

O 31: Molecular Films: Properties and Preparation

Time: Tuesday 10:30–13:00

Location: WIL A317

O 31.1 Tue 10:30 WIL A317

Ultrathin poly(ethylene glycol) films as flexible platform for plasmonics and nanofabrication — NIKOLAUS MEYERBRÖKER and •MICHAEL ZHARNIKOV — Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

We present a novel approach to prepare ultrathin, biocompatible, hydrogel films based on cross-linking of multi-functionalized, star-branched poly(ethylene glycols) (STAR-PEGs) with tunable film thicknesses of 4-200 nm. The films revealed pronounced swelling behavior, which was fully reversible and could be precisely controlled. Additionally, they provided a high affinity to citrate-stabilized gold nanoparticles (AuNP) that could be adsorbed with high densities into the PEG matrix from an aqueous solution. These novel PEG/AuNP composite films offer interesting and potentially useful optical properties. Controlling the accessibility, swelling behavior, and biorepulsive properties of the PEG films lithographically, we prepared nanocomposite patterns of metal nanoparticles and fluorophores imbedded into the PEG matrix as well as protein-affinity patterns in protein-repelling background. Further, using electron beam lithography, we succeeded to fabricate a variety of different nanostructures. Finally, we demonstrated that the PEG films can be separated from the substrate and exist as ultrathin, biocompatible, free-standing membranes. These membranes possess high stability and exceptional elasticity. They can be used in transmission electron microscopy experiments on sensitive biological targets and as a new type of support for the characterization of nanoparticles.

O 31.2 Tue 10:45 WIL A317

X-ray spectroscopic analysis of the electronic structure of aqueous salt solutions — •YEKKONI JEYACHANDRAN¹, FRANK MEYER², ANDREAS BENKERT^{2,3}, MARCUS BÄR^{4,5}, REGAN WILKS⁴, MONIKA BLUM⁵, WANLI YANG⁶, FRIEDRICH REINERT², CLEMENS HESKE^{3,5}, LOTHAR WEINHARDT^{3,5}, and MICHAEL ZHARNIKOV¹ — ¹Angew. Phys. Chemie, Universität Heidelberg. — ²Exp. Phys. VII, Universität Würzburg. — ³Inst. Photon Sci. Synchr. Rad., Karlsruhe Institute of Technology. — ⁴Sol. Energy Res., Helmholtz-Zentrum Berlin. — ⁵Dept. Chem., University of Nevada Las Vegas. — ⁶Advanced Light Source, Lawrence Berkeley National Laboratory.

Modification of the molecular structure of water in the presence of ionic salts is of primary importance for a variety of chemical and biochemical processes. Advanced soft X-ray spectroscopic techniques, which provide information on the local electronic structure of molecules, can be used to probe such a modification. In this work, using a specially designed experimental setup, we studied the electronic structure of water molecules in aqueous alkali halide and calcium chloride solutions by non-resonant and resonant X-ray emission spectroscopy (XES). Significant changes in the characteristic emission spectra of water were observed at the variation of the salt concentration, with the extent and character depending on the size and valence state of the involved anions and cations. The observed spectral changes are discussed in terms of the disturbances of the hydrogen bond network of water molecules induced by the salts. These changes are accompanied by the changes in the electronic structure of water, which can be traced by XES.

O 31.3 Tue 11:00 WIL A317

Thermally induced defects in Langmuir-Blodgett films — JAN WEBER, ECKART HASSELBRINK, and •THORSTEN BALGAR — Fakultät für Chemie, Universität Duisburg-Essen, Germany

In recent years organic monolayers of long-chain aliphatic molecules are intensively discussed in the context of heterogeneous catalysis, microelectronics or biosensing since they allow for chemical tailoring of various surfaces.[1-3] In this context the inner structure of the monolayer regarding a proper chain alignment is of considerable interest. We have utilized vibrational sum-frequency generation spectroscopy (VSFG) to monitor the creation of conformational chain defects at elevated temperatures. Our study is focused on Langmuir-Blodgett monolayers of long-chain carboxylic acids on glass substrates.

