The layered structure of transition metal dichalcogenides (TMDCs) enables the synthesis of single- and few-layer two-dimensional (2D) materials with unique electronic, chemical, and mechanical properties. However, the lateral 2D feature size has limited efforts to quantify the electrochemical response on these types of materials. Using a scanning electrochemical cell microscopy approach, we investigate the effect of layer thickness on electrochemical response on 2D TMDCs, isolating the response from individual layers and quantifying how the electrochemical activity varies with electronic structure.

Hybrid electrochemical scanning probe microscopy: Physical and electrochemical characterization of interfaces
Prof. Dr. Christine Kranz
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Session Wednesday 23 September: Resolving Electrochemical Properties on Functional, Sustainable Materials / ion session

Hybrid scanning probe techniques such as scanning ion conductance microscopy (SCM) – scanning electrochemical microscopy (SECM) and atomic force microscopy (AFM)-SECM have gained tremendous importance in physical and electrochemical characterization of interfaces [1]. Our research team has pioneered combined AFM-SECM using AFM-tip integrated electrodes, which are not in direct contact with the sample surface [2], and therefore allow simultaneous mapping of physical and electrochemical properties at electrified interfaces in contrast to other approaches based on metal/metalized AFM tips [3,4]. Recently, we introduced a new type of electrochemical scanning probe tip for combined AFM-SECM measurements providing instead of a conventional AFM tip, a conductive colloid sphere attached to an otherwise insulated cantilever [5]. Such conductive spherical probes may consist of boron-doped diamond [6], a highly attractive electrode material, or may be electrochemically modified, e.g., with polymers, highly suitable for force spectroscopic measurements such as adhesion measurements under potential control. Within this contribution, selected examples of combined electrochemical and nanomechanical mapping will be presented and discussed along with experimental challenges. In addition, electrochemical force spectroscopic measurements with polydopamine (PDA)-modified colloidal probes will be presented taking advantage of the fact that the surface functionality of PDA and hence the force interaction can be altered by oxidation or reduction of functional groups.

References:

Correlative Electrochemical Multi-Microscopy: Building an Understanding of Electrochemical Interfaces From Local to Global.
Prof. Patrick R. Unwin
Department of Chemistry, University of Warwick, Gibbet Hill, Coventry, CV4 7AL, United Kingdom

Session Wednesday 23 September: Resolving Electrochemical Properties on Functional, Sustainable Materials / ion session

to come
Nanorheologie AFM for Basic Polymer Science

Prof. Ken Nakajima

Department of Chemical Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan

Session Thursday, 24 September: Polymer- and Bionanotechnology | Join the session

Nanorheological measurement based on AFM is reviewed with showing several examples of polymeric materials. Dynamic modulus determination, such as storage ($E'$), loss ($E''$) moduli and loss tangent with wide-frequency range is now realized by this technique. [1, 2] The first example uses its capability of wide frequency measurement and its temperature control function to validate the time-temperature superposition (TTS) principle. We used styrene-butadiene rubber (SBR) vulcanizate of which glass-rubber transition temperature, $T_g$, is $-27^\circ C$. [3] It was confirmed that the viscoelastic values of a pure SBR vulcanizate were quantitatively equivalent to bulk DMA results. TTS holds even at nanoscale if just viewing “average,” while some breakdown occurs due to heterogeneous nature of GR transition. As the second example, we applied this technique to silica-filled SBR to investigate the nature of the interfacial rubber region. [4] Its dynamics properties were different from those of matrix rubber regions. The master curve obtained by this technique perfectly coincided with that by bulk DMA. However, by examining the frequency-dependent change of $E''$, we found that this transition does not occur uniformly depending on spatially heterogeneous polymer segmental dynamics.

(a)

(b)

Figure 1. (a) Loss tangent map of SBR/BR blend by nanorheological AFM ($f=20$ kHz). The scan size is 2.0 $\mu$m. (b) Frequency dependence of loss tangent for both SBR/BR blend and each homopolymer.

The miscibility between two polymer species is the third example. Nanorheological AFM was utilized to investigate the nature of a SBR/butadiene rubber (BR) partially miscible blend. The blend seemed to be immiscible according to SEM and conventional AFM techniques. However, when both $E'$ and $E''$ for the blends were compared with those for the homopolymers, values for both the SBR-rich and BR-rich regions did not coincide with those for the pure components as shown in Fig. 1. In particular, the BR-rich region, exhibited a dynamic heterogeneity, where the frequency responses were much more complicated than those of both the SBR-rich and BR-rich regions. The master curve obtained by this technique perfectly coincided with that by bulk DMA.

References:


AFM-tip-induced strain effects in BiFeO$_3$ films: from structural phase changes to polarization switching and nanofabrication

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Session Thursday, 24 September: Advanced research on ferroelectric materials | Join the session

