O 68: Polymeric biomolecular films

Time: Thursday 11:15-13:00

O 68.1 Thu 11:15 $\,$ WIL B122 $\,$

Dynamic photothermal laser manipulation of surface-grafted thermoresponsive polymer brushes — •CRISPIN AMIRI NAINI, STEFFEN FRANZKA, SVEN FROST, MATHIAS ULBRICHT, and NILS HARTMANN — Fakultät für Chemie, CeNIDE, NETZ, Universität Duisburg-Essen, Universitätsstr. 5, 45141 Essen, Germany

Stimuli-responsive polymers have become a versatile material in designing smart functional devices, e. g. as adaptive microoptics, microfluidic chips, membranes and sensors. Controlled reaction schemes allow one to build up surface-grafted polymer brush films with thicknesses from the submicron down to the sub-100 nm range [1]. This opens up an avenue towards highly integrated device structures with unprecedented functionalities. In order to stimulate miniaturized polymeric components, e. g. for valving, suitable techniques are required. Here, we demonstrate a facile noncontact laser technique for switching of surface-grafted poly-n-isopropylacrylamide brushes at the water/substrate interface. A modulated beam of a microfocused laser at a wavelength of 532 nm is used to heat the substrate surface and locally trigger swelling and deswelling of the polymer film. Switching on length scales from millimeters down to a few microns is feasible at very low laser power densities. Also, in conjunction with masks, parallel switching at distinct surface areas can be carried out. Prospects in micro- and nanofluidic applications, e. g. in designing freely configurable device structures, are discussed.

[1] M. Mathieu, A. Friebe, S. Franzka, M. Ulbricht, N. Hartmann, Langmuir 25 (2009) 12393.

O 68.2 Thu 11:30 WIL B122

Synthesis of 2D COFs through exfoliation and coalesence of nano-crystalls — •JÜRGEN F. DIENSTMAIER¹, WOLFGANG M. HECKL^{2,3}, and MARKUS LACKINGER^{1,2} — ¹Ludwig-Maximilians-University and Center for NanoScience (CeNS) — ²Deutsches Museum — ³Department of Physics, TUM School of Education, Technical University Munich

Self-condensation of Benzene-1,4-diboronic acid can yield highly crystalline Covalent Organic Frameworks (COF). In the COF-1 structure, monomers are covalently interlinked into two-dimensional sheets which are then stacked along the c-axis. These sheets are comprised of a hexagonal alternating arrangement of phenyl and boroxine rings and are an ideal model structure for 2D COF variants. In this contribution we demonstrate a new approach to first synthesize nanocrystalls of COF-1. The product of this synthesis was independently characterized by PXRD, TGA, IR-, and Raman-spectroscopy. After exfoliation, two-dimensional nanocrystalline flakes, whose structure correspond to a single layer of COF-1, are dispersed in solvent and deposited onto a substrate. STM imaging under ambient conditions reveals full monolayer coverage of nanocrystalline COF flakes with well ordered internal structure. Tempering of these highly polycrystalline structures results in ripening and increasing domain size.

O 68.3 Thu 11:45 WIL B122

Contact energy landscapes by means of mobile nanoparticles — ●Ute Queitsch¹, Anja Blüher¹, Alfred Hucht², Berndt Rellinghaus³, Ludwig Schultz³, and Michael Mertig¹ — ¹TU Dresden, Phys. Chem. Measurement & Sensor Technol, D-01062 Dresden, Germany — ²Univ. Duisburg-Essen, Fac. Phys, D-47048, Duisburg, Germany — ³IFW Dresden, P.O. Box 270116 D-01171, Germany The key to successful applications of nanoparticles is their organization at the nanoscale, i.e. the creation of defined nanostructures of particles with controlled morphology in highly ordered arrays. Gas phase preparation has proven to allow for the preparation of nanoparticles of various materials with narrow size distribution. A regular arrangement of the particles can be accomplished by self organization on bacterial S-layer templates [1]. There the main driving force to achieve particle ordering, is the reduction of the surface free energy of the particles by maximizing the contact area between particles and the S-layer surface [2]. The effective contact energy can be quantitatively determined by simulations on the density-dependent particle distribution on the S-layer. Therefore a simple model on the particle diffusion on S-layers including the deposition, diffusion and agglomeration of the particles within the periodic surface potential of the protein template is developed. By means of the presented method for the first time a Location: WIL B122

quantification of the templating effect of S-layer templates is realized.[1] U.Queitsch et al., Appl. Phys. Lett. 90, 113114 (2007)

[2] U.Queitsch et al., J. Phys. Chem. C., 113, 24, 10471 (2009)

