

O 60: Solid-Liquid Interfaces I: Structure and Spectroscopy

Time: Wednesday 15:00–18:00

Location: TRE Phy

O 60.1 Wed 15:00 TRE Phy

Investigation of the water structure at the (001) and (010) orthoclase surfaces with three-dimensional atomic force microscopy — ●FRANZISKA SABATH, RALF BECHSTEIN, and ANGELIKA KÜHNLE — Physical Chemistry I, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld

Feldspars are the most abundant minerals in the Earth's crust and belong to the most effective group of mineral ice nucleating particles (INP) in the atmosphere. In the crystal structure, potassium, sodium or calcium, among others, are incorporated as counterions in varying ratios. Potassium-rich feldspars are more effective INPs than the other feldspars. A representative of a potassium-rich feldspar is orthoclase. Unlike other INPs, such as silver iodide, the surfaces of feldspar do not have an ice-like structure. Therefore, it is interesting to know what other factors, such as hydroxyl groups on the surfaces or defect sites, are responsible for the high ice nucleating efficiency of K-feldspars. In particular, the water structure at the interface of K-feldspars is of interest. Here, we show the three-dimensional water structure at the two natural cleavage planes of orthoclase, the (001) and the (010) surfaces, using three-dimensional atomic force microscopy (AFM).

O 60.2 Wed 15:15 TRE Phy

Influence of substrate on supramolecular nanostructures at the solid-liquid interface — ●BAOXIN JIA¹, MIHAELA ENACHE¹, SANDRA MIGUEZ-LAGO², MILAN KIVALA², and MEIKE STÖHR¹ — ¹Zernike Institute for Advanced Materials, University of Groningen, Netherlands — ²Institute of Organic Chemistry, University of Heidelberg, Germany

Self-assembly of supramolecular nanostructures at the solid-liquid interface has gained increasing academic interest in past recent years. Substrates can influence molecule-substrate interactions, which plays an important role in determining supramolecular nanostructures. In this study, we used scanning tunneling microscopy (STM) to investigate the self-assembly of two carboxylic acids at the nonanoic acid-solid interface. We performed the experiments on four substrates: HOPG, MoS₂, Au(111), and graphene/Cu foil. We also measured the water contact angle of these four substrates to obtain some information on the molecule-substrate interaction. The STM measurements showed that, on HOPG and graphene/Cu foil, both carboxylic acids can form porous and close-packed structures, which depends on the bias voltage polarity during STM measurements. On MoS₂, both carboxylic acids did not form stable self-assembled structures. On Au(111), both carboxylic acids only formed short range-ordered structures in very diluted solutions. The results reveal that the interplay between molecule-substrate, solvent-substrate and molecule-molecule interactions is important to the formation of supramolecular nanostructures at the solid-liquid interface.

O 60.3 Wed 15:30 TRE Phy

Hydrophobic pockets on the hydrophilic In₂O₃(111) surface — CHRISTIAN RITTERHOFF¹, ●BERND MEYER¹, ULRIKE DIEBOLD², and MARGARETA WAGNER² — ¹Interdisciplinary Center for Molecular Materials and Computer Chemistry Center, FAU Erlangen-Nürnberg, Germany — ²Institute of Applied Physics, TU Wien, Austria

Clean oxide surfaces are generally hydrophilic. Water molecules anchor at undercoordinated surface cations that act as Lewis acid sites, and they are stabilized by H bonds to surface oxygens. However, for In₂O₃(111), DFT calculations predict a deviation from this general rule, which has been confirmed by TPD, XPS, STM and AFM experiments. In UHV, the first nine water molecules cover only a part of the unit cell. Within the H-bonded network three out of the nine water dissociate. Additional molecules pile up above the OH groups. The rest of the unit cell is unfavorable for adsorption and remains water-free, despite offering undercoordinated In and O sites. The first water layer thus shows ordering into nanoscopic 3D water clusters separated by hydrophobic pockets. Beyond UHV, our *ab initio* MD simulations of a liquid water layer demonstrate the robustness of the strongly hydrophobic behavior of this region in the unit cell.

