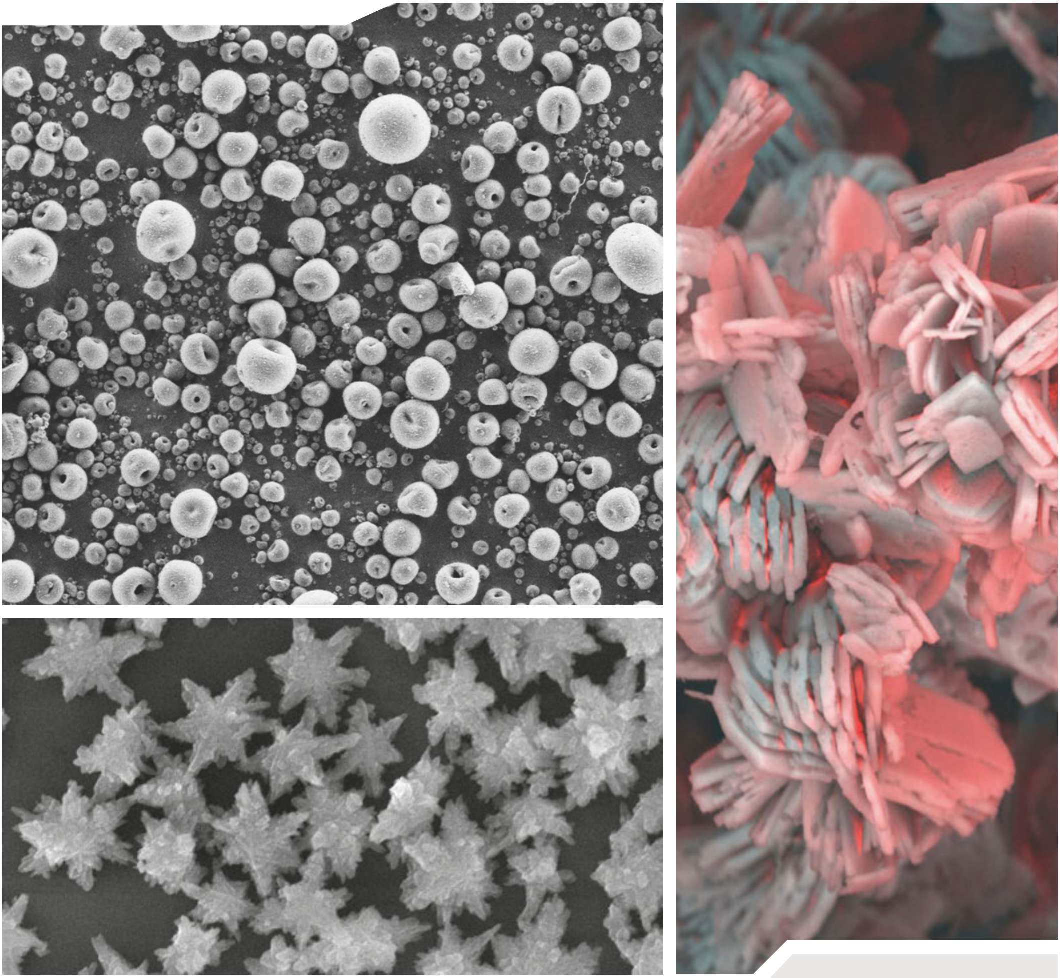

PARTICLE-BASED MATERIALS SYMPOSIUM

NOVEMBER 9–10, 2017
SAARBRÜCKEN, GERMANY

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COVER IMAGES:	Claudia Stauch, Karl Mandel, Fraunhofer ISC: Supraparticles formed by spray-dried silica nanoparticles (top)
	Saeedeh Golkar, FAU: Iron oxide nanostars (bottom)
	Marcus Koch, Sener Albayrak, INM: Zinc phosphate nanoparticles (right)
ABSTRACT BOOK:	Dominik Hell, INM
ISBN:	978-3-00-058162-5

PROGRAM

THURSDAY, NOVEMBER 9, 2017

09:00 Registration and coffee

09:50 Welcome

SESSION 1: **New Building Blocks**

Chair: Karl Mandel

10:00 Shape and Interaction Patchiness for the Self-Assembly of Nanocrystals

Michael Engel, FAU Erlangen-Nürnberg, Germany

10:20 Zwitterionic Supraparticles as Building Blocks for Interlocking Particle Assemblies

Michael Maas, University of Bremen, Germany

10:40 Fabrication and Study of Model Rough Colloids: Rheology and Tribology of Shear-Thickening Systems

Chiao-Peng Hsu, ETH Zürich, Switzerland

11:00 Hybrid Nanocolloids by Shadow Growth

Hyeon-Ho Jeong, Max Planck Institute for Intelligent Systems, Stuttgart, Germany

11:20 Triblock Terpolymer Microparticles

André H. Gröschel, University of Duisburg-Essen, Germany

11:40 Nanoparticle-Based Hierarchical Aggregates with Tailored Structure and Functional Properties

Georg Garnweitner, TU Braunschweig, Germany

12:00 Lunch

SESSION 2: **Optics and Plasmonics I**

Chair: Alexander Kühne

13:00 Colloidal Crystallization in Spherical Confinements: Structure and Optical Properties

Nicolas Vogel, FAU Erlangen-Nürnberg, Germany

13:20 Single-Step Processing of Conjugated Polymer Particles towards Organic Light-Emitting Capacitors

Bastian Haehnle, DWI - Leibniz-Institute for Interactive Materials, Aachen, Germany

13:40 Enhancement of Photoluminescence of a Carbon Dot System through Polymer Nanoparticle Interaction

Rebecca Momper, Max-Planck Institute for Polymer Research, Mainz, Germany

14:00	Porous Stimuli-Responsive Block Copolymer and Colloidal Architectures *Markus Gallei*, Technische Universität Darmstadt, Germany
14:20	Anisotropic Polymer Nanoparticles with Tunable Emission Wavelengths by Intersegmental Chain Packing *Julian Dominik Ruiz Perez*, University of Konstanz, Germany
14:40	Electric Field Optically Responsive Nanowire Colloids *Andris Sutka*, Riga Technical University, Latvia
15:00	Coffee break
	SESSION 3: **Biological Materials** Chair: Tobias Kraus
15:20	Particles as Building Blocks for Tissue Regenerative Materials *Laura de Laporte*, DWI - Leibniz-Institute for Interactive Materials, Aachen, Germany
15:40 – 17:30	POSTER SESSION
19:00	Conference Dinner “Kunstwerk Saarbrücken – Bistro Malzeit”

FRIDAY, NOVEMBER 10, 2017

	SESSION 4: **Catalysis** Chair: Tobias Kraus
09:00	From Colloids to Supported Catalysts *Jörg Polte*, Humboldt Universität zu Berlin, Germany
09:20	Photocatalytic and Magnetic Porous Cellulose-Based Nanocomposites Prepared by a Green Method *Alexandra S. M. Wittmar*, Universität Duisburg-Essen, Germany
	SESSION 5: **Magnetic Materials** Chair: Robin Klupp-Taylor
09:40	Functional Supraparticles From Iron Oxide Based Nano-Building-Blocks *Karl Mandel*, Fraunhofer ISC, Würzburg, Germany
10:00	Magnetic Field-Induced Elastic Deformations in Ni-Nanorod/PAM-Hydrogel Composites *Andreas Tschöpe*, Saarland University, Saarbrücken, Germany

10:20 Magneto-Elastomeric Nanocomposites with Supramolecular Activity

Margarita Kruteva, Jülich Centre for Neutron Science, Germany

10:40 3D Macroscale Self-Assembly

Leon Abelmann, KIST Europe, Saarbrücken, Germany

11:00 Coffee break

SESSION 6: **Electronic and Thermal Materials**
Chair: Matthias Karg

11:20 Block Copolymer Template-Directed Synthesis of Composite Particles with Complex Nanostructures

Shilin Mei, Helmholtz-Zentrum Berlin für Materialien und Energie, Germany

11:40 Structure-Transport Correlations in Superlattices of Coupled Organic-Inorganic Nanostructures

Marcus Scheele, University of Tuebingen, Germany

12:00 Inkjet Printing of CdSe/CdS Nanorods on Conducting Surfaces

Franziska Lübkemann, Leibniz Universität Hannover, Germany

12:20 Lunch

SESSION 7: **Optics and Plasmonics II**
Chair: Nicolas Vogel

13:20 Interface-Mediated Self-Assembly of Soft, Plasmonic Core-Shell Colloids: Structural Control and Functionality

Matthias Karg, Heinrich-Heine-University Duesseldorf, Germany

13:40 Looking for Synergetic Effects in Molecular Plasmonics by Hybrid Functional Nanostructures

Tobias A. F. König, Leibniz-Institut für Polymerforschung Dresden, Germany

14:00 Energy Transfer between Hybrid Metal-Halide Perovskites and Conjugated Polymer Colloids

Annabel Mikosch, DWI - Leibniz-Institute for Interactive Materials, Aachen, Germany

14:20 Monolayer Formation of Gold Nanotriangles for SERS Monitoring of Plasmon-Driven Catalytic Reactions

Ferenc Liebig, University of Potsdam, Germany

14:40 Closing words / Poster Award

▶ SESSION 1

New Building Blocks

O1-1

SHAPE AND INTERACTION PATCHINESS FOR THE SELF-ASSEMBLY OF NANOCRYSTALS

Michael Engel

Institute for Multiscale Simulation, Friedrich-Alexander University Erlangen-Nürnberg, Erlangen, Germany

Chemical methods enable the preparation of colloidal nanocrystals with uniform size and shape. The superlattices these Brownian objects order into depends on particle geometry and enthalpic interactions. Leveraging non-traditional surface chemistries and assembly environments promises control over superlattice structure and the production of non-bulk assemblies. Fundamental principles governing nanocrystal self-assembly have been derived from hard and soft particle perspectives borrowed from the comparatively established fields of micrometer colloids and block copolymer assembly [1].

In this contribution, we discuss recent advancements in the modeling of complex nanoparticle self-assembly processes with the help of computer simulations. The performance of hard particle Monte Carlo simulations is improved by the introduction of collective moves. This allows us to study entropically driven self-assembly significantly faster than before. The assembly of DNA ligand-modified triangular bipyramids into clathrate colloidal crystals is modeled with a generalized patchy particle model [2]. Tetrahedral order found in many ubiquitous substances such as water, silica, and elements of the carbon family can be mimicked in hard particle systems, and with it non-classical, two-step nucleation and growth. These findings demonstrate, for the first time, that nanocrystal shape alone affects not only superlattice structure but also the pathway and kinetics of superlattice formation.

[1] MA Boles, M Engel, DV Talapin, Chem. Rev. 116 (2016), p. 11220.
[2] H Lin et al., Science 355 (2017), p. 931.

O1-2

ZWITTERIONIC SUPRAPARTICLES AS BUILDING BLOCKS FOR INTERLOCKING PARTICLE ASSEMBLIES

Michael Maas[1,2], Kurosch Rezwan[1,2]

[1] Advanced Ceramics, University of Bremen, Bremen, Germany
[2] MAPEX Centre of Materials and Processes, University of Bremen, Bremen, Germany

The colloidal assembly of individually dispersed nanoparticles into well-defined clusters consisting of only a few nanoparticles promises the scalable synthesis of advanced multifunctional supraparticles with well-defined surface moieties, also known as patchy particles. However, electrostatic heteroagglomeration, which is one of the simplest approaches to colloidal assembly, usually results in the uncontrolled precipitation of large particle clusters. In this work, we demonstrate the assembly of oppositely charged silica particles into well-defined core-satellite arrangements via electrostatic agglomeration. To achieve controlled heteroagglomeration, we studied the assembly of oppositely charged silica particles using particles with different sizes ranging from 5 nm to 150 nm at various concentrations. While we achieved controlled agglomeration into colloidally stable and well-defined supraparticles, we observed an uneven covering of a central particles with around 1-6 satellite particles absorbed to the central particle. This behavior is not predicted by simple DLVO theory which would anticipate an even spacing of the satellite particles on the core. We explain our observations by taking into account the interactions of the adsorbing particles within the ionic cloud of the central particle [1]. Based on these findings, zwitterionic supraparticles consisting of positively charged APTES-coated silica particles with diameters of 150 nm and negatively charged silica particles with diameters of 80 nm at a ratio of around 1 to 6 big particles to small particles were tested for their ability to assemble into stable, interlocking thin films. To this end, we studied the formation of Pickering emulsions stabilized by such particles. The zwitterionic core-satellite particles showed strongly increased surface activity compared to single particles. Interfacial dilatational rheological tests supported the observations from the emulsion tests. Accordingly, we show that this relatively unordered ensemble of supraparticles is able to present well-defined functionality at a higher hierarchical level potentially leading to new particle-based materials.

[1] Maas, M.*, Silvério, C. C., Laube, J., Rezwan, K. Electrostatic Assembly of Zwitterionic and Amphiphilic Supraparticles. Journal of Colloid and Interface Science 2017, 501, 256–266.

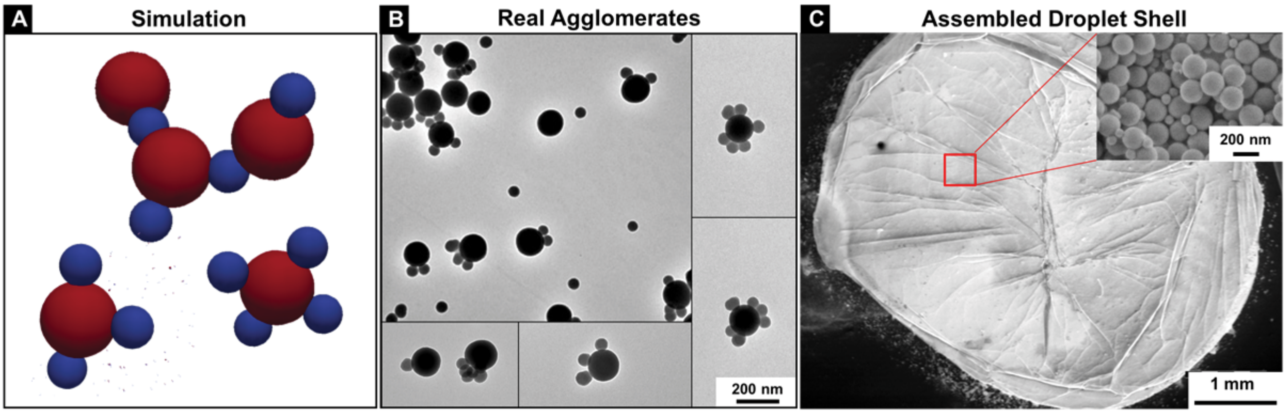

Figure 1. Electrostatic heteroaggregation of zwitterionic supraparticles (A) simple model based on DLVO interactions, (B) zwitterionic supraparticles, (C) thin film assembled from these supraparticles at the surface of an emulsion droplet.

O1-3

FABRICATION AND STUDY OF MODEL ROUGH COLLOIDS: RHEOLOGY AND TRIBOLOGY OF SHEAR-THICKENING SYSTEMS

Chiao-Peng Hsu, Michele Zanini, Shivaprakash Ramakrishna, Nicholas D. Spencer and Lucio Isa

Department of Materials, ETH Zürich, Zürich, Switzerland

Shear thickening is a spectacular and yet only partly explained phenomenon with tremendous technological implications, spanning from shock-absorbing materials to the processing of slurries, such as cementitious materials. In particular, the role played by the surface roughness of the flowing particles on the shear-thickening behavior of dense colloidal suspensions remains unexplored [1]. We aim to shed light on the role of roughness on the onset of shear thickening by investigating the correlation between macroscopic rheological properties and microscopic tribology of model rough colloids.

In this work, we present the fabrication of raspberry-like silica particles with tunable nanoscale surface roughness [2]. We then exaime their compressive rheology via sedimentation experiments to measure their maximum packing fraction [3]. Intrerestingly, we observe a dependence of the sediment's volume fraction on surface roughness. The same behavior is also found by measuring the critical shear rate for the onset of shear thickening, confirming the correlation between the two macroscopic rheological quantities [3]. Here, we propose a novel microscopic mechanism to explain these obervations based on nanoasperity interlocking.

In order to interrogate this mechanism, we have produced planar surfaces with a surface morphology comparable to that of the rough colloids and we have measured their friction using lateral force microscopy with rough colloidal probes. The nanotribology characterization reveals that the rough surfaces with the highest friction correspond to the particles with the lowest maximum packing fraction, which are also those that shear thicken first. The surface furthermore displays stick-slip frictional behavior, indicating that interlocking of the probe with the surface asperities plays a crucial role. In addition to the link between friction and thickening, rough colloids also present harsher discontinuous-shear-thickening behavior at lower concentrations compared to smooth frictional colloids, due to particle-particle interlocking [4].

[1] I. R. Peters, S. Majumdar. and H. M. Jaeger, Nature, 2016 (532) 214-217.
[2] M. Zanini et al., Colloids Surf., A, 2017 (In Press).
[3] N. Fernandez et al., Phys Rev Lett 2013 (111) 108301.
[4] The authors acknowledge funding from the Swiss National Science Foundation grant grants SNSF PP00P2 144646/1 and ETH Research Grant ETH-49-16-1.

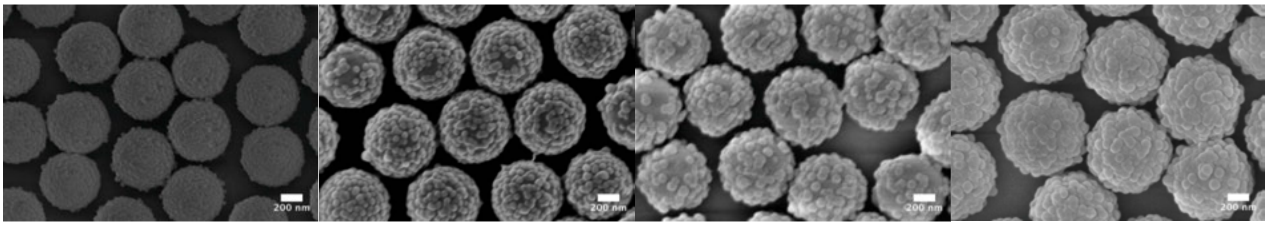

Figure 1. SEM images of raspberry-like silica particles with tailored surface roughness.

O1-4

HYBRID NANOCOLLOIDS BY SHADOW GROWTH

Hyeon-Ho Jeong[1], Mariana Alarcón-Correa[1,2], Andrew G. Mark[1], Tung-Chun Lee[1], and Peer Fischer[1,2]

[1] Max Planck Institute for Intelligent Systems, Stuttgart, Germany
[2] Institute for Physical Chemistry, University of Stuttgart, Stuttgart, Germany

Nanoparticles promise a variety of application in energy, medicine, and biology.[1] However, most nanoparticles' shape and material composition cannot be tuned and their functions have thus far been limited. Moreover many functionally useful materials are prone to corrosion in solution.[2]

Here we show that physical shadow growth is able to grow a series of 3D hybrid nanoparticles with programmed shape and material composition, but also chemically stable against corrosion. We firstly demonstrate a combined fabrication scheme, nano glancing angle deposition (nanoGLAD)[3] with atomic layer deposition (ALD), to design, grow, and protect hybrid nanoparticles.[4] We present Co magnetic nanocolloids that without the protective layer corrode within hours in an acidic environment, but that are stable for weeks and in some cases even months when grown by the scheme we present here. Entirely new applications are possible including chiral plasmonic sensing with Cu, Mg,[5] Ag-Ti,[6] and nanorheology with Au-Fe[7] hybrid nanoparticles in aqueous solutions, which will be also discussed in this presentation.

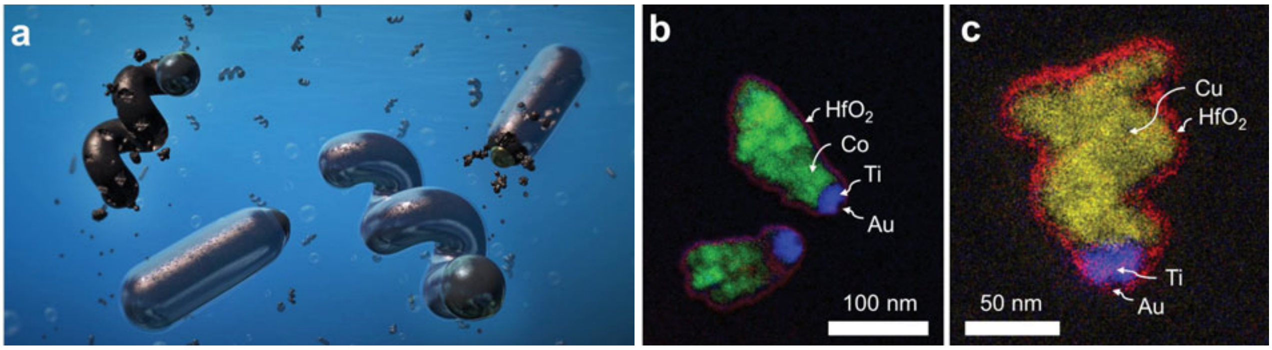

Figure 1. (a) An illustration of corrosion-protected hybrid nanoparticles in solution. Their corresponding experimental images, (b) Co nanorods and (c) a protected Cu nanohelix. Reprinted from Ref. 4.

[1] Y. Xia, Y. Xiong, B. Lim and S. E. Skrabalak, *Angew Chem Int Ed*, 2009, **48**, 60-103.
[2] A.-H. Lu, E. L. Salabas and F. Schüth, *Angew Chem Int Ed*, 2007, **46**, 1222-1244.
[3] A. G. Mark, J. G. Gibbs, T.-C. Lee and P. Fischer, *Nat Mater*, 2013, **12**, 802-807.
[4] H.-H. Jeong, M. Alarcón-Correa, A.G. Mark, K. Son, T.-C. Lee, and P. Fischer, *Adv Sci*, 2017, doi: 10.1002/advs.201700234.
[5] H.-H. Jeong, A. G. Mark and P. Fischer, *Chem Commun*, 2016, **52**, 12179-12182.
[6] H.-H. Jeong, A. G. Mark, M. Alarcon-Correa, I. Kim, P. Oswald, T.-C. Lee and P. Fischer, *Nat Commun*, 2016, **7**, 11331.
[7] H.-H. Jeong, A. G. Mark, T.-C. Lee, M. Alarcón-Correa, S. Eslami, T. Qiu, J. G. Gibbs and P. Fischer, *Nano Lett*, 2016, **16**, 4887-4894.

O1-5

TRIBLOCK TERPOLYMER MICROPARTICLES

Andrea Steinhaus, Ramzi Chakroun, Tai-Lam Nghiem, André H. Gröschel

Physical Chemistry and Centre for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Duisburg, Germany

The self-assembly of block copolymers in solution has brought about a large variety of functional nanoparticles.[1] While most self-assembly processes are conducted under diluted conditions, more recent works on block copolymer microphase separation within emulsion droplets report on the formation of porous inverse morphologies[2–4] and compartmentalized microparticles.[5,6]

In this presentation, I will discuss the microphase separation of triblock terpolymers in the spherical confinement of nanoemulsion droplets (**Figure 1A**). We obtain a large variety of multicompartment microparticles that may serve as templates for complex inorganic replicas or the synthesis of block copolymer toroids, perforated discs, patchy discs, and a range of Janus nanostructures. For instance, the formation of a lamella-cylinder morphology in spherical confinement allows the synthesis of Janus nanorings through cross-linking of B rings sandwiched between axially stacked lamellae (**Figure 1B**). The lamella-ring morphology further poses interesting topological problems that can be visualized by TEM tomography. Depending on the surfactant, we either find concentric rings on 2D discs or cylinders wrapped to cover a 3D concentric lamellae. The preparation of microparticles through emulsions is scalable, and the complex inner structure might be suitable for capture and release, actuation, energy storage and conversion, or applications that require high surface area.

[1] Gröschel AH, Müller AHE. Nanoscale 2015;7:11841–76.
[2] La Y, Park C, Shin TJ, Joo SH, Kang S, Kim KT. Nat Chem 2014;6:534–41.
[3] Yu H, Qiu X, Nunes SP, Peinemann K-V. Nat Commun 2014;5:1–10.
[4] Lin Z, Liu S, Mao W, Tian H, Wang N, Zhang N, et al. Angew Chemie - Int Ed 2017;56:7135 40.
[5] Jang SG, Audus DJ, Klinger D, Krogstad D V, Kim BJ, Cameron A, et al. 2013.
[6] Shin JM, Kim Y, Yun H, Yi G-R, Kim BJ. ACS Nano 2017;11:2133–42.

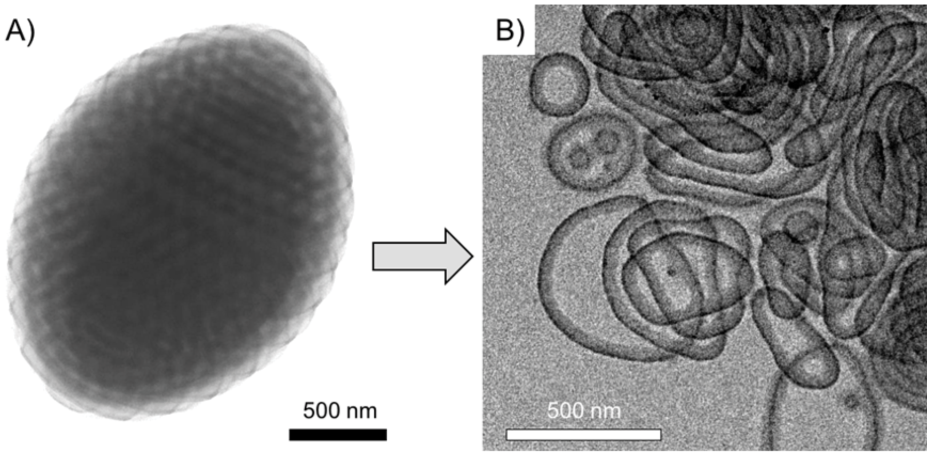

Figure 1. Lamella-ring morphology of a triblock terpolymer in spherical confinement and cross-linking of the ring domain to release Janus nanorings.

O1-6

NANOPARTICLE-BASED HIERARCHICAL AGGREGATES WITH TAILORED STRUCTURE AND FUNCTIONAL PROPERTIES

Georg Garnweitner[1,2], Sabrina Zellmer[1], Lennart Kleinfeldt[1] and Carsten Schilde[1]

[1] Institute for Particle Technology, Technische Universität Braunschweig, 38106 Braunschweig, Germany
[2] Laboratory for Emerging Nanometrology, Technische Universität Braunschweig, 38106 Braunschweig, Germany

Nanoparticle-based aggregate structures are important for new or enhanced applications of high quality products in the chemical, pharmaceutical, food and dye industries. The desired product properties are specified by material characteristics of the particles and the resulting aggregate structures. Apart from the nanoparticle synthesis, the systematic formation of well-defined, even hierarchical nanostructures is a major challenge in research and development. Spray drying processes are suitable for the production of such nanoparticulate hybrid materials with hierarchical structures. Hereby, the systematic formation of these nanostructures depends on formulation, process strategies and process parameters [1, 2].

In this contribution, we demonstrate that both aggregates with tunable microstructure as well as hybrid aggregates with functional properties can be fabricated by spray drying. To obtain defined porous aggregates, a template approach was realized, using both SiO_2 primary particles obtained by Stöber synthesis (with sizes between 50 to 500 nm) as well as polystyrene template particles of various particle sizes (between 20 nm and 500 nm). After spray drying, tempering or solvent leaching was applied to remove the polystyrene, obtaining aggregate particles with tailored porosity. The obtained aggregates were stressed with a flat punch indenter tip via nanoindentation in order characterize the mechanical aggregate properties. The aggregate structure was determined from mercury porosimetry measurements and the analysis of FIB-SEM images (coordination number, porosity, tortuosity, arrangement and size of solid bridges). The mechanical properties were related to structure characteristics derived as function from the aggregate radius via statistical analysis of the FIB-SEM images. Furthermore, functional hybrid particles were obtained by combining dispersions of suitable primary particles of different materials. By variation of spray drying parameters as well as of the particle interactions, different structures, e.g. core-shell particles, were obtained.

[1] S Zellmer, G Garnweitner, T Breinlinger, T Kraft and C Schilde, ACS Nano 9 (2015), p. 10749.
[2] S Zellmer, M Lindenau, S Michel, G Garnweitner, C Schilde, Journal of Colloid and Interface Science 464 (2016), p. 183-190.

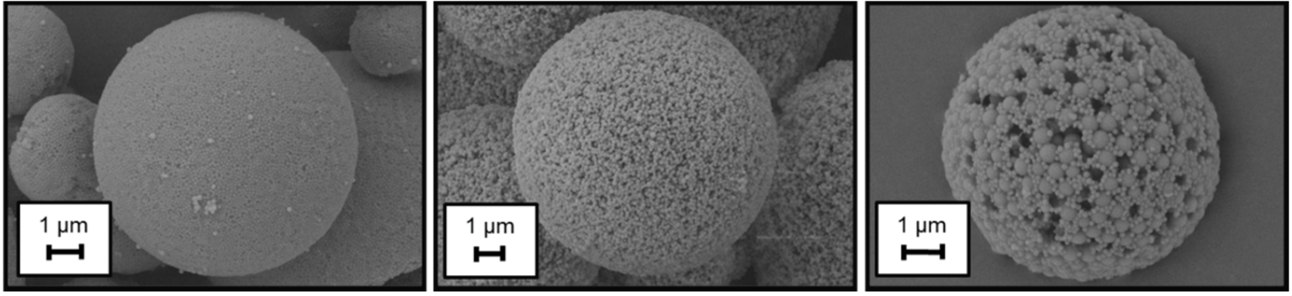

Figure 1. SEM images of silica aggregates with 150 nm-sized primary particles (left); porous aggregate obtained via a templating strategy (middle); and porous core-shell aggregate with 150 nm and 500 nm-sized primary particles (right).

