

O 65: Focus Session: Structure and Chemistry of Metal-Oxide Surfaces III

Time: Wednesday 15:00–16:45

Location: MA 005

O 65.1 Wed 15:00 MA 005

Density functional theory study of water and glycine adsorption at TiO₂-TiN interfaces — ●JULIO GUTIERREZ MORENO and MICHAEL NOLAN — Tyndall National Institute, University College Cork

Titanium nitride (TiN) is used in sensors as a conducting layer with good hardness and resistance to corrosion. TiN can spontaneously form a thin oxide layer when it is exposed to air, which could modify the properties of the coating and the impact on biofouling is not yet clear. Therefore, there is significant interest in studying the biofouling of oxidised TiN to find strategies to inhibit this process. In this work, we carried out Hubbard corrected density functional theory (DFT+U) simulations of the TiO₂-TiN interface, as a model of the oxide layer on TiN. We investigate defects that can form during the oxide growth and are present after TiO₂ formation such as Ti vacancies in TiN, O vacancies or the interdiffusion of O/N atoms within the interface. Our simulations show the formation of Ti³⁺ cations in the TiO₂ that arise upon interface formation. We found that water adsorbs dissociatively on TiO₂-TiN for low surface coverages while molecular adsorption is more stable at higher coverage. Glycine adsorption from gas phase is strong on the TiO₂-TiN interface ($E = -1.6$ eV) compared to bare TiN ($E = -0.4$ eV). However the adherence of glycine is weaker on hydrated surfaces and also depends on the defects that might be present in the interface. The outcomes of these simulations give us a more comprehensive insight on the atomic level structure and the electronic properties of oxidised TiN surfaces and how this is related to biofouling.

O 65.2 Wed 15:15 MA 005

Influence of halic and carboxylic acids on the shape of TiO₂ nanoparticles — KAI SELLSCHOPP¹, WOLFGANG HECKEL¹, ANDREAS HENSEL², CLEMENS SCHRÖTER², TOBIAS VOSSMEYER², HORST WELLER², STEFAN MÜLLER¹, and ●GREGOR FELDBAUER¹ — ¹Institute of Advanced Ceramics, Hamburg University of Technology — ²Institute of Physical Chemistry, University of Hamburg

Titanium (TiO₂) nanoparticles are used for many applications ranging from photo-catalysts to hybrid materials. The faceting and accordingly the shape of the nanoparticles determine the performance of the nanoparticles in these applications. Therefore, shape control during synthesis is essential. It is known that fluoric acid stabilizes the anatase (001) surface through a substitution of surface oxygen atoms. This leads to platelet shaped particles with a large percentage of reactive (001) facets. The influence of other halic and organic acids on the particle shape, however, is rarely studied. Here, we present our latest results on the adsorption and surface energies of all halic acids and some carboxylic acids on the major TiO₂ anatase surfaces. From the surface energies calculated using density functional theory (DFT) we derive the shape of the nanoparticles starting from the Wulff construction. Transmission electron microscopy (TEM) images of TiO₂ nanoparticles synthesized in non-aqueous medium show good agreement with the calculated shapes.

Invited Talk

O 65.3 Wed 15:30 MA 005

Bulk-terminated surfaces of KTaO₃ and SrTiO₃ studied by combined STM/AFM — ●MARTIN SETVIN — TU Wien

Recent development of the noncontact atomic force microscopy (nc-AFM) has opened new possibilities in different fields - imaging of organic molecules [1], controlling the charge state of adsorbed species [2], or measuring forces involved in a single chemical bond [3]. I will focus on the possibilities and opportunities emerging on oxide surfaces. The limits of atomic resolution will be illustrated on clean and water-exposed binary oxides like TiO₂ or In₂O₃. The technique opens new ways towards investigation of complex oxides; this will be illustrated on the (001) surfaces of cubic perovskites KTaO₃ and SrTiO₃. These materials, when prepared by cleaving, consist of a mixture of two terminations (KO/TaO₂, SrO/TiO₂). The layout of these terminations resembles the shape of ferroelectric domains, indicating that the incipient-ferroelectric character of these materials can be used for tuning the surface topography. Basic physical and chemical properties of these surfaces will be discussed, with a special focus on the polar KTaO₃ (001) surface. This surface compensates its inherent instability by various mechanisms like formation of 2DEG-like states in the band

gap, ferroelectricity, point defects, surface restructuring, or adsorbate-induced reconstruction. Tuning the environment allows choosing which mechanism will be in play and controlling the surface termination.

