Invited Speaker

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Mr. Francesco Simone Ruggeri[1]
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Oral Presentation

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[1]Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden
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[1]Institute of Nuclear Physics Polish Academy of Sciences, Krakow, Poland, [2]Jagiellonian Centre for Experimental Therapeutics, Jegiellonian University, Krakow, Poland
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[1]TBI, Université de Toulouse, INSA, INRAE, CNRS, Toulouse, France, [2]IIIA-UNSAM-CONICET, Universidad Nacional de San Martín, Buenos Aires, Argentina

Poster Presentation

307 High-resolution 3D chemical imaging of light elements by time-of-flight mass spectrometry
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Dr James Bowen[1], Dr David Cheneler, Dr James Vicary
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Late Poster Presentation

1253 Computational analysis of the anisotropy of SEM images to quantify nanowire verticality and surface roughness

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Nano-chemical Imaging and Spectroscopy at the Single-molecule Level

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IM-09, Lecture Theater 5, august 29, 2024, 14:00 - 16:00

Background
Biological processes rely on a wide class of biomolecular and macromolecular machines that have nanoscale physical dimensions and whose function emerges from a correlation between their chemical and structural properties. A fundamental objective of modern analytical methods is the comprehension of how physical-chemical properties and heterogeneity of single biomolecules underlie their role in cellular function and disease. While innovative nanoscale imaging methods have been developed to characterise biomolecules, imaging microscopies are to the most part chemically blind; thus, hampering the characterisation of inhomogeneous and complex systems.

Methods
The introduction of photothermal infrared nanospectroscopy (AFM-IR) has revolutionized the field of nano-chemical analysis in a wide-open range of fields, including biological, material and polymer sciences. Here, we will present an overview of our latest development and application of AFM-IR in combination with advanced spectroscopic analysis and chemometrics, as a real breakthrough for the analysis of heterogeneous (bio-)molecular systems and materials down to the single molecule level.

Results
To illustrate our path towards single-molecule AFM-IR, we first show the achievement of single protein molecule detection of infrared absorption spectra and maps by introducing off-resonance, low power, and short pulse ORS-nanoIR. [1] This approach enables the accurate determination of the secondary structure elements of single proteins and amyloids in the amide band I region. We will then showcase the application of this unprecedented single molecule sensitivity to: i) unravel molecular structure and interactions of protein and organic molecules [2]; ii) origin of chirality in click chemistry polymers [3]. Finally, we illustrate the application of this sensitivity to probe the surface and structural properties of functional materials, such as artificial model membranes [4] and functional protein self-assemblies [5].

Conclusion
Overall, our aim is to expand the capabilities of analytical nanoscience to shed light on the structure-activity relationship of biomolecules and functional materials design.

Keywords:

Nano-Imaging;Spectroscopy;Atomic Force Microscopy; Supramolecular Assembly

Reference:

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Enhancing Nanomechanical Properties of MXene through Tailored Surface Potential: PFQNM and Kelvin Force Microscopy Studies

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IM-09, Lecture Theater 5, august 29, 2024, 14:00 - 16:00

2D MXene (Ti3C2TX) possess distinct characteristics such as high electrical conductivity, adjustable surface chemical properties, and mechanical flexibility. These features make them valuable as building blocks for energy storage devices, serving purposes like electrodes, ion transfer regulation, electrocatalysts, and electrodeposition substrates. Enhancing the mechanical strength of MXenes has been achieved by combining them with 1D nanocelluloses from their stable colloidal dispersions. However, the practical application of MXene materials faces obstacles due to their tendency to swell unfavorably caused by weak interactions between nanosheet layers, convoluted pathways for ion transport channels, and susceptibility to oxidation in aquatic environments, consequently impacting the performance of EC devices. The current challenge in optimizing MXene properties is to maintain the EC properties during synthesis. Poly(ionic liquid) treated heterostructure Mexne membranes assembly with layered double hydroxide nanosheets via solution-phase showed high permeability and selectivity, the interaction with the oppositely charged surfaces accerate electrostatic crosslinking between MXene neighboring nanosheets driving the enhanced stability in colloidal phase.1 Up to this point, there has been limited focus on nano-scaled mechanical studies using quantitative peakforce nanomechanical mapping (PFQNM) using a colloidal atomic force microscopy probe to measure the localized mechanical and nano-scaled force origins of HOLO cellulose nanofibers (HOLOCNFs) during interaction with Mxenes in a colloidal phase.