Recent studies have emphasized the critical role that local mechanical stress can play on the functionality of ferroelectric materials. For instance, stress applied from an atomic force microscope (AFM) tip has been shown to induce polarization reversal through the flexoelectric effect in ultrathin films, where the strain gradients can permeate through the film thickness [1]. In addition, local stress can alter electric field-induced switching behavior, affecting hysteresis loop shape, coercive field, and remnant polarization [2]. The mixed phase form of epitaxially-strained BiFeO$_3$ thin films, having a coexistence of rhombohedral-like R phase, comprising needle-like structures, within a tetragonal-like T phase matrix, meanwhile show a particular susceptibility to applied stress. The effects include transitions between phases, with the resulting boundaries demonstrating enhanced conductivity [3], and stress-induced alterations to electric field-induced hysteresis [4]. In this work, a loading-force dependent evolution of strain effects is reported, from structural phase changes at low forces ($< 1 \mu$N) to...
nanomechanical mechanical at higher forces (~ 1 μm). Switching behavior and switching currents are also found to be affected by force, with coercive fields decreasing with increasing loading force. Notably, mechanically-induced increases in applied force may enable polarization state determination in ferroelectric memory applications. Lastly, at high forces > 10 μm, a moving tip can be used to remove material. Through a systematic investigation of a range of AFM parameters, including force, we demonstrate that AFM-based machining is an effective tool for rapid and precise modification of local regions of the sample, as well as for the fabrication of several different nanostructures, including nanocapacitor arrays with individually addressable ferroelectric elements. AFM-based machining of ferroelectric nanostructures offers advantages over established techniques, such as bottom-up approaches and focused-ion beam milling, in select cases where low damage and low-cost modification of already-fabricated thin films are required.

References

Quantification of nanoscale electromechanical responses
Dr. Neus Domingo
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Session Thursday, 24 September: Advanced research on ferroelectric materials | Join the session

In this talk, I will review several different phenomena that directly affect quantification of piezoelectric response at the nanoscale, that is, the determination of the d33 effective piezoelectric coefficient. First, I will show how gradient-based electromechanical effects couple and interfere with PFM measurements. I will start by demonstrating the asymmetry in mechanical properties induced by the coupling of flexoelectricity to ferroelectricity leading to ferroelectrics as smart mechanical materials [2], and opening new opportunities to mechanically read ferroelectric polarization states in both, thin films and single crystals, on the base of Contact Resonance Frequency AFM mode. Then, I will put the light in another new aspect: converse flexoelectric effect [3] due to the presence of strong local electric field gradients at the tip end can induce a mechanical strain of crystals, on the base of Contact Resonance Frequency AFM mode. Nevertheless, when engineering domains across such crystals, domain walls (DWs), i.e. the tiny region that separates adjacent areas of opposite or non-collinear electric polarization, show, to our great surprise, excellent metallic-like properties. When applying a small voltage of ±10 V across such a wall, extremely large DWCs of up to ±1 mV per DW are recorded, and this even at room temperature. Mandatory for this to happen, however, are low injection barriers as well as optimized electron (hopping) transport properties along such DwS, as is experimentally mediated by slightly inclining DWs with respect to the polar LNO axes. In this talk, I will provide clear proof for the existence of this 2-dimensional electron gas (2DEG) in these DWs by exploiting Hall transport properties, excited both with and without external photo-illumination. In addition, I will show how to track the effective trajectory of electrons when flowing along the DW; the latter is achieved by applying a novel type of non-linear optical microscopy, so-called Cherenkov Second Harmonic Microscopy, a method that then reveals a 3-dimensional profile of individual domain walls across the bulk, excellently complementing our PFM surface data. Most interestingly, these large DWCs allow for fabricating nanoelectronics devices, making use of the reconfigurable 2DEG in these DWs.

References

Oxide materials exhibit a broad range of tunable properties, including magnetism, multiferroicity, and superconductivity. Oxide interfaces are particularly intriguing. Their low local symmetry combined with the sensitivity to electrostatics and strain leads to unusual physical properties beyond the bulk properties. Recently, ferroelectric domain walls (DWs) of oxide interfaces, the walls are spatially mobile and allow controlling electronic signals at the atomic scale, holding great potential as multifunctional 2D systems for future nanoelectronics.

In my talk, I will present unique features that occur at improper ferroelectric domain walls in hexagonal manganites and discuss how these walls can be used to emulate the behavior of key electronic components. For our studies, we choose the p-type semiconductor LaMnO3 as it naturally develops all fundamental types of ferroelectric domain wall at room temperature, namely neutral (side-by-side) as well as negatively (tail-to-tail) and positively charged (head-to-head) configurations. The walls are explicitly robust and, hence, represent an ideal template onto which the desired electronic behavior can be imposed. I will show how the electronic properties can be optimized and controlled, and discuss the possibility to use such walls for designing 2D digital switches and half-wave rectifiers [1,2], bringing us one step closer to domain-wall based devices and networks for next-generation nanoelectronics.

References
Finally, I will present an outlook on the characterization of 3D-printed micrometer scale auxetic elastic structures, which extended towards the organization of the collagen networks using AFM based fast force-mapping. 

Next, I will show how a combination of AFM based indentation and fluorescence microscopy is used to correlate nanomechanical properties with the organization of chondrocytes in osteoarthritic cartilage [2]. This correlation is further extended towards the organization of the collagen networks using AFM based fast force-mapping. Finally, I will present an outlook on the characterization of 3D-printed micrometer scale auxetic elastic structures, which underlines the great versatility of today’s AFM-based research.