▸ SESSION 2

Optics and Plasmonics I

O2-1

COLLOIDAL CRYSTALLIZATION IN SPHERICAL CONFINEMENTS: STRUCTURE AND OPTICAL PROPERTIES

Junwei Wang[1], Chrameh Fru Mbah[2], Michael Engel[2] and Nicolas Vogel[1]

[1] Institute of Particle Technology, Department of Chemical and Biological Engineering, Friedrich Alexander University Erlangen-Nürnberg
[2] Institute of Multiscale Modelling, Department of Chemical and Biological Engineering, Friedrich Alexander University Erlangen-Nürnberg

Materials in nature are characterized by structural order over multiple length scales evolved for maximum performance and multi-functionality and are often produced by self-assembly processes. A striking example of this design principle is structural coloration, where interference, diffraction and absorption effects result in vivid colors. Mimicking this emergence of complex effects from simple building blocks is a key challenge for man-made materials.

We crystallize colloidal particles in the confinement of an emulsion droplet using droplet-based microfluidics and study the crystallization behavior. If the crystallization process is fast, we observe spherical colloidal crystals with ordered, crystalline layers and a disordered core. This geometry produces multiple optical effects.[1] The ordered layers give rise to Bragg diffraction that is strongly influenced by the curvature, leading to limited angular dependence of color and cut-off in transmitted light. The disordered core contributes non-resonant scattering that induces a macroscopically whitish appearance, which we can mitigate by incorporating absorbing gold nanoparticles that suppress scattering and macroscopically purify the color. With increasing size of the constituent colloidal particles, grating diffraction effects dominate, which result from order along the crystal's curved surface and induce a polychromatic appearance. When increasing the time scale available for crystallization and thus enabling the system to rearrange into lower energy structures, we find a rich phase behavior of colloidal crystals with icosahedral symmetry and anti-MacKay surface reconstruction. We classify the resulting structures as a function of the number of particles and provide a phase diagram for such confined self-organization processes.

[1] N. Vogel, S. Utech, G. England, T. Shirman, K.R. Phillips, N. Koay, I. Burgess, M. Kolle, D. A. Weitz and J. Aizenberg, Color from hierarchy: diverse optical properties of micron-sized spherical colloidal assemblies, Proc. Natl. Acad. Sci. USA 2015, 112, 10845.

O2-2

SINGLE-STEP PROCESSING OF CONJUGATED POLYMER PARTICLES TOWARDS ORGANIC LIGHT-EMITTING CAPACITORS

Bastian Hähnle and Alexander JC Kuehne

DWI – Leibniz Institute for Interactive Materials, Aachen, Germany

Organic light-emitting capacitors (OLECs) are AC driven light emitting devices, which are a powerful alternative to the DC driven and widely applied organic light emitting diodes (OLEDs). However, conventional manufacturing of organic semiconductors into OLECs is disadvantageous as it requires multiple layers and complicated multistep processing.
Here, we present a new type of OLEC based on monodisperse π-conjugated polymer colloids, which self-assemble into a hierarchical device architecture in a single processing step **(Fig. 1a)**. [1]
The conjugated polymer particles are produced by Suzuki-type dispersion polymerization, leading to sub-micrometer sized and monodisperse conjugated polymer particles. In the conjugated polymer particles there are Pd-nanoparticle residues, which result from catalyst oxidation during the Suzuki-type dispersion polymerization **(Fig. 1b)**. During processing into OLEC devices, the conjugated polymer particles are dispersed in a matrix composed of a high-k dielectric and then sandwiched between two electrodes. The dielectric matrix protects the colloids from moisture and oxygen and prevents direct charge injection from the surrounding electrodes into the semiconducting particles. The devices are driven by an alternating voltage to produce an alternating electric field between the electrodes. Here, these Pd impurities act as nanometer sized ambipolar charge generators, which inject charges into the conjugated polymer semiconductor as a response to the external electric field. This allows for locally induced electroluminescence induced by the applied alternating voltage from the external electrodes. I will discuss the synthesis of Pd-nanoparticle filled conjugated polymer colloids and their assembly into OLEC devices by printing methods.

[1] A. Mikosch, S. Ciftci, A. J. C. Kuehne, ACS Nano, 2016, 10, 10195-10201.

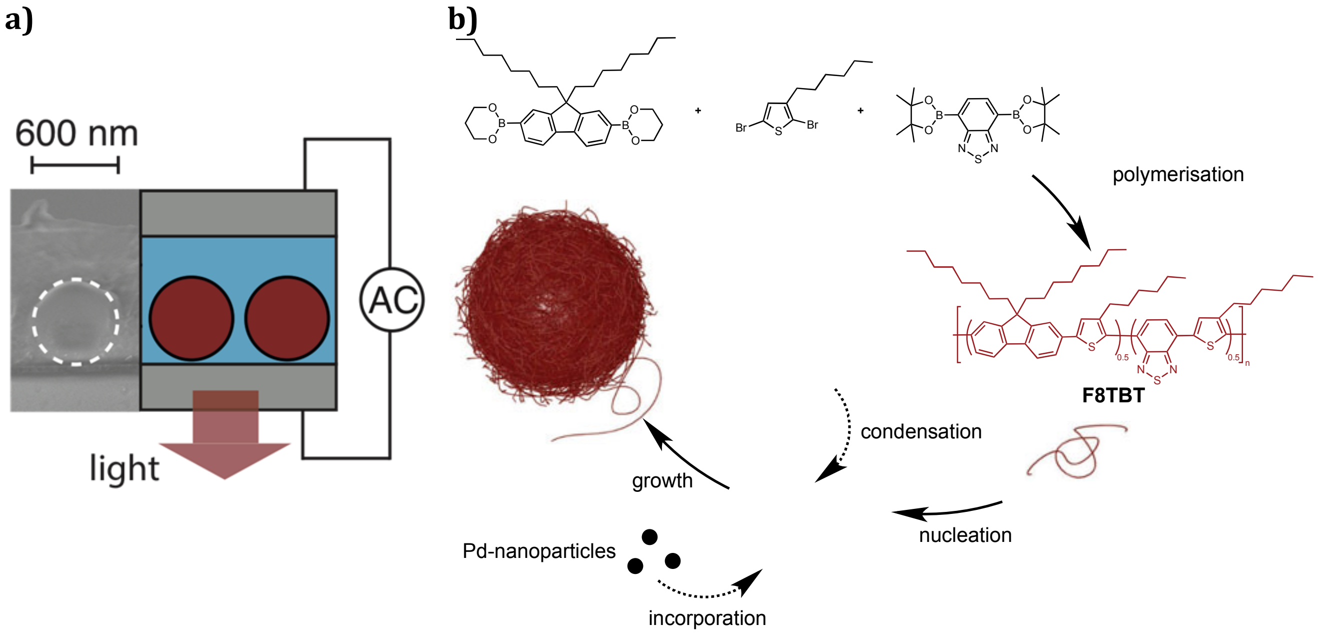

Figure 1. a) SEM image and schematic illustration of the OLEC device cross section.
b) Reaction scheme and dispersion polymerization mechanism for the formation of monodisperse conjugated F8TBT colloids with incorporated Pd-nanoparticles.

O2-3

ENHANCEMENT OF PHOTOLUMINESCENCE OF A CARBON DOT SYSTEM THROUGH POLYMER NANOPARTICLE INTERACTION

Rebecca Momper[1], Julian Steinbrecher[1], Matthias Dorn[1], Irina Rörich[1], Charusheela Ramanan[1], Sandra Ritz[2], Manuel Tonigold[1,3], Volker Mailänder[1,3], Katharina Landfester[1], Markus B. Bannwarth[1]

[1] Max Planck Institute for Polymer Research, Mainz, Germany
[2] IMB gGmbH, Mainz, Germany
[3] Dermatology Clinic, University Medical Center Mainz, Mainz, Germany

Carbon dot systems (CDS) are fluorescent, carbon based nanoparticles in the size of few nanometers. Their fluorescence properties strongly depend on their surface environment. The influence of environmental parameters like pH, small molecules or ions has been widely studied in the literature [1-3]. Often passivation agents, like polymers, such as poly(ethylene glycol) (PEG) or poly(ethylene imine) (PEI), are used to activate or modulate the fluorescence properties of CDS [4]. For passivation a thin layer of polymer is formed around the CDS and protects them from the environment. While the direct attachment of polymer chains to activate or modulate the fluorescence properties of CDS is widely applied, the effect of activating fluorescence properties through physical interaction with surfaces (e.g. of polymeric colloids) has been neglected.

Here we show that CDS selectively interact with polymer colloids, in this case model polystyrene nanoparticles (PS NP) to strongly influence their fluorescent behavior. The CDS was synthesized using a microwave assisted thermal treatment [3].The used PS NPs were prepared by a miniemulsion polymerization technique [5]. To investigate the effect of a colloidal system on the fluorescence properties of CDS, two ways to generate a CDS-NP system were studied. The CDS were either synthesized directly in the presence of PS NP (*in situ)* or mixed afterwards with a PS NP dispersion (mixing). In both cases the combination of CDS with PS NP leads to a strong enhancement of the fluorescence intensity and a prolongation of the fluorescence lifetime from around 1 ns to 5 ns. Interestingly, the enhancement of the fluorescence intensity is independent of the attachment mechanism. For the *in situ* system a covalent binging was found whereas the CDS in the mixing system are electrostatically attached. This finding can be used to apply a new strategy to activate and enhance the fluorescence properties of CDS without an additional passivation step [6].

[1] Jia et al., Nanoscale, 4 (2012) p. 5572.
[2] Shen et al., Anal Chem, 86 (2014) p. 5323.
[3] Gong et al., Anal. Chim. Acta 861 (2015) p.74.
[4] Cao et al., J. Am. Chem. Soc. 129 (2007) p. 11318.
[5] Holzapfel et al., Macromol. Chem. Phys. 206 (2005) p. 2440.
[6] The authors acknowledge the Max Planck Society for the financial support.

O2-4

POROUS STIMULI-RESPONSIVE BLOCK COPOLYMER AND COLLOIDAL ARCHITECTURES

Markus Gallei

Ernst-Berl-Institute for Technical and Macromolecular Chemistry, Technische Universität Darmstadt, Darmstadt, Germany

In the last decade stimuli-responsive block copolymers and core-shell particles have proven their utility for a range of important applications.[1] These polymers are capable of changing their conformation, solubility, or even of breaking or forming covalent bonds upon, for instance, a change of temperature or pH value, light irradiation, electrochemical stimuli or the presence of an electrical or magnetic field, or combinations thereof.[2-4] The presentation focusses on materials which contain at least one selectively addressable segment, either chemically or physically. Nanostructures based on block copolymer self-assembly as well as soft colloidal crystal films prepared by using the so-called melt-shear organization technique will be highlighted. In the case of soft colloidal crystal structures, which are also referred to as *polymeric opals*, applied external triggers lead to a remarkably fast change in optical properties (Figure 1). A great benefit of opal structures by the melt-shear organization is their inexpensive and convenient preparation giving a good optical performance with iridescent reflection colours caused by Bragg diffraction. This talk will give some recent examples for the rational design of functional (hybrid) materials with hierarchical architectures and some of the presented structures could be advantageously used for direct conversion into ordered ceramic or carbonaceous materials. Herein presented functional materials are expected to be interesting candidates for a manifold of applications in the field of sensing and robust membrane technologies.

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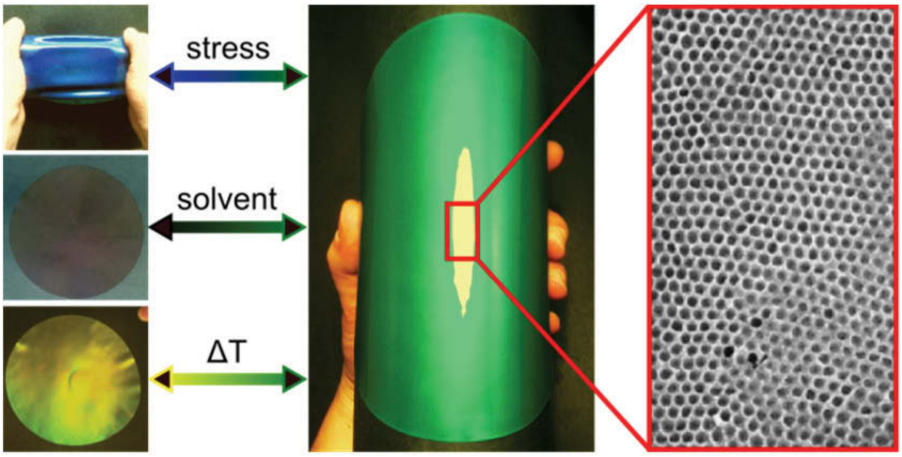

Figure 1. Switching capabilities of stimuli-responsive inverse opal structures.

O2-5

ANISOTROPIC POLYMER NANOPARTICLES WITH TUNABLE EMISSION WAVELENGTHS BY INTERSEGMENTAL CHAIN PACKING

Julian Dominik Ruiz Perez and Stefan Mecking

Chair of Chemical Materials Science, Department of Chemistry, University of Konstanz,
Konstanz, Germany

Beyond their composition, the shape of nanoparticles has a tremendous impact on their properties [1]. This is not limited to individual particles, but also inter-particle interactions are shape dependent. The self-assembly to organized structures is decisively determined by particle shape, particle packing and alignment as well as the directional interactions between the particles. Different from inorganic nanocrystals, the accessibility of anisotropic polymer nanoparticles remains largely unexplored. This applies in particular to conjugated polymer nanoparticles as an important class of materials [2].

We discuss a reproducible preparation method to a range of stable dispersions of ellipsoidal shaped (aspect ratio of around 3.5) conjugated polymer nanoparticles, prepared via heterophase Suzuki-Miyaura coupling polymerization [3]. The conjugated polymer nanoparticles exhibited a bright fluorescence emission with tunable emission wavelengths and quantum yields as high as $\varphi = 78\%$. Structural investigation via UV-vis absorption and photoluminescence spectroscopy along with PXRD studies revealed that the nanoparticles are composed of the highly ordered β- and α'-phase within a nematic matrix. Preliminary studies on the origin of particle anisotropy suggest a concerted mechanism in which anisotropic shape evolves from segmental packing that occurs along with progressing chain formation by polymerization. Further research on the alignment of these novel anisotropic CPNs appears to be promising for particle-based polymer materials with potentially directional properties [4].

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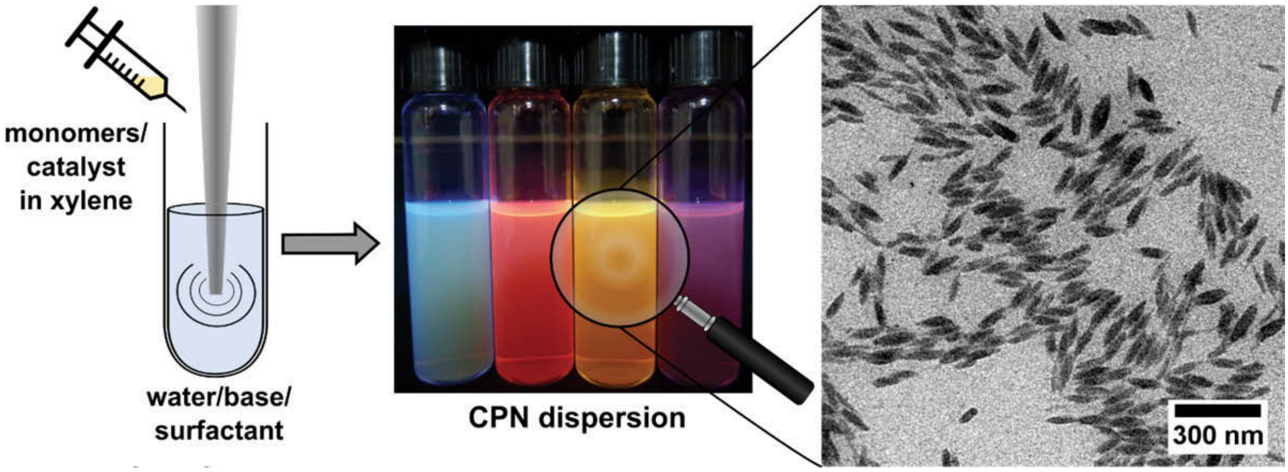

Figure 1. Polymer nanoparticle formation with anisotropic shape and tunable emission.

O2-6

ELECTRIC FIELD OPTICALLY RESPONSIVE NANOWIRE COLLOIDS

Andris Šutka[1,2]

[1] Research Laboratory of Functional Materials Technologies, Riga Technical University, Rīga, Latvia
[2] Institute of Physics, University of Tartu, Tartu, Estonia

Electric field optically responsive nanowire (NW) colloids can be applied for low-cost electro-optical devices (i.e. smart windows, switches) [1], detectors and sensors [2], as well as dielectrophoretic self-assembly of NWs into macroscopic yarns [3]. Smart windows are commonly based on visible light absorbing small oblong nanoparticles where transmittance is modulated by aligning nanoparticles towards direction of electric field and thus changing light absorption cross-section [4, 5]. These devices require high nanoparticle concentrations up to 10 wt%. High concentration hinder oblong nanoparticles to re-align into chaotic state after electric field is switched off and re-alignment may take up to several hours [4, 5]. These devices also switching transmittance between fully non-transparent to approximately 50% transmittance at 550 nm [4, 5], which is not suitable range for practical applications.

Recently we have demonstrated smart window devices based on relatively large size ZnO NW (diameter below 200 nm and length up to 3μm) diluted colloids in amino-PDMS where transmittance can be modulated because of change of scattering (not absorption) cross-section during NW alignment in direction of electric field [6]. We found that high aspect ratio NWs with diameters smaller than 200 nm in the the chaotic state exhibits abnormally low scattering and despite the obvious decrease in the geometrical cross-section upon alignment, the scattering efficiency increases and light undergoes diffuse multiple scattering inside the colloid. The reversible transmittance change from 70% to 20% can be reached by colloids with NW concentrations as low as ~0.25 wt%. The switching time from transparent to untransparent state and back took 25 and 30 min, respectively. The orientation-reorientation kinetics can be modulated by changing viscosity by adding non-polar solvent i.e. hexane, but by decreasing viscosity, decreases stability of colloids and sedimentation occur.

Furthermore, we made colloids from visible light absorbing transition metal doped ZnO NWs [2]. The obtained colloids are “touch sensitive”; filled in glass vial they change color from vivid to black upon touching with rubber gloves. This is related to the formation of electrostatic charges on glass surface. When electrostatic charge is formed, NWs in colloid are aligned towards electric field direction arising from static surface charge and absorption properties are changed. The observed optical behavior could be related to light multiple reflections whereas some portion of light is absorbed at each reflection. By increasing optical path, there is no reflected light and colloid appears black. Transition metal doped ZnO NW colloids can be used for electrostatic charge naked eye optical detection.

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▶ SESSION 3

Biological Materials

O3-1

PARTICLES AS BUILDING BLOCKS FOR TISSUE REGENERATIVE MATERIALS

Jonas Rose, Luis Guerzoni Busca, Abdolrahman Omidinia-Anarkoli and Laura De Laporte

DWI-Leibniz Institute for Interactive Materials, Aachen, Germany

We apply micro-elements as building blocks for tissue regenerative materials. The different types of micro-elements are spherical or anisometric, short fibers or microgels, responsive or hollow, and produced using different methods, such as microfluidics, electrospinning/ micro-cutting, or an in mold polymerization method. We aim to design containers to embed and grow cells to form mini-tissues for transplantation or load specific biological molecules to control temporal release[1], and produce structural magnetic elements that can be aligned for cell guidance. Due to their size, the micro-objects can be injected, with or without a surrounding hydrogel. Their internal structure and degradation properties enable temporal control of tissue formation. To obtain anisotropic matrices after injection, rod-shaped elements are rendered magneto-responsive by the incorporation of superparamagnetic iron oxide nanoparticles (SPIONs). Due to their anisometric shape, the elements align parallel to a low external mTesla magnetic field, after which a surrounding hydrogel can crosslink to fix their unidirectional orientation after removal of the magnetic field. Fibroblasts and nerve cells sense the mechanical anisotropy, induced by the oriented structures, resulting in directed cell growth inside 3D hydrogels.[2] Neurons inside the Anisogel show spontaneous electrical activity proving neuronal functionality and importantly, electrical signals propagate along the anisotropy axis of the material.[3] The developed hybrid hydrogel can be applied as a low invasive, injectable material to repair complex, sensitive tissues, such as the spinal cord.

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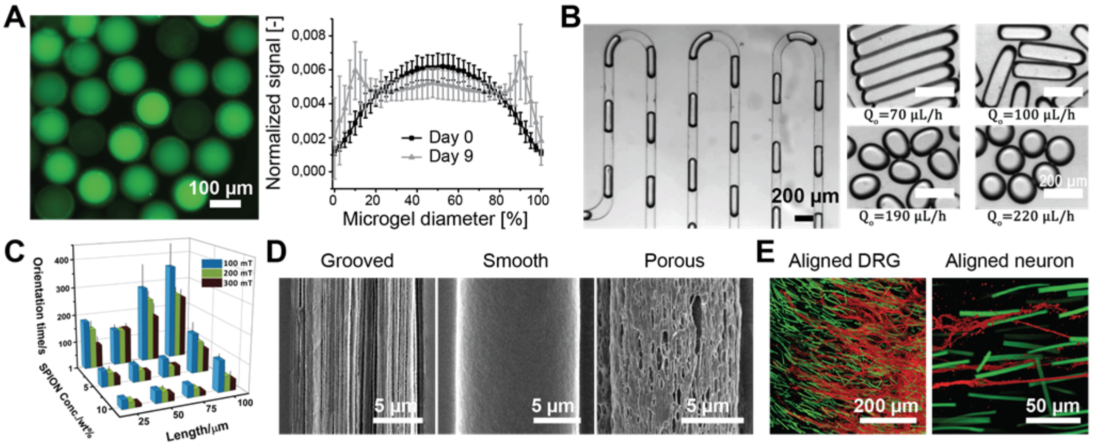

Figure 1. A) Microgel capsules containing encapsulated FITC-dextran and normalized fluorescence spectra across the diameter of the microgels over time. B) Microfluidic production of anisometric microgels with varying aspect ratios depending on the flow rate of the oil phase. C) Short magneto-responsive electrospun microfibers align with an orientation rate depending on the fiber length, SPION concentration, and magnetic field strength. D) Fiber topography (grooved, smooth, porous) can be tuned using different solvent systems. E) Unidirectionally oriented microgels induce aligned nerve growth inside a fibrin gel.

SESSION 4

Catalysis

O4-1

FROM COLLOIDS TO SUPPORTED CATALYSTS

Jörg Polte

Humboldt Universität, Institut für Chemie, Berlin, Deutschland

Many heterogeneous or electro catalysts are based on immobilized noble metal nanoparticles. For these catalysts metal nanoparticles are anchored on substrates such as metal oxide or carbon whereby the nanoparticles are in general formed on the substrate via precipitation or impregnation methods. The metal oxide substrates are typically TiO_2, Al_2O_3 , CeO_2 or SiO_2 and are commonly used in heterogeneous gas phase catalysis. Catalysts for electrochemical applications (e.g. fuel cells) or organic chemistry (e.g. cross coupling reactions) are typically metal nanoparticle anchored on carbon supports such as carbon black or active carbon.

Although literature provides a broad range of syntheses for metal colloids with control over size, shape, structure and composition, commercially used supported metal nanoparticle catalysts are almost entirely not using pre-made colloids. One exception are the Nanoselect™ catalysts (Pd- and Pt-NPs on carbon supports) from BASF.

In contrast, the commonly used preparation techniques of a supported noble metal catalyst comprise the impregnation of a porous support with a molecular precursor and a subsequent thermal treatment. Such preparation techniques allow high metal loadings and can be scaled up. However, the final particle size distribution is in general very broad. In addition, size control is much more difficult and elaborative as for colloidal syntheses since each synthetic step influence the growth leading to a large set of different parameters. Furthermore, the properties of the support (e.g. porosity, surface defects or roughness) affect the outcome of each step which makes it necessary to find the optimal synthesis parameter for each single support material and consistent support properties also need to be assured during production.

This contribution discusses the physico-chemical processes causing the synthetic problems which are responsible that metal colloids are not used for catalytic applications. In addition, it presents synthetic pathways which meet the criteria for commercial catalysts.

O4-2

PHOTOCATALYTIC AND MAGNETIC POROUS CELLULOSE-BASED NANOCOMPOSITES PREPARED BY A GREEN METHOD

Alexandra S. M. Wittmar[1,2], Qian Fu[1] and Mathias Ulbricht[1,2]

[1] Lehrstuhl für Technische Chemie II, Universität Duisburg-Essen, Essen, Germany
[2] CENIDE – Center for Nanointegration Duisburg-Essen, NETZ – Nano Energie Technik Zentrum, Duisburg, Germany

The present work expands our previous studies [1, 2] related to cellulose processing with room temperature ionic liquids and simultaneous integration of functional nanoparticles towards photocatalytically active and easily recyclable nanocomposite porous films based on a renewable matrix material. Porosity can be tuned by the selection of phase separation conditions for films of casting solutions of cellulose in ionic liquids or their mixture with an organic co-solvent. TiO_2 nanoparticles confer to the nanocomposite photocatalytic activity while the Fe_3O_4 make it magnetically active. The co-doping of TiO_2-cellulose composite with Fe_3O_4 nanoparticles did not diminish the photocatalytic activity of the final composite which can be easily separated from solution with a magnet. Additionally, by Fe_3O_4 doping, the composite temperature can be homogenously increased by exposure to a high frequency alternating magnetic field. For an optimal thermal response in such magnetic field the magnetite nanoparticles have to be homogenously dispersed within the polymer matrix. The preparation method for the casting solution has been found to play an essential role for the fabrication of nanocomposite materials in which the functional nanoparticles are homogenously dispersed in a non-agglomerated form. Besides the presented porous flat sheet nanocomposites, by the established non-solvent induced phase separation processes similar photocatalytic and magnetic porous cellulose nanocomposites can be successfully shaped also in spherical form as micro- or macro beads (Fig.1).

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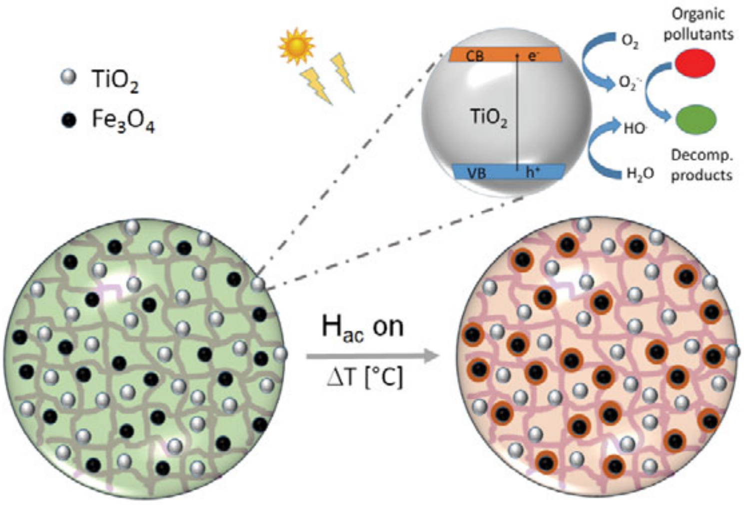

Figure 1. The working principle of the photocatalytic and magnetic components in a photocatalytically and magnetically active porous cellulose-based sphere

▶ SESSION 5

Magnetic Materials

O5-1

FUNCTIONAL SUPRAPARTICLES FROM IRON OXIDE BASED NANO-BUILDING-BLOCKS

Karl Mandel[1,2]

[1] Fraunhofer Institute for Silicate Research, ISC, Neunerplatz 2, 97082 Würzburg, Germany
[2] University Würzburg, Chair of Chemical Technology of Materials Synthesis, Würzburg, Germany

In this talk, functional supraparticle systems will be presented. These are based on iron oxide nano-building-blocks. It will be demonstrated how novel functionalities can emerge simply from arrangement of these nano-building-blocks to entities, which add a certain level of complexity either in terms of structure or composition. A range of examples of functions that can be obtained by colocalisation of nano iron oxide building-blocks will be presented. With these functions, novel particle systems for advanced materials or processes can be generated addressing field such as water purification, substance detection, light-weight materials and magnetically manipulable optically active objects.

O5-2

MAGNETIC FIELD-INDUCED ELASTIC DEFORMATIONS IN NI-NANOROD/PAM-HYDROGEL COMPOSITES

Andreas Tschöpe, Christoph Schopphoven, Kerstin Birster and Rouven Schweitzer.

Universität des Saarlandes, Experimentalphysik, Saarbrücken, Germany

Below a critical diameter of 40 nm, Ni nanorods are ferromagnetic single-domain particles with a substantial magnetic anisotropy along the rod axis. Hence, these nanorods experience magnetic torque in an external field which can be employed for remote mechanical actuation. Analysis of the nanorods dynamics in time-dependent fields has been explored for protein detection and active microrheology. The present study focuses on the torque-driven deformation of textured soft elastic composites with Ni nanorods as the particulate phase.

Ni nanorods were synthesized by the AAO template method, Fig.1 (left) [1], processed to stable colloidal suspensions and dispersed in polyacrylamide (PAM) hydrogels. Polymerization of PAM was performed in homogeneous magnetic field to generate a magnetic texture. Taking advantage of their anisotropic optical extinction cross section, local rotation of the nanorods was investigated using optical transmission of linearly polarized light. The observed dependence on field strength and orientation of the texture axis, Fig.1 (right), was combined with magnetization studies to derive and verify a semi-quantitative microscopic description of the magnetic torque based on the Stoner-Wohlfarth model [2]. On the macroscopic scale, the field-induced torsion of a slender magnetically textured composite cylinder was investigated. The experimental results are quantitatively consistent with the torsion of an elastic continuum as result of microscopic body torques distributed in the composite volume [3].

