

O 88: Molecular Films

Time: Friday 10:30–12:45

Location: H38

O 88.1 Fri 10:30 H38

Chitosan conformation and its supramolecular complex with iodine on the silica surface — ●TETIANA PODUST, TETIANA KULIK, and BORYS Palyanytsya — Chuiko Institute of Surface Chemistry of the NAS of Ukraine, 17 General Naumov str., Kyiv, 03164, Ukraine

Nowadays there are a lot of studies are focused on developing different strategies of nanomaterials surface functionalization with biopolymer. Such studies are of great interest for answering fundamental questions and for solving various practical tasks. Among other materials nanooxides modified with polysaccharides are promising systems due to their high potential for biotechnology, medicine, water treatment, engineering of eco-friendly materials etc. Consideration in this talk will be given to organic-inorganic hybrid nanomaterials based on silicas modified with chitosan. It is desirable to expand number of techniques which allow determining fraction of bound segments (p parameter) that is a key parameter for adsorbed polymer. A new approach based on the temperature-programmed desorption mass spectrometry (TPDMS) data for estimation of the p parameter of chitosan adsorbed on the silica will be proposed. It will be described main features of silicas surfaces modified with chitosan and iodine using a combination of FTIR and UV-vis spectroscopy, SEM, particle size analysis and thermogravimetry. A discussion about chitosan polymeric chains conformation on the silica surface and supramolecular inclusion complex of iodine with surface-immobilized polysaccharide will be given.

O 88.2 Fri 10:45 H38

Characterizing the protein-surface interactions that control diatom biomineralization — ●JOE BAIO¹, ADRIENNE ROHRIG², MISCHA BONN¹, GARY DROBNY², and TOBIAS WEIDNER¹ — ¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany — ²University of Washington, Seattle, WA 98195

The formation of silica-based cell walls in marine, single celled organisms, is regulated by protein-mineral interactions. The diatom species *Cylindrotheca fusiformis* assembles supermolecular silica structures via proteins called silaffins. In a silicic acid solution, specific repeat units within this protein, SSKKSGSYSGSKGSKRRIL (R5), induce the formation of silica-protein composite nanoparticles. The protein-surface interaction that drives self-assembly is likely controlled by specific contacts between the surface atoms and key protein side chains. In this study, we characterized this R5-SiO₂ interaction by both near edge x-ray absorption fine structure (NEXAFS) spectroscopy and in situ sum frequency generation (SFG) spectroscopy. Two peaks within the amide I vibrational band of the SFG spectra, 1640 and 1670 cm⁻¹, indicate that the R5 peptide retains a beta sheet conformation when interacting with SiO₂. While details of the binding geometry of the single tyrosine within R5 is provided by the observed polarization dependence of the NEXAFS C1s to π^* transition related to the tyrosine's phenyl ring.

O 88.3 Fri 11:00 H38

self-assembled monolayers of partially fluorinated alkanethiols on gold and GaAs substrates — ●HAO LU¹, ANDREAS TERFORT², and MICHAEL ZHARNIKOV¹ — ¹Applied Physical Chemistry, Heidelberg University, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany — ²Institute for Inorganic und Analytical Chemistry, Frankfurt University, Max-von-Laue-Straße 7, 60438 Frankfurt, Germany

Self-assembled monolayers (SAMs) of partially fluorinated alkanethiols (PFAT) gained substantial attention during past years because of their rigidity, oleophobicity, thermal stability, and potential use as nanoscale corrosion inhibitors. To better understand and use these properties it is important to obtain information on the structure and organization of the PFAT monolayers. In this context, we studied SAMs of a series of the PFAT molecules with the variable length of the fluorocarbon chain, viz. CF₃(CF₂)_n(CH₂)₁₁SH (FnH₁₁SH, $n = 6, 8, \text{ and } 10$), on Au(111) and GaAs(001) by high resolution X-ray photoelectron spectroscopy, near edge X-ray absorption fine structure spectroscopy, and infrared reflection absorption spectroscopy. We demonstrate that FnH₁₁SH form highly ordered and densely packed self-assembled monolayers on both these substrates, which is mediated by the thiolate-substrate bond. The orientational order is high on both Au and GaAs but deteriorates

to some extent with the decreasing length of the fluorocarbon chain. This deterioration is more pronounced for GaAs which is intrinsically prone to degradation and oxidation and is, therefore, a quite sensitive substrate for molecular self-assembly.

