CPP 10: Bioinspired Functional Materials II

Time: Monday 15:00–18:15 Location: ZEU 114

CPP 10.1 Mon 15:00 ZEU 114

Extreme refractive index wing scale beads cause the bright colors of pierid butterflies — •Bodo Wilts[1], Bas Wijnen[2], Ullrich Steiner[1], and Doekele Stavenga[2] — [1]Adolphe Merkle Institute, University of Fribourg, Switzerland — [2]University of Groningen, Groningen, the Netherlands

Butterflies feature strong, vivid colours due to photonic structures on their surface. Butterflies of the family Pieridae are brightly colored, ranging from white to red, caused by various pterin pigments concentrated in scattering spheroidal beads in the wing scales. Given the sparsity of the beads in the wing scales, the high brightness suggests a scattering strength of the beads that significantly surpasses that of typical cuticular chitin beads with the aereal density found in the wing scales. To elucidate this apparent contradiction, we have analyzed the optical signature of the pierids* highly saturated pigmentary colors by using Jamin-Lebedeff interference microscopy combined with Kramers-Kronig theory and light scattering modeling. We show that extreme pterin pigment concentrations cause a very high refractive index of the beads with values above 2 across the visible wavelength range, thus creating one of the most highly light scattering media thus far discovered in the animal kingdom.

CPP 10.2 Mon 15:15 ZEU 114

Actuated Self-(Un)rolling Silk Microstructures: Rings, Tubules, and Hhelical Tubules — •Chunhong Ye[1,2], Svetoslav V Nikolov[3], Ren Geryak[2], Rossella Calabrese[4], Alexander Alexeev[3], David L Kaplan[4], and Vladimir V Tsukruk[2] — [1]Institute of Physical Chemistry and Polymer Physics, Leibniz Institute of Polymer Research, Dresden, 01169 Germany — [2]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332 USA — [3]Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332 USA — [4]Department of Biomedical Engineering, Tufts University, 4, Colby street, Medford, MA 02155 USA

We demonstrated facile, reversible, fast self-rolling biopolymer microconstructs using sandwiched active-passive, silk-on-silk morphology. We experimentally showed and theoretically confirmed that the shape of individual sheets effectively controls biaxial stresses within these sheets which can self-roll themselves into distinct 3D structures including microscopic rings, tubules, and helical tubules. This is a unique example of tailoring self-rolled 3D geometries though shape design without changing the inner morphology of active bimorph nanomaterials. Furthermore, the self-rolling direction, percentage shape, and diameter of the silk microtubes can be readily controlled over the geometry of the 2D microsheets, such as lateral dimension, thickness and aspect ratio. The microstructrues indicated highly reversible rolling/unrolling by alternating the external pHs, attributed to the significant swelling/deswelling of silk active layer at different pHs.

CPP 10.3 Mon 15:30 ZEU 114

Shear-induced transformation of polymer-rich lamellar phases to micron sized vesicles investigated by small-angle scattering — •Sören Grosskopf[1], Miriam Siebenbürger[2], Oliver Wrede[1], Yvonne Hertle[1], and Thomas Hellweg[1] — [1]Bielefeld University — [2]Helmholtz-Zentrum Berlin

The influence of adding an amphiphilic triblock copolymer to a cationic microemulsion results on the one hand in an increasing viscosity and on the other hand in complexer phase behavior with an enhanced lamellar phase. This is a common feature of amphiphilic block copolymers related to the *efficiency boosting effect*. The aim of this work was to fabricate multi-lamellar-vesicles (MLV) out of a triblockcopolymer-rich lamellar phase applying stress and their identifaction via small angle scattering. The system consists beside the the polymer of a polar and apolar component and an cationic co-surfactant. Such large vesicles are of potential interest for the usage as drug delivery systems. Different *rheo*-small-angle scattering techniques were used to investigate structures while applying shear stress: With neutrons the change in the bilayer spacing can be investigated. For the research of larger structures depolarized rheo-small-angle light scattering (*rheo*-SALS) was used. The *rheo*-SALS experiments shows an inverse dependency of the applied shear-rate on the size of the MLVs. Beside the small-angle scattering experiments different microscopy techniques (polarized light, difference interference contrast microscopy) was used to obtain real space pictures of the resulting particles.

