O 4: Mini-Symposium: Free-standing functional molecular 2D materials I

Time: Monday 10:30–12:30 Location: R2

Invited Talk O 4.1 Mon 10:30 R2

Ion permeation across atomically thin materials — •Marcelo Lozada-Hidalgo — Department of Physics and Astronomy, The University of Manchester

The basal plane of graphene is impermeable to all atoms and molecules - even for helium, the smallest - at ambient conditions. On this basis, it was believed that graphene would be impermeable even to protons, the nuclei of hydrogen atoms. Unexpectedly, we found that graphene is highly permeable to these ions at ambient conditions. Since these early experiments, our research has established that permeation through 2D crystals can be fundamentally different from that in bulk materials. Even basic notions like bulk 3D resistivity need to be considered carefully. Many fundamental questions remain open even for graphene, the most researched of theses crystals - and the vast majority of these materials remain unexplored from this perspective. This talk will provide an overview of this new field of research and discuss some of the recent developments involving new 2D materials.

O 4.2 Mon 11:00 R2

Ultrahigh ionic exclusion through 1-nm-thick carbon nanomembranes — •Yang Yang[1,2], Roland Hillmann[1], Yubo Qi[1], Riko Korzetz[1], Niklas Bierε[1], Daniel Emmrich[1], Michael Westphal[1], Björn Büker[1], Andreas Hütten[1], André Beyer[1], Dario Anselmetti[1], and Armin Gölzhäuser[1] — [1]Faculty of Physics, Bielefeld University, Germany — [2]Department of Chemical Engineering, Imperial College London, UK

The "single-file" transport of water in natural nanoconduits (i.e., aquaporins) inspires the development of high-performance artificial membranes for water purification. In particular, 2D materials open a path to new filtration processes. However, a key challenge has been finding an effective way to create a large number of narrow channels in the material to realize the desired high water permeance and high ion rejection. Carbon Nanomembranes (CNMs) are 2D carbon sheets fabricated from crosslinking of self-assembled monolayers. This work will show that a ~1.2 nm thick CNM made of terphenylthiol (TPT) precursors possesses a very high density (~10^18 m^2, i.e., 1 sub-nm pore per square nanometer) of sub-nm channels. TPT CNMs let water pass very quickly, but hinder the passing of ions including protons. The membrane resistance in 1 M chloride solutions reaches ~104 Ω cm^2, comparably high to that of lipid bilayers. TPT CNMs show a ~80 times enhancement in water productivity over the commercial forward osmosis membranes. These observations encourage the use of CNMs for producing clean water. The versatile manufacturing process also enables CNM functions to be customized at a molecular level.

O 4.3 Mon 11:15 R2

Atomic-scale carving of nanopores into a van-der-Waals heterostructure with slow highly charged ions — Janine Schwestka[1], Heena Inani[2], Mukesh Tripathi[2], Anna Niggas[1], Niall McEvoy[3], Florian Libisch[4], Friedrich Aumayr[1], Jani Kotakoski[2], and •Richard Wilhelm[1] — [1]TU Wien, Institute of Applied Physics — [2]University Vienna, Faculty of Physics — [3]Trinity College Dublin, AMBER School of Chemistry — [4]TU Wien, Institute for Theoretical Physics

Tailoring the mechanical, electronic and chemical properties of functional 2D materials post-growth demands methods with highest surface sensitivity. Especially in van-der-Waals (vdW) heterostructures a method which only modifies a particular layer in the layer stack is highly beneficial. Here we report on nanoscale perforation of a MoS_2 layer on-top of a single layer of graphene by irradiation with individual slow highly charged ions. While we can perforate the MoS_2 layer with a high efficiency, the graphene stays intact. Even more so, when changing the layer order, the graphene facing the ion beam shields the MoS_2 from damage and the entire vdW heterostructure remains intact. While this monolayer sensitivity is based on different susceptibilities of metals and semi-conductors to highly charged ion induced potential sputtering, up to three layers of MoS_2 on-top of graphene also show perforation only in the topmost 1-2 layers. Hence, even a susceptible material can be perforated with monolayer precision. The mechanism of extreme surface sensitive energy deposition is discussed.

