

## CPP 58: Nanostructures, Nanostructuring and Nanosized Soft Matter

Time: Thursday 15:00–18:30

Location: H13

**Invited Talk**

CPP 58.1 Thu 15:00 H13

**Gyroids on the nanoscale: Metamaterials with surprising optical properties** — ●BODO WILTS — Adolphe Merkle Institute, University of Fribourg, Fribourg, Switzerland

Block copolymers can self-assemble into various nanostructured morphologies, such as lamellae, cylinders, spheres and the gyroid. Such polymeric structures can be used as templates to fabricate functional nanostructured materials. This bottom-up fabrication route allows generating materials with different, or entirely novel, properties. One example are optical metamaterials, metallic structures with unit cells smaller than the wavelength of light. Here, I will show that optical metamaterials can be fabricated by replicating gyroid polymeric nanostructures into plasmonic metals. The cubic gyroid structure is of particular interest for optical metamaterials applications due to its inherent chirality, which promises to induce novel optical properties in gyroid metal replica. I will demonstrate that these gyroids indeed show surprising optical properties such as linear and circular dichroism, and will show that these properties originate from a contribution of the surface morphology and the local orientation of the gyroid structure. I will discuss the importance of structural order of the polymeric templates on the resulting optical metamaterials and will further outline how changing the material composition, e.g. by changing the material from gold to silver, changes the optical properties of the nanostructures.

CPP 58.2 Thu 15:30 H13

**The real 3D morphology of cylindrical block copolymer nanomasks** — ●DANIEL KOOL<sup>1,2</sup>, KATHARINA BRASSAT<sup>1,2</sup>, and JÖRG K. N. LINDNER<sup>1,2</sup> — <sup>1</sup>University of Paderborn, Dept. of physics, Paderborn, Germany — <sup>2</sup>Center for Optoelectronics and Photonics Paderborn CeOPP, Paderborn, Germany

Block copolymer (BCP) lithography is a well-established technique which allows for economical large-area patterning of surfaces with self-assembled nanoscale features. We exploit the microphase separation of copolymers, here poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) BCP with a block length ratio of 70:30. This results in the formation of 17 nm diameter PMMA cylinders perpendicular to the surface and hexagonally arranged in a PS matrix. After selective removal of PMMA cylinders the nanostructured PS thin film can be used in common lithography processing steps, as reactive ion etching and lift-off for pattern replication and transfer. Here we demonstrate that the efficiency of replication of the nanostructured features can be drastically improved by modification of the polymer mask prior to lithographic use by an O<sub>2</sub> plasma treatment. We achieved an experimental method of pattern replication without loss of features and the opportunity to tune the feature size precisely on the nanometer scale. By SEM investigations of both interfaces of the lithography mask we were able to reconstruct the 3-dimensional morphology of the polymer mask. Indirect information on the polymer mask morphology is obtained, in addition, from pattern replication studies by lift-off experiments and by RIE, allows to conclude on the real 3D shape of BCP pores.

CPP 58.3 Thu 15:45 H13

**Research of the high loading capacities of amphiphilic Poly(2-Oxazoline)-based Triblockcopolymers with Curcumin** — ●ÖZGÜR DÜDÜKÜ<sup>1</sup>, B. SOCHOR<sup>1</sup>, M. LÜBTOW<sup>3</sup>, B. SCHUMMER<sup>1,2</sup>, R. LUXENHOFER<sup>3</sup>, and R. HANKE<sup>1,2</sup> — <sup>1</sup>Institute of Physics, Chair of X-ray Microscopy, Universität Würzburg, Germany — <sup>2</sup>Fraunhofer Institute for Integrated Circuits IIS, Development Center X-ray Technology EZRT, Fürth, Germany — <sup>3</sup>Functional Polymer Materials, Chair for Advanced Materials Synthesis, Department of Chemistry and Pharmacy and Bavarian Polymer Institute, Universität Würzburg, Germany

