

## CPP 13: Colloidal and Nanoparticles

Time: Tuesday 15:00–18:45

Location: C 264

CPP 13.1 Tue 15:00 C 264

**Micromechanics of gas filled Microballoons** — ●PAULO FERNANDES<sup>1,2</sup>, GEORGE TZVETKOV<sup>3,4</sup>, RAINER FINK<sup>3</sup>, and ANDREAS FERY<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Universität Bayreuth, Bayreuth, Germany — <sup>2</sup>Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Potsdam, Germany — <sup>3</sup>Physikalische Chemie II, Universität Erlangen-Nürnberg, Erlangen, Germany — <sup>4</sup>Swiss Light Source, Paul Scherrer Institut, 5232 Villigen, PSI, Switzerland

Gas filled MicroBalloons (MBs) are today highly valued research subjects mainly due to their potential use in medical applications where they impose themselves as targeted drug delivery systems and contrast agents for ultrasonic imaging. Intense research has been devoted to the development of MB systems. Their mechanical and adhesion properties are of interest since these determine the micro containers behavior and stability in applications. We introduce novel AFM-based methods for quantifying both mechanics and adhesion properties.

We use a combination of the colloidal probe AFM technique and an inverted optical microscope. The deformation behavior of individual MBs is characterized with AFM Force Spectroscopy measurements. We analyze the dependence of the profiles with MB radius at different temperatures (room and body temperature). Scanning Transmission X-ray Microscopy (STXM) experiments proved to be very appropriate to study the MBs. Quantitative analysis of the resulting transmission profiles allowed us to characterize the MBs properties.

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**Fabrication of novel metal oxide hollow spheres with tailored shell thickness** — ●MUKESH AGRAWAL<sup>1</sup>, ANDRIJ PICH<sup>2</sup>, NIKOLAOS E. ZAFEIROPOULOS<sup>1</sup>, and MANFRED STAMM<sup>1</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany — <sup>2</sup>Technische Universität Dresden, Institut für Makromolekulare Chemie und Textilchemie, Mommsenstr. 4, 01062 Dresden, Germany

Sub-micrometer sized polystyrene-metal oxide core-shell composite particles and hollow metal oxide spheres with tunable shell thickness and void size have been fabricated exploiting the sol-gel process. A controlled precipitation of ZnO/TiO<sub>2</sub>/Ta<sub>2</sub>O<sub>5</sub> nanoparticles has been carried out on the template surface by hydrolyzing the metal oxide precursors and subsequently polymer core was removed either via chemical treatment with toluene or calcination at elevated temperature to achieve the hollow spheres. Thickness of the ZnO/TiO<sub>2</sub>/Ta<sub>2</sub>O<sub>5</sub> shell, precipitated on polystyrene core during coating process has been tuned by varying the concentration of metal oxide precursors in reaction media. The obtained core-shell composite particles and hollow microspheres have been characterized by scanning electron microscopy, transmission electron microscopy, infra-red spectroscopy, X-ray diffraction and thermo gravimetric analysis. Due to the unique optical and dielectric properties, these nanostructured materials are envisaged to be used in applications such as novel building blocks for the fabrication of advanced materials, surface coatings, catalysts and drug delivery systems.

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**Temperature, pH, and ionic strength induced changes of the swelling behavior of PNIPAM-Poly(Allylactic-Acid) copolymer microgels.** — ●THOMAS HELLWEG<sup>1</sup> and MATTHIAS KARG<sup>2</sup> — <sup>1</sup>Universität Bayreuth, Physikalische Chemie I, Universitätsstr. 30, 95447 Bayreuth, Germany — <sup>2</sup>TU Berlin, Institut f. Chemie, Stranski-Lab. f. Theoretische und Physikalische Chemie, Strasse des 17.Juni 124, 10623 Berlin, Germany

The volume transition of colloidal microgels made of N-isopropylacrylamide (NIPAM) can be affected by copolymerization. Therefore, a series of poly(N-isopropylacrylamide-co-allylactic acid) copolymers with different contents of allylactic acid (AAA) was synthesized by means of emulsion polymerization. The thermo-responsive behavior of these particles was studied using dynamic light scattering (DLS). Further characterization was done employing transmission electron microscopy (TEM) and zeta potential measurements. The measured zeta potentials provide information about the relative surface charge. Since these copolymers are much more sensitive to external stimuli such as pH and ionic strength than their pure PNIPAM counterparts the volume phase transition was investigated at two different

pH values and various salt concentrations. At pH 10 for some of the copolymer microgels a significant shift of the volume phase transition temperature towards higher temperatures is found. For higher AAA contents a change in pH from 8 to 10 can induce a change in radius of 100 nm making the particles interesting as pH controlled actuators.