References:

Three-dimensional nano-architectures in energy, bio-medical, electronic and sensing applications – optimization based on correlative microscopy and spectroscopy and machine learning
Prof. Dr. Silke Christiansen
Innovation-Institute for Technology and correlative Microscopy, Forschheim, Germany

Session Friday 25 September: Correlative microscopy techniques for comprehensive material characterization

Complex nano-architectures of various material combinations (e.g. Si-nanostuctures such as wires (NW) and cones (NC), GaN nanostructures, transparent conductive oxides e.g. Al doped ZnO, coinage metal nanoparticles e.g. wires, spheres, graphene and other 2D materials) integrated on Si wafer platforms will be presented for light absorption, light emission and sensing applications. In this context, we will show nano-material choices e.g. for surface enhanced Raman spectroscopy (SERS) and chemically functionalized SiNWs, SiNCs, GaN NWs with distinct resonances for optical sensing or distinct electrical performance in e.g. electronic nose devices based on resistors or field-effect transistors. Materials and device optimization will rely on advanced, scale bridging correlated electron-, ion-, optical- and x-ray microscopy and spectroscopy (CROHMIC) including atom probe techniques. The application of nanoGPs to enable true correlation with nanoscale precision between different techniques in different machines is essential and respective workflows will be demonstrated. In addition, we will show the application of machine learning strategies to aforementioned heterogeneous data to further exploit optimisation of materials and device performance.

Introduction of recent SPM hybrid technology development
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Session Friday 25 September: Correlative microscopy techniques for comprehensive material characterization

Over the past three decades, AFM (Atomic Force Microscopy) has evolved into an ideal methodology for non-destructive sample scan with longer tip life, higher accuracy, repeatability, and automation. AFM is improving steadily so that it can be widely adopted like other microscopes, such as optics and scanning electron microscopes (SEM). In addition to the recent advances in AFM technology, it further expands the AFM application area by combining with other metrological technologies such as white interferometer (WI) and photo-induced force microscopy (PFM). By utilizing the vibration-isolated platform and the low noise z scanner of AFM, the performance of WI has been greatly improved achieving unprecedented high z resolution.
Traceably quantitative magnetic field measurements with magnetic force microscopy
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Session Friday 25 September: Overcoming barriers in AFM / join the session

Magnetic force microscopy (MFM) can be considered the standard tool for measuring magnetic stray fields with a spatial resolution down to 10 nm. When measuring nano-scale structures, the size of the MFM probe, a magnetically coated tip, usually becomes comparable to the length scale of the field variations and must hence be considered. This is possible by a transfer function (TF)-based calibration approach that correctly considers the non-point-like character of the magnetic tip. The MFM tip interacts with the sample via its stray field gradient distribution. The TF approach calculates an effective tip stray field gradient distribution, the tip transfer function (TTF), by means of a calibration measurement on a reference sample with well-defined magnetic field distribution. This allows quantitative MFM (qMFM), since the knowledge of the TTF-together with the mechanical properties of the tip cantilever facilitates the calculation of the magnetic field distribution of an unknown sample from a constant height MFM measurement by a deconvolution.

In this talk, we will introduce the TF-based calibration concept and discuss its scope of application as well as the limitations. Reference samples are discussed and the results of an intercomparison are presented. As an outlook, first results on a validation of a TTF using NV centre magnetometry are shown, as a first step towards quantum traceability of qMFM.

References:

A comprehensive study of electrochemical HOPG intercalation with HClO₄ and H₂SO₄ electrolytes by photoemission spectroscopy and atomic force microscopy
Prof. Gianlorenzo Bussetti
Polytechnic University of Milan, Italy
Session Wednesday 23 September: Resolving Electrochemical Properties on Functional, Sustainable Materials / join session

Graphitic materials are employed in many technological applications, from the realization of electrodes in batteries to the production of graphene foils by electrochemical (EC) procedures [1]. In particular, the processes characterizing graphite oxidation have attracted researches in view of understanding the mechanisms of the EC oxidation of graphite electrodes, and in particular the intercalation process that occurs at oxidative EC potential ranges [2].

In this context, highly oriented pyrolytic graphite (HOPG), with its well-defined layered structure, is generally considered a model system to elucidate the mechanisms of the EC oxidation of graphite electrodes, and in particular the intercalation process that occurs at oxidative EC potential ranges [3].

Recently, we demonstrated that anion intercalation can be detected not only at high (within 1.9 and 2.1 V vs SHE) EC potential values, i.e. above literature-reported intercalation stages, but also at lower potentials and allowing for a faster dynamics [4]. Here, we compare the results obtained on HOPG by using two different EC techniques for ion intercalation, namely cyclic voltammetry (CV) and normal pulsed voltammetry (NPV), with two different aqueous electrolytes (i.e. perchloric and sulfuric acid). The samples were analysed in-situ by atomic force microscopy (EC-AFM) and ex-situ by X-ray photoemission spectroscopy (XPS), where ion intercalation results in a shift of the XPS core levels towards lower binding energies, as previously highlighted by one of us [5].

We detect comparable XPS line shapes after intercalation at high potentials, both with CV and NPV and for both electrolytes. Intercalation of perchlorate ions at lower potentials (namely, at the oxygen evolution potential) surprisingly shows a similar spectral evolution, with much less stronger modifications are obtained by applying NPV, compared to CV. Finally, we investigated the effect of increasing the CV scan rate on both sample morphology and chemical surface condition. Our results show that, in spite of a similar XPS behaviour, fast CV scans prevent the development of extended surface defects (such as blisters) usually observed on HOPG due to the formation of gases seeded by ion intercalation.