[1] H. Chen, M.A. Blatnik, C.L. Ritterhoff, I. Sokolović, F. Mirabella, G. Franceschi, M. Riva, M. Schmid, J. Čechal, B. Meyer, U. Diebold, M. Wagner, ACS Nano, accepted, DOI: 10.1021/acsnano.2c09115

O 60.4 Wed 15:45 TRE Phy

Facet-dependent surface charge and hydration of SrTiO₃ nanoparticles at variable pH — ●IGOR SIRETANU, SU SHAOQIANG, BASTIAN MEI, DIRK VAN DEN ENDE, GUIDO MUL, and FRIEDER MUGELE — Physics of Complex Fluids and Photocatalytic Synthesis Groups, MESA+ Institute, Faculty of Science and Technology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

Anisotropy of shape and surface properties determine the functionality of faceted nanoparticles in various contexts including facet selective colloidal self-assembly, biosensing, improved photo/electrocatalytic activity and ions uptake. The characteristic surface properties and function of solid-liquid interfaces of crystalline faceted nanoparticles are believed to be essential for their performance but remains poorly understood and difficult to characterize and quantify. We use dual scale Atomic Force Microscopy to measure electrostatic and hydration forces of faceted SrTiO₃ nanoparticles in aqueous electrolyte at variable pH. We demonstrate (i) the ability to quantify strongly facet-dependent surface charges yielding isoelectric points of the dominant {100} and {110} facets that differ by as much as 2 pH units, ii) fluids composition controlled facet-dependent accumulation of oppositely charged (SiO₂) particles, and iii) that atomic scale defects can be resolved but are in fact rare for the samples investigated. Atomically resolved images and facet-dependent hydration structure suggest a microscopic hydration and charge generation mechanism.

O 60.5 Wed 16:00 TRE Phy

Watching Redox Activation of Gold for Water Electrolysis live: An in-situ Experiment at Home — CHRISTOPH GRIESSER, DANIEL WINKLER, TONI MOSER, ENGELBERT PORTENKIRCHNER, and ●JULIA KUNZE-LIEBHÄUSER — Institute of Physical Chemistry, University of Innsbruck, Innrain 52c, Innsbruck, 6020 Austria

A fundamental understanding of processes that take place at the solid/liquid interface is of utmost importance for a rational design of (electro-)catalysts, and key for advancing energy conversion and storage technologies. We could show with in-situ electrochemical near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) that metallic Au, in alkaline media, reversibly oxidizes to Au⁺ at potentials prior to and during the early oxygen evolution reaction (OER), while it reversibly oxidizes to Au³⁺ at potentials where the OER takes place at high rates. This has previously not been clearly demonstrated in-situ, so that the redox chemistry of Au in alkaline media remains a highly debated topic in the electrochemical community to date. We demonstrate the implementation of a simple, affordable and in-situ/operando- method to track dynamic processes taking place at the electrified solid/liquid interface, utilizing a lab-based NAP-XPS system with a conventional Al K α X-ray source. The method has the potential to become a gamechanger in applied (electro-)catalysis research, which makes our contribution appealing for scientists following either fundamental or applied research interests.

O 60.6 Wed 16:15 TRE Phy

Structure and Reactivity of an Ionic Liquid on Cu(111) investigated by Scanning Probe Microscopy, Photoelectron Spectroscopy and Simulations — RAJAN ADHIKARI¹, STEPHEN MASSICOT¹, LUKAS FROMM², ●SIMON JAEKEL¹, TIMO TALWAR¹, AFRA GEZMIS¹, MANUEL MEUSEL¹, ANDREAS BAYER¹, FLORIAN MAIER¹, ANDREAS GÖRLING², and HANS-PETER STEINRÜCK¹ — ¹Chair of Physical Chemistry II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany — ²Chair of Theoretical Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

We studied the adsorption and reaction behaviour of the ionic liquid (IL) 1,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([C₁C₁Im][Tf₂N]) on Cu(111) in UHV. Our nc-AFM and STM results show that the IL transitions from an ordered structure observed after annealing at 200 K into a different ordered structure and disordered islands after extended annealing at 300 K. Complementary, ARXPS reveals that the IL initially adsorbs intact and that no IL desorption occurs until 300 K but that a significant fraction of the IL is converted to a new species. We correlate the remaining unshifted peaks to the ordered phases observed in AFM and the shifted peaks to decomposition products, which appear as disordered islands. From DFT, we

obtain additional information on the structure of the ordered phases and the interaction of the IL with the substrate.

