# CPP 9: Biopolymers and Biomaterials (joint session with BP)

Time: Tuesday 9:30-13:00

Invited TalkCPP 9.1Tue 9:30H 1058Surface topology effect on cell interaction at the nanoscale— •GIUSEPPE BATTAGLIA — Department of Biomedical Science, The<br/>University of Sheffield, Sheffield, UK

One of the most important classes of synthetic systems for creating self-assembled nanostructures is amphiphilic block copolymers. By controlling the architecture of individual molecules, it is possible to generate nanostructures either in an undiluted melt or in solution. These ordered nanostructures are tunable over a broad variety of morphologies, ranging from discrete micelles and vesicles to continuous network structures. Their synthetic nature allows the design of interfaces with different chemical functional groups and geometrical properties. This, in combination with molecular architecture, determines the levels of ordering in self-organizing polymeric materials. Such an effective control is extremely beneficial when it comes to design materials that have to interact with biological systems. I will be discussing how block copolymers can be used for the design of nanoscopic vectors that go across different biological barriers from the thick tissues to the very cell interior to deliver therapeutic agents and/or diagnostic probes. Similarly exploiting the facile interface engineering of block copolymers I will show how these can be used to design functional interfaces for polymeric scaffolds for cell and tissue engineering.

#### CPP 9.2 Tue 10:00 H 1058

Molecularly imprinted conductive polymers for controlled trafficking of neurotransmitter at solid-liquid interfaces — •NEELIMA PAUL<sup>1,2</sup>, MARKUS MUELLER<sup>1</sup>, AMITESH PAUL<sup>3</sup>, ELKE GUENTHER<sup>4</sup>, IVER LAUERMANN<sup>1</sup>, PETER MÜLLER-BUSCHBAUM<sup>2</sup>, and MARTHA CH. LUX-STEINER<sup>1</sup>—<sup>1</sup>Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — <sup>2</sup>TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str. 1, 85747 Garching, Germany — <sup>3</sup>TU München, Physik-Department, LS Neutronenstreuung, James-Franck-Str. 1, 85748 Garching, Germany — <sup>4</sup>Natural and Medical Sciences Institute at the University of Tübingen, Markwiesenstr. 55, 72770 Reutlingen, Germany

The state of the art approach to restore sight in certain cases of blindness is the replacement of the damaged photoreceptors by a subretinal implant consisting of light-sensitive photodiodes . We suggest to chemically stimulate the neurons by replacing the photodiodes in the subretinal implant by a molecularly imprinted polymer (MIP), imprinted with a neurotransmitter, such as glutamate. By controlling the neurotransmitter trafficking across a solid-liquid interface with voltage, we show the possibility of using this MIP for chemical stimulation of retinal neurons. ATR-FTIR spectroscopy and XPS has been used to chemically confirm the imprint of neurotransmitter in the MIP at the solid-liquid and the solid-air interface respectively. Fluorescence spectroscopy using the dye, fluorescamine, has been used to monitor the changes in neurotransmitter concentration in various solvents.

## CPP 9.3 Tue 10:15 H 1058

Excitation energy transfer processes in coupled phycobiliprotein complexes of A. marina and semiconductor nanocrystals forming hybrid structures — •FRANZ-JOSEF SCHMITT<sup>1</sup>, EVGENY MAXIMOV<sup>3</sup>, PATRICK HÄTTI<sup>2</sup>, VITHIYA JEYASANGAR<sup>2</sup>, JÖRN WEISSENBORN<sup>2</sup>, VLADIMIR PASCHENKO<sup>3</sup>, HANS JOACHIM EICHLER<sup>2</sup>, THOMAS FRIEDRICH<sup>1</sup>, and GERNOT RENGER<sup>1</sup> — <sup>1</sup>Max Volmer Laboratory for Biophysical Chemistry — <sup>2</sup>Institute of Optics and Atomic Physics, Berlin Institute of Technology, Germany — <sup>3</sup>Department of Biophysics, M.V. Lomonosow Moscow State University, Russia