In this project, drug-loaded triblock copolymers in solutions were investigated using small-angle-neutron-scattering (SANS), densitometric measurements and <sup>1</sup>H-NMR Spectroscopy. Curcumin was used as the hydrophobic drug and Poly(2-Oxazoline)-based amphiphilic triblock copolymers as carrier systems. The triblock copolymers consist of a hydrophobic middle block and hydrophilic side chains. Polymer carrier systems in nanomedicine typically have loading capacities of less than 10-20 %. The aim of the project was to clarify the high drug loading capacities up to 80 wt% of the investigated formulations. This

effect is still unexplained. By analysing the scattering curves of the formulations resulting from the SANS experiments, information about the structure and composition of the formulations was obtained. The scattering curves are compared with theoretical models to clarify the structure of formulated drug-polymer-systems. The analysis showed that the drug-loaded polymers form micelles with a hydrophobic core and two outer shells, i.e. a core-shell-shell model. Including <sup>1</sup>H-NMR measurements it was found that curcumin does not only accumulate in the hydrophobic core. Despite its hydrophobic character interacts with the hydrophilic side chains of the triblock copolymer and forms a second shell. Thus this model gives a possible explanation of the high loading capacity of the polymers.

CPP 58.4 Thu 16:00 H13

**Sputter deposition of Al on nanostructured PMMA-*b*-P3HT and PS-*b*-PMMA copolymer thin films** — ●MARC GENSCHE<sup>1,2</sup>, MATTHIAS SCHWARTZKOPF<sup>1</sup>, JONAS DREWES<sup>3</sup>, OLEKSANDR POLONSKYI<sup>3</sup>, THOMAS STRUNSKUS<sup>3</sup>, FRANZ FAUPEL<sup>3</sup>, PETER MÜLLER-BUSCHBAUM<sup>2</sup>, and STEPHAN VOLKHER ROTH<sup>1,4</sup> — <sup>1</sup>Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, D-22607 Hamburg, Germany — <sup>2</sup>Technische Universität München, Physik-Department, LS Funktionelle Materialien, James-Frank-Str. 1, D-85748 Garching, Germany — <sup>3</sup>Lehrstuhl für Materialverbunde, Institut für Materialwissenschaft, Christian Albrechts-Universität zu Kiel, Kaiserstr.2, D-24143 Kiel, Germany — <sup>4</sup>KTH Royal Institute of Technology, Teknikringen 56-58, SE-100 44 Stockholm

Nanostructured polymer-metal-composite films show great perspectives for optoelectronic applications, e.g. as sensors or photovoltaics. To tailor properties of such devices the self-assembly process of the nanostructures needs to be understood. We studied in situ the evolution of the cluster growth morphology by grazing incidence small-angle X-ray scattering (GISAXS), the crystallinity of the nanogranular metal film with grazing incidence wide-angle X-ray scattering (GIWAXS) and the optical properties using surface differential reflectance spectroscopy (SDRS) all simultaneously during Al sputter deposition on nanostructured polymer templates. Our study reveals the selective decoration of Al on the polymer domains and the templates influence on the percolation behavior of the Al layer.

CPP 58.5 Thu 16:15 H13

**Pattern transfer of self-assembled block copolymer nanopores into silicon and silicon dioxide by reactive ion etching** — ●ALEXANDER STRATMANN, DANIEL KOOL, JULIUS BÜRGER, KATHARINA BRASSAT, and JÖRG K. N. LINDNER — Paderborn University, Paderborn, Germany

Reactive ion etching (RIE) is a highly reproducible dry etching method, which combines the benefits of physical sputtering with ions and chemical etching with radicals. By combining RIE processes with block copolymer (BCP) lithography large-area nanopore patterns in the sub-20 nm regime can be created. To this end, the self-ordering of a polystyrene-*b*-methyl methacrylate (PS-*b*-PMMA) BCP is exploited to create hexagonally arranged PMMA cylinders in a PS matrix. After the selective removal of the PMMA cylinders the PS thin film can be used for common lithography processes such as RIE. The pattern transfer was accomplished on silicon and silicon dioxide surfaces by etching with a SF<sub>6</sub>/Ar and a CHF<sub>3</sub>/Ar plasma, respectively. To complete the lithography process, the removal of the mask was done by an O<sub>2</sub>/Ar plasma. We achieved a highly reproducible method to etch nanopores with homogenous etching depth, etch profile, pore diameter and high feature density. The process steps are investigated by SEM, AFM and cross-sectional TEM.

