Symposium on microscopic characterization of the solid/liquid interface

Scientific Committee: Gianlorenzo Bussetti – Klaus Wandelt / Local Committee: Mario Da Prada

Get ready to embark on a captivating exploration of the solid-liquid interface at our upcoming scientific symposium, planned at the picturesque town of Sondalo (IT), from June 21st to 25th, 2024. This event is tailored to bring together young researchers involved in the field and in view of fostering a vibrant network of collaboration. At the heart of our symposium lies the hope to foster connections among emerging scholars, by providing a platform for knowledge exchange, collaborative discussions, and networking opportunities.

Esteemed experts in the field of the solid/liquid interface (see below) will deliver insightful lectures, offering valuable perspectives on the current state and future directions of microscopic investigation at the solid-liquid interface.

Beyond the academic program, Sondalo provides the perfect backdrop for relaxation and rejuvenation. Nestled amidst the breath-taking scenery of the Italian Alps, participants will have the opportunity to unwind, explore the natural beauty of the region, and build friendships that extend beyond the confines of the symposium.

General program

	Thursday 20th	Friday 21st	Saturday 22nd	Sunday 23rd	Monday 24th	Tuesday 25th	Wednsday 26th
		breakfast	breakfast	breakfast	breakfast	breakfast	breakfast
09:15		opening remarks			social journay	WANDELT	
09:30		BUSSETTI	MAISONHAUTE	DE FEYTER			
09:45							
10:00						round table	
10:15		round table	round table	round table		FILONI	
10:30		MENEGAZZO	DEFONTAINE	FU			
10:45						round table	
11:00		round table	round table	round table		coffee break	
11:15		coffee break	coffee break	coffee break		KOSMALA	
11:30		ETRO	YIVLIALIN	CUCINOTTA			
11:45							
12:00		round table	round table	round table		round table	
12:15		MAZZOLETTI	CRAMER	NITU		FUTYMA	
12:30							
12:45		round table	round table	round table		round table	
13:00		lunch time	lunch time	lunch time		lunch time	
13:15							
13:30							
13:45							
14:00							
14:15							
14:30		KRANZ	AGNOLI	DURANTE		RECALCATI	
14:45							
15:00							
15:15		round table	round table	round table		round table	
15:30		DANIELE	CIELO	NALESSO		GUADAGNINI	
15:45							
16:00		round table	round table	round table		round table	
16:15		GOLETTI	CAZZADORI	REGINATO	SEDONA	RIVA	
16:30							
16:45			round table	round table		round table	
17:00		round table	coffee break	coffee break	round table	concluding remarks	
17:15		coffee break	CAMPIONE	FACCHIN	coffee break		
17:30		TOMEI			NT-MDT	volleyball tournament	
17:45			round table	round table			
18:00		round table	CAFOLLA	GIBERTINI	round table		
18:15		VALLE			experiments		
18:30			round table	round table			
18:45		round table	FRANKE	SHINNUR			
19:00		PRADA					
19:15			round table	round table			
19:30	welcome party	dinner	dinner	Valtellina dinner	dinner	dinner	
19:45							
20:00							
20:15							
20:30				poster session			
20:45							
21:00		ALBONETTI	cosmology talk	anticarb talk	gravitation talk		
21:15							
21:30		music party					

Detailed Program

Thursday 20th

7 p.m.: registration

7:30 p.m.: welcome party

Friday 21st

9:15 a.m.: opening remarks

9:30 a.m.: **Bussetti:** *Graphite intercalation: a model system for the electrochemical SPM investigation*

10:15 a.m.: round table for comments and discussions

10:30 a.m.: **Menegazzo:** *Stiffness and mechanical manipulation of blisters grown on electrochemically intercalated graphite*

11:00 a.m.: round table for comments and discussions

11:15 a.m.: coffee break

11:30 a.m.: **Etro:** *Characterization of Porosity and Electrochemical Behavior of C60 Thin Films on HOPG Using EC-AFM*

12:00 a.m.: round table for comments and discussions

12:15 a.m.: **Mazzoletti:** *Stiffness and mechanical manipulation of blisters grown on electrochemically intercalated*

12:45 a.m.: round table for comments and discussions

1:00 p.m.: lunch time

2:30 p.m.: **Kranz:** *Scanning electrochemical probe microscopy: From light-driven molecular catalysis to studies of interfaces of post-Li battery electrodes*

3:15 p.m.: round table for comments and discussions

3:30 p.m.: **Daniele:** *Alumina- and Silica-Coated Platinum Films/Aqueous Solution Interfaces. An Investigation on their Stability by Scanning Electrochemical Microscopy (SECM)*

4:00 p.m.: round table for comments and discussions

4:15 p.m.: **Goletti:** *Corroles at the Real Solid–Liquid Interface: an In-Situ Scanning Tunnelling Microscopy Investigation*

5:00 p.m.: round table for comments and discussions

5:15 p.m.: coffee break

5:30 p.m.: **Tomei:** *A modified reflectance anisotropy spectroscopy spectrometer for ellipticity measurement*

6:00 p.m.: round table for comments and discussions

6:15 p.m.: **Valle:** *Interaction between biological materials and surfaces at the solid-liquid interface*

6:45 p.m.: round table for comments and discussions

7:00 p.m.: **Prada:** *social events during the symposium*

7:30 p.m.: dinner

9:00 p.m.: **Albonetti:** *State-of-the-art of SPM@ISMN: a personal perspective*

9:30 p.m.: music party

Saturday 22nd

9:30 a.m.: **Maisonhaute:** *Transient Electrochemical Tip Surface-Enhanced Raman Spectroscopy (EC-Tip-SERS) : Concept and Applications in Electrocatalysis and Material Science*

10:15 a.m.: round table for comments and discussions

10:30 a.m.: **Defontaine:** *Development of a cell for EC-STM-TERS*

11:00 a.m.: round table for comments and discussions

11:15 a.m.: coffee break

11:30 a.m.: **Yivlialin:** *Microwave-matter interaction for enhanced carbon capture by mineral carbonation*

12:00 a.m.: round table for comments and discussions

12:15 a.m.: **Cramer:** *Quantitative imaging of electroswelling in organic mixed ionic electronic conductors*

12:45 a.m.: round table for comments and discussions

1:00 p.m.: lunch time

2:30 p.m.: **Agnoli:** *Study of model systems at the electrified solid/liquid interface*

3:15 p.m.: round table for comments and discussions

3:30 p.m.: **Cielo:** *Operando study of CoAl-LDH in alkaline conditions*

4:00 p.m.: round table for comments and discussions

4:15 p.m.: **Cazzadori:** *EC-STM and Voltammetric Analyses of Free-base Octaethylporphyrin on Au(111) at the 0.1 M HClO4 Electrolyte Interphase as Heterogeneous Molecular Electrocatalyst for Oxygen Reduction Reaction*

4:45 p.m.: round table for comments and discussions

5:00 p.m.: coffee break

5:15 p.m.: **Campione:** *Nanotribological properties of organic molecular crystals (1/2)*

5:45 p.m.: round table for comments and discussions

6:00 p.m.: **Cafolla:** *Nanotribological properties of organic molecular crystals (2/2)*

6:30 p.m.: round table for comments and discussions

6:45 p.m.: **Franke:** *Modulated signals in electrochemically controlled force microscopy: implementation and application examples*

7:15 p.m.: round table for comments and discussions

7:30 p.m.: dinner

9:00 p.m.: **Lapi:** *Pills of galaxy formation and evolution in a cosmological context*

Sunday 23rd

9:30 a.m.: **De Feyter:** *On-surface synthesis of synthetic two-dimensional materials at the liquid-solid interface: a close-up with scanning probe microscopy*

10:15 a.m.: round table for comments and discussions

10:30 a.m.: **Fu:** *Deciphering the factors influencing electric field-mediated polymerization and depolymerization at the solution–solid interface*

11:00 a.m.: round table for comments and discussions

11:15 a.m.: coffee break

11:30 a.m.: **Cucinotta:** *Investigation of a Porous Metal-Organic Network by Scanning Probe Microscopy at the Solid-Liquid Interface*

12:00 a.m.: round table for comments and discussions

12:15 a.m.: **Nitu:** *Surface self-assembly of molecular motors and switches*

12:45 a.m.: round table for comments and discussions

1:00 p.m.: lunch time

2:30 p.m.: **Durante:** *Revisiting the Oxygen Reduction Reaction at Metal Porphyrins Using Electrochemical Scanning Tunneling Microscopy: A Fresh Look at the Volcano Plot!*

3:15 p.m.: round table for comments and discussions

3:30 p.m.: **Nalesso:** *Studies on* MoS_2 *and Ru-based ultra-thin films supported on Au(111) at the interface with electrolytic solutions*

4:00 p.m.: round table for comments and discussions

4:15 p.m.: **Reginato:** EC-STM study of Nitrate Reduction Reaction on iron-octaethylporphyrins adsorbed on Au(111)

4:45 p.m.: round table for comments and discussions

5:00 p.m.: coffee break

5:15 p.m.: **Facchin:** *Electrochemical redox processes under the Fast electrochemical scanning tunneling microscope*

5:45 p.m.: round table for comments and discussions

6:00 p.m.: **Gibertini:** *Zn^{2+} storage in Ti3C2 MXene: a EC-AFM case of study*

6:30 p.m.: round table for comments and discussions

6:45 p.m.: **Shinnur:** *Studying the photoactivity of Ag-decorated TiO_2 nanotubes with combined AFM and RAMAN spectroscopy*

7:15 p.m.: round table for comments and discussions

7:30 p.m.: special dinner: typical Valtellina dishes

8:30 p.m.: poster session

9:00 p.m.: special talk (in Italian) at the Town Hall - **Malaspina:** *Le ricchezze geologiche della Valtellina: dalle materie prime al loro riciclo e riutilizzo*

Monday 24th

9:15 a.m.: social journey to Rifugio Federico in val Dosdè and lunch!

4:15 p.m.: **Sedona:** *On-surface synthesis, from UHV to electrolytic environment*

5:00 p.m.: round table for comments and discussions

5:15 p.m.: coffee break

5:30 p.m.: **NT-MDT:** *NTEGRA Spectra system*

6:00 p.m.: round table for comments and discussions

6:15 p.m.: experiments at the solid-liquid interface

7:30 p.m.: dinner

9:00 p.m.: **Peron**: *A look at gravitation*

Tuesday 25th

9:15 a.m.: **Wandelt:** *Relevance of Solid-Liquid Interfaces: Macroscopic Phenomena and Microscopic Understanding*

10:00 a.m.: round table for comments and discussions

10:15 a.m.: **Filoni:** *Physical confinement vs adsorption driven reconstruction: the case study of the sulfate anion interaction with vicinal Cu(111) surfaces*

10:45 a.m.: round table for comments and discussions

11:00 a.m.: coffee break

11:15 a.m.: **Kosmala:** *Tuning Graphene-Metal Interactions for Advanced Energy Storage and Catalytic Applications*

12:00 a.m.: round table for comments and discussions

12:15 a.m.: **Futyma:** *Elucidating the Surface Chemistry of TMPyP on Iodine-Modified Au(111) by EC-STM study*

12:45 a.m.: round table for comments and discussions

1:00 p.m.: lunch time

2:30 p.m.: **Recalcati:** *Quantification of mineral dissolution via Atomic Force Microscopy*

3:15 p.m.: round table for comments and discussions

3:30 p.m.: **Guadagnini:** *Scalable statistical behaviour of mineral dissolution rates (1/2)*

4:00 p.m.: round table for comments and discussions

4:15 p.m.: **Riva:** *Scalable statistical behaviour of mineral dissolution rates (2/2)*

4:45 p.m.: round table for comments and discussions

5:00 p.m.: concluding remarks

5:30 p.m.: volleyball tournament

7:30 p.m.: dinner

Graphite intercalation: a model system for the electrochemical SPM investigation

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ABSTRACT

Graphite intercalation through electrochemical methods has garnered significant attention for its suitability in studying scanning probe microscopy systems operating in electrochemical environments (EC-SPM). Since the pioneering studies by Murray in the early 1990s, many questions regarding the mechanisms of the intercalation process remained unanswered. Our recent work aims to bridge this knowledge gap, providing crucial insights into the intercalation mechanisms. These findings are pivotal for enhancing the understanding of processes currently employed in the preparation of lithium battery electrodes. Through our research, we offer a more comprehensive understanding of graphite intercalation, which is essential for advancing the development and optimization of energy storage technologies.

The combined analysis of electrochemical scanning tunneling microscopy (EC-STM) and electrochemical atomic force microscopy (EC-AFM) during the graphite intercalation process has led to significant modifications of Murray's original model. Our studies reveal that blisters become distinctly observable under microscopic investigation only during the deintercalation phase. This suggests that blisters form when the graphite planes collapse following the removal of sulphate ions. Moreover, our real-time investigations indicate that, while intercalation consistently occurs, the formation of blisters is not inherently linked to it.

Keywords: HOPG; anion intercalation, EC-STM, in-situ AFM.

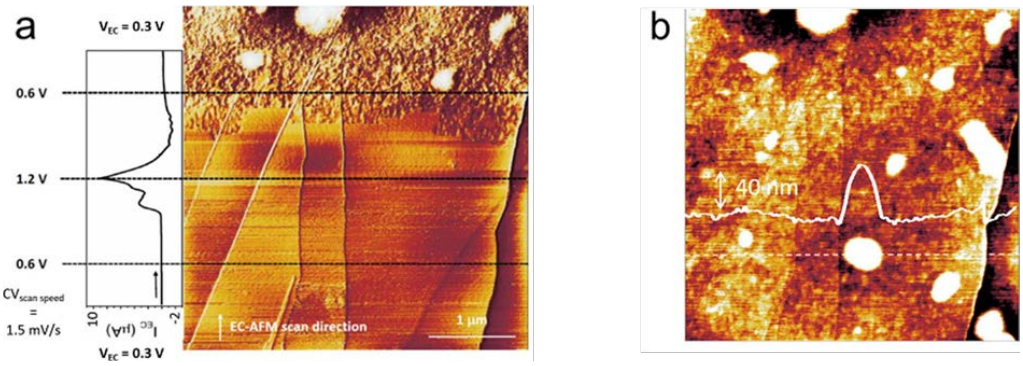

Figure 1: *a) AFM image of blister evolution during the cyclic-voltammetry b)AFM image at constant EC potential after the blister evolution.*

Acknowledgements

We acknowledge funding by: Cariplo Foundation “ANTICARB - Quarry waste ANTIgorite CARBonation: a zero emission platform for re-manufacturing with the benefit of CO2 sequestration” (Grant n. 2020-0977).

