

Surface Science

Room: N - Session SS2-ThM

Electron Activated Molecular Interfaces

Moderator: S.L. Tait, Indiana University

8:00am SS2-ThM1 Thermal Effects of Templated C₆₀ Ordered Structures on AnCA, B. Xu, Yanshan University, China

Anthracene carboxylic acid (AnCA) forms multiphase self-assembly structures on Ag(111). Two of these multiphase structures were employed to investigate the template effects on sequentially deposited C₆₀ molecules using scanning tunneling microscopy. At low C₆₀ coverage, fullerene molecules tend to occupy Ag step edge or AnCA domain boundary sites. With increasing C₆₀ deposition, strong modulation on C₆₀ growth was observed depending on the initially AnCA structures. C₆₀ can either pair into dimers and locate on top of AnCA molecules with the periodicity determined by the underneath AnCA (Interface I), or form small phase-separated C₆₀ and AnCA domains with the width of tens of nanometers (Interface II). Anneal these interfaces at 370 K lead to the desorption of most of the AnCA molecules and the formation of novel C₆₀ structures. For Interface I, the second layer C₆₀ molecules are organized into ordered dimers on top of the first layer zigzag C₆₀ chains running along Ag[1-10] direction. The distance between neighboring zigzag C₆₀ chains is 2 nm, and there are some AnCA molecules left between the zigzag chains to hold the structure stable. For Interface II, parallel C₆₀ chains along Ag[11-2] are observed after annealing. The C₆₀ molecules are close packed along the chain direction and separated by *c.a.* 1.3 nm between neighboring chains. The molecules have alternative heights across the chain direction, suggesting distinct molecular orientations. Our studies suggest a pathway of nanostructure fabrication through the choice of suitable template and annealing treatment.

8:20am SS2-ThM2 Porphyrin Adsorption on Copper Single Crystal Electrodes Studied by SXPS, S. Breuer, D.-T. Pham, University of Bonn, Germany, G. Cherkashinin, T. Meyer, Technical University of Darmstadt, Germany, P. Broekmann, University of Berne, Switzerland, K. Wandelt, University of Bonn, Germany

Porphyrins are well known as biologically active molecules, e.g. as heme in hemoglobin or chlorophyll in green leaves. Their biological functions originate from their redox activity, which makes their investigation in an electrochemical environment interesting. We have investigated the electrochemically deposited monolayers of Tetra-methylpyridinium-porphyrin (TMPyP)-Tetratosylat on chloride and sulphate precovered Cu(100) and Cu(111) surfaces by means of Cyclic Voltammetry (CV), in-situ ElectroChemical Scanning Tunneling Microscopy (EC-STM) as well as ex-situ X-ray Photoelectron Spectroscopy with synchrotron radiation S-XPS at the SoLiAS-station at BESSY II. This station allows the electrochemical preparation of the surfaces and a quick and contamination-free transfer into UHV. The electrochemical preparation includes the formation of the anion preadsorption in diluted hydrochloric- or sulphuric-acid, respectively, and the adsorption and emersion of the porphyrin layer at different potentials within the doublelayer regime.

While the preadsorbed anion layers, i.e. c(2x2) Cl⁻ on Cu(100), (√3x√3)R30°-Cl⁻ on Cu(111), quasi-(√3x√7)R30°-SO₄²⁻ on Cu(111) and a disordered SO₄²⁻-layer on Cu(100), bind the TMPyP-cations electrostatically to the surface variation of the electrode potential causes structural transitions within the selfassembled porphyrin layers, as seen with EC-STM. The S-XPS N(1s) spectra enable a clear correlation of the structural changes with concomitant redox-transition of the TMPyP-cations. As a result structural transitions within the ordered TMPyP-layers are most likely due to different lateral electrostatic interactions between different TMPyP-redox states.