**15 min. break**

CPP 58.6 Thu 16:45 H13

**Dye-Sensitized Ternary Copper Chalcogenide Nanocrystals: Optoelectronic Properties, Air Stability and Photosensitivity** — ●SONAM MAITI<sup>1,2</sup>, SANTANU MAITI<sup>2</sup>, ALI HOSSAIN KHAN<sup>3</sup>, FRANK SCHREIBER<sup>2</sup>, and MARCUS SCHEELE<sup>1</sup> — <sup>1</sup>Institute of Physical and Theoretical Chemistry, University of Tübingen, Germany. — <sup>2</sup>Institute of Applied Physics, University of Tübingen, Germany — <sup>3</sup>Department of Chemistry, Ghent University, Belgium

Copper chalcogenide nanocrystals (NCs) exhibit a great potential for optoelectronic applications and efforts have been made to increase electronic coupling in thin films of these materials. 1-2 We report on the effect of ligand exchange of Cu<sub>2</sub>-xSe<sub>y</sub>S<sub>1-y</sub> as well as Cu<sub>2</sub>-xSe nanocrystals (NCs) with the organic pi-system Cobalt  $\beta$ -tetraaminophthalocyanine (CoTAPc) and analyze changes in the structural, optical as well as electronic properties. A strong ligand interaction with the surface of the NCs is revealed by absorption and Raman spectroscopy. Grazing-incidence small-angle X-ray scattering studies show a significant contraction in the interparticle distance upon ligand exchange. For Cu<sub>2</sub>-xSe, this contraction has a negligible effect on electric transport, while for Cu<sub>2</sub>-xSe<sub>y</sub>S<sub>1-y</sub> the conductivity increases by eight orders of magnitude and results in metal-like temperature-dependent transport. With photocurrent measurements, we demonstrate high optical responsivities for Cu<sub>2</sub>-xSe<sub>y</sub>S<sub>1-y</sub> NCs and show the organic pi-system acts as an electronic linker and an optical sensitizer at the same time. 1. C. Coughlan et al, Chem Rev 2017, 117 (9), 5865-6109. 2. S. Maiti et al, JPCC 2018, 122 (41), 23720-23727.

CPP 58.7 Thu 17:00 H13

**Following the formation of metal electrodes on photoactive polymer thin films** — ●FRANZISKA LÖHRER<sup>1</sup>, VOLKER KÖRSTGENS<sup>1</sup>, SIMON SCHAPER<sup>1</sup>, MATTHIAS SCHWARTZKOPF<sup>2</sup>, ALEXANDER HINZ<sup>3</sup>, OLEKSANDR POLONSKYI<sup>3</sup>, THOMAS STRUNSKUS<sup>3</sup>, FRANZ FAUPEL<sup>3</sup>, STEPHAN ROTH<sup>2,4</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik-Department, D-85748 Garching — <sup>2</sup>Deutsches Elektronensynchrotron DESY, D-22607 Hamburg — <sup>3</sup>CAU zu Kiel, Institut für Materialwissenschaft, D-24143 Kiel — <sup>4</sup>KTH, Teknikringen 56-58, SE-100 44 Stockholm

Although based on organic materials, organic solar cells often include metal electrodes due to their unrivaled electronic conductivity. Thus, polymer-metal interfaces are inherently present in most OPV devices and have a major influence on their behavior. Understanding the growth mechanisms of metal contacts on polymer thin films plays a crucial role in identifying potential ways to enhance the device performance. We investigate the morphological changes at the metal-polymer interface during the sputter deposition of metal contacts onto photoactive polymer films via in-situ GISAXS. This technique allows insights into the structural evolution of the metal on the organic film. A model describing the process is developed based on earlier work on different material systems. Comparing the deposition behavior of typical electrode materials on thin films of photoactive organic materials helps to understand their influence on the respective device performance.

