# CPP 69: Thin Films, Nanostructures and Nanoparticles II

Time: Friday 10:15–13:00

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Shear Exfoliation of layered silica in organic solvents — •MICHAEL HUTH and VEIT WAGNER — Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

There is a large interest in the delamination of layered silica for the production of nanocomposites. Those nanocomposites can be used for several applications, like reinforcement, flame retardant agent, or barrier applications. For all those applications, a uniform dispersion of monolayers in the nanocomposites is essential for the improvement of overall performance. In this work, layered silicaes with different intercalated molecules, so-called intercalated agents are used. Those agents change the interlayer distance between the layers forming the silica flake. The influence of those changes on the dispersion process, as well as on the morphology of the dispersed plates is investigated. The dispersions of clay are processed using a shear exfoliation in chloroform. The dispersions consist of layered silica flakes of  $\sim 1.5 \ \mu m$ length and with a thickness down to 3 nm, equivalent less than four monolayers. The obtained high aspect ratio flakes, were characterized by microscopy (TEM and AFM), UV-Vis and gravimetric measurement. The results show that high interlayer distances favor a stable dispersion of layered silicaes with a thickness of just a few monolayers.

#### CPP 69.2 Fri 10:30 ZEU 114

Gas permeation through free-standing carbon nanomembranes — •PETR DEMENTYEV<sup>1</sup>, POLINA ANGELOVA<sup>2</sup>, HENNING VIEKER<sup>2</sup>, DANIEL EMMRICH<sup>1</sup>, and ARMIN GÖLZHÄUSER<sup>1</sup> — <sup>1</sup>Universität Bielefeld, Fakultät für Physik, Universitätsstr. 25, Bielefeld — <sup>2</sup>CNM Technologies GmbH, Herforder Str. 155a, Bielefeld

Despite membranes-based gas separation can provide lower operation costs compared to distillation and sorption methods, membranes of superior permeance and selectivity are still under development. 2D materials seem to be promising in this context, as nanoporous membranes with the least thickness and no tortuosity would provide the ultimate permeation rate and could potentially work as molecular sieves.

Herein we employ a newly developed high vacuum permeation setup to study mass transport through free-standing carbon nanomembranes (CNMs). CNMs are formed out of self-assembled monolayers of molecules and are mechanically stable. Furthermore, CNMs can be fabricated on a large scale, and their properties are widely tunable depending on the preparation conditions.

Various CNMs were probed towards permeation of helium, neon, nitrogen, oxygen, argon and carbon dioxide. Mass-spectrometry detection enabled to determine the permeation rate and the membrane selectivity. Some of the samples were found to have defects with a characteristic size of 100 nm which was confirmed by helium ion microscopy. In turn, the intact samples were proved to be dense but highly selective to helium. We discuss the mechanism of gas separation as well as the origin of defects.

#### CPP 69.3 Fri 10:45 ZEU 114

Transfer and characterization of covalently modified large area graphene — •FELIX RÖSICKE<sup>1,2</sup>, MARC A. GLUBA<sup>1</sup>, CHRISTOPH KRATZ<sup>3</sup>, TIMUR SHAYKHUTDINOV<sup>3</sup>, NORBERT H. NICKEL<sup>1</sup>, JÖRG RAPPICH<sup>1</sup>, and KARSTEN HINRICHS<sup>3</sup> — <sup>1</sup>Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany — <sup>2</sup>SALSA - School of Analytical Sciences Adlershof, Berlin, Germany — <sup>3</sup>Leibniz - Institut für Analytische Wissenschaften - ISAS - e.V., Department Berlin, Germany

We have investigated the electrochemical grafting of CVD grown large area graphene, as grown on copper, by p-(N-maleimido)phenyl residues from the respective diazonium salt (p (N maleimido)phenylbenzenediazonium tetrafluoroborate). The samples were characterized using Raman backscattering and infrared spectroscopic ellipsometry measurements, both prior and after transfer to a thin gold film on silicon. Optical simulations of the C=O vibrations were performed, determining the thickness of the functional layer to approximately 4 nm, showing the possibility of a lossless transfer. Furthermore, AFM-IR experiments were performed to confirm both the thickness and homogeneity of the maleimido layer. To prove the reactivity of the p-(N-maleimido)phenyl layer, the Michael addition of a thiol was monitored via IR-microscopy. Considering the variety of possible diazonium cations, this opens the possibility to the use of

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modified graphene as tailored modular building block for facile and specific surface functionalization.