The PFQNM morphology results (Fig. 1.A) revealed a uniform distribution of the HOLOCNF network nanostructure, with HOLOCNFs tightly inserted into Mxene thin sheets. The height distribution of the composite indicated that the integration of HOLOCNFs reduced the roughness of the Mxene, enhancing the overall uniformity of the composite. Specifically, the roughness of the Mxene film (1×1 µm) was measured at 56.8 nm ± 71 pm, while that of the composite was 28.4 nm ± 69 pm. The fitted elasticity modulus (Derjaguin-Muller-Toporov model) for the composite was approximately 132.8 GPa ± 0.39 GPa, compared to approximately 27.6 GPa ± 13 MPa for pure Mxene (Fig. 1.B). The Young's modulus of the composite was approximately four times higher than that of pure Mxene films. Force spectroscopy was employed to quantify the adhesion force between HOLOCNF and the Mxene surface using a HOLOCNF-modified AFM probe (Fig. 1.C and D). Statistical Gaussian fitting of the adhesion force measured during the coated probe's departure (retraction) from the Mxene surface revealed a force that was 10 times stronger (17.2 nN ± 77 pN) than the adhesion force measured for the same Mxene film when a naked probe was used (1.5 nN ± 1.2 pN). These results clearly indicate that the force interaction between nanocelluloses and Mxene originated from Van der Waals attraction, with adhesion being a long-range force at a separation distance of 150 nm. Remarkably, the negative force measured in the force-distance (FD) adhesion region during tip retraction showed a significantly larger dissipation of energy (energy loss) compared to the dissipation observed when a naked probe (solid black curve) was used. The difference in dissipation energy can be attributed to the deformation of the monolayer of HOLOCNF attached to the probe, whereas no layer existed when the Si3N3 surface of the naked probe was measured against Mxene. The force-distance curves unveiled a mechanism of force interaction between the surface of Mxene and the surface of HOLOCNF attached to the AFM probe. The revealed force origin elucidates the notable colloidal stability of the HOLOCNF-Mxene suspension during its synthesis procedure and provides quantitative information about the strength of attraction force when Mxene film interacts with nanocellulose during the functioning of Mxene films in real time. The strong

adhesion force between HOLOCNFs originated from various chemical groups covering the entire nanocelluloses, which were retained during the mild synthesis of HOLOCNF, resulting in robust adhesion force against Mxene during tip retraction. In Fig 1 (E), the localized heterogeneous catalysis mechanisms occurring at the active sites of single layer Mxene and the residual chemical groups on the nanocellulose were in situ visualized by amplitude modulated Kelvin probe force microscopy (KPFM). The decreased surface contact potential (Φ) of the Mxene (1.7 eV) measured after its interaction with the HOLOCNFs in colloidal chemical phase, compare the surface potential of Mxene (4.7 eV). This result revealed the doping mechanism the formation of Ti−O···H− hydrogen bonding between MXene and the chemical groups on HOLOCNFs, which modulated the dipolarity of the MXene surface and thus decreased the work function. The results are agreed with previous report.2 In short, the PFQNM and KPFM results revealed relationship between the structure, nanomechanical and surface chemical properties of Mxene-CNF at a single-fibril level and nanoscale. A future study aims to comprehend the mechanisms involved in electrochemical catalytic reactions in the presence of CO2 using HOLOCNF-Mxenes as electrode in electrolytes.

Figure 1. Representative results of (A) PFQNM morphology and Peakforce error of the materials; (B) PFQNM height, elastic modulus using Derjaguin-Muller-Toporov contact model, and adhesion force of the materials; (C) (left)SEM of the HOLOCNF probe;(right) Force-distance curves (curves in red were measured using HOLOCNF colloidal probe); (D) Gaussian fitted adhesion force distribution of the HOLOCNF-Mxene and naked probe-Mxene. (E) KPFM surface potential (work function Φ) maps and fitted distribution of the maps for Mxene and Mxene-HOLOCNF obtained 50 nm lift height.

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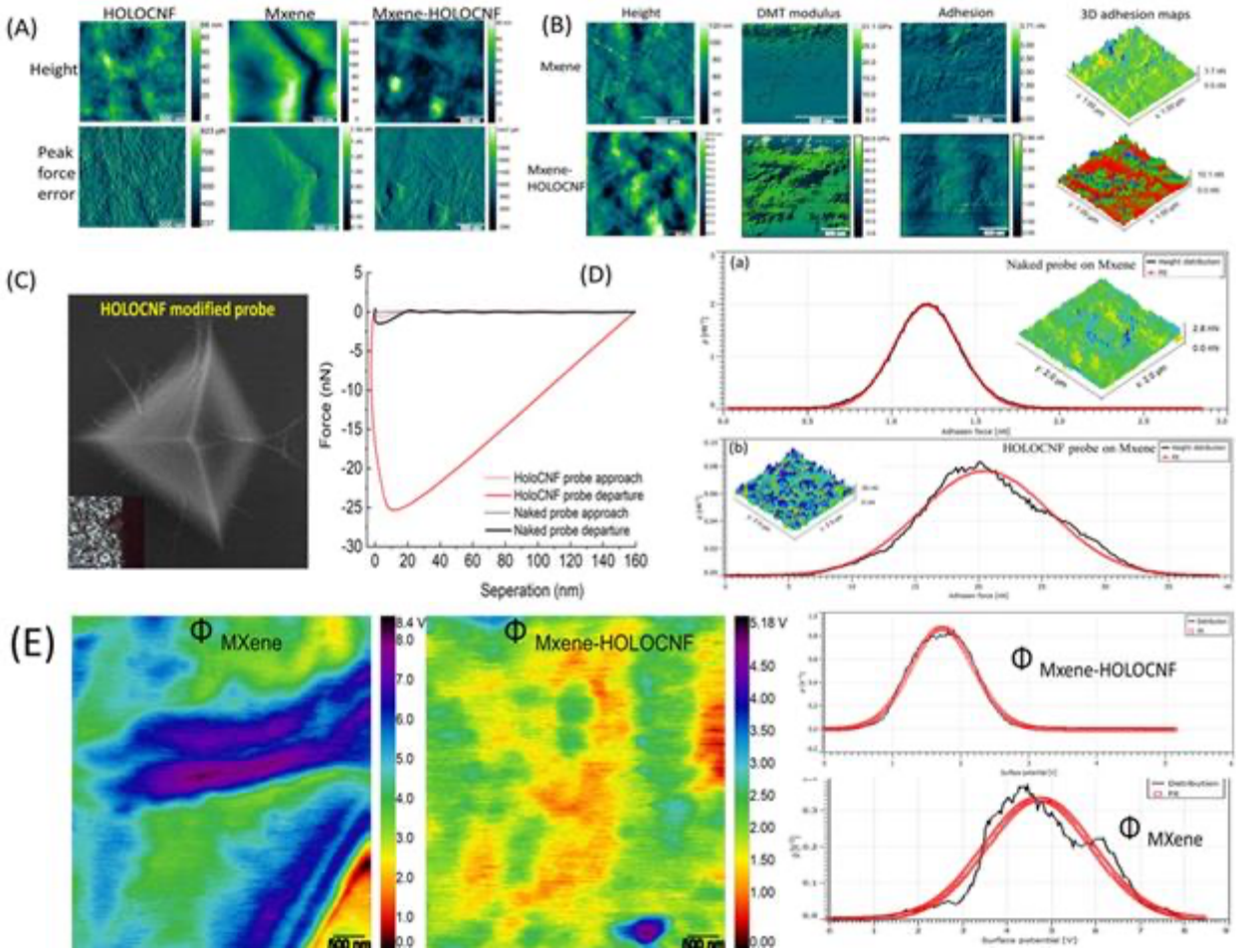

