O 57: Solid / liquid interfaces II

Time: Wednesday 16:45-18:45

Location: A 060

O 57.1 Wed 16:45 A 060

Two-Dimensional Colloidal Alloys — •ADAM LAW¹, MARTIN BUZZA², and TOMMY HOROZOV³ — ¹Max Planck Institute for Intelligent Systems, 70569 Stuttgart, Germany — ²Surfactant and Colloid Group, Department of Physics, The University of Hull, England, HU6 7RX — ³Surfactant and Colloid Group, Department of Chemistry, The University of Hull, England, HU6 7RX

We study both experimentally and theoretically the structure of mixed monolayers of large (3 μ m) and small (1 μ m) very hydrophobic silica particles at an octane/water interface as a function of the number fraction of small particles. We find that a rich variety of two-dimensional hexagonal superlattices of large and small particles can be obtained in this system experimentally due to strong and long-range electrostatic repulsions through the nonpolar oil phase. These represent the first experimental results for long-range order in a 2D binary colloid system. The structures obtained for the different compositions are in good agreement with zero temperature lattice sum calculations and finite temperature Monte Carlo simulations. Our theoretical analysis also reveals that the melting behaviour of the superlattice structures is very rich, proceeding via a multi-stage process, with melting temperatures that have a very strong and non-monotonic dependence on composition.

O 57.2 Wed 17:00 A 060 Photoelectrochemical Characterization of Bimodal ZnO Nanostructures as Photoanodes in Dye-sensitized Solar Cells — •CHRISTOPH RICHTER¹, MICHAEL SCHRÖDER², MELANIE RUDOLPH¹, MAX BEU¹, BERND SMARSLY², and DERCK SCHLETTWEIN¹ — ¹Justus-Liebig-Universität Gießen, Institut für Angewandte Physik, Heinrich-Buff-Ring 16, D-35392 Gießen — ²Justus-Liebig-Universität Gießen, Physiklaisch-Chemisches Institut, Heinrich-Buff-Ring 58, D-35392 Gießen

Bimodal ZnO nanostructures were fabricated by electrochemical deposition from aqueous solution. A layer of monodisperse polystyrene spheres obtained by mini-emulsion polymerization acts as a template for the electrodeposition. EosinY serves as a structure-directing agent towards formation of a mesoporous ZnO/EosinY hybrid material. EosinY can easily be removed by soaking in an aqueous solution of sodium hydroxide. The polystyrene spheres are chemically decomposed and a meso-macroporous network of ZnO is obtained. Following sensitization by a dye monolayer, these films were characterized by intensity modulated photocurrent spectroscopy (IMPS), intensity modulated photo voltage spectroscopy (IMVS), open circuit voltage decay (OCVD) and electrochemical impedance spectroscopy (EIS). Charge transport, recombination and photovoltaic properties are discussed.

O 57.3 Wed 17:15 A 060 Electrocatalytic activity of small Pt nanoparticles on monolayer graphene supported by Ru(0001) — •CHRISTOPH U. LORENZ, OTAVIO B. ALVES, and R. JÜRGEN BEHM — Ulm University, D-89069 Ulm, Germany

With their characteristic Moiré-type nm-scale superstructure, graphene monolayers supported on metal single crystals [1,2] can serve as ideal, chemically inert template for the growth of ordered arrays of very small nano-sized metallic (electro-)catalyst particles. For Pt deposition on gr/Ru(0001), particles fabricated by metal vapor deposition under ultrahigh vacuum conditions, displayed heights of a few layers and lateral diameters in the range of 1-2 nm as measured by STM [3,4]. Based on their narrow size distribution and their regular arrangement, these Pt nanoparticles appear as interesting and promising system for (electro-)catalytic model studies. Cluster arrays with different Pt coverages and cluster size distributions, which were determined by STM, were tested as electrodes for elementary reactions such as hydrogen evolution/oxidation, CO oxidation, and O2 reduction. Potential-dependent reaction rates were measured in a wall-jet type flow cell located in an electrochemical pre-chamber attached to the main UHV system. The electrochemical behavior of the Pt cluster arrays will be discussed in comparison to bulk Pt and realistic carbon supported Pt catalysts. [1] C. Oshima et al., J. Phys. Condens. Matter 9, 1 (1997). [2] S. Marchini et al., Phys. Rev. B 76, 075429 (2007). [3] N'Diaye et al., New J. Phys. 11, 103045 (2009). [4] K. Donner & P. Jakob, J. Chem. Phys. 131,164701 (2009).

O 57.4 Wed 17:30 A 060

EC-STM study of bulk Cu(111) and Cu covered Au(111) electrodes in a phosphate buffer solution — •CHRISTIAN SCHLAUP and SEBASTIAN HORCH — Center for Individual Nanoparticle Functionality (CINF), Department of Physics, Technical University of Denmark (DTU), DK-2800 Kongens Lyngby, Denmark

Copper is known to have an outstanding catalytic activity for the electroreduction of carbon dioxide. For a deeper insight into the involved sites as well as their dynamics under reaction conditions well defined single crystalline copper surfaces can be used as an adequate model system.

In a first step the fundamental interaction of both, a bulk Cu(111) surface and a laterally expanded Cu surface, i.e. an ultrathin Cu film on a Au(111) electrode, in contact with neutral phosphate buffer electrolyte has been studied using in-situ STM. Thereby, depended on the actual sample treatment, several phases, e.g. phosphate adsorbate or copper oxide film, were found and characterized.