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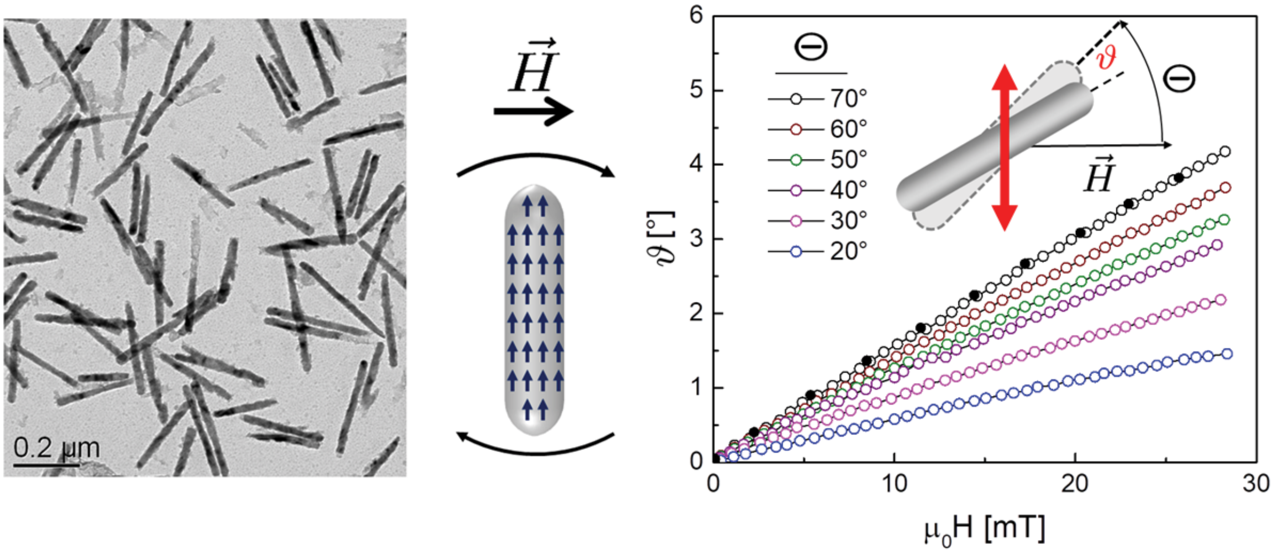

Figure 1. Ni nanorods (TEM image, left) are uniaxial ferromagnetic single-domain particles and experience a torque when exposed to a transversal magnetic field. The field-dependent local rotation of nanorods in a soft elastic hydrogel matrix is determined from optical transmission of linearly polarized light for different orientations Θ of the texture axis (right).

O5-3

MAGNETO-ELASTOMERIC NANOCOMPOSITES WITH SUPRAMOLECULAR ACTIVITY

Margarita Kruteva[1], Lisa Fruhner[1], Rieke Koll[2], Artur Feld[2], Hauke Heller[2], Jürgen Allgaier[1], Wim Pyckhout-Hintzen[1], Horst Weller[2], Stephan Förster[1]

[1]Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH, Jülich, Germany
[2] Intstitute of Physical Chemistry, University of Hamburg, Hamburg, Germany

Recently there is an increasing interest in functional polymer nanocomposites due to emerging novel applications ranging from sensors and plasmonics through stretchable electronics and smart coatings for energy conversion and human health (see e.g. [1-2]). Further exploitation of the huge potential of functional nanocomposites requires full control of the underlying nanostructure and the interaction between the nanoparticles and the host matrix, e.g. by external fields. The present work is focused on synthesis and consecutive structural investigation of magneto-rheological nanocomposites.

The nanocomposites are composed of magnetic polymer-functionalized nanoparticles and a polymeric matrix. These hybrid materials allow classical magnetically-induced ordering effects especially at low matrix viscosities. The thereby achieved stimuli-responsive nanocomposites whose properties (i) depend on the surrounding conditions (temperature, matrix polymer properties) and (ii) can be easy controlled by external fields (magnetic, deformational).

Synthetic procedure to obtain highly monodisperse nanoparticles consisting of a superparamagnetic iron oxide core (SPION) embedded in a polymeric shell we recently developed by us [3]. Using a combination of scattering techniques with TEM we showed that particle agglomeration is largely absent. Our scattering experiments in the presence of a magnetic field demonstrated (i) chain-like ordering of the nanoparticles along the direction of the magnetic field (in solution) and (ii) a pronounced magnetic scattering observed by SANS.

Implementation of supramolecular H-bond functionality in both, matrix polymers and polymer-functionalized nanoparticles allows field-induced ordering at elevated temperatures. On the other hand, the induced structures are “frozen-in” by cooling the system down into the state of closed supramolecular bonds. The matrix then becomes elastomeric and is itself composed of supramolecular units. These units self-assemble linearly and provide a control over the matrix viscosity. Alternatively, similar ordering effects can be achieved by mechanical deformation of the rubber-like nanocomposites. [4]

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O5-4

3D MACROSCALE SELF-ASSEMBLY

Leon Abelmann[1,2,3], Tijmen Hageman[1,2,3], Per Löthman[1,2,3], Marc Pichel[1,2,3], Nuriye Korkmaz[1], Bohyun Ryu[1], Andreas Manz[1,2]

[1] KIST Europe, Saarbrücken, Germany
[2] Saarland University, Saarbrücken, Germany
[3] University of Twente, Enschede, The Netherlands

In particle based materials, not only the particle properties but also their arrangement determines the final macroscopic behavior of the material. In many cases, we try to achieve ordered structures by means of some form of self-assembly. This works very well at the molecular scale, where we can use thermal agitation to minimize the energy of the system and sedimentation plays a negligible role. When increasing the particle size however, we need to resort to agitation and the gravitational force becomes important. Therefore, most micro-scale self-assembly studies are restricted to two-dimensional structures, usually forming at the bottom of some kind of container. There is very little work on true three-dimensional self-assembly on the microscale.

In this work, we jump to the macroscale to learn about self-assembly using levitation and agitation. In the first example (left figure), we study formation of cubic crystals of silicon cubes with an edge length of 500 µm [1]. Gravitation is counteracted by using a paramagnetic fluid in a strong magnetic field gradient. Since silicon is diamagnetic, the cubes are pushed to the region of lowest field. Agitation is achieved by sound waves provided by a piezo transducer. The interaction between the cubes is the external pressure provided by the magnetic field. We observed formation of a cubic crystal, frustrated by the shape of the magnetic force field.

In the second example we move from millimeter to centimeter size. The particles are 3D printed objects with an embedded magnet that causes particle interaction [2]. Levitation is achieved by an upward water flow, which also provides agitation due to turbulence. The interaction can be accurately tuned by modifying the shape of the polymer shell. The right figure shows that by changing the aspect ratio of the shell, one can realize sheets, lines and three-dimensional clusters. The attempt frequencies of these particles are only a few Herz, which allow for detailed study of the self-assembly dynamics.

These experiments deepen our insight into self-assembly at the nano- and micro-scale, which will be instrumental in the search for novel particle based materials.

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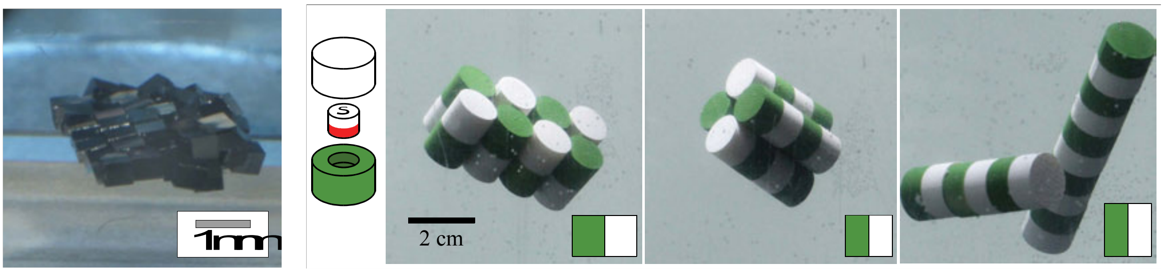

Figure 1 Left: Diamagnetically levitated silicon cubes. Right: 3D printed cylinders with embedded magnets, levitated and agitated in an upward water flow. By changing the cylinder aspect ratio, different geometries self-assemble. The center figure shows 3D self-assembly

▶ SESSION 6

Electronic and Thermal Materials

O6-1

BLOCK COPOLYMER TEMPLATE-DIRECTED SYNTHESIS OF COMPOSITE PARTICLES WITH COMPLEX NANOSTRUCTURES

Shilin Mei[1], Charl. J. Jafta[1], Matthias Ballauff[1, 2], Yan Lu[1, 3]

[1] Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany
[2] Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany
[3] Institute of Chemistry, University of Potsdam, Potsdam, Germany

Nanoparticles with highly ordered or porous structures are of great interest in a broad range of applications, such as catalysis and energy storage materials. Creating such particles with great complexity through templating strategy is a promising but challenging proposition, due to the trade-off between creating well-defined template and preserving the designed structure during the removal of the template. A significant strategy has been developed to utilize block copolymers as temples, which have the ability to self-assemble into highly ordered nanostructures and can be removed simply by dissolving or calcination.

In our study, PS-P2VP is used as the model polymer to direct the spatial assembly of both Au and Pd nanoparticles onto the BCP nanospheres with ordered distribution (Fig. 1a.) [2]. The composite particles can work efficiently as catalyst by using the reduction of 4-nitrophenol as the model reaction. Moreover, a selective swelling process will induce porous structures of the PS-P2VP nanospheres [3]. Porous Ti_4O_7 particles with interconnected pore structures have been developed by using porous PS-P2VP particles as template, which can be applied as a new type of sulfur-host material for lithium-sulfur batteries [4]. In order to improve the conductivity of the obtained particles, a thin layer of carbon has been coated on the surface as shown in Fig. 1b. Enhanced capacity with better cycling stability has been observed for the carbon-coated $Ti4O_7$ particles-based cathode materials.

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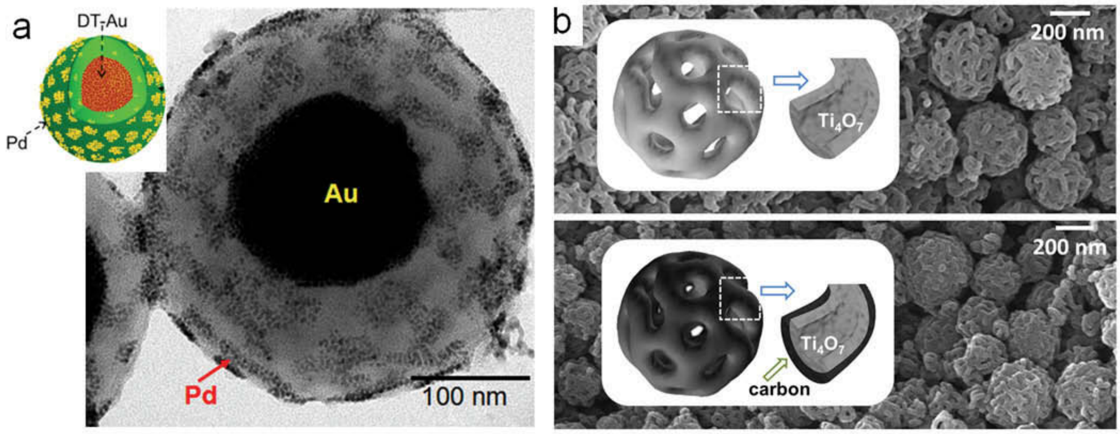

Figure 1. (a) Pd@PS-P2VP@DT-Au composite particles (b) Ti_4O_7 and carbon-coated Ti_4O_7 porous nanoparticles.

O6-2

STRUCTURE-TRANSPORT CORRELATIONS IN SUPERLATTICES OF COUPLED ORGANIC-INORGANIC NANOSTRUCTURES

Marcus Scheele

Institute of Physical and Theoretical Chemistry, University of Tübingen, Tübingen

Mesocrystals are three-dimensional, macroscopic arrays of iso-oriented nanocrystals (NC). In many ways, these arrays mimic classical crystals in which atoms have been replaced by NCs. Sufficient electronic coupling between the NCs provided, it is expected that mesocrystals exhibit a (mini-)band structure in full analogy to periodic arrays of atoms. Engineering such a band structure, e.g. by tuning coupling between NCs or changing their orientation, provides excellent prospects for applications in thermoelectrics, photovoltaics, (magneto-) electronics and optics [1, 2].

This presentation will illustrate how simultaneous self-assembly of semiconductor NCs and surface functionalization with organic semiconductor molecules gives access to macroscopic, conductive mesocrystals. Using different molecules not only affects the degree of coupling and the type of transmitted carriers (electrons, holes or both), but also controls the angular correlation between the superlattice and the iso-oriented atomic lattices of the NCs [3]. Although the particles are intrinsically isotropic, transport anisotropy in these materials arises due to facet-specific binding of surface molecules as well as a facet-dependent wavefunction overlap for holes and electrons[4, 5].

It will be shown how a combination of wide- and small angle X-ray scattering techniques in conjunction with X-ray cross-correlation analysis can elucidate the full mesocrystal structure of the hybrid superlattices, including the angular correlation with the individual atomic lattices.[3] Simultaneous electric transport measurements on the same X-ray transparent substrate allow for a correlation between transport, structure as well as NC orientation, and, ultimately, the revelation of anisotropic transport in such ordered, particle-based materials.

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O6-3

INKJET PRINTING OF CDSE/CDS NANORODS ON CONDUCTING SURFACES

Franziska Lübkemann[1], Ralf Anselmann[2], Torben Kodanek[1], Dirk Dorfs[1], Nadja C. Bigall[1]

[1] Leibniz Universität Hannover, Institute of Physical Chemistry and Electrochemistry, Hannover, Germany
[2] Evonik Resource Efficiency GmbH, Marl, Germany

In recent years the interest of inkjet printing as new methodology to deposit colloidal nanocrystals on different substrates has increased. One of the big advantages is, that lateral structuration can be easily performed.

Here, we want to present the formulation of aqueous inks, which consisting photoluminescent CdSe/CdS core/shell nanorods (NRs)[1] and the deposition on conducting ITO (tin doped indium oxide) by the means of inkjet printing.[2] The work involves the synthesis of organic soluble CdSe/CdS NRs, there phase transfer by ligand exchange[3] and the ink formulation. To improve the connection between CdSe/CdS NRs and the surface the ITO surface was modified with thiol-silanes. Films with increasing homogeneity can be obtain by consequently printing of several layers on each other. Characterization by UV/Vis-NIR absorption spectroscopy and photoluminescent spectroscopy provides us information about the physical properties of the printed nanorod films and about the homogeneity. The film thickness and texture of the printed films were investigated by scanning electron microscopy.

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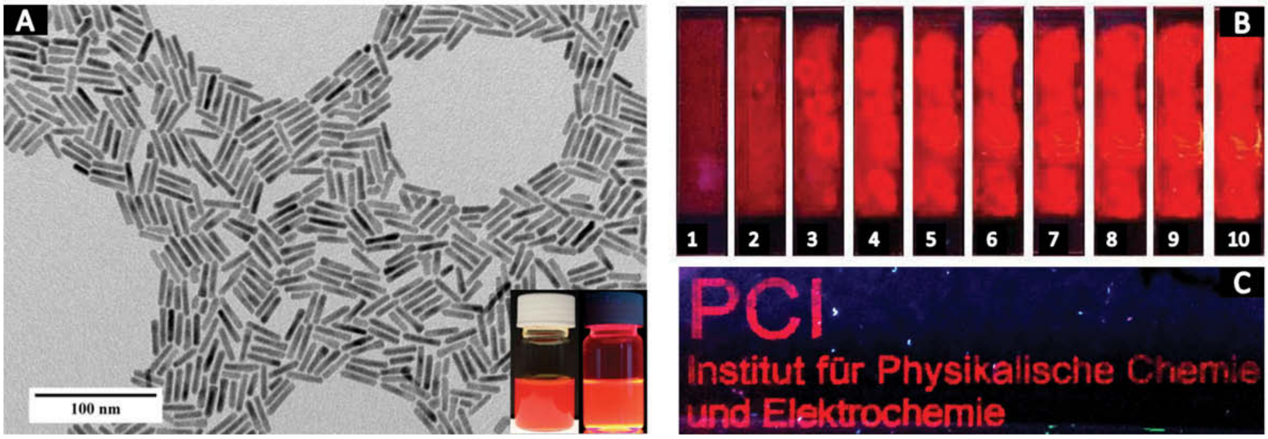

Figure 1: TEM image of CdSe/CdS NRs (A), 1 – 10 printed CdSe/CdS NR layers on ITO coated glass (B) and printed logo of "Institut für Physikalische Chemie und Elektrochemie" of the Leibniz Universität Hannover (C) under UV light illumination.

▶ SESSION 7

Optics and Plasmonics II

O7-1

INTERFACE-MEDIATED SELF-ASSEMBLY OF SOFT, PLASMONIC CORE-SHELL COLLOIDS: STRUCTURAL CONTROL AND FUNCTIONALITY

Kirsten Volk[1], Tobias Honold[2], Markus Retsch[3] and Matthias Karg[1]

[1] Heinrich-Heine-University Düsseldorf, Physical Chemistry I, Düsseldorf, Germany
[2] University of Bayreuth, Physical Chemistry I, Bayreuth, Germany
[3] University of Bayreuth, Physical Chemistry – Polymer Systems, Bayreuth, Germany

The encapsulation of hard, inorganic nanoparticles by linear or cross-linked polymers yields core-shell particles that spontaneously self-assemble at air/liquid interfaces forming highly ordered monolayers[1]. Transfer of the monolayer from the interface to macroscopic solid supports allows the fabrication of hexagonally ordered superstructures with large single crystalline domains. Depending on the length/thickness of the polymer coating of the building blocks such structures possess inter-core distances from a few up to several hundred nm. Multiple depositions on one substrate[2] or deposition to substrates with different contact angles gives access to a broad range of complex superstructures including non-hexagonal 2D Bravais lattices.

In this contribution we will demonstrate the structural diversity that is accessible by interface-mediated self-assembly of hard-soft core-shell particles. Furthermore, we will show how assembly of particles with plasmonic cores can lead to superstructures that show collective optical responses that differ strongly from the single particle behavior. The observed diffractive/plasmonic coupling can be reversibly tuned by addressing the refractive index environment through changing the swelling state of a responsive hydrogel matrix[3]. This way fully reversible resonance tuning becomes possible by either solvent exchange or temperature (see figure 1).

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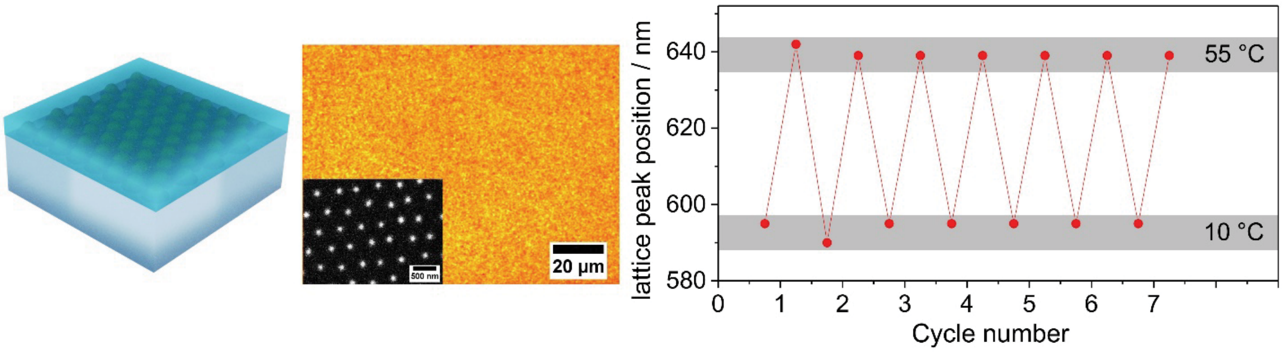

Figure 1. Left: Schematic depiction of a self-assembled plasmonic monolayer on glass (grey) embedded in a hydrogel matrix (light blue). Middle: Optical microscopy image as well as SEM image (inset) of an experimental hydrogel-embedded monolayer sample. Right: Temperature response of the resonance peak (diffractive/plasmonic coupling) for repeated heating/cooling cycles. Adapted from [3].

O7-2

LOOKING FOR SYNERGETIC EFFECTS IN MOLECULAR PLASMONICS BY HYBRID FUNCTIONAL NANOSTRUCTURES

Tobias A.F. König[1,2,3]

[1] Leibniz-Institut für Polymerforschung Dresden e.V., Institute of Physical Chemistry and Polymer Physics, Hohe Str. 6, 01069 Dresden, Germany. E-mail: koenig@ipfdd.de
[2] Technische Universität Dresden, Physical Chemistry, Technische Universität Dresden, Bergstr. 66b, 01062 Dresden, Germany
[3] Cluster of Excellence Centre for Advancing Electronics Dresden (CFAED), Technische Universität Dresden, 01062 Dresden, Germany

For the next generation of optical devices, the possibility of cost-efficient manufacturing requires both tailored control of the nanoparticle building blocks as well as an up-scaleable self-assembly method for macroscopic areas. We address these demands using bottom-up directed self-assembly of plasmonic nanoparticles to achieve collective plasmonic resonances in high quality plasmonic modes.[*Nano Lett.* **2014**, 14, 6863.] A first step toward these tailored modes are the controlled synthesis of the plasmonic building blocks with specific mintage materials (gold or silver), subwavelength dimensions and morphologies with less symmetry axis (*e.g.* cubic shape). For instance, we have recently been able to fabricate core shell nanoparticles with a specific dielectric spacer for controlled electric field enhancement.[*J. Phys. Chem. C* **2015**, 119, 9513 and Nanoscale **2017**, 9, 9376] As a second step, we use a directed self-assembly technique to align these building blocks to achieve collective plasmonic excitations such as constructive interference between plasmonic and diffraction modes (Fano resonance). Finally, we go one step further and use our directed self-assembly approach to discuss a magnetic metasurface. This magnetic mode could be excited using a plasmonic film coupled nanoparticle system.[*Faraday Discuss.* **2016**, 191, 159.] This extraordinary electric field enhancement opens up new possibilities in ultra-sensitive sensing applications, plasmon-induced charge separations and the tailored control of the electric as well as magnetic field, which is important for super-absorber and metamaterial applications.

O7-3

ENERGY TRANSFER BETWEEN HYBRID METAL-HALIDE PEROVSKITES AND CONJUGATED POLYMER COLLOIDS

Annabel Mikosch[1,2], Sibel Ciftci[1], Felix Deschler[2], Alexander JC Kuehne[1]

[1] DWI-Leibniz Institute for Interactive Materials, Forckenbeckstr 50, 52074 Aachen, Germany.
[2] Optoelectronics Group, University of Cambridge, Cambridge, United Kingdom.

Monodisperse π-conjugated polymer colloids self-assemble into periodic optical resonator structures, while simultaneously providing optical gain, and therefore are powerful building blocks for polymer and hybrid material photonics.[1] By contrast, methylammonium lead halide perovskites ($MAPbX_3$, X= Cl, Br, I) are inorganic semiconductors with long charge carrier lifetimes and exciton diffusion lengths. They can be processed at ambient temperatures from solution and by changing the halide combination, the emission of the perovskites is tunable across the entire visible spectrum.[2] The combination of conjugated polymers and perovskites into one co-deposition process leads to new nanostructured, hybrid organic-inorganic materials. Tuning the emission band of the perovskite to overlap with the absorption band of poly(fluorene-co-divinylbenzene) colloids enables energy transfer between the organic and the inorganic materials. The perovskite serves as a functional matrix for the colloids, which increases the optical performance and photoluminescence quantum yield. However, the nature of this energy transfer is unknown. We apply fluorescence lifetime imaging and spectral analysis to investigate the energy transfer from perovskite to the conjugated polymer colloids and differentiate between radiative, resonant and direct electron transport. The new hybrid materials could provide a new way of pumping organic lasers and provide insight into new pathways for electrically driven organic photonics.

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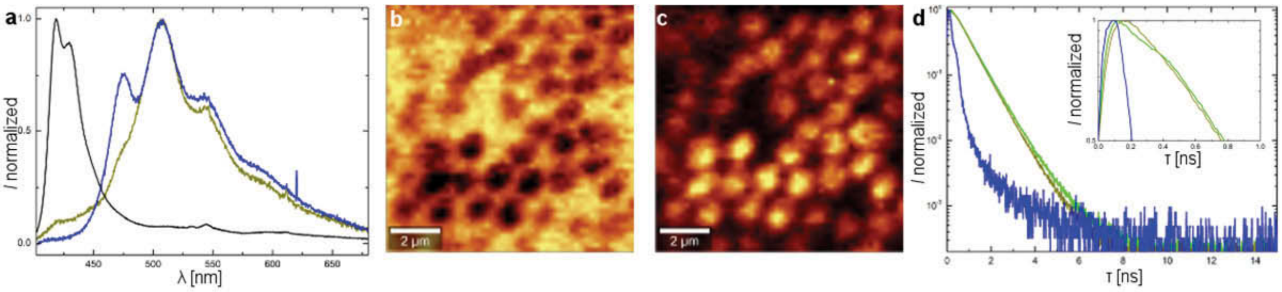

Figure 2. A) Photoluminescence spectra of $MAPb(Br_xCl_{(1-x)})$ x= 0.1 as black line, colloids as blue line, and composite as dark yellow line. B) intensity map of x= 0.1 composite photoluminescence at 450 nm. C) intensity map of x= 0.1 composite emitting at 510 nm. D) fluorescence life time of emission at 450 nm of pure colloids as blue line, x= 0.1 composite as dark yellow line, and x= 0.4 composite as green line. Inset shows a zoom-in on the rise time.

O7-4

MONOLAYER FORMATION OF GOLD NANOTRIANGLES FOR SERS MONITORING OF PLASMON-DRIVEN CATALYTIC REACTIONS

Ferenc Liebig[1], Radwan M. Sarhan[2] and Joachim Koetz[1]

[1] University of Potsdam, Institute of Chemistry, Potsdam, Germany
[2] University of Potsdam, Institute of Physics, Potsdam, Germany

Gold nanotriangles (AuNTs) show unique optical and physical properties, which are useful in many applications. Their absorption in the NIR-region, for example, make them highly interesting for biological applications like hyperthermia of cancer cells and tissue imaging. Another important research field is the performance in surface-enhanced Raman scattering, an analysis technique for the detection of molecules, which also can be used for monitoring plasmon-driven catalytic reactions.

The synthesis of AuNTs in a mixed AOT/phospholipid-based vesicular template phase leads to a yield of 33 %.[1] The separation from the rest of the particles was realized by a combined micelle/polyelectrolyte depletion flocculation.[2] After a subsequently purification, only gold nanotriangles with an edge length of about 175 nm and a defined thickness of about 7 nm were obtained.

By adding an oil mixture to a droplet of an aqueous dispersion of these AuNTs, a particle transfer to the air-liquid interface and a related self-assembled monolayer formation will be induced. After evaporation of the liquid a close-packed monolayer of edge-to-edge ordered AuNTs can be observed. The short distance between the plasmonic particles serves as basis for “hot spots”, which can be directly attributed to the SERS performance. To study the photocatalytic activity of the AuNTs, the dimerization of 4-nitrothiophenol (4-NTP) to 4,4´-dimercaptoazobenzene (DMAB) as a model reaction was used. From this result it can quite clearly be seen that the AuNTs efficiently drive the reaction and allow a real time monitoring of reaction dynamics.

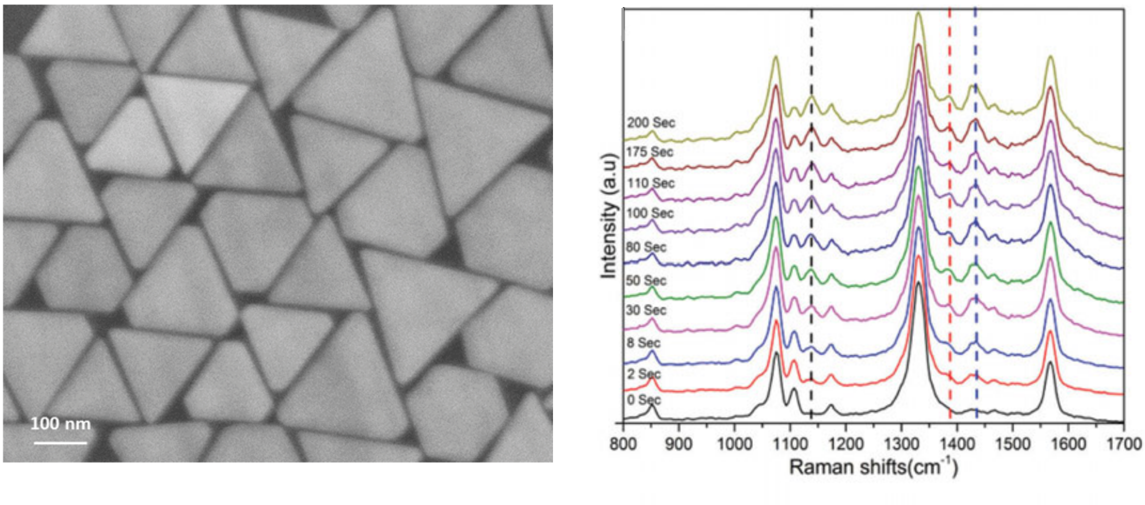

Figure 1. SEM micrograph of the AuNTs monolayer formation (left), time-dependent SERS spectra during the reaction of 4-NTP to DMAB

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POSTER SESSION

P-1

PRODUCTION OF MCM-41 FROM GOLD MINE WASTE

İlayda Acaroglu Degitz[1], Sabriye Piskin[2]

[1] Yeditepe University, Department of Chemical Engineering, İstanbul, Turkey
[2] Yildiz Technical University, Department of Chemical Engineering, İstanbul, Turkey

A member of M41S family, MCM-41 which is a well-known mesoporous molecular sieve, have great attention due to their long range order open pore [1], highly ordered arrays and strong thermal stability, and narrow size[1,2] but large surface area [2,3]. Therefore, MCM-41 has been a great candidate for drug delivery, heterogeneous catalyst, adsorption of toxic metal ions and many other applications [2-4]. MCM-41 had been synthesized by hydrothermal method with using expensive silica sources TEOS, TMOS [5]. In recent years due to the increasing interest on waste recycles processes, many different waste used to synthesize MCM-41 such as rice husk, coal fly ash [6,7].