O 60.7 Wed 16:30 TRE Phy

Influence of Interfacial Water and Cations on the Oxidation of CO at the Platinum/Ionic Liquid Interface — ●BJÖRN RATSCHMEIER, GINA ROSS, ANDRE KEMNA, and BJÖRN BRAUN-SCHWEIG — University Münster, Institute of Physical Chemistry, Münster, Germany

CO oxidation is fundamental key for complete oxidation of small alcohols on Pt catalysts in fuel cells. So far, room-temperature ionic liquids (RTIL) have been used to modify the selectivity in electrocatalysis. In order to understand the mechanism of CO oxidation in RTIL we have investigated this reaction at the Pt(111)/1-butyl-3-methylimidazolium trifluorosulfonylimide [BMIM][NTf₂] electrode/electrolyte interface as a function of H₂O concentration and electrode potential using *in situ* sum-frequency generation (SFG) spectroscopy and infrared absorption spectroscopy (IRAS). Using SFG spectroscopy, we address the changes of CO molecules on Pt(111), while we monitor bulk electrolyte changes with IRAS using vibrational bands from H₂O, CO₂ and CO. The presence of water in [BMIM][NTf₂] shifts the CO onset potential by more than 200 mV with increased H₂O concentration from 0.01 to 1.5 M, which we relate to the incorporation and availability of water at the electrode/electrolyte interface. The nature of the RTIL cation has also a large effect on the surface excess of H₂O since RTILs which are prone to form closed-packed structures like [BMMIM][NTf₂] can block the incorporation of H₂O and lead to more sluggish CO oxidation with larger overpotentials and oxidation in a much broader potential.

O 60.8 Wed 16:45 TRE Phy

Resolving the structure of Cu(100) in iodine containing solutions — ●NICOLAS G. HÖRMANN, NICOLAS BERGMANN, KARSTEN REUTER, BEATRIZ ROLDÁN CUENYA, GEORG H. SIMON, and CHRISTOPHER S. KLEY — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

We present results from our joint experimental and theoretical effort to identify the structure of iodine adlayers on Cu(100) in electrochemical environment – a first step towards understanding the origin of the influence of iodine on the electrocatalytic carbon dioxide reduction (CO₂RR) on Cu. In particular, we resolve stable interface structures as a function of the potential by a detailed analysis of theoretical predictions from density functional theory calculations and *in-situ* EC-AFM measurements. These results are complemented by the comparison of experimental and theoretically simulated Cyclic Voltammograms [1,2], which provide additional information on electroadsorption reactions and thereby the interface composition as a function of the potential.

[1] N.G. Hörmann et al., *J. Chem. Theory Comput.* **17**(3), 1782-1794 (2021). [2] N.G. Hörmann et al., *J. Phys. Condens. Matter.* **33**, 264004 (2021).

O 60.9 Wed 17:00 TRE Phy

Non-Random Island Nucleation in the Electrochemical Roughening on Pt(111) — ●MARCEL ROST¹, LEON JACOBSE², and MARC KOPER³ — ¹Huygens-Kamerlingh Onnes Laboratory, Leiden University, Niels Bohrweg 2, 2333 CA Leiden, The Netherlands — ²Centre for X-ray and Nano Science CXNS, Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, D-22607 Hamburg, Germany — ³Leiden Institute of Chemistry, Leiden University, Einsteinweg 55, 2333 CC Leiden, The Netherlands

Many chemical surface systems develop ordered nano-islands during repeated reaction and restoration. Platinum is used in electrochemical energy applications, like fuel cells and electrolyzers, although it is scarce, expensive, and degrades.

During oxidation-reduction cycles, simulating device operation, nucleation and growth of nano-islands occurs that eventually enhances the dissolution. Preventing nucleation would be the most effective solution. However, little is known about the atomic details of the nucleation; a process almost impossible to observe.

Here, we analyze the nuclei-distance distribution mapping out the underlying atomic mechanism: a rarely observed, non-random nucleation takes place. Special, preferential nucleation sites that a priori do not exist, develop initially via a precursor and eventually form a semi-ordered Pt-oxide structure.

This precursor mechanism seems to be general, possibly explaining also the nano-island formation on other surfaces/reactions.

