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Agglomeration mechanisms and thermodynamic properties of TiO₂ nanoparticles interacting with natural organic matter: an isothermal titration calorimetry study

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Interaction between engineered nanoparticles and natural organic matter is investigated by measuring the exchanged heat during binding process with isothermal titration calorimetry^{1,2}. TiO₂ anatase nanoparticles and alginate are used as engineered nanoparticles and natural organic matter to get an insight into the thermodynamic association properties and mechanisms of adsorption and agglomeration. Changes of enthalpy, entropy and total free energy, reaction stoichiometry and affinity binding constant are determined or calculated at a pH value where the TiO₂ nanoparticles surface charge is positive and the alginate exhibits a negative structural charge. Our results indicate that strong TiO₂-alginate interactions are essentially entropy driven and enthalpically favorable with exothermic binding reactions. The reaction stoichiometry and entropy gain are also found dependent on the mixing order. Finally correlation is established between the binding enthalpy, the reaction stoichiometry and the zeta potential values determined by electrophoretic mobility measurement. From these results two types of agglomeration mechanisms are proposed depending on the mixing order. Addition of alginate in TiO₂ dispersions is found to form agglomerates due to polymer bridging whereas addition of TiO₂ in alginate promotes a more individually coating of the nanoparticles.

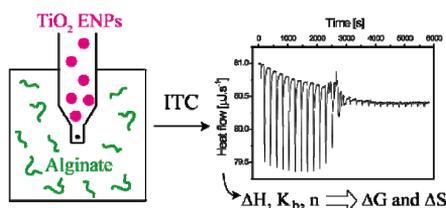


Figure 1 Isothermal titration calorimetry allows the determination of important thermodynamic parameters and assess, when associated with light scattering techniques, the mechanisms of agglomeration.

F. Loosli, L. Vitorazi, J.F. Berret and S. Stoll, *Water Res.*, 2015, **80**, 139.

F. Loosli, L. Vitorazi, J.F. Berret and S. Stoll, *Environ. Science: Nano*, 2015, **2**, 541

Adsorption and Desorption Behavior of Ionic and Nonionic Surfactants

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Surfactants, either designed by nature or synthesized by humans, accumulate at hydrophobic/hydrophilic interfaces. The strength of their adsorption at the interface, which implicitly affects their capacity to reduce the surface tension, can also have practical implications such as those encountered in the process of emulsion polymerization. In this work, we combine experimental and computational techniques to elucidate the adsorption properties of ionic and nonionic surfactants on poly(styrene). To represent these two types of surfactants, we choose sodium dodecyl sulfate and poly(ethylene glycol)-poly(ethylene) block copolymers, both commonly utilized in emulsion polymerization. By applying quartz crystal microbalance with dissipation monitoring we find that the non-ionic surfactants are desorbed from the poly(styrene) surface slower, and at low surfactant concentrations they adsorb with stronger energy, than the ionic surfactant. Of fact, from molecular dynamics simulations we obtain that the effective attractive force of these nonionic surfactants to the surface increases with the decrease of their concentration, whereas, the ionic surfactant exhibits mildly the opposite trend. We argue that the difference in this contrasting behavior stems from the physico-chemical properties of the head group. Ionic surfactants characterized by small and strongly hydrophilic head groups form an ordered self-assembled structure at the interface whereas, non-ionic surfactants with large and weakly hydrophilic head groups generate a disordered layer. Consequently, upon an increase in concentration, the layer formed by the nonionic surfactants prevents the aprotic poly(ethylene glycol) head groups to satisfy all their hydrogen bonds capabilities. As a response, water molecules intrude this surfactant layer and partially compensate for the missing interactions, however, at the expense of their ability to form hydrogen bonds as in bulk. This loss of hydrogen bonds, either of the head groups or of the intruding water molecules, is the reason the nonionic surfactants weakens their effective attraction to the interface with the increase in concentration.

For the ionic surfactant we have not observed this behavior, however, further analyzes were hampered by the large fluctuations in the electrostatic forces.

Charge properties and size of small colloids by electroacoustics: a benchmark system for calibration

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An extensive use of colloids in numerous industrial applications requires a robust characterization of the properties of these systems. A key aspect of colloidal particles is that most of them bear an electrical charge that controls their interactions with the surrounding medium. Hence, the understanding of the properties characterizing this charge is of prime importance. There are a number of techniques used to determine “effective charge” of the colloids. Among them are dynamic methodologies, such as electroacoustic, dynamic conductivity and dynamical light scattering. The former consists in applying an ultrasonic wave to an electrolyte solution and measuring the induced electric field or the inverse, depending on the device. This technique is much less developed than the others despite its advantages: non dilute and non-transparent colloidal systems can be studied, and there is no size limit for the objects. However, the solid theory that would describe extensively nano-sized objects dispersions such as small colloids is still missing. To address this issue, a proper benchmark system is required.

Polyoxometalates (POMs) were already chosen as calibrants for the electroacoustic measurements [1] due to their high electron density and so a good acoustic contrast as well as high polarizability. In a recent work on POMs [2] we demonstrated that these macroions being highly polarizable have the propensity to adsorb on hydrophilic and neutral surfaces. Thus, micelles made of non-ionic surfactant with ethoxy or sugar polar heads in presence of POM in solution constitute the nano-sized charged colloids with tunable properties, for example as a function of their core-swelling. In order to apply this system for electroacoustic calibration, the comprehensive characterization of the micellar aggregates is required. The special interest has the equilibrium, POM in solution and POM adsorbed onto the micelles. Using techniques such as NMR, SAXS, DLS the complementary analysis was performed. We demonstrate that this system can be used as a benchmark system in electroacoustic and for the help in development of the above mentioned theory.

[1] R.W. O'Brien, D.W. Cannon and W.N. Rowlands, *J. Coll. Inter. Sci.*, 1995, **173**, 406.

[2] B. Naskar, O. Diat, V. Nardello-Rataj and P. Bauduin, *J. Phys. Chem. C*, 2015, **119**, 20985.

Phase Behaviour, Dynamics and Directed Self-Assembly of Soft Repulsive Bowl-Shaped Colloids

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We investigate the phase behaviour of soft repulsive charged bowl-shaped colloidal dispersions using confocal laser scanning microscopy (CLSM). These anisotropic particles were obtained by nanoengineering spherical composite microgels, consisting of a polystyrene core surrounded by a crosslinked poly(N-isopropylmethacrylamide) shell, into a bowl shape following the method developed by Im *et al.* [1] as shown in our former study [2]. In deionized conditions, we observe a transition from a fluid to a plastic crystal phase, with freely rotating particles, to a glassy state with increasing number density. In comparison to spherical particles, the glass transition occurs at a significantly lower number density, indicating that the bowl shape frustrates crystallization. The evolution of the structural properties was determined through the analysis of the pair correlation function and the translational and orientational dynamics was followed by computing the respective mean square displacement up to the glass transition. In addition, an AC electric field was employed to manipulate the particle orientation and self-assembly. The field aligns the particles along their long axis and changes the particle interactions from soft repulsive to dipolar. We find that string-like structures are formed at low concentration and, surprisingly, that at high concentrations the field induces a reversible transformation of the glassy state to a BCT-like crystal.

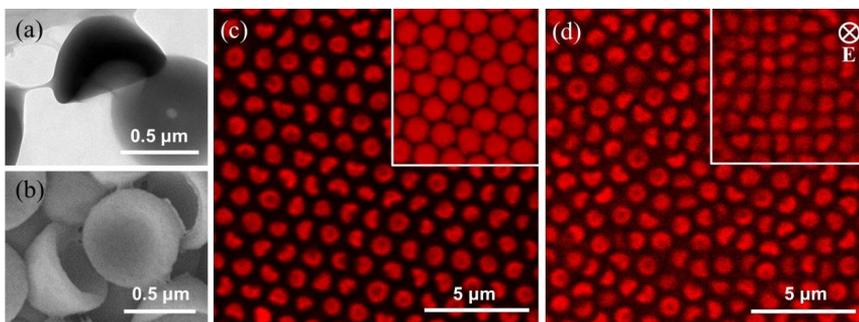


Figure 1 (a) TEM and (b) SEM image of bowl-shaped composite microgels. (c-d) CLSM images of (c) plastic crystal phase (inset) time averaged image showing spherical shapes due to freely rotating particles (d) glassy state (inset) that is transformed into a BCT-crystal by a perpendicular E-field.

[1] S. H. Im, U. Y. Jeong and Y. N. Xia, *Nat. Mater.*, 2005, **4**, 671.

[2] J. J. Crassous, A. M. Mihut, L. K. Månsson and P. Schurtenberger, *Nanoscale*, 2015, **7**, 15971.

Effective temperatures and the breakdown of the Stokes-Einstein relation for particle suspensions

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The short- and long-time breakdown of the classical Stokes-Einstein relation for colloidal suspensions at arbitrary volume fractions is explained here by examining the role that confinement and attractive interactions play in the intra- and inter-cage dynamics executed by the colloidal particles. We show that the measured short-time diffusion coefficient is larger than the one predicted by the classical Stokes-Einstein relation due to a non-equilibrated energy transfer between kinetic and configuration degrees of freedom. This transfer can be incorporated in an effective kinetic temperature that is higher than the temperature of the heat bath. We propose a Generalized Stokes-Einstein relation (GSER) in which the effective temperature replaces the temperature of the heat bath [1]. This relation then allows to obtain the diffusion coefficient once the viscosity and the effective temperature are known. On the other hand, the temporary cluster formation induced by confinement and attractive interactions of hydrodynamic nature, makes the long-time diffusion coefficient to be smaller than the corresponding one obtained from the classical Stokes-Einstein relation. Then, the use of the GSER allows to obtain an effective temperature that is smaller than the temperature of the heat bath. Additionally, we provide a simple expression based on a differential effective medium theory (DEMT) that allows to calculate the diffusion coefficient at short and long times. Comparison of our results with experiments and simulations for suspensions of hard and porous spheres shows an excellent agreement in all cases.

Acknowledgments: Work supported by DGAPA IN-110516

[1] C.I. Mendoza, I. Santamaría-Holek, and J.A. Perez-Madrid, *J. Chem. Phys.*, 2015, **143**, 104506.

Synthesis of colloidal rods and (preliminary) stacking experiments

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Synthesis of monodisperse akageneite rods (β -FeOOH) with tunable aspect ratio (between 4 and 12) is presented [1,2]. The rods are used for coating experiments with silica. The standard Stöber synthesis is applied to obtain silica coatings as well as a method to obtain mesoporous silica coatings [3]. Treatment of both types of particles with strong acid yields hollow silica rods. These rods are intended to be used in stacking experiments with rods only or with rods and other non-spherical particles. Possible applications can be found in membrane science.

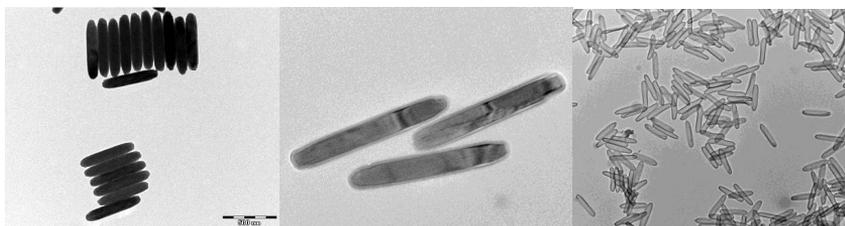


Figure 1 TEM pictures of (from left to right): akageneite rods, akageneite rods coated with silica and hollow silica rods.

1 H. Zocher, W. Heller. *Z. Anorg Allg Chem* 186:75, 1930.

2 Y. Maeda and S. Hachisu, *Coll Surf.* 6 (1983), 1-6.

3 S.I.R. Castillo, thesis Utrecht University 2015.

Interactions of an alkylated antimicrobial peptide, BP100C₁₆, with Phospholipid Vesicles

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Antimicrobial peptides are antimicrobial agents (AMPs) with potential to be used as a therapeutic alternative to the growing antibiotic resistance of microorganisms [1]. BP100, KKLFKKILKYL-NH₂, is an AMP hybrid of Cecropin and Melittin. BP100 has high activity against bacteria, low hemolytic effect and high selectivity for negatively charged membranes, characteristic of bacterial membranes [2]. To obtain an analog with a lower minimum inhibitory concentration, MIC, and greater therapeutic potential we synthesized an alkylated BP100 derivative with a hexadecyl alkyl chain, BP100C₁₆, C₁₆H₃₃-AKKLFKKILKYL-NH₂. Here we describe the interactions of BP100C₁₆ with large unilamellar vesicles, LUV, prepared by extrusion, with pure 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphatidylcholine (POPC) and mixtures of and 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphatidylglycerol (POPG). LUV leakage by BP100C₁₆ was determined using 4,5-carboxyfluoresceine as an internal probe. BP100C₁₆ structure and its interaction with LUV were analyzed by CD, NMR, electrophoretic mobility, DLS and optical microscopy with giant vesicles, GUVs. BP100C₁₆ increased the permeability of LUV of POPC and different POPC: POPG mixtures. BP100C₁₆ was a random coil in water and its structure remained unchanged in the presence of POPC LUV. With PC:PG LUV, BP100C₁₆ exhibited a α -helix structure. BP100C₁₆ aggregated LUV of POPC:POPG 1:1, seen with GUVs, leak the LUV internal content, increased the vesicles hydrodynamic diameter and changed its electrophoretic mobility. We have shown that BP100C₁₆ interacts with vesicles through hydrophobic interactions with the alkyl chain and that the peptidic α -helix structure is dependent upon the presence of negatively charged phospholipids.

Acknowledgements This work received financial support from: CNPq, FAPESP (2013/08166-5), INCT-FCx and NAP-FCx.

[1] R. Ferre, M.N. Melo, A.D. Correia, L. Feliu, E. Bardají, M. Planas and M. Castanho, *Biophys. J.*, 2009, **96**, 1815.

[2] M. C. Manzini, K. R. Perez, K.A. Riske, J. C. Bozelli Jr, T. L. Santos, M. A. Silva, M. J. Politi, A. P. Valente, F. C. L. Almeida, H. Chaimovich, M.A. Rodrigues, M. P. Bemquerer, S. Schreier and I. M. Cuccovia., *Biochim. Biophys. Acta Biomembranes*, 2014, **1838**, 1985.

Normal and shear forces between surfaces bearing stabilized liposomes

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Phosphatidylcholine (PC) liposomes have been shown to lead to a striking reduction in the sliding friction under physiologically-high pressures (1). However instabilities of liposomes during storage are a serious limiting factor for their applicability due to fusion and aggregation. We have synthesized a novel molecule with a structure based on the lipid distearoylphosphatidylethanolamine (DSPE) but with a highly-hydrated, chain-like poly(methacryloylphosphorylcholine) (PMPC), whose monomer contains the phosphorylcholine group (headgroup of lipid), have proved to be extremely efficient boundary lubricants up to quite high pressures. These DSPE-pMPC molecules can be incorporated into PC-SUVs (phosphatidylcholine-small unilamellar vesicles), forming PC-SUV-PMPC liposomes, which stabilize them against aggregation/fusion (Figure 1); at the same time such stabilized liposomes serve as very efficient high-pressure lubricants between sliding surfaces via the hydration lubrication mechanism. This resolves the issue of long shelf life for such lubricating PC liposomes (which, when unstabilized, aggregate within a week, and when stabilized by poly(ethylene glycol) (PEG) provide less good lubrication in salt at high pressures). That is attributed to the stronger hydration of pMPC (ionic solvation) than PEG's (hydrogen bonding).

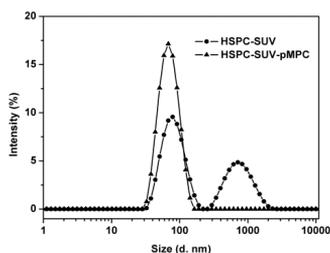


Figure 1 Size distribution of HSPC liposomes (one week after preparation) and DSPE-pMPC polymer stabilized HSPC (three months after preparation) in water.

(1) Goldberg, R.; Schroeder, A.; Silbert, G.; Turjeman, K.; Barenholz, Y.; Klein, J. *Advanced Materials* **2011**, *23*, 3517.

Internally Nanostructured Raspberries

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The use and role of spherical nanocolloids as stabilizers in water of internally self-assembled domains dispersed from lipid-based lyotropic liquid crystalline phases is investigated and discussed. We focus on the relation between stabilization and formation of a colloidal armor around the lyotropic phase drops. The structural parameters are determined by Small and Very Small Angle Neutron Scattering (SANS and VSANS) under contrast matching conditions, and Cryogenic Transmission Electron Microscopy (Cryo-TEM). The adsorption of negatively spherical nanoparticles is low, and creation of armor is only possibly through a hydrophobic modification of the sphere surface during the process by addition of a cationic surfactant [1,2]. The adsorption ratio of the modified nanoparticles on the drops has been investigated, demonstrating the conditions in forming raspberry stabilized particles. The use of SANS and VSANS under contrast matching conditions allow to qualitatively determine the coverage as a function of the ratio between the colloidal concentration and the one of the added surfactant. This is demonstrated the progressive increase of the coverage while the stabilization decrease. These results represent further advances in smart carriers due to the possibilities of hierarchical functionalization of both the internal phase and the stabilizing particles.

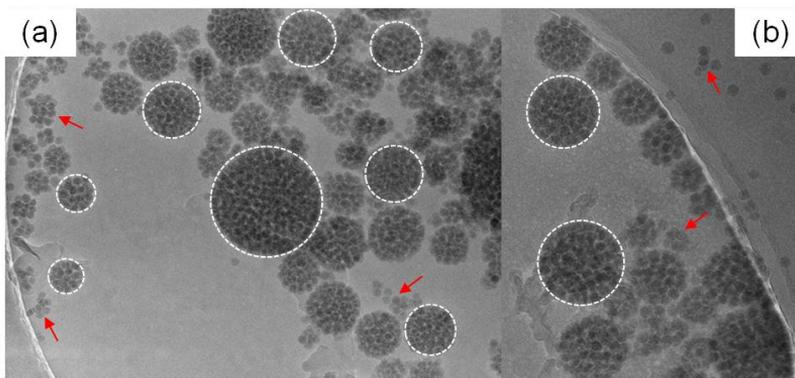


Figure 1. Typical cryo-TEM pictures of a sample composed of 5 wt% of L2 phase (inversed micelles) stabilized in water by silica colloids (14 nm) and $5 \cdot 10^{-5}$ M of CTAB (cationic surfactant).

[1] F. Muller, J. Degrouard, A. Salonen, A.P.L.B.L. Chapter 8, vol 18, 209 (2013).

[2] F. Muller, T. Dégousée, J. Degrouard, A. Brûlet and A. Salonen, *J. Colloids Interface Sci.*, 2015, **446**, 114.

Antioxidant activity of phenolic acids in the nonionic micellar system

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Phenolic compounds are a complex group of substances that have attracted considerable attention due to their role in maintenance of flavor and color characteristics of food as well as in protecting human health. Many of the benefits of phenolic-rich foods consumption are due to their antioxidant activities. The efficiency of a phenolic antioxidant will depend upon the reactivity of its phenolic groups and locations of the radical and the antioxidant in the microheterogeneous food system. The rate of the reaction between an antioxidant and a radical totally incorporated within a microphase will be determined by the antioxidant hydrophobicity. The hydrophobicity will strongly influence its distribution between the microphase and the external medium as well as its location inside the microphase.

To address these two aspects, the reactivity of diphenylpicryl hydracil radicals (DPPH) towards cumaric (CA), ferulic (FA) and caffeic (CAA) acids was investigated in the Triton X-100 micellar solution of various concentrations (0.001M, 0.003M and 0.005M) and at different temperatures. Micellar solutions are often used as simple models of food. The presence of TX-100 micelles increased the rate of DPPH consumption for all investigated acids. The effect was most noticeable for *p*-cumaric and caffeic acids which are insoluble in water. For ferulic acid, which is soluble in water, the kinetics was the slowest because both reagents (DPPH and FA) were located in different microphases.

Studies of Arenediazonium Ions Behavior in the Complex Matrix

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One of the important limiting factors in the application of ArN_2^+ ions for quantitative investigations of the structure and composition of association colloids and emulsions is their stability. In our presentation the spectroscopic and electrochemical studies of dediazonation reaction in aqueous solutions containing surfactants and/or other additives (i.e. phenolic antioxidant) are presented for para substituted arenediazonium salts. The aim of the studies was to figure out the effect of different factors on the kinetics of ArN_2^+ decomposition. By fitting best the integrated first-order kinetic equation to the experimental data (absorbance of ArN_2^+ at the appropriate wavelength vs. time), the dediazonation reaction rate constants k_{obs} were calculated at different temperatures. Then from the Arrhenius plots activation energies and entropies were found. It has been proved that stability of arenediazonium ions depends to a great extent on the character of substituent, e.g. CH_3^- and Br-groups show a retarding effect on the dediazonation reaction. The addition of the increasing amounts of surfactant to the system causes the increase of the reaction rate up to the CMC. Above the CMC, the abrupt drop of rate constant to the values somewhat higher (for CTAB and TX-100) or slightly lower (in the case of SDS) than in the buffered aqueous solution was observed. It means that the SDS micelles stabilize ArN_2^+ ions but the effect is rather poor and depends on the substituent type. Nonionic and cationic surfactants exhibit an opposite effect.

The same systems were investigated by means of the differential pulse voltammetry (DPV) method. The peak potential, E_p , and the peak current, I_p , of ArN_2^+ were measured in the solutions of TX-100, CTAB and SDS. All measurements were carried out at $\text{pH} = 1.81$ and $T = 25^\circ\text{C}$. From the obtained results it can be concluded that the most pronounced changes of the peak potential and peak current are observed at the surfactant concentrations below the CMC. At higher surfactant concentrations these parameters remain approximately constant. The addition of propyl gallate to the p-NOBD solution results in the decrease of reduction current, I_p , which is an evidence of the reaction proceeding between these two reagents.

Calcium hydroxide nanoparticles from solvothermal reaction for the deacidification of degraded waterlogged wood

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The preservation of the Swedish warship Vasa represents a unique and challenging conservation case study. Since its salvage, a combination of sulfuric acid and iron ions inside the wood has been corroding the hemicellulose and cellulose matrices jeopardizing the preservation of the shipwreck [1-3]. Past deacidification treatments displayed poor penetration inside the wood matrix with limited efficacy [4-6]. Alkaline earth metal hydroxide nanoparticles have proved efficient for pHN controlled deacidification to inhibit both the metalN catalyzed oxidation and the acidN catalyzed hydrolysis of cellulose and hemicellulose [7]. In order to improve on the available treatments and make the conservation of larger objects possible, stable and highly concentrated calcium hydroxide nanoparticle dispersions in alcohols were synthesized via a solvothermal reaction, which has also the advantage to be upscalable to industrial level. Nanoparticle dispersions were characterized using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), X-Ray Powder Diffraction (XRPD), High Resolution Transmission Electron Microscopy (HR-TEM), Selected Area Electron Diffraction (SAED), Dynamic Light Scattering (DLS), surface area analysis (BET), and turbidimetry. The efficacy of these nanoparticle dispersions was tested on samples from the Vasa shipwreck using a mild vacuum treatment. Deacidification was assessed by pH determination and Differential Thermal Gravimetric (DTG) measurements, showing that these dispersions represent a very promising tool for the conservation of objects such as statues or decorations of waterlogged and archeological relicts whose preservation is still a challenging issue [8].

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- [1] Y. Fors and M. Sandström, *Chem. Soc. Rev.*, 2006, **35**, 399.
- [2] G. Almkvist and I. Persson, *Holzforschung*, 2008, **62**, 694.
- [3] G. Almkvist and I. Persson, *Holzforschung*. 2008, **62**, 64.
- [4] R. Giorgi, D. Chelazzi and P. Baglioni, *Langmuir*, 2005, **21**, 10743.
- [5] E.J. Schofield, R. Sarangi, A. Mehta, A.M. Jones, F.J.W. Mosselmanns and A. V. Chadwick, *Mater. Today*, 2011, **14**, 354.
- [6] A. V. Chadwick, E.J. Schofield, A.M. Jones, G. Cijin and J.F.W. Mosselmanns, *Solid State Ionics*, 2012, **225**, 742.
- [7] G. Poggi, R. Giorgi, N. Toccafondi, V. Katur and P. Baglioni, *Langmuir*, 2010, **26**, 19084.
- [8] G. Poggi, N. Toccafondi, D. Chelazzi, P. Canton, R. Giorgi and P. Baglioni, *J. Colloid Interface Sci.*, 2016, **473**, 1.

A transient amorphous solid formed from low density aqueous charged sphere suspensions

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Glass transition is one of the fundamental problems in condensed matter physics. Colloidal glasses are most commonly observed in hard spheres or hard sphere polymer mixture systems. In charged sphere systems, they have so far been reported at elevated packing fractions, where strong self-screening renders the electrostatic repulsion very steep. Here we report the observation of a low density amorphous solid, formed in a thoroughly deionized suspension of highly charged latex spheres with diameter of 118 nm. The transition occurs close to the fluid-solid phase boundary with number density of $n = 2 \cdot 10^{-18} \text{ m}^{-3}$ corresponding to a volume fraction of 0.005. From static light scattering experiments, the samples show a liquid-like structure factor. Torsional Resonance Spectroscopy provides a shear rigidity in the range of 0.3-0.5 Pa. The intensity auto-correlation function of samples manifests the typical two-step decay [1]. Although our data are still somewhat preliminary, this seems to be the first experimental observation of a low density Wigner glass in colloidal system.

[1] T. Palberg, E. Bartsch, R. Beyer, M. Hofmann, N. Lorenz, J. Marquis, R. Niu and T. Okubo, arXiv:1602.08947.

Investigations of Structural and Rheological Properties at high and low temperature of bitumen for warm recycling technology

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The low quantity of bitumen (colloidal system) and your expensive cost, the high intrinsic value of resulting materials of the old superstructures have attracted increased attention on the reuse of reclaimed asphalt pavement (RAP) [1].

The goal of this study was to investigate the effects of two different rejuvenation additives on the RAP bitumen. In general, there is still a lack in the comprehension and description of the real mechanism of the additive action on the colloidal structure.

These additives are oil based and surfactant based rejuvenators. In particular, the rheological properties were investigated in order to understand the efficiency of rejuvenation of these additives and the structural changes of the colloidal bitumen system were monitored by ILT NMR analysis [2]. This methodology is very powerful to correlate the mechanical properties and the morphology of the soft matter system.

[1] T. Ma, X. Huang, Y. Zhao and Y. Zhang, *Constr. Building Mat.*, 2015, **98**, 530.

[2] L. Filippelli, L. Gentile, C. Oliviero Rossi, G. A. Ranieri and F. Antunes, *Ind. Eng. Chem. Res.*, 2013, **51**, 16346.

Enhancing colloidal stability of layered double hydroxides by copolymer adsorption

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Layered double hydroxides (LDHs) have been extensively investigated in the recent years due to their promising prospective applications in drug delivery, catalysis, wastewater treatment and polymer nanocomposites formation. In particular, development of novel polymer-inorganic nanomaterials is a thriving research area due to enhanced mechanical, thermal and flammability properties. However, understanding colloidal stability of the LDH based materials and determining proper amount of polymer that can adsorb on the surface of the nanoparticles and furthermore, improve colloidal stability are of crucial importance. The effect of four different macroRAFT (Reversible Addition Fragmentation chain Transfer) copolymers of acrylic acid (AA) and butyl acrylate (BA) monomers on colloidal behavior of LDHs (Mg^{2+} and Al^{3+} - intralayer cations, CO_3^{2-} or NO_3^- - interlayer anions) was investigated by measuring electrophoretic mobilities and stability ratio values (Figure 1). Particles are moderately stable at low copolymer dose, and unstable close to isoelectric point (IEP). However, after IEP, LDH nanoparticles become extremely stable due to substantial charge reversal. Significant effects of AA-to-BA ratio and molecular mass of polyelectrolytes were observed. Larger amounts of butyl groups in the copolymers increase the onset of the adsorption saturation plateau (ASP, the maximum amount of copolymer that can adsorb on the LDH particles), therefore, more macroRAFT agents can be absorbed on the particle surface. In summary, colloidal stability of aqueous LDH dispersions can be well tuned by macroRAFT agents [1].

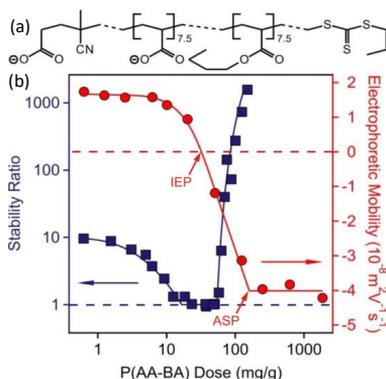


Figure 1 a) Structure of macroRAFT agent of AA-to-BA 1:1; b) stability ratio (■) and electrophoretic mobility (●) of LDH particles decorated by macroRAFT copolymer in different doses.

[1] M. Pavlovic, M. Adok-Sipiczki, C. Nardin, S. Pearson, E. Bourgeat-Lami, V. Prevot and I. Szilagyi, *Langmuir*, 2015, **31**, 12609.

The effect of surface quality on the flow of aqueous kaolin suspensions

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Colloidal dispersions often manifest non-Newtonian behaviour in bulk flow and interfacial anomaly at confining walls. The most common interfacial anomaly is known as the apparent wall slip, caused by depletion of dispersed phase close to solid walls [1-3]. An opposite interfacial anomaly, analogous to the dilatancy phenomenon, was observed in our viscometric measurements with aqueous kaolin suspensions.

The rotational viscometry was carried out at a laboratory temperature (25°C) for samples with three kaolin concentrations (30, 35 and 40 wt.%). Four non-commercial KK-sensors [4] differing in materials and surface finalization were used. These sensors were made from stainless steel with smoothed or sand blasted surfaces, from titanium with smooth surfaces and from aluminium alloy with eloxal coated surfaces.

Apparent wall slip was detected in the sensors made from stainless steel and titanium. Its magnitude was found to be decreasing with increasing roughness of individual surfaces, but even in the case of sand blasted surface the apparent wall slip effect was still important.

In the case of eloxal coated surface, the interfacial anomaly depended on applied shear stress. At lower shear stresses the common apparent wall slip was detected. After exceeding some critical stress level, the standard data treatment detected "negative" apparent wall slip velocity. This fact can be interpreted as formation of a stagnant layer at the wall, whose thickness is independent of the sensor's gap thickness. This highly anomalous wall effect is probably caused by electrochemical interactions of kaolin particles with eloxal coated surface.

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- [1] H.A. Barnes, *Journal of Non-Newtonian Fluid Mechanics*, 1995, **56**, 221.
- [2] R. Buscall, *Journal of Rheology*, 2010, **54**, 1177.
- [3] T. Sochi, *Polymer Reviews*, 2011, **51**, 309.
- [4] O. Wein, M. Večeř, V.V. Tovčigrečko, *Journal of Non-Newtonian Fluid Mechanics*, 2006, **139**, 135.

Electro-optical research of surface conductivity of colloid particles

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In this work we present the experimental results of the study of surface conductivity in colloids and the electro-optical experimental techniques used to obtain them. Surface conductivity is an important characteristic of the interface which, just like charge, surface potential and electro-kinetic potential characterizes the double electric layer of particles and influences the stability of the solution. The theory of particle polarizability [1] defines the relation between specific particle surface conductivity, their size, shape, and their polarizability. This theory considers particle polarization together with that of dispersive media and ionic atmosphere surrounding the particles to describe the dispersion of electric polarizability of particles in the media in a wide range of electric field frequencies. Experimental study of particle polarizability allows to determine surface conductivity and the influence of ionic strength of the media on the latter. Mean values of particle polarizability can also be determined when studying the increment of electric conductivity of the colloid. Application of external fields induces orientation of non-spherical particles, which causes anisotropy of electric, dielectric and optical properties of the colloids. Since most colloids scatter incident light considerably, it is easy to observe electro-optical effects defined by anisotropy of light scattering, such as conservative dichroism. To conduct the experimental study of colloid particle surface conductivity we have constructed an experimental setup that employs electro-optical technique based on the study of conservative dichroism of colloids in electric fields of different types and frequency. The measurement of optical anisotropy using such a technique as a function of field strength and frequency allows to study polarizability and determine the size of colloid particles. In polydisperse systems it is possible to determine the distribution functions on these particle parameters and control the aggregative stability of the system during the experiments. Using particle polarizability model [1] it is then possible to determine the surface conductivity of the interface.

An experimentally determined dispersion of conservative dichroism for diamond aqueous colloid on the frequency of the applied electric field in frequency range 500 Hz – 4 MHz is in good agreement with the theoretically computed dispersion dependence if we take into account the distribution of particles on their size and shape. Good agreement of the theoretical and experimental curves testifies to the applicability of the employed theory of particle polarizability to study particle surface conductivity. The obtained magnitude of diamond particle surface conductivity is in good agreement with the magnitudes obtained using other techniques. Analogous results were obtained for several other colloids with particles of different shape, size, and origin.

Conclusions: 1. The employed theory of particle polarizability is applicable to the study of electric properties of studied colloid particles. 2. The obtained magnitudes of surface conductivity is in good agreement with those obtained before.

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[1] V.N. Shilov, Yu.B. Borkovskaia and S.N. Budankova, In "Molecular and Colloidal Electro-Optics", 2007, Surf. Sci. Series, v. 134, ch.2, pp. 39-57, CRC, Taylor & Francis.

Diamond nanoparticles in aqueous colloids – a complex study

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In this work we performed optical, electro-optical and electro-kinetic of aqueous colloids of nanodiamond at low particle concentration and varying *KCl* electrolyte concentration. Also we determined size and shape distribution histograms by electron microscopy method. The surface of diamond nanoparticles contains different molecular groups, which define the stability of colloids and the processes of their aggregation. Electron microscopy images show cluster-like structures of particles on the film formed, to the most extent for some samples, by small particles (10-40 nm). During gravitational sedimentation of polydisperse aqueous colloids several horizontal layers are formed. These layers contain particles of different size and scatter incident light of different intensity and spectral characteristics. That all testifies to a rather selective character of interaction between diamond particles in water. If the distance between the particles is big, and scattering can be considered single, the light scattering indicatrix is asymmetrical, and the degree of asymmetry is close to that of spheres of size equal to the most probable diamond particle size in the colloid. The distribution function of diamond particles on their size was determined using DLS technique. It was shown that it contains two modes, with the first mode comparable to the size of particles determined from the histogram of particle size distribution obtained from electron microscopy images, and the second corresponding to particle aggregates of size 0.5-1 μm .

For big enough particles the refractive index in dilute colloids does not depend on particle concentration [1], and the turbidity coefficient, being proportional to particle concentration, depends on particle orientational order in electric field and the angle between incident light and particle orientation axis. Thus in this research we studied dichroism and employed a simpler setup to measure the observed effects.

The study of relaxation of the electro-optical effects allowed us to determine the distribution functions of diamond particles and their aggregates on size, which are in good agreement with those determined using DLS. The relaxation curve of electro-optical effect is close to that of autocorrelation function of the depolarized scattered light intensity. During the study of dispersion of electro-optical effect in weak electric fields the dependence of surface conductivity of diamond particles on *KCl* concentration was calculated according to the theory of particle polarizability [2]. At low concentrations of *KCl* this dependence is linear, which is in line with the Henry law. At *KCl* concentration of 4 mMol/l and more we observed aggregation of diamond particles and a loss of stability of the solution. A study of diamond colloids at such electrolyte concentrations is only possible with periodic ultrasonic processing of the colloids. Electro-kinetic potential of diamond nanoparticles almost does not depend on *KCl* concentration up until 1 mMol/l, when it starts to sharply decrease.

The properties of aqueous colloids of diamond considerably depend on particle size and concentration. The study of such colloids must be complex and carried out using several supplemental and independent methods.

Acknowledgements. This work was supported by RFBR grant 16-03-00495A. Scientific research were performed at the Interdisciplinary Center for Nanotechnology of Research park of St.Petersburg State University.

[1] V.V. Voitylov, M.P. Petrov, A.A. Spartakov, A.A. Trusov, *Opt. Spectrosc+*, 114(4) (2013) 630-638.

[2] V. N. Shilov, Yu. B. Borkovskaia, S. N. Budankova. "Molecular and Colloidal Electro-Optics", 2007,

chap.2, Surfactant science series, CRC Taylor & Francis, Boca Raton-London-New York.

Optical sugar sensor based on synthesis of gold nanoparticles

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Gold nanoparticles (AuNP) are widely used in many fields due their unique optical and physical properties [1]. A wide array of solution based approaches has been developed in the past few decades to control the size, shape and surface functionality of AuNP [2]. Formation and growth of AuNP can be used as analytical signal in design of sensors and biosensors [3-5]. Sugars are interesting analyte for sensors development. Determination of sugars is important due their influence to human health and importance for manufacture of foods [6-7]. The main aim of this study was to develop rapid and simple method for sugars detection in different solutions. Optical methods such as UV-Vis absorption spectroscopy and Dynamic light scattering (DLS) were chosen due to their desirable properties such as easy sample preparation and determination of analyte. Formation of gold nanoparticles was observed as an indirect signal of sugars presence in solution. The solution for optical measurements contains a sugar sample, cetyltrimethylammonium bromide (CTAB) as a surfactant, tetrachloroauric acid as a precursor for AuNP and sodium hydroxide as a solvent. In basic conditions at room temperature during sugar oxidation AuCl_4^- ions are reduced to Au^0 creating AuNP. Obtained results showed that surfactant is necessary for AuNP stability in colloidal solution. Furthermore, optimal concentrations of NaOH and CTAB were chosen for quick reaction and for preventing AuNP aggregation. In addition, for quantitative measurements calibration curves were obtained for various sugars (glucose, fructose etc.). Moreover, it was discovered that formation rate of AuNP depends on the type of sugar.

Acknowledgements

AR thanks the Research Council of Lithuania for the financial support (grant No. SEN-15095).

- [1] M. Das, K. H. Shim, S. A. An and D.K. Yi, *Toxicol. Environ. Health. Sci.*, 2011, **3**, 193.
- [2] Y. C. Yeh, B. Creran and V. M. Rotello, *Nanoscale*, 2012, **4**, 1871.
- [3] D. Liu, J. Yang, H. Wang, Z. Wang, X. Huang, Z. Wang, G. Niu, A. R. Walker and X. Chen, *Anal. Chem.*, 2014, **86**, 5800.
- [4] N. Zhou, J. Wang, T.g Chen, Z. Yu and G. Li, *Anal. Chem.*, 2006, **78**, 5227.
- [5] A. Ramanaviciene, J. Voronovic, A. Popov, R. Drevinskas, A. Kausaite-Minkstimiene, A. Ramanavicius. *Colloids Surf. A*, 2016 (submitted).
- [6] P. Moynihan, *Adv Nutr.*, 2016, **7**, 149.
- [7] Y.C .Huang, J. Carragher, D. Cozzolino, *Food Anal. Methods*, 2016, **9**, 1079.

Mixtures of spherical particles - co-existing crystal and liquid phases

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Charged colloidal particles can order as dispersions in deionised water and are well-known to form crystal structures that have a low yield stress and flow readily while exhibiting long-range three dimensional order. Large single crystals can be observed [1]. In practical applications there are often distributions of size and understanding the behaviour of such systems is important. Binary mixtures with different size particles constitute a simple system that can be understood a model for various applications such as coatings.

Small-angle neutron scattering with mixtures of normal hydrogenous and deuterated latex particles in combination with H₂O/D₂O contrast variation allows the partial structure factors for each component in a mixture to be determined. Results for a number of concentrations and compositions of particles in deionised water will be presented. At low ionic strength the constituents on their own form crystals. These will be contrasted with old studies that have investigated dispersions with added electrolyte so as to resemble binary liquid mixtures [2].

Our new results show that mixtures of strongly interacting (repulsive potential) particles with two different sizes display interesting behaviour: small particles can be inserted in the gaps between large particles. We have observed that for systems where each component would on its own form crystals, the crystalline order of the large particles in a mixture is destroyed whereas the structure for the small particles retain sharp Bragg diffraction peaks. The small particles thus act as macroions that screen interactions between large particles as well as cluster within interstices but their order is not significantly perturbed.

[1] M. S. Hellsing, A. R. Rennie, R. K. Heenan and S. E. Rogers, *RSC Advances*, 2012, **2**, 7091.

[2] R. H. Ottewill, A. R. Rennie and G. D. W. Johnson, *Adv. Colloid Interf. Sci.* 2003, **100-102**, 585.

Electrokinetic Properties of Polypyrrole/Expanded Perlite Conducting Composite

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Conducting polymers have attracted attention due to their promising applications in various area of electronics such as magnetic recording materials, effective quantum electronic devices, sensors, toners in photocopying, smart windows conductive paints, rechargeable battery electrolytes [1-6]. PPy is an insulator, which has attracted intense attention due to its environmental stability, ease of synthesis, exciting chemical and electrical properties, but its oxidized derivatives are good electrical conductors. Perlite is a glassy volcanic rock, which is commonly light gray, with a rhyolitic composition and 2 to 5% of combined water, and it is one of the most important material because of its low thermal conductivity, high absorption of sound, low bulk density, and fire resistance, perlite aggregate plasters hold many advantages over conventional plaster [7].

In this study, Polypyrrole/Expanded Perlite (PPy/EP) composites were synthesized different rates (%10, %30 and %50) by in situ radicalic polymerization method with the presence of FeCl₃ in HCl medium. Structural and some physical properties of PPy/EP composites were characterized by using FTIR, TGA, SEM and XRD techniques. Electrokinetic properties of PPy/EP composites in polar and non-polar media were examined as functions of time, pH, various electrolytes, surfactants, and temperature.

Acknowledgements The authors thanks to TUBITAK (214Z199) for the financial support of this work.

- [1] O. Quadrat, J. Stejskal, *J. Ind. Eng. Chem* 2006, **12**, 352-361.
- [2] H.J. Choi, M.S. Jhon, *Soft Matter* 2009, **5**, 1562-1567.
- [3] C.H.A. Esteves, B.A. Iglesias, R.W.C. Li, et al. *Sens Actuators B Chem* 2014, **193**, 136-141.
- [4] L. Duan, J. Lu, W. Liu, et al. *Colloids Surf A Physicochem Eng Asp* 2012, **414**, 98-103.
- [5] G.H. Shim, S.H. Foulger, *Photonic Nanostruct* 2012, **10**, 440-446.
- [6] U. Vanamo, J. Bobacka, *Electrochim Acta* 2014, **122**, 316-321.
- [7] M. Alkan, O. Demirbas, M. Dogan, *Microporous and Mesoporous Materials* 2005, **84**, 192-200.

Physicochemical Identity of Protein-Coated Gold Nanoparticles

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When NPs are exposed to the environment, an undefined protein corona is generated, which changes their colloidal properties (i.e. hydrodynamic size, surface charge and aggregation state) fundamentally. This leads to a completely new and undefined physicochemical NP identity. In the presented study, we used gold NPs as a model system because their colloidal stability can be monitored easily with UV/Vis. The impact of the protein properties (molecular weight and isoelectric point) and that of the environmental conditions (pH and ionic strength) on the final physicochemical NPs' properties was investigated. They form either stable dispersions or agglomerate spontaneously when mixed with protein solutions. This depends on the protein and the experimental conditions. Surprisingly, the agglomerates redisperse to individually dispersed and colloidally stable NPs, depending on the purification pH. The final protein coated NPs exhibit specific stabilities and surface charges that depend on protein type and the conditions during its adsorption. By understanding the interactions of NPs with proteins under controlled conditions, we can define the protein corona of the NPs and thus their physicochemical properties in various media.

Acknowledgements: J.S. thanks the German Federal Environmental Foundation (DBU) for financial support.

[1] I. Dewald, O. Isakin, J. Schubert; T. Kraus, M. Chanana, *J. Phys. Chem. C* 2015, **119**, 25482.

Characterizing generated charged inverse micelles

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We have investigated the generation of charged inverse micelles in nonpolar surfactant solutions relevant for applications such as electronic ink displays and liquid toners [1]. When a voltage is applied across a thin layer of a nonpolar surfactant solution between planar electrodes, the generation of charged inverse micelles leads to a generation current (see Figure 1). From current measurements on the surfactant system poly-isobutylene succinimide (PIBS) in dodecane, it appears that such charged inverse micelles generated in the presence of an electric field behave differently compared to those present in equilibrium in the absence of a field [2,3]. To examine the origin of this difference, transient current measurements in which the applied voltage is suddenly increased are used to measure the mobility and the amount of generated charged inverse micelles. The mobility and the corresponding hydrodynamic size are found to be similar to those of charged inverse micelles present in equilibrium, which indicates that other properties determine their different behavior. The amplitude and shape of the transient currents measured as a function of the surfactant concentration confirm that the charged inverse micelles are generated by bulk disproportionation. A theoretical model based on bulk disproportionation with simulations and analytical approximations is developed to analyze the experimental transient currents.

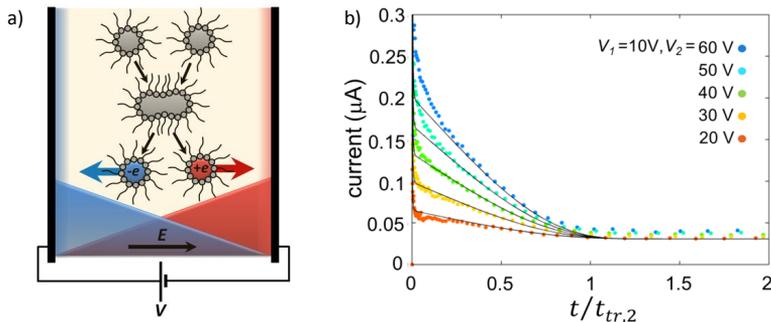


Figure 1 a) Schematic of the steady state concentration profile of newly generated charged inverse micelles at applied voltage V_1 . b) The current measured when switching the voltage to a larger value V_2 (dots) and simulations (lines)

Acknowledgements This research was supported by the Research Foundation Flanders (FWO Vlaanderen), IWT-Vlaanderen, the IAP project photon@be funded by the Belgian Science Policy program, and the Hercules Foundation.

- [1] F. Strubbe, M. Prasad and F. Beunis, *J. Phys. Chem. B*, 2015, **119** (5), 1957.
- [2] F. Strubbe, A.R.M. Verschueren, L.J.M. Schlangen, F. Beunis and K. Neyts, *J. Colloid Interface Sci.*, 2006, **300**, 396.
- [3] M. Prasad, F. Beunis, K. Neyts and F. Strubbe, *J. Colloid Interface Sci.*, 2015, **458**, 39.

Robust boundary integral formulation of Debye-Hückel model

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The calculation of electrostatic interactions in liquids is needed in many chemical and biological applications, including electrostatic interactions between colloid particles, emulsions, and electrostatic interactions between charged proteins as well as drug-substrate interactions.

The Debye-Hückel (linearized Poisson-Boltzmann) model is an effective implicit continuum model to study electrostatic interactions. The boundary integral method is a general, flexible and efficient way to solve problems that arise in the Debye-Hückel model [1-3], as it reduces the dimension of the calculation domain by one. However, there are some drawbacks in the traditional boundary integral method because of the singularities of the Green's function and its normal derivative.

In this talk, we will introduce a novel, robust and non-singular boundary integral method in which all the singular behaviors in the integrands have been analytically eliminated. As such, compared to the traditional boundary integral method, our method is able to calculate accurately the interactions between two objects of general shape even when their surfaces are close (see Fig. 1).

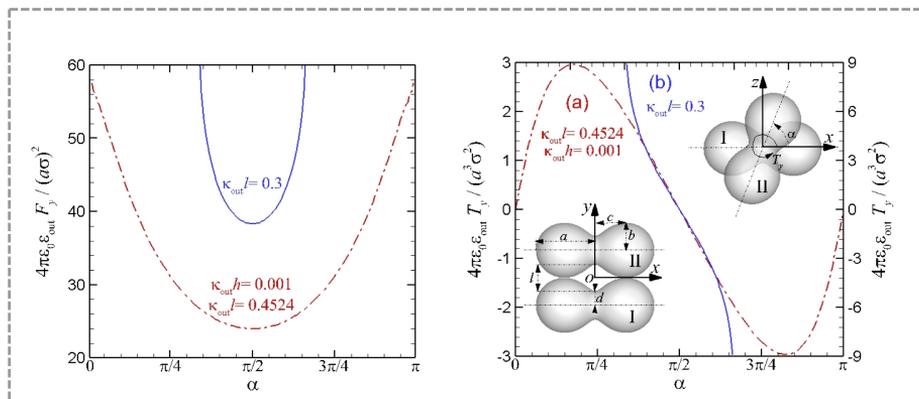


Figure 1 Dimensionless force, F_y , and torque, T_y , due to electrical double layer interactions between two closely spaced dumb-bell shaped particles at constant surface charge, σ , as functions of relative orientation, α , obtained using our non-singular boundary integral method. The dimensionless geometric parameters are: $\kappa a = 1$, $\kappa b = 0.4757$ and $\kappa d = 0.25$, for values of κl shown in the figure.

Acknowledgements This work is supported by the Australian Research Council.

- [1] B.J. Yoon, A.M. Lenhoff, *Journal of Computational Chemistry*, 1990, **9**, 1080.
- [2] M.D. Altman, J.P. Bardham, J.K. White, B. Tidor, *Journal of Computational Chemistry*, 2008, **30**, 132.
- [3] C.D. Cooper, J.B. Bardhan, L.A. Barba, *Computer Physics Communications*, 2014, **185**, 720.

One-pot synthesis of high-aspect-ratio twin gold nanorods

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Large varieties of sizes in gold nanorods are developed. The long nanorods, especially those longer than 1 μm , are well-suited for use as electrodes, nanogap electrodes, nanorod arrays, and new photonic devices. It is well known that there are two kinds of crystal structures in gold nanorods, namely, single crystal and twin. Twin gold nanorods have different crystal planes at the sides and edges of the nanorods. Thus the twin gold nanorods are modified the surfaces in anisotropic way, whereby the side and edge are modified with different molecules. Moreover nanorods, especially those longer than 1 μm , are also easily manipulated. Therefore, for further application, high-aspect-ratio twin gold nanorods will be arranged or moving on a specially-patterned surface by means of the anisotropic interaction between the two surfaces. Here we present a new synthesis of high-aspect-ratio twin gold nanorods by using gelled surfactant solution.

Generally, twin gold nanorods are synthesized using a stepwise additive method [1]. In such method, citrate-stabilized seeds are added to the growth solution that contains the surfactant, Au ions, and the reducing agents. Some part of the mixture is then added to another growth solution, which is composed of the same constituents and the process is repeated. In these cases, the length of gold nanorods is limited to 500 nm and extra processes will be necessary to elongate nanorods longer than 1 μm [2,3]. In our method, however, the nanorods with the length of ca. 1.7 μm grow in a gelled surfactant solution with only one step and no extra processes are necessary (Fig1). The yield is relatively high: ca. 60 %.

In this study, we examined in detail the effects of NO_3^- concentrations or number of seeds on the length of nanorods. As a result, NO_3^- has an influence on the length of the gold nanorods and the longest ones were obtained at an optimal concentration of NO_3^- , even for growth in the gelled surfactant solution as well as the growth in aqueous surfactant solution. On the contrary, the number of seeds in the growth solution has no effect on the lengths of the nanorods[4].

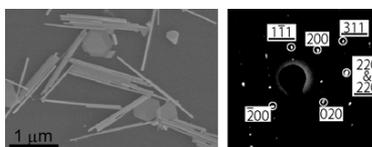


Figure1 SEM image of high-aspect-ratio twin gold nanorods (left). Diffraction pattern from the edge of a present gold nanorod (right). The indices with and without underlines mean two different series of spots.

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- [1] H.-Y. Wu, H.-C. Chu, T.-J. Kuo, C.-L. Kuo and M. H. Huang, *Chem. Mater.*, 2005, **17**, 6447.
- [2] H. M. Chen, H.-C. Peng, R.-S. Liu, K. Asakura, C. L. Lee, J. F. Lee and S.-F. Hu, *J. Phys. Chem. B*, 2005, **109**, 19553.
- [3] K. Critchley, B. P. Khanal, M. L. Gorzny, L. Vigderman, S. D. Evans, E. R. Zubarev and N. A. Kotov, *Adv. Mater.*, 2010, **22**, 2338.
- [4] Y. Takenaka, *RSC Adv.*, 2015, **5**, 34690.

Colloidal Microworms Propelling via a Cooperative Hydrodynamic Conveyor Belt

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We study propulsion arising from microscopic colloidal rotors [1,2] dynamically assembled and driven in a viscous fluid upon application of an elliptically polarized rotating magnetic field. Close to a confining plate, the motion of this self-assembled microscopic "worm" results from the cooperative flow generated by the spinning particles such as an hydrodynamic "conveyor-belt" effect. Chains of rotors propel faster than individual ones, until reaching a saturation speed at distances where flow additivity vanishes. By combining experiments with theoretical arguments, we elucidate the underlying mechanism of motion and fully characterize the propulsion speed in terms of the external field parameters.

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[1] P. Tierno, R. Golestanian, I. Pagonabarraga, and F. Sagués, *Phys. Rev. Letters*, 2008, **101**, 218304.

[2] P. Tierno, S. Schreiber, W. Zimmermann, and T. M. Fischer, *J. Am. Chem. Soc.*, 2009, **131**, 5366

An approach to analysis of optical spectra of colloidal quantum dots and their aggregates: taking account of inhomogeneous broadening, blinking, and FRET

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Förster resonance energy transfer (FRET) in aggregates of colloidal quantum dots with narrow size distribution manifests itself experimentally as a red-shift and quenching of the emission spectrum upon aggregation. A mathematical model has been developed to describe this process [1]. The input data for the model are the absorption and emission spectra of individual particles. However, typical experimental absorption and photoluminescence spectra of colloidal quantum dots are usually considerably inhomogeneously broadened and therefore cannot be directly used for calculations. Fortunately, the total broadening can be easily decomposed into homogeneous and inhomogeneous parts by using the fundamental Kennard–Stepanov–van Roosbroek–Shockley (KSvRS) relation between the absorption and emission spectra. Figure 1 illustrates this issue. As a result, given the experimental absorption and emission spectra of nonaggregated and aggregated particles, the model can be used to calculate the FRET efficiency and the fraction of particles in the OFF state (in the context of blinking).

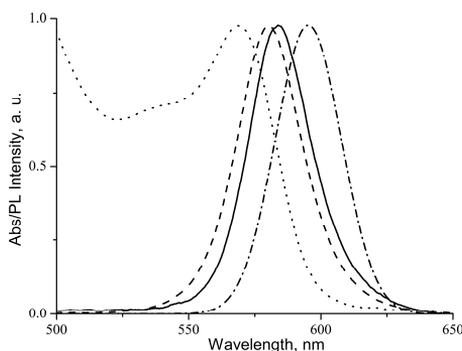


Figure 1 Experimental absorption (dotted curve) and emission spectra of nonaggregated (dashed line) and aggregated (solid curve) CdSe quantum dots with an average diameter of 3.5 nm [2]. The dash-dotted curve shows the emission spectrum of the ensemble of nonaggregated nanoparticles calculated from the KSvRS relation assuming a Gaussian shape of the spectrum and no inhomogeneous broadening. The deviation of this curve from the experimental one contains the information on the inhomogeneous broadening. The dash-dotted curve should also be the aggregate emission spectrum in the limit of infinitely fast FRET and no blinking. Its deviation from the solid line can be used to calculate the FRET efficiency.

Acknowledgements This study is supported by the Russian Science Foundation, project no. 14-13-01426

[1] S. A. Tovstun and V. F. Razumov, *High Energy Chemistry*, 2015, **49**, 352.

[2] S. B. Brichkin, M. G. Spirin, Y. Yu. Gak, *Colloid Journal*, 2014, **76**, 6.

Diffusio-phoresis of photocatalytic particles under self-generated concentration gradients

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The generation of flow within the interfacial structure due to concentration gradients was described quantitatively for the first time by Anderson [1] and extended by Ajdari and Bocquet [2] for solvophobic surfaces. The flow is driven by an osmotic pressure gradient which builds up inside the interfacial layer where the interaction potential between the chemical species and solid spans (Figure 1). Moreover, if the surface is reactive, the diffusio-osmotic flow could be promoted without any external input, through self-generated concentration gradients. If the solid surface is not immobilized, e.g in a colloidal system, the surface flow will propel small particles.

In this project, the migration of photocatalytic particles (TiO_2) under self-generated concentration gradients is studied systematically in a microreactor where an aqueous solution of an organic contaminant is contacted under continuous flow with a particle suspension containing various concentrations of the same contaminant (Figure 2). When UV light is turned on, the photocatalytic particles decompose the contaminant lowering the concentration inside the colloidal stream. The difference in concentration that is generated via the photocatalytic reaction leads to the migration of particles toward the higher concentration site.

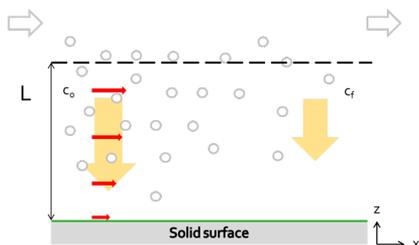


Figure 1 Concept illustration for diffusio-osmosis.

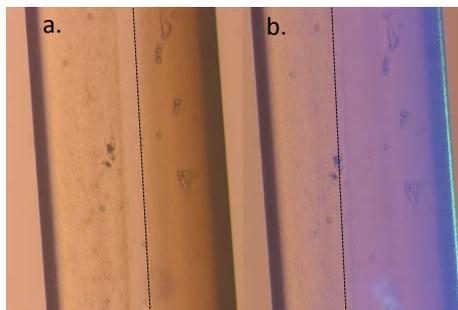


Figure 2: A methylene blue (MB) solution is contacted with a TiO_2 suspension stream in a $200\ \mu\text{m}$ width channel. The dotted line is used as a guideline to show the spreading of the colloidal stream upon illumination. a. UV off; b. UV on.

Acknowledgements This work was supported by the Netherlands Center for Multiscale Catalytic Energy Conversion (MCEC), an NWO Gravitation programme funded by the Ministry of Education, Culture and Science of the government of the Netherlands.

- [1] J. L. Anderson, *Annu. Rev. Fluid Mech.*, 1989, **21**, 61.
 [2] A. Ajdari and L. Bocquet, *Phys. Rev. Lett.*, 2006, **96**, 1.

Investigation of the osmotic deswelling of polystyrene microgels by polymer addition

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The addition of free polymer to a glassy colloidal dispersion leads to the creation of a fluid pocket in the phase diagram at high volume fractions between two glassy states - the "repulsive" and the "attractive" glass. This re-entry effect is extraordinarily strong for polystyrene (PS) microgel colloids in good solvent to which linear PS chains are added - a phenomenon which is still not understood [1]. As the re-entry effect is very robust and can be transferred to technical (aqueous) dispersions, a very interesting application for economic and ecological reasons [2], it is important to understand the physical origin of the differences between typical hard spheres, like PMMA particles [3], and the microgel system which has so far not been achieved. As the microgel particles are swollen in a good solvent typically by a factor 5-6 in volume, osmotic deswelling has been discussed as an obvious explanation, since this would lead to smaller effective volume fractions and resolve the apparent discrepancy with respect to the PMMA system. Measurements of a dilute deuterio PS tracer in a highly concentrated protonated PS host via small angle neutron scattering (SANS), however, showed no difference in the formfactor when we increased the polymer concentration.

The next obvious step is the examination of size and structure of the free polymer in the system and the structural changes it causes in the packing of the colloidal particles. The major part of the huge re-entry region of microgel colloids in mixtures with free polymer is located at effective polymer concentrations $c_{p,free}$ above the overlap concentration. This suggests that the concept of the radius of gyration R_g becomes obsolete in semi-dilute polymer solutions and should be replaced by the screening length ξ . Therefore we determined with SANS the screening length of fully deuterated PS polymer in a contrast-matched host of microgel particles at a colloid volume fraction of ~ 0.74 . We find that the screening length of the polymer confined by the microgel matrix is much smaller than in pure polymer solution at identical reduced polymer concentration c/c^* .

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- [1] S. Burger, E. Bartsch, *Colloids Surf. A: Physicochem. Eng. Aspects*, 2013, **442**, 6.
- [2] N. Willenbacher, J. S. Vesaratchanon, O. Thorwarth, E. Bartsch, *Soft Matter*, 2011, **7**, 5777.
- [3] K. N. Pham, S. U. Egelhaaf, P. N. Pusey, and W. C. K. Poon, *Phys. Rev. E.*, 2004, **69**, 011503.

The electrokinetic behaviour of chitosan-treated TiO₂ suspensions

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Titanium dioxide has been studied for many years as a model oxide and for numerous practical applications. The aim of this investigation was the effect of cationic polysaccharide (chitosan, Fig. 1) on the electrokinetic behaviour of TiO₂ suspensions in NaCl solution at different pH. Chitosan was used because its molecules exhibit various biomedical activities such as antimicrobial, antifungal, anti-allergic, anti-tumour and immune-activating effects. Moreover, chitosan protective barrier can retard ripening and water loss as well as reduce the destruction of products. Besides, because of its positive charge, chitosan strongly interacts with cell membranes and mucosal surfaces, which can be useful in drug delivery systems.

TiO₂ (P-25, Degussa) was purified by the procedure described by Preočanin and Kallay [1]. The electrokinetic behaviour of chitosan-treated TiO₂ suspensions was determined mainly with the help of an optical analyzer and by dynamic light scattering method. The isoelectric point of the investigated TiO₂ suspensions determined from electrokinetic behaviour compares well with literature data [2-3]. The chitosan solution treatment leads to a shift of the isoelectric point. Cationic biopolymer molecules adsorb to the TiO₂ surface, driven by hydrophobic and electrostatic interactions. The charge on both kinds of TiO₂ surfaces can be controlled by pH, due to acid/base reactions of the surface OH groups. In the experiments, the concentration of titanium dioxide, chitosan and pH of the solution were varied. The results obtained show significant influence of the chitosan on the measured quantities. The cationic biopolymer can be also effective in the process of suspension stabilization.

The zeta potential and mean diameter values obtained from dynamic light scattering measurements were compatible with the finding that the properties of titania suspensions show the largest changes for pH next to the isoelectric point, independent of solids concentration. The most important conclusion is that it is possible to control the flocculation state and biocompatibility by chitosan coating of the titanium dioxide system and by adjusting its pH level. Knowledge of the effect of biopolymer adsorption and full understanding of the suspension electrokinetic properties is essential for optimizing production and broadens the spectrum of TiO₂ applications. This study gives full characteristic a well-designed and functional suspension in biotechnological industries for example in cosmetic products, pharmaceuticals and drug delivery.

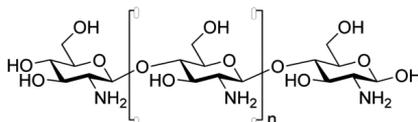


Figure 1 Chitosan structure.

- [1] T. Preočanin and N. Kallay, *Croat. Chem. Acta*, 2006, **79**, 95
- [2] A.E. Wiącek, E. Anitowska, A.V. Delgado, L. Holysz and E. Chibowski, *Colloids Surfaces A*, 2014, **440**, 110
- [3] E. Chibowski, L. Holysz, K. Terpiłowski and A.E. Wiącek, *Croat. Chem. Acta*, 2007, **80**, 395

Hematite Ellipsoids coated with Silica Shell: Phase Behavior and Dynamics

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Colloidal particles showing anisotropy have been commonly observed either in synthetic (coatings, construction materials, oil drilling, etc.) or natural (cells, clays, cellulose, etc.) materials. Such systems display a diverse phase behavior depending on concentration, aspect ratio, and/or presence of external fields (e.g. electromagnetic fields) that can tune the single particle properties and the interparticle interactions. As an example, for simple thin hard rods, the system may undergo a transition from an isotropic to a nematic state when the volume fraction is high enough. For ellipsoidal particles with a smaller axial ratio, additional states are expected such as a stretched FCC crystal as well as a glassy state at very high densities. Moreover, anisotropic systems also exhibit more complex dynamics, with a possibility to observe the different contributions of rotational and translational diffusion, a decoupling of diffusion coefficients in different directions, and a more complex transition to different arrested states. Such kind of information can be obtained by using, for instance, differential dynamic microscopy (DDM), which is based on temporal fluctuations of the intensity in optical microscopy.¹

Here we use dispersions of ellipsoidal particles composed of a hematite core and a silica shell as a convenient model of an anisotropic colloidal system, utilizing features such as an easily tunable aspect ratio which allows to reach a wide region in the phase diagram, and the response to magnetic fields (due to the ferromagnetic core) which that provides control of the rotational degree of freedom.² We describe their structural and dynamic properties from dilute conditions up to the glass transition, while exploiting their ability to orient in a homogeneous external magnetic field. We use DDM to determine the concentration dependence of the diffusion coefficient and its decoupling along parallel and perpendicular directions with respect to the field, and follow the onset of arrest as the system undergoes a glass transition.

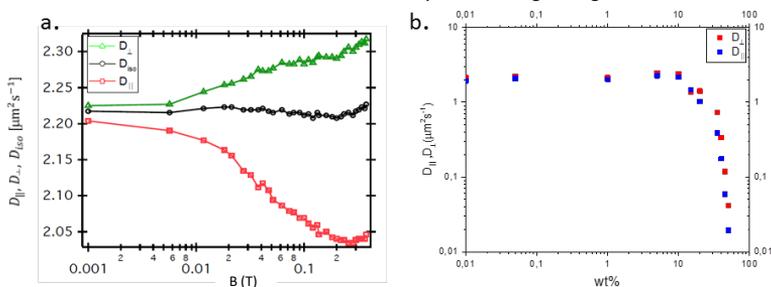


Figure 1 a) Decoupling of the diffusion coefficient along parallel and perpendicular directions with respect to the applied magnetic field as a function of field strength for 0.1 wt% of dispersion. **b)** Variation of the anisotropic diffusion coefficients as a function of the concentration at a magnetic field of 380 mT.

[1] M. Reufer, V. A. Martinez, P. Schurtenberger and W. C. K. Poon, *Langmuir*, 2012, **28**, 4618.

[2] M. Reufer, H. Dietsch, A. Hirt, A. Menzel and P. Schurtenberger, *J. Phys. Chem. B*, 2010, **114**, 4763.

Synthesis of gold and silver nanoparticles functionalized with organic dithiols

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Noble metal nanoparticles represent a very interesting class of materials thanks their unique chemical-physical properties conferred by their nanoscopic scale. In particular gold and silver nanoparticles are largely employed in biomedicine [1], catalysis [2] and optoelectronic [3] applications.

In this work three different bifunctional organic dithiol, the 4,4'-dithiol-biphenyl (BI), the 4,4''-dithiolterphenyl (TR) and the 4,4'-dithiol-*trans*-stilbene (ST), have been used for the stabilization of gold and silver nanoparticles (AuNPs and AgNPs). The ST ligand has been prepared by following a synthetic procedure developed in our laboratory [4] and has been carefully characterized. Then, gold and silver nanoparticles have been prepared by using a double phase reaction through the reduction of the metal precursor, the tetrachloro auric acid and the silver nitrate salt. The obtained NPs have been purified and then characterized with spectroscopic and microscopy techniques. The Uv-Vis investigation carried out on the NPs has showed the Plasmon resonance even if the peak was rather broad and red shifted respect the typical value (more than 550 nm for AuNPs and more than 450 nm for AgNPs) this could be an indication of the networks formation [5]. The PL studies have revealed the fluorescence properties of the NPs whereas the XPS measurement have confirmed the functionalization of the metal surface and has given information about the amount of thiol involved in the metal-sulfur bond. The morphological investigation carried out with the FESEM microscopy, revealed the presence of spherical NPs of less than 10 nm for gold and bigger for silver ones. In particular the FESEM images of the AuNPs stabilized with TR ligand have showed the most ordered arrangement in the space and also the XPS characterization has confirmed that is the system with the highest amount of thiolic functionality involved in the networks formation. So this last sample is the best candidates for the optoelectronic applications.

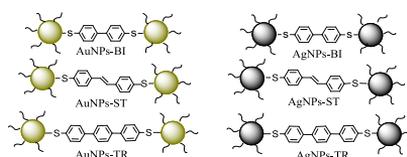


Figure 1 chemical sketch of the synthesized gold and silver nanoparticles functionalized with the organic dithiols: BI, TR and ST

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References

- [1] N.G. Bastús, E. Sánchez-Tilló, S. Pujals, C. Farrera, C. López, E. Giral, A. Celada, J. Lloberas, V.F. Puntes, *ACS Nano*, 2009, 3, 1335-1344.
- [2] G. Li, R., *Jin Accounts of Chemical Research*, 2013, 46, 1749-1758.
- [3] S. Alex, A. Tiwari, *Journal of Nanoscience and Nanotechnology*, 2015, 15, 1869-1894.
- [4] M. Quintiliani, M. Bassetti, C. Pasquini, C. Battocchio, M. Rossi, F. Mura, R. Matassa, L. Fontana, M.V. Russo, I. Fratoddi, *J. Mater. Chem. C*, 2014, 2, 2517-2527.
- [5] S. K. Gosh, T. Pal, *Chem. Rev.*, 2007, 107, 4797-4862.

Ion size effect on electrophoretic mobility of a colloidal particle

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One of the main assumptions of the standard electrokinetic model is that ions behave as point like entities. Many recent works modify this classic model taking into account the finite ion size, introducing steric interactions among ions by means of an excess electrochemical potential. Two main conclusions can be drawn from these studies: the corrections to the standard electrokinetic model are only significant for high surface charges and/or bulk electrolyte concentrations and, in order to fit experimental data, it is necessary to consider effective ionic radii much larger than the hydrated ionic radii appearing in the literature. While the first restriction is not important for microelectrode systems in which high surface charges are used in practice, it is an important limitation for electrokinetic phenomena in colloidal suspensions in which the surface charges are relatively low.

In a recent work [1], we compared the corrections introduced into the equilibrium standard electrokinetic model by the Bikerman and the Carnahan-Starling expressions. Our main conclusion was that high and low surface charge conditions must be examined independently. At high surface charges, both the Bikerman and the Carnahan-Starling models can provide acceptable representations of the same measured results but due to different physical processes. For low surface charge values, however, the Bikerman model nowhere approaches saturation values so that the obtained results are close to the classical Poisson-Boltzmann solution while the Carnahan-Starling equation presents important deviations even in this situation. The bottom line is that the Carnahan-Starling model appears to be able to provide an interpretation of the electrokinetic potential vs. surface charge dependence in the case of colloidal particles suspended in aqueous electrolyte solutions.

In the present work we calculate the out of equilibrium behaviour of a colloidal suspension using both the Bikerman and the Carnahan-Starling equations for the steric interactions. The obtained results agree and extend our previous equilibrium study: in all cases the steric interactions improve upon the standard model predictions so that the surface potential, and electrophoretic mobility are larger (in modulus) [2]. Moreover, unlike the Bikerman equation, the Carnahan-Starling expression leads to corrections that are substantial even for electrolyte solution concentration and surface charge density values typically encountered in colloidal suspensions.

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[1] López-García, J.J., Horno, J., Grosse, C., *J. Colloid Interface Sci.*, 428 (2014) 308.

[2] López-García, J.J., Horno, J., Grosse, C., *J. Colloid Interface Sci.*, 458 (2015) 273.

Novel Hydrophobically Associative Cellulose Nanofibers for Controlled Suspension Rheology of Nanoscale Fluids

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In recent years, cellulose materials have gained significant attentions because of their excellent structural stability as well as unique rheological fluidity [1,2]. This study synthesizes hydrophobically associative cellulose nanofibers (ACNFs) by using combined surface-mediated living radical polymerization and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation. More specifically, cellulose nanocrystals were grafted with poly (stearyl methacrylate-co-2-methacryloxyethyl phosphorylcholine) hydrophobic and zwitterionic polymer brushes. Finally, the TEMPO-mediated oxidation enables production of nanoscale cellulose nanofibers. We have found that the cellulose nanofibers can not only dramatically increases the viscosity of aqueous solution due to the hydrophobic attraction, but also display excellent tolerance to pH changes and salt addition due to formation of structurally fiber gel network. The results obtained in this study highlight that that the incorporation of hydrophobically associative polymer brushes onto the surface of ACNFs is indeed important and play a role in fabrication of high performance nanoscale fluids.

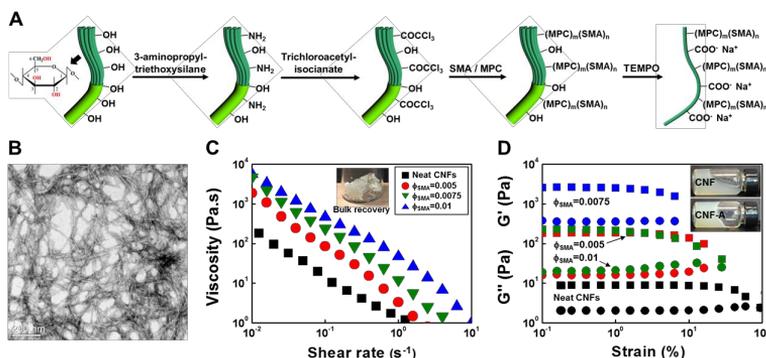


Figure 1. (A) Schematic illustration for grafting poly (SMA-co-MPC) brushes on CNFs by using surface-mediated living radical polymerization. (B) TEM images of poly (SMA-co-MPC) grafted ACNFs. $\phi_{SMA} = 0.0075$. (C) Viscosity behaviors of CNF suspensions as a function of shear rate. The effect of the weight fraction of SMA in the polymer (SMA-co-MPC) brushes. (D) Storage modulus, G' and loss modulus, G'' changes as a function of oscillation strain.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2008-0061891

References

- [1] N. Quennoz, et al. *Soft Matter*, 2015, 12(1), 157-164.
- [2] T. Saito, et al. *Biomacromolecules*, 2007, 8(8), 2485-2491.

Rich-diamond and rich-graphite nanodiamond particles

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Nowadays, nanodiamond (ND) particles are attracting increasing interest for their outstanding properties of the diamond and are excellent candidates for many and disparate applications in the fields of: drug delivery carriers, bio-labelling probes, nanocomposites, single photon sources, electrochemical energy storage, nucleation sites for growth of high performance CVD nanocrystalline diamond films, highly efficient and stable photocathodes [1], just to cite a few. Usually, the nanoparticles exhibit a very high surface-to-volume ratio and therefore they got surface-dependent properties more significantly than their bulk counterparts and tuneable with treatments. For the above applications, the ND particles are generally handled in colloidal dispersion and their behavior in solution is critical. In particular, as received particles with size of few nanometers are hardly separate in monodisperse particle colloids, but high temperature treatment in H₂ gas or air makes easy to get monodispersion and stability.

In this contribution, we present an investigation on two types of ND powders with particle size of about 250 nm and having different sp² (graphite phase) and sp³ (diamond phase) carbon contents; for this the powders are classified as rich-diamond and rich-graphite nanodiamonds. The surface of ND particles has been modified with treatment in H₂ microwave plasma. The presence of hydrogenated surface affects in the solid state the quantum efficiency of ND-based photocathodes [1] and in solution the particle zeta potential and therefore their stability [2].

Many aqueous dispersions were prepared with the two types of powders, as received (ND_{as-rec}) and hydrogenated (H-ND). The more concentrated (1 mg/1 ml) were used to produce photocathodes whose ND layers were deposited by pulsed spray technique [1], whereas more diluted (0.1 mg/1 ml) were examined by dynamic light scattering in the pH range from 2 to 12.

The effect of the hydrogen treatment is beneficial inducing an increase of photocathode quantum efficiency and a correspondent increase of the zeta potential (see Fig. 1).

The ND particles were also characterized by Raman and FTIR spectroscopies, and transmission electron microscopy.

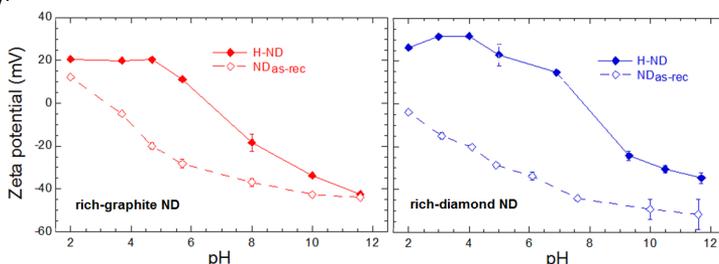


Fig. 1 Zeta potential of untreated and hydrogenated nanodiamond powder as a function of pH.

Acknowledgements The financial support of the Project PON03PE_00067_6 “APULIA SPACE”, (Italy) is partially is acknowledged.

[1] L. Velardi, A. Valentini and G. Cicala, *Appl. Phys. Lett.*, 2016, **108**, 083503.

[2] O. A. Williams et al., *ACS NANO*, 2010, **4**, 4824.

Permittivity of concentrated aqueous colloidal suspensions: the role of water, CO₂, added salt, and ions released from the particles

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In this work, the importance of taking into account the influence that water dissociation, CO₂ contamination, ions released from the particles, and added salt have on the complex permittivity of colloidal suspensions is stressed and analyzed in detail. This study has been carried out for different particle volume fractions, surface charge densities, particle radii, and salt concentrations. A pure salt free suspension is exclusively composed of charged particles and the added counterions that neutralize each particle charge. These added counterions stem from the particles have been released to the solution as the particles get charged. On the other hand, in real aqueous suspensions other ionic species will be present as H⁺ and OH⁻ from water dissociation, and in many cases, ions produced by the atmospheric CO₂ contamination, as H⁺ and HCO₃⁻ from the partial dissociation of the carbonic acid generated by the dissolution of CO₂ in water. A salt-free model which include these real conditions is called "realistic salt-free" [1]. We will modify this model allowing the incorporation of an added salt, and a comparison with the standard model will be done. These previous assumptions have been classically dismissed by the standard model [2,3] because of the major influence on the electrokinetic response of the electrolyte solution in normal conditions. But it has been shown that when the salt concentration is low, the realistic effects of the aqueous solution are of utmost importance in determining the electrokinetic response, while at increasing salt concentrations, it is the salt that plays the dominant role for low to moderate particle volume fractions, although for larger ones they are the added counterions that are determinant for the observed response provided that the salt concentration is not too high. In the present contribution, attention is paid to the relative weight of added counterions and realistic water chemistry in the determination of the complex dielectric dispersion of concentrated suspensions. In addition, a detailed study is carried out concerning the cases where the added counterion species is coincident or not with that of the external salt. The results show the importance of controlling these aspects as quite remarkable and even unexpected discrepancies have been found between standard and realistic dielectric predictions.

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[1] F. Carrique et al., *Adv. Colloid Interface Sci.* 2013, **201**, 57.

[2] S.S. Dukhin and V.N. Shilov, *Dielectric phenomena and the double layer in disperse systems and polyelectrolytes*, 1974, Wiley, New York, USA.

[3] F. Carrique et al., *J. Chem. Phys.* 2003, **118**, 1945.

Colloidal suspensions of Goethite (α -FeOOH) nanorods: effect of synthesis parameters on nanorods morphology and optical properties under magnetic field

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Goethite (α -FeOOH) nanorods have been synthesized using two different methods, by the aging at different temperatures of ferrihydrite suspensions obtained through co-precipitation, or by fast conversion of ferrihydrite through ultrasonic irradiation. The synthesis method and parameters influence the aspect ratio and shape of nanoparticles. Colloidal suspensions of nanorods have been prepared by purification of the precipitates and subsequent dispersion in deionised water by sonication.

The synthesized nanopowders have been characterized by Powder X-ray Diffraction and Scanning Electron microscopy and the colloidal suspensions by Dynamic Light Scattering and ζ -potential measurements. Moreover, since goethite in colloidal suspension is a mineral liquid crystal [1, 2] and due to its peculiar magnetic properties [3, 4], transmittance of colloids in the UV-Vis-NIR range has been determined under different magnetic field directions and intensities. It has been found that the transmittance difference between 0° and 90° radiation polarization with respect magnetic field direction increases in NIR range. The effect is bigger when the aspect ratio of nanorods increases.

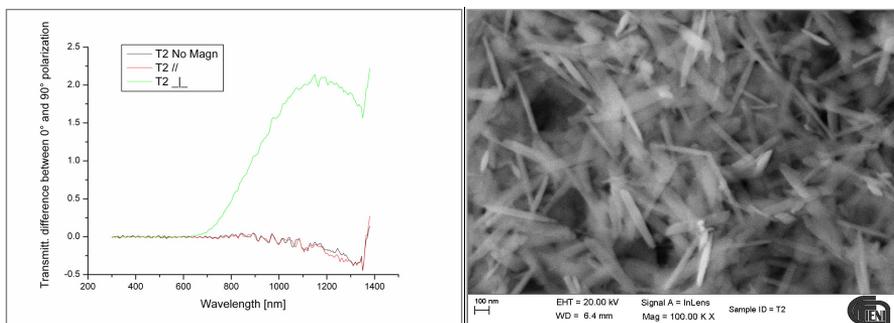


Figure 1 Transmittance difference between orthogonal light polarizations (left), and FE-SEM micrograph of goethite nanorods (right).

Acknowledgements This work has been funded by the National Research Council of Italy – Italian Ministry of Economic Development Agreement ‘Ricerca di Sistema Elettrico Nazionale’.

- [1] P. Davidson, P. Batail, J. Gabriel, J. Livage, C. Sanchez, and C. Bourgaux, *Prog. Polym. Sci.*, 1997, **22**, 913.
- [2] P. Davidson and J.-C. P. Gabriel, *Curr. Opin. Colloid Interface Sci.*, 2005, **9**, 377.
- [3] B. Lemaire, P. Davidson, J. Ferré, J. Jamet, P. Panine, I. Dozov, and J. Jolivet, *Phys. Rev. Lett.*, 2002, **88**, 125507.

Properties of nanocrystalline cellulose hydrosols

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Hydrosols of polysaccharide particles are widely used as biodegradable fillers for gels and plastics, coatings and drug delivery systems. Nanocrystalline cellulose (NC) is broadly used as a catalyst carrier. NC hydrosols are capable of film forming, formation of foams and porous hydrogels of high modulus.

In the current study the NC hydrosols were investigated by the methods of viscometry, refractometry, sedimentation velocity, dynamic light scattering, flow birefringence and induced dichroism. NC was obtained by the controlled hydrolysis of cellulose in the acetic acid/heteropoly acid medium, followed by the purification by dialysis. The values of the density and refractive index increment of NC hydrosol were obtained. The value of the partial specific volume of the investigated particle ($v = 1.0 \text{ cm}^3 \text{ g}^{-1}$) was estimated as well. The value of the intrinsic viscosity of the NC hydrosol was found to be $[\eta] = 0.26 \text{ cm}^3 \text{ g}^{-1}$.

The intensity distribution of the scattered light on the hydrodynamic radius of the particles was obtained by dynamic light scattering. The main contribution in the scattering spectrum was made by NC particles with translational diffusion coefficient $D = 0.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and the hydrodynamic radius $R_h = 65 \text{ nm}$ respectively. The amount of the bigger size particles ($R_h \approx 250 \text{ nm}$) in the distribution was negligible. According to the obtained values of the sedimentation and diffusion coefficients the molar mass of the investigated NC particles was calculated.

Furthermore, the NC hydrosols at different concentrations were studied by the method of flow birefringence. The dependences of the birefringence on the flow velocity gradient g and shear stress coefficient $\Delta\tau$ were obtained. The dependencies are well approximated by the linear extrapolation procedure, which is typical for systems in the absence of a large number of big associates. This, in turn, allowed to determine a value of the optical shear coefficient NC sample. The value was found to be positive and very large in absolute size $\Delta n/\Delta\tau = 12.2 \times 10^{-8} \text{ cm s}^2 \text{ g}^{-1}$.

In addition, the orientation angles at low shear rates g and low concentrations C were determined. The obtained dependency is typical for rigid type particles possessing shape asymmetry. According to the initial tilt angles, the value of the characteristic flow orientation angle NC $[\chi/g] = 0.23 \text{ rad s}^{-1}$ was determined. Moreover, the value of the relaxation time τ_0 of the investigated system was estimated.

The investigation of relaxation of the induced dichroism indicated that the dichroism was caused by the orientation of the NC particles/aggregates under the influence of an external electric field. The field was harmonic with a frequency of 10 kHz and the efficient value of 120 V cm^{-1} respectively. Switching off the field led to the disorientation of the hydrosol particles, which, in turn, led to a decline (relaxation) of the induced dichroism. The analysis of the relaxation curve allowed to evaluate the size distribution of the NC particles/aggregates. Besides that, the effect of the duration of the electric field on the hydrosol NC and the effect of ultrasonic influence on the different durations of the NC particles were studied.

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The influence of surface potential on the relaxation time of hydrogen ion adsorption from solution onto oxides

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The particles of metal oxides dispersed in electrolyte solution obtain a surface charge due to ion adsorption. The pH of solution is key factor determining its value. Nowadays, potentiometric titration is a standard technique of measuring surface charge of oxides. The adsorption of hydrogen ions on oxides is very fast process which can be investigated by using the relaxation method [1,2]. In this technique small perturbation is applied to a system being in chemical equilibrium. Next, the evolution of the system to a new equilibrium state is monitored. In the case of adsorption of protons the pressure jump is used as a stimulus changing an equilibrium in oxide suspension and measurements of solution conductivity are used to determine changes in ion concentrations. From this type of experiments we can determine a relaxation time τ which depends on ion adsorption kinetics (which can be described by the Theory of Activated Adsorption and Desorption). According to this theory the surface coverage by hydrogen ions θ changes with time as follows:

$$\frac{d\theta}{dt} = k_a(1-\theta)a_H \exp\left(-\frac{e\psi_0}{2k_B T}\right) - k_d\theta \exp\left(\frac{e\psi_0}{2k_B T}\right)$$

where k_a and k_d are adsorption and desorption rate constants, and e , k_B and T have their traditional meaning. Exponential factors represent electrostatic activation energy for ion adsorption on the surface with electrostatic potential ψ_0 [3,4].