Pigment-protein complexes isolated from the photosynthetic apparatus provide functionally optimized nanoscaled devices for the construction of light driven operational units. The present work describes results obtained on hybrid systems consisting of CdSe quantum dots (QDs) with ZnS shell and different phycobiliproteins (PBPs) like hexameric phycoerythrin (PE), phycocyanin (PC), allophycocyanin (APC) and rod shaped PBP antenna complexes from the cyanobacterium Acaryochloris marina. The surface of the QDs is functionalised by covering with anionic and cationic groups leading to electrostatic contact with PBP. Excitation energy transfer (EET) from QDs to PBPs occurs with varying efficiency of up to 90 % for coupled QD/PBP hybrid complexes and is highly dependent on the temperature. The study with different Location: H 1058

QDs shows that the Förster Integral crucially determines the efficiency of EET while the electrostatic surface charge is of secondary relevance. Highly efficient EET and fluorescence enhancement of the acceptor was observed for particular stoichiometric ratios between QDs and PBPs.

CPP 9.4 Tue 10:30 H 1058

Neutron radiography study of water migration into casein micellar films — •EZZELDIN METWALLI<sup>1</sup>, HELEN E. HERMES<sup>2</sup>, ELBIO CALZADA<sup>3</sup>, STEFAN U. EGELHAAF<sup>2</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik-Department, LS Funktionelle Materialien, James-Franck-Str.1, 85748 Garching, Germany — <sup>2</sup>Physik der weichen Materie, Heinrich-Heine-Universität Düsseldorf, 40225 Düsseldorf, Germany — <sup>3</sup>Forschungsneutronenquelle Heinz Maier-Leibnitz, TU München, 85747 Garching, Germany

Casein, a milk protein, forms micelles with a radius of about 100-300 nm. Casein-protein based films are widely used as an adhesive for labeling glass bottles and other containers because of their superior mechanical stabilities in different humidities at temperatures between 2 and 40 C. This study demonstrates the use of neutron radiography as a viable method for the determination of the diffusion profile of water in casein films. The dry casein film is contacted with water and neutron radiographs are collected as function of elapsed time. Profiles of the water concentration are successfully measured by imaging. Two diffusion processes are observed: (a) fast diffusion with a decaying diffusion constant, resulting from water exchange with the hydration water bound to the casein proteins, and (b) slow and constant diffusion due to Fickian water transport into the voids and holes between the case in micelles and their aggregates in the porous film. Time evolution of the later diffusion process is compared with our recent GISANS investigation [1] of hydration behavior of case in thin films in water vapor. [1] Metwalli et al., Langmuir 25, 4124 (2009)

CPP 9.5 Tue 10:45 H 1058 Study of lipid and protein coatings on titanium surfaces by neutron scattering — •MAKSYM GOLUB<sup>1</sup>, REGINE WILLUMEIT<sup>1</sup>, BERENGERE LUTHRINGER<sup>1</sup>, FRANK FEYERABEND<sup>1</sup>, ERIC WATKINS<sup>2</sup>, DIETER LOTT<sup>1</sup>, VASYL HARAMUS<sup>1</sup>, BORIS TOPERVEG<sup>3</sup>, and ANDREAS SCHREYER<sup>1</sup> — <sup>1</sup>Helmholtz Zentrum Geesthacht, Geesthacht, Germany — <sup>2</sup>ILL, Grenoble, France — <sup>3</sup>Ruhr-University Bochum, Germany Permanent implants, e.g. using titanium and its alloy, are widely used and successfully implemented in medicine. To improve their performance lipid\*s covering is applied. The study of the structure of the phospholipid (palmitoyl-oleoyl-sn-glycero-3-phosphoethanolamine - POPE) layering under liquid conditions in presence of growth medium and Human Serum Albumin (HSA), which is the favourable condition for cell adhesion, would provide key parameters to understand the interaction between cells and lipid coated implants. Such a system was

measured by neutron reflectivity. Silicon crystals with a Ti layer (36 nm) on the top were covered by POPE lipids and measured at different conditions: D2O, D2O based growth medium and growth medium with protein i.e., HSA. A 2D detector was used for the data collection which allowed us to detect also the diffuse scattering which provides information about the lateral correlations in these films. The neutron reflectivity experiments enabled us to see the changes of layer structure due to adhesion of the protein and will be discussed here in detail.

