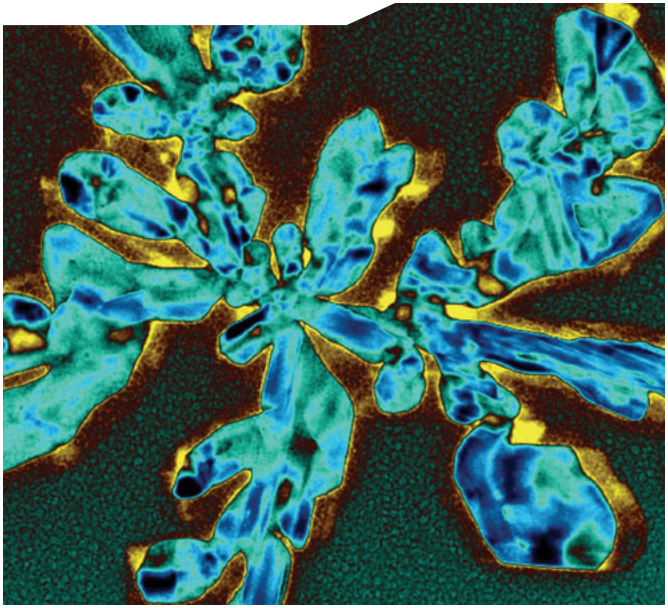

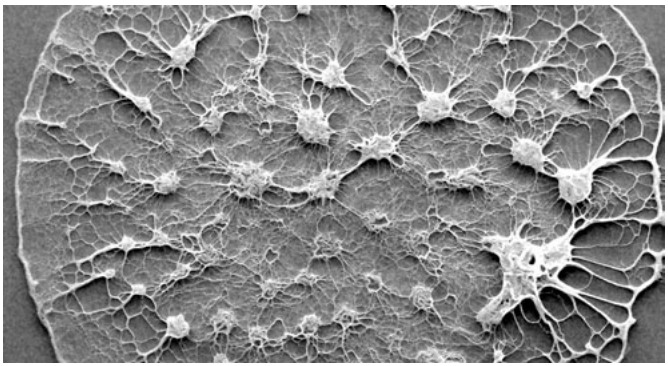

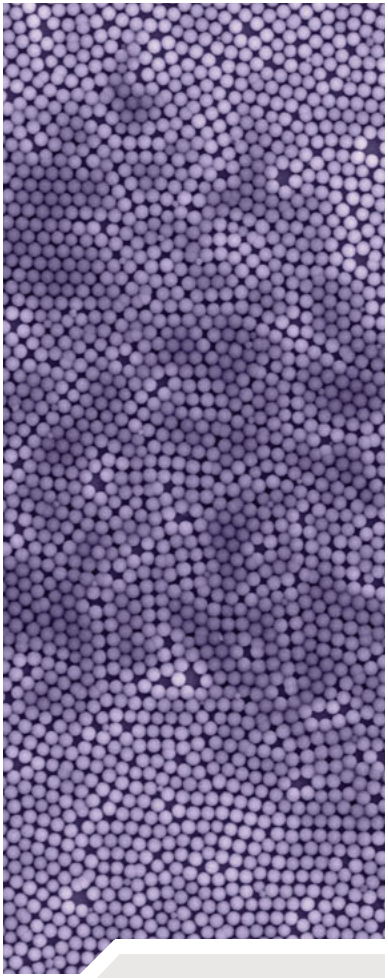

13th ZSIGMONDY COLLOQUIUM

OF THE GERMAN COLLOID SOCIETY

APRIL 5–7, 2017
SAARBRÜCKEN, GERMANY

UNIVERSITÄT DES SAARLANDES

INM

13th ZSIGMONDY COLLOQUIUM of the German Colloid Society

hosted by

INM – Leibniz Institute for New Materials
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Saarbrücken, Germany, April 5–7, 2017

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ABSTRACT BOOK: Dominik Hell, INM

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PROGRAM

WEDNESDAY, APRIL 5, 2017

12:00	Registration and coffee
12:50	Welcome
	SESSION 1 **Synthesis and Processing** Chair: Guido Kickelbick
13:00	"Gold Nanotriangles: Ostwald Ripening Growth Mechanism in Vesicular Template Phases" *Ferenc Liebig,* Universität Potsdam, Germany
13:20	"Protecting Groups in Colloidal Synthesis of Au Semishells" *Daniel Mann,* DWI – Leibniz Institute for Interactive Materials, Aachen, Germany
13:40	"Cellulose Nanocrystals: Excellent Building Blocks for Functional Coatings" *Pascal Buskens,* TNO, Eindhoven, Netherlands
14:00	"Damage Self-Reporting Capsules Indicating Crack Appearance and Healing in Coatings" *Minghan Hu,* Max Planck Institute for Polymer Research, Mainz, Germany
14:20	"Monodisperse Conjugated Polymer Particles – Synthesis, Polymerization Kinetics and Photonic Applications" *Sibel Ciftci,* DWI – Leibniz Institute for Interactive Materials, Aachen, Germany
14:40	Coffee break
15:00	"Synthesis, Characterization, and Application of pH-Responsive Au@p4VP Microgels as Platform for Selective SERS Analysis" *Rafael Contreras-Caceres,* Leibniz-Institut für Polymerforschung Dresden, Germany
15:20	"Continuous Synthesis of ORMOSIL-Particles in a Microreactor" *Christina Odenwald,* Universität des Saarlandes, Saarbrücken,Germany
15:40	"Synthesis of High Organic Loading Hybrid Particles via a Photo Sol-Gel Aerosol Process" *Mathilde Sibeaud,* LPIM, Mulhouse, France
16:00 – 17:30	POSTER SESSION 1
19:00	Conference Dinner "Kunstwerk Saarbrücken - Bistro Malzeit"

THURSDAY, APRIL 6, 2017

	SESSION 2 **Agglomeration and Self-Assembly** Chair: Tobias Kraus
09:00	Invited talk: "Soft Quasicrystals" *Stephan Förster,* Universität Bayreuth, Germany
09:50	"Block Copolymer Hexosomes" *Andre Gröschel,* University of Duisburg-Essen, Germany
10:10	"Colloidal Molecules Fabrication by Assembly of Janus-Like Dumbbells" *Weiya Li,* ICMCB, Pessac, France
10:30	"Fabrication of Oriented Plasmonic Oligomers on Elastomeric Substrate via Macroscopic Strain" *Anja Maria Steiner,* Leibniz-Institut für Polymerforschung Dresden, Germany
10:50	Coffee break
11:10	"Directional Bonding of Silica Particles Bearing Chemically Modified Polystyrene Patches" *Pierre-Etienne Rouet,* Centre de Recherche Paul Pascal, Pessac, France
11:30	"Colloidal Plasmonic Arrays Exhibiting Tunable Surface Lattice Resonances" *Kirsten Volk,* Heinrich-Heine-Universität, Düsseldorf, Germany
11:50	"Spinning of Hierarchical Hybrid Fibers: Controlled Colloidal Assembly" *Beate Reiser,* INM – Leibniz Institute for New Materials, Saarbrücken, Germany
12:10	Lunch
13:10	"Assembly of Isotropic Hard Spheres into Anisotropic Structures at Air/Water Interface in the Presence of Soft Particles" *Marcel Rey,* Friedrich-Alexander-Universität Erlangen, Germany
13:30	"Studying the Self-Assembly, Shape Selectivity and Evolution of Chitosan/Nanoparticle Colloids by Time-Resolved Small-Angle X-Ray Scattering" *Oonagh Mannix,* ESRF: The European Synchrotron, Grenoble, France
13:50	"Colloid Clusters in Confinement" *Junwei Wang,* Friedrich-Alexander-Universität Erlangen, Germany
14:10	Coffee break

	SESSION 3 **Bioactive Colloids and Interphases** Chair: Stephan Förster
14:30	"Membrane Buckling in Macromolecule induced Red Blood Cell Aggregation" *Daniel Flormann,* Saarland University, Saarbrücken, Germany
14:50	"Polysaccharide Sub-Microcarrier for Anti-Infectives Delivery" *Duy-Khiet Ho,* Helmholtz Institute for Pharmaceutical Research, Saarbrücken, Germany
15:10	"Interaction of Biomolecules with Magnetite" *Anna Pohl,* Max Planck Institute of Colloids and Interfaces, Potsdam, Germany
15:30	"Colloidal Apatite Nanoparticles Significantly Improve Trehalose-Enhanced Cryosurvival of Red Blood Cells" *Jean Baptiste Fleury,* Saarland University, Saarbrücken, Germany
15:50	Coffee break
16:10	"The Influence of PEG Density on the Ordering of Proteins on PEGylated Surfaces" *Christoph Bernhard,* Max Planck Institute for Polymer Research, Mainz, Germany
16:30	"Protein Corona *in vitro* as *in vivo*?" *Marijana Mionic Ebersold,* University Hospital Lausanne (CHUV), France
16:50	"An Injectable, Anisotropic Hydrogel for Directed Cell and Nerve Growth" *Jonas C. Rose,* DWI – Leibniz Institute for Interactive Materials, Aachen, Germany
17:10 – 18:40	POSTER SESSION 2

FRIDAY, APRIL 7, 2017

	SESSION 4 **Physical Properties and Characterization** Chair: Marc Schneider / Didier Astruc
09:00	Invited talk: "Polymer and Dendrimer-Stabilized Nanoparticles in Catalysis" *Didier Astruc,* Université Bordeaux I, France
09:50	"Gas Permeation through Pickering Membranes" *Matthias Krejca,* Chemnitz University of Technology, Germany

10:10	"Synthesis of Nanoparticles in Dispersion: Flow Cell Coupled Dynamic Light Scattering as a Way to Follow Particle Growth" *Nicole Meulendijks,* TNO, Eindhoven, Netherlands
10:30	"Investigation and Modification of the Porosity of Supraparticles" *Vivian J. Spiering,* Technische Universität Berlin, Germany
10:50	Coffee break
11:10	"Structure and Dynamics of Polyelectrolyte Complexes with Oppositely Charged Microemulsion Droplets" *Miriam Simon,* Technische Universität Berlin, Germany
11:30	"Online Optical Imaging of Nano-Sized Objects within Polymer/Particle Mixtures During Film Thinning" *Guoxiang Chen,* Max Planck Institute of Colloids and Interfaces, Potsdam, Germany
11:50	Lunch

SESSION 5

Microgels

Chair: Marc Schneider

13:00	"Synthesis and Characterization of Multi-Thermoresponsive Hollow Microgels" *Monia Brugnoni,* RWTH Aachen University, Germany
13:20	"Silver Nanoparticles Fabricated N-Isopropylmethacrylamide Based Hybrid Microgels Catalyst for Reduction of 2-Nitroaniline" *Zahoor Hussain Farooqi,* University of the Punjab, Lahore, Pakistan
13:40	"Mapping the Heterogeneous Modulus of Microgels Adsorbed to an Interface – Comparing Core-Shell and Hollow Microgels" *Marie Friederike Schulte,* RWTH Aachen University, Germany
14:00	"Core-Shell Microgels with Linear Thermo-Response as Smart Surface Coating" *Marian Cors,* Bielefeld University, Germany
14:20	"Investigation of Thermo-Responsive Microgels at Flat Liquid-Liquid Interfaces: Connection between Microgel Softness and Monolayer Properties" *Steffen Bochenek,* RWTH Aachen University, Germany
15:10	Closing words

SESSION 1

Synthesis and Processing

GOLD NANOTRIANGLES: OSTWALD RIPENING GROWTH MECHANISM IN VESICULAR TEMPLATE PHASES

Ferenc Liebig[1], Andreas F. Thünemann[2] and Joachim Koetz[1]

[1] Universität Potsdam, Potsdam, Germany
[2] Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany

The unique optical properties of gold nanotriangles are suitable for a broad range of applications especially in the field of catalysis and biomedicine. The previously described synthesis of gold nanoparticles by a vesicular template phase containing AOT, PL90G and the polyampholyte PalPhBisCarb leads to a yield of 33 % flat nanotriangles with a defined platelet thickness of 8.5 ± 1.5 nm [1]. To understand the mechanism of the gold nanotriangle formation, we used UV-vis and SAXS measurements in addition with transmission electron microscopy and light microscopy to investigate the time-dependent growth of the gold nanoparticles at room temperature [2]. The growth process can be divided in three phases. In the first 60 minutes, small gold nanoparticles with diameter of ca. 5 nm are formed, which build up soft particle aggregates. In a second period from 60 to 180 minutes at the periphery of these aggregates flat gold platelets grow up. The formation of the gold nanoplatelets can be described by an Ostwald ripening-based growth. The 16 times larger growth rate in lateral direction than in vertical direction can be explained by the adsorption of symmetry breaking components, i.e., AOT and PalPhBisCarb. In the third period, a disaggregation into triangles and spherical particles can be observed. Based on a depletion flocculation in presence of polyelectrolytes and AOT-micelles very stable negatively charged gold nanoplatelets can be isolated. These purified gold nanotriangles show promising results in surface-enhanced Raman scattering and vibritions by ultrafast x-ray diffraction [2,3].

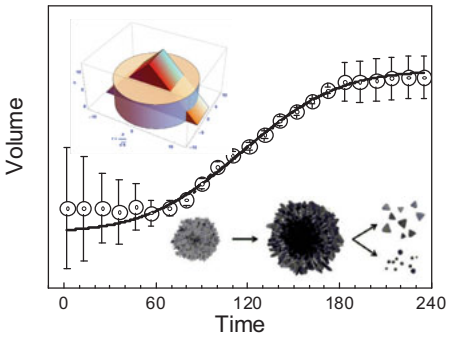

Figure 1. Mean volume of the particles as a function of time and corresponding curve fit; inset (top): nanotriangle and nanodisk with the same thickness and radius of gyration; inset (bottom): time-dependent gold nanotriangle formation

[1] Liebig, F.; Sarhan, R. M.; Prietzel, C.; Reinecke, A.; Koetz, J. RSC Adv. 6 (2016), 33561-33568.
[2] Liebig, F.; Thünemann, A. F.; Koetz, J. Langmuir 32 (2016), 10928-10935.
[3] von Reppert, A.; Sarhan, R.M.; Stete, F.; Pudell, J.; Del Fatti, N.; Crut, A.; Koetz, J.; Liebig, F.; Prietzel, C.; Bargheer, M., J. Phys. Chem. C (2016), DOI: 10.1021/acs.jpcc.6b11651

PROTECTING GROUPS IN COLLOIDAL SYNTHESIS OF AU SEMISHELLS

Daniel Mann,[1] Stefanie Voogt,[1] Ryan van Zandvoort,[2] Helmut Keul,[1] Martin Möller,[1] Marcel Verheijen,[3,4] Daniel Nascimento-Duplat,[5] Man Xu,[2,5] H. Paul Urbach,[5] Aurèle J. L. Adam,[5] Pascal Buskens[1,2]

[1] DWI - Leibniz Institute for Interactive Materials e.V., RWTH Aachen University, Aachen, Germany
[2] The Netherlands Organisation for Applied Scientific Research (TNO), Eindhoven, Netherlands
[3] Philips Innovation Services, Eindhoven, Netherlands
[4] Eindhoven University of Technology, Eindhoven, Netherlands
[5] Delft University of Technology, Delft, Netherlands

Protecting groups are commonly applied in multi-step molecular syntheses to protect one or multiple functional groups from reacting. They can be applied in a wide range of different organic reactions, such as the synthesis of polysaccharides or peptides. Although the concept of protecting one side from reacting seems also to be very helpful in colloidal synthesis, it hasn't been transferred to this growing field of research. Using protecting patches that cover one side of a nanoparticle is a promising synthetic strategy in the synthesis of non-centrosymmetric nanoparticles, where current synthetic procedures are not practical in large scale synthesis. Therefor we developed a synthetic strategy using patches on polystyrene particles as protecting groups in the synthesis of Au semishells. Here we present, for the first time, the synthesis of patches on the surface of cross-linked polystyrene particles that are used to protect one side of the particle in a subsequent two-step Au seeding and plating mechanism. The protecting group can be easily removed from the particle surface to create Au semishells. The reaction mechanism of the newly developed synthesis of these patches on polystyrene particles is investigated intensively. Additionally the optical properties of Au semishells are analyzed and compared with literature as well as theoretical calculations.[1]

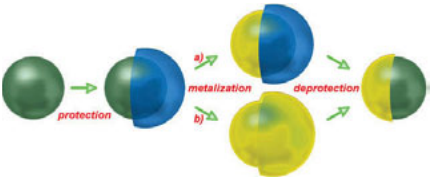

Figure 1. a) Synthesis strategy and b) reaction mechanism to realize Au semishells using a colloidal protecting patch.

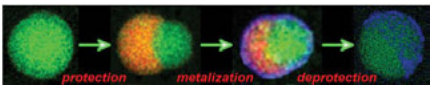

Figure 2. EDS mappings of all reaction intermediates in the synthesis of Au semishells.

[1] D. Mann, S. Voogt, R. van Zandvoort, H. Keul, M. Möller, M. Verheijen, D. Nascimento-Duplat, M. Xu, H. P. Urbach, A. J. L. Adam, P. Buskens, Chem. Commun. (2017) *under revision*.

CELLULOSE NANOCRYSTALS: EXCELLENT BUILDING BLOCKS FOR FUNCTIONAL COATINGS

Pascal Buskens[1,2,3], Nicole Meulendijks[1], Maurice Mourad[1], Renz van Ee[1], Marieke Burghoorn[1]

[1] TNO, Eindhoven, The Netherlands
[2] DWI-Leibniz Institute for Interactive Materials e.V., Aachen, Germany
[3] Zuyd University of Applied Sciences, Heerlen, The Netherlands

Based on their unique properties, for example their high stiffness, their thermal stability, and their ability to form liquid crystalline arrangements, cellulose nanocrystals (CNCs) are powerful natural building blocks for the preparation of functional nanocomposites [1]. Here, we demonstrate their potential as building blocks for nanostructured functional coatings, viz. antireflective coatings (ARCs) and electrically conductive coatings (CCs).

For the preparation of ARCs, we extracted needle shaped CNCs from Avicel and dispersed them in water (Fig. 1a). Subsequently, the CNCs with an average length and width of 125 nm and 5 nm, respectively, were covered with a 10 nm thick silica shell [2]. The CNC-silica core-shell particles were dispersed in ethanol, and applied to float glass through dip coating. The resulting coatings were cured at 450ºC, yielding a highly porous network of hollow silica nanorods. In that way, ultra-low refractive index coatings were achieved (lowest refractive index 1.03, Fig. 1b). These formed the base for robust quarter-wave ARCs on glass [2, 3].

For the preparation of CCs, the same CNCs were applied. In the first step, the crystal surface was oxidized using TEMPO. Subsequently, Ag was deposited on the surface of the oxidized crystals in a seeding-plating sequence, which yielded CNCs with a high degree of Ag coverage on the surface. The resulting CNC-Ag composite particles were applied to float glass through dip coating from an alcoholic dispersion, forming a percolated network (Fig. 1c). After photonic curing, we obtained coatings with an electrical conductivity of $2.9 \cdot 10^4$ S·cm ^{1}, which exceeds the conductivity of the best performing cellulose composites reported to date by a factor 30 [4, 5].

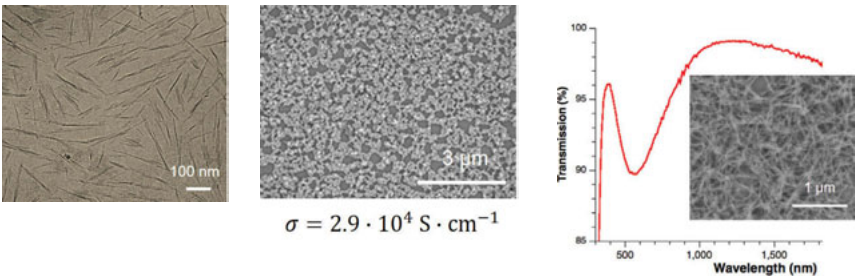

Fig. 1. a) CNCs extracted from Avicel (cryo-TEM), b) ARC comprising hollow silica nanoneedles (SEM), and b) CC consisting of CNC-Ag composite particles (SEM).

[1] Y. Habibi, L. A. Lucia, O. J. Rojas, Chem. Rev. 110 (2010) 3479.
[2] P. Buskens, M. Mourad, N. Meulendijks, R. van Ee, M. Burghoorn, M. Verheijen, E. van Veldhoven, Colloid Surface A 487 (2015) 1.
[3] P. Buskens, M. Burghoorn, M. C. D. Mourad, Z. Vroon, Langmuir 32 (2016) 6781.
[4] Z. Shi, G. O. Phillips, G. Yang, Nanoscale 5 (2013) 3194.
[5] We gratefully acknowledge the European Commission for funding this work as part of the EU FP7 project GREENANOFILMS (grant no. 603519).

DAMAGE SELF-REPORTING CAPSULES INDICATING CRACK APPEARANCE AND HEALING IN COATINGS

Minghan Hu[1], Stefan Peil[1], Michael Kappl[2], Yaowen Xing[2], Katharina Landfester[1], Markus B. Bannwarth[1]

[1] Department of Physical Chemistry of Polymers, Max Planck Institute for Polymer Research, Mainz, Germany
[2] Department of Physics at Interfaces, Max Planck Institute for Polymer Research, Mainz, Germany

The solid shell of capsules can spatially separate the liquid in- from the exterior. The spatial separation allows the protection of the environment from encapsulated active substances and *vice versa* [1]. Ideally, the capsule shell preserves all active compounds inside until the end of the capsule-lifetime: Then, a programmable release is initiated through the influence of a certain stimuli [2-3]. However, the capsule-lifetime can be inadvertently shortened when the shell is accidently damaged. Usually, such microscopic destruction of the shell is not macroscopically visible. Hence, capsules that can macroscopically communicate their destruction would allow life-cycle monitoring of the capsules [4]. Moreover, embedment of the capsules as a fractional part in hybrid polymer systems (e.g. polymeric coatings) would allow life-cycle monitoring of the whole material.

Here, we designed a smart capsule that can autonomously report its microscopic damage *via* macroscopic color-change. By tuning the shell thickness, capsules can be made more or less resistant towards external stresses. As a model-case of using the capsules as life-cycle monitoring systems in hybrid systems, we integrated the capsules in polymeric coatings to successfully visualize the cracks appearance and healing within the coating. Hence, the newly designed damage self-reporting capsules can be applied in various composites to monitor a complete life-cycle of the material [5].

[1] A Kowalczuk et al. *Prog. Polym. Sci.* 39 (2014), p. 43-86.
[2] M Bannwarth et al. *Macromo. Biosci.* 14 (2014), p. 1205-1214.
[3] K Landfester. *Angew. Chem. Int. Edit.* 48 (2009), p. 4488-4507.
[4] JF Patrick et al. *Nature* 540 (2016), p. 363-370.
[5] The authors acknowledge the Max Planck Society for the financial support. M.H. thanks the China Scholarship Council for the graduate scholarship.

MONODISPERSE CONJUGATED POLYMER PARTICLES – SYNTHESIS, POLYMERIZATION KINETICS AND PHOTONIC APPLICATIONS

S. Ciftci[1], A. Mikosch[1], A. J. C. Kuehne[1]

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The production of particles, which spontaneously self-assemble into colloidal crystals with a photonic band-gap, opens pathways towards laser resonators without using time-consuming and costly micro- and nanofabrication techniques.

Here, we present novel dispersion polymerizations yielding monodisperse particles of conjugated polymers with an electronic bandgap (Fig. 1b) [1]. Such hard sphere conjugated polymer particles produced by a cross-coupling dispersion polymerization self-assemble into photonic crystals and at the same time act as a laser gain medium.

Furthermore, seeding of this dispersion polymerization with dielectric particles facilitates the generation of core shell particles, which act as whispering gallery mode resonators (Fig. 1c) [2]. To elucidate the mechanism of our cross-coupling dispersion polymerization, we investigate the kinetics of the underlying particle formation. We find that nucleation of oligomeric species takes place in the pseudo linear kinetic regime followed by a classical growth mechanism. During growth, also limited solid-state coupling occurs leading to fully polymerized particles. The self-assembled colloidal crystals as well as the whispering gallery mode resonators exhibit laser emission at low thresholds.

[1] Ciftci, S.; Kuehne, A.J.C., Marcomolecules 48, (2015), 8389–8393.
[2] Ciftci, S.; Mikosch, A.; Kuehne, AJC., Chem. Commun. 52, (2016), 14222-14225.

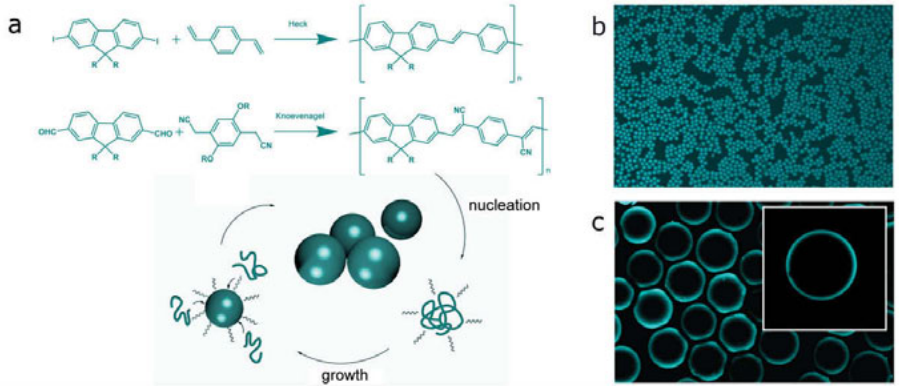

Figure 1. (a) Reaction schemes and dispersion polymerization mechanism for the formation of monodisperse conjugated particles. (c) Conjugated hard sphere particles self-assembled into crystals. (c) Confocal microscopy image of silica core- conjugated polymer shell.

SYNTHESIS, CHARACTERIZATION, AND APPLICATION OF pH-RESPONSIVE Au@P4VP MICROGELS AS PLATFORM FOR SELECTIVE SERS ANALYSIS

Rafael Contreras-Caceres[1*], Joaquim Clara-Rahola[2], Miguel A. Casado-Rodriguez[1], Marco Lanurenti[3], Christian Kuttner[4], Jorge Rubio-Retama[3], Andreas Fery[4,5], Manuel Lopez-Romero[1]

[1] Quimica Organica, Facutlad de Ciencias, Universidad de Malaga, 29071 Malaga, Spain
[2] I2TiC Multidisciplinary Research Group, Open University of Catalonia, 08035 Barcelona, Spain
[3] Physical Chemistry II, Pharmacy Faculty, Complutense University of Madrid, Spain
[4] Leibniz-Institut für Polymerforschung Dresden e.V., 01069 Dresden, Germany
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[*] contreras@ipfdd.de

We present the synthesis, characterization and application as SERS platform of pH-responsive hybrid microgels. This colloidal system is constituted by 55 nm Au cores individually covered by a polymeric pH-sensitive shell of poly(4-vinylpyridine) with controllable thickness shell that we denoted as Au@p4VP.

The synthesized microgels exhibited pH response showing a swelling degree, which depends on the pH of the media and the crosslinker density within the polymer network. As a result, at acidic pH the microgels swell due to the electrostatic repulsion created in the polymer matrix, while at high pH, the microgel structure collapses because of the reduction in the electrostatic repulsion and the increment of the hydrophobic interactions. This property was exploited to create a surface-enhanced Raman spectroscopy (SERS) platform. After increasing the pH of the solution, the captured molecule is brought in close proximity to the surface of the metallic core, enhancing its detection by SERS. The presented system is envisaged to be applied in bio-analysis where the dilution of the analyte would require its concentration prior its analysis.

[1] Clara-Rahola et al. *Langmuir*. Under review
[2] The research leading to these results has received funding from UOC, internal grant N116139473 and from the Spanish MINECO projects CTQ2013-48418P.

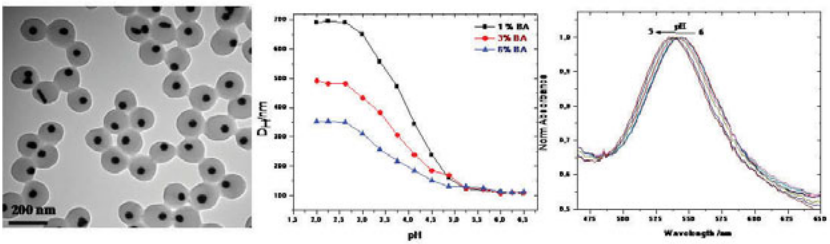

Figure 1. TEM images of the Au@p4VP system (left), DLS measurement at different crosslinking densities (middle), and UV-vis spectra at several pH values (right).

CONTINUOUS SYNTHESIS OF ORMOSIL-PARTICLES IN A MICROREACTOR

Christina Odenwald, Guido Kickelbick

Saarland University, Inorganic Solid State Chemistry, Campus C4.1, 66123 Saarbrücken, Germany
E-Mail: christina.odenwald@uni-saarland.de

ORMOSIL (organically modified silica) particles have a great potential for various applications, such as pigments, in bio-labeling, medical diagnostics, drug delivery, or as fillers for polymers.[1] Materials with a high and uniform quality can only be obtained if particle properties can exactly be adjusted and the reproducibility is guaranteed. Conventional batch and high temperature methods often lead to broad size distributions, aggregation and a batch-to-batch reproducibility. [2] Alternative preparation procedures, especially continuous, wet chemical processes show a great potential for the synthesis of defined particles but by now they are rarely developed.

