

CPP 41: Nanoparticles and Composite Materials II

Time: Thursday 14:00–17:15

Location: H48

CPP 41.1 Thu 14:00 H48

Study of the Defect Structure of SnO₂:F Nanoparticles by High-resolution Solid-State NMR — •YAMINI AVADHUT¹, JOHANNES WEBER¹, ELIN HAMMARBERG², CLAUS FELDMANN², INGA SCHELLENBERG³, RAINER PÖTTGEN³, and JÖRN SCHMEDT AUF DER GÜNNE¹ — ¹Department of Chemistry, Munich University (LMU), Munich, Germany — ²University of Karlsruhe (TH), Germany — ³Universität Münster, Germany

The defect structure of fluorine doped tin oxide (FTO) nano particles was investigated by using ¹¹⁹Sn, ¹⁹F and ¹H solid-state NMR [1]. FTO is a substitute of indium tin oxide, the most commonly used TCO. Fluorine doping is supposed to increase conductivity and is studied by solid state MAS NMR and ¹¹⁹Sn Mößbauer spectroscopy. Quantitative NMR [2], CPMAS, homonuclear dipolar recoupling and rotational echo double resonance experiments allowed us to study the doping homogeneity, dynamics. On the basis of the experimental results we discussed different models which explain the increase in conductivity of SnO₂:F caused by fluorine doping and refine our view by ab initio calculations of different defect models.

[1] Y.S.Avdhut, J.Weber, E. Hammarberg, C.Feldmann, I.Schellenberg, R.Pöttgen, J.Schmedt auf der Günne in preparation.
[2] Y.S.Avdhut, D.Schneider, and J.Schmedt auf der Günne, J. Magn. Reson., 201:1-6, 2009.

CPP 41.2 Thu 14:15 H48

Excitation Dynamics in Polymer-Coated Semiconductor Quantum Dots with Integrated Dye Molecules: The Role of Reabsorption and Radiationless Transfer — •TOBIAS NIEBLING, SEBASTIAN FRIEDE, FENG ZHANG, ZULQUARNAIN ALI, WOLFRAM HEIMBRODT, and WOLFGANG J. PARAK — Department of Physics and Material Sciences Center (WZMW), Philipps University Marburg, Renthof 5, D-35032 Marburg, Germany

Colloidal quantum dots can provide a basis for applications in biolabelling and bioanalytics. Inorganic CdSe/ZnS core-shell quantum dots (QDs) were coated with amphiphilic polymers in order to transfer them to aqueous solutions. The polymer shell allows a functionalization of the nanoparticles. In this work ATTO-dye molecules were linked to the QDs. The excitation dynamics within this system have been investigated by steady state and time-resolved optical spectroscopy. (I) Reabsorption of QD emission by the dye molecules and (II) Förster resonant energy transfer (FRET) from the donor QD to the accepting dye molecules dominate the photoluminescence properties. The spectral overlap between the QD emission and the dye absorption and thereby the transfer efficiency can be tuned by the size of the QDs. Our description of the emission behaviour yields a kinetic model that considers the dynamics of the excited QD and dye molecules with respect to the different transfer mechanisms and reveals the respective contributions of reabsorption and radiationless transfer.

CPP 41.3 Thu 14:30 H48

New Insights to Photo-destructive Effects on Quantum Dots — •DANNY KOWERKO¹, JÖRG SCHUSTER², and CHRISTIAN VON BORCZYKOWSKI¹ — ¹Center of nanostructured materials and analytics, TU-Chemnitz, 09107 Chemnitz — ²Fraunhofer-Einrichtung für Elektronische Nanosysteme ENAS, Technologie-Campus 3, 09126 Chemnitz

Energy and charge transfer in assemblies of semiconductor quantum dots (QDs) and organic (dye) molecules offer numerous applications in science and technology. The surface properties of CdSe and CdSe/ZnS colloidal QDs play a crucial role for the photoluminescence (PL) properties and thus the respective transfer efficiencies. In our contribution we demonstrate how PL quenching and enhancement are related to the surface. Therefore the influence of oxidation and surface adsorption by perylene bisimide (PBI) molecules will be elucidated by time-resolved ensemble and single particle spectroscopy. Irreversible and reversible spectral blue shifts are discriminated and related to surface and intrinsic modifications of the QD and conclusions for the efficiency of energy transfer are drawn.

