CPP 41: Nanoparticles and Composite Materials

Time: Thursday 9:30–13:15 Location: ZEU 222

CPP 41.1 Thu 9:30 ZEU 222

Ultra-fast in-situ SAXS/WAXS on the nucleation and growth of CdS quantum dots — •Andreas Schiener and Andreas Magerl — Lehrstuhl für Kristallografie und Strukturphysik, Staudtstraße 3, 91058 Erlangen

Quantum dots provide due to their unique electrical and optical properties a high potential for applications in solar cells, photo diodes, as medical tracers, and in numerous other fields. Although many synthesis routes for the controlled fabrication are known and well established, a fundamental understanding of the nucleation and growth process is still missing. In this contribution we present a combined ultra-fast in-situ SAXS and WAXS study, which gives for the first time a direct experimental insight into the evolution of the crystalline and morphological structure of CdS quantum dots in the up to now unexplored time regime between 0.1 ms and 2.5 ms with a time resolution of down to 0.01 ms. The precipitation reaction of CdS takes place along a continuous free liquid jet, which converts the time scale into a length scale to address these short reaction times. A prominent cluster structure with the diameter of about 1 nm was observed both in the SAXS and in the WAXS signal. The formation mechanism of the final quantum dots is dominated by oriented attachment of these primary clusters.

CPP 41.2 Thu 9:45 ZEU 222

Simulation of disorder effects in the optical spectra of homogeneously alloyed CdSeS nanocrystals — •Daniel Mourad[1], Tangi Aubert[2], Antoine Guille[2], Edouard Brainis[2], and Zeger Hens[2] — [1]Institut für Theoretische Physik, Universität Bremen — [2]Physics and Chemistry of Nanostructures, Ghent University

Monodisperse, homogeneously alloyed CdSe(x)S$(1-x)$ nanocrystals, which can be grown by means of colloidal synthesis, allow for a gradual tayloring of the absorption/emission properties by variation of the composition. Besides the nonlinear variation of the excitation gap as a function of x ("bowing"), the optical spectra also show an additional alloy-only feature on the S-rich side. The homogeneity of the alloying could be confirmed by Raman spectroscopy [Aubert et al., Chem. Mater. 25(12), 2388 (2013)].

Starting from a tight-binding model for the constituents CdSe and CdS, we try to understand the electronic and optical properties of this quantum dot ensemble system in theory. In our approach alloy effects are simulated exact in the disorder, i.e. the single-particle energies and wave functions are calculated for a large ($N \approx 50$) number of nanocrystals in a stochastical approach for each concentration x. Then, dipole and Coulomb matrix elements are calculated for each realization in order to obtain the light-matter coupling and the many-body properties of this system within the configuration interaction method [Mourad and Czycholl, Eur. Phys. J. B 78, 497 (2010)]. It is shown that alloying relaxes the selection rules that apply to pure CdSe and CdS and the relation between simulation and experimental results is discussed.

CPP 41.3 Thu 10:00 ZEU 222

Templating Carbon Nanotubes with Block Copolymer Micelles — •Matthias M. L. Arras, Christoph Schillai, and Klaus D. Jandt — Chair of Materials Science (CMS), Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, Löbdergraben 32, 07743 Jena, Germany

Control over carbon nanotube dispersion and spatial arrangement are the major issues of carbon nanotube/polymer composites.

In the present study we present the use of an amphiphilic block copolymer as a dispersing agent and its spherical micelles as a template at the same time.

High molecular weight polystyrene-block-poly(2-vinylpyridine) micelles are formed in a selective solvent and ultrasonicated together with unfunctionalized multi-walled carbon nanotubes(MWCNTs). Transmission electron microscopy pictures reveal that the MWCNTs segregate to the interface of the block copolymer.

The obtained structures depend on the length of the MWCNTs and range from split ring to wrapping of multiple micelles. The segregation to the interface is explained by a relieved chain stretching in the block copolymer interface upon crowding with MWCNTs.

We propose application as conducting polymer composites with very low percolation threshold or as a metamaterial.