Stiffness and mechanical manipulation of blisters grown on electrochemically intercalated graphite

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ABSTRACT

Electrochemical anion intercalation of highly oriented pyrolytic graphite in mineral acids (such as sulfuric, perchloric, etc.) represents a model system to study (i) the intercalation process of chemical compounds in stratified crystals; (ii) the evolution of gases at the surface and inside the sample and (iii) the evolution of swollen regions of graphite, called blisters. Although the explanation of the blister evolution mechanism can be dated back to the nineties of the last century, many chemical and physical properties have been explored only very recently. In particular, the mechanical properties of blisters on graphite are not widely discussed in the literature. Here, we employ in-situ atomic force microscopy (AFM) to characterize the blister stiffness. The same AFM tip is used to move mechanically the blister on the basal plane or even cut it. As a consequence of this operation, the entrapped gases (namely, CO, CO_2 and O_2) can deflate and the swollen graphite layers lay down to recompose the graphite basal plane.

Keywords: Atomic force microscopy (AFM), nanoindentation, nanomanipulation, cyclic- voltammetry (CV).

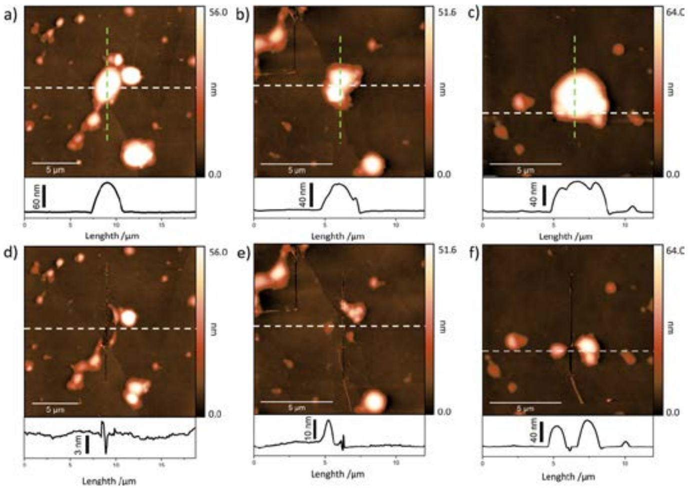

Figure 1. Topography images, acquired *in situ* and in non-contact mode, of three different blisters; respectively before (a, b, c) and after (d, e, f) their cut. The green vertical dash line evidences the path of the tip during the cut. The white dash line is in correspondence of the cross-section, reported at the bottom of each panel.

Acknowledgements

We acknowledge funding by: Cariplo Foundation "ANTICARB - Quarry waste ANTIgorite CARBonation: a zero emission platform for re-manufacturing with the benefit of CO2 sequestration" (Grant n. 2020-0977).

Characterization of Porosity and Electrochemical Behavior of C60 Thin Films on HOPG Using EC-AFM

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ABSTRACT

Recently, fullerene (C60) has attracted a lot of attention in a variety of technological fields. Because of its crucial characteristics, it has been widely used in photovoltaic technology[1] as well as drug delivery[2], proving to be an excellent p-type semiconductor, in the first case, and an effective nano-structuring increasing the active area, in the latter case.

Nevertheless, among the possible applications, a systematic investigation characterizing fullerene thin films at the solid-liquid interface is still missing in the literature. For this purpose, we proposed a research study on the porosity of fullerene thin films, deposited on a highly oriented pyrolytic graphite (HOPG) substrate, when immersed inside an acidic solution. The samples were analysed with a combined electrochemical- atomic force microscopy technique (EC-AFM), to get a detailed analysis of the C60 thin films morphology evolution in real time, while running cyclic voltammetries (CV). In this way, the behaviour of C60 thin films of different thickness on HOPG was compared by dipping them in diluted sulphuric acid electrolyte. In fact, it is now well known that, when graphite is immersed in H_2SO_4 solution, it is exposed to a surface oxidation process when specific positive potentials are applied.[3] From this oxidation process, formation of CO, CO_2 and O_2 gases results on the surface as well as in the underlying layers, leading to a surface swelling process and consequent blisters production. Even if some of these mechanisms are still under debate, it is evident that this process brings to substantial degradation and damages of the crystal.

The aim of this study is to propose a possible solution to the above-mentioned issue, i.e. the HOPG protection, by depositing C60 thin films on top of the surface and analysing their surface characteristics and porosity. The samples were prepared in vacuum, by physical vapour deposition (PVD). Different thicknesses of thin films were chosen, ranging from 1 nm to 125 nm, to have a complete view of liquid percolation through the different surface nanostructures. The EC-AFM measurement revealed that the 1 nm C60 thin film is not able to preserve the HOPG substrate already at a concentration of 1mM of H2SO4; at the intermediate thicknesses, the acidic solution reached HOPG at 10 mM H_2SO_4 concentration; 1M H_2SO_4 concentration is the limit value when the 125 nm fullerene thin film is deposited on the graphite substrate.

Our results reveal that a proportional relationship exists between the acidic concentration and the thickness of the nanostructured thin film: the thicker the C60 thin layer, the higher the acidic concentration to which liquid can percolate trough the surface, reaching the HOPG substrate and bringing to blisters formation and crystal damages.

Keywords: EC-AFM; C60; thin films; HOPG.

References:

[1] Oku, Takeo, et al. "Microstructures and photovoltaic properties of C60 based solar cells with copper oxides, CuInS2, phthalocyanines, porphyrin, PVK, nanodiamond, germanium and exciton diffusion blocking layers." *Materials Technology* **28**.1-2 (2013): 21-39.

[2] Kumar, Manish, and Kaisar Raza. "C60-fullerenes as drug delivery carriers for anticancer agents promises and hurdles." *Pharmaceutical nanotechnology* **5**.3 (2017): 169-179.

[3] Yivlialin, Rossella, et al. "Blister evolution time invariance at very low electrolyte pH: H2SO4/graphite system investigated by electrochemical atomic force microscopy." *Electrochimica Acta* **276** (2018): 352-361.

Acknowledgements

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A combined AFM+Raman statistical analysis on H_2SO_4 intercalated HOPG blisters

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ABSTRACT

Intercalation of highly oriented pyrolytic graphite (HOPG) is a fundamental electrochemical process which consist in ion insertion between graphite layers and may facilitate the production of high quality graphene sheets. Studies on $H_2SO_{4(aq)}$ intercalated HOPG have tried to highlight the most interesting features of this process. One of the consequences of intercalation is the formation of swelled structures on the HOPG basal plane called blisters. These swellings are caused by the formation of gasses during the EC process which remain trapped under few-layers graphene skin. Blisters structure and stratigraphy, however, is still not completely clear. In this work I conducted a combined Atomic Force Microscopy (AFM, figure 1a) and local Raman spectroscopy (figure 1b) in air analysis on HOPG blisters, which revealed the interplay of different phenomena. The strain of the inflated few-layers graphene skin modifies the C-C bond length and results in a blueshift of the G and 2D HOPG Raman peaks. These shift were correlated with the morphology of the AFM scans, which reveal small but not negligible strain values (0,05 - 0,5 %). The intensity and lineshape of the G and 2D peak is influenced by many effects, for example: intercalation, thin skin effects, and the contribution of the underlying HOPG basal plane. This work highlights the potential of the combined analysis in the study of nanostructured surface systems.

Keywords: HOPG; intercalation; Blisters; AFM-Raman correlation.

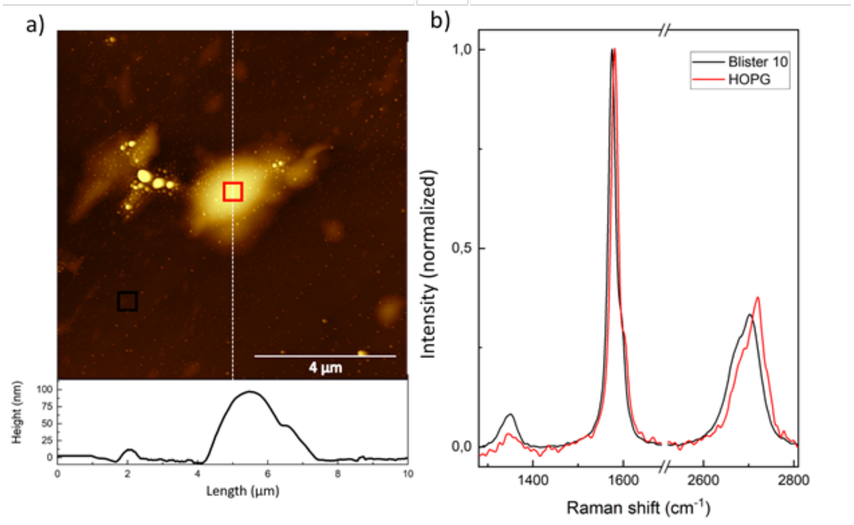

Figure 2: a) AFM image of a blister b) normalized Raman spectrum of the blister and of the HOPG basal plane.

Acknowledgements

We acknowledge funding by: Cariplo Foundation "ANTICARB - Quarry waste ANTIgorite CARBonation: a zero emission platform for re-manufacturing with the benefit of CO2 sequestration" (Grant n. 2020-0977).

Scanning electrochemical probe microscopy: From light-driven molecular catalysis to studies of interfaces of post-Li battery electrodes

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ABSTRACT

Scanning (electrochemical) probe microscopy techniques such as atomic force microscopy (AFM), scanning electrochemical microscopy (SECM), nanopipette derived scanning probe methods (e.g., scanning electrochemical cell microscopy) and hybrid SPM techniques have a long tradition in the study of interfacial processes and heterogeneities of materials at the micro- and nanoscale. Efforts towards carbon-neutral energy conversion and storage such as light- driven water splitting (i.e., artificial photosynthesis), fuel cells, and novel battery chemistries require a fundamental understanding of the processes occurring at interfaces [1] and formed interphases [2].

In this contribution, the potential of scanning electrochemical probe microscopy (SEPM) to gain insight e.g., into light driven catalysis, ranging from nanoscale surface modifications such as the deposition of earth-abundant CAT [3] and the co-deposition of CAT/PS for activity screening experiments using scanning electrochemical cell microscopy (SECCM) will be presented. SECM and AFM-SECM allow spatially resolved in situ / operando detection of light-driven reaction intermediates and products such as H2, O2 and hydrogen peroxide (H2O2) at heterogenized CAT and PS or polymeric carbon nitride (PCN) films [4,5].

In addition, the potential and the challenges of using SEPM for characterization of interfaces and formed interphases at hard carbon composite electrodes for sodium-ion batteries will be discussed.

References:

[1] C. Kranz, M. Wächtler, M. *Chem. Soc. Rev.* **50**, 1407-1437 (2021).

[2] D. Schaefer et al., *Adv. Energy Mater.*, **14**, 2302830 (2024).

[3] E. Oswald et al., *Chem. Eur. J.* **27**, 16897-16903 (2021).

[4] J. Kund et al., *Angew. Chem. Int. Ed.* **62**, e202217196 (2023).

[5] A. Hellmann et al., *Anal. Chem.* **96**, 3308–3317 (2024).

Alumina- and Silica-Coated Platinum Films/Aqueous Solution Interfaces. An Investigation on their Stability by Scanning Electrochemical Microscopy (SECM)

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ABSTRACT

Alumina- and silica- films deposited on metal (or conducting) substrates have been extensively studied and used for a variety of technological applications. Al_20_3 or Si02 thin films act as effective protection coatings of metals against fretting damage or environmental attack, they can also be used for metal insulator-semiconductor capacitor devices, sensor technology, catalyst overcoatings, and barriers to preserve historical metal artifacts. As for the metal substrate, platinum has attracted considerable attention for thin-film applications in micro - and nano-electronic devices because of its chemical inertness, high work function, and excellent electrical properties, including a linear temperature coefficient of resistance over a wide temperature range. In addition, platinum-based materials are still the state-of-the-art catalysts in a wide range of applications for micro-electrochemical systems, energy storage and conversion devices. In most of the above applications, alumina or silica coatings are exposed to potentially reactive aqueous environments, highlighting the importance of the chemical stability of the materials in these media. The main feature affecting stability of the films is the oxide structure, i.e., whether it is amorphous or crystalline, and this, in tum, depends on the preparation methods, as well as on post synthesis treatments. Most studies on stability of Al_20_3 and $Si0_2$ films in water media are performed using surface techniques, such as AFM, SEM, ellipsometry, and a variety of electrochemical techniques, particularly electrochemical impedance spectroscopy. The above surface techniques are mainly employed to establish the change of the surface roughness or other properties (i.e., refractive index) of the coating layers of the samples immersed in water solutions containing electrolytes (acid, base or neutral in nature) for different times, ranging from hours to days. This presentation deals with Al_20_3 and $Si0_2$ thin films, deposited on a Pt thin film by RF-Magnetron Sputtering to investigate the solubility/stability of the coatings in aqueous media containing different electrolytes, at room temperature. The operando SECM approach proposed here is based on imaging the solubility of the Al_20_3 layer of the Al_20_3/Pt samples, immersed in aqueous solutions, containing various electrolytes at different pH values. Series of experiments are also performed varying the pH of the solution locally, over areas of a thousand square micrometres, where etch pits can be locally produced when Al_20_3 or SiO_2 are eroded. The etched features, of tens microns in diameter, can be visualized by SECM in so- called feedback mode, which are quantified to extract kinetic information on solubility

Keywords: SECM; Amorphous Al_20_3; R.F. Magnetron Sputtering; Aqueous Stability

Corroles at the Real Solid–Liquid Interface: an In-Situ Scanning Tunnelling Microscopy Investigation

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ABSTRACT

Investigations of the properties and processes at the solid/liquid interface pose a decisive methodological challenge. Unlike in Ultra High Vacuum (UHV), electron-, ion-, and atom-beam based methods are not applicable or at least of very limited use, because the particles do not penetrate either of the two phases. Therefore, only a much more limited set of experimental methods is available to study a solid surface immersed in a liquid. These are proximity probe-based techniques (like scanning tunneling microscopy and atomic force microscopy) or photon-based techniques, like X-ray and infrared absorption spectroscopy, electroreflectance, ellipsometry, sum-frequency spectroscopy, and lately reflectance anisotropy spectroscopy (RAS).