During relaxation both the hydrogen ion activity a_H and the surface coverage θ change until reaching new equilibrium values. However, it is commonly assumed that the surface potential ψ_0 is constant during relaxation [2]. This is obvious contradiction because the surface potential is a function of the surface coverage by protons: $\psi_0(\theta)$. Assuming that in reality the surface potential depends on temporary surface coverage by ions we developed a new method of interpretation of relaxation experiments. We compared our results with the conventional approach by analyzing experimental data of adsorption kinetics of hydrogen ions for different metal oxides. Our methodology can be extended for investigating the kinetics of adsorption of any ions.

Acknowledgments: The financial support of Łomża State University of Applied Sciences (Grant No. BST-6/IWF/11/2014).

- [1] R. D. Astumian, M. Sasaki, T. Yasunaga, and Z. A. Schelly, *Journal of Physical Chemistry*, 1981, **85**, 3832.
- [2] K. Hachiya, Y. Moriyama, and K. Takeda, (N. Kallay, ed.), *Interfacial dynamics* Vol. 88, 2000, p. 351, Marcel Dekker, New York, USA.
- [3] W. Piasecki, *Journal of Physical Chemistry B*, 2006, **110**, 13138.
- [4] W. Piasecki, P. Zarzycki and W. Rudziński, *Croatica Chemica Acta*, 2007, **80**, 345.

Coumarin derivative for sensing application: nucleotides identification by means of micellar system

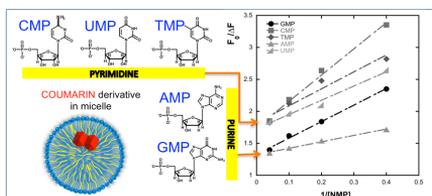
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The recognition of nucleotides is of crucial importance because they are the basic constituents of nucleic acids [1,2]. The present study is focused on the selective interaction between a novel amphiphilic fluorophore containing coumarin and imidazole, CI (1-methyl-3-(12-((2-oxo-2H-chromen-7-yl)oxy)dodecyl)-1H-imidazol-3-ium bromide), and different nucleotide-monophosphates (NMPs). It was supposed that the solubilization of the low water soluble CI in a micelle system of hexadecyltrimethylammonium chloride (CTAC) would make the coumarin moiety of CI available to the interaction with the water-soluble NMPs. Changes in CTAC critical micelle concentration suggested that CI strongly interacted with the host cationic surfactant thus forming a positively charged interface enriched with coumarin able to interact with the anionic NMPs. Steady-state fluorescence quenching revealed that CI/CTAC system was capable of distinguish between purine- and pyrimidine-based nucleotides. A modified Stern-Volmer equation [3] permitted the use of a quenching model that accounted for the possible interactions between the micelles and the nucleotides. The data analysis allowed calculating selective parameters that differentiate according to the type of nucleotide either at 25 or 50 °C. Our results established the utility of the novel coumarin derivative fluorophore, supported by the simple and suitable micellar systems, as a tool for DNA sensing applications.



[1] F. Cuomo, G. Palazzo, A. Ceglie, F. Lopez, *J. Photochem. Photobiol. A*, 2009, **202**, 21.

[2] F. Lopez, F. Cuomo, A. Ceglie, L. Ambrosone, G. Palazzo, *J. Phys. Chem. B*, 2008, **112**, 7338.

[3] D.T. Cramb, S.C. Beck, *J. Photochem. Photobiol. A*, 2000, **134**, 87.

Understanding the aggregation mechanism and stability of asphaltenes

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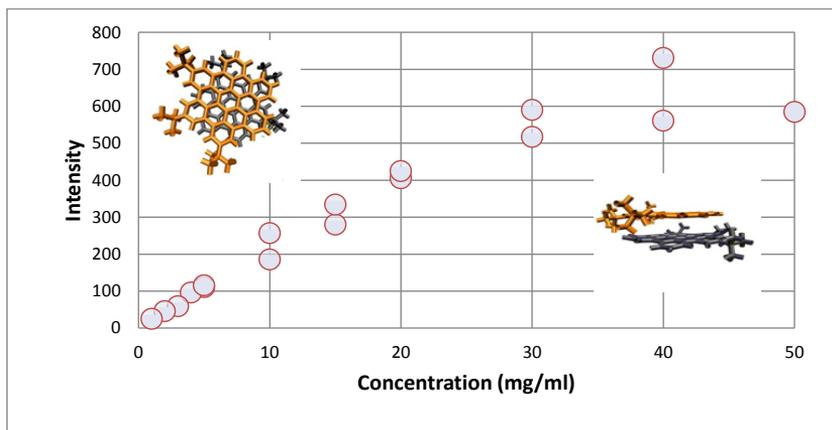
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Asphaltenes, a class of aromatic compounds within crude oil, pose significant industrial challenges such as reservoir impairment, inefficient separation of water from oil, and obstruction of pipelines. Because natural asphaltene possess an undefined molecular structure which results in a complex aggregation mechanism, a model compound, hexa-*tert*-butyl-hexa-*peri*-hexabenzocoronene (HTBHTC) was studied in toluene and heptane, in order to understand the behaviour of natural asphaltene.

The kinetics of the colloidal system are examined as a function of time and concentration by an intensity based light scattering approach, while the molecular interactions were investigated by molecular dynamic simulations.

The intensity of the light scattered by the HTBHTC was measured over a period 366 hours, so that the aggregation kinetics of the polyaromatic compound are established. The intensity was found to be linear to the HTBHTC concentration, while the addition of heptane did not affect the stability of the already formed aggregates. Molecular dynamic simulation results are consistent with the experimental conclusions.



Intensity as a function of concentration and the stacking of HTBHTC molecules

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Synthesis of cubic colloids for as model well-defined depletion interactions

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Recently it was shown that micrometre sized colloidal superballs (rounded cubes) form dense colloidal crystals by adding non-adsorbing polymers[1,2]. These polymers act as a depletant, creating an attraction between individual colloids. It was found that the properties of these crystals are dependent on the particles shape (cube-ness) and the colloid-depletant size ratio. The range of this experimental system, however, is limited by the inherent rounded edges of the superballs. Therefore, we extend on the previous work to further investigate the behaviour and assembly with more cubic colloids. Cuprous oxide (Cu₂O) nanocubes with sharp edges were synthesized [3] and used as a sacrificial template to obtain hollow silica cubes with edge lengths of approximately 100 nm. These well-defined silica cubes are excellent model systems to study the phase behaviour of colloidal cubes with and without depletants. Additionally, the dimensions of the smaller silica cubes allow for other analytical techniques, such as light scattering and ellipsometry.

Acknowledgements: This research is supported by the Dutch Technology Foundation (STW) and DSM

- [1] L. Rossi, S. Sacanna, W. T. M. Irvine, P. M. Chaikin, D. J. Pine and A. P. Philipse, *Soft Matter*, 2011, **7**, 4139.
- [2] L. Rossi, V. Sonia, D. J. Ashton, D. J. Pine, A. P. Philipse, P. M. Chaikin, M. Dijkstra, S. Sacanna, and W. T. M. Irvine, *PNAS*, 2015, **112**, 5286
- [3] J. C. Park, J. Kim, H. Kwon and H. Song, *Advanced Materials*, 2009, **21**, 803.

Quantitative approach to modular micro-swimmer

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Modular micro-swimmer is made of an electrolyte releasing reservoir particle (RP) settled to a charged surface. It may be realized in various ways, e.g. if RP is placed in a dispersion of colloidal spheres (non-active particles or NAPs) a moving complex consisting of the reservoir particles followed by the colloids is formed [1]. The motion mechanism is based on the formation of the electrolyte gradient around the RP. Within this gradient a local electric field is formed, which gives the rise to the electro-osmotic solvent flow along the charged substrate and electro-phoretic motion of NAPs.

To quantify the swimming behaviour of the complex we started with the characterization of the electrolyte gradient. The especially developed microphotography technique was applied to measure the gradients with high temporal and spatial resolution.

The electro-kinetic response of the substrate and NAPs to the field was studied with the integral Doppler velocimetry set up. It allows simultaneous detection and quantification of electro-osmotic and electro-phoretic phenomena [2, 3]. We've implemented a novel experimental cell with exchangeable walls to study influence of different substrate types on the solvent flow.

The length scale of the inner-complex interactions between RP and NAPs was studied with PIV. The range dependent velocity of the non-active particles reflects changes in the forces acting on the non-active particles.

Acknowledgements The financial support of DFG PA459/18 DFG Focus Program "Microswimmers"

[1] A. Reinmüller, *Eur. Phys. J. Special Topics*, 2013, **222** 2835

[2] T. Palberg et al., *J. Phys. Chem.*, 1992, **96**, 8180

[3] T. Palberg et al., *J. Phys.: Condens. Matter*, 2012, **24**, 464109

Magnetic field assisted assembly of DNA coated colloids

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Self-assembly of long, straight, mesoscopic scaffolds can be utilised for building more complicated structures [1,2]. Using the right combination of DNA, it is possible to tune the melt temperatures for single, two and three component systems of DNA coated colloids (DNACC). We present an approach for creating novel superstructures via magnetic field-assisted assembly of DNACC. Recent publications show chains of short lengths [3–5] and/or short persistence lengths [6]. Introducing superparamagnetic beads as one of the components allows us to manipulate their assembly via an externally applied magnetic field. Ring like and long coaxial skeletons of smaller colloids around larger superparamagnetic cores are demonstrated in a two component system. Proof of concept is demonstrated for further stabilizing these structures by adding a suitably functionalized third component. This could pave the way for novel superstructures such as mesoscopic straight coaxial scaffolds, where a bilayer of different colloids is attached to a rigid primary support. These superstructures could also be developed for novel drug delivery systems or utilized as template materials in supercapacitors.

- [1] N. Geerts and E. Eiser, *Soft Matter*, **6**, 4647 (2010).
- [2] L. Di Michele and E. Eiser, *Phys. Chem. Chem. Phys.* **15**, 3115 (2013).
- [3] B. Y. Kim, I.-B. Shim, O. L. a Monti, and J. Pyun, *Chem. Commun.* **47**, 890 (2011).
- [4] R. Dreyfus, J. Baudry, M. L. Roper, M. Fermigier, H. A Stone, and J. Bibette, *Nature*, **437**, 862 (2005).
- [5] V. T. Mukundan, Q. M. Nhat Tran, Y. Miao, and A. T. Phan, *Soft Matter*, **9**, 216 (2013).
- [6] D. Li, J. Rogers, and S. L. Biswal, *Langmuir*, **25**, 8944 (2009).

Dynamics of concentrated core-shell nanoparticle suspensions from confocal differential dynamic microscopy

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Recently, there has been a surge of interest in understanding the dynamical and structural properties of core-shell nanoparticle (CSNp) suspensions due to their importance in a number of applications, including emulsion stabilization, delivery and sensing. In contrast to their counterpart – hard-sphere suspensions – CSNp suspensions have been shown to exhibit fundamentally different hydrodynamic interactions, due both to solvent permeability into the shell and the fuzzy structure of the particle itself [1, 2]. Most of the experimental work on the equilibrium dynamic properties of CSNp suspensions has so far been on particles with a soft core and a soft shell (microgels) [1]. Here, we investigate the dynamics of CSNps dispersed in water with a hard silica core surrounded by a soft shell composed of poly(N-isopropylacrylamide) (PNiPAM) [3]. Their dynamics is probed by confocal differential dynamic microscopy (ConDDM), a technique that has been recently shown to yield information similar to that of dynamic light scattering, but applicable to dense and opaque colloidal suspensions [4]. We found that the behaviour of the intermediate scattering function (ISF) obtained from DDM analysis of concentrated core-shell nanoparticle suspensions is of the form: $F(q, t) = A(q)[1 - \exp(-(\frac{t}{\tau(q)})^{\beta(q)})] + B(q)$. For the case of a dilute suspension, the stretching exponent β is found to have a constant value close to 1, as expected for simple Brownian diffusion [5]. Conversely, for higher volume fraction (ϕ) suspensions, we found that $\beta < 1$ and is not independent of q . The characteristic relaxation time $\tau(q)$ at large ϕ deviates from the dilute $1/Dq^2$ behaviour, indicating structural effects that couple to particle dynamics.

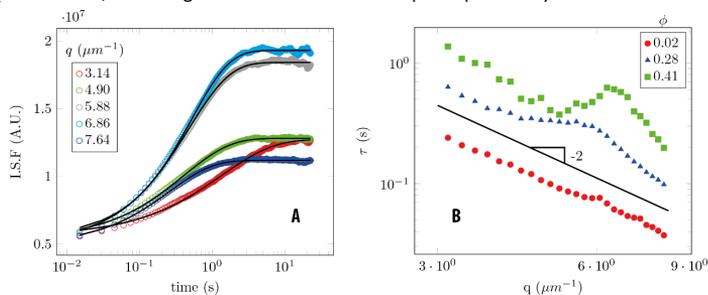


Figure 1: **A)** ISF vs time for $\phi = 0.41$ CSNp suspension at different wave vector q . **B)** Relaxation time τ vs q behavior for different volume fractions ϕ .

1. T. Eckert and W. Richtering, *J. Chem. Phys.*, 2008, 129, 124902
2. G. Petekidis, J. Gapinski, P. Seymour, J. S. van Duijneveldt et al., *Phys. Rev. E.*, 2004, 69, 042401
3. A. Rauh, M. Rey, L. Barbera, M. Zanini, M. Karg and L. Isa, , Submitted to *Soft Matter Journal*
4. P. J. Lu, F. Giavazzi, T. E. Angelini, E. Zaccarelli et al., *Phys. Rev. Lett.*, 2012, 108, 218103
5. R. Cerbino and V. Trappe, *Phys. Rev. Lett.*, 2008, 100, 188102

Nano-composites of DNA-wrapped Carbon Nanotubes and TiO₂ or SiO₂.

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Carbon nanotubes, CNTs, are effectively stabilized by wrapping single strand DNA, ss-DNA, on their surface. The resulting adducts are kinetically and thermodynamically stable. [1] Such entities build up nano-hybrids with SiO₂ or TiO₂ nano-particles, NPs, in presence of surfactant. The conditions leading to a significant adsorption onto such adducts were investigated in some detail. These include optimizing the concentration of the adducts, of NPs, and of the cationic surfactant (CTAB), used as an adjuvant.[2,3] Depending on the working conditions, it is possible getting homogeneously organized hybrids, mostly in case of TiO₂. Characterization by DLS, electro-phoretic mobility, SEM and AFM clarified some details of the surfactant-assisted association between ss-DNA/CNT and SiO₂, or TiO₂. Their clustering on the adducts ends in the formation of hybrids, and is controlled by electrostatic interactions among two such components. Surface coverage of adducts by TiO₂ is significant and homogeneous. In case of SiO₂ the results are erratic, because of the persisting negative charge on such CTAB-covered particles. These hybrids are useful for possible application in heterogeneous catalysis.

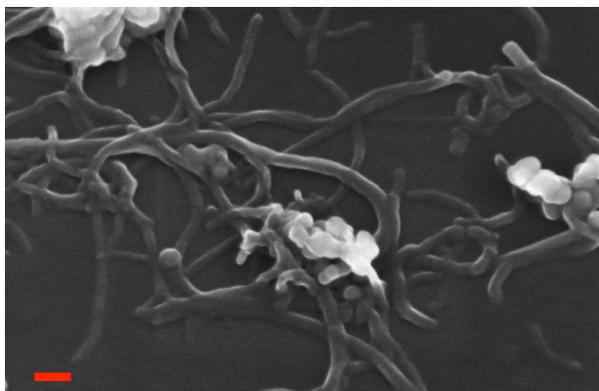


Figure 1 TiO₂ clustering onto DNA-wrapped CNTs. The red bar indicates a 300 nm size.

Acknowledgements The financial support of Sapienza University is acknowledged.

- [1] F. Tardani, C. La Mesa, P. Poulin and M. Maugey, *J. Phys. Chem. C*, 2012, **116**, 9888.
- [2] F. Tardani and C. La Mesa, *Nanomaterials*, 2015, **5**, 1.
- [3] A.A. Ashkarran, M. Fakhari, H. Hamidinezhad, H. Haddadi and M.R. Nourani, *J. Mater. Res. Technol.*, 2015, **4**, 126.

Luminescent platinum complexes-polymer nanoparticles

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We have recently reported luminescent square-planar Pt(II)-complexes with a tunable tendency towards aggregation which is ruled by the establishment of ground-state intermolecular non-covalent interactions[1]. In these compounds the establishment of highly directional metallophilic interactions induces dramatic changes in the electronic spectroscopic properties that can be used as fingerprints to follow the self-assembly process. The control of the environment, is of crucial importance and the interplay between solvents is driven the formation of the aggregates. In this contribution we report on the encapsulation of luminescent platinum complexes using poly (methylmethacrylate)-co-poly(methylacrylic acid) (pMMA-co-pMAA), poly(ethylene glycol) methyl ether-block-poly(D,L lactide) (PEG-b-pDLLA) and other polymers. Using simple “flash-injection” techniques[2,3], we obtained hybrid nanostructures that were characterized by means of different techniques. In particular we have prepared and studied the photophysical properties of two luminescent, hydrophobic platinum complexes, and investigated the formation of nanoparticles of polymers in water.. The resulting water-dispersible polymeric nanoparticles with entrapped either the platinum complexes as monomeric species or as self-aggregated systems, showed emission wavelength, photoluminescence quantum yield (PLQY) and excited state lifetimes which depends on the platinum/polymer ratio and on the concentration of the complex. The size and morphology of these loaded nanoparticles have been studied by scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM) and dynamic light scattering (DLS). These luminescent polymeric nanoparticles made by the biocompatible polymers pMMA-co-pMAA and PEG-b-pDLLA encapsulating the platinum complexes showed particle size in the range 30–300 nm in diameter (see figure 1) and they have been preliminarily applied as bio-imaging probes upon cellular uptake.

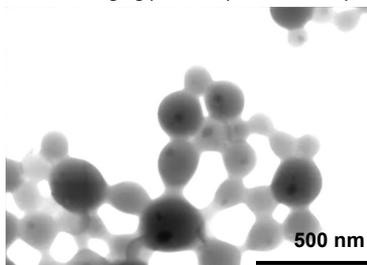


Figure 1. BF-STEM image of platinum complexes loaded polymeric nanoparticles in water

Acknowledgements. We thank the Collège doctoral Européen and the French-German collège doctoral and the French and German governments for financial support.

[1] M. Mauro, A. Aliprandi, C. Cebrián, Di. Wang, C. Kübel and L. De Cola, *Chem. Commun.*, 2014, **50**, 7269; A. Aliprandi, M. Mauro, L. De Cola, *Nature Chemistry*, 2015, **8**, 10.

[2] Pösel, Elmar, Christian Schmidtke, Steffen Fischer, Kersten Peldschus, Johannes Salamon, Hauke Kloust, Huang Tran, *ACS Nano*, 2012, **4**, 3346.

[3] C. Szymanski, C. Wu, J. Hooper, M.A. Salazar, A. Perdomo, A. Dukes, J.D. McNeill, *J. Phys. Chem. B*, 2005, **109**, 8543.

New Stimuli-Responsive Cationic Microgels

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Stimuli-responsive microgels are chemically crosslinked polymer particles of nanometer dimensions that become highly swollen in response to certain external stimuli such as pH, temperature, ionic strength, electric and magnetic field [1]. In recent years, numerous reports on the synthesis of microgels, characterization, modification, and application in biomaterials, sensor technology etc. have emerged demonstrating the importance of these materials both in fundamental and applied research [3,4]. Cationic microgels swell in acidic pH conditions and de-swell or shrink in neutral/basic pH conditions.

In this work, new stimuli-responsive cationic microgels based on *N*-acryloyl-*N'*propyl piperazine (AcrNPP) were synthesized by a surfactant-free emulsion polymerization using water-ethanol mixture. The microgels were responsive to changes in external pH, and temperature. Their size increased or decreased in response to changes in pH or temperature, and the transition was studied using UV-vis spectroscopy, static and dynamic light scattering, and differential scanning calorimetry. Interestingly, the microgels in water showed a lower critical solution temperature (LCST) of 37 °C. This LCST shifted to higher temperature in acidic solution due to increased hydrophilicity as a result of ionization. Using the properties of these microgels, removal of toxic dyes and heavy metals in water is investigated in this project. The core-shell morphology of the water-swollen microgel shown by TEM is presented in Figure 1. .

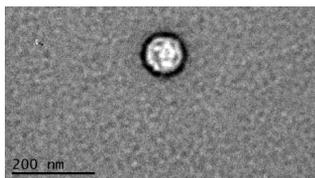


Figure 1. TEM of water-swollen microgel.

Acknowledgements: Nanyang Technological University/National Institute of Education is acknowledged for financial support (NIEAcRF RI 1/15 RGR & NIEAcRF R I6/12 GRD)

- [1] R. Pelton, *Adv. Colloid and Interface Sci*, 2000, **85**, 1-33.
- [2] N. Nath, A. Chilkoti, *Adv. Mater*, 2002, **14**, 1243-1247.
- [3] A. Zillessen, E. Bartsch, *Langmuir*, 2010, **26**, 89-96.

Spontaneous Emulsification of water in oil at appreciable interfacial tensions

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Spontaneous formation of aqueous droplets in kerosene was observed, which was facilitated by the presence of an oil soluble surfactant: Span® 80 at concentrations above CMC. Kerosene/water interfacial tension under all conditions studied was not lower than 4 mN/m. Therefore, ultra-low interfacial tension was not required for this process to occur spontaneously as is usually required [1]. The process was caused by a transfer of water molecules to swollen reversed micelles. The influence of both the surfactant concentration in the organic phase and NaCl concentration in the aqueous phase on spontaneous aqueous droplet formation was investigated. Nano-sizing analysis of the drops was performed, which showed the droplets sizes in between 100 and 400 nm. It is proven that the presence of salt in the aqueous phase inhibits droplet formation. It is shown that big sessile aqueous droplets deposited on a hydrophobic substrate inside the kerosene phase were dissolved in kerosene through formation and growth of droplets, which form an aqueous film at the droplet base.

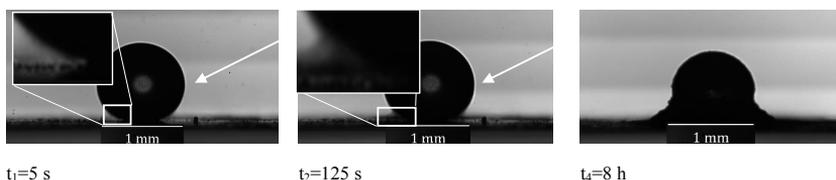


Figure. Formation of a cloud of nano-sized droplets and a film at the droplet base assisted by swollen reverse micelles present in the organic phase (kerosene)

Acknowledgements This work was supported by CoWet Marie Curie Intra-European Fellowship within the 7th European Community Framework Programme, and COST MP1106 project.

References

- 1] Lopez-Montilla, J.C., P.E. Herrera-Morales, S. Pandey, and D.O. Shah, Spontaneous emulsification: Mechanisms, physicochemical aspects, modeling, and applications. *Journal of Dispersion Science and Technology*, 2002. 23(1-3): p. 219-268.

Study of dispersions of non-spherical colloidal aggregates of boehmite

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In the catalyst carriers industry, the production of alumina powders can be achieved by spray-drying boehmite suspensions, this aluminium oxyhydroxyde being often used as precursor for various types of alumina catalyst supports. Well-peptized boehmite ($\text{AlOOH} \cdot n\text{H}_2\text{O}$), is composed of anisotropic particles bearing an electric charge [1]. In the past decade, it has been shown that the properties of the dry powder strongly depends not only on the processing conditions but on physico-chemical of the sprayed suspensions [2]. For instance, different grains morphologies (doughnut-shaped grains, hollow spheres,...) as well as various dry grains properties (textural properties, mechanical resistance,...) may be achieved by tuning the physico-chemical properties of the suspension [2]. Moreover, from a practical point of view, it is important to spray-dry suspensions with the highest solid contents but while keeping low viscosities.

The goal of this communication is to investigate the physico-chemical and rheological properties of aqueous boehmite suspensions. Two industrial boehmites have been studied, the difference between the two is the synthesis route. Suspensions were prepared by peptising the boehmite by nitric acid followed by a dialysis against distilled water. Then, the particles have been characterized by combining DLS, SAXS and TEM analysis. We show that the particles in suspension are aggregates of boehmite elementary crystallites, these aggregates are slightly anisotropic (aspect ratio between ≈ 3 and 4) and tridisperse (≈ 5 , 20 and 60 nm). In order to investigate the behaviour of dispersions of non-spherical colloidal aggregates of boehmite, several dispersions for the two studied boehmite were prepared by osmotic stress for different ionic strengths. For ionic strengths comprised between 10^{-4} and 2×10^{-3} M, we evidence a liquid-gel transition for a constant volume fraction. For the boehmite synthesised by alumina salts precipitation, the volume fraction of the gelation is 2%. For boehmite derived from aluminium alkoxides (Pural SB3), the volume fraction corresponding to the transition is about 1%. For ionic strengths higher than 2×10^{-3} M, the liquid-gel transition is shifted towards lower volume fraction (0.3%). We present a study of the rheological properties of both liquid and gelled dispersions.

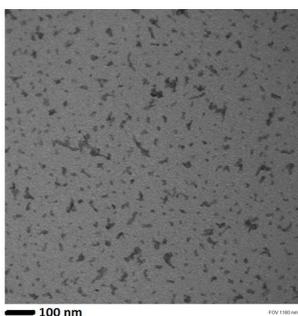


Figure 1 TEM photograph of boehmite (Pural SB3) suspension (magnification: 260kx).

- [1] F. Mange, D. Fauchadour, L. Barré, L. Normand and L. Rouleau, *Colloids and Surfaces A*, 1999, **155**, 199.
[2] S. Lyonnard, J.R. Bartlett, E. Sızgek, K.S. Finnie, Th. Zemb and J.L. Woolfrey, *Langmuir*, 2002, **18**, 10386.

The role of cyclodextrin-tetrabutylammonium interaction on the cellulose dissolution and gelation

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Cellulose dissolution is a challenging process which is typically very sensitive to the solvent characteristics such as pH, temperature or presence of additives. Regarding the later aspect, we here report the interaction between α -cyclodextrin (α -CD) and β -cyclodextrin (β -CD) with the tetrabutylammonium cation (TBA⁺) by ¹H NMR titration experiments. The analysis by the continuous variation method suggests the formation of 1:1 CD:TBA⁺ complexes. However, the computed apparent association constants reveal that the interaction of TBA⁺ with the β -CD ($K=1580$ M⁻¹) is unexpectedly stronger than with α -CD ($K=106$ M⁻¹). In both CD cases, the formation of CD:TBA⁺ complexes decrease the dissolution efficiency of the solvent and this has been rationalized as an effective decrease in the concentration of the amphiphilic cation in solution influencing the overall performance of the solvent. On the other hand, if the cyclodextrins are added after firstly dissolved cellulose, stiff gels can be formed presumably due to CD-TBA⁺ interaction which exposes the less hydrophilic sites of cellulose and allows the formation of a tridimensional gel network. Their rheology and release properties will also be addressed in this communication. Overall, the data supports the fact that amphiphilic species in solution are beneficial for the enhancement of cellulose solubility.

Acknowledgements The authors acknowledge to the Portuguese Foundation for Science and Technology, FCT, projects PTDC/AGR-TEC/4049/2012, PTDC/AGR-TEC/4814/2014 and Pest- OE/QUI/UI0313/2014, researcher grant IF/01005/2014 and PhD grant SFRH/BD/80556/2011. This work was also partially funded by FCT (Foundation for Science and Technology) through the Project No 007630 UID/QUI/00313/2013, co-funded by COMPETE2020-UE.

Cononsolvency vs. temperature: volume phase transition of PNIPAM-based microgels in water/ethanol mixtures in bulk and on surfaces

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Aqueous microgels based on poly(N-isopropylacrylamide) (PNIPAM) exhibit a pronounced response to external stimuli, e.g. temperature. When a critical temperature is exceeded ($\approx 32^\circ\text{C}$ for PNIPAM in water), the swollen microgels undergo a volume phase transition (VPT) and shrink considerably. Additionally, the degree of swelling of those microgels depends on the solvent they are in. A special case occurs when the mixing of two individually good solvents, like water and ethanol, results in a bad solvent. This effect is known as cononsolvency. The microgel shows a minimum swelling for intermediate mixing ratios, and a reswelling for further increase of ethanol content. In the presented study the combination of the temperature response and the cononsolvency effect has been analyzed. Dynamic light scattering (DLS) studies show that the is shifted to lower temperatures in bulk solution with increasing ethanol content. A similar behaviour was observed for gels on a surface with atomic force microscopy (AFM), although the decrease in the volume phase transition temperature was less pronounced here than in bulk. At intermediate ethanol volume fractions at 20-50% the microgels did not swell at all. At higher ethanol volume fractions the gels did reswell, but did not show a clear volume phase transition. The bigger impact of ethanol addition in bulk compared to surface might be due to the preferential interaction of PNIPAM with water. Since the gel is flattened at the surface, the PNIPAM density is higher, so the water ratio inside the gel might be higher than in the surrounding bulk solution. Additionally to pure PNIPAM microgels, microgels with the comonomer acrylic acid have been studied. They generally show a VPT over a broader temperature range. Also here, the VPT occurs at lower temperatures when ethanol is added.

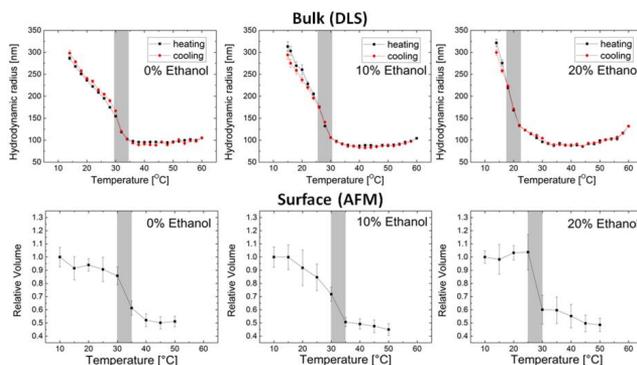


Figure 1 Hydrodynamic radius (upper row, measured by DLS in bulk) and relative volume (lower row, measured by AFM on surface) against temperature for 0, 10, and 20% ethanol volume fraction. The volume phase transition temperature (grey bar) is shown decrease more drastically in bulk than on surface.

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Nanofluids and chemical hydrogels for the selective removal of overpaintings and undesired graffiti from street art

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The removal of graffiti from paintings that must be preserved is a particularly challenging and relatively new issue in conservation of cultural heritage. This is the case of contemporary street art (by unconventional contemporary artists, such as Banksy or Blu) jeopardized by tags, signs and writings. In these conditions, the cleaning action must be extremely selective, as the binder of the undesired paint is likely to have a very similar chemical nature to the one of the underlying original painting. To this aim, in the frame of an Horizon 2020 EU-funded project named Nanorestart, nanostructured fluids, such as micelles and microemulsions, either neat or combined with highly retentive chemical hydrogels was proposed and it is here reported as a selective and controllable cleaning system for the removal of graffiti and overpaintings from street art. The semi-interpenetrating polymer networks-based hydrogels (SIPN) reported in this study are composed by a tridimensional network of poly(hydroxyethyl methacrylate)/N,N'-Methylene bisacrylamide (pHEMA/MBA), interpenetrated by a high molecular weight poly(vinyl pyrrolidone) (PVP). These hydrogels have been shown to be particularly suited to limit the cleaning action to the surface layers of the treated area. pHEMA/PVP hydrogels can be loaded with water, some polar solvents, or with aqueous nanostructured fluids (hereafter, shortly, "nanofluids"), composed by eco-friendly, volatile or auto-degradable compounds, which ensure a residue-free and environmentally compatible cleaning intervention. The studied formulations were structurally characterized by means of scattering techniques and their phase diagram was investigated. Then, they were tested on laboratory samples simulating street art paintings covered by graffiti. The samples were prepared by overlapping different paints in various combinations. The paints included in this study include acrylic, vinyl and alkyd binders, while several colors were tested. The outcome of cleaning tests was investigated by means of visual, photographic and microscopic observation, while micro-reflectance FT-IR spectroscopy was performed on the treated area before and after the application of the cleaning systems, in order to gather information about the chemical composition of the surface, searching for possible residues of the removed paint layer. Setting up application times and performing careful and delicate mechanical action were found to be key factors when removing overpaintings having the same binder as the original paint layer. However the removal of acrylic (or vinyl) paints from other acrylic (or vinyl) paints was achieved with minimum stress for the original paint layer. Microscopic observation and FT-IR analysis of the treated areas confirmed the good results of the cleaning tests.

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Encapsulation of small molecules by poly(ethylene glycol)-*graft*-poly(vinyl acetate) unimer micelles

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Single chain nanoparticles are unimolecular nano-objects typically obtained by the self-folding of linear polymer chains that possess small pendant groups or longer side chain that can interact with each other via intra-chain interactions or by application of external *stimuli*. These systems are typically exploited in the mimicking of the hydrophobic compartments of biomacromolecules and in more technical applications (e.g., catalysis and nanomedicine)[1]. Although from an industrial point of view there is a growing attention towards these nano-carriers, for more technical applications the use of polymer chains with simplified structure and a higher concentration of particles than the typical 1 mg mL^{-1} is recommended [2].

In this work we report on the formation of unimer micelles composed of amphiphilic poly(ethylene oxide)-*graft*-poly(vinyl acetate) copolymers with an extremely low degree of grafting that undergo self-folding in water driven by hydrophobic interactions only. This results in the formation of unimer micelles with a hydrodynamic diameter of about 20 nm. With respect to the typical linear complex-structured polymer chains, this material is best suitable for technical applications because of the simple molecular architecture and stability of unimeric micelle suspensions up to 100 mg mL^{-1} . The so-obtained single-chain globular particles are able to swell upon loading with small hydrophobic molecules therefore promoting micellar solubilization of flavors or drugs, which could be of interest in the food and pharmaceutical industry.

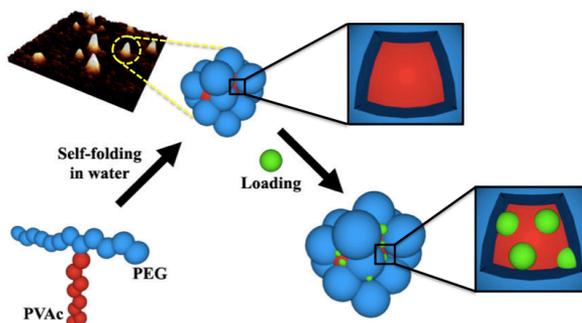


Figure 1 Schematic representation of PEG-g-PVAc chains self-folding into unimer micelles and swelling upon loading of small hydrophobic molecules.

Acknowledgements The financial support of Procter & Gamble.

[1] Hanlon A. M.; Lyon, C. K.; Berda E. B., *Macromolecules*, 2016, **49**, 2-14.

[2] Stals P. J. M.; Gillissen M. A. J. et al., *Macromolecules*, 2014, **47**, 2947–2954.

Microrheology of polymeric gelling systems

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The sol-gel transition of complex fluids, like polymeric gels, is an interesting topic from a fundamental point of view [1]. It is also a very relevant area in many technological applications [2], such as the preparation of different advanced materials, or the use of gelling systems as additive thickeners in many products like foods and personal care, among others.

During gelation a fluid solution (sol) is converted into a disordered solid (gel) usually, but not only, by a change in temperature being this process generally reversible. Furthermore, changes of concentration can lead to the transition at constant temperature, although in this case the process is irreversible. Physical gels, in contrast to chemical ones that occur due to chemical reactions, form as a consequence of intermolecular associations. There is a great variety of intermolecular forces (van der Waals, electrostatic, acid-base, hydrogen bonding, etc.) that can act, individually or in combination, to produce the association, which is the first step before gelation occurs.

We will present results corresponding to two rather different polymeric gelling systems: agarose and pluronic (F68) water solutions, that we have study using diffusing wave spectroscopy (DWS) in combination with other micro-rheological techniques and with a conventional oscillatory rheometer. Those systems have been study in a broad temperature and concentration range, in order to locate the sol-gel transition and then to characterize the viscoelastic behaviour, within the sol regime [3]. The gelling kinetics will also be discussed.

DWS measurement were performed using probe particles (light scatterers) of different nature and size, from the intensity autocorrelation function the mean square displacement, $\langle \Delta r^2(t) \rangle$, of the probes have been obtained and analysed using both model expressions for the mean square displacement and direct Laplace inversion to obtain the complex viscoelastic modulus from the generalized Stokes-Einstein equation.

Both systems present a viscoelastic behaviour that has been described using an extended Maxwell mode, and the results obtained by DWS in the high-frequency range correlate well with the low-frequency ones obtained with the conventional rheometer.

Acknowledgements We are grateful for the financial support of COST MP1106, of CoWet ITN (E.U.), and of MINECO through grants FIS2014-62005-EXP and FIS2012-38231-C02-01.

[1] H.H. Winter, M. Mours, *Adv. Polym. Sci.*, 1997, 134.

[2] E. Faure, E.; C. Falentin-Daudré, T.S. Lanero, C. Vreuls, G. Zocchi, C.V.D. Weerd, J. Martial, C. Jérôme, A.-S. Duwez, C. Detrembleur, *Adv. Funct. Mat.* 2012, **22**, 5271.

[3] T.G. Mason, *Rheol. Acta* 2000, **39**, 371A.

Gelling properties of (bio)polyelectrolyte complexes of ionic polysaccharide with gelatin

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Biopolyelectrolyte complexes formation from complementary polysaccharides and proteins is one of the priorities issues of modern colloid science of biopolymers. These complexes are the basis for creating a wide range of new materials used in biotechnology, biomedicine, pharmaceuticals and food industries.

The characteristics of the intermolecular interaction of κ -carrageenan (an anionic polysaccharide from red seaweeds) and chitosan (a cationic polysaccharide from shrimp shells) with gelatin under the formation of biopolyelectrolyte complexes in the bulk of the aqueous phase have been studied. Spectroscopic methods – ¹H NMR, FTIR spectroscopy, ultraviolet absorption spectroscopy, turbidimetry; scanning electron microscopy, and the rheological techniques – capillary viscosimetry, shear deformation mode at a constant shear rate, dynamic mechanical analysis were used.

The experimental data are interpreted in terms of changes in the role of various intermolecular interactions under the formation of polysaccharide–gelatin complexes. It is shown that at high temperatures hydrophobic interactions contribute significantly to stabilization of the complexes. At the temperatures at which the conformational transition of gelatin occurs (and at a lower temperature) electrostatic interactions and hydrogen bonds play the crucial role [1].

A good correlation between the structure of the polysaccharide–gelatin complexes in solution and rheological properties of gels formed from these solutions has been set up [2]. It is shown that the adding of even a small amount of the polysaccharide causes significant changes in the supramolecular structure of the gelatin gel. The supposed models of the complexes of polysaccharide with gelatin have been discussed.

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[1] N. Voron'ko, S. Derkach, Yu. Kuchina and N. Sokolan, *Carbohydrate Polymers*, 2016, 138, 265.

[2] S. Derkach, I. Zhabyko, N. Voron'ko, A. Maklakova and T. Dyakina, *Colloids and Surfaces A: Physicochem. Eng. Aspects*. 2015, 483, 216.

Understanding Critical Behaviour of pNIPAm: Hydration/dehydration, Solvent Deuterium Isotope Effects, and Cononsolvency

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As is well known, poly(*N*-isopropylacrylamide) (pNIPAm) has a lower critical solution temperature (LCST) in aqueous media [1]; when temperature (T) is raised, pNIPAm chains undergo a coil-to-globule transition at about 32–34 °C. In many small-angle neutron scattering (SANS) studies, D₂O is used as solvent [1][2]. However, solvent deuterium isotope effects are in a sense versatile depending on the system and sometimes cannot be neglected. First, we examined static structure of semi-dilute pNIPAm in H₂O and D₂O by means of simultaneous small- and wide-angle X-ray scattering (SWAXS) in the extended q -range of 0.072 - 20 nm⁻¹. We show how solvent deuterium isotope effects affect T_c and the critical exponents of pNIPAm characterizing the divergence of the length-scale of density fluctuation and the osmotic compressibility. We also used dielectric relaxation spectroscopy (DRS) in the frequency range of $0.2 \leq \nu/\text{GHz} \leq 89$ to monitor the kinetics of hydration and bulk water molecules in aqueous pNIPAm solution. SWAXS and DRS results demonstrate how dehydration of pNIPAm's sidechain groups at high T , mediated by hydrophobic interaction, is closely related to the formation of polymer-rich and water-rich domains and segregation of the polymer chains. Next, we investigated critical behaviour of pNIPAm in water/methanol mixed solvent by means of SWAXS at methanol molar fractions, $X_m = 0.05, 0.10, 0.15, 0.20, 0.45, 0.80, \text{ and } 1$. As we mentioned, water can be either a good or poor solvent for pNIPAm depending on T . On the other hand, methanol is a good solvent independent of T below its boiling point. However, a mixed solvent comprising these two good solvents can be a poor solvent depending on solvent composition [3][4], which is called cononsolvency. Although the underlying mechanisms of cononsolvency of pNIPAm are still in debate, we found that the singular concentration for mixing schemes in methanol/water mixtures as revealed by previous DRS study seems to be linked with the phase boundary of pNIPAm in methanol/water mixtures. We observed critical behaviour depending on T as well as X , the correlation length ξ showing diverging behaviour when either a critical temperature or a critical composition is approached. Addition of methanol to water enhances hydrophobic interaction between the sidechain groups of pNIPAm. Finally, we move on the critical behaviour of pNIPAm-based microgels in dispersion. A series of microgel samples were prepared via aqueous free-radical precipitation polymerization using a water-soluble anionic initiator KPS, in which *N,N'*-methylenebis(acrylamide) (BIS) was used as a crosslinking agent. We observed simultaneous divergence of the correlation length, interpreted as the mesh-size of the transient polymer network, and the asymptotic Ornstein-Zernike forward intensity, being inversely proportional to the osmotic compressibility, when T_c is approached, whose features are, however, considerably different from those of the well-established pNIPAm-based bulk gels belonging to the Ising universality class. We try to explain why the microgels exhibit such unconventional behaviour.

[1] M. Shibayama, T. Tanaka, and C. C. Han, *J. Chem. Phys.* **97**, 6829 (1992).

[2] A. Meier-Koll, et al., *Langmuir* **28**, 8791 (2012).

[3] F. M. Winnik, H. Ringsdorf, and J. Venzmer, *Macromolecules* **23**, 2415–2416 (1990).

[4] I. Bischofberger, D.C.E. Calzolari P. De Los Rios, I. Jelezovor, and V. Trappe, *Scientific Reports* **4**, 4377 (2014).

Kinetic effect of Pluronic F108 aqueous solutions on the gel formation

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It is well understood that temperature induced gelation occurs after the micellization process of Pluronic surfactants allowing for the incorporation of hydrophilic and hydrophobic drugs as formulated injectables and as drug-delivery vehicles. In this study, the thermophysical properties, especially gel formation, of Pluronic F108 aqueous solutions with concentration ranging from 6 to 38 wt% by a heating process from 10 to 90 °C were carefully examined. Tube inversion method was adopted to develop a preliminary outline of gel phase diagram as a reference of no kinetic effect. Rheometry was used to study the kinetics of gelation with heating rate ranging from 0.1 to 10 °C /min to enable us to characterize gelation temperatures. In addition, a differential scanning calorimetry was applied not only to observe the thermal changes of gelation, but also to acquire the critical micellization temperatures (CMT). During the heating process, the F108 aqueous solution would gradually behave a transition from solution to soft gel and then become hard gel at a gelation temperature $T_{\text{soft-hard}}$. Further heating would change the gel structure back to soft gel at another gelation temperature $T_{\text{hard-soft}}$. Both of the CMT and $T_{\text{soft-hard}}$ decrease with an increase in F108 concentration, while the $T_{\text{hard-soft}}$ increases. Based on the experimental results of rheometry, it is interesting to observe that the positive shift of $T_{\text{soft-hard}}$ (compared to that of tube inversion method) becomes more pronounced at higher heating rates. In contrast, the $T_{\text{hard-soft}}$ has a stronger negative shift at higher heating rates. This may be attributed to the weaker gel structure forming at higher heating rates. The extent of the positive/negative shifts of gel phase boundaries was summarized to construct the complete gel phase diagram of F108 aqueous solutions at different heating rates.

Aggregation in wormlike micelles of ternary lecithin, water, sodium deoxycholate systems in organic solvent

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Lecithin Organogels of wormlike micelles usually take place in organic solutions as primer to lecithin ratio increases towards a critical value, where the primer can be represented by water [1], bile salts [2] or other molecules[3].

The role of the primer in the self-assembly process observed in lecithin-primer organic solutions has been partially clarified [4] and only a few bile salts and water effects have been investigated separately[5].

This study wants to elucidate the phase behaviour and the formation of wormlike micelles gels in ternary mixtures of phosphatidylcholine, water, sodium deoxycholate in cyclohexane. The resultant appearance of wormlike micelles as a function of bile salt fraction B_0 and water fraction W_0 and the consequent induction of gel-like behaviour of the colloidal system have been analyzed by rotational rheometry. Structural analysis of the aggregates in solution have been performed by small angle X-ray scattering (SAXS) and Dynamic Light Scattering (DLS).

The main findings are: i) water and sodium deoxycholate, because of their peculiar polar properties, are capable to insert as intercalation agents between heads of lecithins, modifying the packing factor of the aggregation fundamental units, inducing a sphere-to-rod transition of the aggregates. ii) water and sodium deoxycholate give rise to a complementary interaction with the polar head of lecithin, as showed in fig.1. Indeed, a large primer mixture excess determines a phase separation in simple primer lecithin systems and the separation occurs at high B_0 if W_0 is kept low and viceversa. iii) A slight increase in the wormlike micelles cross section is observed by increasing W_0 . v) Despite organogels with two primers have rheological properties very similar to those of binary water lecithin and bile salts lecithin mixtures, still are present many differences when a more accurate investigation of relaxing times of the wormlike micelles network is taken into account.

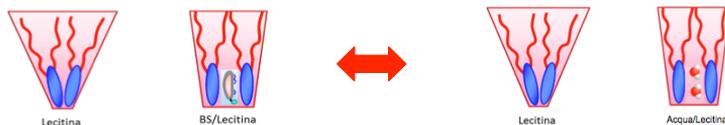


Figure 1 Complementary role of water and sodium deoxycholate as aggregation primer in lecithin wormlike micelles

[1] Angelico R., Ceglie A., Olsson U., Palazzo G., *Langmuir*, 2000, **16**, 2124-2132

[2] Raghavan S.R., Huang Y., *J. Am. Chem. Soc.*, 2006, **128**, 5751-5756

[3] Hashizaki K., Imai M., Saito Y., *J. Coll. Interface Sci.*, 2013, **403**, 77-83

[4] Tung S., Khokhlov A. and Ivanov V., *Langmuir*, 2013, **29**, 3879-3888

[5] Raghavan S.R., Huang Y. and Tung S., *Langmuir*, 2007, **23**, 372-376

Poly(aspartic acid) hydrogels showing reversible volume change upon redox stimulus

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The shortcomings of conventional solid drug formulations – e.g. non-effective or toxic blood levels of drug – might be overcome by the use of formulations providing controlled delivery. Responsive hydrogels can be developed to such formulations because they are able to control the release of their payload by changing their physical properties upon environmental stimuli [1]. Redox sensitive hydrogels have gained particular attention in targeted delivery, since they respond to the redox gradient in the body caused by the different glutathione concentrations in the cytosol (0.5–10 mM) and in the extracellular matrix (2–20 μ M) [2]. Most of the reported hydrogels exhibited only a one-way response and disintegrated upon reduction [3]. Redox-responsive gels with a reversible volume change [4] would have a large advantage: a modulated release controlled by the pathological state of the patient could be achieved similarly to the glucose dependent release of insulin from certain nanogels [5].

Redox and pH sensitive poly(aspartic acid) (PASP) based hydrogels were prepared by cross-linking cysteamine-modified PASP with a non-cleavable (permanent) cross-linker, poly(ethyleneglycol)dyglycidyl ether. The volume of the hydrogels increased upon reduction and decreased upon oxidation (Fig 1) due to the reversible cleavage of disulphide linkages inside the matrix as proven by infrared spectroscopy. The degree of swelling was highly dependent on the thiol-content and the cross-linking ratio. Mechanical stiffness of hydrogels was characterized by their elastic modulus, which was also strongly affected by the composition and oxidation state. To explore the possible biomedical use of the hydrogels, hydrogel loaded with model drug was prepared. Drug release measurement showed that the drug release was remarkably faster in reducing environment, which indicates the potential use of the synthesized hydrogels for redox-modulated drug delivery.

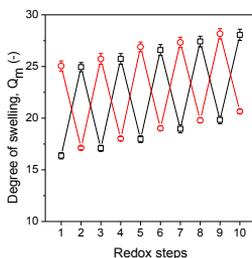


Figure 1 Degree of swelling of redox-sensitive poly(aspartic acid) hydrogels upon repeated oxidation/reduction.

- [1] R. Cheng, F. Feng, F. Meng, C. Deng, J. Feijen, Z. Zhong, *Journal of Controlled Release*, 2011, **152**, 2.
- [2] F. Meng, W. E. Hennink, Z. Zhong, *Biomaterials*, 2009, **30**, 2180.
- [3] B. Gyarmati, A. Nemethy, A. Sziagy, *RSC Advances*, 2014, **4**, 8764.
- [4] E. Krisch, L. Messenger, B. Gyarmati, V. Ravaine, A. Szilágyi, *Macromolecular Materials and Engineering*, 2016, **301**, 260.
- [5] C. Anclá, V. Lapeyre, I. Gosse, B. Catargi, V. Ravaine, *Langmuir*, 2011, **27**, 12693.

Rational design of Au@PNIPAM core-shell nanoreactors with tunable selectivity for catalysis

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Gold nanoparticles have been extensively studied in the last decades due to their catalytic properties, which significantly differ from the bulk metal [1]. Since the free nanoparticles tend to aggregate and are difficult to handle in catalytic applications, stimuli-responsive polymer coatings have been developed to encapsulate and stabilize the nanoparticles [2,3]. The polymer coating not only prevents particles from aggregation but also controls the catalytic activity and selectivity by changing the local environment for the reactants. Thus, the catalytic rate can be flexibly tuned and switched by parameters such as temperature [3,4], ionic strength or pH.

In this work we report the synthesis of thermosensitive core-shell nanoreactors, composed of a polystyrene core, embedded in a poly(N-isopropylacrylamide) (PNIPAM) network in which the gold nanoparticles are immobilized. We demonstrate that the catalytic activity of the gold nanoparticles can be tuned by the volume transition within the polymer shell by using the catalytic reduction of 4-nitrophenol as a model reaction [3,5]. More importantly, we show that the catalytic selectivity of the system can be tuned by temperature as is shown by the competitive reduction of the hydrophilic 4-nitrophenol and the hydrophobic nitrobenzene by borohydride [3,4]. We qualitatively and quantitatively describe the catalytic rates in the stimuli-responsive nanoreactors by using a theoretical framework that extends concepts from the Debye-Smoluchowski theory of diffusion [4].

- [1] R. Sardar, M.A. Funston, P. Mulvaney, R.W. Murray, *Langmuir*, 2009, **25**, 13840.
- [2] Y. Lu, M. Ballauff, *Prog. Polym. Sci.*, 2011, **36**, 767.
- [3] S. Wu, J. Dzubiella, J. Kaiser, M. Drechsler, X. Guo, M. Ballauff, and Y. Lu, *Angew. Chem., Int. Ed.*, 2012, **51**, 2229.
- [4] S. Angioletti-Uberti, Y. Lu, M. Ballauff, and J. Dzubiella, *J. Phys. Chem. C*, 2015, **119**, 15723.
- [5] P. Hervés, M. Pérez-Lorenzo, L.M. Liz-Marzán, J. Dzubiella, Y. Lu, and M. Ballauff, *Chem. Soc. Rev.*, 2012, **41**, 5577.

Polyelectrolytes: solution behavior and application in papermaking process

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Besides rising energy expenses, the rising material costs of raw and auxiliary materials as well as costs for the water demand represent a significant cost factor in the production of paper. Despite water is moved in cycle in the papermaking process, the addition of fresh water is necessary.

Some of the auxiliary materials in papermaking process are polyelectrolytes (PEL) used for flocculation of cellulose fibers. The PEL are added to the cellulose fiber pulp in solute state. Its quality affects the paper quality too.

The objectives of this research project are to minimize fresh water consumption as well as reducing the amount of PEL that is required for an optimum flocculation. For using polymeric additives with their maximum efficiency low recycling costs are consequentially essential to obtain a basic knowledge on PEL and their mode of action available.

A better dissolution of PEL as well as an optimized matching ratio of PEL and pulp should result in a complete conversion of PEL and cellulose. Hence, unnecessary residues and the formation of stickies in the remaining water should be avoided.

To determine the parameters which lead to optimal polymer solutions and their optimum use in the papermaking process different PEL granulates particularly based on polyacrylamide were dissolved with different technical methods (ultrasonic treatment, using a DISPORMAT[®] dissolver and Ultra-TurraX[®] etc.). Subsequently, the states of dissolving were characterized especially by rheology. The determination of storage (G') and loss (G'') modulus allows statements to the inner structure of the polymer solutions in terms of entanglements of polymer chains. Charge densities of the PEL in solution were determined by PEL titration based on streaming potential in each solution state.

In a second step, the dissolved PEL were tested for flocculation on cellulose / CaCO₃ system. The results of flocculation were assessed by centrifugal separation analysis (LUMiSizer[®]), turbidity, COD and TOC.

Acknowledgement

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Nanogels of chitosan and hydrophobically modified chitosan

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The present work is devoted to the study of chitosan and hydrophobically modified (HM) chitosan multichain clusters in dilute aqueous solutions. Clusters were observed by light scattering and transmission electron microscopy (TEM). It was demonstrated that the size of clusters and their aggregation numbers increase at the introduction of hydrophobic side groups into polymer chains. The key result concerns the effect of the chain length of individual macromolecules on the aggregation behavior. It was shown that both for unmodified and HM chitosan the size of clusters is independent of the length of single chains, which may result from the electrostatic nature of the stabilization of clusters. At the same time, the number of macromolecules in one cluster increases significantly with decreasing length of single chains in order to provide a sufficient amount of associating groups to stabilize the cluster. The analysis of the light scattering data together with TEM results suggests that the clusters of chitosan and HM chitosan represent spherical nanogels with denser core and looser shell covered with dangling chains.

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Fast temperature screening for viscosity determination of thermoresponsive polymers by microfluidic

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Viscosity is an essential physical property when studying polymers behavior. However rheological studies remain a challenging task for many laboratories as traditional techniques are time consuming and do not allow to measure samples in desired conditions. We propose a new instrument: FLUIDICAM to measure viscosity as a function of shear rate and temperature in a single experiment set-up. Using a small sample volume, the technology allows flow viscosity measurements of liquid products from water-like inks to thick cosmetic formulations, under a wide range of shear rates (including high values up to 105 s^{-1}).

During the measurement a sample and a viscosity standard are pushed together through a microfluidic chip (Y-junction) at controlled flow rates. Images of the resulting laminar co-flow are acquired with digital camera and the position of the interface is measured. The position is related to the viscosity and the ratio of flow rates between the sample and the reference allowing to determine the viscosity.

In this work, bio triblock copolymers (Ploxamers - $(\text{PEO})_x(\text{PPO})_y(\text{PEO})_x$) and PNIPAm (Poly(N-isopropylacrylamide)) were studied. They are well known for their reversible phase transitions (sol-gel) under specific thermal conditions and thus they are good candidates for innovative drug delivery systems. We have used solutions at various concentrations to measure the viscosity between 5 and 80°C in less than an hour (5min per temperature step). This work will demonstrate the influence of the polymer concentration on viscosity variation and prove the capabilities of FLUIDICAM to conduct fast temperature screening measurements.

Photo-responsive PVA based materials: study of their filming and self-assembling properties

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Poly(vinyl alcohol) (PVA) is a water-processable polymer already employed in a huge variety of industrial applications (adhesives, emulsificants, membranes, etc.). Due to its biodegradable and non-toxic nature it is particularly appropriate as a pharmaceutical and biomedical material; furthermore, because of the readiness to chemical reactions *via* its secondary alcohol functionalities, the controlled modification of the polymer chains allows for conceiving of new compounds with programmed and triggerable physico-chemical properties.¹

In this work, we describe the modification of PVA with small amounts of cinnamic acid moieties resulting in the obtainment of different biocompatible and photo-responsive PVA derivatives. In fact, upon UV light exposure, cinnamic acid pendants are well known to undergo a [2+2]-photocycloaddition between close fragments² resulting in a cross-linked material. Furthermore, cinnamate functionalization definitely represents a cleaner and safer alternative to the use of other photosensitive functional groups (such as acrylates or styrylpyridinium based systems)^{3,4}. Three derivatives of this class, with different loadings of cinnamic acid (namely 0.7, 2.5 and 3.8 mol%), have been prepared through a simple synthetic protocol and characterized by means of NMR, UV/Vis spectroscopy and thermal analysis. Moreover, the efficiency of photo-crosslinking reaction has been measured both in solution and in films through UV/Vis and IR spectroscopy. The extent of functionalization is a crucial parameter in the physico-chemical behavior of these systems: the delicate balance between the very different nature of the hydrophilic backbone and hydrophobic cinnamic acid pendants results in peculiar interfacial and self-assembling properties. In water, the obtained dispersions were characterized by surface tension and dynamic light scattering measurements. Different degrees of functionalization result in a huge variation of the air/water interfacial tension, as well as in the size of the colloidal objects formed in water, which could also be tuned by photoirradiation. In terms of filming properties, different amounts of cinnamic units are responsible for the different macroscopic behaviors and, in the films prepared by solvent casting, for the characteristic morphological features observed by means of atomic force microscopy.

In conclusions, this contribution demonstrates how the introduction of cinnamic moieties along the PVA chain through a facile protocol allows for the tuning of both the self-assembling and filming properties of functionalized PVA, including the possibility to further trigger a change in its structure by photo-irradiation.

Acknowledgements CSGI is acknowledged for financial support.

[1] S. Moulay, *Polymer-Plastics Technology and Engineering*, 2015, **54**, 1289.

[2] C. D. Petruczok, E. Armagan, G. O. Ince and K. K Gleason, *Macromol.Rapid Commun.*, 2014, **35**, 1345.

[3] H. Bai, J. Xu, Y. Zhang, X. Liu and O. J. Rojas, *J. Polym. Sci. B Polym. Phys.*, 2015, **53**, 345.

[4] C. R. Nuttelman, S. M. Henry and K. S. Anseth, *Biomaterials* 2002, **23**, 3617.

Primary Structure and Composition: Tailored Thermo-, Oxidative and Thermo-Oxidative Responsiveness of Polysulfides

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The ability to tune the responsiveness of polymers is of the utmost importance to achieve fit for purpose properties.¹ This work shows how chemical composition and primary structure allows for the fine tuning of both thermal and oxidative responsiveness of polysulfide-based amphiphilic nanomaterials. Poly(ethylene glycol)(PEG)-polysulfide-PEG triblock copolymers were synthesised with the core polysulfide containing various length, monomer composition (different ratios of propylene sulfide (PS) to ethylene sulfide(ES)) and due to the large difference in monomer reactivity different monomer-addition protocols were employed (i.e. one or multiple additions of monomer); this library of polymers were then tested in regards to their thermal-gelling properties and oxidation responsiveness to model oxidant H₂O₂. The results suggest that oxidative responsiveness was solely affected by the molecular composition of the polymer whereas the thermal properties were mainly controlled by the primary structure and the resulting changes in the supramolecular interactions.² With biotechnological applications in mind, the technology has now been extended to larger particle formulations, where the hydrophobic poly(PS-co-ES) have been polymerized in emulsion and crosslinked to afford nanoparticles with a good control over both monomer composition and size, with Z-ave. ranging from 50-170 nm.

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References:

1. N. Kamaly, B. Yameen, J. Wu and O. C. Farokhzad, *Chemical Reviews*, 2016, **116**, 2602-2663.
2. R. d'Arcy, A. Siani, E. Lallana and N. Tirelli, *Macromolecules*, 2015, **48**, 8108-8120.

The Asymmetric Restricted Primitive Model of Molten Salts and Ionic Liquids

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Recall the restricted primitive model (RPM), where ions are modelled as hard spheres, all of diameter d , carrying a charge at their centres. In the simplest charge-symmetric case, this charge has the same absolute value. The presence of any dielectric medium (solvent) is simply represented by its relative permittivity, ϵ_r . The RPM has been very useful for statistical mechanical analyses of electrolyte solutions, molten salts, and plasmas. Here we introduce an extension to the RPM, namely the asymmetric restricted primitive model (ARPM), which allows a new mechanism to enter, controlled by a single parameter b . This parameter measures a displacement of the charge from the centre of the hard sphere. Such a displacement, when uniformly applied to all particles, leaves the model very simple. Nevertheless, b introduces a new mechanism that we believe is of crucial importance to many systems, such as ionic liquids. The presence of a non-vanishing displacement b means that the ions now have an internal structure, generating orientational correlations, with an increased propensity (for a sufficiently large value of b) to form effective dimers (ion pairs) with oppositely charged ions. This is expected to significantly alter the properties of the fluid, including:

- lower freezing temperature
- reduced efficiency of ionic screening, i.e. a longer screening length
- reduced conductivity
- dielectric response, brought about by orientational correlations of dipolar ion pairs

The ARPM is likely to have properties that are reminiscent to a mixture of an RPM fluid and a dipolar fluid, where the dipoles are generated by ion pairs. We believe that the puzzle of room temperature ionic liquid (RTIL) melting points to a large extent can be rationalized in terms of dimerization, as described by the ARPM. There are recent surface force measurements [1,2] that suggest an extremely high degree of ion pairing (more than 99 %) in a typical RTIL, as indicated by measured very long-ranged double-layer interactions.

We have performed simulation studies that confirm the conjecture of a much lower melting temperature of ARPM systems, relative to the corresponding RPM. Simulation works focusing on the remaining conjectures are underway. An interesting structural observation is that radial distribution functions (RDFs) tend to vary with the displacement b in a non-monotonic fashion. This can be rationalized in terms of rotational entropy and orientational correlations.

[1] Gebbie A. M., Valtiner M., Banquy X., et al., *PNAS* **110**, **9674** (2013).

[2] Gebbie A. M., Bobbs A.H., Valtiner, M., et al., *PNAS* **112**, **7432** (2015).

A new model to predict efficiency of cleaning systems: HLD parameter

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Cleaning is crucial to many applications, ranging from detergency processes in laundry and hand-washing applications to the removal of detrimental films from solid substrates. Water-based systems for cleaning typically consist of dispersions in water of surface-active agents and additives such as perfumes and rheo-modifiers. This project aims at identifying a model able to predict the detergency performances of water-based cleaning systems on hard surfaces. In order to reproduce the general composition of commercial detergent formulations[1], we investigated the behavior of a model system made of an anionic surfactant (Sodium Dodecyl Sulfonate, SDS), a cationic surfactant (Benzalkonium Chloride, ADBC) and a non-ionic surfactant (Triton X 100, TX100). Their ternary phase diagram was investigated and the stable compositions were characterized using physico-chemical techniques such as Dynamic Light Scattering, rheometry and Small-Angle X-ray Scattering. Glass surfaces coated with Argan Oil or Artificial Sebum were cleaned using the stable formulations. Atomic Force Microscopy (AFM), Optical Microscopy (OM) and Contact Angle have provided information about the soil removal efficiency. Aiming at modeling the performances of the cleaning formulations towards surfaces coated with soil, the results were then discussed in terms of the Hydrophilic-Lipophilic Difference (HLD) of each formulation. The HLD of a water-in-oil or a oil-in-water surfactant formulation is defined according to the characteristic curvature of the surfactant, to the salinity of the aqueous phase, to the temperature, and to the effective alkane carbon number of the oil phase. The obtained results suggest the possibility to use the HLD parameter to predict the cleaning performances of different formulations [2-3].

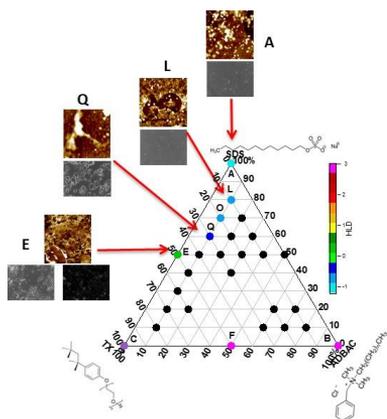


Figure 1 Ternary Diagram: correlation between HLD parameter and AFM e OM measurements for cleaning systems studied.

- [1] P.M. Holland, D. N. Rubingh., *ACS Symposium Series; American Chemical Society*, 1992, **501**.
- [2] J.L. Salager, *Colloid Surf A*, 1995, **100**, 217–224
- [3] E. J. Acosta, S. K. Kiran, C. E. Hammond, *J Surfact Deterg*, 2012 **15**, 495–504

Molecular mechanisms associated with non-linear growth regimes of polyelectrolyte multilayers

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Nonlinear growth regimes of electrostatically assembled polyelectrolyte multilayer films are studied ellipsometrically under in situ conditions. Poly(styrenesulfonate) (PSS) and poly(diallylmethylammonium) (PDADMA) with different molecular weights in 0.1 mol/L NaCl and 30 min adsorption time are used. Always, the linear growth is preceded by a parabolic growth regime. Neutron reflectivity shows that the center of mass of PSS molecules is vertically immobile, in both the parabolic and linear growth regimes. For films made from binary PDADMA mixtures, the compositions in the film and the adsorption solution are nearly identical. The parabolic growth regime is attributed to the different linear charge density of PDADMA and PSS and described by a molecular model.

If the molecular weight of PSS is reduced below a threshold, 25 kDa, the multilayer build-up starts with an exponential growth regime, and pronounced PSS interdiffusion is found with neutron reflectivity. The exponential build-up regime is extended on decrease of PSS molecular weight. For films made from binary PSS mixtures, addition of less than 1 mol % PSS with molecular weight above the threshold prevents the formation of an exponential growth regime.

Aqueous Solutions of Hydrophobically Modified Polyacrylic Acids: Polymer Chain's Length Effect

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In the present study surface characteristics of aqueous solutions of hydrophobically modified polyacrylic acids are systematically explored in order to estimate the polymer chain's length effect. Two types of polyacrylic acids are used: PAA25C₁₂ (MW=25000) and PAA150C₁₂ (MW=150000), both randomly grafted with 3% (units mol) dodecyl (C12) chains. For the studied systems both adsorption layers and microscopic foam films are obtained.

The dynamic, equilibrium and rheological properties of adsorption layers at solution/air interface are investigated by profile analysis tensiometer in a bubble mode (PAT-1, Sinterface). Experiments, concerning foam films properties (kinetic of drainage, disjoining pressure vs. film thickness isotherms, stability, etc.) are conducted using the microinterferometric method of Sheludko-Exerowa and the Thin Liquid Film-Pressure Balance Technique.

The obtained results contain valuable information about the specific behaviour of the investigated systems at the solution/air interface and in foam films. They are interpreted in terms of intramolecular/intermolecular interactions and their response to changes in the polymer chain's length under different experimental conditions.

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Physico-chemical characterization and mineralization of gelatin and poly (vinyl alcohol) hydrogels

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Hydrogels are an important class of materials that are widely investigated for their potential use in soft tissue engineering. Among the hydrogel-forming polymers, gelatin and polyvinyl alcohol (PVA) represent two significant examples since they are biocompatible, biodegradable, and already used in a variety of industrial applications. Gelatin has the same composition of the organic component of the natural extracellular matrix. In tissue engineering, gelatin has been used to develop porous scaffolds^{1,2} and nanocomposites³ for bone remineralization. Gelatin gels have also been used for delivery of growth factors to promote vascularization of engineered new tissue.⁴ However, gelatin's poor mechanical resistance generally requires chemical cross-linking processes and/or the integration with inorganic fillers to produce hybrids with enhanced load bearing properties. Polymer blending is a technique largely applied in polymer science to obtain materials whose physical properties depend on composition and may be modulated through compositional changes. Gelatin and PVA have already been combined to obtain blend hydrogels and films for various applications. It is known from the literature⁵⁻⁶ that PVA forms mechanically compatible blends with collagen and gelatin, and that the turbidity of the mixed solutions results from the formation of uniform particles by coacervation, because of hydrogen bonding interactions between -OH groups of PVA and -COO⁻ and -NH₃⁺ groups of gelatin. However, there is still a need of an extensive physico-chemical understanding, especially regarding the structure and the interactions at the molecular level, as well as the evaluation of their potentials as effective biomaterials.

The present contribution deals with the characterization of the ternary gelatin/PVA/water system, the chemical cross-linking of selected hydrogel-forming compositions, and the study of their mineralization in simulated body fluid (SBF). A stability ternary phase diagram was realized to evaluate the interactions between the two polymers at varying concentration and gelatin/PVA ratio, at 37°C. Then, a point of the phase diagram was selected and fully characterized by means of SEM, DSC, SAXS, FT-IR and rheology (flow curves and frequency sweep). The selected specimen was chemically cross-linked in order to enhance the thermal stability of the hydrogel with two biocompatible bis-epoxy molecules, namely glycerol diglycidyl ether (GDE) and 1,4-butanediol diglycidyl ether (BDGE). The freeze-dried cross-linked hydrogels were soaked in SBF at 37°C, for different times (up to a week), and the mineral phase was characterized through TGA, cross-sectional SEM and XRD. The results demonstrate that the interactions between gelatin and PVA take to the formation of a hydrogel, which could be successfully cross-linked. In particular, hydrogels cross-linked with BDGE show in SBF very promising stability and mineralization properties. Taking into account the biocompatibility and biodegradability of both Gelatin and PVA, we believe that these results could represent a significant contribution in the field of soft biomaterials for bone tissue regeneration.

Acknowledgements Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase (CSGI) is acknowledged for financial support.

[1] S. Van Vlierberghe *et al.*, *Biomacromolecules*, 2007, **8**, 331.

[2] X. Liu, P.X. Ma, *Biomaterials*, 2009, **30**, 4094.

[3] X. Liu *et al.*, *Biomaterials*, 2009, **30**, 2252.

[4] M. Yamamoto *et al.*, *J. Bioact. Compact Polym.*, 1999, **14**, 474.

[5] B. Sarti, M. Scandola, *Biomaterials*, 1995, **16**, 785

[6] T. Tanaka, S. Ohnishi, K. Yamamura, *Polym. Int.*, 1999, **48**, 811.

Influence of compatibility on oligomer partitioning in model adhesives.

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Additive surface segregation is a well-known phenomenon in complex polymer formulations. In industrial adhesives, tackifiers – i.e. aliphatic or aromatic oligomers – are added to enhance adhesion by decreasing the polymer's elastic modulus at the interfaces. However, phase separation between the tackifier and polymer could result in loss of adhesion or contamination of adjacent materials.

We combine experiments with theory and computational simulations to develop and validate a model describing oligomers' segregation. A binary model formulation, consisting of an aliphatic oligomer and a rubbery polymer was chosen to mimic the behaviour of tackifiers in hot-melt adhesives.

Compatibility between the two components was rigorously assessed using differential scanning calorimetry (DSC) to quantify deviations from the Fox equation predictions for ideal mixing. Ion beam analysis and neutron reflectometry were further used to visualise and quantify oligomers' partitioning. Subtle changes in interactions between the polymer and oligomer were explored and found to have a significant influence on compatibility. These small compatibility effects resulted in large, quantitative changes in surface and interfacial segregation and, for some model formulations, led to a clear wetting transition.

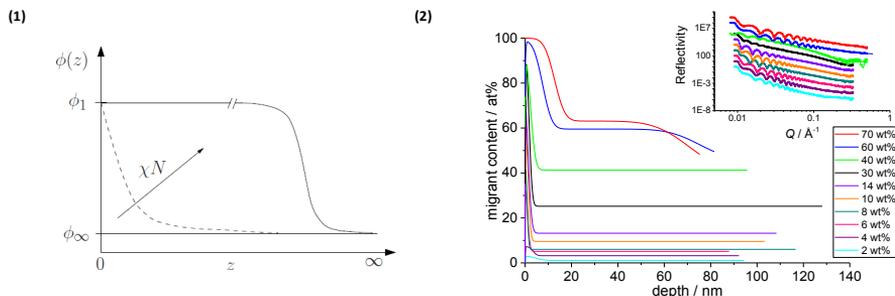


Figure 1 Expected concentration profiles at low (dashed line) and high (solid line) values of χN showing respectively surface segregation and phase separation.

Figure 2 Neutron reflectometry data and fit (inset) and corresponding composition profiles for 2 to 70 wt% d-squalane in thin polybutadiene films reveal distinct wetting transition with increasing oligomer concentration.

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Synergism of DNA-binding agents and macromolecular crowding on DNA condensation

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Genome packaging in prokaryotic cells is believed to be carried out by a combination of DNA binding proteins, crowding effects, and DNA supercoiling. Much is known about DNA – protein interaction as well as the condensation of DNA due to excluded volume effects however, few studies have targeted the potential synergistic role of DNA-binding proteins and crowding agents on DNA condensation.

Here we assess the effect of crowding, induced by polyethylene glycol (PEG), on DNA – H-NS binding, with H-NS a histone-like nucleoid structuring protein that is believed to play a crucial role in gene regulation. In addition, we have also evaluated the non-specificity of the DNA binding and the effect of ionic strength [1].

We have found, using a range of biophysical techniques that PEG enhances the binding of H-NS to DNA, as well as the protection of DNA towards DNase and restriction enzyme digestion.

Acknowledgements This work is supported by the Norwegian University of Science and Technology (NT likestillingsmidler (Startpakke)).

[1] S. K. Ramisetty and R. S. Dias, *J. Mol. Liquids*, 2015, **210**, 64.

Field-Directed Self-Assembly of Soft Thermo-Responsive Colloids

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Ionic poly(N-isopropyl-acrylamide) (PNIPAM) microgels are ideally suited as model systems to study the complex phase behaviour found for particles interacting via a soft potential. Moreover, subjecting the particles to an alternating electric field results in an additional dipolar contribution to the interaction potential, which strongly depends on the strength and frequency of the applied field. Here we use confocal laser scanning microscopy (CLSM) in combination with different scattering techniques to study the system as the dipolar interactions are increased. In the dilute regime, a fluid to string-fluid transition is observed, Fig. 1. [1]. At high densities we see how a face-centred cubic (FCC) crystal diffusively transforms into a body-centred tetragonal (BCT) crystal via nucleation and growth. However, in the reverse direction, the BCT phase transforms cooperatively into a metastable body-centred orthorhombic (BCO) phase, which only relaxes back to the FCC phase as the temperature is increased [2]. The kinetics at this over-packed state is thus either diffusive or martensitic depending on the path. In order to learn more about the origin of this puzzling path dependence, we investigate the influence of the particle softness using ionic microgels with different crosslink densities. We also study the shape and size of the particles as a function of packing fraction and field strength by performing small-angle neutron scattering experiments at so-called zero average contrast conditions as a function of the applied field strength.

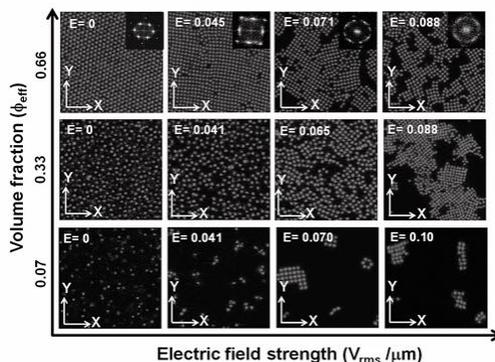


Figure 1 Examples of field-induced structures.

[1] S. Nöjd, P. S. Mohanty, P. Bagheri, A. Yethiraj and P. Schurtenberger, *Soft Matter*, 2013, **9**, 9199.

[2] P. S. Mohanty, P. Bagheri, S. Nöjd, A. Yethiraj and P. Schurtenberger, *Phys. Rev. X*, 2015, **5**, 011030

Hydrogels for Paper Cleaning: the New Entries

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Restoration of paper artworks usually involves the removal of surface grime, cellulosic degradation by-products and naturally aged glues, not only for aesthetic reasons but because these components accelerate ageing processes. In this context, wet cleaning is an important step in paper restoration, but the common procedure –water immersion– may not be the optimal one as it could induce paper fibres swelling and dissolution of components. Therefore, in the last years, the use of hydrogels (as Gellan gel) that allow a valid paper cleaning action by absorbing water-soluble degradation products, inducing, at the same time, a very reduced water uptake by paper, has been proposed and assessed [1]. Moreover, these gels could be loaded with opportune cleaning agents to improve their performances as paper restoration tools [2]. Highly retentive semi-IPN p(HEMA)PVP gels have been recently developed within the EU-funded NANOFORART project [3-4]. These hydrogels, which are nowadays commercially available, could be used for a residue-free and controlled cleaning intervention on water-sensitive works of art. Therefore, these systems have been tested for the selective removal of glues (starch paste and animal glue) from paper samples. In particular, gels capability of loading the hydrolytic enzymes needed for glue removal has been assessed. Data have been compared to those obtained with a well-established gel for paper cleaning artworks that is Gellan gel. To assess the effectiveness of the proposed method, the treated samples have been characterized by comparing the results obtained with different techniques, such as using UV-Vis and FTIR techniques, scanning electron microscopy, high performance liquid chromatography.

Acknowledgements CSGI and the European Union (project NANOFORART, FP7-ENV-NMP-2011/282816) are gratefully acknowledged for partial financial support.

- [1] C. Mazzuca, L. Micheli, M. Carbone, F. Basoli, E. Cervelli, S. Iannuccelli, S. Sotgiu and A. Palleschi, *Journal of Colloid and Interface Science*, 2014 **416**, 205.
- [2] C. Mazzuca, L. Micheli, R. Lettieri, E. Cervelli, T. Coviello, C. Cencetti, S. Sotgiu, S. Iannuccelli, G. Palleschi and A. Palleschi. *Microchemical Journal*, 2016, **126**, 359.
- [3] J. A. L. Domingues, N. Bonelli, R. Giorgi, E. Fratini, F. Gorel, P. Baglioni, *Langmuir*, 2013, **29**, 2746.
- [4] J. A. L. Domingues, N. Bonelli, R. Giorgi, P. Baglioni, *Applied Physics A*, 2013 **114**, 705.

Uniaxial deformation of cross-linked gels

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The similarity of hydrogels with living tissues makes them attractive materials in biomedical applications. Conventional hydrogels, however, suffer from low mechanical strength and toughness which limits their practical use as load-bearing materials, such as artificial cartilage. In addition, the synthesis of cross-linked polymer gels normally introduces inhomogeneities in the form of structural defects (e.g., loops and dangling ends) and a spatially inhomogeneous cross-linking density, which affect the physical properties of the corresponding gel. To fulfil the demands of application, it is of interest to be able to correlate the mechanical properties with the network structure and to be able to improve the mechanical properties.

The mechanical properties may be significantly enhanced by, for example, using interpenetrating (but independently cross-linked) networks (IPN:s) with different cross-linking densities. This improved performance, compared to the corresponding single networks, may be ascribed to the higher strength of the more densely cross-linked (primary) network, which at smaller stresses acts as a rigid skeleton, sustaining the mechanical deformation, as well as to the interactions between the primary and secondary network.

In this work, we use computer simulations to study the deformation behaviour of cross-linked gels. We investigate the impact of spatial inhomogeneities on the deformational behaviour and mechanical properties of gel particles during elongation, for systems ranging from perfectly homogeneous networks to random and bimodal networks with local highly cross-linked clusters of various sizes, with different chain length distributions. We also look at the uniaxial compression of an interpenetrating nanogel bead placed between two parallel surfaces, following the structural and mechanical variations during compression with respect to the cross-linking densities of the pair components, ranging from identical to asymmetric cross-linking, and compare with those of the constituent single networks.

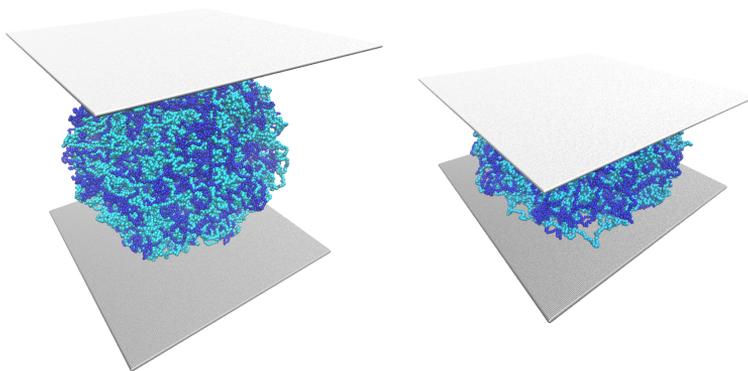


Figure 1 An interpenetrating network prior to and after compression.

Mechanism for Forming Composite Film of Aluminum Salt / Anionic-polymer

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Aluminum chlorohydrate (ACH) has been used widely in deodorants as an antiperspirant active agent over sixty years [1]. ACH forms a film on the skin's surface and covers sweat glands after being applied to the skin, thereby it suppresses perspiration. However, ACH can be removed from skin easily because it is characterized by being fragile and soluble in water, and consequently antiperspirant efficacy becomes lower. Therefore, it is important to retain the ACH on the skin in order to enhance the antiperspirant efficacy. We focused on a film-forming polymer to improve the ACH film properties and found that the retention of ACH film on the model skin increased significantly by a combination with an anionic polymer. As a result, we made a hypothesis that ACH forms a complex with the anionic polymer and began to study the mechanism.

The interaction of ACH and anionic polymer was evaluated by FT-IR measurement and it was found that a carbonyl peak around 1700 cm^{-1} shifted to a high wavenumber by increasing the ACH ratio, then the wavenumber reached a plateau at the ACH/Anionic polymer ratio of 4 to 6. It follows that ACH interacts with anionic polymer. Moreover, the chemical and physical properties of the film surface was analyzed through the surface free energy (SFE) and the structure observation by AFM. SFE changed from high to low by increasing ACH ratio. Film structure was non-uniform and partially aggregated in a low ACH ratio. By contrast, it was intended to be uniform at a high ACH ratio, and the surface roughness values also indicated the same tendency. These results lead to the conclusion that ACH interacts with anionic polymer to form composite film and the film surface structure becomes uniform at the specific ratio of ACH/Anionic polymer mentioned above.

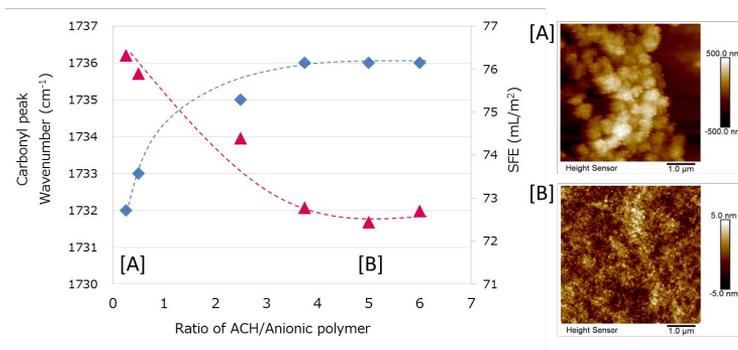


Figure 1 Wave number of carbonyl peak and SFE value with AFM images

[1] T. Govett, M. G. de Navarre, *Amer. Perfum.*, 1947, **49**, 365-8

Efficient simultaneous removal of petroleum hydrocarbon pollutants using a silica aerogel-like material

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Aromatic compounds in the petroleum comprises the polycyclic aromatic hydrocarbons (PAHs) (e.g., benzo(a)pyrene) and the monoaromatic hydrocarbons (MAHs) (e.g. benzene, toluene, and xylene isomers (BTXs)) [1]. The biodegradation of PAHs and BTXs compounds is slow and is associated with mutagenic, teratogenic and carcinogenic effects in humans [2].

Aerogels are nanoporous materials made by a sol-gel process followed by drying at supercritical conditions. The combination of the techniques used for the synthesis of these materials impart into them unique properties such as large surface areas ($\sim 10^6$ m²/kg) and high porosity (>90%), they are easily recovered and they exhibit capacities which enormously exceed that of usually used adsorbents [3-5].

In this work, using methyltrimethoxysilane (MTMS) as the precursor and according to the preparation procedure of Xero-a samples described earlier, a material was obtained with a non-wetting behavior and without significant shrinkage when dried under ambient pressure [6]. The interaction between the aerogel-like material prepared with MTMS and mix solutions containing BTXs and PAHs (pyrene, benzo(b)fluoranthene and benzo(a)pyrene) has been evaluated through sorption isotherms and kinetics.

For the simultaneous quantification of 6 different analytes, we used a HPLC-DAD method, previously optimized. We found that the sorption kinetics follows a pseudo-second order equation and the isotherms can be modelled by using the BET equation. These findings show that a concomitant chemi- and physisorption can happen during the sorption process. Furthermore, we have also observed that the removal efficiency is similar for all adsorbates and are equal to 16-18%, which leads to a total removal efficiency of around 100%. Desorption experiments show desorption rate of ca. 100% for PAHs; however, BTX shows higher interaction with the aerogel and lower desorption rates (below 50%). The silica aerogel-like adsorbent was characterized, before and after equilibrium with BTXs and PAHs solutions, by thermogravimetry (TG), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Finally, the capacity of this aerogel for removing all these pollutants from a real gasoline sample is discussed.