References:
Revealing local ionic conductivity and chemical distribution in solid state electrolytes by Electrochemical Strain Microscopy

Prof. Dr. Florian Hausen
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Session Wednesday 23 September: Resolving Electrochemical Properties on Functional, Sustainable Materials / join session

All Solid State Lithium Ion Batteries (ASS-LIB) are of great economic as well as scientific interest. Substituting the flammable liquid organic electrolyte by a lithium ion conductive ceramic is a promising route. Lithium Aluminium Titanium Phosphate, Li1.3Al0.3Ti1.7(PO4)3, is a typical representative of a solid state electrolyte with NASICON type structure, exhibiting superior lithium ion conductivity. [1] The appearance of secondary phases of aluminium phosphate under certain manufacturing conditions [2] demonstrate the need for understanding the correlation of lithium ion mobility and microstructure on sufficiently small scales in solid state electrolytes. Electrochemical Strain Microscopy (ESM) is employed to investigate the influence of the microstructure of the solid state electrolyte LATP. A clear contrast between LATP and the secondary phase is observed, exhibiting significantly reduced lithium ion mobilities in secondary phase areas. In order to correlate chemical information with the ESM signal, Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX) is utilized in a correlative approach. [3] The contribution of grain boundaries to the overall ionic conductivity is discussed in view of recently published impedance spectroscopy results. [4] Additionally, a correlation between the tip-sample capacitance in contact and the local chemical distribution of LATP is observed, leading to new insights into the complex signal formation process in ESM. [5] The applicability on other solid state electrolytes will be critically discussed.

References

Kinetics of oxidative etching and Mo oxides produced during oxidation of single microscale 2H MoS2 flakes in air and high relative humidity

Asst. Prof. Robert Soós
University of Warsaw, Poland

Session Wednesday 23 September: 2D materials and nanoelectronics / join session

For numerous applications of microscopic MoS2 crystals, one must understand their most expected surface reactions. Ubiquitous examples of these are oxidation reactions in air and water. In this talk, we show how we studied the kinetics of microscopic heat-induced oxidative etching in the case of thick, mechanically exfoliated, geological MoS2 crystals in air. Next, based on the literature we discuss particular reaction mechanisms of oxidative etching as well as mention other competitive processes. In the second part of the talk, we show how to differentiate MoO3 oxides and their derivatives on thermally oxidized microscopic 2H MoS2 flakes. In order to do so, we combined XPS and AFM measurements such as topography, friction, creation of nanoscale ripples and scratches on the MoS2 flakes.

Morphological and electrical characterization of coordination polymers containing rhodium paddle wheels

Dariel Steinbach
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Session Wednesday 23 September: 2D materials and nanoelectronics / join session

The electric conductivity of MOFs is generally considered as a prerequisite for many potential applications such as sensors, transducers, electrodes and others. [1,2] To overcome the disadvantages of most MOFs being insulators, conjugated coordination polymers are investigated regarding their electrical conductivity. Therefore, paddle-wheel structures with a documented metal-metal bond, here rhodium derivatives, were linked via conjugated organic molecules like pyrazine. [3] Coordination polymers of this type were first synthesized as bulk materials, characterized using XRD, BET and XPS and then deposited as coatings on gold surfaces. Subsequently, the topography of the deposited layers was measured. Different morphologies mainly determined by AFM were obtained by using spin coating and dip coating. Depending on the composition of the coordination polymer well distributed crystals or network like structures were found. The surface layers were further investigated by XPS and XRD. Direct current measurements were carried out on such systems by conductive AFM. The results point out, that [Rh(acac)pyz] forms orientated nano crystallites on a gold coated surface (figure 1), which are insulating. Changing the axial bond ligand to acetamide causes a conductive coordination polymer with recognisable currents (figure 2).

Compressed modified interference in boron nitride layers: a conductive two-dimensional BN compound
Prof. Dr. Ana Paula Barboza
Federal University of Ouro Preto, Brazil
Session Wednesday 23 September: 2D materials and nanoelectronics / join session

The ability to create new materials with improved properties upon transformation processes applied to conventional materials is the keystone of materials science. Here, hexagonal boron nitride (h-BN), a large bandgap insulator, is transformed into a conductive two-dimensional (2D) material – boronitrol – that is stable at ambient conditions. The process, which requires compression of at least two h-BN layers and hydrolysis ions, is characterized via scanning probe microscopy experiments and ab initio calculations. This new material and its creation mechanism represent a new strategy on the transformation of known 2D materials into artificial advanced materials with novel properties.

Kelvin probe force microscopy-based direct measurements of contact resistance in 2D semiconductor thin film transistors
Dr. Aleksandar Matevski
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Session Wednesday 23 September: 2D materials and nanoelectronics / join session

This study aims at direct imaging of contact resistance in MoS2-based thin film transistors (TFTs). Exfoliated single-crystal flakes of MoS2 have been used in a bottom-contact TFT configuration. Pyrimidine-containing self-assembled monolayers (SAMs) were employed to tune the work function of gold electrodes. Kelvin probe force microscopy measurements were carried out during operation of the devices in order to directly image potential drops across the channel and to study the influence of different SAM treatments on the contact resistance. By independently imaging potential drops at both channel injection and extraction points, we demonstrate asymmetry of contact resistances in MoS2-based TFTs as well as their non-linear and bias-dependent behavior [1].