O 88.4 Fri 11:15 H38

Modification of nitrile-terminated aromatic self-assembled monolayers by electron irradiation and related applications — NIKOLAUS MEYERBRÖKER and ●MICHAEL ZHARNIKOV — Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany

Here we describe the behavior of self-assembled monolayers (SAMs) of 4'-cyanobiphenyl-4-thiol (CBPT) on Au(111) upon electron irradiation. Under such a treatment, the aromatic framework of CBPT SAMs is laterally cross-linked while the nitrile groups, located at the SAM-ambient interface, are reduced to active amine moieties which can be used as docking sites for the coupling of other species. This makes CBPT monolayers as a promising system for conventional and chemical lithography as well as for nanofabrication. Along these lines, we demonstrate the preparation of complex polymer brushes, patterning of the underlying substrate, and fabrication of molecule-thin, free-standing membranes on the basis of CBPT SAMs. The balance between the application-favorable processes and defragmentation in these films is studied in detail and comparison to the well-established (for the relevant applications) system of 4'-nitrobiphenyl-4-thiols is performed. Taking CBPT SAMs as a model system, the effect of the energy of the primary electrons on the extent of the chemical transformation and cross-linking in substituted aromatic SAMs is investigated.

O 88.5 Fri 11:30 H38

Orientation and ordering in surface-bound DNA hybrids — CAITLIN HOWELL¹, YEKKONI LAKSHMANAN JEYACHANDRAN², PATRICK KOELSCH¹, and ●MICHAEL ZHARNIKOV² — ¹Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany — ²Applied Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

Films of surface-bound homo-oligonucleotides on gold were hybridized and characterized using x-ray photoelectron spectroscopy, near-edge x-ray absorption fine structure spectroscopy, and infrared reflection-absorption spectroscopy. First, the effect of rinsing after the hybridization step was studied. Further, the effects of target sequence mismatches and target length mismatches were investigated. The overall orientation of the probe and target strands was found to remain upright and relatively unchanged despite the presence of up to four sequence mismatches in the target strands, although the total number of hybrids decreased with higher numbers of mismatches. Upright probes were also observed in hybrids formed with targets of shorter length, with a greater number of hybrids present in these films as compared to those formed with longer targets. These results suggest that in DNA films of relatively high densities, such as those tested here, the presence of sequence or length mismatches in target strands does not result in a large disruption of orientation and ordering in surface-bound hybrids. This finding may be useful for nanotechnological applications or utilization of DNA microarrays for biosensing purposes.

O 88.6 Fri 11:45 H38

Thermal Influence on the Structure of Alkylsiloxane Monolayers examined by SFG-Spectroscopy — ●JAN WEBER, THORSTEN BALGAR, and ECKART HASSELBRINK — Fakultät für Chemie, Universität Duisburg-Essen, D-45117 Essen, Germany

As organic monolayers have very diverse characteristics they offer an interesting field of surface science. Especially alkylsiloxane monolayers are of interest because of their potential for modifying surfaces. Promising applications include wetting, fine-scale lithography or protection of metals against corrosion.

Alkylsiloxanes are known to form self-assembled monolayers (SAMs) that are stable under ambient conditions. Since many applications require compatibility with heating it is our goal to get a better understanding of alkylsiloxane SAMs on a molecular level at elevated temperature.

In this study we apply vibrational sum-frequency generation (SFG)

spectroscopy to an octadecylsiloxane (ODS) monolayer on a glass substrate using a picosecond laser system. This method is particularly suitable because its selective surface sensitivity. Our results are discussed with respect to temperature dependent chain disorder and orientation on the surface.

