

O 13: Polymeric biomolecular films

Time: Monday 16:00–18:45

Location: MA 005

O 13.1 Mon 16:00 MA 005

Photoelectron Diffraction on SnPc/Ag(111) — ●MICHAEL GREIF, LUCA CASTIGLIONI, JÜRIG OSTERWALDER, and MATTHIAS HENGSEBERGER — Physik Institut, University of Zurich, Winterthurerstrasse 190, 8057 Zurich

Photoelectron diffraction is a method to monitor the atomic structure of surfaces. From the emitter site in the sample the photoelectron propagates as wave that is then coherently scattered by the neighboring atoms. The directly emitted and the scattered waves create interference fringes in the detector plane. By scanning all emission directions on top of the sample with the detector, a 2-D data set is recorded that gives structural information about the examined system.

In the presented work we investigated Tin-Phthalocyanine molecules (SnPc) on a Ag(111) surface with X-Ray photoelectron diffraction (XPD) and UV photoelectron diffraction (UPD). SnPc shows a well ordered wetting layer growth on a Ag(111) surface. Hence core levels of the Sn-Atom in the center of the molecule serve as well defined emitter sites for photoelectron diffraction experiments.

The diffraction patterns correspond to the structural environment around the Sn-Atoms. Comparing our measurements with simulations using single scattering calculations (SSC), we see indications of the conformational change that the SnPc molecules undergo upon adsorption. Additionally our measurements show the azimuthal orientation of the molecules with respect to the Ag(111) surface. Due to a higher probability of backscattering for low energy electrons, the UPD patterns also show contributions of the substrate structure.

O 13.2 Mon 16:15 MA 005

Core-energy level energy difference between the surface and bulk regions of organic semiconductor films — ●HIROYUKI YOSHIDA^{1,2}, EISUKE ITO³, MASAHIKO HARA³, NAOKI SATO¹, THOMAS ULES⁴, and MICHEL G. RAMSEY⁴ — ¹Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011 JAPAN — ²PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan — ³Flucto-Order Functions Research Team, RIKEN-HYU Collaboration Research Center, RIKEN Advanced Science Institute, 2-1 Wako, Hirosawa, Saitama 351-0198, Japan — ⁴Institute of Physics, Karl-Franzens University Graz, A-8010 Austria

There has been an argument whether the energy level determined by PES is difference between the surface and bulk regions for decades. The reason was that no appropriate experimental method has been available to distinguish the energy levels between the surface and bulk of materials.

We have recently developed a novel analytical method of the core level energies with depth resolution; X-ray photoemission spectra (XPS) are measured at multiple detection angles and the energy profiles are precisely analyzed using target factor analysis.

By applying this method to organic semiconductor thin films, we found that the core-levels of the first surface layer are different from those of the bulk by about 0.3 eV. The origin is also discussed from the systematical study on different organic materials.

O 13.3 Mon 16:30 MA 005

X-ray reflectivity measurements of lipid membranes at the water/oil interface — ●ANNIKA ELSÉN¹, LARS JOERGENSEN², KLAAS LOGER¹, BENJAMIN RUNGE¹, OLIVER H. SEECK³, BEATE KLÖSGEN², OLAF M. MAGNUSSEN¹, and BRIDGET M. MURPHY¹ — ¹Institute for Experimental and Applied Physics, CAU, Kiel, Germany — ²MEMPHYS, Department of Physics, Chemistry and Pharmacy, SDU, Odense, Denmark — ³PETRA III, DESY, Hamburg, Germany

For a better understanding of the function of biological membranes the arrangement of the lipids in the bilayer as well as the structural integration of the proteins, providing the functions of the membrane, has to be known. In a first attempt a biological membrane can be modelled with phosphocholine monolayers at the water/oil interface. Unfortunately the application of structure-sensitive techniques on membranes in such environment is limited. However, with X-ray diffraction techniques it is possible to obtain structural information on the membrane at the liquid/liquid interface on a sub-molecular scale. Here, we present X-ray reflectivity measurements of 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) and 1-palmitoyl-

2-oleoyl-sn-glycero-3-phosphocholine (POPC) monolayers at the water/perfluorohexane interface, the latter with different bulk concentrations, carried out at the new liquid interface scattering apparatus (LISA) at the beamline P08 (PETRA III, DESY). Preliminary results of the vertical monolayer structure at the interface will be presented, giving information on the arrangement of the lipids.

O 13.4 Mon 16:45 MA 005

Interaction of noble gas atoms and aromatic molecules with Au substrates: dispersion-corrected DFT calculations — ●UWE FRIEDEL and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

Dispersion-corrected density functional theory calculations provide a computationally efficient method to evaluate the adsorption properties of atoms and molecules that are bound via van der Waals forces to surfaces. We have used this approach to address the interaction of noble gas atoms and aromatic molecules with metal surfaces. First, the reliability of this approach has been validated by comparing it with high-quality quantum chemical calculations for small finite reference systems. The calculated adsorption energies are in good agreement with available experimental data. The relevance of our results with respect to the interpretation of images obtained with the scanning tunneling hydrogen microscope [1] are discussed.