The presented work focuses on the usage of the microjet technique for the preparation of micro- and nanoparticles, especially ORMOSIL spheres. [3] The continuous, wet chemical sol-gel route offers short mixing times, narrow size distributions and increased process control. [4] A solution of a prehydrolyzed organotrialkoxysilane and an aqueous solution of ammonia are forced with high pressure through narrow nozzles. In the reaction chamber, which is flushed with a gas flow, the solutions collide and generate high shear forces. A fast and homogenous mixing is reached. The dispersion is directly removed from the chamber by the gas flow and is collected in a vessel.

Methyl-, ethyl, propyl-, phenyl-, vinyl-modified SiO_2 particles as well as spheres with mixed groups and unmodified silica particles were produced (Figure 1). By varying the process temperature it was possible to adjust the final particle size. Scanning electron microscopy (SEM) images show that spherical particles in the range of 75 nm to 2 µm were obtained. The presence of functional groups was analyzed with ATR FT-IR- and CP-MAS-NMR spectroscopy. ^{29}Si NMR studies confirm that highly condensated networks solely with T^3 and T^2 groups were obtained. The organic content and the thermal stability of the samples were determined by elemental- and thermogravimetric analysis. Particles with alkyl chains show that the degradation temperature (T_d) of the organic group decreases with increasing chain length. Samples with mixed organic groups show T_ds that lie between the values for the samples with only one of these groups.

[1] J. D. Mackenzie, E. P. Bescher, J. Sol-Gel Sci. Technol. 13, (1998), p. 371–377.
[2] M. Rahman, E. Rebrov, Processes, 2, (2004), p. 466-493.
[3] A. Betke, G. Kickelbick, Inorganics, 2, (2014), p. 1-15.
[4] C. -X. Zhao, L. He, S. Z. Qiao, A. P. J. Middelberg, Chem. Eng. Sci., 66, (2011), p. 1463-1479.

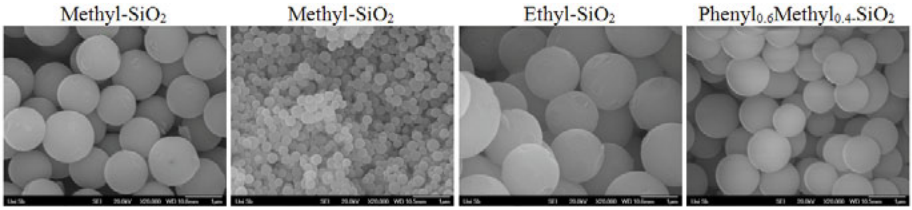

Figure 1: SEM images of prepared ORMOSIL particles (magnification 20.000) prepared at room temperature (a, b, c) and at elevated temperature (d, water bath 55°C).

SYNTHESIS OF HIGH ORGANIC LOADING HYBRID PARTICLES VIA A PHOTO SOL-GEL AEROSOL PROCESS

Mathilde Sibeaud[1-2], Céline Croutxé-Barghorn[2], Séverinne Rigolet[1], Laure Michelin[1], Ludovic Josien[1], Bénédicte Lebeau[1], Michael Wörner[3], Volker Zibat[3], Abraham Chemtob[1]

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Aerosol flame technology is an industrially important process for the manufacturing of many high utility inorganic nanoparticles, including carbon blacks, titania, or fumed silica [1]. However, the very high temperatures inside the conventional flame reactors (as high as 1000°C) prevents the direct incorporation of organic moieties. Because organic-inorganic particles are needed for numerous applications — such as filtration, detection, or to ensure particles/network compatibility in composites — particle hybridization is usually performed subsequently by surface functionalization in costly and time-consuming process.

We describe herein an eco-friendly UV process allowing the one-step synthesis of hybrid particles, either by photocondensation of organosilanes or by encapsulation of organic compounds in a photogenerated siloxane inorganic network [2]. This synthesis is performed at ambient temperature in an annular continuous photoreactor system surrounded by six energy-saving fluorescent UV lamps. Practically, the alkoxysilane (inorganic or hybrid) precursors are atomized into droplets into the reactor. UV irradiation controls the release of a photoacid catalyst, which triggers the sol-gel hydrolysis and condensation reactions [3]. After a single pass into the reactor, solid nanoparticles are collected in the filtration system. Analysis reveals the effective synthesis of spherical polydisperse powder particles with a mean diameter ranging around 400-500 nm. Co-condensation has been proved to be effective with mono and bis-silylated organosilanes, and lead to hybrid organosilica particles with up to 30% wt of organic loading. Finally, encapsulation of photoactive products such as methylene blue [4] has also been investigated, in order to produce particles suitable for photodynamic therapy with increased efficiency.

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AUF DER SUCHE NACH DER **PERFEKTEN OBERFLÄCHE ?**

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▸ SESSION 2

Agglomeration and Self-Assembly

SOFT QUASICRYSTALS

M. E. J. Mauer, M. Dulle, T. Gruhn, S. Förster (invited)

Physikalische Chemie I, Universität Bayreuth, 95440 Bayreuth, Germany

Quasicrystals have a special aperiodic order, which leads to diffraction patterns of 8-, 10-, or 12-fold rotational symmetry. They have been discovered in 1982 by Dan Shechtman. Since then they have been found in more than one hundred binary and ternary metal alloys. Beginning in 2004 there have been reports on quasicrystalline structures formed by soft materials such as dendrimers and polymers. This indicates that there might be very general principles that can lead to the formation of quasicrystals, and if this would be the case, their characteristic length scales could possibly be extended into the submicron range for photonic applications.

We have found quasicrystalline structures with 12- (Q12) and 18-fold (Q18) rotational symmetry in lyotropic liquid crystalline solutions of PI-PEO block copolymer polymer micelles in water, [1] and of PS-PI block copolymer micelles in diethylphthalate. Their stability range and phase transitions into the FCC, BCC and disordered phase as a function of concentration, temperature and molecular weight can be determined by rheo-SAXS experiments and is found to extend to length scales of > 200 nm.

It emerges that a necessary condition for the formation of soft quasicrystals is the existence of two intrinsic length scales, which in our case are the core- and shell dimension of block copolymer micelles. Using 2D- and 3D molecular dynamics (MD) simulations for micellar core/shell systems we identified in addition to the 12- and 18-fold quasicrystals a number of new quasicrystalline phases and rationalized their stability regions in terms of general geometrical packing constraints. [2]

A second method to produce quasicrystals is to realize two length scales using binary colloid mixtures with appropriate diameter and number ratio. We show that the latter can be used to fabricate quasicrystalline structures on length scales up to 800 nm having small-angle laser diffraction patterns with 12-fold rotational symmetry. In order to investigate whether quasicrystals have complete photonic bandgaps, we also fabricated quasicrystalline structures using UV-, two photon-, and electron lithography over length scales from 200 nm to 5000 nm, where the photonic band gap is expected to be in the NIR/IR-range relevant for telecommunication applications.

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BLOCK COPOLYMER HEXOSOMES

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Cubosomes and hexosomes are micron-sized polymorphs of lipids mostly observed for a small family of liquid-crystalline molecules, e.g., oleates and its derivatives.[1,2] Hexosomes in particular feature a monocrystalline internal lattice of inverse cylinders (channels) and a faceted hexagonal prismatic exterior (originating from the liquid crystal).[3] However, the molecular nature of the building blocks greatly limits the variation of structural parameters such as particle size, lattice geometry, lattice parameter, chemistry and mechanical properties. We explore routes to create polymeric analogues of these otherwise intriguing particles with potential as mesoporous scaffolds, for storage and release of nanoparticles, and with enhance mechanical robustness.

In this presentation, I discuss the preparation of hexosomes from block copolymer through a co-assembly and solvent sequence process. Under soft solvent conditions the characteristic monocrystalline lattice of open channels and the flat exterior interfaces form also for all-amorphous polymers (Figure 1). The particles are characterized *in-situ* with cryo-TEM and tomography (cryo-ET)[4] to analyze internal order and to verify the hollow interior of the channel system. The mechanically robust particles can be also transferred to the dry state where we analyze their aspect ratio and surface texture with AFM and SEM. We find that disturbances during the self-assembly process cause coiling of the growing channels into higher-order spinning-top structures with highly complex geometry and composition.

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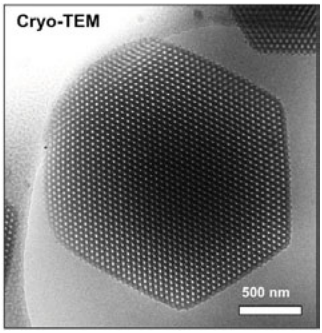

Figure 1. Cryo-TEM of a block copolymer hexosome

COLLOIDAL MOLECULES FABRICATION BY ASSEMBLY OF JANUS-LIKE DUMBBELLS

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Nanoparticles (NPs) used as building blocks for fabricating clusters with higher dimension have attracted much attention due to the potential applications in materials science, photonics, biology, etc. Janus-like particles with a sticky hemisphere are wonderful candidates to prepare colloidal structures of higher dimensions: multipod-like and raspberry-like clusters, linear chains, and even kagome-like lattices [1].

We report the use of dissymmetrical dumbbells made of a soft polystyrene (PS) particle combined to a hard PS@silica core-shell one [2] for successfully assembling them into multipod-like clusters with a controlled number of silica satellites bounded through a PS core. The driving force for assembly is hydrophobic interaction that occurs between PS moieties when the dumbbells are dispersed in a mixture of good and bad solvents for PS. We will discuss about the experimental parameters that allow to tune the aggregation number and in particular how to get raspberry-like morphologies (Figure 1). Interestingly, these silica@PS hybrids are the reverse replicas of the PS@silica clusters that we previously reported [3][4].

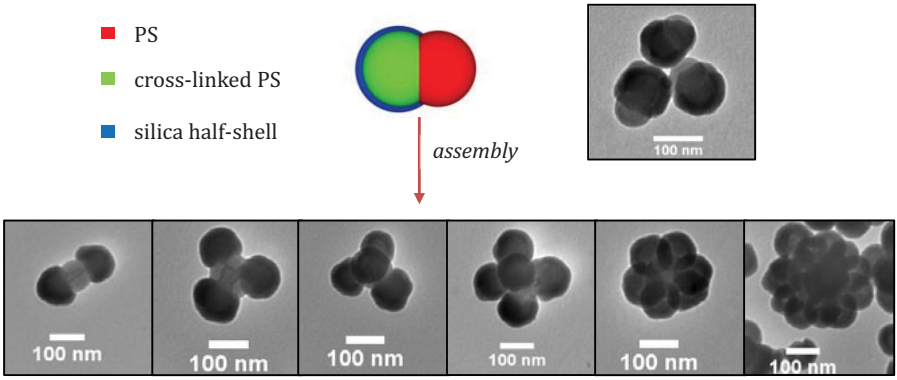

Figure 1. Compositional scheme and TEM images of the precursor Janus-like dumbbells and TEM images of after their assembly into colloidal molecules or raspberry-like clusters

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FABRICATION OF ORIENTED PLASMONIC OLIGOMERS ON ELASTOMERIC SUBSTRATE *VIA* MACROSCOPIC STRAIN

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We present the formation of oriented chains of few plasmonic nanoparticles, so called plasmonic oligomers, by controlled fragmentation of linear particle assemblies [1] into finite subchains. Detailed investigations of the fragmentation process are conducted by *in-situ* atomic force microscopy (AFM) and correlated to UV-vis-NIR spectroscopy. [2]

By evaluation of the strain dependent optical properties we found a reversible, non-linear shift of the dominant plasmonic resonance. These measured optical properties were analyzed by deconvolution for the corresponding ensemble of oligomers by electromagnetic modeling and compared to the oligomer length distribution and dispersity yielded from the AFM measurements. Based on these results and mechanical modeling (lattice spring method), we prove a formation mechanism which provides experimental guiding lines. Following this strain-dependent fragmentation mechanism the chain length can be tweaked depending on the ratio of cohesion between the particles and adhesion of the colloids to the supporting elastomeric substrate.

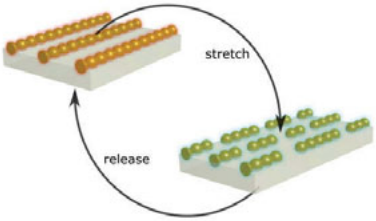

Figure 1: Reversible fragmentation of quasi-infinite gold nanoparticle chains into defined oligomers, induced by macroscopic strain

We demonstrate, that mechanical stimulus is a powerful tool for the scalable fabrication of oriented linear plasmonic oligomers and opens new avenues for strain-dependent optical devises and mechanoplasmonic applications. As an example, for surface-enhanced sensing, the reversible switching of the nanostructure may be utilized to trap/infiltrate target molecules into uniform hot-spots

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[2] Anja Maria Steiner *et al. manuscript submitted*

DIRECTIONAL BONDING OF SILICA PARTICLES BEARING CHEMICALLY MODIFIED POLYSTYRENE PATCHES

Pierre-Étienne Rouet[1,2], Étienne Duguet[2], Serge Ravaine[1]

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The notion of valence is well-known at the level of atoms and is at the origin of the diversity of all molecules and macromolecules. It is a great challenge to reproduce at the scale of colloidal particles the notion of valence, which should allow one to fabricate new colloidal molecules and colloidal crystals. Colloidal particles with chemically distinct surface patches that imitate hybridized atomic orbitals, including sp, sp^2 and sp^3, can be considered as the colloidal analogues of atoms with valence. In this talk, we report on a new route to synthesize patchy particles with a controlled number (*i.e.* 2, 3 or 4) of patches or dimples as well as on their potential use as building blocks for the elaboration of new supracolloids with unusual morphology.

We have recently reported the synthesis of dimpled silica particles through the growth of the silica core of colloidal molecules made of a central silica core surrounded by a precise number of polystyrene satellite nodules, followed by the dissolution of these nodules [1,2]. We have also shown that some organic residues corresponding to the grafted PS chains remain at the bottom of the dimples (Figure 1, left). These organic residues were selectively chloromethylated, which paves the way for further functionalizations such as amination or azidation. We also synthesized silica particles functionalized with a complementary group to the one grafted on the organic residues (respectively carboxylic acid or alkyne) and we adjusted their diameter in order to use them as keys to be locked into each dimple. By assembling the functionalized dimpled particles and the key particles, we obtained supracolloidal structures made of a precise number of silica spheres around a dimpled silica core (Figure 1, right) [3].

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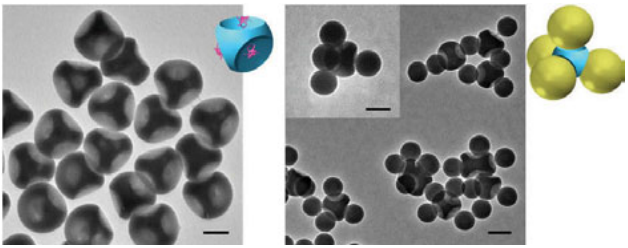

Figure 1. (Left) TEM image and scheme of dimpled silica particles (blue) with polystyrene chains at the bottom of the dimples (pink); (right) TEM image and scheme of supracolloids made of four functionalized silica satellites (yellow) around a dimpled core. Scale bars: 100 nm.

COLLOIDAL PLASMONIC ARRAYS EXHIBITING TUNABLE SURFACE LATTICE RESONANCES

Kirsten Volk[1], Joseph P.S. Fitzgerald[1] and Matthias Karg[1]

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Ordered nanostructures that can guide or manipulate the propagation of electromagnetic fields at optical frequencies are of great importance for applications in sensing, all-optical computing and photovoltaics. Periodic plasmonic nanoparticle arrays can support narrow surface lattice resonances (SLRs) due to coupling between localized surface plasmons and diffractive modes [1,2].

Here, we address a method suitable for fabricating large area devices that support fully reversible, dynamic actuation of SLR modes. We use wet-chemically synthesized core-shell nanoparticles (silver-(poly-N-isopropylacrylamide)) for dynamic assembly at the air-water interface into hexagonally ordered, cm^2- sized, plasmonic arrays [3,4]. In order to obtain a homogeneous refractive index environment we coated the monolayers with a PNIPAM top coating which was then crosslinked in order to create a robust, solvent resistant device (Figure 1a). By carefully choosing the degree of crosslinking a temperature sensitive device in water was developed. The refractive index surrounding the monolayer can be tuned dynamically by swelling and deswelling the polymer film by switching between temperatures below and above the volume phase transition temperature of the coating (Figure 1b,c). This behavior lead to a device with a dynamically tunable and fully reversible SLR.

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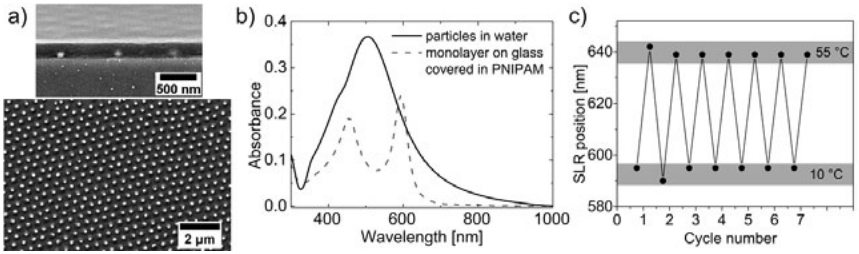

Figure 1. a) Side-view (top) and top-view (bottom) SEM image of PNIPAM-coated monolayer. b) UVvis absorbance spectra of silver-(poly-N-isopropylacrylamide) nanoparticles in dispersion (line) and assembled as monolayer on glass coated with PNIPAM (dashed). c) Experimental reversibility study on SLR tuning of the device with dc-c = 488 nm.

SPINNING OF HIERARCHICAL HYBRID FIBERS: CONTROLLED COLLOIDAL ASSEMBLY

Beate Reiser, Dominik Gerstner, Lola Gonzalez-Garcia, Johannes H. M. Maurer and Tobias Kraus

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Bottom-up fabrication is nature's way of creating a multitude of functional materials. Nanometer scale building blocks assemble into macroscopic hierarchical materials with multiple levels of structural hierarchy and extraordinary properties. Artificial materials can be synthesized on similar routes starting from interacting colloidal building blocks.[1] We are interested in inorganic-organic hybrid materials based on metal-organic hybrid colloids. Ultrathin gold nanowires (AuNWs), stabilized by oleylamine ligands, have diameters below 2 nm, and lengths of several micrometers (Figure 1a). Their dimension and interaction behavior remind of linear polymers.[2,3]Agglomeration of AuNW leads to fibrillar networks rather than globular agglomerates.

Polymers are commercially spun into hierarchical fibers by a process called wet spinning.[4] We show that a similar process, depicted in Figure 1b, can be used to spin AuNW spinning dope. A coagulation bath triggers the formation of AuNW bundles with diameters on the order of 100 nm. These bundles then form a macroscopic hierarchical fiber, where the single AuNWs form the 1st, AuNW bundles the 2nd, and the fiber the 3rd hierarchical level. As-spun fibers are inorganic-organic hybrids with 80% organic content in volume (Figure 1c). The AuNW concentration in the spinning dope and the speed of injection into the coagulation bath control fiber thickness and structure, respectively, as confirmed by scanning electron microscopy and atomic force microscopy. An *in situ* small angle X-ray scattering study of the flowing spinning dope revealed increasing AuNW alignment in direction of the flow with increasing flow speed.

We propose a simple model to explain the impact of flow on the spun fibers' structure. Comparison of fiber structure and tensile testing results provide structure-property relations and prove the importance of hierarchy for fiber tensile properties. The experimental findings on spinnability and structure-property relations of AuNW fibers are in striking analogy with polymer fibers: AuNW fiber spinning is only possible at flow rates that lead to sufficient elongation in the direction of the flow. Spherical gold nanoparticles cannot be spun. This reminds of the minimal polymer molecular weight (that sets the absolute polymer length) required for polymer fiber spinning.[5] We also observed an increase in yield stress but a decrease in the elongation at break for fibers with better alignment that is analogous to polymer fibers.[4]

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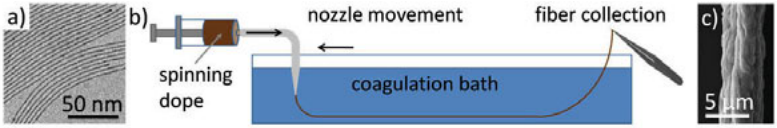

Figure 1. (a) Transmission electron micrograph of AuNWs. (b) Schematic depiction of fiber spinning and collection. (c) SEM image of an as-spun hierarchical AuNW fiber.

ASSEMBLY OF ISOTROPIC HARD SPHERES INTO ANISOTROPIC STRUCTURES AT AIR/WATER INTERFACE IN THE PRESENCE OF SOFT PARTICLES

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The ability of colloidal particles to adsorb to liquid interfaces is of fundamental importance for a range of scientific disciplines and applications. Liquid interfaces confine particles in two dimensions and serve as ideal templates to study self-organisation phenomena.
The symmetry of the assembled structure is determined by the colloidal building blocks. Spherical particles, most commonly applied in colloidal self-assembly, therefore generally form two-dimensional crystals with hexagonal symmetry [1].
However, theoretical predictions have shown that the shape of the interaction potential can greatly affect the assembled structure. By introduction of a soft repulsion shoulder to a hard-sphere potential, Jagla showed that complex, anisotropic assembly phases can be formed from simple, isotropic colloidal particles [2].
Here, we use an in-situ approach to observe the phase diagram of colloids in the presence of soft microgels at the air/water interface of a Langmuir trough equipped with a microscope. This allows us to observe the particle arrangement during compression and relaxation. We find a rich phase diagram including chain-like and rhombohedral packing (Fig. 1). We discuss the appearance of these phases in terms of a soft repulsion potential induced by the presence of the microgel particles at the air/water interface.

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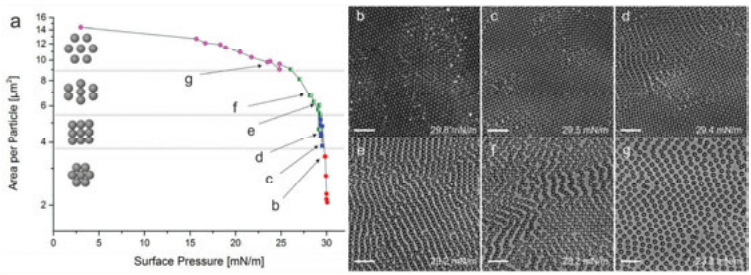

Figure 1. Phase diagram of colloids mixed with microgels observed in situ at the air/water interphase. a) compression isotherm, represented by the area available per particle as a function of the surface pressure. b-g) Representative microscopy images taken at the air/water interface: b) hexagonal close packed, c) rhombohedral packing, d) transition to chain-like packing, e) chain-like packing, f) transition to hexagonal non-close packed, g) hexagonal non-close packed. Scale bar corresponds to 10 µm.

STUDYING THE SELF-ASSEMBLY, SHAPE SELECTIVITY AND EVOLUTION OF CHITOSAN/NANOPARTICLE COLLOIDS BY TIME-RESOLVED SMALL-ANGLE X-RAY SCATTERING

Oonagh Mannix, Sylvain Prévost, Rajeev Dattani and Naryanan Theyencheri

ID02, ESRF-The European Synchrotron, Grenoble, France

Self-assembled particle/chain systems such as micelles with polyelectrolytes [1] or proteins [2], and nanoparticles with polymers [3] or proteins [4] form deformable colloids. Mastering the self-assembly process would lead to easily manufactured products capable of deforming and adapting to environmental conditions, and where controlled disassembly can be triggered. Here we present the self-assembly of a nanoparticle/polyelectrolyte (silica/chitosan) system which forms colloidal structures that we aim to align over large scales under an electric field.

Upon self-assembly a range of structures characterized by their different fractal dimensions is available. These structures are controlled by both (i) microscopic: a combination of electrostatic and depletion interactions; and (ii) macroscopic effects: concentration, ionic strength, and the separate nanoparticle (particle size, surface chemistry) and polyelectrolyte (e.g. Kuhn length) properties.

Focusing on the link between structure and dynamics with time-resolved small and ultra-small X-ray scattering (TR-(U)SAXS) studies probing from 10^{-3} to 10^{7}s (ms to year) we demonstrate that three growth processes are involved at different time scales. Understanding the formation and evolution of these clusters offers insights into the relative effects of the theoretical mechanisms involved, and practically presents the possibility of tailoring the final assemblies.

This work provides information on the thermodynamics of formation of particle/chain systems, including a pathway to shape-selectivity. Control of such systems enables exploitation for other purposes including alignment under electric field [5].

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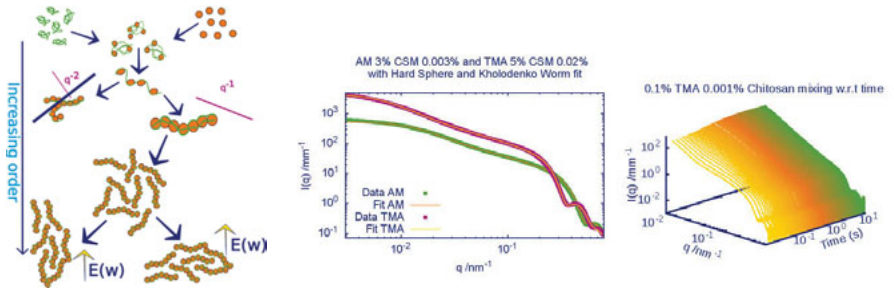

Figure 1. a) Schematic of the proposed self-assembly process and subsequent alignment under electric field, b) USAXS data demonstrating the shape and size of 1-D structures, c) TR-SAXS data demonstrating the self-assembly process.

COLLOID CLUSTERS IN CONFINEMENT

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Colloids assemble upon increase of volume fraction into crystals. Complex structures can be achieved by varying composition, interaction, or shape of the constituent colloidal particles [1,2]. Another method to modify the crystallization process is to utilize interfacial effects resulting from the introduction of confinement [3]. Recently it has been shown that entropy favors icosahedral symmetry for colloids assembling in spherical confinement [4]. Here we use droplet-based microfluidics to create homogeneous emulsion droplets as sources for defined spherical confinement. This allows to systematically explore the assembly behavior of clusters containing between 100 and 10000 near-monodisperse colloidal spheres. We observe a discrete series of colloid clusters with icosahedral symmetry. To understand and explain the formation of the colloidal clusters, we propose a geometric model and extract extremal principles. Our assemblies may find use as templates, photonic materials and building blocks for hierarchical assemblies [5].

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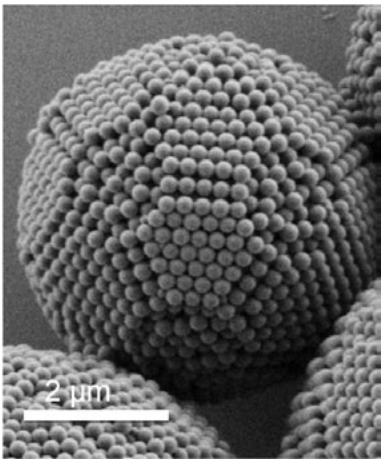

Figure 1. Icosahedral colloid cluster assembled in emulsion droplets.

▸ SESSION 3

Bioactive Colloids and Interphases

MEMBRANE BUCKLING IN MACROMOLECULE INDUCED RED BLOOD CELL AGGREGATION

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Macromolecular plasma proteins such as fibrinogen induce the formation of large aggregates of red blood cells, called rouleaux, which are responsible for the pronounced shear thinning behavior of blood. We use confocal microscopy to characterize the shape of red blood cells within rouleaux at equilibrium as a function of macromolecular concentration, revealing the diversity of contact zone morphology. Our first study on clusters of two cells shows that the deformation of the interacting membranes increases in a nonlinear fashion with the interaction energy. This is corroborated by numerical simulations that indicate a forward bifurcation and an analytical analysis showing that the deformation of the interfacial membrane indeed undergoes a buckling instability from a flat to a deformed contact zone at a critical value of the interaction energy. Once the interface has reached ist final deformation it can be classified into three different shape configurations, so called sigmoid, male-female and parachute shapes that have only been partly predicted before [1,2] as depicted in Fig. 1. These results are not only relevant for red blood cells, but for a whole class of interacting soft deformable objects such as vesicles, capsules or cells.

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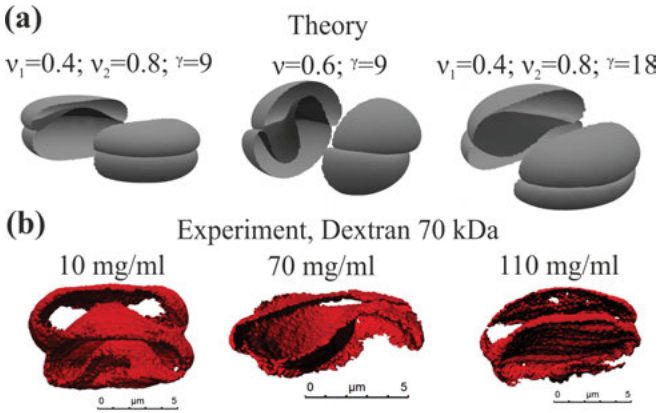

Figure 1. (a) Theoretical results for RBC interaction and resulting contact zones from [1] for different reduced volumes and adhesion strengths. From left to right: Male-female shapes, strong sigmoid shapes and low sigmoid shapes. (b) 3D-confocal imaging of RBC-doublets. The experimental results reproduce qualitatively the theoretical predictions.