CPP 10.4 Mon 15:45 ZEU 114

Carbon-Nanotube Membranes from Self-Assembly in Lipid Bilayers — •Martin Vögele, Jürgen Köfinger, and Gerhard Hummer — Max-Planck-Institut für Biophysik, Frankfurt am Main

Carbon nanotube (CNT) pores in lipid membranes are a promising candidate for applications as molecular filters and in drug delivery. The similarity of such pores to cylindrical membrane proteins raises the question whether they can self-assemble to a thin membrane with a high density of pores in a manner similar to protein 2D crystallization. We apply fully atomistic and large-scale coarse-grained molecular dynamics simulations to explore the hypothetical formation of such a material and to guide future experiments.

We find that indeed carbon nanotubes self-assemble to large clusters in lipid membranes. As the up-right carbon nanotubes induce very strong annular lipid shells around themselves, those clusters include trapped lipids between the CNTs. This trapped state is advantageous as it softens boundaries between otherwise incompatible local crystallization nuclei.

Our simulations suggest that the lipid composition is less important for the experimental procedure to produce such membranes but it will need a very subtle fine-tuning of the CNT properties. If this can be mastered, there is a broad field of applications, e.g. in desalination or dialysis, with many possibilities to tune the desired properties of the material.

CPP 10.5 Mon 16:00 ZEU 114

The impact of surface curvature on growing tissues — •Sebastian Ehrig[1], Alan West[1], Cecile M. Bidan[2], Karen Lam[1], Philip Kollmannsberger[3], Pavel Tomancak[4], Peter Fratzl[1], and John W.C. Dunlop[1] — [1]MPIKG, Potsdam, Germany — [2]CNRS, Université Grenoble Alpes, France — [3]University of Würzburg, Germany — [4]MPICBG, Dresden, Germany

Biological tissues continuously undergo shape changes that effect the development and regeneration of tissues and organs. These changes are regulated by cells confined within a complex environment of mechanical and biochemical constraints. Cells not only respond to the geometry of their local environment but also modify it, through the production of extracellular matrix. How these cells are able to form complex tissue structures over large distances, however, is still elusive. Motivated by the observation that tissues grown on substrates of controlled curvature in-vitro are strongly influenced by the local curvature, we have performed tissue culture experiments on surfaces of constant mean curvature and are able to show that the mean curvature has a strong impact on the rate of tissue growth and on the organization of the cellular structures. We can show that on long time scales the tissue surface behaves like a viscous fluid with an equilibrium shape governed by the Laplace-Young-law. Cells on these surfaces display liquid-crystal like behaviour leading to remarkably symmetric stress patterns that closely resemble geodesics. The emergence of such patterns is a result of the intrinsic surface curvature and can partly be explained by minimizing the free energy of the cells director-field.

CPP 10.6 Mon 16:15 ZEU 114

Colloid Clusters in Confinement: Observation, Modelling and Simulation — •Junwei Wang[1,2], Michael Engel[2], and Nicolas Vogel[1] — [1]Institute of Particle Technology, Friedrich Alexander Universität, Erlangen, Germany — [2]Institute of Multiscale Simulation, Friedrich Alexander Universität, Erlangen, Germany

Natural materials evolve to maximize performance from a limited choice of simple building blocks. Structural coloration is one example where nature utilizes ordered nanostructures to create vivid color. Colloidal particles are ideal building blocks to mimic this design principle, as their sizes match with wavelength of visible light. Colloids assemble upon increase of volume fraction into crystals, driven by entropy. Recent studies show that for colloids in spherical confinement, entropy favors icosahedral symmetry. Here we experimentally realize and geometrically model highly ordered icosahedral colloid assemblies. We discuss and compare stabilization mechanisms. Our study demonstrates the ability to create sophisticated colloid assemblies via con-

finement, which may find use as templates, photonic materials, and building blocks for hierarchical assembly.

