

CPP 64: Nanostructures, Nanostructuring and Nanosized Soft Matter II

Time: Thursday 9:30–12:45

Location: PC 203

CPP 64.1 Thu 9:30 PC 203

Spray deposition of conducting composite films studied with in situ GISAXS — ●VOLKER KÖRSTGENS¹, SENLIN XIA¹, MATTHIAS SCHWARTZKOPF², CALVIN J. BRETT^{2,3}, DANIEL SÖDERBERG³, STEPHAN V. ROTH^{2,4}, and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching — ²DESY, 22607 Hamburg — ³KTH, Fluidmechanics, SE-10044 Stockholm, Sweden — ⁴KTH, Fibre and Polymer Technology, SE-10044 Stockholm, Sweden

In the emerging field of printable electronics there is a growing demand for transparent, flexible substrate materials. Cellulose-based substrates are a promising sustainable alternative to fully synthetic polymers. We present the fabrication of conducting composite films of cellulose nanofibrils (CNF) and PEDOT:PSS. CNF of high surface charge are produced with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation and mixed with PEDOT:PSS in aqueous dispersion. Composite films are produced with a spray deposition process which is followed in situ with GISAXS with sub-second time resolution. GIWAXS applied to the final films is used for the investigation of crystallinity in the composite films. Different CNF/PEDOT:PSS ratios and the influence of the additive glycerol on the film morphology and conductivity are investigated. The improvement of conductivity with the co-solvent glycerol and alternative post-treatment with ethylene glycol for the composite films follows the same trend as for pure PEDOT:PSS films.

CPP 64.2 Thu 9:45 PC 203

Homopolymer and Diblock Copolymer Blends with ABC Miktoarm Terpolymers — ●MATTHIAS M.L. ARRAS¹, HYEYOUNG KIM², MONOJOY GOSWAMI¹, HONG KUNLUN¹, BOBBY G. SUMPTER¹, THOMAS P. RUSSELL^{2,3}, and GREGORY S. SMITH¹ — ¹Oak Ridge National Lab, Oak Ridge, USA — ²University of Massachusetts Amherst — ³Lawrence Berkeley National Lab, Berkeley, USA

The effect of chain configuration in AB/ABC blends is investigated by small angle neutron scattering, transmission electron microscopy and molecular dynamics simulation. Here, the strongly segregating and asymmetric miktoarm star terpolymer poly(styrene)-*arm*-poly(isoprene)-*arm*-poly(2-vinylpyridine), where P2VP is the major component, was blended with equal volume fractions of either a PS/PI homopolymer mixture or an PS-*b*-PI diblock copolymer. We find that, depending on volume fraction, configuration and molar mass of the blended polymers, the morphology of the miktoarm star terpolymer is affected in various ways. In particular, swelling, improved ordering, or order-to-order transitions (OOT) were found. For low molar mass homopolymer blends ($\sim 1/4$ of the miktoarm block's mass) we find examples where the ordering of the blend has improved over the pristine miktoarm star. An OOT from a lamellar to hexagonal phase is induced by the diblock copolymer blend when its molar mass is similar to the one of the miktoarm blocks.

This research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by ORNL. HK & TR were supported by AFOSR (16RT1602) and ARO (W911NF-17-1-0003).

CPP 64.3 Thu 10:00 PC 203

Effect of boehmite nanoparticles on mechanical properties and network architecture of epoxy — ●MEDIA GHASEM ZADEH KHORASANI¹, DOROTHEE SILBERNAGL¹, PAULINA SZYMONIAK¹, and HEINZ STURM^{1,2} — ¹BAM, Berlin, Germany — ²TU Berlin, Germany

Boehmite nanofillers (NP) were found to enhance mechanical properties of epoxy nanocomposites. Understanding the underlying mechanism requires investigations on structure-property relationship. Thus, we study the mechanical properties of anhydride-cured epoxy with boehmite NP (up to 15%wt) using AFM-based methods: force distance curves (FDC) and intermodulation AFM (ImAFM). FDC measurements show increase in stiffness of epoxy in the presence of boehmite but cannot resolve NPs. ImAFM stiffness maps with a resolution of ~ 10 nm reveal an unexpected increase in stiffness of epoxy matrix which implies structural change in the matrix. To investigate these changes dynamic mechanical analysis (DMA) is performed yielding viscoelastic properties and nanostructure of the cross-linked networks. We observe significant inhomogeneity and uncured residues in the neat epoxy which gradually disappear with increasing concentration of NP.

