

O 23: Focus Session: Molecular Nanostructures on surfaces - New Concepts towards Complex Architectures II

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

(Synopsis provided with part I of this session)

Time: Tuesday 10:30–13:00

Location: MA 004

Invited Talk

O 23.1 Tue 10:30 MA 004

Electronic properties of functional organic compounds at surfaces: From zero- to two-dimensional — ●PETRA TEGEDER — Ruprecht-Karls-Universität Heidelberg, Physikalisch-Chemisches Institut

For improvement and optimization of the performance of organic molecule-based devices, comprehensive insight into the physical and chemical properties of the organic material at surfaces is necessary. I will present two case studies in which we investigated the electronic properties of organic/inorganic hybrid systems, namely graphene nanoribbons (GNRs) on gold surfaces and photochromic molecular switches on silicon. The GNRs are generated using a bottom-up approach based on a thermally activated and surface-assisted reaction of suitable precursor molecules. We studied the effect of N-doping on the energy level alignment. Additionally, we identified excitonic states in GNRs on gold surfaces. Incorporating photochromic molecules into organic/inorganic hybrid materials can lead to photoresponsive systems. In such systems, the second-order nonlinear optical properties can be controlled via external stimulation with light at an appropriate wavelength, which we could demonstrate.

O 23.2 Tue 11:00 MA 004

Identifying on-surface reaction products and orbital modifications with photoemission tomography — XIAOSHENG YANG^{1,2}, PHILIPP HURDAX³, LARISSA EGGER³, DANIEL LÜFTNER³, GEORG KOLLER³, PETRA TEGEDER⁴, F. STEFAN TAUTZ^{1,2}, MICHAEL G. RAMSEY³, ●PETER PUSCHNIG³, and SERGUEI SOUBATCH^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — ²Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, Germany — ³Institut für Physik, Karl-Franzens-Universität Graz, NAWI Graz, Austria — ⁴Ruprecht-Karls-Universität Heidelberg, Physikalisch-Chemisches Institut, Germany

Dibromo-bianthracene (DBBA) has been shown to present an effective bottom-up strategy to fabricate atomically precise graphene nanoribbons on metal substrates. Here, we follow the thermally induced chemical reaction of DBBA deposited on Cu(110) to bisanthene (C₂₈H₁₄) by photoemission tomography. By comparison with density functional calculations, we can clearly identify a number of molecular orbitals associated with bisanthene including the filled LUMO. We unambiguously prove the chemical reaction taking place, clarify the molecular conformation and orientation before and after the reaction, and provide information on the charge state as well as on the electronic level alignment of the reaction product. Our work thus demonstrates the potential of photoemission tomography in monitoring complex reactions on surfaces.

O 23.3 Tue 11:15 MA 004

On-surface synthesis and characterization of atomic carbon wires — ●QIANG SUN^{1,2}, SHIYONG WANG¹, WEI XU², PASCAL RUFFIEUX¹, and ROMAN FASEL¹ — ¹Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland — ²Interdisciplinary Materials Research Center, College of Materials Science and Engineering, Tongji University, Shanghai 201804, P. R. China

Carbon-based materials have received tremendous attention, fueled by successive discoveries of novel carbon allotropes such as fullerenes, carbon nanotubes, and graphene. Among others, linear chains of carbon atoms combine ultimately simple structures with intriguing properties. For instance, polyacetylene (PA) is the sp² hybridized one-dimensional hydrocarbon chain. Owing to its simple chemical structure and exceptional electronic properties, PA is an ideal model system for understanding the nature of conducting polymers. Inspired by recent advances in the on-surface synthesis, we aim here at the synthesis of atomic carbon chains by the surface-assisted coupling of ethyne molecule (the simplest alkyne with two terminal alkynyl groups). Here, we report a successful on-surface synthesis of metalated carbyne chains by dehydrogenative coupling of ethyne molecules and copper atoms on a Cu(110) surface, which is characterized by high resolution STM, nc-

AFM, and XPS combined with DFT calculations. Moreover, we have formed both cis and trans PA oligomers on the surface and investigated the electronic properties of trans PA chains through STS and ARPES measurements.