In this study, MCM-41 synthesized from Bergama gold mine waste, which provided a high silicon source. The silicon contents of the gold mine waste were investigated with XRF analysis, which proved the waste contained silicon. The analysis indicated that the gold mine waste contained 77.7% silicon by weight and also has other components (Al_2O_3, K_2O, CaO, TiO_2, MnO, Fe_2O3, MoO_3 and BaO.) For the extraction of silicon from gold mine waste, was achieved using fusion method. The reaction time, temperature, and pH adjustments are the parameters which have most influence on the synthesis' mechanism. For the purpose of examining these parameters, the synthesis was achieved at different reaction times, reaction temperatures and both alkaline pH adjustments and acidic pH adjustments. After the discovery of the optimum conditions for the MCM-41 synthesis, from gold mine waste (MA), and for a comparison, a reference synthesis of MCM-41 (MSS), from a pure silicon source (TEOS), was conducted. The properties of MSS and MA were examined by XRD, FT-IR, SEM and TG/DTG analysis. The effect of calcinations to MSS and MA were studied with XRD and FT-IR analysis and the investigated calcinations assisted the evaporation of surface moisture, surfactant and silanol groups. In addition the thermal analysis were done before calcination process and due to this analysis Kissenger-Akahire-Sunose (KAS) and Friedman (FR) kinetic methods were examined for MSS and MA structures. These two kinetic methods' results were proved to be nearly identical.

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P-2

ROOM TEMPERATURE FERROMAGNETISM IN NANOSTRUCTURED MN-DOPED CUPROUS OXIDE FIBRES

Asar Ahmed

Laxminarayan Institute of Technology Nagpur, India

One-dimensional semiconductors in the nanoscale region are of great interest in the current research because of their interesting properties with varieties of applications. Doping these materials can further tailor their existing properties while inducing some new properties. These materials have the unique combination of different physical properties like semiconductivity and magnetism. It has been reported in the literature that semiconductors doped with transition metal ions can induce ferromagnetism at low temperatures. Here we report the synthesis and characterization of nanostructured Cu_2O fibres doped with Mn ions and the observation of ferromagnetism at room temperature for the same. Room temperature hysteresis curve for the sample clearly showed that the material is ferromagnetic. As both Cu_2O and Mn ions are non-magnetic, therefore it might be suggested that ferromagnetism originated from Mn-induced defects present in the material. These nanofibers were synthesized by employing the polyol method. In this method, precursor of $Cu(CH_3COO)_2.H_2O$ and $MnCl_2.4H_2O$ were used with solvent diethylene glycol and surfactants Tween 80 and Sodium dodecyl sulfate. Parameters like the reaction temperature, the reaction time, the precursor's concentration, surfactant's concentrations and their ratios were carefully controlled during the experiments and were found to have critical influence on the final product and particle shape and size. Nanfibres with a diameter of around 50-70 nm and a length up to 6 μm were obtained. The salient features of this method are the simple and economical methodology, moreover SDS and Tween 80 surfactants are well known for their non-toxic and eco-friendly nature. The nanofibres were characterized by SEM, TEM, XRD, FT-IR and Vibration Sample Magnetometer.

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P-3

FREQUENCY EFFECT ON CARBON NANOTUBE-BASED GAS SENSORS AND CONTACTS

Bahar Meshginqalam[1] and Sholeh Alaei[2]

[1] The Young Researchers and Elite Club, Urmia Branch, Islamic Azad University, Urmia, Iran
[2] Department of Physics, Urmia Branch, Islamic Azad University, Urmia, Iran

The carbon nanotubes (CNTs) due to their specific properties are among promising materials for nanoelectronics, both as elements for MOSFETs and Schottky-junction diodes, opteoelectronics, solar cells, sensors, biosensors, energy sorage, biomedical applications and air and water filterations. Semiconducting or metallic nanotubes are found depending on the topological arrangements, chirality and diameter of carbon atoms in the nanotube matrix. In nanoelectronic applications, the semiconducting nanotubes are very favorable for incorporating in field effect transistors (FETs) and Schottky barriers. Furtheremore, in terms of sensing applications, CNT-based gas sensors are of great interest for detecting various gases like carbon dioxide, hydrogen, nitrogen dioxide and etc [1-3]. Most of these senors are based on electrical conductance variation of semiconduting carbon nanotubes. Many studies have been done in various sensing applications of CNT-based sensors [4,5].

Considering the importance of CNT-based sensors, This study presents our investigation about the effects of frequency on the growth of carbon nano particles and CNTs particularly MWCNTs, development of CNT-based gas sensors and the electrical properties of CNT-metal contacts. High voltage arc discharge method [6] is used for fabrication of CNTs in the form of gas sensors on the base of ohmic or Schottky contacts. The effect of frequency on the performance, sensitivity of gas sensors and electrical properties of CNTs were perused. Electrical properties were characterized by I-V curves after fixing frequency. It is observed that the conductivity of prototype carbon nanotube Schottky contacts and sensitivity of CNTS-based sensors alters under frequency modification. Furthermore, as complementary studies, a model has been developed for CNT gas sensor exposed to various gases to provide a platform for checking the effect of frequency on the performance of CNT contacts.

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P-4

SYNTHESIS AND ELECTRICAL CHARACTERIZATION OF GOLD (AU) EMBEDDED GRAFT COPOLYMER FIBER

Sema Alli[1] and Abdulkadir Alli[2]

[1] Department of Polymer Engineering, Düzce University, Düzce, Turkey
[2] Department of Chemistry, Düzce University, Düzce, Turkey

The poly (linoleic acid)-g-poly (methyl methacrylate) (PLiMMA) graft copolymer was synthesized and characterized. Then, Gold (Au) embedded graft copolymer fiber was prepared via precipitation method using $NaBH_4$. Au particles were distributed in graft copolymer. Electrical characterization of Au embedded graft copolymer fiber was investigated. Main electrical characteristic of the Au/poly (linoleic acid)-g-poly (methyl methacrylate) (PLiMMA)/n-Si diode was investigated. This investigation was realized by using I-V measurements in dark and under illumination at room temperature. It is found that n, and values of the diode are for dark and 100 nW/cm2Ω; 6.3, 0.71 eV, 676 Ω2.8, 0.87 eV, 8096 illumination intensity, respectively. Also, reasons of the deviation from the ideal thermionic emission theory were investigated using Cheung& Cheung method and Card&Rhoderick's function for B (V), series calculating voltage dependence of barrier height resistance and number of surface states (Nss) of the Au/PLiMMA/n-Si diode.

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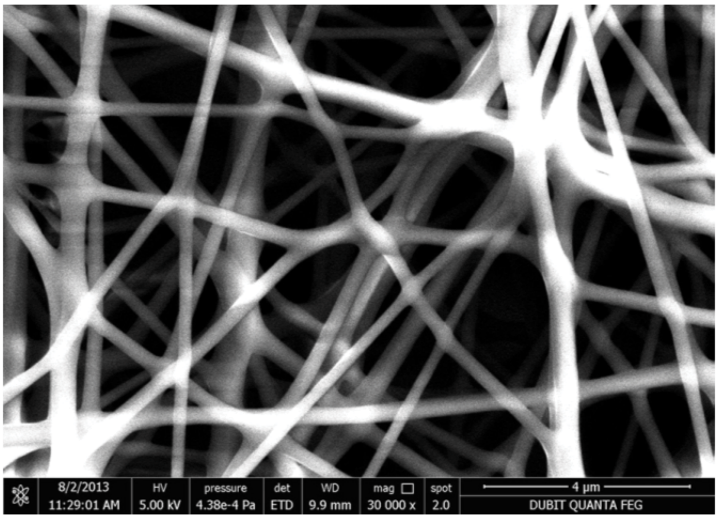

Figure 1. The FEG-SEM micrograph of PLiMMA polymeric interfacial layer.

P-5

SYNTHESIS AND CHARACTERISTICS OF *IN SITU* HARDENED COPPER BASED ALLOYS

Dušan Božić and Jelena Stašić

Materials Science Laboratory/Institute of Nuclear Sciences “Vinča”, Belgrade, Serbia

Copper matrix composites have a wide range of applications because of the combination of high mechanical strength and electrical/thermal conductivity. To improve the interfacial compatibility and avoid serious interfacial reaction, various new processing techniques are being used to fabricate ceramic particle-reinforced metal matrix composites [1]. The basic principle of this technique is that the fine and thermodynamically stable ceramic phases are formed *in situ* by exothermal reaction between elements or between element and compound within a metal matrix. Reaction processes between structural components in obtaining particle reinforcement occur in solid or liquid state. The *in situ* composites exhibit improved mechanical strength, hardness as well as enhanced wear resistance. Titanium diboride is well known for its high stiffness, hardness and high mechanical strength. Furthermore, in contrast to most ceramics, it is electrically and thermally conductive [2]. This suggests that TiB_2 is a potential reinforcing material for copper and its alloys in cases where high electrical conductivity is important. The atomized Cu-0.8 wt.%Ti-1.7 wt.%TiB_2 powders have been used as starting materials. Dispersoid particles TiB_2 were formed *in situ*. The powders have been hot isostatically pressed. Optical microscopy, SEM, TEM, and X-ray diffraction analysis were performed for microstructural characterization. High hardening of Cu-0.8 wt.%Ti-1.7 wt.%TiB_2 is a consequence of the presence of modular structure, $Cu_4Ti_{(m)}$, and TiB_2 particles [3].

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[3] The results presented are realized with financial support of the Ministry of Science and Technological Development of the Republic of Serbia through project no. 172005.

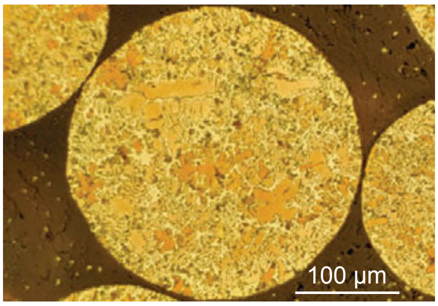

Figure 1. OM: microstructure of as-atomized Cu-0.8Ti-1.7TiB_2 (wt.%) alloy powders.

P-6

ADVANCED LIGHT SCATTERING TECHNIQUES FOR THE CHARACTERIZATION OF CONCENTRATED SYSTEMS.

Coline Bretz, Andrea Vaccaro, Andreas C. Voelker

LS Instruments, Fribourg, Switzerland

Dynamic and Static Light scattering are powerful non-invasive tools widely used to characterize the dynamics and structure of soft matter systems. These techniques traditionally rely on the measurement of singly scattered light, where each photon detected corresponds to a unique scattering event. In this scheme, the sample must be diluted, as a small amount of multiple scattering can result in significant measurement errors. It is often difficult to find an appropriate degree of dilution while keeping a high scattering signal. Moreover, this approach does not allow for the characterization of concentrated, or unconventional systems. To counter this issue, a significant improvement in DLS and SLS has been achieved through the 3D modulated cross-correlation technology: in this scheme, two scattering experiments are temporally separated and then cross-correlated to extract single-scattering information from the same scattering volume and the same scattering vector.

The performance of this 3D technology can be further enhanced through means of optical path length reduction. The ability to modify the position of the sample cell further enables the characterization of concentrated samples through reduction of multiple scattering. The cell can also be continuously rotated during a measurement, allowing for the study of non-ergodic samples such as gels, foams or glasses.

In this presentation, we will give an overview of the 3D technology and its performances. We present SLS measurements performed on suspensions of nanoparticles with long-range interactions. We will show how modulated 3D cross-correlation technology enables us to suppress multiple scattering and hence gain access to the structure factor of highly concentrated suspensions.

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P-7

THE RAPID DIRECTED ASSEMBLY AND FABRICATION OF PARTICLE-BASED OBJECTS USING ACOUSTIC FIELDS

Eunjin Choi[1], Kai Melde[1], Zhiguang Wu[1], Stefano Palagi[1], Tian Qiu[1] and Peer Fischer[1,2]

[1] Max Planck Institute for Intelligent Systems, Stuttgart, Germany
[2] Institut für Physikalische Chemie, Universität Stuttgart, Stuttgart, Germany

Ultrasound offers a convenient and benign way to manipulate particles, including biological cells. Acoustic fields can be used for the directed assembly of particles and cells [1]. However, the acoustic manipulation of particles thus far was limited because it was not possible to generate sophisticated ultrasound fields [2]. We have recently shown that an acoustic hologram can generate highly sophisticated ultrasound fields [3]. Herein, we report the rapid fabrication of arbitrary 2.5 D shapes in solution using ultrasound images reconstructed from acoustic holograms [3]. The ultrasound image is defined by regions of high sound pressure, which form trapping sites for silicone microparticles characterized by a low speed of sound compared to water [4]. The particle assembly is then fixed using a photo-crosslinking scheme that involves pre-loading the initiator onto the particle surface via solvent induced swelling [5]. This limits cross-linking to the object vicinity and leaves the bulk solution largely unaffected. From assembly to confinement, the whole fabrication process is finished in less than 1 min. After cross-linking the objects are self-supporting and mechanically stable. Compared to serial printing techniques, acoustic fabrication thus promises a highly facile and parallel scheme to form arbitrary shaped objects in a matter of seconds [6].

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Figure 1. General scheme of acoustic fabrication. A homogeneous dispersion of functionalized particles (a) is exposed to a structured ultrasound field, which defines trapping regions for particles (b). Then, UV triggers the fixing reaction and thereby permanently fixes the assembled particles to create the object (c).

P-8

MEASURING THE CONCENTRATION OF SELF-ASSEMBLING NANOPARTICLES IN EVAPORATING DROPLETS

David Doblas Jiménez[1], Marina Cano Bonilla[1], Thomas Kister[1], and Tobias Kraus[1,2]

[1] INM – Leibniz Institute for New Materials, Campus D2 2, Saarbrücken, Germany
[2] Colloid and Interface Chemistry, Saarland University, D2 2, 66123 Saarbrücken, Germany

Nanoparticles in the dispersed phase of an emulsion are subject to an interplay between the interfacial energy of the emulsion phases and interparticle forces between the particles. The particles may adsorb on the droplet interfaces and possibly agglomerate or remain in the confined space of the droplets and arrange in reaction to this confinement [1]. Self-assembly may occur if the particles are uniform and can minimize their free energy to reach an ordered state. To understand this process, one would like to know the concentration at which interactions between nanoparticles cause agglomeration or self-assembly.

We observe the behavior of confined particles inside the emulsion droplets using *in situ* techniques [2-3]. Here, we discuss the results of studies of the self-assembly of gold nanoparticles with alkylthiol shells in different solvents. Small angle X-ray scattering of highly concentrated dispersions of stabilized gold nanoparticles during solvent evaporation reveals both the formation of close-packed spherical supraparticles and the remaining amount of solvent with sufficient time resolution (cf. Figure 1a). Following the evolution of those changes, we could estimate that the nanoparticle concentration at which self-assembly occurs is above 100 mg/mL for the shortest ligand (hexanethiol) used in this study (cf. Figure 1b).

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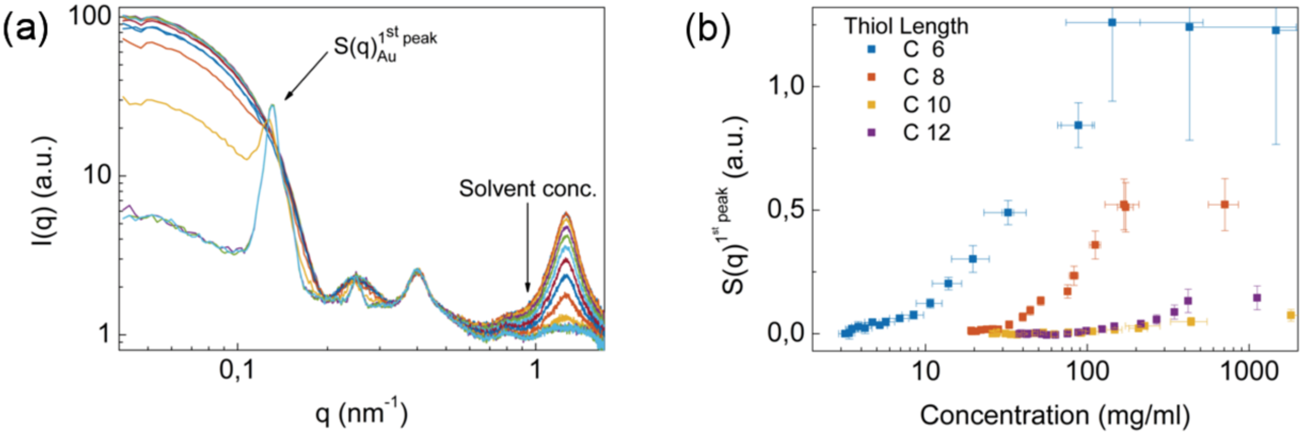

Figure 1. (a) Evolution of the structure factor from small angle X-ray scattering and the overall solvent remaining in an evaporating droplet. (b) Emergence of order with increasing nanoparticle concentration for different ligands shells.

P-9

CARBON ONION / METAL OXIDE: HYBRIDIZATION OR NANOCOMPOSITE? WHAT SYSTEM CAN DELIVER A BETTER PERFORMANCE FOR ELECTROCHEMICAL ENERGY STORAGE?

Simon Fleischmann,[1,2] Marco Zeiger[1,2] and Volker Presser[1,2]

[1] INM – Leibniz Institute for New Materials, 66123 Saarbrücken, Germany
[2] Department of Materials Science and Engineering, Saarland University, 66123 Saarbrücken, Germany

Transitioning from fossil to renewable energy sources is highly dependent on the availability of high power electrochemical energy storage devices that can bridge the fluctuations arising from intermittent solar and wind power. The development of novel electrode materials that enable high charging and discharging rates is at the focal point of current research activities[1]. The main obstacles to overcome are limitations posed by both electron and ion mobility. Consequently, advanced electrode materials have to offer high electrical conductivity and a nanostructured surface yielding a large electrode/electrolyte interface. In this context, the introduction of a nanoparticular carbon to the electrode is a suitable method.

Carbon onions are spherical carbon nanoparticles (5-10 nm) consisting of several concentric shells of sp^2-hybridized carbon[2]. They are derived from nanodiamonds by thermal annealing in inert atmospheres at elevated temperatures. Their high electrical conductivity, spherical shape and nanoscopic size make them ideal candidates for hybridization with Faradaic battery materials that are used in high power lithium ion batteries.

How does the nanoparticle processing influence the desired electrochemical properties? In this contribution, we investigate the properties of carbon onion / vanadium oxide hybrid material as lithium ion intercalation host[3]. The components are hybridized by growing vanadia hydrothermally on the carbon onion surfaces, resulting in a chemically linked and highly intertwined nanostructure. In contrast, mechanical admixing of carbon onions to vanadium oxide post-synthesis yields a less interconnected composite material. Electrochemical investigation in lithium containing electrolyte reveals the advantages of the hybrid design over the composite approach.

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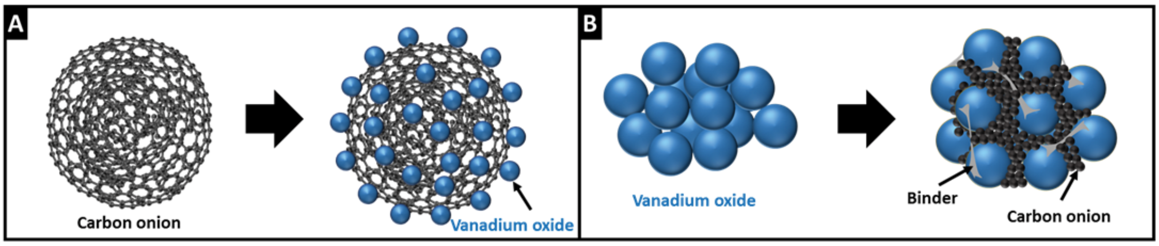

Figure 1. Carbon onion nanoparticles can serve as a substrate for hydrothermally grown vanadium oxide forming a hybrid material (A); or be mechanically admixed as a conductive additive to already synthesized vanadium oxide to form a composite material (B).

P-10

TUNING HYDROPHOBICITY OF GOLD NANOCLUSTERS TO ENHANCE MEMBRANE PENETRATION

Estelle Porret[1], Lucie Sancey[1], Angela Martín-Serrano[2], Maria I. Montañez[2], Ralf Seeman[3], Akram Yahia-Ammar[4], Niko Hildebrandt[4], Jean-Baptiste Fleury[3], Jean-Luc Coll[1] and Xavier Le Guével[1]

[1] Cancer Targets & Experimental Therapeutics, Institute for Advanced Biosciences (IAB), University of Grenoble Alpes, Grenoble, France
[2] Research Laboratory and Allergy Service, IBIMA, Regional University Malaga Hospital and Andalusian Center for Nanomedicine and Biotechnology – BIONAND, Málaga, Spain
[3] Experimental Physics, Saarland University, Saarbrücken, Germany
[4] NanoBioPhotonics, Institute for Integrative Biology of the Cell (I2BC), Université Paris-Saclay, Université Paris-Sud, Orsay, France

Understanding how ultra-small gold nanoparticles (metal core ~ 1–1.5 nm), so-called gold nanoclusters (Au NCs), interact with biological barriers has become highly important for their future bioapplications. The properties of Au NCs with tunable hydrophobicity were extensively characterized in 3 different biological situations: i) interaction with serum in solution, ii) interaction with synthetic free-standing lipid bilayers integrated in a microfluidic device, and iii) cell studies with two different cell types (U87MG human primary glioblastoma and A375 melanoma cell lines). Our results indicate a significant impact of the precise tailoring of the hydrophilicity/hydrophobicity balance on the Au NC surfaces, which could prevent the formation of biomolecular absorption while maintaining excellent colloidal stability in solutions with high serum contents. Increasing the surface hydrophobicity of the Au NCs enabled more efficient lipid bilayer membrane insertion and induced faster cellular uptake. We showed the existence of a hydrophobicity threshold, which resulted in colloidal instability, lipid bilayer damage, and acute cytotoxicity. [1]

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P-11

STABILIZATION OF AL$_2$O$_3$ NANOPARTICLES VIA 3-(TRIMETHOXYSILYL)PROPYL METHACRYLATE IN UV CURABLE INK FOR 3D INKJET PRINTING

Dennis Graf[1,2], Sven Burchard[2] and Thomas Hanemann[1,2]

[1] Karlsruhe Institute of Technology, Institute for Applied Materials-WK, Eggenstein-Leopoldshafen, Germany
[2] University of Freiburg, Department Of Microsystems, Freiburg im Breisgau

Aluminum oxide nanofillers have been stabilized with 3-(trimethoxysilyl)propyl methacrylate (MPS) in a five component acrylate system in order to produce an ink for 3D inkjet printing. The Nanofillers have been added to achieve better, mechanically durable components.
The alumina had an average particle size (APS) of 13 nm (manufacturer information). Together with MPS (50 wt% relative to filler mass) it was introduced into ethanol and grinded with a planetary ball mill (PBM) for 1 h. Afterwards the MPS loaded ceramic was dried in a rotary evaporator. The powder was then suspended in a mixture of isobornylacrylate, tripropylene glycol diacrylate, trimethylpropane(EO)3 triacrylate, di(trimethylpropane)tetracrylate, and polyether acrylate with a high power disperser. The particle size distribution (PSD) has been assessed by dynamic light scattering measurement. Finally, the dispersion was used to produce specimens for tensile tests via drop casting and UV curing layer-by-layer.
The MPS stabilized particles show an APS in acrylate matrix of 0.201 µm. The D10, D50 and D100 values are 0.103 µm, 0.171 µm, and 1.375 µm, respectively (Figure 1. Left). It shows that the filler are agglomerated to a certain extend. The tensile test hints at a general decrease of the mechanical properties with increasing filler concentration (Figure 1. Right).

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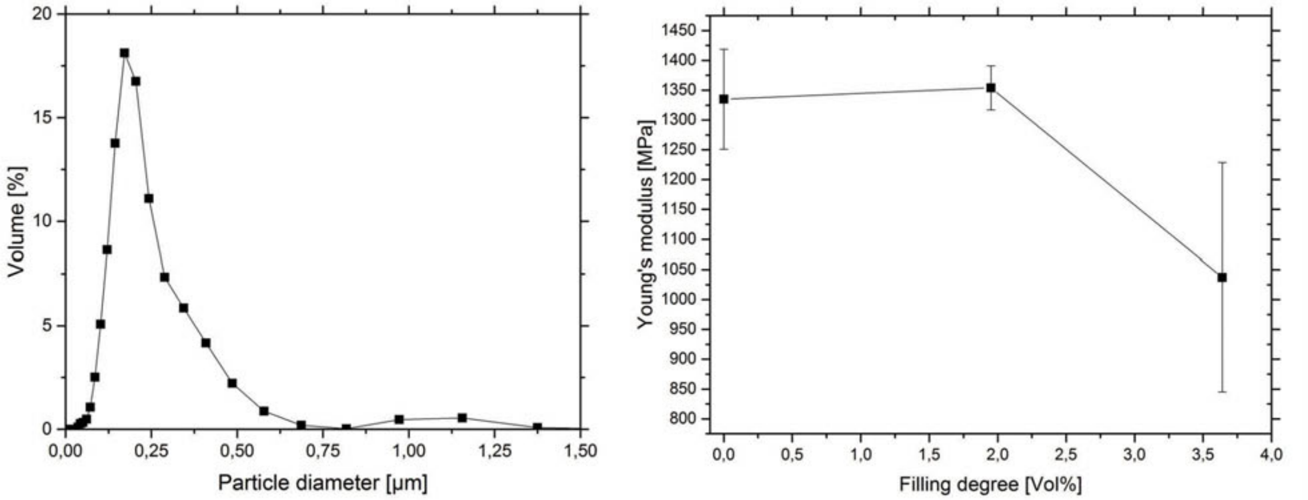

Figure 1.
Left: PSD of MPS stabilized Al$_2$O$_3$ nanoparticles suspended in acrylate matrix.
Right: Young’s modulus of Al$_2$O$_3$-polyacrylate specimens in dependency of the filler degree.

P-12

COLLOIDAL ANALYSIS OF PARTICLES EXTRACTED FROM MICROALLOYED STEELS

Andreas Hegetschweiler[1], Thorsten Staudt[2] and Tobias Kraus[1,3]

[1] INM – Leibniz-Institute for New Materials, Campus D2 2, 66123 Saarbrücken, Germany
[2] AG der Dillinger Hüttenwerke, Werkstraße 1, 66763 Dillingen/Saar, Germany
[3] Colloid and Interface Chemistry, Saarland University, D2 2, 66123 Saarbrücken, Germany

Particles play an important role in modern steels: the advantages of microalloyed steels in mechanical properties, weldability, and relatively low production costs are in no small part due to particles that form during thermo-mechanical rolling. Carbonitride particles with diameters between a few nanometers up to several hundreds of nanometers form from dissolved niobium, titanium, and/or vanadium. Depending on their size, the particles pin grain boundaries or retard the recrystallization during the rolling process, resulting in a very fine-grained microstructure. Very small particles with sizes of a few nanometer lead to precipitation hardening. Control and optimization of particle formation is therefore of interest to the steel industry that requires 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 and colloidal analysis. 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 colloidal dispersion remains. The suspensions are analyzed using Field-Flow-Fractionation (FFF), Analytical Ultracentrifugation (AUC), or Single Particle Mass Spectrometry with Inductively Coupled Plasma (SP-ICP-MS). Here, we evaluate the feasibility of colloidal characterization of the extracted particles. We discuss the particle size distributions measured with FFF and AUC and the assumptions that are necessary to transform these extinction weighted particle size distributions in number weighted size distributions and compare them with the particle size distribution measured on carbon replicas.

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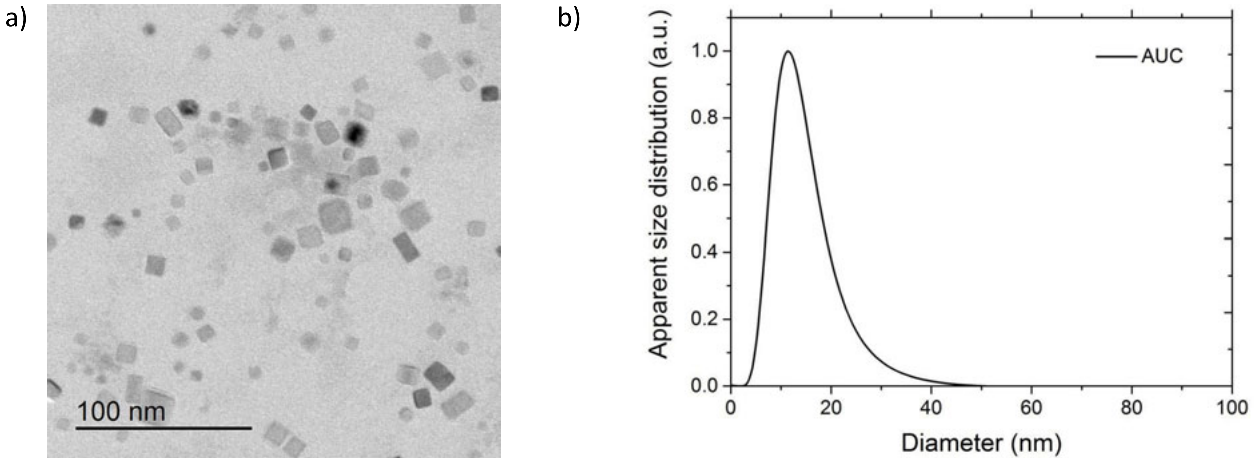

Figure 1. a) TEM micrograph of particles extracted from a microalloyed steel b) size distribution measured with Analytical Ultracentrifugation

P-13

INFLUENCING NOBLE METAL AEROGEL STRUCTURES

Karl Hiekel, Kristian Schneider, Albrecht Benad, Alexander Eychmüller

Physical Chemistry, TU Dresden, Dresden, Germany

Noble metal aerogels are a relative new class of materials that is of great interest e.g. for electrocatalysis [1,2]. In general, the efficiency of the catalyst depends on the used metals or alloys and on the surface area.