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- [1] B.S. Echols, A. Smith, P. Gardinali, G. Rand, *Arch. Environ. Contam. Toxicol.*, 2015, **70**, 392.
- [2] T. Garrison, J.C. Hower, A.E. Fryar, E. D'Angelo, *Environ. Earth Sci.*, 2016, **75**, 1.
- [3] H. Maleki, L. Durães, A. Portugal, *J. Non. Cryst. Solids.*, 2014, **385**, 55.
- [4] T. Matias, J. Marques, M.J. Quina, et al., *Colloids Surfaces A Physicochem. Eng. Asp.*, 2015, **480**, 260.
- [5] M.L.N. Perdigoto, R.C. Martins, N. Rocha, et al., *J. Colloid Interface Sci.*, 2012, **380**, 134.
- [6] L. Durães, M. Ochoa, N. Rocha, et al., *J. Nanosci. Nanotechnol.*, 2012, **12**, 6828.

SAXS study of structure and phase behaviour of pig gastric mucin at different temperatures and hydration levels

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One essential function of mucous gel is to protect the mucosa from dehydration. Mucus properties respond quickly to changes in ambient conditions, and when the relative humidity (RH) of the surrounding atmosphere decreases it undergoes a transition from elastic to glassy state. According to our previous calorimetric studies [1], this mucin glass transition occurs at an RH between 60-70%.

Here, hydration and temperature-induced changes in pig gastric mucin (PGM) in a wide concentration range were studied using small angle X-ray scattering (SAXS). This work demonstrates three ranges of the scattering vector q corresponding to different fractal dimensions in PGM solutions. Such scattering can originate from PGM fiber-like structures that adopt random coil conformation in dilute solutions. Starting from about 20 wt% PGM, three peaks are clearly visible in the scattering pattern and they become more pronounced at intermediate concentrations, indicating structuring in the mucin system at lower levels of hydration. In strongly and fully dehydrated mucin, where the system is in a glassy state, these peaks do not appear. The SAXS data show that the structural changes at about 80 wt% of mucin at 25°C correspond to a mucin glass transition, in agreement with our previous calorimetric results [1].

Temperature-induced changes in the phase behavior of mucin were observed at about 60-70°C at intermediate levels of hydration. Here the single main peak becomes double, indicating formation of a different structure at elevated temperatures. These results are in a good agreement with polarized light microscopy and DSC data. Obtained SAXS data are used to complete the PGM phase diagram.

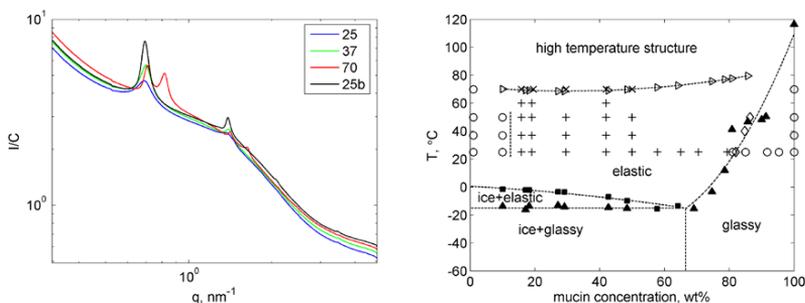


Figure 1 Temperature dependence of concentration normalized intensity I/C versus the scattering vector q for 30 wt% PGM (left image). A phase diagram of PGM constructed using our previously published sorption calorimetry and DSC [1] and present SAXS and DSC data (right image).

Acknowledgements: The MAX IV - laboratory in Lund (Sweden) is acknowledged for providing time to run SAXS measurements. Authors are grateful to Drs. Tomas Plivelic and Sylvio Haas for technical assistance when running X-ray experiments at MAX IV / beamline I-911. Malmö University, Biofilms – Research Center for Biointerfaces, the Knowledge Foundation (KK-stiftelsen) and the Gustav Th Ohlsson Foundation are thanked for financial support.

[1] Y. Znamenskaya, J. Sotres, J. Engblom, T. Arnebrant, V. Kocherbitov, *J Phys. Chem. B*, 2012, **116**, 5047.

New methods of study of reactivity and barrier properties of biocolloids

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The main aim of this work was the study on reactivity, transport and barrier properties of biocolloidal and synthetic polymeric substances by simple diffusion techniques. It was studied mainly the influence of basic physic-chemical parameters (temperature, concentration, pH and modification of material [1]) on the reactivity and barrier ability of chosen compounds. Further substances were chosen as a model compounds: biocolloids (humic acids, alginate, chitosan, hyaluronate) and synthetic polymer (polystyrenesulfonate). Reactivity, barrier and transport properties of chosen substances were studied by interactions with oppositely charged basic organic dyes (methylene blue, rhodamine 6G, amido black 10B respectively) in non-reactive hydrogels matrix based on linear polysaccharide (agarose). The attention was also paid to basic physic-chemical characterisation (infrared spectroscopy, rheology, elemental analysis, thermogravimetry and scanning electron microscopy) of chosen materials and also hydrogels. Key part of the whole work was the optimization of selected diffusion techniques (diffusion cell technique [2] and non-stationary diffusion in cuvettes [3]) designated for the study on reactivity and barrier properties of wide range compounds (optimized method should be used as an universal method for simple and fast determination of reactivity of different compounds at given or changing conditions). The rate of reactivity and barrier properties was determined based on fundamental diffusion parameters such as diffusion coefficients, break-through time so called lag time, interfacial concentration of chosen organic dye, apparent equilibrium constant, tortuosity factor, partition coefficient.

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[1] J. Smilek, P. Sedlacek, M. Kalina and M. Klucakova, *Chemosphere*, 2015, **138**, 503.

[2] P. Sedlacek, J. Smilek and M. Klucakova, *Reactive & Functional Polymers*, 2013, **73**, 1500.

[3] P. Sedlacek, J. Smilek and M. Klucakova, *Reactive & Functional Polymers*, 2014, **75**, 41.

Flocculating activity of exopolymer R_s-202 obtained from *Rhodococcus rhodochrous*

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Different branches of industry produce the wastewater containing suspended solids, inorganic and organic particles, heavy metals and other toxic substances. The removal of these particles is a challenge for the modern techniques of water purification. Relatively small sizes of the particles cause the problems their separation by usually applied methods such as a solvent extraction, an ion exchange, a flotation, a membrane filtration, and a precipitation [1]. Among these processes, the flocculation is the most widely applied the separation method, which could be used for the removal of the suspended particles by their aggregation and sedimentation in the presence of specific factors.

Flocculating agents are mostly classified into three groups: inorganic flocculants (polyaluminium chloride), organic synthetic flocculants (polyacrylamide derivatives) and naturally occurring bioflocculants [2]. Bioflocculants are extracellular polymeric substances produce by microorganisms during their growth. In contrast to their synthetic alternatives, the bioflocculants are more eco-friendly through their biodegradability and biocompatibility, which are highly valued in the increasing of environmental pollution and health problems, caused by various branches of industry. Many factors such as: the bioflocculant concentration, the temperature and pH values, the addition of metal ions, and the mixing speed, could influence on the efficiency of the bioflocculant activity [1]. Therefore, the optimisation of flocculation process and the understanding of the mechanism of flocculation, would highly improve bioflocculants efficiency in their practical applications.

In the present study, the exopolymer R_s-202 was obtained from culture broth of *Rhodococcus rhodochrous*, bacterial strain belonging to Actinobacteria. The flocculating activity of the crude product was examined using kaolin suspension. The basic parameters (temperature and pH values, the presence of ions and the exopolymer concentration) were tested to determine the optimal flocculation conditions of exopolymer R_s-202. The flocculating activity was analysed by the zeta potential and the light transmittance measurements.

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[1] C.S. Lee, J. Robinson and M.F. Chong, *Process Safety and Environmental Protection*, 2014, **6**, 489–508.

[2] H. Salehizadeh and N. Yan, *Biotechnology Advances*, 2014, **32**, 1506–1522.

Physico-chemical characterisation of exopolymer from *Rhodococcus opacus*

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Microorganisms such as bacteria, fungi, algae and yeasts are able to produce biopolymers with multiple biological functions, which can be used for various industrial and medical applications [1]. These extracellular polymeric substances (EPS) are mainly composed of carbohydrates and proteins, however multiple studies had reported the exopolymers containing nucleic acids, lipids, lipopolysaccharides, glycoproteins, and lipoproteins in their structure [2]. Basic functions of exopolymers in natural systems are their abilities to form flocs and biofilms, aggregate bacterial cells, adhere to surfaces, and exhibit enzymatic activities. EPS could be also the structural elements of biofilms and establish protective barrier for cells [3]. Basic features of the natural EPS, such as a biodegradability, a high efficiency, a non-toxicity and a lack of secondary pollution, determine their role as a potential alternative to substitute chemical substances applied in industry [2]. Recently, multiple applications of EPS have been developed in such areas as pharmacology, food and cosmetics industry, production of herbicides and insecticides, and also in medicine as anticoagulant, antithrombotic, immunomodulatory, and anticancer factors [4]. Moreover, exopolymers are widely used in the wastewater treatment, in metals removal and as soil remediation factors known as bioflocculants.

In the present study, the receiving of the exopolymer from culture broth of *Rhodococcus opacus* strain was optimised due to the precipitation parameters, the day of extraction, *inoculum* size, and culture conditions. The chemical components of the studied exopolymer were estimated by series of spectrophotometric analysis. Obtained exopolymer was also characterised by the X-ray photoelectron spectroscopy and the Fourier transformation infrared spectra. The structure of exopolymer was tested by a scanning electron microscopy. Additionally, the crude EPS sample from *R. opacus* was examined for the flocculating activity in the presence of kaolin suspension.

This project was financed by The National Science Centre based on the decision number DEC-2012/07/B/ST5/01799.

- [1] B. Rehm, *Nature Reviews Microbiology*, 2010, **8**, 1-26.
- [2] H. Salehizadeh and N. Yan, *Biotechnology Advances*, 2014, **32**, 1506-1522.
- [3] T. More, J.S.S. Yadav, S. Yan, R.D. Tyagi and R.Y. Surampalli, *Journal of Environmental Management*, 2014, **144**, 1-25.
- [4] U.U. Nwodo, E. Green and A.I. Okoh, *International Journal of Molecular Science*, 2012, **13**, 14002-14015.

Adsorption of reactants on a PNIPAM polymer

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Thermoresponsive hydrogels, such as Poly(N-isopropylacrylamide) (PNIPAM), are recently becoming very popular as 'smart' carriers in modern nanoscience. By changing the temperature, the PNIPAM hydrogel structure can undergo a sharp transition from a swollen into a collapsed state, which alters the selectivity for the solute particles that diffuse through the hydrogel. Catalytic model reactions of the reduction of p-nitrophenol and nitrobenzene nicely demonstrate such a selectivity [1], where the reaction rates of both reactants dramatically change after the transition. In order to gain insights into the nanoscale structure, binding kinetics, and diffusion in such systems, we employ Molecular Dynamics simulations of PNIPAM polymer in explicit water. We model an extended PNIPAM polymer chain in the presence of various solutes dissolved in water, which mimics the hydrogel in the swollen state. We put particular attention on benzene and its derivatives and explore the influence of temperature, polymer stretch, and polymer tacticity on the solute binding affinities.

[1] Shuang Wu, Joachim Dzubiella, Julian Kaiser, Markus Drechsler, Xuhong Guo, Matthias Ballauff, and Yan Lu, *Angew. Chem. Int. Ed.* 51, 2229 (2012).

Poly(vinyl alcohol)-based microgels prepared through salting out: rationalising the aggregation process

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Poly(vinyl alcohol) (PVA) is a biocompatible water-soluble polymer of great interest thanks to its large-scale applications as a material for drug-delivery systems or for building sensors and membranes with selective permittivity. The cryogenic route is one of the most studied and widely employed techniques for the preparation of PVA physical hydrogels [1]: the advantages of such gels is the absence of toxic chemicals for their preparation and the consequent possibility to obtain a completely eco-friendly product [2].

In this work we propose a new route for the preparation of PVA-based microgels through the salting-out effect: after a screening of different salts belonging to the Hofmeister series, sodium chloride represented the best kosmotropic species to use in order to favour the polymer aggregation over a reasonable time-scale. The thermodynamic properties and the kinetics of the aggregation process were deeply studied through a combined Dynamic Light Scattering (DLS), Static Light Scattering (SLS) and Small Angle Neutron Scattering (SANS) study, which allowed rationalising how such process is influenced by different parameters like salt molality, polymer concentration and time from the preparation (fig. 1).

Moreover, we were able to shed light on the structural and morphological properties of PVA particles, showing the role of the salt in the aggregation process and its effect on the supramolecular organization. In particular, we determined the molecular weight and the radius of gyration of the aggregates and we estimated the packing degree of polymer chains within the aggregates, strongly influenced by the time and the salt concentration.

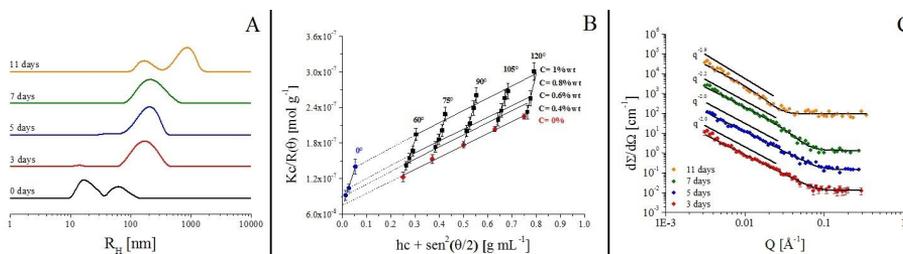


Figure 1 – PVA 1% wt, NaCl 2 mol kg⁻¹: study of the evolution of hydrodynamic radii over time by DLS (panel A); Zimm plot obtained from SLS measurements (panel B); SANS results at different times from the preparation (panel C).

[1] Mangiapia, G., Ricciardi, R., Auriemma, F., De Rosa, C., Lo Celso, F., Triolo, R., Heenan, R.K., Radulescu, A., Tedeschi, A., D'Errico, G., Paduano, L., *J. Phys. Chem. B.*, 2007, **111**, 2166.

[2] Nayak, S., Lyon, A., *Angewandte Chemie*, 2005, **44**, 7686.

Coarse-grained Monte Carlo simulations on the interaction of nanoparticles with weak polyelectrolytes

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Systems comprising of nanoparticles and oppositely charged polyelectrolytes have a great technological interest, being major components in formulations used in pharmaceutical, food, cosmetics, detergents, and paint industries. The stability of colloidal suspensions and the interaction of its constituents are important issues in formulations, and a large effort has been made to understand how the properties of each individual component affect the overall characteristics of the formulations.

Weak polyelectrolytes are especially interesting since their properties can be tuned resorting to pH variations. An additional characteristic of weak polyelectrolytes is the fact that protons can also migrate along the chains and between different chains [1]. It has been shown, using experimental and theoretical tools, that such type of charge correlations enhances the interaction between oppositely charged species. Examples are the adsorption of DNA [2-4] and proteins [5,6] onto lipid membranes and the interaction between annealed polyacids and micelles [7,8].

In this work we have coarse-grained Monte Carlo simulations to systematically study the effect of charge mobility (quenched vs. annealed) on the adsorption of polyacids to a nanoparticle. The effect of polyacid chain length and number number of chains is also evaluated using titration curves.

- [1] D. K. Srivastava, S. Wang and K. L. Peterson, *Biochemistry*, 2007, **36**, 6359-6366.
- [2] B. Maier and J.O. Radler, *Macromolecules*, 2000, **33**, 7185-7194.
- [3] R. S. Dias, A. A. C. C. Pais, P. Linse, M. G. Miguel and B. Lindman, *J. Phys. Chem. B*, 2005, **109**, 11781-11788.
- [4] R. S. Dias and A. A. C. C. Pais, *J. Phys. Chem. B*, 2012, **116**, 9246-9254.
- [5] G. Denisov, S. Wanaski, P. Luan, M. Glaser and S. McLaughlin, *Biophys. J.*, 1998, **74**, 731-744.
- [6] R. S. Dias and P. Linse, *Biophys. J.*, 2008, **94**, 3760-3768.
- [7] J. Norrman, I. Lynch and L. Piculell, *J. Phys. Chem. B*, 2007, **111**, 8402-8410.
- [8] S. Ulrich, M. Seijo, A. Languécir and S. Stoll, *J. Phys. Chem. B*, 1997, **110**, 20954-20964.

The DNA duplex stability: estimation of the energy of hydrogen bonds and reactivity using TATA box as model

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The spatial structure of the DNA molecule determines the physiological and biochemical mechanisms in which this carries out its biological functions. Of particular importance to the spatial structure and stability of the double helix are the hydrogen bonds [1, 2] that join both strands in the chain. Furthermore, the chemical properties of the DNA chain significantly determine the selectivity of certain proteins. In this project the energy associated with the hydrogen bonds in chains of different number of units (from 1 to 14 base pairs) is studied, taking into account two different models: ideal not relaxed model (that obey conditions of symmetry) and ideal relaxed model (relaxed structures from the previous model). On the other hand, a first approach to the selectivity of TBP to the TATA [3] box is done by studying chemical properties of this genomic region. The study was realized under the framework of DFT [4, 5] using the code DMol3 [6] (M06-L/DN) implemented in the Materials Studio software suite [7]. From the analysis could be inferred that the average energy of hydrogen bond of the ideal not relaxed model varies periodically depending on the number of base pairs in the chain. This is related with the border effects associated with the symmetry of the system, allowing the differentiation between chains with even or odd number of base pairs. An analytical model for this development, that allows obtaining the average energy of hydrogen bond for chains of any size, is proposed. While for the ideal relaxed model, the size of the chain has influence in the average energy of hydrogen bond existing between thymine and adenine, because the presence of neighbors tends to stabilize this interaction. Finally, from the Frontier Molecular Orbitals and Fukui functions [8] can explain, from the chain of eight base pairs, the way how the binding protein interacts with the TATA box region.

References:

- [1] F. Weinhold y R.A. Klein. What is a hydrogen bond? Mutually consistent theoretical and experimental criteria for characterizing H-bonding interactions. *Molecular Physics*, 110:565, 2012.
- [2] H. Szaty lowicz y N. Sadlej-Sosnowska. Characterizing the Strength of individual Hydrogen Bonds in DNA Base Pairs. *Journal of Chemical Information and Modeling*, 50:2151, 2010.
- [3] Laszlo Tora y Timmers H.Th.Marc. The TATA box regulates TATA-binding protein (TBP) dynamics in vivo. *Cell Press*, 6:209, 2010.
- [4] P. Hohenberg y W. Kohn. Inhomogeneous Electron Gas. *Physical Review Letters*, 136:B864, 1964.
- [5] W. Kohn y L. J. Sham. Self-Consistent Equations Including Exchange and Correlation Effects.
- [6] B. Delley. From molecules to solids with the DMol3 approach. *Journal of Chemical Physics*, 113:7756, 2000. *Physical Review*, 140:A1133, 1965.
- [7] Materials Studio 2014, Biovia. © 2014 Systèmes, Biovia Software Inc.
- [8] R. G. Parr y W. Yang. Density Functional Approach to the Frontier-Electron Theory of Chemical Reactivity. *Journal of the American Chemical Society*, 106:4049, 1984.

Controlling POEGMA aggregates by varying the copolymer architecture

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Stimuli-responsive polymers have attracted great interest in biomedical applications. The family of poly(oligoethylene glycol methacrylate) (POEGMA) copolymers is ideal for such applications. POEGMA possesses many advantages such as anti-fouling behaviour and reversible phase transitions with tunable lower critical solution temperature (LCST), from 26 to 90 °C [1]. Commonly, POEGMA undergoes a macroscopic phase separation [2]. However, when a monomer with more ethylene oxide (EO) groups is used, the copolymer undergoes a microscopic phase separation with micelle formation [3]. In this work, we studied the phase transition structures in aqueous solutions of various POEGMA copolymers with different monomeric compositions using light scattering and calorimetric techniques.

Random POEGMA copolymers comprising of different monomeric compositions with various EO groups contents, were prepared using the atom transfer radical polymerization (ATRP) method. Our results of UV-vis spectrophotometry and differential scanning calorimetry (DSC) showed that the cloud-point (CP) and LCST of the copolymers increase with an increase in the EO content of the copolymer. For instance, the random POEGMA copolymer with [EO₂]:[EO₄]:[EO₄₅] molar ratios of 99:0:1 displays a CP of 26.5 °C, whereas, for the copolymer with molar ratios of 69:30:1, the CP is 46.0 °C.

Below the LCST, the copolymer in the aqueous solution displayed a random coil structure. Above the LCST, depending on the EO to methacrylate (MA) backbone ratio, the copolymer can undergo either a macro or a micro-phase separation. In case of a lower EO/MA ratio, the copolymer went through a microscopic phase separation, forming a micelle-like structure. Whereas, for a higher EO/MA ratio a macroscopic phase transition took place. There was no significant difference between the enthalpy (ΔH) of both processes.

Furthermore, dynamic light scattering (DLS) and small angle X-ray scattering (SAXS) experiments confirmed that the phase transition is kinetically driven, forming a larger structure that rearranges with time into smaller aggregates containing several dehydrated collapsed copolymer chains.

In conclusion, our results demonstrated that, by varying the content and length of EO side groups, one could control the architecture of the POEGMA copolymers. Therefore, at temperatures above the LCST, different aggregate morphologies can be achieved for the family of POEGMA copolymers, providing different platforms for biomedical applications.

Acknowledgements The financial support of the Brazilian agencies CNPq and CAPES.

[1] J.-F. Lutz, *Advanced Materials*, 2011, **23**, 2237.

[2] J.-F. Lutz, K. Weichenhan, Ö. Akdemir and A. Hoth, *Macromolecules*, 2007, **40**, 2503.

[3] B. Peng, N. Grishkewich, Z. Yao, X. Han, H. Liu and K.C. Tam, *ACS Macro Letters*, 2012, **1**, 632.

Film-forming gels for the removal of corrosion products from copper-based artifacts

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An innovative polyvinyl alcohol-based film forming system was specifically devised for a controllable and selective cleaning of copper-based artifacts, with enhanced performances in terms of both applicability and efficacy. The main advantage of this cleaning system consists in the simultaneous chemical and mechanical action, guaranteed respectively by the presence of a confined complexing agent specific for selected ions (Cu^{2+}), such as EDTA and/or polyethylenamines.

Metallic artifacts are affected by corrosion phenomena that induce the formation of complex *patina* on their surface. Degradation causes the formation of overlapping structures, characterized by a layer of Cu(I) oxide (cuprite Cu_2O) at the interface with the metal, and by an external layer of Cu(II) carbonates, sulphates, chlorides, etc. The presence of copper oxychlorides (atacamite and its polymorphs) is usually considered as a symptom of the 'bronze disease', a cyclic phenomenon that leads to the progressive deterioration of ancient copper alloys. Cleaning procedures of these materials are traditionally performed by mechanical (vibrating or abrasive tools, micro-peening with vegetal granulates, ultra-high-pressure water, laser) and/or chemical methods (complexing agents, bases, acids). Mechanical cleaning presents some limits related to the scarce selectivity and invasiveness of this procedure, while the chemical action is generally affected by an insufficient control over the reactions involved.

The film forming cleaning system, based on polyvinyl alcohol as a polymer and loaded with a complexing agent (EDTA and polyethylenamines), is a promising tool for the selective removal of corrosion products from copper-based artifacts, by respecting the cuprite layer. In fact, this innovative approach permits to achieve: i) improved chemical control, step-by-step, of the cleaning process, thanks to the high selectivity of the chosen complexing agent and to its confinement in the polymeric system; ii) simultaneous chemical (complexation) and mechanical action (favored by the gentle *peeling* of the final film); iii) adjustability of the physico-mechanical properties (consistency, adhesiveness, transparency, etc.), by tuning the additives content to adapt to different substrates (non-horizontal, rough and irregular surfaces).

Two main aspects were studied over both complexing agent-loaded and not loaded systems: i) the kinetics of film formation, by investigating the evolution of the systems from polymeric dispersions towards the formation of elastic films and ii) the evaluation of the formed films properties, through the parameter of crystallinity degree. The techniques used to obtain information over the evolution of the system through time, involved the use of gravimetry, thermogravimetry (both scanning and isothermal), and rheology (both dynamic and rotational experiments). The evaluation of the mechanical properties and of the degree of crystallinity of the dried films was obtained, instead, from differential scanning calorimetry (DSC) and ATR-FTIR spectroscopy experiments.

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Innovative systems for the control of viscosity of polymer dispersions for shale gas applications

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Polymer dispersions are widely used in shale gas extraction and their viscosity is one of the crucial features that need to be modulated. The system needs to be highly viscous in the initial stages of the process and then it has to become more fluid to allow the recovery of the frac fluid and the transfer of the hydrocarbons from underground to the surface. Two innovative systems were studied:

- 1) the application of the cyclic Belousov-Zhabotinsky reaction
- 2) the stimulus-responsiveness of physical gels to external electric fields.

We present our results based on guar gum, sodium hyaluronate and sodium alginate water dispersions that were used as basic ingredients for the formulation of "green" frac fluids.

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Investigating of star - long chain mixtures phase diagram by means of a novel coarse-graining approach

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We present a novel coarse-graining approach, suitable for star-chain mixtures[1-3]. The approach is based on the calculation of the effective interaction between a star polymer and a short chain of length N_0 , which can be used to coarse-grain the interaction between a star and a longer chain or a more complex object. The effective interaction has been calculated numerically for star polymers of different functionalities f and for different degrees of polymerization N . We test our approach, calculating the effective interaction between a star polymer and a long chain of length N_c with both coarse graining and monomer resolved simulations and comparing the results: the comparison yields an excellent agreement between coarse-graining and monomer-resolved simulations. We employ this technique to study star - chain mixtures, focusing on the limit of very long homopolymers. We observe a strengthening of the glassy phase, in contrast with the melting induced by the presence of short chains[4].

- [1] E. Stiakakis, G. Petekidis, D. Vlassopoulos, et al., *Europhysics Letters*, **72:664**, (2005).
- [2] M. Camargo and C.N. Likos, *Physical Review Letters*, **104:078301**, (2010).
- [3] B. Lonetti, M. Camargo, J. Stellbrink, et al., *Physical Review Letter*, **106:228301**, (2011).
- [4] E. Stiakakis, D. Vlassopoulos, C.N. Likos, et al., *Physical Review Letters*, **89:208302**, (2002).

Cation dependence of cellulose solution structure in alkaline solvent

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Cellulose is a readily available and renewable biopolymer. It is fascinatingly insoluble in most common solvents, but may be dissolved in strong alkali, such as 8 wt.% NaOH(aq) and 40 wt. % tetra butyl ammonium hydroxide, TBAH(aq).[1-3] In this study, the dissolution state of microcrystalline cellulose (MCC) has been studied in mixtures of these two solvents to understand if such a mixture could behave as a better or a worse solvent than the precursor. We used 8 wt.% NaOH(aq) and 40 wt. % TBAH(aq) stock solutions and mixed them in different proportions. The mixed solvent composition is expressed as the parameter X_{NaOH} being the fraction of the NaOH solvent in the mixture. The mixtures have been analyzed by scattering, light microscopy, and turbidity experiments. Furthermore the formation of a structured film appears in certain condition and it has been studied by optical and confocal microscopy. When mixing NaOH and TBAH, the cellulose solubility decreases. This is seen in Figure 1 which shows the turbidity of 2 wt.% MCC solutions/dispersions as a function of X_{NaOH} . For $X_{\text{NaOH}} < 0.04$ and $X_{\text{NaOH}} > 0.9$ transparent solutions are formed. For $0.04 < X_{\text{NaOH}} < 0.9$, 2 wt.% MCC can not be fully solubilized. X-ray diffraction indicates that it is Cellulose II that precipitates, possibly as partial sodium salt. MCC in the mixed solvent $x_{\text{NaOH}} = 0.5$, shows precipitation and a pattern formation under confinement between microscope slides. The patterns were characterized using conventional light and confocal microscopy (Fig. 2).

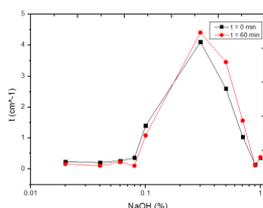


Fig 1. Turbidity curve versus X_{NaOH} in weight %. Black symbols represent the turbidity shortly (minutes) after mixing. Red symbols show the turbidity after 60 minutes.



Fig 2. A) Images of the sample $X_{\text{NaOH}}=0.5$. B) Image of sample $X_{\text{NaOH}}=0.5$ doped with rhodamine recorded with the confocal microscope. C) 3D image of sample $X_{\text{NaOH}}=0.5$ doped with rhodamine, obtained by combining images of different confocal planes. The colour of the picture was adjusted in order to highlight different regions.

References

- [1] Budtova, T; Navard, P. Cellulose in NaOH-Water-Based Solvents: a Review. *Cellulose* **2016**, 23, 5-55
- [2] Alves, L. Medronho, B. Antunes, F.E; Topgaard, D; Lindman, B. Dissolution State of Cellulose in Aqueous Systems. 1. Alkaline Solvents. *Cellulose* **2016**, 23, 247-258.
- [3] Behrens, M.A; Holdaway, J.A; Nostrati, P.; Olsson, U. On the Dissolution State of Cellulose in Aqueous Tetrabutylammonium Hydroxide Solutions. *RSA Advances* **2016**, 6, 30199-30204.

Interpolyelectrolyte interactions: relationship between formation of polyelectrolyte complexes in solution and polyelectrolyte multilayer build-up

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Interpolyelectrolyte interactions in solution and at surfaces lead to the formation of polyelectrolyte complexes (PECs) and polyelectrolyte multilayer (PEMs), respectively. Better knowledge of the relationship between the formation and properties of PEMs and PECs would enable the prediction and the control of deposition of a wide range of polyelectrolytes at various surfaces with important application possibilities. Therefore, we compared the results we obtained earlier [1,2] for the complexation of poly(allylammonium) chloride (PAH) and sodium poly(styrenesulfonate) (PSS) with the results obtained for PAH-PSS multilayer build-up. In order to do so, we studied the formation of PAH/PSS multilayers in aqueous solutions of various electrolytes by means of quartz crystal microbalance with dissipation monitoring (QCM-D) and atomic force microscopy (AFM). The QCM-D measurements indicated that the thickness of deposited layers depends on ionic strength and on the type of the type of salt used. The largest deposition of material was noticed in the case of nitrate and perchlorate anions. This is in accordance with the results obtained for PECs by means of DLS and spectrophotometric experiments which showed anion specific aggregation of positive complexes and the formation of precipitates containing larger amount of PAH with respect to PSS. The thickness of deposited films could be also correlated with the complexation enthalpies of used supporting electrolyte ions. The more enthalpically disfavoured complexation process in solution was, the larger was the amount of material deposited. The results can be explained by different counterion distributions around polyelectrolytes, caused by differences in the corresponding ion hydration enthalpies. The observed strong influence of counterion type on the composition of PAH/PSS nanoassemblies provides a path for the modification of multilayer properties simply by changing the type of salt during their preparation. Although the presented results were obtained solely on the system PAH/PSS, the conclusions could be also applied for various other combinations of polyelectrolytes.

[1] J. Požar and D. Kovačević, *Soft Matter*, 2014, **10**, 6530.

[2] J. Požar, J. Salopek, M. Poldrugač and D. Kovačević, *Colloids Surf. A*, in press.

Optimization of the reaction mixture and validation of the microreactor platform for the stereoselective hydrogenation in presence of ionic liquids

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Stereoselective hydrogenation can be performed using Ruthenium BINAP complex (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) [1]. A pseudo-immobilisation of this complex into an ionic liquid allows for an easy separation of this stereoselective catalyst [2]. In combination with a microreactor platform, which is capable of enhancing the mass and heat transfer, a very flexible reactor for such purposes can be built up. An optimization of a colloidal reaction mixture, containing the Ruthenium BINAP complex in an ionic liquid, methanol, water, source of hydrogen and reactant, consists of various parts:

- (i) A suitable ionic liquids should be selected. A series of tetraalkylammonium bistriflamides (N[R₂][Tf₂N]) with N = 4, 6, 8, 10 and 12 were tested.
- (ii) An optimum amount of water to keep the reaction mixture homogeneous has to be found, because bistriflamide ionic liquids and water show limited miscibility. The three-phase diagram of a mixture IL (N = 8), methanol and water was predicted using the COSMO-RS methodology.
- (iii) A suitable source of hydrogen has to be chosen – either a donor or gaseous hydrogen.

A validation of the microreactor platform for the stereoselective hydrogenation has also been realized:

- (i) A calibration of a micro-pump for the volume flow rate was carried out.
- (ii) Inputs of all reactants including the possibility of gaseous hydrogen were prepared.
- (iii) A correction for the pressure drop on entrance effects was approached by performing comparable measurements using a bypassing of the microreactor.

Acknowledgements The financial support by Czech Science Foundation GACR through contract No. 15-04790S is gratefully acknowledged.

- [1] T. Floris, P. Kluson, M. Slater, *React. Kinet. Catal. Mechan.*, 2011, **102**, 67. A. Name, B. Name and C. Name, *Journal Title*, 2005, **40**, 5432.
- [2] P. Dytrych, P. Kluson, M. Slater, O. Solcova, *React. Kinet. Catal. Mechan.*, 2014, **111**, 475.

Physico-chemical properties of green hydraulic fracturing fluids for European shale gas extraction

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The thermal and rheological behaviour of three different polysaccharide aqueous dispersions (guar gum, sodium alginate and sodium hyaluronate) were investigated in order to evaluate their performance as viscosity-modifiers for water-based, green fracturing fluid formulations [1]. Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and viscosity measurements were performed in the presence of different salts and co-solutes (NaF, NaCl, NaBr, NaI, Na₂SO₄, NaSCN, NaClO₄, Na₃PO₄, Na₂HPO₄, NaH₂PO₄, KCl, trehalose and urea). According to our results, the salt nature and concentration effectively modify the response of these systems in terms of viscosity and thermal behaviour.

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<http://shalexenvironment.org>

[1] Barati, R. and Liang, J.-T., J. Appl. Polym. Sci., 2014, **131**, 40735.

Wetting Properties of Cosmetic Polymeric Solutions on Hair Tresses

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Hair care products are expected to wet hair well, even when the hair is hydrophobic (undamaged or covered with greasy deposits). Thus wetting properties of various cosmetic formulations on hair are very important, as they influence consumer satisfaction with the product. Wettability of a single hair fibre is an important characteristic; however, it may not be representative of a hair array on head, as it does not take into account complex packing of multiple hair strands. Also, wetting behaviour of polymer solutions on hair is less studied than the properties of surfactants. The objective of the present work is to investigate wetting of hair tresses with the solutions of two polyacrylate polymers broadly used in cosmetic products.

Rheology and wetting properties of the neutralized Aculyn22TM (A22) and Aculyn33TM (A33) polymer solutions on dry hair tresses are studied. Spreading kinetics of the solution droplets is analysed, including penetration, spreading and evaporation, as well as the influence of several additives common in cosmetic formulations [1].

The solutions of both polymers spread on hair tresses. However, they show markedly different behavior presented in Fig. 1.

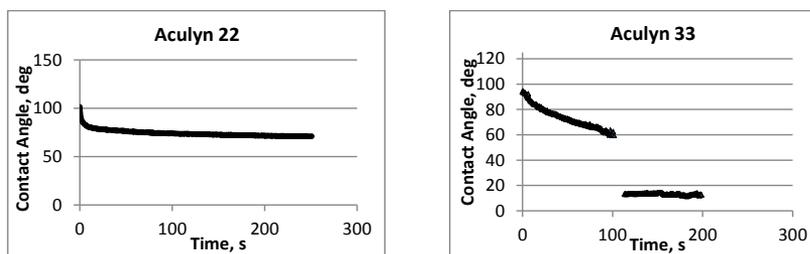


Figure 1 Contact angle of Aculyn 22 and Aculyn 33 solutions on a hair tress.

For the A22 solutions, the droplet remains on the surface of the hair for almost half an hour, and only slow (if any) imbibition is observed. For the A33 solutions, the complete penetration/imbibition happens fast, after the contact angle reaches a critical value (around 60°). This can be attributed to the so-called Cassie–Wenzel wetting transition, when the liquid starts to penetrate inside the hair array. The conditions for this transition are more favourable for the A33 solutions in comparison to the A22.

[1] A. Trybala, A. Bureiko, N. Kovalchuk, O. Arjmandi-Tash, Z. Liu, V. Starov, Wetting properties of cosmetic polymeric solutions on hair tresses. Colloids and Interface Science Communications, COLCOM_2015_69, submitted December 2015

Investigating Structural and Dynamic Roles of Polymers in Model Levan-Based Biofilm Mixtures

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Non-ionic polysaccharide Levan exhibits rather peculiar non-gelling behaviour in pure aqueous solutions up to high polymer concentrations (60 wt. %) [1] that was found to somewhat depend also on the size of levan molecules [2]. On the other hand, Levan is the major polymeric component in biofilms of bacterium *Bacillus subtilis* subsp. *subtilis* str. NCIB 3610 that appear as firm gel-like bacterial coatings. Obviously, the DNA and proteins as additional minor biofilm components have an important role in structuring and dynamic behaviour of such biofilm systems. Our aim was to investigate individual roles that different polymers play in such structurally and dynamically complex systems. To achieve this goal we exploited various physicochemical techniques as the dynamic rheology, small-angle X-ray scattering, dynamic light scattering, microscopy, densitometry, sound velocity measurements, etc. To be as close to reality as possible, we used Levan and DNA that were isolated directly from the biofilm of *B. subtilis* presented in Figure 1, and the fibril forming protein collagen as a model substitute for the native biofilm protein TasA. Macroscopic rheological measurements revealed that the addition of DNA to levan solution contributed mainly to the increase of viscosity and pseudoplasticity of the system. The addition of protein contributed similarly, but also increased the rigidity of the system. Among other, these findings were complemented by the small-angle X-ray scattering results that provided insight into the structure on a molecular scale [2-4].

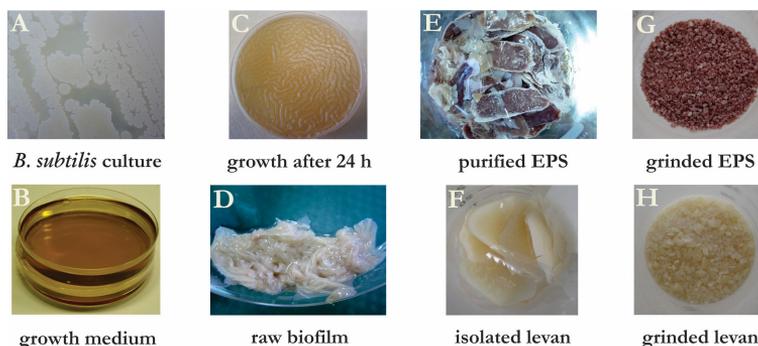


Figure 1 Growth of *B. subtilis* biofilm, purification of extracellular polymeric substances (EPS) and isolation of levan.

Acknowledgements We acknowledge the financial support of Slovenian Research Agency (programs P1-0201, N1-0042 and P4-0116).

- [1] S.A. Arvidson, B.T. Rinehart, F. Gadala-Maria, *Carb. Polymer*, 2006, **65**, 144.
- [2] E. Benigar, I. Dogša, D. Stopar, A. Jamnik, I. Kralj Cigić, M. Tomšič, *Langmuir*, 2014, **30**, 4172.
- [3] E. Benigar, M. Tomšič, S. Sretenovic, D. Stopar, A. Jamnik, I. Dogša, *Acta. Chim. Slov.*, 2015, **62**, 509.
- [4] E. Benigar, A. Zupančič Valant, I. Dogša, S. Sretenovic, D. Stopar, A. Jamnik, M. Tomšič, *in preparation*.

Preparation and Characterization of Hydrogels Containing Biodegradable Materials for Controlled Drug Release

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It is known that the most common eye treatment is eye drops. Approximately 90% of the drug formulation is implemented as eye drops in topical implementation^[1]. However, bioavailability of the eye drop is too low and only 1-5% of the drug can reach the target tissue. The remaining drug is thrown away from the nasal cavity and discarded drugs can cause serious side effects^[2]. Taking into account all of these problems, researchers have developed various approaches to eliminate these disadvantages of the usage of eye drops in recent years. Increasing the viscosity and permeability of eye drop and also loading drugs into micro/nano particles or into contact lenses are some of the approaches that have been published before. Among the others, contact lens based drug delivery systems have two basic advantages which minimize the side effects and eliminate the waste of drugs^[3].

In this study it is aimed to use the drug loaded p-HEMA contact lenses for the treatment of the conjunctivitis, which is one of the common eye diseases. Conjunctivitis is inflammation of conjunctiva and the membrane layer of eyelid on inner surface. Dexamethasone is a hydrophobic drug used for conjunctivitis treatment which was added into hydrogels. Hydrogels were characterized by using FT-IR (Fourier Transform Infrared Spectroscopy), DSC (Differential Scanning Calorimetry). Drug release concentration was measured by using UV-Vis spectroscopy. It was determined that, p-Hema hydrogel released around 40% of the drug in 5 h. However, p-HEMA which loaded in biodegradable materials released approximately 20% of the drug in 5 h. It was demonstrated that the biodegradable materials (EV) which added into the p-HEMA acted as a barrier for drug release. Furthermore, addition of the drug-free Chitosan(Cdf) layer on top of this surface of the hydrogels gave rise to further reduction at the drug release. It was observed that drug release was prolonged with the chitosan layer applied. Thus, controlled drug release was accomplished. Moreover, addition of chitosan layer on top of the contact lenses allowed us to see a prolonge release before the release of drug as well as it prevented the burst release. Also, side effects of the drug were eliminated which was released at the beginning.

This study shows clearly that combining the distinct properties of different materials has been an effective approach for the controlled release of ophthalmic drugs. The dose of drug, which each patient must receive according to his/her drug regimen, can be adjusted by varying the thickness of drug-free Chitosan(Cdf) or loaded biodegradable material applied.

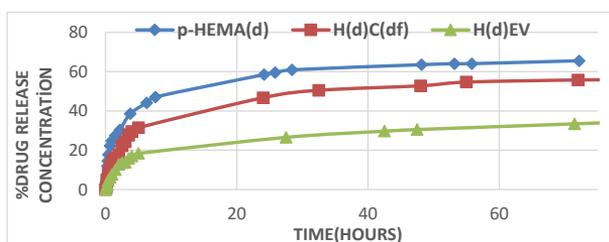


Figure.1. Drug release concentration from p-HEMA contact lenses that were modified by using biodegradable materials as well as drug free chitosan layers

- [1] C. Le Boulrais, L. Acar, H. Zia, P.A. Sado, T. Needham, R. Leverage, 1998, 'Ophthalmic Drug Delivery Systems - Recent Advances', *Progress in Retinal Eye Research*, 17(1),33-58.
- [2] J.C. Lang, 1995, 'Ocular Drug-Delivery Conventional Ocular Formulations', *Adv Drug Deliver Rev*, 16(1), 39-43.
- [3] Y. Kapoor, J.C. Thomas, G. Tan, V.T. John, A. Chauhan, 2009, 'Surfactant-laden soft contact lenses for extended delivery of ophthalmic drugs', *Biomaterials*, 30, 867-878.

Mesoporous Colloidal Gels for Optical Applications - Synthesis and Characterisation

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One of the key drawbacks of equilibrium self-assembly as a fabrication technique for novel microstructures is the requirement for a given system to achieve its ground state. The avoidance of kinetic traps which prevent a mixture from coming to equilibrium has proven experimentally challenging[1].

However, by promoting kinetic arrest via introduction of additional binding mechanisms, it becomes possible to fabricate a wide range of new amorphous or mesoporous materials. By varying the shape and size of particles and the strength of the inter-particle interactions, the characteristics of these arrested phases can be tuned. Such materials would have possible applications in photovoltaics, batteries, and optics[2].

We use DNA-coated polystyrene colloids as building blocks to assemble these non-equilibrium phases. Here we discuss the synthesis of these microstructures and characterise them using structure factor and chord analysis (Figure 1). In particular, we discuss the dependence of the microstructure achieved on particle size and volume fraction for comparison with theoretical results.

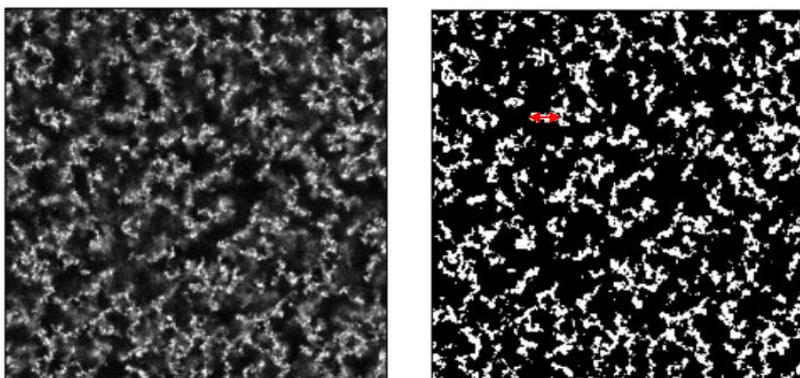


Figure 1: (Left) Micrograph of a typical gel of DNA coated colloids, taken on a confocal microscope using a dye attached covalently to the particle surface. (Right) The same image processed to highlight colloid rich and poor phases for lengthscales analysis.

Acknowledgements

The author would like to thank the EPSRC CDT in Nanoscience and Nanotechnology for the opportunity to undertake this project.

[1] L. Di Michele, E. Eiser, *Phys. Chem. Chem. Phys.*, 2013, **15**, 3115-3129.

[2] L. Di Michele, F. Varrato, J. Kotar, S. Nathan, G. Foffi, E. Eiser, *Nat. Commun.*, 2013, **4**, 2007.

Effect of Eu(III) chloride on the gelification behavior of poly(acrylic acid)

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Supramolecular gels are an important class of soft materials: they are basically formed by solvent molecules inside in a 3D network structure and can be considered from soft and weak to hard and tough, depending on their mechanical properties. [1] The gelation process can be accomplished in different ways through, for example, interaction between a charged polymer and a metal ion. [2]

In this work, the interaction between poly(acrylic acid) (PAA) and the trivalent ion Eu(III), to form luminescent gels, has been studied.

For that, a phase diagram for polymer-ion mixture has been plotted (Figure1) showing that for high molar ratios $\text{Eu}^{3+}/\text{PAA}$ different phase transitions take place. We have focused our work in the region where the formation of weak and strong gels is occurring

From rheological measurements, we have found that the mechanical strength of gels increases by increasing the concentration of PAA, because the elastic module (G') increases when it increases the concentration of PAA. A similar trend is found in yield stress values, from which the gel begins to behave as a liquid. Thus, the higher the concentration of PAA the higher is the yield stress. The frequency sweeps shows that PAA-Eu gels and weak gels exhibit a rheological solid-type behavior, with a storage module (G') predominating over loss modulus (G'') in the studied frequency.

The formation of the gel phase can also be followed by fluorescence spectroscopy. It can be observed that the emission of fluorescence at 424 nm increases by increasing the molar ratio $\text{Eu}^{3+}/\text{PAA}$. Such behavior may be explained both by a decrease in the number of coordinated water molecules and by binding of Eu(III) to deprotonated PAA. However, the formation of gel phase is reversible and dependent on the Eu(III) concentration; in fact, by increasing the molar ratio values, above a certain critical point, it occurs a disaggregation of the gel structure, mainly due to electrostatic repulsions between ions Eu(III) and $\text{Eu}^{3+}/\text{PAA}$; this is supported by the decrease in the emission of fluorescence of Eu(III) mixed solutions.

The effect of Eu(III) in the PAA gel formation mechanism is complemented with the analysis of FTIR, SEM and EDX mapping data.

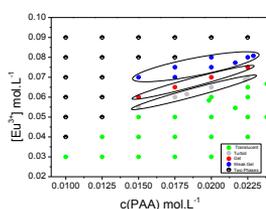


Fig. 1. Phase diagram of $\text{Eu}^{3+}/\text{PAA}$ mixed system.

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[1] Silva, F. F.; Menezes, F. L.; Luz, L. L.; Jr, S. A. *New J. Chem.*, 38, 893-896, 2014.

[2] Qi, X.; Wang, Z.; Ma, S.; Wu, L.; Yang, S.; Xu, J. *Polymer*, 55, 1183-1189, 2014.

Droplets-based millifluidic for the establishment of protein-polysaccharide phase diagrams

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Texture, structure, taste as well as stability of food products are strongly related to its constituent's interactions. The understanding of these interactions is still a challenge in food-processing. Besides lipids or flavour, proteins and polysaccharides are widely used in food products. It is already well known that under specific conditions protein-polysaccharide mixture can lead to liquid-liquid phase separation, of segregative or associative type. To highlight the conditions of phase separation, a phase diagram is established. However, such a study, generally performed in bulk is time and raw material consuming. Therefore alternative strategies for rapid phase diagram determination using microfluidics recently emerged. Microfluidic enables a large reduction of engaged volume, a precise control over experimental conditions and mixed systems composition as well as an acceleration of reaction time. Nevertheless, to the best of our knowledge, these techniques were only described for segregative phase separated systems [1], [2].

In the present work we developed a droplets-based millifluidic device for rapid phase diagram building of associative phase separated system. Binodal curve was determined by turbidity measurements within the droplets using grey balance analysis. Cloud points, corresponding to the onset of phase separation, were defined as the composition corresponding to a 10% increase in turbidity compared to the original reference solution. The first part of the study was dedicated to the proof of concept using a colloidal suspension of titan dioxide (TiO₂). We evidenced proportionality between the turbidity measured in bulk using spectrophotometer and the one determined within the droplet by grey balance analysis. The second part of the study was devoted to establish the phase diagram of an associative phase separated system: β -lactoglobulin (BLG) / Gum Arabic (GA), first in bulk and then using the more innovative droplets-based millifluidic approach where the composition and total concentration were finely tuned by flow rates variation (Figure 1). Considering the high similarities obtained at both scales, we now plan to extend the technic to several protein-polysaccharide mixtures.

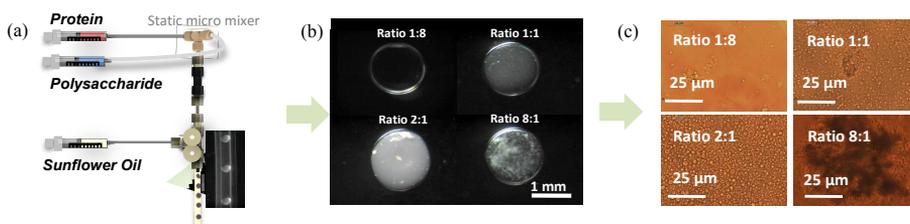


Figure 1: Biopolymers droplets at various protein-polysaccharide ratio (1% total concentration) obtained by millifluidic approach (a) and observed using (b) magnifying glass (c) phase contrast optical microscopy

[1] J. Leng, M. Joanicot, A. Ajdari. *Langmuir*, **23**, 15-17 (2007).

[2] D-F-C. Silva *et al.*, *J.Chromatogr. A.*, **1370**, 115-120 (2014).

Rheology of green gelling agents in fracturing fluid formulation for shale gas exploitation

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Viscosity plays a key role in the performance of a hydraulic fracturing fluid. A viscous media is required in the first steps, in order to carry the proppant down hole and keep the fractures open. In a second phase most of the fluid must be pumped up and recovered [1]. Our aim is the control of the viscosity of the fracking fluid, moving toward a greener formulation by reducing the content of hazardous chemicals that are currently used in shale gas operations [2]. Here we report on the rheological behaviour of Sodium Hyaluronate, Guar Gum and Sodium Alginate dispersions and on the effect of adding different salts and biocompatible additives as thickener agents.

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<http://shalexenvironment.org>

- [1] Ground Water Protection Council, *Modern Shale Gas Development in the United States: A Primer*, 2009.
- [2] D. M. Kargbo, R. G. Wilhelm and D. J. Campbell, *Environ. Sci. Technol.*, 2010, **44**, 5679-5684.

Light-induced heating of gold nanoparticle- microgel hybrids

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The ability of hybrid microgel systems to respond to external stimuli is of great interest in basic research as well as for medical and technical applications. For photo-responsive systems, light-sensitive dyes or nanoparticles are combined with a responsive microgel matrix. Poly(N-isopropylacrylamide) (PNIPAM) - based microgels are sensitive to temperature, pH or ionic strength. The thermosensitive microgel exhibits a volume phase transition at around 32°C. We combine the PNIPAM microgel with spherical gold nanoparticles (Au NP) to create a photo-responsive hybrid material. The incorporation of the Au NP into the PNIPAM microgel influences the optical properties of the microgels via plasmon coupling during their volume phase transition [1] [2]. In order to study their effect as hot spots, we coupled a second laser for plasmon excitation into our dynamic light scattering (DLS) set-up. To improve the photothermal effect for our purpose, the loading density of Au NP within the microgels was varied and the size changes depending on loading, temperature and excitation laser intensity investigated. The plasmon excitation of Au NP by laser irradiation results in local heating providing enough heat to induce a reduction in the microgel size. The light-induced volume change can be controlled by varying the amount and spatial distribution of uptaken Au NP. The apparent internal temperature within the gel can be determined.

[1] H. Lange, B.H.A. Juarez, A. Carl, M. Richter, N.G. Bastus, H. Weller, C. Thomsen, R. von Klitzing and A. Knorr, *Langmuir*, 2012, **28**, 8862.

[2] K. Gawlitza, S.T. Turner, F. Polzer, S. Weller, M. Karg, P. Mulvaney and R. von Klitzing, *Phys. Chem. Chem. Phys.*, 2013, **15**, 15623.

Shearing colloidal gels

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Soft matter systems have the intriguing property to be able to form a variety of different arrested states, encompassing (among others) repulsive, attractive glasses and gels. In this work, we numerically study a gel-forming colloidal system[1,2], modeled as a modified Lennard-Jones potential complemented with a repulsive Yukawa tail, under the effect of shear. Starting from an off-equilibrium arrested state at low temperature, we have sheared the system using Lee-Edwards boundary conditions at different shear rates. We find that at high shear rates the energy of the system increases, reaching a non-equilibrium steady state (Fig.1a). We thus identify a mapping between shear rate and temperature which enables us to connect sheared gels to equilibrium states: for each shear rate we consider the equilibrium system having the same potential energy and we compare the structure of the two states. We find that shear does not significantly alter the local scales but has a profound effect at large length scale, inducing the system closer to a phase separation (Fig.1b-d). For low shear rates, instead the sheared gel is actually able to visit lower energy states with respect to equilibrium simulations (Fig.1a), reaching a crystal state. We then consider a polydisperse version of the model, in order to avoid crystallization and to examine the gel rearrangements at low shear rates.

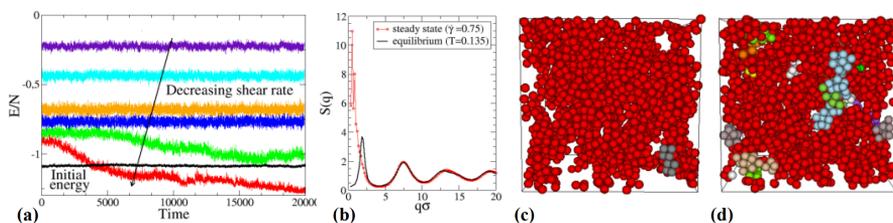


Figure 1 (a) Potential energy per particle E/N versus time for different shear rates starting from an initial gel state; (b) Comparison of $S(q)$ for sheared (shear rate=0.75) and equilibrium ($T=0.135$) states having the same potential energy; (c) Snapshot of a gel sheared into a steady-state at a shear rate 0.75; (d) Snapshot of the corresponding system in equilibrium ($T=0.135$).

Acknowledgements JMRF and EZ acknowledges support from ETN COLLDENSE (H2020-MCSA-ITN-2014, No. 642774).

[1] Campbell, Anderson, van Duijneveldt, Bartlett, *Phys. Rev. Lett.*, **94**, 2005, 208301.

[2] F. Sciortino, P. Tartaglia, E. Zaccarelli, *J. Phys. Chem. B*, **109**, 2005, 21942.

Spherical Nanocomposite Particles Prepared from Mixed Cellulose-Chitosan Solutions

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Novel cellulose-chitosan nanocomposite particles with spherical shape were successfully prepared via mixing of aqueous biopolymer solutions in three different ways. Macroparticles with diameters in the millimeter range were produced by dripping cellulose dissolved in cold LiOH/urea into acidic chitosan solutions, inducing instant co-regeneration of the biopolymers. Two types of microspheres, chemically crosslinked respective non-crosslinked, were prepared by first mixing cellulose and chitosan solutions obtained from freeze thawing in LiOH/KOH/urea. Thereafter epichlorohydrin was applied as crosslinking agent for one of the samples, followed by water-in-oil (W/O) emulsification, heat induced sol-gel transition, solvent exchange, washing and freeze-drying. Characterization by X-ray photoelectron spectroscopy (XPS), total elemental analysis, and Fourier transform infrared spectroscopy (FT-IR) confirmed the prepared particles as being true cellulose-chitosan nanocomposites with different distribution of chitosan from the surface to the core of the particles depending on the preparation method. Field emission scanning electron microscopy (FE-SEM) and laser diffraction was performed to study the morphology and size distribution of the prepared particles. The morphology was found to vary due to different preparation routes, revealing a core-shell structure for macroparticles prepared by dripping, and homogenous nanoporous structure for microspheres. The non-crosslinked microparticles exhibited a somewhat denser structure than the crosslinked ones, which indicated that crosslinking induced a lower degree of freedom during packing of the chains before and under regeneration. From the obtained volume-weighted size distributions it was found that the crosslinked microspheres had the highest median diameter. The results demonstrate that not only the mixing ratio and distribution of the two biopolymers, but also the morphology and nanocomposite particle diameters are tunable by choosing between the different routes of preparation investigated.

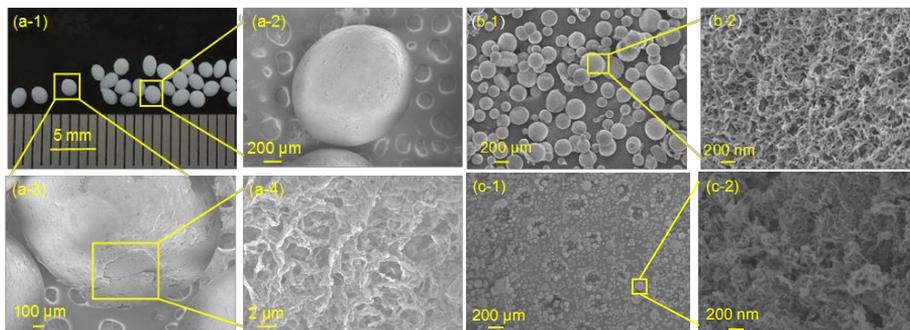


Figure 1. FE-SEM images at different magnification of the biocomposite particles prepared with different routes, (a) macroparticles, CCP; (b) chemically crosslinked microspheres, CCMS-CL and (c) non-crosslinked microspheres, CCMS.

Keywords: cellulose; chitosan; nanocomposite; microspheres; regeneration

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Effect of fluctuations on tracer diffusion in networks

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We study the tracer diffusion in simple Lennard-Jones fluids and semi-flexible chain networks, using coarse-grained molecular dynamics computer simulations. For the fluid system, we find that various dynamic regimes are nontrivially dependent on inter-(tracer-fluid) and intra-(fluid-fluid) interactions, where fluctuations arising in the system largely affect the tracer diffusion. We compute the tracer diffusivities spanning a wide range of the interaction strengths, and reveal that an abrupt diffusivity shift signifies the gas-liquid phase transition. For the network system, we further extend the model towards tracer-hydrogel diffusion by imposing connectivity and semi-flexibility between the fluid particles that constitute the hydrogel network. Depending on the network-network and the tracer-network couplings, the network structure reveals a non-monotonic behaviour, and we discuss how the tracers diffusion and transport show a variety of dynamic regimes in conjunction with the network rigidity and fluctuations.

Flexibility of never dried cellulose fibre measured with AFM

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The fibre wall of cellulose can be considered as a gel and it is the surrounding media that affect the fibre wall properties and the properties can be changed by for example varying the salt concentration in the surrounding media.

The flexibility for the highly anisotropic cellulose fibres is of high importance in almost every pulping and papermaking process. This applies to the complex flow patterns and interactions between the fibres in the forming section, to the formation of a fibre network where the flexibility plays an important role for the paper quality parameters as well as during the fractionation of pulps in different length, diameter and strength fractions. Knowledge about this parameter is thus vital for the papermaking processes.

We have developed a new method to evaluate the flexibility of the cellulose fibre. By using AFM force measurements we have measured the flexibility of never dried cellulose fibres of different origins. The fibre is mounted over a sharp edge in wet state using magnetic force to clamp the fibre to avoiding glue that can penetrate into the gel like fibre wall. Force displacement curves are captured at different length a way out on the fibre from the edge. From these force displacement curves the flexibility can be calculated by using relevant theoretical models. The method has successfully been verified by measuring the flexibility of glass fibre.

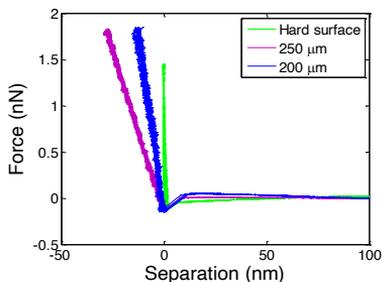


Figure 1 AFM fibre bending data from measurement on never dried pulp fibre.

In search for enhanced stability of biaxial phase in ternary nematic mixtures of hard axially-symmetric particles

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A peculiarity of mixtures of rodlike (R) and platelike (P) particles consists in the formation of a biaxial nematic (\mathbf{N}_b) phase, which may turn out to be either metastable or stable with respect to demixing into the uniaxial nematic phases, a rod-rich \mathbf{N}_+ phase and a plate-dominated \mathbf{N}_- phase. A growing interest towards the study of the biaxial phase in a particular case of systems including long rods is motivated by concepts addressing phase behavior and orientational order in carbon nanotubes/liquid crystal dispersions. The present communication is focused on the effect of doping the binary system of rods and plates with relatively small aspect ratios by an admixture represented by long rods or spacious thin plates upon stability of the biaxial phase. We employ an off-lattice model of n -component athermal nematic system of rectangular prisms having discrete distribution in orientations, collective interactions of particles being treated in the 3rd virial approximation.

The binary R–P sub-system consists of particles having equal volume and aspect ratios ($\gamma_R = 5$, $\gamma_P = 1/5$), whilst the admixture rods (L) or plates (T) have aspect ratios holding $\gamma_R \leq \gamma_L$ and $\gamma_T \leq \gamma_P$. Emergence of biaxial symmetry is inferred by exact calculation of the Gibbs energy (\tilde{G}) along the sections $y_\alpha = \text{const}$ ($\alpha = L$ or T) of the composition triangle (y_α is the mole fraction of the component α) at constant values of t^* defined as proportional to the reduced temperature ($k_B T / P v$). Lines $\mathbf{N}_+ - \mathbf{N}_b$, $\mathbf{N}_- - \mathbf{N}_b$ of the second-order transition, complying with the condition of the equilibrium uniaxial orientational distribution, are located from the matrix singularity: $\left\| \partial^2 \tilde{G} / \partial \Delta_i \partial \Delta_k \right\|_{\Delta_i = 0} = 0$; Δ_i are the biaxial order parameters for each component i . In the R–P system under study, biaxial nematic is metastable with respect to $\mathbf{N}_+ - \mathbf{N}_-$ demixing. Admixing of long rods or thin plates is shown to promote thermodynamic stability for \mathbf{N}_b phase even at very low concentrations within a broad interval of t^* . However, shorter rods (e.g., $\gamma_L = 6$) or thicker plates do not sustain formation of a stable biaxial phase in the ternary system. Data of calculations are discussed in connection with the studies of the effect of polydispersity upon the properties of biaxial phase in mixtures of plates and rods with discrete orientations.

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Physically and chemically gelling hydrogel formulations based on poly(ethylene glycol) diacrylate and Pluronic 407

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Physical hydrogels are viscoelastic solids containing a polymer network held together by physical interactions and which is swollen in water. Due to the reversibility of the cross-links, physical hydrogels are often used as injectable hydrogels, as shear thinning materials in additive manufacturing of hydrogels, as drug delivery devices or in tissue engineering.^[1] However, the mechanical strength of physical hydrogels is often limited. In order to fix the shape of a physical hydrogel after processing into a defined shape, there is a general demand for formulations of physical hydrogels which can be chemically cured. Chemical hydrogels resulting from the curing process then have improved form stability and mechanical strength. An attractive approach for the formulation of both physically gelling and chemically curable hydrogels is the combination of two materials which contribute the two desired properties. In this contribution, the success of this approach is demonstrated using the synthetic hydrogel precursors poly(ethylene glycol) diacrylate (PEG-DA) and Pluronic 407 (P407).

To this end, hydrogel formulations containing P407, PEG-DA ($M_n = 700 \text{ g mol}^{-1}$) and the photo-initiator 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propan-1-one (Irgacure 2959) were characterized concerning their physical and chemical gelling behavior. Upon addition of PEG-DA to P407 solutions, their gel transition temperature T_{gel} was altered and could be adjusted between 10 °C and 39 °C. At P407 concentrations c_{P407} of <22.5 wt.-%, T_{gel} increased compared to P407 solutions by adding PEG-DA. At c_{P407} >22.5 wt.-% T_{gel} decreased. This could be explained by a decrease of P407 micelle size upon PEG-DA addition, as shown by dynamic light scattering. Chemical gelation of the formulations was investigated by FT-IR spectroscopy, by rheology, and by the equilibrium degree of swelling of the cured hydrogels. The shear moduli and equilibrium degrees of swelling of the cured hydrogels could be adjusted by the PEG-DA concentration in the formulation, similar to pure PEG-DA hydrogels.

In order to demonstrate the possibility of using the hydrogel formulations as injectable hydrogels, we used them as inks for the additive manufacturing technique of robotic dispensing. Thus we were able to produce various shapes of spatially well-defined hydrogels (see Figure 1). Our results give rise to the conclusion that the hydrogel formulations are well suited as injectable hydrogels with adjustable properties.



Figure 1 Ear shape produced from the hydrogel formulations by robotic dispensing.

Acknowledgements We gratefully acknowledge generous financial support by the Carl Zeiss Foundation and the University of Stuttgart within the *Projekthaus NanoBioMater*.

[1] T. Jungst, W. Smolan, K. Schacht, T. Scheibel, J. Groll, *Chemical Reviews* **2016**, *116*, 1496-1539.

Organic-inorganic hybrid polysilsesquioxane ionogel electrolyte for energy storage devices

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Hybrid ionogels fabricated with 1M LiTFSI in *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPYTFSI) crosslinked with a ladder-like structured poly(methacryloxypropyl)silsesquioxane (LPMASQ) were investigated as high temperature gel polymer electrolytes for lithium ion batteries. In addition to the exceeding low crosslinker concentration (~2 wt %) required to completely solidify the ionic liquids which allowed for high ionic conductivities comparable to the liquid state ionic liquid (~0.5 mS/cm), these hybrid ionogels exhibited superior thermal stabilities (> 400 °C). Lithium ion battery cells fabricated with these gel polymer electrolytes at various C-rates at various temperatures showed almost same cell performance as the cells with liquid electrolyte. Moreover, these hybrid ionogels exhibited excellent cycling performance after 100 cycles at 90 °C, sustaining over 98 % coulombic efficiency, while conventional organic crosslinking agents suffered from thermal degradation and subsequent cell failure. Highly advantageous properties of these hybrid ionogels, such as high ionic conductivity in the gel state, thermal stability, excellent C-rate performance, cyclability, and nonflammability offer opportunities for applications as high temperature electrolytes.

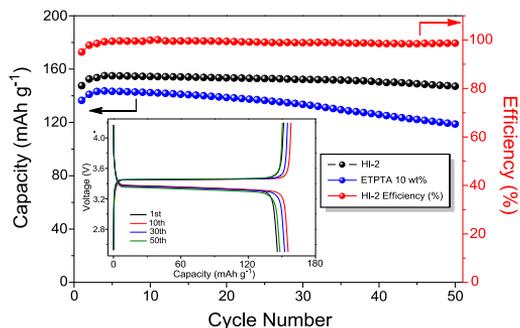


Figure 1. Cyclability of HI-2 ionogel compared with a conventional organic ionogel fabricated with ETPTA, with the inset figure showing the representative discharge profiles

- [1] J. H. Lee, A. S. Lee, J. C. Lee, S. M. Hong, S. S. Hwang, C. M. Koo, *J. Mater. Chem. A*, 2015, **3**, 2226.
- [2] A. S. Lee, J. H. Lee, J. C. Lee, S. M. Hong, S. S. Hwang, C. M. Koo, *J. Mater. Chem. A*, 2014, **2**, 1277.
- [3] A. S. Lee, J. H. Lee, S. M. Hong, J. C. Lee, S. S. Hwang, C. M. Koo, *RSC Advances*, 2015, **5**, 94241.
- [4] W. Na, A. S. Lee, J. H. Lee, S. S. Hwang, S. M. Hong, E. Kim, C. M. Koo, *Electrochimica Acta*, 2016, **188**, 582.

Magnetic PNIPAM Microgels: Towards multi responsive materials

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Multi responsive Microgels are of great interest for sensoric and actuatoric devices and for drug delivery systems. Microgels based on N-isopropylacrylamid (NIPAM) are promising candidates for this purpose since they respond fast to outer stimuli. Depending on the microgel composition the stimuli can be manifold. NIPAM based microgels are temperature sensitive and exhibit a volume phase transition (VPT) at about 32°C (VPTT) due to expulsion of water above the VPTT. The gel structure is collapsing. This process can be reversed by decreasing the temperature below the VPTT where the gel swells again. By adding different co-monomers the volume phase transition can be triggered with the change of pH or ionic strength. In order to let migrate the PNIPAM microgels in an external magnetic field the microgels are doped with magnetic nanoparticles (MNP) in the present work [1].

We control the distribution of the MNP inside the magnetic microgel (Fig. 1) by modification of the microgel structure. The structure of the microgel is varied by changing the cross-linker density and the charge density of the microgels. Furthermore, we report the response of the magnetic microgel to an external static magnetic field both in bulk (migration, UV-VIS spectroscopy) and after adsorption at a surface (deformation, atomic force microscopy (AFM)). The challenge is to optimize the amount of uptaken magnetic nanoparticles that the microgels show pronounced sensitivity to the magnetic field but that the original gel properties (like temperature sensitivity) are still preserved. Therefore the elasticity is studied by indentation experiments with AFM. Temperature sensitivity is investigated with dynamic light scattering (DLS)/zeta potential in bulk and with AFM on the surface before and after embedding of MNP.

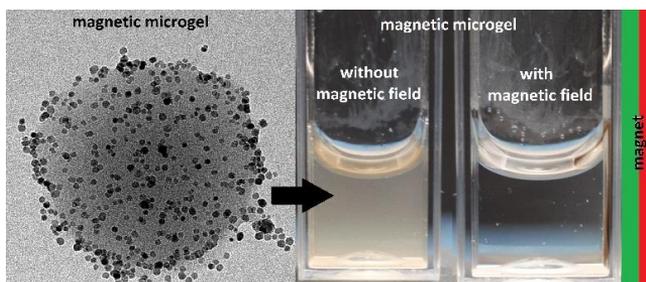


Figure 1: TEM picture of magnetic microgel and the separability by static magnetic fields.

Acknowledgements

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[1] S.Backes, M. U. Witt, E. Roeben, L. Kuhrts, S. Aleed, A. M. Schmidt, R. v. Klitzing, *J Phys Chem B*, 2015, **36**, 119.

Cellulose Dissolved in Aqueous Tetrabutyl Ammonium Hydroxide

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Cellulose is the World's most abundant biopolymer and an important renewable raw material source for many different materials. The spinning of textile fibers or casting of films are typically done from solutions. However, cellulose is fascinatingly insoluble in most common solvents, and finding clean and useful solvents for cellulose, still remains a challenge. One promising solvent that has been proposed is, 40 wt.% aqueous tetrabutyl ammonium hydroxide, TBAH(aq). In this solvent we have characterized the dissolution state of microcrystalline cellulose (MCC, $M_w \approx 29$ kD), and dissolving pulp ($M_w \approx 162.3$ kD), using a combination of ¹H NMR diffusion, rheology, light and small angle X-ray scattering (SAXS). At lower concentrations (< 0.05 g/cm³ for MCC and < 0.02 g/cm³ for pulp) cellulose is molecularly dissolved while at higher concentrations aggregation and gelation is observed, resulting in strongly shear thinning samples. The cellulose is preferentially solvated by TBA⁺ ions, as seen by SAXS and NMR diffusion experiments. From TBA⁺ diffusion we estimate a constant "binding" of 1.2 TBA⁺ ions per glucose monomer unit. From these results we will also briefly discuss some of the particular requirements of good cellulose solvents.

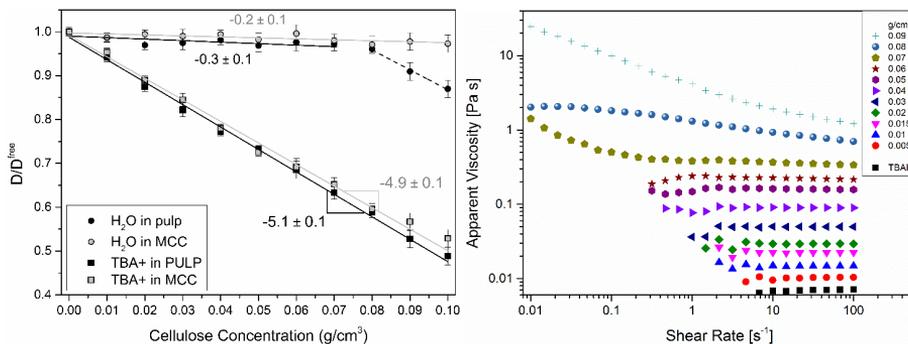


Figure 1 (Left) Relative diffusion coefficients of H₂O-OH and TBA⁺ as a function of cellulose (MCC and pulp, respectively) concentration. **(Right)** Viscosity profiles in the range of shear rate between 0.01 and 100 s⁻¹ from 0.005 to 0.09 g/cm³ of MCC in 40 wt% TBAH(aq).

Acknowledgements The work was supported by the Bo Rydin Foundation for Scientific Research and the Swedish Research Council.

- [1] H. B. Liu, K. L. Sale, B. M. Holmes, B. A. Simmons, S. Singh, *J. Phys. Chem. B* 2010, **114**, 4293.
- [2] J. M. Zhang, H. Zhang, J. Wu, J. Zhang, J. S. He, J. F. Xiang, *Phys. Chem. Chem. Phys.* 2010, **12**, 1941.
- [3] M. E. Ries, A. Radhi, A. S. Keating, O. Parker, T. Budtova, *Biomacromolecules* 2014, **15**, 609–617
- [4] L. Gentile, U. Olsson, *Cellulose* 2016 **Accepted**.
- [5] M. Gubitosi, H. Duarte, B. Medronho, L. Gentile, U. Olsson **in Preparation**.

Biosynthesis of gold nanoparticles using an ecofriendly method and cytotoxicity assessment on Huh7 and HFFF2 cell lines

Introduction:

Gold nanoparticles are one of the most widely used materials in pharmaceutical industries. Due to their detectability in biological systems, suitable electrical and thermal conductivity, etc, gold nanoparticles serve as good vehicles in novel drug delivery systems. A relevant method to produce gold nanoparticles is reducing Au^+ to Au^{0+} , usually using chemical reductants. However, replacing these conventional procedures with less expensive and more ecofriendly methods especially using reductive capability of plants is of utmost importance. The synthesized nanoparticles usually named as *green* nanoparticles. The purpose of this study was the biosynthesis of green gold nanoparticles by gold chloride regenerating methods using the reductive properties of tannins extracted from the plant Sumac (*Rhus coriaria*), a native plant of Iran.

Methods:

The plant gathered from Zanjan, Iran. Aqueous extract of the plant prepared and standardized based on the amount of the Gallic acid. Gold nanoparticles produced using extract sumac with gold chloride regenerating methods. The product was then confirmed by different methods such as XRD, TEM, Particle size analyzing, UV-Vis spectroscopy, etc. Cytotoxic properties of nanoparticles on human hepatoma cell line Huh7 and human normal cell line HFFF2 were investigated in different time periods using MTT assay.

Results:

Our data confirmed the biosynthesis of green gold nanoparticles. The stability, particle size and other properties of the product were acceptable. Furthermore, cytotoxicity evaluations showed no cytotoxic effect on studied cell lines.

Conclusion:

According to our results, we can introduce the plant *Sumac (Rhus coriaria)* as a suitable plant in biosynthesis of gold nanoparticles. This method is environmentally friendly and less expensive than conventional methods. Besides, no cytotoxic effect was observed in our investigations.

Interfacial interactions in the nanocomposites based on thermosetting polyurethane and multi-walled carbonanotubes with surface functionalization

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The multi-walled carbonanotubes (MWCNTs) have excellent thermal, magnetic, electric, mechanical properties which made them the outstanding candidates as nanofillers for polymers. However in the direct mixing of MWCNTs into host matrix it is often difficult to separate agglomerated MWCNTs due to their intrinsic hydrophobic surface. The most effective approach to improve dispersivity of MWCNTs and interfacial interactions in MWCNT-polymer nanocomposites is the chemical functionalization of the outer walls of CNTs that allows covalent attachment of polymer to the nanotubes and as result high impact of nanofiller to the material's properties. The thermosetting Polyurethane-MWCNT nanocomposites with 0.01 - 0.25 wt. % of nanofiller were prepared and studied using chemical analysis, SEM, TEM, DMA, stress-strain testing. Via acid oxidation and reduction chemical procedures hydroxyl, carboxyl, phenol functional groups to be used as cross-linking sites to the matrix were generated on the MWCNT surface¹. Good nanotubes dispersion in the PU matrix were observed by SEM and TEM for the nanocomposites with ultralow contents of functionalized MWCNTs (0.01 and 0.1%) whereas both individually separated nanotubes and their small agglomerates were presented in the matrix at 0.25 % nanotubes (Fig. 1). The strong dependence of nanocomposite's glass transition and dynamic mechanical performance on variations in the nanotube surface chemistry was demonstrated: the large impact of MWCNTs was observed only at direct covalent bonding between PU matrix and nanotube lattice. The pronounced dynamic heterogeneity within the PU glass transition was registered by DMA analysis. The mechanical properties testing indicated that small amount MWCNTs (0.01%) could significantly improve the mechanical performance of the matrix. The tensile strength was increased from 2.0 MPa to 4.0 Mpa (Fig.2). The best results were obtained for nanocomposites containing MWCNTs which covalently bounded to the matrix:the Young's Modulus increased by 2–4 times depending on concentration of nanotubes. Conclusion: chemical functionalization of the outer walls of MWCNTs allows covalent attachment of polymer to the nanotubes that provide good dispersion in the matrix and enhancing of mechanical properties of the nanocomposites.

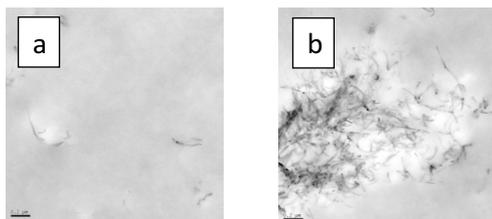


Fig. 1 TEM images of PU containing (a) 0.1 and (b) 0.25 wt% MWCNT-ox.

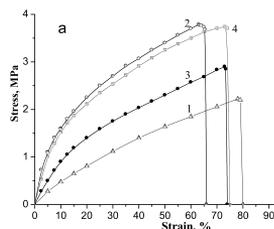


Fig. 2 Stress-Strain curves for the native PU (1) and for the nanocomposites with 0.01 (2), 0.10 (3) and 0.25 (4) wt% of MWCNT-ox

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What is the origin of efficiency of partially burnt rice husk ash as wide-spectrum water filter?

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Rice husk ash burning at controlled temperature and compacted manually (without electrical supply) can be compacted and used as an extremely cheap but efficient water purifier, especially against salt or organic pollutants. Full technology from the field to repository that can be used has been described and openly free-access patented by PC Kumar [1]. At microscopic level rice husk ash fully burnt is a mesoporous silica-based material with local worm-like nanostructure and typical cylindrical pores of 2 nm has been shown to be an extremely efficient absorbers with a broad target range [2]. More recently, partial burning, i.e. using mesoporous material containing some graphitized carbon-rich material resulting from the combustion. In this case, the surface of the mesopores in this material is partly "hydrophilic" and partly "hydrophobic", with afferent ion physisorption mechanisms. These partially burnt rice husk is produced in the form of a black powder have shown extremely improved performance for retaining salts as well as organic materials, and are used as commercially available advanced water filters. Long range interactions can be decomposed in a general hydrophobic interaction[3], combined with electrostatic, depletion well as Hofmeister effects[4]. Hofmeister "inversions" have been known since nearly a century, but the first tentative predictive theory of inverted Hofmeister series are only recent [5]. In the present work, we characterize the nanostructure present by scattering of totally burnt and several batches of partially burnt rice husk prepared by Tata research for real applications. We measure salt and model organic retention, and will compare the results to the current cutting-edge theory of specific adsorption. Since the channels of this mesoporous material are of colloidal size[6], weak long range interactions are dominant [7]. We analyze in the case of rice husk ash in the case of salts and non-electrolytes the complex interplay between hydration force, dispersion forces and depletion effects in the light of most recent predictive theories available in the literature.

- [1] Kapur PC. Production of reactive bio-silica from the combustion of rice husk in a tube-in-basket (TiB) burner. *Powder Technology* 1985;44:63–7. doi:10.1016/0032-5910(85)85022-1.
- [2] Kumar A, Sengupta B, Dasgupta D, Mandal T. Recovery of value added products from rice husk ash to explore an economic way for recycle and reuse of agricultural waste. ... *Science and Biotechnology/ ...*
- [3] Donaldson SH Jr., Røyne A, Kristiansen K, Rapp MV, Das S, Gebbie MA, et al. Developing a general interaction potential for hydrophobic and hydrophilic interactions. *Langmuir* 2015;31:2051–64. doi:10.1021/la502115g.
- [4] Schwierz N, Horinek D, Netz RR. Reversed anionic Hofmeister series: the interplay of surface charge and surface polarity. *Langmuir : the ACS Journal of Surfaces and Colloids* 2010;26:7370–9. doi:10.1021/la904397v.
- [5] Schwierz N, Horinek D, Netz RR. Specific ion binding to carboxylic surface groups and the pH dependence of the Hofmeister series. *Langmuir : the ACS Journal of Surfaces and Colloids* 2015;31:215–25. doi:10.1021/la503813d.
- [6] Cambedouzou J, Diat O. Quantitative small-angle scattering on mesoporous silica powders: specific surface estimation. *J Appl Crystallogr* 2012;45:662–73.
- [7] Gouze B, Cambedouzou J, Rébiscoul D. How hexagonal mesoporous silica evolves in water on short and long term; *Microporous and Mesoporous Materials* 2014;183:168–76.

Polymer Nanocomposite Materials reinforced with amyloid fibrils

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Fibers have fascinated mankind since the very beginning. Most of textile products are made of fibers, which for centuries have been obtained from natural sources. Many biological materials use nano fibers as building block. One of the best examples is spider webs. The incredible properties of spider silk fibers, with their exceptional toughness, have prompted scientist to investigate their structure in the hope of creating light weight but highly resistant materials. Given the difficulty in working with silk proteins, we used instead amyloid fibrils, which are less known but have similar structure to silk and are much easier to prepare, to create an entire new class of reinforced rubber materials.

In this work, a novel type of composite polymeric materials reinforced by protein fibrils has been prepared. Protein fibrils are self-assembled structures resulting from partial denaturation of certain proteins, and the resulting aggregation mediated by beta-sheets interactions. These structures are characterized by an extremely large aspect ratio, with a diameter that changes depending on the age of the fibrils, and on the degree of association of the different strands. For the fibrils used in our experiments, which are prepared by partial denaturation of beta-lacto globulin at pH 2.0 and 80°C for 24 hours, and at a concentration of 10mg/ml, typical diameters are about 25nm with a length of several micrometers. For the first time high concentrations of fibrils have been incorporated into a polymer. The process used to incorporate fibrils is unique. We started from a suspension of polymer particles in water, which are mixed with the fibrils in the aqueous phase. It has been observed that not only the elastic modulus of composite materials with fibrils is increased, but also the ductility of the materials is enormously improved. Further improvement of the properties of the materials have been obtained by combining amyloid fibrils with silica nanoparticles, resulting in the formation of composite materials with mechanical properties even more enhanced, as a result of augmented elastic modulus provided by silica, and ductility increase provided by amyloid fibrils. This procedure to reinforce materials could provide a new alternative to reinforcement of a broad variety of elastomers.