CPP 9.6 Tue 11:00 H 1058

Adhesion of gecko setae reflects nanoscale differences in subsurface energy — •PETER LOSKILL<sup>1</sup>, JONATHAN PUTHOFF<sup>2</sup>, MATT WILKINSON<sup>2</sup>, KELLAR AUTUMN<sup>2</sup>, and KARIN JACOBS<sup>1</sup> — <sup>1</sup>Saarland University, Experimental Physics, D-66041 Saarbrücken, Germany — <sup>2</sup>Department of Biology, Lewis & Clark College, Portland, OR 97219, USA

Surface energies are commonly employed to determine the adhesive forces between materials. However, the component of surface energy derived from long-range forces, such as van der Waals forces, depends on the material's structure below the outermost atomic layers. Prior theoretical results and indirect experimental evidence suggest that the van der Waals energies of subsurface layers will influence interfacial adhesion forces. We discovered that nanometerscale differences in the oxide layer thickness of silicon wafers result in significant macroscale differences in the adhesion of isolated gecko setal arrays. Si/SiO<sub>2</sub> bi-

layer materials exhibited stronger adhesion when the  $SiO_2$  layer is thin (approx. 2 nm). To further explore how layered materials influence adhesion, we functionalized similar substrates with an OTS monolayer and again identified a significant influence of the oxide layer thickness on adhesion. Our theoretical calculations describe how variation in the silicon dioxide layer thickness produces differences in the van der Waals interaction potential, and these differences are reflected in the adhesion mechanics. Setal arrays employed as tribological probes provide the first empirical evidence that the 'subsurface energy' of inhomogeneous materials influences the macroscopic surface forces.

#### 15 min break

CPP 9.7 Tue 11:30 H 1058 Biocompatibility of Fe<sub>70</sub>Pd<sub>30</sub> ferromagnetic shape memory films for cell actuation — •UTA ALLENSTEIN<sup>1</sup>, YANHONG MA<sup>2</sup>, ARIYAN ARABI-HASHEMI<sup>2</sup>, STEFAN G. MAYR<sup>2</sup>, and MAREIKE ZINK<sup>1</sup> — <sup>1</sup>Division of Soft Matter Physics, Institute for Experimental Physics I, University of Leipzig, Germany — <sup>2</sup>Leibniz-Institut für Oberflächenmodifizierung e.V., Translationszentrum für Regenerative Medizin and Fakultät für Physik und Geowissenschaften, Universität Leipzig, Germany

Ferromagnetic shape memory alloys (FSMAs) are a very promising and highly applicable class of smart functional materials which show various interesting features, such as the induction of large reversible strains of several percent due to an external magnetic field at a moderate stress. These properties support the application as actuators or valves in biomedical devices, as well as bone prostheses. Of course in vivo implantation demands good biocompatibility and adhesion of different tissues to the material. Thus, our study investigated the cellular response in contact with single crystalline Fe<sub>70</sub>Pd<sub>30</sub> FSMA films on MgO substrates. The adhesive properties as well as the viability and proliferation of different cell types where tested on the substrates and tuned by coating the substrates with different adhesive materials, such as Fibronectin, Laminin and Poly-L-Lysin. Tests were carried out with NIH 3T3 mouse fibroblasts, MCF 10A human epithelial cells and primary HOB human osteoblasts. We show that these three cell types obtain the ability to adhere and proliferate well on Fe<sub>70</sub>Pd<sub>30</sub> FSMA substrates, demonstrating good biocompatibility of the films.

