

CPP 4: Nanoparticles, Nanocrystals and Composites I

Time: Monday 9:30–12:15

Location: H41

CPP 4.1 Mon 9:30 H41

Protein-Assisted Assembly of Highly Modular Plasmonic Core/Satellite Nanoclusters — ●ROLAND HÖLLER^{1,2}, MARTIN DULLE³, SABRINA THOMÄ², MARTIN MAYER^{1,2}, STEPHAN FÖRSTER³, ANDREAS FERY^{1,2}, CHRISTIAN KUTTNER^{1,2}, and MUNISH CHANANA^{2,4} — ¹Nanostructured Materials, Leibniz Institute of Polymer Research, 01069 Dresden, Germany — ²Physical Chemistry II, University of Bayreuth, 95440 Bayreuth, Germany — ³Physical Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany — ⁴Institute of Building Materials, ETH Zürich, 8093, Zürich, Switzerland

We present a novel protein-assisted self-assembly route of small spherical gold or silver NPs (as satellites) with a hydrophilic protein corona onto larger gold NPs (as cores) into three-dimensional nanoassemblies with core/satellite architecture in dispersion. The highly modular bottom-up fabrication of colloidal stable nanoclusters was shown for homo- and heterometallic core/satellite combinations, with variable sizes of the building blocks, using different proteins. A precise characterization of the morphology of such core/satellite nanoclusters in dispersion was achieved using small-angle X-ray scattering (SAXS). By combining the results from SAXS, UV/Vis spectroscopy, and electromagnetic simulations we were able to correlate the structural parameters with the plasmonic coupling within the core/satellite nanoclusters. Roland P. M. Höller *et al.*, 2015 (submitted).

CPP 4.2 Mon 9:45 H41

Assembly of metal-oxide nanoparticles directed by nanodomain orientation in block copolymer thin films — ●EZZELDIN METWALLI¹, YUAN YAO¹, JEAN-FRANCOIS MOULIN², MATTHIAS OPEL³, and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching, Germany — ²Helmholtz Zentrum Geesthacht, Institut für Werkstofforschung, MLZ, 85748 Garching, Germany — ³Walther-Meissner-Institut, Bayerische Akademie der Wissenschaften, 85748 Garching, Germany

Both, parallel and perforated lamella morphologies of hybrid thin films [1-2] composed of maghemite nanoparticles (NPs) and PS-d-PBMA diblock copolymer (DBC) were investigated. A systematic identification of NP arrangements within the nanostructured DBC films was obtained at different film depths using TOF-GISANS. An enrichment of NPs at the solid interface for both morphologies was observed. The dispersion stability of the PS-coated NPs in the nanostructured DBC films depends not only on the NP size but also on the orientation of the PS nanodomains. The laterally 2D confined PS domains in the perforated lamella initiate an aggregation of NPs at a lower NP concentration compared with 1D parallel lamella morphology. The potential applications in relation to medical instrumentation and magnetic sensors are highly feasible for both morphologies based on the superparamagnetic behavior of the fabricated nanocomposite films, proven with a superconducting quantum interference device magnetometer. [1] Metwalli *et al.*, *ChemPhysChem* 15, 2236 (2014) [2] Y. Yao *et al.*, *ACS Appl. Mater. Interfaces* 7, 13080 (2015)

CPP 4.3 Mon 10:00 H41

Fast and Slow Ligand Exchange at the Surface of Colloidal Gold Nanoparticles — ●BJÖRN BRAUNSCHWEIG, REBECCA DINKEL, and WOLFGANG PEUKERT — Institute of Particle Technology (LFG), FAU Erlangen-Nürnberg, Cauerstrasse 4, 981058 Erlangen, Germany