Up until now, there is no known theory on how to influence the structure of the gels. The aim of this work is to show some possibilities of how to affect the morphology of the noble metal aerogels (gold and silver) and to fine-tune them for their respective application.

The gel morphology depends obviously on the initial particle size and on the number of branching events per volume. For instance, the particle size can be influenced by the ratio of reducing agent to metal salt precursor and other factors like the choice of ligands. The branching on the other side depends on the charge of the metal nanoparticles and therefore of the electrostatic repulsion which can be affected by the addition of ancillary ions or by replacing the solvent [3].

This work will show how to influence the gel structure by changing the reaction conditions and rating their impact using various techniques. The focus will lie on altering the solvent (as seen in Figure 1), the ratio and concentration of the used compounds and other terms. The presented data will finally expand and lead to a better, more detailed understanding and insight in the up until now not fully understood gelation process of noble metal aerogels [4].

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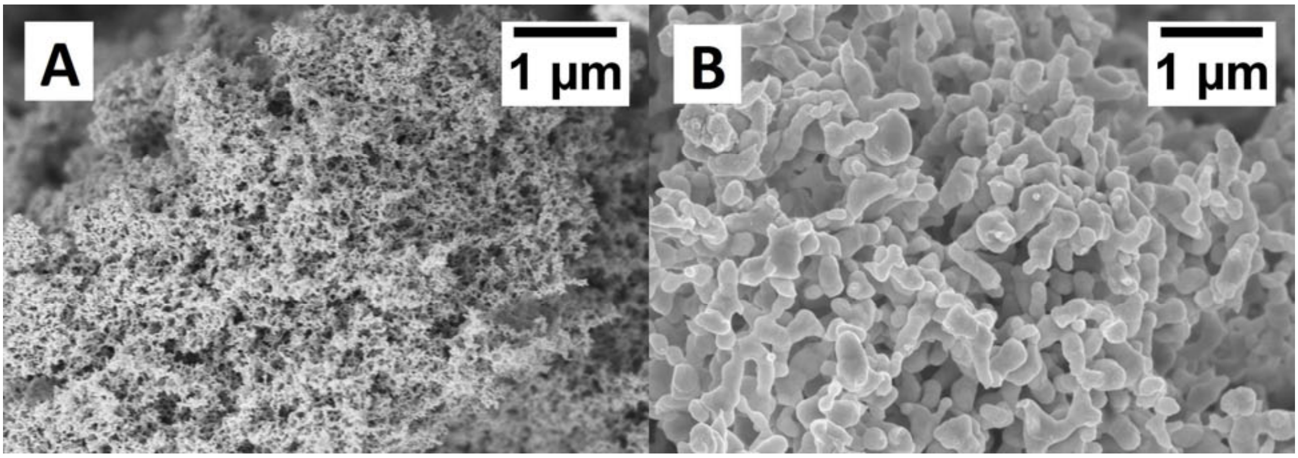

Figure 1. Scanning electron microscopy images of Au-aerogels synthesized in ethanol (“A”, with an average nanochain diameter of ≈ 20 nm) or in water (“B”, with an average diameter of ≈ 150 nm).

P-14

TOWARDS A SURFACE-BOUND MICROGEL SYSTEM USING DNA-HYBRIDIZATION AND SUPER RESOLUTION FLUORESCENCE MICROSCOPY

Laura Hoppe Alvarez[1], Sabine Eisold[2], Ulrich Simon[2], Dominik Wöll[1]

[1] RWTH Aachen University, Institute of Physical Chemistry, Aachen, Germany
[2] RWTH Aachen University, Institute of Inorganic Chemistry, Aachen, Germany

The past decade has witnessed remarkable development in the synthesis of microgels with specific characteristics. Their stimuli-resposive swelling properties opened a large field of applications. Microgels were identified as ideal systems for controlled drug delivery as their temperature-responsive swelling of the inner shell controls the uptake and release, whereas the size of the void is controlled by the outer shell [1]. The production of appropriate applications is highly dependent on the fundamental understanding of the molecular properties and structures of such microgels. Our goal is to build a surface-bound microgel system, which allows us to visualize microgels in their native state using modern super-resolution fluorescence microscopy techniques.

Our approach for such a surface-immobilization takes advantage of the high resolution to write structures with chemical e-beam lithography (C-EBL) and its combination with optical photolithography [2, 3]. Furthermore, our goal is the hybridization of microgels to DNA-strands immobilized to specific spots on the patterned surface.

We could already show how to localize individual spots in the C-EBL pattern in different microscopes (electron and optical) and developed appropriate software routines to address them individually. We were able to successfully attach fluorescently labeled DNA strands to spots in the C-EBL pattern (see figure 1). The next step will include the hybridization of DNA-functionalized microgels to the DNA-strands on the surface. Modern super-resolution fluorescence techniques such as DNA-PAINT will be used in order to image three-dimensional microgel structures.

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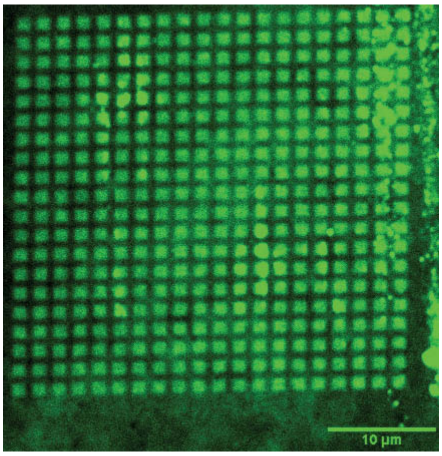

Figure 1. Fluorescently labeled DNA-strands immobilized to the C-EBL pattern.

P-15

SOLID PHASE SYNTHESIS OF ORGANIC SEMICONDUCTOR NANOREACTORS FOR VISIBLE LIGHT PHOTOCATALYSIS

Wei Huang, Katharina Landfester and Kai Zhang

Max Planck Institute for Polymer Research, Mainz-55128, Germany

The development of efficient, stable and cost-effective visible light photocatalysts that enable direct utilization of solar energy for organic transformation represents one of the major targets in organic photosynthesis. Polymeric organic semiconductors have recently emerged as promising alternatives to traditional transition-metal-based photocatalysts owing to their broad visible light absorption, metal-free composition, ease to reuse and highly tunable optoelectronic properties [1]. However, limitations in incident light utilization and charge separation are major drawbacks that restrict the activity of current artificial photosystems. Construction of hollow organic nano-photoreactors is considered as a promising approach to address these issues, since they are able to promote the light absorption efficiency via multiple light reflections during the catalytic process and subsequently enhance photocatalytic activity.

Herein, we developed a facile solid phase synthetic method to produce hollow ordered macroporous and mesoporous organic semiconductor nanoreactors based on trimerization reaction of nitrile-functionalized aromatic units catalyzed by TfOH vapor using nanostructured silica as template. Both variation of molecular and morphological structures, enhanced photocatalytic activity of the organic semiconductors was demonstrated in a series of visible light-promoted photoredox reactions, such as reduction of nitrophenol [2] and selective aerobic oxidation of alcohols [3][4].

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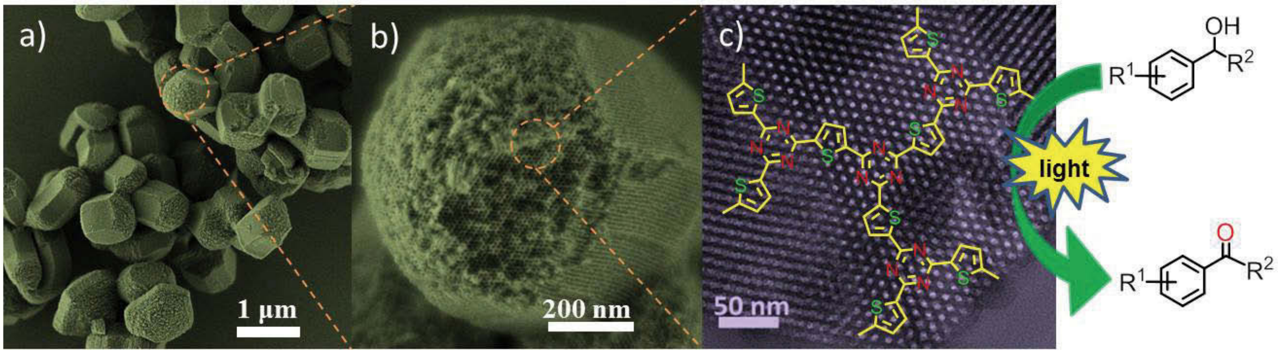

Figure 1. a,b) SEM and c) TEM images of mesoporous trazine-based organic semiconductor nanoreactor for visible light-promoted selective aerobic oxidation of alcohols.

P-16

HYDROXYL-FUNCTIONAL NANOPARTICLES AS PHASE-MODULATING ADDITIVES IN ELECTROSPUN POLYMER NANOFIBERS

Martin Järvekülg [1], Anna Šutka[2] and Andris Šutka[1,3]

[1] Institute of Physics, University of Tartu, Tartu, Estonia
[2] Biomaterials Research Laboratory, Institute of Inorganic Chemistry, Riga Technical University, Rīga, Latvia
[3] Research Laboratory of Functional Materials Technologies, Riga Technical University, Rīga, Latvia

Interface has been found to be critical in maximizing the desired influence of additive on mechanical properties of polymers. In general, the significant enhancements observed in nanoparticle-reinforced polymers are attributed to an interphase, a region surrounding the inclusions where the properties differ from the bulk [1-3].

In this work, we demonstrate extensive hydrogen bonding between Poly(vinyl alcohol) (PVA) and organic or inorganic hydroxyl-functional nanoparticles, such as nano-cellulose (NC) and goethite resulting remarkable reinforcement in electrospun PVA nanocomposite fibers. Our aim has been the development of sustainable cross-linking and stabilization strategies for hydrophilic polymer.

Mechanical properties of the electrospun nanofibers were tested in macro-and nano-scale. We are demonstrating the reason for increased mechanical strength for electrospun PVA fibers doped hydroxyl-functional nanoparticles. We address the relations between the change in inherent Young's modulus of the composite and the stiffness of an electrospun mat. We are reporting a five-fold and seven-fold increase in stiffness of the mat as the result of the goethite and NC additive, respectively.

Especially interesting are goethite nanowires, which have intrinsically high elastic modulus and –OH rich surface, but their use in combination with hydrophilic polymers has not been reported before, even at bulk scale. [4]

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P-17

COLORATION OF TIO_2 NANOPARTICLE COLLOIDS

Urmas Joost[1,2], Andris Šutka[2,3], Marek Oja[2], Krisjanis Smits[4], Nicola Döbelin[5], Ardi Loot[2], Martin Järvekülg[2], Mika Hirsimäki[1], Mika Valden[1], and Ergo Nõmmiste[2]

[1] Surface Science Group, Photonics Laboratory, Tampere University of Technology, Tampere, Finland
[2] Institute of Physics, University of Tartu, Tartu, Estonia
[3] Faculty of Materials Science and Applied Chemistry, Riga Technical University, Riga, Latvia
[4] Institute of Solid State Physics, University of Latvia, Riga, Latvia
[5] RMS Foundation, Bettlach, Switzerland

Energy management and efficiency are becoming more and more important in future due to the on-coming climate change and will impact fields that prioritize optimized consumption such as housing and automotive industry. Development of highly insulating and adaptive smart windows for applications in both commercial and residential sector could save about 4.5% of the annual energy consumption.[1] Control over the transmittance of window materials in the visible (VIS) and near-infrared (NIR) part of the spectrum (and even the thermal black body radiation at 10 μm) will have a positive impact on the living comfort (e.g. less glare and thermal discomfort) and energy-efficiency in commercial and residential environments as well as in automotive applications.

Trong photochromic effects have been observed in case of crystalline TiO_2 quantum dots (mean size ≈ 4 nm) are presented. The quantum dots consist of irregularly shaped anatase TiO_2 nanoparticles (NPs) and are dispersed in alcohol (8 % by mass). Obtained NPs exhibit a dramatic photo-response to UV light, enabling effective transmittance modulation of light in a broad wavelength range extending from visible to near-infrared region, and even the thermal black body radiation regime beyond 10 μm. The exceptional photo-response is attributed to hole-scavenging by alcohol, TiO_2 self-reduction, injection of electrons to the conduction band, and consequent localized surface plasmon resonances in NPs. Observed optical effect is reversible and the initial high transmittance state can be restored simply by exposing the NPs to air. Applied NP synthesis route is economic and can be easily scaled for applications such as smart window technologies.

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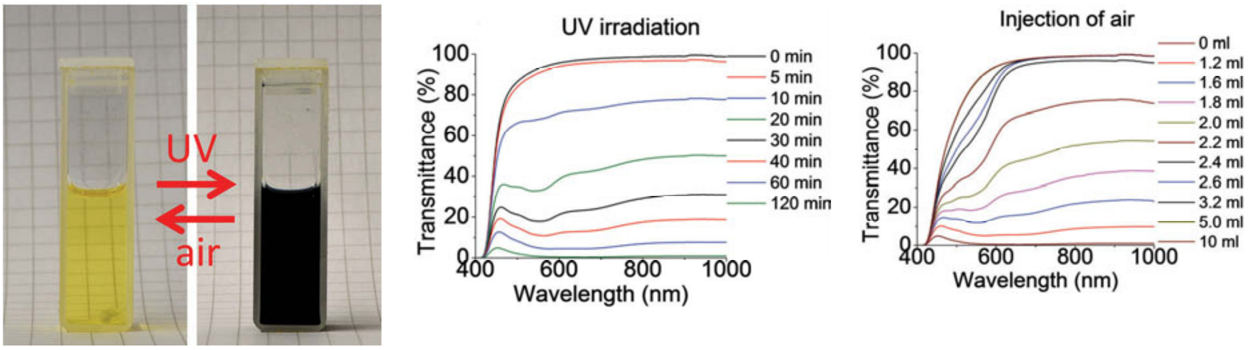

Figure 1. Optical response of TiO_2 NPs to UV irradiation, the color change of the dispersion is relatively fast, the coloration is reversible an can be reversed by exposure to air oxygen.

P-18

EFFECT OF AL$_2$O$_3$ NANOPOWDER ON WETTABILITY OF SILANE-BASED FUNCTIONAL NANOCOATINGS

Mehdi Khodaei, Sepehr Shadmani

Faculty of Materials Science and Engineering, K.N. Toosi University of Technology, Tehran, Iran

Superhydrophobicity is attractive phenomenon in functional surfaces/coatings which leads to the additional properties such as self-cleaning, anti-corrosion, anti-bacterial, anti-fouling. Silanes based sol–gel coatings are the subject of extensive research nowadays [1]. Such coatings have superior properties than conventional organic coating and are in the category of "green coatings". It has been well stablished that hierarchical structure in micro and nano scale on the surface as well as surface energy reduction plays an important role in prompting the superhydrophobic (water contact angle higher than 150) properties [2].

In this work, the combination of hierarchical structure synthesis and surface energy reduction have been done on silane-based coatings. The silane-based coating is selected as TEOS-GPTMS. The substrate is chemically etched aluminum which has micrometer surface roughness. The water contact angle (WCA) of TEOS-GPTMS coating on etched aluminum is about 96. In order to increase the WCA of coating two route have been done, which are the surface functionalization by a surface reduction agent (FAS17) and producing the nanoscale roughness in coating by adding the Al$_2$O$_3$ nanopowder into the coating. This two routs led to increase the WCA of the coating to 112 and 144, as shown in Fig.1. The last strategy was applying these two rout to the coating which increased the WCA of coating to 164 and produced the superhydrophobic coatings. The microstructural characterization has been performed by SEM and corrosion resistant of coatings has been examined.

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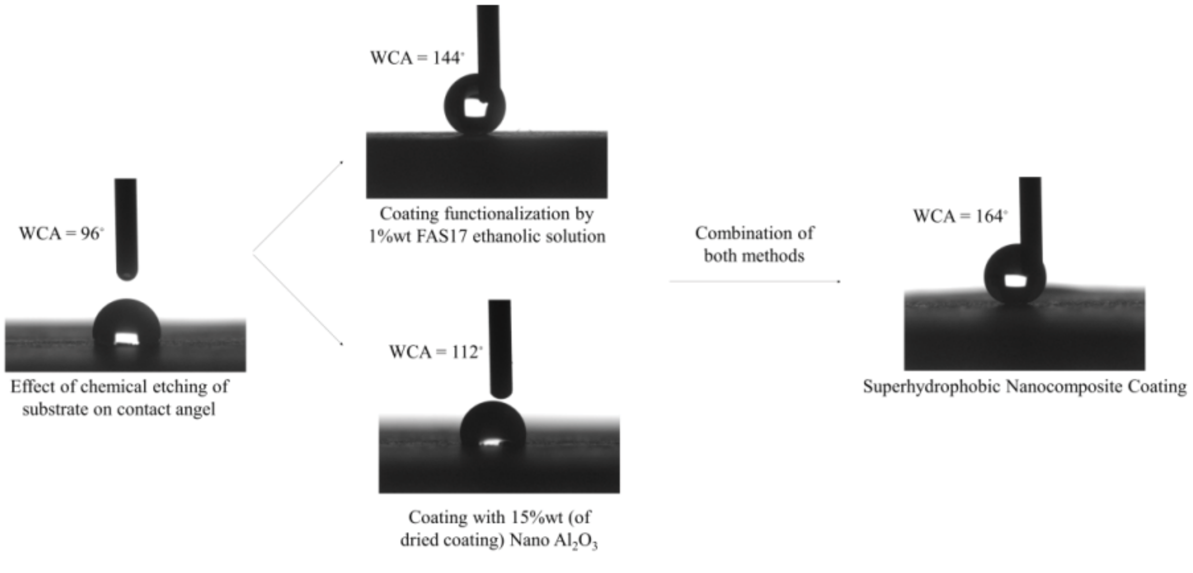

Figure 1. Water contact angle (WCA) of TEOS-GPTMS coatings on chemically etched aluminum substrate with different functionalization routs.

P-19

SYNTHESIS OF METAL NANOPARTICLES AS PRECURSORS FOR SELF-PROPAGATING REACTIONS

Thomas Klein, Guido Kickelbick

Inorganic Solid State Chemistry, Saarland University, Saarbrücken, Germany

Self-propagating reactions are a versatile route for the production of various materials. They allow low energy input for the initiation of the reactions and high purity materials due to an exothermic reaction step leading to the combustion and/or volatilization of side products.[1] While the method is well explored for bulk materials it is only recently that nanoscale structures were studied with this technique. Beside traditional combustion processes, also self-propagating alloying techniques were the target of recent research. An interesting subtopic is the synthesis of aluminide thin films.[2] The precursor structures - before the self-propagating reaction - are generally synthesized via gas phase deposition methods allowing only small areas to be covered. In contrast, a particle-based approach would allow much larger areas to be coated relatively easy. Applying this route towards the formation of new materials it is important to screen various parameters, such as particle size, surface modification, etc.

We synthesized a variety of aluminum nanoparticles using wet chemical approaches via chemical reduction of aluminum salts or catalytic decomposition of alane precursors, respectively. Particle-size was easily adjusted between 45-120 nm by changing the reaction parameters. The particles were stabilized with weakly bound phosphane ligands, which could be easily removed by a simple washing procedure and thus the particles can be switched between a stabilized and an active state.

The reaction of these particles with metallic nanoparticles of silver, ruthenium and nickel resulted in the formation of the corresponding intermetallics, which could be confirmed by STA (Fig. 1a) as well as XRD measurements (Fig. 1b).

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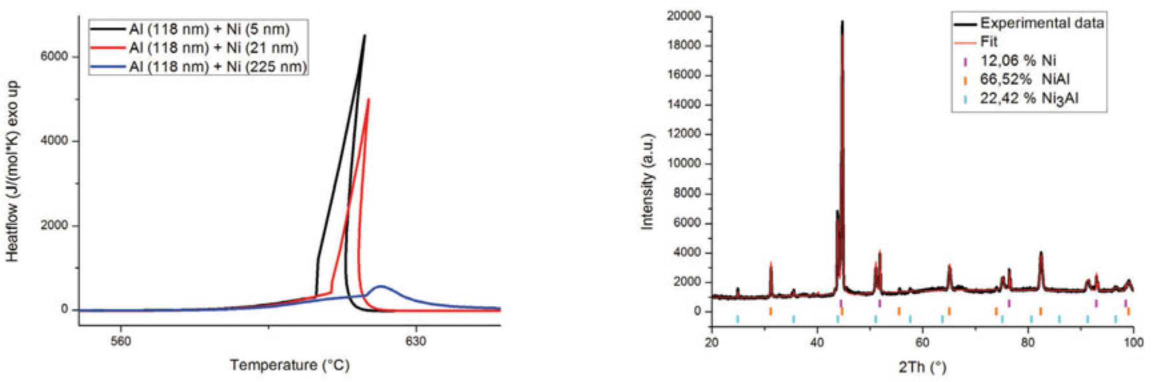

Figure 1. a) STA measurements of Ni-Al particle mixtures (1:1 ratio; Ar, 10 K/min) with varying Ni particle sizes. **b)** XRD measurement of a reacted Ni-Al particle mixture.

P-20

LEACHING AND PHOTOBLEACHING BEHAVIOR OF FLUORESCENT SILICA NANOPARTICLES WITH COVALENTLY AND PHYSICALLY INCORPORATED ORGANIC DYES

Nadja D. Klippel, Guido Kickelbick

Inorganic Solid State Chemistry, Saarland University, Saarbrücken, Germany

For modern research in the fields of nano-, bio- and medicinal sciences, fluorescent markers have to fulfill high requirements. High quantum yields and fluorescence stabilities are desirable to improve and enable possible applications. Semiconductor quantum dots have high quantum yields and are known to be photostable, but their great drawbacks are the comparatively high toxicity and more elaborated synthesis and functionalization of these particles. By labeling metal oxide particles with organic dyes, many of these disadvantages can be avoided. A wide range of organic dyes and potential particle matrices is available, but the efficiency of these systems has to be improved because of problems concerning dye leaching and photostability.[1] To show the relevance of this topic, leaching and photobleaching studies of different particle systems are examined. We distinguish in covalently and physically encapsulated dyes, exemplary shown with the xanthene dyes fluorescein and rhodamine B and with some perylene derivatives which are known for their high photostability. The synthesis of the anchor group functionalized dyes and particles are based on literature methods like a modified Stöber process [2], as well as new methods of production with a microjet reactor [3]. In further studies, particles with optimized properties will be embedded in polymer matrices to investigate in particle migration and agglomeration phenomena.

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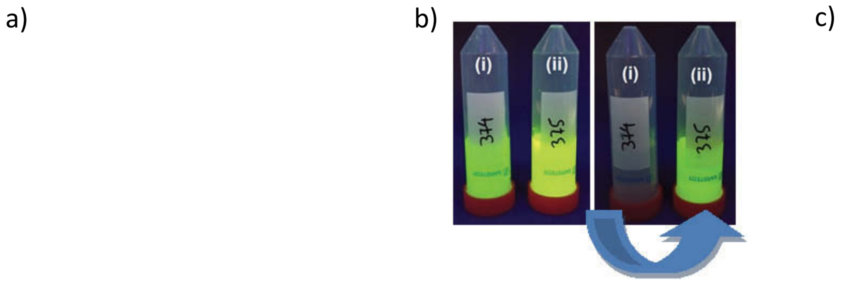

Figure 1. a) leaching behavior of covalently (FITC, (ii)) and physically (uranine, (i)) encapsulated dyes; b) uranine (i) and fluorescein isothiocyanate (ii) doped silica nanoparticles at first and last washing step; c) Solid state photobleaching experiments of different dye labeled silica nanoparticles and their associated dyes.

P-21

APPLICATION OF THE MICROFLUID SEGMENT TECHNOLOGY FOR THE PREPARATION OF NOBLE METAL NANOPARTICLES

Andrea Knauer, J. Michael Köhler

Department of Physical Chemistry and Microreaction Technology, Technische Universität Ilmenau, Ilmenau, Germany

The microfluid segment technology allows the realization of fast mixing processes and thus a very narrow residence time distribution. This enables optimum preconditions for a fast nanoparticle nucleation and opens up the possibility to generate nanoparticles with highly homogeneous shapes and compositions, narrow particle diameter distributions, and thus pronounced sharp absorption bands in optical spectroscopy. Therefore, a microfluid segment based technique was used for the generation of noble metal nanoparticles (Fig. 1).

Within this work, microfluidically processed Au/Ag core/shell nanoparticles [1], triangular silver nanoprisms [2], silver nanoprisms with a gold shell, or gold nanoframes, and single crystalline gold nanocubes [3] are presented as model systems.

By choosing the appropriate reactant ratios, the nanoparticles sizes and thus their optical properties can be tuned with a fine resolution. Depending on size, shape and composition, the spectral position of the absorption maximum can be shifted between 390 and 1000 nm.

Furthermore, the microfluid segment technology provides – under usage of a program-controlled fluid transport – the possibility of tuning the reactant ratios in a fully automatized experimental program [4]. The product particle quality can be read out online by micro-photometry and micro-spectrophotometry.

Here, large series of experiments can be realized by a minimum consumption of chemicals and two or more dimensional parameter spaces can be analyzed in arbitrarily steps.

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The funding from the DFG (KO 1403/39-1) is gratefully acknowledged. Many thanks to Danja Kuhfuß and Toni Schildhauer for their assistance in the lab.

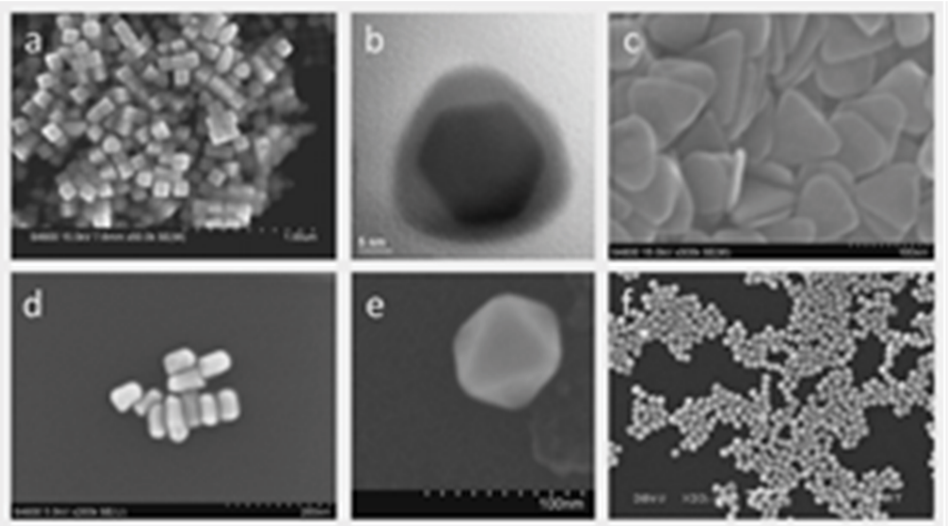

Figure 1: a) Au nanocubes, b) Au/Ag core/shell nanoparticles, c) triangular Ag nanoprisms, d) Au nanorods, e) Au nano-octahedron, f) Au/Ag/Au core/double-shell nanoparticles.

P-22

MICRO FLOW SYNTHESIS OF TUNABLE POLYMER COMPOSITE PARTICLES FOR SERS SENSING APPLICATIONS

Nikunjkumar Visaveliya, Andrea Knauer and J. Michael Köhler

Department of Physical Chemistry and Microreaction Technology, TU Ilmenau, Ilmenau, Germany

Droplet-based microfluidic systems are particularly advantageous for controlling the size and composition of micro- and nanoparticles. Furthermore, surface-enhanced Raman scattering (SERS) is a promising tool for particle-based sensor platforms. Well-defined chemical compositions and tailored physicochemical properties are the requirement for using such particles for sensitive detection. A real challenge is to obtain reproducible and homogeneous nano- and micro particles in a minimum number of preparation steps. In our work, a single-step micro flow process has been successfully implemented for the production of multi-scale sensor particles. The sensor particles consist of a swellable polyacrylamide matrix with in situ incorporated silver nanoparticles. The embedded silver NPs act as seed particles for additional silver reinforcement via a silver-catalyzed silver deposition in order to realize composite microparticles for SERS sensing. The homogeneous size and spatial distribution of silver nanoparticles inside the matrix and the Ag reinforcement at the surface, in combination with controlled pore sizes, provide a high and homogeneous silver loading of the polymer metal composite sensor. Different parameters, such as analyte concentration and particle size have been studied for SERS sensing application of organic molecules (amino acids and vitamins). For micro flow based sequential SERS sensing, several sensor particles have been placed inside a glass capillary. Here, highly reproducible sensor signals were observed with the test analytes adenine and histidine, using a fiber-coupled compact Raman spectrometer. The particles are suited for sequential SERS measurements under flow conditions.