CPP 58.8 Thu 17:15 H13

**Structural and melting properties of low molecular weight PEG confined in nanoporous ITPC** — ●ANN-KATHRIN GREFE, BJÖRN KUTTICH, and BERND STÜHN — Institut für Festkörperphysik, Technische Universität Darmstadt

Ion track-etched polycarbonate constitutes an ideal system for studying confined polymers. Whereas other nanoporous systems often rule out small angle x-ray scattering due to predominant pore scattering and laborious data description, ITPC allows for a more straightforward investigation since the pores are not structurally correlated.<sup>[1]</sup>

Nanopores with radii from 8 to 205 nm are prepared and coated with 10 nm of SiO<sub>2</sub> via ALD in order to obtain a well-defined and homogeneous surface. SAXS reveals the nearly perfect cylindrical geometry of the pores. The linear dependency of the pore radius on the etching time is shown to hold true over the complete range of pore radii.

PEG with  $M_w = 1500$  g/mol and a semicrystalline lamellar bulk structure is introduced into the nanopores via melt infiltration. At high temperatures SAXS confirms a nearly complete filling with amorphous polymer. Upon cooling below the melting point of PEG, a concentric arrangement of semicrystalline lamellae is revealed for pore radii over 71 nm. We introduce models which successfully describe the combined scattering from nanopores and semicrystalline or amorphous PEG inside. DSC measurements of the confined polymer show a decrease of melting temperature and heat of fusion per gram polymer upon reduction of the pore radius and hint at a change in nucleation mechanism.

<sup>[1]</sup> M. Engel et al., Appl Phys A 97, 99-108 (2009)

CPP 58.9 Thu 17:30 H13

**High-resolution multi-channel nanoparticle separation utilizing rocked Brownian motors** — ●CHRISTIAN SCHWEMMER, FRANCESCA RUGGERI, XIAOYU MA, and ARMIN KNOLL — IBM Re-

search - Zurich, Switzerland

Artificial Brownian motors were inspired by how nature achieves directed transport in highly diffusive environments [1]. Their two main ingredients are an asymmetric potential and a zero-mean driving force. Our implementation employs the electrostatic interactions in weak electrolytes between charged nanoparticles and like charged surfaces of a nanofluidic slit [2] to define a ratchet shaped energy landscape [3]. A zero-mean AC electric field across the slit induces an electro-osmotically transduced driving force, resulting in drift speeds of up to 50  $\mu\text{m/s}$  for 60 nm gold spheres. The motors exhibit an Arrhenius-like onset of the particle current with decreasing amplitude of the energy barriers, a promising feature for particle separation [4]. Based on this property, we developed a fast and highly selective nanoparticle sorting device to separate gold spheres of nominally 80 nm and 100 nm diameter along its y-axis into 30 subpopulations with <2 nm sorting resolution. By switching the AC field to the x-direction, the separated populations are transported to compartments for collection. Thus, scalable continuous multi-channel particle separation is within reach.

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

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

[3] Skaug et al., Science, **359**, 1505 (2018)

[4] Bartussek et al., Europhys. Lett., **28**, 459 (1994)

CPP 58.10 Thu 17:45 H13

**Nanoporous Gold supported Polypyrrole: Electrochemically Modulated Elasticity** — ●JIE LI<sup>1</sup>, JÜRGEN MARKMANN<sup>1,2</sup>, JÖRG WEISSMÜLLER<sup>1,2</sup>, and NADIA MAMEKA<sup>1</sup> — <sup>1</sup>Helmholtz-Zentrum Geesthacht, Institute of Materials Research, Materials Mechanics — <sup>2</sup>Hamburg University of Technology, Institute of Materials Physics and Technology