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**Switchable photoluminescent CdTe nanocrystals by temperature responsive microgels** — MUKESH AGRAWAL<sup>1</sup>, SMRATI GUPTA<sup>1</sup>, VERA CIMROVA<sup>2</sup>, NIKOLAI GAPONIK<sup>3</sup>, ALEXANDER EYCHMÜLLER<sup>3</sup>, SPYROS TZAVALAS<sup>1</sup>, ROSANA ROJAS-REYNA<sup>1</sup>, ●JORGE RUBIO-RETAMA<sup>1</sup>, MANFRED STAMM<sup>1</sup>, and NIKOLAOS E. ZAFEIROPOULOS<sup>1</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden, Hohe Strasse 6, Dresden 01069, Germany — <sup>2</sup>Institute of Macromolecular Chemistry Praha, Czech Republic — <sup>3</sup>Physikal-Chemistry Department, Technische Universität Dresden, Dresden 01069 Germany

Microgels are perhaps of the most promising responsive systems due to their high specific surface, which yields materials with very short response time. In the present study we report a facile and reproducible method for preparing fluorescence thermo-sensitive hybrid material based on monodispersed and thermosensitive P(NIPAM) microgels covered with nanocrystals of CdTe of 3.2 nm of diameter. The CdTe nanocrystals were covalently immobilized on the surface of the microgels. Through temperature variation it was possible to modify the chemical environment around the CdTe nanocrystals. This change provoked a variation in the nanocrystal photoluminescence properties in such way that when the temperature was under the LCST of the polymer the photoluminescence of the nanocrystals was strongly quenched, while when the temperature was above the LCST of the microgels (36 C) the photoluminescence properties of the nanocrystals were strongly enhanced.

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**Smart Hybrids made of poly-NIPAM and Gold Nanoparticles:** — ●MATTHIAS KARG<sup>1</sup>, ISABEL PASTORIZA-SANTOS<sup>2</sup>, JORGE PÉREZ-JUSTE<sup>2</sup>, LUIS M. LIZ-MARZÁN<sup>2</sup>, and THOMAS HELLWEG<sup>3</sup> — <sup>1</sup>Berlin, Stranski-Laboratorium, Strasse des 17. Juni 124, 10623 Berlin, Germany — <sup>2</sup>Universidade de Vigo, Grupo de Química Física, 36310 Vigo, Spain — <sup>3</sup>Universität Bayreuth, Physikalische Chemie I, Universitätsstrasse 30, 95440 Bayreuth

Recently, composite materials made of organic polymers and inorganic matter are of high interest. Typically, the aim for the preparation of such kind of hybrids is the combination of the properties of both components, which can be e.g. thermoresponsive behavior for the polymer and optical or magnetic properties for the inorganic component. Here, we present hybrid particles, which were made of thermoresponsive poly-N-isopropylacrylamide (poly-NIPAM) microgels and gold nanoparticles. Characterization of the particles has been done using Dynamic Light Scattering (DLS), Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM) and Small Angle Neutron Scattering (SANS). The thermoresponsive optical properties were investigated using UV-VIS spectroscopy and were found to be fully reversible. [1] M. Karg, I. Pastoriza-Santos, L.M. Liz-Marzán, T. Hellweg, ChemPhysChem., 2006, 7, 2298-2301 [2] M. Karg, I. Pastoriza-Santos, J. Pérez-Juste, T. Hellweg, L. M. Liz-Marzán, Small, 2007, 3, 1222-1229

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**TiO<sub>2</sub> nanoparticles by PEOMA-PDMS-PEOMA block copolymer** — ●MINE MEMESA<sup>1</sup>, JAN PERLICH<sup>2</sup>, SEBASTIAN LENZ<sup>1</sup>, SEBASTIAN NETT<sup>1</sup>, SEBASTIAN EMMERLING<sup>1</sup>, PETER MÜLLER-BUSCHBAUM<sup>2</sup>, and JOCHEN S. GUTMANN<sup>3</sup> — <sup>1</sup>Max-Planck Institute for Polymer Research, Ackermannweg 10, D-55128, Mainz, Germany — <sup>2</sup>TU München, Physik-Dept. LS E13 James-Frank-Str. 1, 85747 Garching, Germany — <sup>3</sup>Institute of Physical Chemistry, University Mainz, D-55099, Mainz, Germany