In the case of 15wt% NP, despite of an increase in storage modulus of the glassy state, the rubbery state storage modulus and the crosslinking density decrease drastically. Based on these observations, we propose a new mechanism in which boehmite particles not only interact with epoxy matrix but also contribute to curing process and network structure.

CPP 64.4 Thu 10:15 PC 203

The influence of interfacial adhesion between a dispersed inorganic phase and a polymer matrix on the overall mechanical properties of composite materials — ●DOROTHEE SILBERNAGL¹, MEDIA GHASEM ZADEH KHORASANI¹, and HEINZ STURM^{1,2} — ¹BAM, Berlin, Germany — ²TU Berlin, Berlin, Germany

The overall mechanical properties of composites are considered to correlate with the mechanical properties of the constituents, i.e. matrix phase (MP) and inorganic dispersed phase (DP). In the case of a MP, e.g. epoxy, which polymerizes in the presence of a DP, the mechanical properties of the interphase (IP), the organic matter in proximity to the filler particle, has to be taken into account. We show the major influence of a third parameter: the interfacial adhesion (IA) between MP and DP. In order to make this effect measurable a nanoparticle based composite was geometrically reduced to a substrate representing the DP and a thin polymer film (10 - 100 nm), representing the MP. Substrates with differently modified moieties enhancing or impeding the IA are used. Mechanical properties of such layered samples (silicon/PnBMA and boehmite/anhydride-cured epoxy) were measured by AFM force-distance curves (FDC), applying forces perpendicular to the interface. FDC curves show significant changes in deformation rates depending on the IA. This implies unexpected long range effect exceeding the effect of an IP.

CPP 64.5 Thu 10:30 PC 203

Self-Assembly of Discotic Rings and Nanowires in a Liquid Crystal Confined in Nanopores — ●KATHRIN SENTKER¹, ARNE ZANTOP², ARDA YILDIRIM³, MILENA LIPPMANN⁴, TOMMY HOFMANN⁵, OLIVER SEECK⁴, ANDRIY KITYK⁶, ANDREAS SCHÖNHALS³, MARCO MAZZA², and PATRICK HUBER¹ — ¹Institut für Werkstoffphysik und -technologie, TU Hamburg — ²MPI für Dynamik und Selbstorganisation — ³BAM, Berlin — ⁴DESY, Hamburg — ⁵HZG für Materialien und Energie — ⁶Faculty of Electrical Engineering, TU Czestochowa

Discotic Liquid Crystals (DLC) tend to stack up into linear columns creating charge carrier pathways along the stacking direction due to overlapping pi - electrons. Embedding DLCs into nanoporous membranes enables the preparation of organic molecular nanowires or nanorings. We show by high-resolution optical birefringence and synchrotron-based X-ray diffraction, as well as Monte Carlo simulations, that confining a thermotropic DLC in cylindrical silica nanopores induces a quantized formation of annular layers consisting of concentric circular bent columns, unknown in the bulk state [1]. Starting from the walls this ring self-assembly propagates layer-by-layer towards the pore center. In addition, we found a pore size dependent orientational transition from the circular to axial orientation in anodic aluminum oxide nanopores allowing the preparation of semiconductive organic nanowires. [1] Sentker et al., Quantized Self-Assembly of Discotic Rings in a Liquid Crystal Confined in Nanopores, 2017, submitted

CPP 64.6 Thu 10:45 PC 203

Unraveling the role of TTBC isomers in self-assembled tubular aggregates — ●JÖRG MEGOW¹, TILLMANN KLAMROTH¹, HANS VON BERLEPSCH², CRAIG N. LINCOLN³, and JÜRGEN HAUER³ — ¹Universität Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam — ²Freie Universität Berlin, Fabeckstr. 34a, 14195 Berlin — ³Technische Universität München, Lichtenbergstraße 4, 85748 Garching

In [1], a structure model for mono-walled tubular aggregates of 1,1',3,3'-tetraethyl-5,5',6,6'-tetrachloro-benzimidazolocarboyanine iodide (TTBC) was proposed. There, the relative intensities and excitation energies of J- and H-bands could be explained satisfactorily. In [2], two isomers of the TTBC molecule have been discussed. In our present work we found a variety of TTBC isomers in the electronic ground state using density functional theory (DFT). Hence, the question arises which of those isomers is/are involved in the building of

TTBC aggregates. Our molecular dynamics simulations together with the DFT results now give a strong hint that TTBC molecules within a tubular structure adopt nearly flat conformations which do not correspond to any of the geometries of the different ground state isomers. This can be explained by the rather flat potential energy surface of the TTBC conformational space.