15 min break

CPP 10.7 Mon 16:45 ZEU 114

Nonclassical Crystallization in vivo et in vitro: origin and mimesis of a fundamental and nanoscale process-structure-property relationship of biominerals — •Stephan E. Wolf — Friedrich-Alexander-University Erlangen-Nürnberg, Erlangen, Germany; Juniorprofessor for Biomimetic Materials and Processes

Hidden within their structural wealth, a distinct nanogranular fine structure is shared by nearly all biominerals. This structural dichotomy of universality vs. diversity roots in a common nanoparticle-mediated growth, i.e. nonclassical crystallization, which underlies the formation of these nanogranular biominerals. This reveals a fundamental process-structure-property relationship of biominerals since the nanoscale organic-inorganic composite design affects multiple properties of the bioceramic. The mimesis of such a nanogranular material can be readily accomplished by exploitation of an in vitro mineralization route which involves accretion of amorphous colloids and their subsequent solid-amorphous to solid-crystalline phase transformation. This model system allows an unpreceded view on the mineral phase transformation and allows further the mimesis of crystal lattice tilting and twisting as observed in biogenic minerals. We discuss the origin of this peculiar crystallographic feature and demonstrate that crystal lattice bending represents a powerful, yet unexploited means to design and dynamically control anisotropic properties of a crystalline material. Revelation of the underlying mechanisms may pave the way to new classes of gradient materials and provide a new view on crystallographic design of solid state materials.

CPP 10.8 Mon 17:00 ZEU 114

Gyroid Optical Metamaterials: Termination-Induced Anisotropy — •Matthias Saba[1], James A. Dolan[2,4], Raphael Dehmel[2], Angela Demetriadou[1], Ilja Gunkel[5], Yibei Gu[3], Ulrich Wiesner[3], Timothy D. Wilkinson[4], Ullrich Steiner[5], Jeremy J. Baumberg[2], Bodo D. Wilts[5], and Ortwin Hess[1] — [1]Department of Physics, Imperial College, Prince Consort Road, London SW7 2BB, UK — [2]Department of Physics, University of Cambridge, J.J. Thomson Avenue, Cambridge CB3 0HE, UK — [3]Department of Materials Science and Engineering, Cornell University, 214 Bard Hall, Ithace, NY 14853-1501, USA — [4]Department of Engineering, University of Cambridge, J.J. Thomson Avenue, Cambridge CB3 0HE, UK — [5]Adolphe Merkle Institute, Ch. des Verdiers 4, 1700 Fribourg, Switzerland

Inspired by gyroid photonic crystals that are found in the wing-scales of several butterfly species, metallic gyroids fabricated via self-assembly constitute the first example of a truly three dimensional optical metamaterial. Gyroid metamaterials (GMMs) are known for their unique optical properties, such as linear and circular dichroism.

We here demonstrate experimentally and theoretically that (a) short range order GMMs essentially behave similar to isotropic nanoporous gold and can effectively be modeled by a Bruggeman approach, and that (b) the strong linear dichroism observed for long range order GMMs stems from a distinct plasmonic response at the GMM surface that breaks the cubic symmetry of the gyroid and is extremely sensitive to the specific surface termination.

CPP 10.9 Mon 17:15 ZEU 114

Immobilization Strategies for Photoactive Metal-Complexes on Carbon Nanomembranes — Maria Küllmer[1], Patrick Endres[2], Christof Neumann[1], •Andreas Winter[1], Andreas Winter[2], Benjamin Dietzek[1,3], Ulrich Schubert[2,4], and Andrey Turchanin[1,4] — [1]Institute of Physical Chemistry, Friedrich Schiller University Jena, 07743 Jena — [2]Institute of Organic Chemistry, Friedrich Schiller University Jena, 07743 Jena — [3]Leibniz Institute of Photonic Technology, 07745 Jena — [4]Jena Center for Soft Matter, Friedrich Schiller University Jena, 07743 Jena