I will present an overview of results recently obtained investigating by scanning tunneling microscopy (STM) at the solution–solid interface the deposition of corrole layers, in particular the self-assembly of corrole molecules dissolved in ethanol or in water, and then adsorbed onto an immersed Au(111) surface. Finally, I will describe a new experimental facility (a UHV chamber for X-Ray Photoemission Spectroscopy) in the Physics Department in Tor Vergata, funded within the PNRR Project STILES (in collaboration with INAF, Istituto Nazionale di Astrofisica), that soon will offer the ambitious opportunity to investigate, also at the solid-liquid interface, the fascinating issue of the origin of life on the Early Earth.

Keywords: Corroles, Scanning Tunnelling Microscope, solid/liquid interface, origin of life.

A MODIFIED REFLECTANCE ANISOTROPY SPECTROSCOPY SPECTROMETER FOR ELLIPTICITY MEASUREMENT

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ABSTRACT

Reflectance anisotropy spectroscopy (RAS) has been largely used to investigate clean surfaces of metals and semiconductors in ultra-high vacuum (UHV), low-dimensionality solid state systems and finally organic layers. In all these experiments, RAS has been limited to the study of the anisotropy of the linear dichroism of matter. The same technique can be used to investigate the ellipticity in transmittance by a proper modification in the experimental apparatus, opening intriguing perspectives in the experimental study of chirality [1]. In a typical RAS system, the photoelastic modulator (PEM) is properly driven by an oscillating circuit at the resonance frequency of the piezoelectric crystal to introduce a phase shift equal to ±π between light beams propagating along ordinary and extraordinary axes, thus modulating the linear polarization of light between two orthogonal independent states. By a proper modification of the applied voltage to introduce a phase shift equal to ±π/2, the PEM produces outgoing light alternatively right and left circularly polarized, with a resulting signal that opens interesting possibilities to investigate the chirality of organic and biological layers. Although commercial spectrometers already exist to measure the ellipticity of substances, the "open structure" of this new spectrometer and its higher flexibility in design makes it possible to couple it with UHV systems or other experimental configurations. Here, we give some insights about the use of this RAS spectrometer in transmission to measure ellipticity features of porphyrins in solution and in solid films, comparing the spectra obtained with the ones produced by a commercial spectrometer apparatus (JASCO).

Keywords: Chirality, Porphyrins, Circular Dichroism, Ellipticity

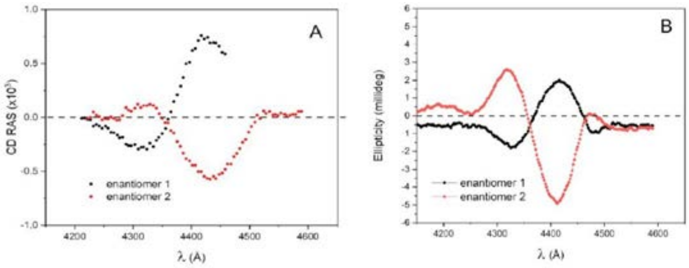

Figure 1. Panel A: CD-RAS experimental spectra for enantiomer 1 (red curve) and enantiomer 2 (black curve). The two enantiomers have been obtained from a 50 μl droplet of a $ZnOEP$ solution in dichloromethane deposited onto a glass substrate and measured in transmission mode. The resulting film has an average thickness estimated in the range 10-15 nm from Atomic Force Microscope images. Panel B: ellipticity spectra measured on the same samples by a commercial spectrometer for Circular Dichroism for enantiomer 1 (red curve) and enantiomer 2 (black curve).

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Interaction between biological materials and surfaces at the solid-liquid interface

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ABSTRACT

Soft matter, in particular the biological molecules and supramolecular constructs, is generally known to be deformable upon interaction with surfaces due to the energy barriers that hold its structures. The latter are in the same order of magnitude of those leading to the adsorption of these objects onto extended surfaces (electrostatic interactions, hydrophobic interactions etc...).

An accurate characterization of the conformation assumed when passing from the bulk solution to the solid- liquid interface might provide insight in the deformation and thus precious information on the interaction force that have lead the adsorption. Nevertheless, to be quantitative one must have tools able to assess quantitatively the conformation and deformations that take place in these processes.

Here I will present two examples where polymer physics (DNA) and morphometric analyses (biogenic nanoparticles) have been applied in this perspective, leading to a characterization of both the strength and the distribution of the interaction spots between biological molecules and extended surfaces at the solid-liquid interface

Keywords: Atomic Force Microscopy; polymer physics, nanomechanics, extracellular vesicles.

State-of-the-art of SPM@ISMN: a personal perspective

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ABSTRACT

If you describe something as state-of-the-art, you mean that it is the best available because it has been made using the most modern techniques and technology (UK Collins dictionary). Our SPM labs in Bologna are surely outdated, and so should be not at the state-of-the-art. Fortunately, the state-of-the-art definition from Treccani dictionary opens to other interpretations; it is in fact the situation, the current stage of development or knowledge achieved in a particular research area as a result of the application of modern methods. Such definition, free from "the most modern" constrains, leaving space to introduce "less" modern SPM in new scientific fields and promote instrumental developments.

Keywords: SPM; State-of-the-art.

Transient Electrochemical Tip Surface-Enhanced Raman Spectroscopy (EC-Tip-SERS): Concept and Applications in Electrocatalysis and Material Science

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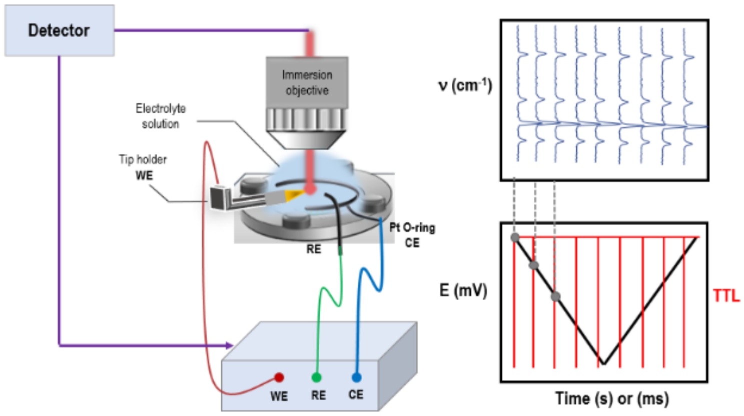
ABSTRACT

The development of electrochemical techniques combined to Raman spectroscopy such as electrochemical Tip- or Surface-Enhanced Raman spectroscopy (EC-TERS or EC-SERS) have attracted considerable attention over the past years by the scientific community. This spectro-electrochemical combination provides an accurate view over electrochemical processes occurring at an electrode by acquiring simultaneously local topography, and vibrational fingerprints about the material or molecules under potential control.[1] Based on the use of an insulated TERS tip, we introduced recently a new approach that we called EC-Tip-SERS (Figure 1). Here, electroactive molecules are adsorbed directly onto the tip that acts both as working microelectrode and single hotspot for SERS.[2] Although the spatial resolution is lost in this configuration, interesting transient mechanistic information can be obtained. In this communication, we will present first the use of this technique on a redox- and Raman- active model molecule, the Nile blue, in which a temporal resolution in the order of millisecond can be easily attained. Then, we will consider the use of Tip-SERS in probing molecular motion within rotaxane-based giant assemblies containing porphyrins derivatives. Finally, we will demonstrate the use of transient EC-Tip-SERS in scrutinizing electrocatalytic transient mechanisms, such as those associated to the oxygen reduction reaction towards hydrogen peroxide in water using viologen SAMs as electrocatalyts.

Keywords: Tip-Enhanced Raman Spectroscopy, Electrochemistry, Nanoscale characterization



Transient electrochemical tip-SERS setup

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Development of a cell for EC-STM-TERS

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ABSTRACT

With the growing desire to use more complex materials to enhance or propose new applications, there is a significant need for powerful, precise analytical techniques that can be used in a variety of situations. These analyses should be capable of being conducted in situ, during experiments, to directly observe the evolution of systems during their future applications. Since interesting phenomena often occur at a nanometric scale, it becomes necessary to characterize the evolution of sample surfaces at this scale. It is also important to perform these analyses in liquid environments, to apply the techniques to the fields of biology or electrochemistry.

Additionally, it becomes important to couple multiple techniques, which allows for the combination of their information and adds a new dimension to certain measurements. This method is notably used with spectroscopic techniques, to visualize spatial defects that may affect measurements, or to precisely target an area of the material. In the context of electrocatalysis, the data obtained at the working electrode are averages of the produced potential, and obtaining this spatial refinement could eventually allow the identification of catalytic sites.

Since 2015, the Laboratoire Systèmes et Interfaces Electrochimiques (LISE) has been working to adapt TERS (Tip-Enhanced Raman Spectroscopy) to electrochemistry. TERS uses local probe microscopies such as STM (Scanning Tunneling Microscopy) linked to Raman spectroscopy to achieve a spatial (vibrational and topographical) resolution of a few nanometers while significantly amplifying the signal. Recent advances have confirmed the possibility of using TERS in liquid environments, and an adaptation to electrocatalysis has been undertaken.

This speech takes place within this context. The main objectives pursued during this work are the development of an electrochemical cell adapted to the system, followed by the study of electrochemical reactions on mica and single-crystal gold, with the goal of demonstrating the feasibility of studying electrocatalysis using EC-STM-TERS.

Keywords: Tip-Enhanced Raman Spectroscopy, Electrochemistry, Nanoscale characterization.

Microwave-matter interaction for enhanced carbon capture by mineral carbonation

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ABSTRACT

The formation of stable and insoluble Mg- and Ca-carbonates and/or hydroxy-carbonate hydrates, through water-mediated reaction of Mg(OH)2 (brucite) and Ca(OH)2 (portlandite) with carbon dioxide, is referred to as mineral carbonation (MC). MC is among the most promising potential solutions for long-term carbon capture and storage (CCS), since it is spontaneous under a wide range of conditions. However, kinetic barriers pose sever limitations to the practical exploitation of MC, implying energy requirements to reach sufficiently high reaction rates. Trying to overcome these hindrances, we show here the application of microwave (MW)-assisted processes for the carbonation of brucite, used as a model system for the carbonation occurring in number of widely diffused minerals, such as serpentine. Preliminary information on the mechanism, kinetics, and energy costs of the reaction, together with the chemical characteristics of the products obtained, are inferred by a combined study, carried out by both a MW reactor on bulk brucite water slurries and ex situ microscopy investigations on micron-scale regions of the surface of brucite single crystals, exposed to MW irradiation in CO2-saturated water.

The challenge is to create a combined MW-microscopy platform to both locally activate and monitor on the micron-scale the carbonation reaction occurring on the brucite surface since the early stages, by using an atomic force microscopy probe.

Keywords: carbon capture and storage and utilization, mineral carbonation, magnesium carbonates, microwave chemistry.

Acknowledgements

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Quantitative imaging of electroswelling in organic mixed ionic electronic conductors

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ABSTRACT

Ionic transport and accumulation into active layers of electrodes is of crucial relevance for energy storage and conversion processes. Organic mixed ionic electronic conductors (OMIECs) are a well characterized model system that exhibits a 3D electrified interface. As a result, unconventional properties emerge such as volumetric capacitance or strong electroswelling. Electroswelling allows to achieve volume changes and mechanical actuation controlled by small electrical potentials. The electroswelling effect is exploited in electrochemical actuators with low-voltage drive, nanoscale precision and miniaturization, with applications in soft robotics, soft micromechanical devices or actuated biomedical devices. However, electroswelling can also trigger delamination in OMIECs thin film devices used for sensors or electrochemical energy storage and puts their long-term stability at risk.

To investigate ionic transport and accumulation at the microscale we introduce a novel type of modulated electrochemically controlled AFM experiment (mEC-AFM) that combines local surface strain measurements with electrochemical impedance spectroscopy. We test the experiment on OMIEC covered microelectrodes and obtain multidimensional spectroscopic data that explains the relevant processes and their timescales in electroswelling. Combining the technique with the PinPoint imaging mode, we record high resolution maps that report the local amplitude and the phase of electroswelling on soft polymer thin films. The data demonstrates that electroswelling in PEDOT:PSS used as OMIEC material is driven by the volume of hydrated ions entering the thin film and does not depend on slower diffusive processes.[1] In more complex materials such as PPY-DBS ionic transport is more hindered and the multidimensional spectroscopic data allows for in-depth profiling of ionic transport and swelling properties.

Keywords: Modulated Electrochemically Controlled Atomic Force Microscopy (mEC-AFM).

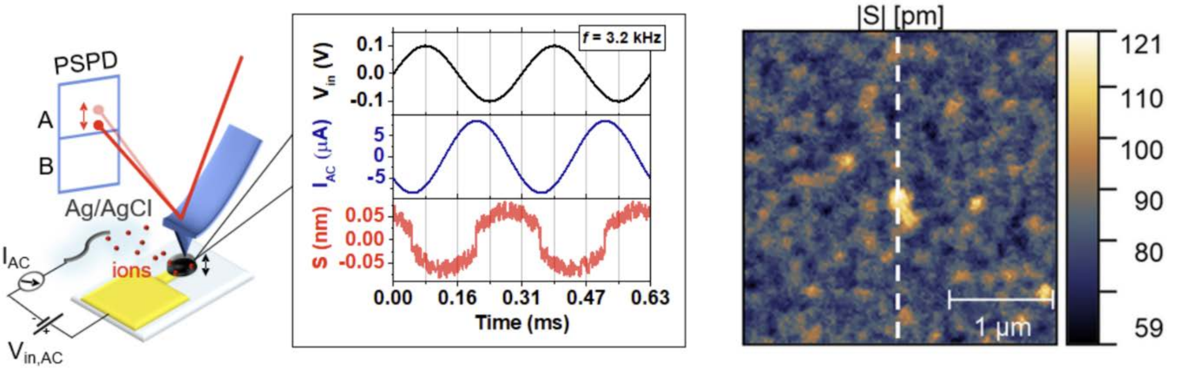

Figure: Schematic showing the modulated EC-AFM experiment and the recorded data traces. The technique allows to map electroswelling in mixed ionic and electronic conductors with nanoscale resolution.