Formation of stable NLC delivery systems for alpha lipoic acid: physicochemical characteristics and release study

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Alpha lipoic acid (ALA) is naturally occurring substance, well-known as strong antioxidant and anti-inflammatory active. Due to its strong antioxidant activity, it may also prevent photooxidative stress in the skin, working as an anti-aging agent. ALA shows favorable physicochemical properties for dermal delivery but low water solubility makes some difficulties in its formulation. Additional problems are that the acid is extremely vulnerable to degradation by sunlight and is characterized by strong sulfur smell. To avoid the problems and improve physicochemical stability of alpha lipoic acid, its encapsulation into nanostructured lipid carries (NLC) can be useful. NLC in comparison to the traditional carriers like emulsions, liposomes and polymeric nanoparticles show some advantages i.a. biocompatible and physiological lipids composition, avoidance of organic solvents in the preparation process, high bioavailability, controlled release rates and suitability to scaling-up production.

The aim of the work was to prepare nanostructured lipid carriers as long term stable carrier systems for the alpha lipoic acid topical delivery. The ALA-loaded NLC were prepared by the ultrasound homogenization method (Sonics Vibra-Cell, Sonics & Materials, INC.), using mixture of Apifil CG and Myritol 312 as the lipid phase. The carriers were stabilized by Plantacare 2000 UP. The stability of obtained formulations was controlled using macroscopic and microscopic analysis. Physicochemical properties of the carriers, such as particle size, polydispersity index and zeta potential were studied by using Zetasizer Nano ZS Malvern Instrument. In vitro release studies of the active were performed at the 32°C, using cellulose membrane and the PBS as a receptor solution.

The obtained results confirmed a high physical stability of the empty and ALA-loaded formulations and showed that the prepared systems are suitable carriers for controlled release of ALA and can be a promising solution for skin delivering of this antioxidant.

Y³⁺ embedded in polymeric nanoparticles: morphology, dimension and stability of colloidal system

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Radiolabeled nanoparticles are promising tools in cancer diagnosis and therapy[1]. Moreover, yttrium-90 (⁹⁰Y) is a good candidate as suitable β - emitting radioisotope for a new approach to radio-guided surgery (RGS) proposed by some researchers of our group[2]. In this work, we developed new composite nanoparticles, based on polymethylmethacrylate (PMMA), and poly(methylmethacrylate-co-acrylic acid), P(MMA-AA), embedded with yttrium ion (⁸⁹Y³⁺), as a first step for the development of ⁹⁰Y³⁺ based nanocomposites. The composite nanoparticles were synthesized by emulsion polymerization technique in the presence of KPS as radical initiator, using different MMA/AA molar ratio in the range 1-20%, and different MMA/Y³⁺ molar ratios, in the range 1-20%. Yttrium doped polymeric nanoparticles were characterized by means of FTIR spectroscopy, DLS and Z-potential measurements and SEM-EDX technique[3,4,5]. The Y³⁺ influence on morphology and dimension of composite nanoparticles was investigated, and monodispersed nanospheres with diameters above 80-150 nm were obtained. The composite material was studied by means of DLS and Z-potential technique and the colloids stability in water solution during 2 weeks, at different temperature (25°C and 37°C), were confirmed. Polymeric nanoparticles (diameter above 130 nm) embedded with ⁸⁹Y³⁺.

Acknowledgements The authors gratefully acknowledge the Sapienza University of Rome, Ateneo Sapienza 2015/C26A15H5J9 and 2015/C26A15LRMA projects for financial support.

[1] V. Rufini, G. Treglia, P. Castaldi, G. Perotti, A. Giordano, *Quarterly Journal of Nuclear Medicine and Molecular Imaging*, 2013, **57**, 122

[2] F. Collamati, F. Bellini, V. Bocci, E. De Lucia, V. Ferri, F. Fioroni, E. Grassi, M. Iori, M. Marafini, S. , R. Paramatti, V. Patera, L. Recchia, A. Russomando, A. Sarti, A. Sciubba, M. Senzacqua, ES.

Camillocci, A. Versari, C. Voena, R. Faccini, *Journal of Nuclear Medicine*, 2015, **56**, 1501

[3] R. D'Amato, L. Medei, I. Venditti, M. V. Russo, M. Falconieri, *Materials Science & Engineering C*, 2003, **23**, 861

[4] R. D'Amato, I. Venditti, M. V. Russo, M. Falconieri, *Journal of Applied Polymer Science*, 2006, **102**, 4493

[5] R. De Angelis, I. Venditti, I. Fratoddi, F. De Matteis, P. Proposito, I. Cacciotti, L. D'Amico, F. Nanni, A. Yadav, M. Casalboni, M. V. Russo, *Journal of Colloid Interface Science*, 2014, **414**, 24

Novel formulation of liposome-encapsulated anthocyanin

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Anthocyanins, natural plants pigments founds in significant amount in edible berries and in many vegetables showed to have high antioxidant activity. Recent data showed that anthocyanins from berries may induce cellular signal transduction events, involved in the cell proliferation [1], induction of apoptosis [2]. Anthocyanins are hydrosoluble macromolecule, unstable and highly susceptible to degradation. For their effective targeted administration, delivery systems, such as liposomes or emulsions are necessary to preserve anthocyanins physicochemical characteristics and protect them against degradation. Nanoscale delivery systems using liposomes and nanoparticles are emerging technologies for the rational delivery of adjuvant treatment with applications in alternative medicine. Liposomes are excellent candidates for anthocyanins delivery due to their biocompatibility, the possibility to fine-tune their physico-chemical properties, according to their lipid composition and content and also, due to the possibility to tailor their surface composition [3].

Based on this, the aim of our study was to prepare liposomes encapsulation anthocyanins (AEL) with size range under 300 nm.

Liposomes containing egg phosphatidylcholine, cholesterol, deoxycholic acid and tween-80 were prepared by the conventional film method with some modifications. The physicochemical characteristics of obtained AEL including particle size, distribution and shape, zeta potential and encapsulation efficiency of liposomal formulations were analysed. Pure anthocyanins were efficiently encapsulated within liposomes. The encapsulation efficiency of anthocyanin in liposome was above 90% for all formulations. Moreover no difference in particle size was observed between empty liposomes and anthocyanin liposomes as obtained by TEM characterisation.

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- [1] Z. Diaconeasa, L. Leopold, D. Rugină, H. Ayvaz, C. Socaciu, *International Journal of Molecular Sciences*, 2015, **16**, 2352-2365
- [2] D.Y. Shin, C.H. Ryu, W.S. Lee, D.C. Kim, S.H. Kim, Y.-S. Hah, , S.J. Le, S.C. Shin, H.S. Kang, Y.H. Choi, *Annals of the New York academy of Sciences*, 2009, **1171**, 137-148.
- [3] N Mignet., J. Seguin, G. Chabot, *Pharmaceutics*, 2013, **5**, 457-471

Rheological performance and high stability of bitumen modified with surfactant, rubber (SBR/BR) and crumb rubber (CR) additives.

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ABSTRACT: In this contribution, the mechanical and physico-chemical properties of a new kind of modified bitumen are presented. The bituminous binder was modified in order to understand the effect on the structural properties of several compounds such as a stabilizing surfactant (S), a Polymer Blend (SBR/BR) and a crumb rubber (CR). Laboratory tests were focused on the characterization of bitumen modified with binary combinations of S-SBR/BR and S-CR additives and compared with binder as a reference. This work deals with the characterization conducted by using conventional as well as advanced methods on bitumens. Fundamental rheological tests, based on dynamic shear rheometer in the temperature range from -30 °C to +160 °C and advanced ¹H Magnetic Resonance Relaxometry analysis were used to evaluate the effect of modifiers on the bitumen structure. Rationalization of all the data was achieved with the aid of X-Ray Photoelectron experiments/

For determination of stability of the surfactant and Rubber, modified bitumen tube testing method was performed. Based on the result analysis, an improvement of the viscoelastic properties of surfactant-modified bitumen was ascertained. The addition of surfactant was crucial and it allowed using both SBR/BR and CR as modifiers to overcome physico-chemical drawbacks such as, e.g., sedimentation phenomena.

Anti-Icing and De-Icing Surfaces Based on Hairy Core-Shell Particles as Building Blocks

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Icing is a common phenomenon in nature and technology that influences our daily lives. In most cases, icing causes severe problems such as, for example, increase in the energy consumption of transport vehicles (aircraft, cars), or alternative energy sources (wind turbines), which eventually leads to increased maintenance costs or failures.

To solve these problems, the design of multifunctional polymeric anti-icing composite materials with controlled wetting and adhesion properties may become essential. The concept used for the fabrication of such surfaces is based either on the reduction of ice adhesion, or the inhibition of ice growth. One approach is the fabrication of superhydrophobic surfaces, where the contact area between the ice and the surface is very low, and the formed ice can easily be removed.[1,2] Another approach is on the use of hydrophilic materials with the function of the reduction of the freezing point as well as antifreeze proteins, which kinetically decrease the ice crystal formation rate.[3] However, there is still a substantial need for simple and scalable approaches for the creation of robust anti-icing materials.

Herein, we propose a new approach for the design of robust heterogeneous ice-phobic surfaces based on the use of polymer-modified core-shell particles. Accordingly, we systematically mix two different types of particles, with controlled and tuneable chemical composition and size, in various mixing ratios to form heterogeneous surfaces, and subsequently investigate the influence of the mixing ratio on the surface characteristics.[4] As a result, simply by varying the mixing ratios, it is possible to influence the anti-icing and de-icing properties of the surface in order to ultimately achieve excellent anti-icing and de-icing capability.

[1] N. Pureskiy, J. Chanda, G. Stoychev, A. Synytska and L. Ionov, *Adv. Mater. Interfaces*, 2015, **2**, 1500124.

[2] J. Chanda, L. Ionov, A. Kirillova and A. Synytska, *Soft Matter*, 2015, **11**, 9126-9134.

[3] A. Narayanan Krishnamoorthy, C. Holm and J. Smiatek, *J. Phys. Chem. B* 2014, **118** (40), 11613-11621.

[4] M. Schwarzer and A. Synytska, under preparation.

Polymer Nanocomposites of Iron Oxides.

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Fundamental understanding of formation and stabilization of metal nanoparticles by polymeric compounds is essential to create metal-polymer nanocomposite systems with flexible customization of the desired properties. Polymers capable of interacting with forming metal nanoparticles are widely used as stabilizing matrices in such compounds. High-molecular compounds containing heterogenic functional groups and capable of stabilizing metal nanoparticles which prevent aggregation are of special interest. In this regard, polyvinyl alcohol which effectively interacts with metal nanoparticles at the earliest stages of their formation regulating their growth, aggregation, size and uniformity of distribution in the polymer matrix [1].

One of the factors that have a great impact on the iron nanoparticles formation is the solvent nature [2]. In order to determine this impact the dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were used. Using the DMF or DMSO as reducing solvent has the important benefit, because the reduction reaction proceeds under mild conditions at room temperature. However, there is no information about iron nanoparticles obtained with reduction with a solvent in the literature.

Chemical synthesis of nanocomposites have been performed with mixing a $[-CH_2CH(OH)-]_n$, $FeSO_4 \cdot 7H_2O$ and $NaBH_4$ with intense spinning of magnetic stirrer (600 rpm) and mix heating at 60°C within 1 hour. After 1 hour DMF batches were added to the reaction mix in a ratio to the blank mix of 20, 40 and 60%. The chemical synthesis was continued at room temperature. The synthesis total time was 8 - 12 hours. In the course of the reaction the color of the reaction mix was changed from rich brown to orange-brown.

The obtained nanocomposites were explored to study the stability over time. The constancy of the optical spectrum of the iron colloidal solution upon storage allows to make a conclusion about the resistance of the obtained systems against aggregation. The iron particles size and shape were determined by the means of a Raster Electron Microscopy (REM) with a Japan high-resolution electron microscope JEOL JSM-7500F with "cold" (field emission) cathode. Reportedly, the average size of iron nanoparticles was 62 nm (Figure 1).

Absorption bands corresponding to stretch and deformation vibrations frequencies of polymer original composition are detected in the obtained IR spectra of nanocomposites: 3330.0 (Intra- and intermolecular H-bonds in dimers and polymers), 2910.4 (-CH₂-), 1735.19 (C=O), 1661.7(O-H). It proves that the structure of PVA during the process of nanocomposites synthesis does not change and the original properties of the polymer matrix are retained. Vibration spectra of the reduced form of metal give the evidence of presence of Fe₃O₄ composition in the iron oxide composite. It is found that the existence of iron ions reducing in the matrix of the polyvinyl alcohol at room temperature is possible in the presence of aqua-organic solvent.

According to the obtained results it may be concluded that the obtained spherical iron nanoparticles with the size of 57-67 nm show plasmon resonance characteristic of metal nanoparticles which characterizes sensitivity to dielectric environment. This fact supports the possibility of using synthesized nanofilms as the biosensors in Biophotonics.

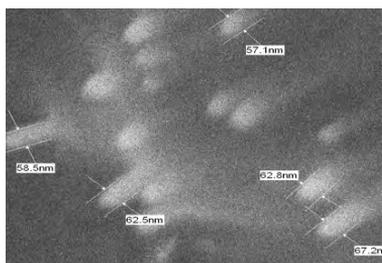


Figure 1 Iron nanocomposite REM -Photomicrography

Acknowledgements

- [1] N.L. Shimanovskiy, V.O.Panov, etc. *Experimental and Clinical Pharmacology*, 2010, 6., 23.
[2] Pastoriza-Santos, L. M. Liz-Marzán, *Adv. Funct. Mater.*, 2009, 19, 679.

Thin film nanostructured materials based on mesogenic mix-substituted phthalocyanines

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Since the middle of the last century, when the solar batteries were created on the base of monocrystalline silicon the researchers on their improving have been continuing. Ultimately, the power conversion efficiency has reached 25%. Since these devices have a number of disadvantages, the scientists focus their attention on getting cheaper and more efficient materials, such as organic semiconductors. They include heterocyclic compounds and discotic mesogens the molecules of which can be arranged in columns that increases the charge transfer. To improve their efficiency, the compositions with organic semiconductors and glass polymers are usually used. Thin film semiconductor materials must be possessed of special physicochemical properties: harvesting of a significant fraction of the solar spectrum with a high molar extinction coefficient, a significant difference in energy between the HOMO / LUMO, the material should be vitrified, optimally in the mesophase.

The report is dedicated to the synthesis and physical and chemical properties of new discotic mesogens – phthalocyanine derivatives and their metal complexes, which can satisfy all the above mentioned requirements. The preparation of thin film nanomaterials based on these phthalocyanines, as well as data on optical and photovoltaic properties of films are described there. Substitution in one molecule by donor and acceptor groups creates unique conditions to form the charge-transfer complexes. It gives special properties to compounds in bulk and thin films. It is shown that all compounds tested (see Figure 1), except for indium complex exhibit thermotropic mesomorphism, type of which depends on the number of chlorine atoms and length of alkyloxy substituents introduced into phthalocyanine molecule. On the basis of the results obtained, we can assume that above mentioned compounds can be used in optical, nanoelectronic and organic photovoltaic devices.

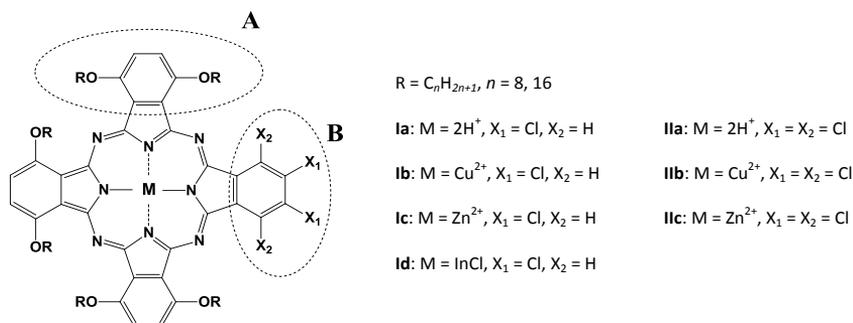


Figure 1. Structural formula of studied mix-substituted phthalocyanines of A₃B type

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Towards development of functional coatings by the synthesis of TiO₂-Fe nanoparticles and its incorporation in a polymeric matrix

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In this work the development of functional coatings by the use of Fe-doped TiO₂ nanoparticles was carried out. TiO₂ has very interesting chemical and physical properties for applications such as functional coatings, photocatalysis, solar cells, and so on [1]. Photocatalytic properties of TiO₂, e.g. activity under visible light can be tuned by doping this material with other transition metal elements.

TiO₂-Fe nanoparticles were prepared by the novel oil-in-water microemulsion reaction method under mild conditions [3]. The microemulsion system used for synthesis was water/Synperonic 91/5 / isooctane. The method allowed the formation of Fe-doped TiO₂ nanoparticles with a tetragonal anatase crystalline structure after calcination at 500°C. The obtained material was dried by two methods: i) the conventional (oven-dried at 120°C) and ii) by the use of a nano-spray drier equipment. The morphology was observed by scanning electron microscopy (SEM), resulting in irregular aggregate structures of globular nanoparticles for the first method and well-defined spheres and donuts assemblies by the second method. The materials were functionalized by chemical solution and incorporated into a polymeric matrix of polyethylene oxide in order to develop the nanocomposite. A film of the nanocomposite onto glass was prepared by spin coating technique. The obtained coatings may possess interesting functional properties which could be useful for its applications in superhydrophilicity, self-cleaning and the photo-degradation of contaminants under solar-light radiation.

Acknowledgements: Were are grateful to CONACYT-SENER, Fondo Sectorial de Sustentabilidad Energética (CEMIESOL Proyecto Estratégico P21).

[1] H. Jiang, L. Gao, *Materials Chemistry and Physics* 2002, **77**, 878–881.

[2] J.I. Garza-Arévalo, I. García-Montes, M. Hinojosa-Reyes, J.I. Guzmán-Mar, V. Rodríguez-González, and L. Hinojosa Reyes, *Materials Research Bulletin*, 2016, **73**, 145-52.

[3] M. Sánchez-Domínguez, K. Pemartin, M. Boutonnet, *Curr. Opin. Colloid Interface Sci.*, 2012, **17**, 297.

MgO/SiO₂ and Portland cement formulations: mutual effects on reaction kinetics and hydration products

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Cement is the binder at the base of one of the most important building material: the concrete. Nowadays, formulations based on reactive periclase (MgO) [1,2] constitute a promising emerging technology toward eco-sustainable binders, with reduced CO₂ emissions as compared to the traditional CaO-based cements. [3,4] In the presence of water, MgO/silicate mixtures hydrate and form a binder phase, M-S-H (magnesium silicate hydrate), a colloidal gel analogue to calcium silicate hydrate, C-S-H, present in traditional Portland cements, but with inferior mechanical properties. The aim of the present study was the investigation of the hydration reaction and of the microstructure development of pastes prepared by mixing Portland cement and MgO/SiO₂ blend. Different percentages of CaO- and MgO-based binders were evaluated to explore the possibility of preparing pastes that could in principle combine the optimal mechanical properties of calcium based cement with the ecological features of MgO-based cement. The hydration kinetics of the mixtures were investigated by means of Differential Scanning Calorimetry. Concurrently, the pastes were characterized by means of a multi-scale approach and the formation of hydrated phases was studied by Thermogravimetric Analysis, Fourier Transform IR spectroscopy and X-ray Diffraction. The structural properties of all samples were investigated by solid state ²⁹Si-NMR. Finally, the morphology of the pastes has been studied by means of Scanning Electron Microscopy. The results showed that in the mixed pastes both C-S-H and M-S-H binder gel phases form, but, as evidenced in Figure 1, their domains remain segregate in different regions. The results evidenced that the kinetics of hydration in the mixed samples is dominated by MgO/SiO₂ hydration in the first period, while the diffusional stage is mostly dependent on the Portland cement presence. Moreover, mutual effects on the formation of the hydration products occur in the mixed pastes.

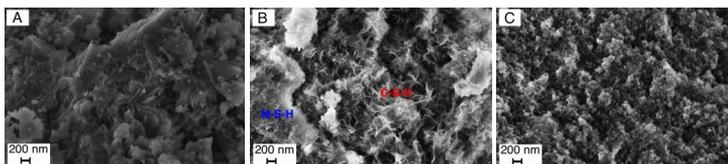


Figure 1 SEM images of CaO-based cement (A), mixed pastes with MgO- and CaO-based cements (B) and MgO-based cement (C).

Acknowledgements CSGI and FIR2013 (Project RBFR132WSM) for financial support.

- [1] Lothenbach, B., et al., *Magnesium and calcium silicate hydrates*, Cement and Concrete Research, 2015. 77: p 60-68
- [2] Chiang, W.-S., et al., *Multiscale structure of calcium and magnesium silicate hydrate gels*, Journal of Material Chemistry A, 2014. 2: p 12991-12998
- [3] Ellis M. Gartner and Donald E. Macphee. 2011. A physico-chemical basis for novel cementitious binders. Cement and Concrete Research 41: 736-749.
- [4] Stuart M Evans and Nikolas Vlasopoulos. 2010. Novacem: Carbon Negative Cement and the Green Cement Bond.

Thermosensitive Brushes Tethered on Wet Bacterial Cellulose Sheets for Improving Their Swelling-Drying Ability

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Thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) brushes were grafted from wet bacterial cellulose (WBC) sheets for the first time using atom transfer radical polymerization (ATRP) method. WBC is recognized as a highly swollen biocompatible material with broad application potential. However, native WBC undergoes drying relatively fast and irreversibly upon losing substantial amount of water. In this work PNIPAM, as a polymer exhibiting Lower Critical Solution Temperature (LCST) at around 32°C was grafted from WBC in order to slow down this irreversible drying especially at elevated temperatures relevant to biomedical applications. Grafting of PNIPAM was realized via surface-initiated ATRP in water/methanol mixture leading to WBC-g-PNIPAM. The modification steps were followed via FT-IR, elemental analysis, and atomic force microscopy. It was concluded that PNIPAM contributes to 22% of dry mass of WBC-g-PNIPAM. The wet WBC-g-PNIPAM samples were subjected to repeating swelling and drying steps at 25°C and 40°C. The obtained results indicated that grafted PNIPAM significantly reduced drying of the modified WBC and enabled better re-swelling after treatment at 40°C with respect to native WBC. The observations may be explained by hydrophobization of the surface of WBC-g-PNIPAM above LCST that can efficiently reduce water evaporation. The reported synthetic method may be also used for grafting other polymers bringing additional functionalities to WBC.

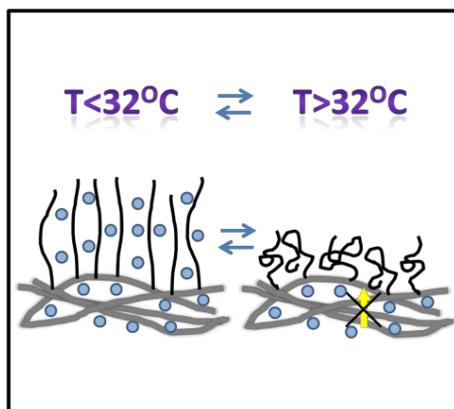


Figure 1. Schematic draw of protective PNIPAM shell on WBC acting below and above LCST.

Oil-core nanocapsules stabilized by graft amphiphilic polyelectrolytes

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A surfactant-free method of preparation of nanocapsules templated on liquid cores using amphiphilic graft polyelectrolytes as stabilizing agents was developed.

For that purpose novel grafting technique was proposed first [1] and both cationic and anionic amphiphilic polyelectrolytes were synthesized using this method. In particular poly(sodium 2-acrylamido-2-methyl-1-propanesulfonate) (PAMPS) and poly(poly(allylamine hydrochloride) (PAH) were grafted with poly(vinyl naphthalene) [2, 3]. Such grafted polyelectrolytes chains were shown to adopt in an aqueous solution “pearl-necklace” type conformation with formation of packed hydrophobic domains that can accommodate functional hydrophobic molecules. Moreover, at the water-oil interface the chains tend to decoil and short hydrophobic chains anchor in the oil droplets phase while polyelectrolyte backbone stays in the aqueous phase. In such a way oil droplets with diameters in the range of a few tens to hundreds of nanometers were stabilized in aqueous dispersions (Fig. 1).

The formed oil-core nanocapsules were shown to serve as high capacity and long-term stability reservoirs of lipophilic molecules. They are not sensitive to dilution and variation of pH in relatively broad ranges. What is more, such nanocapsules may be further modified by applying oppositely charge polyelectrolytes via “layer-by-layer” method that may tune the release rate of the cargo molecules tailor the surface for targeting or stealth properties.

The obtained nanocapsules may find applications not only serve as stable carriers in controlled delivery of drugs, but also as e.g. (photo)nanoreactors for realization of efficient reaction in confined environments or at the interfaces.

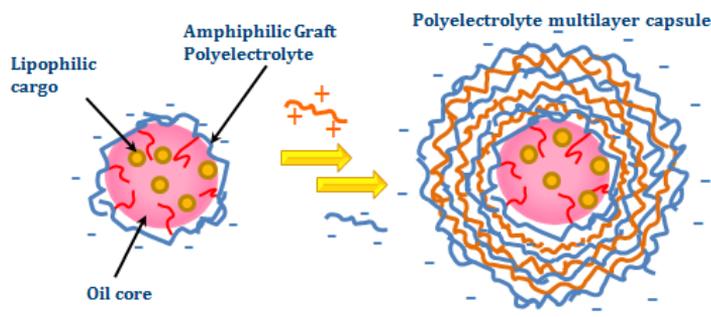


Figure 1 Formation of oil-core nanocapsules stabilized by amphiphilic graft polyelectrolytes and coated by polyelectrolyte multilayer coatings.

[1] M. Rymarczyk-Machał, J. Szafraniec, S. Zapotoczny and M. Nowakowska *Eur. Polym. J.*, 2014, **55**, 76.

[2] J. Szafraniec, M. Janik, J. Odrobińska and S. Zapotoczny, *Nanoscale*, 2015, **7**, 5525.

[3] J. Szafraniec, J. Odrobińska and S. Zapotoczny, *RSC Adv.*, 2016, **6**, 31290.

Simultaneous immobilisation of Glucose Oxidase and Horseradish Peroxidase on SBA-15 mesoporous silica

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In this work an Enzymatic Tandem System (ETS) was prepared by simultaneously immobilizing Glucose Oxidase (GOx) and Horseradish Peroxidase (HRP) on SBA-15 mesoporous silica. The goal of such system is that a controlled amount of H₂O₂ is produced *in situ* by GOx and used for the oxidation of a HRP substrate [1]. This permits to overcome HRP inactivation that occurs in the presence of an excess of H₂O₂ [1]. SBA-15 was synthesized and characterized by N₂ adsorption/desorption isotherms, Fourier-Transform Infrared spectroscopy (FT-IR), Small Angle X-Ray scattering (SAXS), and Transmission Electron Microscopy (TEM). GOx and HRP were then immobilized by either physical adsorption or covalent binding. The kinetics of enzymes immobilization (Fig. 1A), measured through UV-VIS spectrophotometry, was found to follow a pseudo-second order model [3]. The catalytic activity of the obtained ETS was found to be strongly affected by the post immobilization drying step. Indeed, the activity was very high for wet preparations and very low for dried ones, regardless the type of enzyme-support interaction (physical or covalent). ETSs might find application for biosensing[4] or bioremediation [5]. Here, the obtained ETS was used for the degradation of two model phenolic pollutants, namely, ferulic acid and caffeic acid. A conversion of about 70 mol% was obtained for both phenolics after only 15 minutes (Fig. 1B).

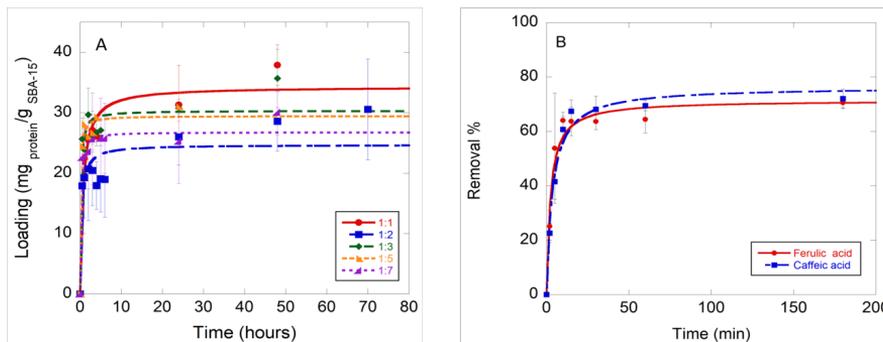


Figure 1: A) kinetics of loading of some mass ratios of GOx/HRP; B) efficiency of the catalyst in the removal% of two fenolic compounds: ferulic and caffeic acid.

References:

- [1] D. Jung, C. Streb, and M. Hartmann, *Int. J. Mol. Sci.*, vol. 11, no. 2, pp. 762–778, 2010.
- [2] K.J. Baynton, J. K. Bewtra, N. Biswas, K. E. Taylor, *Biochim. Biophys. Acta - Protein Struct. Mol. Enzymol.* 1206, 272–278 (1994).
- [3] D. Steri, M. Monduzzi, and A. Salis, *Microporous Mesoporous Mater.*, vol. 170, pp. 164–172, 2013.
- [4] Yu, X., Lian, W., Zhang, J. & Liu, H. *Biosens. Bioelectron.* 80, 631–639 (2016).
- [5] J. Arriel Torres, P. M. Batista Chagas, M. Cristina Silva, C. D. Dos Santos, and A. Duarte Corrêa, *Water Sci. Technol.*, vol. 73, no. 1, pp. 39–50, 2016

Graphene (oxide) – Metal Composites for Electrochemical and Catalytic Applications

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Graphene, the honeycomb 2D network with sp^2 hybridized carbon, has been studied vastly due to its excellent thermal and electrical conductivity, high mechanical strength, and extremely high surface area¹. This wonder material has already expanded its applications by blending with noble metals, metal hydroxides and oxides. Herein, we report utilization of graphene-metal composites as electrode materials for electrochemical capacitors and catalysts for ammonia decomposition reaction. Graphene used in this study was obtained via reduction of graphene oxide synthesized with a modified Hummers method². Graphene oxide and different transition metal cations were combined via utilization of electrostatic interaction and reduced electrochemically. After reduction, almost 20-fold increase in capacitance was observed. From Cyclic voltammetry (CV) measurements, the highest capacitance was observed with addition of iron (II) cation: 135.4 mF cm^{-2} after reduction. On the other hand, metal doped reduced graphene oxide aerogels were tested as catalysts for ammonia decomposition reaction. Prior to catalytic test, aerogels were reduced under H_2 atmosphere at $700 \text{ }^\circ\text{C}$ to grow metal nanoparticles and reduce graphene oxide, simultaneously. At $700 \text{ }^\circ\text{C}$ and 16.7 % ammonia conversion, $42.2 \text{ mmol H}_2/\text{g}_{\text{cat}}/\text{min}$ was produced. The specific surface areas of aerogels were determined via Brunauer–Emmett–Teller (BET) analysis. To investigate the changes in structure during the catalytic test, composites were analyzed by Raman spectroscopy, Scanning transmission electron microscopy (STEM), and X-ray photoelectron spectroscopy (XPS).

[1] M.J. Allen, V. C. Tung and R. B. Kaner, Chem. Rev., 2010, 110, 132.

[2] W.S. Hummers and R.E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339.

Influence of encapsulation process on the optical properties of up-converting NaYF₄ nanoparticles and photosensitizing dyes

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The use of up-converting, lanthanide doped nanoparticles (NPs) as luminescent labels in bioimaging provides the unique possibility to obtain visible luminescence after low power laser diode excitation from nearinfrared region. This lowers the autofluorescence background noise and allows for deep penetration of excitation light into biological tissues [1]. However, as the most commonly used for colloidal NPs synthesis wet chemistry techniques usually yield hydrophobic NPs, the efficient and straightforward NPs surface hydrophilization for bio-related applications remains the main challenge [2]. Recently the encapsulation of multiple inorganic NPs within the various types of polymeric nanocarriers with sizes below 200 nm have received increasing attention, because of the improved solubility, high long-term colloidal stability and biocompatibility of the obtained vehicles, with simultaneous possibility of co-encapsulation with other photoactive compound (i.e. organic photosensitizers) with simultaneous preservation of the optical properties of the hybrid cargo loaded inside the liquid core.

Encouraged by our recent results regarding the encapsulation of different types of inorganic NPs [3-4], we have obtained novel lanthanide-doped NaYF₄ NPs, designed for co-encapsulation with organic photosensitizing dyes via a new nanoemulsion-templated approach. For the synthesis of NaYF₄ NPs we used trioctylphosphine oxide ligands, what allowed us to obtain NPs with sizes ~5 nm, what further facilitated the encapsulation process. The selection of the type of lanthanide ions doping (Er³⁺/Yb³⁺ or Tm³⁺/Yb³⁺) and photosensitizers was made based on the overlap of their emission and absorption spectra, respectively. The physico-chemical properties of the obtained nanostructures were characterized, with the special emphasis put on the measurements of the up-converted emission spectra and luminescence lifetimes. All of the studied systems showed intense, narrow band emission in the visible part of the spectra under 980 nm laser diode excitation, with long luminescence lifetimes in the sub-millisecond range. The investigation of optical properties of the nanocarriers loaded with different concentration of photosensitizers and constant amounts of lanthanide doped NaYF₄ NPs allowed also to study the interaction between NaYF₄ NPs and organic dyes. This in further step allowed for the observation of energy transfer processes between optically active components of the systems, and for showing their potential application as multifunctional agents for simultaneous bioimaging and photodynamic based cancer treatments.

Acknowledgement

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References

- [1] A. Sedlmeier, H.H. Gorris, *Chem. Soc. Rev.*, 2015, **6**, 1526.
- [2] A. Gnach, A. Bednarkiewicz, *Nano Today*, 2012, **7**, 532.
- [3] U. Bazylińska, S. Drozdek, M. Nyk, J. Kulbacka, M. Samoć, K. Wilk, *Langmuir*, 2014, **30** 14931.
- [4] U. Bazylińska, D. Wawrzyńczyk, J. Kulbacka, R. Frąckowiak, B. Cichy, A. Bednarkiewicz, M. Samoć, K.A. Wilk, *Scient. Rep.*, (2016) submitted.

A combined numerical and experimental titration study of mesoporous silica particles.

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Mesoporous silica particles have a large range of potential applications, ranging from chromatography to drug delivery [1]. The key feature of mesoporous silica particles is a very large surface area due to the mesoscopic pores. The large porosity has an enormous impact on the charging behaviour in different salt solutions. To illuminate the physical chemical property of these particles on their surface charge we have conducted both experimental and numerical mean-field (i.e. Poisson-Boltzmann) titration studies, varying both the ionic strength and the pH. We find a good agreement between the experimentally measured and numerical predicted bare silica charge as function of both ionic strength and pH. Accounting also for the ions residing inside the pores the numerical calculations predict an overall charge of these particles several orders of magnitude lower than that of the bare charge of the silica [2]. We furthermore see that the charging behaviour occurs at the silica/salt solution interface (see Fig. 1). The potential and the ion profiles have two decay lengths, one inside the silica particles and one outside. Allowing the salt to penetrate the particle (inside its pores) thus introduces new phenomena absent in non porous silica particle dispersions [3-4].

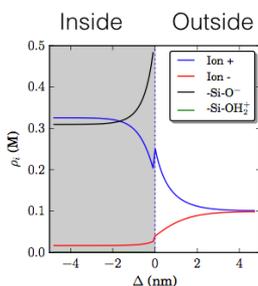


Figure 1: Ion and titratable site profiles across the interface

Acknowledgements M.T. gratefully acknowledges financial support from the Swedish Research Council. S.V. is financed by European Union through FP7-PEOPLE-2013-ITN, Cyclon Hit project (Grant Agreement n°608407).

- [1] V. Mamaeva, C. Sahlgren, M. Lindén, *Advanced Drug Delivery Reviews*, 2013, **65**, 689.
- [2] S. Valetti, A. Feiler, and M. Trulsson, 2016, (In preparation).
- [3] S.H. Behrens and D.G. Grier, *J. Chem. Phys.*, 2001, **115**, 6716.
- [4] A. Salis *et al.*, *Langmuir*, 2010, **24**, 2484.

Conducting inks: extended polypyrrole nanostructured colloids

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Polypyrrole (PPy) [1,2] is one of the most known conducting polymers. PPy has interesting properties, such as biocompatibility and stability under *in-vivo* conditions, reversible doping and redox properties. Globular polypyrrole colloids are produced by the oxidation of pyrrole in the presence of suitable water-soluble polymers, e.g., poly(*N*-vinylpyrrolidone) [3]. When methyl orange is introduced to the polymerization mixture, as the structure-guiding agent, extended PPy colloids based on nanotubes and nanorods are produced instead. The films deposited from colloids of PPy nanotubes/nanorods had conductivity two orders of magnitude higher than those cast from colloid of ordinary PPy nanoglobules. Dynamic light scattering measurement demonstrated that PPy nanotubes/nanorods have average particles sizes around 500 nm with a dispersity index about 0.3. Moreover, the extended PPy nanostructured colloid exhibited improved electrochemical activity. Non-spherical PPy colloids are thus attractive candidates for conducting inks for printing of transparent conducting layers used as flexible sensors or electrodes.

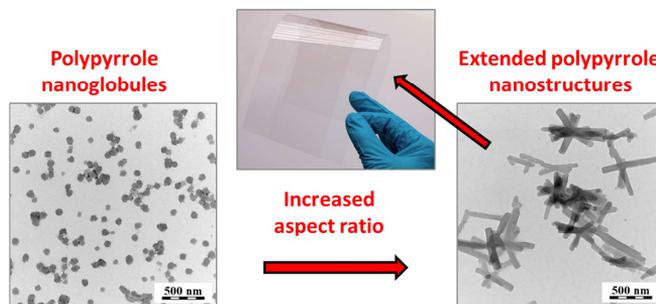


Figure 1. Transmission electron micrographs of PPy colloids and nanotubular PPy colloid coated on flexible poly(ethylene terephthalate) foil.

Acknowledgement: The financial support of the Czech Science Foundation (14-05568P) is gratefully acknowledged.

References

- [1] N. V. Blinova, J. Stejskal, M. Trchová, J. Prokeš and M. Omastová, *European Polymer Journal*, 2007, **43**, 2331.
- [2] J. Škodová, D. Kopecký, M. Vrňata, M. Varga, J. Prokeš, M. Cieslar, P. Bober, and J. Stejskal, *Polymer Chemistry*, 2013, **4**, 3610.
- [3] M. Omastová, P. Bober, Z. Morávková, N. Peřinka, M. Kaplanová, T. Syrový, J. Hromádková, M. Trchová and J. Stejskal, *Electrochimica Acta*, 2014, **122**, 296.

Orientational order of one-patch particles in a quasi-two-dimensional system

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A patchy colloidal particle is an ideal model system of anisotropic colloid due to its well-defined interaction anisotropy. Patchy particles exhibit novel positionally-ordered, i.e. crystalline, phases [1]. In addition, spherical patchy particles exhibit *purely orientationally-ordered phases* when closely-packed [2], which cannot be attained with shape anisotropy. Orientational order is expected to realise unique material properties compared with those by positional order, as known for magnetic or dielectric properties by the orientational order of dipoles in atomic / molecular condensed matter. However, the great variety of the phases in patchy particles often results in the degeneracy of the ground states, and a system falls in a metastable state or several metastable states coexist in a system.

We study the orientational order of closely-packed one-patch particles in a quasi-two-dimensional system between flat substrates. By comparing the experiment and Monte-Carlo simulation results, we found that the degeneracy of orientationally-ordered state is resolved by the lower-dimensionality of the system: A commensurate state(s) with the system geometry and boundary conditions is selected from the (meta)stable options in the corresponding bulk system [2]. In addition, even a unique order appear when all of the states in bulk are incommensurate with the quasi-two-dimensional system. Our study opens a new route for realizing and controlling the mesoscopic order in patchy particles. In addition, the ordering mechanism would be applicable to various other systems where mesoscopic objects are confined in a thin, two-dimensional space.

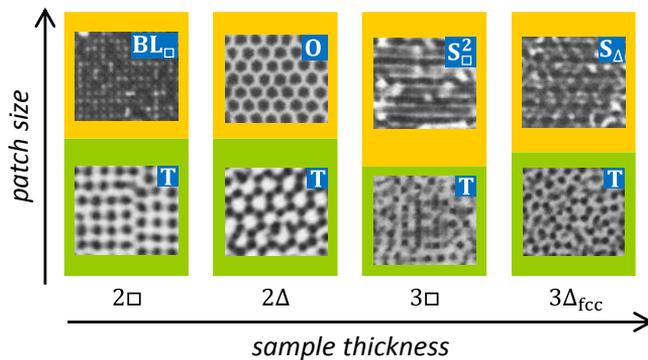


Figure 1 Schematic phase diagram of orientationally-ordered state in one-patch particles, with typical optical microscopy images. The phases are: T; tetrahedron tetramer, BL; bilayer sheet, O; octahedral hexamer, and S; stripe structure.

- [1] e.g., Q. Chen *et al.*, *Nature*, **469**, 381 (2011); D.Z. Rocklin & X. Mao, *Soft Matter*, **10**, 7569 (2014).
 [2] e.g., Z. Preisler *et al.*, *Soft Matter*, **10**, 5121 (2014); Y. Iwashita & Y. Kimura, *Soft Matter*, **10**, 7170 (2014).

Increase of carbonic anhydrase efficiency in amine solutions and using silica matrices as solid supports

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Global warming and climate change are caused by the increasing atmospheric concentration of CO₂. Energy efficiency, low carbon fuel and carbon capture and sequestration can lower the CO₂ emission. Several physical and chemical technologies have been developed and absorption and desorption over an amine solution is one of the most effective approaches to CO₂ capture [1]. Alkanolamines are frequently used because of their good chemical stability and their low regeneration energy. An interesting alternative to classical methods for CO₂ capture is represented by the use of carbonic anhydrase. This zinc containing metalloenzyme belonging to lyase family can efficiently and quickly catalyze the reversible conversion of carbon dioxide to bicarbonate.

Our research group is interested in the study of the effect of water-soluble additives on catalytic properties of different enzymes [2], since enzyme-additive interactions can produce an improvement of enzyme activity and/or stability.

In the present study the esterase activity of bovine carbonic anhydrase (BCA) in the presence of alkanolamines, surfactants and polyethylene glycols was reported. The hydrolysis of the chromogenic substrate, i.e. *p*-nitrophenyl acetate, was monitored spectrophotometrically at different additive concentrations with and without enzyme, to obtain enzyme-catalyzed hydrolysis rates.

The presence of amines generally produced an increase in enzyme activity, even if their effect could be due to a combination of several factors.

More recently, some attempts of BCA encapsulation in silica matrices with or without additives were also performed, with the aim to increase enzyme stability and to achieve the recycling of the catalyst. The experimental protocol of enzyme immobilization was optimized in order to reach the better condition for the enzymatic activity, i.e. variation of aging and drying time, TMOS/H₂O ratio and buffer concentration.

[1] Spigarelli, B.P., Kawatra, S.K. *Journal of CO₂ Utilization* **2013**, *1*, 69-87.

[2] Savelli G., Spreti N., Di Profio P., *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 111-117; Spreti N., Alfani F., Cantarella M., D'Amico F., Germani R., Savelli G., *J. Mol. Cat. B: Enz.* **1999**, *6*, 99-110; Spreti N., Di Profio P., Brinchi L., Marte L., Bufali S., Savelli G., *Eur. J. Biochem.* **2001**, *268*, 6491-6497; Spreti N., Germani R., Incani A., Savelli G., *Biotechnol. Prog.* **2004**, *20*, 96-101; Spreti N., Mancini M.V., Di Profio P., Germani R., Savelli G., *J. Mol. Cat. B: Enz.* **2008**, *50*, 1-6; De Matteis L., Di Renzo F., Germani R., Goracci L., Spreti N., Tiecco M., *RSC Adv.* **2016**, *6*, 46202-46211.

Rheological Behavior of Composite Structurally Reinforced Materials in a Magnetic Field

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For carrying out a monitored change in the strength and damping characteristics of thin-walled structures, use can be made of material layers that are placed inside them and that change their viscoelastic state under the action of external fields (electric or magnetic). This change occurs adaptively to the change in the dynamic state of the structure.

With this aim in view, we have developed magnetosensitive composite dispersion-reinforced materials (MCDRM), which are highly filled pastes on a dispersion base, i.e., on the Mobil synthetic oil. As a dispersed phase we used a complex filler consisting of microparticles, structured under the action of a magnetic field, and the nano- and micro-sized particles that form a thixotropic reinforced lattice. The ferromagnetic particles of carbonyl iron had a size of about 3 μm .

We carried out an investigation of the effect of the type of reinforcing finely dispersed (of size $\sim 1 \mu\text{m}$) particles of bentonite clay, aerosil, and chromium dioxide, on the degree of mechanical response (sensitivity) of the MCDRM to the external magnetic field.

The results of measurements have shown that the values of the rheological parameters of dispersely reinforced magnetorheological fluid without magnetic field effect depend the main on the general concentration of a complex filler and on the mass relationship between its dispersely reinforced and magnetosensitive components. The maximum values of the rheological parameters: yield stress τ_0 and storage modulus G' are typical of the MCDRM-1 paste containing aerosil. The use of mixtures of two types of reinforcing fillers, e.g., aerosil and chromium oxide, CrO_2 (MCDRM-2) as a dispersely reinforcing material leads to the reduction of the mechanical indices of the shear resistance of the paste: τ_0 fivefold and G' fifteenfold, respectively, as compared with the MCDRM-1 sample.

Under the action of an external magnetic field, the value of τ for all of the samples of pastes increases in the measured range of shear rates. Only in the MCDRM-3 samples containing bentonite clay, the shear stress depends on the shear rate in the entire range of change of the magnetic field induction, which allows one to smoothly control its viscoelastic properties.

This characteristic feature of the mechanical behavior of the considered pastes is connected with the effect exerted by the material of reinforcing lattice on the interaction of magnetic particles in a field that determines degree of the strength of the paste or its damping characteristics. Thus, a strong thixotropic matrix produced by the particles of bentonite clay (MCDRM-3) fails gradually with increase in a shear load, impeding the process of structuring of ferromagnetic particles. The lattice of aerosil particles breaks down at the lowest shear rates as compared to the bentonite one, which allows the ferromagnetic particles to easily interact in a magnetic field.

The storage modulus G' increases substantially with the external magnetic field intensity – first linearly and then nonlinearly up to the zone of weak nonlinearity and saturation. In the studied range of the magnetic field induction, G' increases by 1-2 orders of magnitude and in a magnetic field with induction 1000 mT the storage modulus of all of the MRF samples attains 2500 kPa.

The loss modulus G'' of the MCDRM-3 and MCDRM-4 attains maximum values at the magnetic field induction $B < 100$ mT. A further increase in the induction reduces the values of the loss modulus pointing to the decrease in the viscous component.

The possibility of varying the properties of a material by changing the reinforcement structure allows one to additionally “adjust” the mechanical parameters of the elements of thin-walled engineering constructions on change in the viscoelastic properties of layers in the structures of composite beams, plates, and envelopes of the “sandwich” type lamellar structure.

Rheology of Dielectric Suspensions Based on Modified Dual-Doped Titanium Oxide in Electric Field

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Papers on electrorheological effect in suspensions with dispersed phase in form of inorganic powders with a developed specific surface show that the polarization appearing in such suspensions in the electric field and determining the interaction force of the particles of dispersed phase should be mainly "slow" (Maxwell-Wagner). It is due to the difference of the electric parameters on the interface of filler particle-dispersion medium and is linked to the structural defects of the particles themselves. Known heterogeneous and polyphase materials showing this type of polarization consist of either several phases, i.e. amorphous and crystalline, or have dislocations, cracks and etc.

We have earlier shown [1], that the increase of ER-effect can be achieved by a proposed distortion of crystal lattice parameters of titanium oxide, broadly used as ERS filler, by means of doping it with aluminum atoms. In the result of experiments the increase of surface charges quantity has been obtained and the occurring structural interaction of the filler particles due to it, which is fixated by the increase of viscosity at ERF shear under the external constant electric field.

The aim of this work is to strengthen the modification effect of titanium oxide structure by means of dual doping by aluminum and phosphorus atoms. As the titanium component titanium tetraisopropoxide was used and as a template - dodecylamine, at a molar ratio TiO_2 : template equal to 1: 1. The template was removed by washing with water and calcination of the samples at 700 °C for 3 hours, then the modified titanium oxide samples were used for the preparation of suspensions containing 5 and 20 wt. % of the filler in mineral oil.

Electrorheological activity of suspensions was studied by rotational viscometry by means of coaxial-cylindrical cell modified to apply the electric field. The leakage currents were recorded using a microammeter. The dielectric properties of the suspensions were examined using immittance meter E7-20.

The experimental data obtained suggest that the dual modification of titanium oxide with aluminum and phosphorus allows to achieve high levels of ER activity of suspensions thereon. Thus, the shear stress value increased in comparison with the values without influence of the electric field in the 30 and 170 times for 5 and 20 % suspensions, respectively, at an electric field intensity of 4 kV/mm. These values are several times greater than the data previously obtained in experiments when doping titanium oxide only by aluminum atoms.

Participation of both alloying components in the polarization processes occurring on the surface of the modified titanium oxide is confirmed by its dielectric spectrum. Thus, dependence of the imaginary part of the complex effective dielectric constant on the frequency identified two peaks in the frequency range of 1-3 and 20-30 kHz, corresponding to a number of different types of inclusions in the sample. Blur peaks indicative of several polarization processes occurring with different rates at the media interface.

Thus, the prospect of a dual-doping of titanium oxide to obtain effective electrorheological fillers and creation of new smart materials on their basis suitable for usage in modern smart-devices and technologies was shown.

[1] Korobko E., Novikova Z., Sermiyazhko E., Murashkevich A., Eshenko L. Time stability studies of electrorheological response of dispersions with different types of charge carriers. *Journal of intelligent material systems and structures*. – 2015. – VOL. 26, NO. 14. P. 1782–1788.

A Closer Look at the Carbon/Polymer Interface – An AFM Study

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The polymer/carbon interface plays a major role in many polymer matrix composites which use carbon-based fillers/fibres/nanoparticles [1]. Carbon-based particles are widely utilised in polymer composites and nanocomposites for various applications such as; tyre rubbers (carbon black), advanced membranes (carbon nanotubes), medical equipment and super-strong construction materials (carbon fibres) [2-3]. With advances in carbon nanostructures such as graphene [4] and carbon nanotubes [5] the potential for new materials created by polymer/carbon composites is further increasing. However, the carbon/polymer interface itself is poorly understood at a fundamental level [6]. Polymers behave very differently at an interface than in the bulk. This research is focused on exploring the polymer/carbon interface on the nanoscale, primarily using atomic force microscopy (AFM) techniques. Styrene-butadiene random copolymers with varying molecular weights were spin coated onto both mica and graphite surfaces, and the resulting morphology of the polymer aggregates were probed using tapping mode AFM in air. A comparison between the polymer behaviour on the mica surface and the graphite surface is presented.

Figure 1 shows the same concentration of the styrene-butadiene polymer on a mica surface (A) and a graphite surface (B). The morphology of the polymer aggregates are very different on the two surfaces. On the mica surface spherical-cap nanodroplets form with an average height of 87 nm; this morphology can be explained by dewetting; it is not favourable for the hydrophobic droplets to interact with the hydrophilic surface, therefore to reduce free energy, the chains self-assemble into droplets. On the graphite surface a continuous polymer network is formed with an average height of 42 nm, the polymer morphology is much flatter on the graphite; this is attributed to graphite being hydrophobic and the favourable physical interactions between the surface and the polymer.

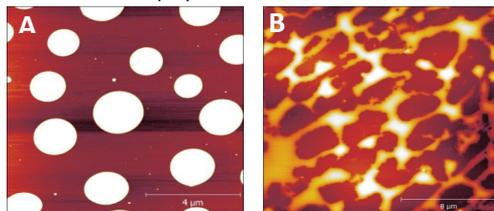


Figure 1: AFM images showing a styrene-butadiene random copolymer ($M_n = 85$ kg/mol) at a concentration of 3.71 mg/ml ($= 1c^*$), on (A) a mica surface and (B) a graphite surface.

[1] K. Yurekli, R. Krishnamoorti, M. F. Tse, K. O. Mcelrath, A. H. Tsou, and H. Wang, *Polym. Phys.* 2001, **39** (2), 256–275.

[2] A. Rahman, I. Rli, S. M. al Zahrani, and R. H. Eleithy, *Nano*, 2011, **6** (3), 85–203.

[3] U. Meier, *Construction and Building Materials*, 1995, **9** (6), 341–351.

[4] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science*. 2004, **306**, 666–669.

[5] S. Iijima, *Nature*, 1991, **354**, 56–58.

[6] National Research Council, *High-Performance Structural Fibres for Advanced Polymer Matrix Composites*, 2011, Preface, ix, The National Academies Press, Washington, D.C. U.S.A.

The effect of the discharge gas on the optical properties and morphology of the silver nanoparticles produced with the aid of the atmospheric pressure glow microdischarge generated in contact with a flowing liquid anode

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Due to many applications of silver nanoparticles (AgNPs) in different areas of science and technology, it is necessary to develop simple, fast, and low-cost production methods that allow to control the optical properties and morphology of the obtained AgNPs. A very rapid method of the synthesis of gold nanoparticles (AuNPs) has recently been reported in our group [1-3] and involved the use of a continuous-flow plasma-reaction system based on direct current, low power atmospheric pressure glow microdischarge (dc- μ APGD) generated in contact with a flowing liquid cathode (FLC) and/or anode (FLA). In the present work, the dc- μ APGD was used for the synthesis of the AgNPs. The microdischarge was ignited in the gap between the surface of solutions of the FLA and a gaseous microjet fed with different gases, i.e., Ar, He, N₂, or air. Solutions containing the AgNPs precursor and a stabilizer were passed through the plasma-reaction system. Samples of the plasma-treated solutions were subsequently collected and taken for analysis by UV/Vis absorption spectrophotometry, dynamic light scattering (DLS), and transmission electron microscopy (TEM). The influence of the gas used for operating the dc- μ APGD system on the optical properties, size, and shape of the obtained AgNPs was examined. It is shown that the use of the mentioned continuous-flow plasma-reaction system with the microjets sustained in N₂ or air, instead of Ar or He, facilitates the production of the highly-stable AgNPs and concurrently reduces the costs associated with this process. Data will also be presented illustrating how the choice of the discharge gas have the effect on the properties of the fabricated AgNPs.

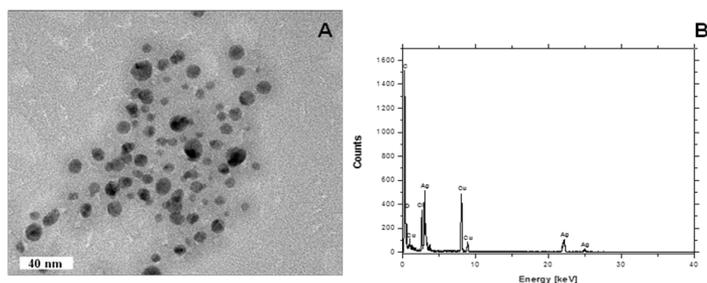


Figure 1 Analysis of the morphology of the AgNPs **A)** Representative TEM micrograph of the AgNPs synthesized using dc- μ APGD in Ar discharge gas; **B)** EDS analysis of the AgNPs.

Acknowledgements The financial support of the research project was provided by National Science Centre (NCN), Poland (UMO-2015/17/N/ST4/03804).

- [1] A. Dzimitrowicz, P. Jamroz, K. Greda, P. Nowak, M. Nyk and P. Pohl, *Journal of Nanoparticle Research*, 2015, **17**, 185.
- [2] A. Dzimitrowicz, T. Lesniewicz, K. Greda, P. Jamroz, M. Nyk and P. Pohl, *RSC Advances*, 2015, **5**, 90534.
- [3] A. Dzimitrowicz, P. Jamroz, M. Nyk and P. Pohl, *Materials*, 2016, **9**, 268.

ZnO Photoinitiators in Production of ZnO/Polymer Nanocomposites

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Zinc Oxide (ZnO) nanocrystals are n-type, wide bandgap semiconductors which are utilized a variety of fields including optoelectronics, piezoelectric devices, sensors, solar cells and sensors. Their antibacterial, UV protective and catalytic properties have been continuously exploited, as well. Synthesis of nanosized ZnO have been demonstrated in a variety of different methods ranging from high temperature thermal decomposition to low temperature solution synthesis [1]. Yet, functionalization of the nanoparticles is an essential issue. Polymers are one of the preferred coating materials for many different nanoparticles due to availability of different functionality and solubility.

Bare ZnO nanoparticles were reported to take part in free radical polymerizations as a photocatalyst in few studies [2,3]. In these systems, ZnO was exploited only as a catalyst and removed after polymerization. Recently, methacrylic acid coated ZnO was used for the synthesis of ZnO/PMMA structure where PMMA was desired as a stabilizer [1]. However, ZnO was not used as a photocatalyst in that synthesis, but a thermal decomposition of a peroxide initiator was used.

Here, utility of surface functional ZnO as a photoinitiator in Free Radical Polymerization to produce an organic/inorganic hybrid material in a simple way is reported. Low temperature synthesis of ZnO was achieved from zinc dimethacrylate under basic conditions and used as a photoinitiator in the production of ZnO/PMMA composites in one pot. In addition, rate of photopolymerization of different monomers such as poly(ethylene glycol) diacrylate (PEGDA) and triethyleneglycol-dimethacrylate (TEGDMA) in the presence of ZnO as a photoinitiator is investigated via Photo-Differential Scanning Calorimetry (DSC). Influence of the excitation wavelength, ZnO concentration and power of the light source on the rate of polymerization and monomer conversion is also studied (Figure 1).

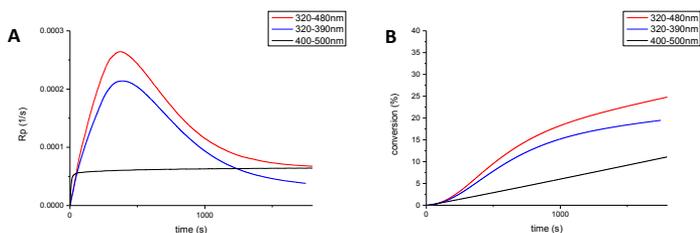


Figure 1. The rate of photopolymerization (A) and conversion (B) of TEGDMA as a function of excitation wavelength.

Acknowledgements. This research is funded by TUBITAK 115Z463.

- [1] A. Gabriela, S. Sreco D., Z. Majda and O. Zorica C., *Journal of Colloid and Interface Science*, 2011, **360.2**, 370-76.
- [2] A. J. Hoffman, H. Yee, G. Millsand M. R. Hoffmann, *J. Phys. Chem.*, 1992, **96**, 5540-5546
- [3] S. Dadashi-Silab, M. A. Tasdelen, A. M. Asiri, S. B. Khan and Y. Yagci, *Macromol. Rapid Commun.*, 2014, **35**, 454-459

Comparison of the electrochemical and photoelectrochemical properties of screen-printed nickel oxide thin films obtained from pastes with different composition

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In the present work the analysis of non-stoichiometric nickel oxide (NiO_x) films obtained from viscous solutions of metal oxide nanospheres is reported as far as the redox properties of the resulting NiO_x deposits are concerned. Films of NiO_x were formed via sintering of slurries consisting in ethylcellulose suspensions of preformed NiO_x nanoparticles (diameter: 20-50 nm), which contained an acid component (HCl or $\text{CH}_3\text{CO}_2\text{H}$) as anti-aggregating agent, and terpineol as solvent. The viscous slurries were screen-printed and sintered onto an opportune substrate of transparent conductive oxide (either indium- or fluorine-doped tin oxide) at temperatures not exceeding 450 °C. The NiO_x deposits were 2-4 μm thick and presented a nanostructured morphology (Figure 1).

The conditions of sintering were chosen in a way that the electrical connectivity between the oxide nanoparticles was warranted and the electrochemical and photoelectrochemical properties were thus imparted in the film. We employed cyclic voltammetry and electrochemical impedance spectroscopy for the electrochemical characterization of the nanostructured electrodes adopting two- and three-electrode configuration of the cell. The effect of film thickness on the electrochemical properties of three different samples of NiO_x was analysed. The NiO_x films thus obtained presented photoelectrochemical activity as *p*-type semiconductors in the pristine state towards the photoactivated reduction of iodine. As a consequence of that the study of screen-printed NiO_x as photoactive cathodes in *p*-type dye-sensitized solar cells was considered.

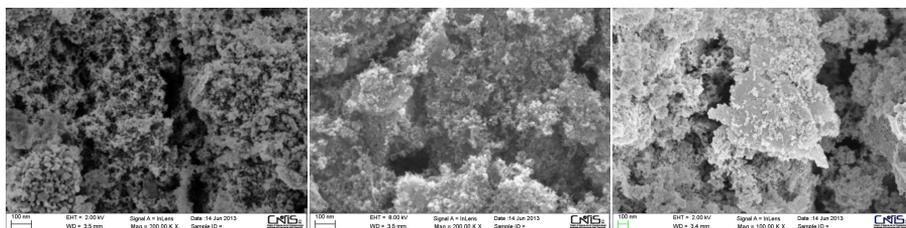


Figure 1. Surface morphology of three different samples of NiO_x obtained from the sintering of slurries with varying composition.

PIC micelles as versatile structuring agents for mesoporous materials: A physico-chemical overview.

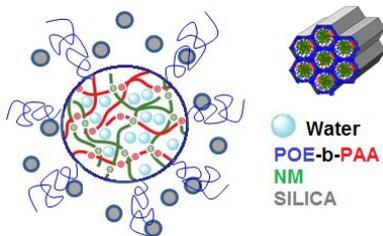
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Polyion Complex (PIC) or Complex Coacervate Core (C3M) Micelles [1] have been used as structuring agents to template ordered mesoporous silica materials [2]. The electrostatic complexation between a double hydrophilic block copolymer (DHBC), polyethylene oxide-b-poly(acrylic acid) (POE-b-PAA), and an polyelectrolyte of opposite charge, neomycin (NM), leads to PIC micelles. Compared to classical structuring agents obtained from amphiphilic molecules, PIC micelles offer several advantages: first, they can be recovered and reused in several mesoporous material synthesis cycles [2]. Secondly, they allow single step preparation of drug-loaded porous materials [3]. Finally, tuning the characteristics of the porous material no longer requires to use several structuring agents: structural characteristics can be adjusted by playing with the physico-chemical conditions, using a unique polyelectrolyte system. The present work aims at correlating the characteristics of the porous materials and the physico-chemical properties of the PIC micelles.

The as-formed hybrid materials obtained right after drying are porous. This is related to the high degree of swelling of the core of the PIC micelles that contains at least 50% of water in weight. Analyses by TEM, N₂ sorption and X-ray diffraction have shown that varying structures and pore sizes can be achieved by simply varying concentration and pH. The associative phase separation of poly(acrylic acid) and neomycin mixtures has been studied as a model system for the core of the PIC micelles. Resulting coacervates were characterized using osmometry, elemental analysis and small angle X-ray scattering. The water content in the coacervates varies with concentration. This translates into variation of porous volume and pore size in the hybrid material. These features are preserved after calcination.



Scheme 1: PIC micelles structuring mesoporous silica materials

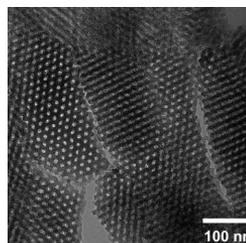


Figure 1: TEM image of a calcined material prepared with PIC micelles

Acknowledgements to the financial support of LabEx CheMISyst Montpellier.

- [1] Voets, I. K.; de Keizer, A.; Stuart, M. A. C. *Adv. Colloid Interface Sci.*, 2009, **147-48**, 300-318.
- [2] Baccile, N.; Reboul, J.; Blanc, B.; Coq, B.; Lacroix-Desmazes, P.; In, M.; Gerardin, C. *Angew. Chem. Int. Ed.*, 2008, **47**, 8433-8437.
- [3] Molina, E.; Warnant, J.; Mathonnat, M.; Bathfield, M.; In, M.; Laurencin, D.; Jérôme, C.; Lacroix Desmazes, P.; Marcotte, N.; Gérardin, C. *Langmuir*, 2015, **31**, 12839-12844.

Hyperuniform materials made with microfluidics

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The hyperuniform materials, being disordered systems with suppressed long-scale fluctuations, now attract a significant scientific interest, especially due to their potential applications for photonic materials production.

We study a jammed packing of oil droplets in water. The droplets are produced in a PDMS microfluidic chip by step emulsification coupled with T junction and directly assembled in a microfluidic channel. By varying the fluid pressures we manage to sharply control the droplet production and thereby govern the structural properties of the obtained material. The hyperuniformity of 3D and pseudo-2D (a monolayer of droplets) systems is investigated. Confocal microscopy is used to determine the position of droplets inside the material. Our results show that at appropriate experimental conditions the droplets self-organize in hyperuniform patterns both in 2D and 3D. The numerical simulations of electromagnetic wave propagation in the obtained materials also predict that they possess interesting optical properties, such as a photonic band gap (PBG). These results supports the hypothesis that hyperuniformity may lead to the PBG in disordered materials [1]. We hope that our studies will help to establish a new way of disordered photonic materials production.

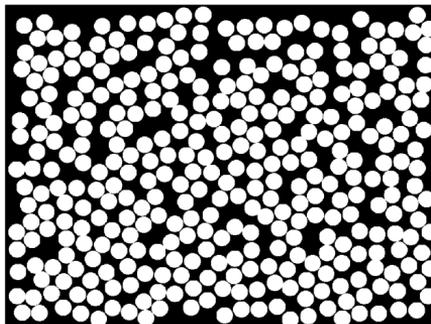


Figure 1 Reconstruction of confocal image.

Acknowledgements The Microflusa project receives funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 664823

[1] M. Florescu, S. Torquato and P. J. Steinhard, *PNAS*, 2009, **106**, 49.

Influence of the shell-to-core ratio of hard core/soft shell particles at liquid/liquid interfaces

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Understanding and controlling the microstructures formed by nanoparticles at liquid/liquid interfaces is of significant importance for many applications including surface patterning, stabilization of emulsions and biological membranes. For a systematic investigation of the effect of shell thickness, we synthesized core/shell particles with hard silica cores encapsulated in soft hydrogel shells of poly-*N*-isopropylacrylamide.[1] In particular, we used silica cores of the same size for all particles and systematically varied the shell-to-core ratio. Due to a similar cross-linking density in the shells with different thicknesses, the degree of swelling was comparable for all samples. The overall particle diameter, however, was significantly different, independently of the swelling state. We assembled these particles at water/*n*-hexane interfaces in a Langmuir-Blodgett trough. Upon compression the particle microstructures were directly transferred onto silicon wafers while the surface pressure was simultaneously measured.[2] The microstructures were investigated by atomic force microscopy (AFM). A representative compression curve obtained for such an experiment is shown in Figure 1. Freeze-Fracture Shadow-Casting cryogenic Scanning Electron Microscopy (FrESCa cryo SEM)[3] was also used to reveal the morphology of the particles at the liquid/liquid interface. The combination of FrESCa cryo SEM and structural analysis by AFM allows drawing conclusions on correlations of the particle architecture to the microstructure as a function of surface pressure. At low surface pressures we found that interfacial distortion caused by the wetting of the particle shells creates attractive capillary forces resulting into crystalline clusters of particles in shell-to-shell contact, at odds with pure microgel particles with a deformable core. At higher compressions, the particles are squeezed into contact. Consequently, adjusting the shell thickness allows tuning the interaction forces and tailoring a specific interface microstructure.[4]

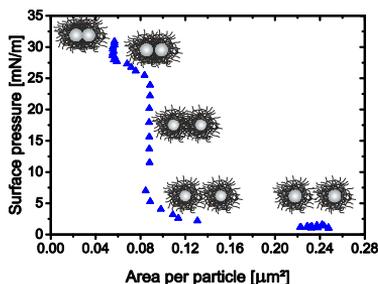


Figure 1: Compression curve for core-shell particles with a shell-to-core ratio of 2.2 adsorbed at the liquid/liquid interface along with a schematic depiction of the underlying microstructure of the particles.

[1]M. Karg *et al.*, *Colloid and Polymer Science*, 2010, **289**, 699-709. [2]M. Rey *et al.*, *Soft Matter*, 2016, **12**, 3545-3557. [3]L. Isa *et al.*, *Nat. Comm.*, 2011, **2**, 1-9. [4]A. Rauh *et al.*, *Soft Matter*, 2016, *in preparation*.

Immobilisation of nanoparticles on polymer surfaces via melt processing

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Nanoparticles and, particularly, nanoparticle aggregates exhibit some very interesting properties which may be used in advanced devices. Some examples are information storage, sensors, microfluidics, or switchable surfaces. For most of the applications, the nanoparticle structures have to be immobilized reliably on solid surfaces.

We followed an approach used for process-integrated surface modification of thermoplastic parts during injection molding. Hereby, the special state of the melt was used for chemical reactions on the melt once it hits a thin layer of a reactive and functional macromolecule, applied on the mold surface in advance. According to our approach, a layer of nanoparticles was prepared on a solid substrate by adsorption from colloid solution. In most cases, a layer of a polycation was adsorbed first to alter the substrate surface charge. Nanoparticles of gold, silica and a polymer were investigated. The surfaces of the particles were chemically modified. The layer was characterized by different spectroscopic and microscopic techniques. The particles were randomly distributed over the surface. In some cases chain-like aggregates were formed. The behavior of the layer in contact with the flowing melt was investigated. Finally, the surface of the part produced by injection molding was characterized.

It was found, that the nanoparticles were not shifted by the flowing melt. No re-mixing with the flowing melt occurred. The distribution on the thermoplastic part surface was also randomly. Even aggregates from the substrate surface were reproduced. This may be a result of the fast cooling of the melt as it comes in contact with the mold. The process is analyzed by thermal simulation. The degree of embedding (see figure 1) depended on the size and surface properties of the particles. Thus, the embedding depth can be controlled. Some of the particle surface area was accessible for small molecules from solution. This was demonstrated by their catalytic activity in a redox reaction and by their adsorption behavior. Those embedded nanoparticle layers may be used in microfluidics or sensor applications.

Consequently, the contribution addresses aspects of manipulation and engineering of nanoparticle systems under conservation of their typical properties. With the method introduced, the economic manufacture of parts with surfaces functionalized with nanoparticles becomes possible.

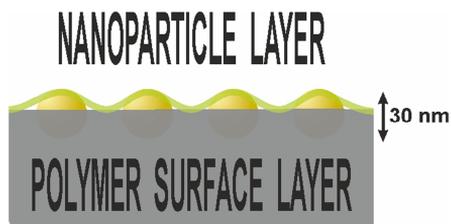


Figure 1 Schematic of the arrangement of nanoparticles on the thermoplastic part surface. The particles are partly embedded, thus immobilized but their surface is still accessible for small molecules.

Optical and structural study of Ga and In co-doped ZnO films

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Zinc oxide is widely known as one of the most significant II–VI semiconductor and an excellent candidate for many technological applications. Doping ZnO films with different metals leads to an effective modification of structural, morphological, optical, electrical, mechanic and chemical properties. Ga-doped ZnO films showed high optical transmittance, Ga can substitute for Zn in the lattice with minimal strain and it possesses very low reactivity towards oxygen. In doped ZnO films become a research focus due to its good electro-optical properties associated with excellent chemical stability. These films are also reported to be good conducting oxide with a high transparency in the visible spectral region and a high electrical conductivity. Ga and In-ZnO system can find applications in gas sensors, in optoelectronic devices and solar cell. The sol for ZnO deposition is synthesized by dissolving zinc acetate in an absolute ethanol (0,4 M concentration). The complexing agent and stabilizer used is monoethanolamine (MEA). The molar ratio MEA/Zn is fixed to 1. The solution has been mixed and stirred on a magnetic stirrer at 50°C/2 hour. InCl₃ and Ga(NO₃)₃·xH₂O have been used as source for In and Ga components. The Zn-In sols are obtained by dissolving 0.5 and 1 wt% InCl₃ into equal Zn sol volume (ZnIn 0.5 and ZnIn 1). Zn-Ga sols are obtained by dissolving 3 wt% Ga(NO₃)₃·xH₂O (ZnGa 3). Two co-doped sols are obtained by mixing equal volumes as follows Sol A (ZnIn 0.5/ZnGa 3) and Sol D (ZnIn 1/ZnGa 3). FTIR detailed study Zn-In-Ga oxides and ZnO shows that Ga and In codoping affects the shapes and the intensity of the absorption bands with no traces of Ga-O and In-O bonds. XRD analysis shows that Zn-In–Ga oxide films possess lower crystallinity compared to pure ZnO and ZnO:Ga films as the XRD lines are broader and less intense. Respectively, the crystallite sizes of co-doped systems are significantly smaller compared to ZnO crystallites and closed to that of ZnO:Ga 3 films. The crystallization appears even at 300°C with clear evidence of amorphous phase. Increasing the annealing temperature (600°C) results in better expressed XRD lines but still amorphous fraction is presented for the doped films. The XRD peaks are assigned to wurtzite ZnO. The lattice parameters, texture coefficients for (100), (002), (101) are determined from XRD data. Optical study shows that the Zn-In–Ga oxide films are not so transparent as ZnO and ZnO:Ga films (Figure 1). The optical band gaps are estimated and it can be seen that they are dependent on doping and annealing temperatures.

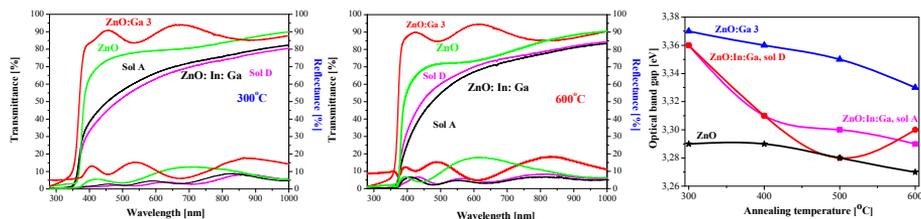


Figure 1. Transmittance and reflectancespectra of ZnO:In:Gafilms, compared with ZnO and ZnO:Ga 3 films annealed at 300 and 600°C. Dependence of the optical band gap on the annealing temperatures of the studied films.

Bifurcation of the dye diffusion coefficient in bulk polymer below the glass transition temperature

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The forced Rayleigh scattering (FRS), or holographic (grating) relaxation technique [1–3] shows itself as particularly sensitive method for estimation of heterogeneities at nanometer scale. The ranges of diffusion coefficients D and spatial scales Λ on which the latter can be measured are $D = 10^{-10} - 10^3 \mu\text{m}^2\text{s}^{-1}$ and $\Lambda = 10^{-1} - 10^2 \mu\text{m}$, respectively, which makes FRS ideal not only for slow diffusion measurements of molecules and particles in polymer systems, but also allows for reaching the superresolution conditions in terms of relaxation times' measurements. The smaller the spatial period Λ the more sensitive is the technique to heterogeneities.

Among other techniques, suitable for heterogeneities sensing, FRS demonstrates superior stability at long times of the measurement. Despite that the minimum spatial scale of this optical technique is in the range of hundreds of nanometers, its sensitivity to the molecular motion is approximately 10 times lower. For example, for a grating distance of 180 nm the characteristic intensity function decreases by a factor e if the particle under investigation performs root mean square displacements (RMSD) of 30 nm: $\text{RMSD} = (2Dt)^{1/2} = \Lambda/2\pi$, where D is the diffusion coefficient and Λ is the spatial period of the induced grating [3].

Holographic (grating) relaxation gives insight into diffusion of the dye molecules in complex environment. It was shown, that this method is particularly useful for investigation of the heterogeneities in wet latex films [4–6], and in dry films with nanofillers [7]. In [4] it was shown that diffusion coefficients in various types of latex film domains and their characteristic size may be defined selectively: in latex particles themselves and in the water-enriched space in between. Core-shell systems were investigated in [5] and [7], while by the same technique the presence of heterogeneities in pure polycarbonate polymer was shown in [6].

In this study the dynamics of 9,10-phenanthrenequinone molecules in the melt of short poly(4-methyl styrene) chains of 15 kg/mol molecular weight with polydispersity of 1.05, which was obtained by freeze drying its non-entangled solution, was investigated below the glass transition temperature (T_g 106 °C) by means of FRS. The bifurcation behaviour of the diffusion coefficient dependency was revealed in this temperature region. Temperature and spatial scale dependencies of apparent diffusion coefficients have shown that the dynamics of the slower process obeys the Williams-Landel-Ferry law, while the faster one demonstrates an activation mechanism of the dye movement. These dependencies were interpreted as evidence for the presence of dynamical heterogeneities in bulk polymer below T_g .

- [1] H. Eichler, P. Günter and D. Pohl, *Laser-induced dynamic gratings*, 1986, Investigation of Physical Phenomena by Forced Light Scattering, 123, Springer, Berlin, Germany.
- [2] M. Antonietti, D. Ehlich, H. Sillescu and M. Wesselmann, *Progress in Colloid & Polymer Science*, 1989, Applications of "Forced Rayleigh Scattering" and "Photon Correlation Spectroscopy" for the examination of transport properties in polymer melts, 83-92, Springer, Berlin, Germany.
- [3] A. Veniaminov and E. Bartsch, *Opt. Spectrosc.*, 2005, **101**, 290.
- [4] A. Veniaminov, T. Jahr, H. Sillescu and E. Bartsch, *Macromolecules*, 2001, **35**, 808.
- [5] K. Suresh, A. Veniaminov and E. Bartsch, *J. Polym. Sci. B*, 2007, **45**, 2823.
- [6] A. Veniaminov, H. Sillescu and E. Bartsch, *J. Chem. Phys.*, 2005, **122**, 174902.
- [7] A. Kiessling, V. Le Houérou, C. Gauthier and E. Bartsch, *Conference talk*, DPG-Frühjahrstagung (Dresden), 2014.

Electro-responsive polymer surfaces

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Polymers are good candidates to build smart materials (materials that can change their properties in response to a changing environment), as their properties can often be tuned by variation of different variables. Thus, changing the conformation of polymers by external stimuli makes it possible to control the properties of polymer-based materials [1-3]. However, The efficient and reversible control of these properties represents an important technological challenge. In this regard, the application of an external electrical stimuli on polyelectrolytes [4] seem to be a convenient control strategy, as the response of polymer chains to physical stimuli is usually faster than the adaptation to chemical stimuli. In this work we discuss the effect of an external electric field on the wettability and adhesion properties of polystyrene-block-polyacrylic acid (PS-b-PAA) copolymer surfaces. The influence of the externally applied electric field is investigated at different pH and salt conditions, as the polyelectrolyte conformation is sensitive to these variables. The figure shows the evolution of the advancing and receding contact angles on a PS-b-PAA surface at pH 4 as a function of the applied voltage. The relatively large variation in contact angle at very low applied voltages and the assymmetric dependence of the response to the sign of the applied field can not be described by conventional electrowetting theories, evidencing the positive effect of the polyelectrolyte coating. We will discuss a model based on polyelectrolyte theories to describe the observed response.

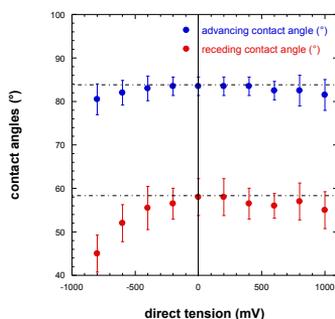


Figure 1: Advancing and receding contact angle of water on polystyrene coated with PS-b-PAA vs. externally applied voltage at pH 4

- [1] D. Julthongpiput, Y.-H. Lin, J. Teng, E. R. Zubarev and V. V. Tsukruk, *Langmuir*, 2003, **19**, 7832
- [2] S. Samanta and J. Locklin, *Langmuir*, 2008, **24**, 9558
- [3] T. Sun, G. Wang, L. Feng, B. Liu, Y. Ma, L. Jiang and D. Zhu, *Angew. Chem. Int. Ed.*, 2004, **43**, 357
- [4] O. V. Borisova, L. Billon, R. P. Richter, E. Reimhult and O. V. Borisov, *Langmuir*, 2015, **31**, 7684

(From material science to biomedicine:) heterogeneous functional materials as seen by synchrotron x-ray (sub)micron beam techniques

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Outstanding structure-function relationship of new functional materials are often due their dynamic heterogeneous structure and composition [1, 2].

We can visualize and quantify this heterogeneity with fine details in real space at nanoscale and mesoscale by i) taking advances from X ray synchrotron radiation features and from optical focusing devices ii) applying advanced spatial statistics tools to big datasets.

Strongly electrons correlated materials constitute an intriguing class of materials where the competition between competing orders due to defects spatial distribution and electronic textures gives mesoscale phase separation (see Fig. 1) that is believed to play a central role for material functionality [3, 4].

We extend our methodology to visualize multiscale complex and heterogeneous structures from nano/mesoscopic to macroscopic scale in different systems, such as biomaterials [5].

The results suggest a complex scenario where materials functionality is related to topology [3].

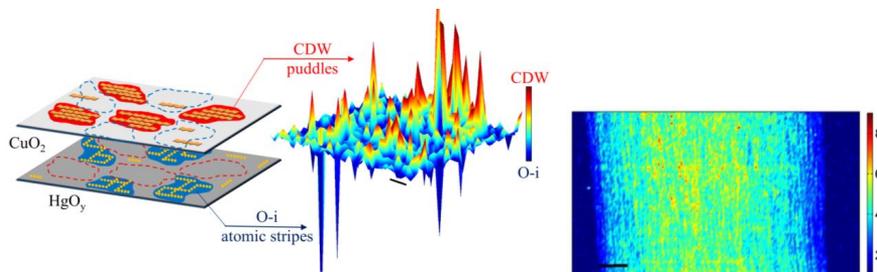


Figure 1 (Left panel) Spatial anticorrelated distribution of charge density waves (CDW) on the CuO₂ planes and atomic stripes of interstitial oxygen dopants, i-O, in the mercury spacer layers of a single layer Hg1201 superconductor. Scale bar, 5 μ m. (Right panel) Inhomogeneous spatial organization of myelin structure in a frog's sciatic nerve. Bar correspond to 100 μ m

- [1] M. Fratini, N. Poccia, A. Ricci, G. Campi, M. Burghammer, G. Aeppli & A. Bianconi, *Nature*, 2010, 466, 841-844
- [2] G. Campi, D. Innocenti, and A. Bianconi, *Journal of Superconductivity and Novel Magnetism*, **2015**, 28, 1355
- [3] G. Campi, A. Bianconi, N. Poccia, G. Bianconi, L. Barba, G. Arrighetti, et al., *Nature*, **2015**, 525, 359
- [4] N. Poccia, M. Fratini, A. Ricci, G. Campi, et al., **2011**, *Nature Materials*, 10, 733-736
- [5] G. Campi, M. Fratini, I. Bukreeva, G. Ciasca, M. Burghammer, F. Brun, G. Tromba, M. Mastrogiacomo, A. Cedola *Acta Biomaterialia*, **2015**, 23, 309

Large-area two-dimensional colloidal crystals of silica particles of different sizes at the air/water interface

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Two-dimensional colloidal crystals have attracted growing interest owing to their potential applications in photonics, surface engineering, biological and chemical sensing, and so on. It is critically important for such applications to prepare highly ordered, uniform mono-particulate films over a wide range on solid substrates. Many approaches have been made with purpose of fabricating such high-quality particulate films. Among them, the use of Langmuir-Blodgett (LB) technique has an advantage in terms of the possibility of controlling film structures (e.g. in-plane density and arrangement of particles) not only by adjusting subphase condition and particle surface property which influence the self-assembly of particles at the air/water interface, but also by lateral compression of films with confining barriers which forces floating particles and their assemblies to get closer. In the present work, we aimed to fabricate large-area crystalline monolayers of silica particles by using the LB technique. As particles, monodispersed silica particles of different diameters (1.62 μm , 500 nm, and 110 nm) were used. The particle surface was chemically modified with organosilanes to control the surface property. Special attempts were made for the smaller particles by adding a surfactant to a spreading dispersion or by partial hydrophobizing of particle surface through Pickering emulsification.

For the particles of 1.62 μm diameter, the surface modification with a polyethylenimine functional silane (SPEI) led to fabrication of a highly ordered, closely packed mono-particulate film over a large area. A surface pressure (π) - particulate area (A) isotherm for the monolayer at the air/water interface and scanning electron microscopic images for films deposited on silicon wafers at several particulate areas suggested that the particles spontaneously assemble into monolayer islands on the water surface after spreading, and then the islands are gathered with in-plane rearrangement of the particles by compression. On the other hand, in the case of SPEI-modified silica particles of 500 nm diameter, some multilayer regions were dispersed in a monolayer matrix. The multilayer formation might occur just after spreading during solvent evaporation and/or by ejection of the particles from the monolayer in the rearrangement process during compression. However, it was also found that the multilayer formation could be effectively suppressed by addition of a small amount of sodium dodecyl sulphate (SDS) into a spreading dispersion: when the particles were spread from the dispersion including 0.1 wt% SDS, a polycrystalline monolayer was formed. In a film of the SPEI-modified silica particles of 110 nm diameter, the number of multilayer region was increased. The addition of SDS again helped the suppression of the multilayer formation, but it was difficult to eliminate the multilayer fraction as small as the case of the particles of 500 nm diameter. To improve the quality of a film of the 110 nm-diameter particles, another attempt in surface modification was conducted, where a part of particle surface was made hydrophobic by means of Pickering emulsification [1]. In the resultant film, the particles were rather well arranged into the monolayer over relatively larger area.

[1] Wei Cao, Renliang Huang, Wei Qi, Rongxin Su, Zhimin He, *ACS Appl. Mater. Interfaces*, **7**, 465-473 (2015).