CPP 69.4 Fri 11:00 ZEU 114 **Pyrolysis of carbon nanomembranes studied by gas per meation measurements** — •ANDRÉ BEYER, NILS KLEMENT, RIKO KORZETZ, XIANGHUI ZHANG, BERTHOLD VÖLKEL, and ARMIN GÖLZHÄUSER — Physics of Supramolecular Systems and Surfaces, Bielefeld University, 33615 Bielefeld, Germany

Carbon nanomembranes (CNMs) from aromatic self-assembled monolayers are made by electron exposure of the molecular monolayers, resulting in cross-linked membranes which are 1 nm thick and exhibit molecular sieving characteristics in gas permeation experiments [1]. Annealing at 1200 K in vacuum transforms CNMs into nanocrystalline graphene [2, 3]. Here, this transformation process is studied by gas permeation measurements of CNMs after annealing at different intermediate temperatures in the range between 600 K and 900 K. To this end, CNMs were placed onto polydimethylsiloxane (PDMS) membranes after completion of the annealing process to determine their gas permeation characteristics with different gases (He, Ne, CO<sub>2</sub>, Ar, Kr, N<sub>2</sub>). A resistance model is employed to discriminate the permeation characteristics of the annealed CNMs from the PDMS support membranes [1]. It is found that a major part of the transformation process occurs at temperatures between 670 K and 770 K.

[1] M. Ai et al., Adv. Mater. 26 (2014) 3421.

[2] A. Turchanin et al., Adv. Mater. 21 (2009) 1233.

[3] A.Turchanin, et al., ACS Nano 5 (2011) 3896.

CPP 69.5 Fri 11:15 ZEU 114 **Transparent Graphene Electrodes for Biomedical Appli cations** — •PRANOTI KSHIRSAGAR<sup>1</sup>, THOMAS CHASSÉ<sup>3</sup>, MONIKA FLEISCHER<sup>2</sup>, and CLAUS J. BURKHARDT<sup>1</sup> — <sup>1</sup>NMI Natural and Medical Sciences Institute at the University of Tübingen, 72770 Reutlingen (Germany) — <sup>2</sup>Institute for Applied Physics and Center LISA+, Eberhard Karls University Tübingen, 72076 Tübingen (Germany) — <sup>3</sup>Institute of Physical and Theoretical Chemistry and Center LISA+, Eberhard Karls University Tübingen, 72076 Tübingen (Germany)

Since its isolated preparation in 2004, graphene is one of the most extensively researched materials. However, the entry of graphene into the field of biomedicine is relatively recent. Microelectrode arrays (MEAs) are often used to record the cellular activity from cells like neurons or cardiomyocytes. Au, TiN, Pt and PEDOT-CNTs are some of the electrode materials which are excellently suited for the cellular recordings. However, all these materials are opaque posing limitation for applications such as optogenetics and calcium imaging.

Here we present the development of MEAs with transparent graphene electrode and their application. 2.5 cm x 2.5 cm largely monolayer graphene is CVD grown and subsequently transferred onto the conduction lines of a MEA substrate. Detailed correlative scanning electron microscopy (SEM) and Raman spectroscopy is performed confirming the presence of graphene after each processing step. SEM is used for visualization of graphene and Raman confirms the number of layers. Graphene micro electrodes of 30 micron diameter are fabricated with this reliable process and successfully tested with cell cultures.

## 15 min break

Self-assembled monolayers (SAMs) of thiols on gold can be patterned using a variety of physical and chemical methods. Irradiation of SAMs on gold with a pulsed 532 nm laser beam leads to thermal desorption of thiol molecules. The gaps are filled with a second thiol SAM and a patterned SAM is obtained. Photothermal patterning of SAMs enables the fabrication of arbitrary structured monolayers with lateral dimensions in the centimetre range. We demonstrate that phothothermal desorption of aromatic thiols can be used to produce patterned twodimensional materials. Patterned carbon nanomembranes have been analyzed by helium ion microscopy, scanning electron microscopy and photoelectron spectroscopy.

# $CPP \ 69.7 \quad Fri \ 12:00 \quad ZEU \ 114$

Surface-Enhanced Characterization of Nanoparticle Surfaces — •CHRISTIAN KUTTNER<sup>1,2</sup>, ROLAND P.M. HÖLLER<sup>1</sup>, MARTIN MAYER<sup>1,2</sup>, MAX J. SCHNEPF<sup>1</sup>, and ANDREAS FERY<sup>1,2,3</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., 01069 Dresden, Germany — <sup>2</sup>Cluster of Excellence Centre for Advancing Electronics Dresden (cfaed), Technische Universität Dresden, 01062 Dresden, Germany — <sup>3</sup>Physical Chemistry of Polymeric Materials, Technische Universität Dresden, 01069 Dresden, Germany

We present the retrieval of molecular information at nanoparticle surfaces using surface-enhanced Raman scattering (SERS). The electricfield enhancement of the localized surface plasmon resonances (LSPRs) of noble metal nanoparticles can be exploited for the local characterization of their molecular surface near field. [1]

Consequently, we studied the nanoparticles' ligand corona in dispersion and its exchange based on the example of low-molecular-weight surfactants against high-molecular-weight proteins. [2]

Höller, R.P.M. et al., ACS Nano 2016, 10, 5740–5750.
Tebbe, M. et al., ACS Appl. Mater. Interfaces 2015, 7, 5984–5991.