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Study of model systems at the electrified solid/liquid interface

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ABSTRACT

The investigation of model systems to determine structure/activity relationships is well-established in heterogeneous catalysis, as masterfully exemplified in Prof. G. Ertls Nobel lecture in 2007. Despite its success, this approach has seen limited application in electrocatalysis due to the technical challenges associated with the atomic-scale characterization in complex electrochemical environments. Recently, a new paradigm has emerged that combines traditional ultra-high vacuum studies, essential for preparing well-defined catalytic systems, with investigations by (pseudo) in situ spectroscopies and operando scanning probe microscopies. In this way, an unprecedented insight into catalytic processes at the solid-liquid interface was achieved.

This presentation will provide an overview of such investigations, with a particular focus on the contribution of electrochemical scanning tunneling microscopy (EC-STM) and its latest advancements, such as the use of the noise detection in the tunneling current to identify electrocatalytic sites. I will present case studies regarding ultrathin films of oxides and chalcogenides supported on metal single crystals, which are used as catalysts in the hydrogen evolution and oxygen reduction reactions. These studies demonstrate the ability to monitor in real-time and at the nanoscale the changes induced by electrochemical potential and to analyse the chemical activity of materials down to the single atom. Additionally, these investigations reveal a wealth of phenomena at the solid-liquid interface, such as the formation of interface-stabilized nanophases and electron tunneling, which are still an uncharted territory, but with a great potential for the design of novel high performing catalysts.

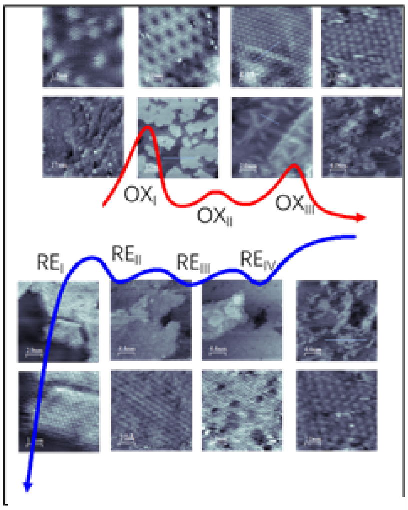

Figure 1: High resolution EC-STM images of iron oxide ultrathin films as a function of the electrochemical potential in alkaline environment.

Keywords: Electrochemical STM; ultrathin films; electrocatalysis.

Operando study of CoAl-LDH in alkaline conditions

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ABSTRACT

The oxygen evolution reaction (OER; $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$) is the half-reaction in the electrolytic generation of hydrogen from electrocatalytic water splitting, the so-called "green hydrogen". It is well known that this reaction represents the bottleneck in terms of efficiency of the process, therefore, improving the performance of the OER is crucial to obtain a sustainable green hydrogen production. From a materials point of view, there is a strong push towards improved, nanostructured, cheap, transition-metal-based electrocatalysts. Crucial is the direct identification of how the material properties influence reactivity during operation. Nanostructured electrocatalysts are reported to show various electrochemical properties across different length scales [1]. These catalytic characteristics, measured at the nanoscale, are proven to be often different from those exhibited at the macro-level, due to higher lateral resolution.

One of the most studied types of electrocatalysts for OER are the transition metal (oxy)hydroxides (MOxHy, M=Fe, Co, Ni) that have emerged as promising electrocatalysts for the OER. These materials can be accurately tuned to form layered double hydroxides (LDH) with a mixed 2+ and 3+ cations. When a potential is applied to these materials, they can undergo a dynamic and heterogeneous changes. Indeed, when a potential is applied, ions can be solubilized [2], converting the usual inactive basal plane of the materials into an active site during OER.

In this work we investigate the physical and chemical changes of CoAl-LDH in relation with the OER performed in alkaline conditions via different techniques. Aging was performed by electrochemical cycling under OER conditions. Electrochemical measurements were carried out by a conventional three electrodes setup system, using drop-casted ink of LDH and carbon as working electrode, Hg/HgO electrode as reference and graphite rod as counter. Similarly to the material β-$Co(OH)_2$, the CoAl-LDH showed two redox pairs in cyclic voltammograms, likely associated with the transitions between β-$Co(OH)_2$ towards α-$CoO_2H_{1.5} \cdot 0.5H_2O$ and α-$CoO_2H_{1.5} \cdot 0.5H_2O$ and β-CoOOH respectively. However, the main difference between these two materials is an increase of the LDH capacitance increases in the first CV cycles. Electron microscopy imaging was used to understand the morphological and stoichiometric changes. These conventional pre/post EC characterization showed a clear transition of the material from hexagonal flakes with homogeneous Co and Al distribution with the expected 3:1 ratio to large Co3O4 crystals with a complete loss of Al. AFM (atomic force microscopy) measurements on the as-prepared LDH show stacked hexagonal flakes, with height approximately between 60 nm and 200 nm and a width ranging from 1 μm to approximately 2 μm, as reported for other transition-metals hydroxides [1,3]. Thanks to the collaboration with SOLINANO Σ-Lab, led by Prof. Gianlorenzo Bussetti, it was possible to perform EC-AFM (electrochemical-AFM), an operando technique that allows performing AFM on a sample subjected to electrochemical analysis. This technique was found to be crucial to define the morphological transition from hexagonal CoAl LDH to a defective phase with loss of Al that explains the superior properties of this material compared to the analogue β-$Co(OH)_2$.

Keywords: LDH; EC-AFM; Microscopy; Operando.

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EC-STM and Voltammetric Analyses of Free-base Octaethylporphyrin on Au(111) at the 0.1 M HClO4 Electrolyte Interphase as Heterogeneous Molecular Electrocatalyst for Oxygen Reduction Reaction

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ABSTRACT

The reduction of oxygen (ORR) process, taking place at the solid-electrolyte interphase, using metal-porphyrin catalysis is currently widely explored.[1] Conversely, metal-free molecular systems are much less investigated, and there is limited information available for molecules such as non-metalated macrocycles capable of catalyzing the ORR.

In this work, metal-free octaethylporphyrin (H2OEP) was adsorbed on Au(111) and immersed in 0.1 M $HClO_4$ electrolyte to investigate ORR electrocatalysis by means of EC-STM and other electrochemical techniques such as cyclic voltammetry and RRDE linear sweep voltammetries. From the EC-STM characterization, a monolayer of H2OEP was observed and proved to be stable to potential variations in the range where ORR occurs with no adsorption / desorption or phase change phenomena occurring, contrary to the case of 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine studied by the Borguet group.[2] Furthermore, a statistical analysis was conducted on high resolution EC-STM images of the H_2OEP monolayer comparing Ar and O_2 saturated electrolyte but with similar tunneling conditions, results revealed a slight increment in the molecular protrusion (ΔZ) when switching to O_2 atmosphere; this increment didn't cause any change of the molecular shape whereas it's homogeneously distributed over the center of the molecule. In addition, a similar trend, only slightly more accentuated, was observed employing ultra-pure water as liquid interphase. This observation, supported by computational calculations, was ascribed to a pre-coordination of molecular oxygen to the central core of the porphyrin. The electrochemical analysis showed a weak improvement in the ORR catalysis caused by the H_2OEP monolayer on Au(111) with respect to the bare substrate, with a threefold increase in the percentage of H_2O_2 produced.

Keywords: EC-STM; ORR; H2O2; Au(111); electrocatalysis.

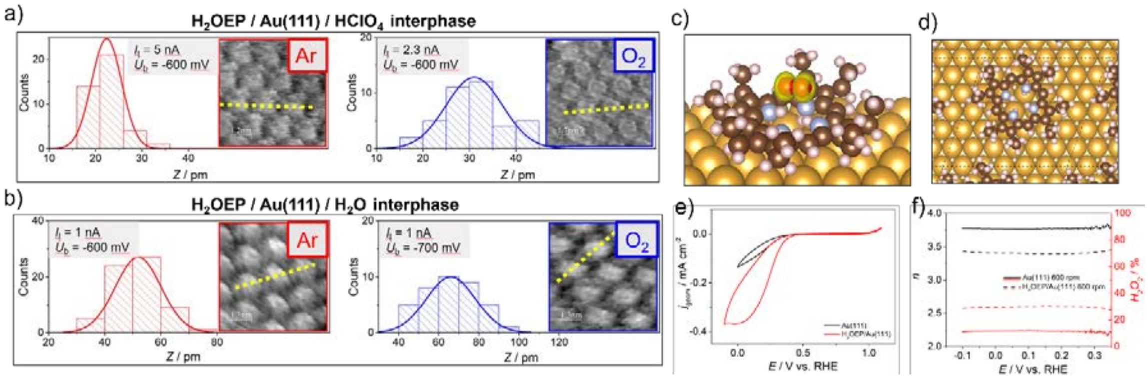

Figure 1. a-b) High resolution EC-STM images with associated histogram of single-molecule heights extracted from topographic profiles, tunnelling conditions are reported in white boxes, the type of interphase (0.1 M $HClO_4$ or ultra-pure H_2O) and atmosphere (Ar or O_2) is indicated in figure; c-d) computational modeling of Au(111) supported H_4OEP^{2+}; e) cyclic voltammetry of bare Au(111) (black curve) and H_2OEP functionalized Au(111) (red curve) in O_2 atmosphere at 50 mV/s scan velocity; f) RRDE results comparing bare Au(111) (straight lines) with H_2OEP functionalized Au(111) (dashed lines).

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Nanotribological properties of organic molecular crystals

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ABSTRACT

Crystalline surfaces show unique properties when at the interface with other solids or fluids. The interaction of the crystal surface with another medium promotes a structural re-arrangement of the surface atoms. Structural surface reconstruction then tunes the physical and chemical properties of the crystal surface. The overall process plays a fundamental role in both science and technology for example modulating the band gap in inorganic semiconductors or tuning the lubricating properties of organic crystal when used as solid lubricants.

While extensively studied in inorganic solids, surface reconstruction has not yet been fully elucidated in organic molecular compounds. According to current models, surface properties of organic molecular crystals can be described assuming a bulk-terminated structure, possibly with a slight relaxation. Within this framework, organic crystals surfaces show marked corrugations, in particular when compared to inorganic surfaces, with deep furrows developing often along more than one crystallographic direction (Fig. 1). Still, our knowledge is limited by only a few experimental studies validating current models' assumptions. A better understanding of surface reconstruction in organic compounds would however have a significant impact in technology with applications ranging from optoelectronic design and thin film synthesis to lubrication.

Here, using atomic force microscopy high-resolution imaging and shear spectroscopy, we explore model organic surfaces in air and at the interface with fluid lubricants. Our results elucidate the key role played by their well-defined corrugations in modulating their tribological properties, giving rise to a strong anisotropy and non-linear behaviour of dry and lubricated friction probed at the nano and microscale.

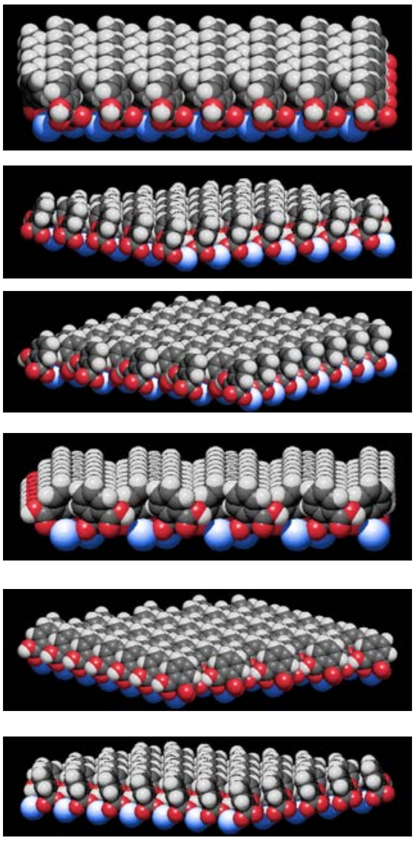

Fig. 1. Cleavage surface of potassium hydrogen phthalate crystal as viewed along six different crystallographic directions.

Keywords: Organic crystal; frictional anisotropy; lubrication; atomic force microscopy.

Modulated signals in electrochemically controlled force microscopy: implementation and application examples

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ABSTRACT

Electrochemically controlled Atomic Force Microscopy (EC-AFM) merges the high-resolution imaging of AFM with real-time electrochemical control, enabling detailed studies of the solid/liquid interface. By applying a potential to the electrode while scanning with an AFM probe, EC-AFM maps how surface morphology and forces change due to electrochemical reactions. However, EC-AFM faces several challenges. The snapshot nature of the image acquisition is in contrast with the dynamic characteristics of the investigated electrochemical processes. Small changes in morphology or forces are hidden by thermal drift and noise. Addressing these issues is crucial for analyzing electrochemical reactions with the AFM.

Here we address these issues by introducing techniques to modulate the electrochemical processes and related signals. We will first discuss how the EC-AFM setup is extended to achieve modulation and filtering. A crucial consideration regards limitation due to the large RC-time constants often found in electrochemical systems. As a first example we will present our investigations of single polymer nanofiber actuators made with electro-spun elastomers. Oscillation of stretched fibers is induced due to electrostriction under electrochemical conditions. With modulated EC-AFM we investigate the nanofiber oscillation as a function of potential and frequency. The measurement allows a quantitative assessment of electrostriction and Poisson effect in single polymer fibers.

A second application example regards the mapping of capacitive and faradaic current density on Au microelectrodes by locally probing the current change due to the presence of the AFM tip. This provides innovative insights into the current distribution on electrochemically active solid/liquid interfaces.