O 60.10 Wed 17:15 TRE Phy

Electrochemical re-structuring of the InP(100)-HCl interface monitored by operando reflection anisotropy spectroscopy — ●MARGOT GUIDAT^{1,2}, MARIO LÖW², DANIEL LÖRCH¹, VIBHAV YADAV¹, JONGMIN KIM^{1,2}, and MATTHIAS M. MAY^{1,2} — ¹Institute of Physical and Theoretical Chemistry, Universität Tübingen, Germany — ²Institute of Theoretical Chemistry, Universität Ulm, Germany

A possible way to achieve a low-carbon energy system consists of hydrogen production by photoelectrochemical water splitting. Here, III-V semiconductors play an important role due to their high solar-to-hydrogen efficiencies. However, surface corrosion limits the overall performance of photoelectrochemical devices. Studies have reported that interface functionalization is a way to protect the surface. In this work, we monitor the potential-dependent restructuring of the electrochemical InP(100) interface in HCl by operando reflection anisotropy spectroscopy (RAS) [1]. We investigate the effect of electrolyte concentration on the ordering and stabilization of the surface film formed at cathodic potentials. Computational RAS qualitatively supports the formation of an InCl_x layer. The latter is further investigated quantitatively with other characterization techniques. Fitting RA-transients measured under applied potentials with adsorption isotherm models gives insight into the lifetime of the involved processes and their adsorption energies. [1] Löw, M.; Guidat, M.; Kim, J.; May, M. M. *RSC Adv.* 2022, 12 (50), 32756-32764.

O 60.11 Wed 17:30 TRE Phy

A femtosecond resolved view of vibrationally assisted electron transfer across the metal/aqueous interface — ●ZHIPENG HUANG, MANUEL BRIDGER, OSCAR ANDRES NARANJO-MONTOYA, ALEXANDER TARASEVITCH, UWE BOVENSIEPEN, YUJIN TONG, and R. KRAMER CAMPEN — Faculty of Physics, University of Duisburg-Essen

Understanding heterogeneous charge transfer is crucial if we are to build the best electrolyzers, fuel cells and photoelectrochemical water splitting devices that chemistry allows. Since the elementary processes involved have characteristic timescales ranging from femto- to milliseconds, direct simulation of all relevant processes is not generally possible.

Here we demonstrate experimentally, using a novel two photon photovoltage approach, that for a prototypical system, a ferrocene terminate alkane thiol self-assembled monolayer (SAM) on gold in contact with aqueous electrolyte, charge transfer from the Au to the ferrocene can be induced by vibrational excitation of the ferrocene aromatic CH. Intriguingly the energy of the aromatic CH vibration, 0.38 eV, is a large fraction of the effective solvent interaction strength inferred for the ferrocene/ferrocenium system in prior electrochemical studies: 0.85 eV. Our results thus imply that, solvent may effect reduction/oxidation rates in electrocatalysis by coupling to a few, perhaps widely different in energy, vibrations. If shown to be generally true such a picture would suggest the necessity of moving beyond a single effective solvent interaction in theoretical descriptions of heterogeneous electron transfer.

O 60.12 Wed 17:45 TRE Phy

Dynamic Polymorph Formation of a Trimesic Acid Derivative at Solid-Liquid Interface — ●RICHA ARJARIYA¹, VIPIN MISHRA¹, GAGANDEEP KAUR¹, SANDEEP VERMA¹, MARKUS LACKINGER², and THIRUVANCHERIL G GOPAKUMAR¹ — ¹Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, UP-208016, India — ²Department of Physics, Technical University of Munich, James-Frank-Strasse 1, Garching 85748 and Deutsches Museum, Museuminsel 1, Munich 80538, Germany

In this work we show the self-assembly of a tricarboxylic acid derivative of trimesic acid (BTA) at heptanoic acid-, nonanoic acid-graphite interface. At both interfaces BTA forms a trimer based-self-assembly, super-flower (SF) pattern. The spontaneously formed SF pattern is observed to be dynamically converting to a dimer-based assembly, chicken-wire pattern (CW), at heptanoic acid-graphite interface while scanning. Interestingly, at nonanoic acid-graphite interface, SF pattern remains stable and not converted to CW pattern. We attribute that the formation energy of both SF and CW patterns is comparable. The difference in the stability of different patterns in heptanoic acid and nonanoic acid is most likely related to the solubility of BTA in these solvents.[1,2] 1) T. N. Ha, T. G. Gopakumar, M. Hietschold, *J. Phys. Chem. C*, 2011, 115, 21743. 2) M. Lackinger, S. Griessl, W. M. Heckl, M. Hietschold and G. W. Flynn, *Langmuir*, 2005, 21, 11, 4984-4988