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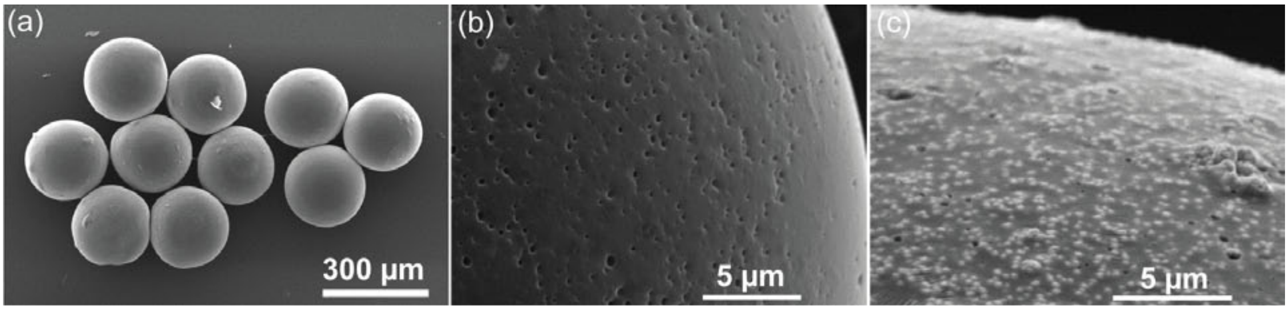

Figure 1. Polyacrylamide microparticles with incorporated Ag NPs before (a, b) and after (c) silver reinforcement

P-23

LUMINESCENT PHOTOCATALYTIC TIO_2-BASED NANOPARTICLE SYSTEMS

S. Koch[1, 2], S. Dembski[1] and K. Heuzé[2]

[1] Fraunhofer Institute for Silicate Research ISC, Würzburg, Germany
[2] University of Bordeaux, Talence , France

In the last decades, the combination of therapy and diagnosis within one tool (also called theranostics), for example within a nanoparticle (NP) system, has really come to the fore in research [1]. The theranostic approach is especially promising for tumour diagnosis and therapy [2]: Particle systems targeting malignant cells or cumulating in the pathologic tissue, can indicate the location and degree of the disease. This is visualized via an imaging method including x-ray computed tomography, ultrasound, bioluminescence or fluorescence imaging [3]. Then, therapy can be conducted thanks to specific particle properties like hyperthermia or photocatalysis but also drug-conjugates incorporated into the NP system. Due to their photocatalytic (PC) activity, titanium dioxide (TiO_2) nanoparticles are a promising potential photosensitizing agent for tumor therapy. However, for theranostics, more complex particle systems have to be developed to add for example photoluminescence (PL) properties.

This study developed two types of photocatalytic luminescent TiO_2-based nanoparticle systems. The first particle system combines the PC activity a TiO_2 core with the cytocompatibility of a SiO_2 shell as well as the PL of a silanized organic Rhodamine B dye incorporated into the shell. The second particle system consists of a TiO_2 nanoparticle functionalized with a self-synthesized Rhodamine B containing organosilane.

The experimental procedure included the synthesis of anatase particles via a hydrothermal process and the synthesis of Rhodamine B organosilanes. Subsequently, the nanoparticles were either coated with luminescent agent dyed silica shells or functionalized with the organosilane. Both systems were characterized thoroughly including TEM, IR, zeta potential, PL, and PC activity measurements.

Both TiO_2-based nanoparticle systems were successfully synthesized: the luminescent TiO_2/SiO_2 core/shell nanoparticles allows the regulation of PC activity and PL intensity by tuning the shell thickness (i.e. the dye content within the system). The Rhodamine dye functionalized TiO_2 system showed a high PL intensity with a superior PC activity compared to pure TiO_2 NPs.

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P-24

MORPHOLOGICAL INFLUENCES ON THE SHEAR THINNING BEHAVIOR OF RODLIKE COLLOIDS

C. Lang[1], J. Kohlbrecher[2], L. Porcar[3], A. Radulescu[1], M. P. Lettinga[1]

[1] Forschungszentrum Jülich, Jülich, Germany
[2] Paul Scherrer Institut, Villigen, Switzerland
[3] Istitut Laue Langevin, Grenoble, France

Although rod-like colloids are used in a broad diversity of industrial branches, e.g. for pharmaceutical-, food-, or dairy products, and also play an important role inside the human body, surprisingly, very little is known about the fundamental parameters that influence their shear thinning behavior under steady flow conditions.

It is known that the phase behavior of suspensions of rods depends on the rod geometry, flexibility and the interaction amongst particles [1]. Also in steady shear flow these characteristics play an important role for semidilute suspensions due to the dependence of the overall rheological response on the underlying particle dynamics [2], [3].

In order to study the impact of morphology on the flow behavior of rods, it is important to develop a suitable model system for which a controlled alternation of particle characteristics is feasible. Probably the best way of producing such a system without introducing an additional effect of polydispersity is bioengineering of rods [4].

We use rod-like viruses, namely fd wild type, fdY21M, M13k07, M13-mini and Pf1, as those species span a range of 0.33-2 μm in length as well as a range of 1.2-9.9 μm in persistence length, pursuing the same thickness of roughly 7 nm and modify the thickness and interaction of these colloidal particles by surface coating and change of ionic strength of the matrix fluid.

For understanding the detailed causes of changes in the rheological behavior of the different systems, we apply rheo-small angle neutron scattering in two different scattering planes, the flow-gradient and the flow-vorticity plane. This enables us to resolve the 3D orientational distribution of rods under steady shear flow.

The low shear behavior is found to be strongly dependent on all morphological characteristics, while, in the high shear rate limit, only length and flexibility play a role, see Figure 1. Additionally, we observe a biaxial orientational distribution for all rodlike systems.

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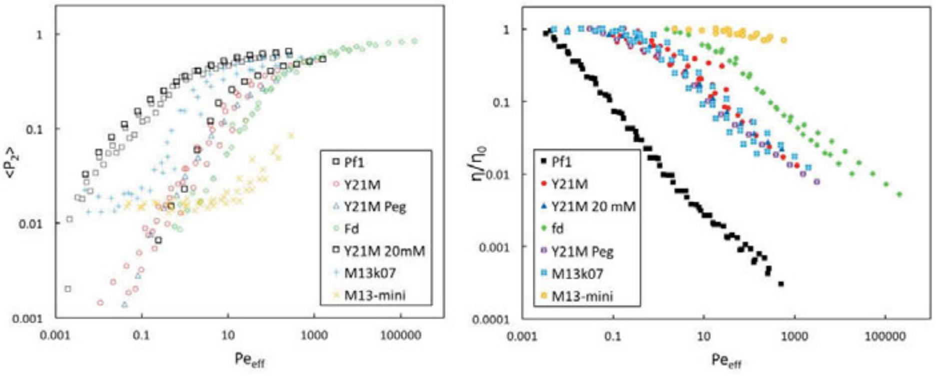

Figure 1. Order parameter and relative shear viscosity vs. effective Peclet number for rodlike viruses of different concentrations.

P-25

SYNTHESIS OF PARTICLE NESTED INVERSE STRUCTURES

Anna M. Lechner, Markus Retsch

University of Bayreuth, Physical Chemistry – Polymer Systems, Bayreuth, Germany

The particle nested inverse structure is a material that consists of an inverse opal/glass sceleton where a single particle is nested in each void of the matrix. The synthesis and characterization of inorganic particle nested inverse opals was first published by Ruhl et al. in 2006 [1]. Eight years later, Rhee et al. showed the synthesis of organic particle nested inverse opals that were used for filtering devices [2]. However, challenges in the preparation of these organic structures still persist.

Here, we demonstrate the preparation of organic particle nested inverse structures with respect to the choice of the right matrix material, removing the polymer overlayer before etching, and approaching free-standing structures.

First, PS@SiO$_2$ core shell particles have to be synthesized. The positively charged polystyrene nanoparticles are synthesized by emulsifier free emulsion polymerization [3], and a modified Stöber process leads to the silica shells [4]. In the next step the particles are assembled by a vertical deposition method on a glass substrate. The colloidal opal/glass is infiltrated with NOA prepolymer in vacuum and the overlayer is removed by spin coating several times with a non-solvent/solvent mixture. After curing the prepolymer with UV light, the silica shells are removed using hydrofluoric acid. Finally, particle nested inverse opals/glasses are obtained [5]. These will be characterized with respect to their mechanical, optical, and thermal properties in the future.

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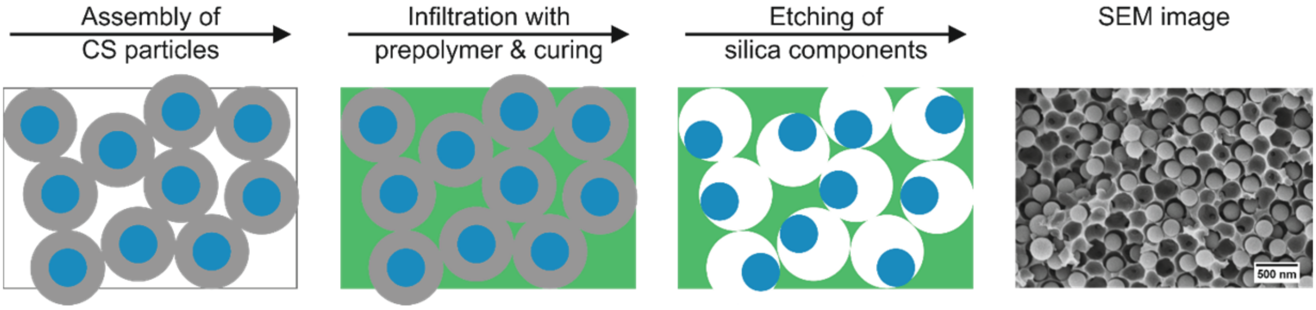

Figure 1. Left: Overview of the preparation steps of particle nested inverse structures, starting with PS@SiO$_2$ core shell nanoparticles. Right: SEM image of a particle nested inverse glass.

P-26

TAILORED SYNTHESIS OF BIMETALLIC SINGLE-CRYSTAL NANOPARTICLES WITH ANISOTROPIC MICROSTRUCTURAL FUNCTIONALITY

Alberto Leonardi, Michael Engel

Institute for Multiscale Simulation, Friedrich-Alexander University Erlangen-Nürnberg,
Erlangen, Germany

Shape- and size- controlled nanoparticles are of great interest for their exceptional chemical-physical properties and selectivity [1-4]. Although techniques for their synthesis are well established, new methods are sought to tailor complex geometry microstructures with controlled anisotropic functionality, especially in low damaging thermodynamic environment (i.e., low temperature). We probe the shape evolution of individual single-crystal bi-metallic core-shell nanoparticles etched in a controlled redox environment as an alternative approach to architecture new particle systems [5, 6]. Characteristic promising non-equilibrium transient configurations are rationalized via Monte Carlo simulations, and further thermodynamically tested and characterized by means of molecular dynamics. Convex platelet, concave polyhedron, pod, cage and *strutted-cage* (e.g., cage embedding a set of struts connecting the shape corners) are easily framed at room temperature with ideally fully coherent structure, exposing different crystallographic facets and chemical elements along distinct particle crystallographic directions. The systematic study of the shape evolution trajectories as a function of the etching environment and the microstructure geometry and element composition of the precursors provides the opportunity to effectively design the spatial and directional distribution of chemical-physical properties of the particles and more in detail of their surface [7].

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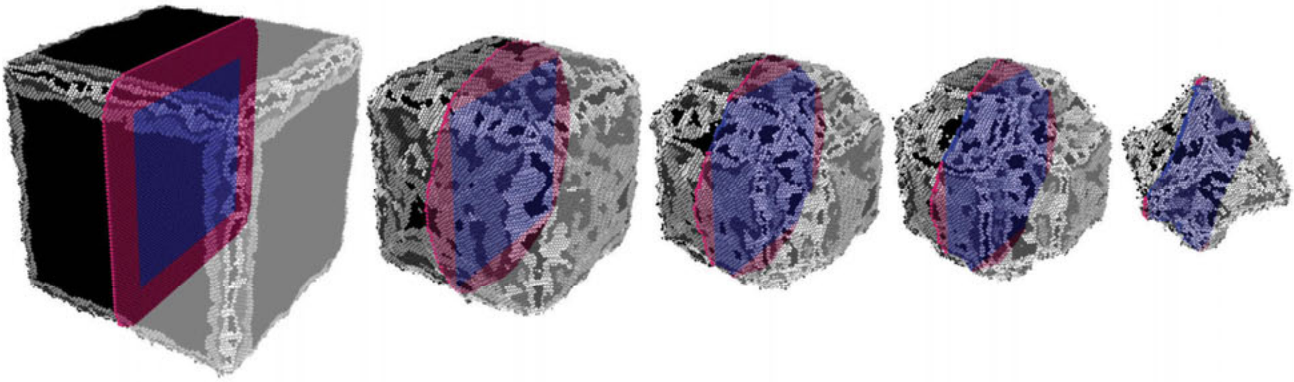

Figure 1. Short-lived non-equilibrium transient shape of an Ag-Au cubic-cubic core-shell nanoparticle as it is etched in a controlled redox environment.

P-27

CONTROLLED AND REVERSIBLE ASSEMBLIES OF HYBRID COLLOIDS WITH ISOTROPIC AND JANUS DESIGN

Olga Diring[1,2], Claudia Marschelke[1,2], Alina Kirillova[1,2], and Alla Synytska[1,2*]

[1] Leibniz Institute of Polymer Research Dresden, Functional Particles and Interfaces Group,
Hohe Straße 6, 01069 Dresden, Germany
[2] Dresden University of Technology, Faculty of Mathematics and Science, Institute of Physical
Chemistry of Polymeric Materials, 01062 Dresden, Germany

Self-assembly is the basic concept to form complex structures in nature and can serve the development of novel materials with controlled properties due to the rich functionality of the individual particles.[1] In this context, the internal dynamics of biological processes are a source of inspiration to form controllable and reversible structures using stimuli-responsive colloidal particles. The variation of a chosen parameter induces a programmable adaption of the system, which is reversible in the absence of the stimulus. Assemblies of isotropic building blocks typically lead to symmetric structures, whereas multifunctional anisotropic building blocks, such as Janus particles, can assemble into more complex structures with significantly different macroscopic properties. Taking advantage of their asymmetric structure, the assembly of Janus particles (also in combination with homogeneous particles) can lead to a variety of sophisticated structures inaccessible to their homogeneous counterparts.
Hence, we report on the synthesis of hairy hybrid poly(2-(dimethylamino)ethyl methacrylate-covered Janus and non-Janus particles with controllable size, chemical functionality and responsiveness to the pH value. Furthermore, we discuss their self-assembly in dispersions with homogeneously polyacrylic acid-decorated stimuli-responsive particles. Both particle types show polyelectrolyte-covered surfaces with pH-dependent opposite charges and swelling behavior, while the Janus particles are partially decorated with an inert, uncharged polymer.[1-3] Driven by electrostatic interactions, the particles enable programmed bottom-up self-assembly into more complex micro-cluster structures (Fig. 1). Different size ratios form characteristic (half-) raspberry clusters, while the degree of coverage depends on the pH value and varies with pH changes. Both fluorescence microscopy and scanning electron microscopy are applied to statistically determine the population of clusters.

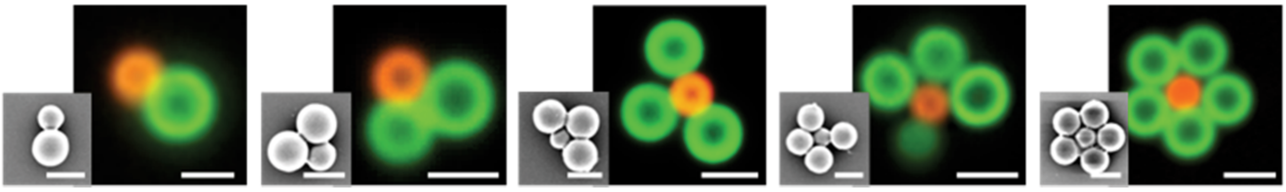

Figure 1: Observed micro-clusters: Representative SEM and fluorescence microscopy images, formed in dispersion from PAA-650 nm and PDMAEMA-1 μm homogeneously decorated particles. Scale bars: 1 μm.

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P-28

CONTROLLED AND TUNABLE DESIGN OF HYBRID UNIFORM AND JANUS PARTICLES FOR INTERFACIAL CATALYSIS

C. Marschelke[1,2], A. Kirillova[1], I. Raguzin[1], A. Matura[3], D. Jehnichen[1], A. Synytska[1,2]

[1] Leibniz Institute of Polymer Research Dresden, Functional Particles and Interfaces Group, Dresden, Germany
[2] Dresden University of Technology, Faculty of Mathematics and Science, Institute of Physical Chemistry of Polymeric Materials, Dresden, Germany
[3] Dresden University of Technology, Institute of Biochemistry, Dresden, Germany

The design of colloidal particles with advanced architectures and controlled chemical functionalities is highly demanding for discovering of responsive and adaptive multifunctional materials. Combining two materials with different properties in the same particle leads to the development of structured hybrid core-shell systems with unique functionalities that can be used as carriers for catalytically active species. Immobilization of nanocatalysts, such as enzymes and metal nanoparticles, onto well-designed polymer interfaces provides an excellent base for their exploitation by enhancing their stability in different environmental conditions, and facilitating their recovery. Herein, we report on the synthesis of hybrid hairy particles with controllable size, grafting density, chemical functionality, heterogeneity, and responsiveness (Fig. 1a). We propose two applications for interfacial catalysis that would benefit from the unique properties and architecture of the hybrid particles: immobilization of enzymes and metallic nanoparticles.

In the first approach, we discuss the correlation between the controlled design of polymeric interface on planar and curved substrates and its impact on the efficiency of immobilization of laccase from *Trametes versicolor*. Therefore, we vary the polymer grafting density prepared using a "grafting from" approach by varying the density of initiator groups. We show how immobilization of laccase via physical adsorption causes changes in the surface properties of the final polymer-enzyme layer.[1,2]

In the second approach, we exploit the superior interfacial activity of Janus particles and apply them for interfacial catalysis through a selective modification of one of their sides with metallic nanoparticles (Fig. 1c). In this way, functional active interfaces loaded with Janus particles are created in an emulsion, resulting in successfully catalyzed reactions in the water phase and the subsequent easy recovery of the hybrid catalyst.[3]

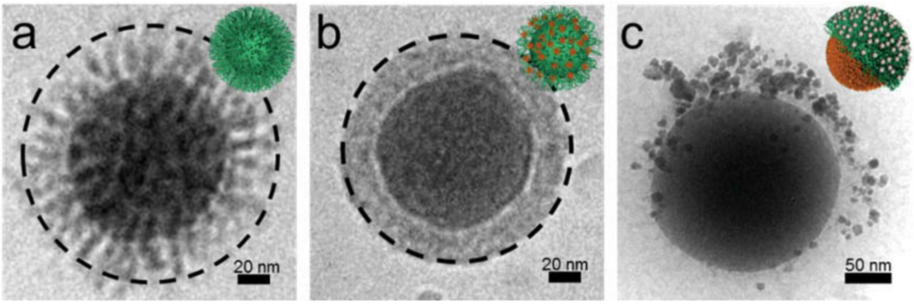

Figure 1. Representative cryo-TEM images of (a) a hybrid hairy particle without any catalytic species, and (b) with immobilized laccase from *Trametes versicolor*, (c) a Janus particle with immobilized Au nanoparticles.

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P-29

SIMULATION OF COLLOIDAL SELF-ASSEMBLY IN SPHERICAL CONFINEMENT

Mbah Chrameh, F.[1], Wang, J. W.[2], Vogel, N.[2], Engel, M.[1]

[1] Institute for Multiscale Simulation, Friedrich-Alexander Universität Erlangen-Nürnberg
[2] Institute of Particle Technology, Friedrich-Alexander Universität Erlangen-Nürnberg

Colloids in suspended emulsion droplets is a promising approach for synthesizing hierarchical assemblies with novel photonic properties [1]. Evaporation causes the packing fraction of the colloids to increase, thereby forming a number of crystalline structures. Packing density influences the stability of the resulting structures, revealing icosahedral geometries [2]. These structures include Mackay type, anti-Mackay type, truncated icosahedral, and face-centered cubic clusters.

In this study we develop a two-step simulation scheme to generate icosahedral clusters of colloidal particles in spherical confinement. First we put a number of hard spheres in a spherical confinement and perform event-driven molecular dynamics whilst successively reducing the radius of confinement. In the second step, we apply a structural relaxation scheme [3] to capture crystalline facets at the surface of the clusters. Our findings are in good agreement with experiment. Also, our simulations confirm the observation that crystallization initiates from the confinement interface. Particles near the interface perform multiple melting and recrystallization cycles [2].

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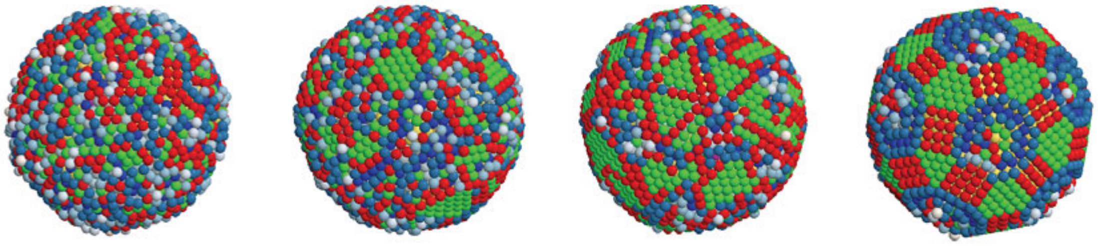

Figure 1. The figure shows the process of crystallization starting from a disordered (leftmost figure)to an ordered (rightmost figure) crystalline structure .

P-30

SPECTROELECTROCHEMICAL ANALYSIS OF NANOPARTICLE BASED POROUS ALIGNMENTS

Jan F. Miethe, Franziska Lübkemann, Jan Poppe, and Nadja C. Bigall

Institute of Physical Chemistry and Electrochemistry, Gottfried Wilhelm Leibniz University,
Hanover Germany

In present state art, several ways to synthesize and modify anisotropic heterogeneous direct semiconductor nanoparticles are known and understood [1],[2],[3]. These crystals show differences in their optical absorption and surface properties. An important property is the specific band structure of heteroparticles, which contributes to the fluorescence but also to the electrochemical attributes of nanoparticle based systems.

The presented work shows the benefits of the application of CdSe/CdS particles as primary building blocks for randomly-ordered porous macroscopic alignments. This structures are based on the interconnection of nanoparticles via grain boundaries and show a by magnitudes lower density in comparison to the bulk material. A possible aspect of these alignments could be the utilization as photoelectrochemical sensors [4].

In our work we apply linear sweep voltammetry (LSV) and a frequency resolved technique like intensity modulated photocurrent spectroscopy (IMPS) to reveal the existing charge carrier transport in these structures [5]. For comparison more optical and electrochemical linear systems like submonolayers are applied as reference samples.

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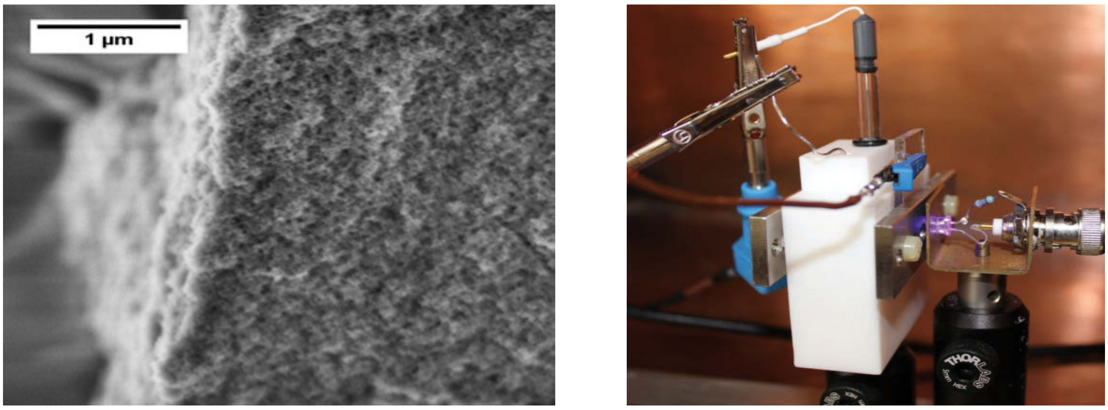

Figure 1. SEM image of a porous CdSe/CdS nanoparticle based macrostructure (left) and three-electrode setup to determine the electrochemical properties of prepared electrodes (right).

P-31

SUPERRESOLUTION FLUORESCENE MICROSCOPY OF NANOCOMPARTMENTALIZED STIMULI RESPONSIVE MICROGELS AT SOLID-LIQUID INTERFACES

Alex Oppermann, Arjan P. H. Gelissen, Walter Richtering, and Dominik Wöll

Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

Microgels are cross-linked, swollen polymer networks with sizes in the range of 100 nm to 100 µm. They show properties of both a macromolecule and a colloid. Depending on the monomer composition, microgels can show a stimuli dependent swelling and deswelling, resulting in a change in size of the polymer network. Stimuli can be for example, temperature, pH, solvent composition or redox potential. These special properties offer a wide range of possible applications for microgels.

Therefore, high quality analytical tools are necessary to investigate different microgel systems. Common analytical tools to characterize microgel systems are scattering methods, electron microscopy and atomic force microscopy. While scattering techniques only yield information on an ensemble level, microscopy techniques have the potential to give information about the polymer network within single microgels. However, swollen polymer networks show only low contrast in electron microscopy. Furthermore, due to their fuzzy surface, imaging with atomic force microscopy is strongly dependent on the force applied to the polymer network and optical (fluorescence) microscopy is limited by diffraction to about half of the wavelength of visible light.

This restriction can be overcome using superresolution fluorescence microscopy methods. We choose single molecule localization microscopy (SMLM) as our method of choice because of several advantages in analyzing soft matter systems compared to other imaging techniques. Using sophisticated labeling strategies, we visualize different compartments of core-shell microgels. Analysis of the two-dimensional distribution of single molecule localizations within single microgels yielded three-dimensional reconstructions of microgel structures [1].

Analyzing the localization distribution of fluorescent dyes inside single microgels we obtain information about the distribution of functional groups within these microgels [2]. In this work, we focus on the investigation of microgels adsorbed to the glass-water interface. Furthermore, we obtain three-dimensional information about fluorophore localizations by point spread function engineering [3]. This enables us to directly access the internal structure of core-shell microgels [4].

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P-32

THERMAL CONDUCTIVITY OF POLYMERIC COLLOIDAL ASSEMBLIES: EXPERIMENT AND SIMULATION

Alexandra Philipp[1], Fabian A. Nutz[1], Martin Dulle[2] and Markus Retsch[1]

[1] Physical Chemistry I – Polymer Systems, University of Bayreuth, Bayreuth, Germany
[2] Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH, Jülich, Germany

Polymers are suitable heat-insulating materials since they have a low thermal conductivity typically around 0.1-0.3 $Wm^{-1}K^{-1}$. Polymeric colloidal crystals consisting of spherical nanoparticles show even lower thermal conductivities due to the decreased density and small contact areas between adjacent particles. It is well known that monodisperse nanoparticles self-assemble in a highly ordered face-centered cubic packing [1]. A rather high density of 74 % of the bulk material's density limits the reduction of the thermal conductivity of such assemblies. One way to decrease the thermal conductivity further is the lowering of the density of the colloidal assembly by introducing disorder.

Here we show that the crystalline structure of a colloidal crystal is transferred from order to chaos by mixing two differently sized polystyrene particles. For a detailed mixing study, the large particle volume ratio is varied between 0 – 100 %. Thereby the colloidal crystallinity is destroyed. The density of the obtained colloidal glass is reduced by maximal 10 % compared to the colloidal crystal. However, the effective thermal conductivity drops even more: from crystalline to amorphous by around 20 %. Thus, this decrease is not only caused by the reduced density. Molecular dynamics simulations were used to determine the structure of the colloidal glass and the number of next neighbors per particle. We find a change from 12 in the crystalline state to an average value of around 10 in the amorphous state. Using finite element modeling, we could show that the lower number of next neighbors leads to increased heat transport pathways. This effectively hinders the heat transport and results in an additional decrease of the thermal conductivity. [2]

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P-33

HIGHLY ORDERED NANOSTRUCTURED MICROCYLINDERS BY TEMPLATE-ASSISTED PARTICLE INFILTRATION

Marcel Pourasghar, Alina Marilena Rus and Marc Schneider

Saarland University, Department of Biopharmaceutics and Pharmaceutical Technology,
Saarbrücken, Germany

Nature-inspired particle engineering is increasingly gaining attention for the development of innovative and efficient drug delivery systems. By mimicking the size, shape, and elasticity, there are new possibilities for the interaction with biological systems [1][2]. Several studies have been done for the understanding of the biological interaction with aspherical particles [3]. However, despite the rising interest within research, methods to produce colloidally dispersible and biocompatible particles with a defined morphology, are mostly limited. Various techniques have been developed to produce aspherical particles, such as self-assembly, template-based, electrospinning and microfluidic. Template-based methods are the most adaptable and flexible for the formation of aspherical particles with nearly infinite possibilities of geometries [4]. But most of the techniques lead to a continuous thin film on the template and thus resulting in severely aggregated particles.

To avoid this technical issue, we have developed a new and unique technique to produce highly ordered nanostructured cylinders, called the template-assisted particle infiltration [4]. We are infiltrating our material of interest in the form of nanoparticles, rather than single molecules, into pores of a track-etched membrane and then stabilising these nanoparticles within these pores by either electrostatic attraction or physical entrapment. Employing a non-destructive release mechanism for the microcylinders from the membrane allows using biodegradable and biocompatible materials, for instance, poly lactic-co-glycolic acid (PLGA), and reuse the template membrane several times (Figure 1A and B). Thus, we achieved two important milestones for a generic pharmaceutical use.

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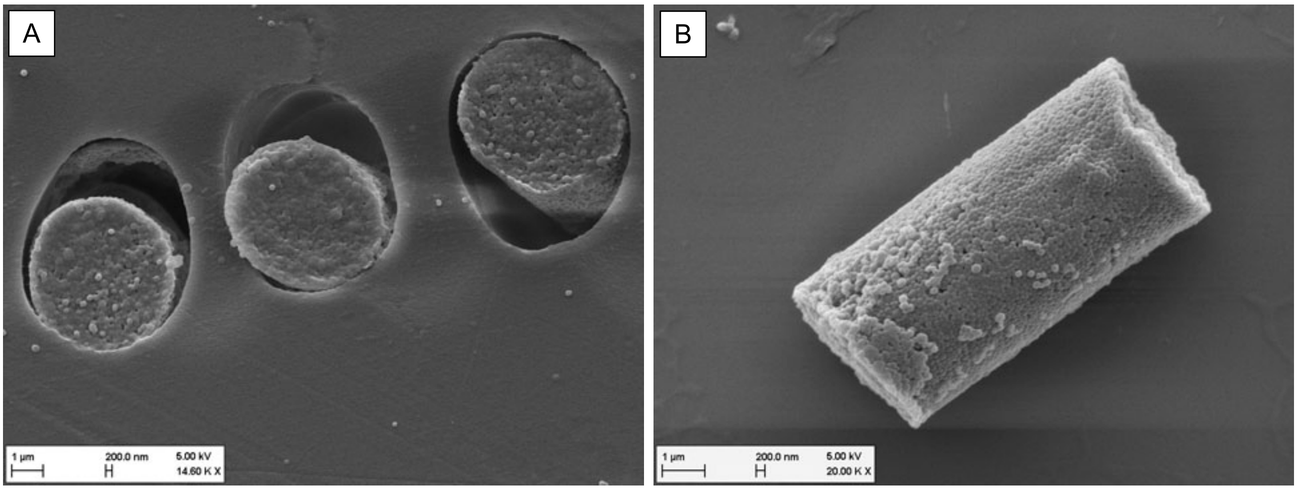

Figure 1. (A) Cylindrically arranged PLGA nanoparticles in template pores. (B) Released nanostructured microcylinder with a length of 9.2 µm and a width of 4.2 µm.