O 23.4 Tue 11:30 MA 004

Novel approach to grow 2D organic topological insulators by on-surface synthesis — ●FABIAN SCHULZ¹, GUOXIAN ZHANG², GERHARD MEYER¹, JULIAN CHAN², and LEO GROSS¹ — ¹IBM Research - Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland — ²University of Ottawa, 120 D'Iorio Hall, Ottawa ON, K1N 6N5, Canada

Honeycomb lattices comprising metal atoms with strong spin-orbit coupling connected by organic linker molecules are predicted to host topologically protected conducting edge states, thus giving rise to two-dimensional organic topological insulators (TIs) [1]. One possible route to create such structures experimentally are self-assembled metal-organic coordination networks grown on surfaces [2]. However, these networks are usually not fully covalently bonded, which would be desirable for realizing organic TIs. Even though there are several strategies to form covalent bonds by on-surface synthesis [3], those are rarely applied to grow metal-organic structures.

Here, the possibility to grow organic TIs by on-surface synthesis is explored. We use atomic force microscopy with CO-functionalized tips to study surface-assisted Ullmann coupling of tris(4-iodobenzene)bismuthine complexes on Ag(111). Our results reveal important challenges that need to be overcome in order for this novel approach to succeed.

[1] Z.F. Wang *et al.*, Nat. Commun. **4**, 1471 (2013).

[2] L. Dong *et al.*, Prog. Surf. Sci. **91**, 101 (2016).

[3] G. Franc *et al.*, Phys. Chem. Chem. Phys. **13**, 14283 (2011).

O 23.5 Tue 11:45 MA 004

Two-dimensional band structure in honeycomb metal-organic frameworks on epitaxial graphene — ●PETER LILJEROTH — Department of Applied Physics, Aalto University, Helsinki, Finland

Metal-organic frameworks (MOFs) are an important class of materials that present intriguing opportunities in, e.g., the fields of sensing, gas storage, catalysis, and optoelectronics. While there is a tremendous number of examples of three-dimensional, bulk, MOFs, synthesis strategies for two-dimensional (2D), monolayer thick MOFs are more limited. These systems are drawing growing interest as a promising platform for realizing designer materials with engineered electronic structures. The synthesis of 2D-MOFs is usually carried out on metal surfaces (e.g. Au, Ag, Cu), where it is difficult to access their intrinsic electronic properties.

We demonstrate synthesis of cobalt-dicyanobiphenyl and cobalt-dicyanoanthracene MOFs on epitaxial graphene and characterize their atomic geometry and electronic structure using atomic force microscopy (AFM), scanning tunneling microscopy and spectroscopy (STM and STS). We show the formation of a strongly coupled 2D electronic system in a MOF synthesized on a weakly interacting substrate. These results open the experimental path towards stand-alone MOF-based designer optoelectronic materials with complex, engineered electronic structures. The direct growth of 2D MOFs on graphene outlines possibilities of heterostructures with inorganic 2D materials with potential applications in sensors, catalysis and optoelectronics.

O 23.6 Tue 12:00 MA 004

Quantum dot coupling modification through barrier width in organo-halide arrays — ●JORGE LOBO-CHECA¹, IGNACIO PIQUERO-ZULAICA², ALI SADEGHI³, ZAKARIA M. ABD EL-FATTAH², TOSHIHIRO OKAMOTO⁴, and SHIGEKI KAWAI⁵ — ¹Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Univ. Zaragoza, Spain — ²Centro de Física de Materiales, CSIC/UPV-EHU. San Sebastian, Spain — ³Department of Physics, Shahid Beheshti Univ., Iran — ⁴Department of Advanced Materials Science, Univ. Tokyo, Japan — ⁵International Center for Materials Nanoarchitectonics, NIMS, Japan

Quantum dot (QD) arrays on surfaces, in the form of nanoporous networks, are candidates for studying fundamental physical phenomena such as 2DEG confinement. Tunability has been accomplished by varying the pore size, geometrical shape and molecule substrate interactions. Moreover, inter-dot coupling is validated by photoemission through the generation of new dispersive bands and modulated through thermodynamics and the condensation of guest elements.

Here, we validate the 2DEGs' modification through inter-dot barrier width by STM/STS/AFM, ARPES and extended model calculations. We engineer the inter-dot barrier width by substitution of a single atom in a haloaromatic compound and tune the confinement properties at each nanopore, affecting the degree of QD intercoupling both on bulk and thin Ag films alike [1].