Molecular decoration of two-dimensional materials: unveiling crystallographic orientation and grain boundaries
Prof. Mariana Prado
Federal University of Ouro Preto, Brazil
Session Wednesday 23 September: 2D materials and nanoelectronics / join session

Following the realization of single-layer graphene atop silicon oxide, much attention has been drawn towards two-dimensional materials. Graphene is a semi-metal, hexagonal boron nitride (hBN) is an insulator and single-layer molybdenum disulfide (MoS2) is a semiconductor with a direct bandgap. Besides these, there are numerous other two-dimensions nanosheets of a variety of materials including other transition metal dichalcogenides and phyllosilicates, minerals composed of parallel sheets of Si2O5 tetrahedra. An example of the latter group is talc [1], a solid lubricant with many industrial applications. Characterizing these 2D materials is a challenge that must be addressed so they can fulfill their potential to revolutionize the industry with their outstanding mechanical, optical, and electrical properties. We present a simple way to reveal the crystallographic orientations of graphene, MoS2, and hBN without the need of acquiring atomic resolution microscopy images. Octadecylphosphonic acid (OPA) is a linear alkyl chain organic molecule that forms self-assembled monolayer (SAM) on top of the cited materials and that keeps registry with the crystallographic substrate beneath it. An atomic force microscopy (AFM) image easily detects the period of the 2D molecular crystal that forms atop the flake, revealing the substrate’s crystallographic orientation. Ab initio calculations reveal that the molecular crystal’s ripples (detected in the AFM image) are aligned with MoS2 [2], hBN [3], and graphene’s [4] armchair directions.

For MoS2, we also found that our samples, purchased from SPI supplies, presented ripples of the molecular crystal-forming 12° angles that did not reflect the substrate’s hexagonal symmetry. Interestingly, Stone-Wales-type defects have been predicted to cause 12°-angled grain boundaries in MoS2 and WS2. Thus, the SAM deposition followed by standard AFM analysis on ambient conditions proposed in this work enables the direct localization of MoS2 grain boundaries. For graphene, ab initio calculations and Raman spectroscopy measurements also show that OPA induces p-type doping of graphene of ~1013 cm-2. Finally, OPA has a different behavior when deposited on top of talc, forming the organized 2D crystal or vertical bilayers, depending on the deposition conditions. Summing it up, spin coating OPA ethanolic solution on 2D materials is a facile way of discovering flake orientation, characterizing grain boundaries of MoS2 samples, and achieving chemical doping of graphene.

Since its discovery in 1986, atomic force microscopy (AFM) has become a powerful tool to address the physical-chemical properties of matter. In the last decades, strong efforts have been made to analyze the intermolecular interactions between biomolecules by AFM through dynamic force spectroscopy (DFS) under near-physiological conditions. DFS is an operation mode which enables not only the acquisition of single force-distance curves but also, combined with scanning to record tip-sample adhesion maps. Adhesion imaging collects with the simultaneous acquisition of topography in force operational mode. When adhesion maps are produced with functionalized tips scanning on samples substrates covered by amino receptors, it is possible to find the conditions to locate the receptors. Several methods were proposed to locate receptors using different modes and strategies, including dynamic modes (e.g. TREC [1]). In this work, we present an intermittent force method able to give adhesion force maps that not only locate the receptors through rupture events but also provide the rupture forces in each pixel of the image at the pN range. These experiments open new possibilities not only for fast analysis of rupture forces but for developing procedures for detection at the single molecule level.

In this work, we show two alternative studies: i) the analysis of the interaction between the flavoenzyme ferredoxin NADP+ reductase and its redox partners, ferredoxin and flavodoxin. We protected the binding site of the enzyme against the tagging molecules to prevent the loss of enzymatic activity evidenced by molecular recognition imaging [2]. Moreover, different loading rates were tested to obtain the energy landscape parameters for both complexes [3]. In the adhesion imaging maps it was possible to distinguish the enzyme molecules and the rupture forces with both protein partners at the tip in the simultaneous images, ii) the analysis of the adhesion forces between streptavidin and biotin. The adhesion maps in implemented certain conditions, indicate that rupture forces of the streptavidin-biotin complexes are 3-fold higher respect to the avidin:biotin complexes (40-80 and 120-170 pN, respectively). This method was probing used mixed protein samples scanned with biotinylated AFM tips, being capable of discriminate among avidin and streptavidin molecules by this molecular recognition imaging method [4, 5].

We expect that these alternative protein-biogenesis conjugation strategies to attach proteins to solid surfaces/AFM cantilevers preserving their enzymatic activity by one side, together with the intermittent force operating conditions allow to get reproducible adhesion force results that achieve characteristicly the identification of protein receptors in mixtures through rupture forces, necessary to design throughputed devices based on forces.


The role of lectins in surface adhesion and virulence of Pseudomonas aeruginosa studied with single molecule force spectroscopy

Joanna Zemła
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Session Thursday, 24 September: Polymer- and Biotechnology | Join the session

On surfaces, bacteria form communities called biofilms, in which a self-produced extracellular matrix acts as a glue and shields bacteria from the environment. In healthcare, biofilm formation plays a crucial role in the development of biofilm resistance [1]. The biofilm formed by Pseudomonas aeruginosa is part of a family of microorganisms exhibiting multi-drug resistant virulence, responsible for most hospital-acquired infections [2]. P. aeruginosa’s matrix is mainly composed of exopolysaccharides (EPS), but extracellular DNA and some specific proteins have been shown to be structurally important [3-6]. Although two main EPS (Pel and Psl) have been identified, the precise composition of the matrix remains elusive. Moreover, its distribution within the biofilm and the temporality of its production are not clear.


