

CPP 3: Nanoparticles and Composite Materials I (joint session CPP, BP)

Time: Monday 9:30–13:00

Location: C 243

CPP 3.1 Mon 9:30 C 243

Iron Oxide Nanocube Monolayers at the Air/Water Interface: Self-Organization on Nano- and Mikroscale — ●HEIKO AHRENS¹, SARAH MEHDIZADEH TAHERI², THOMAS ORTMANN¹, ANDREAS GRÖNING¹, STEPHAN FÖRSTER², and CHRISTIANE A. HELM¹ — ¹Physik, Uni Greifswald, 17487 Greifswald, Germany — ²Physikalische Chemie I, Uni Bayreuth, 95440 Bayreuth, Germany

Monodisperse Cubic Iron Oxide nano particles (5-8 nm) covered in oleic acid form stable films on the air water interface. Isotherms exhibit a plateau at 18 - 20 mN/m, then the pressure increases steeply. At zero surface pressure, Brewster angle microscopy(BAM) shows micrometer sized domains consisting of nanocubes immersed in a matrix of excess oleic acid. These small domains show Brownian motion. Then linear and mesh-like rigid domains (size 100 *m) are observed. The 5.5nm nanocubes form a homogenous monolayer in the plateau region, on further pressure increase large (100 *m) homogenous domains of bi- and even multilayer appear. The films of the larger 8 nm nanocubes remain heterogeneous at all surface pressures. Large (100 *m) patches of oleic acid monolayers coexist with medium sized (50*m) domains of particle monolayer and small domains (10 *m) of bi- and multilayers. All aggregation is irreversible.

These observations are confirmed by X-ray reflectivity and Grazing Incidence X-ray diffraction.

CPP 3.2 Mon 9:45 C 243

ZnO nanoparticle stabilization - How much is necessary? — ●TORBEN SCHINDLER¹, TILO SCHMUTZLER¹, WEI LIN², DORIS SEGETS², WOLFGANG PEUKERT², and TOBIAS UNRUH¹ — ¹Lehrstuhl für Kristallographie und Strukturphysik, Friedrich-Alexander-Universität Erlangen Nürnberg, Staudtstr. 3, 91058 Erlangen — ²Lehrstuhl für Feststoff- und Grenzflächenverfahrenstechnik, Friedrich-Alexander-Universität Erlangen Nürnberg, Cauerstr. 4, 91058 Erlangen

The stabilization of small nanoparticles is of highest importance for their use in different applications. For these applications the stabilizer used in the synthesis is often exchanged by different species which offer the possibility of e.g. light harvesting for solar cells. However, the amount of stabilizer needed in the first place was seldomly addressed in the literature. In the case of solution processed ZnO nanoparticles acetate is often used as primary stabilizer. However, by washing of the samples it was observed that the nanoparticles become unstable and show strong agglomeration after three washing cycles. We investigated the changes in the stabilizing acetate layer by the combination of small angle X-ray and neutron scattering (SAXS&SANS). Initially the shell incorporates about 10% of the total acetate. This factor is clearly reduced in the washed samples which show still stability against agglomeration. Thus only a small amount of acetate is actually needed to stabilize the nanoparticles. In addition to these results the effect of first ligand exchange reactions using different amounts of catechol will be presented.

CPP 3.3 Mon 10:00 C 243

A Toolbox to Connect the Physicochemical Properties of GNPs with their Biological Behavior — ●JONAS SCHUBERT and MUNISH CHANANA — Department of Physical Chemistry II, University of Bayreuth, 95440 Bayreuth (Germany)

Due to their plasmonic properties and their biocompatibility gold nanoparticles (GNPs) are widely used in biological systems. Unfortunately, the colloidal variability is neglected in most studies, so that the chemical identity is not coherent with the biological identity. An undefined absorption alters the properties of the particles fundamentally, so that it is not possible to predict or study their biological behavior in dependence of their original physicochemical properties, e.g. surface charge.

To circumvent these problems, we present a toolbox of GNPs with a defined protein corona.[1,2] This defined protein corona enables the GNPs to meet the first requirement for biological applications: high colloidal stability in the presence of salt, other proteins and over a large range of pH values. A toolbox of more than 10 proteins and different purification procedures allow the exceptional chance of tailoring the physicochemical properties of nanoparticles, such as surface charge, colloidal stability and responsiveness.