Magnetic hybrid nanoadsorbents for the uptake of pharmaceuticals from water

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Pharmaceutical products have been frequently detected in water sources, due to the ineffectiveness of wastewater treatment plants to remove efficiently these compounds [1]. This is a matter of concern due to potential harmful effects on the environment and human health. To overcome this problem alternative treatment methods are needed. Compared to other methods, adsorption is an attractive process in view of its simplicity of implementation. Among available sorbents, magnetic materials present great practical interest for water treatment because, besides being inexpensive, the pollutants may be removed by the application of an external magnetic gradient.

Keeping these features in mind, the present investigation reports the development of magnetic nanosorbents based on organic-inorganic coated magnetite (Fe_3O_4) particles for the uptake of pharmaceuticals from water. The sorbents were prepared using a new approach for the surface modification of Fe_3O_4 particles with biopolymer-silica hybrid shells [2]. The materials were characterized using electron microscopy (TEM/SEM), FTIR spectroscopy, elemental analysis and zeta potential measurements and tested for the uptake of three distinct pharmaceuticals from water: diclofenac (DCF), tetracycline (TET) and metoprolol (MTP). The kinetics and equilibrium adsorption onto the produced materials was investigated and modeled. κ -carrageenan based hybrid sorbents removed efficiently metoprolol tartrate from water, a beta-blocker widely used. The maximum MTP adsorption capacity of these hybrids was *c.a.* 300% higher than the adsorption capacity of others sorbents reported in literature. The high adsorption performance could be ascribed to reduced particle dimensions and the high surface to volume ratio combined with a relevant sulfonate groups content arising from κ -carrageenan incorporation, which have high affinity for MTP molecules.

Acknowledgements This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), financed by national funds through the FCT/MEC (project PTDC/CTMNAN/ 120668/2010) and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement.

- [1] T. Deblonde, C. Cossu-Leguille, and P. Hartemann, *International Journal of Hygiene and Environmental Health*, 2011, **214**, 442–448.
- [2] S. F. Soares, T. Trindade and A. L. Daniel-da-Silva, *European Journal of Inorganic Chemistry*, 2015, **27**, 4588-4594.

Degradation of Azo-Dyes with PEI/Au Nanoparticles: Influence of the PEI Structure and Molecular Weight

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Gold nanoparticles has a very old history yet are still extremely popular due to size and shape dependent optoelectric properties, inertness and biocompatibility. In addition to applications in nanobiotechnology as diagnostic and therapeutic agents, there are a lot of effort in using Au NPs for sensors and as catalyst. One catalytic application of Au NPs is the reduction of pollutants, such as azo-dyes. Recently, synthesis of Au nanoparticles and clusters by the reduction of Au³⁺ to Au⁰ with linear 25kDa polyethyleneimine (PEI) was reported [1].

In this study, we report the effective catalysis of azo-dye reduction with PEI/Au nanoparticles. We have investigated the influence of the PEI molecular weight (0.6Da-25kDa) and structure (linear versus branched) on the catalytic effect of the NPs. As the azo-dyes, three structures with different net charges were selected to elucidate the effect of dye-NP interaction in the reaction kinetics. Studies were performed with methyl orange, methylene blue and ponceau 4R.

Methods

Synthesis of gold nanoparticles were conducted in aqueous solutions using polyethyleneimine and auric acid. After purification from ultrafiltration tubes, NPs were characterized by DLS, UV-spectrophotometer, SEM, XRD, XPS and FTIR. Nanoparticles were mixed with azo-dyes and NaBH₄ and the reduction of dyes were tracked with UV-Vis spectrophotometer.

Results

Stable, aqueous colloidal Au nanoparticles with PEI coating were prepared and used as a catalyst in the reduction of azo-dyes with NaBH₄. Concentration of both nanoparticles and NaBH₄ was changed.

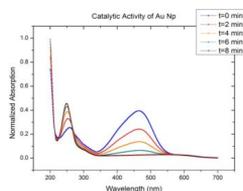


Figure 1 Absorption spectrum of catalytic activity of gold nanoparticles on methyl orange.

- [1] Florian Kretschmer, Ulrich Mansfeld, Stephanie Hoepfner, Martin D. Hager, and Ulrich S. Schubert, *Chem. Commun.*, 2014, **50**, 88.

Contact Angle Hysteresis of a Water Droplet on Regular Pillar-like Hydrophilic Patterned Surfaces

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A series of pillar-like patterned poly(ethyleneterephthalate) (PET) hydrophilic surfaces with different pillar sizes and spacing were fabricated by soft photolithography. The advancing/receding contact angles of water on these PET patterned surfaces were carefully measured by using embedded-needle method and evaporation method, and compared to the theoretical predictions of the Cassie model and the Wenzel model. When a water drop is in the Wenzel state, its contact angle hysteresis increases along with an increase in the surface roughness. While the surface roughness is further increased beyond its transition roughness (from the Wenzel state to the Cassie impregnating wetting state), the contact angle hysteresis (or advancing contact angle) discontinuously drops to a lower value. Even for a hydrophilic surface, the advancing contact angle may still exhibit a value larger than 150° for high surface roughness.

Catalytic investigation of Pd-graphite oxide nanocomposites

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Graphite-oxide (GO) is a layer-structured material, produced by the controlled oxidation of graphite. In contrast to pristine graphite, the GO lamellae contain hydroxyl and epoxide functional groups on their basal planes, in addition to carbonyl and carboxylic groups located at the sheet edges. The presence of these functional groups makes the graphene oxide sheets strongly hydrophilic. As a result, GO readily adsorbs water and other polar liquids and exhibits one-dimensional swelling, similarly to clay minerals [1,2]. GO is a two-dimensional solid, with strong covalent bonding within the layers and weaker interlayer contact between intercalated water molecules. GO readily undergoes disaggregation and has an excellent intercalation ability and cation exchange capacity. The favourable properties of GO make it particularly suitable for application as a host material of catalytically active metal nanoparticles [3]. Cationic surfactant-GO nanocomposites have been synthesized via reactions between aqueous solutions of surfactants and colloidal GO suspensions. Various kinds of surfactants were intercalated into GO and their structures were investigated [4].

In the present study, hydrophobic GO nanocomposites were synthesized and applied as host materials of monodispersed Pd nanoparticles. GO was prepared according to Brodie's method. Low-loaded organophilic Pd-GO nanocomposites were synthesized in micellar systems, by using the precursor K_2PdCl_4 and the aqueous solution of the cationic surfactant tetradecylammonium bromide ($C_{14}TAB$) as a stabilizer. Reduction of the precursor was performed by an excess of $NaBH_4$, which resulted in the formation of a stable Pd sol. The Pd particles were surrounded by a protective layer of the cationic surfactant molecules. Upon mixing the Pd sol with an aqueous GO suspension, the surfactant molecules were released from the surface of Pd and irreversibly bound to the cation exchanger positions of GO. Simultaneously, the Pd particles were immobilized on the surface of the GO lamellae via adhesion. The amount of surfactant cations on the surface sites of GO was equal to its cation exchange capacity. The surfactant cations made the surface of GO hydrophobic, which ensured that Pd-GO could be readily dispersed in organic solvents. The Pd-GO nanocomposites were characterized by ICP-AES, XRD and TEM measurements. The catalytic performances of the samples were investigated in an automated hydrogenation reactor, for the liquid-phase hydrogenations of terminal and internal alkynes under mild conditions (101325 Pa, 298 K). The hydrogen consumption was recorded as a function of reaction time. The reaction rates were determined from the slopes and the turnover frequencies (TOF) were calculated. Experimental results indicated that the Pd/GO samples were highly active and selective catalysts for alkyne hydrogenations. It was also established that a considerable proportion of the particles was accommodated in the interlamellar space of GO, which was found to have a crucial effect on the catalytic behaviour.

Acknowledgements Financial support through Grant OTKA K109278 is gratefully acknowledged.

- [1] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, *Nature*, 2006, **442**, 282.
- [2] I. Dékány, R. Krüger-Grasser, A. Weiss, *Colloid Polym. Sci.* 1998, **276**, 570.
- [3] Á. Mastalir, Z. Király, M. Benkő, I. Dékány, *Catal. Lett.* 2008, **124**, 34.
- [4] Y. Matsuo, T. Niwa, Y. Sugie, *Carbon* 1999, **37**, 897.

Nanotechnology

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The objective of this work is study the synthesis and the characterization of nanostructured catalysts, consisting of association of metal oxides nanoparticles and evaluation of their catalytic proprieties. Four types of nanostructured catalysts have been synthetised in basic medium that are Al₂-SiO₂, MoO₂-Al₂O₃-SiO₂, CeO₂-Al₂O₃-SiO₂ and MoO₂-CeO₂-Al₂O₃-SiO₂ by sol-gel process (supercritical spraying of sol). These catalysts were characterized by various methods such as transmission electronic microscopy (TEM), X-ray diffraction (XRD), infrared spectroscopy Fourier transform (FTIR), the BET method and the zeta metry. These catalysts nanostructured exhibit a good selectivity in the izomerization reaction of normal hexane and in the transformation of cyclohexane.

The synthesis of these nanostructured catalysts at different concentrations is made pae soft chemistry, sol-gel method. The interest of this method lies in its flexibility in effect, and from soils prepared was obtained nanopowder.

The developed nanostructured catalysts are characterized by different physicochemical methods of analysis that revealed several conclusions .

References:

- [1] Q. Yuau , H.Duan,L.Li, Controlled synthesis and assembly of ceria-based nanomaterials, Elsevier Inc,2009
- [2] KarzynaRaulin-Woznika,these de doctorat 2009
- [3] Indirka .Udaikourama Arachchidje;Sol-gel route for mrtal 2008

An alternative diabetic retinopathy therapy: a laser triggered microsystem for controlled release of resveratrol

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Diabetic retinopathy (DR) is one of the most severe ocular complication that causes visual impairment and blinding due to retina and optic neuronal path damage. During recent years, there was expressed a general interest in using **resveratrol (RV)** (3,5,4'-trihydroxystilbene) for prevention or complementary therapy for eye diseases. However current challenges in RV delivery and bioavailability require a targeted delivery strategy. Our current approach is to load **RV** as a cargo molecule, **into polyelectrolyte multilayer microcapsules (PEM)**, with RV's controlled release by a **laser triggered** procedure into **retina pigmented epithelial cells (RPE cells)**. Mimicking the hyperglycemia physiology which occurs in DR patients by using D407 cells as a platform for an *in vitro* experimental model for this eye disease, we assessed the therapeutic potential of RV-loaded PEM. The synthesis process of the RV-PEM complex is based on a simple layer by layer assembly approach. During this procedure the capsules walls are decorated with gold nanoparticles for laser controlled release facilitation. The RV-loaded PEM obtained by this procedure were characterized using spectroscopic and microscopic methods. Next, the laser triggered release process of RV was optimized. Quantification of the RV released from microcapsule was assessed by HPLC-ESI-MS. The RV entrapment efficiency and the yield of production were determined in order to determine the amount of therapeutic agent who reaches the target site. Moreover, confocal and transmission electron microscopy proved that RV-loaded PEM were internalized in RPE cells. Raman/SERS spectroscopy, a rapid and non-invasive biochemical analysis of cells, has been used for detection and imaging applications of RV-loaded PEM inside RPE living cells. The results obtained show a promising strategy to enhance the bioavailability of RV and to increase its solubility, stability and release, by developing an efficient controlled-release delivery system for RV specifically targeted toward retina.

Acknowledgements The financial support of UEFISCDI (Executive Agency for Higher Education, Research, Development and Innovation Funding) through grant with code PN-II-RU-TE-2014-4-1135, 14/01.10.2015 is highly acknowledged. The authors would like to thank Dr. Flaviu Tăbăran and Dr. Maria Suci for help with the confocal and TEM microscopy experiments.

Solidification of Magnetic Liquid Marbles

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Liquid marbles, which are formed usually by rolling a liquid droplet over a hydrophobic powder, are attracted much more attention due to increasing demands to transport or manipulation of small volumes of fluids, micropumps, sensors and miniature reactors. Stimuli-responsive liquid marbles can be manipulated with the changing pH, temperature or magnetic field and allows to use in various applications. Especially, magnetic liquid marbles provide transportation of core liquid and serve as miniature reactors by means of opening and closing the top of the marble with a permanent magnet.

We have studied to form magnetic liquid marbles with hydrophobic iron oxide nanoparticles. Then, obtained liquid marble was used as a model miniature reactor. First of all, approximately 6 nm sized water soluble magnetite nanoparticles (MNPs) were synthesized via a well known co-precipitation method [1]. To modify the surface of iron oxide nanoparticles, a perfluorinated ligand was added to the MNPs solution and interacted. Thus, hydrophobic iron oxide nanoparticles were obtained. To form liquid marbles, particles were dried, ground and various volumes of water droplets were rolled over this hydrophobic powder. Magnetic actuation can be performed when a permanent magnet is approached to the liquid marble and it was determined that the velocity of marbles under a magnetic field were considerably high. When a liquid marble was hold above a magnet, top of the marble was opened, and when the magnet was removed, top of the marble was closed again. This process is a reversible process and can be repeated for more than 10 times. As a reactor, opening and closing process allows adding various reactants after the formation and transportation of marble. A linear relation was determined between the height and diameter values, that means formation of approximately spherical shaped small magnetic liquid marbles and gravitationally flattened puddles were obtained when the large volume of water droplets was used to form liquid marbles.

As a model reaction, gelation of a gelatin solution was performed inside of the liquid marble. To achieve this, a gelatin solution was prepared at 50°C and this solution was used to form the liquid marble. When this solution was cooled to room temperature, reaction was completed in 3 minutes and gelation was occurred. Also, gelation reaction provided a mechanical robustness for marbles. Therefore, solidification of a liquid marble was obtained and it was possible to pick it up and press or stick a needle through it without rupture of the marble.

[1] W. Wu, Z. Wu, T. Yu, C. Jiang and W. Kim, *Sci. Technol. Adv. Mater.*, 2015, 16, 023501. (43pp).

Functional ZnO nanoparticles as photo-initiators

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Semiconductors like ZnO are well-known for their charge transfer potential and their photo-catalytic properties. Recently we have proven that modified nanoscaled ZnO have the potential to be useful as photo-initiator for radical polymerisation of bulk materials[1][2]. NanoPI can be migration-less/free, “harmless” photo-initiators with tuneable, selective absorbance. Such initiators are of dire need for applications resulting to products like food packages. In addition to the demonstration of a possible non-fragmenting system this contribution deals with the effect of modifier content (e.g. levulinic acid) during the synthesis. Levulinic acid is a small molecule which to not contain reactive or aromatic/ chromophore functionalities. The synthesis is maximal a two-step procedure whereby the injection procedure leads to non-surface modified (eventually doped) bare, well-defined nanoparticles (spherical, smaller than 10 nm). A non-doped batch was used for different modifications so that the effect of the modifier can be analysed independent from the influence of the precipitation. Monitoring of the polymerisation of a multifunctional acrylic ester resin took place by using novel transition UV-curing equipment[3], compare to Figure. Thereby an absolute and spectral calibrated xenon flash light illuminates the sample and a diode array detector measures the reaction progress down to the time range of the flash distance (down to 30 ms).

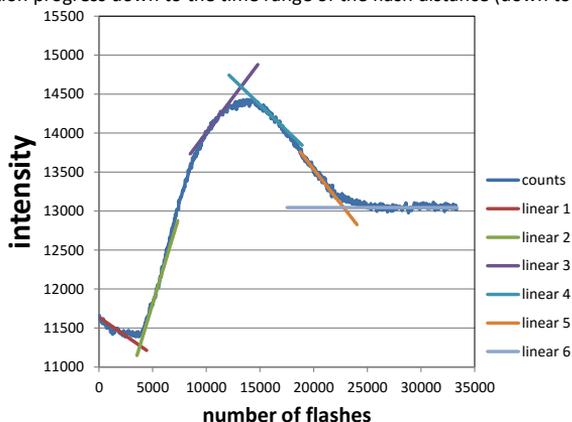


Figure 1 Example analysis for one wavelength point of the UV-curing experiment. The transmitted intensity results in a reaction dependent slope.

- [1] M. Schmitt; *Macromol. Chem. Phys.* ZnO nanoparticles induced Photo-Kolbe-reaction, fragment stabilization and effect on photo polymerization monitored by Raman-UV-Vis-measurements, 2012, **213**, 1953.
- [2] M. Schmitt, *Nanoscale Synthesis and testing of ZnO nanoparticles for photo-initiation: Experimental observation of two different non-migration initiators for bulk polymerization*, 2015, **7**, 9532.
- [3] M. Schmitt; *Macromol. Chem. Phys.* New method for real-time monitoring of photo-polymerization by UV-Vis-spectroscopy, 2011, **212**, 1276.

Investigating the Interactions of Nanoscale Calcium Phosphates with Polymer additives

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Current challenges involved in the design and preparation of functional nanoparticles include the difficulty of overcoming nanoparticle aggregation. The formation of aggregates is thermodynamically favourable; however it prevents the full functionality of nanoparticles from being expressed. If the nanoparticles could be dispersed, this would increase their functionality and improve their application to medicine and dentistry. The project aims to encapsulate apatite nanoparticles with functional polymer coatings to demonstrate an enabling technology with the possibility of opening new opportunities in medicine, dentistry and other non-health sectors.

Commercial low and high molecular weight poly(acrylic acid) was added to the synthesis of fluorhydroxyapatite (FHA) and hydroxyapatite (HA) nanoparticles. Analysis via FTIR, XRD, TGA and TEM showed the inclusion of the polymer in the (F)HA samples had an effect on the morphology and size of the particles. Other polymer additives including linear copolymers of poly(ethylene glycol-b-hydroxyethyl acrylamide), synthesised by SET LRP polymerisation were included in the synthesis of (F)HA showing varying effects on the morphology and size of these particles. Ongoing work is looking into the effects of other polyelectrolytes and phosphorylated polymers to determine their effect on the growth of (F)HA nanoparticles.

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Multiscale Self-Assembly of Microtubes

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Mixtures of β -cyclodextrin (β -CD) and sodium dodecyl sulfate (SDS) form complexes in a 2:1 molar ratio at elevated temperatures [1]. Upon cooling to room temperature these SDS@2 β -CD complexes self-assemble into hollow ‘annular ring’ microtubes. By adding colloidal particles into the mixture colloid-in-tube assemblies are obtained after a heating/cooling cycle [2]. Depending on the ratio of colloid-to-tube diameters various structures can be formed such as zigzag, zipper and helical sphere chains (see figure 1). The self-assembly of this complex system was characterized by small-angle x-ray scattering at the ESRF, covering a total of three orders of magnitude of spatial scales. Furthermore, the response of this system to variations in temperature and concentration was probed.

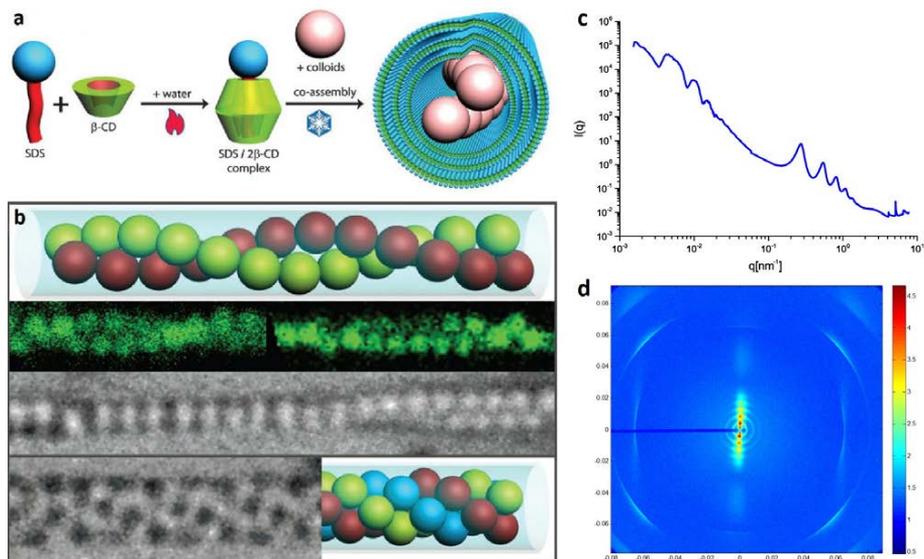


Figure 1 (a) Co-assembly of SDS@2 β -CD microtubes and colloids. (b) Helical structures are formed upon confining colloidal spheres in microtubes. (c) Radial intensity profile and (d) 2D SAXS pattern of microtubes.

[1] L. Jiang, Y. Peng, Y. Yan, M. Deng, Y. Wang and J. Huang, *Soft Matter*, 2010, **6**, 1731.

[2] L. Jiang, J.W.J. de Folter, J. Huang et al., *Angewandte Chemie Int. Ed.*, 2013, **52**, 3364.

Raman imaging and chemisorption studies of methylene blue dyeing of antimicrobial textile fibres

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Since its discovery, surface enhanced Raman scattering (SERS) spectroscopy has been used to detect organic molecules adsorbed at metallic nanoparticles (NPs), typically Au and Ag.[1,2] Numerous works have reported the development of efficient SERS substrates to detect analytes in multiple domains.[1,2]

On the other hand, in the past decade, the textile industry has applied new techniques for the deposition of nano-sized particles on textile fibres in order to enhance properties of conventional fabrics.[3,4] Moreover, the new functionalities arising from the incorporation of metal nanoparticles (NPs) on textile fibres make them good candidates in domains such as wound dressing, smart textiles, water treatment, biosensors and paper industry. Additionally, textile fibres containing Ag nanoparticles have been widely explored for a number of antimicrobial fabrics.[3,4]

This research shows that Raman and SERS mapping can be used with advantage in the monitoring of textile dyeing process, which is a critical stage in the manufacture process of fabrics.[5] Using Ag containing linen fibres stained with methylene blue (MB), it was possible to map the local distribution of the MB dye in the fibres by Raman imaging. MB was selected as the molecular probe not only as a model dye but also because it occurs in aqueous solution in the form of dimer or monomer species each having different characteristic optical absorption, hence resulting in hue variations. Our results demonstrate that by using Raman imaging, it is possible to distinguish the preferred adsorbate form on distinct types of nanocomposite fibres and their local distribution. This investigation allows to foreseeing the use of this technique in terms of quality control of antimicrobial Ag containing fabrics, which is a market in great expansion.

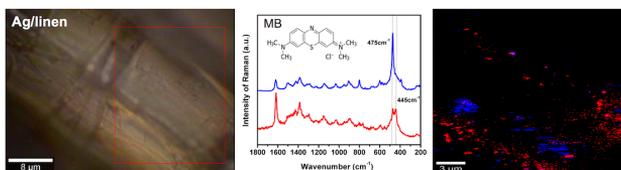


Figure 1: Optical photograph (right) and combined Raman image (left) using two different Raman spectra of MB (10^{-4} M) adsorbed on Ag/linen composite; chemical structure of MB and Raman spectra of MB species used for the combined Raman image (633 nm excitation laser source) (middle);

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- [1] K. Kneipp, *Physics Today*, 2007, **60**, 40.
- [2] S. Fateixa, H. I. S. Nogueira, T. Trindade, *Phys. Chem. Chem. Phys.*, 2015, **17**, 21046.
- [3] R. Dastjerdi, M. Montazer, *Colloids Surfaces B Biointerfaces*, 2010 **79**, 5
- [4] R. J. B. Pinto, M. C. Neves, C. P. Neto, and T. Trindade, "Composites of Cellulose and Metal Nanoparticles," in *Nanocomposites - New Trends and Developments*, 2012, 73.
- [5] S. Fateixa, M. Wilhelm, H. I. S. Nogueira, T. Trindade, *J. Raman Spectrosc.*, 2016 *in press*

Spherical porous polymer particles prepared by phase inversion emulsification process

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Polymer particles with micrometers size have attracted attention due to their potential applications in modifiers of cosmetics, additives of toners, rheology control agents of paint, diagnostic testing agents for medical treatment and automotive materials. In particular, porous polymer particles are a favorable candidate for their applications because of their low-specific-gravity and large apparent surface area. In this study, we demonstrate that spherical porous polymer particles can be prepared by a combination of a phase inversion process from W/O emulsions to O/W emulsions and a removal process of water-soluble organic solvents, and discuss about the effects of surfactants and poor solvents on the formation and porous structure of polymer particles.

A MEK solution of poly(styrene-co-acrylonitrile)(SAN) was mixed with an aqueous solution of copoly(vinyl alcohol-vinyl acetate)(PVA) to prepare W/O emulsions. The sufficient PVA aqueous solution was successively added under a vigorous stirring to induce the phase inversion from W/O emulsions to O/W emulsions. The total volume of water phase was 0.8~1.6 times as much as that of oil phase. Here, since the subsequent addition of water causes exuding water-soluble MEK predominately from the surface of the oil droplets in O/W emulsions, we can obtain solidified SAN particles.

Fig.1(a) shows representative scanning electron micrograph (SEM) images of the solidified SAN particles without porous structure prepared at a stirring rate of 500 rpm. The resultant particle size was about 4 μ m. It was found that the size distribution is improved by adding hydrophobic surface-active agents having low HLB into the oil phase or by increasing the stirring rate. Further, we found that the addition methylcyclohexane (MCH), which is a poor solvent of SAN, into MEK resulted in the formation of various shape of SAN particles. We successfully prepared disc-like (Fig.1b) and porous (Fig.1c) SAN particles at MEK/MCH=8/2 and MEK/MCH=7/3, respectively.

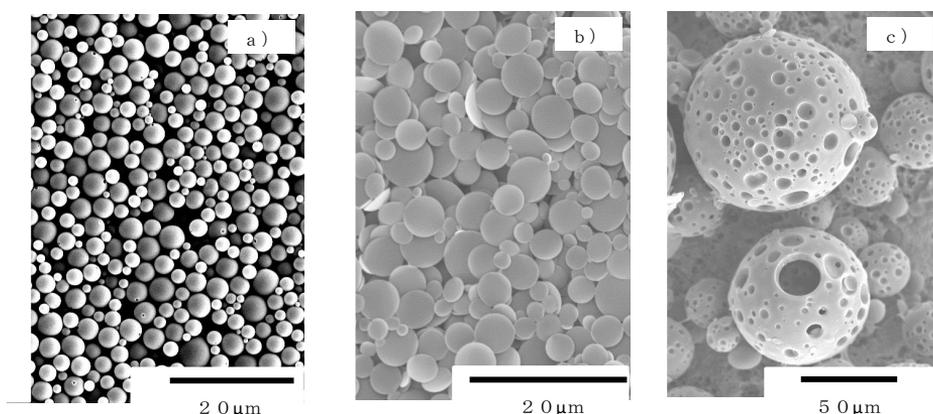


Fig.1 SEM images of (a) spherical SAN particles, (b) disc-like SAN particles, and (c) SEM porous SAN particles.

Morphology control of zinc oxide particles in the presence of anionic surfactants

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Zinc oxide (ZnO) is one of the promising materials applicable for photocatalyst, sunscreen agent and medicine. The fabrication condition such as reaction temperature, reaction time, pH and additives can control the morphologies of the obtained ZnO particles. Amphiphilic molecules are well known as a structure directing agents to synthesize the structure controlled inorganic materials due to self-assemblies and specific adsorption. In this study, we focused on anionic surfactant as an additive to synthesize ZnO particles. We synthesized ZnO particles in the presence of anionic surfactant and investigated the effect of anionic surfactant on the shape of ZnO particles. Sodium hexadecyl sulfate (SHS) was used as an anionic surfactant. ZnSO₄ aqueous solution was added in SHS aqueous solution adjusted pH with ammonia water. The obtained solution was stirred at 70°C for 24 h. Then, hydrothermal treatment (HT) at 150 °C for 24 h was carried out. For comparison, the particles were synthesized without HT and addition of SHS.

First, we investigated the crystal structural properties of the obtained particles using XRD measurements. All XRD patterns of the particles fabricated through HT process had only the diffraction peaks assigned to ZnO. However, peaks assigned to ZnO were not confirmed in the XRD patterns of the particles synthesized without HT.

Next, the morphologies of the obtained particles were investigated using SEM observations. SEM images of the particles obtained without HT showed that amorphous particles were formed (Figure 1 (a) and (b)). In contrast, the morphologies of the particles obtained with HT in the absence and presence of SHS were nanorods and hexagonal platy particles, respectively (Figure 1 (c) and (d)). These results indicated that the hexagonal platy ZnO particles were formed through HT process in the presence of SHS.

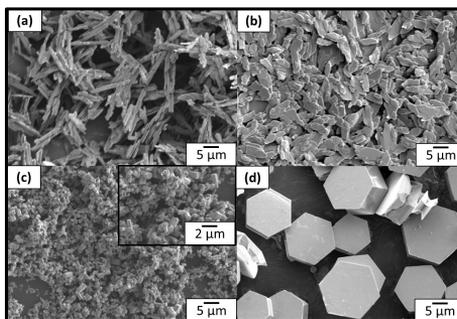


Fig.1 SEM images of the particles synthesized (a, b) without and (c, d) with HT in the (a, c) absence and (b, d) presence of SHS .

Synthesis of macro-porous materials via controlled aggregation of colloidal polymer particles

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Porous materials are widely used for many different applications, ranging from catalysis to chromatography to thermal and sound insulation. In particular, macro-porous polymers exhibit unique behaviors in chromatographic applications thanks to the large set of macro-pores, which allow internal convective flow, quickly carrying large molecules (such as biomolecules) to interact with the pore surface. These materials, also called perfusive materials, allow to establish good separation performance at high flows, due to their flow-independent behavior.

Different manufacturing methods can be applied to produce macroscopic porous polymer particles. Most of them involve a poor solvent of the polymer (the so-called porogen) as pore generating component, which needs to be fully extracted after the synthesis. An alternative is to use controlled aggregation of colloidal polymer nanoparticles and take advantage of the structure and morphology of the formed clusters. Thanks to their fractal nature, such clusters have pore sizes ranging from few nanometers to microns, thus suitable to fulfill the perfusive behavior requirements [1]. A method based on this concept is explored in this contribution. Named “Reactive Gelation”[2], it is composed of three major steps: starting from an aqueous dispersion of colloidal polymer nano-particles (so-called latex) swollen by a mixture containing monomer and initiator, micron-size clusters are formed by controlled aggregation of the primary particles and finally hardened by post-polymerization through heating. This last process “freezes” the aggregate structure, ensuring the mechanical stability required to withstand high flowrates and pressure drops.

Aiming at developing an easily scalable process for the production of optimized and versatile perfusive materials for chromatographic applications, in this contribution we present novel manufacturing methods involving different aggregation regimes. In particular, the first approach is based on shear-induced aggregation performed by passing the latexes through a Z-shaped microchannel at high flow-rate. On the other hand, segmented stagnant aggregation is applied in the second approach taking advantage of an initial water-in-oil emulsion, finally reversed to produce suitable polymer aggregates. The different aggregation mechanisms result in clusters of several micron in size with different porous structure, as shown in Figure 1. The cluster morphology as well as the pore size distribution of the different materials have been systematically investigated through adsorption and intrusion methods and their respective chromatographic performance assessed by standard pulse experiments.

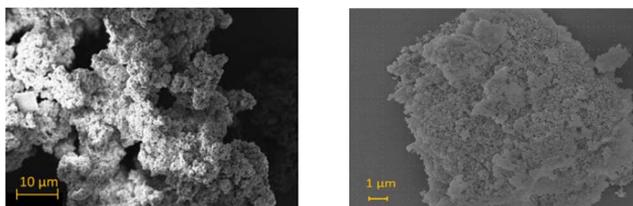


Figure 1: Cluster morphologies obtained by shear aggregation (left) and salt-induced aggregation (right)

- [1] B. Brand, M. Morbidelli, and M. Soos, *Langmuir*, 2015, **31**, 12727.
- [2] N. Marti, F. Quattrini, A. Butté, and M. Morbidelli, *Macromol. Mater. Eng.*, 2005, **290**, 221

SLN versus Vegetable Oils Consist NLC for Drug Delivery Application

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In recent years, especially in cosmetic industry there is an orientation for vegetable oils which are renewable, natural and used as a raw material for eco-friendly cosmetics [1]. Oils consist different unsaturated fatty acids, small amounts of phospholipids, tocopherols, free sterols, hydrocarbons and fat soluble vitamins [2]. All of these ingredients in oils has an antioxidant property are provide skin protection and also they can be used as moisturizers [1]. However, there is a problem with these oils in their instability and low bioavailability. To overcome this problem, oils can be encapsulated within different systems such as micelles, polymers and lipid based nanoparticles. In these mentioned systems, lipid based nanoparticles have high biocompatibility, controlled drug release and loading capacity. Solid lipid nanoparticles (SLN) and Nanostructured lipid carriers (NLC) whose constituent is physiologically related lipids are considered as the most promising encapsulation systems for cosmetic and pharmaceutical industries. Because of the drawbacks of SLN such as low encapsulation efficiency, NLC are developed as second generation of SLN. NLC consist of solid and liquid lipid mixture which leads to decrease the degree of organization of lipid matrix. This structure and high solubility of active ingredients in oils, increase the encapsulation efficiency.

In the light of these information, we have prepared SLN and NLC which composed of vegetable oils such as olive oil and centaury oil with different liquid oil ratios and tocopherol acetate (Vitamine E). Besides, a model drug was loaded into SLN and NLC. The size of particles and morphology were observed with Light Scattering (LS), Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). Also measurement of zeta potential and stability of particles were investigated. The entrapment efficiency and drug release behavior of loaded particles were studied. The size and zeta potential values are demonstrated at Table.1. These particles considered as good candidates for drug delivery applications with their tunable size, surface charge and drug entrapment/release efficiencies. Additionally, these alternative carriers can be used in different applications such as cosmetics by benefiting from their biocompatibility and biodegradability.

Table.1 Size and zeta potential values of particles

Oil Type	% Oil Content	LS (nm)	Zeta Potential (mV)
	0	170±4	24±2
Olive Oil	10	190±8	N.A.
	20	180±7	N.A.
	30	165±4	14±1
	40	210±6	11±1
	50	250±5	N.A.
Centaury oil	10	180±2	N.A.
	20	270±7	N.A.
	30	160±3	10±1
	40	157±1	9±1
	50	220±8	N.A.

REFERENCES

- [1] G. Badea, I. Lăcătușu*, N. Badea, C. Ott, A. Meghea, *Ind. Crops and Prod.* 67, 2015, 18–24
 [2] N. Karak, 2012. Woodhead Publishing Limited, 2012, 54–95.

Breaking Nano-Spaghetti: Bending and Fracture Tests of Nanofibers

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Nanofibers composed of silica nanoparticles, used as structural building blocks, and polystyrene nanoparticles introduced as sacrificial material were fabricated by bicolloidal electrospinning [1]. During fiber calcination, sacrificial particles are combusted leaving voids with controlled average sizes. Mechanical properties of the sintered silica fibers with voids were studied by suspending nanofibers over a gap and performing three-point bending experiments by atomic force microscopy. We investigated three different cases: fibers without voids and with 60 or 260 nm voids, elucidating how the introduction of the voids can be used to control the mechanical stiffness and fracture properties of the fibers. Fibers without voids break mainly at a single fracture point (70% of cases), while the remaining cases (30%) fracture at multiple points, leaving a gap in the suspended fiber. On the other hand, fibers with 60 nm voids fracture predominantly at multiple points (75%), Finally, fibers with 260 nm voids fracture roughly in equal proportions leaving two and multiple pieces (46% vs 54%, respectively). This fracture behaviour was compared to that of macroscopic brittle fibers (i.e. spaghetti) with predefined defects. The present study is a prerequisite for processes involving the controlled sectioning of nanofibers to yield anisometric particles [2].

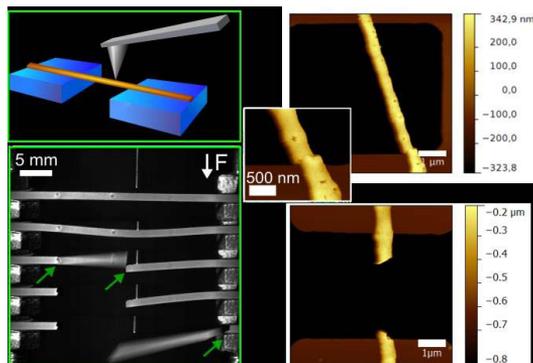


Figure1: upper left: schematic of bending test. Upper and lower right: fracture of supported nanofibers with defined defects (voids). Lower right: fracture behaviour of macroscopic spaghetti with predefined defects.

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[1] K. Friedemann, T.P. Corrales, M. Kappl and D. Crespy, *Small*, 2012, **8**, 144.

[2] T.P. Corrales, K. Friedemann, R. Fuchs, C. Roy, D. Crespy and M. Kappl, *Langmuir*, 2016, **32**, 1389.

Surface modification of graphene oxide flakes with copper sulfide nanophases aiming at applications in photocatalysis

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Semiconductor nanocrystals (NCs) have been extensively explored due to their unique size dependent optical and electronic properties, which are of interest in a number of applications including photocatalysis [1]. In particular, copper sulphide has been investigated as a photocatalyst of interest due to the ability to harvest photons efficiently in the visible spectral region, exhibiting a band-gap (E_g 1.2-2.2 eV), which is dependent on the crystalline phase present [2]. On the other hand graphene based materials have also attracted great importance due to their unique properties [3]. The implementation of chemical routes aiming to combine these two types of materials opens new routes for the development of innovative nanodevices. For example, the combination of graphene oxide with copper sulphide materials has been reported as a promising strategy for the development of hybrid photocatalysts [4]. In this context, we have investigated the *in situ* growth of copper sulphide ($Cu_{2-x}S$) nanocrystals, in the presence of graphene oxide (GO) flakes dispersed in ethanol, by the sonolytic degradation of dissolved Cu(II) dialkyldithiocarbamate complexes. The new materials were firstly tested as photocatalysts using a visible light photoreactor and an organic dye as the water contaminant model. The photocatalytic activity of the hybrid photocatalysts will be discussed on the basis of relevant literature, namely by putting in perspective their application in the photodegradation of emergent pollutants such as pharmaceutical compounds dissolved in water.

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- [1] T. Trindade and P. J. Thomas in *Comprehensive Inorganic Chemistry II: From Elements to Applications* (Eds.: J. Reedijk and K. Poepplmeyer), Elsevier, Oxford, **2013**, 4, 343-369
- [2] (a) R. K. Upadhyay, N. Soin and S. S. Roy, *RSC Adv.*, 2014, **4**, 3823; (b) A. C. Estrada, F. M. Silva, S. F. Soares, J. A. P. Coutinho and T. Trindade, *RSC Adv.*, 2016, **6**, 34521.
- [3] Y. Zhao, H. Pan, Y. Lou, X. Qiu, J. Zhu and C. Burda, *J. Am. Chem. Soc.*, 2009, **131**, 4253.
- [4] Y. Wang, L. Zhang, H. Jiu, N. Li, and Y. Sun, *Appl. Surf. Sci.*, 2014, **303**, 54; (b). M. Saranya, R. Ramachandran, P. Kollu, S. K. Jeong and A. N. Grace, *RSC Adv.*, 2015, **5**, 15831.

On-line characterization of micro- and nanostructured materials in Process Analytical Technology (PAT)

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PAT focusses on process monitoring, which is driven by industry for economic reasons and legal authorities for the sake of consumer safety (e.g. Hazard analysis and critical control points (HACCP) in food industry). Its application focusses on observing the progression of reactions and processes (in batches) as well as controlling process stability (continuous processes). The process monitoring encompasses the continuous observation of product streams or batch processes. This monitoring is involved in complicated physical-chemical condition and process control parameters (e.g. no chance of repeating the measurement, typically harsh conditions, high polydispersity and multiple particle species).

It is important for the PAT that applications of the process analyser concentrate on real time measurement (on-line, in-line and in-situ [1]) in the process and not on measuring situation with time delay or separated from process in time and location (off-line, at-line). This different measuring situation requires measuring methods based on different measurands, for particle size and material composition, i.e. equivalent diameters, and also on different types of quantity of particle size distribution (PSD).

An overview of the state of the art related to research about on-line analytic processes is important in order to understand and compare the advance of the techniques for the determination of physico-chemical properties of matter (e.g. zeta potential). For the characterization of micro- and nanostructured materials targeting the improvement of PAT, the present study contains complete information about the relevant research and implementation of new measurement methods such as imaging methods (e.g. Dynamic Image Analysis (DIA)[2][3] and Particle Vision and Measurement (PVM)[4] versus traditional sizing techniques for process monitoring such as laser diffraction (LD)[5] and acoustic spectroscopy [6].

Acknowledgements

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- [1] M. Stieß, *Mechanische Verfahrenstechnik - Partikeltechnologie 1*, Springer (Berlin, Heidelberg) (2008)
- [2] V. R. Nalluri, *Novel Process Analytical Technological Approaches of Dynamic Image Analysis for Pharmaceutical Dry Particulate Systems*, Universität Basel, 25-26, 2011
- [3] Rabinski G., Thomas D., *Dynamic digital image analysis: Emerging Technology for Particle Characterization*. *Water Sci. Technol.* 50, 19-26, 2004
- [4] M. Kempkes, J. Eggers, M. Mazzotti, *Measurement of Particle Size and Shape by FBRM and in situ Microscopy*. *Chem Eng Sci.*; 63(19): 4656–75, 2008
- [5] M. Juhnke, E. John, *Evaluation of an On-line Particle Sizer for Rotor Impact Milling applied in Drug Development and Manufacturing*, Fachtreffen der Partikelmesstechnik, Magdeburg, ProcessNET, 2015
- [6] R. Weser, S. Wöckel, B. Wessely, U. Steinmann, F. Babick, M. Stintz, *Ultrasonic Backscattering Method for in-situ Characterisation of Concentrated Dispersions*. *Powder Technol.*, 268:177-190, 2014. doi: 10.1016/j.powtec.2014.08.026

Local resolution of the flow field and the slip length of a superhydrophobic surface

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Superhydrophobic surfaces can provide a significant slip to a fluid flowing over the surface, making them attractive for the development of functional coatings. This slip is related to air being entrapped in the indentations of the structured surface that can act as a lubricant. Although the global behaviour of flow past superhydrophobic surfaces has been widely investigated, the local physical fundamentals leading to slippage still remain unclear.

Using fluorescence correlation spectroscopy (Fig. 1), we performed detailed measurements of the local flow field and the local slip length for water in the Cassie state on a structured superhydrophobic surface [1]. We revealed that the local slip length of a superhydrophobic surface is finite, non-constant and anisotropic. Furthermore, it can be strongly influenced by the presence of surface active substances.

All these properties can be explained by the local hydrodynamics within the air layer and at the air-water interface, such as the local flow field depending on the surface geometry or Marangoni forces. For this purpose, we performed numerical calculations of the flow that confirm the complexity of the local flow field found in the experiments.

On a more general level, these findings are also of relevance for the development of theoretical models of slippery surfaces that rely on a fluid being in the Cassie state, because to date, such models typically do not take into account the aforementioned properties of the local slip length.

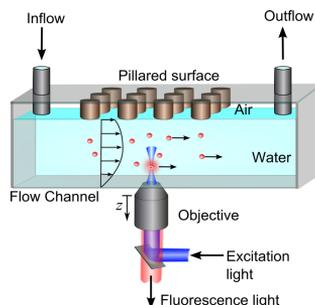


Figure 1 Schematic of the experimental setup.

Acknowledgements Financial support from ERC (Advanced Grant No. 340391-SUPRO) and HFSP (RGP0013/2015) is gratefully acknowledged.

- [1] D. Schäffel, K. Koynov, D. Vollmer, H.-J. Butt and C. Schönecker, Local flow field and slip length of superhydrophobic surfaces, *Physical Review Letters*, 116, 134501, 2016.

Stimuli responsive lipid nanotubes-gel complexes for doxorubicin delivery

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Doxorubicin (DXR) is an anthraquinone based antibiotic which is commonly used for cancer treatment. However, it has various important side effects such as cardiotoxicity, suppressing blood cell production, low therapeutic index, etc. Developing effective carrier systems for DXR is a widely interested topic [1]. One of the most common cancer types for which DXR is used as the therapeutic agent is the colorectal cancer (CRC). Although parenteral ways are generally preferred for the treatment of the colorectal cancer, oral or intracolonic administrations can also be used.

Lipid nanotubes (LNT) are one of the most effective drug delivery systems due to their superiorities provided by their asymmetric geometry such as high interior volume, high drug loading capacity, easy surface modifications and high circulation persistence. Thus, LNTs formed by the specially designed AQUA (AQ-NH-(CH₂)₁₀COOH), AQ: anthraquinone) has a high potential to be an efficient controlled drug delivery agent for DXR. The pH sensitive character of the AQUA LNTs is advantageous for increasing their efficiency on drug entrapment and release as well as providing selective release of the DXR to the tumor cells. Here, the DXR-laden AQUA LNTs which are placed in different gel matrices are investigated for their usability in the intracolonic administration. The aim for placing the drug-laden LNTs in the gel matrices is to locate them in the region that should be cured for a longer time and to provide the sustainable drug release there. AFM and TEM images show that the LNTs are distributed homogeneously in the gel matrix preserving their original structures.

DXR loading capacity is effected by the parameters such as drug concentration, pH, drug to carrier mass ratio and it has been found that the maximum loading capacity is reached at pH 9 when the DXR/LNT ratio is 1/1 (g/g). In this condition AQUA LNTs can entrap almost as much DXR as their own mass. This loading capacity is significantly higher than the ones previously reached in the literature [2] and the existence of the specially selected AQ and COOH functional groups and the tubular morphology provide AQUA LNTs to reach that high drug loading capacity. The release profiles of DXR from the DXR-laden LNTs, which have been placed into various (chitosan, alginate, HPMC, polyacrylic acid) gel formulations, through dialysis membrane or sheep's colon are investigated. Franz diffusion cells are used for the release studies and the released amounts and permeation fluxes are determined from the fluorescence intensity of DXR at 580 nm. The release of DXR from the LNTs lasts for 7 days and the released amount changes depending on the gel type used. Chitosan gel increases the DXR release and almost all of the initially loaded DXR is released from the LNTs through the sheep's colon after 7 days. The chitosan-DXR-LNT system increases the penetration through the colon and can be used as an appropriate drug delivery system. In vitro cytotoxicity measurements were also performed by the MTT method using human breast cancer (MCF-7) and mouse fibroblast (L929) cell lines. The cytotoxic effect of the DXR-laden AQUA LNTs are higher than the DXR solution although AQUA LNTs themselves do not show cytotoxic effect. This means that biocompatible AQUA LNTs increase the effectiveness of the DXR. These abovementioned results show that our new AQUA LNT system is a non-toxic, effective, biocompatible and stable system which is very promising for the intracolonic administration of DXR in colorectal cancer therapy.

[1] B.D. Weinberg, H. Ai, E. Blanco, J.M. Anderson, J. Gao, *J Biomed Mater Res.*, 2007, **81**, 161.

[2] S. Ilbasmis-Tamer, H. Unsal, F. Tugcu-Demiroz, G.D. Kalaycioglu, I.T. Degim, N. Aydogan, *Colloids Surf B Biointerfaces*, 2016, **143**, 406.

Simulation of molecular structure and electrical conductivity of metal phthalocyanines as the basis of the self-assembly monolayers

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Layer-by-layer assembly method is widely used for the creation of ultra-thin organic films. This method solves the problem of creating layers with specified properties that include molecules oriented in definite direction relative to each other and the substrate. One variation of the layer-by-layer assembly method is the polycation/polyanion self-assembly. It allows you to receive a variety of polymer coatings that are used extensively to create new generation devices. Synthesis of molecules with pre-defined structure is promising for manufacturing the various organic electronics materials [1].

Layer-by-layer assembly method is also used for adsorption of organic semiconductors, for example, based on metal phthalocyanine molecules [2]. Organic semiconductors based on metal phthalocyanine molecules are photosensitive and, therefore, are used to make solar cells, photovoltaic cells and other electronic devices. Photovoltaic cells are used in optical fiber of communication systems, measurement technology and energy industry [3]. Phthalocyanine dyes are also used to create new generation displays, as these dyes exhibit nonlinear optical properties [4] and optical memory [5].

The aim of our work is the simulation of molecular structure properties and electrical conduction through metal phthalocyanines and polyelectrolytes implementing Gaussian 09[6,7] software. In particular, we have calculated molecule's conformation, binding energies and their alterations under illumination as well as charge transfer through the film. The copper phthalocyanine (CuPs) and hydroxy-aluminum trisulphonated phthalocyanine (AlPcS) complexes have been studied. Geometry optimization of metal phthalocyanine molecules has been performed by density functional theory (DFT) using B3LYP theoretical model and the standard 6-311G basis set.

As a result, the quantum chemical simulations of metal phthalocyanines confirm the fact of illumination-driven alteration of their adsorption properties, however, only for nonsymmetrical molecules (AlPcS), not for symmetrical ones (CuPc). The following explanation of this fact is proposed: illuminating the nonsymmetrical phthalocyanine molecule increases its AlPcS dipole moment and thereby enhances its hydrophilicity that facilitates molecule's adsorption onto PEI layer.

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- [1] G. Decher, Y. Lvov and J. Schmitt, *Thin Solid Films*, 1994, **1**, 772.
- [2] M. Krzywecki and L. Grzadziel, *Material Science-Poland*, 2008, **26**, 287.
- [3] A. Ulman, *Academic Press: Boston*, 1991, **18**, 159-167.
- [4] R.J. Iller, *Colloid Interf. Sci.*, 1966, **21**, 569-575.
- [5] J. Frueh, G. Reiter, H. Mohwald, Q. He and R. Krastev, *Phys. Chem. Chem. Phys.* 2013, **15**, 486.
- [6] A.A. Kletsov, *Chemical Physics Letters*, 2014, **612**, 203 – 208.
- [7] A.A. Kletsov, E.G. Glukhovskoy, A.S. Chumakov, J.V. Ortiz, *Biochimica et Biophysica Acta (BBA)-General Subjects* 2016, **1**, 140-145.

Stimuli-Responsive Hairy Particles for Enzymatic Catalysis in Bulk and at Interfaces

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Enzymes are versatile but highly specific and selective biocatalysts which act under mild conditions. In particular, enzyme-based processes are more environmentally friendly, cost-effective and sustainable than conventional catalytic methods. Therefore, enzymatic catalysis is of great interest for the food and textile industry as well as for pharmaceutical transformations.

The effective immobilization provides an excellent base for enzyme exploitation by enhancing their structural and catalytic stability in different environmental conditions, and reducing product inhibition. However, separation and increasing their reusability still remains a challenging task.

Herein, we report the synthesis and study of stimuli-responsive carrier systems for an efficient immobilization, high catalytic activity and reusability of laccase from *Trametes versicolor*. The series of stimuli-responsive core-shell particles with controlled and tunable chemical functionality, surface charge and grafting density were synthesised using ATRP. [1], [2] A very easy approach for the control of grafting densities between 0.1 and 0.8 nm⁻² and of lengths of polymeric chains was suggested. [2] The hairy core-shell particles were functionalized with the enzyme by physical adsorption. Correlation between the grafting density of the polymer brush shells and the efficiency of immobilisation, as well as the effectiveness of the catalytic performance of laccase was studied in details. [2]

[1] A. Kirillova, C. Schliebe, G. Stoychev, A. Jakob, H. Lang and A. Synytska, *ACS Appl. Mater. Interfaces*, 2015, **7**, 21218.

[2] C. Marschelke, A. Matura and A. Synytska: manuscript under preparation.

Hybrid Hairy Janus Particles as Novel Building Blocks for Active Surfaces and Interfaces

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Janus particles represent a class of multifunctional anisotropic building blocks, combining two distinct functions at their opposite sides.[1,4] The unique asymmetry of the Janus particles allows them to target complex self-assembled architectures and materials inaccessible for homogeneous building blocks.[2-4] Despite the numerous reported synthetic strategies for the preparation of Janus particles, their truly large-scale synthesis and technological applications are still highly challenging tasks.

We developed a systematic library of hybrid hairy Janus particles with controllable size, geometry, chemical functionality, Janus balance, and responsiveness/adaptability.[1,5] Such Janus particles can be prepared on a large scale, thus opening new perspectives for their applications. Furthermore, we propose two application directions that would benefit from the unique properties and architecture of the Janus particles: active surfaces and interfaces.[2-3,6-8]

In the first approach, we exploit the superior interfacial activity of the Janus particles and apply them for interfacial catalysis through a selective modification of one of their sides with metallic nanoparticles.[6] In this way, functional active interfaces loaded with hybrid hairy Janus particles are created in an emulsion, resulting in successful catalysed reactions in the water phase and the subsequent easy recovery of the hybrid catalyst.

In the second approach, we use the hybrid hairy Janus particles as building blocks to create robust active structured surfaces with controllable adhesion properties under dry, wet and icing conditions.[7-8] In particular, we apply the fabricated surfaces in different environments and test their anti-icing as well as anti-fouling performance. The designed Janus particle-based surfaces allow a rational design of composite materials and advanced coatings with controllable adhesiveness.

- [1] S. Berger, A. Synytska, L. Ionov, K.-J. Eichhorn and M. Stamm, *Macromolecules*, 2008, **41**, 9669.
- [2] S. Berger, L. Ionov and A. Synytska, *Adv. Funct. Mater.*, 2011, **21** (12), 2338.
- [3] A. Synytska, R. Khanum, L. Ionov, C. Cherif and C. Bellmann, *ACS Appl. Mater. Interfaces*, 2011, **3**, 1216.
- [4] A. Synytska and L. Ionov, *Particle & Particle Systems Characterization*, 2013, **30**(11), 922.
- [5] A. Kirillova, G. Stoychev, L. Ionov, K.-J. Eichhorn, M. Malanin and A. Synytska, *ACS Appl. Mater. Interfaces*, 2014, **6**, 13106.
- [6] A. Kirillova, C. Schliebe, G. Stoychev, A. Jakob, H. Lang and A. Synytska, *ACS Appl. Mater. Interfaces*, 2015, **7**, 21218.
- [7] A. Kirillova, L. Ionov, I. V. Roisman and A. Synytska, *Submitted*.
- [8] A. Kirillova, C. Marschelke, J. Friedrichs, C. Werner and A. Synytska, *Submitted*.

Intrinsic peroxidase-like activity of Pt nanoparticles immobilized in spherical polyelectrolyte brushes

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Peroxidase-like nanoparticles have been established as low cost and highly stable alternatives of natural peroxidase in wide range of applications [1]. Recently, a significant amount of research has been focused on imitating peroxidase activity with various nanomaterials. The mechanism of the peroxidase-like activity is still under debate. Usually, the kinetic data of nanoparticles are interpreted by Michaelis-Menten equation (MM). However, the mechanism can hardly be revealed by this enzyme model.

In our study, Pt nanoparticles about 5 nm immobilized in spherical polyelectrolyte brushes (SPB-Pt) were found own high peroxidase-like activity. Owing to the excellent colloidal stability in solution [2-3], the kinetics and mechanism of peroxidase-like activity can be precisely analyzed. The oxidation of 3,3',5,5'-tetramethylbenzidine (TMB) with hydrogen peroxide (H₂O₂) was used as a model reaction. The kinetic data was modelled by Langmuir-Hinshelwood (LH) model for the first time. In this model, both TMB and H₂O₂ are assumed to adsorb on the surface of the nanoparticles to react. Based on this, the time evolution of product can be well modelled up to the conversion of 50%. Excellent merging of the theory with the experimental data is found for both SPB-Pt and Fe₃O₄ nanoparticles. Compared with MM kinetics with initial reaction rate at the beginning several or tens of seconds, the LH kinetics responsible for the whole period is more reliable. All these provide hints to design effective peroxidase-like nanomaterials.

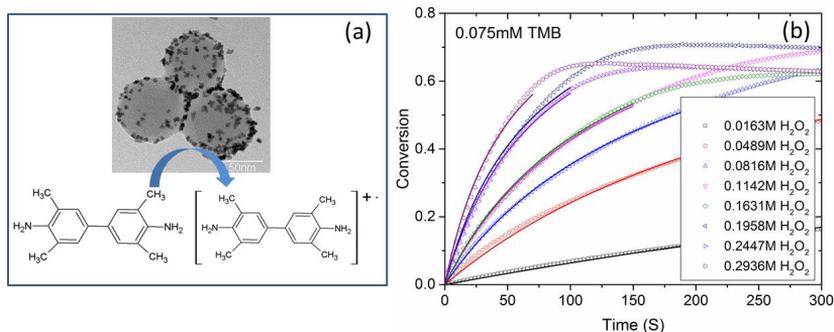


Figure 1 (a) TEM graph of the peroxidase-like Pt nanoparticles immobilized in spherical polyelectrolyte brushes (SPB-Pt), (b) kinetic analysis of peroxidase-like activity of SPB-Pt nanoparticles: conversion evolution at different substrate concentrations, the solid lines are fitting lines based on Langmuir-Hinshelwood model.

- [1] L. Gao, J. Zhuang, L. Nie, J. Zhang, Y. Zhang, N. Gu, T. Wang, J. Feng, D. Yang, S. Perrett and X. Yan, *Nanotechnol.*, 2007, **2**, 577.
- [2] S. Gu, S. Wunder, Y. Lu, M. Ballauff, R. Fenger, K. Rademann, B. Jaquet and A. Zaccone, *J. Phys. Chem. C*, 2014, **118**, 18618.
- [3] S. Gu, Y. Lu, J. Kaiser, M. Albrecht and M. Ballauff, *Phys. Chem. Chem. Phys.*, 2015, **17**, 28137.

Electrochemical synthesis of dendritic gold nanostructures for glucose biosensor design

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Nowadays gold nanoparticles, nanorods, nanocages, and nanostructured surfaces have been applied in many areas such as electronics, photonics, catalysis, imaging, chemical and biochemical sensing, and therapy. Gold micro- and nano-structures have received considerable attention due to their attractive physical and chemical properties [1]. Some challenging bioanalytical problems, such as sensitivity, specificity, reproducibility, duration and cost of analysis can be resolved by micro- and nanostructure-based electrochemical and optical biosensors [2-4]. The aim of this work was to synthesize dendritic gold nanostructures (AuNS) on the graphite rod electrode surface using different electrochemical methods and various conditions in order to develop sensitive and convenient amperometric glucose biosensor. AuNS modified electrodes were characterized using electrochemical methods, scanning electrochemical microscopy and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

SEM images and results obtained by ICP-AES showed that duration of synthesis at the optimal conditions has effect on the gold amount and the shape of structures. However, it has minor effect on the performance of developed biosensor, thus for the further studies 200 s lasting synthesis of AuNS was used. Two different strategies in the construction of glucose biosensor were examined: (i) glucose oxidase (GOx) together with red-ox mediator covalently immobilized on AuNS and (ii) covalently immobilised GOx with red-ox mediator in the solution. All electrochemical measurements were performed in a constant potential amperometry mode using a conventional three-electrode system. Detection of glucose was performed at room temperature in acetate buffer solution with KCl under stirring conditions. The maximal current of the developed glucose biosensors in the presence of glucose, apparent Michaelis constant, limit of detection and linear range of glucose detection were determined for both types of biosensors.

Acknowledgements

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- [1] N. Li, P. Zhao, D. Astruc. *Angew. Chem. Int. Ed.* 2014, **53**, 1756-1789.
- [2] Y. Li, Y. Li, M. Hong, Q. Bin, Z. Lin, Z. Lin, Z. Cai, G. Chen. *Biosens. Bioelectron.* 2013, **42**, 612-617.
- [3] N. German, A. Ramanavicius, A. Ramanaviciene. *Sensor Actuat. B: Chem.* 2014, **203**, 25-34.
- [4] A. Ramanaviciene, J. Voronovic, A. Popov, R. Drevinskas, A. Kausaite-Minkstimiene, A. Ramanavicius. *Colloids Surf. A* (submitted).

Gold nanostructures for surface enhanced vibrational spectroscopy

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Gold nanoparticles (AuNPs) have exceptional properties which have promoted their use in many fields such as biomedical imaging and diagnostic tests, biological applications, as catalysts, and for applications taking advantage of their enhanced optical properties. Bare AuNPs have been synthesized from tetrachloroauric acid solution using steel or stainless steel as solid reducing agent [1, 2]. Photoenhanced adsorption of water on AuNPs has been employed for *in-situ* monitoring of the synthesis of bare AuNPs via surface enhanced infrared absorption attenuated total reflection spectroscopy (SEIRA-ATR) [3].

Bare AuNPs produce an enhancement in the Raman spectrum of e.g., carboxylated single walled carbon nanotubes (c-SWNTs) [4]. On the other hand, SEIRA using an ATR configuration has been used to analyze protein bovine serum albumin (BSA) adsorbed onto these bare AuNPs (Fig. 1). Bare gold nanoparticles forming the SEIRA-active substrate were synthesized *in-situ* inside the ATR compartment taking advantage of the stainless steel walls of the liquid cell inherently acting as reducing agent. BSA has a high affinity towards AuNPs due to external thiol functions available for conjugation to the AuNP surface [5]. Consequently, SEIRA studies take advantage of the affinity of the protein to bare AuNPs present within the evanescent field at the ATR crystal surface. The absorbance of BSA onto AuNPs deposited at the Si waveguide is distinctly enhanced vs. bare Si, thus improving the sensitivity of the measurement. Furthermore, it was shown that the presence of an AuNPs layer does not affect the secondary structure of the protein.

Last but not least, alternative gold nanostructures such as gold nanostars [6] are currently being investigated for surface enhanced vibrational spectroscopy applications. Gold nanostars are immobilized onto a silicon wafer or silicon waveguide via a gold layer and thiol-functionalized polyethylene glycol (PEG) for further application in SERS or SEIRA based analyses.

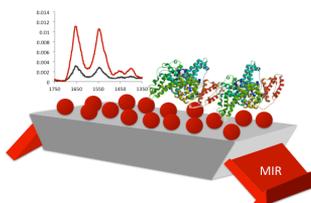


Figure 1 Bare AuNPs for surface enhanced infrared spectroscopic studies on bovine serum albumin.

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- [1] A.I. López-Lorente, B.M. Simonet, M. Valcárcel, S. Eppler, R. Schindl, C. Kranz, B. Mizaikoff, *Talanta*, 2014, **118**, 321.
- [2] A.I. López-Lorente, M. Valcárcel, B. Mizaikoff, *Microchim. Acta*, 2014, **181**, 1101.
- [3] A.I. López-Lorente, M. Sieger, M. Valcárcel, B. Mizaikoff, *Anal. Chem.*, 2014, **86**, 783.
- [4] A.I. López-Lorente, B.M. Simonet, M. Valcárcel, B. Mizaikoff, *Anal. Chim. Acta*, 2013, **788**, 122.
- [5] D.H. Tsai, M. Davila-Morris, F.W. DelRio, S. Guha, M.R. Zachariah, V.A. Hackley, *Langmuir*, 2011, **27**, 9302.
- [6] O. Bibikova, A. Popov, A. Bykov, A. Fales, H. Yuan, I. Skovorodkin, M. Kinnunen, S. Vainio, T. Vo-Dinh, V. Tuchin, I. Meglinski, *IEEE J. Sel. Top. Quantum Electron.*, DOI: 10.1109/JSTQE.2016.2526602

Ribavirin entrapment into PLGA NPs by using a novel microfluidic approach

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The chemical treatment called "chemotherapy of plants" consists in the "in vivo" administration of substances capable of interfering with the viral replication. The current availability of synthetic molecules with a high chemotherapy index, i.e. with a high ratio between the maximum concentration tolerated and the minimum effective, together with the possibility to further widen the therapeutic window by the use of appropriate nanocarriers, seems to open on the application level of a novel chemical approach to treat plant viral infections. Ribavirin, for example, is a synthetic water-soluble nucleoside that possesses broad spectrum activity against a variety of DNA and RNA plant viruses. As well known, water-soluble drugs are generally difficult to encapsulate in solid particles[1]. Chemical modification of these drugs, such as esterification, may increase their encapsulation efficiency, but may also decrease bioactivity.

In this work we have synthesized stable solid monodispersed PLGA (poly-D,L-lactic-co-glycolic acid) NPs with diameters ranging from 50 – 200 nm containing ribavirin by using a microfluidic reactor with a flow-focusing geometry. In the flow-focusing-based microdevice the dispersed organic phase containing PLGA (i.e., acetonitrile) is continuously focused by the continuous phase (i.e., ribavirin in acetate buffer pH 5.5) using 2 syringe pumps (Fig. 1 left). Previous works carried out in our labs [2] showed an improvement of drugs loading efficiency when using a microfluidic approach in comparison with traditional nanoprecipitation methods for nanoencapsulation. On this basis we optimized Ribavirin loading within PLGA NPs by investigating the influence of different operating conditions, such as polymer molecular weight and concentration, flow rate ratio, tmix, microreactor-focusing channel diameters and length, on nanoparticles' size and morphology and drug loading. NPs' characterization was performed by Dynamic light scattering (DLS) measurements (size and Z-potential), and by scanning electron microscopy (SEM). The determination of free ribavirin was carried out spectrophotometrically. Synthesized NPs, although the study is still preliminary, showed significant drug loading and entrapment efficiency[3].



Fig. 1 (left) CFM reactor system used for the synthesis of PLGA NPs. One outlet(c) connected by a cross junction (d), creating a hydrodynamic flowfocusing with a central stream (b) and 2 side streams (a and a').(r) can be varied by altering the Volumetric flow rates of the 3 inlets or the internal dimensions of the mixing channel. (right) SEM micrograph of PLGA ribavirin loaded NPs. Scale bar 2 micron

- [1] Astete, C.E., Sabliov, C.M., 2006. *Synthesis and characterization of PLGA nanoparticles*. J. Biomater. Sci. Polym. Ed. 17, 247–289.
- [2] Chronopoulou et al., 2014. *A modular microfluidic platform for the synthesis of biopolymeric nanoparticles entrapping organic actives*, J. Nanopart. Res. 16:2703.
- [3] Tsutomu Ishihara et al., 2014. *Development of Biodegradable Nanoparticles for Liver-Specific Ribavirin Delivery*, J. of Pharmac. Sci. 103:4005–4011.

Nano-sized self-assemblies of biocompatible amphiphilic diblock copolymers as nanocarriers for hydrophobic photosensitizers

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Polymeric micelles (PMs) are a colloidal carrier system formed through molecular assembly of amphiphilic block copolymers in water. The size distribution of PMs is fairly narrow and is related to their unique core-shell architecture. The PMs are suitable for systemic circulation as they are large enough to prevent their rapid leakage into blood capillaries but small enough to escape capture by macrophages in the reticuloendothelial system (RES) [1-3]. The formation of polymeric micelles, including the critical micelle concentration determination, and solubilization process may be investigated by the use of high resolution diffusion-ordered nuclear magnetic resonance spectroscopy (DOSY NMR). For the direct investigation of the interactions between block copolymer fragments and cargo the Nuclear Overhauser Effect, including basic measurements, such as 1D NOE or 2D NOESY, is a crucial analytical method. Complex polymeric micelles systems analysis by a variety of NMR methods includes spin-lattice relaxation times and self diffusion coefficients determination followed by calculation of the crucial parameters describing micellization and solubilization.

The aim of this work was to determine the solubilization loci of tetra *tert*-butyl zinc (II) phthalocyanine (ZnPc-*t*-but₄), a potential second generation photosensitizer for photodynamic therapy (PDT), loaded in polymeric micelles of amphiphilic diblock copolymers of poly(ethylene oxide) and poly(ϵ -caprolactone) (PCL) or poly(D,L-lactide) (PDLLA). The main tool in these investigations was NMR spectroscopy, including through-space magnetic interactions by 1D NOE effect. Primarily, pulsed field gradient spin-echo (PGSE) and spin-lattice relaxation time (T_1) measurements were used to measure self-diffusion coefficients for the studied PMs as well as to determine nanoparticles hydrodynamic diameter. The cargo encapsulation in the nanocarriers was determined and quantified by the percent loading efficiency, the photosensitizer/copolymer (ZnPc-*t*-but₄/copolymer) ratio, and the polymeric micelles - water partition coefficient. The polymeric micelles systems stability was determined by combination of ¹H NMR spectroscopy with other analytical methods.

The ZnPc-*t*-but₄ - loaded PMs exhibited good physical stability, high drug loading, and size of less than ca. 100 nm with low polydispersity indices – the parameters that meet the requirements for nanocarriers in PDT. NMR spectroscopy measurements allowed to acquire crucial information about interactions in the studied PMs systems, affecting their structure, properties and stability. The present contribution may open a new possibility of selecting more suitable materials as useful photosensitizer delivery systems, while self-assembly analysis showed important features for their future research.

Acknowledgements

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- [1] K. Kataoka, A. Harada, Y. Nagasaki, *Adv Drug Deliv Rev* 2012, **47**, 113.
- [2] Ł. Lamch, U. Bazylińska, J. Kulbacka, J. Pietkiewicz, K. Bieżyńska-Kusiak and K. A. Wilk, *Photodiagnosis Photodyn Ther.*, 2014, **11**, 570.
- [3] Ł. Lamch, J. Kulbacka, J. Pietkiewicz, J. Rossowska, M. Dubińska-Magiera, A. Choromańska and K. A. Wilk, *J. Photochem Photobiol B: Biology* 2016, **160**, 185.

Simultaneous encapsulation of biological and chemical agents for plant protection/nutrition

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Novel chitosan/alginate microcapsules simultaneously loaded with copper and *Trichoderma viride* have been prepared and characterized. FTIR spectroscopy was used in order to obtain information about encapsulated bioactive agents and biopolymers interactions. Copper concentration and microcapsule size were considered as variables with possible influence on essential microcapsule parameters (loading capacity and efficiency, swelling behavior and releasing of active agents). All measured parameters depended on both, the kind of encapsulated agents and microcapsule size. The increase in copper concentration promoted swelling, but there existed obvious differences with regard to loaded agents and microcapsule size. Higher swelling extent and greater amount of released copper of microcapsules loaded only with copper than those simultaneously loaded with copper and *TV* were attributed to the differences in chitosan layer thickness. The in vitro copper release profile was fitted to Korsmeyer–Peppas empirical model. Fickian diffusion was found to be rate-controlling mechanism at smaller microcapsules, whereas release from larger microcapsules was controlled anomalous transport kinetics (combination of the diffusion mechanisms and Type II transport). While the copper release exhibited initial burst followed by a slower release, *Trichoderma viride* releasing profile increased exponentially after initial lag time. Much slower release at the early stage may be ascribed to the higher size of *Trichoderma viride* spores in comparison with copper ions. In the light of importance of *Trichoderma viride* as a biocontrol agent simultaneous encapsulation of copper and *Trichoderma viride* will give wider opportunity in the plant nutrition and protection.

Keywords: micrencapsulation, biopolymers, bioactive agents (copper, *Trichoderma viride*)

How surfactants affect the wetting of superhydrophobic surfaces

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Recent advances in the control of surface wetting lead to the development of the diversity of functional materials with the special wettability for industrial applications. Superhydrophobic surfaces have aroused researchers' intense interests due to their importance in both academic science and practical applications. One of the key points for academic studies is the behavior of superhydrophobic surfaces in outdoor conditions of exploitation where the organic airborne contaminations are ubiquitously present. Typically such contaminations act as surfactants for aqueous medium/air and aqueous medium/solid interfaces. At the same time, for the superhydrophobic coatings fabricated on the basis of fluorine-containing hydrophobic agents such contaminations are surface inactive with respect to the superhydrophobic coating/air interface. Thus the evolution of wettability of superhydrophobic surfaces with respect to aqueous phases will be significantly affected by the surface activity of organic contaminations present in the atmosphere, their solubility in water, vapor pressure, and chemical structure.

In this talk we will demonstrate the intriguing peculiarities of contact angle behavior for water droplets atop of superhydrophobic surfaces in the presence of various types of surfactants and will discuss physics underlying the three phase equilibrium.

The release of perillyl alcohol from the different kind of vehicles

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Terpenoids are the largest group of natural bioactive compounds exhibiting multiple nutraceutical activities, they are also known as active cosmetic ingredients [1]. They exhibit unique biological and pharmacological activities such as: anti-inflammatory, antimicrobial, antiviral properties, cytotoxic effects, against cancer and cardiovascular diseases [2].

One of the promising anticancer monoterpene is perillyl alcohol (POH). Perillyl alcohol is isolated from the essential oils of lavender, peppermint, spearmint, cherries and several other plants. So far published studies have indicated that topical application of POH may improve a skin cancer chemoprevention therapy [3]. In animal studies it has been shown to be therapeutic for pancreatic, mammary and liver tumors. It has also been shown to inhibit photocarcinogenesis and UVB-induced skin carcinogenesis [4]. Moreover perillyl alcohol exhibits chemopreventive properties for colon, skin, breast and lung cancer. Its activity is associated with a selective inhibition of isoprenylation of oncoprotein P21, which regulates cell division [5].

A review of the literature shows that there are very few information concerning the release of perillyl alcohol. Gupta et al. [6] were working on determination the influence of several factors on the stability of POH in solution and develop a topical formulation of POH. Farazudin et al. [7] obtained a novel poly-lactic glycolic acid (PLGA)-based microparticle formulation of perillyl alcohol.

The aim of this work is to study the release kinetic of perillyl alcohol from the various kind of vehicle (oil, macroemulsion, gel, nanoemulsion, NLC) using the selected mathematical models. The aim of this work is also reference the physicochemical properties of obtained formulations to the process of bioavailability of the carrier from the group of monoterpenes with antitumor activity.

Macroemulsion, nanoemulsion and nanostructured lipid carriers contained Polysorbate 80 as emulsifiers and caprylic/capric triglyceride as the oils phase. The water – glycol gel was stabilized by carbomer. The active release study of the actives was carried out using the Spectra/Por Standard Regenerated Cellulose (RC) membrane, at the temperature $T=32^{\circ}\text{C}$. The concentration of active agents in the receptor solution was analyzed by HPLC analysis. The results have shown that nanoformulations are the promising carriers for controlled release of perillyl alcohol. The physicochemical properties of obtained formulations have a high impact on the mechanism of drug release process.

References:

1. G. Wang, W. Tang, R.R. Bidigare, *Terpenoids As Therapeutic Drugs and Pharmaceutical Agents in Natural Products: Drug Discovery and Therapeutic Medicine*, Humana Press Inc., Totowa, NJ, 2005.
2. M. Silva, J. David, L. Silva, R. Santos, J. David, L. Lima, P. Reis, R. Fontana, *Molecules*, 2012, 17, 12197.
3. J. Belanger, *Alternative Medicine Review*, 1998, 3(6), 448.
4. S. Greay, K. Hammer, *Phytochem Review*, 2011.
5. M. Trytek, R. Paduch, J. Fiedurek, M. Kandefer-Szerszeń, *Biotechnologia*, 2007, 76, 135.
6. A. Gupta, P. Myrdal, *International Journal of Pharmaceutics*, 2004, 269, 373.
7. M. Farazuddin, B. Sharma, A. Khan, B. Joshi, M. Owais, *International Journal of Nanomedicine*, 2012, 7, 35.

Study of silver nanoparticles release from antibacterial gel formulations

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Silver nanoparticles (nAg) thanks to their unusual bactericidal, fungicidal and virucidal properties are widely synthesized and applied in various branches of science, industry as well as in many consumer products of daily use, including cosmetics [1]. From toxicological point of view, it is important to determine the mechanisms of the nanoparticles penetration thorough the skin as well as their interactions with human cells [2]. Although the importance, the controlled release of nAg from different forms still has not been developed.

For this reason, the aim of our work was to determine and compare the release kinetics of four types of silver nanoparticles of similar average size (c.a. 10-17 nm) and different surface properties from the gel formulations. The influence of the products viscosity and kind of used stabilizer systems on nAg release was determined. Charge-stabilized silver nanoparticles were prepared by the chemical reduction of silver nitrate using: tannin acid, sodium hexametaphosphate, borohydride and glucose. The surface properties of nanoparticles were determined by measurements of electrophoretic mobility. Additionally, the range of the nanoparticles stability at various pH and ionic strength conditions was determined using dynamic light scattering (DLS) technique and UV-vis measurements [3]. The aqua gel formulations were obtained by use of various thickening agents (sodium hyaluronate, xantan gum and polyacrylic acid). The physicochemical properties (stability, viscosity, pH) of the nAg-loaded gel formulations were investigated. Microbiological stability of the formulations was checked using Mikrocount® Combi kit. The release study was carried out at the temperature T=32°C, in thermostatic diffusion cells system, using the Spectra/Por Standard Regenerated Cellulose (RC) membrane. The concentration of nAg in the receptor solution (i.e. deionized water, 1μS) was analyzed by UV-VIS spectroscopy.

The physicochemical and biological stable gel formulations were prepared based on sodium hyaluronate. The obtained results showed that the gels viscosity and the type of silver nanoparticles significant influence on the nAg release.

References:

- [1] M. Rai, A. Yadav, A. Gade, Silver nanoparticles as a new generation of antimicrobials, *Biotechnology Advances*, 2009, 27(1), 76.
- [2] A. Barbasz, M. Oćwieja, J. Barbasz, Cytotoxic activity of highly purified silver nanoparticles sol against cells of human immune system, *Applied Biochemistry and Biotechnology*, 2015, 176, 817.
- [3] M. Oćwieja, Z. Adamczyk, Monolayers of silver nanoparticles obtained by chemical reduction methods, *Surface Innovations*, 2014, 2(3), 160.

Intensification of environmental photodegradation of pollutants by Pickering emulsions

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Pickering emulsion provides a new way to achieve enhancement of the photocatalysis process efficiency when the solid particles that stabilize the emulsion droplets are made of the photocatalyst itself. Such dual role of the photocatalyst particles is of particular interest for the degradation of non-soluble organic pollutants present as emulsion droplets in the environment. The close proximity of the photocatalyst particles and oil in Pickering emulsions allows a faster photocatalytic degradation of oil.

The present work aims at the validation of this concept. To this end, o/w Pickering emulsions were investigated for their stability and the photocatalytic degradation of the oil inside emulsion droplets was studied.

O/w Pickering emulsions of various models of organic pollutants with low solubility in water were prepared by using titanium dioxide catalysts as stabilizers. So as to allow for adsorption to a wide range of oils, two types of solid particles were investigated: pure TiO₂ having Ti-OH groups at its surface and fluorinated TiO₂ having Ti-F groups at its surface (TiO₂-F). Those particles were prepared by a sol-gel process and characterized by XRD, BET, SEM, DRS and TG-TD-MS.

The present results indicate that stable Pickering emulsions can be formed using nanometer-sized titanium dioxide particles. The type and stability of emulsions depend on the wettability of the stabilizing TiO₂ nanoparticles assessed by contact angle measurements. Wettability of TiO₂ and TiO₂-F surfaces strongly depends on the type of oil because of the contributions of the different polarity of the surface groups and of specific interactions with oils. Investigation of Pickering emulsions by electrical conductivity, optical microscopy and light scattering showed that high stability was achieved when conditions of partial wetting with a contact angle in water between 70° and 110° were met. A relationship between oil droplets size and oil-to-TiO₂ mass ratio confirmed the strong adsorption of catalyst particles to oil droplets.

The oils contained in the Pickering emulsions were photocatalytically degraded under UV radiation. The kinetics of photodegradation of organic pollutants measured by HPLC showed the higher degradation rate in emulsion with respect to control experiments in homogeneous solution.

The results proved that use of a Pickering emulsion stabilized by TiO₂ nanoparticles provides an effective and novel way to intensify the photocatalytic degradation of organic pollutants.

Aggregation and stability in solution of plasmonic active nano-biocolloids

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The capability of gold nanoparticles (AuNps) to form hybrid assemblies with biomolecules provides the basis to engineer innovative systems with potential applications in nano-medicine and nano-biotechnology [1,2]. Great interest in these systems arose in recent years due to the peculiar optical properties of gold at the nanoscale, whose interaction with electromagnetic radiation can be tuned by manipulating the dielectric constant of the environment or the size and shape of the assembly [2,3]. Biocompatibility, versatility, and “tunability” of these systems make them suitable for applications in sensing and therapy [4]. We recently employed mesoscopic aggregates of AuNps on solid support as substrates for Surface Enhanced Raman Spectroscopy and demonstrated their capability to provide huge signal enhancements in sensing applications [3,5,6]. Here we focus on the colloidal aggregation in solution of anionic AuNp (60 nm and 100 nm sized) mediated by lysozyme: a robust, globular and functional protein, with a pH-dependent positive charge. The process was studied by Dynamic Light Scattering (DLS) and Z-potential measurements at varying the AuNps-lysozyme relative molar ratio for different pH of the solution. The aggregation was also monitored following the Surface Plasmon Resonance (SPR) of the aggregates by UV-Visible Absorption Spectroscopy (UV-Vis). A study of the reversibility of the process was carried on by varying the pH of the solution after the clusters were formed. Analogously to the aggregation of biocolloids mediated by linear polymers [7], experiments showed that stable clusters can be obtained with a finite size depending on the AuNps-lysozyme relative molar ratio and on the pH of the solution. The comparison between DLS and UV-Vis measurements enlightened the higher sensitivity of the plasmonic absorption to disentangle the adsorption of lysozyme on the gold surface and the AuNps aggregation. Interestingly enough, we obtained intriguing protein-AuNp bioplasmonic assemblies with a size within few hundred nanometers, exhibiting colloidal stability in physiological condition and a large dynamic range of SPR frequencies from visible to near-infrared spectral region.

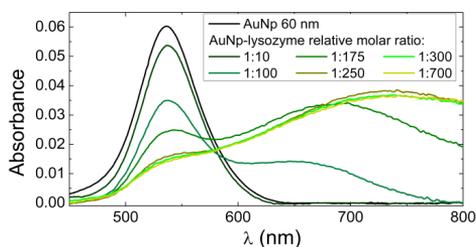


Figure 1 SPR of AuNps-lysozyme aggregates, measured with UV-Vis at varying the relative molar ratio.

- [1] A. Polman, *Science*, 2008, **322**, 868.
- [2] P. K. Jain et al., *Accounts of Chemical Research*, 2008, **41-12**, 1578.
- [3] F. Domenici et al., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2016, **498**, 168.
- [4] F. Domenici et al., *Analytical Biochemistry*, 2012, **421**, 9.
- [5] C. Fasolato et al., *AIP Conference Proceeding*, 2015, **1667**, 020012.
- [6] F. Brasili et al., *IEEE-NANO 2015 - 15th Int. Conference on Nanotechnology*, 2016, **33323**, 1023.
- [7] S. Sennato et al., *Soft Matter*, 2012, **8**, 93.

Nanofibrous polyaspartamide matrices

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Pharmaceutical industry shows a high interest in sublingual delivery, because this route of administration provides much faster absorption and higher bioavailability of several drug molecules compared to gastrointestinal delivery. Electrospun polymer nanofibers have attracted particular attention in sublingual drug formulation due to their unique morphological properties ensuring rapid drug release. In addition, contrary to other oral drug formulations such as suspensions or sprays, predetermined amount of the active molecule can be administered into the body by these drug delivery systems [1].

Several nanofibrous matrices have been reported for pharmaceutical uses, but these polymers are often non-biodegradable (e.g. poly(ethylene oxide)), their chemical structure and related properties can hardly be modified (e.g. poly(vinyl alcohol)) or in many cases electrospinning of the polymers requires harmful solvents (such as trifluoro-acetic acid, chloroform, etc.). These drawbacks might be overcome by the application of polyaspartamides which can be synthesized with high chemical versatility under mild reaction conditions, and due to the protein like structure, they are presumably biocompatible and biodegradable [2].

Our goal was to prepare polyaspartamide based nanofibrous matrices providing rapid sublingual release of the encapsulated drug. Polysuccinimide was reacted with dialkylaminoalkylamines and alkylamines resulting in cationic polyaspartamides. ¹H NMR and FTIR data confirmed the structure of the polymers. Nanowebs with narrow fiber diameter distribution were successfully fabricated from the polymers using ethanol as solvent. Both the starting polymer and the fibrous matrices showed thermal stability up to ~200°C. Glass transition temperature (around 40 °C) of the nanofiber matrices depended on their morphology, especially on the fiber diameter. Drug release and disintegration of the nanowebs were characterized simultaneously by using a fluorescently marked polymer. Rapid liberation of the encapsulated active molecule, Vitamin B was observed at the pH of the oral cavity (pH = 6.8). In the light of these results it can be concluded that nanofibrous matrices based on cationic polyaspartamides can be applied as a starting material of sublingual drug delivery formulation

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[1] S. Agarwal, A. Greiner, J. H. Wendorff, *Progress in Polymer Science*, 2013, **38**, 963.

[2] J. R. Moon, M. W. Kim, D. Kim, *Colloid Polymer Science*, 2011, **289**, 63.

Thermal transport of hollow silica sphere and polystyrene-silica core-shell particle colloidal crystals

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Monodisperse hollow silica nanoparticles and polystyrene-silica core-shell particles are well-defined colloidal building blocks. Due to their low polydispersity, these particles assemble into highly ordered three-dimensional colloidal crystals [1]. Thus a well-defined material with a remarkably precise structural control is obtained. This offers the opportunity to study nanoscale thermal transport in great detail. For silica hollow sphere colloidal crystals we were able to determine the contribution of the silica shell microstructure and the contact area between particles to the overall thermal transport [2].

Here, we extend this study to the influence of the geometric structure of hollow silica nanoparticles (size and shell thickness) on the thermal conductivity. Therefore silica hollow spheres in the size range of 270 – 470 nm and shell thicknesses of 14 – 40 nm were synthesized (Fig. 1). With this wide range of particle geometries, the thermal transport properties can be studied in detail. From the structure-property relationship we can conclude a lower limit of the effective thermal conductivity achievable with such materials. Aspects we focused on were, aspect ratio of the hollow particles (size and shell thickness), the symmetry of the colloidal ensemble (close packing vs. random-close packing) and the sensitivity to the surrounding atmosphere (pressure-dependent thermal conductivity). Particularly hollow silica spheres with a large diameter and thin shell thickness, assembled into a large random-close packed structure, exhibit an extremely low thermal conductivity. This opens the opportunity to use these particles as dispersion processable insulation material.