Further development of AFM-based imaging techniques for tracking fenestrae in living Liver Sinusoidal Endothelial Cells

Dr. Bartosz Zapotoczny
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Session Thursday, 24 September: Polymer- and Biotechnology | Join the session

Atomic Force Microscopy (AFM) imaging technique, based on force-distance curve acquisition in time of a few milliseconds each allowed for the first visualization of fenestrae in living Liver Sinusoidal Endothelial Cells (LSECs). Fenestrae – transcellular pores of the size in a range of 50-300 nm, remained undiscovered in living LSECs for nearly 50 years(2). They play a prominent role in maintaining liver homeostasis and integrity. Variations in size and diameter can be used as morphological indicators for LSEC health status. Fenestrae were reported to respond to a variety of external stimuli becoming a great marker for the functional responsiveness of LSECs (3). Understanding the processes of their formation, lifespan, and closing would allow for the therapy enabling restoration of the proper porosity of LSECs.

With the AFM, high-resolution imaging of fenestrae became possible. Single frames collected in the time of tens of seconds allowed us to repetitively collect images in the same area and - as a result - tracking changes in the actin-spectrin structures forming fenestrae. Our recent advances in AFM imaging provided new insights into the dynamic processes of fenestrae formation, migration, disappearance, and closing(4). We succeeded to estimate the mean fenestrae lifespan, describe three different ways of closing of fenestrae, and showed that individual fenestrae can be in an open or closed state(5, 6). Here, we show that elasticity (described as Young modulus) and porosity can be simultaneously tracked in living LSECs. Further development of AFM-based imaging techniques for tracking fenestrae in living Liver Sinusoidal Endothelial Cells (LSECs). Initial results of the ongoing project and future outlook for research of LSECs will be presented.

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References:
The presence in human biopsies of polymorphic protein assemblies is associated with the onset of several neurodegenerative diseases. On the other hand, several organisms exploit amyloid fibrils functionally, for instance as bio-adhesives or as scaffolding material. Taking inspiration from nature, ordered amyloid-based materials paved the way for the development of robust and biocompatible materials for materials science and biomedical applications. Here we show that atomic force microscopy and force spectroscopy provides a unique window into the morphology, mechanics, and structure of proteins and amyloids on the nanoscale. Furthermore, the combination of high-resolution AFM with microfluidic methods enables to investigate amyloids thermodynamic equilibrium, ultrastructure and formation at the single molecule scale with angstroms resolution. We first demonstrate the identification and characterisation of the smallest elementary unit in the hierarchical assembly of amyloid fibrils, which we termed single-strand protofilaments. Remarkably, these aggregates are present in blood serum, cerebral spinal fluid and brain biopsies obtained from patients affected by Alzheimer’s and Parkinson’s diseases. Then, in parallel, we demonstrate the capability to tune the biophysical properties of these highly biocompatible aggregates for the development of innovative biomaterials that in contrast enable the enhancement of neuronal regeneration in animal models of nerve damage. Unveiling the biophysical properties of amyloidogenic structures at the nanoscale is central to understand how proteins misfold and aggregate for understanding the molecular processes underlying the onset of neurodegenerative disorders, as well as to produce a new class of functional materials for biomedical and materials science application.

References

High-Aspect Ratio Polymeric Nanoneedle Arrays
James McCormack
University College Dublin, Ireland

High aspect ratio (HAR) nanoneedle arrays are metastructures that can tune the intrinsic properties of substrates such as wettability, reflectivity and biocompatibility by virtue of their physical properties regardless of the substrate’s chemical properties. However, engineering dense arrays of HAR nanoneedles using polymeric substrates remains a challenge in soft lithography.

Piezoelectric and electrostatic properties of electrospun PVDF-TrFE nanofibers and their role in electromechanical transduction in nano-generators and strain sensors
Asst. Prof. Tobias Cramer
University of Bologna, Italy

Piezo- and ferroelectric nanofibers of the polymer poly(vinylidene fluoride) (PVDF) have been widely employed in strain and pressure sensors as well as nanogenerators for energy harvesting. Despite this interest, the mechanism of electromechanical transduction is under debate and a deeper knowledge about relevant piezoelectric or electrostatic properties of nanofibers is crucial to optimize transduction efficiency. Here we prepare PVDF-TrFE nanofibers at different electrospinning conditions. We compare macroscopic electromechanical response of fiber mats with microscopic analysis of single nanofibers performed by piezolectric and electrostatic force microscopy. Our results show that electrospinning favors the formation of the piezoelectric beta-phase in the polymer and leads directly to piezoelectric properties that are comparable to annealed thin films. However, during electrospinning the electric field is not strong enough to induce direct ferroelectric domain polarization. Instead, we observe accumulation of triboelectric surface charges and trapped space charge in the polymer that explain the electret-like macroscopic electromechanical response.


Figure 1: AFM topography scans and tilted FESEM images of Si nanoneedle arrays (top row) and their PEG replica (Bottom row). The PS-b-P2VP template used to define the Si nanoneedle array is indicated. All tilted images were obtained at 45o. (Scale bar: 1 μm) (deposited [Rh] [acac] 2) (100 cycles).
Further acceleration of electronics requires new flexible concepts for on-demand-devices. In ferroic materials, atomically sharp domain walls (DWs) may offer an ideal platform to realize such versatile microelectronic building blocks because they can be created, manipulated and erased by external fields. However, conducting DWs have been exclusively studied in ferroic oxides so far, in which domain-wall conductivity usually requires a specific strain configuration of the crystal, an improper character of the ferroelectricity or other unusual properties which render the walls immobile and thus curtail their usefulness and flexibility. Additionally, oxide materials are prone to defects, significantly hampering the utility of their conducting DWs.

