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 electrochemical 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 colloidal 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 conducting nanostructures or electrochemical measurements such as adhesion measurements and 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.

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

Electrodes used in electrochemistry, with applications in electrocatalysis, energy storage, sensor technologies and corrosion, are heterogeneous and complex on a range of length scales. We advocate new approaches to study electrochemical and electrocatalytic phenomena, whereby the activity of an electrode is visualized by electrochemical microscopy in the form of “activity maps” and “potentiodynamic movies”. These quantitative data are then related to co-located electrode structure from complementary high-resolution microscopy and spectroscopy techniques applied in the same area of the electrode. This correlative electrochemical multi-microscopy approach seeks to relate electrode structure to activity clearly and unambiguously. In our work, scanning electrochemical cell microscopy (SECCM) and scanning ion conductance microscopy (SCM) are key techniques that are used for the acquisition of both electrochemical activity maps/movies and topography – synchronously and with nanoscale spatial resolution. These techniques use nanopipette electrochemical (half) cells as probes, which can be made easily in a variety of formats, characterised in detail, and their response modelled. By overlaying data from these measurements with images from co-located microscopy techniques, e.g. electron microscopy and electron backscatter diffraction, micro-Raman spectroscopy and atomic force microscopy, we obtain a deep view of electrochemical interfaces and processes. This is a general platform for investigating electrochemical interfaces, and illustrative examples of this approach will be...
Keynote Talk Abstracts

2020 NanoScientific Forum Europe
Scanning Probe Microscopy (SPM)

Characterization of metallo-DNA nanostructures properties with AFM
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Session Thursday, 24 September: Polymer- and Biotechnology (Join the session)

Nanotechnology applications rely on the capability to prepare and control functional materials at the nanoscale with high precision [1–3]. The development of novel methodologies that enhance this control has attracted the attention of scientists worldwide. In particular, the development of new strategies towards the fabrication of nanowires with tailored electronic and optical properties has been the subject of extensive efforts due to the practical applications they may offer for the miniaturization of electronic circuits. Importantly, in order to design new nanocircuits the correct organization of the nanowires must be precisely controlled. In this context, DNA has become an important tool for scientists, since intrinsic functional nanostructures can be prepared based on its sequence programmability, which offers potential applications in nanomedicine, sensing devices, drug delivery, and information processing [4–6]. However, the concept of exploiting the self-organizing properties of DNA to create nanocircuits remains a great challenge and the source of much contentious discussion. This is due to the debatable conducting properties in natural DNA molecules, with some reports pointing towards the insulating behavior of long DNA molecules, whilst other studies have demonstrated charge transfer in short DNA molecules. The electronic properties of DNA molecules have been enhanced using various strategies, including the covalent attachment of functional groups [7,8] or the deposition of a conducting material [9] including different metal atoms (i.e. Ag, Au, Cu, and Rh). Metalization of DNA molecules has proved to afford DNA nanowires with improved conductivity [10–14].

In this work, we show results for three different helical silver complexes whose molecular structure revealed the formation of helix consisting of stacked μ1–AgII–μ1–homo base pairs, with the presence of contiguous AgII) chains running through the centre of the helices and building nanowires structures. Their morphology and conductivity behavior were studied by means of AFM, EFM and c-AFM.

References:

AFM tip-induced strain effects in BiFeO3 films: from structural phase changes to polarization switching and nanofabrication
Prof. Brian Rodriguez
University College Dublin, School of Physics, Conway Institute Belfield Dublin 4, Ireland
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 BiFeO3 thin films, having a coexistence of rhombohedral-like R phase, comprising needle-like structures, within a tetragonal-like T phase matrix, meanwhile shows a particular susceptibility to applied stress. In this context, this work presents examples of nanoscale phase changes, 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 µN) to...
nanomechanical machining 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 increase with applied force and 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 film, 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
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Session Thursday, 24 September: Advanced research on ferroelectric materials | Join the session

Surface electromechanics at the nanoscale are typically studied by Piezoresponse Force Microscopy (PFM), based on the inverse piezoelectric effect. As a first approach, generally only homogeneous responses are taken into account, but it has been realized that the effect of gradients in electromechanical phenomena at the nanoscale can become dominating: the generation of electrical signals after the application of mechanical strain gradients with an AFM tip has been proved, and it has been shown that it is possible to write ferroelectric domains (1) or to move oxygen vacancies and charges.

