

O 32: Poster Tuesday: Adsorption and Catalysis 1

Time: Tuesday 11:00–13:00

Location: P3

O 32.1 Tue 11:00 P3

Analysis of Electron-Transfer in Water-Based Dye-Sensitized Solar Cells — •DANIEL HOLZHACKER¹, ANDREAS RINGLEB¹, RAFFAEL RUESSE², and DERCK SCHLETTWEIN¹ — ¹Justus-Liebig-Universität Gießen, Institut für Angewandte Physik — ²Justus-Liebig-Universität Gießen, Physikalisch-Chemisches Institut

Dye-sensitized solar cells (DSSCs) present a possible low-cost technology for the conversion of sunlight into electrical energy. Most DSSCs are based on electrolytes with organic solvents. Due to environmental reasons it is attractive to replace organic solvents by water. In view of the damage typically caused to DSSCs by water contaminations, the use of water as contact solution represents a big challenge. Complete aqueous DSSCs were assembled with a combination of different organic dyes (D51, D35 and Y123) and organic redox mediators (TEMPO, AZADO and TEMPOL). The combination of Y123 and TEMPO yielded remarkable efficiencies of up to 4.4%. Although heavily limited in the fill factor, TEMPOL proved to be an interesting alternative, as its solubility in water is dramatically increased in comparison to TEMPO. Similar open circuit voltages and short circuit currents were reached but large overpotentials of electron transfer at the electrodes still limited TEMPOL-based cells. Subsequently, the electrolyte and electrode surfaces were modified in order to reduce the respective overpotentials.

O 32.2 Tue 11:00 P3

Novel corrugated geometric moiré pattern of a semi-periodically buckled, zebra-like topography of Xe on Ag(110) — •INGA CHRISTINA LANGGUTH and KARINA MORGENSTERN — Chair of Physical Chemistry I, Ruhr-Universität Bochum, Bochum, Germany

Solid rare gas films on metal single crystals are currently gaining interest due to their beneficial properties. As non-ionic, low interacting insulator surfaces they offer a potential application for unperturbed surface science studies. STM investigations of a thin xenon (Xe) film of several monolayers on Ag(110) reveal a novel corrugated structure of a semi-periodically buckled, zebra-like topography. The outstanding feature of this surface is a non-uniform distribution of buckled row orientations and distances. Instead of domain boundaries separating different phases, a gradual transition of row orientations is observed. The corrugated row pattern can be attributed to a geometric moiré pattern at the interface of the incommensurable Ag(110) and Xe(111) crystal lattices. A gradual change of the row orientation can further be explained by a gradually changing Xe-lattice orientation with respect to Ag(110) within a narrow angle regime. The stability of this semi-periodic structure against annealing reveals a remarkably flat potential energy surface for the turning of the Xe layer relative to the Ag(110) surface. The corrugated surface may serve as an interesting substrate for further studies of geometric confinement effects in an anisotropic environment.

O 32.3 Tue 11:00 P3

On-surface Synthesis of Naphthalocyanines with Extended π -Systems — •LUKAS J. HEUPLICK¹, QITANG FAN¹, DMITRIY A. ASTVATSATUROV², DENNIS KÖRNER¹, TATIANA V. DUBININA², and J. MICHAEL GOTTFRIED¹ — ¹Fachbereich Chemie, Philipps-Universität Marburg, Marburg, Germany — ²Moscow

The distinct optical and electronic properties of phthalocyanines (Pc) make them interesting in a wide field of applications. Here we report the on-surface synthesis of new naphthalocyanines with differently extended π -systems. This reaction in form of a cyclization is studied for different dicyanotrioles on the Ag(111) and Au(111) surfaces by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). 6,7-Diphenyl-2,3-naphthalenedicarbonitrile (DPNDN) forms naphthalocyanines only with co-adsorbed Fe atoms on Ag(111) and Au(111). The larger 6,7-di(2-naphthyl)-2,3-naphthalenedicarbonitrile (DNNDN) can undergo this reaction directly on Ag(111) without co-adsorbed metal, resulting in the corresponding Ag-NPc.

