

## O 66: Oxide Surfaces II

Time: Thursday 10:30–13:15

Location: H42

O 66.1 Thu 10:30 H42

**Atomic-scale insights into geometrical and electronic properties of the N3 dye on TiO<sub>2</sub> anatase (101)** — ●C. S. KLEY<sup>1</sup>, C. DETTE<sup>1</sup>, S. J. JUNG<sup>1</sup>, G. RINKE<sup>1</sup>, J. CECHAL<sup>1</sup>, S. RAUSCHENBACH<sup>1</sup>, C. PATRICK<sup>2</sup>, F. GIUSTINO<sup>2</sup>, S. STEPANOW<sup>1</sup>, and K. KERN<sup>1,3</sup> — <sup>1</sup>MPI for Solid State Research, Stuttgart, DE — <sup>2</sup>University of Oxford, Department of Materials, Oxford, UK — <sup>3</sup>EPFL, Institut de Physique de la Matière Condensée, Lausanne, CH

Dye-sensitized solar cells (DSSCs) constitute a promising approach to sustainable and low-cost energy production with considerable light conversion efficiencies. Among many efforts, the understanding of the dye adsorption geometry, its electronic alignment and mutual lateral interaction is of paramount importance to optimize the photovoltaic performance of DSSCs. Here, we study the geometric and electronic properties of N3 dye molecules on the TiO<sub>2</sub> anatase (101) surface by means of scanning tunneling microscopy and spectroscopy methods in UHV. Electro spray ion beam deposition is employed to deposit the thermally fragile photosensitizer onto the substrate. In contrast to theoretical predictions suggesting a specific thermodynamically most stable N3 adsorption configuration, our studies reveal variable N3 adsorption geometries on the TiO<sub>2</sub> anatase (101) surface. The role of kinetics, photosensitizer ionization and substrate defects will be discussed and additional studies of the N3 anchor ligand BINA will be correlated to our findings. Further, the electronic configuration of the adsorbed N3 molecules will be presented. Our experimental results are supported by first-principle DFT based calculations.

O 66.2 Thu 10:45 H42

**Carboxylic acid on all stable TiO<sub>2</sub> rutile surfaces: Comparison of DFT and DFTB potentials** — ●WOLFGANG HECKEL, BEATRIX ELSNER, and STEFAN MÜLLER — Hamburg University of Technology, Institute of Advanced Ceramics, Denickestr. 15, D-21073 Hamburg

In order to control the mechanical properties of hybrid materials, the detailed knowledge of the interfaces, the atomic structure and stability is crucial. Both methods, density functional theory (DFT) and density functional based tight binding (DFTB) allow for the investigation of the local electronic structure and the determination of desired observables like binding energy, while growing further towards about 5-10 times larger model systems with the latter.

As a prototype adsorbate we tested acetic acid on TiO<sub>2</sub> (110), (011) and (100) surfaces for two DFT exchange-correlation functionals (PBE and PBEsol) and for DFTB being able to estimate the accuracy of results for arbitrary adsorbates in the future.

We put the focus on the ability of the methods to describe correctly the role of the carboxylic hydrogen ion, which dissociates during adsorption and forms an OH species stabilizing the adsorption, as shown in experiments (e.g. [1]). All methods applied prefer the dissociated adsorption mode to the molecular mode, however the results differ about preferring acetic acid or acetate.

Supported by DFG, SFB 986, project A4.

[1] Sayago et al., *J. Phys. Chem. B* **108**, 14316 (2004)

O 66.3 Thu 11:00 H42

**Photodesorption in the CO/TiO<sub>2</sub>-system** — ●HENDRIK SPIEKER and THORSTEN KLÜNER — Theoretical Chemistry, Carl von Ossietzky Universität, PO Box 2503, 26111 Oldenburg

Due to its high photocatalytic activity, titanium dioxide is of application-oriented interest. Unfortunately, the fundamental mechanisms of surface chemistry are completely unknown. The adsorbate-substrate-system CO/TiO<sub>2</sub>(110) has recently been studied as a model system concerning a fundamental understanding of adsorption and desorption phenomena. [1]

Making use of an embedded cluster approach, two- and three-dimensional potential energy surfaces (PES) for the ground state and relevant excited states of the CO molecule are calculated on a post Hartree-Fock level of theory. These PES serve as potentials for quantum dynamical stochastic wave packet studies, yielding quantum state resolved final state product distributions. Furthermore, the desorption mechanism for the CO molecule interacting with a TiO<sub>2</sub>(110)-surface in consequence of a vertical excitation will be elucidated in detail. Concerning these results, the correction of the basis set superposition error

within the quantum chemical calculations is found to be essential.

