

O 53: Solid / liquid interfaces III

Time: Wednesday 15:00–16:45

Location: WIL C107

O 53.1 Wed 15:00 WIL C107

The adsorption and in situ characterization of viologen monolayers at copper/electrolyte interfaces. — ●EMILIA SAK¹, RALF TROFF², CHRISTOPH SCHALLEY², and KLAUS WANDEL¹ — ¹Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstr.12, 53115 Bonn, Germany — ²Institute Chemistry and Biochemistry, Free University of Berlin, Takustr.3, 14195 Berlin, Germany

Different redox-active 1,1'-Dibenzyl-4,4'-bipyridinium (or "viologen") molecules (DBV) adsorbed on a chloride - modified Cu(100) electrode have been studied by means of cyclic voltammetry (CV) and in-situ scanning tunneling microscopy (STM). At anodic potentials unsubstituted DBV forms a laterally well ordered quadratic array of dicationic "cavitand" ensembles which at negative potentials transform into a stripe phase of π -stacked monocation radicals. Likewise with Dimethyl-DBV (DMDBV) a pair of redox peaks P1/P1' (-305 mV / -240 mV) is found which is accompanied by a transition from a "cavitand" to a dimer phase. Quite in contrast, Tetramethyl-DBV (TMDBV) does not show redox peaks in CV and, accordingly, only a "cavitand" phase. Also the adsorption kinetics of all three molecules is significantly different, it slows down with increasing methylation.

O 53.2 Wed 15:15 WIL C107

Adsorption of TMPy-porphyrin on iodine-modified Pt(100) electrodes — ●KLAUS STALLBERG^{1,2} and WINFRIED DAUM^{1,2} — ¹Institute of Energy Research and Physical Technologies, TU Clausthal, Leibnizstr. 4, 38678 Clausthal-Zellerfeld — ²NTH School for Contacts in Nanosystems

The adsorption of free-base meso-tetra(N-methyl-4-pyridyl)porphyrin (TMPyP) cations on Pt(100)($\sqrt{2} \times 5\sqrt{2}$)I electrode surfaces in 0.1 M HClO₄ was studied in situ with STM and cyclic voltammetry (CV). To facilitate ordered porphyrin adsorption under electrochemical conditions, the Pt(100) surface was precovered with a monolayer of iodine. With a porphyrin surface coverage of 0.7 ML, ordered ($5\sqrt{2} \times 5\sqrt{2}$) superstructures were observed only on parts of the surface indicating a high mobility of the adsorbed molecules. Ordered porphyrin structures were preferentially detected on defect-free terraces but not at the line defects of specifically structured iodine adlayers [1]. The characterization of TMPyP adsorption by means of their pronounced redox current peaks in CV turned out to be complicated: CV experiments performed with porphyrin adlayers adsorbed under different experimental conditions suggest that initially adsorbed molecules may have a low 'redox activity' which increases in time. A possible relation of the increase of this activity with a protonation of TMPyP in acidic electrolytes will be discussed.

[1] B. Braunschweig et al., Surf. Sci. 603 (2009) 3361

O 53.3 Wed 15:30 WIL C107

Self-organized Porphyrin monolayers on iodine-modified noble metal surfaces — ●MICHAEL SCHNEIDER¹, THOMAS KOSMALA², and KLAUS WANDEL^{1,2,3} — ¹Institut für Physikalische Chemie und Theoretische Chemie, University of Bonn, Wegelerstr. 12 D-53115, Bonn, Germany — ²Institute of Experimental Physics, University of Wrocław, Maxa Barna 9, 50-204, Wrocław, Poland — ³Department of Physics, University of Rome Tor Vergata, Via Delle Ricerche Scientifica 1, 00133 Rome, Italy

In the field of template chemistry, new and interesting phenomena can be discovered at noble metal /electrolyte interfaces in the presence of anions and molecules as function of electrode potential. The spontaneous self-assembly of organic molecules is considered a promising *bottom-up* technique in nanotechnology to create surface patterns and electronic devices. Porphyrins, for example, are important organic compounds for potential applications in cancer therapy, or as catalysts and sensors. Halide-modified noble metal surfaces are suitable substrates due to their long range order. Moreover, iodide anion layers on Au(111)-surfaces show electrocompression and phase transitions depending on the electrode potential.

Our studies with in-situ STM and cyclic voltammetry not only reproduce previous works about Tetra(N-methyl-4-pyridyl)-porphyrin molecules (TMPyP) on iodide-modified gold and copper surfaces, but firstly reveal new TMPyP phases on gold not previously described, and secondly are extended to bimetallic Cu/Au surfaces providing new template properties.

O 53.4 Wed 15:45 WIL C107

Competing Phase Transition in Binary Viologen Layers on Cl/Cu(001) — ●MARTINO SARACINO¹, NGUYEN THI MINH HAI², PETER BROEKMANN², and KLAUS WANDEL¹ — ¹Institute of Physical and Theoretical Chemistry, Bonn University, Wegelerstr. 12, D-53115 Bonn — ²Interfacial Electrochemistry Group, Department of Chemistry and Biochemistry, Bern University, Freiestr. 3, CH-3012 Berne