Keywords: Modulated Electrochemically Controlled Atomic Force Microscopy (mEC-AFM), nanofiber actuators, electrostriction.

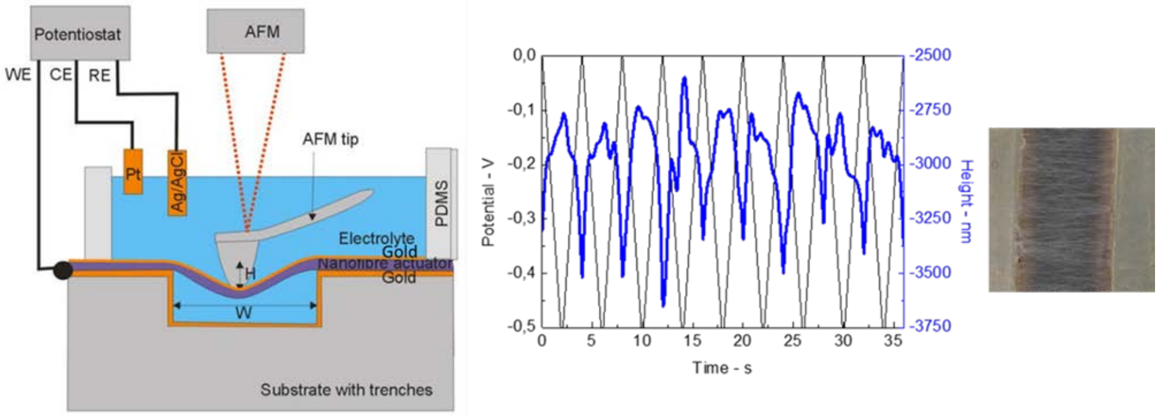

Figure: EC-AFM experiment to detect the actuation of polymer nanofibers, change of the AFM tip height as a response to the applied potential in time and top view of the investigated nanofiber sample.

Pills of galaxy formation and evolution in a cosmological context

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ABSTRACT

In this (semi-)outreach talk, I will describe the properties of present-day galaxies, both star-forming and quiescent, and of their large-scale cosmological environment. Then I will provide a quick look at distant galaxies, and in particular at the cosmic history of star formation and of chemical elements production. I will comment on the current status of theoretical and observational research in galaxy formation and evolution, and highlight the challenges posed to the community by the upcoming massive amount of data that will be delivered by next-generation facilities. Finally, I will offer a glimpse at some open issues in galaxy evolution, with specific focus on the puzzling observations of massive galaxies and black holes at very high redshift, and on the search for the cradles of life across cosmic times.

Abstracts June 23rd

On-surface synthesis of synthetic two-dimensional materials at the liquid-solid interface: a close-up with scanning probe microscopy

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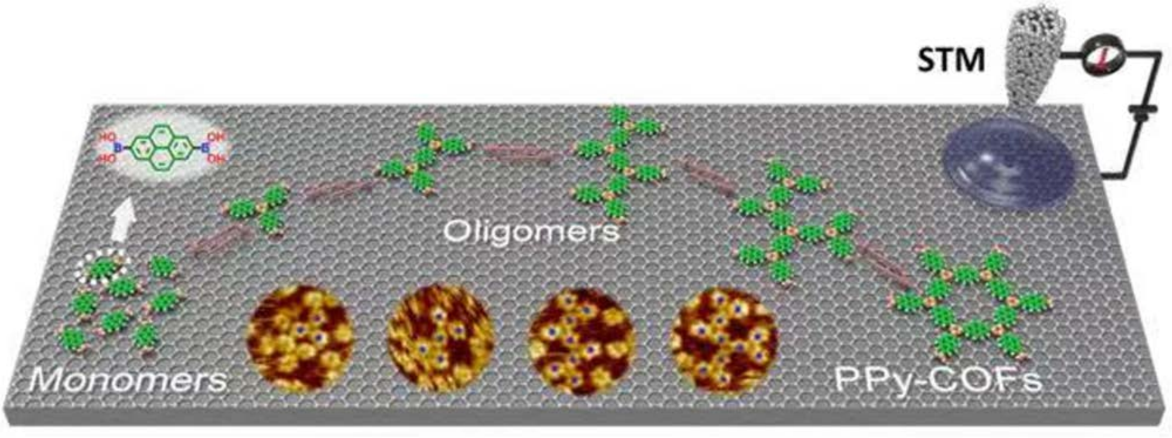
ABSTRACT

Unraveling the structure and dynamics of the formation of covalent and non-covalent synthetic 2D crystalline materials is key to controlling the quality of these materials, i.e. the defect density, and their size. These characteristics are important to understand and control their properties. Here we will highlight the power of scanning probe microscopy, and in particular scanning tunneling microscopy (STM), to visualize the structure and the dynamics of formation of these substrate-supported synthetic 2D materials, with a focus on the liquid-solid interface.

Keywords: STM, dynamics, 2D polymers



Deciphering the factors influencing electric field-mediated polymerization and depolymerization at the solution–solid interface

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ABSTRACT

Covalent organic frameworks (COFs) are a class of materials composed of light elements such as carbon, oxygen, and nitrogen, arranged in a crystalline structure via covalent bonds[1]. They have attracted significant attention due to their unique properties, including high surface area, tunable pore size, and structural stability. Classified by different dimensionalities, they are categorized into three types: bulk COFs, two-dimensional COFs (2D COFs), and two-dimensional polymers (2DPs). 2D COFs refer to a collection of single-molecule thick polymer films stacked vertically through physical interactions, whereas these single-molecule thick, sheet-like macromolecules are referred to as 2DPs[2].

Strong and oriented electric fields are known to influence structure as well as reactivity. The strong electric field (EF) between the tip of a scanning tunneling microscope (STM) and graphite has been used to modulate two-dimensional (2D) polymerization of aryl boronic acids where switching the polarity of the substrate bias enabled reversible transition between self-assembled molecular networks of monomers and crystalline 2D polymer (2DP) domains[3].

Here, we untangle the different factors influencing the EF-mediated (de)polymerization of a boroxine-based 2DP on graphite4. The influence of the solvent was systematically studied by varying the nature from polar protic to polar aprotic to non-polar. The effect of monomer concentration was also investigated in detail with a special focus on the time-dependence of the transition. Our experimental observations indicate that while the nucleation of 2DP domains is not initiated by the applied electric field, their depolymerization and subsequent desorption, are a consequence of the change in the polarity of the substrate bias within the area scanned by the STM tip..

Keywords: scanning tunneling microscopy; boroxine two-dimensional polymer; solvent; concentration

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Investigation of a Porous Metal-Organic Network by Scanning Probe Microscopy at the Solid-Liquid Interface

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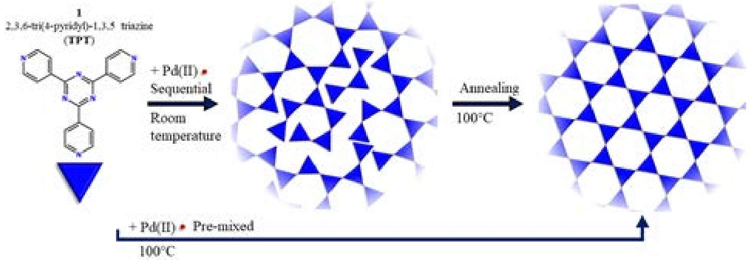
ABSTRACT

Metal-organic networks (MONs) and frameworks (MOFs) are porous crystalline materials constituted by metal nodes coordinated to organic ligands. More than 100,000 MOF crystal structures have been reported up to now, and for many of them, applications in fields including gas storage, sensing, catalysis, and drug delivery are envisioned owing to their high porosity as well as the presence of metal centers. However, while the contemporary MOF research is focused on finding new and better-performing materials, there is still a lack of complete, in-depth understanding of their dynamic processes such as guest adsorption/release or solvent exchange. Moreover, conventional scattering techniques provide space- and time-averaged structural information, while the compatibility of electron microscopy techniques is limited by the organic nature of these materials.

Scanning probe microscopy (SPM), as a space-resolved and less invasive technique, overcomes these problems: atomic force microscopy (AFM) is routinely employed to characterize microscopic features of MOF surfaces, while molecular resolution studies of surface-supported porous MONs have been carried out by ultra-high vacuum scanning tunneling microscopy (UHV-STM). In a pioneering work, Kitagawa and co-workers showed AFM at the solid-liquid interface to be suitable for the investigation of MOF surfaces with molecular resolution, providing insights into guest adsorption and release and delamination processes1. We used ambient STM to study, at the molecular scale, the chiral phases in a surface-supported MON containing prochiral hydrogen-bonded supramolecular building blocks2.

In the work presented here, we report on the molecular resolution SPM characterization of a porous MON formed at the solid-liquid interface under ambient conditions, solely stabilized by metal coordination. Starting from the ligand 2,4,6-tri(4-pyridyl)-1,3,5-triazine (TPT, 1) compact self-assembly on highly-oriented pyrolytic graphite (HOPG), the in-situ addition of a Pd(II) salt solution leads to the formation of a single-layered porous, albeit amorphous assembly. A temperature-driven disorder-to-order transition leading to a porous MON honeycomb is observed when an annealing step is introduced after the metal addition. Differently, pre-mixing the reactants at high temperature followed by dropcasting on pre-heated HOPG leads to the crystalline MON honeycomb, which features different dimensionalities in relation to the starting concentration (from sub-monolayer to bilayer). This study paves the way for the investigation of analogous systems at the solid-liquid interface, concerning their synthesis, temperature effect and concentration effect.

Keywords: Metal-organic networks; STM; Porosity; Amorphous



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Surface self-assembly of molecular motors and switches

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ABSTRACT

The surface confinement of overcrowded alkene-based molecular switches and motors is a promising approach to restrict their Brownian motion. As a result, their photoinduced molecular switching or rotation can be harnessed towards useful work. [1,2] Considering the inherent helicity of such compounds, surfaces can be potentially imparted not only with dynamic properties but also with supramolecular chirality. Molecular motors and switches have already been physi- and chemisorbed onto carbon, quartz and metallic substrates. [2] In the context of non-covalent attachment, the realization of systems in which the physisorbed optical isomers are distinguishable and the photoswitching process between the chiral states can be visualized with scanning probe microscopy techniques remains challenging. [3] A possible strategy towards this purpose is to create systems in which the helicity of the individual motor/switch molecules gets translated to the supramolecular level, into two-dimensional chiral patterns.

This work presents Feringa-type molecular motors and switches that were designed to self-assemble at the liquid-solid interface on highly oriented pyrolytic graphite (HOPG). Aromatic overcrowded alkene cores are equipped with long alkyl chains (-$C_{18}H_{37}$) to facilitate Van der Waals interactions with the surface and between the building blocks themselves. Following the organic synthesis and the solution characterization of such compounds, the self-assemblies on HOPG of racemic versus enantiopure samples are analyzed with scanning tunneling microscopy (STM) to investigate the chirality imparted at the nanoscale by the overcrowded alkenes. Additionally, dynamic aspects of the assembly are investigated using STM in-situ irradiation.

Keywords: molecular motors; self-assembly; chirality; solid-liquid interface

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Revisiting the Oxygen Reduction Reaction at Metal Porphyrins Using Electrochemical Scanning Tunneling Microscopy: A Fresh Look at the Volcano Plot!

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ABSTRACT

M-N-C single site catalysts have emerged as a highly promising alternative to Pt group metals for various electrocatalytic reactions, including the critical O2 reduction reactions (ORR). While M-Nx sites have demonstrated exceptional catalytic properties, there remains a lack of understanding regarding the precise configuration of M-Nx single sites during the catalytic process. To address this challenge, metal porphyrins have been identified as valuable model systems for simulating M-N4 sites [1-4]. In this study, we utilized EC-STM to investigate ORR at metal centered octaethylporphyrins. Through the use of STM imaging, we were able to observe the absorption of O2 as a variation in the tunneling cur-rent. Depending on the metal center, this variation could manifest as either a protrusion or a depression (ΔZ) relative to the non-coordinated metal center. We leveraged ΔZ as a key parameter to describe the electrocatalytic process. (Fig. 1a,b). The study was extended to potentiodynamic measurements and, at potentials where ORR occurs rapidly, the adsorption of oxygen is not observed and the metal center appears as free of axial ligand. For those metal-centered molecules exhibiting a redox couple, the ORR occurred within a redox-like catalysis, where the metal center mediates the reduction of the oxygen molecule, recovering its original oxidation state by reduction at the electrode (Fig. 1c,d). Conversely, molecules lacking redox behaviour exhibited inferior performance, although some catalysis was still observed, as in the case of Pt or Cu OEP. In line with the Sabatier principle, an effective catalyst must bind reactants with neither excessive strength nor weakness, and the same applies to reaction products Transferring this concept to the volcano-plot of Fig. 1e, where ip/2 is plotted versus ΔZ, Fe could be related to an intermediate binding strength, while Pt and Mn could be associated to strongly binded O_2. This leads to the assumption that ΔZ can be assumed as an independent descriptor of the catalytic behaviour of a single site catalyst.

Keywords: EC-STM; Electrocatalysis; oxygen reduction reaction; Volcano plot

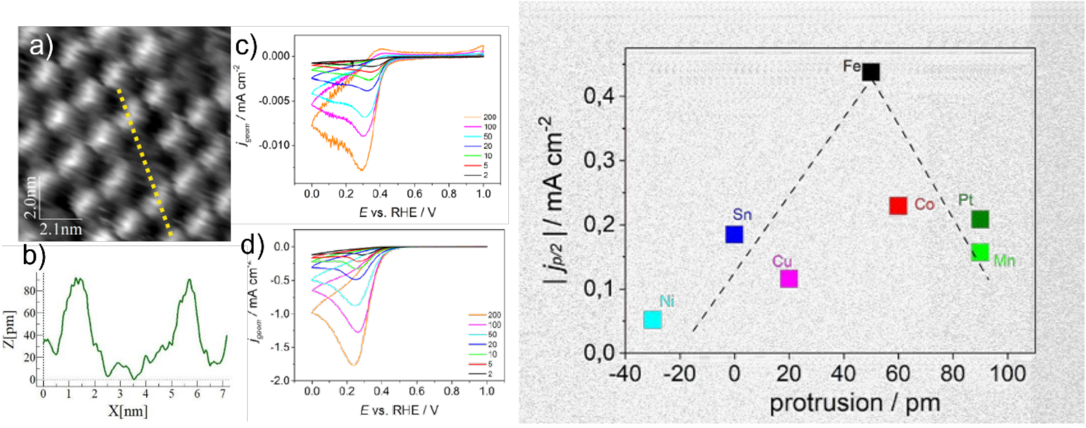

Figure 1. a) Potentiodynamic EC-STM images of a mixed H_2OEP / FeOEP adlayer adsorbed on HOPG in O_2 saturated 0.1 M $HClO_4$. b) topographic profiles corresponding to the yellow dashed; CV of FeOEP @ HOPG in c) Ar purged and d) O_2 saturated 0.1 M $HClO_4$, e) correlation of the STM revealed protrusion and the half-peak potential for all the investigated metal porphyrins.