Keywords:

SPM and AFM, Force spectroscopy

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Breaking the limits of functional Atomic Force Microscopy imaging using Focused Electron Beam Induced Deposition

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IM-09, Lecture Theater 5, august 29, 2024, 14:00 - 16:00

Atomic Force Microscopy (AFM) has evolved into an indispensable characterization method as it provides quantitative 3D surface information with spatial nanometer resolution. It also enables access to electric, magnetic, optical and thermal properties using specialized functional AFM tips. However, achieving this functionality necessitates additional coating on AFM tips, resulting in increased tip apex size and thus limiting resolution. Moreover, coating introduces the risk of delamination, which could compromise or entirely diminish the functionality of the tip. The aim of our research is to surpass the limitations of functional image quality. To be more precise, it was of interest to achieve (1) higher resolution for functional AFM tips, (2) higher sensitivity for e.g. EFM/MFM phase signal, (3) good signal to noise ratio, and (4) higher wear resistance, compared to commercially available tips.
We have utilized the additive direct-write technology Focused Electron Beam Induced Deposition (FEBID), which enables fabrication of all-functional nano-probes that do not require additional coating. Depending on the application, different requirements become relevant such as tip design, type of precursor (elemental composition), spring constants, and so on. The 3D nano-printing process [1] and a variety of advanced, FEBID-based tip concepts for CAFM, EFM [2], and MFM [3] will be briefly discussed.
Ideal fabrication parameters were individually identified with subsequent determination of post-processing steps based on the required precursor, if needed. The FEBIP tips were then compared with commercially available products in terms of image quality, including resolution, signal-to-noise ratio, wear resistance, among others. After thorough testing of magnetic (M) and conductive tips (C), we give an outlook on further expanding AFM tip capabilities by combining both functionalities, produced with a single precursor. While in the past, MFM and CAFM measurements are operated via different modes, the here introduced MC fusion-probes contain unique possibilities, as both techniques can be performed in a single AFM-CAFM-MFM experiment. We present first results, which form the basis of this new type of nanoprobes.
FEBID presents an ideal technique for pushing boundaries in functional AFM measurements. All probes share the coating-free character, thereby mitigating the delamination risks during operation. Furthermore, tip apexes are consistently within the sub-10 nm range, enabling high-resolution imaging beyond alternative products.
(could not be inserted)

Keywords:

FEBID, AFM, EFM, CAFM, MFM

Reference:

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Single-cell pharmacology: atomic force microscopy and spectroscopy for multiparametric imaging of drug-induced alterations in vitro

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IM-09, Lecture Theater 5, august 29, 2024, 14:00 - 16:00

Since its first construction by Gerd Binnig, Calvin F. Quate, and Christoph Gerber in 1986 [1], it took only a few years to disclose the tremendous potential of atomic force microscopy (AFM) in the research of biological objects [2]. It is mainly because AFM does not need sample modification and labelling. Freedom of selection of conditions, including performing measurements in culture media, control of pH, and temperature combined with large x,y, and z piezo-scanner ranges all have led to the rapid development of live cell imaging. Finally, novel AFM imaging modes, based on a fast acquisition of force-distance curves, such as Quantitative Imaging (QI), PeakForce Tapping, or PinPoint have enabled 4D (3D plus time) imaging of changes in biological samples.