Applications of gold nanoparticles often demand that the particle's ligand shell is modified after particle formation. Obviously, there is a great need for a molecular understanding of this process which is often not accessible in situ. Here, we have applied second-harmonic light scattering (SHS) to investigate the ligand exchange at the surface of colloidal gold nanoparticles in situ and in real time. We demonstrate that the ligand exchange at the surface of citrate-covered Au nanoparticles with 3-mercapto-1-propanesulfonate (MPS) must be described by a fast (<100 s) and a slow reaction process (<23 min) which can be attributed to MPS adsorption on low- and high-coordinated Au surface sites. Using a modified Langmuir isotherm, the average Gibbs free energy of adsorption ΔG (-46 kJ/mol) and the surface coverage Γ ($\approx 3.5 \mu\text{mol}/\text{m}^2$) for MPS on Au nanoparticles were determined. The latter was found to be much smaller compared to planar gold surfaces which points to co-adsorption of MPS with citrate on high-coordinated

sites, i.e. Au terraces. On more reactive low-coordinated Au sites, i.e. edge sites, citrate is easily replaced by MPS. In fact, we find that a substantial portion (49 %) of the surface-adsorbed MPS is present on these low-coordinated sites.

CPP 4.4 Mon 10:15 H41

Tailoring the Physicochemical Properties of Protein-Coated Gold Nanoparticles — ●JONAS SCHUBERT¹, INNA DEWALD², OLGA ISAKIN², TOBIAS KRAUS³, and MUNISH CHANANA⁴ — ¹Leibniz Institute of Polymer Research Dresden, 01069 Dresden, Germany — ²Physical Chemistry II, University of Bayreuth, 95447 Bayreuth, Germany — ³INM Leibniz-Institut für New Materials, 66123 Saarbrücken, Germany — ⁴Institute of Building Materials (IFB), ETH Zurich, 8093 Zurich, Switzerland

The investigation of the behavior of nanoparticles in the environment begins with the detection of their physicochemical properties. It has up to now not been successful to connect their properties with their behavior because of the undefined adsorption of proteins onto the surface of the nanoparticles, which changes their properties drastically. One approach to circumvent this is to generate a defined protein corona. In this work, we present gold nanoparticles successfully coated with a variety of proteins, which differ in their physicochemical properties (MW, pI). These properties and the environmental conditions (pH, ionic strength) determine the colloidal stability of the nanoparticles during and after the protein adsorption in a certain pH range. Eventually, the physicochemical properties of the successfully coated NPs can be tailored by the choice of protein, the coating pH and the purification pH.

Dewald, I.; Isakin, O.; Schubert, J.; Kraus, T.; Chanana, M., *J. Phys. Chem. C*, 2015, 119, 25482-25492.

CPP 4.5 Mon 10:30 H41

Halloysites stabilized Pickering-emulsions: Is this the way to green chemistry? — ●DMITRIJ STEHL¹, REGINE VON KLITZING¹, YURI LVOV², TOBIAS POGRZEBA¹, MARCEL SCHMIDT¹, REINHARD SCHOMÄKER¹, LENA HOHL³, MATTHIAS KRAUME³, JOACHIM KOETZ⁴, TINA SKALE⁵, and ANJA DREWS⁵ — ¹TU-Berlin, Straße des 17 Juni 124, 10623 Berlin — ²Louisiana Tech University, 911 Hergot Ave, Ruston, LA 71272, USA — ³TU-Berlin, Frauenhoferstr. 33-36, 10587 Berlin — ⁴Universität Potsdam, Karl-Liebknecht-Straße 24-25, 14476 Potsdam — ⁵HTW Berlin, Wilhelminenhofstr. 75 A, 12459 Berlin

Pickering-emulsions (PEs) are particle-stabilized emulsions. In the combination with Halloysites as stabilizing nanoparticles, PEs fulfil the qualifications of green chemistry and open up new industrial possibilities. Halloysites are multiwall, inorganic tubes with negative charges at the outer surface and positive charges at the inner surface. In this study, the hydroformylation of long chained olefins (1-Dodecene) in PEs was used as a model system, to prove the catalytic power of Halloysites. The water phase contains the homogeneous catalyst and the oil phase (1-Dodecene) is simultaneous the reactant. After the hydroformylation the expensive rhodium-catalyst can be easily separated from the product (Tridecanal) and can be reused. The effect of different parameters such as concentration of the Halloysites, energy input by the PE-fabrication, water/oil ratio and the reaction parameters were analyzed. Furthermore, we study the essential interfacial interactions between water, oil and Halloysites. In order to control the emulsion properties the Halloysites were partially hydrophobized.