[1] A. Corma and H. Garcia, *Adv. Synth. Catal.* 348 (2006) 1391[2] T. Balgar, S. Franzka, E. Hasselbrink and N. Hartmann, *Appl. Phys. A* 82 (2006) 15[3] F. Schreiber, *Prog. Surf. Sci.* 65 (2000) 151

O 31.4 Tue 11:15 WIL A317

Molecular level insights into diatom biomineralization — •HELMUT LUTZ¹, JOE BAI², ADRIENNE ROEHRICH³, MISCHA BONN¹, GARY DROBNY³, and TOBIAS WEIDNER¹ — ¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz — ²Oregon State University, Merryfield South 102A, Corvallis OR 97331 — ³University of Washington, Seattle, Washington 98195, United States

The nano-patterned silica shells of diatoms represent a remarkable example for biomineralization, a process controlled by protein*mineral interactions. Within the unicellular algae *Cylindrotheca fusiformis*, the silaffin proteins play a crucial role in the molecular biomineralization machinery. A specific repeat unit within the silaffin precursor protein, SSKKSGSYSGSKGSKRRIL (R5), precipitates silica-peptide nanoparticles out of a solution of silicic acid. We found that artificial peptides consisting of lysine and leucine (LK peptides) can mimic this capability of forming various biosilica structures. These peptides were designed to adopt helical or beta-sheet structures due to their hydrophobic periodicities and represent simple model systems to study the effect of protein folding on mineralization. In order to propose rational protein- and surface design rules it is essential to elucidate the driving force of the biosilification process. By means of surface sensitive techniques, e.g. sum frequency generation (SFG) we have studied the interactions of R5 and the LK peptides within biosilica composites and on silica surfaces.

O 31.5 Tue 11:30 WIL A317

Core-Level Spectroscopy Studies on Self-Assembly and Switching of Mixed Azobenzene Monolayers — •DANIEL PRZYREMBEL¹, THOMAS MOLDT¹, DANIEL BRETE¹, JOEL R. GOLDMAN², RAFAL KLAJN², CORNELIUS GAHL¹, and MARTIN WEINELT¹ — ¹Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — ²Department of Organic Chemistry, Weizmann Institute of Science, 76100 Rehovot, Israel

We have prepared mixed self-assembled monolayers (SAMs) containing photochromic azobenzene derivatives.[1] Besides this, our approach allows creating layers of, e.g., an 11-(4-(phenyldiazenyl)phenoxy)alkyl-1-thiol diluted with a C₁₂ alkane thiol on Gold(111) substrates from solution in a controlled way. Like this we obtained monolayers with tuneable packing density of the azobenzene units that are stable and durable under ambient conditions. Moreover, the attained increase in free volume around the chromophores in combination with efficient decoupling from the substrate yields reversibly switchable SAMs, responsive to ultraviolet and visible light. Here we present our results from investigating by means of core-level spectroscopies the self-assembly process and the photoswitching. The samples exhibit a complex mixing behaviour with preferential adsorption of one component; and we observed a changing degree of ordering depending on the time the samples are immersed during preparation. The measured changes due to photoswitching vary for different surface component ratios.

[1] D. Brete, D. Przyrembel, C. Eickhoff et al. *J. Phys.: Condens. Matter* 24, 394015 (2012).

O 31.6 Tue 11:45 WIL A317

Molecular Orientation and Excitonic Coupling in Photoswitchable Azobenzene-Based SAMs on Gold(111) — •THOMAS MOLDT¹, DANIEL BRETE¹, DANIEL PRZYREMBEL¹, JOEL R. GOLDMAN², RAFAL KLAJN², CORNELIUS GAHL¹, and MARTIN WEINELT¹ — ¹Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ²Department of Organic Chemistry, Weizmann Institute of Science, 76100 Rehovot, Israel

We present results of polarization-dependent UV/vis Differential Reflectance Spectroscopy (DRS) and Near Edge X-Ray Fine Structure (NEXAFS) spectroscopy measurements performed on mixed self-assembled monolayers (SAMs). The layers consist of 11-(4-(phenyldiazenyl)phenoxy)undecane-1-thiol (Az11) and dodecane-1-thiol (C12). The average orientation of the azobenzene moieties and the strength of the excitonic coupling between the chromophores depend on the component ratio in the SAM. Likewise, this influences the efficiency of the reversible photoswitching of the layer.

O 31.7 Tue 12:00 WIL A317

New Chemistry of Metal-Protein Systems: S-Layer Protein

Interaction with Copper and Iron under Ultra-High Vacuum — ●ANNA A. MAKAROVA^{1,2}, VERA S. NEUDACHINA³, ELENA V. GRACHOVA², LADA V. YASHINA³, ANJA BLÜHER¹, MICHAEL MERTIG¹, SERGUEI L. MOLODTSOV⁴, CLEMENS LAUBSCHAT¹, and DENIS V. VYALIKH¹ — ¹Technische Universität Dresden, Dresden, Germany — ²St.Petersburg State University, St.Petersburg, Russia — ³Moscow State University, Moscow, Russia — ⁴European XFEL GmbH, Hamburg, Germany

In recent years an increasing interest in the design of bio-metal hybrid structures and their application in electronics and robotics has led to a need of understanding of the mechanisms involved in chemical interaction between metals and biosystems under vacuum conditions. Herein by means of photoelectron spectroscopy we characterize interaction occurring between protein and technologically essential metals (copper and iron).