O 68.4 Thu 12:00 WIL B122

NEXAFS of azobenzene-based molecular photoswitches — •ERIC LUDWIG¹, SONJA KUHN¹, THOMAS STRUNSKUS², ALEXEI NEFEDOV³, ULRICH JUNG¹, JENS KUBITSCHKE⁴, RAINER HERGES⁴, CHRISTOF WÖLL³, OLAF MAGNUSSEN¹, LUTZ KIPP¹, and KAI ROSSNAGEL¹ — ¹Institut für Experimentelle und Angewandte Physik, Universität Kiel, D-24098 Kiel — ²Institut für Materialwissenschaft, Universität Kiel, D-24098 Kiel — ³Institut für Funktionelle Grenzflächen, Karlsruher Institut für Technologie, D-76344 Eggenstein-Leopoldshafen — ⁴Otto-Diels-Institut für Organische Chemie, Universität Kiel, D-24098 Kiel

The adsorption behavior of azobenzene-based molecular switches was investigated by NEXAFS. We deposited pure azobenzene on weakly interacting surfaces of layered compounds. Furthermore, we report results of photoswitches employing molecular platforms based on the triazatriangulenium (TATA) ion with functional groups attached to the central carbon atom which form self-assembled monolayers on Au(111) surfaces. This "platform approach" enforces equal spacing of the molecules as well as decoupling of the functional group from the substrate. NEXAFS measurements were performed at BESSY (beamline HE-SGM) utilizing a Prevac endstation.

Results on azobenzene indicate flat-lying molecules when preparing monolayer systems and a non-planar configuration within multilayer systems. Data on Azo-TATA molecules corroborate successful and non-destructive sample preparation. This work was supported by the DFG through SFB 677.

O 68.5 Thu 12:15 WIL B122 Polariton effect in α -Sexithiophene films revealed by reflectance difference spectroscopy — •GÜNTHER WEIDLINGER, LI-DONG SUN, and PETER ZEPPENFELD — Institute of Experimental Physics, Johannes Kepler University Linz, Altenberger Straße 69, A-4040 Linz, Austria

 α -Sexithiophene (α -6T) films consisting of either flat-lying or standing molecules were prepared on clean and carbon-terminated Ag(110) surfaces, respectively, using organic molecular beam epitaxy. The optical properties of the α -6T films were investigated by reflectance difference spectroscopy (RDS). For films composed of flat lying molecules the higher Davydov component derived from the intramolecular HOMO-LUMO transition is located at 2.6 eV, whereas for standing α -6T molecules the transition is shifted to 3.5 eV. This observation can be explained by the so-called polariton effect, i.e., the interaction between photons and excitons [1]. The energetic position of the higher Davydov component thus becomes a function of the angle between the α -6T molecular axis in the films and the propogation direction of the light. This result demonstrates that crystalline orientation and thus the excitonic optical properties of organic thin films can be controlled by the substrate and thin film preparation. Furthermore, RDS is shown to be a sensitive method not only for the determination of the in-plane alignment of organic molecules, but also for their out-of-plane orientation.

[1] G. Weiser and S. Möller, Organic Electronics 5 (2004) 91-97

O 68.6 Thu 12:30 WIL B122 Vibrational spectroscopy of organic monolayers by sumfrequency generation — •JAN WEBER, RAISSA MONGO, THORSTEN BALGAR, and ECKART HASSELBRINK — Fakultät für Chemie, Universität Duisburg-Essen, D-45117 Essen, Germany

Organic monolayers display an interesting field of surface science because of their diverse characteristics. Prominent examples are siloxanes on silica surfaces which are stable under ambient conditions. These self-assembled monolayers have been of interest since the 1980's yet the mechanisms of ordering, degredation or adsorption of other molecules is not fully understood on the molecular scale. In this context we analyze Octadecyltrichlorosilane (OTS) and Aminopropylmethoxysilane (APS) with regard to orientationally ordering and thermally induced degradation mechanisms.

The experiments are carried out via sum-frequency generation (SFG)

spectroscopy by using a picosecond laser system, which provides visible light as well as tunable infrared light. SFG spectroscopy is a convenient method because it provides a very high surface sensitivity for the analysis.

O 68.7 Thu 12:45 $\,$ WIL B122 $\,$

The effect of chain-length on the branching of irradiationinduced processes in alkanethiolate molecular films — •FREDERICK CHESNEAU, HICHAM HAMOUDI, and MICHAEL ZHARNIKOV — Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany

The effect of X-ray and low-energy (50 eV) electron irradiation on short-chain alkanethiolate (AT) self-assembled monolayers (SAMs)

on Au(111) was studied by synchrotron-based high-resolution X-ray photoelectron spectroscopy and infrared reflection absorption spectroscopy. As a test system, a SAM of hexanethiolate (C6) was used. An analogous long-chain film, dodecanethiolate (C12) SAM, was taken as reference. Whereas both C6 and C12 films exhibited a full range of irradiation-induced reactions characteristic of AT SAMs on coinage metal substrates, the branching of the reactions in these two systems was distinctly different. Whereas in the case of C12/Au, the dominant processes were decomposition of the alkyl chains and capture of the released alkylsulfide moieties in the aliphatic matrix, desorption of the complete molecular species emerging after the cleavage of the thiolate-gold bond prevailed in the case of C6/Au. A tentative explanation for this behavior will be proposed.