GRADUATE SCHOOL
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Book of Abstracts

YOUNG RESEARCHERS’ DAY 2018

4 October
Hans-Georg-Waeber-Saal
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Young Researchers’ Day 2018
Hans-Georg-Waeber-Saal
Fraunhofer IISB
October 4th, 2018

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Program

Thursday, October 4th, 2018

12.30 – 13.00  Registration
13.00 – 13.10  Welcome
13.10 – 13.40  Tao Xu, Aarhus University, Denmark
               “Atomic level understanding of selective catalytic reduction of NOx and anchoring of organic molecules on oxide surfaces: a surface science study” (Opening Lecture)

Session 1 | Chair: Bianka Puscher

13.40 – 13.55  Olaf Brummel, FAU, PCI
               “Electrochemically controlled solar energy storage in strain organic molecules: in-situ spectroscopy in the norbornadiene-quadricyclane system”

13.55 – 14.10  Annkatrin Lennert, FAU, PCI
               “Efficient and stable solid-state dye-sensitized solar cells by the combination of phosphonium organic ionic plastic crystals with silica”

14.10 – 14.25  Christina Harreiß, FAU, CENEM
               “Influence of different post-treatment processes on the nanomorphology of organic bulk heterojunction solar cells”

14.25 – 14.30  Uladzislau Zubets, FAU, WW5
               “Region-selective formation of metal oxide layer via solution-based deposition techniques”

14.30 – 14.35  Baolin Zhao, FAU, WW5
               “Functionalized self-assembled monolayer for field effect transistors (SAMFETs)”

14.35 – 14.55  Coffee Break

Session 2 | Chair: Muhammad Ali

14.55 – 15.10  Chandra Macauley, FAU, WW1
               “Cryo-FIB tomography of electrochemical devices”

15.10 – 15.25  Silvan Englisch, FAU, CENEM
               “Magic clusters: investigation of polystyrene particles self-assembly forming agglomerations in crystalline order using 3D X-ray nano tomography and electron tomography”
15.25 – 15.40  Andreas Späth, FAU, PCII  
“Focused soft X-ray beam induced deposition of metallic nanostructures”  

15.40 – 15.55  Christian Dolle, FAU, CENEM  
“Atomically resolved imaging of dodecyl functionalized graphene and defect engineering in bilayer graphene”  

15.55 – 16.10  Judith Wittmann, FAU, WW5  
“Tunable fluorescence of mixed shell monolayers on oxide nanoparticles”  

16.10 – 16.30  Coffee Break  

**Session 3 | Chair: Junwei Wang**

16.30 – 16.45  Eric Görlitzer, FAU, LFG  
“Large-area chiral plasmonic crescents”  

16.45 – 17.00  Marcel Rey, FAU, LFG  
“Anisotropic self-assembly of isotropic colloidal building blocks”  

17.00 – 17.15  Praveen Bommineni, FAU, MSS  
“Effect of static and dynamic size-dispersity on the crystallization of hard spheres”  

17.15 – 17.30  Henning Stumpf, FAU, TP I  
“Effect of membrane mediated interactions on protein organisation”  

17.30 – 17.45  Stefan Zitz, FAU, IEK-11  
“Patterned substrates and sliding drops”  

17.45 – 17.50  Short Break  

17.50 – 18.00  Closing Remarks, Award Ceremony  

18.00  Beer and Brezels
Atomic Level Understanding of Selective Catalytic Reduction of NO\textsubscript{x} and Anchoring of Organic Molecules on Oxide Surfaces: a Surface Science Study.

Tao Xu,\textsuperscript{a} Tobias Waehler,\textsuperscript{a} Julia Vecchietti,\textsuperscript{b} Adrian Bonivardi,\textsuperscript{a} Tanja Bauer,\textsuperscript{b} Johannes Schwegler,\textsuperscript{b} Peter S. Schulz,\textsuperscript{b} Peter Wasserscheid \textsuperscript{d} Joerg Libuda \textsuperscript{b} Jeppe V. Lauritsen \textsuperscript{a},\textsuperscript{+} Stig Kaust \textsuperscript{a},\textsuperscript{+} Kræn C. Adamsen \textsuperscript{a},\textsuperscript{+} Stefan Wendt \textsuperscript{a}.