In this talk, I will review 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 and can induce a mechanical strain of the sample in dielectric centrosymmetric materials with magnitudes comparable to piezoelectric d33 coefficient. Finally, I will go over the effect of Schottky barriers on the determination of the d33 coefficient of piezoelectric semiconductors, and show how the metal-insulator junctions can induce non-linear and multiharmonic electromechanical responses (4).

References
[4] Lozano, E; Catalan, G; Esteve, J; Murillo, G; Domingo, N, Non-linear and Multiharmonic Nanoscale Piezoresponce of Single ZnO nanowires with Schottky Junctions, (under review)

Reconfigurable 2D Electron Gases in Ferroelectric Domain Walls
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Session Thursday, 24 September: Advanced research on ferroelectric materials | Join the session

For the last 10 years, domain wall conductivity (DWC) in ferroelectrics has become a very attractive and prospective field of research. We intensively explore DWs in bulk and thin-film Lu10Bi2O3 (LNO) single crystals, a material that is known for its large bandgap of ~4 eV, optical endurance, and excellent CMOS compatibility, with the help of dedicated scanning force-microscopy (SFM) methods (i.e. AFM, cAFM, PFM, KPFM, etc.). Nevertheless, when engineering domains across such crystals, domain walls (DWs), i.e. the tiny region that separates adjacent areas of opposite or non-collinear dielectric 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 mA per DW are recorded, and this even at room temperature. Mandatory for this to happen, however, are low injection barriers as well as optimized electrode (hopping) transport properties along such DWCs, as is experimentally mediated by slightly inclining DWs in 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 exploring Hall-transport properties, excited both with and without external photo-illumination. In addition, I will show how to follow and 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 SFM surface data. Most interestingly, these large DWCs allow for fabrication nanoelectronics devices, making use of the reconfigurable 2DEG in these DWs.

Advanced functionality in ferroelectric oxides - creating building blocks for nanoscale circuitry
Prof. Dennis Meier
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Session Thursday, 24 September: Advanced research on ferroelectric materials | Join the session

Oxide materials exhibit a broad range of tunable phenomena, 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) with respect to the polar LNO axes.

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 (LNO) 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) walls 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
The AFM is a versatile tool to investigate a large and still growing number of systems, in particular in combination with fluorescence microscopy. Here I will first show how unique insights into polymer physics can be obtained by single molecule force spectroscopy. Temperature dependent experiments combined with molecular dynamics simulations could quantify entropic and energetic contributions to the elasticity of polymers and showed that neither PEG nor PNIPAM are pure entropic chains [1]. Then I will show how the mobility within polymer coatings can be determined with AFM-based scratching experiments. This mobility can be surprisingly high in cross-linked coatings. 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 extended towards the organization of the collagen networks using AFM based fast force-mapping.

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, Forchheim, Germany

Complex nano-architectures of various material combinations (e.g. Si-nanostructures 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. Three-dimensional nano-architectures in energy, bio-medical, electronic and sensing applications – optimization based on correlative microscopy and spectroscopy and machine learning

Materials and device optimization will rely on advanced, scale bridging correlated electron- ion-, optical- and x-ray microscopy and spectroscopy (COHRMIC) including atom probe techniques. The application of nanoGFP 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 optimization of materials and device performance.

Introduction of recent SPM hybrid technology development
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Fig 1: AFM images of various metallic adatoms using a CO terminated tip. A Copper adatom on Cu(111). B Copper adatom on Cu(110). C Iron adatom on Cu(111).

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-punctiform 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.
Contributed Talk Abstracts

2020 NanoScientific Forum Europe
Scanning Probe Microscopy (SPM)

Contributed Talk Abstracts

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

Prof. Dr. Florian Hausen
RWTH Aachen University, Aachen, Germany, Forschungszentrum Jülich, Germany

Session Wednesday 23 September: Resolving Electrochemical Properties on Functional, Sustainable Materials I Join session 9:

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 Aluminum Titanium Phosphate, Li1.3Al0.7T1.7P0.43, 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 aluminum phosphate under certain manufacturing conditions [2] demonstrates 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 Li-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

Ad. Prof. Robert Sadowski
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

Daniel 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 network or model 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] demonstrates oriented 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 recognizable currents (figure 2).

