CPP 52: Focus: Two Dimensional Functional Materials I

Organizers: Armin Goelzhaeuser (Universität Bielefeld), Holger Frauenrath (EPFL Lausanne)

Two-Dimensional Functional Materials are characterized by having one dimension in the molecular or atomic length scale, whereas the other two dimensions are extended. This 2D geometry allows a use as functional components or hybrids in electronics, fluidics, sensing or filtration. The Focus Session will cover a variety of materials, their fabrication processes, properties and applications. A particular emphasis is laid on 2D materials whose fabrication includes molecular assembly: 2D polymers, bio membranes, covalent organic frameworks (COFs), functionalized graphene, Carbon Nanomembranes (CNMs) and others.

Time: Thursday 9:30–12:30 Location: H51

Invited Talk CPP 52.1 Thu 9:30 H51

Synthesis of 2D polymers — •Dieter A. Schlüter — ETH Zurich, Department of Materials, Zurich, Switzerland

Two-dimensional materials (2DM) are sheet-like entities and of great interest for their manifold properties. Famous representatives are graphene, boronitride or molybdenum disulfide. 2DMs are often provided by nature or are obtained under harsh conditions. Such conditions exclude the synthetic arsenal of organic chemistry to be used for rational sheet creation, sheet structure variation and sheet engineering on a molecular level. Recently it was shown that covalent monolayer sheets can be easily accessed at room temperature by genuine two-dimensional polymerizations of organic monomers applying simple protocols. They include spreading of monomers at an air/water interface or crystallizing them into layered single crystals followed by metal complexation or light-induced growth reactions. These growth reactions result in macroscopic sheets of considerable mechanical strength. Some of them are composed of planar repeat units over their entire expanse and were introduced as synthetic two-dimensional polymers (2DP). Particularly in view of the ease of synthesis and the high level of structure control during polymerization we consider this the onset of a major research activity with serious applications at the horizon. Synthetic sheets and 2DPs will increasingly complement graphene and other known sheets. The contribution addresses strategic, synthetic and analytical issues and provides a view into future.

Invited Talk CPP 52.2 Thu 10:00 H51

Carbon nanomembranes as a platform for engineering of functional 2D materials — •Andrey Turchanin — Institute of Physical Chemistry, Friedrich Schiller University Jena, 07743 Jena, Germany — Jena Center for Soft Matter (JCSM)

Carbon nanomembranes (CNMs) are ultrathin molecular sheets (~1 nm) which can be generated via electron, ion or photon induced crosslinking of aromatic self-assembled monolayers. Similar to graphene or other atomically thin 2D materials (hBN, MoS2, etc.) they possess mechanical integrity and therefore can be transferred from their original substrates onto new substrates, fabricated as suspended sheets or stacked into van der Waals heterostructures with a precise control over their thickness. Their physical and chemical properties can be tuned via an appropriate choice of molecular precursors or their post modification, providing a flexible platform for engineering of functional 2D materials. In this talk, some examples of these materials and their applications in devices will be presented. These examples include: (i) biofunctional and photoactive CNMs; (ii) gratings for matter-wave interferometry; (iii) growth of graphene with adjusted electronic and structural properties; (iv) chemical functionalization of graphene and MoS2 field-effect devices; (v) novel hybrid 0D/2D layered materials.

CPP 52.3 Thu 10:30 H51

Functional Carbon Nanosheets From Amphiphilic Hexayne Precursors At Interfaces — •Bjoern Schulte, Stephen Schrettl, and Holger Frauenrath — École Polytechnique Fédérale de Lausanne, Institute of Materials, Laboratory of Macromolecular and Organic Materials, Station 12, 1015 Lausanne, Switzerland

The access to functional two-dimensional carbon nanomaterials remains challenging despite intensive research. Established synthetic routes follow either top-down or bottom-up strategies. Top-down approaches yield materials with a high degree of structural perfection but are mostly limited to small-scale production. Bottom-up approaches promise to be better scalable, but often preclude chemical functionalization of carbon nanomaterials due to the high temperatures required for the carbonization of the precursors. Recently, our group reported on a new approach to obtain two-dimensional carbon nanomaterials from hexayne amphiphiles as molecular precursors. The amphiphilic precursors contain a segment of sp-hybridized carbons that is highly reactive and undergoes carbonization upon irradiation with UV light at room temperature. These mild conditions allow to transfer the chemical functionality of the precursor to the carbon nanomaterial. Based upon the formation of a dense self-assembled monolayer of hexayne precursors at the air-water-interface amphiphilic carbon nanosheets with a thickness of less than 2 nm and lateral dimensions of square centimeters are obtained. Further extending our work, we will provide a more detailed study of the properties of hexayne amphiphiles at interfaces.