POLYSACCHARIDE SUB-MICROCARRIER FOR ANTI-INFECTIVES DELIVERY

Duy-Khiet Ho[1], Ana Margarida Martins Maia da Costa[3], Chiara De Rossi[1], Cristiane de Souza Carvalho-Wodarz[1], Brigitta Loretz[1] and Claus-Michael Lehr[1,2]

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The enormous potential of micro-/nano-sized carriers to improve the therapy of severe infectious diseases yet appears to be underexplored. Multidrug-resistance of bacteria may be better overcome by improving the local delivery of anti-infectives across cellular biobarriers. However, the search for materials that could balance requirements of bio-medical applications and engineering aspects is still challenging. This project aims to develop sub-microcarrier (SMC) for poorly soluble anti-infectives, such as quinolones, based on ß-cyclodextrin (ß-CD) and chitosan using a facile method. Anionic ß-CD was synthesized by selective primary alcohol oxidation in presence of TEMPO and sodium-hypochlorite. SMCs formation was achieved by controlled self-assembly of anionic ß-CD and chitosan derivative (MW 90kDa). SMC characteristics could be varied by (i) polymer concentration, and (ii) molar ratio of carboxylic to amine groups (C/N). Resulting SMC were loaded with Ciprofloxacin and characterized. Their biocompatibility was evaluated by performing MTT assay on differentiated-THP1 and NIC-H441 cells. Particle uptake by differentiated-THP1 macrophages was investigated by using laser scanning confocal microscopy and fluorescence-activated cell sorting. The SMC's size could be controlled from 0.4µm to 1µm by varying the C/N ratio and polymer concentration (Fig.1A). Encapsulation efficiency of Ciprofloxacin was higher than 90%. The SMCs showed no severe cytotoxicity (cell viability>80%) up to 500µg/ml SMC concentrations. The amount of SMC uptake by activated-THP1 cells depended on particle size (Fig.1B).

The results clearly demonstrate: (i) stable SMC's of controllable size by self-assembly of chitosan and ß-CD after gentle chemical modification (ii) effective encapsulation of a poorly soluble anti-infective quinolone (iii) biocompatibility (iv) size-dependent uptake by macrophages. This SMC platform has good prospects for improving the treatment of bacterial infections

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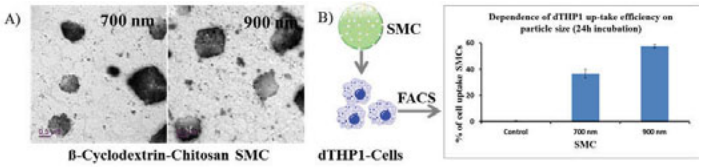

Figure 1. A) Representative TEM images of different size SMC, B) SMC up-take of differentiated-THP1 macrophages.

INTERACTION OF BIOMOLECULES WITH MAGNETITE

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Magnetotactic bacteria are motile aquatic prokaryotes that mineralize magnetite crystals. These crystals are enveloped in a lipid membrane and aligned in a chain along the bacteria cell axis. Bacterial magnetite crystals have outstanding properties, such as a narrow size distribution and a strain-specific shape. In particular, some strains of magnetotactic bacteria are able to synthesize elongated magnetite crystals. Such morphologies are extremely difficult to obtain synthetically. In the bacteria, biomineralization of these elongated structures is genetically controlled and involves a large number of proteins with different functions. In this context, it remains unclear how bacteria mineralize these elongated structures.

We are therefore investigating specific proteins putatively involved in magnetite mineralization with the aim to understand their exact role in controlling the growth of elongated magnetite crystals. Towards this goal, we are developing methods to screen and quantify the interaction of magnetosomal proteins with magnetite. In our experimental setup, we express and purify these proteins recombinantly in *E. coli*, using a standardized expression system. For screening, these proteins are subsequently tested for their interaction with magnetite in a binding assay using synthetic magnetite nanoparticles and fluorescent tags. In a second step, single molecule force spectroscopy is performed to quantify the binding strength between proteins and magnetite surfaces.

These investigations will extend the knowledge about how magnetosome associated proteins interact with magnetite and how different strains of magnetotactic bacteria mineralize magnetite crystals. This mechanistic, molecular level understanding will aid the development of green synthetic routes for magnetite particles towards applications in bio- and nanotechnologies.

COLLOIDAL APATITE NANOPARTICLES SIGNIFICANTLY IMPROVE TREHALOSE-ENHANCED CRYOSURVIVAL OF RED BLOOD CELLS

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Apart from bone repair, biomimetic apatites' intrinsic biocompatibility and nanoscale dimensions allow imagining other biomedical applications as in nanomedicine. Previous data reported the preparation of colloidal apatite nanoparticles (NPs) stabilized by an organic corona, and *in vitro* analyses confirmed their high biocompatibility and absence of detectable pro-inflammatory potential [1]. Recently, the good hemocompatibility of such NPs was also evidenced [2], especially when contacted with Red Blood Cells (RBC). One international issue in blood banks is the low viability of RBC over time, requiring the development of cryopreservation procedures. However, taking into account the drastic character of a freeze-thawing cycle, there is a need to add to the RBC suspension a cryoprotecting agent. Glycerol has been proposed and approved by the FDA, however its toxicity necessitates the setup of a long deglycerolization process which, along with its toxicity, is not suited for a globalized and rapid provision of RBC to blood banks. Alternative solutions are thus under investigation. Sugar-based additives such as trehalose, a dimer of glucose, have been proposed as non-toxic cryoprotectant. However, to be efficient, these agents must be present on both sides of the cell membrane, and the low naturally low permeability of RBC's membranes to trehalose limits drastically its applicative use.

In this work, we have investigated a way to increase RBC viability by freeze-thawing by increasing the permeation of trehalose through RBC membranes, via the addition in the medium of engineered colloidal apatite nanoparticles. Results pointed out a colossal increase of RBC viability (up to 91 %) after freeze-thawing when the NPs (~ 30-40 nm size) were added in the medium prior to freezing. The effect of incubation conditions was also noticed. To further understand this effect, probably linked to an increased permeation of trehalose in the presence of the NPs, additional experiments were carried out on synthetic free-standing lipid bilayers to approach RBC membranes' behavior. Results obtained using Eu-doped luminescent apatite NPs indicated that (in absence of active processes like endocytosis as is also the case for RCB) the apatite NPs could not cross the lipid bilayer. However, the enhanced permeation of a trehalose-mimicking fluorescent probe, FITC, through lipid bilayers was clearly observed in the presence of apatite NPs. In contrast, no transfer was noticed in the absence of apatite NPs. Measurements of the electrical capacitance of the bilayer using a patch-clamp amplifying method indicated a noticeable local change in the presence of NPs. By exposing adequately surface charges on their surface, the NPs are thought to alter locally and transiently the physical properties/3D organization of the membrane, thus increasing momentarily permeation for small molecules like trehalose. This hypothesis seems to be confirmed by computational calculations. Colloidal apatite NPs coupled to trehalose thus appear as a good alternative to the use of toxic agents like glycerol or else DMSO for the cryopreservation of RBC.

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THE INFLUENCE OF PEG DENSITY ON THE ORDERING OF PROTEINS ON PEGYLATED SURFACES

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Nanoparticles and liposomes can be used as versatile drug nanocarriers. Upon injection into the bloodstream a protein layer will immediately coat the nanocarrier surface, the so-called protein corona. This alteration of the nanocarrier surface chemistry can induce changes of the drug carrier properties and interfere with the carrier's targeting mechanism [1]. In order to prevent this non-specific protein adsorption the drug nanocarriers are often coated with a protein repelling poly(ethylene glycol) (PEG) layer, which had been hypothesized to suppress non-specific adsorption by steric repulsion [2]. However, recently, it has been shown that the adsorption of certain proteins can be beneficial and promote specific cellular uptake [3]. A deeper understanding of protein adsorption to PEGylated surfaces would therefore be desirable to control the protein corona composition. Here we use mixed lipid monolayers consisting of 1,2-ditetradecanoyl-sn-glycero-3-phosphoethanolamine (DMPE) and 1,2-dimyristoyl-*sn*-glycero-3-phosphoethanol-amine-N-[methoxy(polyethylene glycol)-2000] (PEG2000 PE) as model systems for PEGylated surfaces. We study the influence of interaction between the lipid head groups and the proteins as well as steric repulsion from the PEG chains on the adsorption behavior of bovine serum albumin (BSA) and fibrinogen. Surface sensitive vibrational sum-frequency generation (SFG) spectroscopy is used to probe the orientation and structure of the proteins at the lipid/water interface. Figure 1 shows a scheme of the SFG experiment and the chemical structure of the lipids. The results suggest that a balance exists in the amount of adsorbed protein and its ordering on the surface which depends on the PEG density.

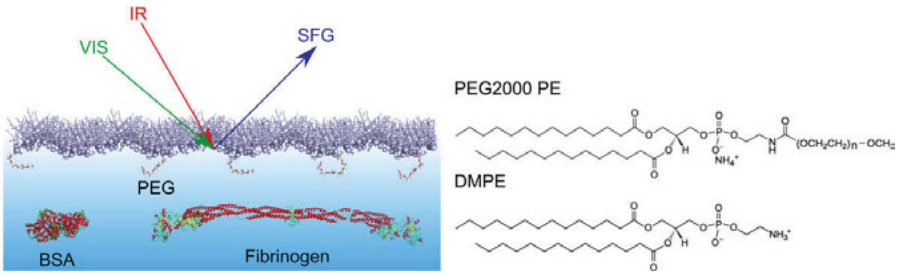

Figure 1. Scheme of the SFG experiment to measure the amide carbonyl stretching vibration of the proteins as well as the chemical structures of the lipids DMPE and PEG2000 PE used as model layers.

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PROTEIN CORONA *IN VITRO* AS *IN VIVO*?

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The key issue in clinical translation of nanoparticles (NPs) for biomedical applications is discrepancy between *in vivo* and *in vitro* studies. Therefore, it is essential to establish novel approach to *in vitro* experiments which would give as-*in-vivo* results. The hallmark of the biological behavior of nanomaterials is protein corona (PC) which forms by NPs-protein interactions upon exposure of NPs to the biological environment. Thus, we studied the specificity of NPs-protein interactions from the physical and chemical point of view and the PC composition in the complex *in vitro* environment including variation of few study parameters [1]. In this study iron oxide NPs (IONPs) were used as a NPs' model due to large potential of IONPs for biomedical applications and numerous previous studies of PC on this type of NPs. PC isolation from IONPs was done by our method developed for magnetic NPs [2]. The obtained PC proteins were analyzed by liquid chromatography-tandem mass spectrometry (LC-MS^2). The detailed physical and chemical characterization was done (FTIR, Transmission electron microscopy (TEM) and HRTEM of native and negatively stained IONPs with PC (see Figure 1)). Finally, by studying the PC composition in complex *in vitro* incubation conditions varied in accordance with their appearance *in vivo*, we found the novel key parameters which determine the PC composition and correlated PC with clinical facts (different administration routes or illnesses lead to different biodistributions) [3].

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[3] D. B., H. H. and M. M. E. acknowledge the MagnetoTeranostics project that was scientifically evaluated by the SNSF, financed by the Swiss Confederation and funded by NanoTera (N°530627). U. A. was supported by the SNSF Project 157615. We thank Prof. Dr. med. H. Thöny, Prof. Dr. med. G. Thalmann and Dr. S. Barbieri (all at Inselspital Bern), and Prof. Dr. F. Stellacci (EPFL).

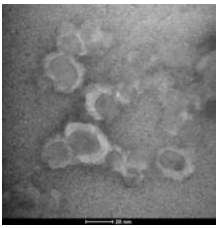

Figure 1. TEM micrograph of IONPs with negatively stained PC in order to increase the contrast of organic material (proteins) on the surface of NPs and carbon-background film on the TEM grid. The lighter parts around the surface of IONPs show proteins in PC.

AN INJECTABLE, ANISOTROPIC HYDROGEL FOR DIRECTED CELL AND NERVE GROWTH

Jonas C. Rose[1], David Gehlen[1], Esther Jaekel[1], María Cámara-Torres[1], Jens Köhler[1], Khosrow Rahimi[1], Martin Möller[1,2], and Laura De Laporte[1]

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Many biological tissues consist of complex, anisotropic, and hierarchical structures, such as nerve, bone, enamel, and heart. For these tissues, regenerative matrices have to mimic the biological architecture to guide cell organization during the healing process. However, up to now, most injectable materials, which allow a minimal-invasive application, are isotropic and therefore, lack the ability to template complex tissues with directionally organized functions and mechanical properties. Here, we demonstrate a new injectable composite material, which has the ability to direct cell growth. The composite hydrogel contains rod-shaped microgel objects with variable mechanical properties, geometry, and porosity, which are incorporated into a surrounding biocompatible hydrogel. The microgels are doped with a low amount of superparamagnetic iron oxide nanoparticles (SPIONs), which induce longitudinal alignment *in situ* within a magnetic field in the milli tesla range. This study encloses the development and characterization of this low-invasive, injectable, anisotropic hydrogel ('Anisogel'), and the cellular response, induced by this novel scaffold material.

Rod-shaped microgels were fabricated with a mold-based soft lithography approach. The microgels consist of a UV-crosslinking star-shaped poly(EO-stat-PO)-acrylate, which was supplemented with SPIONs. The harvested microgels can be tuned in regard to their size, aspect ratio, stiffness, and porosity, as well as modified in their interaction with cells by covalently attached cell adhesion peptides. Furthermore, doping microgels with SPIONs allows their orientation within less than 60 s in a magnetic field of ~100 mT. Interestingly, microgels that have an aspect ratio of 10 exhibit an ultrahigh magnetic response, which allows significant microgel alignment in only 1.9 mT, which corresponds to only 19 times the earth's magnetic field. In order to create a regenerative anisotropic hydrogel, microgels were aligned in a fibrin gel, which enzymatically polymerizes within 120 s, allowing prior microgel alignment. After fibrin gelation, the microgels maintained their position and orientation in the absence of a magnetic field. To investigate the material's functionality in regard to neural tissue, fibroblasts, primary neurons or dorsal root ganglions (DRGs) were inserted into the Anisogel (see Figure 1). When the microgels were randomly oriented, cells infiltrated the matrix less and showed isotropic morphologies. In the case of oriented microgels, extending cells were affected by the aligned physical barrier, resulting in linear cell outgrowth.

By applying magnetoceptive, tailorable microgel rods in a fibrin hydrogel, a global material anisotropy was created after injection. The biomaterial is the first that can achieve highly controlled and ordered structures *in situ* and demonstrated to guide neurite growth in a linear manner. This feature could be groundbreaking as supporting therapeutic material for spinal cord repair.

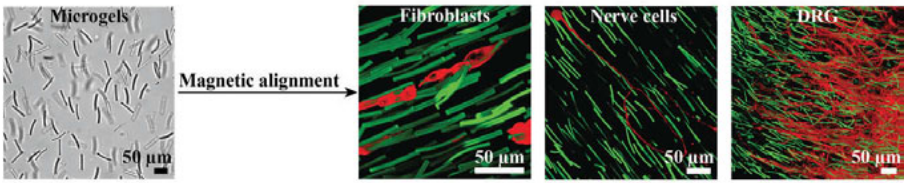

Figure 1. Magnetic alignment of microgels in fibrin to induce oriented and nerve cell growth.

SESSION 4

Physical Properties and Characterization

POLYMER AND DENDRIMER-STABILIZED NANOPARTICLES IN CATALYSIS

Didier Astruc[1] (invited), Christophe Deraedt[1], Dong Wang[1], Jaime Ruiz[1], Changlong Wang[1,2], Lionel Salmon[2]

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Macromolecules containing heteroatoms are very good stabilizers for nanoparticle catalysts. This concept, initiated by Toshima and Yonesawa with polymers [1] and Crooks with dendrimers [2] has produced significant advances in catalysis by late transition-metal nanoparticles. We have initiated and developed the encapsulation of catalysts including nanoparticles and molecular catalysts by CuAAC "click" dendrimers for a number of major organic reactions [3,4]. Moreover, if the dendrimer possess water-soluble termini, it behaves as a unimolecular micelle, a concept (Figure 1) proposed by Newkome for molecular recognition [5] that we have extended to catalysis [6-8] and biomedicine [9]. Exemples will be provided during the lecture.

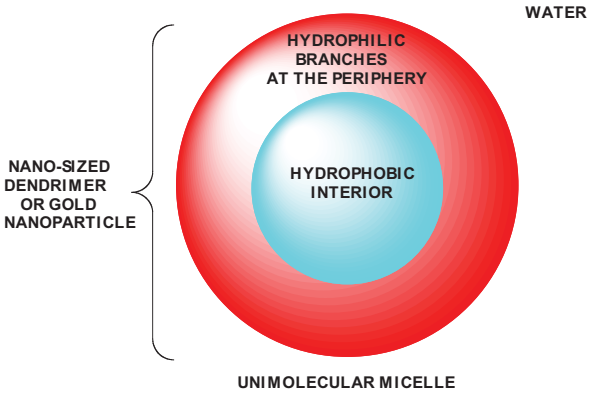

Figure 1. General scheme representing the encapsulation of hydrophobic catalysts and drugs in dendritic molecular micelles for solubilization in water.

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GAS PERMEATION THROUGH PICKERING MEMBRANES

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As described by S. U. PICKERING in 1907 [1], particles spontaneously adsorb to the surface of droplets and emulsify them for a long period of time (so-called Pickering emulsions – see Figure 1 a)). This effect can be enhanced by giving the particle a hydrophilic and hydrophobic region (Janus particles) [2]. These particles arrange themselves preferably at interfaces between two non-miscible fluids (see Figure 1 b)) [3]. Our idea is: We increase the number of regions on the surface of the particles by one. We then should be able to stabilize membranes instead of spherical droplets (see Figure 1c)). We call these membranes *Pickering membranes,* and the particles we use for this approach *Saturn particles* (others call them triblock Janus or patchy particles).

The used Saturn particles are produced by masking the caps of hydrophobic coated silica particles and etching the equatorial region in between them via hydrofluoric acid in one step [4].

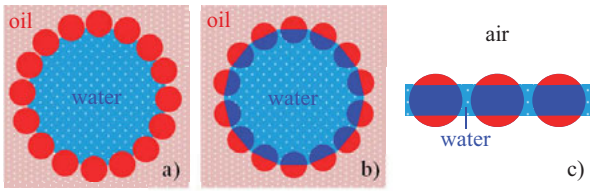

Figure 1: a) Pickering emulsion with particles. b) Pickering emulsion with Janus particles. c) Pickering membrane with Saturn particles. Red areas are hydrophobic, blue areas are hydrophilic.

According to our experience it is far easier to create such water membranes in air than in a hydrophobic fluid. We do this by suspending Saturn particles in ultrapure water and carefully pumping one air bubble into the water from below (see Figure 2). When replacing the air above the Pickering membrane with one of various gases (such as CO_2, SF_6, or NH_3), the gas or air permeates through the water of the Pickering membrane and the membrane moves. When replacing the gas with air, the membrane moves back again. We capture the movement of the Pickering membrane on video to determine the movement speed and therefrom calculate the experimental permeance in quite good agreement with theoretical predictions.

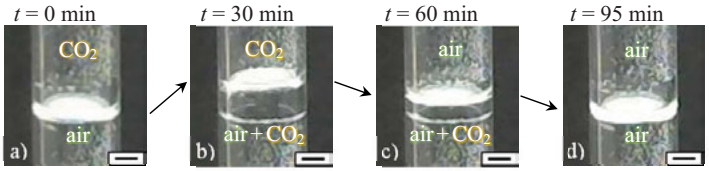

Figure 2: The permeation of CO_2 through a Pickering membrane. The CO_2 above the membrane permeates through it (a–b). The CO_2 is replaced by air after 30 min. The CO_2 below the membrane permeates back through the membrane until there is only air left (c–d). Scale bar is 2 mm.

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SYNTHESIS OF NANOPARTICLES IN DISPERSION: FLOW CELL COUPLED DYNAMIC LIGHT SCATTERING AS A WAY TO FOLLOW PARTICLE GROWTH

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Control of the precise size and morphology of nanoparticles is key to their successful application in optical grade composites. In this work, dynamic light scattering (DLS) has been used to follow the growth from molecular precursors to nanoparticles in a pilot scale reactor. DLS is the standard tool for sizing of nanoparticles in solution. The coherent light scattered from particles carries a fingerprint of the particle motion, which is described by the diffusion coefficient of the particles which is in direct relation to the hydrodynamic radius Rh. The principle is based on the correlation of photons scattered from the sample and detected by a suitable photon detector. It requires that only single scattered photons arrive at the detector. While the criterion of single scattering imposes no problems for solutions of very low turbidity, it renders measurement of slightly turbid solution impossible, because this results in undetectable systematic errors. Since dilution may modify the sample this needs to be reduced as much as possible. This can be done with the 3D modulation technology. It suppresses multiple scattering to filter out only the single scattering (fig. 1).

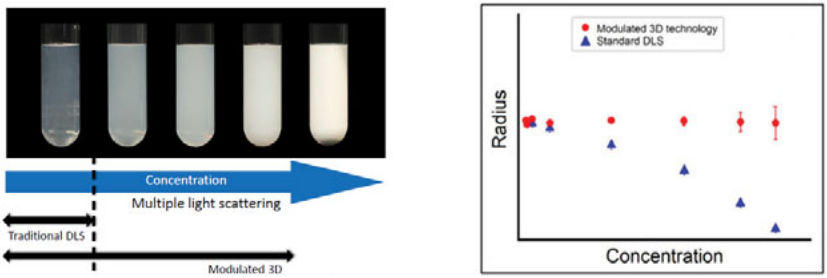

Fig 1: Modulated 3D technology. The triangles indicate the systematic deviation from the true radius at higher concentration.

The instrument's design was adapted in order to accommodate a flow cell including tubing material to enable online measurements. A direct connection of the sample cell to the reactor via a tubing system could easily transmit vibration and cause movement of the particles larger than that caused by Brownian motion. It was thus necessary to decouple and reduce the vibration sufficiently such that the thermal motion of particles in the measured sample volume dominates. We show that real-time measurements of particle size, using a bypass loop and flow cell, can be performed directly on very turbid reaction mixtures without the need for dilution, as a result of the design of the light scattering setup. This is demonstrated using size-tunable reaction systems of nano-silica and nano-titania in dispersion [1].

[1] This work has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 645993.

INVESTIGATION AND MODIFICATION OF THE POROSITY OF SUPRAPARTICLES

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This study presents the investigation of formation and modification of porous spherical supraparticles by evaporation-induced self-assembly (EISA) from multi component colloidal dispersion droplets deposited on superhydrophobic surfaces based on investigations by Sperling *et al.* [1,2].

The porosity of supraparticles from silica nanoparticles and biopolymers (DNA, carboxymethyl cellulose) results from separation of negatively charged SiO_2-NP and biopolymers based on electrostatic repulsion. SiO_2-NP and DNA provide characteristic separation patterns in their drying films, as investigated by Joksimovic *et al.* [3]. The formed micrometer sized pattern found as pores within the supraparticles depend on the relative polymer concentration and the size of the SiO_2-NPs.
Increasing the ionic strength (NaCl) leads to a reduced separation of SiO_2-NP and polymer resulting in smaller pore structures and agglomerates. For further modification polystyrene (PS) can be added to the colloidal dispersion droplets before evaporation. Thus, PS accumulates at the pore structures and at the edge of the supraparticle. As a result an extended pore network of hierarchical architecture can be build.
Subsequent pyrolysis of the polymers leads to porous SiO_2-supraparticles and this process was monitored and characterized by scanning electron microscopy (SEM) and confocal laser scanning microscopy (CLSM) and the pore size can be controlled via ratio SiO_2-NP/DNA (Fig. 1C). This controlled pore network within the SiO_2-supraparticles then can be applied as a support material for catalysts. As an example the functionalization of porous supraparticles with silver nanoparticles (Ag-NP) was done via an in situ synthesis and an incubation method shows the application potential of porous SiO_2-supraparticles. In summary, such porous silica based supraparticles are interesting functional colloidal system with a high degree of versatility towards applications.

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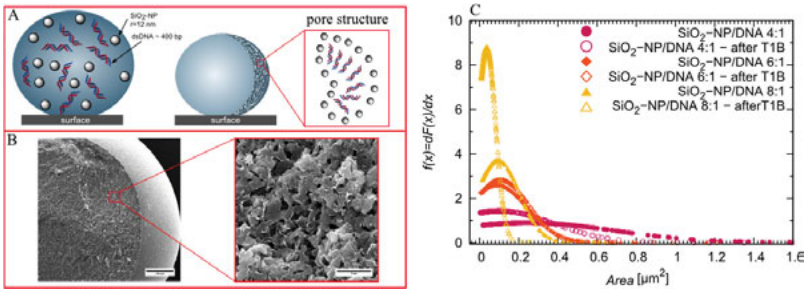

Figure 1. A graphical illustration of the evaporation process of SiO_2-NP and DNA dispersions on superhydrophobic surfaces and pore formation due to separation of SiO_2-NP and DNA. **B** SEM images of a SiO_2-NP/DNA supraparticle and its pore structure. **C** Size distribution function of the pore structure before and after pyrolysis of DNA.

STRUCTURE AND DYNAMICS OF POLYELECTROLYTE COMPLEXES WITH OPPOSITELY CHARGED MICROEMULSION DROPLETS

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By mixing polyelectrolytes (PE) with oppositely charged colloids one gains control of the structural and rheological properties of the system. In most applications, micelles are used as carriers for drug molecules, pollutants, reactants and similar substances that otherwise couldn't be dispersed in the solvent. It is therefore of great importance to investigate the behavior of 'loaded carriers', such as microemulsion droplets, as it can be different to that of normal (empty) micelles.

For this reason we studied the interactions of positively charged O/W microemulsion (ME) droplets that already contain a substantial load of solubilized molecules with negatively charged polyelectrolytes. With small-angle neutron scattering (SANS) it was possible to characterize the formed complexes in terms of size, shape and composition.

The interconnected nature of the droplet aggregates leads to changes in dynamics which was studied using pulsed field gradient NMR (PFGNMR), neutron spin-echo (NSE) and fluorescence correlation spectroscopy (FCS). This way, it was possible to investigate the dynamical behavior of free microemulsion droplets as well as of droplets bound in complexes, information that gives detailed insights into the dynamic aspect of such mixed colloidal systems.

These experiments together give a comprehensive picture of the formed complexes and allow for a detailed understanding of the interactions between charged microemulsion droplets and polyelectrolytes. The ME – PE aggregates serve as a model system for complexes with a high solubilization capacity that could find potential applications in formulations which contain a large amount of oil or hydrophobic agents with tailor-made viscosity and internal mobility, both required for optimized delivery. Thereby these mixtures open up the way for tailor-made formulation with a much higher loading capacity than normal surfactant/polymer complexes.

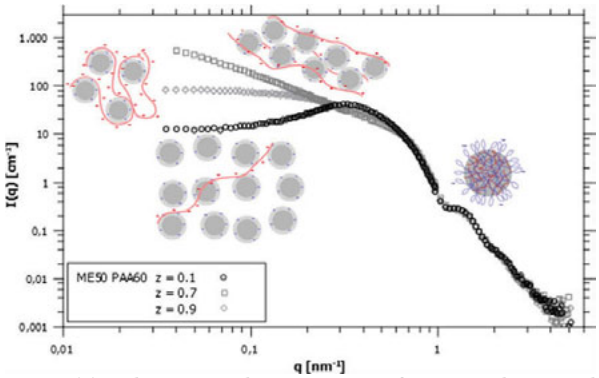

Figure 1. SANS curves I(q) and corresponding structures of microemulsion – polyacrylate complexes for three different charge ratios z = [-]/([+]+[-]).

ONLINE OPTICAL IMAGING OF NANO-SIZED OBJECTS WITHIN POLYMER/PARTICLE MIXTURES DURING FILM THINNING

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We present a new approach to visualize by conventional (interference-enhanced) optical reflection microscopy [1] the location of individual nano-size objects (e.g., nano particles) immersed in thin films. Although the immersed objects are much smaller than the optical resolution limit, their position can be visualized optically through their distortion of the film/air interface. Optimum imaging is thus possible when the film thickness is in the range of the size of the objects (see Fig.1).

With this method we study particle-particle and polymer-particle interactions in ultrathin films of polymers [2-4] containing platinum nano particles with diameters of about 100nm. We prepare the films by consecutive spin casting [5] of platinum nanoparticles from aqueous solution followed by casting PMMA from a PMMA/toluene solution. Real time optical imaging reveals the position of the nanoparticles, their interactions (e.g., lateral movement), the film surface morphology, and the lateral thickness variation of the film. The optical imaging of deposited structures is complemented by AFM.

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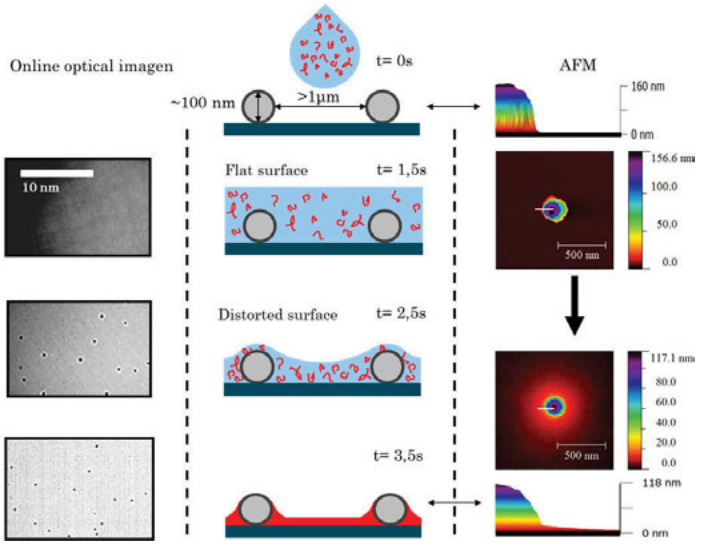

Figure 1. Direct observations of nano objects in consecutive particle-polymer deposition.