P-34

STUDIES ON THE INFLUENCING FACTORS OF THE NANOPARTICLE SELF-ASSEMBLY INTO SUPERCRYSTALS

Annett Reichhelm, Danny Haubold, Alexander Eychmüller

Physical Chemistry, TU Dresden, Germany

Similar to atoms in classic crystals, nanoparticles self-assemble into ordered superstructures with symmetric shapes and defined facets and edges. With sizes up to some hundreds of micrometers, supercrystals are macroscopic objects which preserve the unique properties of the nanoscale building units. The size and morphology of the superstructures depend strongly on the formation conditions. Thus, the investigation of the preparation parameters is crucial for the understanding and control of the supercrystal formation.

In this study, we prepared supercrystals by the self-assembly of silver nanoparticles via a gas phase diffusion method[1] and investigated their morphologies by scanning electron microscopy.[2] By varying the concentration of the initial NP solution, the size of the superstructures has been tuned. Thereby, supercrystals with diameters from 10 to 40 micrometers have been prepared (figure 1). Additionally, the influence of the precipitation agent has been examined. The use of ethanol and methanol led to the formation of symmetrical supercrystals, while *i*-propanol and *n*-propanol produced irregular aggregates. The size of the crystals was also influenced by the precipitant.[3]

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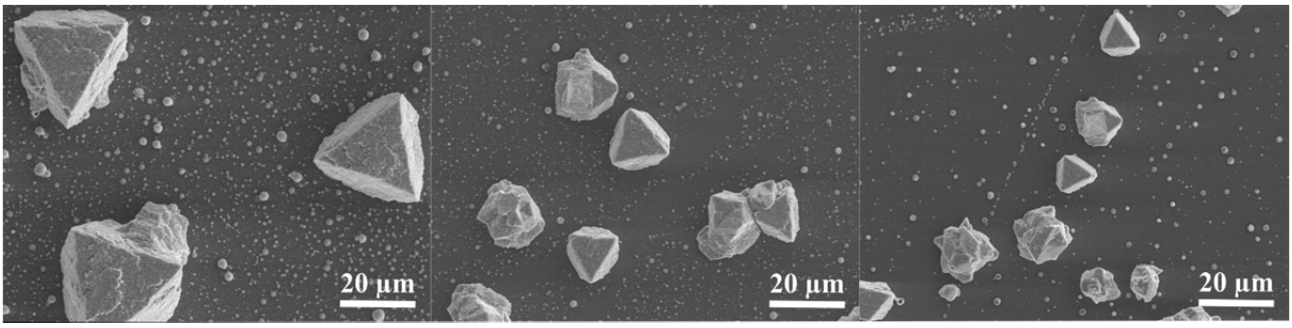

Figure 1. Silver supercrystals with different sizes depending on the concentration of the initial NP solution.

P-35

INDUSTRIAL POLYMER PROCESSING INSPIRED GOLD NANOWIRE MICROFIBER SPINNING

Beate Reiser[1], Dominik Gerstner[1], Lola Gonzalez-Garcia[1], Johannes H. M. Maurer[1] and Tobias Kraus[1,2]

[1] INM - Leibniz Institute for New Materials, Saarbrücken, Germany
[2] Colloid and Interface Chemistry, Saarland University, Saarbrücken, Germany

Simple and efficient methods to assemble "nano-monomers" into novel functional materials are a key step towards their application in marketable products.[1,2] Many nano-objects are dispersed in solvents to form colloidal inks that can be processed from solution. This opens the possibility to profit from decades of experience in the solution processing of polymers.[3] Ultrathin gold nanowires (AuNWs) that have diameters below 2 nm and lengths of several micrometers and are capped with a thick shell of organic ligand can be seen as polymer analogues (Figure 1a).[4] They are ideal candidates to apply polymer processing principles to colloids. Polymers are commercially spun into hierarchical fibers by a process called solution spinning.[5] Analogously, spinning of AuNWs should lead to hierarchical inorganic-organic hybrid fibers.

We used a custom-built spinning setup (sketched in Figure 1b) that mimics polymer spinning for a colloidal dispersion of AuNWs as spinning dope.[6] As-spun fibers consisted of 80 vol.-% organic matter and 20 vol.-% metal and had several hierarchical levels of self-assembled structures (Figure 1c). Despite of the inorganic content of the fibers, we find remarkably good analogy to polymer spinning. Like in polymer spinning, the AuNW concentration in the spinning dope and the speed of injection into the coagulation bath control fiber thickness and structure as confirmed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Furthermore, fibers could only be obtained at flow rates that led to sufficient elongation in the direction of the flow, as confirmed by an *in situ* small angle X-ray scattering (SAXS) study. Spherical gold nanoparticles could not be spun at all. This resembles the minimal polymer length required for polymer fiber spinning.[3] Finally, tensile testing of fibers obtained at different spinning-dope flow rates yield structure-property relations that are similar to polymer fibers.[5]

In summary, we demonstrated the applicability of polymer processing principles to obtain materials from a colloidal ink. The process that we use is simple and fast and fulfills important requirements for industrial scale material production.[6]

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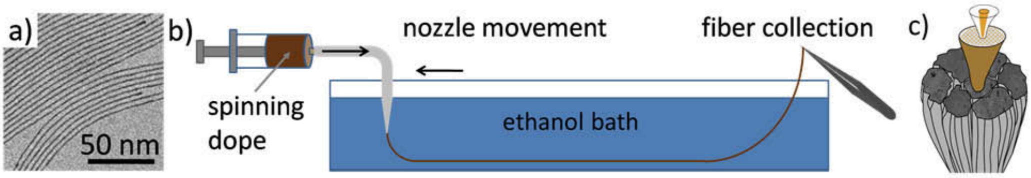

Figure 1 (a) Transmission electron micrograph of dried AuNWs. (b) Scheme of fiber spinning and collection. (c) Scheme of as-spun AuNW fiber showing hierarchical levels (adapted from Reference 6).

P-36

THE EXTRACTION OF HYDROCARBON CONTAMINANTS FROM WATER WITH PHOSPHONIC ACID FUNCTIONALIZED IRON OXIDE NANOPARTICLES.

Sarcletti M.[1], Luchs T.[2], Hirsch A.[2] and Halik M.[1].

[1] Organic Materials and Devices (OMD), Department of Materials Science, Friedrich-Alexander University Erlangen-Nuremberg, Martenstraße 7, 91058 Erlangen
[2] Institute of Organic Chemistry, Department of Chemistry and Pharmacy, Friedrich-Alexander University Erlangen-Nuremberg, Henkestraße 42, 91054 Erlangen

Major disasters in the production and transportation of crude oils and its products, such as the Deepwater Horizon explosion or the Exxon Valdez incident, result in a vast release of hydrocarbons (HCs) and consequently, lead to a dramatic impact to the environment [1]. The State-of-the-Art remediation mainly consists of the dispersion in the water column and the in-situ burning of the HCs [2]. However, these methods are not sustainable and of enormous ecological impact.

We have developed a nanoparticle (NP) based system for the efficient removal of the HCs from the water surface. The magnetite (Fe_3O_4) NPs are functionalized with a hydrophobic and oleophilic phosphonic acid (PA) self-assembled monolayer (SAM) that allows the highly selective adsorption of HCs. Due to the high surface area to volume ratio and the magnetic core of the NPs, this system features high extraction rate and easy collection of the adsorbed HCs by a magnetic field. Due to the stability of PA on oxide surfaces, the functionalized NPs showed very good reusability over several cycles for the extraction of single components as well as different crude oils. By fine-tuning the chemical structure of the SAM molecules with different PAs, the collection of specific HC groups may be improved.

The commercial availability of the magnetic nanoparticles as well as of suitable PAs and the simple and fast functionalization process [3], in combination with the eminent, selective HC extraction make this system a cheap and competitive HC cleanup agent [4].

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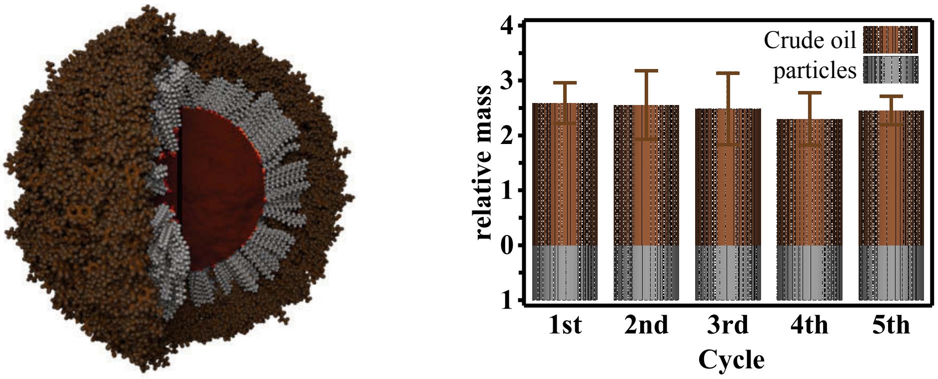

Figure 1. Left: Model of a functionalized Fe_3O_4 NP, loaded with crude oil. Right: Extraction rates (mass[crude oil]/mass[Fe_3O_4-HDPA]) of crude oil with Fe_3O_4-PA over five cycles.

P-37

RESISTIVE SWITCHING OF SUB-10 NM TIO_2 NANOPARTICLE SELF-ASSEMBLED MONOLAYERS

Dirk Oliver Schmidt[1,2], Nicolas Raab[3,4], Michael Noyong[1,2], Venugopal Santhanam[5], Regina Dittmann[3,4] and Ulrich Simon[1,2]

[1] JARA-FIT, Aachen, Germany
[2] Institute of Inorganic Chemistry, RWTH Aachen University, Aachen, Germany
[3] JARA-FIT, Jülich, Germany
[4] Peter Grünberg Institut 7, Forschungszentrum Jülich GmbH, Jülich, Germany
[5] Department of Chemical Engineering, Indian Institute of Science, Bangalore, India

Resistively switching devices are promising candidates for the next generation of non-volatile data memories. Such devices are up to now fabricated mainly by means of top-down approaches applying thin films sandwiched between electrodes. Recent works have demonstrated that resistive switching (RS) is feasible also on chemically synthesized nanoparticles (NPs) in the 50 nm range [1]. Following this concept, we developed this approach further to the sub-10 nm range. In this work, we present the synthesis of sub-10 nm TiO_2 NPs [2] and their characterization by means of powder X-Ray diffraction (XRD) as well as transmission electron microscopy (TEM). Self-assembly experiments were performed in order to obtain hexagonally close-packed TiO_2 NP films on a water surface and we obtained TiO_2 NP monolayer films with lateral dimensions of 1 μm^2. We transferred the self-assembled films to planar Pt/Ir surfaces, which function as bottom electrodes, *via* two different approaches. The transferred films were characterized using a scanning electron microscope (SEM), atomic force microscope (AFM) and transmission electron microscope (TEM). Finally, we investigated the RS properties of the films by means of a nanorobotics setup in a SEM and found typical features of bipolar resistive switching [4].

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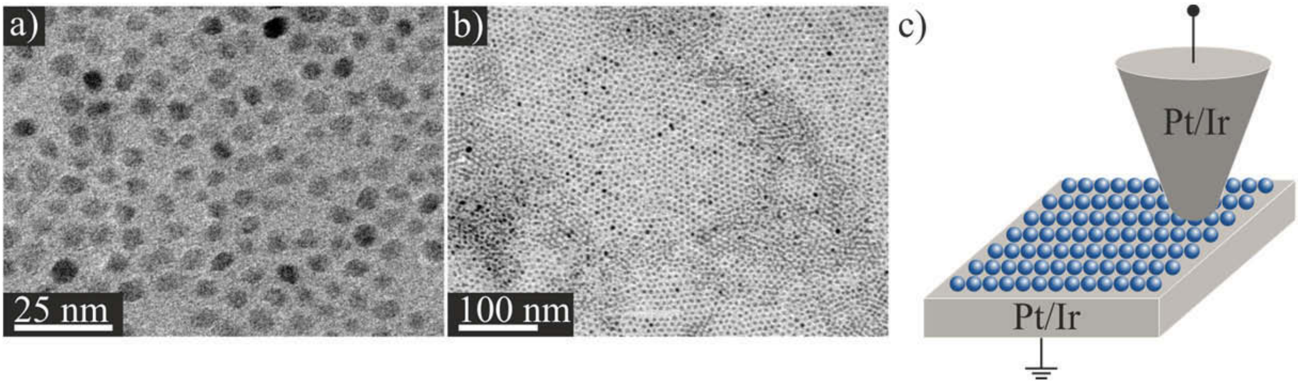

Figure 1. Representative TEM images of the synthesized TiO_2 NPs (a), of the self-assembled TiO_2 NP film (b) and schematic illustration of the [Pt/Ir]/TiO_2 NP film/[Pt/Ir tip] device (c) utilized for the electrical characterization of the devices in a SEM.

P-38

FORMATION, CHARACTERIZATION AND FUNCTIONALIZATION OF CASEIN MICROPARTICLES

Jann Schulte, Dimitrij Rogalski and Ronald Gebhardt

Chair of Soft Matter Process Engineering (AVT.SMP), RWTH Aachen University, Aachen, Germany

In recent years, the demand for polymer based nanoparticles and microparticles has increased drastically [1].Milk proteins, for instance, have been used as a natural, nontoxic, delivery system for bioactive substances and drugs with a broad range of applications in food and pharma industry [2]. Casein micelles are colloidal particles of spherical shape in milk with many structural and functional similarities to microgels. The key properties of microgels are architectural versatility, permeability, functionality and deformability [3].

Our research focuses on the formation, soft properties and functionalization of biopolymer based microparticles. The formation of casein microparticles is driven by depletion forces which occure when casein micelles (Figure 1 A) are mixed with polysaccharides [4]. Film drying of the protein polysaccharide mixture leads to deformation of the particles. A Raman depth profile of the blend film (figure 1 B) shows the compression of the blend particles in vertical direction. This deformation stabilizes the microparticles, so that they can be resuspended after hydrolysis of the polysaccharide film [5].

We are currently studying the influence of different process parameters like the protein-polymer ratio, and the drying conditions on the shape, size and stability of the casein microparticles.

After destruction through shear stress, fragments of film dried casein microparticles act as surfactants to stabilize α-tocopherol droplets (Figure 2) [6]. We present an approach that grants us the possibility to adjust the stability in a way that may allow their use as functional microparticles.

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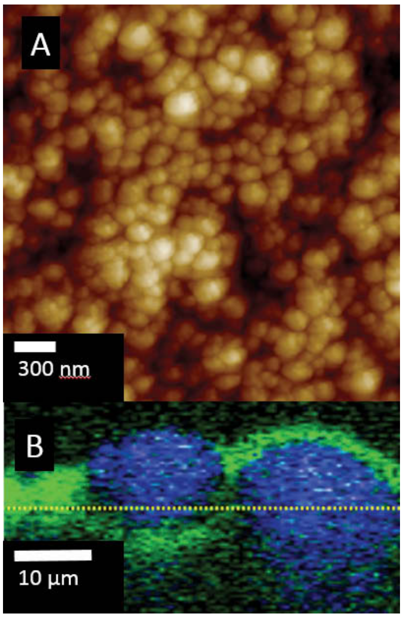

Figure 2.
A: AFM-image of casein micelles from milk powder
B: Color coded Raman depth profile of pectin/casein blend films, casein rich region (blue) pectin rich region (green)

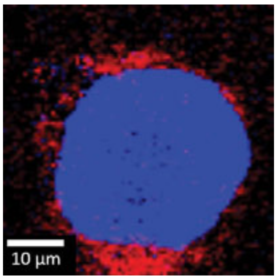

Figure 3. Color coded Raman image of a α–tocopherol droplet stabilized by casein microparticle fragments

P-39

JANUS PARTICLES AND MULTI-FUNCTIONAL COATINGS WITH CONTROLLABLE FOULING AND ICING

M. Schwarzer[1,2], A. Kirillova[1,2], C. Marschelke[1,2], A. Synytska[1,2]

[1] Leibniz Institute of Polymer Research Dresden, Functional Particles and Interfaces Group, Dresden, Germany
[2] Dresden University of Technology, Faculty of Mathematics and Science, Institute of Physical Chemistry of Polymeric Materials, Dresden, Germany

The design of multifunctional polymeric anti-icing and anti-fouling composite materials with controlled wetting and adhesion properties based on colloidal particles with advances anisotropic architectures and controlled chemical functionalities is highly promising. The combination of two chemical functionalities in the same particle leads to construction of new materials with advanced features.

Herein, we propose new approaches for the design of heterogeneous surfaces with anti-icing and anti-fouling capabilities based on core-shell Janus particles, which consist of an inorganic core and hairy polymer shells, and possess controllable size, geometry, surface chemical functionality, and Janus balance.[1-3]

For both applications the coatings prepared from anisotropic Janus particles (Fig. 1A) are found to be very promising for the design of novel multifunctional materials with desired properties. In case of the anti-icing application the heterogeneous coatings 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 (Fig. 1B). This leads to an extremely low ice adhesion.[1, 2] For anti-fouling applications Janus particles based coatings were investigated using the marine biofilm-forming bacteria *Cobetia marina* and it results that the coatings are robust and reduce significantly bacterial retention under static and dynamic conditions.[3] The presented concept opens new paths for the applications of hybrid core-shell particles with “Janus architecture” towards rational design of materials with multi functions.

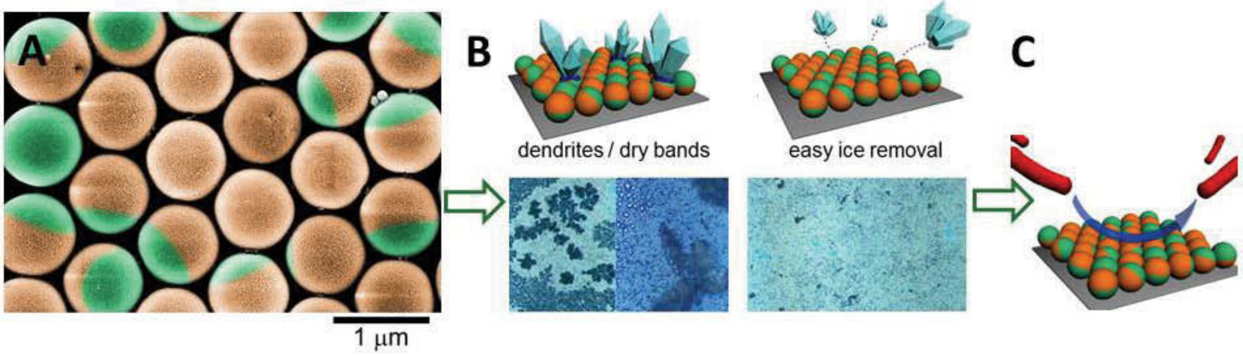

Figure 1. A) SEM image of the SiO_2-P(PEGMA)/PDMS-Janus particles and schematic representation of surfaces applications in B) anti-icing and C) anti-fouling materials.

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P-40

EFFECT OF SIC NANOPARTICLE ON CORROSION BEHAVIOR OF NI-P ELECTROLESS COATINGS

Majid Seyed Salehi, Alireza Mohammad Gholizadeh, Mehdi Khodaei

Faculty of Materials Science and Engineering, K.N. Toosi University of Technology, Tehran, Iran

Electroless nickel-phosphor coatings (Ni-P) have a wide range of industrial applications as a result of their corrosion resistance and good wear resistance. Nowadays, Ni-P coatings have been able to replace hard-chrome coatings, as an environmental friendly coating. Ni-P composite coatings, especially Ni-P-SiC coatings, have been commercially developed. Literature reviewing have shown that with using nanoparticles as a secondary phase in Ni-P composite coatings, better properties are obtained [1]. The purpose of this study was to
investigate the effect of the addition of SiC nanoparticles as a secondary phase in Ni-P on corrosion behavior of nanocomposite coating. Corrosion resistance of nickel coating increased significantly with the addition of a secondary phase of SiC nanoparticle. The corrosion current density of the Ni-P coating decreased from 2.97 (μA / cm^2) to 0.710 for Ni-P-1SiC coating (coating obtained by a Ni bath containing 1 gram SiC nanoparticles per liter).

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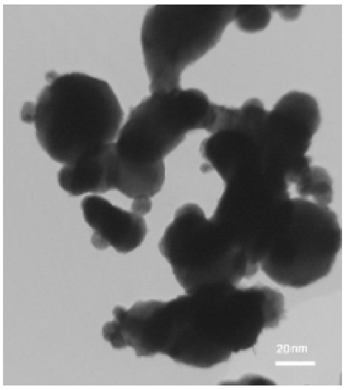

Figure 1. TEM image of SiC nanoparticle used in this research.

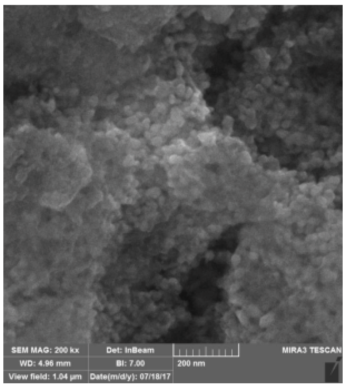

Figure 2. SEM image of etched surface of Ni-P coatings containing SiC nanoparticle.

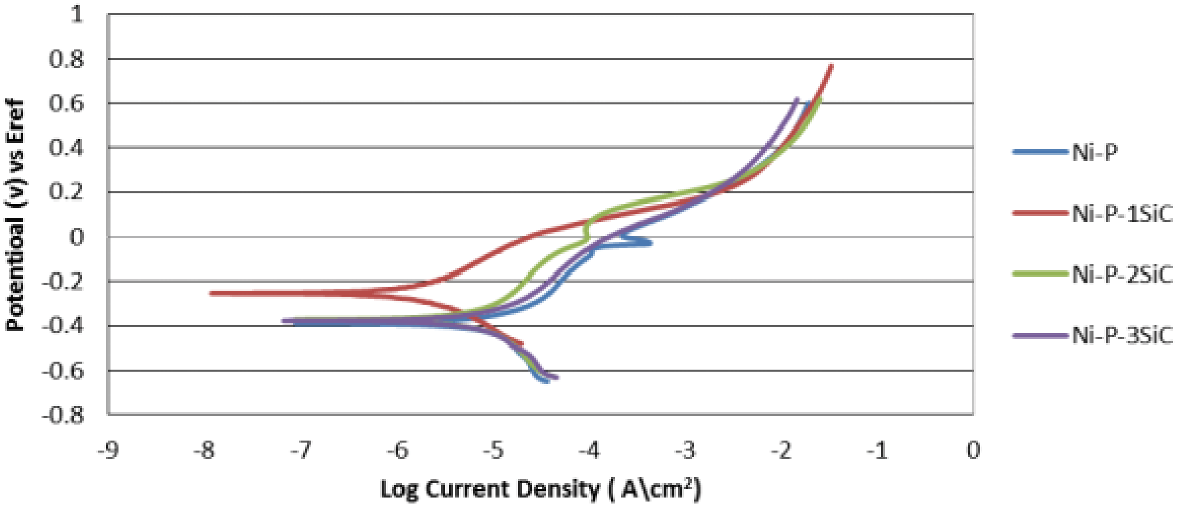

Figure 3. Polarization curves in corrosion tests of different nanocoatings obtained by a Ni bath containing 0 to 3 gram SiC nanoparticles per liter.

P-41

FABRICATION AND PROPERTIES OF SELF-ASSEMBLED THREE-DIMENSIONAL SUPERCRYSTALLINE SYSTEMS PREPARED FROM MAGNETIC IRON OXIDE NANOPARTICLES

Michael Smik[1], Genevieve Wilbs[1], Emmanuel Kentzinger[1], Ulrich Rücker[1], Stefan Mattauch[2], Oleg Petracic[1], Thomas Brückel[1]

[1] Jülich Centre for Neutron Science JCNS and Peter Grünberg Institute PGI JARA-FIT,
Forschungszentrum Jülich GmbH, Jülich, Germany
[2] Jülich Centre for Neutron Science JCNS at Heinz Maier-Leibnitz Zentrum (MLZ),
Forschungszentrum Jülich GmbH, Garching, Germany

Magnetic nanoparticle assemblies form a novel type of artificial material which hold the promise to display properties that are not found in nature. We have succeeded in fabricating large three-dimensional polycrystalline nanoparticle structures (‘nanoparticle macrocrystals’) using a novel centrifuge assisted sedimentation technique from commercially available spherical iron oxide nanoparticles.

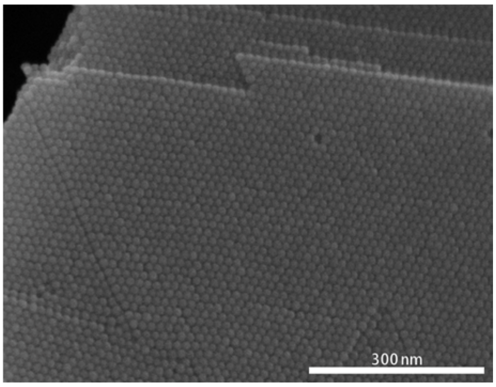

Figure 4: Scanning electron microscopy image of a nanoparticle macrocrystal.

The size and size distribution of the individual nanoparticles were characterized using both dynamic light scattering and small angle X-ray scattering (SAXS) using the new in-house instrument GALAXI (Gallium Anode Low-Angle X-ray Instrument).

The particle dispersions were dried on top of a silicon substrate using our novel fabrication method. The morphology of the crystals was examined using scanning electron microscopy (SEM), which showed that the growth of macrocrystals up to 300-1000µm in size was possible. Their structure was then investigated using SEM and SAXS (see figures 1 & 2).

The magnetic behavior was characterized using magnetometry including zero field cooled, field cooled and aged zero field cooled curves, as well as thermoremanent and isothermal remanent measurements. The systems exhibit characteristics of spin glasses, but show intriguing deviations from canonical spin glasses, hinting at probably a novel class of frustrated magnetic behavior.

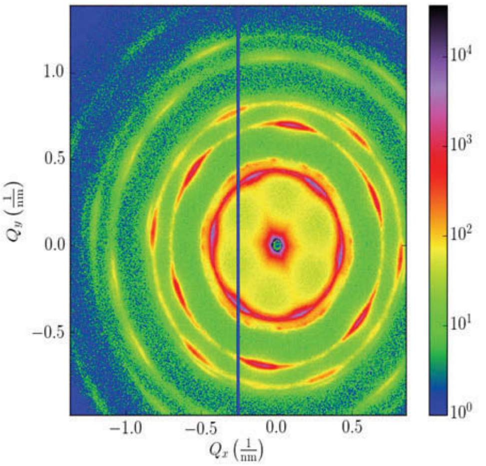

Figure 5: Detector image of a small angle X-ray scattering experiment performed on a single macrocrystal. Indexing of the diffraction pattern allows identifying the supercrystalline structure as an fcc-lattice.

P-42

OBTAINING OF REINFORCED CU-TI, CU-TI-TIB$_2$ AND CU-TIB$_2$ FOILS THROUGH GREEN COMPACT LASER SINTERING

Jelena Stašić and Dušan Božić

Materials Science Laboratory/Institute of Nuclear Sciences "Vinča", Belgrade, Serbia

One of the techniques, which started to develop 30 years ago [1] and is increasingly used nowadays in order to obtain rapidly solidified metal alloys, is synthesis of the starting materials (powders or compacts) by laser radiation. The advantages of this technique are in selectivity of location, time and energy efficiency, flexibility, versatility, automation worthiness, and faster heating and cooling rates including transient heating to elevated temperature [2]. Homogenized Cu-4Ti (wt.%), Cu-1.4Ti-0.45B (wt.%) and Cu-4TiB$_2$ (wt.%) powders were cold pressed and sintered by pulsed, millisecond Nd:YAG laser system. Microstructural parameters of laser sintered foils were studied using optical microscopy, scanning electron microscopy with an energy dispersive X-ray spectroscope and X-ray diffraction. In binary Cu-Ti alloy, after aging at 550 °C, rapidly solidified structure and metastable Cu$_4$Ti precipitates affected high degree of copper matrix strengthening at room and elevated temperature. In ternary Cu-Ti-TiB$_2$ alloy, after aging at 550 °C, rapidly solidified structure, as well as the presence of TiB$_2$ particles and metastable Cu$_4$Ti precipitates, also affected high degree of copper matrix strengthening which, thanks to the ceramic particles, is retained at high temperatures. In case of Cu-TiB$_2$ alloy high starting values of strength and strength on the elevated temperatures result from the presence of finely distributed TiB$_2$ particles in copper matrix. It was determined that the best structural and mechanical properties of laser-sintered foils were reached using the following parameters: laser frequency 4 Hz, laser pulse duration 9 ms, pulse energy ~20 J, number of scans 2 [3].

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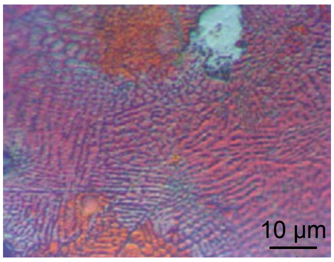

Figure 1. OM: microstructure of laser sintered Cu-1.4Ti-0.45B (wt.%).