Besides silica hollow spheres, we also investigated particles, which are filled with polymer instead of air. With these particles, the thermal transport properties of core-shell particles with different aspect ratios of polystyrene/silica ranging from 0 – 100 % were studied.

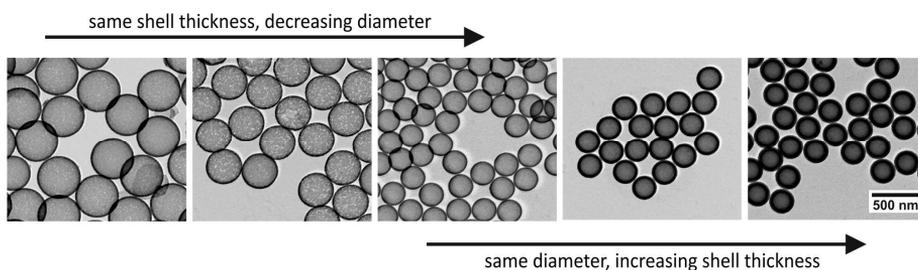


Figure 1 Geometric variation of the silica hollow sphere particles used to investigate the thermal properties.

- [1] P. Ruckdeschel, M. Dulle, T. Honold, S. Förster, M. Karg, M. Retsch, *Nano Research*, 2016, **9**, 1366.
- [2] P. Ruckdeschel, T.W. Kemnitzer, F.A. Nutz, M. Retsch, *Nanoscale*, 2015, **7**, 10059.

Role of vertical ZnO nanowires on modulating the myogenic differentiation of primary mesangioblast cells

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The possibility to control stem cell differentiation processes is a major goal of regenerative medicine. A great interest has recently been directed towards mesangioblasts (Mabs), perivascular myogenic progenitors employed in phase I-II clinical trial for muscular dystrophy cell therapy. Mabs displayed a remarkable capability to regenerate injured muscle and is desirable to maintain them in an undifferentiated state in order to enhance the reparation process before being implanted to recover damaged muscles. In this work, we have investigated the effect of ZnO nanowires on the growth and differentiation of *in vitro* cultured Mabs. Thus, we analysed in a comparative study Mabs grown on a standard glass (control samples) and on a standard glass covered with almost vertical ZnO nanowires (samples under test). As expected, we observed different behaviour of Mabs on the functionalized samples with respect to the control samples: strikingly the cells do not differentiate when grown on the surface functionalized with ZnO nanowires as shown in the bright field image showing Mabs maintaining full spherical shape instead of the normal spindle one observed in standard glass culture condition. This is confirmed by the fluorescent image highlighting the nuclei and the F-actin. In presence of the ZnO nanowires the Mabs maintain a spherical morphology whilst in their absence they manifest spindle appearance revealing full adhesion to the substrate and then prone differentiation attitude. The lack of adhesion and then of differentiating attitude in the Mabs grown above ZnO nanowires is confirmed by the complete absence of Myosin Heavy Chain (MyHC) that contrariwise is well expressed in the differentiated cells grown in the nude control glass. Amazingly the differentiation inhibition has been induced by the contact with the nano-structured material and is not to be related to the specific material, since Mabs grown on a glass coated with a permanganate layer or on a glass coated with a not nano-structured ZnO bulk layer undergo the spontaneous myogenic process. Hence, here we demonstrate that stem myogenic process can be controlled simply by structuring at the nanoscale the substrate, since with respect to control samples ZnO nanowires could effectively modify Mabs morphology, adhesion and differentiation capabilities.

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Temperature for tuning the surface of hybrid nanogels

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In the design of a thermoresponsive polymer hydrogel, the poly(N-isopropylacrylamide), p(NiPAAm), moiety is often included. Its lower critical solubility temperature (LCST) displayed in water is close to the physiological temperature and is used to obtain a “smart” structural responsivity, consisting in the hydrogel shrinking [1]. However, in a hybrid network, the presence of other components is equally important in determining the overall hydrogel behaviour. In this respect, hyaluronic acid (HA), the co-participant with p(NiPAAm) in this hybrid nanogel, is known to be stable, biodegradable, and able to interact preferentially with tumour cells overexpressing integrins, thus adding a huge therapeutic value to the construct. In this framework, we recently realized nanosized, chemically cross-linked, HA-p(NiPAAm) hydrogel particles, in which HA is derivatized with azide-bearing side chains and “clicked” with a telechelic p(NiPAAm) synthesized by reversible addition-fragmentation chain transfer, RAFT, and bearing terminal alkyne groups [2].

In this contribution, we highlight the peculiar temperature behaviour of the HA-p(NiPAAm) hybrid nano-hydrogels in connection to their biomedical relevance. Photon correlation and z-potential spectroscopies show that at 25°C the nanogel particles have a size of ~150 nm. Around a temperature of 33 °C, in the place of the expected shrinking, a change of the surface properties of the hybrid HA-pNiPAAm nanogel particles occurs. In particular, we observe a dramatic change of the zeta-potential of the water-hydrogel particles, suggesting a prevalence of HA at the surface and a transfer of p(NiPAAm) in the core of the nanogel particles. This process was monitored by small angle neutron scattering (SANS) and atomic force microscopy (AFM) to corroborate such hypothesis and to give a further detailed description of the process at the nanoparticle interface. We found that that below LCST the particles surface is biphasic and patchy (Fig. 1), probably reflecting a limited compatibility between the two polymer components. Approaching the temperature of 33°C, the particles form clusters, which break apart once they reach physiological temperature, where they exhibit a smoothest surface of almost only HA. Moreover, we demonstrated that such a reorganizational process of the nanogel surface has remarkable fallout in terms of selective targeting of anticancer drugs in tumour cells. In particular, the delivery of doxorubicin drug via the HA/p(NiPAAm) nanogel particles reduced by 50% the viability of HT 29 tumour cells with respect to healthy fibroblasts NIH3T3.

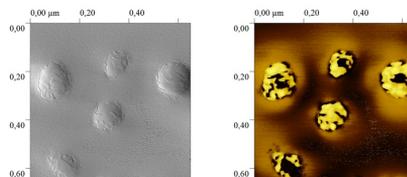


Fig. 1. Tapping mode AFM topography (left side) and phase images of HA-pNiPAAm nanogels laid on a flat silicon surface in water condition.

References

- [1] Hamner, K. L.; Alexander, C. M.; Coopersmith, K.; Reishofer, D.; Provenza, C.; Maye, M. M. *ACS Nano* 2013, 7, 7011. [2] Cerroni B. et al, *Biomacromolecules* 2015, 16, 1753.

Conformations of a colloidal magnetic filament under flow and external field

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Colloidal magnetic filaments are linear arrangements of magnetic colloids—either magnetic micro- or nanoparticles—that have been crosslinked with polymers to form permanent chains [1]. Magnetic colloids assembled into chains have emerged in recent years as building blocks of magneto-responsive systems with a broad potential for technological applications [2]. The stabilization of such chains with polymer crosslinkers to form magnetic filaments provides important advantages, like a strong resistance to shear stresses and an enhanced magnetic response [3]. This makes magnetic filaments promising candidates for many applications, like the creation of magnetically actuated artificial cilia and microswimmers, pumps and mixers for micro- and nanofluidic devices, micromechanical sensors or improved contrast agents for magnetic resonance measurements in biomedicine [1, 4]. In many of such applications, the nonequilibrium structural behavior of the filaments exposed to flows in the background fluid is a key factor. This is one of the central topics of our current theoretical studies on magnetic filaments.

In this contribution, we present the results of a numerical study of the conformational behavior of a flexible filament formed by ferromagnetic colloids when it is placed in a channel and exposed to the combined action of a flow and an external magnetic field. In particular, we study two types of flows (a uniform shear and a Poiseuille flow) and stationary external fields perpendicular to the flow lines. For the zero field case, we found that the filament undergoes coiling-stretching structural transitions. When the perpendicular field is applied, these transitions are strongly hindered and the filament tends to adopt rather straight conformations with an angle of alignment with respect to the field that depends on the balance between hydrodynamic and magnetic torques. For the case of Poiseuille flow, we found that the initial position of the filament in the channel has an unexpectedly long lasting influence on its conformational behavior.

Acknowledgements TTS and JJC acknowledge Project FIS20015-63628-C2-2-R (funded by the Spanish MINECO), as well as a grant awarded by the Conselleria d'Innovació, Recerca i Turisme del Govern de les Illes Balears and the European Social Fund (ESF). PAS and SSK acknowledge the support of the Austrian Research Fund (FWF), by means of the START-Projekt Y 627-N27, and the Ural Federal University stimulating program. SSK is also supported by RFBR mol-a-ved 15-32-20549 and the Ministry of Education and Science of the Russian Federation (Contract 02.A03.21.000, Project 3.12.2014/K).

- [1] R. Dreyfus *et al.*, *Nature*, 2005, **437**, 862; Z. Zhou *et al.*, *ACS Nano*, 2009, **3**, 165; J. Byrom *et al.*, *Langmuir*, 2014, **30**, 9045.
- [2] H. Wang *et al.*, *Nano*, 2011, **6**, 1.
- [3] P. A. Sánchez *et al.*, *Soft Matter*, 2015, **11**, 2963.
- [4] M. Belovs and A. Čēbers, *Phys. Rev. E*, 2009, **79**, 051503; C. Goubault *et al.*, *Physical Review Letters*, 2003, **91**, 260802; S. A. Corr *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 4214.

Development of pH-responsive hyaluronan-boronate nanocarriers

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Hyaluronic acid (HA) has been extensively studied for applications both as a biomaterial and in drug delivery, being non-toxic, biodegradable and allowing target cells *via* binding CD44¹, its most important receptor. Boronic acids (BA) and diols form cyclic boronate esters in a pH-dependent fashion (acid dissociation)², and their stability at neutral pH is maximal with catechols.

We have developed boronate-containing HA (HA-APBA) as a versatile building block for pH-responsive constructs. Here we present A) an innovative spectroscopic method for the evaluation of the boronate/catechol equilibria; B) the nanoparticles obtained *via* solution complexation between HA-APBA and a polycatechol, tannic acid (TA); C) the conjugates obtained by complexing HA-APBA with peptides and proteins (enkephalin, HA-Tag and insulin).

With the aim to obtain HA-APBA derivatives, 3-amino-phenyl boronic acid (3-APBA) was linked to the sodium salt of HA ($M_w = 44, 375, 737\text{kDa}$) *via* amide bond, using DMTMM, in HEPES buffer (pH = 7.4); the degree of functionalization (df) was obtained *via* ¹H NMR giving 4.3-5% and 7.6-8.8% mol/mol (df of 5 and 10% were targeted, respectively). Molecular weight distributions were determined by triple detection GPC. A) Alizarin Red S (ARS) assay: The equilibrium constants (K_{eq}) between HA-APBA and catechols were calculated by using competing equilibria between HA-APBA and given catechols, and HA-APBA and a reference catechol (ARS), whose free/bound concentrations can be calculated on the basis of its bathochromic shifts. The binding HA-APBA and model boronates to a variety of catechols (also enzymatically generated *in situ*) showed equilibrium constants in the range of several 10^3 M^{-1} (kd in the hundreds of μM) at neutral pH, dropping virtually to zero at pH < 5.5.

B) Formation of HA-APBA/TA nanoparticles: A solution of HA-APBA was added to TA in deionized water; the pH ~ 5 is raised to 7.4 by gradual addition of PBS, and nanoparticles spontaneously form. Size and Z-Potential were studied as a function of pH. MTS assay of HA-APBA/TA NPs was performed on Raw 264.7 macrophages. HA-APBA/TA nanoparticles were obtained with average sizes and Z-potentials respectively ranging between 150 and 400 nm (depending on HA-APBA molecular weight) and -38 and -42 mV at physiological pH. At acidic pH (< 5.7) their size increased up to above $1\mu\text{m}$. The nanoparticles showed negligible toxicity on Raw 264.7 macrophages.

C) Development of bio-conjugates: Tyrosine (tyr), enkephalin (enk), hemagglutinin peptide (HA-Tag) and insulin (ins) were conjugated to HA-APBA (44kDa) using resin-supported tyrosinase for phenol-catechol conversion. Peptide/protein oxidation was studied *via* UV-Vis and RP-HPLC analysis. The K_{eq} between tyr or enk and HA-APBA was determined *via* the ARS assay.

Tyr was used as a benchmark for the conversion of phenols into catechols by a resin-supported tyrosinase. Then enkephalin, HA-Tag and insulin were also transformed in their catecholic species and site-specifically conjugated to HA-APBA, as demonstrated *via* gel filtration chromatography, gel electrophoresis and ARS assay.

HA-APBA derivatives showed the capability to build complex and pH-sensitive constructs (nanoparticles, protein/peptide conjugates) in combination with appropriate catechol groups.

1. H. Ponta et al., "CD44: From adhesion molecules to signalling regulators", *Nat. Rev. Mol. Cell Bio.*, 2003, 33-45
2. G. Springsteen et al., "A detailed examination of boronic acid-diol complexation", *Tetrahedron*, 2002, 5291-5300

Preparation of poly(N-isopropylacrilamide) / polyacrylic acid IPN microgels at different composition

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Nanometre- or micrometre-sized hydrogel particles able to change their behaviour between hard- and ultra-soft colloids are interesting model materials to study the dynamic of the arrested state.¹ Colloids displaying this change are those that undergo a rapid but reversible volume phase transition, at critical values, from a swollen hydrophilic state to a collapsed hydrophobic state in response to rapid change of temperature, pH, ionic strength or electric field.

The most known colloidal system exhibiting this behaviour is poly(N-isopropylacrilamide) (PNIPAM) which exhibit a transition from a hydrophilic to hydrophobic state, typically at 32°C. The insertion of polyacrylic acid (PAAc) into colloidal PNIPAM particles to give an interpenetrated network (IPN) allows combining the thermo-responsivity of the latter polymer with the pH-responsivity of the former while keeping independent the response of the two components.² The response of any actual system depends not only on the chemical nature of its components but also on their weight ratio, as well as the polymers architecture and the colloid size. Therefore, tuning these chemical parameters is a key step to access the multivariate physical behaviour of these soft colloidal materials. In this framework, the purpose of this work was to deepen the knowledge on the synthesis of colloidal IPN microgels made of PNIPAM/PAAc IPN to achieve the control over the composition and architecture of particles.

To this aim, microgels have been prepared under the standard procedure based on two sequential radical polymerization steps in aqueous phase.^{3,4} In the first step, particles made of an homopolymeric network of poly(N-isopropylacrilamide) was prepared with a good control over their size (100 nm), then in the second step acrylic acid was added to the dispersion to synthesize the second network within the first one. Systems with different concentration of polyacrylic acid in the particle were prepared and the effect of reagent concentration on the final composition and morphology of the particles were investigated. The actual composition were analysed by FT-IR and NMR spectroscopies, while particle size and morphology were investigated by dynamic light scattering, TEM and viscosity tests.

Acknowledgements The financial support from MIUR-PRIN(2012J8X57P).

¹ V. Nigro, R. Angelini, M. Bertoldo, V. Castelvetro, G. Ruocco, B. Ruzicka, *J. Non-Cryst. Solids*, 2014, **407**, 361

² K. von Nessen, M. Karg, T. Hellweg, *Polymer*, 2013, **54**, 5499

³ N. A. Peppas, *Materials Research Society Symposium Proceedings*, 1994, **331**, 211

⁴ X. Xia, Z. Hu, *Langmuir*, **20**, 2004, 2094

Drops on slippery surfaces

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Here, we consider the shape of a sessile drop embedded in a lubricant film spread on a planar solid substrate both experimentally and theoretically. The lubricant film forms a liquid meniscus around the central drop. In particular the meniscus height is analyzed because it is relevant for a possible drainage and depletion of the lubricant film by sliding drops. Experimentally, a quantitative examination of the shape of the interface between both liquids is generally hindered by poor optical contrast. Laser scanning confocal microscopy enables to measure all curvatures and angles between the different interfaces.

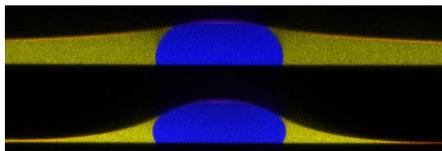


Abb. 1: Snapshots of a drop of ionic liquid (blue) embedded in n-decane (yellow). Top: Initial situation. Bottom: The height of the lubricant film decreased due to evaporation.

We investigated the temporal evolution of the interfaces, the angles and the shape of the wetting ridge for a nonvolatile drop (blue) embedded in a film of slowly evaporating lubricant (yellow). The experimental data quantitative agree with the calculated data for the shape of the drop, the wetting ridge, the Neumann triangle and its evaporation induced rotation.

Acknowledgements The financial support of ERC Advanced Grant 340391-SUPRO and COST MP1106.

[1] F. Schellenberger, J. Xie, N. Encinas, A. Hardy, M. Klapper, P. Papadopoulos, H.-J. Butt, D. Vollmer; *Soft Matter* (2015), 11, 7617.

A New Approach to Fabricate Colloidal Pressure Sensors Using Monodisperse Conducting Elastomer Microparticles

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This study introduces a novel colloidal pressure sensing platform with monodisperse conducting elastomer microparticles. Monodisperse polyurethane (PU) elastomer microparticles were synthesized using the microfluidic technique and consecutive photo-polymerization. For the precise detection of conductance changes, the PU elastomer microparticles were coated with PEDOT:PSS, silver nanowires, and CNTs, respectively. The conducting shell layers had the different coating density, which was possibly achieved by regulation of the coating formulations during the layer-by-layer deposition. We experimentally demonstrated that the conducting elastomer microparticles fabricated in this study could efficiently transduce the pressure changes into electrochemical signals via the piezo-resistive effect in response to the variation of contact area. Combining the characteristics of elasticity and conductivity, the conducting elastomer microparticles showed surprisingly sensitive pressure sensing in the broad pressure range from 5 kPa to 200 kPa and with excellent sensitivity from 10^{-8} ~ 10^{-2} A. The results obtained in this study highlight well that the conducting elastomer microparticles could be used to develop a new type of stretchable, flexible sensing devices.

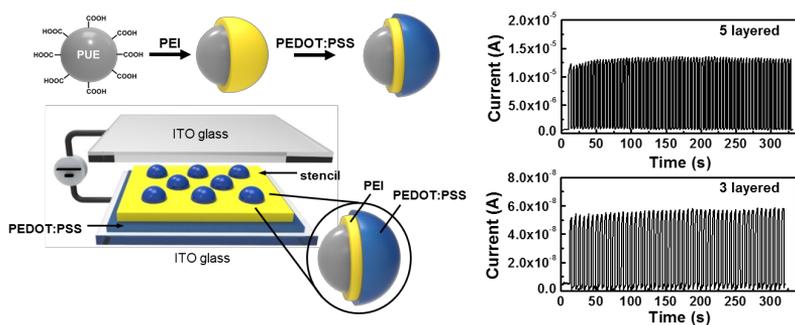


Figure 1 Schematic illustration for fabrication of PEDOT:PSS-layered PU elastomer microparticles and their pressure sensing performance.

Acknowledgements This work was supported by the Samsung Research Funding Center of Samsung Electronics under Project Number SRFC-MA1301-07.

[1] B. C. Tee, C. Wang, R. Allen and Z. Bao, *Nature nanotechnology*, 2012, 7, 825-832.

[2] M. Ziabari, J. Razal, P. Innis, and G. Wallace, *Advanced Functional Materials*, 2014, 24, 2957–2966.

Alcohol dehydrogenase amperometric biosensor based on a hybrid electropolymerised nanocomposite

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In this work, a novel ethanol biosensor was developed using alcohol dehydrogenase (ADH). Ethanol is the most common toxic substance consumed by humans and it is often a contributory factor in a variety of accidents. Usually, the pharmacological effects are observed at blood ethanol concentrations of approximately 10 mmol L⁻¹, whereas lethal levels are ten times higher than this concentration [1]. The measurement of ethanol is particularly relevant in the industry of beverages as beer, wines and spirits.

Electrochemical techniques, with particular reference to amperometric biosensors, are particularly suited to this kind of analysis [2,3]. In ADH-based biosensors, the enzyme catalyzes the oxidation of ethanol to acetaldehyde in the presence of nicotinamide adenine dinucleotide (NAD⁺) and the reduced NADH can be amperometrically detected. It is well known that the direct oxidation of NADH is affected by electrode fouling, hence to minimize this effect several strategies have been employed, often based on the use of either nanomaterials or conducting polymers. To this aim, several dyes such as phenothiazines, phenazines and phenoxazines can be used as redox mediators and can be electropolymerized in aqueous solution on the surface of solid electrodes to obtain electroactive polymers [4,5]. Their advantages are: simplicity (one-step preparation and utilization), high stability and reproducibility. In this research, alcohol dehydrogenase was immobilized, firstly, on the surface of glassy carbon electrode (GCE) modified by co-electropolymerization of the phenoxazine dye Nile Blue-A (NB) and 3-Aminobenzoic acid (2-ABA). The employment of these polymers assess that the immobilization procedure does not disrupt the protein structure and preserve the enzymatic catalytic features.

Secondly, the electrode surface was further modified by nanomaterials as carbon nanotubes (CNTs) and gold nanoparticles (AuNPs) to obtain better electrochemical performances than conventional carbon electrodes. The influence of various steps of modification was investigated for the characterization of the optimum analytical biosensor performances.

Goal of this work was to carry out an electrochemical and morphological study of the nanocomposite-modified electrode using different techniques as cyclic voltammetry (CV), chronoamperometry (CA) and scanning electron microscopy (SEM) and to develop a sensitive and selective biosensor for ethanol determination in real samples.

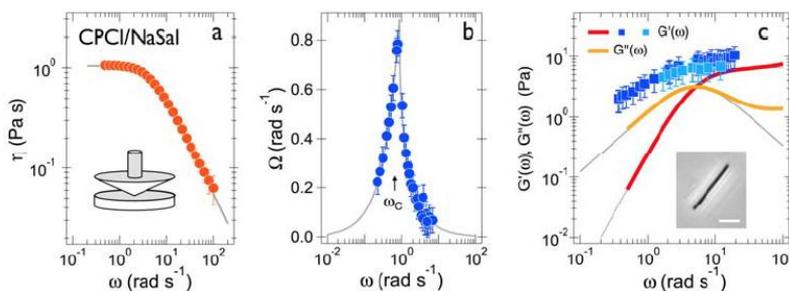
- [1] H. Liden, A.R. Vijayakumar, L. Gorton and G. Marko-Varga, *J. Pharm. Biomed. Anal.*, 1998, **17**, 1111.
- [2] A.S. Santos, A.C. Pereira, N. Durán and L.T. Kubota, *Electrochimica Acta*, 2006, **52**, 215.
- [3] M. Boujtita, J.P. Hart and R. Pittson, *Biosensors and Bioelectronics*, 2000, **15**, 257.
- [4] M.E. Ghica and C.M.A. Brett, *J. Electroanal. Chem.*, 2009, **629**, 35.
- [5] R. Pauliukaite, M.E. Ghica, M.M. Barsan, C.M.A. Brett, *Anal. Lett.*, 2010, **43**, 1588.

Magnetic wire microrheology to differentiate viscoelastic liquids from yield stress gels

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Magnetic rotational spectroscopy using superparamagnetic wires, made of iron oxide nanoparticles, is used to have a rapid and accurate determination of the rheological behavior of viscoelastic liquids or gels. Model solutions were investigated including micellar surfactant solutions and polysaccharide gels to assess the reliability of this technique by comparing experimental results with the Maxwell and Kelvin-Voigt models. Important experimental parameters when investigating the wire rotation behavior submitted to a magnetic field and using optical microscopy allows to relate the frequency dependence of the wire motion to the rheological properties. In particular, synchronous and asynchronous regimes, critical frequency, amplitude of the oscillation and wires average rotation speed were measured and found in good agreement with theoretical models [1-3].



Linear and microrheology measurements of micellar like surfactant solutions. Experimental data obtained by magnetic rotational rheology were found in good agreement with linear rheology and theoretical model.

[1] B. Frka-Petesic, J. Fresnais, J.-F. Berret, V. Dupuis, R. Perzynski and O. Sandre, Stabilization and controlled association of magnetic nanoparticles using block copolymers, *J. Mag. and Mag. Mat.* 2009, **321**, 667 – 670

[2] L. Chevry, N. K. Sampathkumar, A. Cebers and J.-F. Berret, Magnetic wire-based sensors for the μ -rheology of complex fluids, *Phys. Rev. E* 2013, **88**, 062306.

[3] J.-F. Berret, Local viscoelasticity of living cells measured by rotational magnetic spectroscopy, *Nature Comm.* 2016, **7**, 10134.

Thiol-functionalized gold and silver nanoparticles using mixed ligands: a close look at the atomic structure and chemico-physical properties by SR-XPS and SERS

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In recent years, thiol-functionalized noble metal nanoparticles (MNP-s) have been synthesized, characterized and developed to be used in many different fields such as optoelectronics, sensors, catalysis, and biomedicine [1]. Gold and silver nanoparticles, composed of a metallic core and a ligand shell show a peculiar optical behavior and provide a very powerful tool for biotechnological applications. Mixtures of ligand molecules can be used to coat the nanoparticles, controlling the toxicity, the stability and the surface charge density of the system. Typically, this is done so that each of the ligand shell components provides a different property to the nanoparticles. In this work we present gold and silver nanoparticles functionalized by sodium 3-mercaptopropylsulfonate (3MPS) and 2-diethylaminoethanethiol hydrochloride (DEA), chosen on purpose for the biomedical applications [2,3]. The MNP-s were synthesized with different thiols molar ratios with the aim to investigate the properties of the functionalized nanoparticles.

The characterization of the nano-systems was carried out investigating the chemical and electronic structures at the MNP-organic ligand interface by means of Synchrotron Radiation induced X-ray Photoelectron Spectroscopy (SR-XPS). SR-XPS provides information on the local bonding environment of a given species and it has been demonstrated to be a unique tool for investigating the nature of the interaction at the capping agent/metal nanoparticle interface, as well as the chemical structure of MNPs surface [4,5]. FESEM measurements showed dimensions from few nanometers up to 10 nm. The localized surface plasmon resonance (LSPR) of the MNP-s allow the use of another useful technique, Surface Enhanced Raman Spectroscopy (SERS). In SERS, the Raman intensity diffused by molecules close to a nano-curved metallic surface is highly enhanced by the LSPR, allowing the spectroscopical investigation of molecular monolayers [6]. Moreover, structural information on the nanosystem has been gathered by means of Nuclear Magnetic Resonance (NMR) and Dynamic Light Scattering (DLS). In this work we compared the semi-quantitative SR-XPS and SERS analysis to obtain a better understanding of the system. The reported results show a possible correlation between the molar ratio and the thiol affinity for the metal. In conclusion, the present study explores the potential synergy between different techniques in order to give new insights in the field of nanomaterials.

- [1] F. Porcaro, C. Battocchio, A. Antoccia, I. Fratoddi, I. Venditti, A. Fracassi, S. Moreno, I. Luisetto, M. V. Russo and G. Polzonetti, *Colloids and Surfaces B* 2016, **142**, 408-416.
- [2] I. Venditti, L. Fontana, I. Fratoddi, C. Battocchio, C. Cametti, S. Sennato, F. Mura, F. Sciubba, M. Delfini and M. V. Russo, *Journal of Colloid and Interface Science* 2014, **418**, 52-60.
- [3] I. Venditti, C. Palocci, L. Chronopoulou, I. Fratoddi, L. Fontana, M. Diociaiuti and M. V. Russo, *Colloids and Surfaces B: Biointerfaces* 2015, **131**, 96-101.
- [4] C. Battocchio, C. Meneghini, I. Fratoddi, I. Venditti, M. V. Russo, G. Aquilanti, C. Maurizio, F. Bondino, R. Matassa, M. Rossi, S. Mobilio and G. Polzonetti, *J. Phys. Chem. C* 2012, **116**, 19571-19578.
- [5] C. Battocchio, F. Porcaro, S. Mukherjee, E. Magnano, S. Nappini, I. Fratoddi, M. Quintiliani, M. V. Russo and G. Polzonetti, *J. Phys. Chem. C* 2014, **118**, 8159-8168.
- [6] C. Fasolato, F. Domenici, S. Sennato, F. Mura, L. De Angelis, F. Luongo, F. Costantini, F. Bordini and P. Postorino, *Appl. Phys. Lett.* 2014, **105**, 073105.

Nanosecond laser treatment for the design of superhydrophobic coatings with extremely long-ranged freezing delay, robustness to long-term contact with water, corrosion active media, cavitation, and abrasion

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An existing and emerging applications of laser-driven methods make an important contribution to the advancement in nanotechnological approaches for the design of superhydrophobic surfaces. In this study we describe the superhydrophobic coatings on various metals, designed by nanosecond IR laser treatment with subsequent chemisorption of fluorooxysilane. We have shown that one of the most important steps in fabricating the superhydrophobic coatings, i.e., surface texturing, applied to impart multimodal roughness, may be simultaneously used for modifying the physicochemical properties of the thick surface layer of the substrate itself.

Coating characterization reveals extreme water repellency, chemical stability in long-term contact with water, durable corrosion resistance in concentrated potassium halides solutions and excellent durability of functional properties under prolonged abrasive wear and cavitation loads. Besides, we will also show that the statistics of crystallization of ensembles of water and brine droplets deposited on the superhydrophobic coating show the long-term (hours) freezing delay at temperature of -20 °C.

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Strategies to Influence the Crystallization Process of Calcium Silicate Hydrates

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Calcium silicate hydrate, the reaction product of cement with water, is the main binding phase in hardened cement pastes and the principal reason for the strength of concrete. Therefore it is of major importance in various fields of research [1]. Cement clinker as the corresponding "starting-material" and essential component for concrete-formation, is produced by high-temperature treatment of carbonate minerals. This leads to release of carbon dioxide, mainly resulting from process- and fuel-combustion-emissions. Due to rising global production volumes (4.3 billion t in 2014) caused by economic growth, cement manufacturing contributes up to 7 % to the worldwide man-made CO₂-emissions. One conceivable approach to produce sustainable cements is clinker substitution by natural pozzolanes. [2] However, they are not suitable for all kinds of cements, for instance because of low early strength. In order to solve this issue, application of organic additives or so-called templates which directly influence the physicochemical properties are imaginable.

The presence of templates affects the product formation during a chemical reaction or crystallization process, leading to different morphologies, phase compositions or geometries of the final compounds in comparison with the template-free reaction. The most interesting structures with regard to shape, phase composition and mechanical characteristics are created by nature itself. Therefore, the research area of biomineralisation is closely related to approaches that use organic templates in order to create new functional "biomimetic" materials with practical applications. While many scientific publications deal with biomineralisation of calcium carbonate, silica or hydroxyapatite, research on biomimetic approaches of influencing calcium silicate hydrates or cements in general is very scarce so far [3]. Hence, the current work demonstrates and evaluates the impact of different approaches to influence the crystallization process of calcium silicate hydrates (Fig. 1). Various organic additives, herein, the selection of additives aims at organic compounds showing similarities to natural templates regarding partial structural elements or functional groups, e.g. imidazole-rings or carboxy and amino functionalities. Calcium silicate hydrates are grown via the pozzolanes method by using pure SiO₂ and CaO as starting materials and under variation of reaction parameters like time and temperature.

The final products are analyzed via x-ray powder diffraction and gas-adsorption measurements. In order to obtain detailed information regarding structural parameters like crystallite-size, lattice-parameters and interplanar spacing, the Pawley method is applied.

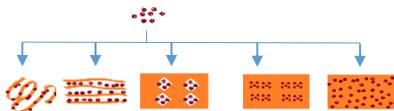


Fig. 1: Influencing strategies for crystallization (nano fibers, layer-by-layer, templating, imprinting, sol-gel method)

Acknowledgements This work was supported by BMBF, IngenieurNachwuchs, AktivPuzzolan [] Persolimplant, [03FH019IX5].

[1] G. Richardson, *Acta Crystallogr. B* 2014, 70, 903.

[2] E. Benhelal, *J. Clean Prod.* 2013, 51, 142.

[3] A. Arakaki, *Org. Biomol. Chem.* 2015, 13, 974.

Phospholipid coatings of fluorescent nanodiamonds

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Nanodiamonds (NDs) are being thoroughly studied as a promising non-toxic material for fluorescent imaging. The combination of physical and chemical properties of diamond and its size in the range of tens of nanometers make these particles a viable option for such applications. In contrast to fluorescent proteins and other organic fluorescent dyes, which suffer from photobleaching, NDs are extremely photoresistant and well suited to be used for long-term imaging in vitro. Although the bare nanodiamonds are chemically inert, they suffer from aggregation in biological environment. Here, we addressed this issue by deposition of self-assembled phospholipid bilayers on NDs. Silica was proven to be an ideal substrate for assembly of supported lipid bilayers. We therefore developed a method to grow silica shells of controlled thickness on the surface of NDs. The formation of supported phospholipid bilayers on silica-coated NDs was confirmed using cryoTEM and fluorescent assay and their increased colloidal stability tested in series of buffer solutions. We will present these composite nanoparticles as new platforms for construction of optical nanosensors based on self-assembly in solution.

Synthesis of novel nanocomposites based on silver nanoparticles and epoxy-amine polymers

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We report a new procedure for the direct synthesis of silver nanoparticles without the traditional reductants in epoxy matrix. Therefore the novel nanocomposites are produced.

Two epoxy oligomers (EOs) of different chemical structure were employed: diglycidyle ether of bisphenol A (Epikote 828[®], Hexion) and polyglycidyl ether of oligoxypropylenetriol (Laproxide 703[®], Macromer, Russia). Also we used the oligoamine hardener, oligoxypropylenediamine (Jeffamine D-230[®], Hunstman). They were the main components of the polymer matrix. Silver nitrate (analytical grade, Sigma Aldrich) was used as a metal precursor.

Cross-linked nanocomposites were synthesized in two stages. At the first one, a mixture of the Epikote 828 and Laproxide 703 (1 : 1 wt/wt) was thermostated in an oil bath for 30 min at 145°C; then, a preset amount of AgNO₃ (no more than 0.6 wt %) was introduced. The reaction mixture acquired brown colour in 5 min; after that, the reaction was stopped by immersing the reactor in cold water (6–8°C) and, then, placing it into a freezing chamber (–16°C). At the second stage, the cooled binary mixture of EOs containing silver nanoparticles, formed at the first stage of the synthesis, was heated to room temperature, and a stoichiometric amount (calculated for the total content of epoxy groups in the system) of the curing agent was introduced. The mixture was thoroughly stirred and heated to 60°C; the curing was performed to the maximum possible conversion [1].

The formation of silver nanoparticles in epoxy mixtures at room temperature was confirmed by dynamic light scattering measurements. The distributions of intensity and particles number by size were monomodal and had similar patterns. The average diameter of silver particles determined from the number distribution was approximately 15 nm. There is a peak maximum at 420 nm in samples extinction spectra. The peak is typical for plasmon resonance of silver nanoparticles.

The addition of the oligoamine into the obtained system followed by heating from 22 to 60°C promotes more reduction of silver ions. The cross-linked metal-polymer composites were obtained after cross-linking of the system. These composites are brown at a thickness of 1–2 mm. The scanning electron microscopy of the cured nanocomposites visualized chain fractal aggregates formed by silver nanoparticles. The sizes of individual nanoparticles in the aggregates (30–45 nm) were obviously larger than those in the uncured first stage product. In such a way, the nanoparticles formed at the first stage may be regarded as inoculating particles for the nanoparticles, formed at the second one.

We suppose, that the performed investigations give new possibilities of producing metal-polymer nanocomposites.

Acknowledgements The financial support of the Russian Foundation for Basic Research, project no. 15-08-02351_a.

[1] Zhavoronok E.S., Senchikhin I.N., Kolesnikova E.F., Chalykh A.E., Kiselev M.R. and Roldughin V.I., *Polym. Sci., Ser. B*, 2010, **52**, 235.

Polymer Colloidal Assemblies: From Film Formation to Order-Disorder Thermal Transport Properties

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In the past decades, polymer colloidal assemblies from monodisperse, spherical particles have been extensively investigated, mostly for their commonly known photonic properties. Based on the well-defined geometry of their building blocks and the possibility to easily adjust the properties of such assemblies, e.g. by changing the material of the building blocks or mixing of different particles, they can additionally serve as an extremely flexible platform to study fundamental thermal transport in nanostructured, colloidal materials.

We recently have shown the unique thermal transport properties of polystyrene (PS) colloidal crystals by temperature-dependent XFA measurements.^[1] Due to their high interface density, these crystals show a very low thermal conductivity in the range of only $51 \text{ mWm}^{-1}\text{K}^{-1}$ at room temperature. Furthermore, the thermal conductivity increases sharply by almost 270 %, once exceeding the glass transition temperature T_g . This increase is mainly due to an enlargement of the particle-particle interfaces between adjacent spheres during the film formation process.

In this contribution, we want to focus on how to tailor this transition temperature by changing the polymer composition of the colloidal particles. Using random copolymers, consisting of methyl methacrylate (MMA) and *n*-butyl methacrylate (nBA), gives access to a precise control over the transition temperature of the assembly. Based on the nBA content, it is possible to systematically shift the T_g of the particles to lower temperatures.

We further utilize time-dependent XFA as a novel approach to study the kinetics of colloidal film formation in nBA-co-MMA colloidal crystals. From our experiments, it is possible to determine a temperature-dependent time constant, which is governed by the respective polymer viscosity. Using an Arrhenius evaluation we find an activation energy of $\sim 283 \text{ kJmol}^{-1}$ for the film forming process.

Besides the particle composition, the influence of the symmetry and order of the colloidal ensemble plays an important role for its effective thermal conductivity. Therefore, samples with different number particle ratios were prepared from two monodisperse PS particles, possessing a diameter of 243 nm (S) and 305 nm (L). The increasing, yet controlled polydispersity disturbs the evolution of a crystalline structure within the assembly. We support our experimental results with molecular dynamics (MD) simulations of the assembling process of such binary mixtures. We found a significant drop of the thermal conductivity of binary mixtures with compositions of 10% to 75% of large spheres (disorder), compared to higher conductivities of the crystalline samples at both edges of the mixing diagram (order). This drop is based on a decreased number of next neighbor particles within the assembly. This geometric constriction can be understood as a bottleneck for thermal transport within these binary structures.

Acknowledgements This research was funded by the Volkswagen foundation.

[1] F.A. Nutz, P. Ruckdeschel, M. Retsch, J. Colloid Interface Sci., 2015, **96**, 457.

Elastocapillary self-assembly of silicon nanopillars

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Nanostructured materials exhibit fascinating physical properties that can be utilized for many applications, and recently there is a rising interest in using elastocapillary self-assembly of vertically oriented nanopillars to fabricate highly ordered hierarchical structures [1–3]. In this work, dense arrays of silicon nanopillars with different dimensions are used to study the capillary-force-induced structural self-organization. The observed bending and aggregation of nanopillars result from the competition between the elastic restoring energy and the capillary interactions. Different surface functionalizations are applied to fine-tune the delicate balance between the mechanical and interfacial energy, as a result various hierarchical morphologies of the clustered nanopillars can be achieved. Reverse self-assembly is also investigated by chemical removal of native oxide from the silicon structures. After breaking the covalent bonds formed between bridging structures, the deformed silicon pillars can recover to their initial free standing states because the reduced adhesion energy is not sufficient to counter balance the elastic restoring energy. Recovery of big clusters is found to be more challenging, and for heavily bended nanopillars, high resolution TEM inspections reveal stress induced crystal defects which are believed to have a catastrophic effect on reversible self-assembly of crystalline structures.

- [1] S.H. Kang, B. Pokroy, L. Mahadevan, and J. Aizenberg, *ACS Nano*, 2010, **4**, 6323.
- [2] M. De Volder and A.J. Hart, *Angew. Chemie Int. Ed.* 2013, **52**, 2412.
- [3] B. Pokroy, S.H. Kang, L. Mahadevan, and J. Aizenberg, *Science*, 2009, **323**, 237.

Description of catalytic rates in stimuli-responsive nanoreactors

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In recent years, the use of stimuli-responsive polymer coatings has come out as a possible new way to control the catalytic activity of colloids and nanoparticles [1,2]. The polymer coating not only prevents particles from coagulation or aggregation, but actively participates in the catalytic process by changing the local environment for the reactants. The catalytic rate can be thus flexibly tuned and switched, e.g., by the temperature [1,2], ionic strength, or pH.

In this work we present a comprehensive theoretical framework that, by extending concepts from the Debye-Smoluchowski theory of diffusion [2,3], allows to qualitatively and quantitatively describe the influence of all major experimentally tunable parameters on the nanoreactors' catalytic rate. We pay special attention to the case of multicomponent systems by analyzing the temporal and spatial distribution of reactants and products. Besides, we study the effect of electrostatic interactions on the catalytic rate. This theoretical framework is also useful to find out what parameters most sensitively tune such rate, therefore providing theory-guided design principle for stimuli-responsive nanoreactors' synthesis.

- [1] S. Wu, J. Dzubiella, J. Kaiser, M. Drechsler, X. Guo, M. Ballauff, and Y. Lu, *Angew. Chem., Int. Ed.*, 2012, **51**, 2229.
- [2] S. Angioletti-Uberti, Y. Lu, M. Ballauff, and J. Dzubiella, *J. Phys. Chem. C*, 2015, **119**, 15723.
- [3] D. F. Calef, and J. M. Deutch, *Ann. Rev. Phys. Chem.*, 1983, **34**, 493.

Preparation of SiO₂/Au/TiO₂ Core-Shell Nanoparticles and Their Photocatalytic Properties

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Titanium dioxide (TiO₂) is a very attractive photocatalyst in practical applications such as water splitting and photodegradation of organic pollutants, due to its chemical stability and non-toxicity. However, TiO₂ has a wide band gap of 3.2 eV, which limits their photocatalytic activity under the ultraviolet light. Therefore, it is important to endow TiO₂ with photocatalytic activity under the visible light. Noble metal nanoparticles absorb visible light due to the localized surface plasmon resonance (LSPR), in which light absorption and/or amplification of the electric field have been shown to depend strongly on the particle size, shape and local dielectric environment. Gold nanoshells are a type of spherical nanoparticles consisting of dielectric core such as SiO₂ particles covered by a thin Au shell. These nanoshells can absorb the light of broad wavelengths ranging from the visible to the near-infrared region depending on the core/shell thicknesses. If gold nanoshells/titania composite particles are prepared, the light source available for the photocatalyst can be extended from the conventional ultraviolet region to the visible and the near-infrared regions, leading to an effective use of sunlight energy.

The SiO₂/Au core-shell nanoparticles were prepared by the deposition-precipitation (DP) process and the seed-mediated growth method [1, 2]. Firstly the surface of SiO₂ particles was functionalized with amino groups by 3-aminopropyltriethoxysilane (APTES). Subsequently Au nanoparticles were deposited on the APTES-grafted SiO₂ surfaces by controlling temperature, pH, and reaction time (70 °C, pH 8, 1 h). Using the Au-supported SiO₂ particles as seed solution, the Au particles grew and formed a uniform shell on the SiO₂ surfaces. Finally addition of titanium tetrabutoxide (TTBO) in the mixed butanol/acetonitrile solvents to aqueous Au nanoshells dispersion gave rise to the formation of TiO₂ shell [3, 4]. The TEM image (Figure 1) reveals that SiO₂/Au (120 diam. / 20 nm thickness) core-shell nanoparticles are covered by a uniform TiO₂ layer of 20-nm thick. The UV-vis extinction spectra (Figure 2) indicates a broad absorption from the visible to the infrared due to the Au nanoshell, as well as the UV absorption by TiO₂ shell. Photocatalytic properties of as-prepared SiO₂/Au/TiO₂ samples were evaluated by oxidation of 2-propanol under visible light ($\lambda > 420$ nm). A high photocatalytic activity was observed under the visible light for the SiO₂/Au/TiO₂ core-shell NPs.

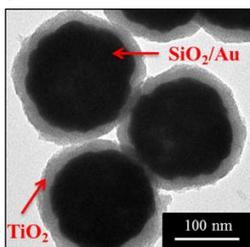


Figure 1. TEM image of SiO₂/Au/TiO₂ core-shell NPs.

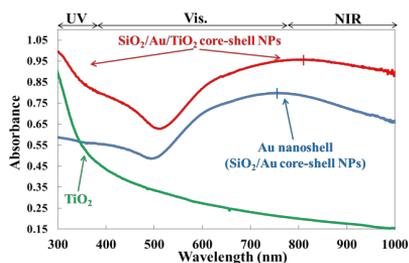


Figure 2. UV-vis extinction spectra.

[1] N. Phonthammchai et al., *Langmuir*, 2008, **24**, 5109.

[2] J. C. Y. Kah et al., *Gold Bull*, 2008, **41**, 23.

[3] T. Ogihara, N. Mizutani, *Inorg. Mater.*, 1996, **3**, 177.

[4] T. Kojima, T. Sugimoto, *J. Phys. Chem. C*, 2008, **112**, 18445.

Sol-gel derived ZnO:Y nanostructured films: structural and optical study

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ZnO has various applications such as solar cell, gas sensors, optoelectronic devices, biological applications and UV photodetector etc. ZnO has a low material cost and low deposition temperature. Yttrium is an environmentally friendly and abundant rare earth element, and yttrium oxide (Y_2O_3) has important parameters such as thermal and crystallographic stability (2325°C), mechanical strength, dielectric constant (~18), band gap (~5.8 eV), optically transparent over a wide spectral range (0.28–8 μm), refractive index ($n = 2$). Y_2O_3 , both a rare-earth oxide and a transition oxide, is claimed to be a theoretically interesting and technologically useful material [1]. Y_2O_3 films are found to be applicable for electroluminescent devices due to high dielectric constant and thermal stabilities.

Previously [2], it has been reported a study of sol-gel ZnO:Y nanostructured films with small concentrations. There, we continue to investigate sol-gel ZnO:Y films prepared from sols with higher concentrations of yttrium precursor $Y(NO_3)_3$. The precursor used is zinc acetate, dissolved in an absolute ethanol (0,4 M concentration). As a complexing agent and stabilizer is used monoethanolamine. The yttrium is involved by adding $Y(NO_3)_3$ in the weight percent : 2 and 3. The corresponding sols and the obtained films are labeled ZnO:Y 2, ZnO:Y 3. The sol-gel Y doped ZnO films have been successfully deposited on Si and quartz substrates by spin coating method, then annealed at the temperatures 300-800°C. XRD and FTIR analyses are applied to reveal structural and vibrational properties. The optical behavior, depending on Y dopant and annealing has been studied by UV-VIS spectrophotometry, optical band gaps are estimated.

XRD patterns have been compared with standard JCPDS data. It is noticeable that the XRD peaks of Y doped ZnO films are significantly broader and less intense compared to single ZnO. The XRD analysis reveals that higher Y concentrations result in the formation of cubic yttrium oxide appeared as separate phase in the film structure after high temperature annealing (Figure 1). The crystallite sizes, lattice parameters and texture coefficients for lines (100), (002) and (101) of wurtzite phase are estimated. This conclusion has been confirmed by FTIR analysis. Optical transmittance in the visible spectral range diminishes with yttrium doping especially significant for ZnO:Y 3. The determined optical band gaps of ZnO:Y are widening compared to single ZnO.

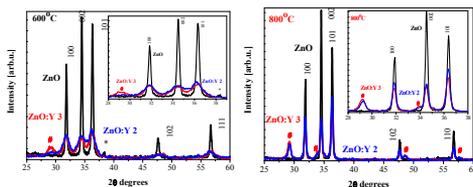


Figure 1. XRD spectra of ZnO:Y 2 and ZnO:Y 3, compared with ZnO and annealed at 600 and 800°C. The inset figures show enlarged part of the spectra 28 – 38 degrees.

[1] P. Lei, B. Dai, J. Zhu, X. Chen, G. Liu, Y. Zhu and J. Han, *Ceramics International*, 2015, 41, 8921.

[2] T.Ivanova, A. Harizanova, T. Koutzarova and B Vetruyen, *IOP Confer. Series* 2016, 682, 012023

Disclosing weak phenomena at multiple scales in soft matter using simultaneous SAXS/WAXS laboratory system

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The physico-chemical behavior of soft materials is often complex since it relates the relationship not only between the chemical species in presence [1] but also couples with the environmental conditions as such as but not limited to temperature, stress, ... Most of these external fields being essentially subtended by intensive variables, it is particularly adapted to study in the bulk of materials the slow variations of the structure over 2 or 3 decades in space, i.e. from atomic scale up to the mesoscale.

For instance, first order transitions are known for sharp changes in conformation, inducing strong variations on the signal of the detecting instruments, with time constant being relatively small. In liquid-solid transition, the latent heat associated with thermal first order transitions should lead to broad times of observation: “water does not turn into vapor” in a short time. But locally, the transition is almost instantaneous. And the fact is that most x-ray analytical methods are usually probing small volumes, for which the transition will undergo in a short time.

In case of already solid or semi-solid systems, the mass exchange is severely slowed down, leading to much extended transition times. Then in comparison, second order transition being also called “continuous transition” can exhibit a wide variety of paths that are sometimes very much kinetic dependent. In this broad panorama, the recent discovery of order-order transitions as such as quasicrystals in polymers [2] or more lately the Frank-Kasper phases in tetrablock copolymer systems [3] is highlighting the wide variety of time constants in phase transition, from ms up to several days.

As a matter of fact, if fast transitions require intense flux of third generation synchrotrons [4], slow phenomena are ubiquitous and can be studied fruitfully in laboratory systems, offering in one hand less instantaneous flux but with unrivalled availability of beam time. This provides strong support in disclosing slow evolutions of nanostructures and at the same time avoids any severe beam damage. Among others, this paper will be illustrated by the SAXS/WAXS kinetic study of washing powder exposed to moisture. It will be shown that presence of moisture increases mobility at surface of grains, leading to local mass exchange and final formation of cakes, having practical consequences both for washing application and for the environment.

- [1] A.V. Zvelindovsky Editor, *Nanostructured soft matter: experiment, theory, simulation and perspectives*, 2007, Springer
- [2] K. Hayashida, T. Dotera, A. Takano and Y. Matsushita, *Phys Rev Lett*, 2007, **98**, 195502
- [3] S. Lee, C. Leighton and F. S. Bates, *PNAS*, 2014, **111**, 17723
- [4] T. Narayanan, R. Borsali and R. Pecora Editors, *Synchrotron small angle x-ray scattering in Soft Matter Characterization*, 2008, **2**, Springer Reference

Magnetoliposomes for Sequential Controlled Release

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The design of efficient and non-toxic drug delivery systems (DDS) that selectively release therapeutic or diagnostic payloads to their biological target in a controlled way is one of the main objectives of nanomedicine [1]. The simultaneous or sequential delivery of therapeutic active principles to the same site of action is particularly challenging. Self-assembled architectures, made of different building blocks, each providing a specific functionality to the final construct combine a facile synthetic route with a high tunability and structural control. For the first time we provide proof-of-principle of a DDS made of (i) liposomes, providing a fully biocompatible lipid scaffold suitable to host both hydrophobic and hydrophilic drugs [2]; (ii) a double stranded DNA zipper conjugated with a cholesteryl unit that spontaneously insert in the lipid membrane and (iii) hydrophobic and hydrophilic superparamagnetic iron oxide nanoparticles (SPIONs) embedded inside the lipid membrane of liposomes or connected to the DNA zipper, respectively. Upon the application of an alternating magnetic field (AMF), SPIONs can trigger, through thermal activation, the release of DNA or of the liposomal payload, depending on the frequency and the application time of the field, as proved by steady-state and time-resolved fluorescence studies. This unique feature, here presented for the first time, is due to the different localization of the two kinds of SPIONs within the construct and demonstrates the feasibility of a multifunctional DDS, built-up from self-assembly of biocompatible building blocks. Even if additional experiments are needed to determine the stability and leakage characteristics in serum and *in vivo*, this contribution shows for the first time an easily self-assembled build-up system for the sequential or simultaneous release of different therapeutics, which would be paramount to handle diseases that requires a multifaced approach addressing both causal and symptomatic features of the pathology [3].

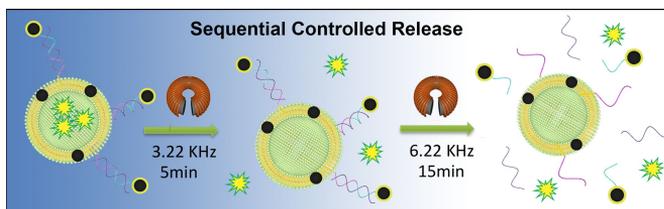


Figure 1 Representative scheme of the DDS functionality for sequential controlled release: the application of a 3.22 KHz AMF for short times is sufficient to provoke the release of the hydrophilic drug contained in the aqueous pool of magnetoliposomes. Subsequently, the application of a 6.22 KHz AMF for longer times allows reaching the DNA melting temperature and the release of the *staple* therapeutic oligonucleotide.

Acknowledgements The financial support from MIUR through the project PRIN 2010- 2011 grant 2010BJ23MN

- [1] Spsford, K.E. *et al*, *Chem. Rev.* **113**, 1904–2074 (2013).
- [2] Allen, T. M. & Cullis, P.R. , *Adv. Drug Deliv. Rev.* **65**, 36–48 (2013).
- [3] Wirtz, S. & Neurath, M. F. *Gene Ther.* **10**, 854–860 (2003), Teo, P. Y., Cheng *e tal*, *Adv. Drug Deliv. Rev.* **98**, 41–63 (2016).

Nano-, Meso- and Macro-swelling characterisation of impregnated compression wood cell walls

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Wood cell walls behavior when contacted with humid atmosphere or an aqueous solution containing electrolytes or polymers show the phenomenon of swelling. The maximum swelling is the point for which the osmotic pressure is zero in the case of pure water, or when the RH of the atmosphere considered is matched (51% TH) in industrial norm.

In order to link the observed behaviour, it is necessary take into account, in the form of the master equation, geometrical and compositional data to quantitatively predict the water sorption. Experimental data are produced to test the prediction by exploring the effects of water and solutes, introduced by equilibration with a solution used as osmotic reservoir. Environmental setups have been developed, allowing the control of temperature, water chemical potential, ionic strength. In this work, we will describe the three techniques available to follow changes occurring in wood cell material:

- at the nanometric scale (Small Angle X-ray Scattering) in tomographic mode at BESSY,
- at the microscopic level (Environmental Electron Scanning Microscopy) made in Marcoule,
- and at macroscopically observable scale under controlled mechanical stress, via a Mechanical Tensile device developed in Potsdam.

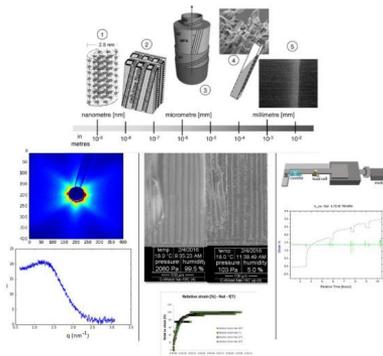


Figure 1: Wood material hierarchical levels (represented on top) can be experimentally explored with different techniques: SAXS measurements give indications concerning the distance between cellulose crystals (bottom left: diffraction pattern and integration results for a sample immersed in NaI solution), ESEM is useful for studying the influence of temperature and humidity (bottom center: images of a sample treated with NaI at different relative humidities, and results obtained at different temperatures), the mechanical tensile device is able to quantify sample swelling due to solution sorption (bottom right: schematic representation of the device, and results of cycles of sample immersion in NaI solution).

By comparing salt and base sorption results obtained from experiments with the three devices, we show that results obtained at the three scales are consistent and can be interpreted within the frame of a single general equation of state combining chemical, colloidal and macroscopic scale.

BSA and PEG Coated Colloidal Gold Nanoparticles: Characterization, Cellular Uptake and Biocompatibility

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The use of nanoparticles in therapeutics and imaging and understanding their effect on the cell functions are among the current challenges in nanotechnology and nanomedicine. Even if currently there is a wide range of materials used for producing gold nanoparticles [1-3] there is a continuous need for the development of new synthesis protocols. Moreover, the applicability of such biosynthesized nanoparticles needs further investigation. Their biocompatibility, cellular uptake and bio-distribution are important aspects that require careful assessment.

In this study we report the synthesis of colloidal gold nanoparticles by reducing the tetrachloroauric acid with short chain polyethylene glycol (PEG200). The nanoparticles were obtained by a one step protocol [3]. For *in vitro* experiments, in order to minimize aggregation in the cell culture media, the nanoparticles were further coated with bovine serum albumin (BSA). The nanoparticles were characterized by UV-Vis spectroscopy, Fourier Transform Infrared Spectroscopy, and Transmission Electron Microscopy. The UV-Vis absorption spectra show narrow absorption bands, with absorption maxima characteristic for AuNPs, at 522 nm. FTIR confirms nanoparticle coating with PEG and BSA. *In vitro* studies were performed on the adenocarcinomic human alveolar basal epithelial A549 cell line. The nanoparticles biocompatibility was assessed and the cytotoxicity threshold was identified. The cellular uptake and intracellular localization of the nanoparticles was assessed by transmission electron microscopy and scanning confocal laser microscopy. Exposure of cells to different concentrations of nanoparticles for 24 h produced a decrease in the cellular viability in a dose dependent manner. Good biocompatibility of the nanoparticles was observed, with high IC₅₀ values, of 0.45 μM. Regarding the cellular internalization, formation of nanoaggregates is observed intracellularly. The nanoparticles are internalized in the cells and localized in the cell cytoplasm, in the region surrounding the nuclei.

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- [1] E.C. Dreaden, A.M. Alkhalifa, X. Huang, C.J. Murphy, M.A. El-Sayed, *Chemical Society Reviews*, 2012, **41**, 2740.
- [2] C. Coman, L.F. Leopold, O.D. Rugină, L. Barbu-Tudoran, N. Leopold, M. Tofană, C. Socaciu, *Journal of Nanoparticle Research*, 2014, **16**, 2158.
- [3] N. Leopold, V. Chiș, N.E. Mircescu, O.T. Marișca, O.M. Bujă, L.F. Leopold, C. Socaciu, A. Irimie, I. Berindan-Neagoe, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2013, **436**, 133.

Formation of gold nanoparticle monolayers of controlled structure and electrokinetic properties

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Deposition mechanism of gold nanoparticles on poly(allylamine hydrochloride) (PAH) modified gold substrate was studied under *in situ* conditions by using quartz crystal microbalance (QCM), streaming potential measurements and scanning electron microscopy (SEM). The studies were carried out for various bulk concentrations of gold suspensions, flow rates, ionic strengths and pHs. It was shown that the particle deposition for the low coverage regime was governed by the bulk mass transfer step that results in a linear increase of the coverage with the time indicating that the hydration of the monolayers was negligible. This allowed one to derive a universal kinetic equation that describes the mass transfer rates in the QCM cell for various flow rates and diffusion coefficients. Kinetic measurements were also performed for longer times and for various ionic strengths and pHs. Negligible desorption of particles was confirmed that allowed one to precisely determine the maximum coverage of monolayers. A significant increase in the maximum coverage with ionic strength was interpreted as due to the decreasing range of the lateral electrostatic interactions among deposited particles.

The experimental results were quantitatively interpreted in terms of the extended random sequential adsorption (eRSA) model where the bulk and surface transfer steps were simultaneously considered. It was also shown that the QCM data matched the *ex situ* SEM results indicating that the monolayer hydration was also negligible for higher coverage range. The structure of monolayers obtained for various ionic strength was analyzed in terms of the radial distribution function by using the SEM micrographs of deposited particles. In this way, the significance and the range of electrostatic interactions was directly determined. Besides significance to basic sciences, the obtained results can be exploited for developing an efficient procedure of preparing gold-nanoparticle monolayers of desired coverage and structure having potential applicability as biosensors.

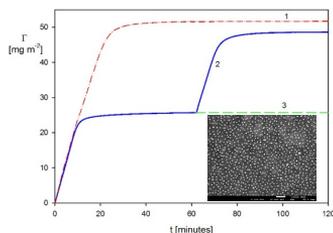


Figure 1. The kinetics of gold nanoparticle deposition on PAH modified Au sensor determined by QCM, pH 7.4 (PBS). Lines 1 and 3 show the results obtained for single step gold nanoparticle deposition for ionic strength 10^{-2} M (red) and 10^{-3} M (green) whereas line 2 presents a two-stage deposition kinetics obtained for ionic strength change from 10^{-3} M to 10^{-2} M. The inset shows the SEM image of nanoparticle monolayer at the gold sensor of the coverage of 0.15.

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Stress triggered colour-changing elastic materials for motivational dental applications.

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Patient motivation to undergo treatment is very important in dental healthcare. A particularly challenging group are children, where the lack of willingness to follow a prescribed medical regimen can lead to ineffective therapy, especially in orthodontics. This problem is predominantly observed when everyday elastic ring-bands have to be worn between the fixed upper and lower orthodontic appliances (braces), even during daily activities including eating or teeth brushing. To overcome this problem, we propose to design and synthesize a colour-changing elastic material (**Figure 1**) for the elastic ring-bands. The dye molecules enclosed in capsules within the elastic matrix is released in response to mechanical stresses (**Figure 1c-e**), leading to colour changes and motivating child patients. In addition, the change in colour can inform an orthodontist and parents of whether these bands are worn.

In this work we will use *Pickering emulsions* stabilised by clay particles as templates for pigment encapsulation. Pickering emulsions consist of two or more immiscible liquids, either water-in-oil, oil-in-water, or multiple, which is stabilised by solid particles instead of surfactant molecules. Our experimental challenges include modification of clay particle surface chemistry for tailored capsule mechanical properties, optimization of interfacial polymerisation at the Pickering emulsion interior, toxicity of the capsules, and incorporation of the capsules in the ring-bands.

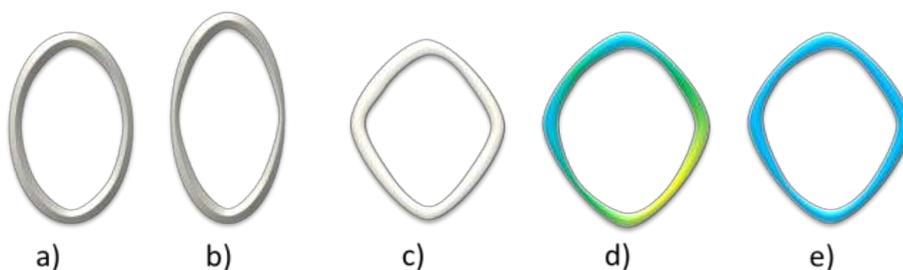


Figure 1. A schematic of elastic rings in dental applications: a) standard, b) the same ring after a day of usage, c) intelligent elastic colour-changing material before application, d) during the day, and e) after worn for a day.

Acknowledgements

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In situ growth of silver sulfide nanocrystals onto graphene oxide flakes: synthetic, spectroscopic and photocatalytic studies

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Graphene based materials have emerged as promising materials in many technologies due to their structure-dependent physical and chemical properties [1]. Metal chalcogenide nanocrystals have also attracted great attention because of their size-dependent properties and their potential application in diverse areas, which include sensors, solar cells, catalysts and optoelectronic devices [2]. For example, Ag₂S (E_g = 1.08 eV) has been reported to harvest photons efficiently in the visible spectral region, which makes this semiconductor an interesting material to be explored in visible light photocatalysis.

The combination of the above types of nanomaterials can be regarded as a promising strategy to develop efficient photocatalysts for water treatment technologies [3]. However, there are few synthetic routes that result in morphological uniform hybrid materials comprising both components, which in some cases can be related to lack of knowledge about surface chemical effects on the synthesis itself. Hence, in this research we have studied the in situ growth of Ag₂S nanocrystals, in the presence of graphene oxide (GO) flakes dispersed in ethanol, by the sonolytic degradation of a Ag(I) dialkyldithiocarbamate complex [4].

Several synthesis parameters have been investigated in order to optimize experimental conditions for obtaining morphological uniform hybrid nanomaterials. In particular, Raman spectroscopic methods have been applied to monitor the surface nature of GO obtained from the exfoliation of graphite, due to their potential impact on the nucleation and growth of the metal sulfide nanophases onto the GO surfaces. Preliminary experiments aiming the evaluation of the photocatalytic activity of the as prepared hybrid materials were carried out, by using an organic dye as the water contaminant model and a visible light photoreactor.

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- [1] A. Ciesielski and P. Samori, *Chemical Society Reviews*, 2014, **43**, 381.
- [2] T. Trindade and P. J. Thomas, *Comprehensive Inorganic Chemistry II: From Elements to Applications*, 2013, 4, 343-369, Elsevier, Oxford, England.
- [3] Y. Wang, L. Zhang, H. Jiu, N. Li and Y. Sun, *Applied Surface Science*, 2014, **303**, 54.
- [4] A. C. Estrada, E. Mendoza and T. Trindade, *European Journal of Inorganic Chemistry*, 2014, **2014**, 3184.

Preparation and Characterization of Bio-Nanocomposite Films with Antibacterial Properties from Mixed Cellulose and Chitosan Solutions

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Natural biopolymer-based nanocomposite films of cellulose and chitosan were prepared via mixing 4 wt% cellulose and 4 wt% chitosan aqueous solutions. The cellulose and chitosan solutions were firstly prepared by dissolution in LiOH/urea/water and LiOH/KOH/urea/water, respectively. Then the bio-nanocomposite films with different properties were prepared by tuning the cellulose-chitosan ratio. Morphology and physicochemical properties of the films were studied with field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). The mechanical properties of the films were evaluated by means of stress-strain curves. The cellulose-chitosan bio-nanocomposite films were also tested for their antibacterial efficiency against *Escherichia coli* (gram negative) and *Staphylococcus aureus* (gram positive).



Figure 1. Pictures showing the transparency and flexibility of bio-nanocomposite film made from cellulose and chitosan solutions.

Keywords: cellulose; chitosan; bio-nanocomposite films; antibacterial properties;

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Control of axial symmetry and structure of concentrated spin coated colloidal deposits by external sources

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Spin coating technique is very fast, cheap, reproducible, simple and needs less material to fabricate colloidal crystals. However, they present the emergence of colored arms imposed by axial symmetry of spin coating, causing orientationally correlated polycrystals (OCP) [1]. The OCP character of spin coated colloidal deposits is challenging and of competitive interest. In spin-coating, the thickness and the uniformity of the films are important and strongly dependent on the key parameters including: the spin time and speed, the viscosity of fluids, the density and the evaporation rate of the fluids, concentration of the suspension as well as the substrate surface characteristics [2,3]. We study the influence of substrate wettability on the behavior of concentrated non magnetic colloidal deposits, spin coated on topographically patterned substrates. Polycrystals of mono-layer on photo-patterned substrates are obtained by using concentrated colloidal suspension of 458-nm diameter silica spheres dispersed in ethanol at 20% (V/V) concentration. We break the axial symmetry imposed by spin axis and eliminate the emerging OCP character (6- or 4-arms). The effect of the characteristic scale of surface pattern on the different structures formation of the spin coated deposits has been studied. Moreover, we modify spin coating technique by applying uniform magnetic field during spin coating of concentrated magnetic colloids to orient colloids in the field direction and break the axial symmetry. The experimental results under different conditions will be discussed in detail.

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[1] C. Arcos, K. Kumar, W. González-Viñas, R. Sirera, K. M. Poduska, A. Yethiraj. Phys. Rev. E77, (2008), p. 050402(R).

[2] M. Giuliani. Ph.D. thesis, University of Navarra (2010)

[3] M. Pichumani, P. Bagheri, K. M. Poduska, W. González-Viñas, A. Yethiraj. Soft Matter 9 (12), (2013), pp. 3220-3229.

Active micromotors: efficient Marangoni-driven microgears and self-assembling Janus micromachines

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In the first part of the talk I will present a new type of light-activated motors with unprecedented efficiency[1](Fig.(a), (b)). These consist in asymmetric microfabricated gears covered by an absorbing coating that converts the energy of wide-field illumination into rotational motion. These micromotors are suspended at an air-liquid interface and produce a non-homogenous heating of the fluid that, in turn, causes a surface tension-driven torque spinning the rotor up to 300 rpm. It is shown that these microdevices have an efficiency orders of magnitude higher than rotors relying on direct optical momentum transfer or on thermophoresis. In the second part of the talk I will show how we were able to design self-assembling micromotors from catalytic (Janus) self-propelling particles and passive microgears[2](Fig.(c)). This combination leads to the fully autonomous construction and propulsion of rotors via the almost perfect alignment of Janus particles with the gear's edge. It will be discussed how the performances of these motors are affected by hydrodynamics and competition for fuel.

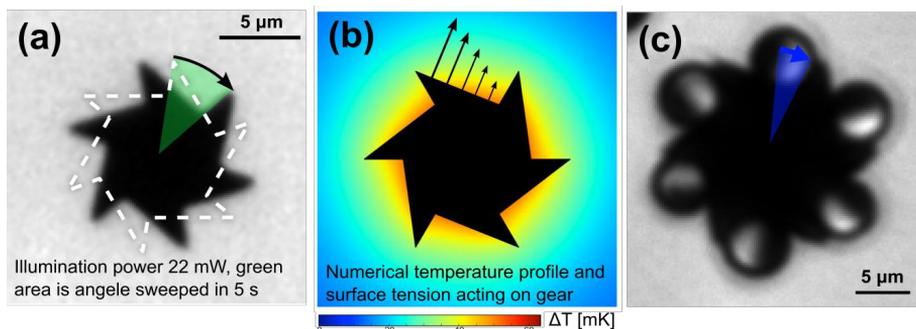


Figure (a) Microscopy picture of a light-activated micromotor spinning at the air-liquid interface. (b) The inhomogenous temperature profile generated unbalances surface tension (arrows) and drives the rotation of the gear. (c) Self-assembled micromotor composed by a passive rotor and Janus particles that are randomly distributed before addition of hydrogen-peroxide, coloured area is the angle spanned in 4 s.

[1] C. Maggi, R. Di Leonardo et al. *Nature Communications*, 2015, **6**,7855.

[2] C. Maggi, R. Di Leonardo et al. *Small*, 2016, **12** 446.

Preparation of self-cleaning AG/AR film with hollow structured layer of titania particles.

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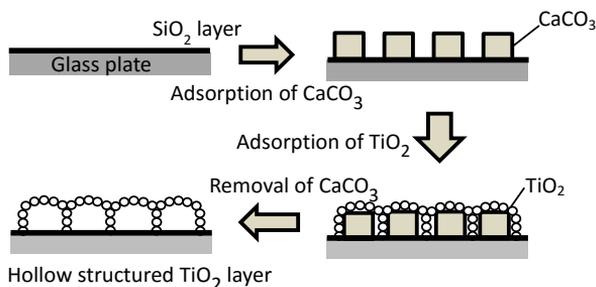
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Anti-reflection or anti-glare films are widely used in order to improve the visibility of displays. Among the several ways for achieving the AG/AR properties,[1] preparation of air-containing layer on the top of substrate to make lower refractive index compared with the substrate material is effective to prepare a film with gradation of refractive index on the top of the substance. To achieve such structure, we attempted to prepare hollow structure on the glass slide. And TiO₂ nanoparticles were employed as building blocks of the film to endow the photo induced self-cleaning activity.[2]

A glass substrate with silica layer was hydrophilized by alternative adsorption of oppositely charged linear polymers (Layer-by-Layer method). Cubic submicron calcite particles were casted onto the glass substrate by dip coating method. Then Layer-by-Layer deposition of charged polymers was applied to the glass substrate again. The positively charged glass was immersed into the titania nanoparticle dispersion. Then the glass plate heated to fuse the surface of titania particles to connect each other and fix their location. Polymer molecules were burnt out during this process. The glass slide with calcite / titania film was immersed in hydrochloric acid to remove calcite. Finally the glass with titania film was calcined again and obtain hollow titania coated glass. The obtained film was observed by FE-SEM, and analyzed by EDX. Optical property was evaluated by UV-vis absorption spectroscopy. And the self-cleaning properties were evaluated by contact angle recovery of the oleic acid and heptanes casted surface.

Many voids were seen in the titania particles accumulated layer. Transmittance of visible light was increased for the hollow structured titania film compared to those of glass substrate surface or the dense titania surface of film on the glass substrate. And the water contact angle of the oil wetted surface was rapidly decreased by irradiation of UV light.



Scheme : Preparation of hollow structured TiO₂ layer on top of glass substrate with calcium carbonate template.

References

- [1] Raut et al., Energy & Environmental Science (2011), 4(10), 3779-3804.
 [2] Fujishima et al., Surface Science Reports (2008), 63(12), 515-582.

Nano-mechanical characterisation of pea protein shell encapsulates produced via ultrasound

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Microcapsules produced via a one-step ultrasonic method are of particular interest in industry due to the simplicity of production of these capsules, and can be used in the food and personal care products. Our study investigated the ultrasound synthesis of microcapsules consisting of a pea protein isolate shell and a tetradecane core using high intensity ultrasonication at 20 kHz to form the m emulsion and crosslink the shell. The pea protein isolate was denatured via sonication in either PBS buffer at pH 7.4 or Tris/HCl buffer at pH 8. It was found that the sonication increased the solubility of the pea protein, which was confirmed by the sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) analysis. This analysis also showed that the increase in solubility due to using Tris instead of PBS stems from PBS indiscriminately shielding the exposed charged groups in the proteins, and preventing charged interactions and hydrogen bonding.

The microcapsules made from the denatured pea proteins were compressed using Atomic Force Microscopy (AFM) and analyzing the force spectra via Reissner's model. This showed that the strongest capsules were made with the Tris buffer, with a stiffness ranging from 9.9 to 18.2 mN/m, and a Young's modulus of 1.19 to 2.35MPa. The weaker PBS buffered capsules became weaker as further denaturation occurred as expected from our mechanism, with stiffness ranging from 9.5 to 22nN/M and Young's modulus ranging from 1.2 to 0.58MPa. The PBS produced thicker shells of the same stiffness. The shells were also tested for their stability, where both systems were stable for 1 month at 4°C.

Complexation of aromatic surfactants

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Bioactive surfactants are molecules with broad applications as complexation agents, antimicrobials or transfections agents [1]. Some hydrophobic ethers obtained from 4-nitro-3-hydroxybenzoic acid have shown to be active in enzymatic processes [2]. These compounds also show antimicrobial activity. Complexation of hydrophobic molecules with cyclodextrins could enhance the bioavailability and also improve properties such as solubility and stability [3].

Based on these considerations, we synthesized an octyl ether of 4-nitro-3-hydroxybenzoic acid, characterized the aggregation of this compound and its complexation with α and β cyclodextrins. After surface tension measurements, we obtained a CMC for this compound.

The ROESY spectrum shows that the aliphatic chain of the surfactant molecule protrudes into the cavity of both cyclodextrins.

[1] Yoon, K.; Jackman, J. A.; Min C. K.; Nam-Joon C.; *Langmuir*, 2015, **31**, 10223

[1] Shin, H.; Gennadios, H.; Whittington, D.; Christianson, D. W.; *Med. Chem.* 2007, **15**, 2617

[2] Mura, P.; *J of Pharmaceutical and Biomedical Analysis*, 2015, **113**, 226

Preparation, physico-chemical characterization and in vitro test of a Silybin–phospholipid complex encapsulated into liposomes.

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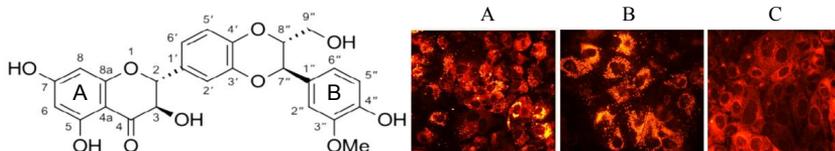
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Silybin is the main polyphenolic component of silymarin, a flavonoid complex extracted by the milk thistle plant *Silybum marianum*. Silybin possesses many health-promoting activities, such as antioxidation, anticancer and hepatoprotective [1]. However, the benefits are curtailed by its extremely poor water solubility [2]. Consequently, the bioavailability and therapeutic effective of silybin is also limited. Nanotechnology is an available approach to solving these issues. Currently, the efficacy of natural extracts may be improved through their incorporation into liposome, thanks to their versatility to load and protect unstable/photosensitive molecules having different structure and molecular weight, and their ability to facilitate and control the delivery of the loaded drug to the target. Here, we tested a formulation based on the encapsulation of a silybin–phospholipid complex, commercially available with the trade name Siliphos™, into liposomes to yield a new type of supramolecular aggregates, also called *Phyto-Liposomes* [3].

First, we set up a simple preparation protocol through the reverse-phase evaporation method and investigated the physico-chemical properties of the obtained liposomal suspensions. A careful investigation of host-guest interactions was carried out by performing UV–vis, spectrofluorimetry and NMR experiments both in aqueous and non-polar solvents to probe the influence of phospholipids on the electronic properties of silybin and its propensity to engage H-bonding with the lipid headpolar groups. Then, it was demonstrated the ability of phyto-liposomes to be internalized in human hepatoma Huh7.5 cells, being 2.4 fold more efficient than the pristine silybin. Finally, the new formulation was tested on cell systems supporting HCV replication and infection, and its spectrum of pharmacological activities was compared with that of the active principle dissolved in DMSO revealing a three hundreds fold more potent pharmacological activity [4]. A striking anti-viral effect was also manifested by empty liposomes used as control. We suspect that the presence of a minor non-phospholipidic component in the raw lecithin used to produce liposomes might be responsible for the inhibitory activity observed by naïve vesicles.

This research was supported by MIUR-PRIN 411 2010–2011, Project No. 2010BJ23MN_006.



Left: Molecular structure of silybin. **Right:** Fluorescent microphotographs at 40X of Huh7.5 human hepatoma cellular monolayers incubated at 37°C for 72 h with (A) Liss-Rhod-PE labelled phyto-liposomes loaded with silybin; (B) Liss-Rhod-PE labelled empty liposomes; (C) free red-emitting Liss-Rhod-PE labelled phospholipid.

References.

- [1] S.J. Polyak, C. Morishima, V. Lohmann, S. Pal, D.Y. Lee, Y. Liu, T.N. Graf and N.H. Oberlies, *Proc. Natl. Acad. Sci.* 2010, **107**, 5995.
- [2] G. Yang, Y. Zhao, Y. Zhang, B. Dang, Y. Liu and N. Feng, *Int. J. Nanomedicine*, 2015, **10**, 6633.
- [3] R. Angelico, A. Ceglie, P. Sacco, G. Colafemmina, M. Ripoli and A. Mangia, *Int. J. Pharm.* 2014, **471**, 173.
- [4] M. Ripoli, R. Angelico, P. Sacco, A. Ceglie and A. Mangia *J. Biomed. Nanotech.* 2016, **12**, 770.

Exploring the impact of molecular weight of fucoidan polysaccharides on the adsorption of protein to a PEM surface

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Wound care is an area of active research where surface and materials chemistry has the potential to improve healing outcomes for patients, through the creation of bioactive wound dressings. Polyelectrolyte multilayer (PEM) films have been shown to be an effective method of constructing surface coatings that can be applied to different surfaces to encourage tissue repair and growth. Naturally occurring biopolymers show great promise as biocompatible, bioactive components for PEM systems in wound care.

Fucoidan, a polysaccharide mainly extracted from seaweeds, has the ability to bind and protect biomolecules in wound fluids to promote healing. This work is focused on investigating two different molecular weight fractions of fucoidan in PEMs (in combination with chitosan, a well-studied biopolymer for biological applications) and their interactions with bovine serum albumin (BSA) as a model protein. The two fractions encompass low molecular weight fucoidan (peak MW 12.2 kDa) and unfractionated fucoidan (peak MW 61.7 kDa) from the seaweed species *Fucus vesiculosus*.

The layer-by-layer (LbL) build-up of the fucoidan-based PEMs, and their interactions with BSA, have been monitored using zeta-potential measurements, Quartz Crystal Microscopy with Dissipation monitoring (QCM-D), and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). Similar build-up has been observed for both systems. However, protein adsorption is seen to be very different, with low molecular weight fucoidan PEMs giving rise to lower adsorption, and a degree of PEM degradation due to BSA-fucoidan complexation. The implications of these observations for the use of fucoidan PEMs in wound dressings will be discussed.

Composition dependent Equation of State of Cellulose Based Plant Tissues

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Wood consists of parallel cylindrical cells. Cell walls so-called "wood materials" are constituted by a complex, highly anisotropic and hierarchically organized nanocomposite, characterized by stiff crystalline cellulose nanofibers, parallel to each other, embedded in a softer and less anisotropic matrix of hemicelluloses and lignin. This matrix is hygroscopic, and it swells with increasing humidity. Consequently, wood cells undergo large dimensional changes.

We developed a minimal model of wood secondary cell walls to predict water absorption, in the form of an Equation of State (EOS) that represents water sorption isotherm in wood and osmotic pressure variations versus swelling. Starting from compositional and structural considerations, and including chemical and mechanical terms, modelization leads to a multi-scale force balance, in which molecular and macroscopic forces between wood building blocks that are responsible for the solvent uptake are independently considered and then balanced.

In the present communication, we will compare the expected experimental EOS (i.e pressure vs distance) in four different cases: 1) the standard compression wood, 2) the hemicellulose-rich example found in mistletoe berries from *Viscum album*, 3) the lignin-rich example composed by coir fibers, 4) with synthetic cellulose gel made of osmotically compressed cellulose crystals, separated by aqueous solution without lignin or hemimethylcellulose.

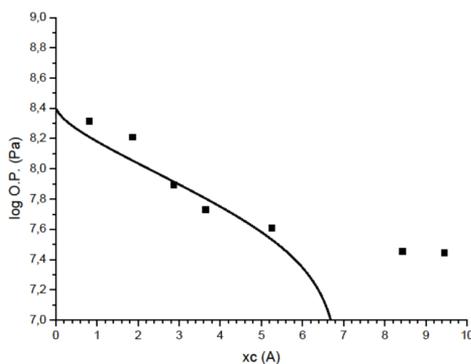


Figure 1 Swelling in terms of center-to-center distance of cellulose nanocrystals as a function of osmotic pressure (OP): experimental data of mistletoe (black dots) and calculated model of compression wood (black line)

Cu-Zn and Cu-Zn-Co nanosized mixed oxides for biocide action against *Escherichia coli*

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Single oxides nanoparticles, especially CuO, ZnO and Co₃O₄ [1-2] proved to be an efficient tool against *E. coli*. On the other hand, mixed oxides are quite often employed in a large number of processes, as more performing than the single oxides [3].

Here we present the enhanced effects of nanosized mixed Cu/Zn and Cu/Zn/Co oxides against *E. coli*. The mixed oxides were synthesized from hydroxycarbonates precursors and fully characterized by XRD, IR and SEM, hence their structure and size were determined. The metal oxide nanoparticles were dispersed thoroughly in a culture medium, and *E. coli* bacteria were cultivated on Tryptic Soy Agar plates containing different concentrations of metal oxide nanoparticles (50-100-200-400 µg/mL). Bacteria were counted in terms of colony forming units (CFU). *E. coli* counts decreased in the culture medium containing metal oxide nanoparticles, and the dose-response relationship was calculated [4].

The nanosized mixed oxide nanoparticles exhibit a higher biocidal power against *E. coli* compared to the corresponding single oxides. Furthermore, tests were performed also in comparison with single oxides mechanically mixed in the same proportion of the solid solution mixed oxides. The increase in concentration of nanoparticles, also increases the bacterial inhibition rate. The highest viability reduction values (> 99%) were obtained at the highest doses with the longest expositions.

[1] Brayner R., S.A. Dahoumane, C. Yéprémian, C. Djediat, M. Meyer, A. Couté, F. Fiévet, *Langmuir* 2010, **26**(9), 6522.

[2] Azam A., A. S. Ahmed, M. Oves, M.S. Khan, A. Memic, *Int. J. Nanomed.* 2012, **7**, 3527.

[3] Wachs I. E., K. Routray, *ACS Catalysis*, 2012, **2**, 1235.

[4] Yong-Wook Baek, Youn-Joo A., *Science Total Environ.* 2011, **409**,1608.

Injectable peptidic hydrogels for bone tissue repair and regeneration

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The ongoing growth in the incidence of bone injuries and diseases is producing an increment in the demand of medical and healthcare resources, with an urgent need to identify suitable alternatives to current common clinical treatments. In this context, bone tissue engineering is part of an emerging interdisciplinary field that applies the principles of engineering and life sciences towards the development of biological substitutes. Peptide hydrogels may be used in this context as biocompatible and biodegradable materials suitable for cell encapsulation and for the controlled spatial and temporal delivery of biomolecules (e.g. growth factors) able to direct cell differentiation.

Recently, we developed an enzymatic approach for the preparation of injectable, self-assembling materials based on Fmoc-oligopeptides¹. The reaction products (Fmoc peptides) spontaneously self-assemble in water to originate fibrils, that become entangled to form a three-dimensional structure of fibers with a diameter of approximately 7 nm, as evidenced by atomic force microscopy (AFM) measurements. Macroscopically, a stable, self-supporting hydrogel material is produced. These materials can be used as controlled drug delivery systems for a wide spectrum of bioactive molecules² and may enhance cell production of growth factors³. Our results suggest the possibility of using Fmoc oligopeptides as building blocks for a new class of injectable scaffolds that could play an important role in bone regeneration, i.e. to reconstruct anatomical defects caused by cancer surgery, malformations and trauma. We employed such hydrogels for the preparation of composite materials specifically designed for bone tissue regeneration. These tailor-made hydrogel systems contain biopolymeric spheres delivering bioactive molecules, as well as pure and substituted calcium phosphate (CaP) nanoparticles to provide bioactivity, osteoconductivity and improved mechanical properties. The morphological and viscoelastic properties of the synthesized hydrogels were investigated and their biocompatibility with different mammalian cells was assessed. Ongoing work is aimed at investigating the biological properties of the composite hydrogel systems, in terms of adhesion, growth and differentiation of human mesenchymal stem cells.