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Radius of gyration	5 nm to 5 µm*
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Detectors	Two high sensitive APDs, QE 65%, dark count < 250 count/s
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Laser power	Wide range of choices: 20 to 500 mW
Laser control	Fully automated active Laser intensity optimization
Detection	Single mode fiber detection system with integrated collimation optics
Sample celles	Fits 5 and 10 mm diameter cylindrical cells (min sample volume 50 µl)
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SESSION 5

Microgels

SYNTHESIS AND CHARACTERIZATION OF MULTI-THERMORESPONSIVE HOLLOW MICROGELS

Monia Brugnoni[1], Andrea Scotti[1], Arjan P.H. Gelissen[1], Andreas M. Stadler[2], Aurel Radulescu[3] and Walter Richtering[1]

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Hollow doubly thermoresponsive microgels built up of two spatially separated polymeric shells reveal promising properties for applications as novel carrier systems [1]. The multi-step synthesis originates from the generation of surface modified silica nanoparticles serving as sacrificial cores onto which a first inner and then a second outer polymeric shells were subsequently polymerized. The corresponding hollow microgels were obtained by basic core dissolution [2]. Distinct volume phase transition temperatures (VPTTs) of the two networks lead to an advanced responsiveness which enables to separately control the interactions between both the microgel and its surrounding and the microgel and possible guest species inside the cavity. This makes these microgels interesting as potential thermoresponsive nanocapsules. Here, we present core-double-shell microgels and the corresponding hollow spheres made of an inner poly(*N*-isopropylmethacryl-amide) (pNIPMAM) and an outer poly(*N*-isopropylacrylamide) (pNIPAM) shell. The distinct VPTTs of 44 °C for pNIPMAM and 34 °C for pNIPAM lead to doubly temperature sensitive microgels. The shell thicknesses and permeabilities are of great importance regarding the stability and structure of the hollow microgels. The changes in size and structure have been investigated by dynamic light scattering (Fig. *left*) and small-angle neutron scattering showing a strong interplay of the distinct shells. Cryogenic transmission electron microscopy (Cryo-TEM) was applied to determine the hollowness of the microgels (Fig. *right*). Especially interesting effects on the relative polymer volume fraction as well as the cavity of the microgels were observed at the temperature range between the two VPTTs, meaning the state with a collapsed outer shell and a swollen inner shell. We observed a strong compenetration of the shells at their peripheries in the presence of the stiff silica core. The corresponding hollow spheres show conservation of the cavity at all swelling degrees. Temperature induced changes in the polymeric network densities combined with persistent cavities lead to required properties for a controlled uptake, storage and release of guests. [3]

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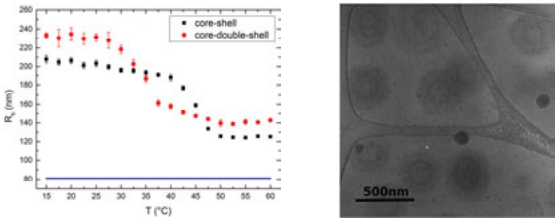

Figure. *Left:* Thermoresponsiveness of silica-core pNIPMAM-shell and silica-core pNIPMAM-shell pNIPAM-shell microgels. *Right:* Cryo-TEM image of hollow double-shell microgels 50 °C.

SILVER NANOPARTICLES FABRICATED N-ISOPROPYLMETHACRYLAMIDE BASED HYBRID MICROGELS CATALYST FOR REDUCTION OF 2-NITROANILINE

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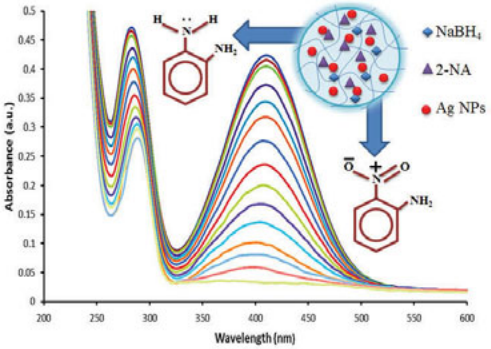
Silver nanoparticles incorporated smart polymer microgels are widely used in catalysis due to their easy synthesis, their efficient removal from reaction mixture after completion of reaction and triggered controlled activity. Most researchers have reported the use of N-isopropylacrylamide based hybrid microgels in catalysis for reduction of nitroarenes and toxic dyes [1-3]. Here, we reported the synthesis of silver nanoparticles fabricated N-isopropylmethacrylamide based hybrid microgels for rapid degradation of 2-nitroaniline (2-NA).



We prepared Ag NPs-Poly(N-isopropylmethacrylamide-acrylic acid) [Ag-p-(NIPMAM-AAc)] hybrid microgels by precipitation polymerization [4] and chemical reduction method [5]. Pure and hybrid microgels were characterized by TEM, DLS, UV-Visible and FTIR spectroscopy. It was observed by TEM analysis that Ag NPs were uniformly distributed inside the microgels sieves and their average diameter was found to be 20±5 nm.

The catalytic activity of Ag-p(NIPMAM-AAc) hybrid microgels was investigated by degrading 2-NA into 2-aminoaniline (2-AA) using sodium borohydride as reducing agent. Pseudo first order kinetic model was found to be fitted for catalytic reduction of 2-NA. The observed apparent rate constant for degradation of 2-NA into 2-AA in the presence of hybrid microgels catalyst at T ≈ 14 ºC was 0.278 min^{-1}. This high value of apparent rate constant indicates the efficiency of our synthesized catalyst for reduction of 2-NA. Reduction reaction was also carried out under different conditions to find the mechanism of catalysis. It was observed that 2-NA reduction reaction follows the Langmuir Hinshelwood mechanism.

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MAPPING THE HETEROGENEOUS MODULUS OF MICROGELS ADSORBED TO AN INTERFACE – COMPARING CORE-SHELL AND HOLLOW MICROGELS

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Microgels exhibit special properties. They are highly interfacial active, not only to liquid/air or liquid/liquid interfaces, but also to solid interfaces. Compared to solid colloidal particles, microgels show remarkable effects, such as deformation upon adsorption and increased adsorption dynamics [1]. Silica core – PNIPAM (poly(*N*-isopropylacrylamide)) shell microgels combine the unique temperature-responsive behavior of PNIPAM and the rigidity of silica. Dissolution of the core leads to hollow microgels [2]. Investigations of such core-shell and hollow microgels at the solid/liquid interface are of great importance to form a basis for the development of advanced polymeric coatings.

We studied the influence of the microgel architecture on their behavior at a solid interface. In particular, we determined the elastic modulus of core-shell and hollow microgels by atomic force microscopy at the solid/liquid interface. The initial thermo-sensitivity is preserved, indicated by the increase of the E-modulus by one order of magnitude upon heating above the volume phase transition temperature of PNIPAM ($T = 32$ °C). Young's modulus maps, resolved on a nanoscale, show that the elasticity is not only a function of the temperature, but also of the radial position across a microgel. The difference in elastic modulus of the periphery compared to the one in the center of the microgel is more pronounced for the core-shell microgels [3].

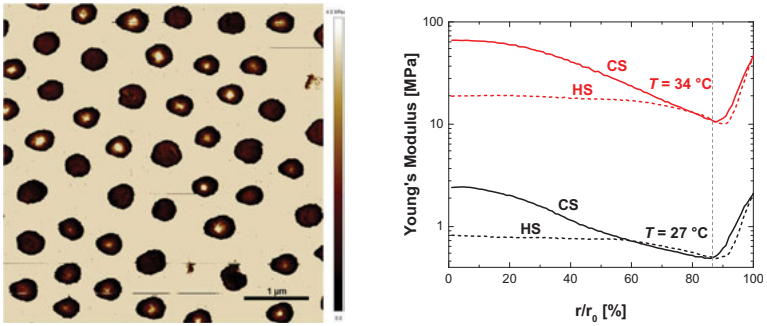

Figure 1. left: Young's modulus image of rehydrated core-shell (CS) and hollow (HS) microgels on a solid substrate at $T = 27$ °C. right: Young's modulus along the normalized radial position of CS and HS microgels on a solid substrate in dependence of their swelling state.

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CORE-SHELL MICROGELS WITH LINEAR THERMO-RESPONSE AS SMART SURFACE COATING

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A gel is a dispersed system, which consists of at least two different components: a solid or flexible network and a fluid. If the fluid is water, the gel is called a hydrogel. Microgels are gels smaller than 10 µm and can be used in a wide range of applications like drug delivery and smart surface coatings [1]. Microgels consisting of acrylamides like *N*-isopropylmethacrylamide (NIPMAM) or *N*-n-propylacrylamide (NNPAM) as network component, show a volume phase transition (VPT) at a certain temperature, the volume phase transition temperature (VPTT). At this point, a change of temperature leads to abrupt reversible changes in size. The VPTT is specific for each monomer.

To use microgels in sensors or for nanoactuators[2] the thermoresponse has to be precise and well known. That is why we investigated microgels with a complex architecture containing NIPMAM and NNPAM (Figure 1b). These particles show a linear thermoresponse between the two VPTTs of NNPAM (22 °C) and NIPMAM (43 °C) (Figure 1a) [2]. Furthermore, we coated surfaces with these microgels. Such surfaces show the same linear thermoresponse in size as the microgels in solution. Furthermore, the properties of the coatings (like layer thickness and phase behavior) can be adjusted by selecting specific synthesis conditions.

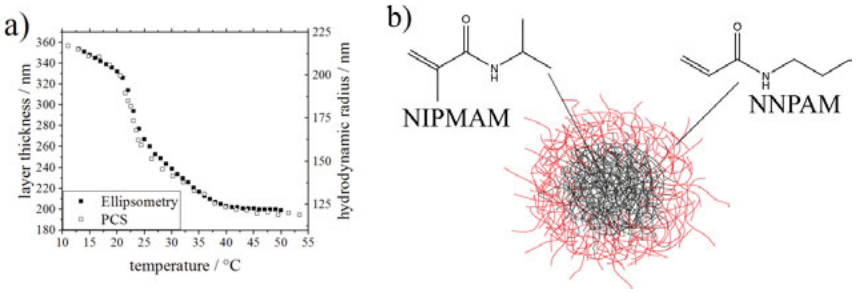

Figure 1. a) Hydrodynamic radius of microgels as well as the layer thickness of a microgel coating as a function of the temperature b) schematic drawing of the microgel architecture with NIPMAM in the core and NNPAM in the shell.

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INVESTIGATION OF THERMO-RESPONSIVE MICROGELS AT FLAT LIQUID-LIQUID INTERFACES: CONNECTION BETWEEN MICROGEL SOFTNESS AND MONOLAYER PROPERTIES

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Microgels are 3D, cross-linked polymer networks, typically spherically shaped and in the size range of 50 nm to 10 µm. The network is swollen in a good solvent and adjusts its dimensions, density and related properties according to the environmental conditions. Microgels are highly interfacial active and can be employed as emulsion stabilizers. Their usage bears a significant advantage, the stimuli-responsiveness of the microgels leads to stimuli-responsive emulsions. For example, Monteux *et al.* have shown that *N*-isopropylacrylamide (NiPAM) based microgel-stabilized emulsions have a lower stability when heated to above 40 °C, resulting in phase separation [1].
The special properties of microgels as emulsifiers are far from being fully understood. The aim of this study is to elucidate the connection between the microgels temperature-dependent swelling state (e.g. softness) and monolayer properties at liquid-liquid interfaces. Thus, thermo-responsive model systems with equal cross-linker densities were synthesized from NiPAM and *N,N*-Diethylacrylamide (DEAAM); the incorporation of DEAAM leads to a reduction of the volume phase transition temperature of the microgels. Langmuir compression isotherms were recorded at different temperatures. In accordance with literature two-staged progresses are obtained in swollen state [2]. In contrast, collapsed microgels show only a one-staged progress (Figure 1 a), similar to rigid particles at liquid-liquid interfaces [3]. Freeze-fractured shadow-casting (FreSCa) cryo-SEM images were recorded (Figure 1 b). The images give us information about protrusion height, size and morphology of the microgels as a function of the swelling state. Further, Interfacial rheology is used to determine the viscoelastic properties of the monolayers at different temperatures [4].

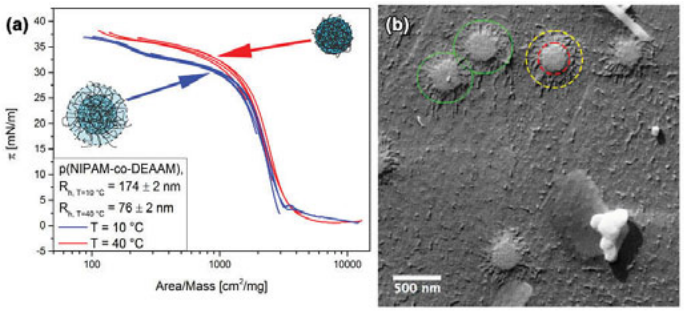

Figure 1. a) Compression isotherms of soft (blue lines, T = 10 °C) and rigid (red lines, T = 40 °C) p(NIPAM-*co*-DEAAM) microgels. **b)** FreSCa cryo-SEM image. The sample was prepared at 10 °C. Yellow dashed circles: Fuzzy corona. Red dashed circles: highly cross-linked core. Green circles: overlapping coronae of two microgels.

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POSTER SESSION 1

A – K

LARGE-SCALE PREPARATION OF BIODEGRADABLE NANOCARRIERS

Mohammad Shafee Alkanawati, Heloise Therien-Aubin, Frederik R. Wurm, Katharina Landfester

Max Planck Institute for Polymer Research, Mainz, Germany

Smart nanocarriers are used in the transport and controlled delivery of payloads [1]. Fundamental studies and practical uses depend on our ability to synthesize large quantities of these nanomaterials in a reproducible and controlled manner. This work was dedicated to establishing reliable protocols for the large-scale and consistent preparation of biodegradable nanocarriers. A microfluidizer was used to prepare of large-scale quantities of miniemulsions (up to several liters), leading to the formation of nanocapsules with a narrow and uniform size distribution. This process was used to prepare a variety of nanocapsules made of polysaccharides, proteins or lignin using a crosslinking reaction at the droplet interface [2,3] in the miniemulsion. In the future, this processing method will be used to encapsulate biologically-relevant payloads for in vivo applications.

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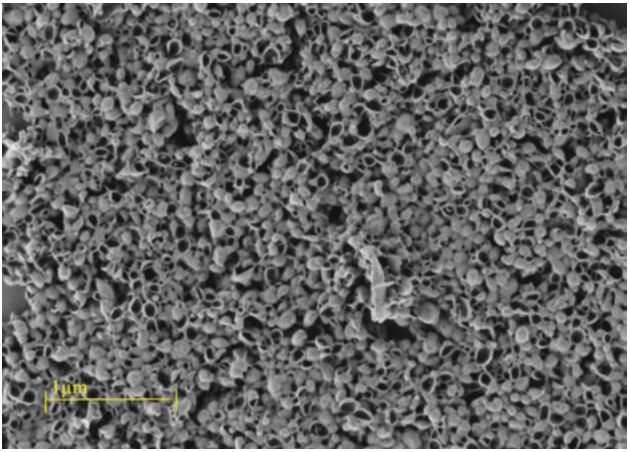

Figure 1. Scanning electron microscopy image of nanocapsules made of hydroxyethyl starch prepared using a microfluidizer.

MONODISPERSE VESICLES AS TEMPLATES FOR SILICATION

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Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Berlin, Germany

In our department, a vesicle system has been developed where the vesicle size is not governed by thermodynamics, but by the kinetics of the growth process[1-3]. Due to this kinetic control, monodisperse (PDI 5-10%) vesicles can be formed with a radius ranging from 30 to 100 nm, controlled by the concentration of triblock-co-polymer. These structures can be retained over a period of weeks.

The positive features of this vesicle system, monodispersity and adjustable, relatively small size compared to other vesicular structures, render it an ideal template for other, more rigid structures such as nanocapsules. Therefore, in this work an approach is presented to form hollow silica particles based on such vesicles.

These particles have been characterized via static and dynamic light scattering, small angle neutron scattering (SANS), and transmission electron microscopy (TEM) imaging. Results show that silication is taking place at the surface of the vesicles, during which the vesicle size and monodispersity is retained.

Such hollow silica structures are candidates for drug encapsulation and delayed release for crop science. Accordingly as a next step for our work investigations of the release kinetics of active agents from such capsules are planned.

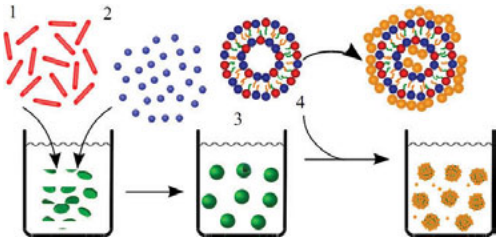

Figure 1. Synthesis scheme: Tetradecyldimethylamine oxide (TDMAO) (1) and lithium perfluorooctane sulfonate (LiPFOS) (2) are mixed and form small disklike micelles that grow, bend and close at a defined point to form vesicles (3). Addition of a silicate source like tetramethyl orthosilicate (TMOS) (4) forms dense silica nanoparticles at the surface of the vesicle.

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HIGHLY STABLE SILVER NANOPARTICLES GENERATED IN RESPONSIVE MULTI-MICROGELS FOR EFFICIENT CATALYTIC REDUCTION

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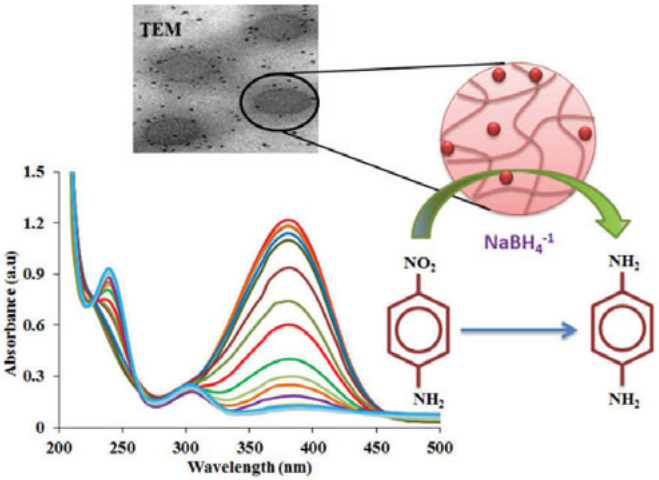
Hybrid polymer microgels combine the properties of both organic and inorganic materials and are used as fascinating catalysts in recent research for reduction of toxic compounds. In this work, we prepared Poly (N-isopropylacrylamide-hydroxy ethyl methacrylate-acrylic acid) [p(NIPAM-HEMA-AAc)] microgels and used them as micro-reactors for fabrication of silver nanoparticles. Polymer microgels suspension was prepared by emulsion polymerization method [1,2] while Ag NPs were fabricated inside inside the microgels by in-situ chemical reduction of $AgNO_3$ salt [3]. Pure and hybrid microgel samples were analyzed by UV-Visible spectroscopy, Fourior transform infrared spectroscopy, Dynamic light scattering and Transmission electron microscopy. TEM analysis shows the monodispersity of Ag NPs inside the microgels network. 4-Nitroaniline was reduced to 4-Aminoaniline using $NaBH_4$ as reducing agent in the presence of Ag-p(NIPAM-HEMA-AAc) catalyst. Effect of $NaBH_4$, 4-NA and catalyst concentration on the rate of reduction of 4-NA was studied by monitoring catalytic reduction by UV-Visible spectroscopy as shown in Figure.



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GRADIENTIAL PLASMONIC NANOCAVITY ARRAY ON THE MACROSCOPIC SCALE AS SCREENABLE AND TUNABLE METASURFACE

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We study the optical properties of a metal-film-coupled gold nanoparticle system, separated by a Poly(N-isopropylacrylamide) (PNIPAM) layer, as up-scalable and cost-efficient platform for screening of plasmonic properties. The electromagnetic interaction of Au nanoparticles and a gold film is achieved using a lithography free fabrication method. As we have shown in earlier work, a monolayer of gold-core/PNIPAM-shell particles featuring a gradient in core-sizes, results in lateral variation of plasmonic properties [1]. Coverage with a 35 nm gold layer induces plasmonic coupling between cores and film. Interestingly, the responsive behavior of the hydrogel is still maintained under the film, resulting in switchable optical properties. We study the tunability of the metasurface by reversible swelling of PNIPAM for various particle sizes, which reveals a reversible plasmonic shift of up to 40 nm. With this adjustable and up-scalable method we produce a platform for systematic screening of fundamental optical effects and application in surface plasmon resonance (SPR) sensing [2].

[1] M.B. Müller *et al.*, ACS Nano, 2014, 8, 9410
[2] The authors acknowledge funding from ERC Starting Grant METAMECH-306686

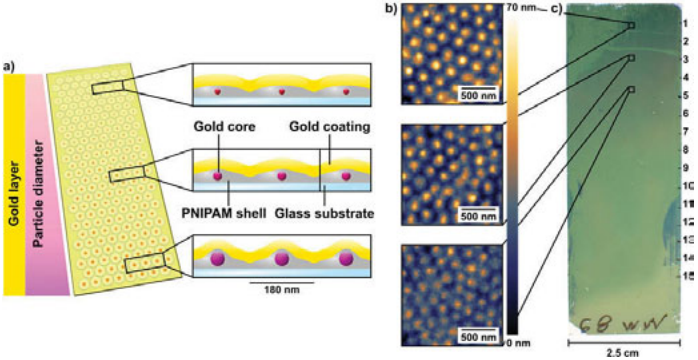

Figure 1. Concept of the screenable and tunable metasurface. a) A monolayer of Au@PNIPAM particles on a microscope slide is covered with a layer of gold. The core diameter is dependent on the lateral position while the covering gold layer thickness remains constant. b) AFM height images of three different positions of the coated substrate. The cores get more pronounced with increasing diameter. c) Photography of the macroscopic substrate with numbered spots from UV/vis-characterization.

THE PREPARATION OF HIERARCHICALLY STRUCTURED MICROSIEVES FOR AIR FILTRATION

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The particle-loaded air, like from traffic or industry, and natural sources, such as pollen and bacteria, strain people and disturb industrial processes [1]. One possibility to minimize these particles is air filtration [1]. Until now mainly fiber filters are used [2]. However, these filters are usually not regenerable and cause high energy costs because of a high pressure drop across the filter [2]. To overcome these disadvantages, microsieves can be used. Microsieves have a uniform pore size and a membrane thickness which is lower than their pore diameter [3]. Moreover, they do not have a branched and complex pore system [3]. This results in a low flow resistance and, additionally, in the possibility for an easy and complete regeneration [3,4].

Microsieves first were outlined by van Rijn with the technique of photolithography [3]. One other technique to produce microsieves is the float-casting process. With this technique, mixtures of hydrophobic colloidal particles and a hydrophobic liquid form wetting layers on a water surface (even though the liquid is non-wetting – therefore, the process is also called particle-assisted wetting) [5]. To form microsieves the hydrophobic liquid is a mixture of monomer, initiator and solvent. This mixture is polymerized and the particles are removed. The sieve is formed at the interface of water and air and afterwards transferred to a support. The supporting structure can also be a microsieve itself but with larger pore sizes. This approach made it possible to form a hierarchically structured microsieve from three differently sized sieves (see Figure 1). The large-pored microsieve has a pore diameter of about 53 µm, the medium-pored of about 6 µm and the fine-pored sieve, which is the actual filter membrane, of about 325 nm.

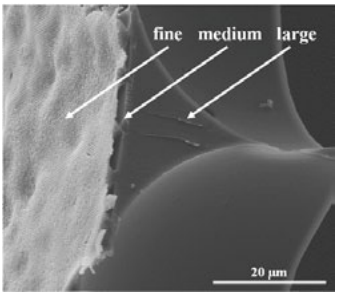

Figure 1. SEM image of the cross section of the hierarchically structured microsieve.

Mass flow measurements with water show that these hierarchically microsieves have a much higher permeability coefficient than common cellulose acetate and polymeric netlike membranes with comparable pore sizes. It is assumed that this high permeability also takes effect in air filtration. This claim should be examined with air filtration tests. So far, simulations with the software GeoDict® support this conjecture [6].

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COLLOIDAL PROPERTIES OF CHITOSAN/EXPANDED PERLITE COMPOSITES IN AQUEOUS AND NON-AQUEOUS MEDIA

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Perlite is a glassy volcanic rock which consists mainly of fused sodium, potassium, aluminum silicate (greater than 70%) and 3-5% water. When it is heated at temperatures in the range of 850-1100 ºC, it expands 4–35 times of its original volume and is called 'expanded perlite'. Due to its excellent surface chemical properties, expanded perlite has been intensively studied and widely used in many industrial products and process [1]. Chitosan [Poly (β-(1-4)-2-amino-2-deoxy-d-glucan] is N-deacetylated derivative of chitin, extracted from the shells of crustaceans like crabs and shrimps, which is a very interesting material due to its characteristics such as biodegradability, chemical inertness, biocompatibility, high mechanical strength, and low cost.

Electrokinetic measurements are one of the effective tools to determine the surface properties of colloidal particles and interactions between different particles. Zeta potential (ζ) is a physical property and represent the surface charge of particles in a dispersion. It has a great importance in many fields such as food, medicine and materials science [2]. The surface properties of expanded perlite can be altered by modification process, changing the pH of the solution, and adding the some molecules.

In this study, a series of chitosan/expanded perlite (CS/EP) composites with different chitosan mass fractions (10%, 20% and 50%) were chemically synthesized. Characterizations of the composites were carried out by FTIR, XRD, TGA and SEM-EDS techniques. Electrokinetic properties of the composites in aqueous and non-aqueous (silicone oil) media were examined by zeta-potential measurements as functions of time, pH, various electrolytes (NaCl, $BaCl_2$, $AlCl_3$, Na_2SO_4 and MgCl2), surfactants (CTAB, SDS and Triton-X) and temperature. It was observed that the ζ-potential of EP shifted from negative region to positive region after the modification process with chitosan. It can be attributed to the strong interactions between negatively charged EP and polycationic CS chains. The most effective electrolyte and surfactant on the ζ-potential was determined to be trivalent ($AlCl_3$) electrolyte and SDS (anionic surfactant) [3].

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REDOX ACTIVE SOLUTION/SUSPENSION FOR FLOW BATTERIES

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Due to the high modularity, electrochemical energy storage techniques using batteries have received great success for transportable applications, and are promising for large-scale stationary energy storage in the future. In contrast to traditional lead acid and lithium-ion batteries, redox flow batteries can easily be designed to meet the needs of a broad range of applications with low self-discharge, long life time and low cost. Particularly, redox flow batteries have merits of decoupled energy storage and power generation capability. Electrolyte chemistry is a key consideration for the performance enhancement [1,2]. Among various redox couples for flow batteries, much attention has been focused on the vanadium redox chemistry with redox couples of V^{2+}/V^{3+} and VO^{2+}/VO_2^{+} [3]. Compared to the limited number of metal ions suitable for flow batteries [4], a wide range of organic molecules and polymers for flow batteries can be obtained by the diversity of synthetic organic chemistry [5].

Herein, we report new electrolytes for redox flow batteries with (i) polymer-based, (ii) organic functional groups grafted/modified materials as energy storage media. The flow battery was constructed with two graphite felt electrodes and a piece of ion exchange membrane sandwiched between graphite felts and two copper current collectors. The structure and electrochemical properties of the synthesized materials were analyzed.

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DROPLET IMPACT ON SOFT VISCOELASTIC SURFACES

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In this work, we experimentally investigated the impact of water droplets onto soft viscoelastic surfaces with a wide range of impact velocities. Several impact phenomena, which depend on the dynamic interaction between the droplets and viscoelastic surfaces, have been identified and analyzed. At low Weber number, the air film formed at the liquid-solid interface causes impinging droplets to rebound when the impact velocity is between a lower and an upper threshold, beyond which deposition is observed. At intermediate Weber number, this air film leads to the entrapment of an air bubble inside the impinging droplets on soft surfaces, while a bubble entrapment on surface is observed on rigid surfaces. At high Weber number, the wetting ridge formed near the contact line hinders droplet recoiling and the partial rebound is only observed on the most rigid surface at $We \gtrsim 92$. In general, rebounding droplets show characteristics similar to elastic drop rebounding on superhydrophobic surfaces and the impact process is independent on surface stiffness. Further, surface stiffness does not influence drop spreading after impact – as the surfaces behave like rigid surfaces – but it does affect retraction of depositing droplets. We also show that the post-impact droplet oscillation on soft viscoelastic surfaces is influenced by their dynamic wettability. By analogy of sessile drop oscillation with a damped harmonic oscillation, we could conclude that surface stiffness affects the damping coefficient, while the liquid surface tension determines the spring constant. These findings indicate that the dynamic response of viscoelastic surface to drop impact is the key to understand the complex impact dynamics of liquid drops on soft surfaces.