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Studies on MoS_2 and Ru-based ultra-thin films supported on Au(111) at the interface with electrolytic solutions

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ABSTRACT

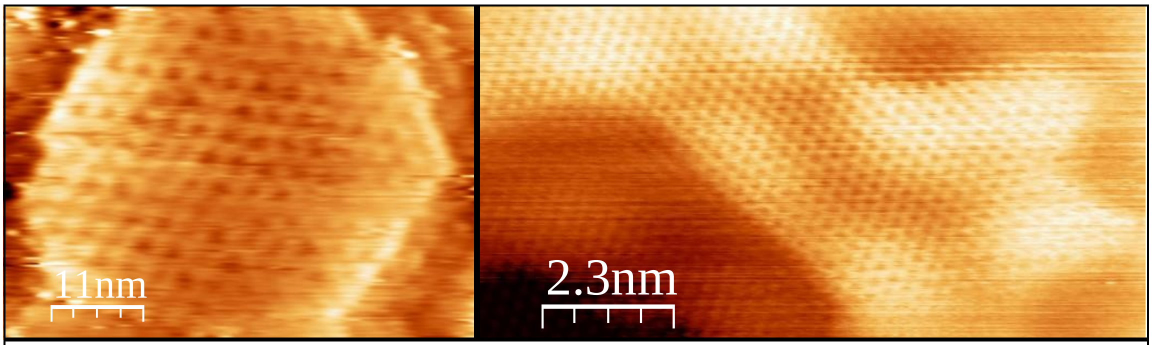
Transition metal dichalcogenides (TMDCs), such as MoS2, are of significant interest for the hydrogen evolution reaction (HER) due to their relatively low cost, primarily composed of non-precious and non-noble elements, and their two-dimensional nature. These materials are known for their largely inert basal plane, onto which electron transport is particularly rapid, and highly active edges. The edges and grain boundaries are two critical defects, with much to learn about their orientation and behaviour with respect to the substrates onto which the TMDCs are deposited.

In this context, Electrochemical Scanning Tunneling Microscopy (EC-STM) can be especially beneficial, as it enables the examination of symmetry, morphological characteristics, and transformations of single crystal surfaces and ultra-thin films through potentiodynamic imaging. This process can span from the open circuit potential (OCP) to pre-catalytic conditions, to hydrogen or oxygen evolution conditions, and back.

In recent years, we have utilized Ultra-High Vacuum (UHV) bottom-up methods to carefully prepare and characterize molybdenum sulphide and ruthenium-based ultra-thin films and nanostructures. We have also studied their electrocatalytic properties in both acid and alkaline electrolytes. Their two-dimensionality and the higher order of symmetry provided by Moiré patterns facilitate tunneling when atomic resolution cannot be achieved, especially in solution.

We discovered a substantial overlap between the surface structures observed in UHV and the measurements in the electrolytic solution. A review of the observed nanostructures and their changes between non-faradaic and hydrogen evolution conditions will be presented, along with some thoughts on the differences between imaging in alkaline and acid environments.

Keywords: EC-STM, hydrogen evolution, transition metal dichalcogenides



Left: EC-STM image of Gr/Ru/(S)Au(111)Moiré pattern in 0.1 M KOH electrolytic solution, collected inpre-HER conditions. U(T)=-0.932 V, i(T)=2.3 nA, V(WE)=-0.832 V vs Pt/PtO; Right: EC-STM image of MoS$_2$/Au(111) edge in 0.1 M KOH electrolytic solution. U(T)=0.031 V, i(T)=6.0 nA, V(WE)=-0.451 V vsPt/PtO.

EC-STM study of Nitrate Reduction Reaction on iron-octaethylporphyrins adsorbed on Au(111)

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ABSTRACT

The nitrate reduction reaction (NO_3RR) is attracting a lot of attention not only as a greener alternative synthesis of ammonia to the high energy-consuming Haber-Bosch process, but also for new perspectives of wastewater treatment. For this purpose, following the guidelines of what has been done for ORR and CO_2RR, single-atom catalysts are being studied to investigate their catalytic activity towards NO_3RR, but a proper description of the reaction mechanism still lacks.

In this work, iron-octaethylporphyrin (FeOEP) adsorbed on Au(111) is studied via EC-STM to investigate its capability to catalyze the NO_3RR, with the objective to observe its pathway and some intermediates or final products, such as nitrite, nitric oxide and hydroxylamine. High-resolution EC-STM images were taken to characterize the FeOEP monolayer in different environmental conditions but similar tunneling parameters. Statistical methods were employed to evaluate the porphyrin height (ΔZ) and to eventually discriminate adsorbed molecules on the metal center. In an argon-saturated $HClO_4$ 0.1 M electrolyte the ΔZ was found to vary between 50 and 60 picometers (figure 1.a), which is coherent with other studies. The protrusion undergoes a significant variation when nitric acid is added to the very same electrolyte as a source of nitrate. In a HClO4 0.1 M + HNO_3 1 µM solution the protrusion was found to be more than double with respect to the previous case, with values of 130-140 pm (figure 1.b). For comparison, the ΔZ in the case of an O_2-saturated $HClO_4$ 0.1 M was found to range between 90 and 100 pm (figure 1.c), thus confirming that other effects are occurring in the presence of nitrate, whether its adsorption or other phenomena related to it.

Keywords: EC-STM; NO3RR; Au(111); FeOEP

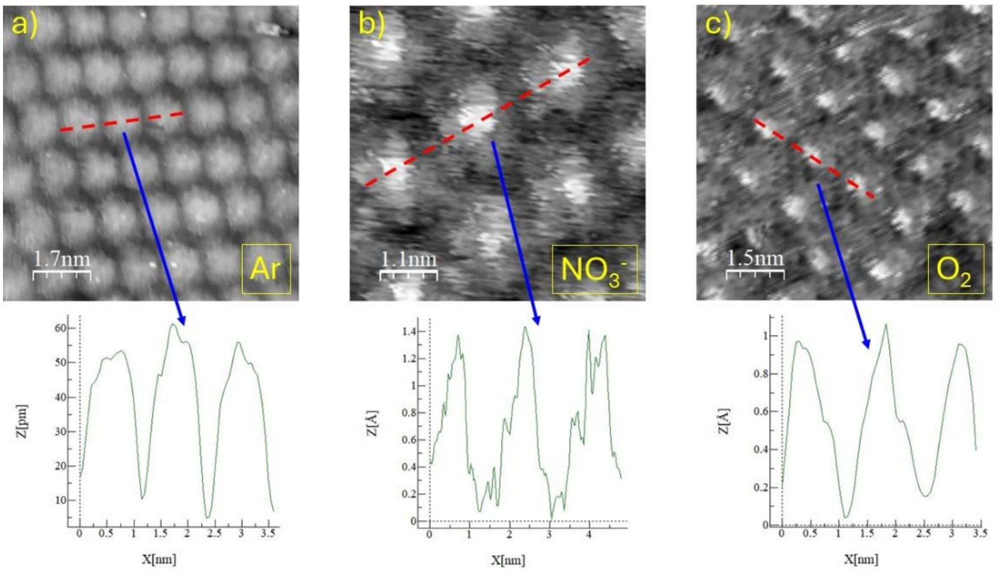

Figure 1. EC-STM images and extracted topographic profiles of FeOEP@Au(111) monolayer in a) Ar-purged $HClO_4$ 0.1 M, b) Ar-purged $HClO_4$ 0.1 M + HNO_3 1 µM, c) O_2-saturated $HClO_4$ 0.1 M. Tunneling parameters are Ub = -300 mV and It = 1 nA.

Electrochemical redox processes under the Fast electrochemical scanning tunneling microscope

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ABSTRACT

EC-STM is regarded as an advanced in situ imaging technique sensitive to non-equilibrium dynamics triggered by electrochemistry. However, it is typically limited by its rather slow acquisition rate. While dedicated fast instruments already exist, as shown by the Magnussen and the Rost groups, [1,2] we accelerate a standard beetle-type EC-STM (Wandelt et al. [3]) with an add-on Fast control module developed by the group of Cautero et al. [4]. This module allows (i) to take constant height images at and beyond video rate - e.g. for investigation of nanoparticle surface dynamics in reactive environments, (ii) to track the apex of single nanoparticles down to 50 µs time resolution under full lateral and vertical feedback - e.g. for investigation of particle diffusion mechanisms and energetics, and (iii) to precisely position the tip on surface features for fast current detection down to 5µs time resolution.

Here, we present our studies on HOPG functionalized with iron octaethylporphyrin (FeOEP) molecules in the presence of $HClO_4$ and phosphate buffer electrolyte. Figure 1 depicts the Fe(III)→Fe(II) reduction upon working electrode potential cathodic sweep (a). [5,6] This redox process can be imaged by means of Fast EC-STM, which tracks the redox process as a change of contrast (b,c). We will give examples of hitherto inaccessible dynamic processes that can now be explored.

Keywords: EC-STM, fast STM

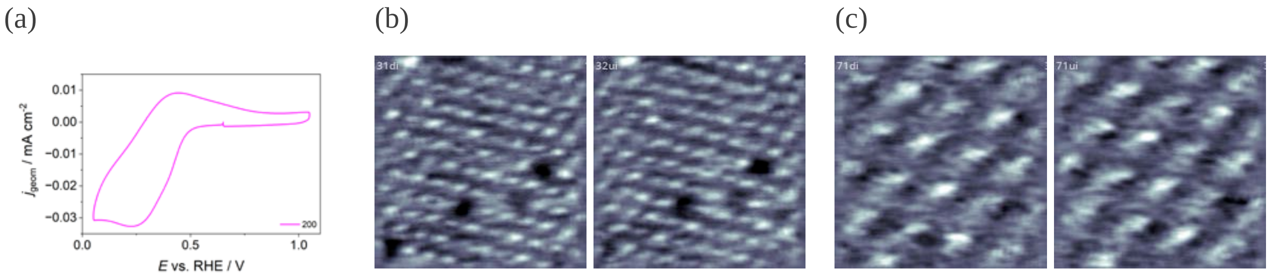

Figure 1. FeOEP adlayer on an HOPG substrate in the EC-STM in a 0.2 M phosphate buffer (pH = 7). a) CV of recorded at 200 mV/s (pH 7); b and c) successive EC-STM images taken with 4 frames/s under potential control ($E = 0.75\ V_{RHE}$); 100 x 100 px^2, line frequency 400 Hz, pixel frequency 80 kHz; U_{Tun} = 800 mV, I = 1 nA. Image size: 14 x 14 (b), resp. 5x5 nm^2 (c). Single molecules and mobile vacancies can be resolved.

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Zn^{2+} storage in Ti3C2 MXene: a EC-AFM case of study

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ABSTRACT

The search for alternative electrochemical energy storage technologies beyond conventional lithium-ion batteries is driving the exploration of non-lithium chemistries. Zinc ion chemistry, in particular, shows promise for revolutionizing the energy storage field by offering higher energy density, faster charging times, and enhanced safety, making it an appealing option for various applications [1].

In zinc ion batteries (ZIBs) or hybrid zinc ion supercapacitors (ZISCs), zinc ions are reduced to metallic zinc during the charging process, while in traditional ZISCs, they are stored as Zn^{2+} species [2]. In this context, MXene materials, especially Ti_3C_2 MXenes (MX), are emerging as promising candidates. These materials not only serve as effective interfacial regulators for highly reversible and smooth zinc plating/stripping but also function as ZISC anodes due to their high Zn^{2+} storage capacity in their interlayer spaces [3]. However, a comprehensive understanding of the electrochemistry of Zn^{2+} at the MX interface remains incomplete.

In this work, we describe the case of study of the application of electrochemical atomic force microscope (EC-AFM) for the investigation of the interface evolution of Ti_3C_2 MX thin film under polarization in $ZnSO_4$ electrolyte. In particular, EC-AFM was employed to detect evidence of underpotential deposition pseudocapacitive storage of zinc ions. The advantages and limitations of the samples and techniques are herein addressed, also comparing the result of EC-AFM with ex-situ analyses as scanning electron microscopy (SEM).

Keywords: Zinc ion; Ti_3C_2; MXene; EC-AFM; underpotential deposition

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Studying the photoactivity of Ag-decorated TiO2 nanotubes with combined AFM and RAMAN spectroscopy

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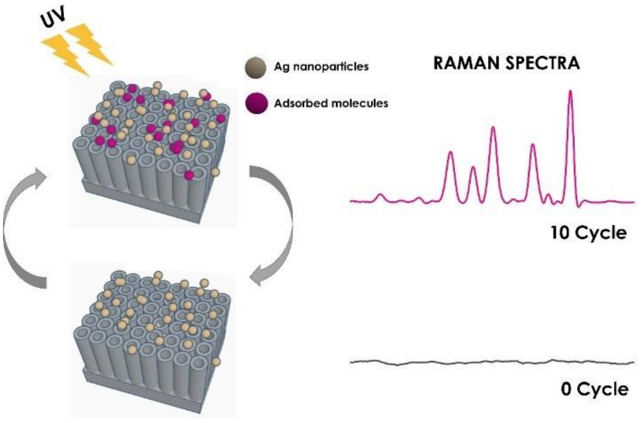
ABSTRACT

The drive for the development of systems that can simultaneously investigate chemical and morphological information comes from the requisite to fully understand the structure and chemical reactivity relationships of materials; this is particularly relevant in photocatalysis, a field ruled by surface interactions. In-detail understanding of these complex interactions could lead to significant improvements in materials design, and consequently in photocatalytic performances.

