

O 54: Focus Session: Molecular Nanostructures on surfaces - New Concepts towards Complex Architectures III

Organizers: Sabine Maier, FAU Erlangen-Nürnberg; Meike Stöhr, University of Groningen

(Synopsis provided with part I of this session)

Time: Wednesday 10:30–13:00

Location: MA 004

Invited Talk

O 54.1 Wed 10:30 MA 004

Molecularly functionalized surfaces and interfaces — ●ADAM FOSTER — Department of Applied Physics, Aalto University, Finland — NanoLSI, Kanazawa University, Kanazawa 920-1192, Japan — Graduate School Materials Science in Mainz, Staudinger Weg 9, 55128, Germany

Many ideas in next generation technology are predicated on atomic and molecular control of surfaces and interfaces. A natural route to providing this level of control is to design the interface directly using molecular building blocks via self-assembly. Using a combination of modelling approaches in partnership with Scanning Probe Microscopy experiments, in this work we consider several examples where the interface has been designed by the controlled assembly of molecular layers. We first introduce the computational tools at the heart of our methodology, and discuss the challenges when simulating complex assembly processes and comparing to experiment. We then compare the adsorption and reaction mechanisms on a benchmark insulator system [1], and also contrast to processes on conducting surfaces [2]. Finally, we build upon this to consider new insights offered by modern machine learning simulation approaches.

[1] J. Phys. Chem. C 120 (2016) 14730, Phys. Chem. Chem. Phys., 19 (2017) 15172

[2] J. Phys. Chem. C 120 (2016) 8772, Nat. Commun. 7 (2016) 11559, Nat. Commun. 7 (2016) 12711, ACS Nano 11 8122 (2017)

O 54.2 Wed 11:00 MA 004

Artificial Intelligence for Molecules on Surfaces — ●MILICA TODOROVIĆ¹, MICHAEL U. GUTMANN², JUKKA CORANDER^{3,4}, and PATRICK RINKE¹ — ¹Aalto University, Espoo, Finland — ²University of Edinburgh, Edinburgh, UK — ³University of Oslo, Oslo, Norway — ⁴University of Helsinki, Helsinki, Finland

Quantum mechanical accuracy is required to simulate the structures and properties of molecules on surfaces. However, accurate calculations are costly and extensive sampling is prohibitive, so studies into molecular assembly and surface-supported processes like diffusion are guided by human intuition. To promote unbiased studies into molecular surface structures and phenomena, we have combined atomistic simulations with Bayesian optimisation - an artificial intelligence (AI) technique designed for complicated optimisation tasks [1]. We demonstrate how the AI was adapted to learn surface and property landscapes of molecules on surface with minimal computational sampling [2], delivering most stable surface structures with favorable designer properties. Energy landscapes can be further data-mined for low energy paths and associated trajectories to reveal the atomistic mechanisms behind key processes. We showcase the capability of AI to infer complex properties on several examples of atomic and molecular surface adsorbates. [1] M.U. Gutmann and J. Corander, J. Mach. Learn. Res. 17, 1 (2016). [2] M. Todorović, M. U. Gutmann, J. Corander and P. Rinke, arXiv:1708.09274 (2017).

O 54.3 Wed 11:15 MA 004

Monte Carlo simulation of the 2D self-assembly of functional molecules — ●PAWEŁ SZABELSKI¹, DAMIAN NIECKARZ¹, and WOJCIECH RZYSKO² — ¹Department of Theoretical Chemistry, Maria Curie-Skłodowska University, Lublin, Poland — ²Department for the Modeling of Physico-Chemical Processes, Maria Curie-Skłodowska University, Lublin, Poland

Controlled self-assembly of molecular building blocks on solid substrates is a versatile method to create low-dimensional structures with preprogrammed morphology and functions. In this contribution, using theoretical tools, we demonstrate how the structure of large self-assembled molecular systems can be predicted based on individual properties of building blocks at play. In particular we focus on the role of directionality of interactions provided by discrete active centers being part of model star-shaped tectons. Our theoretical predictions are compared with available experimental data and hints on synthesis of organic functional molecules able to form various superstructures

are given. The findings from the Monte Carlo modeling can be useful in designing of 2D supramolecular architectures as well as of covalently bonded structures resulting from on-surface polymerization reactions.