References

Indentation of metallic thin film on soft substrate: insights for stretchable conductors

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

Microstructured gold thin films on poly(dimethylsiloxane) (PDMS) are used as stretchable metallic conductors in low-invasive bioelectronic interfaces [1,2], electronic skin [3], or dielectric elastomer actuators (DEAs). Understanding of the micromechanical properties in such metallic hard-on-soft systems is of crucial importance to ensure device functionality and to optimize device design. Here we perform AFM nanoindentation experiments on thin films of gold on PDMS. In the experiments, we vary systematically film thickness and tip curvature. Force – indentation curves show two regimes. In the first regime, the response is completely elastic, without plastic deformation and fracture. Above a critical force, a second regime sets in, where fracture of the thin
filament is observed, and conductivity changes occur as confirmed by conducting AFM. In the elastic regime, force-indentation curves differ significantly from the one predicted by the Hertz model. The results depend on the metallic film thickness, while they are found to be independent of the tip curvature. To interpret the experimental data, we perform FEM simulations of the indentation process. The simulations are consistent with the bending of a thin plate on an elastic medium that can be analytically described by a so-called Winkler model. The deformation of the nanoscale thin film is derived from the experimental data.

References

Compression induced modification of boron nitride layers: a conductive two-dimensional BN compound
Prof. Ana Paula Barboza
Federal University of Ouro Preto, Brazil
Session Wednesday 23 September: 2D materials and nanoelectronics

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 – boron nitride nanosheets – that is stable at ambient conditions. The process, which requires compression of at least two h-BN layers and hydroxyl 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. Alexeandr Matkovic
Montanuniversität Leoben, Leoben, Austria
Session Wednesday 23 September: 2D materials and nanoelectronics

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 carrier 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

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 those, there are numerous other two-dimensional 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 a 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 with +103 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 graphene 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.


Wet Graphene Membranes on a Microfluidic Platform
Prof. Ivo Almeida
Federal University of Ouro Preto, Brazil
Session Wednesday 23 September: 2D materials and nanoelectronics

Graphene is regarded as the toughest two-dimensional material (highest in-plane elastic properties) and, as a consequence, it has been employed/proposed as an ultrathin membrane in a myriad of microfluidic devices. Yet, an experimental investigation of eventual variations on the apparent elastic properties of a suspended graphene membrane in contact with air, water and other liquids is still missing. In this work, the mechanical response of suspended monolayer graphene membranes on a microfluidic platform is investigated via scanning probe microscopy experiments. A high elastic modulus is measured for the membrane when the platform is filled with air, as expected. However, a significant apparent softening/hardening of graphene is observed when water/oleic acid fills the microfluidic system. Through molecular dynamics simulations and a phenomenological model, we tried to understand these behaviors. These results may bring substantial modifications on the design and operation of microfluidic devices which exploit pressure application on graphene membranes.
The role of lectins in surface adhesion and virulence of Pseudomonas aeruginosa studied with single molecule force spectroscopy

Joanna Zdzień
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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 antibiotic resistance [1]. The biofilm-former 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 Pai) 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.

Bacterial lectins are sugar-binding proteins that mediate adhesion to host surfaces, and are also important for biofilm formation. In the widespread pathogen Pseudomonas aeruginosa, lectins LeaC and LebC are known to be key pathogenicity factors, yet their exact role in surface colonization and their implication in virulence pathways are unclear. LeaC and LebC structures suggest that they function as tetramers, and could create cell-bacteria, matrix-bacteria, and bacteria-bacteria interactions, which could explain why they are important for adhesion as well as biofilm cohesion. We have used single molecule force spectroscopy (SMFS) to investigate the composition and structure of the EPS of P. aeruginosa with LeaC and LebC molecules covalently attached to the scanning probe. Our recent experiments have shown that both lectins interact specifically with early matrix deposits. Our analysis points to a mannose and galactose-rich matrix, and suggests that lectins could play a role as building blocks and crosslinkers in the matrix. Additionally, freely jointed chain (FJC) model indicates that both Pel and Pai contain galactose units.

References:
Single Molecule Atomic Force Microscopy to Unravel Protein Misfolding and Aggregation

Dr. Francesco Simone Ruggeri
University of Cambridge, United Kingdom
Session Thursday, 24 September: Polymer- and Biotechnology - Join the session

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 pave 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
Session Thursday, 24 September: Polymer- and Biotechnology - Join the session

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 substrates’ chemical properties. However, engineering dense arrays of HAR nanoneedles using polymeric substrates remains a challenge in soft lithography.