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STRUCTURAL AND MAGNETIC PROPERTIES OF SELF-ASSEMBLED IRON OXIDE NANOPARTICLE FILMS

X. Sun[1], M. Smik[1], E. Kentzinger[1], A. Ullrich[2], U. Rücker[1], O. Petracic[1] and Th. Brückel[1]

[1] Jülich Centre for Neutron Science JCNS and Peter Grünberg Institut PGI, JARA-FIT, Forschungszentrum Jülich GmbH, Jülich, Germany
[2] Lehrstuhl für Experimentalphysik II, Universität Augsburg, Augsburg, Germany

Self-assembled NP films using iron oxide nanoparticles (NPs) were fabricated using various methods e.g. drop-casting and liquid-air-interface self-assembly. The 2D hexagonally ordered superstructures were characterized by scanning electron microscopy and Grazing Infcidence Small Angle X-ray Scattering (GISAXS). The GISAXS patterns are compared with scattering simulation results using the software BornAgain (Fig.1). The phases of iron oxide are determined by combining x-ray powder diffraction and magnetometry measurements. An exchange bias effect is found in the hysteresis loops at low temperatures. By comparing hysteresis loops after cooling in different magnetic fields, a hardening effect is observed, i.e. the squareness and hardness of the hysteresis loops is significantly enhanced with increasing magnetic cooling field. This is due to an antiferromagnetic wustite component, which pins the ferrimagnetic spins of magnetite/maghemite via exchange coupling. By this an additional anisotropy axis is induced. Also, the influence of the induced anisotropy onto the magnetic correlations of the NP superspins was investigated. The hardening effect in diluted iron oxide NPs is compared to self-assembled NP films. Due to the dipolar interactions between NPs, a memory effect was found in ordered NP films. This effect was not observed in diluted samples.

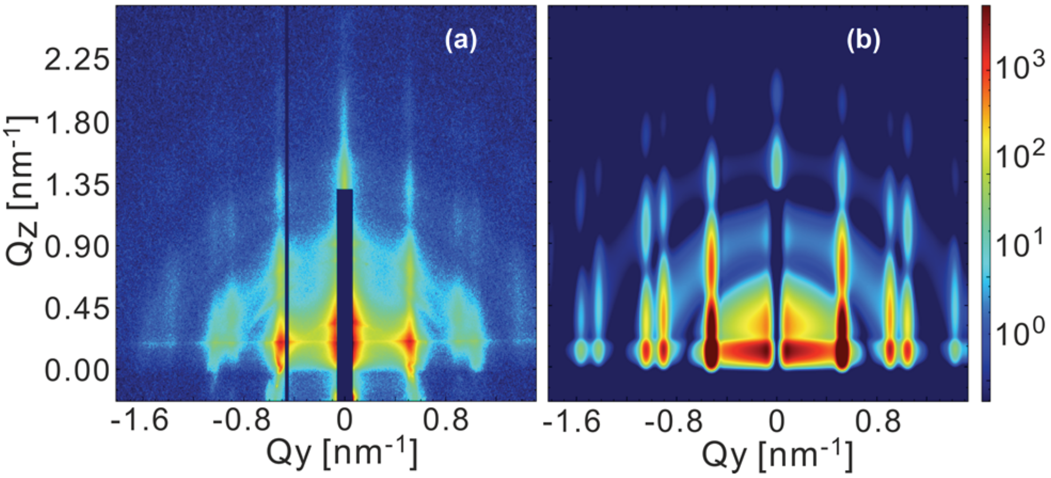

Figure 1. (a) GISAXS pattern of self-assembled iron oxide NPs with 15nm diameter using drop-casting plus toluene method. (b) GISAXS pattern simulated for hexagonally ordered spheres with 13nm diameter. The lattice constant of the hexagonal lattice is 18 nm.

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NANOGLASS AS TEMPLATE FOR FOAMING

Sandra Teusch, R. Strey and A. M. Schmidt

Department Chemie, Institut für Physikalische Chemie, Universität zu Köln, Köln, Germany

An important goal in current material science research is the production of nanoporous materials for a wide variety of applications, for instance as advanced thermal insulation materials, i.e. *Knudsen* materials. However, the foaming of such materials is challenging and therefore a topic of ongoing research. Here, we adapt the Continuity Inversion of Dispersions (NF-CID) procedure [1,2] using glass (nano-) particles to fabricate a highly porous glass foam. To this end, monodisperse solid nano- (or micro-) particles are closely packed and soaked with a super- or near critical fluid within a pressure-proof, locked container. A continuity inversion occurs upon melting of the particles, which creates *sc*-fluid inclusions within the now continuous glass matrix. A foam is obtained by expansion, whereby the foam solidifies due to expansion cooling. We examine the foaming process as it depends on temperature, pressure and the nature of the applied particles.[2,3] The most relevant properties of the particles are size and composition. On the one hand, the size correlates directly with the pore diameter of the resulting foam and should preferably be in the nanometer range. On the other hand, the composition is important for the thermal behavior of the material. Nanosized particles with a composition close to soda-lime-silicate glass are identified as promising candidates with a low glass temperature T_g.

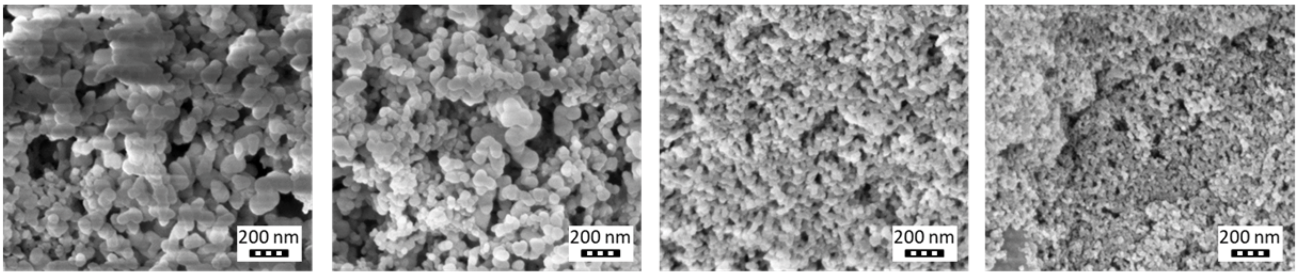

Figure 1. SEM images of calcium-doped SiO_2 particles of different size.

Calcium and sodium doped silica particles were generated employing different synthetic strategies.[4-7] By varying the reaction conditions, particles of different composition and size are now available (see Fig. 1). The thermal behavior and structure of the doped particles is examined by differential scanning calorimetry, X-ray diffraction and scanning electron microscopy to ensure their suitability for the NF-CID approach. First foaming experiments show the applicability of the approach to glass particles aiming at highly porous glass (nano-)foams.

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P-45

UNDERSTANDING AND CONTROLLING SURFACE LATTICE RESONANCES IN SELF-ASSEMBLED PLASMONIC MONOLAYERS

Kirsten Volk and Matthias Karg

Heinrich-Heine-University Düsseldorf, Physical Chemistry I, Düsseldorf, Germany

Plasmonic monolayers have recently gained attention in research due to their potential applications in nanooptics. The precise arrangement of single plasmonic nanoparticles into large ordered arrays leads to far-field coupling of the localized surface plasmon resonances (LSPR) of the particles with diffractive modes. This effect enables the formation of surface lattice resonances (SLRs) with peak positions determined by the lattice and narrow bandwidths indicating long lifetimes of the plasmons. As a result, SLRs are an exciting area of active research into using plasmon resonances for coherent optical processes, such as lasing.

It was found that a homogeneous refractive index environment surrounding the particle monolayer is vital for the formation of surface lattice resonances [1,2]. In fact, inhomogeneities, e.g. given by a materials' interface close to the particle monolayer, lead to little to no diffractive mode coupling. However, the transition between this weakly coupled case and the strong SLR in the effectively infinite medium has not been experimentally investigated and remains poorly understood.

Here we provide a systematic study of the influence of the homogeneity of the refractive index environment on the strength and wavelength of SLR modes in self-assembled plasmonic monolayers. The refractive index environment is manipulated by application of a polymeric top coating onto the monolayer that is deposited on glass [2,3]. Monitoring the single LSPR contribution to the overall extinction spectra is used to quantify the coupling strength as its appearance is dramatically influenced by the surrounding refractive index [4]. We do this by systematically varying the distance between the lattice plane, in a medium with refractive index ~1.5 (glass + NOA 81), and the medium interface with air (refractive index 1) over a large range of thicknesses using small, nanometer-scale increments. In order to better understand the physical origin of the observed resonances, we compare the spectra to theoretical calculations using FDTD simulation and a simplified, coupled dipole approximation (CDA) model.

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P-46

TUNABLE FLUORESCENCE BY HIERARCHICAL STRUCTURE FORMATION BASED ON FUNCTIONALIZED OXIDE NANOPARTICLES

Judith Wittmann[1], Lisa Stiegler[2], Christian Henkel[3] and Marcus Halik[1]

[1] Department Werkstoffwissenschaften, Lehrstuhl für Polymerwerkstoffe, Organic Materials and Devices (OMD), 91058 Erlangen, Germany
[2] Department Chemie und Pharmazie, Institut für Organische Chemie, 91054 Erlangen, Germany
[3] Department Chemie und Pharmazie, Institut für Physikalische Chemie I, 91058 Erlangen, Germany.

Core- shell systems, such as oxide nanoparticles (NP) functionalized with chained phosphonic acid derivatives, are applicable in various contexts. By a careful choice of the phosphonic acid derivative (PA), the NPs solubility [1] or reactivity [2] can precisely be adjusted. The NPs surface properties, respectively zeta potential and solubility change upon interactions with complementary amphiphiles that is for example the interaction between hexadecylphosphonic acid (C_{16}-PA) bound to an oxide NP and dodecylbenzenesulfonate (SDBS). Hereby, a “second shell” is formed through noncovalent interactions between C_{16}-PA and SDBS [3].

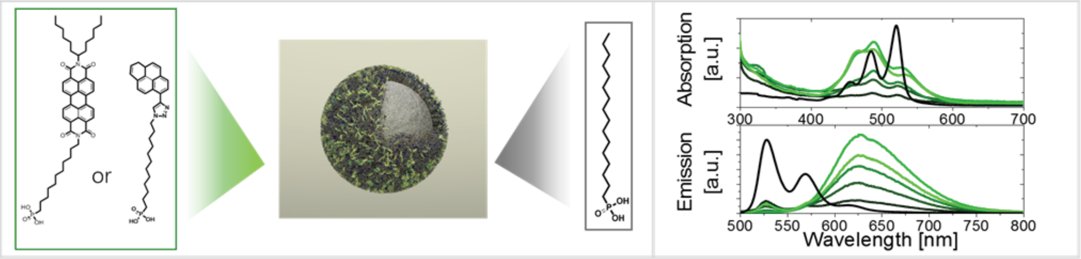

Figure 1. Functionalization of oxide nanoparticles with mixtures of phosphonic acid derivatives (left) allows the precise control of the NPs optical properties (right).

This toolbox is applied for the precise tuning of the optical properties of functionalized oxide nanoparticles (Figure 1). Therefore, fluorescent polyaromatic hydrocarbons (PAHs) are linked to aluminum oxide nanoparticles either directly as phosphonic acid derivatives, or indirectly via “click chemistry”. By functionalizing NPs with a mixture of optical active and “spacing” PA, the aggregation of PAHs is controlled by the molecular ratio. Furthermore, the optical behavior is influenced by the chemical nature of the “spacing” PA (e.g. alkyl-, glycol-, fluorinated chains). By forming a “second shell”, corresponding to the nature of the “spacing” PA, the aggregation of PAH is further influenced. This changes the optical properties by providing a distinguished chemical environment to the chromophore. Additionally, the changed solubility of the NPs, upon the formation of a “second shell”, allows the maintenance of optical features corresponding to e.g. an alkyl environment in e.g. an aqueous solution [4].

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TEMPLATING OF THE CRYSTALLINE STRUCTURE OF INJECTION-MOLDED ISOTACTIC POLYPROPYLENE/TIO2 NANOCOMPOSITE BY NANOPARTICLES

Peng Zhang[1] and Tobias Kraus[1,2]

[1] INM – Leibniz Institute for New Materials, Campus Saarbrücken, Germany
[2] Colloid and Interface Chemistry, Saarland University, Saarbrücken, Germany

Structure formation in semicrystalline polymers involves molecular assembly at different length and time scales. Here, we consider the phase transition of a polypropylene melt into a semicrystalline solid involves packing the molecular chains into nanoscale lamellae and microscale spherulites that contain many chains. Inorganic nanofillers can drastically change this transition even at low volume fraction and strongly affect the mechanical behavior of the resulting nanocomposites. They nucleate the formation of crystallites that serve as crosslinks and increase the filler's effect on mechanical performance [1]. In this work, we revisit the role of polymer crystallization in a semicrystalline polymer nanocomposite and focus on the effects of anisotropic nanofillers.

We find that injection-molded isotactic polypropylene/titanium dioxide (IPP/TiO_2) nanocomposites exhibit preferential molecular alignment and a higher elastic modulus than neat IPP [2]. Both effects are too strong to be solely explained by the shear alignment of nanorods during injection molding. We show that the nanorods have an unexpectedly strong templating effect on the crystalline IPP structure. It is likely that polymer molecules adsorb on shear-aligned nanorods and interconnect through supramolecular "bridges" [3].

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FUNCTIONAL NANOPARTICLES FOR RESPONSIVE PHOTONIC CRYSTALS

Xuyang Zhang, Dominik Rengel and Thorsten Wagner

Paderborn University, Faculty of Science, Department of Chemistry, Paderborn, Germany

Responsive photonic crystals (R-PhCs) are periodical dielectric structures. Their optical properties depend on symmetry and geometry, the refractive indices of the constituting phases [1], the volume fraction of these phases and the periodicity of the R-PhC. Rational design of the structure and composition allows for manipulation of the optical properties by external stimuli. Therefore R-PhCs are suitable for biological and chemical sensing [2].

In the here presented work we focus on new sensing concepts based on opals and inverse opals, a subcategory of PhCs. Opals and inverse opals offer highly accessible surface areas and are therefore most suitable for this application. One promising approach to achieve and control responsivity in these structures is the utilization of functional nanoparticles (see Figure 1, left and caption).

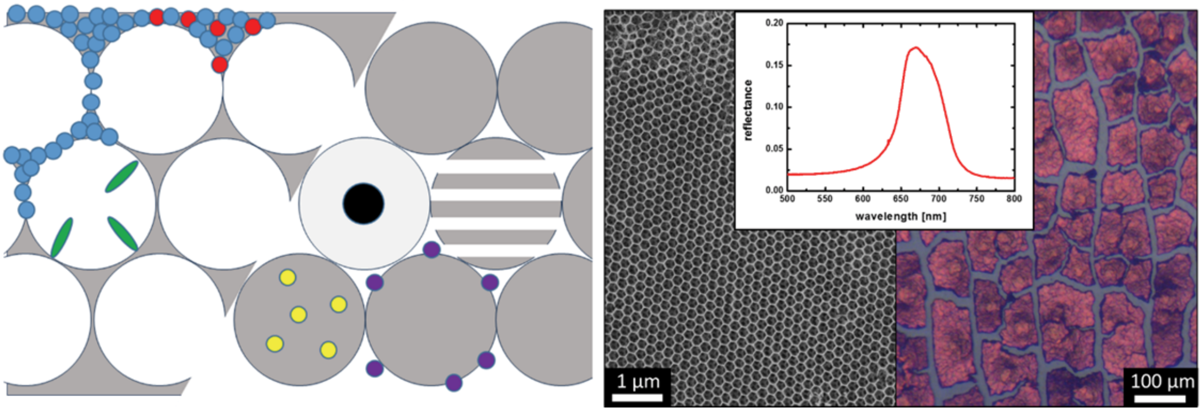

Figure 1. (left) Functional nanoparticles in responsive photonic crystals: as responsive wall material (blue, red) and surface modifications (green) in inverse opals; as sensitive luminophores or dyes (yellow), catalyst (violet), core shell (black-grey) or porous particles in opals. (right) SEM image of a SnO_2 inverse opal and photograph; inset shows reflectance spectrum of the structure.

Among others, results on metal oxide structures will be presented. A tin dioxide (SnO_2) inverse opal (Figure 1, right) composed hierarchically of responsive building blocks (SnO_2 nanoparticles) and an optical transducing PhC structure exhibits excellent structural and optical properties. Based on this material a new type of optical gas transducer will be created. The working principle relies on a change of structural color caused by gas reactions inducing a refractive index change in the SnO_2 particles. The iridescent coloration is due to the formation of photonic band gaps, the optical analogy to the electronic bands of semiconductors. Light with the frequency in these gaps is reflected resulting in a color impression if the gaps locate in the visible range [3]. Measurements and simulations on the optical properties and the gas response will be presented [4].

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PATCHY SILICA PARTICLES VIA MICRO CONTACT PRINTING

Marc Zimmermann[1,2], Dmitry Grigoriev[1], Nikolay Puretskiy[1], Alexander Böker[1,2]

[1] Functional Protein Systems | Biotechnology, Fraunhofer Institute for Applied Polymer Research, Potsdam-Golm, Germany
[2] Polymer Materials and Polymer Technologies, University of Potsdam, Potsdam-Golm, Germany

The precise and selective modification of silica microparticles is a challenging task, which led to very different approaches over the years reaching from dip coating, etching processes and interface reactions in two phase systems [1 – 3].

While there are several studies concerning the preparation of patchy or janus-like polymer particles with micro contact printing (µCP), only very few studies use this technique to create patchy silica particles. A great stability concercing temperature and various solvents and a broad selection of alkoxysilanes for surface modification make these silica particles very attractive for further investigations.

Our group works with PDMS as a substrate for µCP. In comparison to other researches concerning µCP of particles we work with polymeric inks instead of molecular inks, in particular with polyelectrolytes[4]. This gives us enhanced control over patch size, geometry and pH dependent patch release. After printing, these patches can be modified with reversible (supramolecular) or irreversible crosslink chemistry (click reactions) to achieve the possiblity of switchable colloidal assemblies. Additionally we aim to create multivalent patchy particles which are not constrained to a high symmetry of the patches (e. g. 60° angle) by using our µCP approach with a combination of structured and unstructured PDMS substrates [5].

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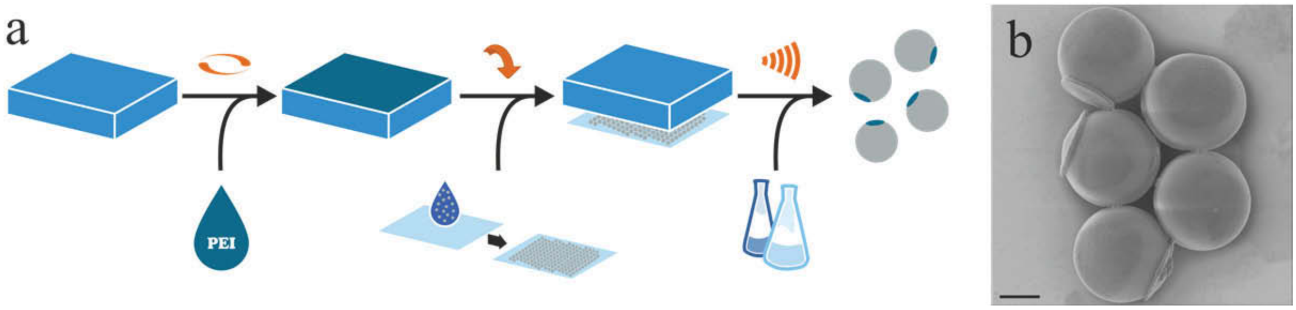

Figure 1 a) Visualization of our micro contact printing approach: Production of loaded PDMS stamps; silica monolayer creation; printing process and particle release from stamp in a suitable solvent. b) REM image of printed patchy silica particles (2µm scale bar).

▶ PARTICIPANTS

Leon Abelmann
KIST Europe
Saarbrucken, Germany
l.abelmann@kist-europe.de

Ilayda Acaroglu Degitz
Yeditepe University
Istanbul, Turkey
ilaydacaroglu@gmail.com

Asar Ahmed
Laxminarayan Institute of Technology
Nagpur, India
asar.ahmed@nagpuruniversity.nic.in

Sholeh Alaei
Islamic Azad University
Urmia, Iran
sh.alaei@iaurmia.ac.ir

Abdulkadir Alli
Düzce University
Düzce, Turkey
abdulkadiralli@duzce.edu.tr

Dušan Božić
University of Belgrade
Belgrade, Serbia
dbozic@vinca.rs

Coline Bretz
LS Instruments
Fribourg, Switzerland
coline.bretz@lsinstruments.ch

Eunjin Choi
Max Planck Institute for Intelligent Systems
Stuttgart, Germany
choi@is.mpg.de

Laura De Laporte
DWI - Leibniz Institute for Interactive Materials
Aachen, Germany
delaporte@dwi.rwth-aachen.de

David Doblas Jimenez
INM - Leibniz Institute for New Materials
Saarbrücken, Germany
David.DoblasJimenez@leibniz-inm.de

Sabine Eisold
RWTH Aachen University
Aachen, Germany
sabine.eisold@ac.rwth-aachen.de

Lukas Engel
INM - Leibniz Institute for New Materials
Saarbrücken, Germany
Lukas.Engel@leibniz-inm.de

Michael Engel
FAU Erlangen-Nürnberg
Erlangen, Germany
michael.engel@fau.de

Simon Fleischmann
INM - Leibniz Institute for New Materials
Saarbrücken, Germany
simon.fleischmann@leibniz-inm.de

Jean Baptiste Fleury
Saarland University
Saarbrücken, Germany
jean-baptiste.fleury@physik.uni-saarland.de

Markus Gallei
TU Darmstadt
Darmstadt, Germany
m.gallei@mc.tu-darmstadt.de

Georg Garnweitner
TU Braunschweig
Braunschweig, Germany
g.garnweitner@tu-bs.de

Dennis Graf
Karlsruhe Institute of Technology
Eggenstein-Leopoldshafen, Germany
Dennis.Graf@kit.edu

André Gröschel
University of Duisburg-Essen
Duisburg, Germany
andre.groeschel@uni-due.de

Bastian Haehnle
DWI - Leibniz-Institute for Interactive Materials
Aachen, Germany
haehnle@dwi.rwth-aachen.de

Andreas Hegetschweiler
INM - Leibniz Institute for New Materials
Saarbrücken, Germany
andreas.hegetschweiler@leibniz-inm.de

Karl Hiekel
TU Dresden
Dresden, Germany
karl.hiekel@chemie.tu-dresden.de

Laura Hoppe Alvarez
RWTH Aachen University
Aachen, Germany
hoppe.alvarez@pc.rwth-aachen.de

Chiao-Peng Hsu
ETHZ
Zurich, Switzerland
chiao-peng.hsu@mat.ethz.ch

Wei Huang
Max Planck Institute for Polymer Research
Mainz, Germany
huangwei@mpip-mainz.mpg.de

Kentaro Iwasaki
Sumika Ceramics Poland Sp. z o.o
Wroclaw, Poland
kentaro.iwasaki@sumikaceramics.com

Hyeon-Ho Jeong
Max Planck Institute for Intelligent Systems
Stuttgart, Germany
hjeong@is.mpg.de

Urmas Joost
University of Tartu
Tartu, Estonia
urmas.joost@ut.ee

Matthias Karg
Heinrich-Heine-University Duesseldorf
Duesseldorf, Germany
karg@hhu.de

Mehdi Khodaei
K.N. Toosi University of Technology
Tehran, Iran
khodaei@kntu.ac.ir

Thomas Klein
Saarland University
Saarbrücken, Germany
thomas.klein1@uni-saarland.de

Nadja D. Klippel
Saarland University
Saarbrücken, Germany
nadja.klippel@uni-saarland.de

Robin Klupp Taylor
FAU Erlangen-Nürnberg
Erlangen, Germany
robin.klupp.taylor@fau.de

Andrea Knauer
TU Ilmenau
Ilmenau, Germany
andrea.knauer@tu-ilmenau.de

Tobias A. F. König
Leibniz-Institut für Polymerforschung
Dresden, Germany
koenig@ipfdd.de

Tobias Kraus
INM – Leibniz Institute for New Materials
Saarbrücken, Germany
tobias.kraus@leibniz-inm.de

Margarita Kruteva
Jülich Centre for Neutron Science
Jülich, Germany
m.kruteva@fz-juelich.de

Alexander Kuehne
DWI - Leibniz Institute for Interactive Materials
Aachen, Germany
ajckuehne@gmail.com

Christian Lang
Forschungszentrum Jülich
Jülich, Germany
c.lang@fz-juelich.de

Anna Lechner
University of Bayreuth
Bayreuth, Germany
Anna.Lechner@uni-bayreuth.de

Jun Tae Lee
Korea Testing Laboratory
Ansan-si, Korea
leejt@ktl.re.kr

Alberto Leonardi
FAU Erlangen-Nürnberg
Erlangen, Germany
alberto.leonardi@fau.de

Siham Lhimr
Faculty of Science
Khemisset, Morocco
siham.lhimr@gmail.com

Ferenc Liebig
Universität Potsdam
Potsdam, Germany
ferliebi@uni-potsdam.de

Franziska Lübkemann
Leibniz Universität Hannover
Hannover, Germany
Franziska.Luebkemann@pci.uni-hannover.de

Michael Maas
University of Bremen
Bremen, Germany
michael.maas@uni-bremen.de

Karl Mandel
Fraunhofer ISC
Würzburg, Germany
karl.mandel@isc.fraunhofer.de

Claudia Marschelke
Leibniz-Institut für Polymerforschung e.V.
Dresden, Germany
marschelke@ipfdd.de

Fru Mbah Chrameh
FAU Erlangen-Nürnberg
Erlangen, Germany
fmbah.chrameh@fau.de

Shilin Mei
HZB für Materialien und Energie
Berlin, Germany
shilin.mei@helmholtz-berlin.de

Jan Frederick Miethe
Leibniz Universität Hannover
Hannover, Germany
jan.miethe@pci.uni-hannover.de

Annabel Mikosch
DWI - Leibniz Institute for Interactive Materials
Aachen, Germany
mikosch@dwi.rwth-aachen.de

Rebecca Momper
Max Planck Institute for Polymer Research
Mainz, Germany
momper@mpip-mainz.mpg.de

Alex Oppermann
RWTH Aachen University
Aachen, Germany
oppermann@pc.rwth-aachen.de

Alexandra Philipp
University of Bayreuth
Bayreuth, Germany
alexandra.philipp@uni-bayreuth.de

Jörg Polte
Humboldt Universität zu Berlin
Berlin, Germany
joerg.polte@hu-berlin.de

Marcel Pourasghar
Saarland University
Saarbrücken, Germany
marcel.pourasghar@uni-saarland.de

Annett Reichhelm
TU Dresden
Dresden, Germany
Annett.Reichhelm@chemie.tu-dresden.de

Holger Reiner
University of Constance
Konstanz, Germany
holger.reiner@uni-konstanz.de

Beate Reiser
INM - Leibniz Institute for New Materials
Saarbrücken, Germany
beate.reiser@leibniz-inm.de

Julian Ruiz Perez
University of Constance
Konstanz, Germany
julian.ruiz@uni-konstanz.de

Marco Sarcletti
FAU Erlangen-Nürnberg
Erlangen, Germany
marco.sarcletti@fau.de

Marcus Scheele
Universität Tübingen
Tübingen, Germany
marcus.scheele@uni-tuebingen.de

Annika Schlander
TU Darmstadt
Darmstadt, Germany
A.Schlander@MC.tu-darmstadt.de

Dirk Oliver Schmidt
RWTH Aachen University
Aachen, Germany
oliver.schmidt@ac.rwth-aachen.de

Marc Schneider
Saarland University
Saarbrücken, Germany
Marc.Schneider@mx.uni-saarland.de

Jann Schulte
RWTH Aachen University
Aachen, Germany
jann.schulte@avt.rwth-aachen.de

Madeleine Schwarzer
Leibniz-Institut für Polymerforschung e.V.
Dresden, Germany
schwarzer@ipfdd.de

Majid Seyed Salehi
K.N. Toosi University of Technology
Tehran, Iran
seyedsalehi@kntu.ac.ir

Michael Smik
Jülich Centre for Neutron Science 2
Jülich, Germany
m.smik@fz-juelich.de

Jelena Stašić
University of Belgrade
Belgrade, Serbia
jelsta@vinca.rs

Xiao Sun
Jülich Centre for Neutron Science
Jülich, Germany
x.sun@fz-juelich.de

Andris Sutka
University of Tartu
Tartu, Estonia
andris.sutka@rtu.lv

Sandra Teusch
Universität zu Köln
Köln, Germany
sandra.teusch@uni-koeln.de

Andreas Tschöpe
Saarland University
Saarbrücken, Germany
a.tschoepe@nano.uni-saarland.de

Nicolas Vogel
FAU Erlangen-Nürnberg
Erlangen, Germany
nicolas.vogel@fau.de

Kirsten Volk
Heinrich-Heine University
Duesseldorf, Germany
kirsten.volk@hhu.de

Tamara Winter
TU Darmstadt
Darmstadt, Germany
t.winter@MC.tu-darmstadt.de

Susanne Wintzheimer
Fraunhofer ISC
Würzburg, Germany
susanne.koch@isc.fraunhofer.de

Judith Wittmann
FAU Erlangen-Nürnberg
Erlangen, Germany
judith.wittmann@fau.de

Alexandra S. M. Wittmar
Universität Duisburg-Essen
Essen, Germany
alexandra.wittmar@uni-due.de

Xia Wu
Paderborn University
Paderborn, Germany
xia.wu@upb.de

Xuyang Zhang
Paderborn University
Paderborn, Germany
xuyangz@mail.uni-paderborn.de

Peng Zhang
INM - Leibniz Institute for New Materials
Saarbrücken, Germany
peng.zhang@leibniz-inm.de

Marc Zimmermann
Fraunhofer IAP
Potsdam-Golm, Germany
marc.zimmermann@iap.fraunhofer.de

INM – Leibniz Institute for New Materials
Campus D2 2 · 66123 Saarbrücken, Germany

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