CPP 41.4 Thu 10:15 ZEU 222

Harnessing thermoplasmonics for actuation of hydrogel — •Hang Zhang, Martin Möller, and Ahmed Mourran — DWI - Leibniz Institut für Interaktive Materialien, Aachen, Germany

Significant attention has been drawn in the last decades on the localized surface plasmon resonance (LSPR) of noble metal nanoparticles featuring remarkable photothermal energy conversion. In this regard, we report on a near-infrared driven hydrogel actuation system consisting of gold nanorods (AuNRs) embedded in Poly(N-isopropylacrylamide) (PNIPAM) network. Illuminations instantly heat the AuNRs and transform the hydrogel from the swollen state to the state above the lower critical solution temperature, causing the polymer network and the water to segregate. As a result, the expansion or contraction of the hydrogel can be remotely modulated, which is reversible, fast and local. The report discusses the possibility for actuation (amplitude, frequency) and the significance of the irradiation time and frequency on the hydrogel response dynamics.

CPP 41.5 Thu 10:30 ZEU 222

Tracer Diffusion Studies of Tailored Nanostructured Composites — •Andy Kiessling[1], Vincent Le Houérou[2], Christian Gauthier[2], and Eckhard Bartsch[1] — [1]Department of Physical Chemistry, Albertstr. 21, 79104 Freiburg, Germany — [2]Institut Charles Sadron - CNRS UPR 022, 23 rue du Loess - BP 84047, 67034 Strasbourg cedex 2, France

Volatile organic compounds in solvent cast film formation act as softener and leave behind films of high material strength after evaporation. Water-based systems lack this ability, but this drawback can be circumvented by the combination of components with complementary properties like high Tg core - low Tg shell polymer dispersions. The improved properties of coatings from water-based core-shell polymer dispersions like enhanced scratch resistance are attributed to a layer of restricted mobility of the polymer surrounding the high Tg cores. Studies addressing the molecular origin of the observed macroscopic enhancements are scarce. Applying a tracer diffusion method (Forced Rayleigh Scattering) allows an analysis of the nanostructured composites on a molecular level on different length scales. Through the superposition of two laser beams, a holographic grating is created. The diffusion of the dye is detectable as time decay of an optical Bragg scattering signal. Interpretation and modeling of the signal provide information about the mobility of the tracer in various film compartments, which is characterized by diffusion coefficients and diffusion lengths. These investigations are complemented by studies on the macroscopic film properties, notably the behavior when submitted to sliding contact.

CPP 41.6 Thu 10:45 ZEU 222

Temperature Dependent Luminescence and Dephasing of Gold Nanorods — •Alexander Konrad[1], Frank Wackenhut[1], Martin Hussels[1], Alfred J. Meixner[1], and Marc Brecht[1,2] — [1]Universität Tübingen, IPTC, 72076 Tübingen, Germany — [2]Zürcher Hochschule für Angewandte Wissenschaften, IAMP, 8401 Winterthur, Switzerland

The one-photon luminescence of noble metal nanoparticles is a well known phenomenon, but its underlying physics is not yet completely understood. The reason for the common use of nanoparticles in optics is lying in their ability to exhibit plasmons, which are responsible for a large scattering cross section of nanoparticles and probably also partly for their photoluminescence. Quantifying plasmons is possible spectroscopically by their resonance frequency and dephasing time, depending on intrinsic and extrinsic properties. We present measurements of the one-photon luminescence emitted by single gold nanorods (GNR) to propose its causally underlying processes. Therefore, we determined the resonance frequency and dephasing times of single GNRs as a function of temperature from ambient down to cryogenic temperatures (295K-1.6K) and assumed the plasmon as a Lorentzian oscillator. The determined increase of the dephasing times with decreasing temperature follows a simple Debye-model for electrons and phonons in bulk materials confirming the plasmonic origin of the one-photon luminescence. The temperature independent contributions for dephasing are assigned mainly to the processes: electron-electron-scattering, electron-surface-scattering and radiative damping.