Here, the results of the development of so-called in vitro pharmacology on a single cell will be presented [3-5]. Briefly, the methodology allows tracking the single-cell morphology and its nanomechanical properties over time. Then, a drug is injected into the culture medium and the cell response to the drug is further observed. It allows monitoring of morphological features and the cytoskeleton remodelling, including its effect on alterations in Young's modulus distribution. Depending on the area of interest single frame is collected in the range of minutes to several seconds allowing observation of drug-induced changes in the morpho-mechanics of cells.

The main focus will be devoted to primary murine liver sinusoidal endothelial cells (LSEC) in vitro. LSEC have transcellular pores, called fenestrations, that are indicators of the healthy phenotype of the liver. These nanostructures – 50-350 nm in diameter – participate in the transport of lipoproteins and solutes (e.g. hormones) between the vascular system and the liver parenchyma. AFM remains the exclusive tool allowing monitoring of drug response in living LSEC for up to 6 hours. Fenestration number, diameter, lifespan, migration range, and deformability can be quantified [3]. Moreover, Young's modulus distribution over the whole cell can be calculated [5]. We show that fenestration lifespan varies from minutes to hours. During this time fenestration changes their diameters and migrates within the cell as far as several micrometers. We employed so-called loading force-dependent tomography to assess the deformability of fenestrations. We test the established methodology in several pharmacological strategies aiming to restore fenestrations in LSEC originating from wild-type animals and genetic knockouts.

We conclude that novel AFM provides multiple parameters for quantifying drug responses in LSECs and their fenestrations in real time. Introducing in vitro pharmacology on LSEC fenestrations will enhance understanding of the mechanisms underlying fenestration formation and function.

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Keywords:

fenestration, live cell imaging, AFM

Reference:

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Nanoendoscopy-AFM: A new technique to explore Focal Adhesions in living cells

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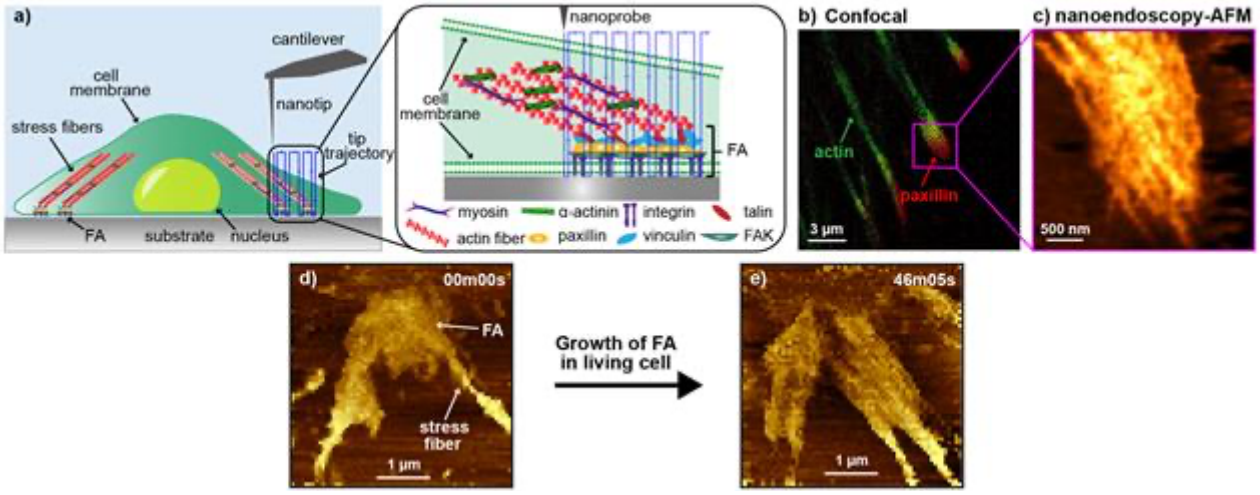
IM-09, Lecture Theater 5, august 29, 2024, 14:00 - 16:00

Introduction: Focal Adhesions (FAs) are complex structures containing several adapter proteins such as paxillin, vinculin, FAK, talin, and zyxin, which together create a dynamic nanostructure that mechanically links intracellular actin bundles to the extracellular matrix (ECM). They play important roles in various cellular processes including cell adhesion, cell migration, force transmission between the intracellular structures and ECM, or vice versa. Although several microscopic techniques have been employed to explore FA architecture, many of these methods face limitations when applied to living cells or involve complex sample preparation that can impact the natural function of FAs. Consequently, there is a strong demand to investigate various aspects including the dynamics of these multiprotein complexes in living cells using new techniques. A recent advancement in this regard is Nanoendoscopy-Atomic Force Microscopy (AFM), a technique that measures intracellular structures of living cells without disassembling the cell, maintaining intracellular structures in their physiological environment [1]. Here we use this advanced nanoendoscopy-AFM technique to visualize and study the dynamics behavior of FAs in living cells.
Methods: Fig. 1a shows the schematic of the 3D nanoendoscopy-AFM technique. A long and sharp AFM nanoprobe fabricated by electron beam deposition (EBD) or focused ion beam (FIB) milling is inserted into living cells to visualize FAs by collecting force versus distance (F-z) curve maps. The continuous penetration of the cell by this ultrathin nanoprobe does not damage the cell or negatively impact cell viability.
Results: We succeeded in imaging FA structure directly within living fibroblast cells by nanoendoscopy-AFM, as confirmed by complementary confocal microscopy (Fig. 1b,c). FA indentation or penetration by the AFM nanoprobe does not trigger FA disassembly. Using this approach we can monitor FA growth over time, as well as the dynamic rearrangement of stress fibers connecting to individual FAs (Fig. 1d,e). Moreover, FA thickness is reduced when it matures or grows from the cell periphery to the center. In addition, this technique enables us to obtain insights into the mechanical characteristics of FAs. Our findings reveal that FAs exhibit increased stiffness during maturation and undergo softening upon disassembly.
Conclusion: Our results provide a new nanoscale look at FA ultrastructure inside living cells and at the dynamic processes regulating stress fiber attachment to these structures. In the future, we aim to gain more detailed information on the structural and biomechanical intricacies of FAs in living cells.
Fig. 1. (a) 3D nanoendoscopy-AFM measurement of FAs. (b) Confocal image of actin stress fibers (green) connected to FAs (paxillin; adapter protein in red) and (c) a corresponding AFM image of an individual highlighted FA. (d) and (e) represent contact point mapping images of the same FA at 0 and 46 minutes of imaging, indicating the maturation of the FA.