SPECTROSCOPIC ENDOSCOPY WITH SILICA NANOPARTICLE

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Proton transfer reactions are some of the most fundamental processes in chemistry. The photoacid hydroxypyrene and its derivatives undergo an increase of acidity upon electronic excitation[1], which leads to a release of proton to the solvent (excited-state proton transfer). In the past, we modified the prototypic photoacid 8-Hydroxy- pyrene-1,3,6-trisulfonic acid (HPTS, pyranine) and synthesized derivatives which carry three identical substituents at the 1, 3, and 6 position [2], there recently, one of the three substituents was selectively modified to enable further derivatization for analytical and spectroscopic studies [3].

Currently we are adapting the synthetic pathway, to functionalize the position 6 or 8 with (3-Amino-propyl)triethoxysilane (APTES). These compounds allow for immobilization on a glass surface and subsequently observation by total internal reflection fluorescence (TIRF) microscopy. In addition, they are suitable for the functionalization of silica-based nanoparticles. The functionalized nanoparticles can be used for *in-vivo* ratiometric pH measurements or to retrieve information about the environment within the nanoparticle core, based on the well-studied solvatochromic behaviour of the recently described photoacid [4].

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SELF MARGINATION IN SICKLE CELL ANEMIA BLOOD FLOW

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The origin of sickle cell disease (SCD) lies in a recessive point mutation in the gene that encodes for the hemoglobin molecule of its carrier called HbS. Although HbS affinity for oxygen is not much different from its healthy homologe HbA, when it releases its oxygen, the HbS polymerizes into long rope like fibers that give to the cells it chacarteristic sickled shape. This shape was believed in the sixties to be responsible of the characteristic vaso-occlusion phenomena known for sickle cell disease since the more rigid cells will have difficulty to pass in the microcirculation like normal red blood cells do.

However, in the last three decades, SCD pathobiology has been proven to be more complex to explain general vaso-occlusion than the logical and recently, simulations are shown that the rigid, crescent-shaped red blood cells that are the hallmark of sickle cell disease don't cause the red cell blockages on their own [1].

Then, SCD is still a perplexing disease and almost no consequent cellular scale approaches of the study of capillary obstruction dynamics have been proposed in microflow, although the problem of obstruction is in essence a circulatory one.

Knowing that stiffer cells like white blood cells [2] or platelets migrate toward the vessel walls in blood flow through a process called margination, that depends mainly on local hematocrit, flow rate, red blood cell aggregation, deformability of different cell components [3], but that also could depend on size and shape [4,5] in this research we investigate experimentally the collective behavior of oxygenated arteriol-like sickle red blood cells and their margination process on flow through cylindrical channels with inner diameters comparable in size to a human arteriol. The cells are labeling accordingly to their density, that is associated mainly to their rigidity and flash under different flow conditions on pressure and solutions, including solutions inducing and non-inducing red blood cell aggregation.

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GETTING THE INSIDE VIEW OF COLLOIDS WITH A SAXS/WAXS INSTRUMENT

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Small Angle X-ray Scattering (SAXS) is proving to be a powerful technique for getting information related to the structure of nano-materials. By recording the x-ray scattering pattern, one obtains reciprocal space information that can be transformed or modeled to extract real-space information from the sample [1]. Information such as nanoparticle size, size-distribution and surface to volume ratio can be obtained in the range from 1 nm to beyond 100 nm. This is related to form factor of particles. Furthermore, particle interactions in colloids is readily obtained, as known as structure factor.

The method requires little sample preparation, is non-destructive and in contrast to microscopy probes a volume of the sample thus giving a statistically meaningful result. When combined with Wide Angle X-ray Scattering (WAXS) one can also get information on crystalline structure.

A broad range of materials and applications can be addressed by SAXS and WAXS techniques, ranging from soft condensed matter, polymers, bio-materials to nanoparticles, fibers and even structured surfaces which can be measured in the Grazing Incidence (GISAXS) geometry. This paper present results from various material systems including biological solutions, nanoparticles, highlighting how the provided information can be complementary to other analytical methods.

A short review of the considerable progress made in laboratory SAXS/WAXS instrumentation such as high brilliance microsource and advanced detectors will be done. Rapid measurements and high data quality opens the way towards dynamic measurements with parameters like temperature, humidity, flow, DSC as well as high precision structure resolutions on highly diluted and low contrast solutions, that is ideally suited for the study of most demanding colloidal systems.

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MOTH-EYE TEXTURED RESIST TO IMPROVE THE EFFICIENCY OF CIGS SOLAR CELLS

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The transmission of a maximum number of photons to the active layers of solar cells is highly desired. A flat transparent conductor layer is generally applied on copper indium gallium (di-)selenide (CIGS) solar cells; however, when flat this layer causes reflection of light. Thus a texturing of this top layer is desired in order to reduce reflection. Additionally, the texturing might change the angle of the photons through the layers, and thus will allow a longer path length through the CIGS absorber layer.

We, a consortium of Zuyd University of Applied Sciences, TNO, DWI and Kriya Materials BV have coated the top conductor layer of a CIGS solar cell with a UV curable resist incorporating Ti_2O nanoparticles (see Figure 1) [1]. This textured layer increases the efficiency of the solar cell on average by 6.0% compared to a non-textured CIGS solar cell [1,2].

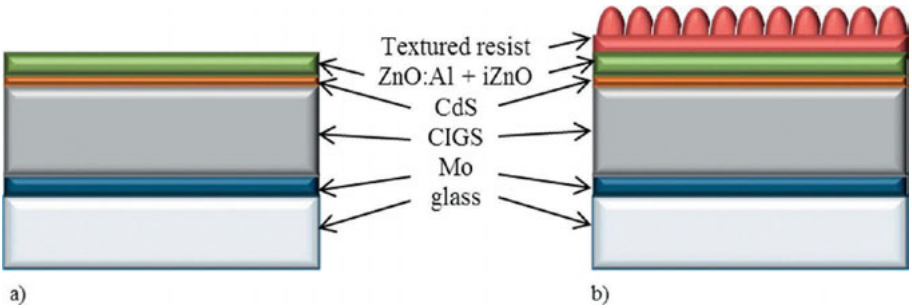

Figure 1. Composition of a CIGS solar cell without (left) and with textured resist (right) [1].

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[2] The authors acknowledge funding from RAAK/SIA in the RAAK Pro project “UV absorberende nanodelen.”

ACTIVE NANOPARTICLES DISPERSION EMBEDDED IN A SOLID POLYMER MATRIX

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We discuss “active nanocomposites” that reversibly change optical properties upon stimulation. We develop them based on current nanocomposite technology using functional nanoparticles that have sufficient mobility to rearrange under specific conditions. The classical scheme “process→ structure→ function” of passive nanocomposites is thus replaced by “stimulus → structural change → functional change”, enabling materials that can adapt to different use cases.

Previous work has shown how liquid nanoparticles dispersions can reversibly agglomerate after stimulation by temperature, ion concentration, electric field strength, surface tension, and other stimuli producing changes in colour, reflectivity and scattering due to plasmonic interactions between densely packed nanoparticles[1,2]. Here, we discuss strategies to bring this functional principle from liquids to solids. We show experimental data on a temperature-sensitive dispersion of stabilized gold nanoparticles in an organic solvent of which submicron droplets were embedded in a polymer matrix. *In situ* small angle X-ray scattering during repetitive cycling between high and low temperatures indicated fully reversible agglomeration. Kinetic studies show that the agglomeration is diffusion-limited. This change of the scattering of the nanoparticles is responsible for the transition of macroscopic properties such as color and haze.

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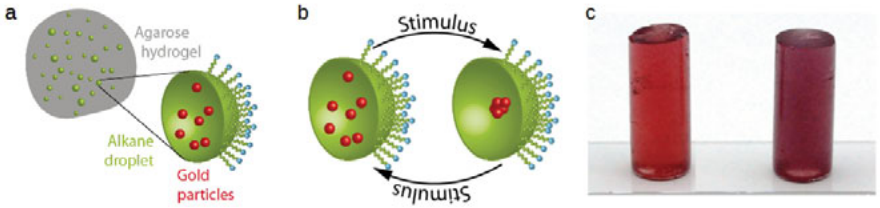

Figure 1. Principle of the Active Nanocomposites: (a) emulsion droplets containing Au nanoparticles are embedded in a polymer matrix, (b) upon stimulation, Au nanoparticles agglomerate (right) or deagglomerate (left), (c) Final result of the solid when it is heated up (left) and cooled down (right).

NOVEL TYPES OF CATIONIC PYRIDINIUM SURFACTANTS: SYNTHESIS, PROPERTIES AND TECHNICAL APPLICATIONS

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Cationic surfactants play an important role for research and industrial applications. In industry they have been used for considerable time as preserving agents, fabric conditioner, corrosion inhibitors, water repellents, antistatic agents and floatation agents [1, 2].

In the present research project, we synthesized a new series of cationic pyridinium gemini-surfactants, linked by a propylene-spacer in γ-position, and their monomeric analogues. We used these cationic surfactants as simple model systems for investigating the effects of the counter ions on the adsorption and aggregation properties of these cationic surfactants. We performed these investigations in order to get a better understanding of the role of the anions.

We systematically determined Krafft-temperatures, micelle formation concentrations (cmc) and several thermodynamic parameters. These data confirmed the assumption, that the counter ions had a large influence on the surface-active properties of these cationic detergents.

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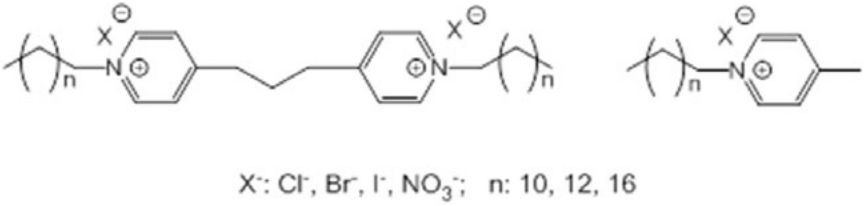

Figure 1. The cationic gemini surfactants (left) and its monomeric analogues (right).

A VERSATILE POLYSTYRENE MICROGEL SYSTEM WHICH FITS YOUR NEEDS

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Colloidal particles are widely used as model systems for studying condensed matter phenomena like the glass transition, nucleation and growth or dynamic heterogeneities close to kinetic arrest lines [1, 2, 3]. These systems are investigated by dynamic or static light scattering, optical microscopy techniques or by Forced Rayleigh Scattering (FRS) [1,4,2,3,5,6]. The main problem in using these techniques is the poor scientific comparability between the different results. Since every technique has different requirements for the preparation of the sample and for the nature of the sample itself, it is difficult to use one system for all techniques. Light scattering studies on typical hard sphere colloid like silica or PMMA require a nearly perfect refractive index match between particles and suspending medium and submicron particle sizes [1,4]. Optical microscopy on the other hand needs less perfect index matching conditions, but particle sizes of the order of 1 micro which in turn require special buoyancy-matching solvent mixtures to avoid sedimentation [2,3,5]. Techniques using an additional dye like fluorescence microscopy or FRS lead to even greater challenges in preparing a comparable system, since the dye molecule may alter the interaction potential of the particle surface [2,3,6]. Another example for the comparability problem are crosslinked polystyrene microgels. Light scattering studies and alike are achievable with particles following a standard synthetic approach, but for the attachment of a dye or to get tracer particles for microscopy it is necessary to switch to a two-step synthetic route [7,8,5]. The resulting core-shell particles may be inhomogeneous and differ in their interactions compared to the standard particles or the host. Therefore many groups focus on one main technique and are forced to make assumptions in order to be able to compare different techniques. This practice is far from an ideal case in which one sample can be used in different techniques without larger alterations of the physical properties of the model particle.

In this work, we present particles which are applicable to vast variety of different techniques without major changes in their physical properties. The fundamental synthesis consists of two main parts. In the first part the primary particles are synthesized via a one-step semi-batch polymerization. In the second part the particles can be modified in a simple two-step procedure without changing the size or the surface potential of the particles. This leads to a model system whose particles can be used e.g. in light scattering, fluorescence microscopy and FRS at the same time by a simple adjustment of the second synthetic part. The particles provide therefore the possibility of comparable results with different techniques. Another advantage of these particles is that properties like the softness of the primary particles can be tuned also in this case via the variation of the crosslinking degree.

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SOFT MICROGEL BUILDING BLOCKS FOR DIRECTED SELF-ASSEMBLY AND SELF-ORGANIZATION

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We will present an aqueous colloidal system consisting of core-shell particles with a solid core and a soft microgel shell bearing functional groups, which allow for triggered responses of microgel assemblies. The hard sphere-like core particles are fluorescently labeled to allow three-dimensional imaging by means of confocal microscopy.

If the microgels are functionalized with charged groups, they be assembled into defined clusters of oppositely charged microgels or be switched from crystalline to amorphous states using pH as a handle to fine tune the assembly.

Furthermore, we will show that the assembly and disassembly of the systems can be coupled to photoacids, pH gradients in time and pH-oscillators.

By introducing more selective functional association motifs, we also show how these particles can be used to study social and narcissistic self-sorting amongst families of microgels with orthogonal recognition motifs.

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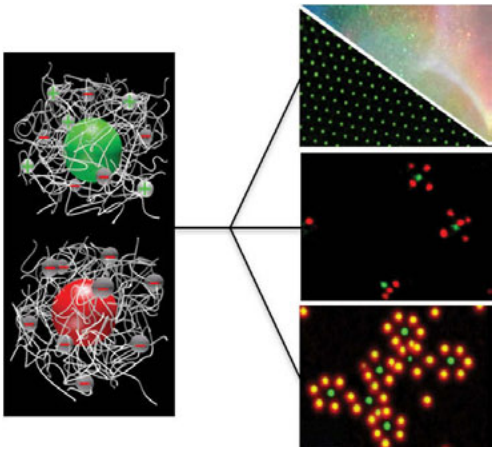

Figure 1. Schematic illustration of the soft microgel building blocks and their possible assemblies into soft colloidal crystal arrays or well defined structures.

HYBRID NANOPARTICLE INKS FOR PRINTED ELECTRONICS

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The accelerating market of printed electronics requires high performance, stable inks that are suitable for large-area, high-throughput, and low-cost production. Inks that contain dispersed metal nanoparticles can satisfy market requirements. We study the role of the stabilizing ligands on different properties of electronic inks such as shelf life, particle agglomeration during printing, and the electrical properties of printed patterns. New colloidal concepts are used to improve the inks. For example, existing metal nanoparticle-based inks require a sintering process after deposition to remove the stabilizing ligands and to provide conductive patterns [1]. Standard thermal sintering limits substrate compatibility and causes volume shrinkage that can rupture the material. We introduced ligands that enable softer sintering processes or lead to sinter-free inks. A second challenge of the field is the reduction in characteristic feature sizes. Currently possible minimal line width limits applications of printed electronics for example in the fabrication of thin grids for transparent electrodes or highly integrated patterns for microelectronics [2]. We show that particle-particle interaction can be exploited to enhance the deposition process and increase the printing resolution while ensuring percolation of the printed patterns.

We will discuss two ink concepts based on hybrid nanoparticles: sintering-free, conductive inks and self-organizing inks. Sintering-free inks exploit conductive polymers as nanoparticle ligands [3]. They provide good colloidal stability at high particle loading. We demonstrate that metal content and solvent composition can be tuned to formulate inks that are suitable for inkjet printing. The conductive polymer ligands bridge the gaps between the inorganic cores during drying and establish electrical contact. Electrical characterization confirms the ohmic conductivity of the printed lines without any further treatment. Self-organizing inks contain interacting particles, for example ultrathin gold nanowires (AuNWs) that exhibit unusual colloidal behavior that is the basis of a new printing process. The oleylamine-capped AuNWs that we use here have diameters below 2 nm and lengths of several micrometers. Ligand-ligand and ligand-solvent interactions govern their self-assembly into hexagonal arrangements (“bundles”) [4]. We use a silicone elastomer stamp to template their self-assembly and form transparent and conductive grids. The ink fills the cavities of the stamp that confines the AuNWs; during solvent evaporation, the wires form bundles and ensure percolation [5]. A soft-sintering plasma process [6] coarsens the grids until they exhibit high optical transmittance (> 92 %) at low sheet resistance (106-168 Ω/sq). Electrodes prepared by this method have been successfully employed as capacitive and resistive touch sensors.

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HETEROMERIC MAGNETITE-GOLD NANOPARTICLES

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Magnetite nanoparticles have a broad application profile due to their magnetic properties. Their size-controlled synthesis in organic phase under high-temperature conditions was shown by Sun and Zeng [1]. The use of hydrophobically modified poly(isobutylene-alt-maleic anhydride) (PMA) as a coating agent enables an applicable method to transfer the as-synthesized nanoparticles into the aqueous phase. By linking them with other water-dispersed nanoparticles, e.g., gold nanoparticles, it becomes possible to combine the optical characteristics of colloidal gold to the magnetic properties of magnetite nanoparticles.

In our system, magnetite nanoparticles with diameter of about 8 nm are synthesized in diphenyl ether and transferred into chloroform. PMA is modified with 1-octylamine by the formation of amides with a degree of substitution of 75%. By choosing different amines, the functionality and hydrophobicity of the polymer can be tuned [2]. The polymer-coated, water-dispersable magnetite nanoparticles are negatively charged. Linking them with positively charged gold nanoparticles leads to heteromeric nanoparticles. A conceivable application of this and similar systems is the use as contrast agent for MRI diagnostics or in cancer therapy [3].

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Figure 1. Phase transfer of magnetite nanoparticles from *n*-hexane to water in presence of modified PMA.

COLLOIDAL ANALYSIS OF PARTICLES EXTRACTED FROM MICROALLOYED STEELS

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Microalloyed steels are widely used in oil and gas industry. These steels provide good mechanical properties combined with good weldability and relatively low production costs. The improvement of the mechanical properties over regular plain carbon steels is due to particles composed of niobium and/or titanium carbonitride with sizes between several hundreds of nanometers down to a few nanometers that are embedded in the steel. The particles strongly influence the microstructure of the steel during the production process depending on their size. Hence, control and optimization of the rolling process needs information on the size distribution, composition and volume fraction of the particles. Today electron microscopy is used to image particles in electron transparent steel samples or on carbon replicas. These area-based methods survey a relatively small number of particles, which may not be representative for the whole sample volume.

We use a colloidal approach based on matrix dissolution to amend microscopy. In this volume-based method, a steel sample with a representative volume is dissolved by chemical dissolution using a chemical etchant or by electrolysis [1]. The iron matrix is removed until a particle dispersion remains. Our goal is to produce suspensions that can be analyzed using colloidal characterization methods such as dynamic light scattering (DLS), Field-Flow-Fractionation (FFF), Analytical Ultracentrifugation (AUC) or Single Particle Mass Spectrometry with Inductively Coupled Plasma (SP-ICP-MS). These methods require stable colloidal solutions with unagglomerated particles. We found, in accordance with earlier studies [2], that silicate networks form during the dissolution of silicon-containing steels that embed the particles and inhibit their characterization. Here, we discuss improved extraction routes that avoid silica formation and their influence on the colloidal stability on the particle suspensions. We evaluate the feasibility of colloidal characterization of the extracted particles.

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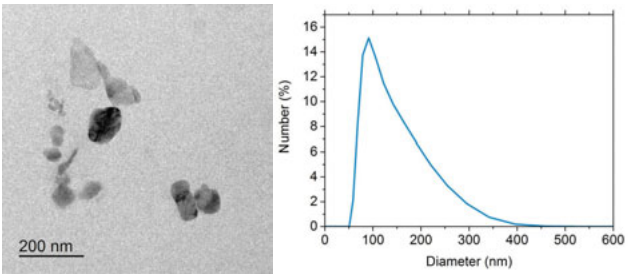

Figure 1. a) TEM micrograph of particles extracted from a microalloyed steel b) number weighted size distribution measured with dynamic light scattering

RHEOLOGICAL CHARACTERIZATION OF WORMLIKE MICELLES BY COMBINING DIFFERENT LIGHT SCATTERING TECHNIQUES

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Viscoelastic surfactants and their rheological properties in solution have been of considerable interest in recent decades. This is mainly due to the formation of entangled networks of wormlike which exhibit striking viscoelastic properties. Because micellar networks are, in contrast to polymer solutions, continuously breaking and reforming again, these surfactant solutions provide ideal model systems for advanced studies of fundamental principles of flow.

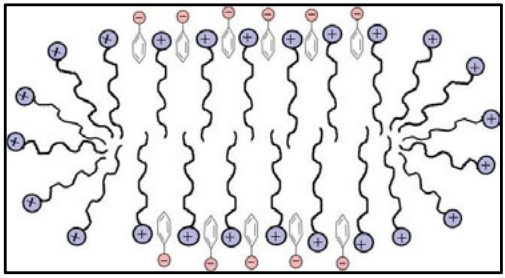

Figure 2 Stabilization of a rodlike micelle by benzoic acid derivate cosurfactants

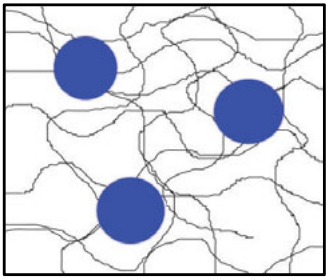

Figure 1: Tracer Particles trapped in entangled micelles

In a series of experiments we investigated different aqueous solutions of Cetylpyridiniumchloride at various Sodiumsalicylate concentrations. Commercially available microrheology software was used to evaluate values for the storage and loss moduli. In these experiments, we added tracer particles to the samples and observed the diffusion process of these particles. Furthermore we studied the autocorrelation function of the quiescent surfactant solutions which allowed further insights into the stress relaxation properties of these solutions. We also determined the zeta potentials for a series of co-surfactant concentrations in order to describe the elastic properties as a function of the ionic strengths and the salt concentration. We finally compared all these measured values with the rheological results obtained in commercial rheometers.

THE BIDIRECTIONAL INFLUENCE OF SEA URCHIN PROTEINS ON CALCIUM CARBONATE MINERALIZATION AT PHYSIOLOGICAL pH

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Biomineralization refers to the study of hybrid biogenic minerals such as shells, skeletons and teeth. The fascinating material properties of biominerals arise due to hierarchical structures and complex morphologies, biologically tailored for specific functions. Calcium carbonate ($CaCO_3$), the most abundant biomineral in Nature, is the major inorganic component in mollusk shells, corals and sea urchins. Studies show that pre-nucleation clusters play important roles during the nucleation of $CaCO_3$.[1, 2] Subsequently formed amorphous intermediates exhibit certain pre-structures, which relate to different crystalline forms, and appear to play a key role in polymorph selection.[2, 3] Recently, Evans has highlighted the value of the non-classical nucleation pathway for understanding protein-mineral interactions during biomineralization.[4] Although the pH value significantly influences $CaCO_3$ nucleation during mineral precipitation, the assessment of physiological i.e. near-neutral pH has not yet been explored using a quantitative titration assay, [1, 3] complemented by further in situ techniques. Given that the pH of seawater is between 7.5 and 8.4, an understanding of $CaCO_3$ nucleation at such pH levels will provide insights into physiological biomineralization and also its relation to environmental factors such as pollution and climate change. In this study, experimental challenges due to CO_2 out-diffusion at physiological pH levels (pH 8-9) are addressed and resolved in order to implement a quantitative titration assay. This methodology provides quantitative information on the early stages of calcium carbonate precipitation. As the pH level decreases, the stability of pre-nucleation clusters decreases and the time required for nucleation increases. The data also strongly suggests that although calcium bicarbonate ion association is weak, bicarbonate binding plays a distinct role during nucleation of the initial phases in this pH regime.

The titration methodology further shows the effects of recombinant proteins on mineralization at physiological conditions, which are not evident at higher pH levels, and shed light on the biochemical mechanisms regulating crystal nucleation and growth. Bioinformatics studies indicate that several proteins involved in biomineralization contain C-type lectin-like domains (CTLDs).[5, 6] This implicates that CTLDs play an essential role in biomineralization. We show that three C-type lectin-like proteins from sea urchin do not significantly affect the stability of pre-nucleation clusters, however inhibit the nucleation of $CaCO_3$ at pH 8.5. Circular dichroism and Small Angle X-ray scattering analyses reveal that these proteins aggregate or change conformation during mineral formation. In all, our work suggests that biomineralization encompasses bidirectional processes involving (i) biomolecules that modulate nucleation and crystallization behavior of inorganics and (ii) inorganics that tune the secondary structure and self-association of biomolecules.

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A SYSTEMATIC INVESTIGATION OF NANOPARTICLE SAMPLE LOSSES DURING AF4: COLLOIDAL INTERACTIONS AS ORIGIN OF LIGAND-DEPENDENT LOSS MECHANISMS

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Standard nanoparticle (NP) sizing techniques, such as light scattering methods or electron microscopy imaging, are often associated with limited resolution for multimodal size distributions and low sample throughput. Asymmetrical flow-field flow fractionation (AF4) is a chromatography-like colloidal fractionation and sizing method that separates particles according to their diffusion coefficient without a stationary phase [1]. AF4 in combination with a multi-detector approach enables fast and automatable analysis of multimodal size distributions, even for samples with complex matrices [1].

However, nanoparticle characterization using AF4 is often accompanied by sample losses that depend on particle properties and details of the analysis method. The choice of parameters for AF4 analysis ("method development") therefore requires basic knowledge of colloidal properties such as the surface charge in order to avoid particle- and size dependent NP losses that would lead to biased results [2].

Here, we present a systematic investigation of loss mechanisms for gold NPs during AF4. Our results suggest that losses of metal nanoparticles are dominated by their surface modification and the colloidal stabilization mechanism. We believe that gold nanoparticles that are stabilized with polyethylene glycols are lost at the separation membrane through a bridging adsorption mechanism, while citrate-stabilized gold nanoparticles are lost throughout the system by particle degradation (Figure 1) [3]. We will give an overview of the current understanding of NP losses in flow analysis and discuss how nanoparticles with tuned properties can be employed as reference nanoparticles to resolve some of the loss-related limitations of AF4 and similar methods.

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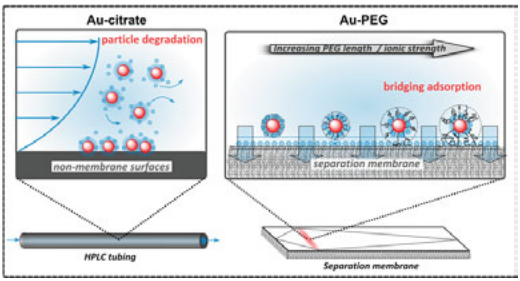

Figure 1. Ligand-dependent gold nanoparticle loss mechanisms of citrate- and polyethylene glycol-stabilized gold nanoparticles [3].

A PLATFORM FOR THE SCALABLE SYNTHESIS OF INORGANIC JANUS PARTICLES WITH DUAL FUNCTIONAL PROTEIN FACES AT A NANOSCALE

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Janus particles with tailored surface chemistry have been gathering interest for applications as catalysts, multifunctional cell surface targets, nanomotors and drug delivery agents. The dual nature of the surface chemistry of Janus particles can be exploited to immobilize drugs, cell surface targets, and/or other functional molecules on both sides of the particle surface [1]. In our work, we developed a model system for the preparation of nano-sized Janus particles with dual protein functionalization. To allow the widespread utilization of nano-sized Janus particles, it is necessary to develop a highly scalable synthesis approach that also allows highly diverse chemical compositions. To this end, we adapted the wax Pickering emulsion technique which has been proposed by Granick et al. [2]. We used 150 and 80 nm silica nanoparticles (SiNPs) modified with an azidosilane to prepare Pickering emulsions using molten wax as the droplet phase (**Figure 1**). The presence of the azide groups (N_3) on the SiNPs enables the subsequent use of click chemistry [3]. The azide functionalized SiNPs on the Pickering emulsion droplets were further subjected to a second silane, biotin-polyethylene glycol (PEG) ethoxy silane. The biotin groups were then conjugated with streptavidin which was labeled with ultra-small gold nanoparticles. Afterwards, we grafted ferritin on the azide functionalized side via a click-reaction. The results demonstrate that it is possible to prepare nano-sized Janus NPs with dual functionalities on two separate sides of a homogenous silica nanoparticle surface. This method represents a scalable platform for preparation of as-desired protein-protein Janus nanoparticles.

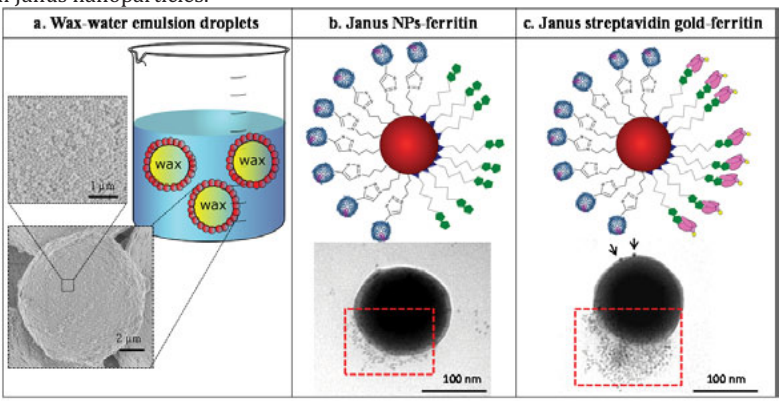

Figure 1. Janus particle preparation technique a. wax in water emulsion droplets stabilized on the surface with SiNPs and SEM micrographs of Pickering emulsion droplets. b. Janus SiNP with two different silanes and ferritin grafted on a single face c. Janus SiNP with ferritin and gold-labeled streptavidin on the respective sides.

