

O 30: Focused session: Functional molecules at surfaces I

Time: Tuesday 10:30–13:15

Location: A 053

O 30.1 Tue 10:30 A 053

Activation of surface hydroxyl groups by modification of H-terminated Si(111) — ●PETER THISSEN¹, TATIANA PEIXOTO¹, ROBERTO CARLOS LONGO¹, WOLF GERO SCHMIDT², KYEONGJAE CHO¹, and YVES JEAN CHABAL¹ — ¹Department of Materials Science and Engineering, University of Texas at Dallas, Richardson, USA — ²Lehrstuhl für Theoretische Physik, Universität Paderborn, Paderborn, Germany

Most approaches to self assembled monolayer grafting on silicon surfaces rely on chemical reactions with hydroxyl groups. To date, such groups have only been prepared on silicon oxide surfaces, leading to poor reactivity with only low number of important organic molecules. For instance, phosphonic acids are attractive because they can in principle attach to surfaces in different (mono-, bi- or tri-dentate) configurations that control their arrangement. However, all attempts to directly graft phosphonic acids on silicon has in the past decades not been possible, requiring a perturbing annealing step at 140° C. Here, we demonstrate, using a model surface prepared by functionalizing atomically flat, hydrogen terminated Si(111) with exactly 1/3 hydroxyl monolayer, that hydroxyl on oxide free silicon is more reactive than on oxides. With this model surface, we demonstrate that a perfectly ordered layer of phosphonic acid molecules can be directly grafted at room temperature, and explain why it can remain completely stable in aqueous environments in contrast to phosphonates grafted on oxides. This work opens new possibilities for surface functionalization needed for sensors, photovoltaic devices and fundamental studies.

Topical Talk

O 30.2 Tue 10:45 A 053

Surface-supported molecular assemblies: insight from scanning tunneling microscopy and photoemission experiments — ●MEIKE STÖHR — Zernike Institute for Advanced Materials, University of Groningen, Netherlands

The interest in studying organic nanostructures on surfaces emerges from their prospective applications in nanoscale electronic or optoelectronic devices, in which the spatially addressable functional units are to be assembled on the molecular level. By making use of molecular recognition processes based on non-covalent interactions, well-ordered 1D and 2D molecular structures can be formed on surfaces. The understanding of the interplay of the underlying intermolecular and molecule substrate interactions is highly important since the resulting molecular structures are based upon these two interactions. For the formation of molecular structures with improved stability and conductivity, the concept of on-surface polymerization has been introduced recently.

In my presentation, I will focus - on the basis of perylene derivatives adsorbed on Cu(111) - on surface-supported molecular assemblies based on non-covalent interactions [1]. The assembly structures can be altered through post-annealing of the sample. Thereby, also the intermolecular interactions are varied. Through the combination of experimental and theoretical methods, the electronic and structural properties have been elucidated.

[1] J. Lobo-Checa et al., Science 325 (2009) 300; M. Matena et al., Chem. Eur. J. 16 (2010) 2079.

Topical Talk

O 30.3 Tue 11:15 A 053

How metal surfaces control adsorbate functionality: cooperativity, adatoms, and substrate interactions — ●FELIX HANKE — University of Liverpool, Liverpool, UK

Achieving complete atomic-level control and understanding of functional nanostructures in contact with a metal surface is one of the outstanding challenges in surface science. One of the most interesting issues is the role of the surface in driving the function and assembly of adsorbates and molecular switches. Here I will outline the impact and control of substrate reactivity and adatom incorporation on different molecular systems. These theoretical concepts will be illustrated in detail for two systems using van der Waals density functional theory calculations and STM simulations. First, the assembly of single porphyrins on Cu(110) leads to highly oriented one-dimensional nanostructures despite the complete lack of functionality to direct the self-assembly [1]. The porphyrin macrocycles are coupled by covalent C-Cu-C bonds, which result from the incorporation of adatoms into the structure. The one-dimensional nature of the chains is inherited from the substrate structure. Second, the recent synthesis of

graphene nanoribbons (GNR) on the Au(111) surface will be discussed [2]. Again, the substrate plays a fundamental role in catalyzing the coupling reactions from a polyanthracene precursor to the full GNR. Successive couplings start at one end of the precursor and proceed cooperatively through the molecule in a domino-like fashion [3].