Keywords:

focal adhesion, nanoendoscopy-atomic force microscopy,

Reference:

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Nanoscale tribology of hair fibres over large displacements

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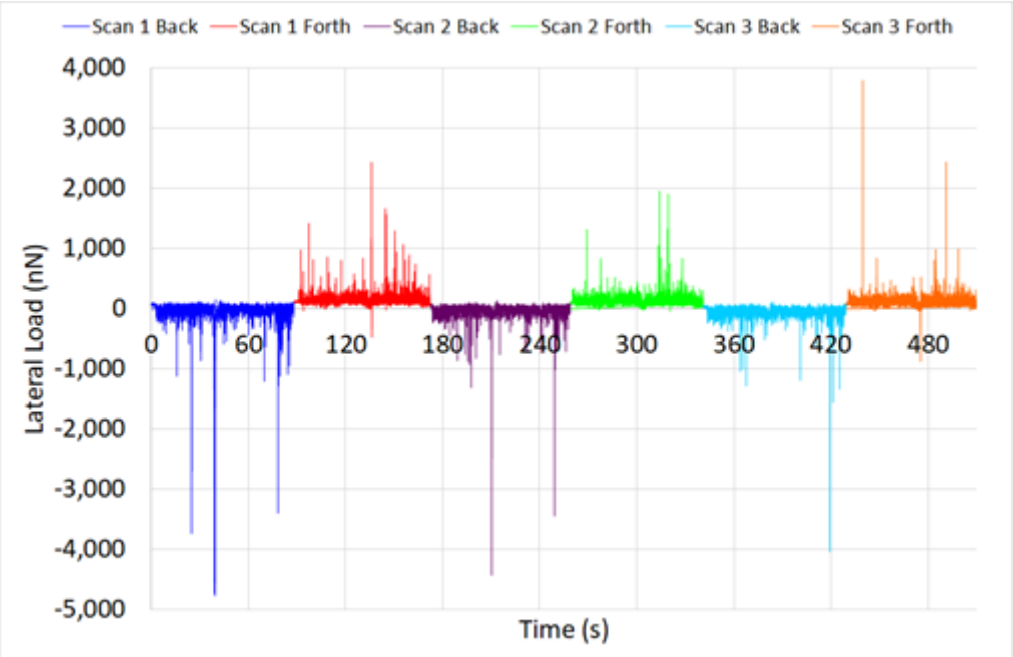
IM-09, Lecture Theater 5, august 29, 2024, 14:00 - 16:00

Background incl. aims
Hair is a protein-based, filament-like biomaterial that grows from follicles beneath the surface of the skin. The evolution, structure and function of human hair is of great interest to anatomists and anthropologists, and the use of hair for social and cultural functions is well established. There have been many scientific studies regarding hair structure, the physicochemical properties of the hair cuticle surface, and hair damage mechanisms. Atomic force microscopy has played a crucial role for studies of friction and conditioners applied to single hair fibres.
Methods
This work reports the development of a method for measuring the tribological properties of two orthogonally crossed cylinders over a 2 mm displacement with nanoscale precision in loads and displacement. Specifically, a human hair fibre was used as the lower cylinder, while the upper cylinder was a 0.5 mm section of 75 µm diameter tungsten wire. Measurements were performed at a sliding velocity of 20 µm/s, the compressive normal load between the cylinders was 600 nN, and data were recorded every 2 nm.
Results
Topography and lateral load were recorded throughout the bidirectional measurement, with differential friction observed upon comparison of the 'with cuticle' and 'against cuticle' sliding directions (Fig. 1). To assess the influence of sliding velocity on the frictional behaviour a sequence of increasing velocities in the range 0.01-1.0 mm/s was programmed; the total displacement of this measurement covered 5 mm.
Conclusion
The mean friction coefficient did not vary significantly with sliding velocity, although occasional high lateral loads were observed at velocities in excess of 0.1 mm/s.