8:40am SS2-ThM3 STM and XPS Study on the Reactive versus Non-Reactive Adsorption of Viologens, D.-T. Pham, C. Safarowsky, S. Huemann, S. Breuer, University of Bonn, Germany, R. Hunger, Technical University of Darmstadt, Germany, P. Broekmann, University of Berne, Switzerland, K. Wandelt, University of Bonn, Germany

The reactive and non-reactive adsorption of redox-active viologens (1,1'-disubstituted-4,4'-bipyridinium molecules) on a chloride modified copper electrode has been studied using a combination of cyclic voltammetry (CV), in-situ scanning tunneling microscopy (STM) and ex-situ photoemission techniques. Two prototypes of viologens, 1,1'-dibenzyl-4,4'-bipyridinium molecules and 1,1'-diphenyl-4,4'-bipyridinium molecules (abbreviated as DBV and DPV respectively), are studied here with respect to their redox

behaviour upon adsorption on a chloride modified copper surface. DBV molecules can be adsorbed and stabilized on a chloride modified Cu(100) electrode surface in their di-cationic state at potentials above the main reduction wave in the cyclic voltammogram. Electrostatic attraction between the solvated viologen di-cations and the anionic chloride layer is the main driving force for the DBV adsorption onto the electrode surface. By reducing the adsorbed dicationic DBV²⁺ species to the corresponding radical mono-cation DBV^{•+}, a quasi-reversible phase transition is initiated from a "cavitand" to a "stripe pattern" phase on the chloride layer. Analysis of the N1s and O1s core level shifts of the adsorbed DBV molecules points to a non-reactive DBV adsorption leaving the DBV²⁺_{ads} solvation shell partly intact. The laterally ordered DBV²⁺_{ads} monolayer is highly hydrophilic with at least 8 water molecules per viologen present within this cationic organic film. The analysis of the Cl2p core level shift reveals that no other chloride species is present on the surface than the one underneath the organic molecules in direct contact with the metallic copper surface.

DPV²⁺ molecules are much more reactive upon adsorption and cannot be stabilized on the electrode surface in di-cationic state, at least within the narrow potential window of copper. The N1s core level shift points to DPV²⁺ molecules which are upon adsorption instantaneously reduced to the corresponding mono-reduced DBV^{•+}_{ads} species even at potentials above the main redox wave in the voltammogram. This process leads to the formation of a highly hydrophobic monolayer film with polymeric DBV^{•+}_{ads} stacking chains as the characteristic structural motif.

9:00am SS2-ThM4 Interfacing Electrocatalytic Molecules with Vertically Aligned Carbon Nanofibers through Click Chemistry: An Approach to "Smart", Highly Functional Nanostructures, E.C. Landis, R.J. Hamers, University of Wisconsin, Madison

Vertically Aligned Carbon Nanofibers are a unique form of nanoscale carbon comprised of graphene cups nested together to form a nanofiber. A unique feature of VACNFs is that they expose large amounts of graphene edge-planes along the nanofiber sidewalls. The high electron transfer rates associated with edge plane graphite suggest that VACNFs should be an excellent support for electrocatalysis. However, nanofibers alone lack the specificity often desired in electrochemical reactions. We have developed a method for covalently binding redox active molecules to the VACNF surface based on "click" chemistry as a pathway toward combining the high stability of VACNFs with the selectivity provided by molecular redox-active groups. This binding method creates a highly stable linkage of VACNFs to a 'smart' ligand with well defined redox properties. Using XPS, FTIR, and other surface analytical methods in conjunction with electrochemical measurements, we have investigated how the nanoscale structure of the fibers and the nature of the surface ligands impacts the surface chemistry and subsequent electron transfer processes. Our results demonstrate that the graphitic edge-plane sites of VACNFs play a key role in the chemical reactivity of VACNFs and in the subsequent electron-transfer processes on VACNFs functionalized with redox-active groups. These results demonstrate that VACNFs are a promising material for functional nanostructures using covalently tethered molecular catalysts.