#### CPP 9.8 Tue 11:45 H 1058

Direct Laser Writing for Three-dimensional Biological Application — •BENJAMIN RICHTER<sup>1,2</sup>, ALEXANDRA GREINER<sup>1</sup>, CLEMENS FRANZ<sup>1,2</sup>, MARTIN WEGENER<sup>2,3,4</sup>, and MARTIN BASTMEYER<sup>1,2</sup> — <sup>1</sup>Zoologisches Institut, Karlsruher Institut für Technologie, 76131 Karlsruhe — <sup>2</sup>DFG-Center for Functional Nanostructures (CFN), Karlsruher Institut für Technologie, 76131 Karlsruhe — <sup>3</sup>Angewandte Physik, Karlsruher Institut für Technologie, 76131 Karlsruhe — <sup>4</sup>Institut für Nanotechnologie, Karlsruher Institut für Technologie, 76021 Karlsruhe

Direct laser writing (DLW) is a versatile technique to fabricate tailored three-dimensional (3D) cell-culture scaffolds in the micrometer to nanometer range. By sequential DLW of two different photoresists, composite-polymer scaffolds with distinct protein-binding properties are fabricated and selectively bio-functionalized thereafter. Cells cultured in these scaffolds selectively form cell-adhesion sites with the functionalized parts, allowing for controlling cell adhesion and cell shape in 3D \* forming the basis for future designer tissue-culture scaffolds. To go one step further photoactivation of 3D scaffolds might play an important role in the future. One application realized by using these two-component polymer scaffolds is measuring forces of cells in a three-dimensional environment. With our technique we can control the number, size, and geometry of adhesive cubes. The forces induced by a single cell onto the scaffolds are proportional to the bending of the beams.

### CPP 9.9 Tue 12:00 H 1058

Superparamagnetic Iron Oxide Nanoparticles as Radiosensitizer for Radiation Therapy — •ANJA SOMMER<sup>1</sup>, STEFANIE KLEIN<sup>1</sup>, LUITPOLD DISTEL<sup>2</sup>, and CAROLA KRYSCHI<sup>1</sup> — <sup>1</sup>Department of Chemistry and Pharmacy, Institute of Physical Chemistry I, University of Erlangen, Egerlandstr. 3, 91058 Erlangen, Germany — <sup>2</sup>Department of Radiation Oncology, University of Erlangen, Universitaetsstr. 27, 91058 Erlangen, Germany

Superparamagnetic iron oxide nanoparticles (SPION) have been widely used experimentally for numerous in vivo applications such as magnetic resonance imaging (MRI) contrast enhancement, hyperthermia and targeted drug delivery. we present the synthesis of surface-stabilized ultrasmall superparamagnetic iron oxide nanoparticles. In this contribution, we will report on functionalized SPION with sizes between 4 and 15 nm which were synthesized by alkine coprecipitation or thermal decomposition and subsequently coated with biocompatible acids. The differently stabilized SPION were fully characterized using HRTEM, XRD, SQUID, FTIR and Raman spectroscopy, XPS, TGA-MS and TGA-IR coupling and zeta potential measurements. Furthermore we present studies about their biocompatibility for cancer cell lines and their potential as radiosensitizer in radiation therapy.