CPP 41.4 Thu 14:45 H48

Controlled embedding of semiconducting nanoparticles in a conducting polymer template — •MATTHIAS A. RUEDERER¹, STE-

FAN M. PRAMS¹, WEINAN WANG¹, QI ZHONG¹, ROBERT MEIER¹, STEPHAN V. ROTH², and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department LS E13, James-Franck-Str. 1, 85747 Garching (Germany) — ²HASYLAB at DESY, Notkestr. 85, 22603 Hamburg (Germany)

Photovoltaic based on organic compounds such as conjugated polymers attracted increasing interest during the last two decades. Beside of all organic systems, the combination of an inorganic and an organic component, so called hybrid composites, have shown promising properties. In a typical hybrid system an inorganic porous template is filled with an organic photoactive material. Our approach is based on the selective embedding of nanoparticles in a diblock copolymer matrix. [1] We use a rod-coil like copolymer, with a photoactive conjugated and a styrene block, as a template for embedding titania nanoparticles which are directed into the coil like part. The structural length is defined by the copolymer and is in the range of the exciton diffusion length which is crucial in organic systems. The evolving structures are investigated with imaging methods like SEM and grazing incidence small angle X-ray scattering (GISAXS). The influence on the optical and electrical properties are investigated with UV/Vis and conductivity measurements and compared with the structural results. [1] M.M.Abul Kashem, J.Perlich, L.Schulz, S.V.Roth, P.Müller-Buschbaum; Macromolecules 41, 2186-2194 (2008)

CPP 41.5 Thu 15:00 H48

Symmetry and Shape dependent Properties of CdSe Nanostuctures — •FARZANA ASLAM¹ and CHRISTIAN VON FERBER^{2,3} —

¹Department of Mathematics, Statistics and Engineering Sciences, Coventry University, UK — ²Applied Mathematics Research Centre, Coventry University, UK — ³Physikalisches Institut, Universität Freiburg

We investigate the impact of symmetry, shape and size of CdSe particles on their electrostatic and structural properties and discuss consequences for their role as sensitizers. Other than previous theoretical studies which have focussed on a fixed particle shape and a small set of sizes we systematically investigate a large set of more than a thousand nanocrystals with different shapes, sizes, and aspect ratios. This unusual approach allows us to draw conclusions on significant correlations of the relevant properties of these crystals with symmetry, shape, surface character and size. In particular, we find significant differences between the properties of approximately spherically shaped particles, and particles with well defined surfaces along crystal planes but also between particles of the latter class. A surprisingly strong impact of the specific shape and surface configuration is found for the internal structure well inside the crystal as measured by bond lengths correlated with coordination numbers.

CPP 41.6 Thu 15:15 H48

Net Charge on Colloidal CdSe/ZnS Evidots in Nonpolar Solvents — •NICOLE AMECKE-MÖNNIGHOFF and FRANK CICHOS — Molecular Nanophotonics Group, University of Leipzig, Linnéstraße 5, 04103 Leipzig

An interesting and promising class of materials studied over the last years are semiconductor Quantum Dots (QDs). Many applications seek to make use of their favorable fluorescence characteristics, like tunable emission wavelength, high quantum yield and antibunching. Additionally they show certain peculiarities like power-law blinking, lifetime-fluctuations and spectral diffusion which can be explained by charges close to or in the dot center leading to Auger processes and the quantum confined Stark effect. Those charges can arise from ejection of electron or hole via tunneling leaving behind the counterpart and changing the matrix charge constellation. So far the model, assuming the net charge of a QD plus close surroundings to be zero. When applying an electric field to a solution of QDs in toluene, we surprisingly find a net positive charge on a great part of QDs, even though being dispersed in a nonpolar solvent. As those charged QDs still fluoresce the charge will most likely be located at the surface. Since this surface charge is very unlikely to be formed in the nonpolar toluene, we suggest that it is the result of the synthesis of the QDs. Such a charge should definitely influence blinking and probably all the characteristics mentioned above. It even might bias electron tunneling and should thus be included in blinking models. Our first goal is to find its origin, amount

and precise location, including also that of the counter charge.