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Nitrogen oxides (NO\textsubscript{x}) from flue gas are in concern as major sources of air pollution. Increasingly stricter NO\textsubscript{x} emission control policies (e.g. Euro VI) demand innovation and better performance of NO\textsubscript{x} reduction technology. The Selective Catalytic Reduction (SCR) of NO\textsubscript{x} via anatase titania (and ceria more recently) supported vanadia catalyst is used for this service and attracted much research attention. However, many aspects of the SCR catalysis process remain poorly understood at the atomic level. In this work, we aim to unravel, at a fundamental level, what factors make the a-TiO\textsubscript{2} and CeO\textsubscript{2} different in SCR reactivity. By using mineral a-TiO\textsubscript{2} single crystals exposing the (101) facets and growing well-defined CeO\textsubscript{2}(111) thin film on Ru(0001) surface, the atomic and electronic structures of VO\textsubscript{x} supported on a-TiO\textsubscript{2}(101) and CeO\textsubscript{2}(111) will be studied with state-of-the-art Scanning Tunneling Microscopy (STM) and other surface science techniques. The adsorption of ammonia (an important reactant for SCR) on these model catalysts is studied by STM, temperature programmed desorption (STM) and X-ray photon-electron spectroscopy (XPS). The project will provide systematic insights into the interactions between VO\textsubscript{x} and different oxide facets, elucidating how this would influence SCR catalysis.

Organic thin films on oxide surfaces are essential in many applications like photovoltaics and molecular electronics. For such applications, the organic entities are often bound to the surface using anchor groups such as carboxylic acids, phosphonates or hydroxyl groups. The associated binding mechanisms, kinetics and energetics are critical for the growth and the structure formation processes at organic-oxide interfaces. They are the key to control the growth and structure of the film and, therefore, their electronic and chemical properties. We have performed surface science model studies to explore the influence of (1) the carboxylic acid functional group (2) the surface structure on the anchoring and thermal stability of organic molecules on oxide surfaces. Specifically, we investigated the adsorption and desorption of phthalic acid (PA) on atomically defined (i) MgO(100) grown on Ag(100), (ii) Co\textsubscript{3}O\textsubscript{4}(111), (iii) CoO(111) and (iv) CoO(100) grown on Ir(100). Formation of the PA films and interfacial reactions were monitored in-situ during growth by isothermal time-resolved infrared reflection absorption spectroscopy (TR-IRAS) under ultrahigh vacuum (UHV) conditions. We observe pronounced structure dependencies on the three cobalt oxide surfaces with different binding geometries and characteristic differences as a function of temperature and coverage.\textsuperscript{[1][2]} In addition, we present a new method to prepare a chemically well-defined interface between an oxide and an ionic liquid (IL) film. We used the functionalized IL 3-(4-isopropoxyl-4-oxobutyl)-1-methylimidazolium bis(trifluoromethyl-sulfonyl) imide ([IPBMIM][NTf2]) that carries an ester group at the imidazolium cation. The IL was deposited by Physical Vapour Deposition (PVD) onto atomically defined Co\textsubscript{3}O\textsubscript{4}(111) and CoO(100) surfaces under ultraclean UHV conditions. The [IPBMIM][NTf2] was found to be anchored on the CoO(100) surface through cleavage of the ester bond and formation of a bridging surface carboxylate. This anchoring reaction is thermally activated and shows high structure dependency.\textsuperscript{[3][4]}

Electrochemically Controlled Solar Energy Storage in Strained Organic Molecules: In-Situ Spectroscopy in the Norbornadiene-Quadricyclane System


Olaf Brummel, FAU Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

Energy conversion, storage, and release can be combined in a single system using pairs of valence isomers. The most prominent example is norbornadiene (NBD) and its strained and energy-rich valence isomer quadracyclane (QC). Conventionally, the energy release is triggered by the use of mild oxidants, which provides a poor level of control. We demonstrate greatly enhanced control by triggering the reaction electrochemically.