O 57.5 Wed 17:45 A 060 Analyzing the hydrodynamic boundary condition at solidliquid interfaces with fluorescence correlation spectroscopy — STOYAN YORDANOV, DAVID SCHÄFFEL, ROMAN SCHMITZ, BURKHARD DÜNWEG, KALOIAN KOYNOV, and •HANS-JÜRGEN BUTT — Max-Planck-Institut für Polymerforschung, Mainz, Deutschland

An important step towards an understanding of hydrodynamics is determining the correct boundary conditions. A new method for direct studies of flows in the close proximity of a solid surface has been developed. It is based on total internal reflection fluorescence cross-correlation spectroscopy (TIR-FCCS).

The effect of TIR is used to create an evanescent optical field that excites fluorescent tracer particles flowing with the liquid. A high numerical aperture microscope objective is employed to monitor simultaneously the fluorescent light from two small and laterally shifted (in flow direction) observation volumes. A cross-correlation of the fluorescent signals from these volumes yields the tracers and hence the flow velocity. By tuning the TIR conditions and therefore the evanesced wave penetration depth we can determine flow velocity profiles in the range 0-300 nm from the interface.

O 57.6 Wed 18:00 A 060 **Dynamic Electro-Chemo-Mechanical Analysis** — •QIBO DENG¹, MAXIM SMETANIN¹, and JÖRG WEISSMÜLLER^{1,2} — ¹Institut für Werkstoffphysik und -Technologie, Technische Universität Hamburg-Harburg, Hamburg — ²Institut für Werkstoffforschung, Werkstoffmechanik, Helmholtz-Zentrum Geesthacht, Geesthacht

In various instances in surface science it is of relevance to study coupling between mechanical stress or strain of surface and its thermodynamic or electrochemical properties. Experiments use alternatively cantilever bending measurements of the variation of surface stress f, with charge density q, during electrochemical cycles or Dynamic Electro-Chemo-Mechanical Analysis(DECMA), which detects the coupling between electrode potential E, and strain e. At equilibrium, a Maxwell relation equates relevant response parameters, $\zeta_E{=}\zeta_f$ where $\zeta_f = df/dq|e$ and $\zeta_E = dE/de|q$. The surfaces under study are not perfect single crystals. They contain defects such as step edges and terraces. Indeed ζ_E or ζ_f vary significantly between as-prepared and annealed states of electrode. A recent analysis of surface stress measurements on rough electrode surfaces finds corrugation has an important effect on the way in which f is transferred into the substrate. The action of f can even invert its sign; this appears at moderate values of roughness. We adopt theory to correct DECMA data. Our analysis shows the variation of ζ_E between different states of surface is indeed controlled by mechanics and can be precisely corrected. The finding has implications for reported values of ζ and for the design of commercial cantilever arrays exploiting surface stress changes for sensing.

O 57.7 Wed 18:15 A 060 Diffuse scattering of Hg-electrolyte interface — •BENJAMIN RUNGE¹, ANNIKA ELSEN¹, SVEN FESTERSEN¹, MOSHE DEUTSCH², OLIVER H. SEECK³, OLAF M. MAGNUSSEN¹, and BRIDGET M. MURPHY¹ — ¹Institute for Experimental and Applied Physics, CAU, Kiel, Germany — ²PETRA III, DESY, Hamburg, Germany — ³PD, Bar-Ilan University, Ramat-Gan, Israel

Surface x-ray scattering methods belong to the very few experimental approaches that allow access to data on the nano-scale structure of liquid surfaces and in particular liquid-liquid interfaces. Here first x-ray diffuse scattering studies of a liquid-liquid interface are presented for the case of an interface between liquid Hg and electrolyte solutions. By these studies the lateral correlations caused by surface capillary waves were investigated. The measurements were carried out at the new liquid interface scattering apparatus (LISA) at the high resolution X-ray diffraction beam line P08 at the PETRA III synchrotron radiation source. Previous x-ray reflectivity studies [1] revealed a dependence of the interface width on the applied potential, not consistent with capillary wave theory. The diffuse scattering studies focus on obtaining further insight into the origin of this dependence and on the effect of the potential on the capillary waves.

[1] A. Elsen, et al., Phys. Rev. Lett., 104. 105501 (2010)

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Development of an electrochemical flow-through cell for in situ characterization of UHV-fabricated model surfaces —

•OTAVIO B. ALVES and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, 89069 Ulm, Germany

We report on the assembly of a wall-jet type electrochemical flow cell for electrochemical and electrocatalytic characterization under controlled and continuous electrolyte flow, which is connected to an ultrahigh vacuum scanning tunneling microscopy (UHV-STM) system via a sample transfer system. The electrochemical set-up exhibits a "true" wall-jet hydrodynamic characteristics [1-2]; and offers a high sensitivity, low solution hold-up and reproducible mass-transfer conditions when coupled to a closed loop miniature flow controller. We will discuss the experimental verification of the theoretical predictions for the limiting diffusion current [2] at UHV prepared single crystalline electrodes. It will also be examined in how far the Frumkin-Tedoradze [3] or an analogous treatment [4-5] is suitable for describing the measured kinetic data.

- [1] M. B. Glauert, J. Flui Mech. 1, 1956, 625.
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- [4] W. J. Albery, J. Electroanal. Chem. 191, 1985, 1.
- [5] R. G. Compton et al., J.Appl. Eletrochem. 21, 1991, 295.