Invited Talk O 4.4 Mon 11:30 R2

Macroscopic Two-Dimensional Polymers: Synthesis and Structure Control — •Zhikun Zheng — Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, P. R. China

At present, one of the key challenges faced by the scientific community is to go beyond graphene, a prototypical two-dimensional polymer (2DP, a laterally infinite, one atom- or monomer-unit thin, free-standing network with long-range order along two orthogonal directions), to synthesize its analogues with structural control at the atomic- or molecular- level under mild conditions. Here we present the rational synthesis of monolayer and multilayer 2DPs at an air-water interface. Such 2DPs are highly crystalline with controlled aggregate structure and microstructure and tunable single-crystal domain size in the range of tens of nanometers to several micrometers. They have a tunable thickness ranges from 0.7 nm to around 1μm and a lateral size up to 4-inch wafer, and can be freely suspended over 40 μm * 40 μm sized holes. They are rigid and flexible, and can be conformed and bonded robustly to nearly any surface, facilitating their integration with target supports or into devices for the extraction of properties. On the basis of the elucidation of their molecular structures, near atomic structures, grain boundaries and edge structures, some preliminary structure-property relationships of the 2DPs were obtained.

O 4.5 Mon 12:00 R2

Low-energy electron irradiation induced synthesis of molecular nanosheets: Influence of the electron beam energy — •Christof Neumann[1], Richard A. Wilhelm[2,3], Maria Küllmer[1], and Andrey Turchanin[1] — [1]Institute of Physical Chemistry, Friedrich Schiller University Jena, 07743 Jena, Germany — [2]Institute of Applied Physics, TU Wien, 1040 Vienna, Austria — [3]Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany

Aromatic self-assembled monolayers (SAMs) can be cross-linked into molecular nanosheets - carbon nanomembranes (CNMs) - via low-energy electron irradiation. Due to their favorable mechanical stability and tunable functional properties, they possess a high potential for various applications including nanosensors and separation membranes. Here, we studied the cross-linking of 4'-nitro-1,1'-biphenyl-4-thiol SAM on gold. The SAM samples were irradiated with different electron energies ranging from 2.5 to 100 eV in ultra-high vacuum and subsequently analysed by complementary techniques including X-ray photoelectron spectroscopy (XPS). To demonstrate the formation of CNMs, the formed two-dimensional molecular materials were transferred onto grids and oxidized wafer and analyzed by different microscopy techniques. We found a strong energy dependence for the cross section for the cross-linking process and conducted a comparative analysis of the cross sections for the C-H bond scission via electron impact ionization and dissociative electron attachment. C. Neumann et al., Faraday Discuss. 2020 DOI: 10.1039/C9FD00119K

O 4.6 Mon 12:15 R2

On-surface synthesis of nonbenzenoid planar carbon allotropes — •Qitang Fan[1], Linghao Yan[2], Daniel Martin-Jimenez[3], Daniel Ebeling[3], Matthias W. Tripp[1], Ondřej Krejčí[2], Stefan R. Kachel[1], Claudio K. Krug[1], Adam S. Foster[2], Ulrich Koert[1], André Schirmeisen[3], Peter Liljeroth[2], and J. Michael Gottfried[1] — [1]Department of Chemistry, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany — [2]Department of Applied Physics, Aalto University, FI-00076 Aalto, Finland — [3]Institute of Applied Physics (IAP), Justus Liebig University Gießen, Heinrich-Buff-Ring 16, 35392 Gießen, Germany

The quest for new carbon allotropes with unusual properties persistently intrigues scientists from various fields. However, the challenge of synthetic carbon allotropes still remains in the limited protocols for their controlled bottom-up construction. To date, no planar sp^2 carbon allotropes other than graphene have been achieved. Here, we show the bottom-up growth of sheets of monoatomically-thick nonbenzenoid carbon allotropes via an Ullmann-type coupling followed by dehydrogenative/dehydrofluorinative C-C coupling reactions on metal surfaces.

Such carbon allotropes consist of periodically arrayed non-hexagonal rings of sp^2 carbon atoms, exhibiting electronic properties contrasting those of the benzenoid graphene. We expect that our surface-science based strategy will enrich the bottom-up toolbox for the synthesis of other planar carbon allotropes.