O 32.4 Tue 11:00 P3

Adaptive training of a machine-learned model for nonadiabatic hydrogen chemistry on multiple facets of Copper. — •WOJCIECH G. STARK, JULIA WESTERMAYR, OSCAR A. DOUGLAS-

GALLARDO, JAMES GARDNER, and REINHARD J. MAURER — University of Warwick, Coventry, United Kingdom

Traditionally, molecular dynamics methods utilise the Born-Oppenheimer approximation and dynamics are governed by a single potential energy surface. However, on metallic surfaces often the energy exchange between adsorbate and electronic excitations in the metal is significant and causes the breakdown of the Born-Oppenheimer approximation. There are multiple methods to include such nonadiabatic effects, with one of the most efficient being molecular dynamics with electronic friction (MDEF). MDEF introduces nonadiabatic effects via additional electronic friction forces, which can be calculated with time-dependent perturbation theory based on Density Functional Theory. However, a meaningful comparison between computational simulations and experiments demands the capability to run tens of thousands of MDEF trajectories. We present high-dimensional machine-learning based iteratomic potential and electronic friction models that enable the simulation of nonadiabatic molecular dynamics of hydrogen scattering and associative desorption at different copper surfaces. We construct deep neural network representations via iterative adaptive sampling based on the target dynamical observables, namely the scattering and reaction probabilities.

O 32.5 Tue 11:00 P3

Adsorption and Diffusion of NH₃ on Rutile TiO₂(110): An STM Study — •HANNA BÜHLMAYER¹, KRAEN CHRISTOPHER ADAMSEN², TAO XU¹, LUTZ LAMMICH², JÖRG LIBUDA¹, STEFAN WENDT², and JEPPE VANG LAURITSEN² — ¹Interface Research and Catalysis, ECRC, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany — ²Interdisciplinary Nanoscience Center, Aarhus University, Gustav Wieds Vej 14, 8000 Aarhus, Denmark

The adsorption of NH₃ on TiO₂ is an important step for many reactions in environmental catalysis such as the selective catalytic reduction (SCR) of NO_x over V₂O₅/TiO₂ and the removal of NH₃ from air and water over TiO₂. To obtain a detailed understanding of the surface chemistry of NH₃ on TiO₂, we investigated the adsorption of sub-monolayers of NH₃ on clean, hydroxylated, and O-precovered rutile TiO₂(110) surfaces by means of scanning tunneling microscopy (STM) under ultrahigh vacuum (UHV) conditions. We found that on the clean TiO₂(110) surface at 120 K, NH₃ adsorbs exclusively as monomers. On the hydroxylated TiO₂(110) surface at 160 K, we observe 2(NH₃) pairs and (NH₃)₂ dimers in addition to the majority of monomeric NH₃. At 270 K, monomeric NH₃ and surface hydroxyls diffuse together along the [001] direction. Additionally, NH₃ can also diffuse along the surface hydroxyl bridge in the [1-10] direction. On the surface precovered by O adatoms (Oot) at 160 K, we observe the formation of NH₂OH and 2(NH₂OH) species formed by the interaction of NH₃ monomers with Oot and Oot pairs.

O 32.6 Tue 11:00 P3

Real-space study of carbenes using a diazofluorene precursor adsorbed on a Cu(111) surface — •HUSSAIN MAZHAR¹, JULIEN ROWEN², WOLFRAM SANDER², and KARINA MORGENSTERN¹ — ¹Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, 44801 Bochum, Germany — ²Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany

Carbene is a reactive intermediate playing a vital role for many synthesis in the pharmaceutical industry [1]. Here, we study their properties on a metal substrate in real space using scanning tunnelling microscopy (STM) at 5 K. As carbenes are highly reactive species, they cannot be deposited directly on metal surfaces. The arrangement of their precursors on the surface is crucial for the carbene reactivity upon carbene formation. Diazofluorene molecules, already studied on the Ag(111) surface [2], are used as a precursor of the carbene to compare the influence of the surface on carbene reactivity. The STM study reveals dimer and cluster formation of the carbene precursor molecules on Cu(111) when deposited at 50 K and 100 K. While at 50 K more dimer formation occurs, at 100 K cluster formation is noticeable. An electrostatic surface potential map is used to determine charge distribution of the dimers. For carbene formation, a particular energy is required to cleave the diazo part from the molecule. In this study, we used STM manipulation to estimate the energy for the dissociation of

the molecule. [1] Patil, Siddappa A, *Future Med. Chem.* 7. (2015) 1305-1333 [2] Mieres-Perez, Joel, *J. Am. Chem. Soc.* 143. (2021) 4653-4660