O 88.7 Fri 12:00 H38

Confinement of electrons in metal-coordinated and covalently bonded two dimensional nanoporous molecular networks — ●ANELIJA SHCHYRBA¹, SUSANNE MARTENS¹, CHRISTIAN WÄCKERLIN², TONI IVAS¹, JORGE LOBO-CHECA³, MANFRED MATENA⁴, LUTZ H. GADE⁵, MEIKE STÖHR⁶, and THOMAS A. JUNG² — ¹University of Basel, Switzerland — ²Paul Scherrer Institut, Switzerland — ³Spanish National Research Council (CSIC), Spain — ⁴Donostia International Physics Center (DIPC), Spain — ⁵Universität Heidelberg, Germany — ⁶University of Groningen, Netherlands

Two dimensional (2D) nanoporous networks are intensively studied for their capability to act as quantum wells confining the surface state of a suitable substrate like Cu(111) or for the study of host-guest assemblies. Structures which are stabilized by strong interactions (i.e. by metal-coordination or by covalent bond-formation) are of special interest as they are more stable and therefore better suited to host strongly interacting guest molecules without collapse, up to elevated temperatures. Herein, we review the strictly regular, hexagonal DPDI (4,9-diaminoperylene-quinone-3,10-diimine) network which is based on metal-coordination to proceed towards novel, irregular 2D nanopores based on covalent bond-formation. While the former allows even to observe the confined surface state by spatially averaging, angle-resolved photoemission since the same confinement is repeated over-and-over, the irregular pores are observed to lead to a whole collection of differently sized and shaped quantum wells.

O 88.8 Fri 12:15 H38

High Resolution Core-Level Spectroscopy of Molecular Switches at Silicon(111) Surfaces — ●DANIEL PRZYREMBEL¹, MICHAEL ÅXMAN PETERSEN², ANDREAS HEBERT², KAROLA RÜCK-BRAUN², and MARTIN WEINELT¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin — ²Institut für Chemie, Technische Universität Berlin

Si(111) surfaces, functionalised with organic molecular switches of the fulgimide[1] and dihydroazulene[2] (DHA) type, have been investigated by means of high resolution X-ray photoelectron spectroscopy (XPS). The versatile anchoring strategy involves first the attachment

of alkyl acid chains to the H-terminated Si(111) single crystal surface and second coupling of the molecular switches to these carboxyl linkers. This leads to very stable and durable self assembled monolayers (SAMs). The linker chain-density can be adjusted by mixing in inert alkyl chains. Thus the packing density of molecular switches becomes tuneable. All steps of the sample preparation have been monitored and their efficiency proven. Fulgimides are optically switchable between open and closed forms by irradiation with UV and visible light, DHA turns into its isomer vinyl heptafulvene (VHF) upon optical stimulation and reacts back thermally. The reversible switching of the molecules leads to small, reproducible modifications of the XP spectra, i.e. peak shifts and shape changes, only weakly affected by successive beam damage. A reduced packing density of molecular switches improves the switching efficiency. [1] Y. Yokoyama *Chem. Rev.* **2000**, *100*, 1717-1739; [2] J. Daub, T. Knöchel, A. Mannschreck *Angew. Chem.* **1984**, *96*, 980-981

O 88.9 Fri 12:30 H38

Determining excitation pathways in a hybrid metal-organic interface state using coherent 2D nanoscopy — M. AESCHLIMANN¹, T. BRIXNER², M. CINCHETTI¹, N. GROSSMANN¹, M. HENSEN³, C. KRAMER², P. MELCHIOR¹, W. PFEIFFER³, M. PIECUCH¹, C. SCHNEIDER¹, S. STEL¹, C. STRÜBER³, and ●P. THIELEN^{1,4} — ¹Fachbereich Physik and Research Center OPTIMAS, Technische Universität Kaiserslautern, Erwin-Schrödinger-Str. 46, 67663 Kaiserslautern, Germany — ²Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ³Fakultät für Physik, Universität Bielefeld, Universitätsstr. 25, 33615 Bielefeld, Germany — ⁴Graduate School Materials Science in Mainz, Staudinger Weg 9, 55128 Mainz, Germany

Coherent 2D nanoscopy combines the principle of conventional 2D spectroscopy with photoemission electron microscopy (PEEM). While 2D spectra are well suited for studying the dynamics of quantum states as well as interactions between them, PEEM allows for detection of the electrical near field of nano-structured samples with a resolution beyond the optical diffraction limit. We use coherent 2D nanoscopy to study the hybrid electronic state forming at the interface between cobalt and the organometallic complex tris(8-hydroxyquinolinato)aluminium (Alq3). We observe the excitation paths at such a hybrid metal-organic interface and monitor the subsequent electron dynamics in the hybrid interface state. The lateral resolution enables us to address small ensembles of quantum systems rather than large-scale averaging.