First, we studied the electrochemically triggered cycloreversion of QC to NBD by electrochemical infrared reflection absorption spectroscopy (EC-IRRAS) at a single-crystalline Pt(111) electrode. To identify the different isomers, the IR bands of NBD and QC in fingerprint region between 1100 and 1600 cm\(^{-1}\) were assigned on the basis of density functional (DF) calculations. Specific bands enable straightforward identification of NBD and QC, and allow monitoring the reaction in-situ. The spectroscopic results are in line with voltammetric data.\(^1\) To study the complete storage cycle we developed a new photoelectrochemical IRRAS (PEC-IRRAS) experiment. It allows us to monitor and quantify the products both during the photochemical conversion and during the electrochemically triggered cycloreversion. We monitored the highly selective photochemical conversion in-situ, and could show that a follow up reaction with the photosensitizer (Michler’s ketone, MK) decreases the selectivity at longer irradiation times. During electrochemically triggered cycloreversion, oxidation of MK competes with conversion of QC.\(^2\) In order to avoid the use of an external photosensitizer, we used UV light-absorbing NBD derivatives, such as 2-cyano-3-(3,4-dimethoxyphenyl)-norbornadiene. In PEC-IRRAS, we obtained high selectivities in both the photochemical conversion and the electrochemically triggered cycloreversion, demonstrating operation over many storage cycles.


Efficient and Stable Solid-State Dye-Sensitized Solar Cells by the Combination of Phosphonium Organic Ionic Plastic Crystals with Silica

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For more than two decades dye sensitized solar cells (DSSC) have been the focus of intensive research in the field of renewable energies. Easy fabrication out of low cost materials render them a promising candidate for commercialization to supply future energy demands. [1] However, there is still room for improvement in terms of lifetime and stability, traits mainly dependent on the electrolyte used in the devices. Commonly used solvent based electrolyte are prone to leakage and evaporation over time, limiting the device performance. To circumvent this and create longer lasting devices the concept of solid state electrolytes has come into focus more and more in recent years. [2]

Here, plastic crystals constitute a feasible solution. The most commonly used plastic crystal is succinonitrile, which has also been one of the first to be tried in ssDSSC. [3] Other plastic crystals are usually based on a cation from the pyrrolidinium family or quaternary ammonium salt and applied in a melt with various ILs. Plastic crystals containing a phosphor bearing cation have, so far, been mostly overlooked, although they have the potential to be more stable and, thus, longer lasting than their ammonium counterparts. Presented here are two new plastic crystals based on quaternary phosphor cations, which are implemented as electrolytes without any addition of solvent or ILs. Using I3- /I- as the redox couple our devices feature excellent values, reaching 4.1% efficiency under 1 sun with N719 after an optimization of the device architecture. Further improvement through the addition of fumed silica particles to the plastic crystal electrolyte lead to increased electrode/electrolyte contacts, as well as decreased transport resistance, resulting in a record PCE of 7.4% under 1 sun, which is comparable to liquid reference devices.

Influence of Different Post-treatment Processes on the Nanomorphology of Organic Bulk Heterojunction Solar Cells

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During the past decades the power conversion efficiency of solution-processed bulk heterojunction (BHJ) solar cells could be highly improved using new donor and acceptor materials as well as by developing new processing conditions. Since the nanoscale morphology of organic BHJ solar cells determines the charge separation at the interfaces and the subsequent electron and hole transport to the respective electrode, it highly influences the device performance. The morphology of BHJ solar cells is not only dependent on the involved materials but also on their post-processing treatment like thermal or solvent vapor annealing.

Analytical Transmission Electron Microscopy (TEM) techniques like electron energy-loss spectroscopy (EELS) and energy filtered TEM (EFTEM) are approved techniques to study and characterize the morphology of organic solar cells since conventional imaging techniques are mostly not sufficient to visualize and identify the small molecule and fullerene component. Due to the very similar chemical composition of the donor and the acceptor material in the active layer, conventional TEM delivers rather uniform contrast where no significant structures can be identified. In contrast, rich information about the elemental distribution and the local thickness of BHJ layers can be obtained using EFTEM and combining signals from high and low loss regions.

Here we present results on a high-efficiency photovoltaic system composed of a small molecule (DRCN5T) as electron donor and a fullerene derivative (PC70BM) as electron acceptor. [1] The active layers were treated by different post-treatment processes including thermal annealing (TA) and solvent vapor annealing (SVA). Furthermore the SVA was performed with different solvent atmospheres like chloroform (CHCl3), tetrahydrofuran (THF) and carbon disulfide (CS2) and for different annealing times. The morphology was revealed for all different post-treated active layers by EFTEM. Currently we are performing the thermal annealing directly in our TEM device by an in situ heating technique. By this, we can simultaneously observe the nanoscale phase separation and the formation of an interpenetrating network of donor and acceptor phases. This gives us new insights into the kinetics of BHJ film formation.

