O 34: Solid-Liquid Interfaces: Reactions and Electrochemistry - Experiment II

Time: Tuesday 10:30–12:15 Location: HSZ 101

Invited Talk O 34.1 Tue 10:30 HSZ 101
Self-Assembly at the Liquid/Solid Interface: Playing on the Nanoscale and Taming Molecules — •Manfred Buck — University of St Andrews, St Andrews, United Kingdom

The combination of intrinsic atomic precision with structural and functional versatility, and spontaneous assembly on surfaces make organic molecules essential components of a developing toolbox aimed at the routine access to the bottom end of the nanoscale. With options ranging from two-dimensional porous networks of flat lying to densely packed layers of upright standing molecules, thermodynamically and kinetically controlled processes at the liquid-solid interface (including the electrochemical interface) offer a rich playground for surface functionalisation, templating, and patterning on the ultrasmall scale. However, progress on the route to ultimately functional nanostructures will be critically dependent on how well we can control the energy landscape of molecular assemblies. This comprises both static and dynamic aspects and involves the spectrum of intermolecular and molecule-substrate interactions, diffusion processes, and boundary conditions imposed by a highly confined space. Presenting illustrative examples of our work which range from hierarchical assembly based on supramolecular networks to molecular monolayers involving metal-organic coordination, the talk will provide a critical account of achievements and challenges ahead.

O 34.2 Tue 11:00 HSZ 101
Low-frequency conductivity of clay suspensions: Electrokinetic potentials, surface conductance and counterion mobility — •Christian Weber[1], Helge Stanjek[2], and Markus Valtiner[1] — [1]Institut für Physikalische Chemie, TU Freiberg, Leipzigerstrasse 29, 09599 Freiberg — [2]Ton- und Grenzflächenmineralogie, Bunsenstrasse 8, 52072 Aachen

This work presents results on the low-frequency electric conductivity of kaolinite dominated clay suspensions. The theoretical interpretation of conductivity data is guided by the theory of O'Brien & Ward [1] which accounts for the non-spherical particle shape and surface conductance. Essential outcomes of the conductivity experiments are the surface conductance and electrokinetic potential. Alongside with the conductivity experiments the surface charge density of the particles has been measured under similar conditions. A correlation of the surface conductance and the surface charge density allows to estimate tangential counterion mobilities in the Stern layer and a consistency check of the conductivity interpretation.

References

[1] O'Brien R. W. & Ward D. N. (1988) The electrophoresis of a spheroid with a thin double layer. Journal of Colloid and Interface Science, 121(2), 402-413.

O 34.3 Tue 11:15 HSZ 101
Atomic-level electrochemical surface science of TiO$_2$ rutile (110) — •Matthias Müllner, Jan Balajka, Michael Schmid, Ulrike Diebold, and Stijn Mertens — TU Wien, Institut für Angewandte Physik, Wiedner Hauptstrasse 8-10/134, 1040 Vienna

The rational design of catalysts and other functional materials requires an atomic-level understanding of their structure and of the interface to supporting surfaces.

Here, we present an in situ electrochemical STM study of TiO$_2$ rutile (110) with atomic resolution. This is achieved using a new wet-chemical cleaning procedure for the substrate and with Pt-Ir tips. If tungsten tips are used, WO$_3$ is spontaneously formed at the tungsten liquid interface and strongly adsorbs on oxide surfaces below their point of zero charge through an electrostatic mechanism. The tungsten oxide forms 1D oligomers up to a coverage of one monolayer, and can be manipulated and nanopatterned in situ with the scanning probe tip. Under clean conditions, the TiO$_2$ rutile (110) surface shows a bulk-like, unreconstructed structure, which resembles its appearance in vacuum, even though the surface is probably fully hydroxylated.