9:20am SS2-ThM5 Fabrication of a Full-Coverage Polymer Nanobrush on Electron-Beam-Activated Monomolecular Template, S. Schilp, N. Ballav, M. Zharnikov, University of Heidelberg, Germany

Along with chemistry, morphology is an important tool to adjust properties of surfaces and interfaces. One of the most promising approaches to control over surface morphology down to the nanometer scale is the fabrication of 3D polymer brush patterns by surface-initiated polymerization (SIP) combined with electron beam lithography (EBL). However, polymer brush patterns made by EBL-SIP are chemically inhomogeneous. Whereas the polymer brush itself is comprised of a polymer, the areas between the 3D features have a different chemical identity determined by the original template. As a result, the effects of morphology on one side and chemistry and surface energy on the other side can be entangled when using such patterns as model surfaces for, e.g., biology-inspired research. Here, we show that this drawback can be overcome by using a sophisticated primary template comprised of monomolecular film with mostly deactivated amino tail groups suitable for SIP. Whereas SIP on such a template gives a thin, homogeneous "background" brush, the regeneration of these groups by electron beam activation lithography promotes the controlled growth of 3D polymer features on this background, resulting in the formation of chemically homogeneous morphology pattern exclusively comprised of the polymer material. The technique relies upon commercially available compounds and requires a comparably low patterning dose. Using a biologically relevant polymer, poly-N-isopropylacrylamide, as a test system, we demonstrated the fabrication of both complex gradient-like

brushes and marine-mammals-skin-inspired surfaces on the electron-beam-engineered monomolecular templates.

9:40am **SS2-ThM6 Self-assembled Monolayers as Templates for Electrochemical Nanotechnology**, *C. Shen*, University of St Andrews, UK, *C. Silien*, University of Limerick, Ireland, *M. Buck*, University of St Andrews, UK

Electrochemistry and self-assembled monolayers (SAMs) are a versatile combination as, on the one hand, SAMs can be used as templates to control electrochemical processes whereas electrochemistry, on the other hand, allows manipulation of SAMs [1,2].

Within this context underpotential deposition (UPD) of metal, i.e. intercalation of a metal monolayer at the SAM-substrate interface, is particularly interesting as this alters the electrochemical stability of a SAM. However, to exploit this for a controlled manipulation of SAMs on the nanoscale it is mandatory to use SAMs of very high quality in order to eliminate uncontrolled metal UPD caused by defects in a SAM [3]. In our experiments we use a class of thiol SAM whose molecules are characterized by the combination of a rigid aromatic moiety with an aliphatic spacer. Forming layers of high structural perfection defects are then introduced in a controlled way by

local modification of a SAM using, for example, the tip of a scanning tunneling microscope. By this means UPD of metal and subsequent modification of the SAM can be controlled on a length scale ranging from micrometers down to nanometers.

[1] Thom, I.; Hähner, G.; Buck, M. *Appl. Phys. Lett.* 87, 024101 (2005).

[2] Oyamatsu, D.; Nishizawa, M.; Kuwabata, S.; Yoneyama, H. *Langmuir* 14, 3298 (1998).

[3] Silien, C.; Buck, M. *J. Phys. Chem. C* 112, 3881 (2008).

10:40am **SS2-ThM9 XPS and AFM Characterization of Two Component Self-Assembled Monolayers on Au(111)**, *M.H. Cheng, T. McIntire, R.L. Grimm, J.C. Hemminger*, University of California, Irvine

Water uptake on organic films is of great importance in a number of fields. We have used two-component alkanethiol self-assembled monolayers (SAMs) to prepare surfaces with varied hydrophilic character. These surfaces have been used to study water uptake as a function of hydrophilic/hydrophobic character. The chemical composition and morphology of the two two-component alkanethiol self-assembled monolayers on Au(111) were characterized by x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Gold films on glass were prepared by piranha cleaning and *in vacuo* argon ion sputtering yielding carbon- and oxygen-free surfaces. Solution-phase chemistry forms a two-component SAM comprised of the octanethiol and 6-mercaptohexanoic acid. These components were selected for comparison with previous research in our laboratory regarding the interaction and temperature-programmed desorption (TPD) of water from organic surfaces of tuned hydrophobic and hydrophilic character. The ratio of the O(1s) to the Au(4f) peak areas in the XPS quantify the relative fraction of the carboxylic acid-terminated thiol in the SAM. The XPS spectra indicate that the relative fraction of the two thiol components in the surface adsorbed SAM phase does not correspond to the relative solution-phase concentrations. By comparison with water thermal desorption experiments, we discuss the implications for the interaction of water with methyl-terminated and carboxylic acid-terminated organic surfaces and partially-oxidized organic aerosol.

