CPP 37: Biopolymers, Biomaterials and Bioinspired Functional Materials (joint session CPP/BP)

Time: Thursday 9:30–13:00 Location: H 0111

Invited Talk CPP 37.1 Thu 9:30 H 0111

Self-organized protein/polysaccharide nano-assemblies for applications in biomedical and food sciences — •Aristeidis Papagiannopoulos — Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vass. Constantinou Ave. 11635 Athens, Greece

Multifunctional nanocarriers of drugs and nutrients are very important for applications in the food industry and pharmaceutics. Proteins and polysaccharides are extensively used in these fields as they are biodegradable, metabolizable, nontoxic and biocompatible. Nanostructures from these two biopolymer classes combine the multifunctionality of the proteins (hydropathy and pH-dependent charge surface distributions) with the hydrophilicity and hydrogen-bonding property of the polysaccharides. Our recent work on protein/polysaccharide nanoparticles by electrostatic self-organization and thermal treatment without the use of chemical reactions or toxic solvents will be presented. Examples will include fibrinogen-hyaluronic acid nanoformulations, bovine serum albumin-chondroitin sulfate or -xanthan nanoparticles, trypsin- and hemoglobin-based nanoparticles. The discussion will be focused on the stimuli-response, molecular interactions and hierarchical morphology of the protein/polysaccharide systems and the binding of bioactive compounds. Physicochemical characterization and optimization of the nano-assemblies by light scattering, small angle scattering and spectroscopy techniques will be analyzed. These works motivate the development of other novel protein/polysaccharide biomaterials.

CPP 37.2 Thu 10:00 H 0111

Dichroic ATR-FTIR studies on thin bioinspired films of spider silk related peptide blends — Mirjam Hofmaier[1], •Thomas Scheibel[2], Andreas Fery[1], and Martin Müller[1] — [1]Leibniz Institute of Polymer Research Dresden (IPF), Institute of Physical Chemistry and Polymer Physics, 01069 Dresden, Germany — [2]University of Bayreuth, Chair of Biomaterials, 95447 Bayreuth, Germany

Bioinspired binary blends of a crystalline (C) and amorphous (A) peptide sequence were prepared addressing analogy to C-A multiblockcopolymer-like spider silk proteins. C/A blends were prepared in hexafluoroisopropanol for molar mixing ratios C/(C+A)=0, 25, 50, 77, 100%, deposited as thin films (d=31-44nm) onto silicon substrates and checked for secondary structure and orientation by dichroic transmission (T-) and ATR-FTIR spectroscopy. Amide I band analysis revealed little β-sheet (<15%) and much disordered (>79%) structure and dichroic ratios (R) of Amide I components indicating no β-sheet orientation for all C/(C+A) values. Whereas, after swelling in methanol vapor C/A blend films revealed increasing β-sheet up to 54% and decreasing disordered structure down to 42% with increasing C/(C+A). Furthermore, R values of Amide I components assigned to antiparallel beta-sheet were found by T-FTIR indicating no in-plane orientation, while ATR-FTIR revealed R values indicating significant out-of-plane orientation of β-sheet crystallites for blend films with C/(A+C)>0. SFM microscopy showed larger needle-like fibrillar structures for C/A blend films, while C-A copolymer films revealed smaller fibrillar or spherical structures correlating with the lower orientation obtained by ATR-FTIR.

CPP 37.3 Thu 10:15 H 0111

Exploring deposition conditions for antibacterial thin films via GISAXS measurements — •Joanne Neumann[1,2], Maria J Garcia[1,3], Holger Sondermann[1,3], Matthias Schwartzkopf[1], and Michael Martins[2] — [1]DESY, Photon Science, Notkestr. 85, D-22607 Hamburg — [2]UHH, Physics Department, Luruper Chaussee 149, D-22607 Hamburg — [3]CSSB, Center for Structural Systems Biology, Notkestr. 85, D-22607 Hamburg

During the last decades, the rate of multiresistant microbes against antibiotics increased dramatically. Moreover, biofilm-based contaminations complicate cleaning procedures and require cost-intensive methods in industrial processes. In this context, Pseudomonas aeruginosa (PA) is one of those bacteria that forms biofilms at liquid/air interfaces as a protective shell, e.g. against antibiotics. To investigate the influence of nanostructured silver layers as antibacterial coatings on the initial bacterial growth, we employed micro-focused Grazing incidence Small Angle X-ray Scattering (GISAXS) as a very surface-sensitive X-ray-based method providing structural information about electron density distributions. In our experiments we characterized PA biofilms, grown under different deposition conditions at the P03 beamline at Petra III / DESY.