Here we present a first approach to a combined atomic force microscopy (AFM) and Raman spectroscopy characterization of anodic TiO2 nanotube arrays, decorated with Ag nanoparticles electrodeposited from organic and aqueous electrolytes and employed in photocatalytic degradation of an organic dye, rhodamine B (RhB). Characterization of obtained photocatalysts was carried out using scanning electron microscopy (SEM), X-ray diffraction (XRD) and Energy-dispersive X-ray spectroscopy. The formation of Ag nanoparticles on TiO2NTs were confirmed by the EDX analysis. Two photocatalytic samples (one cleaned, the other uncleaned after each photocatalysis cycle) were used in 12 consecutive photocatalysis tests for photodegradation of Rh- B aqueous solution under UV light irradiation, to prove possible deterioration with reuse. Sample aging can produce changes in both the morphology and the chemical compounds that characterize the photocatalyst surface; adopting multiple characterization techniques, such as a combination of AFM and Raman spectroscopy in an original set-up, can profitably enable the observation of surface contamination with reaction byproducts and possible morphological alterations.

In comparison to the uncleaned samples, cleaning the samples after every photocatalysis cycle did not significantly alter photocatalytic activity. A significant drop-in photocatalytic activity was observed at the 10th cycle in samples where silver was deposited from the organic electrolyte, with degradation efficiency dropping from 65% to 25% and from 67% to 33% for cleaned and uncleaned samples, respectively. Such drop was ascribed to photocatalyst deactivation, but chemical and thermal recovery treatments only allowed partial photoactivity restoration. In contrast, samples where Ag was deposited from aqueous electrolytes remained stable even after 10 cycles.

Keywords: Ag-decorated TiO2 nanotubes; photocatalysis; AFM; Raman spectroscopy



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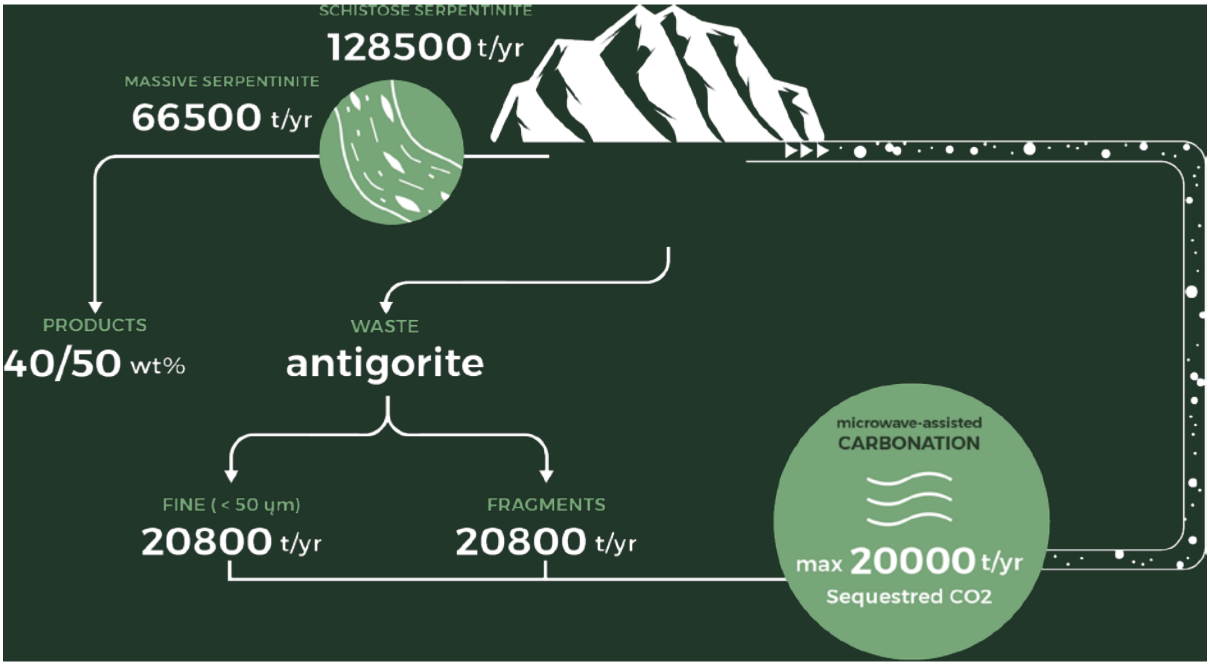
ABSTRACT

Le attività estrattive di geomateriali rappresentano una realtà industriale diffusa in tutto il mondo dove la Lombardia gioca un ruolo da leader, grazie alla sua lunga tradizione di estrazione specialmente nell'area della Valtellina. Tra queste si distinguono il quarzo di Sondalo e le serpentiniti della Valmalenco, che trovano applicazioni in svariati campi e vengono esportati in tutta Europa. Purtroppo, più del 50% della produzione delle cave è costituita da scarto, polvere e frammenti di silicati. I silicati di calcio e di magnesio però sono potenzialmente in grado di sequestrare anidride carbonica (CO_2) emessa dalla stessa industria per produrre calcite o magnesite (carbonati di calcio o magnesio), composti che trovano ampio utilizzo sia come materiale grezzo sia come prodotto finito con un valore economico. Sfruttare queste potenzialità significherebbe rendere questo settore dell'industria un esempio virtuoso di piattaforma a "emissione e scarto zero".

In questa presentazione vedremo come si formano le ricchezze della Valtellina, la loro origine geologica e le caratteristiche che le rendono uniche. Vedremo inoltre quali sono i principali metodi di riutilizzo degli scarti di cava e, tra i più promettenti, ci concentreremo sulla carbonatazione mineralogica, un processo che permette di catturare e stoccare la CO_2 in maniera definitiva e al contempo di produrre nuovi materiali dal riciclo degli scarti di cava. Semplice a dirsi ma difficilissimo a farsi, in quanto affinché la reazione avvenga in tempi gestibili industrialmente occorre assicurare condizioni supercritiche ($P > 73.8$ bar, $T > 31.1$ °C), ottenibili solo in grandi impianti industriali con un dispendio energetico sfavorevole. Tra i vari metodi, l'utilizzo delle microonde per favorire la reazione di carbonatazione si è dimostrato uno dei più promettenti per sequestrare la CO_2 nei silicati di magnesio come il serpentino. L'antigorite (una tipologia di serpentino) ad esempio, reagisce molto velocemente con la CO_2, grazie alla particolare "morfologia" della sua struttura cristallografica. Verrà descritto lo sviluppo di un sistema innovativo di carbonatazione ottimizzato, per il momento, per gli scarti di antigorite provenienti dalle cave più importanti della Valmalenco, convertendo una frazione sostanziale dell'industria estrattiva della Lombardia in economia circolare. I ricercatori dell'Università di Milano-Bicocca e del Politecnico di Milano stanno investigando il meccanismo di reazione di carbonatazione dell'antigorite alla scala atomica, sfruttando il riscaldamento indotto dalle microonde, di monitorare la reazione in tempo reale e in situ, al fine di individuare strategie di catalisi a impatto zero. I risultati di questa ricerca scientifica saranno utilizzati per trattare le polveri di scarto delle cave della Valmalenco (e potenzialmente della Valtellina) e per ottenere un modello di economia circolare basato sulla riconversione dei prodotti di scarto e il sequestro simultaneo di CO_2 emessa dagli impianti.

Keywords: Quarzo; Serpentinite; Cave; Stoccaggio CO2



Abstracts June 24th

On-surface synthesis, from UHV to electrolytic environment

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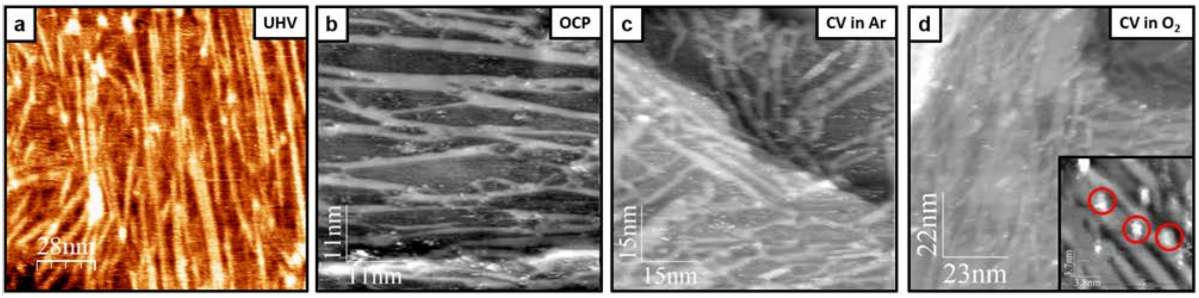
ABSTRACT

In the last decades the study of organic monolayers on surfaces has experienced a revolution with the introduction of a new synthetic strategy known as On-Surface Synthesis (OSS). This approach, based on a bottom-up methodology, involves the precise construction of covalent surface organic frameworks (SCOFs) from carefully designed molecular precursors that self-organize and react at metal surfaces, forming new covalent bonds in the process. These SCOFs, synthesized under ultra-high vacuum (UHV) conditions, exhibit unparalleled extension and order that are unachievable with liquid-phase synthesis. The covalent bonds formed during OSS impart significant stability to these structures, allowing for their study beyond UHV conditions, including ambient environments and electrolyte solutions. Since 2012, the Surface Supramolecular Chemistry (SSC) Group at the University of Padua has been actively engaged in the OSS field, notably focusing on the synthesis of linear conductive polymers and graphene nanoribbons (GNRs).

In this talk, we report preliminary results on the transfer and study of these SCOFs-fabricated by OSS in electrochemical environments. Using electrochemical scanning tunneling microscopy (EC-STM), we have investigated the stability and reactivity of linear conductive polymers and GNRs synthesized on Au(111) surfaces. Our findings demonstrate that these structures, despite being initially fabricated under UHV, maintain their integrity at solid/liquid interphase and that the EC-STM can be used to study their possible catalytic properties.

Keywords: On-surface synthesis; Ultra high vacuum; Electrochemical STM



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A look at gravitation

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ABSTRACT

The study of gravitation and of gravitationally induced phenomena walked along the discovery path of humanity. Indeed, several of the great scientific achievements involved this fundamental interaction. The current best theoretical description of gravitation, the theory of general relativity by Albert Einstein, explains a large amount of phenomenology over a huge range of scales. In this talk, after a brief overview on the foundations of the relativistic description of gravitation, examples will be provided of the current experimental activities devoted to test its most important predictions.

Keywords: Gravitation; General relativity; Fundamental Physics; Satellites

Relevance of Solid-Liquid Interfaces: Macroscopic Phenomena and Microscopic Understanding

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ABSTRACT

The relevance of the research of surfaces and interfaces is reflected in the ubiquitous application of low-dimensional materials in most modern technologies like catalysis, nano-electronics etc., that shape our daily life. The necessary understanding for their controlled design and production arose from the so-called "surface science approach", i.e. the investigation of well-prepared single-crystal surfaces with a plethora of high-sensitivity, high-resolution surface specific methods in ultra-high vacuum (UHV). On the other hand, however, many macroscopic phenomena in the earth's hydrosphere and in technological processes at solid-liquid interfaces such as e.g. electro-plating, electro-catalysis, corrosion, flotation etc. are still awaiting similarly detailed in situ investigations as they are standard in UHV surface science.

A breakthrough in the microscopic understanding of solid/liquid interfaces happened shortly after the realization of the Scanning Tunneling Microscope (STM) that turned out to provide atomic scale structure data also from solid/liquid interfaces [1,2]. This together with the ongoing development of methods providing precise in situ chemical information, such as near-ambient X-ray photoelectron spectroscopy or alike [3,4], is the basis for the growing microscopic understanding of macroscopic phenomena also at solid/liquid interfaces.

In this talk I will address some technologically important solid/liquid interface processes [5], and will specifically present and discuss selected structures of metal/aqueous electrolyte interfaces studied with in situ STM as well as advocate a liquid ↔ UHV transfer XPS approach [6] that provides, though ex situ, valuable chemical information of solid/liquid interfaces.

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Physical confinement vs adsorption driven reconstruction: the case study of the sulfate anion interaction with vicinal Cu(111) surfaces

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ABSTRACT

Research in electrochemical processes is usually based on (sub-)millimetric (mesoscopic) description by looking at average charge fluxes and reaction rates. Nonetheless the advent of methods for preparing, studying and interacting with matter of dimensions close to single molecules brings new fundamental insights and experimental potentialities. In addition, there is much to be learned from probing the behavior of single redox molecules, individual catalytic sites, and single-electron transfer events. Despite these facts, systematic studies on the so-called nanoelectrochemistry (i.e., the influence and even the processes related to nanometric structures) are still missing.

In this talk, we propose an original approach where molecules adsorption (namely, sulphates) on the electrode surface is influenced by the presence of steps, as naturally observed in vicinal Cu(111) surface. The electrochemical scanning tunneling microscopy (EC-STM) locally detects the formation of a well-ordered sulphate superstructure (Moiré pattern) in case that the copper terrace size is larger with respect to the Moiré lattice parameter. If the potential applied to the Cu electrode is close to- or within- the anodic corrosion regime, i.e., when copper undergoes a dissolution process that releases copper ions (Cu^{2+}) in solution, EC-STM acquisition becomes difficult, due to the significant detriment of the electrode surface flatness. In the corrosion regime, we successfully exploit the EC-atomic force microscopy (EC-AFM) to prolong the surface characterization towards relatively high anodic potentials. The combined experimental investigation, which is able to follow the electrode morphology on different length scales, highlights the effect of the redox processes and the role of steps during the sulphate molecules adsorption and desorption processes at the Cu surface.