15 min. break

CPP 41.7 Thu 15:45 H48

Synthesis of stable bimetallic AuAg and CoPd colloids via diblock copolymer micelle nanoreactors — •WILLIAN G. MENEZES¹, VOLKMAR ZIELASEK¹, CHRISTIAN KÜBEL², KARSTEN THIEL³, and MARCUS BÄUMER¹ — ¹Universität Bremen, Institut für Angewandte und Physikalische Chemie — ²Forschungszentrum Karlsruhe / KIT — ³Fraunhofer IFAM, Bremen

The preparation of metal nanoparticles (NPs) by using block copolymers (BCP) as encapsulating agent yields NPs with narrow size distributions and outstanding control over the inter-particle distance. Various metal salts, also in combination, can be easily loaded as precursor for NPs into the micelle cores.[1] We will demonstrate the synthesis of AuAg and CoPd bimetallic NPs by using PS-*b*-P4VP as stabilizing agent and N₂H₄·H₂O as reducing agent. TEM images show spherical crystalline NPs with diameters varying between 3 and 6 nm, for both, AuAg and CoPd. In UV-vis only one plasmon band at 460 nm was observed for Au-Ag NPs, indicating the formation of truly bimetallic NPs. STEM and EDX confirm that single NPs contain both metals, in the case of AuAg with atomic ratios of Au:Ag as 1:1, in agreement with the metal salt concentrations used. In catalysis, bimetallic systems can demonstrate unique properties distinct not only from the bulk metals but also from the corresponding monometallic NPs. The results of first catalytic tests for CO oxidation at titania loaded with AuAg and CoPd NPs prepared via the BCP route will be presented. Despite the organic matrix, the NPs are active for CO oxidation under certain conditions.

[1] S. Förster, M. Antonietti, *Adv. Mater.* 10 (1998) 195.

CPP 41.8 Thu 16:00 H48

Hybrid raspberry particles for superhydrophobic surfaces — •DORIS VOLLMER, MARIA D'ACUNZI, LENA MAMMEN, and HANS-JÜRGEN BUTT — Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128, Mainz (Germany)

On superhydrophobic surfaces, water droplets roll off even at inclinations of just a few degrees, taking up any contaminants encountered on their way. In nature, the lotus leaf is one of the most efficient examples of a superhydrophobic surface. Its superhydrophobicity is conferred by surface roughness on the nano- and micrometer scale.

Here we report a novel method to prepare superhydrophobic films from raspberry particles. The term *raspberry particle* refers to the topography of their surfaces with nano-sized secondary spheres attached to a considerably larger primary particle. Our particles consist of a polystyrene core and a rough silica shell. The hybrid nature of our particles offers the possibility to design a completely new approach to prepare superhydrophobic surfaces.

Multilayers of particles are formed by evaporation of the aqueous dispersant. By exposure of the hybrid particles to tetrahydrofuran vapour, polystyrene leaks out of the core and forms bridges between the particles, thereby providing mechanical stability. The films are hydrophobized by silanization with a semifluorinate silane. Films show static contact angle for water of about 160° and roll-off angle of 1°.

CPP 41.9 Thu 16:15 H48

Electron beam-induced nanoparticle formation in Au and Pt salt-loaded polystyrene-block-poly(4-vinylpyridine) micelles — •VOLKMAR ZIELASEK¹, CHRISTIAN KÜBEL², WILLIAN G. MENEZES¹, KARSTEN THIEL³, and MARCUS BÄUMER¹ — ¹Universität Bremen, Institut für Angewandte und Physikalische Chemie — ²Forschungszentrum Karlsruhe/KIT — ³Fraunhofer IFAM, Bremen

Using diblock copolymer micelles as nanoreactors for the generation of metal colloids has proven to be a universal route to regular arrays of uniformly sized nanoparticles (NPs) for a variety of metals [1]. When PS-*b*-P4VP micelles in toluene are loaded with metal salts, the formation of a single NP in each P4VP core can be achieved in a subsequent reduction step induced either chemically, by plasma or by UV or electron irradiation. We will present a detailed TEM study of metal colloid formation during this reduction step in Au and Pt salt-loaded PS-*b*-P4VP micelles at variable temperature in the range 95 - 300 K. Electron irradiation-induced coagulation of metal and initial formation of particulates with subnanometer diameters within the P4VP cores is observed in the entire temperature range for Au as well as for Pt. Particle coarsening and ripening, however, strongly depend on the

metal, the electron dose and, in particular, on temperature. Counter-intuitively, the dynamics of metal aggregation into a single NP within each micelle core is faster at low temperature whereas at 300 K even high densities of subnanometer particulates remain stable. Stability of the P4VP is probably essential for metal mobility within the core.