CPP 37.4 Thu 10:30 H 0111

Colored CNC films reflect left and right circular polarized light. — •Silvia Vignolini — MPI Colloids and Interfaces Potsdam DE

The chiral self-assembly of nanoscale building blocks is a universal phenomenon that demonstrates the emergence of large-scale structures from the properties of individual sub-units. In many self-organising colloidal systems, such as cellulose nanocrystals (CNC), the emergence of chirality in the mesophase can be correlated to the properties of the building blocks and is therefore necessarily fixed. CNC chiral nematic suspensions are, in fact, always left-handed, giving rise when dried, to colored films reflecting only circular left-polarized light. In this talk, I will review some tricks that can be used to achieve CNC-colored films with circular right-polarized light reflection.

CPP 37.5 Thu 10:45 H 0111

Tailoring morphologies of protein-templated titania nanostructures — •Linus F. Huber[1], Stephan V. Roth[2], Manuel E. Scheel[1], and Peter Müller-Buschbaum[1,3] — [1]TUM School of Natural Sciences, Chair for Functional Materials, 85748 Garching, Germany — [2]Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, 22607 Hamburg, Germany — [3]TUM, MLZ, 85748 Garching, Germany

Biotemplating is an effective technique for structuring hybrid inorganic-organic materials at the nano scale. This method facilitates the fine-tuning of material characteristics such as porosity and structure sizes. Therefore, parameters like the electronic conductivity can be adjusted for different applications. This work focuses on titania thin films with different structures, for their application in thermoelectric generators. Beta-lactoglobulin, a bovine whey protein, serves as a template in the sol-gel synthesis process. The Seebeck effect allows the conversion of waste heat into electrical energy. This research aims to address the scarcity, toxicity, and costliness of current state-of-the-art thermoelectric materials. To investigate the morphologies of titania, a combination of in situ GISAXS, GIWAXS, and SEM techniques are used. In particular, in situ GISAXS printing allows for a time-resolved exploration of the structure formation, domain sizes, and domain distances.These observed structural differences are subsequently correlated with measurements of the Seebeck coefficient, electrical conductivity and optical properties.

CPP 37.6 Thu 11:00 H 0111

Sustainable photonic glass pigments from brush block copolymers — •Zhen Wang[1], Ruiting Li[2], Richard Parker[1], and Silvia Vignolini[1,2] — [1]Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK — [2]Department of Sustainable and Bio-inspired Materials, Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Potsdam, Germany

Growing societal concerns over microplastic pollution and resource sustainability is driving the pigment industry to search for sustainable alternatives. One promising avenue is block copolymer (BCP), which is known to self-assemble into structurally coloured materials. However, its real-world application has been hindered by limited exploration into the suitability of biocompatible and (bio)degradable monomers. In this talk we will show that biocompatible BCPs can be self-assembled within emulsified microdroplets, which upon drying form microparticles with a porous photonic glass architecture. The colour from these pigments can be tuned by either the BCP properties or the fabrication conditions. Finally, the relationship between the microparticle morphology and its optical response was investigated for BCPs with similar composition but different thermal behaviour. This revealed the formation mechanism for the porous structure and allowed for a strategy to enhance colour purity.