CPP 41.7 Thu 11:00 ZEU 222

A drug delivery system based on calcium carbonate sub-micron particles — Bogdan Parakhonskiy[1,2], •Albrecht Haase[3], Yulia Svenskaya[1,4], and Renzo Antolini[1] — [1]BIOtech center, Dept. of Industrial Engineering, University of Trento, Mattarello (TN), Italy — [2]A.V. Shubnikov Institute of Crystallography Russian Academy of Science, Moscow, Russia — [3]Department of Physics, University of Trento, Povo (TN), Italy — [4]Saratov State University, Saratov, Russia

We present synthesis, loading, and release of sub-micron carriers in form of polycrystalline vaterite. The experimental characterization of the system shows excellent suitability for drug delivery applications, like perfect biocompatibility, high substance loading, and multiple controllable payload release mechanisms. We present in detail two of these mechanisms, one is a fast pH-dependent release due to a rapid degradation of the carriers in buffers below pH 7. The second is a delayed burst release due to a crystal phase transition from vaterite to calcite, predestined for scheduled admission. The release dynamics of both processes can be further controlled by the molecular properties of the payload, variation of carrier size, or additional layers. First in vitro experiments show high cellular uptake efficiency of the vaterite carriers. Possible applications in photodynamic therapy of cancer in the gastrointestinal tract will be discussed.

15 min break

CPP 41.8 Thu 11:30 ZEU 222

Morphological and swelling behavior of Block Copolymer/Nanoparticles Composites — •Christian Lewin, Larisa Tsarkova, and Alexander Böker — DWI at the RWTH Aachen, Forckenbeckstraße 50, 52074 Aachen, Germany

Among polymer-inorganic composites, block copolymers loaded with metal particles attract particular research interest due to their technological potential in nanoelectronics, nanolithography and sensing applications. We study the influence of selectively deposited gold nanoparticles (Au-NPs) on the micro-phase separation behavior and on macroscopic swelling of block copolymer films. We report solvent vapor annealing of Polystyrene-block-poly(2-vinylpyridine)/gold nanoparticles composites with varying concentration of loaded Au-NPs that have been subjected to solvent vapor annealing under controlled temperature and partial vapor pressure of the solvent vapor. Measurements of the swollen film thickness with in-situ ellipsometry revealed that the NPs concentration has a clear effect on the solvent up-take, as well as on the phase behavior of composite films. In particular we observed an unusual type of surface patterning which was attributed to fine tuning of interfacial interactions by NPs. Performing swelling experiments using controlled annealing set up is essentially important for generating reproducible and therefore comparable data on the behavior of composite films in confined geometry and hence for providing novel insights into the understanding of complex nanoheterogeneous systems.

CPP 41.9 Thu 11:45 ZEU 222

Anomaly in thermal and mechanical properties of SBR/alumina nanocomposites — •Rymma Sushko, Jörg Baller, Marlena Filimon, and Roland Sanctuary — Laboratory for the Physics of Advanced Materials, University of Luxembourg, 162a avenue de la Faiencerie, L-1511, Luxembourg

Filling elastomers with nanoparticles generally leads to changes in the relaxation behavior of the matrix molecules. Using dynamic mechanical analysis (DMA) and temperature modulated calorimetry (TMDSC), we investigated the influence of different amounts of untreated, hydrophilic alumina nanoparticles on the properties of a model rubber system (SBR). Beside a reinforcement effect seen in the complex elastic moduli, small amounts of nanoparticles of about 2 wt% interestingly lead to an acceleration of the relaxation modes responsible for the thermal glass transition. This leads to a minimum in the glass transition temperature as a function of nanoparticle content in the vicinity of this critical concentration. The frequency dependent elastic moduli are used to discuss the possible reduction of the entanglement of rubber molecules as one cause for this unexpected behavior.

CPP 41.10 Thu 12:00 ZEU 222

Resolving the inner structure of nanoparticles by means of solvent contrast variation with SAXS — •Raul Garcia-Diez, Christian Gollwitzer, and Michael Krumrey — Physikalisch-Technische Bundesanstalt, Berlin, Germany

Synthetic latex prepared by multiple-addition emulsion polymerisation present a spherical core-shell structure which can be revealed by Small Angle X-ray Scattering (SAXS) and resolved in conjunction with solvent contrast variation. This method allows the traceable characterization of the size and size distribution of the particles in suspension as well as an insight in its radial structure and an electron density determination, using both the Guinier and Fourier region of the scattering curves along an extended q-range.[1] A novell approach to contrast variation based on the anomalous scattering effect of the solvent close to an X-ray absorption edge is presented and compared to the more classical case of latex suspensions in sucrose solutions.