[1] S. Tautz *et al.*, Direct Imaging of Intermolecular Bonds in Scanning Tunneling Microscopy, *J. Am. Chem. Soc.* **2010**, *132*, 11864-11865

O 13.5 Mon 17:00 MA 005

Controlling on-surface polymerization by hierarchical and substrate-directed growth — ●LEIF LAFFERENTZ¹, VOLKER EBERHARDT², CARLO DRI³, CHRISTINA AFRICH³, GIOVANNI COMELLI³, FRIEDRICH ESCH³, STEFAN HECHT², and LEONHARD GRILL¹ — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Department of Chemistry, Humboldt-Universität zu Berlin, Berlin, Germany — ³IOM-CNR Laboratorio TASC, Basovizza-Trieste, Italy

The on-surface synthesis of oligomers under ultra-high vacuum conditions has been intensely studied in the last years [1,2] as such processes allow the formation of stable covalently bound molecular structures on surfaces. However, so far all experiments relied on a one-step polymerization, which limits the control of the process and leads to rather simple architectures. Another issue that needs to be addressed is the reduction of defects, because covalent linking processes are typically irreversible and therefore lack a capability for self-repair. We present experiments that address these issues by employing a sequential connecting process, which achieves greater control of the network formation and reduces the number of defects. This novel approach opens the possibility for the formation of more sophisticated structures.

[1] Grill, L. *et al.* *Nat. Nanotechnol.* **2**, 687-691 (2007)

[2] Gourdon, A. *Angew. Chem.-Int. Edit.* **47**, 6950-6953 (2008)

O 13.6 Mon 17:15 MA 005

Bis(terpyridine) adsorption on graphite and graphene: Theoretical studies — ●DANIELA KÜNZEL and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

Bis(terpyridines) (BTPs) form various self-assembled monolayer structures on different surfaces such as graphite or graphene [1]. Their adsorption properties and the structure formation are of interest from a fundamental point of view and for possible applications. The ordered adsorption process is governed by strong van der Waals interactions between the BTP molecule and the surface and by weak intermolecular hydrogen bonds. Using dispersion-corrected DFT, the surface-adsorbate interaction of isolated molecules can be described accurately [2].

Interesting effects on the structure formation can occur when the surface shows periodic lateral variations on a larger scale in its properties. As an example, force field results addressing the BTP adsorption on a buckled graphene adlayer on Ru(0001) will be presented [3].

[1] C. Meier, D. Künzel *et al.*, *J. Phys. Chem. C* **2010**, *114*, 1268.

[2] D. Künzel, K. Tonigold, J. Kucera, M. Roos, H. Hoster, R.J. Behm, A. Groß *ChemPhysChem* **2011**, *12*, 2242.

[3] M. Roos, D. Künzel, B. Uhl, H. Huang, O.B. Alves, H. Hoster, A. Groß, R.J. Behm *J. Am. Chem. Soc.* **2011**, *133*, 9208.

O 13.7 Mon 17:30 MA 005

Structure-property relation in oligoethylene glycol terminated alkanethiol monolayers under electron irradiation as applied to specific and non-specific protein adsorption —

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We investigated the possibility to use electron irradiation for the controlled modification of the protein-repelling and protein-affinity properties of oligoethylene glycol (OEG) terminated alkanethiol (AT) monolayers. The modifications were induced either directly by electron irradiation or in combination with the successive exchange reaction with the molecular substituents bearing special anchor group for protein adsorption. The direct irradiation treatment allowed for controlled non-specific adsorption of proteins, whereas the irradiation-promoted exchange reaction (IPER) enabled their controlled specific adsorption. Combining these two approaches with lithography, we fabricated both non-specific and specific protein patterns of various shapes, including gradient ones, on different length scales. The specific protein adsorption relied on well-known biotin-avidin interaction, utilising biotinylated-OEG-AT molecules as the substituents in IPER. Potential applications of gradient protein patterns for cell adhesion and mobility analyses, as well as novel strategies for multi-protein patterning by a combination of direct writing and IPER will be discussed.

O 13.8 Mon 17:45 MA 005

Biocompatible Nanomembranes based on PEGylation of Cross-Linked Self-Assembled Monolayers —•NIKOLAUS MEYERBRÖCKER¹, ZI-AN LI², WOLFGANG ECK¹, and MICHAEL ZHARNIKOV¹ — ¹Angewandte Physikalische Chemie, 69120 Heidelberg, Germany — ²Fakultät für Physik und Center for NanoIntegration, Universität Duisburg-Essen, 47048 Duisburg, Germany

Self-assembled monolayers (SAMs) represent an efficient means to modify the properties of surfaces by covering them with an uniform monomolecular layer. Because of weak intermolecular interactions, SAMs cannot exist without a substrate as support. However, if these films consist of an aromatic framework, they can be laterally cross-linked by electron irradiation and persist as a freestanding membrane after the removal from the substrate. If, additionally, nitro-substituted aromatic molecules are used, they can be not only cross-linked by the irradiation but also reduced to reactive amines which can serve as binding sites for further species. As such species we used poly(ethylene glycols), which made the resulting bilayer protein-repelling. Using this approach, we prepared an ultrathin, mechanically stable and protein-repelling membrane which can be used as highly transparent support in transmission electron microscopy (TEM). Whereas the low Z character and ultimate thinness (ca. 5 nm) of this support guarantees high imaging quality, protein-repelling ensures the lack of protein denaturing, which extend the possibilities of TEM experiments in their applications to sensitive biological targets.