[1] M. Mehring, T. Klüner, *Chem. Phys. Lett.* **513**, 212-217 (2011).

O 66.4 Thu 11:15 H42

**Ab initio calculations on the adsorption energy of NO on TiO<sub>2</sub>(110)** — ●MARIE ARNDT and THORSTEN KLÜNER — Theoretische Chemie, Carl von Ossietzky Universität Oldenburg, Germany

Photocatalytic reactions on metaloxide surfaces are an important section in technical industries. An outstanding photocatalyst is the semiconductor titaniumdioxide. In this context, the adsorption and desorption processes of small molecules on the substrate surfaces play an important role in theoretical and experimental analysis. This study focuses on the characterization of the adsorption of NO on a rutile(110) surface. We investigated the adsorption by using ab initio calculations, such as restricted open shell Hartree-Fock and restricted open shell Møller-Plesset second order perturbation theory. To describe the electronic ground state of this open shell system, an embedded cluster model of the type Ti<sub>9</sub>O<sub>18</sub>Mg<sub>7</sub><sup>14+</sup> was used. Using the *Molcas*[1] quantum chemistry package, the goal is to find the global minimum of the adsorption energy. Within our model, six degrees of freedom of our diatomic NO molecule on a rigid TiO<sub>2</sub> surface are defined. In this study, we varied the desorption coordinate  $z$  and the polar angle  $\theta$ , by keeping the lateral coordinates  $x$  and  $y$ , the azimuthal angle  $\varphi$  and the NO bond length  $r$  fixed. The preferred orientation of NO on the rutile(110) surface has been found by modeling a 2D potential energy surface and is discussed in terms of a molecular orbital picture. The results revealed a tilted orientation of the NO at a distance of 3.0 Å to the surface. [1] Division of Theoretical Chemistry, Molcas 7.6, Lund University, 2011.

O 66.5 Thu 11:30 H42

**Co-Salen on NaCl(001) and NiO(001): Substrate influence on adsorption geometry and growth** — ●JOSEF GRENZ<sup>1</sup>, ALEXANDER SCHWARZ<sup>1</sup>, DAVID GAO<sup>2</sup>, MATTHEW WATKINS<sup>2</sup>, ALEXANDER SHLUGER<sup>2</sup>, and ROLAND WIESENDANGER<sup>1</sup> — <sup>1</sup>Inst. of Ap. Phys., University of Hamburg, Germany — <sup>2</sup>University College London, UK

By depositing the same molecule, i.e., Co-Salen, on two chemically different substrates, i.e., NaCl(001) and NiO(001), with the same surface structure disparities as well as equalities regarding adsorption geometry and growth were investigated.

Since these materials are bulk insulators, atomic force microscopy in the non-contact mode operated was applied to simultaneously resolve the atomic structure of the surface and to image individual molecules. On both ionic substrates the molecule adsorbs on top of the anions, i.e., chlorine and oxygen. However, on NaCl(001) 16 stable orientations are observed [1], while only 8 are present on NiO(001). Moreover, tip-induced translational motion of individual Co-Salen molecules occur along preferred crystallographic directions and coincide with stable orientations of the molecule on the respective substrate. Tip-induced motions are more frequent on NaCl(001) than on NiO(001), indicating a larger binding energy on the latter. This presumption is supported by the initial layer-by-layer growth observed on NiO(001), while island growth is observed on NaCl(001) [2]. All these experimental findings are in agreement with density functional theory (DFT) calculations.

[1] K. Lämmle, *et al.*, *Nano Lett.* **10**, 2965-2971 (2010).