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O 54.4 Wed 11:30 MA 004

Kinetic control in molecular self-assembly on an insulating surface — ●LEV KANTOROVICH¹, CHIARA PARIS¹, ANDREA FLORIS^{1,2}, SIMON AESCHLIMANN³, JULIA NEFF³, FELIX KLING³, and ANGELIKA KÜHNLE³ — ¹King's College London, Strand, London, WC2R 2LS, U.K. — ²University of Lincoln, Brayford Pool, Lincoln LN6 7TS, U.K. — ³Johannes Gutenberg-University Mainz, Duesbergweg 10-14, 55099 Mainz, Germany

We present a new route for creating a set of metastable molecular architectures on surfaces. This approach relies on two key aspects: First, the suitable choice of the initial state of the molecules triggers a well-defined transformation path. Second, the observed path is entirely controlled by kinetics rather than thermodynamics. The feasibility of this route is demonstrated using a model system of dihydroxybenzoic acid molecules on the (10.4) surface of calcite. An initial state of molecular dimers undergoes, upon increase of temperature, a series of structural transitions from clusters to ordered striped and then dense networks, and finally to a disordered structure. Combining high-resolution dynamic atomic force microscopy experiments and density-functional theory calculations, we provide a comprehensive analysis of the fundamental principles driving this sequence of transitions. Our study opens new avenues based on kinetic control as a promising strategy for achieving tailored molecular architectures on surfaces.

O 54.5 Wed 11:45 MA 004

Bishop diffusion involving a chiral flip — ●SIMON AESCHLIMANN^{1,4}, FELIX KLING¹, CHIARA PARIS², ANDREA FLORIS^{2,3}, LEV KANTOROVICH², RALF BECHSTEIN¹, and ANGELIKA KÜHNLE¹ — ¹Institute of Physical Chemistry, Johannes Gutenberg-University Mainz, Duesbergweg 10-14, 55099 Mainz, Germany — ²Department of Physics, King's College London, London WC2R 2LS, United Kingdom — ³School of Mathematics and Physics, University of Lincoln, Brayford Pool, Lincoln LN6 7TS, United Kingdom — ⁴Graduate School Materials Science in Mainz, Staudingerweg 9, 55128 Mainz, Germany

Molecular surface diffusion is one of the most fundamental process in nature with far-reaching impact on a wide range of fields including, e.g., catalysis, sensing and surface functionalization. So far, molecular surface diffusion studies have mainly been limited to high-symmetry surfaces possessing rotational symmetry. Here, using the low-symmetry (10.4) surface of calcite, we present a novel molecular diffusion mechanism that can be described by the bishop move in chess, meaning that only half of the existing lattice sites are accessible for an individual molecular species. Interestingly, due to the only existing symmetry operation of the surface, a glide reflection symmetry, this bishop movement is inevitably associated with a flip in the chiral adsorption footprint of the molecular species towards the surface. Here, we demonstrate the pivotal influence of the surface symmetry on the detailed diffusion mechanism, including the adsorption chirality.

O 54.6 Wed 12:00 MA 004

Tuning the self-assembly of carboxyl-substituted triphenylamine-derivatives on bulk NaCl(001) and KBr(001) — ●MIRUNALINI DEVARAJULU¹, JIA LIU¹, MIN KEN LI¹, CHRISTIAN STEINER¹, BETTINA GLIEMANN², YI LIU¹, TUAN ANH PHAM¹, MILAN KIVALA², and SABINE MAIER¹ — ¹Department of Physics, University of Erlangen-Nürnberg, Erlangen, Germany — ²Department of Chemistry and Pharmacy, FAU Erlangen-Nürnberg, Erlangen, Germany

While most molecular self-assemblies so far have been studied on metallic substrates, comparatively little is known about molecular

self-assemblies on insulating surfaces. One reason is the weak and often unspecific molecule-substrate interaction on bulk insulating surfaces. Therefore, the structure of the self-assemblies is challenging to predict. Here, we present a study on the self-assembly of a carboxyl-substituted dimethylmethylene-bridged triphenylamine derivative [1] on bulk NaCl(001) and KBr(001) by non-contact AFM at low temperature. The intermolecular hydrogen bonding contributes to the formation of 2D monolayers on NaCl(001) and KBr(001). We observed structurally different self-assemblies of the carboxyl-substituted triphenylamine derivative on NaCl(001) and KBr(001), respectively, due to a significant change in lattice mismatch [2]. The surface templating effect and binding motifs will be discussed in detail.