[1] J. Am. Chem. Soc. **133** 12031 (2011); ACS Nano **5** 9093 (2011); [2] Nature **466** 470 (2010); [3] J. Am. Chem. Soc. **133** 14884 (2011)

O 30.4 Tue 11:45 A 053

On-surface covalent linking of organic building blocks on a bulk insulator — MARKUS KITTELMANN¹, PHILIPP RAHE¹, MARKUS NIMMIRICH¹, ●ROBERT LINDNER¹, ANDRÉ GOURDON², and ANGELIKA KÜHNLE¹ — ¹Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, Germany — ²CNRS, CEMES, Nanoscience Group, 29 Rue J. Marvig, 31055 Toulouse, France

On-surface synthesis in ultra-high vacuum provides a promising strategy for creating thermally and chemically stable molecular structures at surfaces. Very recently, few pivotal experiments have been presented, demonstrating the potential of this concept on metallic substrates.

However, many of the envisioned applications require non-conductive rather than metallic substrates to prevent electronic coupling and leakage or non-radiative quenching. Thus, it becomes exceedingly important to transfer this technique to bulk insulators.

Here, we demonstrate the covalent linking of organic molecules on a bulk insulator, namely calcite. We deliberately employ the strong electrostatic interaction between the carboxylate groups of halide substituted benzoic acids and the surface calcium cations to reach homolytic cleavage temperatures before molecular desorption. This allows for the formation of aryl radicals and intermolecular coupling. By varying number and position of the halide substitution, we rationally design the resulting structures, revealing straight lines, zigzag structures as well as dimers, providing clear evidence for the covalent linking [1].

[1] Kittelmann, M., et al., ACS Nano 2011, 5 (10), 8420-8425

O 30.5 Tue 12:00 A 053

Redox mediation by immobilised centres in the pores of a SURMOF metal-organic framework — ●ANDRÉ DRAGÄSSER¹, OSAMA SHEKHAH², OLEXANDRA ZYBAYLO², CAI SHEN³, MANFRED BUCK³, CHRISTOF WÖLL², and DERCK SCHLETTWEIN¹ — ¹Justus-Liebig-Universität Gießen, Institut für Angewandte Physik, Heinrich-Buff-Ring 16, D-35392 Gießen — ²Karlsruhe Institute of Technology, Institute of Functional Interfaces, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen — ³University of St Andrews, EaStCHEM School of Chemistry, St Andrews, KY169ST, UK

Functionalizing surfaces by a highly ordered porous layer and loading of its pores with functional molecules appears very attractive. Very flexible frameworks are available in the form of metal-organic frameworks (MOFs). These frameworks are highly oriented thermally stable porous powders with a pore size of about 1 - 10 nm useful for gas separation, chromatography, and also for electrical and electronic applications. MOFs can be prepared on highly ordered surfaces to yield so-called SURMOFs. Their charge transport characteristics and redox properties are of pronounced interest. In this work, a layer of a metal-organic framework (SURMOF) was prepared by liquid-phase epitaxy on a self-assembled thiol monolayer on polycrystalline Au. Cyclic voltammetry in contact with a redox-active electrolyte was performed to probe charge transport through such SURMOF phases. Charge transport across these insulating membranes could be established by ferrocene as an immobilised redox mediator. Reversibility of the immobilisation and its role in the electrode kinetics is discussed.

O 30.6 Tue 12:15 A 053

STM investigations of functional platform adlayers on Au(111) surfaces — ●SONJA KUHN¹, FRAUKE CLAUSSEN¹, JIYAPA SRIPROM², ULRICH JUNG¹, JENS KUBITSCHKE³, SANDRA ULRICH³, ALBERT SCHULTE², RAINER HERGES³, and OLAF MAGNUSSEN¹ — ¹Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Leibnizstr. 19, 24118 Kiel, Germany — ²Biochemistry-Electrochemistry Research Unit, Suranaree University of Technology 30000, Thailand — ³Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel, Otto-Hahn-Platz 4, 24098 Kiel, Germany

For preparation of functionalized molecular adlayers, we have introduced the platform approach, where derivatives of the Triaza- [1,2,3] or Trioxatriangulenium [4] ions are used, which can be functionalized at the central carbon atom to control orientation and spacing of the functionality as well as at side positions to control the steric demand. Here, we present STM studies of these platform adlayers on Au(111) surfaces in air and in electrochemical environment [1,2,4]. These compounds form highly ordered hexagonal structures and thus are important example systems exhibiting a high degree of lateral and vertical order. We will also present in situ STM studies by a novel kind of carbon fiber tips, which exhibit superior electrochemical properties [5].