The effect of titanium oxide (TiO<sub>2</sub>) nanoparticles on the efficiencies of conjugated polymer photovoltaics has been widely studied. Preparation of TiO<sub>2</sub> nanoparticles by using an amphiphilic block copolymer as a templating agent via a sol-gel process resulted in different morphologies. In this study, TiO<sub>2</sub> nanoparticles are prepared by a poly(dimethylsiloxane) (PDMS) containing block

copolymer, poly(ethyleneoxide)methacrylate(PEOMA)-block-PDMS-block-PEOMA via sol-gel chemistry. By varying the components of the sol gel, the morphology of the particles formed is investigated by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Grazing Incidence Small Angle X-ray Scattering (GISAXS). The ability of PDMS to turn into silicon-oxi carbide (Si-O-C) after being heated to elevated temperatures is believed to act as an alternative to the conventional blocking layer between conducting transparent electrode (FTO) and the photoactive layer in hybrid organic solar cells. The results of the ongoing study on the morphology of the particles and resultant physical properties will be presented.

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**Depletion-Driven Aggregation Kinetics and Protein Resistance of Surface Decorated Au Nanoparticles** — ●FAJUN ZHANG<sup>1</sup>, DONALD G. DRESSEN<sup>1,2</sup>, MAXIMILIAN W. A. SKODA<sup>1,3</sup>, ROBERT M. J. JACOBS<sup>3</sup>, STEFAN ZORN<sup>1</sup>, RICHARD A. MARTIN<sup>4</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany — <sup>2</sup>Department of Physics and Astronomy, University of Denver, USA — <sup>3</sup>CRL, University of Oxford, UK — <sup>4</sup>Department of Physics, University of Bath, UK

Self-assembled monolayers with oligo(ethylene glycol) (OEG) termination are of great importance in biomedical applications due to their protein resistance. We have successfully prepared OEG-thiol decorated gold colloids and studied various interactions, stability and aggregation kinetics of colloid in the mixture of protein and colloid by SAXS and UV-vis spectroscopy [1]. Results proved the protein resistance of the OEG SAM at curved interfaces. Above a critical protein concentration,  $c^*$ , the colloids lose their stability and form aggregates due to the depletion-attraction [1]. Depletion-driven aggregation kinetics was studied under various protein concentrations and ionic strength. A kinetic crossover from RLCA to DLCA is observed at low salt addition, which is caused by the effective repulsive interaction barrier between colloids within the oscillatory depletion potential. Above 0.5 M NaCl, the surface charge of proteins is screened significantly, and the energy barrier disappears, thus the growth kinetics becomes DLCA only [1]. [1] F. Zhang, et al., J. Phys. Chem. B. 2007, 111, 251. J. Phys. Chem. A. 2007, DOI: 10.1021/jp074293v. Euro. Biophys. J. Submitted.

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**Frustration-induced magic number clusters of colloidal magnetic particles** — ●LARYSA BARABAN<sup>1</sup>, DENYS MAKAROV<sup>1</sup>, MANFRED ALBRECHT<sup>2</sup>, NICOLAS RIVIER<sup>3</sup>, PAUL LEIDERER<sup>1</sup>, and ARTUR ERBE<sup>1</sup> — <sup>1</sup>University of Konstanz, Department of Physics, Konstanz, Germany — <sup>2</sup>Chemnitz University of Technology, Surface and Interface Physics, Chemnitz, Germany — <sup>3</sup>Institut de Physique et Chimie des Matériaux de Strasbourg, Strasbourg, France

We report the formation of stable two-dimensional clusters consisting of long-range interacting colloidal particles with pre-defined direction of macroscopic magnetic moments. The colloids can find the global minimum of the structure driven by magnetic frustration. This solution coincides with the ground state configuration of a two-dimensional triangular antiferromagnet, which is consistent with an XY-spin model. By satisfying the criteria of stability, a series of 'magic number' clusters is formed. Since the ground state follows the rules for compensation of magnetic moments and chirality, it is likely that conclusions can be drawn for spin systems as well, although the exact nature of the interactions is different. Thus, the system can be regarded as a mesoscopic model system for spin arrangements in antiferromagnets.