CPP 4.6 Mon 10:45 H41

Lifetime-encoded Microparticles — ●DANIEL KAGE¹, KATRIN HOFFMANN¹, WOLFGANG GÖHDE², THOMAS THIELE³, UWE SCHEDLER³, and UTE RESCH-GENGER¹ — ¹Federal Institute for Materials Research and Testing (BAM), Richard-Willstätter-Str. 11, 12489 Berlin — ²Quantum Analysis GmbH, Mendelstr. 17, 48149 Münster — ³PolyAn GmbH, Rudolf-Baschant-Straße 2, 13086 Berlin

Analytical methods require efficient and versatile strategies to measure an increasing number of analytes that can be used in conjunction with established platforms like flow cytometry. Spectral multiplexing suffers from problems such as spectral crosstalk and often requires different excitation light sources increasing instrumentation costs [1]. Thus, the number of distinguishable reporters with intensity-based barcodes is limited. An alternative can be lifetime encoding for discrimination of

fluorophores based on their fluorescence decay kinetics [2].

We report on the suitability of μm -sized polymer particles stained with organic dyes for lifetime encoding. These dyes are excitable at a standard laser diode wavelength and detectable within a single spectral window. For lifetime-based discrimination, these dyes display sufficiently different luminescence decay kinetics. We present the spectroscopic properties of these beads and address challenges like the limited number of detectable photons in a flow for the reliable discrimination. These studies are expected to pave the road to new applications of fluorescence lifetime multiplexing for time-domain flow cytometry.

1.*Hoffmann, K., et al., ACS Nano, 2013. 7(8): p. 6674-84. 2.*Cao, R., et al., Opt Express, 2013. 21(12): p. 14816-31.

15 min. break

CPP 4.7 Mon 11:15 H41

Reversible switching between self-assembled nanoribbons and nanotubes — •ASAD JAMAL^{1,2}, PHILIPPE MESINI³, and GÜNTER REITER^{1,2} — ¹Physikalisches Institut und — ²Freiburger Materialforschungszentrum, Albert-Ludwigs-Universität Freiburg, 79104 Freiburg, Germany — ³Institut Charles Sadron, 23 rue du Loess BP 84047, 67034 Strasbourg Cedex 2, France

The self-assembly of achiral 3,5-bis-(5-hexylcarbamoylpentyl)oxy)-benzoic acid decyl ester (BHPB-10) molecules in solution and on substrate was investigated as a function of solvent quality. Tubular structures nanotubes with diameters of ca. 30 nm were favoured in solvents having weak interactions with the molecules (cyclohexane) while in solvents with comparatively strong molecule-solvent interactions (cyclohexanone) 12 nm wide nanoribbons were formed. Both structures were several micrometers long. A switching from nanoribbons to nanotubes was observed during solvent vapour annealing in cyclohexane vapour. Nanotubes could be switched back into nanoribbons by destroying the hydrogen bonding between BHPB-10 molecules via exposure to cyclohexanone. Atomic force microscope (AFM) revealed that nanoribbons first switched to helical twisted nanosheets which were subsequently transformed into tubular structures. Thus, tuning the interactions between BHPB-10 with the quality of the solvent, we were able to form nanoribbons, which can turn into helical twisted nanosheets or nanotubes but also to reversible switch between nanoribbons and nanotubes.