[1] C. Friedl, T. Renger, H. v. Berlepsch, K. Ludwig, M. Schmidt am Busch, and J. Megow, *Phys. Chem. C*, 2016, 120 (34), 19416 [2] M. Aydin, Ö. Dede, and D.L. Akins, *J. Chem. Phys.*, 2011, 134(6):064325

15 min. break

CPP 64.7 Thu 11:15 PC 203

Time resolved analysis of a Brownian motor — ●CHRISTIAN SCHWEMMER¹, STEFAN FRINGES^{1,2}, URS DÜRIG^{1,3}, and ARMIN KNOLL¹ — ¹IBM Research - Zurich, Switzerland — ²Institute of Physical Chemistry, University of Zurich, Switzerland — ³SwissLitho AG, Zurich, Switzerland

Artificial Brownian motors mimic the mechanism behind intracellular transport in nature [1] and enable a controlled transport of particles in a fluid [2]. In our implementation, we use a novel approach based on geometry induced trapping [3] to define a ratchet shaped potential landscape inside a nanofluidic slit. By applying a zero-mean AC electric field across the slit, we observed transport of 60 nm gold nano particles at drift speeds of 50 $\mu\text{m/s}$. The high temporal resolution of our experimental setup allowed us to measure the probability density *in-situ* and its temporal evolution with sub millisecond resolution. We observed current reversal at 250 Hz, an effect predicted more than 20 years ago [4], illustrating the nonlinear character of the motor. Comparison with a parameter-free theoretical model based on the Fokker-Planck equation shows excellent agreement. Using the model we traced the origin of the current reversal to the asymmetric, almost static probability density distribution at high frequencies, which leads to a faster increase of the backward current after switching the field direction.

[1] Vale et al., *Science*, **288**, 88, (2000)

[2] Hänggi et al., *Rev. Mod. Phys.*, **81**, 387, (2009)

[3] Krishnan et al., *Nature*, **467**, 692, (2010)

[4] Bartussek et al., *Europhysics Letters*, **28**, 459, (1994)

CPP 64.8 Thu 11:30 PC 203

Interaction of Cationic Surfactants with Protein in Tubular Silica Nanopores Studied by Small-Angle Neutron Diffraction — ANJA F. HÖRMANN¹, ●ALBERT PRAUSE¹, VIVIANA CRISTIGLIO², MICHAEL GRADZIELSKI¹, and GERHARD H. FINDENEGG¹ — ¹Department of Chemistry, Technical University of Berlin, Berlin, Germany — ²Institut Laue-Langevin, Grenoble, France

The interactions of surfactants with porous materials play an important role in environmental, chemical and medical applications. We studied nanostructures formed by adsorption and self-assembly of the cationic surfactants dodecyl pyridinium chloride (DPCl) and hexadecyl pyridinium chloride (CPCl) in the tubular mesopores of SBA-15 with pore diameter of 7 nm. Small-angle neutron diffraction (SAND) was used at silica contrast-matching conditions to obtain structural information from diffuse scattering contributions and the reappearance of the SBA-15 Bragg reflexes. For CPCl it could be shown that due to its high affinity to the negatively charged pore wall and the strong hydrophobic interaction of its tails the surfactant forms a monolayer *via* the growth of monolayer patches with increasing bulk concentration. Furthermore, we studied the co-adsorption of the globular protein lysozyme (Lyz) and CPCl. Whereas the pre-adsorption of CPCl is found to hinder the adsorption of Lyz sterically, the presence of Lyz seems to promote the homogeneity of the adsorbed material at the pore wall, as visible in the appearance of hollow cylinder scattering at lower adsorption fraction of surfactant f_s .

CPP 64.9 Thu 11:45 PC 203

Salt-induced microheterogeneities in binary liquid mixtures — ●MARKUS BIER¹, JULIAN MARS², HAILONG LI², and MARKUS MEZGER² — ¹Max Planck Institute Int. Sys. and University of Stuttgart, Germany — ²Max Planck Institute Poly. Res. and University of Mainz, Germany

The formation of microheterogeneities (MHs) in binary liquid mixtures due to the presence of salt is investigated by means of small-angle X-ray scattering (SAXS) and liquid state theory. The phenomenon is experimentally known to occur for antagonistic salts, whose cations

and anions prefer different components of the solvent mixture. However, up to now the origin of the characteristic length scale of MHs was unclear. In this contribution it is shown that MHs can be generated by an interplay between short-ranged interactions and long-ranged monopole-dipole interactions. This conclusion has been reached by performing SAXS measurements and comparing the solvent structure factor with a general expression derived without assuming any specific model. This method allows one to analyse the dependency of the MH structure with respect to ionic strength and temperature. Upon approaching the demixing phase transition, critical-like behaviour occurs close to the spinodal line in the phase diagram.