[2] S. Frey, *et al.*, *Nanotechnology* **20**, 405608 (2009).

O 66.6 Thu 11:45 H42

**Boron nitride as a template for molecular adsorption, self-assembly and electronic decoupling of the prototype macrocycle porphine.** — ●FELIX BISCHOFF, SUSHOBHAN JOSHI, KNUD SEUFERT, DAVID ECIJA, SARANYAN VIJAYARAGHAVAN, WILLI AUWÄRTER, and JOHANNES BARTH — Physik Department E20, TUM, James Franck Str. 1, 85748 Garching, Germany

Motivated by its bulk and thin film properties and successful incorporation into graphene nanodevices, boron nitride (BN) has gained great attention. Recently, a vapor-deposited BN monolayer on a Cu support was comprehensively characterized [1]. It is topographically smooth, yet electronically patterned and therefore provides a versatile template for molecular adsorption, self-assembly and electronic decoupling of molecular nanosystems. In this work, these properties are exemplified by systematic STM and STS experiments. The macro-

cyclic model compound porphine (2H-P) does not spontaneously form ordered structures on bare Cu at room temperature due to strong substrate-adsorbate interactions. However, a BN spacer layer electronically decouples these molecules and enables 2-D self-assembly. It also serves as an electronic template due to variations in its potential landscape and traps 2H-P at specific sites. At low- and intermediate coverages, arrays of well-separated, but highly-ordered porphine islands are observed, following the BN moiré structure. The inhomogeneous BN template also dictates the electronic level alignment, as evidenced by a spatial modulation of the energy of porphine frontier orbitals.

[1] Joshi et al., *Nano Lett.*, 2012, 12 (11), pp 5821-5828

O 66.7 Thu 12:00 H42

**Single molecules in a petri dish: Iodine dissociation of CHP on a hexagonal boron nitride monolayer** — •THOMAS DIENEL<sup>1</sup>, ROLAND WIDMER<sup>1</sup>, ARI P. SEITSONEN<sup>2</sup>, JÜRIG HUTTER<sup>2</sup>, and OLIVER GRÖNING<sup>1</sup> — <sup>1</sup>nanotech@surfaces Lab, Empa, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland — <sup>2</sup>Physical Chemistry Institute, University of Zurich, CH-8057 Zurich, Switzerland

Well-defined monolayers of hexagonal boron nitride (h-BN) can be produced by thermal decomposition of borazine (HBNH)<sub>3</sub> on transition metal surfaces. On Rh(111) a strongly corrugated superstructure of depressions with a periodicity of 3.22nm is formed. There weakly bonded h-BN regions called "wires" separate strongly bonded "pores" with a diameter of 1.5nm, where organic molecules can be efficiently trapped[1]. We report on the adsorption behavior and properties of hexaiodo-substituted macrocycle cyclohexa-m-phenylene (CHP) on corrugated h-BN. The CHP molecules adsorb within the pores and are aligned in [12] direction of the superstructure reflecting the inner structure of the h-BN monolayer. The terminal iodine atoms of the CHP can be dissociated by thermal annealing [2, 3]. Contrary to the case on metals, the h-BN substrate imposes a distinct abstraction sequence, which we follow in situ by scanning tunneling microscopy and DFT calculations. With these insights to the catalytic properties of h-BN we pave the road to bottom-up fabrication of graphene by aryl-aryl coupling on h-BN. [1] S. Berner et al., *Angew. Chem. Int. Ed.* 46 (2007) 5115. [2] M. Bieri et al., *Chem. Commun.*, 45 (2009) 6919. [3] M. Bieri et al., *JACS*, 132 (2010) 16669.

O 66.8 Thu 12:15 H42

**Stability of self-assembled organic monolayers on ZnO** — •PHILIPP HERRMANN and GEORG HEIMEL — Institut für Physik, Humboldt Universität zu Berlin, Germany

Its wide bandgap and natural abundance make ZnO a promising material for optoelectronic devices. Particularly tempting is the use of ZnO in conjunction with organic semiconductors, but this requires detailed information on the interfaces in such hybrid systems. Given the complex phase diagram of ZnO surfaces, reliable means to control the interfacial properties are needed for real applications.