CPP 52.4 Thu 10:45 H51

Touchless finger motion tracking with humidity sensitive 1D Photonic Crystals — •Katalin Szendrei — Max Planck Institute for Solid State Research, Stuttgart, Germany — Ludwig Maximilians Universität, München, Germany

1D Photonic Crystals (1D PCs) are periodic multilayered nanostructures exhibiting a photonic band gap - a forbidden spectral range for photons propagating through the nanostructure. These structures are promising candidates for smart optical detectors as the structural color can be dynamically changed by external chemical, physical or biological stimuli. Herein we present 1D PCs fabricated by bottom up assembly from colloidal metal oxide nanoparticles and colloidally stable suspensions of antimony phosphate 2D nanosheets, which show an ultrasensitive response to local humidity changes caused by the moisture induced swelling of the nanosheets. Integrated into a PC, a resulting full spectrum color change is indicative of ultrahigh sensitivity towards water vapor. The combination of a high selectivity, high reproducibility and response time in the subsecond time scale allowed us to detect minute humidity changes. As the human finger is surrounded by a humid atmosphere, finger positions and motions can be tracked and indicated by color changes of the BS in realtime under touchless conditions. These experiments suggest a new device architecture as alternative to the common touchscreen technology. With the touchless technology, the disadvantages of hygienic aspects, mechanical vastage could be avoided, while at the same time the user receives a direct feedback of the finger motion through the optical answer of the display.

15 min. break

CPP 52.5 Thu 11:15 H51

Making atomically thin perforated nanomembranes — •Andreas Winter^{1}, Yasin Ekinci^{2}, Armin Gölzhäuser^{3}, and Andrey Turchanin^{1,4} — ^{1}Institute of Physical Chemistry, Friedrich Schiller University Jena, 07743 Jena — ^{2}Laboratory for Micro- and Nanotechnology, Paul Scherrer Institute, 5232 Villigen, Switzerland — ^{3}Faculty of Physics, Bielefeld University, 33615 Bielefeld — ^{4}Jena Center for Soft Matter, 07743 Jena

Two-dimensional (2D) materials like graphene, hexagonal boron nitride or carbon nanomembranes (CNMs) have recently attracted enormous interest due to their potential use in electronics, chemical and biological sensors, nanofilters, and hybrid materials. Lithographic patterning of 2D materials allows to form nanostructures required e.g. in filter or nanosensoric applications. In this respect, extreme UV interference lithography (EUV-IL) provides possibilities for large-scale and high resolution patterning with an ultimate size limit in the 10 nm-range. Here we present the preparation of atomically thin perforated nanomembranes and their characterization with a helium ion microscope (HIM), which is especially suitable to image topographic features of freely suspended membranes. Examples for the area-selective crosslinking of self-assembled monolayers and resist-based lithography as well as the use of perforated membranes for interferometry of massive molecules will be given.

CPP 52.6 Thu 11:30 H51

Transfer of covalently modified large area graphene

— •Felix Rösicke[1,2], Marc A. Gluba[1], Guoguang Sun[3], Karsten Hinrichs[3], Jörg Rappich[1], and Norbert Nickel[1] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany — [2]SALSA - School of Analytical Sciences Adlershof, Berlin, Germany — [3]Leibniz - Institut für Analytische Wissenschaften - ISAS - e.V., Department Berlin, Berlin, Germany

We have investigated the electrochemical grafting of CVD grown large area graphene by p-aminophenyl residues from the respective diazonium salt (p-aminobenzenediazonium tetrafluoroborate). Subsequently, these amino functional groups were modified by activated p-nitrobenzoic acid via an amidation reaction. All processes were performed before and after the transfer of graphene onto SiO2 coated silicon wafers. After the electrochemical grafting the samples were characterized using Raman backscattering and infrared spectroscopic ellipsometry measurements. The data show that similar results were obtained for grafting of graphene on Cu foil and SiO2 coated silicon. Moreover, electrochemically functionalized graphene on Cu was successfully transferred to other substrates without damaging the functional groups. Considering the variety of possible diazonium cations, this opens the possibility to the use of modified graphene as tailored modular building block for specific surface functionalization.