1Chanana, M.; Correa-Duarte, M. A.; Liz-Marzan, L. M., *Small* 2011, 7 (18), 2650-2660.

2Chanana, M.; Gil, P. R.; Correa-Duarte, M. A.; Liz-Marzan, L. M.; Parak, W. J., *Angewandte Chemie-International Edition* 2013, 52 (15), 4179-4183.

CPP 3.4 Mon 10:15 C 243

Electrochemical growth of ZnO nanostructures for biosensing applications — ●RALUCA - ANCUTA SUCIU, NIVEDITA YUMNAM, and VEIT WAGNER — Jacobs University, Bremen, Germany

Biosensors have been used in applications such as blood glucose measuring or pregnancy tests already for a long time, and their improvement is of high interest in many fields of research such as medicine (e.g. diagnostics), military (e.g. monitoring of poison gases) and industry (e.g. food and drink process control). The sensitivity of biosensors can be improved by increasing the surface area where the molecules under observation can bind. Therefore, we have employed ZnO nanorods grown via electrochemical deposition on Au covered flexible PET (polyethylene terephthalate) substrate. The size and distance of ZnO nanostructures can be effectively controlled by tuning the electrochemical deposition parameters. Furthermore, self-assembled monolayer (SAM) of 1-octadecanethiol has been applied on Au to tune the nucleation density of ZnO. Application of SAM prevents overly dense growth of ZnO and instead allows ZnO to electrochemically grow through the pinholes in the SAM. To realize a capacitive sensor additional Au finger contacts have been fabricated using optical lithography. The sensor operation is verified by detection of Streptavidine biomolecules.

CPP 3.5 Mon 10:30 C 243

In situ Study of Spray-deposited Gold Nanoparticles Assemblies on Polymer Substrates Using GISAXS — ●PENG ZHANG¹, KOYILOTH V. SARATHLAL¹, SANTORO GONZALO¹, NIPAM SHAH², GUANGSU HUANG³, and STEPHAN V. ROTH¹ — ¹Deutsches Elektronen Synchrotron, Notkestr. 85,22607 Hamburg — ²Fachbereich Maschinenbau und Wirtschaft, Fachhochschule Lübeck, 23562 Lübeck — ³College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

The assembly of the nanoparticles from the solution still remains challenging, namely inhomogeneous material dispersion for example, coffee-stain-like or clumps of particles is observed. To get designed nanocomposite in thin films, controlling the solution evaporation and promoting the ordering of nanoparticles on the templated substrates is a smart and feasible choice. Spray deposition is one of the desirable techniques to manipulate solvent evaporation by atomizing the solution. Here we present our recent in situ studies on the directed assembly of spray deposited gold nanoparticles on patterned substrates. By manipulating the assembly process, we find that the well-ordered gold nanoparticles show enhanced optical properties. These findings are attractive for the applications such as solar cells and antireflection coating. [1] Yunker et al. *Nature* 476, 308 (2011); [2] Al-Hussein et al. *Langmuir* 29, 2490 (2013); [3]Herzog et al. *Langmuir* 29, 11260 (2013).

Invited Talk

CPP 3.6 Mon 10:45 C 243

Functional Nanocomposites: Disordered media with a cooperative macroscopic action — ●MADY ELBAHRI — Nanochemistry and Nanoengineering, Institute for Materials Science, Faculty of Engineering, Christian-Albrechts-University Kiel, Germany

So far, research on polymer based nanocomposites mostly centered on structural composites where little attempt was made to precisely control the nanostructure. During the last years, however, there has been increasing interest in functional nanocomposites due to novel applications ranging from sensors and plasmonics through stretchable electronics and smart coatings to energy conversion and human health. In this context the concept of a disordered "glassy" nanocomposite with a cooperative macroscopic action has not been suggested so far. The present talk aims at introducing a particularly promising new class of functional optical materials based on closely spaced ultrafine nanoparticles acting as "artificial molecules" embedded in a polymeric host where the unique properties arise from the strong and cooperative near field coupling between neighbouring nanoparticles. This gives

rise to coherent cooperative action thus determining the macroscopic properties.