Figure 1: AFM topography scans and tilted FESEM images of Si nanoneedle arrays (Top row) and their PEG replicas (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)
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, GaV4S8. 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 GaV4S8 DWs, unprecedented in oxide materials and possibly allowing for π-n junctions inside domain walls. Most importantly, GaV4S8 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.

Screening charge on patterned domain structures in films with 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.

Ferroelectric materials, such as lead titanate, show differently oriented domains of spontaneous electric polarisation. The walls between domains have been modelled as a distorted elastic system, both statically and during displacement under an applied electric field [1,2], where their motion has been observed to follow avalanche statistics via the detection of Barkhausen noise [3]. The universality of these classifications allow for modelling of domain walls at larger scales than typically possible via ab initio methods, and integrating the effects of material defects, which can present a complex and heterogeneous disorder landscape, particularly in thin film ferroelectric samples. Here we report scanning probe microscopy studies into the switching dynamics of lead titanate thin films with varied and controlled defect disorder. The films, grown on strontium titanate substrates, present strain-relieving a-domains that extend through the film, in-plane, along the crystallographic axes. Varying point defect densities have also been introduced via bombardment with He²⁺ ions. The gradual motion of 10⁵ domain walls in these films under incrementally increasing bias applied by a scanning probe tip was imaged using piezoresponse force microscopy. Computational tools were also developed to access information pertaining to the rate of switching at the nanoscale, as a function of both point defect density and a-domain proximity.

We observe that increasing point defect density significantly increases the average voltage required for switching, as well as the voltage range over which domain wall motion is observed. Domain nucleation also appears preferentially in more heavily bombarded samples. The a-domains appear to act as extended strong pinning sites, imposing directional constraints on the domain wall motion along the film crystallographic axes. In the non-irradiated sample, the effect of these a-domains appear to dominate, leading to large scale domain wall jumps to configurations determined by a-domain position. In contrast, all samples have been observed to express Barkhausen behaviour with similar critical exponents, regardless of defect implantation. In this complex disorder landscape, preliminary observations therefore suggest point defects may apply a screening effect to the impact of a-domains, yielding anomalous behaviour that is locally constrained around a-domains in the non-bombarded sample, while being statistically similar on a larger scale to ion-bombarded datasets.

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 CH3NH3PbBr3 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.

Figure 1: PFIR-KPFM measurement of a naturally degrade CH3NH3PbBr3 perovskite single crystal. (a) Topography. (b) Mechanical modulus. (c) Contact potential difference (CPD). (d) Nano-IR imaging at 1585 cm⁻¹. (e) Correlation analysis between CPD and IR signal. (f) Correlation between CPD and modulus.
Instrument Development for New AFM Capabilities
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Session Friday 25 September: Overcoming barriers in AFM / join the session

Microscopy instruments are important in nanotechnology research for imaging of nanoscale phenomena. Among such tools is the atomic force microscope (AFM) for nanoscale imaging and surface characterization. An AFM scans a micro-cantilever over the sample surface to measure various quantities from the probe-sample interaction. With high-speed imaging, dynamic processes can be visualized to improve fundamental understanding of microscopic interactions. Scientists can use videos, in addition to images, to observe and compare experimental data with theoretical predictions, and verify models without speculating about intermediate dynamics. However, conventional AFMs have limited throughput that allows for static imaging only and require transparent working environments. In our group, we develop AFM subsystems to remove such AFM restrictions and enable advanced visualization capabilities. Example applications include visualizing chemical reactions and biological responses in their native environments. We design new generation nano-positioners to address the low imaging throughput limitation and enabled high-speed video-rate AFM imaging. To resolve the transparency limitation, active cantilever probes with embedded piezoresistive sensing and thermomechanical actuation are developed with nano-fabrication techniques. We apply coating to protect the functional structures to enable AFM imaging in chemically harsh opaque liquid enabled. This allows observations of samples in their native environment such as non-transparent acid, crude oil, cells in blood, etc.

In this talk, the development of high-bandwidth nano-positioning systems, active cantilever probes and other enabling technologies will be presented. We will show AFM images and videos to demonstrate the new capabilities. The high-speed imaging capability is used to capture videos for calcite etching process and electrochemical deposition of copper on gold substrate. Images taken in opaque acidic liquid and crude oil are used to verify the functionality of the coated active cantilever probes. We conclude by discussing related applications and broader impacts of the development on both the AFM user and instrument designer communities.