[1] I. Piquero-Zulaica et al., *Nat. Commun.* **8**, 787 (2017).

O 23.7 Tue 12:15 MA 004

Engineering the surface state of Au(111) by molecular patterning — JUN LI¹, ●NICO SCHMIDT¹, STEFANO GOTTARDI¹, LEONID SOLIANYK¹, JUAN CARLOS MORENO-LOPEZ², ZAKARIA M. ABD EL-FATTAH^{3,4}, IGNACIO PIQUERO-ZULAICA⁵, JORGE LOBO-CHECA⁵, and MEIKE STÖHR¹ — ¹Zernike Institute for Advanced Materials, University of Groningen, Netherlands — ²Faculty of Physics, University of Vienna, Austria — ³Faculty of Science, Al-Azhar University, Nasr City, Egypt — ⁴ICFO-Institut de Ciències Fotoniques, The Barcelona Institute of Science and Technology, Spain — ⁵Materials Physics Center, San Sebastian, Spain

The controlled tuning of material properties on the nanometer scale is a central goal in nanoscience. Artificial nanostructures can be built by STM in an atom-by-atom fashion. Corral structures built in this way were shown to confine the surface state electrons and locally modify the electronic surface properties. However, the manipulation process is impractical to change the properties of the entire surface. In contrast, molecular self-assembly offers the possibility to build well-ordered and defect-free nanostructures. By using different molecular building blocks, networks of different sizes and symmetries can be formed, which allows for tuning the electronic structure not only locally but also surface wide. Here, we report on tuning the electronic structure of Au(111) by adsorbing a porous molecular network made from 1,3,5-benzenetribenzoic acid molecules. With ARPES the formation of an artificial band structure based on surface state confinement was detected.

O 23.8 Tue 12:30 MA 004

The chemistry of artificial 2D atoms implemented at a metal-molecule interface — AIZHAN SABITOVA^{1,2}, JEFFREY RAWSON^{3,4,2}, RUSLAN TEMIROV^{1,2}, and ●F. STEFAN TAUTZ^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — ²Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, Jülich, Germany — ³Peter Grünberg Institut (PGI-6), Forschungszentrum Jülich, Germany — ⁴Institute of Inorganic Chemistry, RWTH Aachen, Germany

Localising the hybrid metal-molecule interface state of PTCDA/Ag(111) at artificially patterned vacancies we form atom-like structures whose electronic states exhibit well-defined angular momenta, giving rise to direction-specific bonding interactions. These two-dimensional artificial atoms can be constructed into multianometer-scale molecules whose wavefunctions exhibit features, such as sigma and π -bonding configurations, previously only attributed to natural molecular orbitals.

O 23.9 Tue 12:45 MA 004

Band structure of a metal-molecule interface state revealed by feature recognition scanning tunneling spectroscopy — ●AIZHAN SABITOVA^{1,2}, RUSLAN TEMIROV^{1,2}, and F. STEFAN TAUTZ^{1,2} — ¹Peter Grünberg Institute (PGI-3), Forschungszentrum Jülich, Germany — ²JARA - Fundamentals of Future Information Technology

Adsorption of a monolayer of 3,4,9,10-perylenetetracarboxylicdianhydride (PTCDA) on Ag(111) leads to emergence of an unoccupied free electron-like interface state [1]. Although the state is believed to be a hybrid of the Shockley surface state of Ag(111) and unoccupied molecular orbitals [1-4], the impact of the molecular overlayer has not been probed directly. Combining Fourier transform scanning tunneling spectroscopy with a new approach called feature recognition scanning tunneling spectroscopy (FR-STs) we map the dispersion of the PTCDA/Ag(111) interface state, resolve the gaps at the boundaries of its Brillouin zone, and image the corresponding standing wave band states. This information allows to reconstruct the scattering potential introduced by the molecular lattice.

[1] R. Temirov et al., *Nature* **444**, 350-353 (2006)

[2] C.H. Schwalb et al., *Phys. Rev. Lett.* **101**, 146801 (2008)

[3] M. Dyer and M. Persson, *New. J. Phys.* **12**, 063014 (2010)

[4] N.L. Zaitsev et al., *J. Exp. Theor. Phys.* **110**, 114-120 (2010)