15 min. break

CPP 3.7 Mon 11:30 C 243

Self-assembly of nanoparticles in block copolymer nanotemplates — ●MANFRED STAMM^{1,2}, ANDREJ HORECHY¹, and BHANDU NANDAN³ — ¹Leibniz-Institut für Polymerforschung Dresden — ²Technische Universität Dresden — ³Indian Institute of Technology, Delhi

Nanotemplates generated by microphase segregation of diblock copolymers can be used for directed self-assembly of nanoparticles. There are several routes possible where functional nanoparticles are either added to the copolymer solution prior to film formation and then preferentially migrate to one of the phases or where the nanoparticles are added after copolymer nanotemplate formation and then show preferential adsorption to one of the phases. In both cases ordered nanoparticle arrays are obtained and by combination of the two approaches dual structures /1/ may be formed. With hexagonal structures and removal of the majority phase, nanorods are generated /2/. Under certain conditions helical arrangements of nanoparticles inside the cylinders are observed /3/ which are due to dense packing in confined geometry. Copolymer nanotemplates thus provide an interesting tool for generation of ordered nanoparticle structures. We acknowledge funding by DFG. /1/ Adv.Fun.Mater. 23 (2013) 483-90; /2/ J.Mater.Chem. 22 (2012) 25102-7; /3/ Angew. Chem. Int. Ed. 53 (2014) 1-5.

CPP 3.8 Mon 11:45 C 243

Insulin capped gold nanoparticles-polymer brush composites — ●MURIEL ROVIRA ESTEVA, ZULEYHA YENICE, STEPHANIE CHRISTAU, STEFAN WELLET, and REGINE VON KLITZING — Stranski Laboratorium für Physikalische und Theoretische Chemie, Technische Universität Berlin, 10623 Berlin, Germany

Polymer brushes are polymers grafted to a surface by one end, with a density high enough to induce the polymer chains to stretch away from the surface. This stretching is often responsive to environmental conditions, which makes them a suitable candidate for the design of smart coatings, among a number of other applications. Polymer brush-nanoparticle composites allow to combine the responsive properties of the brush with the physico-chemical properties of the particles. Therefore, determination of how the geometric parameters affect the behavior of the composite is of high scientific and technological significance.

Gold nanoparticles capped with sodium citrate are often used in these composites, but they pose a series of instability problems. In this work, monodisperse gold nanoparticles with sodium citrate and tannic acid cappings were synthesized, and their capping was replaced by insulin, adapting a method by M. Chanana et al. The higher stability against strong pH variations of the insulin capped particles was confirmed with UV-Vis. Incorporation of particles with different cappings into brushes with different geometries allowed to obtain a variety of polymer brush-gold nanoparticle composites, and the effect of the geometrical parameters on the brush-nanoparticle interactions was then explored using a number of techniques, such as AFM and reflectometry.

CPP 3.9 Mon 12:00 C 243

Drug delivery to cancer cells by nanodiamonds — ●ANNA ERMAKOVA¹, YUZHOU WU², BORIS NAYDENOV¹, TANJA WEIL², and FEDOR JELEZKO¹ — ¹Institute of Quantum Optics, University Ulm, Ulm, Germany — ²Institute of Organic Chemistry III, University Ulm, Ulm, Germany

The numbers of new cancer cases increase every year, and only few last years in some country the numbers of deaths were stable or decreased [1], this is result of progress in medicine. The main problem of the cancer therapy is the precise drug delivery to cancer cells with the exception of healthy cells. The direct drug delivery can bring a lot of advantages: reduction of the total amount of uptaken drug, more stable drug level in the specific sides, potential reduction of the drug in healthy unaffected tissues, and reduction of dosages frequency. Nanodiamonds (NDs) are potentially good drug carriers since they are non-toxic [2], their surfaces can be chemically functionalized [3] and they can be easily inserted into cells [4]. Furthermore, colour defect centres in NDs can be used as photostable biomarkers compared to quantum dots and dyes. In our work to release drug we used the property of the tumour

tissue to have on average a lower pH level than healthy tissue [5]. We demonstrate a drug release from NDs in the solution, triggered by change in the pH, and inside HeLa cells. We show that only drugs penetrate into a cell nucleus and NDs stay at the cytoplasm. [1]R.Siegel et al,CA Cancer J Clin,63(2013) [2]A.M.Schrand et al,J Phys Chem B,111(2007) [3]A.Datta et al.,Nanotechnology,22(2011) [4]F.Neugart et al.,NanoLett.,7(2007) [5]R.Jain,J of Controlled Release,53(1998)