Keywords:

fibre, friction, hair, load, tribology

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Understanding how microalgae cells remediate heavy metals using Atomic Force Microscopy (AFM)

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IM-09, Lecture Theater 5, august 29, 2024, 14:00 - 16:00

Background incl. aims
Microalgae have recently emerged as a promising biomass for the biosorption of heavy metals from aqueous environments, by offering an efficient and cost-effective alternative compared to conventional remediation techniques. However, to date, the mechanisms by which microalgae can remediate these pollutants is still not entirely clear. In this work, we investigate the role of extracellular polymeric substances (EPS) of a green microalgae species, Parachlorella kessleri, isolated from the polluted Reconquista River in Argentina, in the biosorption of zinc.
Methods
For that, we use an original approach based on atomic force microscopy (AFM) experiments. This technique, developed in 1986, relies on the control of a force acting between a sharp tip and a surface, while scanning a sample. In force spectroscopy mode, AFM can record force-distance curves, where the force experienced by the probe is plotted as a function of the probe-sample separation distance (typically from 0.5 to 6 µm). These curves can then be analyzed to extract several information on the sample morphology, on its nanomechanical properties, and on the physico-chemical nature and strength of interactions that can take place between the tip and the sample. In addition, while the tip used can be bare, it can also be functionalized with any type of molecules or particles, making it possible to access specific interactions between these functionalized tips and cell surfaces.
Results
A first step in the study was to optimize a culture medium favoring the production of EPS by cells. It was showed that cells cultivated in the presence of nitrates could produce EPS while the cells had much less EPS when cultivated with ammonium as a nitrogen source. This was confirmed by nanomechanical experiments performed with AFM that showed that cells cultivated with nitrates were covered by a thick layer of a soft material (200 Pa approximately), corresponding to the EPS layer. Then, our hypothesis is that EPS play a key role on the biosorption of metals. To test this hypothesis, AFM force spectroscopy experiments were performed using zinc-functionalized AFM tips, this way allowing to probe directly the interactions between zinc and cell surfaces at the molecular level. The results obtained showed that zinc could interact with the EPS present at the surface of cells cultivated with nitrates with a force of up to 1 nN. Since no interactions were recorded when cells cultivated with ammonium were probed, this confirms that the EPS of P. kessleri can interact directly with and absorb zinc, thereby remediating it from the medium.
Conclusion
Overall, these experiments provide a new understanding of biosorption mechanisms using an original biophysical approach, and show the potential of P. kessleri for heavy metal biosorption.

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High-resolution 3D chemical imaging of light elements by time-of-flight mass spectrometry

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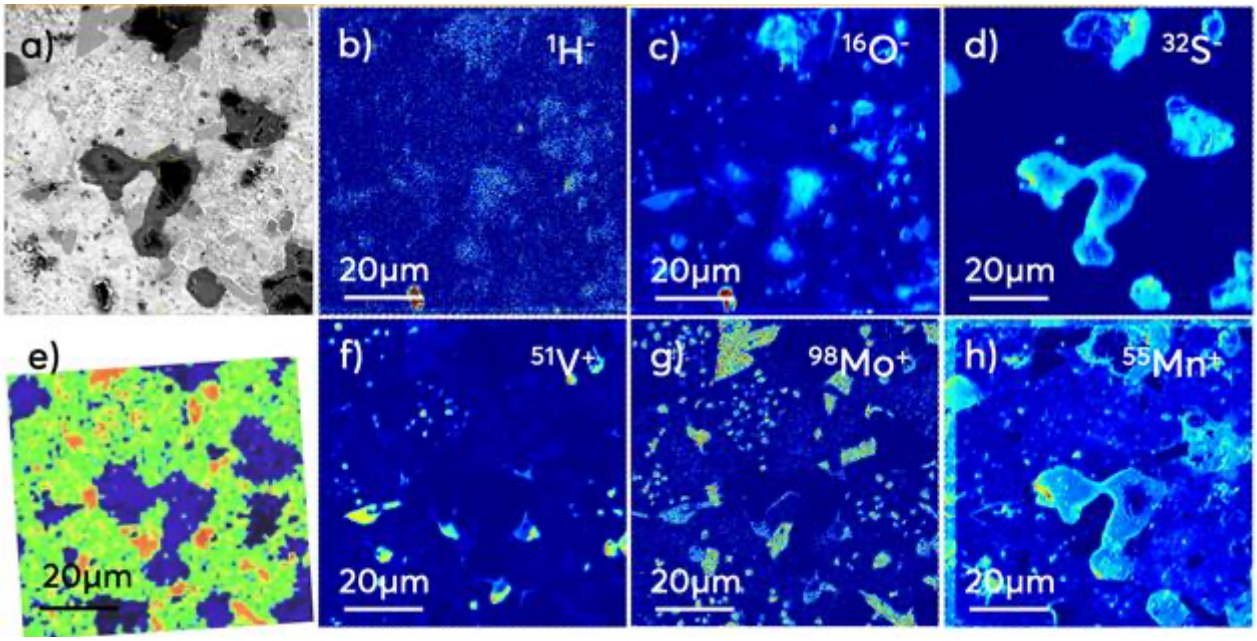
Poster Group 2