15 min. break

CPP 37.7 Thu 11:30 H 0111

Reservoir computing with organic fiber networks — •Richard Kantelberg, Anton Weissbach, Peter Steiner, Peter Birkholz, Hans Kleemann, and Karl Leo — Technische Universität Dresden, Dresden, Germany

Reservoir computing (RC) is a promising paradigm for machine learning that utilizes dynamic systems, known as reservoirs, to process and analyze complex temporal data. Organic mixed ionic electronic conductors (OMIECs) have emerged as a novel class of materials with intriguing properties, such as their ability to exhibit both electronic and ionic conductivity, as well as their biocompatibility, flexibility, and low power consumption. These features make OMIECs particularly suitable for the development of unconventional computing architectures. Conducting fiber networks grown by field-directed polymerization have been proven to be a suitable candidate for, e.g., heartbeat or image classification tasks. However, the dependency between classification accuracy and device parameters is still rather unclear. We present recent findings interlinking electronic conductivity, system nonlinearity and reservoir size with the neuromorphic functionality and RC performance. The recent progress in reservoir computing using organic mixed ionic electronic provides valuable knowledge for the targeted development of fiber reservoirs. Given these findings, we are confident to further increase the classification accuracy by adopting the system to specific application scenarios, paving the way to future commercialization.

CPP 37.8 Thu 11:45 H 0111

Paper Fibers Beyond Saturation: μ-CT Analysis of Prolonged Structural Changes — •Maximilian Fuchs[1,2], Raimund Teubler[1,3], Daniel Kollreider[1,2], Maximilian Grillitsch[1,2], Ekaterina Baikova[1,2], and Karin Zojer[1,2] — [1]Institute for Solid State Physics, Graz University of Technology, Austria — [2]Christian Doppler Laboratory for Mass Transport through Paper — [3]Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Austria

The uptake of water or dimethylsulfoxid (DMSO) by a cellulose-lignin based fiber network, in this case paper, is a complex interplay between capillary transport and sorption of these polar volatiles into the fibers. Microcomputed tomography (μ-CT) allows us to correlate this uptake with changes in the microstructure, with water and DMSO being offered either as a liquid or additionally via the gas phase to prevent capillary uptake. A pore network analysis of the 3D images shows that uptake from liquid and gas cause similar initial structural changes, although the fiber space and pore space between the fibers swells to different extents. Interestingly, fibers and pores continue to expand long after mass uptake from gas phase has ceased. This long-lasting expansion is most likely caused by an increasing amount of detached fibril bundles in the fiber wall.

CPP 37.9 Thu 12:00 H 0111

Microgels for Enhanced Adsorption of Endothelial Cells on Artificial Networks — •Souraj Mandal and Regine von Klitzing — Soft Matter at Interfaces, Department of Physics, Technical University of Darmstadt, Darmstadt 64289, Germany

In human physiology, endothelial cells (ECs) form a lining inside blood vessels, which is essential for cell maturation and the development of capillary vessels. However, replicating this process ex vivo, especially ensuring the adequate adherence of ECs to the surfaces of 3D-printed artificial networks, presents a significant challenge. In this study, we focus on designing an effective mediator between the inner wall of the artificial network and endothelial cells that would remain mechanically stable against the flow of the nutrient solutions for cell maturation. Our strategy involves the use of Poly(N-isopropylacrylamide) (PNIPAM) microgels (MGs) as mediators for cell culturing surfaces. To enhance their attachment, we synthesized charged MGs and tested their adhesion on plasma-treated silicon (Si), glass, and 3D-printed polymeric surfaces. The MG particles were characterized based on their Zeta potential and hydrodynamic radius. To achieve rapid deposition, we employed spin coating to form a thin polymeric layer of MG particles on the substrates. We conducted atomic force microscopy (AFM) analyses and observed stable adhesion of MG particles on flat surfaces, even after water washing and exposure to mechanical stress. Moreover, we observed that these MG coatings yield superior endothelial cell adhesion and spreading compared to non-coated substrates.