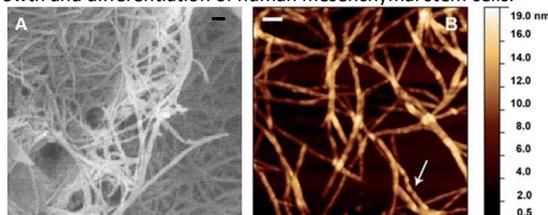


Fig.1 SEM (A) and AFM (B) images of Fmoc-Phe₃ hydrogels. Scale bars = 100 nm.

[1] L. Chronopoulou et al. *Soft Matter*, 2010, **6**, 2525.

[2] L. Chronopoulou et al. *Soft Matter*, 2014, **10**, 1944.

[3] L. Chronopoulou et al. *Soft Matter*, 2012, **8**, 5784.

Antifolate functionalized SERS-active nanovector: from cell targeting to theranostics

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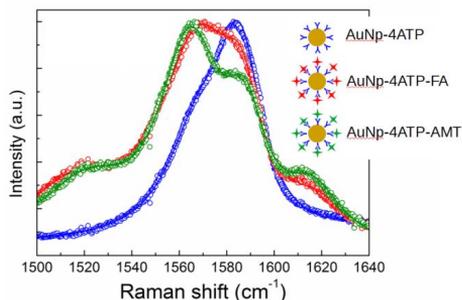
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Nowadays, early diagnosis of cancer is one of the main biomedical proposes that involve physics, chemistry, biology and nanotechnology. Over the last few years, several methods have been tested and developed from standard assays to really innovative techniques. One of the most exploited technologies for the early detection of cancer involves the well-known, molecular based SERS-active nanovectors [1,2] for selective bio-recognition of cancer cells. A SERS-active nanovector consists in a metallic nanoparticle (Np) core functionalized with a suitable molecular layer. Due to the excitation of the electron cloud inside the metal nanostructure, when the Np is illuminated by a light beam (visible/IR), the localization of extremely intense electromagnetic fields occurs at the metal surface [3]. This field can be exploited as a spectroscopic probe for Surface Enhanced Raman Scattering (SERS) experiments. Beside specific bio-recognition, the advantages of SERS in biomaterials investigations are the possibility of tracing Nps across sample, to produce imaging and, if necessary, to perform photothermal effect therapy. Nanovectors are often functionalized with antibodies or other small molecules, which are chosen based on specific properties of cancer cells (e.g. overexpression of certain receptors or membrane protein, differences in the cell cycle, etc.) [2,4]. In our recent work, we proved high sensitivity and selectivity of folate-conjugated Nps and suggested the possibility to add theranostic features by substituting folate with antifolate drugs [2]. We are here presenting our result in the characterization of different theranostic nanovectors (functionalized with folate and with antifolates, as aminopterin and methotrexate) performed through SERS, UV-visible and Z-potential measurements. We proved the successful functionalization of the Nps and we investigated the different spectroscopic features of these nanovectors (Fig.1). Moreover, through a titration experiment, we are able to predict how many molecules are covalently bound with the Nps.

Fig.1: SERS comparison of the three nanovectors in the region of 1585 cm^{-1} : in blue the first step of functionalization of gold nanoparticles with 4-aminothiophenol (4-ATP); in red the second step of functionalization with folic acid (FA) and in green the antifolate conjugation with aminopterin (AMT).



[1] Salvati et al., *Nanomedicine* 10.23 (2015): 3495-3512.

[2] Fasolato et al., submitted to *Biomaterials* (2016).

[3] Fan et al., *Science* 328.5982 (2010): 1135-1138.

[4] Pallaoro et al. *Proceedings of the National Academy of Sciences* 108.40 (2011): 16559-16564.

Surface Enhanced Raman Microimaging Allows for Screening Single Cells With Different Folate Binding Capability

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In the last few decades, the development of novel spectroscopic techniques, often combining a very high sensitivity with huge spatial resolution, allowed the possibility of investigating down-scaled phenomena, as for example biochemical and biophysical processes in living systems. Among these, Surface Enhanced Raman Spectroscopy (SERS) is based on plasmonic excitations in metallic nanostructures [1]. The oscillation of the free electron gas in metallic nanoparticles (Nps) causes the confinement of strong electromagnetic fields, which can be used for spectroscopy, at the Np surface. Moreover, SERS-labelled nanomaterials, such as properly functionalized Nps, paved the way for applications in the emerging field of nanomedicine [2], e.g. in the early detection of cancer. Addressing this problem, we designed a biocompatible system based on SERS-labelled gold Nps conjugated with folic acid, a biomolecule essential in cell reproduction. Folic acid receptors are overexpressed in many types of cancer cells, as these reproduce more frequently than ordinary ones [3]. The presence of folate receptors on the membrane strongly depends on the physiology of the cell line considered. In this presentation, after briefly exposing the system characterization, we will illustrate the interaction of our nanovector with different cell cultures. SERS mapping, performed on different cells, allowed us to detect our nanovector bound to the cell membrane and, therefore, to map the presence of the folate receptors even at subcellular level. A SERS screening protocol used to measure wide cell populations allowed us not only to discriminate between healthy and cancer cells, but also to distinguish two types of cancer cells showing differential folate-receptor expression (see Fig. 1) [4]. These results suggest the possibility to combine the nanovector plasmonic properties with opportune chemical conjugations, aiming at SERS-based biophysical investigations, e.g. mapping the molecular receptors on cell membranes. Preliminary results on the functionalization of the nanovector with antifolate drugs will also witness the potential theranostic application of this nanovector.

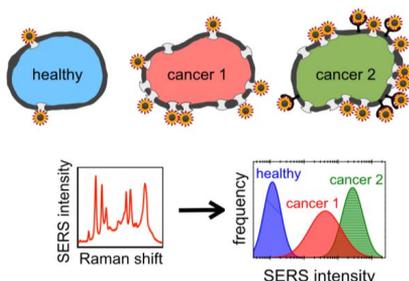


Figure 1: Sketch of the experiment, which consists in the treatment of three different cell lines (one healthy, two cancerous) with the folate-functionalized nanovector. By measuring the average SERS signal on the cells, it is possible to discriminate between healthy and cancer cells and to distinguish three different populations, namely HaCaT (human keratinocytes, “healthy”), PC-3 (prostatic cancer cells, “cancer 1”) and HeLa (cervical cancer cells, “cancer 2”).

- [1] W. Kiefer, S. Schlücker (ed.), John Wiley & Sons (2011);
- [2] S.M. Janib, et al., *Advanced drug delivery reviews* 62 (2010) 1052-1063;
- [3] C.M. Paulos, et al., *Mol. Pharmacol.* 66 (2004) 1406;
- [4] C. Fasolato, et al., submitted to *Biomaterials*.

Remote loading of voacamine in cationic liposomes

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The inclusion of an active principle in liposome formulations can increase its potential applications by i) rendering it soluble in water, ii) controlling its pharmacokinetics and biodistribution, iii) increasing its accumulation in target tissues and iv) avoiding or reducing its accumulation in healthy tissues, thus reducing toxic effects. Compounds with basic/acidic properties can be concentrated into the liposome aqueous compartment in response to specific pH transmembrane gradients ($pH_{in} < pH_{ext} / pH_{in} > pH_{ext}$). This method exploits the different permeability of the lipid bilayer to the charged and the neutral form of small lipophilic compounds containing titratable groups, in fact neutral molecules permeate the lipid bilayer of liposomes many orders of magnitude faster than their charged forms [1,2].

This methodology was applied to the inclusion of voacamine (Figure 1), a bisindolic alkaloid that displays several pharmacological properties [3,4], into cationic liposomes by a remote loading technique.

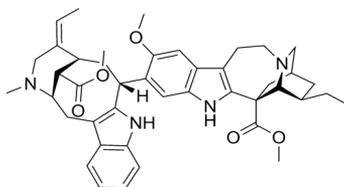


Figure 1 Voacamine structure.

Acknowledgements LG thanks the FIRB project 2012 RBFR12BGHO for the financial support.

- [1] G. Haran, R. Cohen, L. K. Bar and Y. Barenholz, *Biochim. Biophys. Acta*, 1993, **1151**, 201.
- [2] S. Hwang, Y. Maitani, X. R. Qi, K. Takayama and T. Nagai, *Int. J. Pharm.*, 1999, **179**, 85.
- [3] D. Ramanitrahambola, P. Rasoanaivo, S. Ratsimamanga-Urverg, E. Federici, G. Palazzino, C. Galeffi and M. Nicoletti, *Phytother. Res.*, 2001, **15**, 30.
- [4] S. Meschini, M. Marra, A. Calcabrini, E. Federici, C. Galeffi and G. Arancia, *Int. J. Oncol.*, 2003, **23**, 1505.

Functionalized lipid bilayer on LbL-microcarriers – mimicking a cell for targeted drug delivery

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Common systemically applied therapeutics may cause side effects due to non-targeted transport and highly dosed amounts of active agents. Therefore, new drug delivery systems are needed which exhibit a targeted transport, time controlled release and are able to transport multiple active agents safely and in a defined dosage in just one carrier system.

One promising approach which provides all these features is based on the combination of the (1) Layer-by-Layer-technique (LbL) with the (2) Liposome-Spreading-technique (LS) and (3) antibody surface modification.

(1) The LbL-technique allows the integration of defined amounts of multiple active agents into specific layer depth and/or the microcarrier core, facilitating a time dependent release within the targeted cell [1,2].

(2) The LS-technique uses the fusion of small unilamellar vesicles on surfaces to create a lipid bilayer, reducing the risk of opsonization and enhancing biocompatibility [3].

(3) Specific functionalized lipids (e.g. biotinylated lipids) can be easily integrated into this lipid bilayer to provide a binding site for specific antibody coupling and targeted cell interaction.

The combination of all three techniques results in a smart drug delivery system with unique features. However, for the fabrication of an effective microcarrier system it is essential to create a homogeneous and regular lipid bilayer on top of the microcarrier to inhibit unspecific serum protein interaction and to reduce microcarrier uptake by non-targeted cells.

Using SiO₂ microparticles and an LbL multilayer consisting of protamine sulfate and dextran sodium sulfate, we could show that the lipid bilayer formation is strongly influenced by the applied lipid mixture as well as the LS coating conditions. For instance, the integration of the functional lipid PE-PEG-biotin into a homogeneous POPS/POPC lipid membrane leads to a concentration dependent disturbance of the lipid bilayer homogeneity [4].

In this study we demonstrate that suitable adjustments of the incubation conditions (e.g. concentration of liposomes, microcarriers and functional lipid PE-PEG-Biotin) can be made in order to obtain a homogenous functionalized lipid bilayer on top of LbL-microcarriers. Such microcarriers exhibit a highly specific streptavidin as well as optimal antibody binding. Cell approaches show the specificity and adaptability of the smart drug delivery system.

Acknowledgements The research was made possible by funding from the German Research Foundation (DFG), the European Union and the Free State of Saxony and was supported by the DFG project RE 2681/2-2 and the DFG graduate school 185 "Leipzig School of Natural Sciences Building with Molecules and Nano-objects" (BuildMoNa).

- [1] U. Reibetanz, M. Schönberg, S. Rathmann, V. Strehlow, M. Göse and J. Leßig, *ACS Nano*, 2012, **6**(7), 6325-6336.
- [2] B. G. De Geest, S. De Koker, G. B. Sukhorukov, O. Kreft, W. J. Parak, A. G. Skirtach, J. Demeester, S. C. De Smedt and W. E. Hennink, *Soft Matter*, 2009, **5**, 282-291.
- [3] M. Fischlechner, M. Zaulig, S. Meyer, I. Estrela-Lopis, L. Cuéllar, J. Irigoyen, P. Pescador, M. Brumen, P. Messner, S. Moya and E. Donath, *Soft Matter*, 2008, **4**, 2245-2258.
- [4] M. Göse, P. Pescador and U. Reibetanz, *Biomacromolecules*, 2015, **16**(3), 757-768.

Interactions of lipidic cubic phase nanoparticles with lipid membranes

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Phospholipid monolayers and bilayers have been used as model systems for biological membranes in studies of the effect of drug and drug carriers on the properties of the biomembranes.

The interactions of liquid-crystalline monoolein (GMO) cubosome nanoparticles with various model lipid membranes spread at the air-solution interface by the Langmuir technique were investigated. Cubosomes have attracted attention as potential biocompatible drug delivery systems, and thus understanding their mode of interaction with membranes is of special interest. Cubosomes spreading at the air-water interface as well as interactions with a monolayer of 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) compressed to different surface pressures were studied by monitoring surface pressure-time dependencies at constant area. Progressive incorporation of the nanoparticles was shown to lead to mixed monolayer formation. The concentration of cubosomes influenced the mechanism of incorporation, as well as the fluidity and permeability of the resulting lipid membranes.

Brewster angle microscopy images reflected the dependence of monolayer structure on the cubosomes presence in the subphase. A parameter C_{sat} was introduced to indicate the point of saturation of the lipid membrane with the cubosomal material. This parameter was found to depend on the surface pressure showing that the cubosomes disintegrate in prolonged contact with the membrane, filling available voids in the lipid membrane. At highest surface pressures when the layer is most compact, the penetration of cubosomal material is not possible and only some exchange with the membrane lipid becomes the route of including GMO into the layer. Comparative studies of the interactions of lipids with various head group charges with cubosomes suggest that at high surface pressure the exchange of lipid component between the monolayer and the cubosome in its intact form may occur.

Nanocomposite membraneous vesicles for controlled encapsulation, transport and release

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Functional nano-engineered materials formed by natural or biocompatible components are necessary for bio-medicine and other important fields of science and engineering [1].

We present results of design, preparation and characterization of new nanocomposite biocompatible membraneous vesicles based on the interfacial polycomplexes of biogenic lipid phosphatidylcholine, synthetic amphiphilic polyamine stearyl spermine, polyelectrolytes and functional inorganic nanoparticles (magnetic iron oxide nanoparticles and metallic Au nanoparticles with mean diameter less than 10 nm). Amphiphilic water-insoluble polyamine stearyl spermine was synthesized and characterized by FTIR and NMR spectroscopy techniques.

Nanocomposite membraneous vesicles were prepared successfully by adsorption of colloid magnetite and gold nanoparticles onto the membrane surface of hybrid phosphatidylcholine/stearyl spermine liposomes with diameter 100-200 nm preliminarily formed using conventional ultrasound method. The obtained nanocomposite vesicles were characterized by transmission electron microscopy, AFM, electron magnetic resonance technique, laser light scattering and electrophoresis techniques.

The study of the effects of ultrashort high strength electromagnetic pulses and of applied external magnetic field on those vesicles have been carried out and the non-thermal decapsulation effect and efficient release of encapsulated model compound was observed. TEM and AFM data showed that the structure of vesicles was changed substantially by those external physical factors. It was experimentally demonstrated and theoretically proved that the presence of conducting nanoparticles in the vesicle membrane can decrease substantially the voltage of applied electric pulses resulting in the substantial membrane structural changes and efficient vesicle "opening" [2]. It was found that additional polyelectrolyte complex layers formed on the surface of nanocomposite vesicles can change substantially the physical-chemical characteristics of such vesicles and their stability and resistivity against external stimulating physical factors as electromagnetic fields.

The data obtained give evidence that the synthesized stable biocompatible nanocomposite magnetic membraneous vesicles can be prospective for development of novel efficient means for encapsulation, controlled spatial localization, remote non-thermal release of various compounds in aqueous media for biomedical controlled drug delivery and other applications.

Acknowledgements This work was supported by Russian Scientific Fund (Grant 14-12-01379).

[1] M. Giersig and G.B. Khomutov (Editors), *Nanomaterials for application in medicine and biology*, 2008, Springer, Dordrecht, The Netherlands.

[2] Yu.V. Gulyaev, V.A. Cherepenin, V.A. Vdovin, I.V. Taranov, A.A. Yaroslavov, V. P. Kim and G.B. Khomutov, *J. Communications Technology and Electronics*, 2015, **60**, 1097.

Polyelectrolyte films with the „antifouling” properties

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The formation of bacterial slime or biofilms at the surface of biomaterials, e.g. diagnostic devices and a variety of biomedical implants, represents a major medical problem leading, if untreated, to chronic microbial infection. One of the most significant issue is the process of biofouling, i.e. the unwanted adsorption of proteins occurring at surfaces exposed to solutions containing biological material. Therefore, the development of the „antifouling” coatings protecting against non-specific protein adsorption or bacteria and fungi colonization are an important area of research within a broader field of biointerface science. The goal of our work was to develop the method for formation of ultrathin anti-adhesive coatings for biomedical applications. The Layer-by-Layer (LbL) technique of electrostatic self-assembly of charged nanoobjects has been proved to be a versatile technique for the formation of multilayer ultrathin films. The method is based on the sequential adsorption of the oppositely charged species on solid surfaces [1]. The „LbL” method, which is considered as one of the most promising techniques of surface modification, can be used for formation of those coatings.

Immobilization of neutral hydrophilic polymers (e.g. poly(ethylene glycol)) (PEG) at surfaces is one of the promising methods to reduce non-specific adsorption of proteins or microorganisms. Pegylation of polyelectrolyte films is expected to reduce/eliminate the non-specific adsorption of proteins at surface as well as the bacterial colonization of implanted materials. Synthesized copolymers of poly(glutamic acid) or poly(L-lysine) with grafted PEG chains with various grafting ratio and various PEG chain lengths were used for formation of the external pegylated layer of multilayer films. The synthesized copolymers were characterized by NMR method. The biofouling process was investigated by Quartz Crystal Microbalance (QCM) by studying the adsorption of different proteins: HSA, Fibrinogen as well as proteins from Human Serum. We found that pegylated films have antifouling properties decreasing adhesion of microorganism to the ultrathin films.

Acknowledgements: The financial support of NCN project UMO 2012/07/N/ST5/00173 and Norwegian Financial Mechanism grant Pol-Nor/199523/64/2013 NanoNeucar.

[1] G. Decher, J. B. Schlenoff, *Multilayer Thin Films Sequential Assembly of Nanocomposite Materials*, 2002, ISBN 978-3-527-31648-9 - Wiley-VCH, Weinheim, Germany.

Thermodynamic analysis of Human Serum Albumin interaction with uremic toxins.

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Uremic toxins accumulate in large numbers in the blood of patients suffering from chronic kidney disease (CKD) and interact detrimentally with plasma proteins [1-3]. Thereby, several protein-bound toxins mainly bind to the transport protein Human Serum Albumin [1]. A well-studied toxin is Indoxylsulfate (IS), where binding to HSA is known to inhibit the drug binding ability of the protein in addition to structural modifications []. Another representative member of small hydrophobic uremic toxins, which has not been well studied yet is Phenylacetic acid (PhAA) [4]. Jankowski et al. have achieved a more effective clearance of PhAA and IDS under high ionic strength, where the fraction of uremic toxins was significantly decreased during hypertonic predilution hemodiafiltration [5]. However the mechanisms underlying the interaction have not been fully explored. Furthermore, albumin is modified in pathophysiological condition as in chronic renal failure: urea-induced carbamylation on multiple lysine and arginine chains occur [6]. To elucidate thermodynamic information, isothermal titration calorimetry (ITC) is the best method of choice to measure enthalpy, entropy and binding affinity directly in one experiment [7]. We therefore use ITC to investigate the binding of IS and PhAA to HSA under the influence of varying temperature and ionic strength to access full thermodynamic information. Additionally, the effect of in vitro urea modification of HSA upon its binding affinity towards the uremic toxins is studied.

It is found that two PhAA molecules bind to HSA in a sequential binding process with a binding constant k_b in the order of $\approx 10^4$ and $\approx 10^3$. In contrast, IDS binds much stronger to HSA with a total of 3 molecules to a high and low affinity binding site in the order of $\approx 10^5$ and $\approx 10^3$. All binding isotherms show negative binding affinity dependency with increasing temperature and higher ionic strength. Representative binding isotherms are shown in Fig. 1 with the binding of PhAA to native HSA at (a) different temperature and constant ionic strength $I=20\text{mM}$ and (b) constant temperature 37°C and varying ionic strengths.

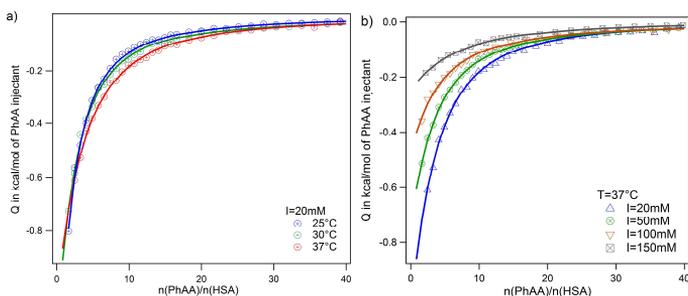


Fig. 1: Binding isotherms for the binding of PhAA to native HSA. (a) Influence of temperature varying from room to body temperature at ionic strength $I=20\text{mM}$. (b) influence of ionic strength at body temperature 37°C .

- [1] Y. Itoh, A. Ezawa, K. Kikuchi, Y. Tsuruta, T. Niwa, *Anal. and Bioanal. Chem.*, 2012, **403**, 1841.
- [2] E. Devine, D. H. Krieter, M. R uth, J. Jankowski, H. D. Lemke, *Toxins*, 2016, **6**, 416.
- [3] S. Liabeuf, T. B. Dr ucke, Z. Massy, *Toxins*, 2011, **3**, 911.
- [4] T. Sakai, A. Takadate, M. Otagiri, *Biol. Pharm. Bull.*, 1998, **18**, 1755.
- [5] F. B ohringer, V. Jankowski, P. R. Gajjala, W. Zidek, J. Jankowski, *ASAIO Journal*, 2015, **61**, 55.
- [6] A.H. Berg, C. Drechsler, R. Thadhani, S.A. Karumanchi et al., *Science Translational Medicine*, 2013, **5**, 175.
- [7] S. Leavitt, E. Freire, *Curr. Opin. Struct. Biol.*, 2001, **11**, 560.

Phosphatidylcholine with conjugated linoleic acid in fabrication of custom-designed lipid nanocarriers

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Exploration of novel lipid-based formulations has been an aim for researchers over the last decades. Lipid nanoparticles have been extensively studied as bioactive agent carriers in the biochemical and biotechnological fields. In our studies we have provided properties of two different types of lipid nanocarriers, i.e., solid lipid nanoparticles (SLN) and nanostructured lipid carriers (NLC) prepared via high pressure homogenization method. The choice of surfactants in the structural design of the lipid nanoparticles is one of the most significant approaches to achieve nanosystems with desirable parameters, that acquire both good stability and requested physical state.

The present work has been carried out to explore the potential for fabrication of stable and nearly monodisperse lipid nanoparticles stabilized by two of recently synthesized phosphatidylcholine-type surfactants, i.e., 1,2-distearoyl-sn-glycero-3-phosphocholine (Fig.1a) and 1,2-di(conjugated)linoleoyl-sn-glycero-3-phosphocholine (Fig.1b), which are potential lipid prodrugs. The sizes of the studied nanosystems (about 100-200nm) along with the size distribution (below 0.3) were determined by dynamic light scattering (DLS), while shape and morphology – by atomic force microscopy (AFM). The physical state of the studied nanoparticles was characterized by differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The NLCs had a less ordered crystalline structure than the SLNs, which is conferred by the inclusion of the liquid lipid; in result, they had lower values for phase transition temperature and melting enthalpy. The delivery efficiency *in vitro* was evaluated with human cancer cell lines – epidermoid carcinoma (A431) and skin melanoma (MeWo) compared to normal human keratinocytes (HaCaT). The *in vitro* cytotoxicity evaluation of the studied nanosystems was performed after 24 and 48 hours using the MTT assay. The obtained results indicated an increased cytotoxicity of nanocarriers against cancer cells in relation to free phospholipids. The most significant antiproliferative effect was observed in the case of nanocarriers where the molar ratio of phospholipid to T80 was 1:1 and 3:1. Additionally, the nanocarriers based on 1,2-distearoyl-sn-glycero-3-phosphocholine revealed not significantly increased cytotoxic effect in melanoma cells. The most safe were the NLC nanocarriers where the molar ratio of phospholipid to T80 was 5:1.

Our results give new insights into the lipid nanoparticles containing phosphatidylcholine-type surfactants and may serve as guidelines for design and preparation of new delivery systems for pharmacological activity, including anti-cancer applications.

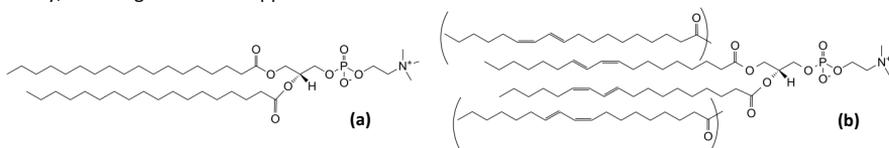


Figure 1 Structures of the studied phosphatidylcholine-type surfactants.

Acknowledgements

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Encapsulation of DNA by cationic and anionic disc-shaped bicelles

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Nanosize disc-shaped bicelles can be formed spontaneously by mixing long-chain lipids with short-chain lipids at suitable ratios with a relatively uniform size around a few tens of nanometers in diameter [1]. Bicelles can be doped with cationic or anionic long-chain lipids to vary their surface charges for interacting with various charged biomaterials and polyelectrolytes [2]. Charged bicelles can be used to pack the DNA for biomedical applications with the advantage of the size tenability and the relatively smaller size as compared with the encapsulation of DNA by liposomes. We demonstrated that both cationic lipid bicelle-DNA (CB-DNA) and anionic lipid bicelle-cation-DNA (AB-DNA) complexes can be prepared in aqueous solutions. As revealed by small-angle X-ray scattering and TEM, disc-shaped cationic bicelles and DNA form alternate layers in the one-dimensionally stacked aggregate. DNA molecules form ordered array encapsulated between the cationic bicelles with a DNA to DNA repeat distance of around 4~5 nm [3]. The number of the stacking layers can be easily varied from a few stacks to more than one hundred stacks by adjusting the doping percentage of the charged lipids. Such CB-DNA complexes are promising as a novel nonviral vector for gene delivery. It is also possible to form anionic bicelle-DNA complexes with the help of the divalent cation. The AB-DNA complexes can be formed in the investigated range of 10 to 100 mM calcium ion concentration using bicelles doped with 15% anionic lipid [4]. At above the critical calcium ion concentration, DNA can be packed more tightly and excess lipids are released from the DNA-ion-disk complexes to form the multilamellar ion-membrane complexes in coexistence with the AB-DNA complexes.

References

- [1] P.-W. Yang, T.-L. Lin, Y. Hu and U.-S. Jeng, *Chinese J. of Phys.*, 2012, **50**, 349.
- [2] P.-W. Yang, T.-L. Lin, Y. Hu and U.-S. Jeng, *Soft Matter*, 2015, **11**, 2237.
- [3] P.-W. Yang, T.-L. Lin, T.-Y. Lin, C.-H. Yang, Y. Hu and U.-S. Jeng, *Soft Matter*, 2013, **9**, 11542.
- [4] P.-W. Yang, T.-L. Lin, Y. Hu and U.-S. Jeng, *Soft Matter*, 2014, **10**, 2313.

MicroRNA detection through upconversion emission enhancement between NaYF₄:Yb,Er nanoparticles and carbon dots

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MicroRNAs are non-coding sequences of 20-25 nucleotides and they are important in the transcriptional mechanisms of gene expression. Many viruses such as HIV, Ebola, Hepatitis C, Dengue, etc. can encode and express specific viral miRNAs that help the viral replication facilitating the host infection [1]. Those miRNAs can be found in sera samples at relatively high concentration opening the possibility to be used as early diagnosis biomarkers [2]. We have developed a novel sensor for the detection of specific miRNA sequences that was based on graphene quantum dots (GQDs) and upconversion nanoparticles (UCNPs) functionalized with SiO₂ and single stranded DNA (ssDNA). The proposed sensor exploits the interaction between the sp² carbon atoms of GQDs and the ssDNA anchored on the UCNPs. This interaction brings the GQD to the surface of the UCNPs-SiO₂-ssDNA system enhancing the fluorescence emission of the upconversion nanoparticles. On the other hand, the hybridization of the ssDNA chains on the surface of the nanoparticles with their complementary miRNA sequence blocks the capacity of the UCNPs to interact with the GQD reducing the fluorescent enhancement that is dependent on the concentration of the miRNA sequence. Using a relative emission/upconversion measurements compared to a reference, the miRNA sensor showed a detection limit of 10 fM.

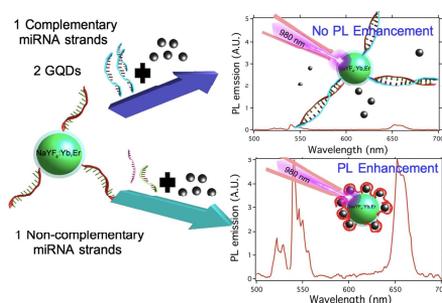


Figure 1. Schematic representation of the proposed sensor platform based on UCNPs-SiO₂-ssDNA and GQDs.

Acknowledgements. The financial support of this work was granted by Bill and Melinda Gates Foundation (OPP1128411) and Spanish Ministry of Economy and Competitiveness (MAT-2014-55065R).

- [1] Gilad, S.; Meiri, E.; Yogev, Y.; Benjamin, S.; Lebanony, D.; Yerushalmi, N.; Kushnir, M.; Cholakh, H.; Melamed, N.; Bentwich, Z.; Hod, M.; Goren, Y.; Chajut, A. *PLoS One*, 2008, **3**, 1.
- [2] Yeung, M. L.; Bennasser, Y.; Le, S. Y.; Jeang, K. T. *Cell Res.*, 2005, **15**, 935.

Functionalization of inorganic nanoparticles for specific applications

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By combining the properties of inorganic nanoparticles and the possibilities that offers the silica coating, it is possible to make nanoengineering. The silica coating method permits to obtain inorganic nanoparticles covered with a silica shell that can be controlled with nanometric precision. Thus, the production of structured nanoparticles with a remarkable homogeneity enables their use in different applications that will be defined by the functionalization done on its surface [1,2]. In this work, the surface of silica coated inorganic nanoparticles has been functionalized with DNA, a doxorubicin-photoactive molecule, and poly(ethylene glycol). The resulting hybrid nanomaterials demonstrate that the combination of the properties of the inorganic nanoparticles with specific molecules is a potential tool for the creation of advanced functional nanomaterials. What makes this strategy interesting is that is an open-source-like method that offers a high versatility making possible to combine almost any nanoparticle in the core with a wide variety of surface functionalization. For example, we have developed a photoresponsive material [3] based on $\text{NaYF}_4:\text{Yb,Tm}@SiO_2$ nanoparticles and its surface was functionalized with PEG and a derivative of the photoresponsive molecule *ortho*-nitrobenzylalcohol (*o*-NBA) that was conveniently modified so that, when the system was exposed to a light stimulus the drug Doxorubicin was released (see Figure 1).

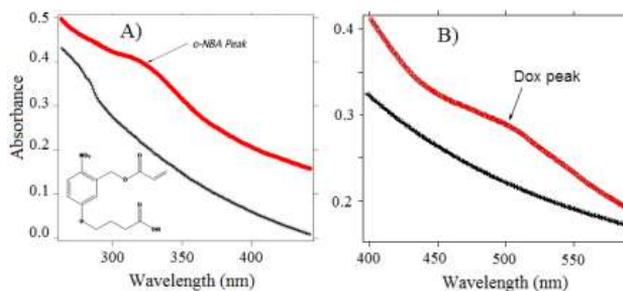


Figure 1. A) UV-Vis spectra of bare $\text{NaYF}_4:\text{Yb,Tm}@SiO_2$ nanoparticles (black) and the photoresponsive *o*-NBA-functionalized $\text{NaYF}_4:\text{Yb,Tm}@SiO_2$ nanoparticles (red). Inset: structure of the modified *ortho*-nitrobenzylalcohol photoresponsive molecule. B) UV-Vis spectra of the $\text{NaYF}_4:\text{Yb,Tm}@SiO_2$ nanoparticles (black) and Dox-loaded $\text{NaYF}_4:\text{Yb,Tm}@SiO_2$ nanoparticles (red).

Acknowledgements: The financial support of the Spanish MINECO (project MAT2014-55065R), the BSCH-UCM program for research groups (MATNABIO-911033). Paulino Alonso acknowledges the Spanish Ministry of Education for FPU Grant to perform this work (No. AP2010-1163).

- [1] H. Ding, Y. Zhang, S. Wang, J. Xu, S.C. Xu and G. Li, *Chem. Mater.*, 2012, **24**, 4572.
- [2] A. Guerrero-Martinez, J. Perez-Juste and L.M. Liz-Marzan, *Adv. Mater.*, 2010, **22**, 1182.
- [3] P. Alonso-Cristobal, O. Oton-Fernandez, D. Mendez-Gonzalez, J.F. Díaz, E. Lopez-Cabarcos, I. Barasoain and J. Rubio-Retama, *ACS Appl. Mater. Interfaces*, 2015, **7**, 14992.

Membrane interactions of mesoporous silica nanoparticles as carriers of antimicrobial peptides

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Membrane interactions are critical for the successful use of mesoporous silica nanoparticles as delivery systems for antimicrobial peptides (AMPs). In order to elucidate these, we here investigate effects of nanoparticle charge and porosity on AMP loading and release, as well as consequences of this for membrane interactions and antimicrobial effects. Anionic mesoporous silica particles were found to incorporate considerable amounts of the cationic AMP LLGDFFRKSKEKIGKEFKRIVQRIKDFLRNLPRTES (LL-37), whereas loading is much lower for non-porous or positively charged silica nanoparticles. Due to preferential pore localization, anionic mesoporous particles, but not the other particles, protect LL-37 from degradation by infection-related proteases. For anionic mesoporous nanoparticles, membrane disruption is mediated almost exclusively by peptide release. In contrast, non-porous silica particles build up a resilient LL-37 surface coating due to their higher negative surface charge, and display largely particle-mediated membrane interactions and antimicrobial effects. For positively charged mesoporous silica nanoparticles, LL-37 incorporation promotes the membrane binding and disruption displayed by the particles in the absence of peptide, but also causes toxicity against human erythrocytes. Thus, the use of mesoporous silica nanoparticles as AMP delivery systems requires consideration of membrane interactions and selectivity of both free peptide and the peptide-loaded nanoparticles, the latter critically dependent on nanoparticle properties.

Liposomal delivery of oligonucleotide therapeutics against antibiotic-resistant bacteria

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Microbial resistance to antibiotics has grown over the last few decades into a serious global threat [1], which must be tackled with innovative therapeutics. We propose to address it by coupling the action of a strong antibacterial, the bolaform cationic surfactant [12-bis-THA]Cl₂, with specifically engineered oligonucleotides (TFDs, Transcription Factor Decoys) that can block essential genomic targets in bacteria [2,3]. In order to improve the bioavailability and antibacterial activity of the [12-bis-THA]Cl₂/TFD complex, we incorporated it in fusogenic liposomal carriers with controlled composition and morphology. We investigate the effect of the inclusion of the bolaamphiphile in the lipid bilayer and optimize the encapsulation of the oligonucleotide. We characterize the structure of the liposomes by means of dynamic light scattering (DLS), Zeta potential measurements, small-angle X-ray scattering (SAXS), cryogenic electron microscopy (cryo-TEM), UV-Vis absorption and fluorescence spectroscopy. The antibacterial activity and cytotoxicity of these delivery systems are evaluated with *in vitro* assays, while confocal microscopy experiments on fluorescently labelled samples allow us to assess the delivery of the TFD into model bacterial systems (Figure 1).

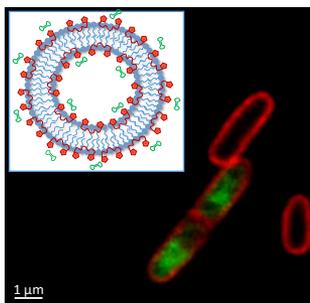


Figure 1 Confocal microscopy: liposomes containing the [12-bis-THA]Cl₂/TFD complex (green) are delivered into *E. coli* (red). Insert: schematic representation of the liposomes (blue = POPC/DOPE, red = [12-bis-THA]Cl₂, green = TFD).

Acknowledgements Research funded by the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n. 612338.

[1] E. Leung, D. E. Weil, M. Raviglione and H. Nakatani, *Bulletin of the World Health Organization*, 2011, **89**(5), 390.

[2] M. McArthur and M. J. Bibb, *Proceedings of the National Academy of Sciences*, 2008, **105**(3), 1020.

[3] M. Mamusa, C. Resta, F. Barbero, D. Carta, D. Codoni, K. Hatzixanthos, M. McArthur, D. Berti, *Journal of Colloids and Surfaces B: Biointerfaces*, 2016, **143**, 139.

A general approach to the encapsulation of glycoenzymes chains inside calcium alginate gel beads.

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In this work an enzyme encapsulation general approach, based on the use of calcium alginate hydrogels, is reported. Alginate gels are biodegradable and low cost and have been found to provide a good matrix for the entrapment of sensitive biomolecules. Alginate is an anionic polymer whose gelation occurs by an exchange of sodium ions from the polymer chains with multivalent cations, resulting in the formation of a three dimensional gel network. For gelation alginate is dripped into a calcium chloride solution. The cations diffuse from the continuous phase to the interior of the alginate droplets and form a gelled matrix. By means of this “external gelation method” beads with a diameter of few millimeters can be obtained (see figure 1).

The entrapment of enzymes in alginate beads suffers some disadvantages, like as low enzyme loading efficiency with reduction of the immobilization yields and reusability, related to the enzyme leakage from the large beads pores (cut off of about 100 kDa).

We used alginate beads to entrap, as model system, three glycoenzymes (trehalase, glucose oxidase and horseradish peroxidase) acting in series. Leakage of entrapped enzymes after gelation has been avoided using the biospecific complexation between concanavalin A and sugar residues of glycoenzymes to form large enzyme networks, that cannot go through beads pores. The aggregation process has been monitored by dynamic light scattering technique, while both enzyme encapsulation efficiency and leakage have spectrophotometrically been quantified. Moreover, operational stability of “as prepared” beads has been largely improved by a coating of alternated shells of polycation poly(diallyldimethylammonium chloride) and of alginate.

As a test for the effectiveness of the overall procedure, analytical bio-assays exploiting the enzyme containing beads have been developed for the optical determination of glucose and trehalose [1].

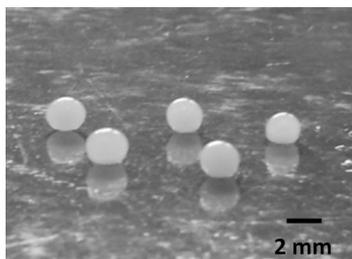


Figure 1 Calcium alginate gel beads.

[1] A. Mallardi, V. Angarano, M. Magliulo, L. Torsi and G. Palazzo, *Anal. Chem.*, 2015, **87**, 11337.

Poly(amino acid) based nano gel fibers for tissue engineering

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The importance of nanotechnology is well recognized in the area of biomedical applications. The interest in the development of biocompatible and biodegradable polymer matrices has increased with their usability in wide range. In many biological applications, such as tissue engineering, there is a desire for well-defined 3D scaffolds with high surface area for cell attachment and growth. The use of electrospinning enables the possibility to prepare such tailored meshes, however the use of water soluble polymers is inappropriate because of their fast dissolution in biological fluids. By utilizing reactive electrospinning technique, chemically crosslinked gel fibers can be created which without enzymatic or chemical degradation will not dissolve in physiological conditions.

Poly(amino acid)-based polymers that have desirable chemical, mechanical and biological properties have recently emerged as promising new class of biomaterials [1]. In our work we have utilized the anhydrous form of poly(aspartic acid), the poly(succinimide) as base polymer. In order to imitate the structure of the backbone of the connective tissue, electro-spinning technique was applied to prepare artificial extracellular matrix. To prevent the polymer fibers from dissolution poly(succinimide) molecules were grafted by thiol side chains. During the electro-spinning process at 10 kV (0.8 ml/h flow rate and 15 cm target distance) cross-linking reaction took place between the side chains. The mean value and distribution of the fibre diameter were determined with AFM and light microscope after the sample preparation [3]. Investigation of swelling behaviour due to the change of pH was carried out on the macroscopic matrix of nanofibers. In vitro biocompatibility test with human fibrosarcoma (HT1080) and human fibroblast cells was performed. It was followed by in vivo experiments on 6-6 albino rats for 72 h and 1 week period. We have found that cross-linked poly(succinimide) based fiber matrix hydrolyzes in 72 hours and turns into poly(aspartic acid) based hydrogel matrix degrades in 1 week. Our novel biocompatible and biodegradable artificial scaffold seems to be a promising poly(amino acid) based fiber matrix for tissue replacement.

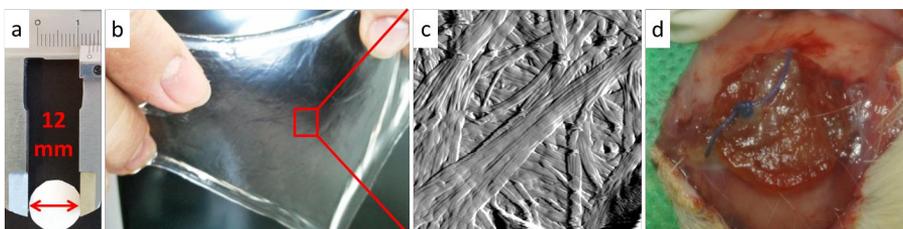


Figure 1.: (a) dry PSI based matrix before implantation, (b) the poly(aspartic acid) based system in wet state after preparation, (c) the AFM image of the dried PASP based fibers and (d) hydrolysed sample after 72 h *in vivo*.

Acknowledgements The financial support of OTKA 115259, OTKA 105523.

[1] Zrínyi, M.; Gyenes, T.; Juriga, D.; Kim, JH.; *Acta Biomaterialia*, 2013, **9**, 5122

[2] Molnár, K., Juriga, D., Nagy, P. M., Sinkó, K., Jedlovsky-Hajdú, A., Zrínyi, M., *Polymer International*, 2014, **63**,

Translocation, biological fate, stability and effective dose of engineered NMs

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There is an urgent need for a deeper understanding of the impact of engineered nanomaterials (ENMs) on human health resulting from deliberate exposure to ENMs, such as in nanomedicine, or from accidental exposure due to handling or using devices or products containing ENMs. The characteristics of ENMs, such as shape, size, degradability, aggregation, surface and core chemistry determine their interaction with biomolecules and the ENMs fate both intracellularly and at body level. Therefore, for the assessment of ENMs toxicity is necessary to correlate ENMs characteristics with the fate and biological interactions. ENMs fate *in vivo*, distribution per organ, accumulation and biodegradability are fundamental to assess how ENMs affect biological functions. ENMs translocate and may finally reach the cell interior. The physical state of the ENMs, including aggregation, the interaction with biomolecules in different cellular environments, and the dynamics of ENMs will guide the intracellular action of nanomaterials.

Several aspects of ENMs fate *in vitro* and *in vivo* will be discussed. Cell uptake and intracellular fate of ENMs will be presented. The intracellular dose for metal oxides NPs will be measured with Ion Beam Microscopy. Relations between exposure dose, intracellular dose and cell viability will be established. The bio distribution, organ accumulation and fate of radiolabelled ENMs will be studied in animal models by means of Positron Emission Tomography (PET)¹. NPs dose per organ will be evaluated. A dual radiolabelling strategy of nanoparticle core and coating is presented using gamma emitters with different energy spectra. After intravenous administration into rats, energy-discriminant Single-Photon Emission Computerised Tomography (SPECT) resolved each radioisotope independently revealing different fates *in vivo* for the core and coating ².

Acknowledgements The financial support of the FP7-Eranet SINN 2015 FATENANO project

- [1] C.Perez-Campaña, V. Gómez-Vallejo, A.Martin, E. San Sebastián, S.E.Moya, T. Reese, R.F. Ziolo and J. Llop ACS Nano 2013, 7, 3498
- [2] J.Llop, P Jiang, M Marradi, V Gómez-Vallejo, M Echeverría, S Yu, Ch.Gao and S.E. Moya J. Mat. Chem. B 2015, 3, 6293.

Liquid Crystalline Nanoparticles for Cancer Theranostics

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Docetaxel-loaded cubic bicontinuous nanoparticles (cubosomes) were stabilized in water by a mixture of commercial Pluronic F108 (PF108) and rhodamine- and folate-conjugated PF108 so that the nanoparticles simultaneously possess targeting, therapeutic, and imaging properties.

These nanoparticles were investigated by DLS, cryo-TEM, and SAXS to confirm their structural features. Taking into account the possible use of the system under study as a theranostic nanocarrier, the variations of the size and inner structure upon temperature changes were monitored in the range of 10–50 °C. The fluorescent emission characterization of the proposed formulation indicated that the rhodamine conjugated to the PF108 experiences an environment less polar than water (similar to chloroform), suggesting that the fluorescent fragment is buried within the poly(ethylene oxide) corona surrounding the nanoparticle. These nanoparticles were successfully used to image living HeLa cells. Furthermore, viability tests revealed a significant cytotoxic effect (more than 1 order of magnitude larger than the molecularly dispersed drug) of the Docetaxel-loaded nanoparticles against HeLa cells [1].

Taken together, these findings encourage the investigation of cubic bicontinuous liquid crystalline dispersions for possible applications as theranostic tools in oncology.

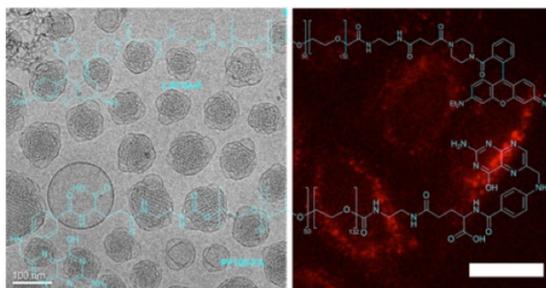


Figure 1 Docetaxel-loaded nanoparticles stabilized in water by a mixture of commercial, rhodamine- and folate-conjugated PF108 (left) used to image HeLa cells (right).

[1] V. Meli, C. Caltagirone, A. M. Falchi, S. T. Hyde, V. Lippolis, M. Monduzzi, M. Obiols-Rabasa, A. Rosa, J. Schmidt, Y. Talmon, S. Murgia, *Langmuir*, 2015, **31**, 9566.

Waste water treatment by natural sorbents

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Water is the most valuable natural resource. It plays a crucial role in the metabolic processes that form the basis of human life. It is well known the need for domestic human needs. At the same time the water needs are enormous and are increasing every year. The water cycle in nature, it is a long way of its movement. Throughout its path the water has the ability to be cleaned of dirt falling into it - the products of decay of organic matter, dissolved gases and minerals, suspended solid material. But this self-cleaning ability is not unlimited. In recent years, the environmental system hits a huge number of pollutants, from which they are unable to protect themselves. And mostly untreated or poorly treated wastewater.

Wastewater treatment is a treatment for the removal or destruction of harmful substances. The release of wastewater from pollution is a complex process. There are a variety of techniques and methods of wastewater treatment. In the present study we have investigated samples of waste (municipal) water of Almaty city. The composition of wastewater is studied, its organoleptic properties, electrical conductivity, optical density is determined. Adsorption performed on samples of wastewater by using of natural adsorbents of Kazakhstan (diatomite, kaolin and bentonite) for 1 week.

It is found that kaolinite, bentonite and diatomite used as adsorbents exhibit considerably good adsorption properties: pH of the water dropped from 9 to 7.5; conductivity of waste water samples is increased by 17%, 24.6% and 22.4%. Results of the study of the absorption of UV waves after adsorption showed in the composition of wastewater the absence of indole, furan and fluorobenzene.

These results suggest the use of domestic adsorbents kaolinite, bentonite and diatomite to improve wastewater treatment.

Lipid-liquid crystalline nanoparticles in drug delivery system

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Hydrated lipids exhibit polymorphism, thereby forming a variety of lyotropic liquid crystalline phases with distinct 3D liquid-crystalline structures such as lamellar, hexagonal or cubic phases. Bicontinuous lipidic cubic phases (LCPs) exhibit a combination of material properties that makes them highly interesting for various biomaterial applications: they are non-toxic, biodegradable, optically transparent, thermodynamically stable in excess water, and can incorporate active molecules of virtually any polarity. An interesting property of cubic phase is also their ability to disperse into nanoparticles called "cubosomes". Cubosomes are less viscous and they can stably exist in equilibrium with aqueous solution and retain an internal bicontinuous structure unchanged. In contrary to liposomes or micelles cubosome is more resistant to mechanical or osmotic rupture. The cubic phase nanoparticle delivery system can be used to improve the oral bioavailability of poorly water-soluble drugs. The structure and dynamics of lipidic mesophases, and their interactions with guest molecules can be tailored by applying additives, thereby achieving novel materials with improved functions for drug delivery. [1, 2]

Here we present lipid-liquid crystalline nanoparticles as effective and safe anticancer drug delivery system. Doxorubicin, a model drug that contains an amine group and a hydrophobic part, was loaded into the cubic phase and cubosomes. As the pH sensitive release is crucial for a delivery system to release drugs at the target tumor cells, the release behavior of DOX was evaluated by using electrochemistry and UV-vis spectroscopy in two buffered solutions at pH 5.5 and 7.4. The release behavior *in vitro* indicated that the DOX was removed from nanoparticles faster at pH 5.5 than at pH 7.4. The size and morphology of the prepared nanoparticles were characterized using dynamic light scattering and cryo-transmission electron microscopy. The inner cubic structure of the prepared materials was confirmed by SAXS. SAXS and DLS results demonstrate that the introduction of DOX does not significantly modify the inner structure of the cubosome, as well as their size and charge. A bicontinuous cubic phase of cubic Im3m was obtained with the particle size of each cubosome formulation of about 170 nm. The cytotoxicities of cubosomes and cubosomes containing DOX were evaluated using *in vitro* cytotoxicity assay on the glioma cells.

Acknowledgements This work was supported by Sinergia project no. CRSII2 154451 financed by the Swiss National Science Foundation and National Science Centre of Poland (2013/09/D/ST5/03876).

[1] E. Nazaruk, M. Szlęzak, E. Górecka, R. Bilewicz, Y. M. Osornio, P. Uebelhart, E. M. Landau, *Langmuir*, 2014, **30**, 1383.

[2] E. Nazaruk, E. Górecka, R. Bilewicz, *J. Colloid and Interface Sci.*, 2012, **385**, 130.

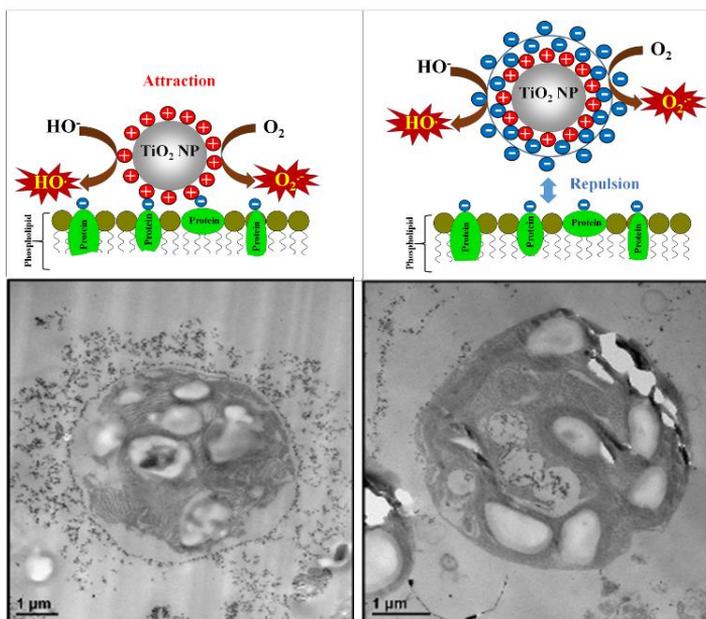
Control of the Nanotoxicity of Polymer-Coated Titania Nanoparticles

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This study gives important insights of the various factors controlling the nanotoxicity of titania nanoparticles (TiO₂NPs). We studied the nanotoxicity of TiO₂NPs of various hydrodynamic diameters and crystallite sizes on *C. Reinhardtii* (microalgae) and *S. cerevisiae* (yeast) upon illumination with UV/visible light [1]. The cell viability was assessed for a range of nanoparticle concentrations and incubation times. Bare TiO₂NPs affect the microalgae viability at much lower particle concentrations than for yeast. We also found an increased nanotoxicity upon illumination with visible light which indicates that they may also interfere with the microalgae photosynthetic system leading to decreased chlorophyll content upon exposure to TiO₂NPs. The results indicate that the larger the hydrodynamic diameter of the TiO₂NPs the lower is their nanotoxicity, with anatase TiO₂NPs generally being more cytotoxic than rutile TiO₂NPs. We also prepared a range of polyelectrolyte-coated TiO₂NPs using the layer by-layer method and studied their nanotoxicity on yeast and microalgae. The toxicity of the coated TiO₂NPs alternates with their surface charge. TiO₂NPs coated with cationic polyelectrolyte as an outer layer exhibit much higher nanotoxicity than the ones with an outer layer of anionic polyelectrolyte. TEM images of sectioned microalgae and yeast cells exposed to different polyelectrolyte-coated TiO₂NPs confirmed the formation of a significant build-up of nanoparticles on the cell surface for bare- and cationic polyelectrolyte-coated TiO₂NPs. The effect is coming from the increased adhesion of cationic nanoparticles to the cell walls. Significantly, coating the TiO₂NPs with an anionic polyelectrolyte as an outer layer led to a reduced adhesion and much lower nanotoxicity due to electrostatic repulsion with the cell walls. This suggests a new way of making the TiO₂NPs potentially safer for use in different formulations by pre-coating them with anionic polyelectrolytes.



[1] M.J. Al-Awady, G.M. Greenway and V.N. Paunov, *RSC Advances*, 2015, 5, 37044.

Electrochemical study of drug release from hybrid cubic phases

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Bicontinuous lipid cubic phases (LCPs) formed by mixing glycerol monooleate with water are highly interesting as the matrix for drug delivery because they are non-toxic, bioadhesive and biodegradable in the body. LCPs have a large inner surface and can accommodate the appropriate amount of active molecules of any polarity. Cubic phase is employed to protect the body cells from the harmful effects of the drug and to stabilize the drug when it is unstable. We have reported that the diamond cubic phase can be a carrier of e.g. anticancer drug – doxorubicin [1]. Now we present application of this drug in monoolein cubic phase doped with magnetic nanoparticles. Lipidic hybrid materials have magnetic properties allows to move in a magnetic field. To stabilize nanoparticles we can use compounds with different hydrophobicity thus NPs can be located in the LCP's water channels or in the lipidic domain. Different localization of the nanoparticles affected the drug release rate from the cubic phase. We studied the physical and chemical properties of hybrid materials containing hydrophobic and hydrophilic NPs. Release profiles of Dox from the hybrid LCPs were monitored electrochemically using Differential Pulse Voltammetry. The addition of hydrophobic nanoparticles located in the lipidic parts of the phase affect only slightly the drug release rate. On the other hand, in the presence of hydrophilic nanoparticles occupying the water channels the release rate is slowed down. The reasons are: larger size of hydrophilic nanoparticles that can affect the transport through channels and electrostatic attraction between the negatively charged hydrophilic nanoparticles and positively charged doxorubicin. The structural parameters of hybrid mesophases were characterized by Small Angle X-ray Scattering. The structure of diamond cubic phase is maintained after the addition 0.2% - 2% w/w of the nanoparticles and 0.5% w/w of drug, but at temperatures higher than 40°C hexagonal phase signals become visible in the presence of hydrophilic magnetic nanoparticles. Release from hexagonal phase is also slower than from the cubic phase.

Acknowledgements The financial support of Sinergia project no. CRSII2_154451/1 “Design, synthesis and characterization of lipidic nanomaterials for biomedical and biosensing applications”.

[1] E. Nazaruk, M. Szlezak, E. Gorecka, R. Bilewicz, Y. M. Osornio, P. Uebelhart, E. M. Landau, *Langmuir*, 2014, **30**, 1383

Interaction of the E2-GBV-C derived peptide, P6-2-VIR576, with Phosphatidylcholine rich Membranes.

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The human immunodeficiency virus type 1 (HIV-1) is an enveloped viruses that must overcome membrane barriers to deliver the viral nucleocapsid into the cytoplasm. It is the causative agent of the acquired immunodeficiency syndrome (AIDS). A key step in the virus entry is the fusion with host membranes mediated with a fusion peptide (HIV 1-FP). In recent years, many synthetic peptides have been assayed as possible HIV-1 FP inhibitors [1]. P6-2-VIR576, a 40 amino acid negatively charged peptide, is a derived peptide from E2-protein of GBV-C virus, which has demonstrated anti-HIV-1 FP activity [2]. The aim of this work is to study the effects of the peptide on the structural properties of lipid membrane using dipole-potential membrane probes and fluorescence microscopy. As model membranes, LBs composed of DMPC/DMPS (3:2), DMPC/EDMPC (3:2), DPPC/DPPS (3:2), containing 1% NBD-PC fluorescence probe, on silica as a solid support were used. Significant spectral shifts of the fluorescence dye di-8-ANEPPS induced by the peptide occur in lipid membranes studied due to the electrostatic interaction. In addition, fluorescence microscopy images revealed a noticeable change on lipid structure. The results obtained for DMPC/DMPS (3:2) in absence and presence of P6-2-VIR57 are shown in Figure 1.

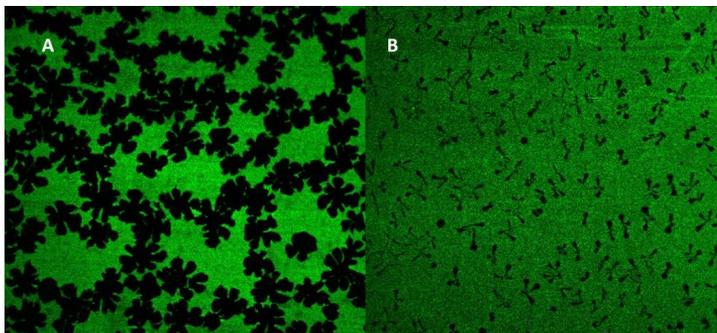


Figure 1 Effect of P6-2-VIR576 on the topography of DMPC/DMPS (3:2) Langmuir-Blodgett films at 12 mNm⁻¹. A) DMPC/DMPS (3:2), B) DMPC/DMPS (3:2) in presence of P6-2-VIR576. Lipid/peptide ratio (9:1)

Acknowledgements This work was supported by Grants CTQ2012-37589-C02-01/02 from the *Ministerio de Economía y Competitividad* and 2014 SGR 216 from the *Generalitat de Catalunya*

[1] J. M. White, S. E. Delos, M. Brecher and K. Schornberg, *Clin. Rev. Biochem. Mol. Biol.* 2008, **443**, 189

[2] N. Lev, Y. Fridmann-Sirkis, L. Blank et al. *Biochemistry*, 2009, **48**, 3166.

The comparison of absorptivity and wettability of powder and tablets containing mixture of mucoadhesive polymers and Fluconazole as active pharmaceutical ingredient

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Mucoadhesion is the process in which two materials adhere to each other for extended periods of time with the help of interfacial forces and when one of these materials is biological in nature, the phenomenon is known as bioadhesion. The theory of mucoadhesion was introduced in the controlled drug delivery field in the early eighties of the last century. A basic mechanistic approach of mucoadhesion involves two steps: (i) intimate contact between a bioadhesive and a membrane (wetting or swelling phenomenon) and (ii) penetration of the bioadhesive into the tissue or into the surface of the mucous membrane (interpenetration) [1]. A mucoadhesion promoting agent or the polymer is added to the formulation which helps in promoting the adhesion of the active pharmaceutical ingredient (API) to the oral mucosa [2-4]. In recent years many efforts have been made aiming to select not only the appropriate mucoadhesive polymers useful in drug delivery but also the best dosage form.

The main goal of our study was to determine the influence of simulated biological fluids on the wetting properties and the absorbency of the selected mucoadhesive polymers and their mixtures containing Fluconazole as active pharmaceutical ingredient (API). Moreover, to shed light on the relation between the dosage form and its wettability as well as absorptivity both the tablets and powders were studied.

The investigated materials were polymers commonly used in the mucoadhesive drug delivery systems: Carbopol 974P NF (carboxy polymethylene), Noveon AA-1 (polycarbophil), Kollidon VA 64 (poly[1-(2-oxo-1-pyrrolidinyl)ethylene]), HEC (cellulose 2-hydroxyethyl ether). Moreover, mixed systems of polymers with components at different weight ratios were considered. For the research was used three types of simulated biological fluids: saliva, gastric and vaginal fluids. The measurements of advancing contact angle of simulated biological fluids on the polymeric matrix tablets (as a measure of wettability) were carried out using the sessile drop method with the instrument KSV Theta Optical Tensiometer (TL 101). The determination of the absorbency of the polymer powders were performed by the Washburn capillary rise method (WCR) using an instrument KSV Sigma 700/701.

It was found that the wettability and absorptive properties of the examined mucoadhesive powders and tablets containing Fluconazole are strongly affected by the type of polymers and the biological fluids, as well as the composition of the formulations. However, the dosage form also possess significant influence.

Acknowledgements This work was financially supported by the statutory activity (Faculty of Chemical Engineering, Poznan University of Technology), grant no. 03/32/DSMK/0615 and 502-01-03314429-03439.

[1] S. Mansuri, P. Kesharwani, K.Jain, R. K. Tekade, N.K. Jain, *React. and Funct. Poly.*, 100 (2016) 151-172.

[2] V. Khutoryanskiy, *Macromol. Biosci.*, 11 (2011) 748–764.

[3] R. Shaikh, T. Raghu Raj Singh, M. J. Garland, A. D. Woolfson, R. F. Donnelly, *J. Pharm Bioall Sci.*, 3 (2011) 89-100.

[4] J. M. Llabot, R. H. Manzo, A. Allemandi, *Pharm.Sci.Tech.*, 3(2002) 47-52.

Absorptivity and wettability of mucoadhesive polymers containing fluconazole in systems with simulated biological fluids

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Mucoadhesive dosage forms are modern and promising drug delivery systems for many active pharmaceutical ingredients (API) and can be used to adhere to any mucosal tissue including oral cavity, gastrointestinal or urogenital tract [1,2]. A basic mechanistic approach of mucoadhesion involves two steps: intimate contact between a bioadhesive and a membrane (wetting or swelling phenomenon) and penetration of the bioadhesive into the tissue or into the surface of the mucus membrane (interpenetration) [1,3]. Mucoadhesive polymeric excipients have many hydrophilic groups which combine with mucus or the cell membrane by various interactions. Some of mucoadhesive polymers can generate a gelled structure which allow to release API in a specified time [4]. From this reason, the swelling degree of polymer plays an important role in conditioning drug release kinetic.

In our work we analyzed how the type of biological fluid (pH, presence of a mucin) and a composition of formulations influence on the wetting properties and absorptivity of mucoadhesive polymers and their blends. New formulations were prepared by mixing the commercial mucoadhesive polymers (derivatives of cellulose and polyacrylic) with fluconazole as API, in two forms: powders and discs.

Measurements of an advancing contact angle of simulated biological fluids were carried out using the sessile drop method with the instrument Theta Lite Optical Tensiometer TL101 (Attension, KSV). The confocal microscope were used in order to a qualitative evaluation of polymeric surfaces of discs formulation (eg. roughness). On the basis of contact angle values were estimated surface free energy of investigated matrixes according to the theoretical models propose in the literature. Additionally, the swelling index of the polymeric matrix discs tested in biological fluids was determined and also the release kinetics of API were analyzed. Our research indicated that the wettability and absorptivity of mucoadhesive polymers depends on the structure of polymers, the type of biological fluids as well as the type and composition of pharmaceutical formulation.

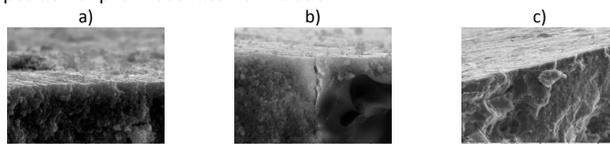


Figure 1. SEM images of discs:

a) Carbopol 974PNF b) Carbopol 974PNF: Kollidon VA64 (1:1) c) Carbopol 974PNF: Kollidon VA64: HEC (1:1:1)

Acknowledgements The financial support of 03/32/DSMK/0615, 502-01-03314429-03439, 06/62/DSPB/0216.

- [1] S. Mansuri, P. Kesharwani, K. Jain, R.K. Tekade, N.K. Jain, *Reactive and Functional Polymers*, 2016, **100**, 151.
- [2] F. Russo, F. Selmin, S. Baldassari, C.G.M. Gennari, G. Caviglioli, F. Cilurzo, P. Minghetti, B. Pardo, *Journal of Drug Delivery Science and Technology*, 2016, **32**, 113.
- [3] M.T. Cook, S.L. Smith, V.V. Khutoryanskiy, *Chemical Communications*, 2015, **51**, 14447.
- [4] A. Ciurba, L. Lazar, P. Antonoaea, A.M. Georgescu, C.-E. Vari, N. Todoran, *Farmacia*, 2015, **63**, 11.

Novel Antibacterial Peptide Modified Contact Lenses

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Soft contact lenses are hydrogel materials recently receiving increasing attention due to their high potential for ophthalmic medical applications [1]. In this work, we present a new method to modify commercial soft contact lenses for the incorporation of antibacterial molecules. It is well known that one of the most common problems related to contact lenses is associated with the risk of eye microbial infection. This is a significant health issue given the large population of contact lenses wearers worldwide [2]. Previous studies demonstrated that many bacteria and fungi may cause corneal infections, and identified *Pseudomonas aeruginosa* and *Klebsiella pneumoniae* as the most common pathogen agents [3]. Two short antimicrobial peptides (AMPs) specifically effective against the aforementioned bacteria were anchored on the hydrogel contact lens materials, with the objective of imparting bactericidal activity on those materials. The hydrogel chemical modification was performed under mild conditions (room temperature, pH=7.4) following two approaches: physisorption and covalent binding (Figure 1A). Physisorption was carried out by simply immersing the samples in a PBS solution containing the peptide, whereas covalent bonding was achieved through a linker capable of binding the hydrogel surface at one end and the approaching peptide at the other end. Both methods proved to be effective for incorporating the selected peptides at various concentrations. However, stability studies, with a fluorescently tagged peptide, demonstrated that covalently bound peptides show a higher stability in PBS solution (Figure 1B). The modified contact lenses were characterised through several analytical techniques including wettability, Raman confocal microscopy, and fluorescence studies. These systems offer the potential to minimise corneal bacterial infection and represent a suitable platform for future ophthalmic devices. All these aspects will be herein discussed within the frame of product development.

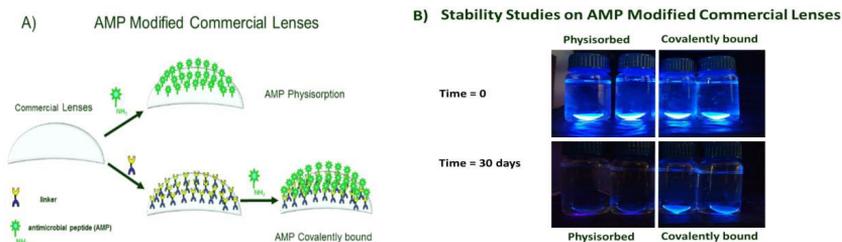


Figure 1. A) Schematic representation of AMP modified soft contact lenses. B) Fluorescence stability studies on the AMP modified commercial contact lenses.

Acknowledgements We would like to acknowledge the TECNIOspring programme for funding (TECSPR14-2-0044 project).

- [1] C. Alvarez-Lorenzo, H. Hiratani and A. Concheiro, *Am. J. Drug Deliv.*, 2006, **4**, 131.
- [2] S.A. Collier, M.P. Gronostaj, A.K. MacGurn, J.R. Cope, K.L. Awsumb, J.S. Yoder and M.J. Beach, *Morbidity and Mortality Weekly Report*, 2014, **63**, 1027.
- [3] P. Preechawat, U. Ratananikom, R. Lerdvitayasakul and S. Kunavisarut, *J. Med. Assoc. Thai*, 2007, **90**, 737.

Investigation of the adsorption process of heavy metal ions from aqueous solutions on chitosan by SEM-EDX analysis

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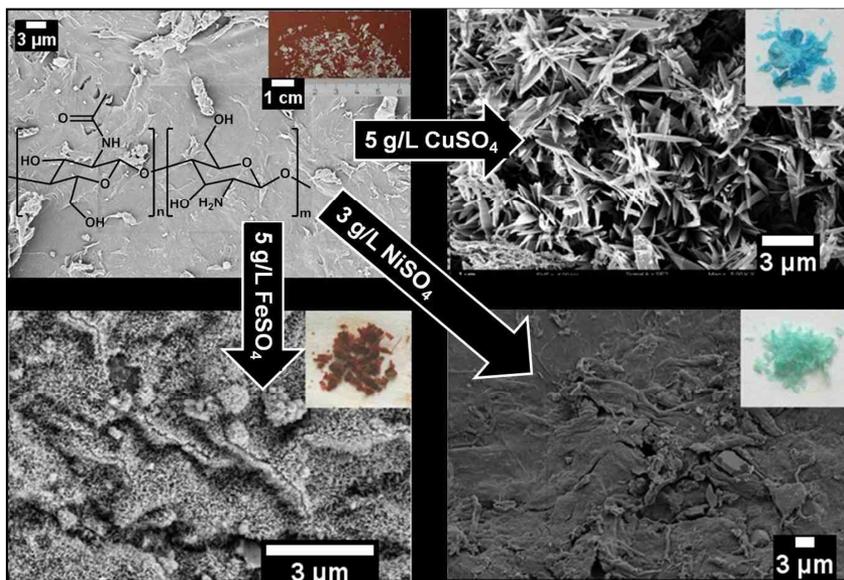
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Chitosan (flakes with a degree of deacetylation of 90 %) was used as adsorbent for heavy metal ions in solution (copper, iron, nickel). The adsorption capacities were determined in dependence on the adsorption time and the initial metal salt concentration. With increasing adsorption time as well as the initial metal salt concentration the adsorption capacities increased. Highest adsorption capacity was achieved for copper(II) ions with 110 mg/L. Iron(II)- and nickel(II) ions adsorbed with an adsorption capacity of 80 mg/L.

The surface of chitosan flakes were investigated before and after the adsorption process by SEM and SEM-EDX, respectively. The formation of crystal-like structures was observed by SEM analysis for the investigation of copper(II)sulfate and iron(II)sulfate. It has been noticed that iron(II) ions oxidized before the adsorption on chitosan occurs. In comparison, the adsorption of nickel salt resulted in a smooth layer on the chitosan surface. SEM-EDX analysis revealed that sulfate adsorbs on the chitosan surface besides the metal cations used.



Bacterial adhesion on food contact material surfaces

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Interactions between bacteria and food contact material surfaces [1] play an important role in the field of food safety. Microbial contamination of food-contact surfaces is an ongoing concern for the food industry. Poor sanitation of food contact surfaces, equipment, and processing environments has been a contributing factor in food borne disease outbreaks. The objective of this study is to identify the most susceptible kitchen surfaces to bacterial adhesion. We analysed the adhesion rate of *E. coli*, *P. aeruginosa* and *S. aureus* on common kitchen food contact materials e.g. polyethylene terephthalate, silicone, aluminium, Teflon and glass. Our results have shown that from adhesion point of view the most hygienic materials are Teflon and aluminium. Teflon possesses low adhesion due to its hydrophobicity and aluminium due to its low roughness. Contrary to that the most predominant adhesion has been analysed on PET and glass surfaces, due to high roughness. Contamination of food contact materials, due to bacteria presence is one of the main causes of foodborne outbreaks. Therefore selection of proper material with lowest adhesion potential is the best strategy to prevent bacterial adhesion.

[1] K. Bohinc, G. Dražič, R. Fink, M. Oder, M. Jevšnik, D. Nipič, K. Godič Torkar and P. Raspor, *Int. J. of adhesion and adhesives*, 2014, **50**, 265.

Near-Infrared-Sensitive Nanomaterials based on Ru Complex-Functionalized Upconverting Nanoparticles for Biomedical Applications

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Upconverting Nanoparticles (UCNPs) convert near-infrared light to UV or visible light, which can trigger photoreactions. Many applications based on the UCNP-assisted photochemistry including multimodal bioimaging, photodynamic therapy, and drug/gene delivery, photoisomerization, photocleavage, photopolymerization, cell adhesion, and bending of elastomers have been developed. The reported excitation intensity for UCNP-assisted photochemistry is typically between several hundred mW/cm² to several hundred W/cm². The relatively high-intensity NIR light required by UCNP-assisted photochemistry may damage cells, tissue, and other biomaterials. Therefore, the reduction of the excitation intensity for UCNP-assisted photochemistry to a medically harmless level is an important objective. Here, we demonstrate how to reduce the intensity of NIR light for UCNP-assisted photochemistry^[1]. Based on the low excitation intensity for UCNP-assisted photochemistry, the applications including the photon upconverting lithography^[2](Figure 1) and drug delivery system^[3](Figure 2) were developed.

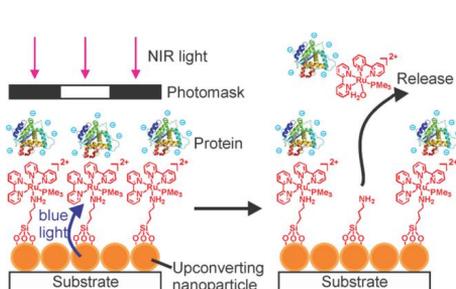


Figure 1 Schematic of photon upconversion lithography (PURL) for the patterning of proteins. Note: Polyethylene glycol, which is co-grafted with Ru complexes on the upconverting nanoparticles (UCNPs), is not shown for clarity.

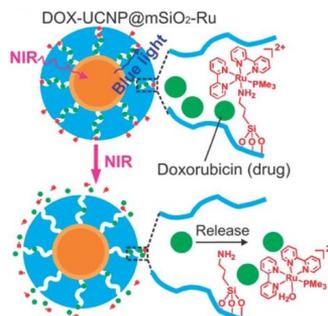


Figure 2 Schematic illustration: upconverted blue luminescence triggers cleavage of Ru complexes and release of doxorubicin from DOX-UCNP@mSiO₂-Ru nanoparticles.

[1] Z. Chen, W. Sun, H.-J. Butt, S. Wu, *Chem. Eur. J.*, 2015, **21**, 9165.

[2] Z. Chen, S. Q. He, H.-J. Butt, S. Wu, *Adv. Mater.*, 2015, **27**, 2203.

[3] S.Q. He, K. Krippes, S. Ritz, Z. Chen, A. Best, H.-J. Butt, V. Mailänder, S. Wu, *Chem. Commun.*, 2015, **51**, 431.

Antimicrobial films containing microparticles for the enhancement of long term sustained release

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Coated packagings with thin films containing antimicrobial agents are an alternative technology to ensure the protection of products against microbial contaminations. Indeed, they allow lowering the antimicrobial concentration in the bulk of the product while meeting the safety requirements and the growing consumer demand for low preservative concentrations. Microencapsulation is a suitable way for controlling active agent release and providing a long term activity. This work aims at combining both technical solutions with coatings containing antimicrobial microparticles for the achievement of long term sustained release. Polyethylene surfaces were functionalized with microparticles of poly(methyl methacrylate) (PMMA) loaded with phenylethyl alcohol (PEA) as antimicrobial agent by the dip coating process using a polyurethane binder. The release of PEA into water from coated polyethylene surfaces and from PMMA microparticles was investigated to assess the sustained release and its mechanisms. Films with various thicknesses of 400-1000 μm containing antimicrobial microparticles demonstrated unusual long term release longer than 3 months. The diffusion of the antimicrobial agent through PMMA was the rate limiting step of the sustained release. PEA release increased as the contact area of the protruding microparticles with the external medium increased and the thickness of the film decreased. Such antimicrobial agents encapsulated inside thin coatings are promising with regards to antimicrobial preservation of products along their full shelf-life.

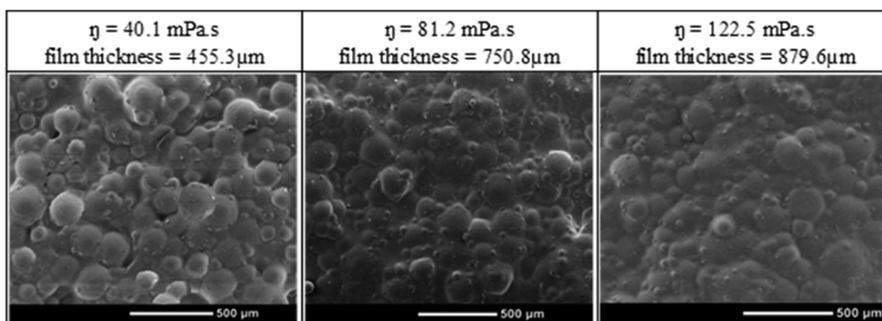


Figure 1 Various morphologies polymer microspheres deposited onto a polyethylene surface.

The parameters influencing the morphology of poly(ϵ -caprolactone) microspheres and the resulting release of encapsulated drugs

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Polymer microparticles used for drug encapsulation and delivery have various surface morphologies depending on the type of formulation ingredients and parameters of the manufacture process. This work aims at investigating the critical parameters governing the morphology of microparticles and to underline the influence of their surface state on the drug release. The classical fabrication process by the "emulsion - solvent evaporation" is addressed using poly(ϵ -caprolactone) as the polymer and methylene chloride as the volatile organic solvent. The typical surfactants poly(vinyl alcohol) and polysorbate 80 have been considered. Scanning electron microscopy observations showed the various surface morphologies mainly depending on the stirring rate, the viscosity of the oil phase and by the presence of inappropriate surfactants. Because of arrested coalescence during solvent evaporation, the evaporation of the organic solvent causing particles hardening is the most important parameter that controls the morphology. Indeed, slow evaporation allows partial coalescence of the soft particles swollen by the organic solvent, whereas the particles morphology is frozen rapidly upon fast evaporation, thus preventing damaged surface states. Moreover, an effective stabilizing system for the primary emulsion is also a determining factor to control the final morphology. The morphology of the particles has a definite influence on the drug delivery of cholecalciferol. The surface morphology should be taken into consideration in the design of polymer microparticles because it allows a control over the drug release kinetics.

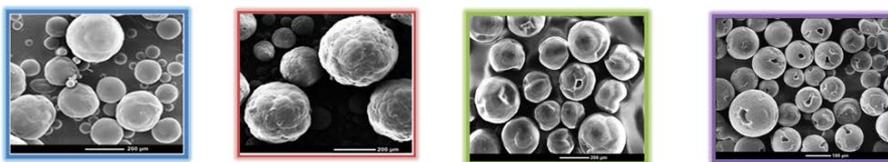


Figure 1 Various morphologies of the polymer microspheres.

[1] J. Bile, M.-A. Bolzinger, C. Vigne, O. Boyron, J.-P. Valour, H. Fessi and Y. Chevalier, *Int. J. Pharm.* **2015**, **494**, 152.

Encapsulation of curcumin in polyelectrolyte nanocapsules and their neuroprotective activity

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Curcumin, diferuloylmethane, is a component of turmeric, which comes from *Curcuma longa* herb. The studies have shown that curcumin reveals various biological actions. It exhibits prominent antioxidant and anti-inflammatory, antiviral, antibacterial and antifungal activities and it is used as a potential preventive agent in the treatment of many types of cancer. There is also evidence that curcumin exhibits neuroprotective effects. Poor water solubility and low bioavailability of lipophilic drugs like curcumin, can be potentially improved by use of delivery systems. In this study, encapsulation of nanoemulsion droplets was utilized to prepare curcumin nanocarriers. The droplets contained curcumin were encapsulated in polyelectrolyte shell formed by the layer by layer (LbL) adsorption of biocompatible polyelectrolytes: poly-L-lysine (PLL) and poly-L-glutamic acid (PGA). The size of synthesized nanocapsules was ~100 nm. Biocompatibility of synthesized nanocapsules and neuroprotective potential of encapsulated curcumin against the H₂O₂-induced cell damage of SH-SY5Y was evaluated using cell viability/toxicity assays. Curcumin encapsulated in our nanocapsules showed the improved neuroprotection activity when compared to curcumin pre-dissolved in DMSO. The obtained results indicate the utility of PLL/PGA nanocapsules as a promising alternative way of curcumin delivery for neuroprotective purposes with improved efficiency and reduced toxicity

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Magnetic nanocapsules for delivery of therapeutic compounds

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Synthesis of theranostic nanoparticles, which combine both therapeutic and diagnostic capabilities in one platform, is the first step forward personalized medicine. Increasing concentration and bioavailability of drugs, prolonging circulation of actives in the body fluids, is essential for future success of many therapies (e.g. cancer, diabetes). Systems based on micelles, vesicles, nanospheres and nanocapsules are commonly used for transport of therapeutic agents. Incorporation in the structure of carriers compounds like peptide, antibody, carbohydrates, magnetic particles allow to transport of drug at the exact location for its pharmacological action.

The aim of this work was preparation and characterization of nanocapsules with iron oxide nanoparticles (MP) for magnetic targeting. Specifically, we explore the development of theranostic nanoparticles that may simultaneously monitor and treat disease. Nanocapsules were prepared by LBL method using biocompatible polyelectrolytes (Poly L-lysine and Poly Glutamic acid), with low-energy microemulsification. We obtained 100 nm nanocapsules with concentration 10^{11} particles/ml. Model drug as well as iron oxide magnetic particles were encapsulated inside nanocapsules. Morphology of magnetic carriers were investigated by Cryo-Scanning Electron Microscopy. We performed stability and cytotoxicity tests (MTT reduction, LDH release). Additionally, magnetic properties of synthesized nanocapsules were examined using Mossbauer Spectroscopy.

This magnetically responsive drug nano delivery system may be a promising platform for future targeted therapies or other biomedical applications.

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Lytropic Liquid Crystal Based on Nonionic Surfactants as Media for Encapsulation of Bioactive Molecules

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In the last decade increasing interest in the use of lyotropic mesophases as matrices for delivery and controlled release of drugs and bioactive substances has been. The fact that many of the lyotropic liquid crystalline phases (in particular reverse hexagonal and cubic) have a priori nanoscale pore space with an ordered distribution in the bulk mesophase, provides high and uniform loading of the drug. LLCs based on nonionic surfactant are self-assembled into a large variety of morphologies that exist between isotropic liquid and solid crystalline. The dendrimers have gained interest in various applications in pharmaceuticals and biomedical systems, especially in the treatment of cancer. These macromolecules have a unique well defined "treelike" branching structure, which spreads out from a central core under systematic introduction of branching sites. The combination of dendrimer with LLCs may provide an advantageous drug delivery system.

In the present work, we demonstrate for the first time a complex prospective drug delivery system, based on a third generation poly(propylene imine) dendrimer (DAB-16) solubilized in the aqueous domains of lamellar mesophases $C_{12}EO_4/La(III)/H_2O$. Liquid crystal properties and structure parameters of LLC were established by methods of POM and SAXS.

The structure of complex was determined by FTIR and UV adsorption. The DAB-16 encapsulation concentration into structure to the two basic systems $C_{12}EO_4/La(III)/H_2O$ with a water content of 36 wt. % and 63 wt. % were found. According to SAXS the incorporation of dendrimer molecules into the bilayer structure was proved. Fourier transform infrared were utilized to study the structural behavior of the mesophases, the localization of DAB-16 within the system, and the interactions between the guest molecule and the system's components. Based on results of spectral studies the interaction between lanthanum ions and dendrimer functional groups was established.

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Interfacial behavior of gemini type perfluorinated surfactants with DPPC at the air-water interface - effect of spacer length

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A fluorocarbon chain is lower cohesiveness and higher rigidity than hydrocarbon chains. In addition, a fluorocarbon has hydrophobicity and lipophobicity simultaneously. Hence, Fluorinated surfactants show some special properties such as high surface activity, and chemical and biological inertness. In terms of surface activity, fluorinated surfactants are more efficient than hydrogenated surfactants because of the surface tension can be reduced by small amounts of fluorinated surfactants. Moreover, the feature of hydrophobicity and lipophobicity provides phase separation and selfm assembly. These properties are useful for applications in various fields such as biomedical and industry fields [1]. The perfluorinated double long chain salts with divalent counterions which have various hydrocarbon spacer lengths have been synthesized in recent years. The solution properties and the interfacial behavior of the fluorinated compounds have been investigated previously [2,3]. It is found that the solution properties and the interfacial behavior depend on the spacer length. Herein, in this study, the binary monolayer properties of the fluorinated compounds and dipalmitoylphosphatidylcholine (DPPC) were investigated to understand the spacer length effect and an aspect of biomembrane interaction on their interfacial behavior.