[1] L. Gross et al., Science 2009, 325, 1110 [2] L. Gross et al., Science 2009, 324, 1428 [3] Y. Sugimoto et al., Nature 2007, 446, 64

O 65.4 Wed 16:00 MA 005

On the role of strong metal-support interactions in the activity of Metal/CeO₂ catalysts — ●M. VERONICA GANDUGLIA-PIROVANO¹ and PABLO G. LUSTEMBERG² — ¹ICP-CSIC, Madrid, Spain — ²IFIR-CONICET-UNR, Rosario, Argentina

Ceria (CeO₂) is the most significant of the oxides of rare-earth elements in catalysis. Specifically, the role of ceria in the catalytic activity of metal-ceria systems is still not fully understood. The non-innocent role of ceria as catalyst support will be analyzed using ceria-supported metal nanoparticles as experimental and theoretical model catalysts [1-4]. Co-, Ni- and Cu-ceria systems will be used for methane dry reforming ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$), a relevant process from the environmental standpoint [1-3]. Ni-ceria will also be considered for hydrogen production [4]. The ability of ceria to stabilize oxidized species (Co²⁺ and Ni²⁺) on the stoichiometric CeO₂ surfaces, by relocalizing electrons on localized f-states, and metallic ones (Co⁰, Ni⁰) on the reduced CeO_{2-x} support, is essential for catalytic activity.

- [1] Z. Liu et al., Angew. Chem. Int. Ed. 55, 7455 (2016).
- [2] P. G. Lustemberg et al., ACS Catal. 6, 8184 (2016).
- [3] Z. Liu et al., Angew. Chem. Int. Ed. 56, 13041 (2017).
- [4] J. Carrasco et al., Angew. Chem. Int. Ed. 54, 3917 (2015).

O 65.5 Wed 16:15 MA 005

Structural and electronic differences between tetragonal and monoclinic ZrO₂ films on Rh(111) — ●PETER LACKNER, ZHIYU ZOU, SABRINA MAYR, ULRICH DIEBOLD, and MICHAEL SCHMID — Institute of Applied Physics, TU Wien, Vienna, Austria

The applications of zirconia (ZrO₂) are manifold, e.g. as catalyst support or solid electrolyte in fuel cells. Despite the importance of the material, its surface has not yet been studied thoroughly on an atomic level. This has a simple reason: ZrO₂ has a band gap of more than 5 eV and is therefore non-conductive, which makes the study of bulk zirconia with methods like x-ray photoelectron spectroscopy (XPS) impracticable, and scanning tunneling microscopy (STM) close to impossible.

To circumvent this issue, we prepared five-monolayer-thick layers of ZrO₂(111) [1] on Rh(111) using a home-build UHV-compatible sputter source [2]. By annealing in $p_{\text{O}_2} = 10^{-6}$ mbar at $T < 700^\circ\text{C}$, we prepared tetragonal ZrO₂, while above 700°C a phase transformation to monoclinic ZrO₂ – the stable bulk structure – was observed. Tetragonal ZrO₂ was atomically resolved, showing the expected (2×1) structure (w.r.t. cubic ZrO₂). The domain size grows with annealing temperature; at 650°C , domains of $40 \times 40 \text{ nm}^2$ are common. For monoclinic ZrO₂, a (2×2) structure was resolved. The two phases have distinct binding energies in the Zr3d region, with an unexpectedly high ΔE_B of 1.4 eV, pointing towards an unusual structure in one of the two.

- [1] Meinel et al., Phys. Rev. B 74, 235444 (2006).
- [2] Lackner et al., Rev. Sci. Instrum. 88, 103904 (2017).

O 65.6 Wed 16:30 MA 005

Structure and stability of the vicinal ZnO(10-14) surface — ●ELIN GRÄNÄS¹, BJÖRN ARNDT^{1,2}, MARCUS CREUTZBURG^{1,2}, GUILLERME D.L. SEMIONE^{1,2}, HESHMAT NOEI¹, ANDREAS SCHAEFER³, JOHAN GUSTAFSON³, VEDRAN VONK¹, and ANDREAS STIERLE^{1,2} — ¹Deutsches-Elektron Synchrotron (DESY), Germany — ²University of Hamburg, Germany — ³Lund University, Sweden

Zinc oxide (ZnO) based catalysts are commonly used, often together with Cu nanoparticles, in important chemical reactions such as methanol synthesis low temperature water-gas shift, and methanol steam reforming. ZnO plays not only the role as nanoparticle support; instead it is much more actively involved in many reactions, with detailed reaction mechanisms under discussion.

The commonly studied low index surfaces of ZnO are polar, resulting in surface instability, while the most stable surface has been suggested

to be the vicinal ZnO(10-14) surface. However very little is still known about the equilibrium structure of the vicinal surface and its stability upon gas exposures. Here first studies performed on vicinal ZnO(10-14) single crystals will be presented. Using techniques such as scanning probe microscopy (STM), surface x-ray diffraction (SXRD), and x-ray

photoelectron spectroscopy (XPS) we have characterized the bare and water exposed ZnO(10-14) surface. We have confirmed that the bare vicinal surface is stable in UHV and will discuss the atomic structure based on SXRD measurements. We will also discuss chemical and structural changes upon water exposure.