[1] N.Dingenouts, J.Bolze, D.Potschke, M.Ballauff; *Analysis of polymer latexes by small angle x-ray scattering*, Advances in Polymer Science Vol. 144, pp 1-47 (1999)

CPP 41.11 Thu 12:15 ZEU 222

Using the Interplay of Different Techniques to Understand the Microscopic Origin of the Macroscopic Material Behavior — •Gerald Schneider, Thomas Glomann, Jürgen Allgaier, and Dieter Richter — Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science and Institute for Complex Systems, Germany

Intense research has led to substantial progress towards understanding polymer melts and nanocomposites. For that purpose, knowledge of the single chain dynamics is of particular interest. It is important for modeling or predicting the macroscopic material response needed for the target oriented engineering of new hybrid materials starting from the single molecule. It may lead to optimized materials ranging from the classical car tire to battery or fuel cell applications.

In polymer melts, different microscopic processes, such as diffusion, reptation, contour length fluctuations, etc. add up to the total response at the macroscopic length-scale. Additionally, in composites with inorganic nanoparticles hard impenetrable walls impose constraints on polymer melts, by limiting the accessible regions. Such a confinement significantly affects the polymer dynamics when the interparticle distances and the dimensions of the embedding polymer chains are comparable.

The talk illuminates the relationship between the microscopic dynamics and the macroscopic application, exploiting different experimental techniques, such as dielectric spectroscopy, rheology, neutron scattering and spectroscopy.

CPP 41.12 Thu 12:30 ZEU 222

Method for quantitative and qualitative detection of nanosized particles emitted from paper and packaging materials — •Volker Uhl[1], Ricardo Vizcaya[1], and Andreas Kornherr[2] — [1]Austrian Research Institute for Chemistry and Technology (OFI), Vienna, Austria — [2]Mondi Uncoated Fine & Kraft Paper GmbH, Austria

Paper is a complex material which consists of an organic fiber matrix with embedded inorganic filler particles and various different additives. Such a compound material tends to the emission of various fiber fragments, filler particles, and additive residues when being exposed to mechanical stress. We present the acoustic dust tester - a new method to qualitatively and quantitatively determine particulate matter emissions in the nanosized range from paper surfaces: In a measuring chamber the paper is exposed to a well defined mechanical stress induced via acoustic waves. The exit air from the chamber is led to aerosol characterizing and sampling instruments, e.g. a condensation particle counter and an electro-mobility spectrometer. We present the concentration and particle size distribution of emitted nanoparticles from a number of different paper and packaging materials determined via this method. The detection of nanoparticles is of increasing importance both because a very low level of paper dusting is a quality characteristic for high grade papers and also to ensure that any possible health risks arising from small respirable dust particles due to the handling of paper can be completely excluded.

Invited Talk CPP 41.13 Thu 12:45 ZEU 222

Growth kinetics of metal nanoparticles on polymer surfaces — •Ezzeldin Metwalli — TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching

Dispersed metal nanoparticles (nps) in a polymer matrix are essential for many technological applications, including biological imaging, thin film technology, magnetic recording media, optoelectronics and sensors. Real time investigation of the evolution of nps size and shape

during the in-situ metal deposition on polymer thin films enables a fine tune of magnetic and electric properties. Metals in their atomic state are deposited on several homopolymer and block copolymer films by DC magnetron system [1]. With the unprecedented time resolution of 10 milliseconds, the growth kinetics of the metal nps on the polymer surfaces is monitored using in-situ GISAXS. An exponential growth of nps size on all polymer surfaces is observed. Below a certain critical nps size, an initial fast particle growth is due to high particle mobility. A slower kinetics at concentrated metal dispersion is due to the strong metal-metal interactions. The metal growth kinetics study for many chemically different homopolymer films explains the long-time debated high selectivity characteristics of metals towards one block in block copolymer based nano-templates. 1- E. Metwalli et al. Langmuir 29, 6331 (2013)