Region - selective formation of metal oxide layer via solution - based deposition techniques

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Metal oxides nanomaterials have a versatile usage as catalysts, ceramics, electronic and etc. In order to achieve further development of such applications, it is required to establish simple and universal method for the region-selective formation of the layer. Unlike the complex vapor phase deposition, solution-based deposition techniques are preferred for easy handling and simplifying the reaction chemistries. Two representative strategies are proposed in this manner, a region-selective thin film formation with solution-based atomic layer deposition (sALD) technique and preferential deposition of nanoparticles (NPs) by tuning the functionalities of the surface of NPs. By creating the contrasts of surface functionalities, both methods are expected to create a region-selective metal oxide layer. To proof of the concepts, these layers will eventually be used as a functional layer of the electronic devices to analyze their properties. In terms of the second strategy is intended to be realized the region - selective deposition of core-shell nanoparticles (NP) for 3D hierarchical assemblies. At this moment is pretended to agglomerate the aluminum oxide (AlOx) NPs functionalized by Phosphomycin Disodium Salt (PDS) where is presented the epoxy group to control the over layer thickness. The AlOx thin film on Si substrate behaves as substrate for deposition reaction of self - assembled monolayer (SAM) of amine phosphonic acid (PA) over which occurs deposition reaction of AlOx NPs functionalized by PDS. During research project the nanoassemblies can be rearranged permuting core-shell NPs. The NP functionalization is analyzed by IR - spectroscopy and deposition stack are characterized by SEM, AFM, Surface Contact Angle technique with definition of region selectivity. As final part of this research project, the nanostructure is pretended to be tested and analyzed as electronic device for different objectives.

Functionalized Self-assembled Monolayer for Field Effect Transistors (SAMFETs)

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The organic molecules enable the fabrication of large-area and flexible electronics with low energy consumption.[1] The method of functionalized self-assembled monolayers (SAMs) enhances the ordered morphology and reliable performance via a simple solution process by only one layer of active molecules. Newly designed organic molecules with specific anchor groups provide a tool box for p- and n-type self-assembled monolayer field-effect transistors (SAMFETs). The talk will stress recent achievements in SAMFET devices based on small molecules,[2] oligomers,[3] and provide concepts for integrated circuits.

Cryo-FIB Tomography of Electrochemical Devices

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The performance of electrochemical devices such as fuel cells or electrolyzers is often dictated by material properties at interfaces.[1] Both fuel cells and electrolyzers contain interfaces between catalysts and Nafion® (DuPont), a proton conducting polymer film. To investigate the relevant interfaces between the Nafion®, catalyst layers and gas diffusion layers, it is essential to conduct 3D-characterization in the near-operando and post-operando state.

Utilizing techniques developed to study biological materials, focused ion beam (FIB) tomography of hydrated fuel cell/electrolyzer components was conducted at cryogenic temperatures using a Quorum Technologies PP3005 cryo-stage in a FIB-SEM. By combining images from several different detectors, such as the secondary electron (SE), energy selective backscattered (ESB), and in-lens detectors, different types of information could be gathered. Advanced image tracking algorithms based on the Kanade–Lucas–Tomasi (KLT) technique[2] were used in combination with a custom MATLAB code to register, align and crop the stack of images, and create a 3D-reconstruction.

To study materials containing low viscosity liquids like water, a custom transfer arm was also designed and built, thus enabling rapid cryo-fixation and transfer directly to the pre-cooled cryo-stage. Although the resulting tomograms provide a qualitative view of the structure of fuel cell layers, it is also possible to obtain quantitative information. For example, catalyst and pore-size distribution can be determined, as well as pore-connectivity within the catalyst layer. Ideally, the 3D-reconstructions can also be used by researchers in the simulation community as a ‘digital twin’ to simulate critical transport phenomena that dictate cell performance. The implications for improving the performance of electrochemical devices will be presented.