Improving image contrast and estimating material properties by Biharmonic AFM
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Session Friday 25 September: Overcoming barriers in AFM / join the session

Since invention of atomic force microscopy (AFM) in 1980s, researchers have focused on developing new characterization methods to measure different materials properties. These efforts have been mostly toward characterizing soft matters such as polymers or biological samples with the goal of minimizing surface damage during imaging process. One way to increase accuracy and sensitivity in AFM is exciting the cantilever’s higher modes (i.e., Higher Modes AFM) or exciting multiple modes simultaneously (Multifrequency AFM). Bimodal AFM captures both topography and material composition of a material especially for soft heterogeneous material in a single-pass measurement. Based on the rectangular beam theory, the cantilever’s second to first eigenmode frequency is 6.27. Due to the fact that they are not multiple integers, there are irregular raps over the surface and high signal-to-noise ratio for the higher modes excitations. This can cause nonlinear vibrations in the cantilever in addition to the fact that the probe does not interact with each pixel similarly. Therefore, exciting the cantilever with higher harmonics instead of the eigenmodes in multifrequency AFM mechanisms and its advantages are discussed.

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. The second excitation frequency is the closest harmonic frequency to the second eigenmode frequency. Based on this theoretical discussion, this study provides the guideline for selecting the correct harmonic according to cantilever’s type and geometry. It is found that the ratio of second to first eigenmode frequency heavily depends on the geometry of the cantilever and applicable environment. Additionally, it is found that cantilevers with lower eigenmode frequency ratio, excited with the first eigenmode frequency and higher harmonic, can provide higher phase contrasts in comparison to bimodal AFM. Numerical and experimental studies prove that for enhancing phase contrast and accurately measuring material properties the ratio of 2nd to 1st frequency should be minimized. Additionally, the second excitation frequency should be the closest n-th harmonic to this ratio.

Pulsed Force Kelvin Probe Force Microscopy for < 10 nm Contact Potential Mapping in Ambient Conditions
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Session Friday 25 September: Overcoming barriers in AFM / join the session

Measurement of the contact potential difference (CPD) and work functions of materials are crucial in the development and study of new electronically active materials and devices. Kelvin probe force microscopy (KPFM), an imaging technique based on atomic force microscopy, is a robust and popular tool for CPD and work function mapping at the nanoscale. However, the conventional KPFM variants are typically limited in their spatial resolution to 30–100 nm under ambient conditions. The continually decreasing size and increasing complexity of photovoltaic materials, semiconductor devices, and related materials present challenges in uncovering their important electrical properties through KPFM. In this talk, a new paradigm of contact potential measurement in KPFM is presented. The new imaging technique, pulsed force Kelvin probe force microscopy (PF-KPFM), is developed and can reliably obtain CPD and work function images with ~10 nm spatial resolution, on a wide range of samples.

The operating principle of PF-KPFM deviates from the fundamental paradigm of all current KPFM techniques, as 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 variants which limit their achievable spatial resolution; most notably the requirement for lift mode and the stray capacitance effect. Here, we explain the operating principle of PF-KPFM, how it compares to conventional frequency modulated KPFM (see Figure 1a-d), and present results on several materials to exemplify the robustness of our technique. In particular, we 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 perovskite domains. From these measurements, new insights into the nanoscale electrical properties are established.

Figure 1. Comparing the spatial resolution of FM-KPFM and PF-KPFM on a standard KPFM sample composed of silicon (on the left) and gold (on the right). (a) FM-KPFM on the sample. (b) KPFM over the same area. (c) The spatial resolution for FM-KPFM is estimated at 39 nm, found from the signal cross section marked by the red line in (a). (d) The spatial resolution of PF-KPFM over the same area is estimated to be 10 nm. (e) Topography of a BaTiO3 ferroelectric sample. (f) PF-KPFM measurement on the region, showing the heterogeneity of the contact potential over nanoscale domains.
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 / Join session

Stochastic collision electrochemistry\(^1\) 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.\(^2,3\) Noise levels are very sensitive to the input capacitance of the current amplifier when operating at high bandwidth.\(^4\) In this presentation a new strategy will be introduced to minimise 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,\(^5\) 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.