CPP 3.10 Mon 12:15 C 243

Metal nanopatterning using block copolymers: Differences between ionic and atomic metal selectivity — ●EZZELDIN METWALLI¹, YUAN YAO¹, VOLKER KÖRSTGENS¹, MATTHIAS SCHWARTZKOPF², STEPHAN V. ROTH², and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching — ²DESY, Notkestr. 85, 22607 Hamburg

Metal nano-patterns with a particular structural symmetry, characteristic length scale and periodicity are of growing interest, e.g. for photonic applications and high-density memory devices. The characteristic metal affinity towards the minority block of the self-assembled block copolymer (BC) templates plays an essential role to fabricate highly-order and well-defined metal nanopatterns [1]. Though, ions of metal are highly selective towards the ionic polymer block, the metal atoms show an opposite behavior, an extreme selectivity towards the neutral block. A simple explanation based on like-dissolves-like is ruled out. Experiments are performed by depositing gold in its atomic state on several homopolymer and block copolymer films with DC magnetron sputtering. At time resolution of 15 milliseconds, the nucleation/growth kinetics of gold nanoparticles on the polymer films is monitored using in-situ GISAXS. An extreme selectivity of the metal atoms is observed on the neutral block with an exponential growth of metal particle size. The coalescence behavior of the inert metal is mainly dominated by the improved atom mobility within the neutral polymer block. [1] Metwalli et al. ChemPhysChem 15, 2236 (2014)

CPP 3.11 Mon 12:30 C 243

Nanocomposites of colloidal triglyceride platelets and DNA — ●MARTIN SCHMIELE, CHARLOTTE KNITTEL, and TOBIAS UNRUH — Physik Department, Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstr. 3, 91058 Erlangen, Germany

Aqueous suspensions of colloidal tripalmitin platelets, stabilized by a mixture of soybean lecithin, Poloxamer 188 (or Polysorbate 80) and the cationic surfactant dioctadecyldimethylammonium bromide (DODAB), are prepared by high-pressure melt homogenization. DODAB provides the platelets with a positive surface charge. DNA complexes are prepared by addition of herring DNA to the suspensions.

The structure of the DNA complexes, ranging from the molecular to the micron scale, is investigated by small- and wide-angle x-ray and neutron scattering, microcalorimetry, photon correlation spectroscopy, transmission electron microscopy and computer simulations.

Complexes prepared from native suspensions with low concentrations of DODAB and high +/- charge ratios (DODAB:DNA) exhibit sizes in the colloidal range. Higher concentrations of DODAB and charge ratios close to the isoelectric point promote platelet agglomeration, leading to very large complexes of several microns.

Small-angle scattering and computer simulations reveal a lamellar arrangement of the platelets in the complexes, with the DNA being most probably sandwiched between the platelets. Such nanocomposites of macromolecules (DNA) and tripalmitin platelets could provide a good protection of the intercalated macromolecules and can be regarded as a potential carrier system for them.

CPP 3.12 Mon 12:45 C 243

Nanocomposites composed of HEUR polymer and magnetite iron oxide nanoparticles — ●ANTONELLA CAMPANELLA¹, HENRICH FRIELINGHAUS¹, ZHENYU DI¹, MARIE-SOUSAI APPAVOU¹, ALESSANDRA LUCHINI², LUIGI PADUANO², ALICE KLAPPER³, OLEG PETRACIC³, PETER MÜLLER-BUSCHBAUM⁴, and DIETER RICHTER¹ — ¹JCNS@FRMII, Lichtenbergstrasse 1, 85747 Garching — ²University of Naples, Federico II, Dipartimento di Scienze Chimiche, Via Cinthia, 80126 Naples, Italy — ³JCNS-2, Forschungszentrum Jülich GmbH, 52425 Jülich — ⁴TU München, Physik-Department, Lehrstuhl für Funktionelle Materialien, James-Franck-Strasse 1, 85748 Garching

We study nanocomposites of a polymer matrix which consists of hydrophobically modified ethoxylated urethane polymers (HEUR) with embedded coated magnetite nanoparticles. Two different kinds of coatings are compared namely, the hydrophobic coating, composed of

oleic acid and oleylamine, and the hydrophilic coating composed of a cationic surfactant, C18TAB, as an additional layer to the hydrophobic magnetic nanoparticles. We focused on the structural characterization of such nanocomposites in two different morphologies: as thin dry films

and as hydrogels.