O 31.8 Tue 12:15 WIL A317

Hybrid organic-inorganic systems: metal nanoparticles (Au, Al and Ag) embedded into organic semiconductor thin film — ●OLGA MOLODTSOVA¹, IRINA ARISTOVA², OLEG VILKOV³, ANETTA PIETZSCH^{3,4}, MAXIM TCHAPLYGUINE⁴, SERGEY BABENKOV¹, VITALY KVEDER², and VICTOR ARISTOV^{1,2} — ¹HASYLAB at DESY, D-22607 Hamburg, Germany — ²Russian Acad. Sci, ISSP, Chernogolovka 142432, Russia — ³HZB für Materialien und Energie, BESSY II, D-12489 Berlin, Germany — ⁴Lund Univ, MAX-lab, S-22100 Lund, Sweden

Materials with a high on-off resistance ratio could become the basis for resistive random-access memory (RRAM). Such a storage class memory would revolutionize the information technology industry. One type of RRAM can be based on hybrid organic*inorganic systems, mainly consisting of inorganic nanoparticles (NP) blended into an organic matrix. The evolution of the morphology and the electronic properties of the hybrid organic-inorganic systems composed of aluminum, silver and gold NPs distributed in an organic matrix, CuPc and CuPcF₄, as a function of nominal metal content was studied by TEM and PES using synchrotron radiation. Strong difference in morphology and electronic properties were observed for aluminum nanoparticles self-assembled in a wide-gap organic semiconductor matrix if compare to gold and silver NPs in the same matrix. E.g., on the very first stage of aluminum deposition, aluminum atoms show strong chemical interaction with substrate atoms. Supported by RFBR grant N 13-02-00818.

O 31.9 Tue 12:30 WIL A317

The influence of annealing temperature on molecular structure on HOPG — PENG JIANG and ●MICHAEL HIETSCHOLD — Solid Surfaces Analysis Group, Institute of Physics, D-09107 Chemnitz, Ger-

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As an n-type organic molecule, F16CoPc film on HOPG is investigated by UV STM. The ultrathin molecular film is prepared by OMBE, and then annealed at 375K for 20min. The influence of temperature on molecular adsorbate structure is investigated in this work.

At submonolayer coverage, molecules form large areas with ordered arrangement, where the structure of HOPG can be considered as the template: F16CoPc employs hexagonal structure, with a unit cell of about 1.5nm.

After annealing at 375K, there are two new structures observed: unidirectional row structure and near-square structure with molecular unit cells characterized by side lengths of 1.3nm*2.2nm and 1.4nm*1.7nm and angles 91° and 95°, respectively. In addition, a new effect is found simultaneously: smaller protrusions appear at the original sites of some molecules, which form only after annealing; and some of them disappear later again after scanning. This effect happens only to single molecules in closed packed structures, such as hexagonal and square structure.

O 31.10 Tue 12:45 WIL A317

Biomimetic solid-supported polymer bilayer incorporated with natural membrane proteins — ●XIAOYAN ZHANG¹, WANGYANG FU², CORNELIA G. PALIVAN¹, and WOLFGANG MEIER¹ — ¹Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland — ²Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland

Lipid cell membrane is the most important interface in biological systems, which is able to selectively control the transport by their specific proteins. Reconstitution of membrane proteins in artificial membranes creates a platform for exploring their potential for pharmacological or biotechnological applications. Previously, we demonstrated amphiphilic block copolymer is a relatively stable substitute for a lipid and is able to be used as promising building blocks for artificial membranes with long-term stability and tailorable structural parameters. However, the insertion of membrane proteins has not previously been realized in a planar large-area, stable, and solid-supported artificial membrane. Herein we present our recent work on the first, preliminary model of a channel protein that is incorporated in block copolymer, tethered, solid-supported bilayer membrane (TSSBM). Unprecedented ionic transport characteristics that differ from previous results on protein insertion into planar, free-standing membranes, are identified. For the unique variation in conductance in a TSSBM, a model describing channel protein mediated ion transport was introduced. Our findings mark a change in understanding protein insertion and ion flow within natural channel proteins when inserted in an artificial TSSBM.