[1] C. Steiner et al. J. Phys. Chem. C, 2015, 119 (46), 25945-25955

[2] S. Maier et al. Phys. Rev. B, 2007, 75, 195408

O 54.7 Wed 12:15 MA 004

Porphyrins on Titania — •THILO GLATZEL¹, RES JÖHR², ANTOINE HINAUT¹, SILVIO DECURTINS³, SHI-XIA LIU³, TOBIAS MEIER¹, RÉMY PAWLAK¹, and ERNST MEYER¹ — ¹University of Basel, Department of Physics, 4056 Basel, Switzerland — ²Lehrstuhl für Angewandte Physik, Ludwig-Maximilians-Universität, 80799 Munich, Germany — ³University of Bern, Department of Chemistry, 3012 Bern, Switzerland

Titania surfaces sensitized with metallo-porphyrins are of increasing interest for photocatalysis or photovoltaics. In these applications, the dye absorbs light and injects the excited electron into the conduction band of the titania. The binding configuration is thereby of great importance for the electron transfer process. To simultaneously investigate the binding configuration and its influence on the charge transfer process, nc-AFM and in particular KPFM are the methods of choice. We studied the adsorption configurations of single Cu-TCPP molecules, a sensitizer commonly used for photocatalysis, on anatase and rutile TiO₂(110). Bimodal nc-AFM at room temperature and under UHV was applied to obtain high resolution on the molecules as well as on the substrate. KPFM was used to investigate the electronic properties of the adsorbed Cu-TCPP. The experimental data reveals that the Cu-TCPP molecules align themselves with respect to the substrate structure resulting in two main orientations. In both cases the KPFM showed a lowered LCPD on the sensitizer, indicating that adsorption is accompanied by charge transfer from the sensitizer to the substrate.

O 54.8 Wed 12:30 MA 004

Anchoring of a dye precursor on NiO(001) studied by non-contact atomic force microscopy — •SARA FREUND¹, ANTOINE HINAUT¹, NATHALIE MARINAKIS², EDWIN C. CONSTABLE², ERNST MEYER¹, CATHERINE HOUSECROFT², and THILO GLATZEL¹ — ¹Department of Physics, University of Basel, Klingelbergstrasse 82,

4056 Basel, Switzerland — ²Department of Chemistry, University of Basel, BPR 1096, Mattenstrasse 24a, 4058 Basel, Switzerland

The properties of metal oxides can be modified when functionalized with complex molecules. These kinds of organic/inorganic surfaces have become important for enabling technologies such as hybrid photovoltaic p-type dye sensitized solar cells. A key parameter for optimized interfaces is not only the choice of the functionalization compounds but also their adsorption geometry on the substrate. The latter requires fundamental studies of such surface-molecule interactions at the nanoscale.

In this contribution, we describe the use of non-contact atomic force microscopy at room temperature to investigate the adsorption of a common organic dye precursor molecule on a NiO(001) single crystal surface. Depending on the degree of surface coverage, single molecules, groups of adsorbates with random or recognizable shapes, or even islands and domains can be identified. The interfaces were imaged with sub-molecular resolution, revealing that the dye precursor lies flat on the surface in a trans-conformation. A charge transfer from NiO to the molecular layer was observed and quantified by Kelvin probe force microscopy, only in the areas, where the molecules are closed packed.

O 54.9 Wed 12:45 MA 004

Infrared Reflection Absorption Spectroscopy Study of Phenylphosphonic Acid on Co₃O₄(111), CoO(111), and CoO(100) — •MATTHIAS SCHWARZ, CHRISTIAN SCHUSCHKE, CHANTAL HOHNER, THAIS NASCIMENTO SILVA, and JÖRG LIBUDA — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg

We applied infrared reflection adsorption spectroscopy (IRAS) in a surface science model study under ultra-high vacuum (UHV) conditions to investigate the coverage dependent growth and thermal stability phenylphosphonic acid (d1,d2-PPA) multilayer and monolayer films on well-ordered Co₃O₄(111), CoO(111) and CoO(100) films on Ir(100). At 180 K, identical amorphous multilayers of intact d1,d2-PPA form on all three surfaces. They rearrange at 250 K, leading to similar recrystallized phases for all three surfaces, however with different molecular orientations. Above 340 K the multilayers desorb and only the chemically anchored monolayers remain on the surface. These are stable up to at least 550 K for all surfaces. However, surface binding and coverage dependencies in the monolayer are highly structure dependent. For d1,d2-PPA on Co₃O₄(111), a tridentate binding mode and full deprotonation was found for low coverages. At higher coverage, this species is replaced by partly protonated bidentate. In contrast, fully deprotonated tridentate dominates for all coverages on CoO(100). On the oxygen terminated CoO(111) bidentate species are found in the zero coverage limit. With increasing coverage, the surface restructures such that tridentate binding mode is enabled. Close to saturation, bidentate binding dominates again, presumably enabling more dense packing.