The investigation of artificial molecular photo catalysts plays an important role in the development of novel energy sources. In this respect, the incorporation of photoactive compounds into nanomembranes is a promising approach for such applications in the field of light harvesting and electron transfer. Ruthenium-complexes are well-known photo-sensitizers and photocatalysts, which facilitate the utilization of light energy by electron transfer to/from the actual catalyst. The preparation of photoactive nanomembranes requires selective immobilization of these species on the nanomembrane surface. Here we present various immobilization strategies of ruthenium-II-photosensitizers on 1 nm thick carbon nanomembranes (CNMs). We use thiol-ene click reactions and amide-bond formation via active esters to couple the complexes to the CNM. Alternatively the metal-capturing unit was formed intrinsically by the crosslinked self-assembled monolayer units. The functionalized CNMs have been characterized by means of X-ray photoelectron spectroscopy as well as atomic force and optical microscopy.

CPP 10.10 Mon 17:30 ZEU 114

Bio-inspired photonic structures as blueprints for compact polarization converters — •Xia Wu[1], Fernando Luis Rodríguez Gallegos[2], Marie-Christin Angermann[3], Bertram Schwind[1], Helge-Otto Fabritius[4], Georg von Freymann[3], and Jens Förstner[2] — [1]Department of Chemistry, University of Paderborn, Warburger Straße 100, D-33098, Paderborn, Germany — [2]Theoretical Electrical Engineering, University of Paderborn, Warburger Straße 100, 33098 Paderborn, Germany — [3]Physics Department, University of Kaiserslautern, Erwin-Schroedinger-Strasse, 67663 Kaiserslautern, Germany — [4]Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, 40237 Düsseldorf, Germany

Polarization conversion is often needed in many optical applications. In nature, many species of insects have evolved photonic structures can convert the polarization state of light upon reflection[1,2]. We reveal a new type of biological polarization converter found in the scales of weevil Entimus imperialis. We show that the D-structures in (and only in) the green domains of scales (i.e. {001} lattice plane parallel to scale surface) can act as a linear polarization converter. Furthermore we show that the D-structures in green domains preserve the handedness of the incident circularly polarized light upon reflection. Inspired by this finding, we synthesized woodpile structures by direct laser writing. We show that the well-known woodpile structure has very similar polarization conversion effect like that of D-structure. References: [1] K. Zhang et al., RSC Adv. (2014) 4, 51865-51871 [2] P. Vukusic et al., Nature (2000) 404, 457

CPP 10.11 Mon 17:45 ZEU 114

Soft and Tough as well: Morphology and Functional Structure of Spider Silk — A. Markus Anton and •Friedrich Kremer — Institute of Experimental Physics I, University of Leipzig, Germany

Spider dragline silk exhibits remarkable characteristics, such as exceptional biocompatibility or high tensile strength combined with great elasticity. Its mechanical properties are based on a refined architecture on the molecular scale: Proteins with highly repetitive core motifs aggregate into nanometer-sized crystals, rich on alanine in β-sheet secondary structure, surrounded by an amorphous glycine-rich matrix. During spinning the amorphous parts are elongated, which orients both substructures and gives rise to an inherent non-equilibrium state. Thus, external stress is directly transferred to the nanocrystals, while the tendency to contract is counterbalanced by surrounding fiber structure, as demonstrated by FTIR experiments in combination with uniaxial stress [1] or hydrostatic pressure [2].

Until recently it was not possible to artificially recreate this exceptional architecture [3]. We show that wet spinning and post-treatment of a novel biomimetic protein results in fibers with a similar nanostructure and comparable toughness as the natural template [4].

[1] P. Papadopoulos et al., *Eur. Phys. J. E* **24** (2007) 193–199; [2] A. M. Anton et al., *Macromolecules* **46** (2013) 4919–4923; [3] A. Heidebrecht et al., *Adv. Mater.* **27** (2015) 2189–2194; [4] A. M. Anton et al., *Manuscript in preparation*

CPP 10.12 Mon 18:00 ZEU 114

Hyperbolic surface decorations and novel materials — •Myfanwy Evans — Mathematics Institute, TU Berlin, Berlin, Germany

Hyperbolic surfaces form the basis of a wide array of biological structure. This talk explores the mathematical construction of secondary structures, or symmetric decorations, on these surfaces as a way to construct complex entangled materials with novel physical behaviour.