11:00am **SS2-ThM10 Vacancy Diffusion in Self-Assembled Organic Monolayers and its Role as a Roughening Mechanism in Organic/Organic Interfaces**, *C. Urban, D. Ecija, M. Trelka*, Universidad Autonoma de Madrid, Spain, *R. Otero*, UAM & IMDEA-Nano, Spain, *J.M. Gallego*, ICMM-CSIC, Spain, *N. Martín*, Universidad Complutense de Madrid, Spain, *R. Miranda*, UAM & IMDEA-Nano, Spain

Molecular diffusion on solid surfaces is of fundamental importance for surface chemistry and also because of the important role it plays in the formation of self-assembled molecular mono and multilayers. Many studies have discussed the diffusion processes of a single, isolated molecule on the surface and the self-assembly process in terms of molecule-molecule and molecule-substrate interactions, but the relevant kinetic aspects have mostly not been dealt with. In addition, the growth of organic multilayers of two different types of functional molecules (e.g. donor and acceptor or magnetic and non-magnetic) with enough structural perfection requires a knowledge of intermixing processes at interfaces not yet available and intimately related to vacancy diffusion.

We directly visualized the surface diffusion of molecular vacancies in monolayers of exTTF (2-[9-(1,3-dithiol-

2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole) self-assembled on Au(111) under UHV conditions. exTTF is a strong electron donor, and in

combination with PCBM, it has been shown to produce a phase-segregated, mixed layer with optimal morphology for bulk heterojunction solar cells [1]. When deposited on Au(111), exTTF molecules modify the substrate surface reconstruction and self-assemble to form long rectangular islands, the space between them being occupied by a sea of diffusing, non-nucleated molecules, which are very mobile even down to 150 K. The continuous exchange of molecules between the islands and this sea creates many vacancies within the islands. By means of a variable temperature fast-STM, we have quantified the diffusion of these vacancies within the islands. The results indicate a non-isotropic, Brownian-type diffusion. The implication of these results and the relevance of this diffusion mechanism for the exchange processes observed in the growth of exTTF-PCBM mixed layers and multilayers will be discussed.

[1] R. Otero, D. Ećija, G. Fernández, J.M. Gallego, L. Sánchez, N. Martín, R. Miranda, *Nano Letters* 7 (2007) 2602-2607.

11:20am **SS2-ThM11 Local Fluctuations in Organic Adlayers - a Quantitative Video-STM Study**, *M. Roos, T. Waldmann, H.E. Hoster, R.J. Behm*, Ulm University, Germany

Bis(terpyridine)derivatives (BTP) form highly ordered hydrogen-bonded networks on different substrates at solid surfaces.^{1,2} Using time resolved scanning tunneling microscopy we have studied selected dynamic phenomena in such adlayers on Au(111) and Ag(111) at around room temperature. Specifically, we have evaluated the mobility of defects in ordered adlayers, exchange of molecules between 2D phases of different local coverage and structure and fluctuations within disordered phases. Such data not only provide important information about typical rates in self assembly processes, but also give quantitative insights into molecular-scale aspects that govern the adlayer thermodynamics. Apart from the balance of molecule-molecule and molecule-substrate interactions, we find a surprisingly high influence of molecular entropy due to rotation and translation on the stability of the distinct phases. We will discuss the relevance of our findings for these particular model systems for the growth and stability of supramolecular structures in general.

¹ M. Roos et al., *Phys. Chem. Chem. Phys.* 9 (2007) 5672.

² H. E. Hoster et al., *Langmuir* 23 (2007) 11570.

11:40am **SS2-ThM12 From Self-Assembled Monolayers to 1 nm Thin Conducting Carbon Nanosheets**, *A. Turchanin, A. Beyer, Ch.T. Nottbohm, X. Zhang*, University of Bielefeld, Germany, *R. Stosch*, PTB-Braunschweig, Germany, *A. Sologubenko, J. Mayer*, University of Aachen, Germany, *P. Hinze, T. Weimann*, PTB-Braunschweig, Germany, *A. Götzhäuser*, University of Bielefeld, Germany