Magic Clusters: Investigation of Polystyrene Particles Self-assembly Forming Agglomerations in Crystalline Order using 3D X-Ray Nano Tomography and Electron Tomography

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X-Ray Tomography (XRT) and Electron Tomography (ET) allow non-destructive three-dimensional (3D) investigations of materials and related structures across multiple length scales. By morphological segmentation of the tomographic reconstructions a quantitative and position-correlating analysis can be conducted. In particular, complex sample structures can be investigated in depth, where merely surface information is insufficient. Liquid crystals, which are structures generated by a self-assembly process, resemble complex configurations with alternating lattice structures. Those so-called “Magic Clusters” are self-assembled agglomerations of polystyrene balls forming solid crystal or shell structures depending on their manufacturing process and number of primary particles (polystyrene) (see Fig. 1).

In this contribution, we report on correlative 3D studies of “Magic Clusters” which recently showed an exceeding impact on material science of photonic structures and on fundamental research. The agglomeration size is varying from 1 µm to 14 µm in diameter with a correlating primary particle diameter of 50 nm to 400 nm and primary particle numbers of 1000 up to 15,000.

In order to study the composition of individual 3D positions (x, y, z) of each primary particle inside the agglomeration of a “Magic Cluster”, XRT and ET was instrumented. Achieving a sufficiently high contrast (signal-to-noise ratio) for further segmentation was found to be challenging since imaging was exploiting the limits of XRT (resolution) and ET (size limitation). A morphology threshold filter in the software Arivis was used for segmentation (see Fig. 1d). The primary particles are visualized in their original size at the positions evaluated from the prior segmentation (see Fig. 1e). Utilizing this workflow, it is possible to investigate the individual 3D positions of the primary particles in the agglomeration and, in particular, the lattice of these liquid crystals.

Figure. 1: “Magic Clusters”: Polystyrene primary particles with a diameter of 400 nm forming an agglomeration with a diameter of 14 µm. a) Scanning Electron Microscopy: overview of agglomeration; b) XRM projection image (phase contrast imaging mode) of one “Magic Cluster”; c) Volume rendering of 3D reconstruction of XRM tomographic dataset (density coloring); d) segmentation with morphology-threshold filter in 3D; e) Virtual primary particle (spheres) positions evaluated by using the prior segmentation.
Focused Soft X-Ray Beam Induced Deposition of Metallic Nanostructures

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Focused X-ray beam induced deposition (FXBID) is a maskless direct-write technique that combines the concepts of focused electron beam induced deposition (FEBID) and X-ray lithography (XRL). We use the focused beam of a scanning X-ray microscope (STXM) for energy-selective photo-excitation and subsequent decomposition of metal-organic precursor molecules in the gas phase. The main advantage of our new technique is the selectivity of the decomposition trigger by the incident photon energy. Therefore, it is possible to optimize deposition rates by tuning of the excitation energy according to the absorption cross-section of the precursor and, in perspective, to evaluate optimum parameters for deposition of monometallic structures from precursor mixtures. Furthermore, we target the fabrication of nanostructures with superior purity compared to FEBID by evaluation of photon energy dependent fragmentation processes and plan to exploit the comparably high penetration depth of X-rays for functionalization of porous substrates.

We will present photon energy dependent growth rate studies for several metal-organic precursor molecules and the respective in-situ characterization in terms of purity, chemical composition and magnetic properties of the deposited nanostructures.[1,2] Furthermore, we have recently studied the photon energy-dependent resonant and off-resonant fragmentation of Fe(CO)5 and Co(CO)3NO at all relevant absorption edges in the gas-phase. We observe a high degree of fragmentation with the respective metal ion M+ as main component as well as significant differences in the relative intensities of various fragments with respect to the incident photon energy.[3] These results are correlated with insights on the energy distribution of secondary photo-electrons by resonant / off-resonant photoemission spectroscopy. We will also discuss future developments of the current deposition set-up in terms of in-situ cleaning procedures and annealing of our deposits.

The project is funded by DFG grant SP 1775/1-1.