[1] Baisch et al., J. Am. Chem. Soc. (2009), 131, 442, [2] Kuhn et al., PCCP (2010), 12, 4481, [3] Kubitschke et al., Eur. J. Org. Chem. (2010), 5041, [4] Kuhn et al., Chem. Commun., 2011, 47, 8880-8882, [5] J. Sripirom et al., Carbon, 49, 2011, H. 7, 2402-2412

O 30.7 Tue 12:30 A 053

Disorder-order transition at coverages above one monolayer in 2H-tetraphenylporphyrins on Cu(111) — ●MICHAEL STARK, STEFANIE DITZE, MARTIN DROST, FLORIAN BUCHNER, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058

The understanding of the adsorption behavior of functional molecules on surfaces is a prerequisite for using them as building blocks in molecular devices. In this study, we investigate the coverage dependent supramolecular arrangement of 2H-tetraphenylporphyrin (2HTPP) on Cu(111) with scanning tunneling microscopy at room-temperature (RT) in ultra-high vacuum. At low coverage, "slow" diffusion of individual 2HTPP molecules along the close-packed atomic rows of the substrate is observed [1,2]. Up to saturation of the first layer, no supramolecular ordering occurs. However, at higher coverage, the formation of ordered domains is found. This behavior is attributed to a complex interplay of intermolecular and molecule-substrate interactions upon increasing 2HTPP coverage.

This work has been funded by the DFG through Sonderforschungsbereich 583.

[1] F. Buchner et al., Chem. Eur. J., (2011), 17, 10226.

[2] F. Buchner et al., J. Phys. Chem. C, (2011), DOI: 10.1021/jp206675u.

O 30.8 Tue 12:45 A 053

Lichtinduzierte Knüpfung von kovalenten Bindungen auf Isolatoren — ●ROBERT LINDNER, MARKUS KITTELMANN, PHILIPP RAHE, CHRISTOPHER HAUKE, MARKUS NIMMICH und ANGELIKA KÜHNLE — Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, Germany

Die Ausbildung von kovalent gebundenen Netzwerken auf Isolatoren ist ein vielversprechender Schritt auf dem Weg zu molekularer Elektronik. Die Knüpfung von kovalenten Bindungen ermöglicht stabile Netzwerke, deren Eigenschaften und Struktur sich über funktionelle Gruppen gezielt beeinflussen lassen. Thermisch induzierte Bindungsknüpfungen auf Metallen [1] und Isolatoren [2] wurden schon auf eindrucksvolle Weise gezeigt. Um das Wachstum der Lagen und die Vernetzung selektiv voneinander zu trennen, stellen photochemische Reaktionen eine sehr elegante Methode dar.

In diesem Beitrag stellen wir erstmals die Photoreaktion des C₆₀-Fullerens auf einem Isolator vor. C₆₀ Monolagen wurden auf einer Calcit (10.4)-Oberfläche durch Laserbelichtung photochemisch zweidimensional vernetzt und mit einem Nicht-Kontakt AFM untersucht. Hierbei wurden, neben Änderungen der Molekülabstände auch Änderungen der C₆₀-Überstruktur beobachtet. Dadurch können umfangreiche Aussagen über die Polymerisation der Fullerene auf der Calcitoberfläche dargelegt werden.

[1] Grill, L., et al., Nature Nanotechnology 2007, 2, 687-691

[2] Kittelmann, M., et al., ACS Nano. 2011, 5 (10), 8420-8425

O 30.9 Tue 13:00 A 053

Molecular orientation of tetracene in ordered and disordered layers on Ag(111) — ●TOMOKI SUEYOSHI¹, MARTIN WILLENBOCKEL¹, MICHAEL NABOKA², ALEXEI NEFEDOV², SERGEY SOUBATCH¹, CHRISTOF WÖLL², and STEFAN TAUTZ¹ — ¹Peter Grünberg Institut (PGI-3), JARA, Forschungszentrum Jülich, Germany — ²Institute of Functional Interfaces, Karlsruhe Institute of Technology (KIT), Germany

Tetracene on Ag(111) forms different structural phases depending on preparation condition. Based on scanning tunneling microscopic/spectroscopic studies, we indicated that variation of the tilt angle of tetracene molecule (and local molecular environment) results in different electronic properties of tetracene layers. This demonstrates how it is important to know the molecular orientation in the layer to understand the electronic structure of molecular layers. Here, we investigate tetracene molecular orientation in ordered and disordered layers on Ag(111) using near edge X-ray absorption fine structure (NEXAFS) spectroscopy. Quantitative analysis of NEXAFS intensity reveals that monolayer alpha-phase consists of flat-lying molecule with a tilt angle of less than 10 degrees whereas complex bi-layer beta-phase includes tilted molecule with an average tilt angle of 36 degrees. At room temperature the monolayer alpha-phase gets disordered and the average tilt angle of tetracene molecules changes to 15 degrees, accordingly. The increase in the tetracene tilt angle suggests that an order-disorder transition of tetracene monolayer is achieved by getting additional degree of freedom for tetracene to move.