CPP 37.10 Thu 12:15 H 0111

A Computational Investigation into the Oxidation of Cytosine Epigenetic Modifications — •Vasilii Korotenko[1] and Hendrik Zipse[2] — [1]Forschungszentrum Jülich, IEK-9 — [2]LMU München, Fakultät für Chemie und Pharmazie

Studying the (aut)oxidation of 5-methylcytosine (5mC) is crucial for understanding the dynamic control of DNA methylation - a pivotal epigenetic modification linked to gene expression, cellular differentiation, and disease development. In this work, the oxidizing properties of oxygen-centered radicals and the reducing properties of epigenetically modified cytosines were studied. The O-H bond dissociation energies BDE(O-H) were calculated for various alcohols using selected theoretical methods. BDE(C-H) and pKa values have been calculated for various oxidation product of 5mC. Special attention was paid to the equilibrium of the hydration reaction of 5-formylcytosine (5fC), because the corresponding hydrate product can be very easily oxidized. All this together allowed us to propose and thermodynamically evaluate the mechanism of the 5mC (aut)oxidation reaction. The (aut)oxidation of 5mC is unlikely to occur through initiation by triplet dioxygen or through unimolecular decomposition of hydroperoxides. In the proposal mechanism, neural molecules react with free radicals, transferring hydrogen atoms to create products with higher BDE values. The thermodynamics of the presented mechanism agrees with the experimental kinetics. We assume that the protonation (pH $<$ 7) of oxidizable nucleic acids inhibits the (aut)oxidation process by increasing the BDE(C-H) values.

CPP 37.11 Thu 12:30 H 0111

Arylazopyrazole Amphiphiles as New Candidates for Photo-Induced Drug Delivery — •Ipsita Pani, Michael Hardt, Dana Glikman, and Björn Braunschweig — Institute of Physical Chemistry, University of Münster, 48149 Münster, Germany

Photo-responsive materials have been extensively explored to meet the demands for high precision drug delivery. Azobenzene-based amphiphiles have been the focal point of research in photo-responsive drug delivery systems. However, most azo amphiphiles suffer from low thermal stabilities of the cis-isomer. Consequently, the drug carriers are subjected to prolonged and periodic UV irradiation of high intensity for the release of the encapsulated drug. Therefore, the design of nanocarriers for light-induced drug delivery demands innovations to achieve targeted release at low intensities and short exposure times of the UV irradiation. Arylazopyrazoles (AAPs) have emerged as novel photoswitches with superior thermal stability of the cis-isomer and photo-stationary states (>90%) for trans/cis photo-isomerization in both directions.[1,2] In this contribution, we report on the potential of an anionic AAP surfactant (octyl arylazopyrazole butyl sulfonate) as a micellar nanocarrier for doxorubicin which is the most widely used anti-cancer drug. Using surface specific tools such as surface tensiometry and vibrational sum-frequency generation (SFG) spectroscopy we demonstrate the UV-induced release of doxorubicin at the air-water interface, while the release of doxorubicin in aqueous solution is studied by UV-visible and fluorescence spectroscopy. [1] Hardt et al. *Langmuir* **2023**, 39, 5861 [2] Honnigfort et al. *Chem. Sci.* **2020**, 11, 2085

CPP 37.12 Thu 12:45 H 0111

Untangling the stabilizing effects of proteins as foaming agents — •Kevin Gräff[1], Sebastian Stock[1], Luca Mirau[1], Sabine Bürger[1], Larissa Braun[1], Annika Völp[2], Norbert Willenbacher[2], and Regine von Klitzing[1] — [1]Soft Matter at Interfaces, Technische Universität Darmstadt, Darmstadt, Germany — [2]Institute of Mechanical Engineering, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Foams appear in many applications such as in personal care products, firefighting and food technology. Macroscopic foams consist of air bubbles separated by foam films. Therefore, it is crucial to untangle electrostatic, steric and network stabilization effects in foam films to understand macroscopic foam properties. We compare globular proteins (β - lactoglobulin and bovine serum albumin), a flexible protein (whole casein) and lupine protein isolate with varying solution pH. In a Thin Film Pressure Balance (TFPB) we use image intensity measurements to record spatially resolved disjoining pressure isotherms and to gain information about structure formation. We introduce feature tracking as a novel method to measure the interfacial mobility and stiffness of foam films. Around the isoelectric point, stable Newton Black Films (NBFs) for the globular proteins form in contrast to the unstable NBFs for the flexible proteins due to different characteris-

tics of the network structures. To evaluate the foam films impact on macroscopic foams, we use a Bikerman cell to measure foam parameters (e.g. foamability). Small Angel Neutron Scattering (SANS) on macroscopic foams completes the picture.