CPP 69.8 Fri 12:15 ZEU 114 In-situ Small-angle X-ray Scattering and UV-vis spectroscopy Investigations of the Formation and Growth of Inorganic Nanoparticles by Microwave-Assisted Solvothermal Synthesis — •ROBERT WENDT<sup>1</sup>, EIKE GERICKE<sup>1</sup>, DRAGOMIR TATCHEV<sup>2</sup>, ARMIN HOELL<sup>3</sup>, MARKUS WOLLGARTEN<sup>3</sup>, SIMONE RAOUX<sup>3</sup>, and KLAUS RADEMANN<sup>1</sup> — <sup>1</sup>Humboldt-Universität zu Berlin, Berlin, Germany — <sup>2</sup>Bulgarian Academy of Sciences, Sofia, Bulgaria — <sup>3</sup>Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany

Microwave-assisted solvothermal syntheses (MWASS) have become subject of renewed fundamental interests in the preparation of crystalline and monodisperse inorganic nanoparticles (NPs). Main features of MWASS are distinguished control and exact on-line determination of pressure and temperature inside the autoclave-type reactors. The advantage is the efficient internal volumetric "in-core" heating by direct coupling of MW energy to the reaction molecules. It allows high heating rates with small thermal gradients and strongly decreased reaction times based on the Arrhenius law. This work includes innovative *in-situ* investigations of the formation and growth mechanisms of inorganic NPs by this new developed MWASS-system. It allows exact additions of precursor solution into the sealed reactor and withdrawals of colloid solution at any time. Thereby, we are able to investigate and characterize the NPs in a time-range of seconds by *in-situ* UV-Vis spectroscopy and SAXS and *ex-situ* by TEM, EELS and EXAFS. These results provide new insights in the formation and growth mechanisms.

### CPP 69.9 Fri 12:30 ZEU 114

Metrology on Nascent Soot Particles from Flames by Helium Ion Microscopy — •DANIEL EMMRICH<sup>1</sup>, MAURIN SALAMANCA<sup>2</sup>, LENA RUWE<sup>2</sup>, HENNING VIEKER<sup>1</sup>, ANDRÉ BEYER<sup>1</sup>, KATHARINA KOHSE-HÖINGHAUS<sup>2</sup>, and ARMIN GÖLZHÄUSER<sup>1</sup> — <sup>1</sup>Physics of Supramolecular Systems, Bielefeld University, 33615 Bielefeld, Germany — <sup>2</sup>Department of Chemistry, Bielefeld University, 33615 Bielefeld, Germany

Soot emissions from combustion processes are a problem for environment and health. A detailed understanding on the formation process of soot is a prerequisite for the development of strategies to reduce the emission of soot. While mature soot particles are spherical aggregates with dimensions of 20-50 nm, nascent soot particles are smaller and structurally inhomogeneous. Thus, especially the latter poses challenges in their characterization. In this study, we extracted soot particles from flames of different fuels and use helium ion microscopy (HIM) to determine size and shape of the particle down to a size of 2 nm. HIM is a scanning technique similar to scanning electron microscopy (SEM) but taking advantage from the higher mass of the helium ions. The use of helium ions in comparison to electrons in SEM enables higher contrast accompanied with high resolution, high surface sensitivity and low beam currents resulting in low sample damage. This microscope enables high throughput and high resolution to follow the growth of nascent soot particles taken at different distances from the burner surface [1, 2]. [1] M. Schenk et al., ChemPhysChem, 14, 3248 (2013) [2] M. Schenk et al., Proc Combust Inst, 35, 1879 (2015)

### CPP 69.10 Fri 12:45 ZEU 114

Mean free path of slow electrons retrieved from velocity map imaging of aerosol particles — •MAXIMILIAN GOLDMANN<sup>1</sup>, BRUCE L. YODER<sup>1</sup>, STAVROS AMANATIDIS<sup>1</sup>, EGOR CHASOVSKIKH<sup>1</sup>, LUKAS LANG<sup>1</sup>, ANDRAS BODI<sup>2</sup>, DAVID LUCKHAUS<sup>1</sup>, and RUTH SIGNORELL<sup>1</sup> — <sup>1</sup>Laboratorium für physikalische Chemie, ETH Zürich, 8093 Zürich — <sup>2</sup>Swiss Light Source, Paul Scherrer Institut, 5232 Villigen

Electron mean free paths are important quantities for a number of physico-chemical phenomena ranging from aerosol physics and chemistry to radiation damage of biological tissues. We introduce and apply a novel method to determine the electron mean free path of low energy electrons in solid and liquid materials by velocity map imaging photoelectron spectroscopy of neutral aerosol particles using vacuum ultraviolet light. We extract the electron mean free path by comparing experimental with simulated photoelectron velocity map images of aerosol particles. For the simulation, we use a detailed scattering model [1].

Experimental photoelectron spectra of potassium chloride nanoparticles [2], liquid water droplets [1], and liquid-coated nanoparticles are presented. These photoelectron images were recorded at the VUV beamline at Paul Scherrer Institute and by means of a home-built table-top laser system.

[1] R. Signorell et al., Chem. Phys. Lett. 658, 1 (2016).

[2] M. Goldmann et al., J. Chem. Phys. 142, 224304 (2015).