In this study, we present a non-oxide material, GaV$_4$S$_8$. This multiferroic material combines crucial domain-wall functionalities which are not found combined in any oxide material. For example, eight orders of magnitude conductivity contrast between walls and bulk lets the walls dominate the overall conductivity behavior. Furthermore, a change from hole-like to electron-like conductivity over smallest length scales occurs in GaV$_4$S$_8$ DWs, unprecedented in oxide materials and possibly allowing for p-n junctions inside domain walls. Most importantly, GaV$_4$S$_8$ is a proper ferroelectric in which conductive DWs emerge in the unstrained crystal spontaneously, such that they retain their flexibility and can be manipulated by electric and magnetic fields.

Probing the behaviour of surface water and ferroelectric PbTiO$_3$ thin films as a function of relative humidity and temperature

Loïc More, University of Geneva, Switzerland

Session Thursday, 24 September: Advanced research on ferroelectric materials | Join the session

Surface adsorbates play an essential role in the stability of as-grown and written ferroelectric domains, particularly in thin films, since they provide the screening necessary to stabilize polarisation bound charge. The study and control of the ferroelectric-adsorbate interaction is, therefore, key to the engineering of complex ferroelectric patterns which could be used for electromechanical actuation and sensing applications as well as catalytic processes [1,2,3]. Previous studies have demonstrated that polar adsorbates such as water are strongly influenced by both the direction of the polarisation and the switching history of the ferroelectric [3], with screening strongly dependent on the relative humidity [4]. Here, we report on our investigation of the behaviour of water on ferroelectric PbTiO$_3$ thin film surfaces as a function of relative humidity and temperature at the nanoscale using Kelvin probe force microscopy, piezoresponse force microscopy and high resolution non-contact resonant imaging, and a home-built humidity control system [5]. We observe extremely low charge dissipation, and high localisation of both positive and negative screening charge on patterned domain structures in films with varying as-grown polarisation states, which we attribute to the extremely high quality and low surface roughness of the films, as compared with previous studies where much more extensive charge dynamics were observed [6]. Local measurements of the surface water layer during temperature cycling at low and high humidity will be presented, where the charge between a purely solid-like molecular arrangement and the formation of a liquid-like surface layer [7] strongly affects screening charge dynamics.


Quantifying the Impact of Varying Defect Landscapes on Domain Wall Motion

Ralph Bulanard, University of Geneva, Switzerland

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Piezoresponse force microscopy on ZnO platelets, thin films, and sintered material

Dr. Markus Kratzer, Montanuniversitaet Leoben, Austria

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As a nano/micro–scale method, piezoresponse force microscopy (PFM) is on the rise for the characterization of ferroelectric/piezoelectric properties of microsystems. Frequently PFM is utilized to study ferroelectric domain patterns, which can be challenging already. However, usually, the materials are smooth, strongly responsive, and strictly insulating allowing the extraction of quantitative information. [1] By using vector piezoresponse force microscopy [2], we could reconstruct the domain distribution function on lead zirconate titanate (PZT) as well as on polycrystalline ZnO samples [4]. We also measured the piezoelectric material zinc oxide (ZnO) in form of crystalline ZnO films [4], CdO deposited thin films, sintered polycrystalline vanadate. In these cases, the measurements are experimentally more challenging and the interpretation/quantification is difficult. Significant surface roughness, finite conductivity, and poor mechanic stability are parameters that should be considered.

Contributed Talk Abstracts

Integrated Simultaneous Chemical, Surface Potential, Mechanical, and Topographic Imaging at <10 nm Spatial Resolution

Prof. Xiaoji Xu
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Session Friday 25 September: Correlative microscopy techniques for comprehensive material characterization | Join the session

Multimodal measurements of chemical composition, electrical properties, mechanical properties, and topography by scanning probe microscopy (SPM) deliver correlations across properties at the nanoscale, and provide clues to the structure-function relationship of materials. In the past, measurements with these modalities are operated separately with different operational modes of SPM. Not only the sequential measurements require additional operation time, are subject to scanner-sample drift, but also, different modalities of SPM have different spatial resolutions, which undermine correlative analysis. For example, the popular frequency-modulated Kelvin Probe Force Microscopy measures the surface potential with 30–50 nm spatial resolution under the ambient conditions, whereas the SPM measurements of chemical composition, mechanical properties, and topography can routinely achieve < 10 nm spatial resolution.

At the conference, we will present our invention of an integrated SPM mode that can simultaneously provide chemical, surface potential, mechanical, and topographic imaging at < 10 nm spatial resolution under the ambient conditions. We name it peak force infrared-Kelvin probe force microscopy (PFIR-KPFM), as we achieved it through an integration of peak force infrared microscopy and pulsed force Kelvin probe force microscopy. In a single scan, the integrated PFIR-KPFM delivers simultaneous multimodal measurement at a comparable and high spatial resolution of < 10 nm. As a demonstration, we measured a naturally-degraded CH$_3$NH$_3$PbBr$_3$ perovskite single crystal. AFM topography, mechanical modulus, contact potential difference (CPD), and nano-IR imaging at infrared absorption of perovskite are simultaneously acquired and shown in Figure 1 (a-d) respectively. Correlation analysis among infrared absorption, mechanical modulus, and CPD are performed and displayed in Figure 1e-f.