O 34.4 Tue 11:30 HSZ 101
Ion Exchange: Reactions of Porphyrins on Oxides and in Liquids — •Ole Lytken[1], Matthias Franke[1], Quratulain Tariq[1], Daniel Wechsler[1], Julia Köbl[1], Norbert Jux[1], Hubertus Marbach[1], Hans-Peter Steinrück[1], Florencia Marchini[2], Federico Williams[2], Tao Wang[3], Cici Wang[3], Qian Xu[3], and Junfa Zhu[3] — [1]Universität Erlangen-Nürnberg — [2]University of Buenos Aires — [3]University of Science and Technology of China

Porphyrins and their analogues are large organic molecules that play significant roles in vivo, e.g. in light harvesting and photosynthesis (chlorophyll) and oxygen transport and storage in the blood cells of mammals (hemoglobin and myoglobin). In recent years the adsorption of porphyrins on metal surfaces has been studied extensively, but, despite the technological importance of oxides, much less work exists on the adsorption of porphyrins on oxide surfaces. Using X-ray photoelectron spectroscopy to study the adsorption and reactions of 5,10,15,20-tetraphenylporphyrin on MgO(100) and TiO2(110) surfaces, the behavior on oxide surfaces is shown to have a lot in common with reactions known from the liquid phase, such as ion exchange and protonation.

O 34.5 Tue 11:45 HSZ 101
Probing surface electrochemical oxidation of gold by non-linear optical vibrational spectroscopy — •Yujin Tong, Felix Gerke, Martin Wolf, and R. Kramer Campen — Fritz-Haber-Institut, Abt. Physikalische Chemie, 14195 Berlin, Germany

Electrochemical water splitting on noble metal surface is an important reaction of both fundamental and application interest. It is well known that the bottleneck of this reaction is the poor kinetics for oxygen generation from water oxidation. In spite of years study, the mechanisms in terms of the roles of the thin oxides film that formed on the metal surface before/during oxygen evolution are still inexplicit. One of the main reasons is the lack of molecular level information about the oxide thin film structures. In this study, we investigated the electrochemical oxidation of gold in solutions with different pH by employing surface specific vibrational sum frequency spectroscopy (VSFS). By analyzing the potential dependent behaviors of different types of adsorbed species, we could gain molecular level information regarding the structures and formation mechanisms of gold-oxides. The results of this study will provide essential data toward understanding the oxygen evolution mechanism and may suggest strategies for developing better water splitting catalysts.

O 34.6 Tue 12:00 HSZ 101
Stability of metallo-porphyrin networks under oxygen reduction and evolution conditions in basic media — •D. Hötger[1], C. Morchutt[1], M. Etzkorn[1], J. Dreiser[2], S. Stepanow[3], D. Grumelli[4], R. Gutzler[1], and K. Kern[1,5] — [1]MPI for Solid State Research, D-70569 Stuttgart — [2]SLS, PSI, CH-5232 Villigen — [3]ETH Zürich, CH-8092 Zürich — [4]CONICET, ARG-1900 La Plata — [5]EPFL, CH-1015 Lausanne

Oxygen reduction and evolution reaction (ORR and OER) are two relevant reactions in important devices like fuel cells, electrolysers and metal-air batteries. The catalytic stability of a catalyst is commonly well explored, but little focus is given to the structural integrity of molecule-based catalysts. We study iron-tetrapyridyl porphyrines (FeTPyP) co-deposited with Co on Au(111). The bimetallic network is bifunctionally active for OER and ORR.[1]

FeTPyP-Co is characterized before and after electrocatalysis by scanning tunneling microscopy (STM) to explore the geometric structure of the molecules on the Au(111) surface. STM shows that the molecules remain intact after ORR but decompose during OER. X-ray absorption spectroscopy (XAS) yields insight into the electronic structure of the metal centers. XAS confirms the integrity of TPyP after ORR. In contrast, after OER XAS reveals the presence of Co and Fe oxide on the surface in absence of TPyP. Thus, OER conditions are more aggressive on organic molecules than ORR. This finding is of great importance for the design of molecule-based electrocatalysts.

[1] B. Wurster, *et al.*; J. Am. Chem. Soc.; **2016**, 138, 3623-3626.