[1] S. Förster, M. Antonietti, *Adv. Mater.* 10 (1998) 195.

CPP 41.10 Thu 16:30 H48

Ground state structures in ferrofluid monolayers: influence of an external magnetic field — •TAISIA PROKOPIEVA¹, VICTOR DANILOV¹, SOFIA KANTOROVICH^{1,2}, and CHRISTIAN HOLM² — ¹Ural State University, Ekaterinburg, Russia — ²ICP, University of Stuttgart, Stuttgart, Germany

More and more attention is given to ferrofluid monolayers recently because they find different applications in various disciplines. Based on our previous results [Prokopieva et al. *Phys. Rev. E* (2009), V.80, P. 031404], we investigate the microstructure of ferrofluid thin films at low temperatures under applied external magnetic field. Using a combination of analytical methods and Monte Carlo simulations we have studied the ground state structures in two cases: the field aligned perpendicular and parallel to the layer. The crucial influence of the external field is demonstrated. We find different configurations for different magnetic fields. The critical parameters of structural transitions for different fields are proved to depend on the number of particles in the system.

The results of the ground state structures in the presence of the external field will be used to understand the microstructure of ferrofluid monolayers at room temperatures.

CPP 41.11 Thu 16:45 H48

Ferrofluids With Shifted Dipoles — •RUDOLF WEEBER, SOFIA KANTOROVICH, JOAN J. CERDÀ, and CHRISTIAN HOLM — Institute for Computational Physics, Pfaffenwaldring 27, 70569 Stuttgart, www.icp.uni-stuttgart.de

In the last decades, ferrofluids and magnetic colloids have become relevant in many applications ranging from engineering to medicine, and therefore have attracted the interest of scientists from many fields. We present simulations and analytical calculations for a model system for magnetic nanoparticles that have a dipole moment shifted out of the center of mass, towards the surface. I.e., the spherical symmetry of the particle is broken. This model is inspired by experiments on colloidal particles with magnetic caps by Erbe et. al. While it does not attempt to reproduce the experiments exactly, similar structures can be observed already for intermediate shifts of the dipole. In our contribution, we discuss ground state properties for small clusters, which help us to understand the building blocks of larger systems. For moderate shifts of the dipole moment, the ground state structure changes from chains and rings with parallel alignment of moments, usually observed in dipolar particles, to pairs and triangles with close to anti-parallel orientation of moments. We also present magnetization properties of larger systems at finite temperature and observe the influence of the shift in particular on the initial slope of the magnetization curve, namely, the initial susceptibility.

CPP 41.12 Thu 17:00 H48

Molecular Dynamics Simulations of Thermal Decomposition of Methane using a Reactive Force Field — •NORBERT LÜMMEN — University of Bergen, Department of Physics and Technology, Allégaten 55, 5007 Bergen, Norway

Incomplete combustion of carbon based materials produces fine carbon rich particles. Controlled manufacturing of very pure carbon nanoparticles (Carbon Black) can be achieved by, for example, thermal decomposition of gaseous precursors like acetylene or methane.

Molecular dynamics simulations of hydrocarbon growth after non-catalyzed thermal decomposition of methane were carried out in order to understand the impact of the thermal decomposition reaction of methane on the formation of large hydrocarbon molecules and their role in formation of carbon nanoparticles [1]. A reactive force field (ReaxFF [2]) was employed to model the interactions of the involved hydrocarbons.

After thermal decomposition of methane the formation of molecular hydrogen, a broad range of hydrocarbons and carbon dimers was observed. The basic reactions are in agreement with existing models of thermal decomposition of methane. An increasing variety of hydrocarbons is observed with increasing temperature. The largest molecules formed within 1 ns of simulation time contain enough carbon atoms to be able to form 5- or 6-membered carbon ring structures.

[1] Lümmen, submitted for publication.

| [2] van Duin et al., J. Phys. Chem. A 105, 9396 (2001).