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LIPID BASED LIQUID CRYSTALLINE NANOPARTICLES AS POTENT THERAPEUTIC MODULES FOR ANTI LEPROSY DRUGS

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This report aims at unveiling the potential of nanostructured lipid-based liquid crystalline systems for improving the therapeutic efficiency of anti-leprotic drugs i.e. Rifampicin and Dapsone. Lipid based liquid crystalline nanoparticles (LCNP) have been fabricated by employing the hot micro-emulsification methodology in which the hot microemulsion becomes rapidly diluted by water [1]. Dialkyldimethylammonium bromide (D_xDAB) surfactants (where, x=12,14,16,18) as the liquid crystalline solid lipid part and oleic acid as the liquid core, are employed owing to their contribution towards the enhancement of encapsulation and release property of hydrophobic drugs [2]. The effect of D_xDAB as a function of the chain length of the double alkyl chain on the characteristics of LCNP was investigated to completely understand its physiochemical aspects in association with its *in-vitro* release performance. In depth characterization of the LCNP placebo has been done by using various techniques such as DLS, SLS, ZP, TEM, SEM, AFM etc. *In-vitro* cytotoxicity evaluation put forth that toxicity is totally concentration dependent phenomena and LCNP with less than 50 µg/mL is preferred for better *in-vivo* tolerance [3]. High encapsulation efficiency and i*n-vitro* release has been achieved by employing these LCNP nano vehicles for drug delivery. Therefore, this class of D_xDAB based LCNP has become a potent candidate for anti leprosy medicaments as carriers, targeting for pharmaceutical and medicinal purposes. In summary, these LCNPs are an interesting way of colloid formulation for delivering a large variety of different active agents

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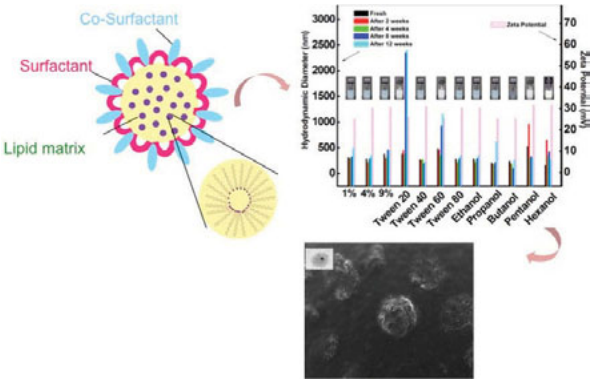

Figure 1. Structure of optimized lipid based liquid crystalline nanoparticles (LCNP) formulation verified by TEM and SEM analysis.

TEMPERATURE INDUCED AGGLOMERATION OF ALKANETHIOL STABILIZED GOLD NANOPARTICLES

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Many inorganic nanoparticles (NP) with organic ligand shells undergo a reversible, temperature-dependent agglomeration [1]. Here, we study the agglomeration process for alkanethiol coated gold NPs in detail. We used protocols to prepare such particles with diameters between 4 nm and 9 nm, a narrow size dispersion of 8 %, and oleylamine ligand shell. Ligand exchange was performed to coat the NPs with the desired ligand at reproducible densities [2]. Agglomeration was induced by cooling the dispersions. The transition between the dispersed and agglomerate state and the crystallinity of the agglomerates was reconstructed from small-angle X-ray scattering and other methods.

This contribution will focus on the size dependent "critical" agglomeration temperature of alkanethiol-coated gold NPs in alkanes. Born et al. showed that such particles can undergo a "ligand-dominated" transition between dispersed and agglomerated state [1] and that the structure of the agglomerates depend on temperature [3]. We will present systematic data on this transition and show that it also depends on the diameter of the particles. Small angle X-ray scattering (SAXS) measurements were used to follow the agglomeration *in situ* and to concurrently analyze the agglomerate structure. Transmission electron microscopy (TEM) was used to create real-space models for SAXS analysis. The figure below shows TEM micrographs and SAXS pattern of the same NPs in different states: dispersed (left), amorphous agglomerated (center) and crystalline agglomerated (right).

The transition temperature also depended on ligand shell thickness and solvent quality. Using certain solvent-ligand combinations with the same NP core allowed changing the agglomeration temperature and the structure of the agglomerate.

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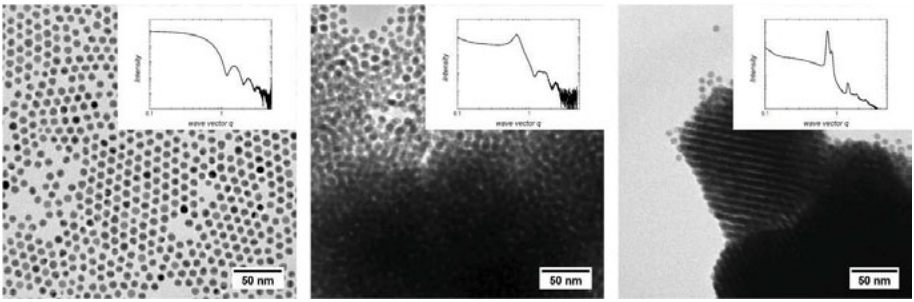

Figure 1. Transmission electron micrographs of alkanethiol stabilized gold NPs prepared on grids from their dispersed state (left), amorphous agglomerated state (center), and crystalline agglomerated state (right). Inserts show the corresponding SAXS pattern.

SYNTHESIS AND FUNCTIONALIZATION OF FLUORESCENT SILICA NANOPARTICLES FOR APPLICATION IN NANOCOMPOSITES

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Modern nanoscale fluorescent materials find numerous applications as markers in biology, medicine and in materials science. So far, quantum dots were often used for these applications, for which the band gap and thus the emission is based on the size of the particles. These materials have many properties, limiting their potential applications, i.e. their composition, stability, limited size variation and lack of possibilities for surface functionalization. Dye-doped nanoparticles based on silica as the matrix overcomes many of these disadvantages. The aim of the research project is the synthesis of fluorescent nanoparticles with organic fluorescent dyes encapsulated in an inorganic shell. Systematic studies aim at optimizing the synthesis of these nanoparticles and an investigation of influences of reaction parameters on particle morphology and fluorescence behavior. The synthesis of the anchor group functionalized dyes and particles are based on literature methods like the Stöber process [1], as well as new methods of production with a microjet reactor [2]. For further applications the stability of fluorescence and brightness is important. The incorporation of fluorescent dyes in a silica matrix increase their lifetime due to a protection of the dye from environmental influences like light or oxidizing agents. Covalent bonding of the dye is necessary for fluorescence performance, since dyes bound by physical interaction tend to leach out of porous silica networks. The particles with optimized properties will be embedded in polymer matrices to investigate agglomeration phenomena.

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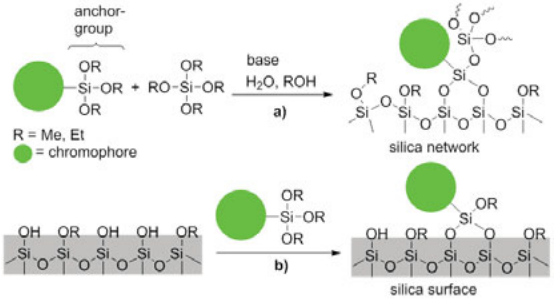

Figure 1. Covalent dye doping a) in situ dye incorporation, b) dye functionalization after particle synthesis

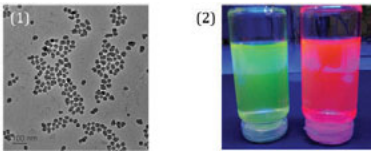

Figure 2. (1) TEM picture of FITC doped silica particles, average size 27.8 ± 4.0 nm, (2) left: FITC functionalized silica particles in ethanol, right: R6G doped silica particles.

CO-MONOMER ASSISTED SYNTHESIS OF CATIONIC POLYSTYRENE PARTICLES WITH EXCELLENT SIZE CONTROL AND THEIR USE AS CORES FOR GOLD PATCHY PARTICLES PRODUCED IN A CONTINUOUS FLOW PROCESS

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In this presentation we will show a novel combination of initiator and co-monomer in the radical emulsion polymerization synthesis of cationic polystyrene (PS) particles with impressive size tunability. The influence of temperature, styrene and co-monomer concentration on the PS particle size will be demonstrated. Especially, the effect of the co-monomer concentration on the nucleation rate will be highlighted. In addition, the use of the synthesized PS particles as core particles for the fabrication of surface conformal gold patches will be shown. This approach is based on the heterogeneous nucleation of gold at the PS particles' surface initiated by the chemical reduction reaction between chloroauric acid and ascorbic acid under highly diluted conditions. Particularly, we will demonstrate the advantage of using a continuous flow mixing procedure rather than the poorly reproducible batch process of our original work [1]. Depending on process parameters like mixing conditions, concentrations and PS particles dimensions, various gold patch morphologies from spot- and cone like gold patches to very thin dendritic patches having different sizes up to complete nanoshells can be synthesized. Due to the plasmonic properties of gold, the variation of the gold patch morphology allows the optical properties of the product particles to be tailored, opening up their potential use in applications in nanomedicine, functional films or sensors. At the end of the talk initial results of the colloidal stabilization of such highly complex particles and their application in dip coated functional films on glass substrates will be shown.

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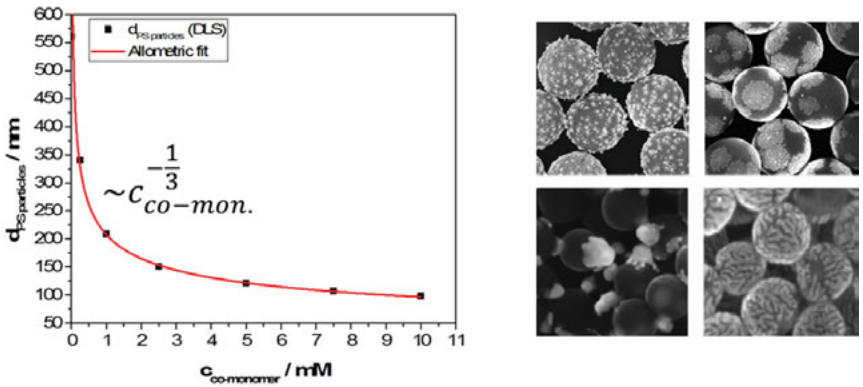

Figure 1. Dependency of PS particles diameter on co-monomer concentration, SEM images of synthesized gold patches showing different morphologies and patch coverages.

ANIONIC RING-OPENING POLYMERIZATION ON THE SURFACE OF SILICON DIOXIDE NANOPARTICLES

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Saarland University, Inorganic Solid State Chemistry, Campus C4.1, 66123 Saarbrücken, Germany

The grafting-from polymerization on the surface of inorganic nanoparticles is a widely used technique to synthesize nanocomposite materials that can be used as drug carriers or for applications in material science. Usually, radical polymerizations are employed in grafting-from applications because of the mild reaction conditions and broad spectrum of potential monomers. The rare occurrence of anionic ring opening polymerizations in this field is due to the high sensitivity towards impurities, despite the advantages of highly controlled polymer weights and interesting possible monomers.

In this work, we present the functionalization of silicon dioxide nanoparticles with haloalkyl groups as initiators for anionic polymerizations and the synthesis of polysiloxane nanocomposites by a ring opening grafting-from polymerization of various cyclosiloxanes. So far, silicon dioxide nanoparticles with a diameter of 20 nm were synthesized with standard Stöber conditions [1] and the functionalization reaction with haloalkylsilanes has been optimized to yield a high surface density of halogen functionalities. However, the lithiation step proved to entail a complex array of different side reactions leading to alkylated particle surfaces [2]. Different strategies have been chosen to obtain a surface, which is lithiated solely at the halogen center of functionalized particles, e.g. lithiation with *n*-butyllithium, *tert*-butyllithium and lithium naphthalenide. The effect of these lithiation reagents on the surface structure of particles is studied in detail using solid state NMR techniques.

Results show, that *n*-butyllithium preferably alkylates the particle surface while *tert*-butyllithium and lithium naphthalenide show no signs of attacking the particle surface directly. Nonetheless, a successful grafting-from polymerization of hexamethylcyclotrisiloxane was carried out using *n*-butyllithium and is expected to give even better results when using other lithiation reagents, which is currently under investigation.

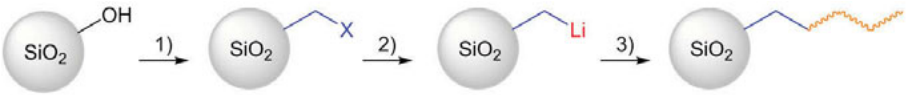

Figure 1: Aim of the research.
1) Functionalization of silica nanoparticles with haloalkylsilanes
2) Lithium halogen interconversion on the surface of functionalized particles
3) Anionic ring-opening grafting-from polymerization of cyclosiloxanes

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[1] W. Stöber, A. Fink, E. Bohn, *J. Colloid Interface Sci.* **1968**, *26*, 62–69
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INFLUENCE OF DIFFERENT EXCIPIENTS ON MORPHOLOGY AND DISINTEGRATION BEHAVIOR OF NANO-EMBEDDED MICROPARTICLES

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* both authors contributed equally

The embedding of nanoparticles (NPs) into microparticles is a promising approach for pharmaceutical application as it allows the combination of two size ranges within one system. NPs can be used to improve the drug transport across biological barriers and to protect drugs from deactivation. However, for an application as dry powder formulation, they need to be embedded into microparticles having an appropriate size to be inhaled. In this context, we embedded PLGA-NPs into a matrix of mannitol or hydroxyethyl starch (HES) by spray drying. Furthermore, we investigated the influence of the excipient content on morphology and disintegration behavior of the microparticles.

Microparticles were prepared by spray drying pure PLGA-NPs, pure excipient and mixtures of both in three different ratios. Morphology was analyzed by SEM and CLSM. The disintegration behavior was investigated under conditions similar to the lungs by distributing the microparticles on a membrane and exposing them to 90-99% rel. humidity. Evaluation of the redispersibility was performed by white light interferometry and SEM.

Considering the mannitol particles, different morphologies occurred depending on the mannitol ratio. Spray drying of pure mannitol produced spherical solid particles, while the addition of nanoparticles resulted in raisin-shaped, hollow particles with a solid shell. In comparison HES particles show a raisin-shaped structure, regardless of the used ratio (Fig. 1).
The tendency to form hollow particles can be explained by a high Péclet number, which is comparing diffusion time of a substance to the drying time of a droplet upon spray drying [1]. The degree of buckling is associated with the nanoparticle content defining the mechanical properties of the shell [2].

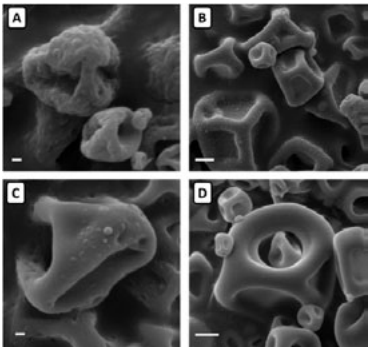

Figure 1. SEM image of spray-dried microparticles with different ratios of HES to PLGA- NP. A: 1-1; B: 1-5; C: 1-10; D: pure HES. Scale bar represents 1 μm.

Exposure to high air humidity turned out to be sufficient for the disintegration of microparticles containing mannitol. To ensure a fast redispersion of NPs, high mannitol content is recommended. The presented nano-in-micro particles combine the advantages of both nano- and microparticles and thus bear the potential to be used as a pulmonary drug delivery system.

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RECOMBINANT BACTERIOPHAGES AS PROGRAMMABLE FUNCTIONAL BIONANOMATERIALS

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Filamentous bacteriophages (M13, fd and f1) are a group of viruses which can only infect male Gram (-) bacteria carrying pili [1]. Filamentous phages are used for phage display technique to identify short peptide sequences which can specifically recognize and bind surfaces, proteins or living cells [2]. Ease of genetic modification of phage genetic material makes bacteriophages programmable nanomaterials.

fd- bacteriophage is a member of filamentous phages (1 µm in length and 6 nm in diameter) composed of a circular single stranded DNA (ssDNA) packed in a protein cage [1]. In this study, fd-phages are genetically engineered to display various gold binding peptides along the body part on pVIII (major coat protein) subunits [3], at the head on pIX (minor coat protein) and at the tail on pIII (minor coat proteins) subunits (Fig. 1a). Resulting recombinant virus particles have been investigated in terms of their gold binding affinities and metallization potential.

Quartz crystal microbalance (QCM), Energy dispersive X-ray spectroscopy (EDX), Atomic force microscopy (AFM) and Scanning electron microscopy (SEM) analyses were performed in order to investigate binding affinities of genetically modified phages to gold surfaces and nanoparticles (NPs). Expression of Tyr amino acids on pVIII coat protein subunits enhanced Au binding affinities of geneticaly modified phages (Fig. 1b). YYYYY phages showed the strongest Au surface and AuNP binding (Fig. 1c). Bacteriophage nanorods can be reprogrammed by genetic engineering and used as biotemplates for bottom-up fabrication of nanowires or as functional bioactive scaffolds for tissue engineering and cancer research studies.

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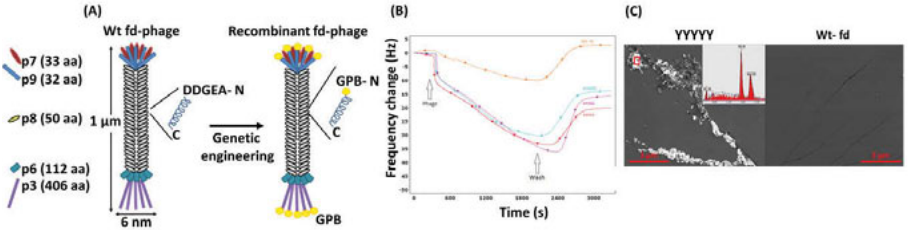

Figure 1. fd- phages were genetically modified to display Gold binding peptides (GBP) on minor and major coat protein subunits (A). Au binding affinities of recombinant phages were investigated by QCM analyses on Au coated quartz sensor chips. Net frequency changes were calculated at the 3rd frequency overtone (n=3) (B). SEM and EDX analyses showed that engineered YYYYY-phages were decorated with 5 nm AuNPs after AuNP binding tests (C). Pictures were taken at 30 kV in high vacuum. EDX analysis was performed inside the red box.

CHARACTERIZATION OF GOLD NANOPARTICLES AND THEIR ASSEMBLIES BY SURFACE-ENHANCED RAMAN SPECTROSCOPY

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[2] Cluster of Excellence Centre for Advancing Electronics Dresden (cfaed), TU Dresden, Germany
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We present two examples for the retrieval of molecular information at nanoparticle surfaces using surface-enhanced Raman scattering (SERS): The first example shows that the electric-field enhancement of individual noble metal nanoparticles can be exploited for the local characterization of their surface near field. Here, we studied the ligand corona in dispersion and its quantitative exchange of low-molecular-weight surfactants against high-molecular-weight proteins [1].

The second example focuses on the application of protein-linked particle assemblies as colloidal SERS sensors (see **Fig. 1**) [2]. For this purpose, we report the detection of low-molecular-weight analyte molecules in the gaps of the particle assemblies despite the broad spectral fingerprint of the protein linker. That enabled us to compare the SERS signals to the non-enhanced volume-Raman signals of the medium (EtOH/H_2O) as reference.

[1] M. Tebbe *et al.*, *ACS Appl. Mater. Interfaces* **2015**, *7*, 5984–5991.
[2] R.P.M. Höller *et al., ACS Nano* **2016**, *10*, 5740–5750.
[3] The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement No. METAMECH-306686.

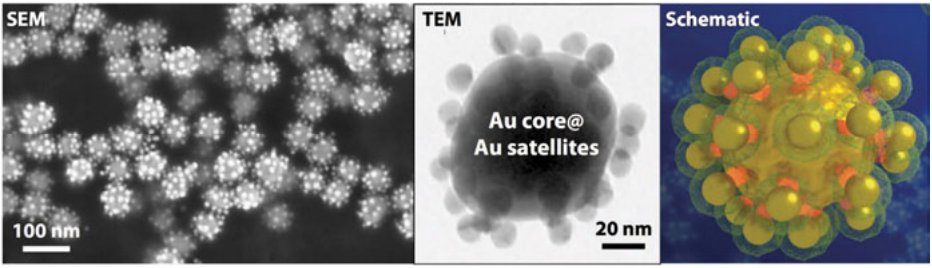

Figure 1. Self-assembled nanoassemblies of small gold nanoparticles (16nm) as satellites on larger gold nanoparticles (84nm) as cores.

POSTER SESSION 2

L – Z

DEVELOPMENT OF PROTEIN-RESISTANT SURFACE FUNCTIONALIZATIONS FOR BIOMATERIALS

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Adsorption of proteins on surfaces crucially influences the performance of biomaterials in the human body [1, 2]. Processes, such as thrombosis, inflammation as well as encapsulation are governed by the initially formed protein layer [2, 3]. Understanding the influence of surface properties on protein adsorption as well as the development of protein-resistant surfaces is thus vital in order to improve the functioning of biomaterials.

For this purpose, a variety of novel surface modifications was developed. Silicon or silica based model substrates were functionalized with self-assembled monolayers (SAMs) via silane chemistry, introducing terminal succinic anhydride, carboxylic acid or amine groups. These SAMs served as a basis for the subsequent immobilization of various reagents with terminal amine groups but varying structure. In summary, polyamines and poly(amidoamine)s (PAMAM) with oligomeric, polymeric or dendritic structure were investigated. All surface functionalizations exhibited moderate hydrophilicity and medium surface free energies, whereas their amino group densities and zeta potentials differed strongly.

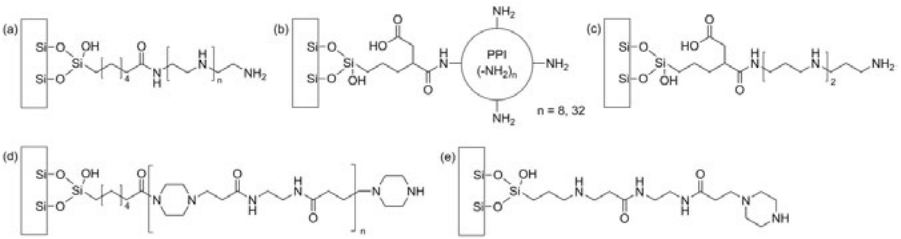

Figure 1: Overview of the surface modifications: (a) linear poly(ethylene imine) (PEI) polymer, (b) poly(propylene imine) (PPI) dendrimers of generation 2 or 4, (c) N,N'-bis(3-aminopropyl)-1,3-propanediamine (APD), an oligo(propylene imine), (d) linear PAMAM polymer or (e) PAMAM oligomer.

Protein adsorption on those modified surfaces was investigated with the bicinchoninic (BCA) assay. Preliminary tests were performed with human serum albumin (HSA, pI 4.7). Low amounts of HSA were found to adsorb to APD, PEI or PAMAM polymer covered surfaces (< 70 ng cm^{-2}) compared to PPI dendrimer or PAMAM oligomer functionalized substrates (~160-430 ng cm^{-2}). Thus, APD, PEI or PAMAM polymer functionalized surfaces exhibited promising protein-resistant properties. Adsorption of proteins with different isoelectric points (e.g. lysozyme) as well as from complex physiological fluids (such as whole saliva) is currently investigated.

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LOW-VOLTAGE ELECTROWETTING ON MULTILAYER-DIELECTRICS CONSTRUCTED WITH TANTALUM PENTOXIDE AND SILANE

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Electrowetting on dielectric (EWOD) is a phenomenon, which can be used to change the wettability of a small scale (µL) conductive droplet on an electrode with a dielectric coating by applying a voltage. EWOD is used in liquid lenses [1,2], displays [3,4] and various lab-on-a-chip microsystems e.g. in the biological analysis [5].

To improve the electrowetting performance, one of the biggest obstacles is the need of high voltages about 25-50 V. To reduce the necessary voltage for electrowetting applications, a low-potential EWOD electrode was constructed in this work as a multi-dielectric-thin-layer electrode. It consists of an anodic tantalum pentoxide (Ta_2O_5) thin layer and a self-assembly hydrophobic silane thin layer. The thickness, dielectric constant, capacitance and layer growth rate of the tantalum pentoxide layer were characterized using impedance spectroscopy and ellipsometry. Its high relative dielectric constant was determined to be comparable with the literature value (27.5 [6]). Furthermore, the hydrophobicity, morphology and roughness of the silane surface were investigated with measurements of contact angle and contact angle hysteresis as well as atomic force microscopy. The coating with hydrophobic silane results in a significant change of the surface properties.

Based on this multilayer-EWOD electrode, electrowetting of an aqueous µL-droplet in an oil environment under low voltages was investigated with optical imaging and impedance spectroscopy. The experimental results were evaluated with a modified Young-Lippmann equation. Further results will be shown in the presentation.

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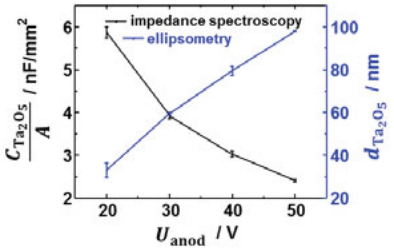

Figure 1: Capacitance per unit area determined by impedance spectroscopy (black) and layer thickness by ellipsometry (blue) for anodic tantalum pentoxide layers anodized at different voltages.

TEMPERATURE-DEPENDENT OPTICAL PROPERTIES OF ALKYLTHIOL-STABILISED GOLD NANOPARTICLE DISPERSIONS

Hei Tung Lin[1,2], Thomas Kister[1,2] and Tobias Kraus[1,2]

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The agglomeration of metallic nanoparticles has been studied by researchers partially because of their interesting optical properties [1]. Various ligands are used to stabilise nanoparticles by introducing repulsive interactions between the particles. The ligands also affect the optical properties of nanoparticles [2]. Agglomeration of ligand-stabilised metallic nanoparticles can be induced by a temperature decrease that causes attractive interactions [3].

In this contribution, we discuss the agglomeration behaviour of gold nanoparticles (AuNPs) stabilised by alkylthiols. We investigated the influence of particle size, solvent and ligand length on the temperature dependence of agglomeration and studied the change in their optical properties.

Systematic measurements on the agglomeration behaviour were performed using dynamic light scattering (DLS) and UV-Vis spectroscopy (UV-Vis). Critical agglomeration temperatures were obtained from the change in the hydrodynamic diameter (DLS), changes in the scattering intensity (DLS), the absorbance change in the visible range (UV-Vis), and the plasmon peak shift of the AuNPs (UV-Vis).

Figure 1 shows AuNPs of 3.7 nm radius covered in 1-hexadecanethiol dispersed in hexane, decane, and hexadecane at different temperatures. The colour changes due to agglomeration of the particles were clearly visible to the naked eye. Strong agglomeration was observed in decane and hexadecane, as indicated by their blue colour at room temperature. Gradual changes in the colour shift of the AuNPs dispersed in solvents of increasing chain length were detected.

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Figure 1. AuNPs of 3.7 nm radius covered with C16 thiol in hexane (left), decane (middle) and hexadecane (right) at (a) 20°C (b) 35°C and (c) 55°C.

IMPACT OF VISCOUS DROPLETS ON SURFACES WITH DIFFERENT WETTABILITY

Shiji Lin, Binyu Zhao and Longquan Chen

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The effect of surface wettability, liquid viscosity and impact velocity on the maximum spreading ratio, impact time and the oscillation has been studied. With the systematic research, we demonstrate that a single power law could not be applied to predict the maximum spreading ratio for all cases, but the exponent dominantly decreased with the viscosity, then based on the low viscous liquid and high viscous liquid, two exponent limits are proposed. And we found all of the impact time normalized by $\sqrt{\frac{\rho r_{\max}{}^3}{\gamma}}$ collapsed onto one master curve $1.25We^{-0.46}$, where the maximum spreading radius $r_{\max}$ is used. Furthermore, two different oscillation behaviors were distinguished: oscillation with pinned contact line and with mobile contact line. We interpreted different features of oscillation, such as a larger viscosity causes a bigger damping coefficient, and the range of the impact velocity which left the oscillation is smaller on hydrophilic surfaces than that on less wettable surfaces.

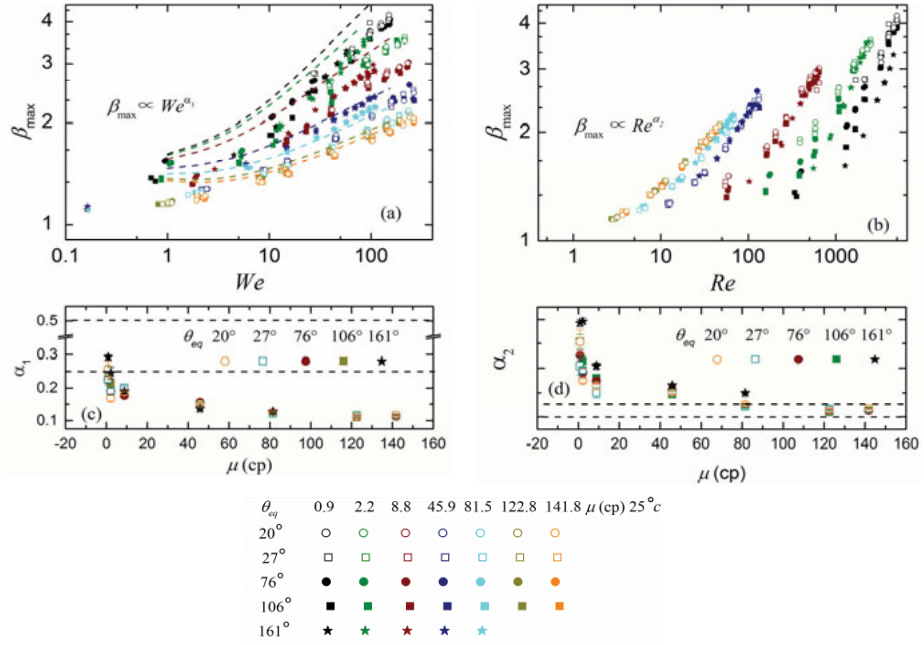

Figure 1 : Log-log plot of β_{max} of different liquids on surfaces with different wettability as a function of We (**a**) and Re (**b**). The dash lines are the theoretical values. (**c**) Plot of the fitting exponent α_1 on different surfaces with $\beta_{max} \propto We^{\alpha_1}$, two black dash lines indicate 1/2 and 1/4, respectively. (**d**) Plot of the fitting exponent α_2 on different surfaces with $\beta_{max} \propto Re^{\alpha_2}$, two dash lines indicate 1/4 and 1/5, respectively.