Polypyrrole (PPy), an intrinsic conducting polymer, has drawn widespread attention in many fields, such as, displays, ion exchange membranes and actuators, where mechanical integrity is required by functionalities. Thin films preparation and their mechanical properties, say, strength, have been widely studied, whereas the elastic modulus, especially the modulus under stress coupled with electrochemical conditions, remains to be clarified. Herein, PPy film is electropolymerized on mm-size nanoporous gold (NPG), a 3D bicontinuous network of nanoscaled ligaments and pores with large surface area [1]. Uniform PPy coatings with various thicknesses in bulk NPG are achieved without blocking the original nanopores. The elastic modulus measurements of NPG-PPy composites were performed in situ during potential cycling in aqueous electrolyte in a dynamic mechanical analyzer (DMA). In situ DMA experiments reveal a non-monotonic modulus response versus the potential during charging-discharging processes, as opposed to nearly linear variation of the macroscopic length. Moreover, the modulus variation amplitude increases with the PPy film thickness. Possible mechanisms for the stiffness behavior will be discussed. [1] Mameka et al, Mater. Res. Lett., 2016, 1:27.

CPP 58.11 Thu 18:00 H13

**Structural Characteristics of Small and Stable Coenzyme Q10 Nanoparticles produced by Antisolvent Precipitation** — ●ISABEL SCHULDES, DENNIS M. NOLL, TOBIAS ZECH, and TOBIAS UNRUH — Institute for Crystallography and Structural Physics, Friedrich-Alexander Universität Erlangen-Nürnberg, Erlangen, Germany

The production of organic nanoparticles (NPs) via antisolvent precipitation (AP) is a less-invasive and low-cost alternative to top-down methods like high-pressure homogenization. Thus, AP is receiving growing attention, e.g. for the preparation of nanodispersions of pharmaceutical ingredients. For instance, the antioxidant coenzyme Q10 (Q10) has several health protective effects and Q10 NPs showed improved bioavailability compared to free Q10.

Here we report the structural characterization of Q10 NPs produced by AP. The NPs are analyzed by photon correlation spectroscopy (PCS), cryogenic transmission electron microscopy (CryoTEM), small-angle X-ray and neutron scattering (SAXS; SANS, KWS-1 at MLZ). In particular, the combination of SAXS and SANS studies allows the investigation of the molecular structure of the NPs and the interface between the NPs and the dispersion medium. Our experiments revealed, that Q10 NPs prepared by AP are stable with and without added stabilizer, have a particular small size (down to  $\sim 20$  nm in diameter), and exhibit a specific stabilizing layer, suggesting a self-stabilizing process of the Q10 molecules.

CPP 58.12 Thu 18:15 H13

**The impact of inhomogeneous distributions and magnetisation of nanoparticles on the equilibrium structure of magnetic filaments** — ●DENIZ MOSTARAC<sup>1</sup>, PEDRO A. SANCHEZ<sup>1,2</sup>, OLEG GANG<sup>3,4</sup>, and SOFIA KANTOROVICH<sup>1,2</sup> — <sup>1</sup>University of Vienna, Vienna, Austria — <sup>2</sup>Ural Federal University, Ekaterinburg, Russia — <sup>3</sup>Columbia University, New York, USA — <sup>4</sup>Brookhaven National Laboratory, New York, USA

Construction of smart materials with sophisticated magnetic response by incorporating magnetic particles (MNP's) within permanently cross-linked structures, opens the possibility for applications to highly magneto-responsive systems [1]. Construction of magnetic filaments (MF's polymer-like structures in which as monomers are the magnetic

beads) is possible using DNA origami technique [2,3]. Structural inhomogeneities alter the equilibrium properties and the magnetic response of MF's. Using MD simulations, we show that coiling and persistence length of MF's depend on the magnetic particle distributions, along with temperature and applied magnetic field. We compare the structural properties and magnetic behaviour of different configurations of MF's, highlighting that our model takes in to account superparamagnetic effects. We present an exhaustive, comparative analysis of the field dependent, structural behaviour of MF's.

[1] Sánchez, P. A., et al. *Macromolecules* 48.20 (2015): 7658-7669.  
[2] Liu, W., et al. *Nature chemistry* 8.9 (2016): 867. [3] Tian, Y., et al. *Nature materials* 15.6 (2016): 654.