References:

Contributed Talk Abstracts

Accelerating Your Research Using Nature Research Group's AI Powered Nanotechnology Platform

Pranoti Kshirsagar
Database Group, Nanoscience & Technology, Springer Nature, Heidelberg, Germany

Session Friday 25 September: Correlative microscopy techniques for comprehensive material characterization | Join the session

Growing public and private investment into nanotechnology has led to a significant rise in nanotechnology data generation, with increasing research output and patents over the last decade. Nanotechnology has made a significant impact on a wide range of industries from medicine to aerospace – in developing new products and applications. However, utilizing this rapidly growing data remains a critical challenge. The increasing number of research articles and patents leads to a gap between data generation and data access. Nano (nano.nature.com) is an artificial intelligence powered research solution under the Nature Research portfolio that aims to provide highly indexed and structured information related to nanoscience derived from peer-reviewed journals across all major publishers. Figure 1 shows the three categories on Nano and the content. Scanning probe techniques are crucial in understanding the correlations between surface structure and property of nano- and bio-materials. As seen in figure 2, 22,000+ nanomaterials characterized by atomic force microscopy, 120,000+ Articles and 66,000+ Patents are part of the Nature Nano database. This talk will illustrate how Nano can aid nanotechnology research communities to obtain fast and precise insight into the wealth of nanotechnology based scholarly knowledge.

References:
In this talk, a new imaging technique known as biharmonic AFM is presented. Similar to bimodal AFM, in biharmonic AFM, the cantilever is excited with two frequencies simultaneously. The first excitation frequency is at or near the first eigenmode frequency, while the second excitation frequency is the closest harmonic frequency to the second eigenmode frequency. Based on the rectangular beam theory, the cantilever’s second to first eigenmode frequency ratio is 6.27. Due to the fact that they are not excited at the same time, there is no requirement of external oscillating voltage to produce the KPFM signal. As a result, PF-KPFM can avoid many of the intrinsic limitations associated with other KPFM techniques, such as the need for lift mode and the stray capacitance effect. In this talk, we will present the operating principle of PF-KPFM, how it compares to conventional frequency modulated KPFM (FM-KPFM), and present results on several materials to exemplify the robustness of our technique. In particular, we will show that PF-KPFM is suitable for probing the interfaces between metals and semiconductors, for probing individual ferroelectric domains and boundaries on ferroelectric materials (see Figure 1e-f), and for imaging nanoscale chemical reactions and biological responses in their native environments. Scientists can use videos, obtained from PF-KPFM, to gain unprecedented insight into the spatial and temporal characteristics of these systems. PF-KPFM can be considered as a “super” KPFM, since it is capable of measuring CPD and work function images with ~10 nm spatial resolution, on a wide range of samples.

The new imaging technique, pulsed force KPFM (PF-KPFM), is developed and can reliably obtain CPD and work function images with ~10 nm spatial resolution. The PF-KPFM signal is derived from the probe-sample interaction, without the requirement of external oscillating voltage to produce the KPFM signal. As a result, PF-KPFM can avoid many of the intrinsic limitations associated with other KPFM techniques, such as the need for lift mode and the stray capacitance effect. In this talk, we will present the operating principle of PF-KPFM, how it compares to conventional frequency modulated KPFM (FM-KPFM), and present results on several materials to exemplify the robustness of our technique. In particular, we will show that PF-KPFM is suitable for probing the interfaces between metals and semiconductors, for probing individual ferroelectric domains and boundaries on ferroelectric materials (see Figure 1e-f), and for imaging nanoscale processes. Scientists can use videos, obtained from PF-KPFM, to gain unprecedented insight into the spatial and temporal characteristics of these systems. PF-KPFM can be considered as a “super” KPFM, since it is capable of measuring CPD and work function images with ~10 nm spatial resolution, on a wide range of samples.
Using scanning electrochemical cell microscopy (SECCM) architecture for high-temporal resolution stochastic electrochemistry
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Session Wednesday 23 September: Resolving Electrochemical Properties on Functional, Sustainable Materials

Stochastic collision electrochemistry requires high-resolution and high-bandwidth current amplification due to the low magnitude and short duration of the current signals. However, increasing the current amplifier bandwidth leads to increased current noise levels, which in turn obscures the current signal generated from stochastic collision electrochemistry experiments.1,2 Noise levels are very sensitive to the input capacitance of the current amplifier when operating at high bandwidth. In this presentation, we introduce a new strategy to minimize the parasitic effect contribution over the input capacitance to a current amplifier for stochastic collision electrochemistry. This is achieved by using a movable microscale electrochemical cell, formed at the end of a micropipette using a scanning electrochemical cell microscopy approach,3 to conduct electrochemical experiments in close proximity (~300 µm) to a custom design transimpedance amplifier. We demonstrated this via electro-oxidation of single Ag nanoparticles detected at 1 MHz bandwidth.


Figure 1: On the left, scheme of SECCM set-up. On the right, magnification over the end of the nanopipette, where a microscale electrochemical cell is formed in close proximity of the transimpedance amplifier (TIA). It is also detailed the nano-impact oxidation of silver nanoparticles.