Experimental:

The fluorinated compounds, 1,1'-(1, ω - alkanediyl)- bispyridinium perfluoro-tetradecanecarboxylate (abbreviation: CnBP(FC14)₂; n = 2, 6, 10), were synthesized. DPPC was obtained from Avanti Polar Lipids (Alabaster, AL). Surface pressure (π)-molecular area (A) and surface potential (ΔV)-A isotherms were measured on 0.15 M NaCl at 298.2 K.

Discussion:

We have investigated that the binary monolayers of DPPC and CnBP(FC14)₂ behavior were also employing Brewster angle microscopy (BAM), fluorescence microscopy (FM) and atomic force microscopy (AFM). Twom dimensional phase diagrams were constructed on the basis of the disordered/ordered phase transition pressure and the monolayer collapse pressure versus the molar fraction of CnBP(FC14)₂ (XCnBP(FC14)₂). The transition pressures and collapse pressures changed against XCnBP(FC14)₂. In the morphology (BAM and FM), the dispersion degree of two regions (ordered and disordered) were depending on the spacer length. The miscibility is also confirmed visually by AFM at nanometer scales.

[1] M. P. Krafft, *Soft Matter*, 2015, **30**, 5982.

[2] Y. Matsumoto, H. Nakahara, Y. Moroi and O. Shibata, *Langmuir*, 2007, **23**, 9629.

[3] J. Masuda, H. Nakahara, S. Karasawa, Y. Moroi and O. Shibata, *Langmuir*, 2007, **23**, 8778.

Calcium carbonate formation on mica supported extracellular polymeric substance produced by *Rhodococcus rhodochrous*

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Biom mineralization is a process by which organisms precipitate inorganic minerals usually to harden or stiffen their tissues. This widespread phenomenon in nature has important consequences for evolution and the environment. Hence, the study of biom mineralization is an interdisciplinary discipline at the borderline of chemistry, biology and materials science whose results are important for the fields of paleontology, marine chemistry, sedimentology, medicine and dentistry [1]. It is also known that not only living cells but also extracellular polymeric substances of microbial origin can be involved in mineral precipitation and this process is called biologically influenced [2].

In the present study extracellular polymeric substance (EPS) extracted from *Rhodococcus rhodochrous* bacterial strain was used as a matrix for calcium carbonate precipitation using the vapour diffusion method. The total exopolymer and water-soluble exopolymer fraction of different concentrations were spread on the mica surface by the spin-coating method and the obtained layers were characterised using the atomic force microscopy measurement and XPS analysis. The effects of polymer concentration, initial pH of calcium chloride solution and precipitation time on the obtained crystals properties were investigated. Raman spectroscopy and scanning electron microscopy were used to characterize the precipitated minerals. It was found that the type of precipitated CaCO₃ polymorph and the crystal size depend on the kind of EPS fraction, its concentration and solution pH. The obtained results indicates that the total EPS favours vaterite dissolution and calcite growth, whereas the water-soluble EPS fraction stabilizes vaterite and this effect is stronger at basic pH. It seems to be due to different contents of the functional group of EPS fractions.

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[1] F. Nudelman and N.A.J.M. Sommerdijk, *Angew. Chem. Int. Ed.* 2012, **51**, 6582.

[2] A.W. Decho, *Ecol. Eng.* 2010, **36**, 137.

The polymer-based nanoparticles as neuroprotectants-loaded carriers for brain drug delivery

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Prevention and treatment of stroke-related brain damage and neurodegenerative diseases such as Alzheimer's and Parkinson's are major and still unresolved problems of contemporary medicine. In the clinical trials we may find only few neuroprotective substances, however their efficiency in the treatment is not satisfactory. One of the major limitations is an inefficient delivery of neuroprotectants by the blood-brain barrier (BBB). Therefore, the main aim of the research is to develop a new strategy of delivery of neuroprotective drugs by the nanocarriers that are able to cross the BBB without imposing side effect on its normal function.

In the present work we were focused on preparation of neuroprotectants-loaded nanoparticles (NP's) from nanoemulsion by the Phase Inversion Composition (PIC) technique. The NP's were composed of the biodegradable and biocompatible polymers (polycaprolactone, PCL and/or poly(lactic acid), PLA) containing active neuroprotective agents (Curcumin, Undecylenic acid, MDL28170) as well as model drug (Cumarin-6 and/or Cyclosporin). Moreover, the surface of received NP's were functionalized by poly(ethylene glycol), PEG chains. All synthesized nanocarriers were characterized by size, size distribution, zeta potential, imaged by Cryo-SEM and their stability in the simulated body fluid (SBF) was also determined. The neuroprotective action of encapsulated drugs were evaluated in the SH-SY5Y human neuroblastoma cell line. Cytotoxicity, cellular uptake and transport through the blood-brain barrier were also tested.

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Highly thiolated and S-protected poly(aspartic acid) derivatives as *in situ* gelling ophthalmic drug delivery formulation

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Conventional ophthalmic drug formulations such as eye drops have generally poor bioavailability due to the limited area of absorption and protective mechanisms of the eye. This problem might be overcome by the utilization of mucoadhesive polymeric dosage forms which adhere to mucosal membranes providing a longer residence time and a controlled rate of drug release.

Strong mucoadhesion can be achieved by the use of thiolated polymers as they can form covalent bonds, i.e. disulphide linkages with cysteine rich subdomains of the mucus layer. Thiolated polymers might show also *in situ* gelling property due to the oxidation of thiol groups to intermolecular disulphide linkages or thiol/disulphide exchange reactions. The increase in thiol content of polymers usually results in stronger mucoadhesion [1]. However, the stability of liquid formulations of thiolated polymers is limited because of the oxidation of thiol groups in the presence of air. The protection of thiol groups can be advantageous for two reasons. First, the stability of liquid formulation is largely improved and secondly, the presence of protected thiol groups might further improve mucoadhesion because of the exchange reaction between disulphide groups of the polymer and thiol groups of mucin [2].

In our work poly(aspartic acid) (PASP), a synthetic polyamino acid was chosen as the backbone of the mucoadhesive polymers. Thiolated PASP with various degree of modification was synthesized by reacting cysteamine with polysuccinimide and the subsequent hydrolysis of the polymer. S-protected PASP was synthesized by the attachment of thiopyridyl substructure to the thiol groups on the polymer. Structure of the polymers was confirmed by ¹H-NMR and UV-Vis spectroscopy. Oxidation induced gelation of the thiol containing derivatives and gelation of the S-protected derivative by thiol-disulphide exchange reaction were monitored by oscillation rheology. Mucoadhesion of the polymers were compared by tensile tests. Release kinetics of a commonly used ophthalmic antibiotic, ofloxacin from the polymer matrix was determined. According to the results to be presented, mucoadhesive PASP derivatives may serve as excipients of *in situ* gelling ophthalmic drug delivery formulations.

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[1] A. Bernkop-Schnürch, *Adv. Drug Deliv. Rev.*, 2005, **57**, 1569.

[2] F. Hintzen, S. Hauptstein, G. Perera and A. Bernkop-Schnürch, *Eur. J. Pharm. Biopharm.*, 2013, **85**, 1266.

[3] G. Horvát, B. Gyarmati, S. Berkó, P. Szabó-Révész et. al. *Eur. J. Pharm. Sci.*, 2015, **67**, 1.

Towards modern drug carriers: physicochemical characterization of protein using simulation and experiment

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Nanotechnology, especially nanomedicine is a rapidly growing field that has captured worldwide attention. A large number of nanoparticle drug delivery systems have been developed for cancer treatment. Natural biomolecules such as proteins are an attractive alternative to synthetic polymers which are commonly used in drug formulations. Protein nanoparticles are biocompatible, biodegradable, metabolized and are easily amenable to surface modifications to allow attachment of drugs and targeting ligands. Many drugs molecules are known to bind to albumins. This work focusses on bovine serum albumin (BSA), because of its structural homology with human serum albumin (HSA) - their tertiary structures are 76% similar. The understanding of how the protein interacts with model surfaces is of major interest in both fundamental research and applications such as nanomedicine. One of the new promising composite device for protein controlled delivery is silica surface due to its weak interactions with proteins. Despite the constant development of research in biomedicine, there are few systematic reviews about protein adsorption from a molecular point of view.

The use of precise, analytical techniques such as multi-parametric surface plasmon resonance (MP-SPR) and quartz crystal microbalance with dissipation monitoring (QCM-D) allowed us to determine the structure of the layers formed on a nanometric scale under precisely defined and controlled conditions (concentration, ionic strength, pH). A combination of QCM-D and MP-SPR complementary techniques has provided crucial information on the mechanisms behind the protein- silica surface interaction, protein structural changes and biomolecular rearrangements. Both the kinetics of BSA deposition and the maximum surface concentration were determined. The dependence of the maximum coverage on the pH, ionic strength and the experimental kinetic runs were quantitatively interpreted in terms of the Random Sequential Adsorption model. It is shown that using the SPR measurements, one can determine the mechanisms of BSA adsorption, namely the reversibility and orientation of molecules at interfaces. Furthermore, from the comparison of the MP-SPR and QCM-D data we have estimated the hydration of the film on the silica surface.

We combine our experimental measurements with fully atomistic molecular dynamics (MD) simulations to gain new insight into the BSA adsorption on silica surfaces. The simulation work is challenging due to the negative charge on both the BSA and silica under physiological conditions, nevertheless we are able to examine in detail how the protein interacts with surface. In particular, we make strong predictions about the orientation of the adsorbed BSA and its conformational stability. We discuss how the simulations help the interpretation of our experimental observations. These results are essential for designing an alternative scheme for drug delivery systems.

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Double-compartment hydrogel particles for targeted delivery and sustained release of hesperidin

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There has been considerable interest in application of hydrocolloids as stable targeted delivery systems for therapeutic agents [1]. Double-compartment (complex) nano- and microsized structures, composed of biocompatible and biodegradable materials (eg. sodium alginate (SA) and carboxymethylcellulose (CMC)), are being increasingly exploited for successful encapsulation of pharmaceuticals [1]. The polymeric particles have been in focus of our actual research due to their functionality and ease of controlled cargo release in response to a particular trigger - ionic strength, pH or temperature.

The objective of our study was to develop a targeted delivery system for hesperidin - a low-molecular phenolic glycoside of natural origin, in order to enhance its pharmacological activities: antioxidant [2], anti-inflammatory [3], and recently revealed therapeutic potential in the treatment of nephrolithiasis [4]. We designed, developed and extensively studied pH-responsive biodegradable double-compartment hydrogel carrier system devoted to encapsulate the bioactive compound to facilitate its protection in adverse environment and distribution to specific locations within the organism. We fabricated a double-compartment delivery system composed of CMC microparticles filled with SA nanoparticles loaded with hesperidin. Nanoparticles were formed with methods based on internal and/or external gelation, and subsequently were incorporated into CMC microparticles with dripping technique. Additionally, hesperidin was also encapsulated directly in single-compartment SA and CMC microparticles fabricated with the external gelation method. All obtained particles were characterized in terms of their morphology and size using polarization microscopy and scanning electron microscopy (SEM). Furthermore, the hydrodynamic diameter, size distribution and zeta potential of the nanoparticles were measured by dynamic light scattering (DLS). The cargo encapsulation was confirmed by spectroscopic analysis (FTIR), while the processes efficacies were derived from the spectrophotometric measurements (UV-Vis). The effect of different pH values (2, 7, 10) on the stability and diffusion kinetics of the microparticles was evaluated. The release profiles of the fabricated microsystems were studied *in vitro* in the simulated gastric (pH 2, 37°C) and intestinal (pH 7.5, 37°C) environment in order to provide the most effective carrier system in terms of functionality of the fabricated hydrocolloid particles, their ability to encapsulate the studied cargo, protect it under adverse conditions and release it under required ones.

The optimization of the fabrication processes provided nano- and microproducts with sizes in range of 100 – 300 nm and 800 – 1000 µm respectively, and of acceptable loading efficiency, but different stability within various pH conditions. Comparing results obtained for single-compartment and double-compartment microparticles it can be concluded, that filling micro-hydrogel structures with nanoparticles loaded with hesperidin provided more stable carrier protecting the bioactive compound from uncontrolled leaching more effectively, and significantly prolonged its release under simulated intestinal conditions.

Acknowledgement

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[1] S. Labbaf, S. Deb, G. Gamma, E. Stride and M. Edirisinghe, *J. Colloid. Interface. Sci.*, 2013, **409**, 245

[2] K.M. Kamel, O.M. Abd El-Raouf, S.A. Metwally et al., *J. Biochem. Mol. Toxicol.*, 2014, **28**, **7**, 312.

[3] A.S.A. Abuelsaad, G. Allam and A.A.A. Al-Solamani, *Mediat. Inflamm.* 2014, **1**, 13

[4] R. Gancarz and E. Klepacz, Patent application P.410626, 2015

**Lactic acid and glucose-responsive micelles
of poly(ϵ -caprolactone)-*b*-poly(ethylene oxide) block copolymers
with phenylboronic ester as a sensitive blocks connector**

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Synthesis, self-assembly and responsiveness to glucose and lactic acid of a novel biocompatible and biodegradable block copolymer micelles that contains phenylboronic ester as a blocks linker between the hydrophobic poly(ϵ -caprolactone) (PCL) and the hydrophilic poly(ethylene oxide) (PEO) is described herein. Synthetic procedure to prepare successfully PCL block with pendant phenylboronic acid (BA) combines ring-opening polymerization (ROP) of ϵ -CL initiated by 4-hydroxymethyl(phenylboronic) acid pinacolate and pinacol deprotection step. The second block glucose terminated PEO was obtained by 1,3-dipolar cycloaddition Cu(I)-catalyzed alkyne-azide reaction of α -methoxy- ω -propargyl PEO and 1-azido-2,3,4,6-tetra-O-acetyl glucopyranoside. All new compounds were evaluated by ¹H NMR spectroscopy and SEC analysis. PCL and PEO blocks were connected in NaOH acetone solution and this feature has been confirmed by fluorescence measurements using Alizarin Red as a model compound as well as by ¹H NMR spectroscopy. The block copolymer was transformed into physiological relevant phosphate-buffered saline (PBS) solution via dialysis and self-assembled nanoparticles were characterized by static and dynamic light scattering (SLS, DLS) and cryogenic transmission electron microscopy (cryo-TEM). Furthermore remarkable sensitivity of nanoparticles can be triggered by addition of a surplus of glucose or lactic acid (simulating acidic cytosolic or endosomal conditions in tumor cells) that binds to BA competitively. The latter feature has been confirmed by fluorescence and light scattering measurements [1].

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- [1] A. Matuszewska, M. Uchman, A. Adamczyk-Wozniak, A. Sporzynski, S. Pispas, L. Kovacik, M. Stepanek, *Biomacromolecules*, 2015, **16**(12), 3731.

Preparation and characterization of modified inulin particles by spray-drying regarding release behaviour and cytotoxicity

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In our work, we investigate the application of carbohydrate based polymers from renewable resources as encapsulation material using the spray-drying technology. Therefore inulin is used as a fructan from the chicory root which has already several biomedical applications, e.g. drug-delivery for colon targeted substances and adjuvants for vaccines. [1] Chemical modifications are applied to adjust the release behaviour of the particles. We investigate the influence of several functional groups towards particle formation and encapsulation of low molecular substances (hydrophobic vs. hydrophilic and solid vs. liquid) such as dexpanthenol or vitamin C via spray-drying as well as the release behaviour.

Herein, the modified inulin was characterized by NMR, IR, SEC and DSC. The spray-dried formulations were analysed via SEM and static light scattering methods. Figure 1 shows an example of native and modified inulin particles that were spray-dried with a content of 1 % dexpanthenol. The particles showed a spherical structure with a size range from 0.7 μm to 5 μm . In order to determine the release behaviour, an USP apparatus 4 method with standardized dialysis adapter was used which is suitable for micro particle testing. [2] The release of substances like dexpanthenol or vitamin C were determined in phosphate buffer solutions and quantified via HPLC methods. We investigated and applied different substances regarding the chemical modifications of inulin. To ensure non toxicity of the modified inulin towards organism and cells the cytotoxicity of the obtained materials according to the DIN EN ISO 10995-5 was investigated.

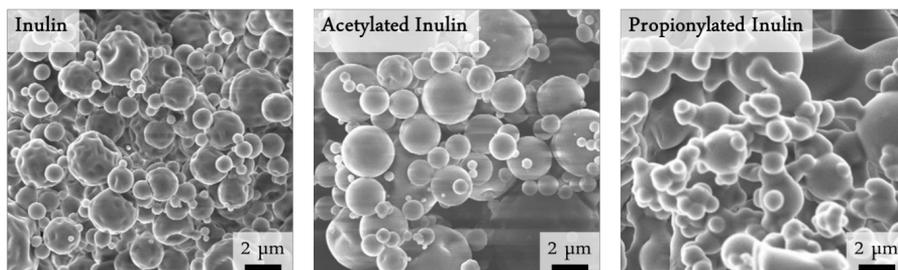


Figure 1 Inulin derivatives obtained by spray-drying containing 1 % dexpanthenol.

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- [1] M.A. Mensink, H.W. Frijlink, K.V. Maarschalk and W.L.J. Hinrichs, *Carbohydrate Polymers* 2015, **134**, 418.
- [2] A. Rawat, E. Stippler, V.P. Shah and D.J. Burgess, *Int. J. Pharm.*, 2011, **420**, 198.

Chitosan/DPPC coated polymer surfaces activated by air plasma

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The development of biocompatible polymers and membranes has been a major subject of research in recent years. Biomimetic systems can be used in a variety of applications including molecular recognition, membrane fusion, implants and controlled drug delivery devices. Of particular interest for this work is chitosan which has several unique characteristics that are beneficial for biomedical applications, such as its biodegradable, biocompatible, nontoxic, and antibacterial properties. Another area of growing interest is the preparation of antimicrobial edible films and coatings [1]. Chitosan can be used as a hypocholesterolemic agent when added to the diet. In these applications, chitosan interacts in most cases with biomembrane surfaces. The bactericidal activity of chitosan is due to the electrostatic interactions between the NH_3^+ groups of chitosan and the phosphoryl groups of the phospholipid component of the cell membrane [2]. Accordingly, chitosan can interact with liposomes [3] and other mimetic systems, but few studies are reported on its interactions with the Langmuir and Langmuir-Blodgett/Schaefer films [4]. Strong interactions of chitosan with phospholipids may cause morphological changes and influence the membrane permeability.

In our studies the chitosan/phospholipid (DPPC) films on air plasma treated polyethylene terephthalate (PET) plates were prepared by two methods. One-step hybrid chitosan/DPPC coating was spreading of the chitosan solution onto the PET surface activated with air plasma. In the first method this stage was followed by spreading of the DPPC solution onto the previously dried chitosan film. In the second one a two-layered coating consisting of chitosan and DPPC was prepared by deposition of the phospholipid DPPC monolayer-onto the PET/chitosan plate by means of the Langmuir-Blodgett/Schaefer techniques. The latter techniques offered the advantage of tightly packed phospholipid molecules. The wetting properties of the prepared layers were measured by determining the contact angles of water, formamide and diiodomethane. Moreover, the theoretical models were used to study the surface thermodynamics, i.e. surface free energy and its components.

It was found that the way of layers preparation had a significant effect on the wetting properties and surface free energy of the PET/chitosan/DPPC films. Both topographic features and surface chemistry influenced the surface hydrophilicity of materials. Polarity of the activated PET considerably decreased with the deposition of chitosan layer and then increased when the chitosan/DPPC film was present. Moreover, the study gives information on the film permeability strongly affected by the molecular packing. It is important to understand how chitosan interacts with cell membrane models and changes their organizations, because of great potential use of chitosan in several areas, including its application in cosmetics, biotechnology, medicine, and food preservation.

- [1] M.Z. Elsabee and E.S. Abdou, *Mater. Sci. Eng. C*, 2013, **33**, 1819
- [2] H. Liu, Y. Du, X. Wang and L. Sun, *Int. J. Food Microbiol.*, 2004, **95**, 147
- [3] O. Mertins and R. Dimova, *Langmuir*, 2013, **29**, 14552
- [4] F.J. Pavinatto, T.M. Nobre, L. Caseli, M.E.D. Zaniquelli, A. Pavinatto, H.S. Silva, D.S. dos Santos Jr., P.B. Miranda and O.N. de Oliveira Jr., *Langmuir*, 2007, **23**, 7666

Encapsulation efficiency and release rate of water-soluble drug in ethosome-like cationic vesicles

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Cationic surfactants have emerged as the new materials for preparing vesicular carriers of potential drug and gene delivery systems [1-3]. This work aimed at developing competent ethosome-like cationic vesicles for transdermal drug delivery. Three cationic surfactants- decyltrimethylammonium-dodecylsulfate (DeTMA-DS), decyltrimethylammonium-tetradecylsulfate (DeTMA-TS) and dodecyltrimethylammonium-dodecylsulfate (DTMA-DS)- were synthesized and thereafter used as the raw materials for preparing stable ethosome-like cationic vesicles with the aid of ethanol and cholesterol in buffer solution by a simple semispontaneous process. Potential applications of the vesicles were demonstrated by the encapsulation and release of a water-soluble drug Arbutin. Cholesterol effects on encapsulation efficiency and release rate in vesicles with 20% ethanol at 25 °C were systematically studied. Experimental results showed that encapsulation efficiency was increased with cholesterol addition in all three systems. Release rate, however, was decreased in DeTMA-DS and DeTMA-TS systems and increased in DTMA-DS system with cholesterol addition. The encapsulation efficiency results were supported by the vesicle size and therefore the vesicle core volume, which were also increased with cholesterol addition in all three systems. On the other hand, vesicular membrane rigidity was found to be a dominant factor in determining release rate. The opposite effects of cholesterol on the release rate in different cationic surfactant systems were explained by the opposite effects (that is, condensation and disordering effects prevailing in vesicular bilayers at liquid-crystalline phase and gel phase, respectively) on their membrane rigidity.

[1] C. W. Chiu, C. H. Chang and Y. M. Yang, *Soft Matter*, 2013, **9**, 7628.

[2] Y. S. Liu, C. F. Wen and Y. M. Yang, *Sci. Adv. Mater.*, 2014, **6**, 954.

[3] C. H. Lee, Y. M. Yang, K. L. Leu, H. Y. Lin, C. H. Liang and C. H. Chang, *Colloid Polym. Sci.*, 2015, **293**, 2239.

Lipid-liquid crystalline cubic phase in drug diffusion studies

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Reverse cubic phase can be used to accommodate and controlled release of bioactive molecules ranging from the low molecular weight drugs to peptides or proteins. Efficiency of transport of the drug in the LCP (liquid-crystalline cubic phase) can be described e.g. by the diffusion coefficient. Diffusion of an incorporated drug from the LCP depends on the size and polarity of the molecules, the rate of transport can be tuned, e.g. by applying lipids with various acyl chains to modify the charge delineating the aqueous channels. To form the pH sensitive LCP a weak acid - linoleic acid (LA, $pK_a=5.6$) was added to the neutral monolinolein (ML) [1]. Tunable interactions with the lipidic matrix led to the observed pH-dependent drug release from the phase. Here AQ2S, negatively charged neuroprotective drug was incorporated into monolinolein (ML) based LCP undoped or doped with linoleic acid. Structural parameters of the cubic phases formed with the incorporated lipids and AQ2S were characterized by small-angle X-ray scattering (SAXS). Because AQ2S is electroactive, its release profile was evaluated based on its electroreduction current. Release behavior of the drug was determined at pH 3 where phase was neutral because of the presence of protonated form of LA and at pH 7, where carboxyl groups were ionized. It was found that doping ML based LCP with linoleic acid have a major impact on the drug release at neutral pH, where electrostatic repulsion exists between negatively charged drugs and negatively charged lipidic domains [2]. Electrochemical methods - chronocoulometry and voltammetry at micro and normal size electrodes – were also applied to simultaneously determine the diffusion coefficients and effective concentrations of AQ2S in the LPCs. Using steady-state voltammetry on microelectrode and macroelectrode both diffusion coefficient (D) and concentration of the electroactive probe in the cubic phase were evaluated. It was shown that the concentration of AQ2S in the phase depends on the charge of the aqueous channel, and was found to be smaller than that introduced to the cubic phase, which reflects the contribution of drug interactions with the lipid bilayer.

Acknowledgements This work was supported by Sinergia project no. CRSII2 154451 financed by the Swiss National Science Foundation.

[1] R. Negrini and R. Mezzenga, *Langmuir*, 2011, **27**, 5296.

[2] R. Negrini, A. Sanchez-Ferrer and R. Mezzenga, *Langmuir*, 2014, **30**, 4280.

RAMAN APPROACH TO MONITOR THE INTERNALISATION OF PEG COATED COLLOIDAL GOLD NANOPARTICLES IN CELLS

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In the last decade gold nanoparticles (AuNPs) were proposed as targeted drug delivery platforms. The conventional method used to monitor the cellular internalization of AuNPs is fluorescence spectroscopy, when dye molecules as labels are needed.

In this work we propose Raman mapping as a label-free method for monitoring the internalisation of AuNPs in A549 cells. Raman mapping provides chemical information coupled with spatial information. Raman spectra of cells were analyzed by using principal component analysis (PCA).

Short chain PEG (PEG 200) was used for the one step synthesis of AuNPs, following a procedure reported previously [1]. In this case PEG 200 was the reducing agent and surfactant, as well. Moreover, PEG 200 as surface coating agent, confers high biocompatibility to the AuNPs, as proved by MTT assay. TEM micrographs revealed a spherical morphology and a mean diameter of 12 nm.

Raman mapping enabled the discrimination between cellular compounds and the label free detection of internalized AuNPs in cells.

References

Leopold N., Chis V., Mircescu N.E., Marisca O.T., Buja O.M., Leopold L.F., Socaciu C., Braicu C, Irimie A., Berindan-Neagoe I., (2013). One step synthesis of SERS active colloidal gold nanoparticles by reduction with polyethylene glycol. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 436: 133– 138

Acknowledgement

Financial support from UEFISCDI (Executive Agency for Higher Education, Research, Development and Innovation Funding) through grant PN-II-RU-TE- 2014-4-2211, grant PN-II-RU-TE-2014-4 0944 and grant PN-II-RU-TE-2014-4-1135 is highly acknowledged.

Phosphate based cross-linking agents for poly(vinyl alcohol): physico-chemical characterization and bio-mineralization

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PVA is a highly hydrophilic, water-soluble polymer with chemical versatility and stability. Its properties have been widely investigated also because of its ability to form physical and chemical hydrogels that have already found use in personal care and biomedical applications, including cosmetics, drug-delivery, cartilage replacement. Despite its biocompatibility and biodegradability, PVA is not commonly used as a load bearing biomaterial *per se*, due to the lack of mechanical integrity in physiological conditions. Thus, several strategies to improve its mechanical properties were investigated so far, including the use of cross-linking agents¹ (such as aldehydes, anhydrides, polycarboxylic acids), freeze-thawing cycles,² as well as the integration of organic³ and inorganic fillers⁴. Phosphate-based crosslinkers have been recently reported as valuable alternatives to more traditional cross-linking agents⁵ thanks to their non-toxicity and to the ability of forming phosphate esters with hydroxyl groups under relatively mild conditions.⁶

In this contribution we present our latest results on the physico-chemical characterization of phosphate-based cross-linked poly(vinyl alcohol) (PVA) hydrogels, in view of their application as biomedical materials.

We investigated the use of sodium trimetaphosphate and hexametaphosphate to produce cross-linked PVA hydrogels, and we characterized the obtained materials in view of their application as bio-mineralizable orthopedic substitutes. The materials have been fully characterized by means of thermal analysis (DSC, TGA), rheology (amplitude/frequency sweep, dynamic mechanical analysis) and microscopy (SEM, AFM). The results demonstrate that materials with different properties could be obtained by the careful control on experimental conditions (*i.e.*, pH, T, reaction time, concentration). In particular, the study is focused on the effect of the different phosphate esters (both in terms of their presence and chemical nature) in the PVA hydrogel. The influence of phosphates on the mineralization properties (evaluated in simulated body fluid at 37°C) was also evaluated, in the attempt of relating the morphology and the amount of the mineral phase to the composition of the cross-linked PVA hydrogels.

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- [1] B. Bolto *et al.*, *Prog. Polym. Sci.*, 2009, **34**, 969.
- [2] C.M. Hassan, N.A. Peppas, *Biopolymers: PVA Hydrogels, Anionic Polymerisation Nanocomposites*, 2000, 4, 37-65, Springer, Heidelberg, Germany.
- [3] M. Roohani *et al.*, *Eur. Polym. J.*, 2008, **44**, 2489.
- [4] M. Kokabi, M. Sirousazar, Z.M. Hassan, *Eur. Polym. J.*, 2007, **43**, 773.
- [5] G. Leone *et al.*, *J. Mater. Sci. Mater. Med.*, 2010, **21**, 2491
- [6] S. Lack *et al.*, *Carbohydrate Research*, 2007, **342** 943.

Mesoporous Silica Nanoparticles Functionalized with Hyaluronic Acid and Chitosan Biopolymers. Effect of Functionalization on Cell Internalization

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Mesoporous Silica Nanoparticles (MSNs) are being used as carriers for drug delivery systems because of their particular features as high surface areas (up to 1400 m²/g), high pore volumes (1-3 cm³/g) and a narrow pore size distribution (2-5 nm). In the last few years the attention has been focused on the synthesis of bio-conjugates functionalized with saccharide-based biopolymers, proteins and peptides [1,2]. These can be useful not only for specific cell targeting [3] but also for obtaining stimuli-responsive systems with a lower toxicity and a higher biodistribution than non-functionalized MSNs [4]. In this work mesoporous silica nanoparticles (MSNs), based on the MCM-41 matrix, were functionalized with amino groups, and then with hyaluronic acid (HA) or chitosan (CHIT) to fabricate bioactive conjugates. The role of functionalization toward cytotoxicity and cellular uptake, using 3T3 mouse fibroblast cells, was investigated. A very high cell viability was obtained regardless the type of MSNs functionalization. On the contrary, fluorescence microscopy and transmission electron microscopy give evidence of significant differences in terms of cellular uptake and stability of the particles in the biological medium depending on the type of MSNs functionalization. Indeed, MSN-NH₂ and MSN-HA are easily internalized in the cytoplasm, whereas MSN-CHIT tend to give large aggregates that cannot be internalized by 3T3 cells.

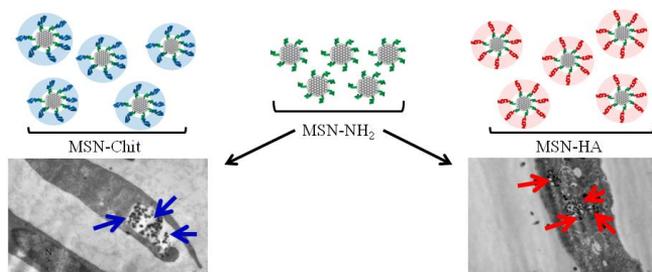


Figure 1 Electron micrographs of mouse fibroblast 3T3 incubated for 24 h with 100 µg/mL of MSN-CHIT and MSN-HA respectively in the culture medium.

- [1] A. Baeza, M. Colilla, M. Vallet-Regí, *Expert Opin. Drug Deliv.* 2015, **12**, 319.
- [2] L. Medda, M.F. Casula, M. Monduzzi, A. Salis, *Langmuir* 2014, **30**, 12996.
- [3] G. Villaverde, A. Baeza, G.J. Melen, A. Alfranca, M. Ramirez, M. Vallet-Regí, *J. Mater. Chem. B* 2015, **3**, 4831.
- [4] Y. Chen, H. Chen, J. Shi, *Adv. Mater.* 2013, **25**, 3144.

Hydrodynamic Trapping of Immune Synapse Proteins in Supported Lipid Bilayers

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Background: Much research has been devoted to the study of important proteins in the immune system and especially in the immunological synapse (IS). The IS functions as the contact area between immune cells and is crucial for initiating an immune response. However, static and kinetic information about intermolecular interactions in the IS are to a large extent lacking. We here use supported lipid bilayers (SLBs) to trap proteins on a planar SLB (1). This allows us to study intermolecular forces between different membrane proteins providing biophysical knowledge about their molecular behavior. The aim of this project is to investigate the intermolecular forces of characteristic molecules in the IS, including: CD45, CD4 and CD2, coupled to an SLB.

Methods: Hydrodynamic trapping of fluorescently-labelled human CD45 (hCD45), human CD4 (hCD4), rat CD2 (rCD2) and Streptavidin (SA) was done as previously described by Jönsson et al. (1). In brief, SLBs were prepared with vesicles containing 5 wt% 1,2-dioleoyl-*sn*-glycero-3-[(N-(5-amino-1-carboxypentyl)iminodiacetic acid)succinyl] (nickel salt) (DGS-NTA) mixed with 95 wt% 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) lipids. Alternatively, vesicles containing 0.05 wt% 1,2-dipalmitoyl-*sn*-glycero-3-phosphoethanolamine-N-(cap biotinyl) (sodium salt) (biotin-PE) mixed with 99.95 wt% POPC lipids was used for experiments on the protein streptavidin. A micropipette was mounted on a custom made micropipette holder that was placed above the SLB. Applying negative pressure over the micropipette allows for accumulation of the proteins below the pipette, which was captured using total internal reflection fluorescence microscopy (TIRFM).

Results and Discussion: We studied the trapping and accumulation of the T-cell proteins hCD45, hCD4 and rCD2, and the protein SA as a model protein. Accumulation of the proteins occurred in a circular area distinguishable from the surrounding bilayer by a higher fluorescence intensity, shown for hCD45 in Figure 1. The relative accumulation of proteins varies across the trap and is dependent on the applied hydrodynamic energy per μm^2 , ϵ_{hydro} , at each position. The accumulation is also dependent on the dimensions of the protein as well as the intermolecular interactions between the proteins. The initial linear increase in Figure 1F is due to the hydrodynamic force from the trap being balanced by entropic forces, whereas at higher applied energies (protein densities) the concentration levels out at a value where repulsive intermolecular interactions between the proteins is high. We also saw that the taller molecules, hCD45 and hCD4, seem to bend at higher hydrodynamic forces.

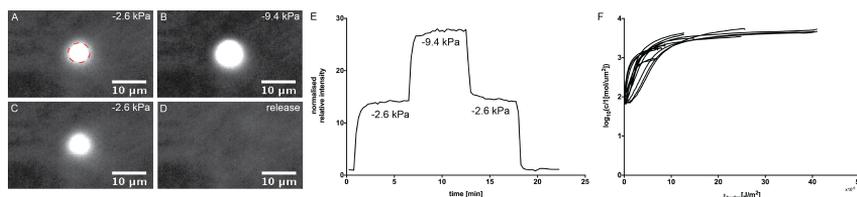


Figure 1. Hydrodynamic trapping of hCD45.

Human CD45 accumulating under different pressures: (A) -2.6 kPa, (B) -9.4 kPa and (C) -2.6 kPa on the SLB. (D) Turning off the applied pressure leads to release of the trapped hCD45. (E) The intensity of trapped hCD45 (area indicated with the dashed circle) versus time at different applied pressures. (F) The relative accumulation of hCD45 as a function of ϵ_{hydro} from different experiments.

References:

1. Jönsson P, et al. Proc. Natl. Acad. Sci. U.S.A., 109:10328–10333 (2012).

New concept of mesoporous nanocontainers synthesis and loading

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Mesoporous silica nanoparticles (MSNs) are characterized by a large specific area and an ordered system of pores which diameter can be varied from 2 to 50 nm. Such particles are of significant interest as nanocontainers for different substances, primarily – for drugs [1]. The main approach of the MSNs' creating is a sol-gel synthesis using "inert" surfactant micelles as a template. After the synthesis completed, the template is removed by chemical etching or high-temperature treatment of the MSNs and a targeted functional compound is loaded.

The drawbacks of this classical scheme are its multistage nature and a relatively low uptake of the targeted substance by silica vehicles; generally it does not exceed 0.3 g per 1 g of SiO₂ [2]. Moreover, in most cases, it is necessary to modify the inner/outer surface of the MSNs by grafting some functional compound; this allows one to control the sorption kinetics of the targeted substance and its release rate.

We propose a new approach that allows one to combine the stages of silica nanocontainers synthesis and their loading with the targeted substance. Moreover it is greatly facilitate the control of the uploaded substance release without any additional modification of the nanocontainers' internal or external surface. This approach is based on the use of micelles (or vesicles) of the *targeted substance itself* (instead of *inert* surfactant ones) as templates in the MSNs synthesis [3, 4].

The prospects and benefits of such route are exemplified by the encapsulation of various functional amphiphilic compounds (for example, bactericidal drugs and corrosion inhibitors). Wherein, the possibility of silica nanocontainers synthesis using hydrolyzable drug as a templating agent has been demonstrated for the first time.

It is shown that the synthesized nanocontainers are characterized by an extremely high capacity with respect to templating functional compound (about 1 g and over per 1 g of SiO₂) and are also pH-sensitive.

The kinetics of the template molecules release from the MSNs has been studied at various pH and temperature values; and the features of this process in static and quasi-dynamic conditions have been analyzed.

We also discuss the possibility of such MSNs use as a basis to creation of protocells – fundamentally new means of drug delivery.

Acknowledgements The work was supported by the Russian Foundation for Basic Research; Project no. 16-03-00118.

1. H. Mekaru, J. Lu and F. Tamanoi, *Adv. Drug Delivery Rev.*, 2015, **95**, 40.
2. C. Bharti, U. Nagaich, A. K. Pal and N. Gulati, *Int. J. Pharm. Invest.*, 2015, **5**, 124.
3. O.V. Dement'eva, I.N. Senchikhin, E.M. Sedykh, I.N. Gromyak, V.A. Ogarev and V.M. Rudoy, *Colloid J.*, 2016, **78**, 52.
4. O.V. Dement'eva, and V.M. Rudoy, *RSC Adv.*, 2016, **6**, 36207.

Inducing an order-order morphological transition via chemical degradation of amphiphilic diblock copolymer nano-objects

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The disulfide-based cyclic monomer, 3-methylidene-1,9-dioxo-5,12,13-trithiacyclopentadecane-2,8-dione (MTC), is statistically copolymerized with 2-hydroxypropyl methacrylate (HPMA) to form a range of diblock copolymer nano-objects via reversible addition-fragmentation chain transfer (RAFT) polymerization. Poly(glycerol monomethacrylate) (PGMA) is employed as the hydrophilic stabilizer block in this aqueous polymerization-induced self-assembly (PISA) formulation, which affords pure spheres, worms or vesicles depending on the target degree of polymerization for the core-forming block. When relatively low levels (< 1 mol %) of MTC are incorporated, high monomer conversions (> 99%) are achieved and high blocking efficiencies are observed, as judged by ¹H NMR spectroscopy and gel permeation chromatography (GPC), respectively. However, the side reactions that are known to occur when cyclic allylic sulfides such as MTC are statistically copolymerized with methacrylic comonomers lead to relatively broad molecular weight distributions. Nevertheless, the worm-like nanoparticles obtained via PISA can be successfully transformed into spherical nanoparticles by addition of excess tris(2-carboxyethyl)phosphine (TCEP) at pH 8-9. Surprisingly, DLS and TEM studies indicate that the time scale needed for this order-order transition is significantly longer than that required for cleavage of the disulfide bonds located in the worm cores indicated by GPC analysis. This reductive degradation pathway may enable the use of these chemically-degradable nanoparticles in biomedical applications, such as drug delivery systems and responsive biomaterials.

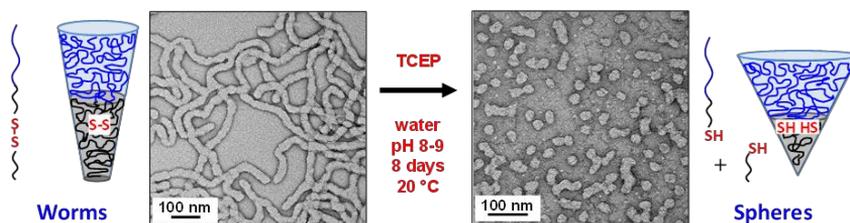


Figure 1 TEM images obtained for a 0.20 % w/w aqueous dispersion of PGMA₅₆-P(HPMA₁₇₀-*stat*-MTC_{0.85}) before and after exposure to TCEP, including a Cartoon representation of how the worm-to-sphere transition is likely to have affected the copolymer chain packing.

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Synthesis of new bile alcohols in 24 position

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Bile salts are natural surfactants with a diverse biological activity. Some of its derivatives, have shown antiproliferative, antimicrobial and anticancer activity [1]. Lately, new compounds have been synthesized with a hydrophobic expansion in the region 3 β ; as a result, interesting supramolecular properties arise and some of them even show cytotoxic activity in tests recently conducted [2]. In our lab, we synthesized two new deoxycholic acid with adamantyl and nicotinamyl derivatives with moieties at 3 β position. The compounds were obtained from methyl 3 β -aminodeoxycholate and adamantyl and nicotinamyl acyl chlorides. The resultant amide was hydrolyzed and reduced with borane, to generate the desired compounds. [2] Products were fully characterized by NMR, Mass and Monocrystal X ray diffractometry. Biological tests are being carried out these days.

References

[1] Huang, L.; Sun, Y.; Zhu, H; Zhang, Y.; Xu, J.; Shen, Y.; Steroids, 2009, **74**, 701

[2] Trillo, J.; Meijide, F.; Jover, A.; Soto V.H.; de Frutos, S.; di Gregorio, M.; Galantini, L.; Vázquez- Tato, J.; RSC Adv. **4**, 2014, 5598

Design of hyaluronic acid hydrogels: Effect of crosslinker concentration on drug release and toxicity

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Hyaluronic acid (HA) is a natural polysaccharide widely distributed into the human body. The physicochemical properties and biocompatibility make it a suitable candidate to be used in biomedical and pharmaceutical applications [1]. As HA is degraded *in vivo* by hyaluronidase [2], the preparation of materials based on chemically crosslinked HA for drug delivery could represent a useful approach for increasing the *in vivo* resistance to degradation [3]. Hydrogels are crosslinked networks of hydrophilic polymers. These materials are very similar to biological tissues in terms of their physical properties, due to their high water content and soft consistency. Furthermore, the capacity of hydrogels to contain molecules of different sizes enables using them as drug delivery systems via several administration routes [4,5]. The aim of this work was to study the crosslinking effect of HA hydrogels on drug release properties and *in vitro* cytotoxicity. HA hydrogels were prepared with different degrees of crosslinking using butanediol diglycidyl ether (BDDE) as a crosslinking agent. A lipophilic model drug, ketoprofen (KP), and a hydrophilic model drug, theophylline (TH), were incorporated to HA hydrogels and the release properties of HA hydrogels as a function of the degree of crosslinking were studied. The results showed that, while a fast release was observed for a low crosslinking degree, a more sustained release was obtained for HA hydrogels with a high degree of crosslinking. The mathematical models applied to fit the experimental values show that the dominant mechanism in the drug release is Fickian diffusion. Furthermore, the MTT test was applied to study hydrogels toxicity and the influence of crosslinker concentration on cells viability was determined. Preliminary results evidenced that HA hydrogels induce low cytotoxicity in HeLa human cell line, showing more than 80% of cell viability. In conclusion, the results obtained on the release properties of HA hydrogels indicate that there are suitable for controlled drug delivery due to the possibility of modifying the crosslinking degree that influence release kinetics. Likewise, *in vitro* assays show that these materials could be considered as good candidates for implant developments due to their low cytotoxicity.

Acknowledgements The financial support of the Ministerio de Economía y Competitividad (project CTQ2011-29336-CO3) and the Generalitat de Catalunya (consolidated research group 2014SGR1655)

- [1] L. Lapčák, L. J. Lapčák, S. De Smedt, J. Demeeste, et al. Chemical Review. 1998, **98**, 2663-2684.
- [2] R. Stern, M.J. Jedrzejew. Chem. Rev. 2006, **106**, 818-839.
- [3] T. Segura, B. Anderson, P. Chung, R. Webber, et al. Biomaterials. 2005, **26**, 359-371.
- [4] N.A. Peppas, P. Bures, W. Leobandung, H. Ichikawa. European Journal of Pharmaceutics and Biopharmaceutics. 2000, **50**, 27-46.
- [5] F. Roig, C. Solans, J. Esquena, M.J. García-Celma. J. Appl. Polym. Sci. 2013, **130**, 1377-1382.

Structure-activity relationships of a series of self-assembling compounds on 1,4-dihydropyridine core as delivery agents

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Recently development of new non-viral vectors as DNA or drug delivery systems has resulted in elaboration of various nanopharmaceutical applications. Polyfunctional pyridinium derivatives on the 1,4-dihydropyridine (1,4-DHP) scaffold form liposomes and efficiently act as gene delivery agents, for example, 1,4-DHP **1**. [1,2] The influence of lipid head-groups [2] and linker structure [3] on transfection activity as well as properties of 1,4-DHP **1** formed liposomes [4] were studied.

The aims of the work are: 1) modification of substituents on the 1,4-DHP cycle; 2) studies of biological activity and physical-chemical properties; 3) characterisation of nanoparticles formed by modified delivery agents; 4) clarification of the structure-activity relationships.

A series of amphiphiles as putative gene delivery agents differing in the substituents of 1,4-DHP core have been designed and synthesised. It can be concluded that structure of substituents of at positions 2 and 6 of 1,4-DHP molecule are important for radical scavenging properties. The buffering capacity of studied N-unsubstituted 1,4-DHPs were in the pH range 6.8–8.8. All amphiphiles possessed self-assembling properties, formation of nanoparticles with the average size 79–273 nm, which was dependant from the structure of compound. 1,4-DHPs with modifications at the positions 2 and 6 or 4 of 1,4-DHP molecule showed highest transfection activity of pEGFP-C1 plasmid DNA delivery into the BHK-21 cell line.

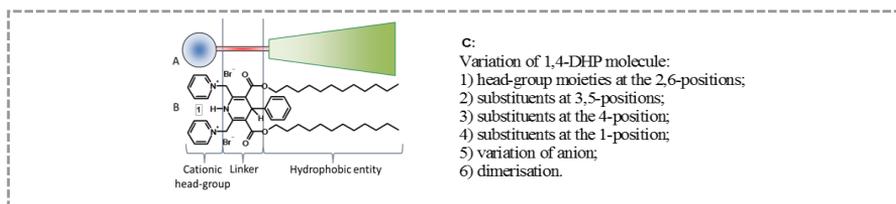


Figure 1. General structure of cationic lipids (A) [5]; structure of cationic 1,4-DHP amphiphile **1** (B); planned structural variations (C).

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- [1] Z. Hyvönen, A. Plotniece, I. Reine et al, *BBA*, 2000, **1509**, 451.
- [2] K. Pajuste, Z. Hyvönen, O. Petrichenko et al., *New J. Chem.*, 2013, **37**, 3062.
- [3] O. Petrichenko, M. Rucins, A. Vezane et al., *Chem. Phys. Lip.*, 2015, **191**, 25.
- [4] M Rucins, O. Petrichenko, K. Pajuste et al., *Adv. Mater. Research*, 2013, **787**, 157.
- [5] G. Byk, C. Dubertret, V. Escriou et al., *J. Med. Chem.*, 1998, **41**, 224.

Macromolecular HPMA-Based drug delivery system - behavior in protein environment

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Polymer drug carriers based on N-(2-hydroxypropyl) methacrylamide (HPMA) copolymers, which have cholesterol moieties and anti-cancer drug bound via cleavable bond, have been studied extensively over the past few years, to understand the self-assembly in dilute aqueous solutions [1,2]. Above a certain concentration, micelle-like nanoparticles (NPs) having ellipsoidal shape are observed. However, there is a lack of knowledge on the behavior of these drug carriers in human blood environment.

We use synchrotron small angle X-ray scattering (SAXS) to investigate HPMA copolymers that are dissolved in an aqueous solution of human serum albumin (HSA), as a step on the way to the blood environment, to reveal the interaction between the NPs and HSA. We find that the size of the NPs is reduced when HSA is present. We suggest that some of the cholesterol moieties from HPMA copolymer bind to HSA and are removed from the nanoparticles, which changes their size and shape.

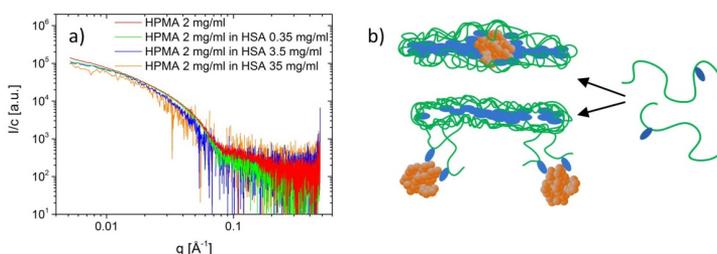


Figure 1 a) SAXS curves of HPMA copolymers ($M_w = 33290$ g/mol, with 2 mol% cholesterol) having a concentration of 2 mg/ml in HSA solution of various concentrations. b) HSA interacts with the NPs by forming complex with the NPs (top) or removing cholesterol groups from the NP core (bottom).

Acknowledgements We thank DFG for financial support.

- [1] S. K. Filippov, P. Chytil, P. V. Konarev, M. Dyakonova, C. M. Papadakis, A. Zhigunov, J. Plestil, P. Stepanek, T. Etrych, K. Ulbrich, D. I. Svergun, *Biomacromolecules*, 2012, **13**, 2594
- [2] S. K. Filippov, J. M. Franklin, P. V. Konarev, P. Chytil, T. Etrych, A. Bogomolova, M. Dyakonova, C. M. Papadakis, A. Radulescu, K. Ulbrich, P. Stepanek, D. I. Svergun, *Biomacromolecules*, 2013, **14**, 4061

Super Liquid Repellency

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The Pandora box of surfaces able to repel liquids is still a hot research topic. These surfaces are able to remove dust (self-cleaning) and can even hinder the growth of microorganism colonies.

Over the past years we have created superhydrophobic coatings (water repellent) where water droplets sit on microscopic pockets of air, which are trapped beneath the liquid drops. We even designed superamphiphobic coatings (i.e. water and oil repellent). One of these types are the so called slippery surfaces, where after infusing a rough/porous structure with a lubricant a deposited drop will slip by tilting the surface by a few degrees. This pressure-stable omniphobicity opens exciting applications for anti-biofouling, anti-icing or anti-frost performances.

However, the mechanism how a drop moves on slippery surfaces is still unclear.

In this case, we used Laser Scanning Confocal Microscopy (LSCM) to observe the contact angles and evaluate the dynamics of droplet motion on the microscale.

Dynamic light scattering study of amorphous calcium phosphate formation

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Amorphous calcium phosphate (ACP) attracts attention as a precursor to calcium phosphates (CaPs) formation *in vitro* and *in vivo* and due its excellent biological properties [1-3]. In general, the dominant mechanism of ACP formation *in vitro* is aggregation. Calcium and phosphate ions associate forming prenucleation clusters, which aggregate to spherical ACP nanosized particles, which in turn aggregate to chain-like aggregates [1,4]. A widely used technique for following nanoparticles aggregation in general is dynamic light scattering (DLS). However, DLS was scarcely used for the investigation of calcium phosphates [5]. The aim of this research was to use DLS for following ACP formation kinetics at different supersaturations.

Precipitation of ACP was initiated by fast mixing of equimolar reactant solutions. Induction time for nucleation of crystalline phase, i.e. time needed for the commencement of ACP transformation, was determined from potentiometric measurements. DLS was used to follow the changes in ACP particles sizes during induction time. Information about initial formation rates was obtained from initial change of hydrodynamic diameter of particles with time, when this change was linear [6]. Formed ACP was characterized by FT-IR spectroscopy and atomic force microscopy (AFM).

During induction time spherical particles and their chain like aggregates, characteristic for ACP, were formed as confirmed by AFM and FTIR. The initial formation rates, as well as the size of the particles, depended on the initial supersaturation.

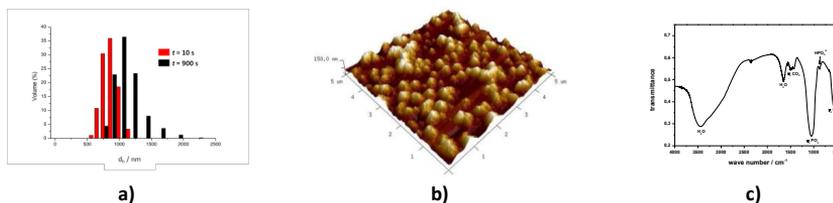


Figure 1 Distribution of hydrodynamic diameter (a), atomic force micrographs (b) and FTIR spectra of amorphous calcium phosphate particles formed at highest investigated supersaturation.

Acknowledgements The financial support of Croatian Science Foundation, Grant HRZZ-5055 is greatly acknowledged.

- [1] C. Combes, and C. Rey, *Acta Biomater.*, 2010, 6, 3362.
- [2] J. Mahamid, A. Sharir, L. Addadi and S. Weiner, *Proc. Natl. Acad. Sci. U.S.A.*, 2008, **105**, 12748.
- [3] E. Beniash, R. A. Metzler, R. S. K. Lam and P. U. P. A. Gilbert, *J. Structural Biology*, 2009, 166, 133
- [4] P. Bar-Yosef Ofir, R. Govrin-Lippman, N. Garti and H. Füredi-Milhofer, *Cryst. Growth Des.*, 2004, **4**, 177.
- [5] C.-G. Wang, J.-W. Liao, B.-D. Gou, J. Huang, R.-K. Tang, J.-H. Tao, T.-L. Zhang and K. Wang, *Cryst. Growth Des.*, 2009, 9, 2620.
- [6] R. A. French, A. R. Jacobson, B. Kim, S. L. Isley, R. L. Penn, and P. C. Bavey, *Environ. Sci. Technol.* **43** (2009) 1354.

Influence of structurally different amino acids on calcium phosphate precipitation

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Knowledge about the mechanisms of interactions of soluble small organic molecules and/or macromolecules with inorganic crystals is of major importance in understanding the crystallization processes in nature, as well as for the production of materials whenever precise control of crystal size, morphology and texture is required [1]. Among different biogenic crystals, calcium phosphates (CaPs) attract attention due to their role in the normal and pathological mineralization, as well as in industrial processes [1-3]. Recent investigations of influence of additives on CaP formation described in literature are mostly focused on proteins and their synthetic analogous [4]. Although general principles of these interactions are known, the role of specific amino acids is still not clear.

The aim of this research was to investigate the influence of structurally different amino acids on CaP formation and transformation. The selected amino acids differ, either in their charge (Asp, Asn, Lys) or in polarity (Ser, Tyr versus Ala, Phe).

Calcium phosphates precipitation was initiated by mixing the equimolar calcium and phosphate solutions, at strictly controlled hydrodynamic and thermodynamic conditions. The progress of reaction was continuously followed potentiometrically and induction time for nucleation of crystalline phase, i.e. time needed for the commencement of amorphous calcium phosphate (ACP) transformation, was determined. Precipitates were isolated at predetermined intervals during 1 hour and analysed by means of PXRD, FT-IR and SEM.

It was found that in the control system the initial CaP phase that precipitated was ACP which transformed to calcium deficient apatite (CaDHA). Similar mechanism of solid phases formation was observed in the presence of Asn, Lys, Ser, Ala, Phe as well, but the ACP transformation was slightly inhibited, as evidenced by increased induction time. No specific effect on morphology of CaDHA, precipitated in the presence of these amino acids, was observed. However, the formation of CaDHA was progressively inhibited with increasing Asp and Tyr concentration and in these systems DCPD was formed. The obtained results indicated that, in addition to charged, the hydrogen bonding amino acids can be of importance in CaPs formation.

Acknowledgements The financial support of Croatian Science Foundation, Grant HRZZ-5055 is greatly acknowledged.

[1] M.D. Sikirić and H. Füredi-Milhofer, *Adv. Colloid Interface Sci.*, 2006, **128-130**, 135.

[2] L. Wang and G.H. Nancollas, *Chem. Rev.* 2008, **108**, 4628.

[3] S.V. Dorozhkin and M. Epple, *Angw. Chem. Int. Ed.*, 2002, **41**, 3130.

[4] K. Bleek and A. Taubert, *Acta Biomater.*, 2013, **9**, 6283.

Comparative study of amorphous phases formation and transformation in calcium phosphate and calcium carbonate precipitation systems

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A number of recent studies pointed out that the amorphous calcium phosphate (ACP) or amorphous calcium carbonate (ACC) are the first step in either, invertebrate or vertebrate hard tissues formation [1-3]. Therefore, the renewed interest for *in vitro* and *in vivo* investigations of mechanisms of their formation and transformation is not surprising. In spite of the fact that the calcium carbonates and calcium phosphates occur in different organisms, there are a number of similarities in mechanisms of their formation and transformation, as well as in their role in organisms. A number of researchers point out the usefulness of comparing those two systems, but this is still not fully exploited approach [4,5].

In order to contribute to elucidation of a role of amorphous phases, the physical chemical properties of ACP and ACC formed in the systems at defined and comparable initial experimental conditions (supersaturation, constituent ions ratio, ionic strength and presence of relevant inorganic additives) have been studied. At that, the formation and transformation of ACP and ACC in three model precipitation systems of increased complexity were investigated: (a) system containing only constituent ions, (b) system with increased ionic strength and (c) system containing physiologically relevant co-ions.

The experiments were initiated by mixing the reactant solutions at strictly controlled hydrodynamic and thermodynamic conditions, while the progress of reaction was continuously followed potentiometrically. Precipitates obtained after up to 10 minutes were isolated and analysed by means of IC, PXRD, FT-IR, TEM, EPR and TG.

The results have shown that ACP is more stable and nucleated at lower relative supersaturations in comparison to ACC formation. Typically, ACC preceded the formation of either, thermodynamically stable calcite or metastable vaterite, aragonite and/or monohydrocalcite, while ACP always transformed to metastable calcium deficient apatite. The exact transformation mechanisms were found to depend on complexity of the precipitation systems, while the magnesium ions were found to strongly stabilize both amorphous phases.

Acknowledgements The financial support of Croatian Science Foundation, Grant HRZZ-5055 is greatly acknowledged.

- [1] L. Addadi, S. Raz and S. Weiner, *Advanced Materials*, 2003, **15**, 959.
- [2] J. Mahamid, A. Sharir, L. Addadi and S. Weiner, *Proc. Natl. Acad. Sci. U.S.A.*, 2008, **105**, 12748.
- [3] E. Beniash, R. A. Metzler, R. S. K. Lam and P. U. P. A. Gilbert, *J. Structural Biology*, 2009, **166**, 133.
- [4] K. Bleek and A. Taubert, *Acta Biomater.*, 2013, **9**, 6283.
- [5] D. Gebauer, M. Kellermeier, J. D. Gale, L. Bergström and H. Cölfen, *Chem. Soc. Rev.*, 2014, **43**, 2371.

Structure and mechanical properties of castor oil hybrid Films

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Castor oil has been used as a matrix material to synthesize bio-based films with promising applications in pharmaceuticals. Properties of vegetable oils such as biocompatibility, biodegradability and cost-effectiveness make them very good candidates for the production of new bio-friendly films that can replace conventional medical devices in pharmaceuticals. Such medical devices include dressings [1] aiming in wound healing and transdermal drug delivery systems [2]. The novelty of the present castor oil hybrid inorganic-organic films was based on their environmentally friendly chemical synthesis that is based on sol-gel reaction preventing the use of organic solvent and curing. The synthesis procedure included, the functionalization of castor oil with an inorganic precursor (isocyanatopropyltriethoxysilane/IPTES) and afterwards the spreading of the functionalized oil onto a water surface (Fig.1A). The whole system was sealed and the control of the humidity during the evaporation of the water induces the cross-linking reaction via hydrolysis and condensation procedure (sol-gel reaction). After one 1 day we observed the formation of solid-like films, transparent with a micrometric thickness and characterized by a steady value of the elastic modulus (Fig.1B). The goal of this work was to characterize the physical properties of castor oil hybrid films and to highlight their pharmaceutical potential. More specifically, our approach aimed to investigate the kinetics of the castor oil cross-linking by means of rheology and Wide angle X-Ray Scattering. The structural and viscoelastic studies of the final state films revealed their solid-like nature. In addition to that, we performed complementary experiments to study their mechanical properties by nanoindentation technique allowing us to measure their Young modulus. Finally, their capacity to entrap model drugs was evaluated as well as their stability in physiological media. Their interaction with cellular elements such as fibroblasts was assessed to confirm their biocompatibility.

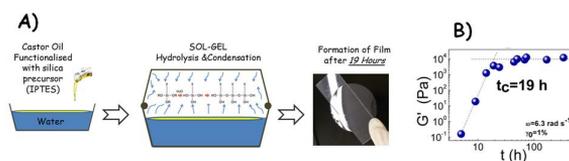


Figure 1 A) Schematic representation of the formation process of the castor oil hybrid films. B) The time evolution of the elastic modulus (G') of the film.

[1] A. M. Díez-Pascual, A. L. Díez -Vicente , *Biomacromolecules*, 2015, **16**, 2631.

[2] R. Guo, X. Du, R. Zhang, L. Deng, A. Dong, J. Zhang, *Europ. J. Pharmaceutics and Biopharmaceutics*, 2011, **79**, 574

Controlled Drug Release from Contact Lenses Prepared by Using the Layer-by-Layer Method

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In recent years, researchers focus on the controlled release of ophthalmic drugs from contact lenses. Synthetic polymer p-HEMA is widely used as soft contact lens material in the biomedical applications. However, drug loaded p-HEMA contact lenses release the drug in a few hours, which is an undesirable situation. Even though it is more successful than eye drops and ointment, sustained drug release cannot be provided as desired^[1]. Thus, there are some methods to slowdown the drug release such as surface of hydrogels modification using micro and nano particle^[2].

In this study, it is aimed to develop drug loaded p-HEMA contact lenses for the treatment of the conjunctivitis, which is one of the common eye diseases. Dexamethasone is one of the drugs used for the treatment, was added into hydrogels. The surface of hydrogels is modified via "Layer By Layer" (LbL) technique, in which chitosan (cationic) and hyaluronic acid (anionic) were used to form layers. By using this technique, it is possible to obtain up to ten layers. The formation of each layer was monitored by measuring absorbance, light transmittance and water contact angle of the lenses. Moreover, a thick layer of drug free chitosan was added on the top of the contact lenses, which already had five layers formed via LbL technique, as mentioned before. Addition of 5 layers on the top of the contact lenses was reduced the drug release from 60 % to 30 % in 50 hours. It was demonstrated that the formed chitosan/hyaluronic acid layers act as a barrier for drug release. Moreover, addition of chitosan layer on top of the contact lenses allowed us to see a delay time before the release of drug as well as it prevented the burst release. The observed delay time varied with the changing thickness of the chitosan layer applied. As it is seen from Fig.1, the delay time increased from 15 minutes to 45 minutes with the increase in thickness. Thus, controlled drug release was accomplished.. Also, side effects of the drug are eliminated which is released at the beginning. These experiments show clearly that drug release rate and released drug amount can be adjusted according to the patient's suggested drug regimes without losing the other functions of contact lenses such as correcting the vision.

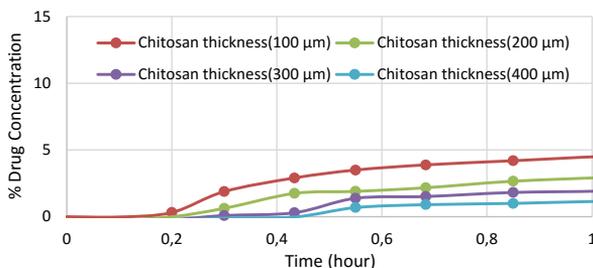


Figure 1. Drug release from p-HEMA contact lenses that were modified by using LbL method as well as drug free chitosan layers with different thickness.

[1] C. Le Boulrais, L. Acar, H. Zia, P.A. Sado, T. Needham and R. Leverge, *Prog. Retinal Eye Res.*, 1998, **17**, 33.

[2] Y. Kapoor, J.C. Thomas, G. Tan, V.T. John and A. Chauhan, *Biomaterials*, 2009, **30**, 867.

The structural response of albumin to oxidation

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The most abundant plasma protein, Human Serum Albumin (HSA), plays a key part in the body antioxidant defense against reactive species [1]. This study was aimed at correlating oxidant-induced chemical and structural effects on HSA and was performed thanks to the use of a multi-probe platform allowing for the simultaneous collection of small angle x-ray scattering (SAXS), UV-vis absorption spectra and fluorescence emission [2].

We demonstrated that, despite the chemical damage of the protein occurs since the very first addition of the potent oxidant sodium hypochlorite, its structure is fairly preserved up to relevant oxidative modification (oxidant/HSA molar ratio of 80). At stronger oxidation conditions a dose-dependent unfolding of HSA occurs in a critical range of oxidant/HSA molar ratio of 80-120 that is given by a progressive detachment of one of the protein end-domains (Figure 1). This conformational variation, which implies the loss of roughly one third of the α -helix and the increase of the protein negative charge (detected by means of complementary circular dichroism and zeta potential measurements), is highly reproducible and represents a further fundamental property of this widely studied protein. The ability to tolerate high level of oxidation in a folded or only partially unfolded state, together with the stability to aggregation, confer to albumin optimal feature as a biological buffer to local formation of oxidants.

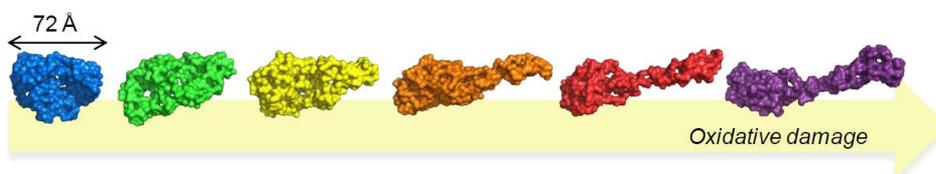


Figure 1 Representative dummy-residue models fitting SEC-SAXS data of increasingly oxidized HSA samples. The hypochlorite/HSA molar ratios are: 0 (blue), 80 (green), 90 (yellow), 105 (orange), 120 (red), 170 (violet).

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[1] M. Roche, P. Rondeau, N. R. Singh, E. Tarnus and E. Bourdon, E., *FEBS Lett.*, 2008, **582**, 1783.

[2] S. Haas, T. S. Plivelic and C. Dicko, *J. Phys. Chem. B*, 2014, **118**, 2264.

Towards the Study of Exosomal Membrane Phase Transition

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In the last few years, it has been discovered that the majority of eukaryotic and prokaryotic cells release small lipid vesicles. These vesicles, generally called micro-vesicles or exosomes, are becoming the object of a great scientific interest, because of their role as carrier of information about progenitor cells, through their cargo of proteins and nucleic acids and the biochemical composition of their membrane [1]. Indeed, the discovery of this important role of exosomes opened a completely new scenario for therapeutic and diagnostic applications.

Here we present a study of the temperature-induced phase transitions in the membrane of bacterial Outer-Membrane-Vesicles (OMVs) that are the bacterial analogous of exosomes from eukaryotic cells. In particular, we study the OMVs produced by *Escherichia Coli* because they are considered a model system for biological studies. Indeed, as known from the literature [2], *Escherichia Coli* membrane presents different temperature phase transitions due to structural changes in the organization of the lipid bilayer. In our study, we have studied the phase transition behaviour of the OMVs membrane by Light Scattering measurements at varying temperature [3]. OMVs were characterized by the presence of phase transitions similar to those revealed for *E. Coli* membrane but occurring at slightly different temperatures. This preliminary result suggests the possibility of distinguishing exosomes from different progenitor cells based on their phase transition profiles.

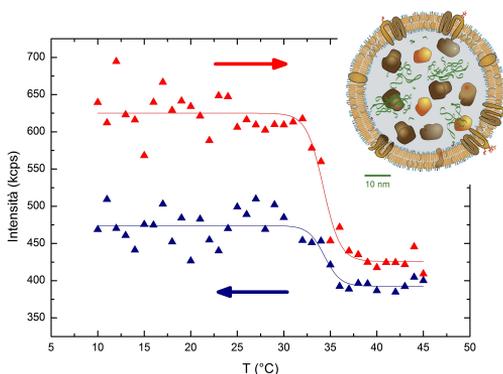


Figure 1: Light scattered intensity as function of temperature for a population of exosomes (size 70 nm). For both increasing (red) and decreasing (blue) temperature it is clear that a membrane phase transition occurs.

[1] A. V. Vlassov et al., *Biochimica et Biophysica Acta*, 1820 (2012) 940-948;

[2] H. Trauble et al., *Biochimica et Biophysica Acta*, 307 (1973) 491-512;

[3] N. Michel et al., *Chemistry and Physics of lipids*, 139 (2006) 11-19;

Investigation of the interaction between P6-2-VIR and lipid bilayers by fluorescence techniques

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The beneficial effect of co-infection with the GB virus C (GBV-C) in HIV-infected patients has been described (1), although its mechanism of action is yet to be determined. The physical principles governing interactions between peptides and lipids and peptide-peptide in lipid environments are important in the design of peptides with therapeutic properties, such as enveloped virus entry inhibiting peptides. P6-2-VIR576 (VIR-LCDCPNGPWVWPVAVCQAVG) showed high potency in HIV replication trials performed on TZM-bl cells (2) thus, it was selected to ulterior studies. Here we investigate the importance of lipid phase in the interaction of P6-2-VIR576 with anionic lipid membrane systems composed by DMPC/DMPS (3:2) and DPPC/DPPS (3:2) by fluorescence spectrometry. The interaction was assessed by binding and quenching experiments. Binding experiments showed that the peptide interacts with DMPC/DMPS (3:2). Concerning acrylamide quenching assays figure 1 shows the quenching profiles in the presence and absence of 0.24 mM of DMPC/DMPS (3:2) at 25 °C and 37 °C and DPPC/DPPS (3:2) at 25 °C. A characteristic negative deviation to the linear Stern-Volmer relationship was observed at 25 °C unlike to results obtained at 37 °C. By Lehrer equation, the fraction of peptide that is accessible to the quencher in solution was calculated.

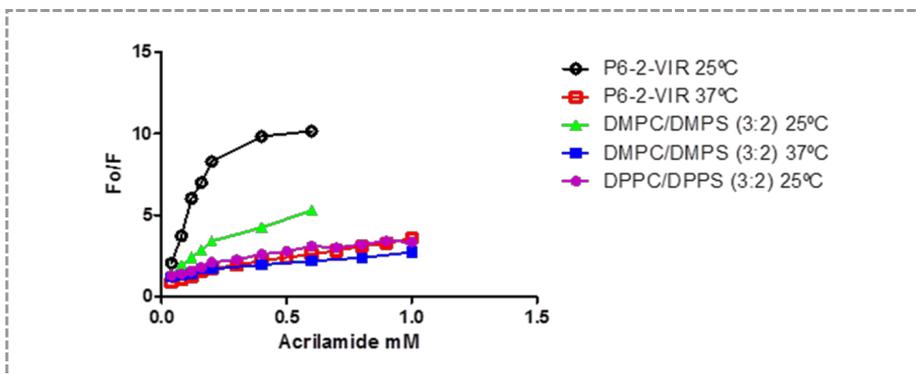


Figure 1 Stern-Volmer plots of fluorescence quenching of P6-2-VIR576 (1.023 μ M) in the absence and presence of 0.24 mM lipid vesicles.

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[1] Willians, C.F. et al. *N.Engl.J.Med.* 2004, **350**, 981-990

[2] Koedel, Y.; Eissmann, K.; Wend, H.; Fleckenstein, B.; Reil, H. *Journal of Virology.* 2011. **85**, 7037-7047.

Few-layer graphene dispersion in liposomes with antibacterial activity

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In recent years graphene and its derivatives, due to their unique physicochemical properties, have aroused interest in many research fields. As a matter of fact, applications in electronic [1] and photonic devices [2], clean energy [3], energy storage [4] and sensors [5] have been well demonstrated. In addition, graphene-based materials appear as promising scaffolds in biomedicine [6-8]. For application in biomedicine one of the most important and fundamental goal to be achieved is to make graphene soluble in water. Up to now, almost all the studies on graphene in the biomedical field have been focused on the production and characterization of hydrophilic graphene oxide (GO). The functionalization of graphene to get GO has revealed undisputed advantages, but it involves the breakdown of the continuous honeycomb backbone of pristine (non-functionalized) graphene compromising several of the peculiar properties of the original material.

In order to preserve graphene structural integrity and to use an absolutely green process of exfoliation and functionalization, inspired by Titov's molecular dynamics simulation [9] that showed the theoretical insertion of a "graphene sheet in the hydrophobic interior of biological membranes", in the present study we succeeded to realize a facile and prompt exfoliation protocol for graphite in aqueous solution.

We obtained a liposomal formulation in which graphene is sandwiched between phospholipid alkyl chains by simply sonicating graphite into POPC large unilamellar vesicle aqueous solution for 2 h. The obtained results were validated and quantified by the use of different methods of investigation such as: UV-Vis spectrophotometry to quantify the exfoliated graphene (yield~15%) and the liposomal entrapment efficiency (E.I.~2%), Raman spectroscopy to demonstrate the presence of non-oxidized double layer graphene as well as amphiphilic phospholipid molecules organized in bilayers in the samples, TEM to point out that sonication allows the formation of nanometric double-layer graphene sheets embedded into liposomes, DLS and ζ -potential analyses to evaluate the suspension stability over time and homogeneity of the dispersion.

The as-prepared graphene aqueous dispersion is stable for days and demonstrates significant antibacterial activity against both Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) strains. In particular, it almost completely inhibits the microbial growth of Gram-positive bacteria whereas Gram-negative bacterial growth is reduced to a mere three-fold.

- [1] K. Bourzac, *Nature*, 2012, **534**, 483.
- [2] F. Bonaccorso, Z. Sun, T. Hasan, A. C. Ferrari, *Nat. Photonics*, 2010, **4**, 611.
- [3] J.-Y. Hong, J. Jang, *J. Mater. Chem.*, 2012, **22**, 8179.
- [4] L. Dai, *Acc. Chem. Res.*, 2013, **46**, 31.
- [5] Y. Song, W. Wei, X. Qu, *Adv. Mater.*, 2011, **23**, 4215.
- [6] A. K. Geim, *Science*, 2009, **324**, 1530.
- [7] A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, *Rev. Mod. Phys.*, 2009, **81**, 109.
- [8] V. C. Sanchez, A. Jachak, R. H. Hurt, A. B. Kane, *Chem. Res. Toxicol.*, 2012, **25**, 15.
- [9] A. V. Titov, P. Kral, R. Pearson, *ACS Nano*, 2006, **4**, 229.

Effect of external factors on the human skin corneocyte morphology

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Stratum corneum (SC) located in the outermost layer of human skin consists of about a dozen layers of corneocyte cells, working as an intelligent interface between the skin and the environment. In this study we focused on the corneocyte morphology, which is thought to be related to the skin barrier function. We evaluated the shape of corneocytes tape-stripped from the skin surface of three healthy male subjects by the simple cryo-section technique we have developed for its ex vivo observation. The corneocytes transferred onto an adhesive tape were covered by another adhesive tape (sandwich method) and rapidly frozen in liquid nitrogen slush to make an ultrathin section with an ultramicrotome Leica EM FC6. The sections were observed with an electron microscope (JEM1400, JEOL). We compared the cross-sectional shape of the corneocytes collected from various body sites and found that the thickness of corneocyte is widely distributed from 200 nm to 1500 nm, depending on the body site. In particular, the corneocytes collected from the palm and the sole had irregular shapes with larger thickness than the typical flat cell.

Moreover, in some body sites there seemed to be a dependence of the corneocyte thickness on the subject. Interestingly, the thickness of the corneocyte from the wrist was evidently smaller in the subject wearing a wristwatch than in the one with a bare wrist. To clarify the influence of wearing a wristwatch, we examined the thickness of the corneocyte from the wrist of a subject, who usually wore a wristwatch, a month after his taking it off. As a result, we found that the thickness became more than five times larger by eliminating the influence of the wristwatch. These results suggest that the corneocyte morphology is very sensitive to the external factors imposed onto the skin surface.

The external factors could include temperature, mechanical stimulation, humidity, occlusive environment, and so on. We carried out some experiments to identify the factor responsible for the change in the corneocyte morphology induced by wearing a wristwatch. Our simple cryo-section technique used in these experiments was very useful in quantitative evaluation of the corneocyte morphology because it allowed us to obtain sufficient data for statistical analysis. We will discuss the influence of the external factors on the corneocyte morphology and its mechanism on the basis of our observations.

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Hybrid Organosilica for Smart Drug Delivery System

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The global market of nanomedicine and vectorization is predicted to be worth 225 billion dollars in 2017; and so far is dominated with the use of polymeric based materials. As an alternative, silica based nanomaterial is promising candidate for future development in this field due to its advantage. In particular, the appealing multifunctionality that can be built around this system.

In this poster, the functional systems created using inert or active inorganic nanocontainers such as microporous and mesoporous silica based nanoparticles will be presented. In particular, examples using the crystalline allumino silicates, zeolite L, will be discussed since these materials can act as nanocontainers and due to their biocompatibility used for biomedical applications. However, as many nanoparticles, they are not biodegradable. Recently, we developed hybrid organosilica system by incorporating physiologically responsive functional groups in the framework. Following this approach, it is possible to design a drug delivery platform, which able to break apart after reaching the target cell. Not only for small drugs, using slightly different strategy, we are able to deliver bigger size bioactive molecules such as oligonucleotide, protein, and enzymes. Furthermore, after release the cargo payload, we could expect the remaining materials leave the cells and eventually the body in the case of in vivo delivery.

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- [1] Drug Delivery Technologies: Commercial Prospects 2013-2023. Available from: <https://www.visiongain.com/Report/1042/Drug-Delivery-Technologies-Commercial-Prospects-2013-2023>.
- [2] E. A. Prasetyanto, A. Bertucci, D. Septiadi, R. Corradini, P. Castro-Hartmann, L. De Cola, *Angew. Chem. Int. Ed.* 2016, **55** (10), 3323–3327
- [3] Bertucci, E. A. Prasetyanto, D. Septiadi, A. Manicardi, E. Brognara, R. Gambari, R. Corradini, L. De Cola, *Small*, 2015, **11**, 5687-5695.
- [4] L. Maggini, I. Cabrera, A. Ruiz-Carretero, E. A. Prasetyanto, E. Robinet, L. De Cola, *Nanoscale*, 2016, **8** (13), 7240-7247.
- [5] R. Marega, E. A. Prasetyanto, C. Michiels, L. De Cola and D. Bonifazi, *Small*, 2016, DOI: 10.1002/smll.201601447.

New chemical routes to Biocompatible Gold Nanoparticles: a cheap two steps approach.

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In recent years, the development of Nanotechnology opened new perspectives for the synthesis of highly versatile materials of nanometric dimensions [1]. Among others, Gold Nanoparticles (AuNP) have obtained an outstanding outcome in a huge variety of biomedical applications like radioenhancers for radiotherapy, or chemotherapeutic carrier for drug delivery [2]. Although the extraordinary success of AuNP in these frameworks, great challenges for new generation of nanoscience chemists are still open. Above all, the tuning of nanostructure chemical proprieties in order to obtain specific delivery in the tumor site still remains a critical aim [3]. Glucose functionalization of AuNP surface leads to an increased uptake in tumor cells and offers an interesting chance to face the tumor delivery problem [4]. In this context, we are developing a new cheap synthetic procedure to synthesize Glucose functionalized gold nanoparticles (GNP). Our approach consists of two synthetic steps. In the first step, a two phase the synthesis of AuNP stabilized by means of very cheap thiolated Glucose precursor, 1-Thio- β -D-glucose tetraacetate, is performed. In the second step, an *in situ* deacetylation of the hydroxyl protected groups will lead to the final glucose exposure on AuNP surface.

In this research work we will discuss some preliminary results concerning the synthesis and the characterization of new kind of stable AuNP (Figure 1) functionalized with 1-Thio- β -D-glucose tetraacetate molecule. The AuNP formation and its chemical surface integrity was assessed by means UV-Vis spectroscopy and X-Rays Photoelectron Spectroscopy (XPS). The UV-vis spectrum shows the typical gold nanometric plasmonic absorption profile with a maximum at 527 nm (Figure 1, c). Moreover, ultrastructural study were performed by means Transmission Electron Microscopy (TEM) and confirmed a very small AuNP diameter of 5 ± 1 nm.

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[1] P. Zhao, N. Li, D. Astruc, *Coordination Chemistry Reviews*, 2013, **257**, 638

[2] S. Her, A. Jaffray, C.Allen, *Advanced Drug Delivery Reviews*, 10.1016/j.addr.2015.12.012. *In Press*

[3] Z. Yuanyuan, L. Lianming, *Journal of Nanoscience and Nanotechnology*, 2015, **15**, 4753

[4] F. Porcaro, C. Battocchio, A. Antocchia, I. Fratoddi, I. Venditti, A. Fracassi, S. Moreno, I. Luisetto, M. V. Russo and G. Polzonetti, *Colloids and Surfaces B*, 2016, **142**, 408-416.

New colloidal frontiers as radiosensitizers agents : a smart chemical approach to Biocompatible Gold and Platinum Nanoparticles.

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The recent explosion of Nanobiotechnology, an interdisciplinary research area between Physics, Chemistry and Biology, gives new tools for developing new therapeutic approaches and also for the improvement of the efficacy of radiotherapy by means of a new generation of radiosensitizers materials [1]. Dose absorption increase at the tumor site is usually achieved through administration of compounds containing high atomic number (Z) atoms like Iodine (Z=53) or Gadolinium (Z=63) [2]. Despite that, a trade off is often mandatory between the drug induced cytotoxicity to healthy tissues and the amount of High Z atoms delivered to the tumor. Noteworthy, noble metals such as Gold (Z=79) or Platinum (Z=78) Nanoparticles (NP) offers many advantages in radiotherapy application due to very low cytotoxicity and the huge number of atoms delivered inside the cells [1]. Moreover, the extreme chemical versatility of NP surface allow a stable conjugation with biomolecules in order to further increase the targeting of cell tumor only [3]. Among such molecules, Glucose is taking the scene due the high bio-effectiveness and binding simplicity to NP surface [4]. Although the great success of metal nanoparticles in this framework, there is still need to open new routes for the synthesis of more stable and functional nanoparticles.

Herein are reported some results concerning with the synthesis, the characterization and the bio-response assessment of new kind of stable Gold and Platinum NP (Figure 1) stabilized with the organic thiol 3MPS (3-mercaptopropylsulfonate) and 1- β -thio-D-glucose (TG). X-Rays Photoelectron Spectroscopy (XPS) was performed in order to study the chemical surface integrity of the nanostructure. The radiosensitizers effect of the nanostructured systems were tested with clonogenic assay on Human Salivary Gland Tumor cells.

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- [1] J.A. Coulter, W.B. Hyland, J. Nicol, F.J. Currell, *Clinical Oncology*, 2013, **25**, 593-60
- [2] K. A. Bradley, I. F. Pollack, J.M. Reid, P. C. Adamson, M.M. Ames, G. Vezina, S. Blaney, P. Ivy, T. Zhou, M. Krailo, G. Reaman, M.P. Mehta, *Neuro Oncology*, 2008, **10**, 752
- [3] S. Her, A. Jaffray, C. Allen, *Advanced Drug Delivery Reviews*, 10.1016/j.addr.2015.12.012. *In Press*
- [4] F. Porcaro, C. Battocchio, A. Antocchia, I. Fratoddi, I. Venditti, A. Fracassi, S. Moreno, I. Luisetto, M. V. Russo and G. Polzonetti, *Colloids and Surfaces B*, 2016, **142**, 408-416.

Electroosmotic flow through an α -hemolysin nanopore

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The determination of structures and sequences of macromolecules is a key element in modern biology and medicine. A relevant innovation in the biomolecule sensing is the employment of nanopore based devices for the analysis of macromolecules at a single molecule level [1]. In a nanopore sensor the interaction between the macromolecule and the pore alters the ionic current flowing through a single pore that separates two chambers containing an electrolyte solution. The typical signal in a nanopore based devices is a multilevel current trace where the baseline level corresponds to no macromolecule inside the pore and the other levels correspond to specific interactions between the pore and the macromolecule, such as the presence of a specific monomer inside the pore. Although the method is quite simple, only recently it was possible to rescaling the principle down to the nanoscale enabling, for instance, the development of a nanopore based DNA sequencer [1].

In this framework, a fundamental nanofluidic issue is the characterization of the open pore current level, i.e. the baseline signal when no molecules occupies the pore. Although the electrolyte solution is globally neutral, nanopores typically present a surface charge that alters the ion distribution at the pore interface. In addition, positive and negative ions have different hydration shells the behavior of which is strongly altered by the nanoconfinement. All these circumstances result in a complex electro-hydrodynamical phenomenology. In general, the unbalance between positive and negative ions distribution give raise to an electroosmotic flow [2] that has a strong impact on the macromolecule capture by the pore and on its translocation [2-3].

In this study, we characterize the water and the ion flows through a nanopore. In particular, we studied the α -hemolysin [4] pore (the widely employed biological nanopores for sensing devices) via all-atom molecular dynamics. We explored the electro-hydrodynamical response of the system for different ionic concentrations and applied potentials. Our simulations provide a first extensive set of data at atomic scale that clarify the role of electroosmotic flow in α -hemolysin based nanopore sensing devices.

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[1] Cressiot, Benjamin, et al. *BioNanoScience* 4.2 (2014): 111-118.

[2] Piguët, Fabien, et al. *The Journal of Physical Chemistry Letters* 5.24 (2014): 4362-4367.

[3] Mereuta, Loredana, et al. *Scientific reports* 4 (2014).

[4] Song, Langzhou, et al. *Science* 274.5294 (1996): 1859-1865. 8/10

[5] Bhattacharya, Swati, et al. *The Journal of Physical Chemistry C* 115.10 (2011): 4255-4264.

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