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**Metal-precursor loaded polymer-particles: a basis for ordered arrays of nanoparticles** — ●ACHIM MANZKE<sup>1</sup>, FABIAN ENDERLE<sup>1</sup>, STEFAN WIEDEMANN<sup>1</sup>, CHRISTIAN PFAHLER<sup>1</sup>, ALFRED PLETTL<sup>1</sup>, PAUL ZIEMANN<sup>1</sup>, EYK SCHREIBER<sup>2</sup>, ULRICH ZIENER<sup>2</sup>, and KATHARINA LANDFESTER<sup>2</sup> — <sup>1</sup>Institut für Festkörperphysik, Universität Ulm, D-89069 Ulm — <sup>2</sup>Institut für Organische Chemie III, Universität Ulm, D-89069 Ulm

The fabrication of metal precursor loaded colloidal polystyrene (PS) particles in aqueous solution is carried out by a miniemulsion technique. We will report on colloids loaded with Pt-, Fe- as well as with Fe- and Pt-complexes. Dropped on hydrophilic Si substrates, hexagonally ordered monolayers of colloids are generated. By applying optimized plasma and temper processes, metallic nanoparticles can be

obtained which still exhibit the original ordered arrangement. The metal content in the colloid defines the size of the final particle, which could be varied between 6 and 14 nm, so far. The interparticle distances is determined by the diameter of the starting PS-particles and could be varied between 80 and 230 nm. This new technique has the potential to extend the limits of the micellar technique [1] regarding the particle distance and order.

[1] G. Kästle et al. , Adv. Funct. Mat. 13, 853 (2003)

[2] A. Manzke et al. Adv. Mater. 19, 1337 (2007)

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**X-ray investigations for determining the aspect ratio in CdSe nanorods** — ULLRICH PIETSCH and ●ÖZGÜL KURTULUS — Festkörperphysik , Universität Siegen, Siegen, Germany

Semiconductor based 1D nanostructures are of high technological interest due to potential application in 1D conductivity measurements and optical devices. Catalyst assisted solution-liquid-solid synthesis is a new method where nanocrystal catalysts are used to grow CdSe nanorods (NR) from solution. The aim of this study is to investigate CdSe samples prepared with this new method by means of x-ray diffraction. The measurements have been performed at DELTA synchrotron using a beam of wavelength 1.127 Å and an image plate system. It is found that the CdSe NRs have a crystal structure of wurtzite with an aspect ratio changing between 2 and 10. This is in contradiction with the results obtained from TEM measurements, according to which the lengths of the NRs are in the order of  $1\mu$  and the widths are around 20nm. Presently the results are interpreted by the appearance of stacking faults which separate uniformly stacked AB, AB layers from each other. It is planned to measure an individual NR using a nanofocused x-ray beam. Once an individual NR could be observed, the next step is to measure the powder spectrum using a CCD as a function of the position of the beam spot along the nanorod. Depending on this information, the parameters affecting the structure of the NRs would be clear by making experiments with samples prepared in different conditions.

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**A new method to detect and characterize single metallic nanoparticles using confocal microscopy** — ●TINA ZÜCHNER<sup>1</sup>, ANTONIO VIRGILIO FAILLA<sup>1</sup>, ACHIM HARTSCHUH<sup>2</sup>, and ALFRED JOHANN MEIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Tübingen, Germany — <sup>2</sup>present address: Department für Chemie und Biochemie, LMU München, Germany

A new confocal microscopy method for imaging single metallic nanoparticles is presented. It provides information about the particle's shape, size and orientation. For excitation azimuthally and radially polarized doughnut modes [1] were used. The particles were immobilized on glass or embedded in media of different refractive indices. Both the scattered light from the particles and the light reflected at the glass slide were collected and contributed to the image. The resulting patterns were studied experimentally and theoretically. Particles of different shapes (spheres, rods and triangles) could be distinguished [4] and the refractive index mismatch at the sample interface could be detected. For metallic nanorods the 2-dim. orientation can be directly imaged [2] with high precision [3]. Preliminary data shows that the method also allows to determine the 3-dim. orientation of nanorods.

[1] R. Dorn, S. Quabis and G. Leuchs, Phys. Rev. Lett. 91, 233901 (2003). [2] A.V. Failla, H. Qian, H. Qian, A. Hartschuh and A.J. Meixner, Nano Lett. 6, 1374 (2006). [3] A.V. Failla, S. Jäger, T. Züchner, M. Steiner and A.J. Meixner, Opt. Expr. 15, 8532 (2007). [4] T. Züchner, A.V. Failla, A. Hartschuh and A.J. Meixner, J. Microsc., in print (2007).