Reference:

M. Bier, J. Mars, H. Li & M. Mezger, *Phys. Rev. E* **96**, 022603 (2017).

CPP 64.10 Thu 12:00 PC 203

AC electrokinetic manipulation of nanoparticles and molecules — EVA-MARIA LAUX¹, XENIA KNIGGE¹, CHRISTIAN WENGER², FRANK F. BIER¹, and ●RALPH HÖLZEL¹ — ¹Fraunhofer Institute for Cell Therapy and Immunology, Bioanalysis and Bioprocesses, Potsdam-Golm (IZI-BB), Germany — ²IHP GmbH - Leibniz Institute for Innovative Microelectronics, Frankfurt (Oder), Germany

AC electric fields are increasingly exploited for the separation of nanoparticles and molecules in micro- and nanoelectrode systems. AC electrokinetic phenomena like dielectrophoresis (DEP) and AC electroosmosis allow a robust non-contact spatial manipulation. Here we present results of dielectrophoretic experiments on nanoparticles and proteins in various electrode systems. Numerous protein species have been successfully manipulated: intrinsically fluorescing proteins like eGFP, DsRed and RPE, and fluorescently labeled BSA; specific antibody binding as well as enzymatic function are shown to be retained after DEP immobilisation. Depending on electrode size, molecules and nano-particles are isolated as singles between planar triangular electrodes or on arrays comprising up to 500,000 conical electrodes. Using fluorescence polarisation microscopy, permanent dielectrophoretic immobilisation of eGFP molecules is demonstrated with parallel alignment of the proteins' main axis along the electric field, and the relative orientation of the molecule's fluorophor is determined.

CPP 64.11 Thu 12:15 PC 203

Efficient hydrogen evolution on triple point fermion semimetal MoP — ●GUOWEI LI¹, GUDRUN AUFFERMANN¹, JIAN ZHANG², XINLIANG FENG², and CLAUDIA FELSER¹ — ¹Max Planck Institute for Chemical Physics of Solids, 01187, Dresden, Germany — ²Center for Advancing Electronics Dresden (cfaed), Department of Chemistry and Food Chemistry, Dresden University of Technology, 01062, Dresden, Germany

Materials in topological state result in many exotic properties such as large magnetoresistance, high conductivity, and an intrinsic Hall effect. However, their function in the field of chemistry has generally been overlooked and has attracted little attention. The observation of extremely high conductivity and Weyl nodes in MoP motivates us to design high performance electrocatalyst. Mo-P co-doped carbon layer@MoP was synthesized and exhibits outstanding electrocatalytic activity for the hydrogen evolution reaction (HER) with an overpotential of 49 mV at the current density of 10 mA/cm², and a Tafel slope of 54 mV per decade in alkaline media. All these make it one of the best non-noble metal hydrogen evolution electrocatalysts and even approaches to that of commercial Pt/C catalyst. The formation of P-C and Mo-C bonding in the interface and layers were able to shape the band structure more favoring for the electron accumulation and de-localization, resulting the high HER activity with a large exchange current density. The results here show a new way for the modification of carbon coating, which we can use for designing of high-performance HER electrocatalysts in both acid and alkaline media.

CPP 64.12 Thu 12:30 PC 203

13C isotope enriched graphitic material for operando NMR studies of processes in electrochemical cells — ●ANASTASIA VYALIKH¹, VICTOR KOROTEEV², WOLFRAM MÜNCHGESANG¹, LYUBOV' BULUSHEVA², ALEXANDER OKOTRUB², and DIRK C. MEYER¹ — ¹TU Bergakademie Freiberg, Freiberg, Germany — ²Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia

We provide a multi-scale characterization of a 13C-enriched fine-grained graphitic material and explore two different ways of its modification through a high-temperature high pressure annealing and a room-temperature chemical treatment. It has been found that such

modifications result in structural and textural changes caused by carbon layer arrangement and carbon hybridization state, that can significantly affect the behavior in various applications, including batteries. We have shown that a high degree of ^{13}C isotope enrichment, as well

as good long-term performances in Li-ion batteries, and, in particular, an improved NMR spectral resolution in the bromine-treated sample provide the materials studied in the present work to be suitable candidates for ^{13}C NMR study of processes in electrochemical cells.