Atomically Resolved Imaging of Dodecyl Functionalized Graphene and Defect Engineering in Bilayer Graphene

Christian Dolle 1,*, Peter Schweizer 1, Daniela Dasler 2, Sebastian Gsänger 3, Gonzalo Abellán 2, Frank Hauke 2, Andreas Hirsch 2, Bernd Meyer 3 and Erdmann Spiecker 1

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2D-materials keep exciting the scientific community and have done so for decades due to their exceptional optical, mechanic and electronic properties. Within this family, graphene takes the most prominent position, as it was the first widely investigated monolayer material worth a Nobel prize for its isolation and the experimental description of charge transport within the single atomic layer.

To harvest these exceptional properties for conceivable electronic applications, the zero-bandgap semiconductor graphene has to be structurally altered. We will present the microscopic characterization of two approaches for possible band gap tuning on a road for a use of mono- or bilayer graphene to be a building block in device structures.

The covalent functionalization of free-standing monolayer graphene with individual dodecyl chains is presented and the atomically resolved imaging of the dynamic behavior of individual alkyl chains will be shown.

To separate contamination traces from covalently bound addends, the interface is cleaned by a mechanical filtering approach with two precisely controllable “nano-brooms”. After mechanical filtering the atomically clean surface can be imaged and individual carbon chains on graphene are resolved.

Furthermore, the direct in situ manipulation of individual dislocations in freestanding bilayer graphene[1] has the potential to enable the switching of graphene’s functional properties.[2] The observation of reactions between these topological defects helps to unveil fundamental concepts of crystalline defect theory and lets us anticipate the construction of an all-carbon defect-based functional switch.

Tunable Fluorescence of Mixed Shell Monolayers on Oxide Nanoparticles

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Metal oxide nanoparticle (NP) surface functionalization with phosphonic acid derivatives (PA) is a widely applied tool to control colloidal stability, hinder Ostwald ripening and precisely tune NPs reactivity and solubility.[1] By a chemical surface modification, a monolayer of ligands (here PAs) covalently links on the NPs surface. As such, NP surfaces offer a template where various properties, such as solubility and optical properties, can easily be combined by a suitable choice of ligands. To introduce optical activity to intrinsic colorless NPs, surface functionalization with dyes, among those aromatic systems, is a well-known tool.[2] By applying a mixture of optical active (polyaromatic hydrocarbons) and optical inactive PAs the aggregation behavior of aromatic dyes is controlled, allowing a precise tuning of the resulting fluorescence properties. Furthermore, the utilization of optical inactive PAs of different chemical nature further influences the fluorescence properties.

With this motivation at hand, we aim to investigate the relationship between different NP surface functionalization and the resulting optical properties, depending on the ligands polarity and morphology. For this we combine several spectroscopic methods and X-ray reflectivity with molecular dynamic simulations of self-assembled monolayers on NPs surfaces in order to explain our observations.

The subdiscipline of chiral plasmonics studies the interaction of circularly polarized light with metallic nanostructures. Planar crescent shaped plasmonic structures have shown strong near-field enhancement, and can be produced easily by colloidal lithography. This technique is very versatile, and can produce cheap large-area samples (1cm²) in contrast to e.g. costly ebeam lithography. To gain a chiroptical response this technique was further developed to gain 3-dimensional single crescents, rather than planar ones. The systems show promising optical properties in the range of $\lambda = 600$ to 3000 nm, and circular dichroism values of up to 20%.

Chiral single objected have been produced by a modified on-edge lithographic approach. Here, the gold crescents are evaporated on twisted silica crescents. The silica introduces an edge, and by that also 3-dimensionality. The spectral properties are mainly determined by the resonator size, i.e. they behave similarly as planar crescents. The chiroptical response crucially depends on the structural chirality, which can be tuned by the position of the edge or the edge thickness. Thus, large degrees of freedom are given for chiral single crescents (cSC). The first three harmonic resonances are excited within the visible to near-IR range. We corroborate our model by finite elements simulations. By this, we can employ multipole decomposition to gain an understanding of the chiroptical response and the nature of these resonances. These intrinsic chiral nanostructures are dominated by electric and magnetic moments with overlapping projection.
Anisotropic Self-assembly of Isotropic Colloidal Building Blocks

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The ability to control the assembly behavior of colloidal building blocks is of fundamental importance for a range of scientific disciplines and applications. At an air/water interface, spherical particles generally form two-dimensional crystals with hexagonal symmetry.[1]

However, theoretical predictions have shown that even simple, isotropic colloidal building blocks can form complex anisotropic assemblies, if their interaction potential is described by a hard sphere potential modified with a soft repulsion shoulder.[2]

In our recent work, we were able to proof these predictions experimentally.[3] We engineered the interaction potential of colloids by the addition of soft amphiphiles including microgels, proteins or block-copolymers. We use an in-situ approach to observe the phase diagram of colloids directly at the air/water interface of a Langmuir trough equipped with a microscope. We find a rich phase diagram including hexagonal non-close packed, chain, square and hexagonal close packed phases (Fig. 1). We discuss the appearance of these phases in terms of a soft repulsion potential induced by the presence of the amphiphiles at the air/water interface.