CPP 9.10 Tue 12:15 H 1058 X-ray diffraction on biocomposite materials at high hydrostatic pressure — •Christina Krywka<sup>1</sup>, Roxana Ene<sup>2</sup>, SHIN-GYU KANG<sup>3</sup>, and MARTIN MÜLLER<sup>3</sup> — <sup>1</sup>Christian-Albrechts-Universität zu Kiel, Institut für Experimentelle und Angewandte Physik, Leibnizstr. 19, D-24098 Kiel — <sup>2</sup>Universität Leipzig, Fakultät für Physik und Geowissenschaften, Linnéstr. 5, 04103 Leipzig — <sup>3</sup>Helmholtz Zentrum Geesthacht, Max-Planck-Str. 1, D-21502 Geesthacht

The anisotropic compressibilites of the crystalline fractions of biocomposite materials (spider silk, silkworm silk, cellulose etc.) were analysed using wide angle X-ray scattering (WAXS) at moderate high pressure (0.01 to 0.5 GPa) using a hydrostatic high pressure cell. With this method, the compression moduli of the biocomposite materials were determined for the first time with high pressure resolution in a pressure range that corresponds to loads as they occur under natural conditions. Exemplarily, for spider silk the compression modulus of the nanocrystals is proven to be highest in the direction of intra-sheet hydrogen bonds. In addition, it is found that the applied pressure may increase the organization of the amorphous phase, indicated by a pressure enhanced diffraction ring.

CPP 9.11 Tue 12:30 H 1058

Subspecies of nacre protein "perlucin" favors binding to aragonite over binding to calcite microcrystals — •HANNA RADE-MAKER, MALTE LAUNSPACH, and MONIKA FRITZ — Institute for Biophysics, University of Bremen, Germany

Nacre is a compound material of calcium carbonate platelets and organic layers of chitin and proteins. The outstanding mechanical properties of nacre make it desirable to understand the details of the biomineralizing process. The calcium carbonate platelets in nacre show the crystal structure of aragonite and not of calcite. Therefore we are especially interested in proteins which favor binding to aragonite over binding to calcite. We adapted a simple detection method from Suzuki et al. [1] for this purpose.

In this work [2] biomineralizing proteins were chemically removed from the acid-insoluble matrix of nacre from *Haliotis laevigata* and incubated with aragonite and calcite microcrystals, respectively. The crystals were washed and then dissolved. SDS-PAGE of these solutions showed that one protein, a subspecies of perlucin, favors binding to aragonite crystals. This might be a hint that perlucin plays a key role in the biomineralization process.

[1] M. Suzuki et al., Science, **325** (5946), 1388-1390, 2009

[2] H. Rademaker and M. Launspach, Beilstein J. Nanotechnol., 2, 222-227, 2011

CPP 9.12 Tue 12:45 H 1058

Assessment of swelling driven actuation in a two-phase cellular material — •LORENZO GUIDUCCI<sup>1</sup>, YVES J. M. BRECHET<sup>2</sup>, PE-TER FRATZL<sup>1</sup>, and JOHN W. C. DUNLOP<sup>1</sup> — <sup>1</sup>Max Planck Institute of Colloids and Interfaces, Department of Biomaterials, Am Mühlenberg 1, Science Park Golm, Potsdam, Germany — <sup>2</sup>SIMaP-Grenoble Institute of Technology, Saint Martin d'Hères, France

Natural systems that are able to actuate -that is, generate stress/strain- have recently drawn the attention of scientific community. Examples include the seed dispersal unit of the wild wheat and stork's bill awn, which are able to crawl on the ground following the daily humidity cycle and the hydro-actuated unfolding of the ice-plant seed capsule.

In natural actuators, the extent of max elongation/forces depends on underlying microstructure, and swelling properties of the constituents: here we present a finite element (FE) simulation study that aims to assess the actuation performance -eigenstrains and effective stiffness at a certain swelling level- of an ideal two-phase cellular material. The eigenstrains assessment is rigorously performed simulating a tessellation of the bidimensional space with given unit cell. As observed in preliminary simulations of a finite patch of material with free boundaries, the resulting two-phase material deforms in a highly anisotropic way. For each value of swelling pressure, we get an equilibrated configuration of the unit cell that becomes the starting point for the calculation of the effective mechanical properties. Finally, we show that the FE results can be understood in terms of a simpler lattice spring model.