We therefore explore the functionalization of ZnO surfaces with self-assembled monolayers (SAMs) of covalently attached organic molecules. The stability of these SAMs against water and oxygen is investigated by first-principles thermodynamics based on periodic density functional theory calculations.

Once an effective docking chemistry is found, these SAM molecules can be chemically modified with dipolar docking groups to control the alignment between the electronic levels of ZnO and a subsequently deposited organic semiconductor.

O 66.9 Thu 12:30 H42

**Diffusion and Reaction on ZnO surfaces** — •NAVID ABEDI and GEORG HEIMEL — Institut für Physik, Humboldt-Universität zu Berlin, Brook-Taylor Straße 6, 12489 Berlin, Germany

In an attempt to develop a systematic strategy for the concomitant stabilization and functionalization of ZnO surfaces, we computationally explore the formation of self-assembled monolayers (SAMs) of covalently attached organic molecules. To this end, we perform density functional theory (DFT) based periodic band-structure calculation and use the nudged elastic band (NEB) method to study reaction barriers and -paths as well as transition states on ZnO surfaces. Particular emphasis has been put on hydrogen, oxygen, and hydroxide diffusion, as well as water and methanol dissociation. From these results we derive guidelines for the design of kinetically stabilized SAMs which can subsequently be modified to tune surface properties.

O 66.10 Thu 12:45 H42

**Density Functional Theory study of adatom adsorption on metal supported thin Zirconia films** — •WERNFRIED MAYR-SCHMÖLZER, FLORIAN MITTENDORFER, and JOSEF REDINGER — Center of Computational Materials Science, Technical University of Vienna, Austria

Zirconium dioxide is a material with many interesting properties, which make it useful for various technological applications, for example as a solid electrolyte in solid-oxide fuel-cells or as an oxygen gas sensor.

We present the results of DFT calculations of the interface between thin zirconium oxide films and supporting metals like Pt<sub>3</sub>Zr and Pd<sub>3</sub>Zr. Both substrates are very stable and can be used to experimentally grow thin ZrO<sub>2</sub> films by oxidation. Using the Vienna Ab-initio Simulation Package (VASP) employing both standard PBE and van-der-Waals density functionals a thorough investigation of the structural and electronic properties was done of both small model cells and the experimentally found large super cells. Furthermore the changes induced by oxygen vacancies were studied. The ground state structure was confirmed by simulation of the resulting core level spectra.

Additionally we investigated the adsorption of late transition metals such as Gold or Nickel on the supported zirconium oxide film. Furthermore the behavior of water molecules on the surface generated by the thin Zirconia film was investigated.

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O 66.11 Thu 13:00 H42

**Ab Initio Study of Amino Acid Adsorption on ZnO (10-10)** — •SVEVA GROSSE HOLTHAUS, SUSAN KÖPPEN, THOMAS FRAUENHEIM, and LUCIO COLOMBI CIACCHI — University of Bremen, Bremen Center for Computational Material Science

In a recent study the toxicity of ZnO nanoparticles towards mammalian cells was found to be directly related to particle dissolution causing an uptake of particle remnants and toxic Zn{2+} ions into the cell. In this context the release of Zn{2+} ions was found to be different in cell culture media containing various amino acids [1]. The adsorption of different amino acids on ZnO constitutes a first step in describing the overall solid liquid interface of a nanoparticle in a biological environment.

In our study the adsorption of two charged (Arginine, Glutamic Acid) and three polar (Serin, Cystein, Glutamine) amino acids on ZnO(10-10) embedded in water are investigated using ab initio molecular dynamics simulations. An analysis of the obtained dynamics implies that the ampholytic backbone forms bond to the first water layer. Furthermore the presence of the amino acid is seen to influence the hydroxylation of the first water layer compared to pure surface water systems. Depending on the local water structure surrounding the back bone amino group, a hydrogen transfer to the first water layer is observed.

[1] Xia, T.; Kovoichich, M.; Liong, M.; Mädler, L.; Gilbert, B.; Shi, H.; Yeh, J. I.; Zink, J. I.; Nel, A. E. *ACS Nano* 2008, 2, 2121-2134.