In-situ STM and cyclic voltammetry are employed to analyze the competing adsorption of Diphenyl- (DPV) and Dibenzylviologen (DBV) on a chloride precovered Cu(001) surface. This model system for similar N-containing aromatic molecules is studied for the significant role of this type of organic and inorganic additives in metal plating processes. DPV²⁺ is reduced even at most anodic potentials to the monocationic radical DPV^{+•} and forms a full monolayer of a hydrophobic π -stacked stripe-phase, preventing the post-adsorption of the di-cationic DBV²⁺. Lowering the concentration of DPV in solution till only a sub-monolayer coverage with mono-cationic π -stacked DPV^{+•} stripes is obtained permits the co-adsorption of the less stable di-cationic DBV²⁺ in its characteristic quadratic cavitand structure next to the DPV^{+•} stripe-phase. Lowering the electrode potential to the DBV²⁺ reduction potential at -250mV_{RHE} leads first to a complete replacement of the more stable DPV^{+•} stripe-phase by a π -stacked stripe-phase of mono-cationic DBV^{+•}. The resulting proximity of DBV^{+•} stripes and DBV²⁺ cavitands now permits the decay of the cavitand-phase starting at the domain boundaries to the mono-cationic DBV^{+•} stripe-phase, which finally fully covers the whole surface.

O 53.5 Wed 16:00 WIL C107

co-operative adsorption of TMA-alcohol mixture controlled by sonication time — ●NGUYEN THI NGOC HA¹, THIRUVANCHERIL G. GOPAKUMAR², and MICHAEL HIETSCHOLD¹ — ¹Solid Surfaces Analysis Group, Institute of Physics, Chemnitz University of Technology, D-09107 Chemnitz, Germany — ²Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany

Trimesic acid (TMA) dissolved in alcoholic solvents shows linear pattern of straight-chain aliphatic alcohols co-adsorbed with TMA on highly oriented pyrolytic graphite (HOPG). According to literature the detailed structure of these patterns depends on the number of carbon atoms in the alkyl chain of alcohols, the so called odd-even effect. In odd alcoholic solvents, dimer rows of TMA molecules are interacting with interdigitating alcohol molecules in a nearly perpendicular (86°) manner with respect to the direction of the TMA tapes, and the alkane chains of alcohols oriented orthogonally with respect to HOPG surface. However, in aliphatic alcohols with even number of carbon atoms dimer rows of TMA interact with alcohol molecules with an angle of 64° and alcoholic molecules adsorbed parallel on HOPG surface. By adjusting the sonication time of TMA-alcohol mixture, here we show that the geometry of adsorption pattern, packing density etc. of TMA and alcohol molecules can be controlled within one type of alcoholic solvent.

O 53.6 Wed 16:15 WIL C107

Quantitative studies of adsorbate diffusion and interactions at Cu(100)-electrolyte interfaces by in situ Video-STM — ●ANDRIY TARANOVSKYY, SOPHIE GUÉZO, YAW-CHIA YANG, HISAYOSHI MATSUSHIMA, TUNAY TANSEL, and OLAF MAGNUSSEN — Institut für Experimentelle und Angewandte Physik, Universität Kiel, D-24098 Kiel, Germany

Quantitative data for adsorbate tracer diffusion and adsorbate-adsorbate interactions at solid-liquid interfaces were obtained from the analysis of high-speed in situ STM data [1,2]. Here we present a comparison of the results for lead, sulphur and methyl thiolate adsorbates on Cu(100) electrodes in 0.01 M HCl. Even though the mobility of these different adsorbate species can differ by one or two orders of magnitude, it exhibits a similar potential dependence, with the hopping rates increasing towards negative electrode potentials. This could be explained by the strong influence of the coadsorbate layer on the hopping process. Furthermore, the adsorbate-adsorbate interactions of sulphur and thiolate depend on the lattice direction, whereas those of lead are attractive for the nearest and next nearest sites, as expected

for metal adatoms.

[1] T. Tansel, O.M. Magnussen, Phys. Rev. Lett. 96, 026101 (2006).

[2] A. Taranovskyy, T. Tansel, O.M. Magnussen, Phys. Rev. Lett. 104, 106101 (2010).

O 53.7 Wed 16:30 WIL C107

Adsorption of phthalocyanine molecules on an iodide modified cu(100) electrode studied by means of in-situ stm and ex-situ xps — •THANH HAI PHAN¹, STEPHAN BREUER¹, UWE HAHN², THOMAS TORRES², and KLAUS WANDELT^{1,3,4} — ¹Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstr. 12, D-53115 Bonn, Germany — ²Departamento de Química Organica C-I-305, Universidad Autónoma de Madrid, Campus de Cantoblanco, 28049 Madrid, Spain — ³Institute of Experimental Physics, University of Wrocław, Maxa Born 9, 50-204, Wrocław, Poland — ⁴Department

of Physics, University of Rome Tor Vergata, Via Della Ricerca Scientifica 1, 00133 Rome, Italy

A combination of CV, in-situ STM and ex-situ XPS studies were performed to gain information about an iodide modified Cu(100) electrode surface exposed to an acidic electrolyte containing a redox-active phthalocyanine (abbreviated as [ZnPcPyMe]⁺⁴). In the CV, four single electron transfer steps were observed, which lead to the formation of tri-, di-, and mono-cations, respectively. The XPS data reveal not only the strong adsorption of molecules, but also the replacement of the zinc atoms by hydrogens. The well-ordered self-assembled adlayer of metal-free phthalocyanine seen in STM forms a (quasi) square-shaped lattice (angle of $92 \pm 2^\circ$, intermolecular distance of 19.5 \AA) which coincide neither with the iodide nor with the copper lattice underneath. A detailed molecular structure model is proposed in agreement with the experimentally observed pattern.