THE INFLUENCE OF PARTICLE SIZE DISTRIBUTION AND SHELL IMPERFECTIONS ON THE PLASMON RESONANCE OF Au AND Ag NANOSHELLS

Daniel Mann,[1] Daniel Nascimento-Duplat,[2] Helmut Keul,[1] Martin Möller,[1] Marcel Verheijen,[3,4] Man Xu,[2,5] H. Paul Urbach,[2] Aurèle J. L. Adam,[2] Pascal Buskens[1,5]

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[2] Delft University of Technology, Delft, Netherlands
[3] Philips Innovation Services, Eindhoven, Netherlands
[4] Eindhoven University of Technology, Eindhoven, Netherlands
[5] The Netherlands Organisation for Applied Scientific Research (TNO), Eindhoven, Netherlands

Au and Ag nanoshells are of interest for a wide range of applications. The plasmon resonance of such nanoshells is the property of interest and can be tuned in a broad spectral regime, ranging from the ultraviolet to the mid-infrared. To date, a large number of manuscripts have been published on the optics of such nanoshells. Few of these, however, address the effect of particle size distribution and metal shell imperfections on the plasmon resonance. Both are inherent to the chemical synthesis of metal nanoshells and therefore to a large extent unavoidable. It is of vital importance to understand their effect on the plasmon resonance, since this determines the scope and limitations of the technology and may have a direct impact on the application of such particles. Here, we elucidate the effect of particle size distribution and imperfections in the metal shell on the plasmon resonance of Au and Ag nanoshells. We prepared the particles with desired core diameter and shell thickness using cross-linked polystyrene particles tailored for both the deposition of Au and Ag through reduction of tetrachloroauric acid and silver diammine, respectively, in a two-step procedure. In the first step, small Au or Ag seeds were selectively deposited on the polystyrene particle surface, covering all particles with homogeneously distributed metal seeds.[1] In the second step, the particles decorated with metal seeds were subjected to metal plating, resulting in well-defined Au and Ag nanoshells. The size of the polystyrene core and the thickness of the Au and Ag shells were systematically varied to study their influence on the plasmon resonance, and the results are compared to values obtained through optical simulations using extended Mie theory and finite element method. Discrepancies between theory and practice were studied in detail and discussed extensively. Quantitative information on the minimum thickness of the metal shell, which is required to realize a satisfactory plasmon resonance of a metal nanoshell, is provided for Au and Ag.[2]

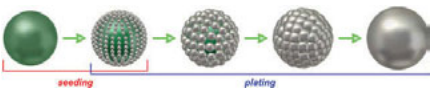

Figure 1. Schematic representation of the formation of metal nanoshells (green = polystyrene, silver = metal)

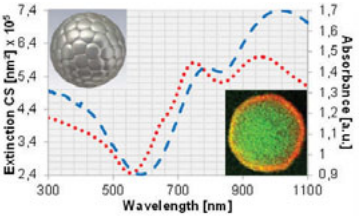

Figure 2. UV/Vis absorbance spectrum (blue) and calculated ECS (red) for Au nanoshells.

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CONTROLLED AND TUNABLE DESIGN OF POLYMER INTERFACE FOR IMMOBILIZATION OF ENZYMES: DOES CURVATURE MATTER?

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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. Thus, enzymatic catalysis is of great interest for the food and textile industry as well as for pharmaceutical transformations.

The effective immobilization of enzymes provides an excellent base for their exploitation by enhancing their structural and catalytic stability in different environmental conditions, and reducing product inhibition. For this, the tunable and controllable design of polymer interface is necessary, which can be realized by polymer brush modification. Particularly, polymeric brush-modified colloids can be used as carrier materials for enzyme immobilization. Although it is of prime importance to control the brush architecture, there is still a lack of systematic investigations concerning the impact of grafting density on the properties of the designed interface, as well as on the immobilization of biomolecules.

Herein, we will present the experimental results and the relationship between the controlled design of polymeric interface on planar and curved substrates and its impact on the effectiveness of immobilization of laccase from *Trametes versicolor*. Thus, the interfacial properties of polyelectrolyte brushes with different grafting densities prepared using a "grafting from" approach on flat and on colloidal particle substrates by changing the density of initiator groups will be varied. In this way, we control the interfacial properties of the carrier material such as swelling, charge, and adhesion, which are strongly determined by the grafting density. We also show that there is no direct transferability of the results received from planar to curved substrates regarding the swelling behavior. Specifically, the immobilization of laccase via physical adsorption causes changes in the surface morphology, charge and adhesion performance of final polymer-enzyme layer which is proved by cryo-TEM and AFM force distance measurements. Furthermore, correlation between the grafting density of the polymer brush shells and the efficiency of immobilization, as well as the effectiveness of the catalytic performance of laccase are studied in details.[1,2]

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NANOSCALE TOPOGRAPHY DETERMINES THE CAPILLARY ASSEMBLY OF NANOPARTICLES

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Predetermined and selective placement of metallic nanoparticles onto large-area substrates with nanometre-scale precision [1] is essential to harness the unique properties of nanoparticle assemblies, particularly for the realization of functional electro-optical nanodevices [2].
Here we show that tailored nanoscale topography can determine the capillary assembly of Au nanorods on solid substrates to attain 1) ultimate and simultaneous control of position, orientation and interparticle distance at the nanometre level, and 2) up to 100% assembly yield over centimetre-scale substrates [3]. This is achieved by optimizing three-dimensional topographic features on substrates to benefit from three sequential stages of capillary assembly: insertion of nanorods into commensurate traps, resilience against the receding suspension front, and drying of residual solvent. The novel insights into the technique allow the predictable assembly of nanorods over arbitrary two-dimensional multimeric motifs and also to tailor their precise three-dimensional orientation. The spectral response and near-field properties of spatially programmed Au nanorod multimers, characterized using electron energy-loss spectroscopy, highlights the opportunities for precise tunability of plasmonic modes in large nanoparticle assemblies towards sensing applications.

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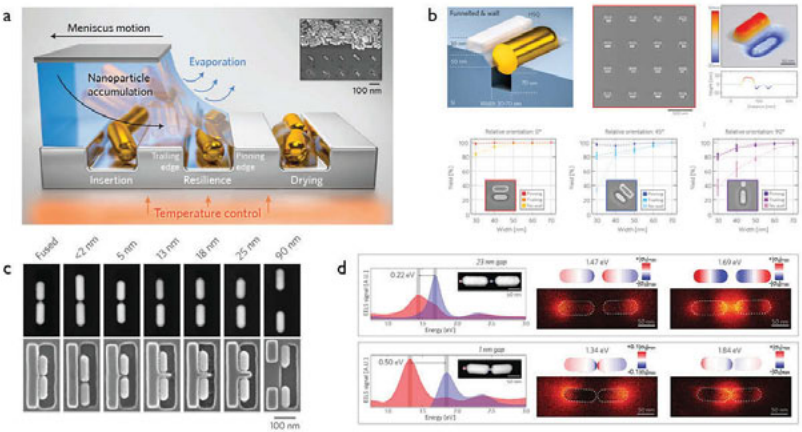

Figure 1. a) Stages of capillary nanoparticle assembly. b) Assembly yield of Au nanorods in commensurate funneled traps with single auxiliary sidewall. c) Control of interparticle gap in assembled Au nanorod dimers. d) Electron energy-loss spectroscopy maps of bonding and anti-bonding plasmonic modes in assembled Au nanorod dimers. (Adapted from [3]).

BIMETALLIC COLLOIDS: MERGING THE ADVANTAGES OF SILVER AND GOLD NANOCRYSTALS

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We present a general approach to achieve narrow distributions in size, chemical variability, and oxidant stability, which are well-known for gold nanocrystals, while maintaining the advantageous plasmonic properties of silver. This is achieved by consequent control of the growth *via* balancing the reduction potentials and enforcing adequate reaction kinetics (*"living conditions"*) [1].

The use of gold cores as seeds enables the controlled synthesis of various silver morphologies in aqueous dispersions. Exploiting specific gold colloids as seeds for silver overgrowth *via* facet-selective capping allows for the preparation of Ag nanocubes[2], Ag cuboids[3] and Ag nanowires[1] with sharp edges/tips and extraordinary narrow distributions (see Figure). Hence, we selected seed-mediated growth of spherical single-crystalline Au nanoparticles, single-crystalline and pentatwinned Au nanorods as seeds, respectively.

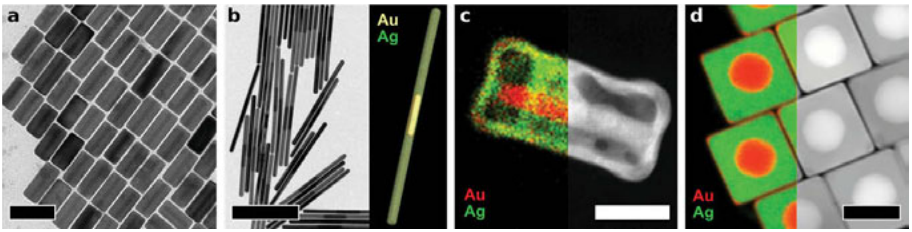

Figure: TEM and EDX images of different bimetallic morphologies, which combine the advantages of silver and gold**.** Ag cuboids (a), Ag nanowires (b), nanorattle with dielectric cavity (c), and Ag nanocubes with protective gold shell (d). Scalebars: 100 nm, 500 nm, 25 nm, and 50 nm, respectively.

Finally, we achieved a thin protective gold shell, which ensures oxidant stability, but also facilitates a variety of chemical functionalization protocols in aqueous suspension[2]. Alternatively, we further increased the complexity of silver colloids by employing controlled galvanic replacement reactions resulting in axisymmetric nanorattle particles[4].

To verify the homogeneity and distribution of the obtained bimetallic morphologies we performed a comprehensive characterization by high-angle annular dark field transmission electron microscopy (HAADF-TEM), energy dispersive X-ray (EDX) mapping, small-angle X-ray scattering (SAXS), optical spectroscopy (UV-vis-NIR), electron energy loss spectroscopy (EELS) and electromagnetic simulations (FDTD).

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NEW ENCAPSULATION MATERIALS FOR HIGH ENERGY LEDS

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High energy LEDs (light emitting diodes) require transparent electronic packaging materials in order to maximize the light emission and the durability [1-3]. Based on their superior properties compared to epoxides or polyphthalamides, functionalized polysiloxanes as well as hybrid materials show a rising popularity in optoelectronic encapsulation devices. The main advantages are their high transparency, adjustable refractive index (RI), as well as improved UV- and thermal stability. Furthermore, excellent control over their composition can be achieved applying polycondensation reactions and sol-gel chemistry starting from molecular precursors [4-6].

In this study we present principle approaches regarding the molecular composition in order to improve the final macroscopic properties of the packaging materials. For this, nanoparticles were synthesized and modified with various polysiloxanes. These were substituted with various high diffractive index delivering side groups and incorporated into new polymers for the 2K packaging materials. Small metal oxide nanoparticles increase the thermal stability, the refractive index and serve as an additional tuning tool to receive an outstanding packaging material.

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MOLECULAR DIFFUSIONAL DEGRADATION OF SERIES ALCOHOLS COSURFACTANT ON MINIEMULSIONS SYSTEM

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The success of miniemulsion polymerization is greatly dependent on the quality of miniemulsions produced prior to polymerization in the monomer droplets which is involves the free radical polymerization of monomer in discrete droplets. Miniemulsions are classically defined as aqueous dispersions of relatively stable droplets where it is stable by kinetically within a size range of 50-500 nm prepared by shearing a mixture containing oil, water, a surfactant, and additionally a cosurfactant/costabilizer. The molecular diffusional degradation (Ostwald ripening) behaviour of the two-component miniemulsions of monomer Styrene (ST) with series alcohol cosurfactant was investigated. Ostwald ripening rate determine by fitting a semi-empirical equation from extended of Kabalnov equation with two adjustable parameters K1 and K2. Corresponding to the single component of ST on stable volume fraction, the value Ostwald ripening of $C_{12}OH > C_{16}OH > C_{18}OH$. Its describe increasing the capability of alcohol cosurfactant to enhance the storage stability of miniemulsion products. TEM figure and FTIR data also applied to observe the morphology and functional groups in the miniemulsions system

Keywords: miniemulsions, Ostwald Ripening, molecular diffusional degradation, alcohol, cosurfactant.

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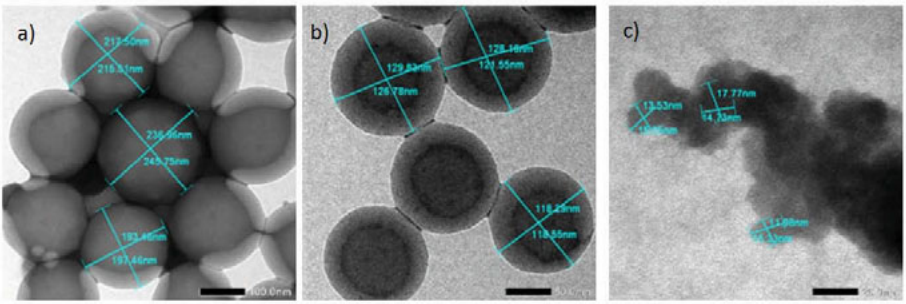

Figure 1. TEM results of two-component miniemulsions of monomer Styrene with cosurfactant: a) $C_{12}OH$ b) $C_{16}OH$ c) $C_{18}OH$

A NEW INTERFACIAL POLYMERIZATION TECHNIQUE CONTROLLED BY GAS-PHASE ADSORPTION OF REACTIVE MONOMERS

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The properties of ultra-thin films or layers with the thickness of just a few nanometers may deviate from the features of bulk-sized materials based on size induced functionalities. This enables a large variety of new capabilities in modern technology, making nano-scaled substances an interesting field for scientific research and industrial applications. However, obtaining these homogenous nano-layers is still a challenge of modern times.

By adsorption of reactive monomers from the gas phase, followed by autopolymerisation at the water surface, we succeeded to create ultra-thin cross-linked polymer films through polycondensation reactions. In a series of experiments, we used highly reactive organosiloxanes, silane, stannane and germane compounds, which polymerized immediately, after getting in contact with the water surface. Depending on the vapor pressures of the monomers, we enhanced the evaporation by heating the beaker, which contained the monomer and was streamed by argon gas. This inert gas stream, containing tiny amounts of the reactive monomers, was then directed towards the water surface. The ultra-thin siloxane films, which were formed after polymerization, had typical thicknesses between a few nano- and micrometers, depending on the used volumes of the monomers. By observation of the reaction process via Time-Sweep-Experiments, we succeeded to create a homogenous monolayer of Octadecyltrichlorosilane by interrupting the gas stream immediately after the time the first coherent network structure was confirmed.

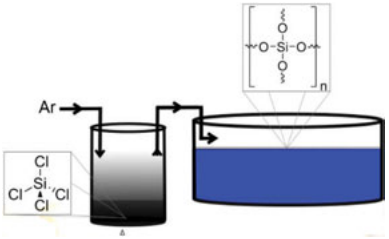

Fig. 1. Schematic drawing of the experimental technique for the synthesis of ultra-thin polymer films.

We systematically analyzed the elastic and viscous properties of the obtained films by means of different rheological techniques. In a series of experiments, we investigated the film stabilities as a function of the structure and size of ligands, chain length and thickness of the ultra-thin silane layers.

In additional experiments, we tried to functionalize the silane films by adding magnetic nanoparticles to the water surface. The resulting flexible polymer films could be deformed by applying a magnetic field. It was also possible to enclose surfactants and other surface-active molecules in the very thin and stable film. We also investigated the possibility of copolymerizing different silane monomers. With these special monomers, we observed under the scanning electron microscope the formation of polymer films with mixed structural compositions.

STABILITY STUDIES ON AQUEOUS POLYURETHANE DISPERSIONS

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An aqueous polyurethane dispersion (PUD) is a heterogeneous colloidal system, in which PU particles are dispersed in a continuous aqueous medium [1]. PUDs belong to the so-called secondary dispersions [2]. The main ingredients of a PUD are in general long and short polyols chains, aliphatic or aromatic isocyanates, an internal emulsifier and a chain extender. The colloidal stability of PUDs in terms of electrolyte, storage or shear sensitivity is of great importance for the process industry. It is affected by several factors, amongst others, the attractive van der Waals forces between the PU particles and various repulsive forces. These may be formed by electrostatic and steric interactions [3]. Therefore, a distinction can be made between ionically and non-ionically stabilized polyurethanes. This work focuses on the synthesis of ionically stabilized PUDs and the study of their stability compared to electrolytes. Electrokinetic and photometric methods are used in order to elucidate the stabilizing mechanism.

For this purpose, PUDs with different amounts of ionic groups were prepared according to the classical acetone process. First of all, the prepolymer, consisting of a polyester polyol and isophorone diisocyanate (IPDI), was synthesized and dissolved in acetone. Then, the chain extension step was carried out using isophorone diamine (IPDA) and sodium 2-[(2-aminoethyl) amino] ethanesulfonate (AAS). The latter also provides the stabilizing ionic groups and its amount was varied. Finally, the PU polymer was dispersed in water and the acetone was distilled off.

Measurements of the average particle size were performed. This is an important factor for further applications involving PUDs. It was observed that the particle size decreases with the increase of AAS content. This phenomenon is well known and can be explained in terms of surface enlargement. This is due to electrostatic repulsion of the increasing particle charges [4].

The stability of colloidal dispersions and the electrokinetic behaviour of the particles are decisively determined by the surface potential of the particles, which for its part is a function of the surface charge density. The latter was investigated by charge titration. As expected, it was found that the effective specific surface charge increases almost linearly with the increase of AAS content. The degree of sodium dissociation can also be calculated. Surprisingly, only 10 % of all sodium ions are dissociated. This shows that almost 90 % of the incorporated sulfonate groups do not contribute to the electrostatic stabilization of the dispersion. The stability of polymer dispersions can also be expressed as a critical coagulation concentration (ccc). Sodium chloride was used as monovalent electrolyte for the determination of the ccc. As expected the dispersion stability increases with the increase of AAS content. This is due to the enhancement of electrostatic repulsive forces. Therefore, we have strong evidence that the electrostatic repulsion plays an important role in the stabilization of the investigated PU dispersions.

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WRINKLE-ASSISTED GRAZING INCIDENCE SPRAYING: ROBUST ALIGNMENT OF NANOWIRES

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In current microelectronics, silver nanowires (AgNWs) represent promising building blocks for transparent, flexible conducting films. Building devices like field-effect transistors requires additionally the uni-directional alignment of these thin films. Recently, we introduced the Grazing Incidence Spraying (GIS) approach to obtain linear alignment of AgNWs on flat substrates with an orientational order parameter $S_{2D} > 0.9$ [1,2]. Briefly, the linear shear forces arising from the liquid flow on the substrate direct this uni-axial alignment. As a spraying technique using nano-sized building blocks from large-scale synthesis, this approach can easily be implemented in existing production lines. Its compatibility with Layer-by-Layer techniques further allows the fabrication of multi-component systems or complex sandwich structures.

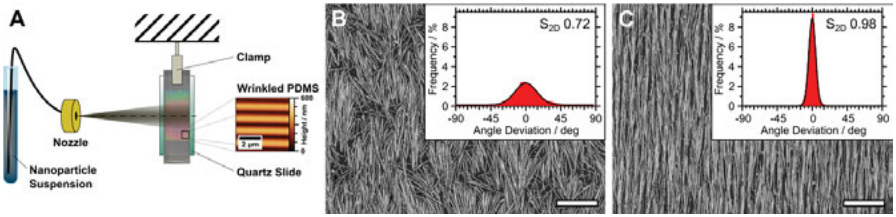

Figure 1. Grazing Incidence Spraying on corrugated receiver substrates enhances the linear order of AgNWs. (A) Schematic illustration of the setup. There is a significant improvement of unidirectional order from flat (B) to corrugated PDMS (C), as shown by the narrowed distribution of angular deviation from the predominant direction determined from SEM images. Scale bars: 5 µm.

Here, we report that corrugated, wrinkled receiver substrates for GIS significantly increase the AgNW ordering and extend the area of highly oriented AgNW thin films: the parallel channels foster the linear flow at the substrate-liquid interface and reduce turbulences. The resulting microscopic linear arrangement of AgNWs evaluated by scanning electron microscopy (SEM) reflects in a pronounced macroscopic optical anisotropy, measured by conventional polarized UV-vis-NIR spectroscopy. Surprisingly, the alignment along the corrugations is very robust concerning in-plane rotation of the substrate relative to the spraying direction. Even when spraying perpendicular to the channels, we find preferred alignment parallel to the wrinkles in regions close to the impact point of the spray. As a general technique for linear alignment independent of material (metal, semiconductor, nanofibrils), this robust method paves the way for large-scale production in microelectronics.

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TRAJECTORIES OF CERAMIC PARTICLES IN NONPOLAR MEDIA IN AN ELECTRIC FIELD

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Electrophoretic deposition (EPD) as technique for ceramic processing is gaining increasing interest in academia and industry as novel applications in the processing of advanced ceramic materials emerge [1]. This is not surprising regarding the high versatility, low costs and simple equipment needed in EPD. EPD rests on the motion and deposition of charged particles in media under the influence of an external electric field. Much effort has gone in the investigation of aqueous systems due to environmental reason as well as to minimize the troublesome formation of bubbles caused by electrolysis. However, other media are available for EPD like ethanol, acetone or toluene, which can be used instead [2–4]. As a result, EPD offers a plethora of experimental variables including different media and materials, like alumina, zirconia and silica in different shapes and sizes down to nanopowder [4–6]. Even biomaterials like hydroxyapatide can be deposited and open a field for fabrication of bio application [7]. Generally, the velocity of the particles in an electric field during EPD are described by the equations of Hückel and Smoluchowski. Nevertheless, other electrokinetic phenomena by induced charge on the particles may have to be taken into account [8]. Less effort has been put in the investigation of nonpolar, organic media with low dielectric constant so far. Here, we present results on the velocity of particles during EPD in nonpolar media. By measuring their velocity, we can investigate and evaluate the validity of Smoluchowski's and Hückel's equation and determine if additional electrokinetic phenomena occur during EPD.

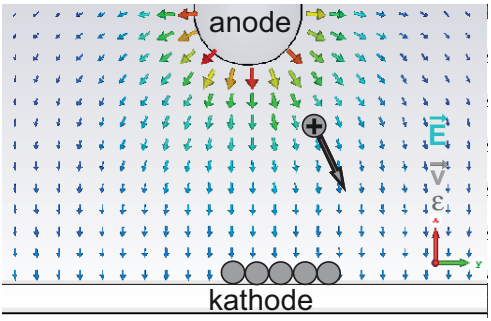

Figure 1. Particle with positive charge in an electric field *E* with velocity *v* dispersed in a medium with dielectric constant *ε*.

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A COFUNCTIONALIZATION STUDY ON SPHERICAL SILICA AND MAGNETITE PARTICLES TO EXAMINE THE REACTIVITY OF SURFACE GROUPS

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Surface functionalized nanoparticles are the basis for self-healing polymer nanocomposites. [1, 2] One of the most well-known triggered reactions for intrinsic self-healing properties is the thermoreversible Diels-Alder (DA) reaction.[3] In this work both scientific concepts were joined and nanocomposites with intrinsic thermoreversible crosslinking were studied as potential self-healing materials.

In nanocomposite synthesis the tailoring of the interface between the inorganic nanoparticles and the polymer matrix is one of the crucial parameters for the desired homogenous distribution of the inorganic moiety. We designed appropriate coupling agents for the attachment on surfaces with the required DA groups. Both, diene or dienophile can be attached via a spacer such as an alkyl chain to the particle surface using appropriate anchoring groups, like alkoxysilanes or phosphonic acids. The resulting surface-functionalized inorganic particles act as crosslinking units in the nanocomposite.

In this study we present our systematic studies on the influence of functional group density attached to the surface of silica and other particles on the self-healing capacity of the materials.[4] Major parameters beside the surface coverage are the temperature and the flexibility of the matrix.

One focus of our ongoing work is the modification of magnetic Fe_3O_4 nanoparticles. In this case, phosphonate coupling agents were used. Again, a cofunctionalization of DA groups with sterical less demanding methyl groups was carried out. A TG-IR evolved gas analysis reveals the dependence of the DA kinetics on the cofunctionalization ratio.

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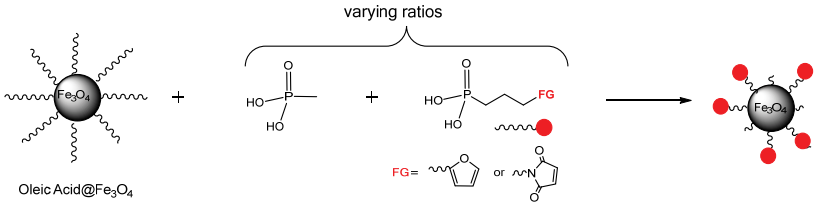

Figure 1. Cofunctionalization of magnetite using phosphonates.

SYNTHESIS OF SINGLE-CRYSTALLINE AND PERFECTLY ROUND SILVER NANOSPHERES AS BUILDING BLOCKS FOR LOW LOSS PLASMONIC MATERIALS

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We present a scalable and cost-efficient synthetic pathway to obtain highly monodisperse, single-crystalline and gold core at silver shell nanoparticles, which are close to a perfect sphere. These were synthesized by a three step, seed-mediated growth procedure (see Figure). In the first and second step, single-crystalline gold nanospheres of defined size were synthesized, followed by an epitaxial silver overgrowth resulting in Au@Ag nanocubes.[1] Finally, the corners of the Au@Ag nanocubes are selectively etched to Au@Ag nanospheres in a catalytic reaction step. The kinetics of this reaction were studied by variation of the synthesis parameters (*e.g.* catalyst concentration) and using time-resolved UV-Vis spectroscopy.

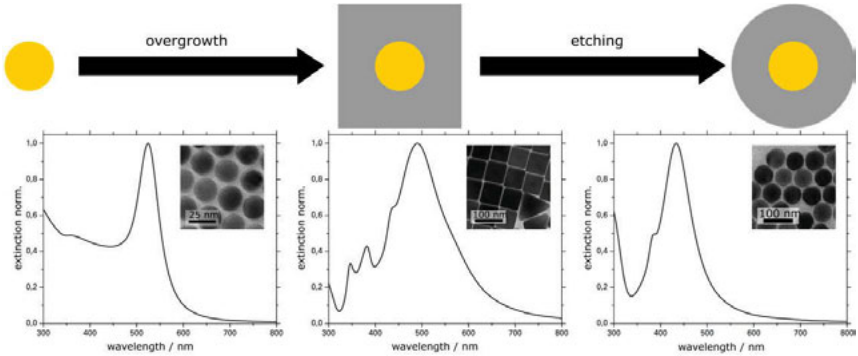

Figure 1: Schematic description of the synthetic pathway, corresponding UV-vis spectroscopy measurements and TEM images (inset). Synthetic pathway starting from spherical gold nanoparticles, overgrown to Au@Ag nanocubes and subsequently etched to highly monodisperse, single-crystalline and spherical Au@Ag nanoparticles, which are close to a perfect sphere.

Due to the high monodispersity of the final Au@Ag nanospheres, the particles show a narrow dipole plasmon resonance signature and a quadrupolar mode shown as left shoulder in the extinction cross-section. Spectroscopic results of all synthesis steps are in very well agreement with electromagnetic modeling (FDTD) methods. Based on the employed *living reaction conditions*,[2] the resulting size, edge-rounding from cube to sphere, and plasmon resonance position can be continuously adjusted over a wide range. With this scalable and cost-efficient synthesis approach we obtained ultra-spherical silver shelled nanoparticles, which can be used as unique building blocks for bottom-up assemblies[3] or to improve the efficiency in photovoltaics[4].