Whereas the fabrication of free-standing 0D and 1D nanomaterials like clusters, nanoparticles, nanowires, nanotubes etc. is well established at present, the fabrication of free-standing 2D materials with atomic thicknesses is not routine. In this contribution we present a route for the fabrication of novel ultrathin (~1 nm) free-standing carbon nanosheets with adjustable sizes based on molecular self-assembly. Self-assembled monolayers (SAM) of aromatic biphenyl molecules are first cross-linked by electrons [1]. Vacuum pyrolysis of the cross-linked films transforms them into a mechanically stable and conductive 2D graphitic phase consisting of nanosize graphene patches [2, 3]. Resistivity and stiffness can be tuned by the annealing temperature [3]. The transition from insulator to conductor (~100 kΩ/sq) is characterized by a variety of complementary spectroscopic and microscopic techniques (Raman Spectroscopy, XPS, UPS, NEXAFS, TDS, HTEM, STM, AFM). A plethora of applications of this novel material is visible taking advantage of the fact that size, shape, and resistivity of the nanosheets in supported and suspended states (nanomembranes) are easily controlled.

[1] W. Geyer, V. Stadler, W. Eck, M. Zharnikov, A. Götzhäuser, M. Grunze, *Appl. Phys. Lett.* 75, 2401 (1999)

[2] A. Turchanin, M. El-Desawy, A. Götzhäuser, *Appl. Phys. Lett.*, 90, 053102 (2007)

[3] A. Turchanin, A. Beyer, Ch. T. Nottbohm, X. Zhang, R. Stosch, A. Sologubenko, J. Mayer, P. Hinze, T. Weimann, A. Götzhäuser, *Adv. Mater.* 21, 1233 (2009)

Authors Index

Bold page numbers indicate the presenter

— B —

Ballav, N.: SS2-ThM5, 1
Behm, R.J.: SS2-ThM11, 2
Beyer, A.: SS2-ThM12, 2
Breuer, S.: SS2-ThM2, **1**; SS2-ThM3, 1
Broekmann, P.: SS2-ThM2, 1; SS2-ThM3, 1
Buck, M.: SS2-ThM6, 2

— C —

Cheng, M.H.: SS2-ThM9, 2
Cherkashinin, G.: SS2-ThM2, 1

— E —

Ecija, D.: SS2-ThM10, 2

— G —

Gallego, J.M.: SS2-ThM10, 2
Gözlhäuser, A.: SS2-ThM12, 2
Grimm, R.L.: SS2-ThM9, 2

— H —

Hamers, R.J.: SS2-ThM4, 1
Hemminger, J.C.: SS2-ThM9, 2
Hinze, P.: SS2-ThM12, 2
Hoster, H.E.: SS2-ThM11, 2

Huemann, S.: SS2-ThM3, 1

Hunger, R.: SS2-ThM3, 1

— L —

Landis, E.C.: SS2-ThM4, **1**

— M —

Martin, N.: SS2-ThM10, 2
Mayer, J.: SS2-ThM12, 2
McIntire, T.: SS2-ThM9, 2
Meyer, T.: SS2-ThM2, 1
Miranda, R.: SS2-ThM10, 2

— N —

Nottbohm, Ch.T.: SS2-ThM12, 2

— O —

Otero, R.: SS2-ThM10, 2

— P —

Pham, D.-T.: SS2-ThM2, 1; SS2-ThM3, 1

— R —

Roos, M.: SS2-ThM11, 2

— S —

Safarowsky, C.: SS2-ThM3, 1

Schilp, S.: SS2-ThM5, **1**

Shen, C.: SS2-ThM6, **2**

Silien, C.: SS2-ThM6, 2

Sologubenko, A.: SS2-ThM12, 2

Stosch, R.: SS2-ThM12, 2

— T —

Trelka, M.: SS2-ThM10, 2

Turchanin, A.: SS2-ThM12, **2**

— U —

Urban, C.: SS2-ThM10, 2

— W —

Waldmann, T.: SS2-ThM11, 2

Wandelt, K.: SS2-ThM2, 1; SS2-ThM3, **1**

Weimann, T.: SS2-ThM12, 2

— X —

Xu, B.: SS2-ThM1, **1**

— Z —

Zhang, X.: SS2-ThM12, 2

Zharnikov, M.: SS2-ThM5, 1