Background incl. aims
It is a common practice to correlate multiple imaging techniques to achieve a comprehensive understanding of the interplay between material structure and function. Beyond the geometric structure, the chemical composition, particularly at the nanometer scale, plays an essential role. However, there is a shortage of instruments capable of imaging light-mass elements with sufficiently high spatial resolution and sensitivity. This gap is addressed by TOFWERK's fibTOF platform, offering high spatial resolution and 3D chemical imaging of all the elements of the periodic table, including light-mass elements. This capability is demonstrated through the application examples below, which are taken from the battery and metallurgy sectors.
Methods
fibTOF is a Secondary Ion Mass Spectrometry (SIMS) detector designed to be attached to a Focused Ion Beam (FIB) Scanning Electron Microscope (SEM). fibTOF extends microscopic analysis to probe the chemical composition of solids at the nanometer scale with sensitivities down to the ppm range. The properties of a FIB as a primary ion source to erode and ionize material is used. For each pixel probed by the FIB, the released secondary ions are extracted and characterized. The combination of the mass spectra/pixel, results in an intensity map of elements for a mass range of 0-500 Th. As the FIB repeatedly scans the region of interest (ROI), a 3D data set is generated.
Results
The value of the fibTOF is demonstrated by the investigation of a Solid-Electrolyte Interface (SEI) composition at the anode after galvanostatic cycling. We explore how various molecular additives affect its stability.
Lithium ions have been observed at various penetration depths, indicating differences in SEI formation efficacy based on the additives used. The lower SEI formation efficiency explains the diminished battery performance due to ongoing electrolyte degradation. In addition, measurements of Mn and Ni on the anode corroborate irreversible phase changes and metal dissolution of the cathode.
The use of the fibTOF has been shown as well in correlation with hardness tests done by nanoindentation of an M3 high-speed steel alloy. Certain regions of the sample, chemically characterized as hard phases, exhibited soft mechanical properties. These regions also showed the presence of hydrogen, hinting at a potential link to hydrogen embrittlement. Notably, both case studies were carried out using elevated sputtering and detection rate of the fibTOF.
Conclusions
The studies presented demonstrate fibTOF's efficacy in light-mass element imaging, showcasing its versatility and reliability in analyzing diverse materials and complex microstructures. Furthermore, the demonstrated capability of fibTOF to manage enhanced signals bolsters its potential for a broad spectrum of applications.



Keywords:

FIB-SIMS, high-resolution imaging, lithium, battery

Reference:

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Manufacture and calibration of high stiffness AFM cantilevers

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Poster Group 2

Background incl. aims
Atomic force microscopy (AFM) employs microfabricated cantilevers as sensing elements, which are used to measure surface topography and interaction forces. The flexible free end of a cantilever often presents either a pyramidal tip or a colloid probe particle. Force-displacement measurements have been applied to a wide variety of scientific and engineering disciplines, and across many industrial sectors. For many studies, the use of colloid probes or chemical functionalisation permits the selective study of a particular material/material interaction, often under non-ambient environments. Force-displacement measurements can provide information regarding sample mechanical properties, during tip/sample approach and contact, as well as adhesive properties, during the tip/sample separation. The spring constant is a measure of the cantilever stiffness, i.e. the resistance to bending. The spring constant of a rectangular cantilever can be estimated using Euler-Bernoulli beam theory. Once calibrated, the spring constant is used to convert normal (i.e. vertical) deflections into normal forces using Hooke's law.
Methods
The range of AFM cantilevers commercially manufactured means that spring constants in the approximate range 0.001 to 100 N/m are available. Deflections in the range 0.1-100 nm are typically measurable on the PSD, and hence forces can be measured in the picoNewton to microNewton range. Accurate control of the beam thickness during fabrication is particularly difficult to achieve, due to the nature of the etching process employed. The width and length of the beam are generally much more reliable and repeatable. Given the sensitivity of the spring constant to the beam thickness, typically proportional to the (thickness) cubed, accurate calibration is a necessity for accurate force-displacement measurements.
Results
We are currently calibrating 40 different designs of rectangular AFM cantilever, designed using Timoshenko beam theory, manufactured from Si. The various designs incorporate a range of widths, lengths, and thicknesses. These cantilevers are expected to exhibit spring constants in the range 100 to 10,000 N/m. This would afford researchers the opportunity to perform adhesion, indentation, and tribological testing with normal loads approaching 1 mN, whilst retaining the displacement resolution of the AFM.
Conclusion
We present the latest results of this project, including measured cantilever resonant frequencies and calculated spring constants, which are compared to analytic expressions and finite element models.

Keywords:

cantilever, load, microfabrication, spring constant

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Computational analysis of the anisotropy of SEM images to quantify nanowire verticality and surface roughness

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Poster Group 1

Background incl. aims
Surface texturing on micro and nanoscale plays a fundamental role in many applications of nanotechnology due to its effects on almost all surface properties such as wetting, wear, reflectance, bioactivity to name just a few. A chief feature of surface texture is its isotropy/anisotropy. Anisotropy (i.e. directionality of surface texture) is encountered in a wide gamut of cases since it can be caused by a plethora of processes on different scales and can have strong impact on applications at a variety of scales. Based on its importance, the characterization of surface texture anisotropy has been incorporated in the ISO 25178-2 and two parameters have been proposed to characterize the degree and directionality of anisotropy using the autocorrelation function and Fourier transform respectively. The ISO characterization assumes full measurement of 3D topography by 3D profilometer or AFM. However, since height information is not critical in anisotropy identification, SEM images can also be used and provide a straightforward way to surface anisotropy characterization.