CPP 4.8 Mon 11:30 H41

Oxidative etching of silver nanowires for improvement of structural integrity — •EGON STEEG¹, FRANK POLZER¹, HOLM KIRMSE¹, YAN QIAO¹, JÜRGEN P. RABE^{1,2}, and STEFAN KIRSTEIN¹ — ¹Department of Physics, Humboldt-Universität zu Berlin — ²IRIS Adlershof, Humboldt-Universität zu Berlin

Silver nanowires with diameter of 6.5 nm are grown within tubular J-aggregates by reduction of silver ions. The nanowire growth starts with small isolated crystallites within the tubular aggregate that grow into pieces of wires that finally coalesce into continuous wires that homogeneously fill the template. This growth continues due to remaining silver ions within solution. The resulting crystals are wire-like, but are inhomogeneous and non-uniform in diameter. Addition of NaCl allows precipitation of the remaining silver ions in form of AgCl at defined

times stabilizing the structure of the wires. The influence of oxygen is critical for this process, since the silver can be oxidized by oxygen in the solution with the chloride acting as a ligand due to oxidative etching. This etching is most effective at silver structures that contain defects or twin boundaries. The selective etching efficiency allows removing the parts of the wires that have lower structural integrity which leaves pieces with length of several hundred nanometers. This allows us not only to produce well-defined silver nanowires but to preserve their morphology in solution for weeks.

CPP 4.9 Mon 11:45 H41

Enhanced Dispersion and Alignment of Carbon Nanotubes by a High Molar Mass Amphiphilic Block Copolymer — •MATTHIAS M. L. ARRAS, ROY ZITZMANN, BOJIA HE, and KLAUS D. JANDT — Chair of Materials Science (CMS), Otto-Schott-Institut für Materialforschung, Friedrich-Schiller-Universität, Jena, Germany

In this contribution multi-wall carbon nanotubes (MWCNTs) were simultaneously dispersed *and* aligned in a nanocomposite by using a high molar mass amphiphilic block copolymer (HMMABCP) matrix. HMMABCPs are promising because they are blendable with homopolymers of technically relevant molar masses. The hypotheses were tested that a HMMABCP can (i) disperse MWCNTs (ii) by a mechanism similar to low molar mass BCPs and (iii) be melt-drawn to align the MWCNTs while maintaining the degree of dispersion. The dispersion of MWCNTs within poly(styrene)-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) ($\bar{M}_w \approx 500 \text{ kg mol}^{-1}$) and its homopolymers (control) in non-selective and selective solvents were investigated. PS-*b*-P2VP greatly improved the MWCNT dispersion which was long-term stable. The dispersion mechanism was identified as BCP micelle mediated steric stabilization. A melt-drawn MWCNT/PS-*b*-P2VP nanocomposite film showed a high degree of MWCNT dispersion *and* alignment. In comparison to a similarly processed MWCNT/poly(ethylene) nanocomposite film, the MWCNT dispersion in PS-*b*-P2VP was strongly enhanced. This contribution highlights the advantages of an intrinsically dispersive matrix which may facilitate the future application of functional nanocomposites.

CPP 4.10 Mon 12:00 H41

Dynamics and interfaces in functional polymer nanocomposites — •ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden e.V.

Nanoparticles from hydroxyapatite (HAp) and layered double hydroxides (LDH) have been investigated using solid-state NMR. ²⁷Al NMR provides a local probe for the interface of the nanoparticles and the modifications applied to enhance to compatibility with the polymer matrix. The coordination and the local symmetry manifested in the quadrupolar coupling constant is monitored. Dedicated solid-state NMR experiments permit the selective excitation of the protons in the HAp particles. Spin diffusion from there transfers the magnetization to the nearby protons in the polymer matrix. Thus distance-dependent solid-state NMR spectroscopy becomes feasible, allowing the investigation of structure and local mobility of the polymers in contact with the inorganic filler compared to the bulk material, showing reduced polymer segment motion in the vicinity of the the particles. Additional dynamic information is available from EPR using spin-labelled polyelectrolytes in multilayers covering the nanoparticles.