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**Femtosecond Spectroscopy Study of the Exciton Relaxation Dynamics in Silicon Quantum Dots** — ●CAROLA KRYSCHI<sup>1</sup>, VOLKER KUNTERMANN<sup>1</sup>, CARLA CIMPEAN<sup>1</sup>, and DIETRICH HAARER<sup>2</sup> — <sup>1</sup>Institut für Physikalische Chemie I, FAU, Egerlandstr. 3, D-91058 Erlangen — <sup>2</sup>BIMF, Universität Bayreuth, D-95440 Bayreuth

This contribution is targeted to the development of surface-modified silicon quantum dots (Siqdots) with tailored luminescence properties. The surface modification of Siqdots with sizes between 1 and 5 nm has been successfully achieved via two different synthesis routes, first, by controlled oxidation followed from silanization and second, by thermal hydrosilylation with chromophores. The luminescence properties of ethanolic Siqdots dispersions were characterized using stationary and time-resolved luminescence spectroscopy techniques, whereas the

ultrashort exciton relaxation dynamics were examined using femtosecond transient absorption spectroscopy. Silanized Siqdots were observed to exhibit two species of photoluminescence (PL): the blue emission at 380 nm is assigned to localized surface states, whereas radiative recombination of quantum confined excitons gives rise to a broad PL band around 800 nm. Whereas the latter is ascribed to Siqdots with sizes larger than 3 nm, for Siqdots smaller than 1.5 nm exciton relaxation dynamics is understood to occur predominantly by trapping due to lower-lying surface states which may radiatively decay. Siqdots terminated with suited chromophores were observed to exhibit only one PL band in the visible that is ascribed to exciton states involving resonant couplings to the conjugated electron system of the chromophores.

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**Spectroscopic fingerprints of single dye - quantum dot nanoassemblies** — •DANNY KOWERKO, JÖRG SCHUSTER, and CHRISTIAN VON BORCZYKOWSKI — Center of nanostructured materials and analytics, TU-Chemnitz, 09107 Chemnitz

Self assembled nanoassemblies of semiconductor quantum dots (QDs) and organic molecules are of interest for numerous applications in science and technology. However, physics and chemistry of coupling mechanisms and possible interactions (i.e. energy transfer) are complex and thus not yet fully understood. Spectroscopic analysis of nanoassemblies in solution is difficult, since many complex dynamical processes are involved [1]. We have chosen an alternative approach to study nanoassemblies by freezing all of the solution dynamics while depositing the nanoparticles in a low concentration on a silicon oxide surface. The solution which we deposit the nanoassemblies from always contains the unbound building blocks too. We may compare spectroscopic properties of the free and bound species on one and the same sample under identical conditions. By recording series of emission spectra of individual quantum dots, dyes and nanoassemblies we obtain very detailed spectroscopic information which allows us to com-

pare the spectroscopic observable quantities for the free and the bound species. We are thus able to extract spectroscopic fingerprints of the nanoassemblies. In this talk we will present results for CdSe quantum dots and functionalized perylene bisimide dye molecules as building blocks for the aforementioned nanoassemblies.

[1] E. I. Zenkevich, C. von Borczykowski, J. Lum., 122, 784, 2007

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**Optical measurements on periodically ordered nanoscopic metal clusters on glass substrates** — •MICHAEL WEINL, DANIEL KRAUS, JÖRG K. N. LINDNER, and BERND STRITZKER — University of Augsburg, Institute of Physics, 86135 Augsburg

Nanosphere lithography (NSL) is a versatile, fast developing tool for fabricating large areas of nanoscopic, highly ordered metallic particles on a substrate surface. NSL uses self-assembled monolayers of colloidal particles as a deposition mask with the empty space between three adjoining nanospheres acting as mask opening. In comparison to e-beam lithography, NSL produces a great amount of defects but on the other hand it is a very fast and cost-effective technique. The fixed triangle geometry of pure nanosphere lithography can be augmented by angle-resolved evaporation or by plasma and ion beam modification of the masks. In this work, polystyrene nanospheres with a diameter of 200 to 1000 nm were used to fabricate colloidal mono- and doublelayers on glass and silicon substrates. Double layers can be used as masks with smaller mask openings and larger pitch, as compared to monolayers. Regular arrays of metallic nanodots were formed by physical vapour deposition of Au and Ag through these masks. The metal particle shape and size was determined by ESEM, AFM and TEM. An apparatus for the spatially resolved measurement of optical absorption and transmission in the spectral range of 400 to 950 nm was developed to examine the optical properties of regular metal dot arrays. The lateral resolution also allows to observe the optical properties of structures created at mask defects.