CPP 52.7 Thu 11:45 H51

Gas permeation through carbon nanomembranes

— •Vahe Chinaryan[1], Sergey Shishatskiy[2], Jan Wind[2], Xianghui Zhang[1], Henning Vieker[3], Polina Angelova[3], Volker Abetz Abetz[2], André Beyer[1], and Armin Gölzhäuser[1] — [1]Physics of Supramolecular Systems, University of Bielefeld, 33615 Bielefeld, Germany — [2]Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, 21502 Geesthacht, Germany — [3]CNM Technologies GmbH, 33609 Bielefeld, Germany

The gas permeation characteristics of carbon nanomembranes (CNMs) from self-assembled monolayers are reported. CNMs are 1 nm thick sheets, made by the cross-linking of molecular monolayers. CNMs were placed onto polydimethylsiloxane (PDMS) membranes to determine the gas permeation characteristics for single- and multi-layers of CNMs. CNMs made from different molecules having thicknesses from 0.6 nm up to 1.2 nm were investigated with regard to the permeation of different gases (He, H2, CO2, O2, N2,...). The CNM-PDMS composites were also characterized by X-ray photoelectron spectroscopy and helium-ion microscopy. The permeation characteristic of CNMs indicates a molecular-sieve-like transport mechanism which can be attributed to molecular-sized channels in CNMs. Additionally, the permeance of CNMs is adjustable by varying the length of the precursor molecules, i.e. the thickness of single-layer CNMs. Multilayers of CNMs show a permeation that differs significantly from single-layer CNMs, possibly due to the diffusion of the permeating molecules in between the CNM layers.

CPP 52.8 Thu 12:00 H51

Covalent functionalisation of pristine and vacancy defective single-walled carbon nanotubes with diisocyanates

— •Mariana Kozlowska — University of Bialystok, Ciolkowskiego Str. 1K, 15-245 Bialystok, Poland

Mechanical properties and thermal stability of polyurethanes can be improved with the addition of small amounts (0.1 wt%) of carbon nanotubes (CNTs). The formation of such hybrid systems may be proceeded via covalent grafting of polyurethanes to reactive isocyanate groups located on the sidewalls and at the ends of CNTs. The isocyanate groups can be attached to the CNT surface during the reaction between the aromatic diisocyanates with the carboxyl or hydroxyl groups on its surface.

The present work focuses on the structural properties of aromatic diisocyanates (4,4-methylene diphenyl diisocyanate, toluene-2,4-diisocyanate) covalently attached to the pristine and defective (single vacancy and 5-8-5 divacancy) SWCNT(10,0). The detailed analysis of the results obtained using static DFT calculations in combination with Car-Parrinello molecular dynamics simulations at 300 K will be shown.

The authors gratefully acknowledge the financial support of the University of Bialystok within the Grant for Research of Young Scientists, grant number BMN 175.

CPP 52.9 Thu 12:15 H51

Quantitative SFM-Imaging of Graphene Functionalization: Toward Well-Defined Wrappings for Multivalent Virus Interactions

— •Mohammad Fardin Gholami[1], Daniel Lauster[2], Kai Ludwig[3], Julian Storm[2], Benjamin Ziem[3], Nikolai Severin[1], Christoph Böttcher[3], Jürgen P. Rabe[1], Andreas Herrmann[2], Rainer Haag[3], and Mohsen Adeli[3] — [1]Institut für Physik & IRIS Adlershof, Humboldt-Universität zu Berlin — [2]Institut für Biologie, Humboldt-Universität zu Berlin — [3]Institut für Chemie und Biochemie, Freie Universität Berlin

Multivalency is widely used by nature to control biological interactions. Therefore, we also considered it for the design of a new generation of anti-viral drugs. Two-dimensional materials are promising carriers for multivalency. Graphene, in particular, is very robust yet chemically rather inert and therefore it is difficult to control the density distribution of its functionalization. We employed Scanning Force Microscopy (SFM) in quantitative imaging mode to investigate the functionalization of thermally reduced graphene oxide sheets and further used the sheets for the inhibition of the vesicular stomatitis virus (VSV) as a model virus. The functionalization of the sheets was carried out using a [2+1] nitrene cycloaddition reaction at ambient conditions. SFM imaging reveals a high density and homogenous distribution of the functionalization, depending on reaction conditions. Moreover, it allows to gain insight into the interaction of the multivalently functionalized sheets with VSV depending on the type and density of the functionalization.