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ZWITTERIONIC MICROGELS AS MODEL SYSTEMS FOR AMPHOTERIC MICROGELS: PROPERTIES IN DILUTE AND CONCENTRATED SOLUTION

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Microgels are intramolecularly cross-linked, mostly spherical colloidal particles with properties from linear polymers, latex particles and macroscopic gels. They are swollen with a good solvent and the volume-swelling ratio is mainly determined by the polymer-solvent interactions.
Microgels based on *N*-isopropylacrylamide (NIPAm) show a so-called volume phase transition (VPT) in aqueous solution where the volume-swelling ratio depends strongly on temperature. PNIPAm microgels collapse when the volume phase transition temperature (VPTT), which is about 32 °C in water [1], is exceeded as the polymer-polymer interactions become more favorable as compared to the polymer-solvent interactions. The incorporation of different co-monomers, e.g. ionizable groups leads to multi-sensitive microgels, which are additionally sensitive to for example pH or salinity. The term amphoteric microgels refers to a very interesting sub-class of multi-sensitive microgels containing positive and negative charges simultaneously.
We used a zwitterionic co-monomer, which carries a positive and negative charge in one molecule, to synthesize a series of small zwitterionic microgels as model systems for amphoteric microgels with equal numbers of opposite charges and a defined distance between the opposite charges. [2,3]
The effect of the zwitterionic co-monomer content in the microgel network on the particle size and size distribution, the VPTT and the degree of swelling was investigated by various scattering techniques. [2] We found a different trend of the particle size with the amount of zwitterionic co-monomer in the microgel as was reported for a similar system of zwitterionic microgels [4]. We could attribute this contradictory behavior to an increasing surface activity of the zwitterionic co-monomer in mixtures with the surfactant sodium dodecylsulfate (SDS), which was used during the synthesis to control the particle size.
In a second study [3], the influence of the zwitterionic co-monomer on the pair-interaction potential was investigated. Therefore, static structure factors $S_M(q)$ of the series of zwitterionic microgels were measured using small angle neutron scattering (SANS). The experimentally determined $S_M(q)$ of the zwitterionic microgels were thereby compared with the classical hard sphere (HS) system and a reference system of pure PNIPAm. No significant influence of the zwitterionic co-monomer on the pair interaction potential was found as all static structure factors $S_M(q)$ could be described by the HS pair potential up to effective volume fractions $\phi_{eff} < 0.4$ only. [5]

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PHOTOINDUCED FORMATION OF SILVER NANOPARTICLES IN DNA-CONTAINING LYOTROPIC LIQUID CRYSTALS

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Metal nanoparticles have attracted a lot of attention in the field of colloidal and material science due to their unique electronic and optical properties. Because of the broad field of potential applications, there is also a growing interest in developing new green methods for the controlled synthesis of nanomaterials. Due to the rich polymorphism, lyotropic liquid crystals formed by amphiphilic molecules are particularly interesting templates to control size and morphology of nanoparticles.

Both DNA and surfactants have been successfully used for the synthesis of silver nanoparticles.
However, the templating properties of DNA-cationic surfactant complexes are almost unknown.
In this contribution, we report the photochemical synthesis of silver nanoparticles in various lyotropic liquid crystalline phases formed by the dodecyltrimethylammonium-DNA complex in the presence of an aqueous solution of 2-hydroxypropyl-β-cyclodextrin [1]. Silver nanoparticles were synthesized via photoreduction of the DNA-Ag^+ complexes where the Ag^+ ions are embedded in the DNA helical structure [2]. The reported method does not require any external reducing or stabilizing agents since DNA acts as a photosensitizing agent and a template for the nanoparticle formation. Size and morphology of the resulting nanoparticles can be controlled by the Ag^+/DNA ratio and the structure of the liquid crystalline phase.

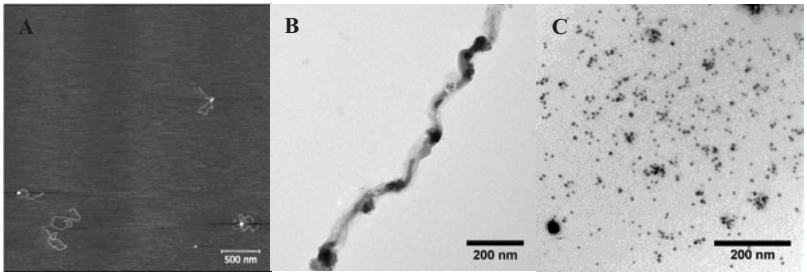

Figure 1. AFM (A) and TEM (B) images showing the formation of particles in DNA and TEM image of nanoparticles synthesized in tetragonal phase (C).

The effect of the formation of silver nanoparticles on the lyotropic liquid crystalline phase was investigated by small angle x-ray scattering, ^2H and ^{31}P NMR spectroscopy. The influence of the template mesophase on the formation rate and nanoparticle size and morphology was studied using UV-spectroscopy, TEM and AFM.

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TAILORED ELECTRIC-FIELD ENHANCEMENT: COMPREHENDING PLASMONICS OF AXISYMMETRIC NANORATTLES

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Nanorattles are metal-insulator-metal nanoparticles, which were synthesized starting from a gold core [1], followed by a silver overgrowth [2], and a final galvanic replacement reaction step. Due to their intrinsic nanocavity between core and shell, these nanorattles have been identified as a promising class of nanoparticles for sensing, because they offer high field enhancement [3]. Limiting factors are reproducibility and loss of axial symmetry due to the movable metal-core resulting in fluctuation of nanocavity size and consequently enhancement factor variations. We present a novel approach to ensure robust fixation of the central gold rod in a well-defined frame, which results in an axisymmetric nanorattle. Therefore, the desired axial symmetry can be guaranteed, as systematic studies by small-angle X-ray scattering (SAXS) show. Based on the retrieved geometry, finite-difference time-domain (FDTD) simulations predict high and homogenous field enhancement. These predictions are in excellent agreement with electron energy-loss spectroscopy (EELS) mapping on single-particle level and with various UV-vis-NIR spectroscopy techniques on the macroscopic level. With this synthesis and comprehensive characterization methods, a reliable nanoparticle cavity is now available and well understood for applications where field enhancement is crucial [4,5].

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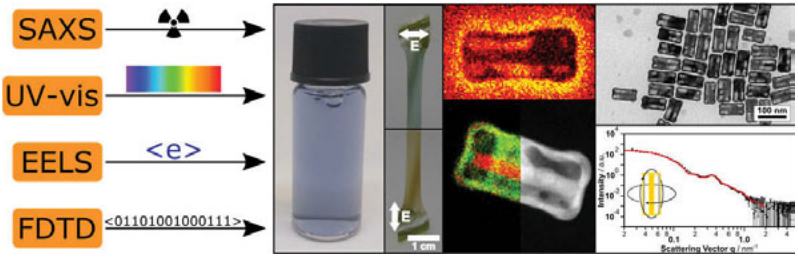

Figure 1. We performed SAXS measurements, advanced UV-vis-NIR spectroscopy, and FDTD calculations on axisymmetric nanorattles and the previously synthesized particles, as well as EELS measurements on axisymmetric nanorattles in order to comprehend the plasmonic properties for tailored field enhancement.

ANTI-ICING AND DE-ICING SURFACES BASED ON CORE-SHELL PARTICLES AS BUILDING BLOCKS: DOES HETEROGENEITY MATTER?

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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 based 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 new approaches for the design of heterogeneous surfaces with anti-icing and de-icing capabilities based on polymer-modified core-shell particles. First, we use a mixture of different types of particles with controlled and tuneable chemical composition and size in various ratios to form heterogeneous surfaces and to fundamentally investigate their wettability, ice nucleation and grow as well as ice adhesion.[4] We will discuss the impact of chemical and topographical heterogeneities on the mentioned above phenomena.

Second, we compare these results with the findings obtained on a heterogeneous surfaces made of hybrid polymeric modified Janus particles. The heterogeneous surfaces formed by Janus particles exhibit special surface “edge” morphologies and show a synergism of two main effects, the area is free of ice and they form large unstable dendrites at the edges of heterogeneities. This leads to an extremely low ice adhesion.[5]

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PHENYLTRIMETHOXYSILANE AS SURFMER FOR THE ONE-POT SYNTHESIS OF SUB-MICRON SIZED SPHERES WITH COMPLEX ARCHITECTURES

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Sub-micron sized hollow, multiporous and hybrid spheres are interesting building blocks for nanocomposite coatings and polymer nanocomposites. In spite of their large potential for application, these particles are not yet widely used in commercial products. This is caused by the lack of efficient synthesis routes with stringent control over particle size and architecture that are suitable for scale up.

Here we present a facile one pot synthesis of sub-micron sized hollow, multiporous and hybrid organosilica spheres, using only low cost, commercially available chemicals, that can be performed in a standard emulsion reactor. The synthesis is based on an oil-in-water emulsion and merely involves one organosilica precursor, phenyltrimethoxysilane (Ph-TMS), that serves as monomer, precursor for a surface active species and oil phase [1, 2, 3]. For this reason no free surfactant remains in the particle dispersion after the synthesis.

We managed to prepare organosilica spheres with a programmable outer diameter between approx. 300 and 1000 nm and a narrow size distribution, simply by varying the volume ratio Ph-TMS to water. As the particles grow from the outside inwards, the average outer diameter is fixed in an early stage of the reaction. For hollow particles the shell thickness and core size could therefore be tuned through variation of the reaction time. Through addition of inert solvents to the dispersed phase, whilst keeping all other reaction parameters constant, we managed to synthesize sub-micron sized multiporous spheres. Addition of organic monomer led to the formation of hybrid particles with different architectures, depending on the ratio organosiloxane to organic monomer.

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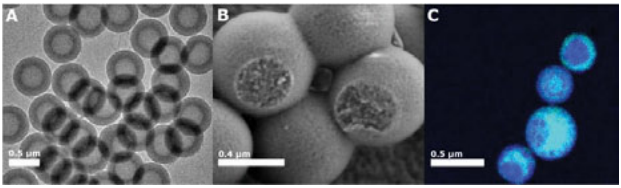

Figure 1. A) SEM-image of hollow phenylsiloxane particles; B) STEM-image of multiporous phenylsiloxane particles; C) STEM-EDS mapping of hybrid particles obtained from the mixture Ph-TMS/styrene (volume ratio Ph-TMS: styrene = 1:1). The light blue areas are Si-rich and the dark blue areas are C-rich.

TWO-DIMENSIONAL MICROGELS (JANUS PARTICLES) FORMED AT THE INTERFACE BETWEEN OIL AND WATER – SYNTHESIS, PROPERTIES AND TECHNOLOGICAL APPLICATIONS

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Microgels are colloidal particles of polymer networks with typical diameters between 100 nm and 100 µm. These small sizes lead to large surface areas, which have attracted considerable interest as model colloids and for various potential applications[1]. Previous publications mainly focused on the synthesis and features of three-dimensional microgels. In this poster, we shall for the first time describe the typical properties of two-dimensional microgels. We obtained these special aggregates using the polymerization of amphiphilic monomers at the interface between oil and water. The reactive monomer n-octadecyltrichlorosilane (OTS) was first dissolved in dodecane, and after the addition of water an interfacial polymerization immediately took place[2] [Fig. 1]. If OTS was used below the threshold concentration c^*, two-dimensional microgels were formed instead of coherent film structures as shown in *Brewster-angle microscopic* images [Fig. 2]. These aggregates can also be denoted as Janus particles, since they have a hydrophilic and a hydrophobic surface. In the framework of this research project, we examined the properties of these special microgels in more detail, with a special focus set on the applicability of these particles to stabilize foams and emulsions.

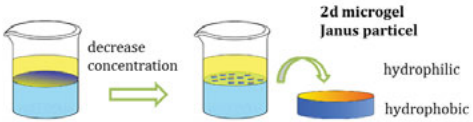

Fig. 1: Schematic drawing of the formation of two-dimensional microgels at the interface between oil and water by polycondensation processes of n-octadecyltrichlorosilane (OTS).

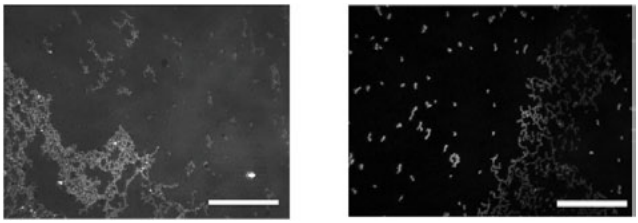

Fig. 2: *Brewster-angle microscopic* images of OTS at the water surface after compression in the *Langmuir through*. **Left**: Coherent OTS film structures obtained at elevated concentrations ($c > c^*$). **Right**: OTS microgel particles obtained in the regime below c^*.

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COLLOIDAL ROUTE FOR THE SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALLY STABILIZED GOLD NANOPARTICLES THROUGH ULTRASONIC SPRAY PYROLYSIS

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The investigation reports the successful synthesis of colloidal spherically shaped AuNPs with Gold (III) acetate and Gold (III) Chloride through USP. [1,2] The synthesis parameters, such as concentration, evaporation & reaction temperature and gas flow rate, were varied in order to observe its effect on the final characteristics (morphology, purity and concentration) of these AuNPs through TGA-DT, TEM-EDX, DLS, FTIR, ICP-MS and UV-vis spectroscopy. These AuNPs were stabilized with different mediums such as PEG-5000 and sodium citrate. [3]

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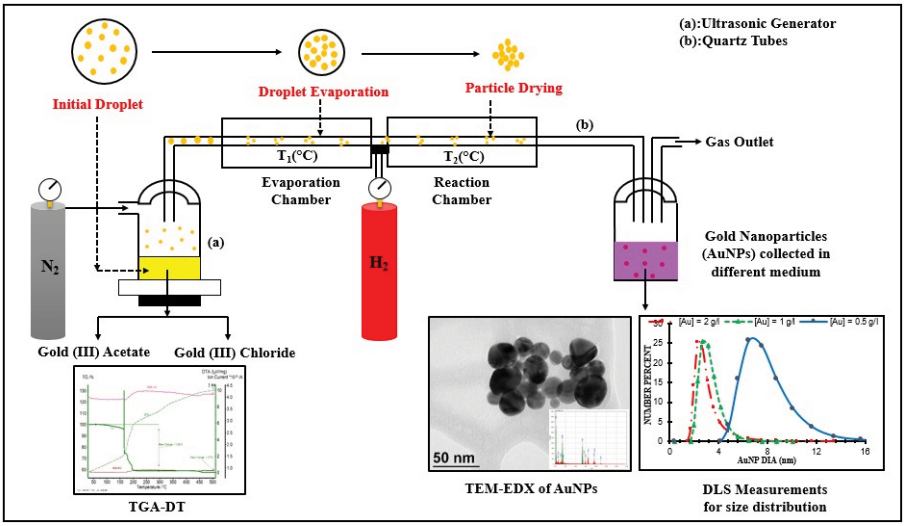

Figure 1. Schematic Diagram of Experimental Setup of Ultrasonic Spray Pyrolysis comprised of Ultrasonic Generator, Evaporation Chamber, Reaction Chamber, Quartz Transport Tubes and Collection bottles for AuNPs.

NEW STRATEGIES TOWARDS RATIONAL DESIGN OF MULTIFUNCTIONAL INTERFACES BASED ON POLYMERS AND ANISOTROPIC COLLOIDS

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Our group aims for a rational design of interfaces with tailored and controllable adhesion properties under dry, wet, underwater or extremely cold conditions/icing environmental conditions. We address key questions concerning the molecular origins of wetting and adhesion as well as their correlation to chemical functionality, polymer architectures, surface charge, structural and topographical features and elasticity of materials.

For this we develop new chemical approaches for the targeted interface design and modification using polymer grafting and coatings with core-shell hybrid colloids. [1-2] Herein, I will present and discuss new strategies for design of surfaces, which combine anti-icing and de-icing as well as anti-(bio) fouling and fouling release properties in one material. [3-7]

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FORCE MEASUREMENTS OF MICROSPHERES TRAPPED WITH A LASER AT HIGH HYDROSTATIC PRESSURE

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Colloids and microspheres are often used as a probe for investigations of surface interactions. One instance is colloidal probe force microscopy. Here, we use a different approach; in which a microbead is trapped with optical tweezers. One big advantage of using optical means is that no mechanical access is required to the sample volume, thus enabling an increase in hydrostatic pressure of the environment (Fig. 1). Using this set-up the force between a glass bead and a glass wall were investigated in water at hydrostatic pressures up to 1 kbar [1].

At my poster, I will explain the basic principles of this set-up, discuss the procedure to record force distance curves, and evaluate Brownian motion of the colloid that is trapped. One interesting extension to the set-up is to add heating. This extension allows investigating supercritical CO_2, with a relatively mild critical point at 73 bars and 31 °C. Supercritical CO_2 is a commonly used solvent in extraction and polymer synthesis. Supercritical CO_2 was also proposed for storage of CO_2 or as a heat carrier [2]. Surface forces play a role in e.g., interactions between synthesized polymer colloids, or in rock layers for the case of CO_2 storage in old gas or oil reservoirs. However, there are very few reports on direct measurements of surface forces in supercritical CO_2 [3].

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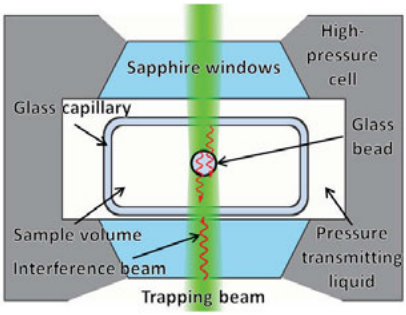

Figure 1. Schematic of the high-pressure sample cell used in the set-up. The sample volume was separated from the (dirty) pressure-transmitting liquid by means of a glass capillary, which was sealed by a non-dissolving pressure-transmitting paste. The capillary contains the beads, dispersed in a NaCl solution. Due to the sapphire windows optical manipulation and detection are possible. Note that the image is not drawn to scale. Image reproduced from [1].

INSIGHT IN THE VISCOELASTIC CHARACTERISTICS OF GELATIN NANOPARTICLES AS DRUG DELIVERY SYSTEM

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In the research of drug delivery systems, nanoparticles (NPs) are in focus due to their advantages in drug targeting. In recent years the elasticity was shown to have a high impact on the retention time in the blood and the cellular uptake [1]. Both are important parameters for the successful delivery of drugs to their site of action. Even though crosslinked gelatin NPs are well studied and characterized their stiffness and its tenability remains unknown.
The aim of this study was to design a setup to measure and evaluate the viscoelastic parameters of gelatin NPs. Therefore crosslinked NPs with an average hydrodynamic diameter of around 200 nm are used. First of all, we investigated different crosslinking reaction times which should lead to differently crosslinked and hence variously elastic particles.

The viscoelasticity can be determined by force-distance-measurement with atomic force microscopy (AFM). When the tip and the NPs are in contact, either the force or the height is kept constant for 10 sec. The resulting creep and force relaxation curves can be fitted to the Zener model [2] by a single exponential decay and the parameters c_0, c_1 and x_1 or a_0, a_1 and tau_1 are extracted. To check the linear relation of stress and strain we applied different forces between 0.5 and 2.5 nN. The read out were the time-dependent parameters x_1 and tau_1. Their consistency is shown and proves the linearity of the relation. The linear dependence between stress and strain was examined for particles with crosslinking times of 3, 15 and 18 hours.
For the following experiments, a load of 1 nN was chosen. This allows evaluating the obtained results by Zener´s model. From the extracted parameters the elasticity is calculated. For E_1 and E_∞ there is a slight increase visible in the elasticity from 6 to 18 hours crosslinking time. The NPs which are crosslinked for only 3 h do not show this trend but the standard deviation is very high for these particles. Even though there is a small increase in the elasticity the aging of crosslinked gelatin nanoparticles after a storage time of approx. 4 weeks at 4 °C has an influence on the stiffness which is much bigger. For E_0 there is no influence observed of the crosslinking time looking at the freshly produced NPs. With the influence of the storage time, this changes whereas the elasticity increases from 40 to 69 MPa for the 15 h crosslinked NPs the values for the NPs with 18 h crosslinking are more than double as high after storage. The viscous characteristics show the same tendency as E_1 and E_∞.

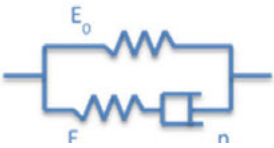

Figure 1. Zener´s model. E indicates the elasticity and η the viscosity. E_0 and E_1 is E_∞.

From the performed experiments, we can conclude that the crosslinked gelatin NPs show linear (visco)elasticity in the examined range. Furthermore, the crosslinking time of the NPs seems to have only a small or no influence on the stiffness of the particles. In contrast, the aging of the NPs showed a high influence to our NPs and changed the stiffness clearly.

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SELF-ASSEMBLY OF LOW MOLECULAR WEIGHT GELLANTS IN PRESENCE OF SURFACTANTS

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Low molecular weight gellants (LMWGs) with a molecular mass lower than 1000Da are capable of spontaneous thermo-reversible non-covalent orthogonal self-assembling into a stable three-dimensional network of solid fibers that are able to immobilize the solvent in the meshes[1]. LMWGs often show an orthogonal self-assembled behavior which means that two self-assembled structures coexist within the same system without influencing one another. In recent times, LMWGs have been developed as organogellants and it has been observed that the ability to gelate water was found by serendipity rather than by design [2]. Now low molecular weight hydrogellants have a growing interest in the scientific literature since it is known that they include positive aspects like the simplicity of their synthesis, setting of their properties, high level of molecular organization and their biocompatibility. Furthermore, a small amount of the gellant agent is sufficient to form a strong gel network [3]. They have an increasing potential in industrial, pharmaceutical, cosmetic and food sections [4]. When the LMWGs are contacted with amphiphilic additives, a complex rheology can occur. In this work, the interactions of low molecular weight hydrogellants are studied in mixture with surfactant molecules to work out the effects of different surfactant concentrations on the rheological behavior of LMWGs and to understand their impact on the gel network.

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STRUCTURE FORMATION OF WET-DEPOSITED Au NANOROD THIN FILM OBSERVED USING TWO-DIMENSIONAL CORRELATION GRAZING INCIDENCE SMALL-ANGLE X-RAY SCATTERING

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Anisotropic Au nanoparticles like nanorods that lend material anisotropic properties have attracted broad interest of material scientists, especially in electronics and optics.[1] Our work focuses on the wet preparation of anisotropic nanoparticle thin films. We are interested in the localized alignment of nanoparticles during the drying of thin films of their liquid dispersion. Synchrotron based micro-beam grazing incidence small-angle X-ray scattering (μGISAXS)[2] experiments combined with generalized two-dimensional correlation (2DC) analysis[3] gives insight into structure formation in real time at high time resolution. This correlation analysis determines the direction of intensity changes ("synchronous spectrum", Figure 1a) or sequences of events ("asynchronous spectrum", Figure 1b) during the first 15 s after coating. Figure 1c shows a typical instantaneous 2DC-GISASX scattering image of the film 15 s after coating. Four typical Yoneda peaks from surfactant, solvent, substrate and Au are marked with arrows. We find the changes of the Yoneda peaks of surfactant, solvent, substrate and Au during drying are positively correlated with each other. The change in the solvent Yoneda peak during drying is faster than that of the surfactant, that of Au, and that of the substrate, indicating that structure formation in the drying nanoparticle thin film is first dominated by solvent evaporation, then by surfactant layer formation, and finally by Au layer formation. We demonstrate that 2DC-GISAXS is a powerful tool in deciphering the structure formation of wet-deposited nanoparticle thin film.

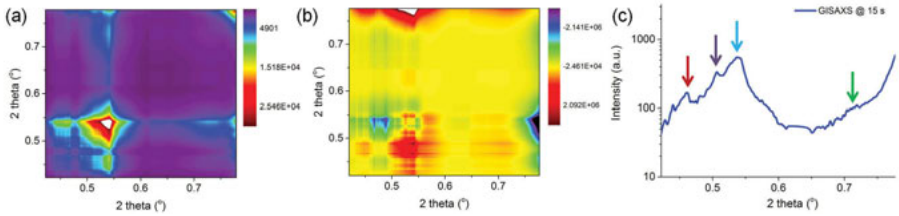

Figure 1. (a) Synchronous 2D correlation GISAXS spectrum showing variations of the Yoneda peaks' intensity during the first 15 s after coating. (b) Asynchronous 2D correlation GISAXS spectrum showing sequential changes of the Yoneda peaks' intensities during the first 15 s after coating. (c) Vertical integration of GISAXS scattering showing Yoneda peaks of surfactant, solvent, substrate and Au, indicated with arrows from left to right. Colorbars in panels a and b indicate the magnitude and sign of the correlation strength.

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MACROMOLECULAR HPMA-BASED DRUG DELIVERY SYSTEM – BEHAVIOR IN PROTEIN ENVIRONMENT

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Copolymers based on N-(2-hydroxypropyl)methacrylamide (HPMA) having cholesterol side groups self-assemble into ellipsoidal nanoparticles (NPs) in aqueous solution [1,2], with the core and the shell being formed by cholesterol and by HPMA, respectively. They have been proposed as drug carriers. However, little is known on their behavior in human blood environment.

In our synchrotron small-angle X-ray scattering (SAXS) experiments at beamline P12, EMBL, HPMA copolymers bearing 2.1 mole% cholesterol, with ($HPMA_{50k}$) and without ($HPMA_{33k}$) 6 wt% anticancer drug doxorubicin (Dox) bound to them were investigated in a phosphate buffered saline (PBS) solution of human serum albumin (HSA). Upon addition of HSA to $HPMA_{33k}$, a decrease in forward scattering as well as a shift of the shoulder towards lower q values are observed (Fig. 1a). The model fits confirm a decrease in the major axis of the NPs along with a slight increase in the minor axis (Fig. 1b). This is in accordance with the well-known fact that the role of HSA in the body is to transport hydrophobic ligands, among others, cholesterol. When Dox is present ($HPMA_{50k}$), a good overlap of the SAXS curves having varied HSA concentration is observed (Fig.1c), meaning that there is no structural change of the NP. However, dynamic light scattering (DLS) results on the same polymer show that the hydrodynamic radius of the NP, increases with HSA concentration (Fig.1c inset) [3]. Therefore, we speculate that HSA adsorbs onto the NP's surface by binding to Dox, without influencing the core [4].

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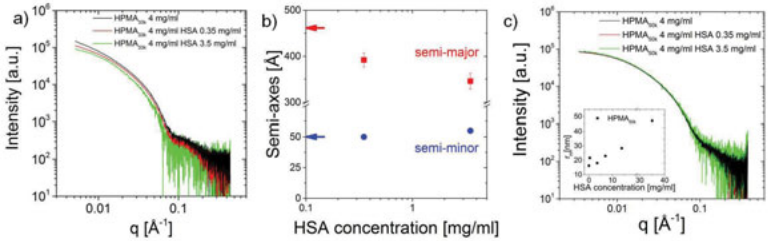

Figure 1. a) SAXS curves of $HPMA_{33k}$/HSA mixed solutions. b) Corresponding fitting results. The two arrows to the left indicate radii of the NPs without HSA. c) SAXS curves of $HPMA_{50k}$/HSA mixed solutions. The inset shows DLS result from the same sample.

IMPACT OF VISCOUS DROPLETS ON SUPERAMPHIPHOBIC SURFACES

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Superamphiphobic coating is promising for various applications in industry, e.g. self-cleaning windows, where the impingement of droplets on the surface is commonly encountered [1]. In this work, we experimentally investigated the impact of droplets with much different viscosity (1-150 mPa s) on superamphiphobic surfaces. We found that droplets can rebound from the superamphiphobic surface when the impact velocity is larger than a critical value, which linearly increases with the liquid viscosity. Droplets with higher viscosity spread, retract slower, and eventually rebound lower and fewer times than that of low viscous droplets. These findings have important implications for surface engineers to use superamphiphobic coatings. Furthermore, we measured the maximum spreading factors for droplet impact on superamphiphobic surfaces and performed a simple scaling analysis based on energy conversation to describe its relationship to Weber number and Reynolds number. In comparison to other models [2-6], it was found that our model could well predict the maximum spreading factors of viscous droplets impacting on the superamphiphobic surface, especially for high-viscosity droplets.

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HEMATITE α-Fe_2O_3 NANOPARTICLES OF GREEN SYNTHESIS AS AN ACTIVE MATERIAL IN SUPERCAPACITORS APPLICATION

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As an n-type semiconductor, hematite (α -Fe_2O_3) has attracted a great deal of attention from researchers in different fields because of its nontoxicity, low cost, high stability under ambient conditions, and multiple functions. It has been intensively investigated for different applications such as lithium batteries [1-2], sensors [3], catalysts, [4] pigments [5].

In particular, α -Fe_2O_3 is chosen as supercapacitor electrode due to its large theoretical specific capacitance (3625 F.g-1), low cost, thermal stability, corrosion resistant, abundant in nature and environmental friendliness [6].

In this work, hematite nanoparticles are prepared by a simple green method at low temperature (Polyol) using $Fe(NO_3)_3$-$6H_2O$ as a reagent (0.6M), olive leaves extraction as a surfactant and distilled water as a solvent. In order to understand the influence of the extract solution of olive leaves, α-Fe_2O_3 powders has been characterized by XRD Pattern, Raman spectroscopy, FTIR measurements, BET for the specific surface area and Field emission scanning electron microscopy.

This material α-Fe_2O_3 could be used as active material for the energy storage application where we have check this material for one of the supercapacitors application as active material.

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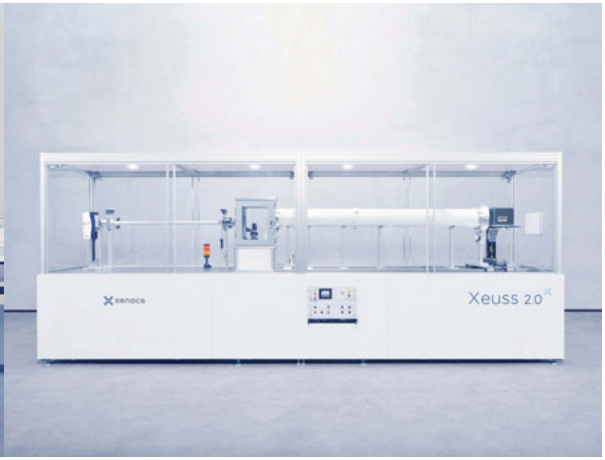

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