Moreover, surfaces with nanowires have been used in various fields of applications from electronics and photonics to bio-devices and energy harvesting systems. One of the critical properties of nanowire patterns is their alignment and verticality since it tunes the contact area with the attached body and hence their performance in their applications.

The aim of this work is firstly to implement a methodology for the quantification of SEM image anisotropy based on 2D Fourier spectrum analysis to conclude about surface anisotropy and secondly to characterize indirectly the verticality of nanowires (NWs) developed on substrates.

Methods
Here, we propose a fast and easily implemented method to characterize the degree of surface anisotropy1, which can also be applied to surfaces with nanowires to assess their verticality. First, we apply a threshold to the Fourier spectrum values to identify the low-frequency region in the 2D Fourier space with amplitudes higher than this threshold. Then, we calculate the anisotropy ratio A by dividing the smallest radius of this region by the largest one and then substract it from 1 (see Fig. 1). An A value close to 0 indicates an isotropic surface, whereas a value close to 1 indicates an anisotropic surface.
A top-down SEM image of a fully vertical nanowire (NW) with a cylindrical shape is isotropic, as it displays the circular shape of its cross-section. When the NW is tilted from verticality, the SEM image shows a portion of its axis, indicating local anisotropy. Therefore, the deviation from full verticality can be quantified by an index characterizing the anisotropy of NW spots in top-down SEM images.

Results
Our methodology was applied to SEM images of inclined polymer surfaces after plasma etching with oxygen gas. We observed that at the bottom part of these surfaces, near the electrode plate of plasma reactor, anisotropic morphologies were emerged, forming horizontal ripples at large inclination angles2 (see Fig. 2). As we are moving upwards, there is a noticeable transition from anisotropy to isotropy with ripples qradually replacing by nanowire bundles. Using Fourier-based anisotropy indices, we can quantify this transition and establish a link to plasma etching conditions

and inclination angles. Figure 2 illustrates the change in low-frequency Fourier contour lines (blue for bottom areas vs. red for top areas), from which we calculated the anisotropy index A increase from 0.13 at the top to 0.82 at the bottom.
To study the change in the verticality of the nanowires, Figure 3 presents the anisotropy index used to assess the verticality of nanowires on the polymer surface before and after water condensation. The anisotropy index, A, decreased from 0.51 to 0.26, indicating degradation of nanowire verticality by nearly 50%.

Conclusion

In conclusion, we developed a fast and easily implemented method to characterize surface anisotropy, which is also applicable to assessing the verticality of surfaces with nanowires. This method successfully quantified the transition from anisotropic to isotropic morphologies on inclined polymer surfaces after plasma etching with oxygen gas, linking these changes to etching conditions and inclination angles. The anisotropy index proved to be an effective tool in determining nanowire verticality, demonstrating significant sensitivity and accuracy. These findings pave the way for optimizing plasma etching processes and enhancing the design and fabrication of nanowire-based materials and devices.

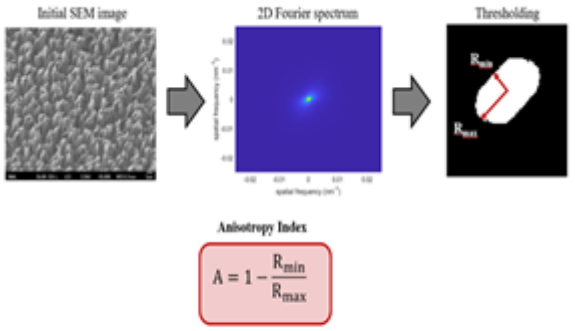

Figure 1. Representation of the computation of anisotropy index.

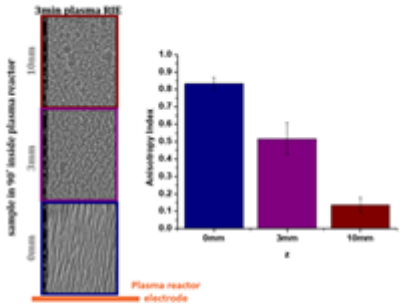

Figure 2. Polymer surface being etched in oxygen plasma in 90 degrees angle. The results of anisotropy index for each region are provided in the graph .

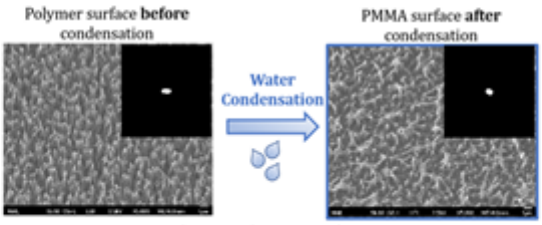

Figure 3. Polymer surfaces before and after water condensation along with their thresholded Fourier spectra.

Keywords:

anisotropy, Fourier spectrum, Nanowire verticality

Reference:

1. Quantitative characterization of nanowire verticality using SEM images (to be submitted)
2. Plasma-induced maskless formation of periodic nanoripples on polymeric substrates (to be submitted)