O 32.7 Tue 11:00 P3

Thickness-dependent energy level alignment of terrylene molecules on WS₂ monolayer — •QIANG WANG¹, SIFAN YOU³, BJÖRN KOBIN², PATRICK AMSALEM¹, LIFENG CHI³, STEFAN HECHT², and NORBERT KOCH¹ — ¹Institut für Physik & IRIS Adlershof Humboldt-Universität zu Berlin, Berlin, Germany — ²Department of Chemistry & IRIS Adlershof Humboldt-Universität zu Berlin, Berlin, Germany — ³Institute of Functional Nano and Soft Materials (FUN-SOM), Soochow University, Suzhou, China

The exceptional large surface ratio makes 2D TMDC notably sensitive to extrinsic modification. In particular, we study the Van der Waals structure of WS₂ monolayers modified by the conjugated terrylene molecules. We show the terrylene/WS₂ heterostructures exist in different stacking configurations dependent on the layered coverage, revealed by photoemission spectroscopy and scanning tunnelling microscopy (STM). Electronically, the hybrid heterostructures exhibit type-II energy level alignment. It is further determined that the ionization potentials of terrylene, are reduced by 0.54 eV as the molecule switching from flat-lying to standing orientation. The adsorption behaviour is spatially resolved by STM, indicating two different atomic assembles. As determined by photophysical characterization, low energy electron-hole pairs are also populated upon molecule deposition. Meanwhile the external dielectric screening lowers the Rydberg states of WS₂. Our findings reveal the vertical 2D heterostructures enable effective tailoring of both electronic and photophysical properties, which can be applied for various optoelectronic devices.

O 32.8 Tue 11:00 P3

Nanocar Race II: How fast and how long can we drive nano-vehicles? — •TIM KÜHNE¹, KWAN HO AU YEUNG¹, SUCHETANA SARKAR¹, OUMAIMA AIBOUDI², SOYOUNG PARK², FRANZISKA LISSEL², and FRANCESCA MORESCO¹ — ¹Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — ²Leibniz Institute of Polymer Research, 01062 Dresden, Germany

Scanning tunneling microscopy has progressed far beyond just being a probing technique. We can now address and manipulate single molecules and atoms with a great degree of precision and repeatability. The 2nd Nanocar Race saw surface science groups from across the globe design and synthesize molecules of at least 70 atoms with the intent of driving it on Au(111). The conversion of electric impulse from the tip to controllable translation of the nanocar along the FCC sites of Au(111) was demonstrated by each team, although the design philosophy and mediating physics theories varied across the board. Here, we present the TU Dresden nanocar. It was successfully manipulated via inelastic tunneling electrons for 290nm during the 24-hour race.

O 32.9 Tue 11:00 P3

First-Principles Study of Methanol and Benzene Adsorption on In₂O₃(111) — •ANDREAS ZIEGLER¹, MARGARETA WAGNER², ULRIKE DIEBOLD², and BERND MEYER¹ — ¹Interdisciplinary Center for Molecular Materials and Computer Chemistry Center, FAU Erlangen-Nürnberg, Germany — ²Institute of Applied Physics, TU Wien, Austria

Indium oxide is widely used as transparent conductive oxide for electrodes in semiconductor devices, but it is also a promising new catalyst for hydrogenation and dehydrogenation reactions, e.g. methanol synthesis. To probe the reactivity of the most stable (111) termination of In₂O₃, we studied the adsorption of methanol and benzene, two prototypical polar and nonpolar molecules, by DFT geometry optimizations and Car-Parrinello molecular dynamics (CPMD) simulations. We find that the unit cell of the In₂O₃(111) surface is chemically quite heterogeneous: by searching for the most favorable configurations of methanol with increasing coverage from one to nine molecules per unit cell we find that the first three methanol molecules dissociate in one specific region of the unit cell, followed by molecular adsorption on neighboring sites, confirmed by TPD, XPS and ncAFM experiments. Also benzene prefers to adsorb at one specific site in the unit cell. Due to the large size of the unit cell, the benzene molecules are well separated. CPMD simulations show that the molecules can freely rotate and are well trapped at their adsorption site. However, rotation is suppressed for benzene derivatives with additional side groups.