O 13.9 Mon 18:00 MA 005

Mechanical Metamaterials —•TIEMO BÜCKMANN¹, NICOLAS STENGER¹, MICHAEL THIEL², CHRISTOPH EBERL³, TOBIAS KENNERKNECHT³, and MARTIN WEGENER^{1,2,4} — ¹Institut für Angewandte Physik und DFG-Center for Functional Nanostructures (CFN), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany — ²Nanoscribe GmbH, 76344 Eggenstein-Leopoldshafen, Germany — ³Institute for Applied Materials, Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany — ⁴Institut für Nanotechnologie (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany

Auxetic materials attract attention due to their mechanical properties for over 100 years. These advanced materials with negative Poisson's

ratio have recently gained special interest. State-of-the-art fabrication techniques allow for greater design freedom and systematic investigation. We consider the characteristics and the design of structured polymeric materials with the aim to create three-dimensional (3D) mechanical metamaterials with negative Poisson's ratios. 3D models of different structures are simulated with finite-element methods using the software package Comsol Multiphysics. Samples of relevant geometries with sizes between tens of micrometers and 0.3 millimeters are fabricated using direct laser writing (DLW). Arbitrary 3D manufacturing offered by DLW allows for tuning the Poisson's ratio of the material. The fabricated mechanical metamaterials are well structured, show a high degree of translational symmetry, and maintain fidelity to the blueprint over the extent of the entire structure.

O 13.10 Mon 18:15 MA 005

Reaction mechanism of debromination on coinage metals —•JONAS BJÖRK¹, FELIX HANKE², and SVEN STAFSTRÖM¹ — ¹Linköping University, Sweden — ²University of Liverpool, UK

Covalent bonded molecular networks can be formed through self-assembly on various surfaces. A successful approach has been to use molecular building blocks with specific hydrogen atoms replaced by bromine atoms. The bromine atoms can split-off, allowing covalent coupling between the un-saturated carbon atoms. However, despite the experimental success in the field, there is a lack of theoretical understanding of covalent self-assembly. In particular, a coherent picture is lacking for the temperature dependence of the debromination reaction and the adsorption properties of reactants and products.

Here, we present a theoretical study of the debromination on the close-packed (111)-facets of coinage metals, commonly used in covalent self-assembly. Within the framework of van der Waals density-functional theory, and using bromobenzene as model component for the debromination, the catalytic activities of the Au, Ag and Cu surfaces are compared. It is found that the reactions are described by similar mechanisms on all surfaces, in that the C-Br dissociation follows an almost identical path and that there are no radical products. The reaction proceeds easiest on the Cu(111) surface, while it is associated with the largest energy barrier on Au(111). Finally, the consequences of the energy barriers on the temperature dependence for each surface will be discussed.

O 13.11 Mon 18:30 MA 005

Molecular polymerisation on a stepped surface —•ALEX SAYWELL¹, JUTTA SCHWARZ², STEFAN HECHT², and LEONHARD GRILL¹ — ¹Department of Physical Chemistry, Fritz-Haber-Institute of the Max-Planck Society, Berlin, Germany — ²Department of Chemistry, Humboldt University, Berlin, Germany

On-surface reactions have the potential to provide new synthetic routes for the production of novel molecular species. In such reactions the surface is likely to play a more complex role than simply functioning as a flat, inert support. Step edges and defect sites of catalytic surfaces are considered as 'active sites' for chemical reactions.[1] Probing a surface with atomic resolution allows site specific information to be obtained about the structure and location of these active sites.[2]

Here we investigate the influence of the step edges of the Au(10,7,7) surface on a model chemical system, with respect to the catalytic activity of the step edges and the adsorption geometry of monomer units and polymer chains. Low temperature UHV-STM provides the spatial resolution to identify catalytic sites and facilitates the characterisation of molecular structures. Our results demonstrate that the Au(10,7,7) surface possesses catalytically active sites, and that the local geometrical structure of these sites plays an important role in the on-surface chemistry. The step edges also provide a template for highly orientated polymers formed via the on-surface reaction.

[1] Taylor, H.S. *Proc. R. Soc. London Ser. A* **108**, 105-111 (1925).[2] Vang, R.T. *et al. Chem. Soc. Rev.* **37**, 2191 (2008).