Figure 1. Phase diagram of colloids mixed with microgels observed in situ at the air/water interphase a) compression isotherm b-g) Representative microscopy images taken at the air/water interface: Scale bar corresponds to 10 µm.

References
Effect of Static and Dynamic Size-dispersity on the Crystallization of Hard Spheres

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Colloids are never synthesized perfectly identical but follow a distribution of particle sizes, shapes, and charges. Such static dispersity is commonly attributed to the inhibition of crystallization. Spontaneous symmetry breaking can also cause dynamic dispersity in micelles and certain metal atoms via molecule and electron exchange, respectively. Here, we systematically investigate the effect of size-dispersity on the crystallization of hard spheres. We accelerate event-driven simulations with particle swap moves for static dispersity and with particle resize moves for dynamic dispersity. We observe a competition of dense packing into the face-centered cubic crystal and the propagation of icosahedral order. At dispersity above 7%, Laves crystals, AB13, and a highly complex phase with predominantly icosahedral order self-assemble in simulation. Our findings demonstrate new ordering phenomena by the controlled introduction of dispersity not possible with identical colloids.
Effect of Membrane Mediated Interactions on Protein Organisation

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There is a manifold of interactions between proteins and membranes including local modulation of membrane thickness, curvature, or structure, as well as forces induced by pinnings to external structures, for example the cytoskeleton or a second membrane. Due to their long range nature and non-specificity,[1] membrane mediated interactions may be vitally important for clustering of membrane proteins. In turn, this is important for a number of biological processes among which are cell adhesion, where binding to an adhesion junction and growth of domain may be affected,[2] but also for the interactions between membrane attached, functionalised nanoparticles.

We use the Helfrich Hamiltonian [3] to model the membrane, and a harmonic point force to model the effect of the membrane inclusion on the membrane. The latter is deforming the membrane and induces local reductions in membrane fluctuations. Using a mean field model, we analyse the resulting potentials and forces between proteins.[1] By studying the second virial coefficient, we estimate the position of the gas-liquid critical point.[4] We show that, depending on the membrane and inclusion parameters, the membrane mediated forces can be enough to drive clustering [5]. The effect of these interactions on the diffusion of proteins[5] is analysed through the mean first passage time.

Patterned Substrates and Sliding Drops

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We study the interactions of a Newtonian droplet with structured wetting defects numerically. Although this system has been studied already we show that several limitations are imposed. Either the patterning is much smaller than the droplet or the shape of the assumed defect is trivial.\cite{1,2} For the case of a defect which has a finite curvature and is of comparable size to the droplet a new interaction is observed. We refer to this state as splitting which is generated only by the means of a wettability defect. Systematically scanning through the parameter space of aspect ratio and wettability difference allows us to obtain a phase diagram. Our findings confirm that not only the wettability difference is a key parameter but also the impact curvature of the defect. Further we show that computing the defect-droplet overlap is not sufficient to describe the energy loss.\cite{2} In turn we observe a transition from finite overlap to no overlap for increasing wettability difference. We argue that the energy that is needed to wet the defect is higher than the energy which is needed to deform the three phase contact line as well as the surface of the droplet. Similar arguments apply for the splitting in which the impact curvature of the defect has to be larger than a critical curvature. Our numerical approach is a shallow water lattice Boltzmann method.\cite{3} There are two reasons for this choice. The first one being efficiency. A single GPU is suitable for most systems we are interested in. The second one is simplicity. Instead of a two phase 3D model we manage to capture the leading order physics of the problem with our 2D single fluid model.

Our plan is to use this in the future for complex coating problems and fluid substrate backcoupling.

\cite{3} S. Zitz et al., preprint (2018).