Keywords: Nanotechnology, nanomaterials, nanowires, electrochemical STM

Acknowledgements

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Tuning Graphene-Metal Interactions for Advanced Energy Storage and Catalytic Applications

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ABSTRACT

Developing and researching new materials for energy storage and conversion is a top priority in modern scientific research and represents a crucial challenge within sustainable energy development. In this talk, I will showcase our recent work on the use of graphene interfaced with specific metal substrates—platinum, ruthenium, and iron (Fig. 1)—tailoring their properties for enhanced energy storage and catalytic applications.

Our research focuses on how different substrate materials tune graphene-metal interactions, leading to diverse functionalities and efficiencies. A prime example is electrochemical hydrogen storage, conducted at room temperature and ambient pressure, with atomic hydrogen absorbed through hydrogen underpotential deposition of H^+ [1]. However, long-term stability due to self-discharge remains a challenge [2]. Notably, graphene on Ru(0001) demonstrates exceptional hydrogen storage capabilities, significantly surpassing the Gr/Pt(111) model system. This has been rigorously examined using Electrochemical Scanning Tunnelling Microscopy (EC-STM), allowing us to monitor the proton intercalation process through the graphene layer. Conversely, the Gr/Fe/Pt(111) system shows a remarkable improvement in catalytic activity for the hydrogen evolution reaction (HER) [3], driven by iron atoms trapped in graphene defects during sample growth. Using an innovative in operando and in situ method known as cr-EC-STM [3,4,5], we accurately identify catalytically active sites and assess their relative activity with atomic precision.

Our findings highlight the transformative potential of engineered graphene-metal interfaces in advancing energy storage and catalysis, providing a deeper understanding of how specific atomic arrangements and interactions at the interface can drastically influence material behavior, opening new avenues for sustainable energy technology innovations.

Keywords: graphene; energy storage; catalytic activity; graphene-metal interface

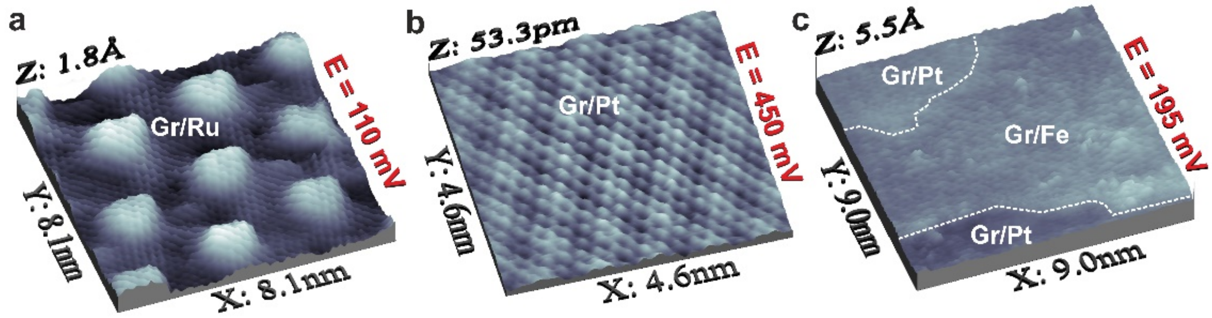

Fig. 1. High-resolution EC-STM images of (a) Gr/Ru(0001), (b) Gr/Pt(111), and (c) Gr/Fe/Pt(111) acquired in 0.1 M $HClO_4$ Ar-saturated electrolyte. Tunneling conditions: (a) $U_b = -20$ mV, $I_t = 27$ nA; (b) $U_b = -12$ mV, $I_t = 1$ nA; (c) $U_b = -16$ mV, $I_t = 1.4$ nA.

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Elucidating the Surface Chemistry of TMPyP on Iodine-Modified Au(111) by EC-STM study

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ABSTRACT

This study delves into the self-assembly dynamics of Tetra(N-methyl-4-pyridyl)porphyrin (TMPyP) molecules on an I-modified Au(111) electrode by in situ electrochemical scanning tunneling microscopy (EC-STM). Detailed observations were made under acidic conditions at a pH of 2.3, closely matching the TMPyP's pKa of 2.2 [1,2]. Under these conditions, two distinct ionic species, H2TMPyP(0)$^{4+}$ and H4TMPyP(0)$^{6+}$, coexisted in the solution, providing a unique opportunity to study their electrochemical behaviour on the electrode surface.

At electrode potentials approaching the first reduction process of TMPyP, the molecules arranged into rows, labelled as types A and B (Fig. 1). Each row type exhibited unique molecular orientations, with rotations of ± 22° (± 1°) relative to the c1 vector direction. By modifying the tunneling conditions, observation of the iodide layer and the underlying Au(111) (1 × 1) surface was achieved, enabling a direct structural correlation across all three layers and contributing to a robust structural model (Fig. 1c). This model demonstrated that the centers of the molecules in rows A and B adsorb onto equivalent iodine sites. High-resolution STM imaging (Fig. 1b) revealed varied LDOS within these rows, suggesting different protonation states that appear to significantly influence the electronic properties of the assembled molecules. Notably, molecules in row B exhibited characteristics—such as noise at low bias exclusive to this row and changes in the apparent height that vary with the applied bias potential—that are conducive to facilitating reduction processes or promoting the adsorption of a second molecular layer, both of which are intriguing from a surface chemistry perspective.

The study highlights the complex interplay between molecular protonation states and their assembly behaviour on modified electrode surfaces, providing a deeper understanding of the molecular mechanisms at play, which could be crucial for future innovations in molecular electronics and sensor design.

Keywords: porphyrin; EC-STM; protonation; self-assembly

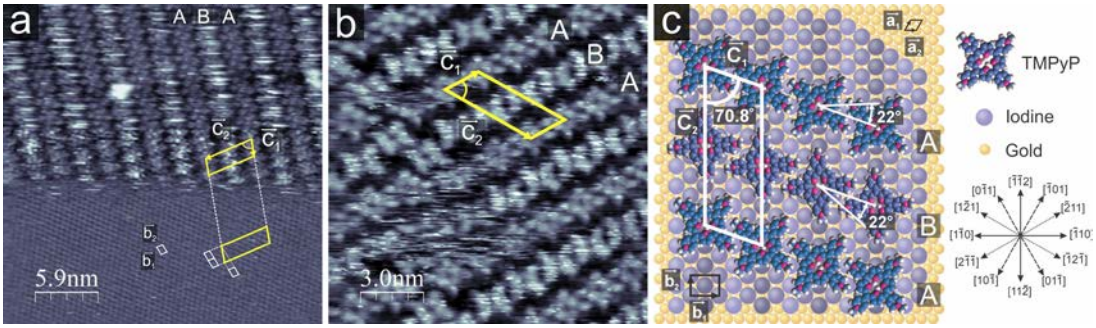

Fig. 1. (a) STM image of structural correlation between the TMPyP layer and the underlying iodine (c(p × √3)R30°; p = 2.5) and gold layer; (b) high-resolution STM images of self-assembled TMPyP molecules on I/Au(111) surface; (c) structural model. STM image parameters: (a-b) E = -297 mV vs Pt; (a) upper part: I_t = 1 nA, U_b = -500 mV, lower part: I_t = 5 nA, U_b = -105 mV; (b) I_t = 0.48 nA, U_b = -354 mV.

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Quantification of mineral dissolution via Atomic Force Microscopy

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ABSTRACT

We illustrate an experimental platform resting on the use of Atomic Force Microscopy (AFM) imaging for accurate evaluate nanometer-scale absolute material fluxes across a mineral surface sub-ject to dissolution while in contact with a continuous fluid flow. These types of reactive phenomena drive the evolution of geologic systems, also in terms of the alteration of their macro-scale attributes (such as, e.g., porosity, permeability, and storage capacity). High resolution experimental observations document that several kinetic processes contribute to the overall reaction. These, in turn, yield spatially heterogeneous reaction rates. Establishing a sound integrated experimental platform that allows em-ploying AFM imaging to evaluate real-time and in situ absolute material fluxes across the mineral sur-face is a critical challenge still hampering our ability to characterize such heterogeneity. Our experi-mental approach and design provide absolute topographic measurements (referenced to an engineered non-reacted surface) to document the spatial heterogeneity of the surface of a calcite crystal in contact with a flowing fluid and subject to dissolution. The ensuing high-quality data are then employed to ob-tain spatial fields of corresponding absolute reaction rate. Coupling the high horizontal resolution al-lowed by AFM with a tailored experimental procedure for the application of an inert metallic mask on the crystal surface provides an original way to directly observe absolute material fluxes and their space-time heterogeneity.

Keywords: Atomic Force Microscopy; Mineral - fluid interaction; Dissolution kinetics

Acknowledgements
Funding from the European Union Next-Generation EU (National Recovery and Resilience Plan – NRRP, Mission 4, Component 2, Investment 1.3 – D.D. 1243 2/8/2022, PE0000005) in the context of the RETURN Extended Partnership is acknowledged. The experiments have been performed at the Solid-Liquid Interface Nanomicroscopy and Spectroscopy laboratory (SoLINano-∑ LAB) at Politecnico di Milano.

Scalable statistical behavior of mineral dissolution rates

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ABSTRACT

We rely on high-quality data stemming from Atomic Force Microscopy (AFM) imaging of nanometer-scale absolute material fluxes across a mineral surface subject to dissolution under continuous flow. These are employed to enrich and expand typical analyses of the evolution of surface morphology going beyond studies rendering the system behaviour through bulk/average quantities. We interpret experimental observations through a stochastic approach. The latter is designed to embed the action of diverse kinetic modes corresponding to different mechanistic processes taking place across the surface and driving the spatial heterogeneity of the reaction. In this context, we view spatial distributions of rates as multi-modal (spatially correlated) random fields. Reliance on a rich and high-quality data set of absolute rates enables us to (a) accurately assess the detailed features (including tailing and extreme values) of the ensuing probability density function (PDF) and (b) accurately characterize the statistical traits of each component of the PDF. As a distinctive element, our approach and ensuing formulations embed the joint assessment of the probability distribution of a target variable and its associated spatial increments (taken between locations separated by any given distance or lag). Relying on such interpretive approach is consistent with the observation that there is mounting evidence that many spatially varying quantities exhibit a dependence of their stochastic behaviour on a multiplicity of scales. Such scaling behaviour is ubiquitously observed and transcends a given scientific field (be it, e.g., hydrology, or Earth sciences in general). We illustrate its applicability upon focusing on our very recent advances in the recognition and analysis of this phenomenon. These include the establishment of a theoretical framework that captures major documented aspects of scalable behaviour of spatial random fields in a comprehensive manner. We further focus on the analysis of sample structure functions. With reference to these, we identify power-law scaling ranges and explore behaviours such as Extended Self-Similarity.

Keywords: Stochastic modeling; Dissolution rate heterogeneity; Statistical scaling

Acknowledgements
Funding from the European Union Next-Generation EU (National Recovery and Resilience Plan – NRRP, Mission 4, Component 2, Investment 1.3 – D.D. 1243 2/8/2022, PE0000005) in the context of the RETURN Extended Partnership is acknowledged. The experiments have been performed at the Solid-Liquid Interface Nanomicroscopy and Spectroscopy laboratory (SoLINano-∑ LAB) at Politecnico di Milano.

Extra Abstracts (poster session, extra talk)

Characterization of Post-lithium Battery Materials using Scanning Electrochemical Probe Microscopy

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ABSTRACT

Among the post-lithium batteries, aluminum-ion batteries represent a promising frontier in energy storage, offering a range of benefits such as high energy density, safety, and environmental friendliness.[1,2] As the global demand for efficient, sustainable, and cost-effective energy storage solutions intensifies, Al-ion batteries have emerged as compelling alternative to lithium-ion batteries (LIBs), since the metal is highly abundant, low-cost and recyclable. However, challenges related with an Al_2O_3 passivation layer and the use of acidic ionic liquid (IL)-based electrolytes, which causes corrosion, affect the plating and stripping efficiency, thus impacting the overall performance of rechargeable aluminum batteries (RABs).

We propose a novel approach to investigate the electrochemical properties and formed interphases of polished polycrystalline aluminum foils as anode materials for RABs. Crucially, the concept is not confined to a single battery chemistry. This flexibility allows for exploration of other advanced ma-terials such as hard carbon[3] for sodium-ion batteries or to study magnesium electrodes for recharge-able Mg-ion batteries, which are also very abundant and inexpensive, offering another pathway to cost-effective and sustainable batteries. Scanning electrochemical probe microscopy (SEPM), in-cluding techniques like scanning electrochemical cell microscopy[4] (SECCM), to conduct localized charging-discharging experiments are performed on polished Al foils to examinate the electrochemi-cal, morphological, and nanomechanical properties of cycled Al spots, correlating them with electron backscatter diffraction (EBSD) maps to understand how crystal orientation and defects affect strip-ping and plating performance. Additionally, SEPM will be utilized to analyze the interphase layers formed on cycled Al foils.

Keywords: AFM; Post-Li batteries; SECCM; SPEM

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From AFM to TERS: Unveiling the Nanoscale Morphological and Chemical Composition of Bovine Milk-Derived Extracellular Vesicles

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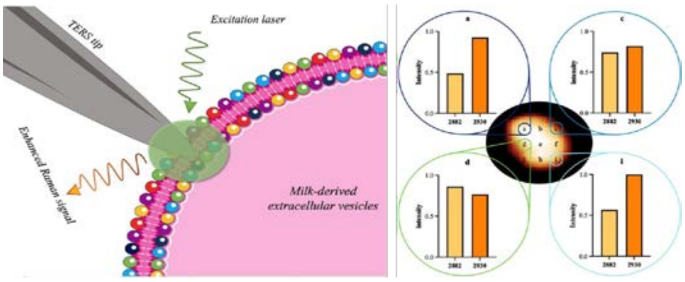
ABSTRACT

Tip-enhanced Raman Spectroscopy (TERS) is an advanced technique that combines Raman spectroscopy and Atomic Force Microscopy (AFM) to perform local chemical analysis of sample surfaces at nanoscale resolution.

This work demonstrates the innovative application of TERS for analyzing bovine milk derived extracellular vesicles (mEVs). These nanostructures have significant potential in drug delivery and therapeutic applications. Traditional Raman spectroscopy has been used to analyze mEVs, providing a detailed spectrum that identifies the “signature” of mEVs based on their characteristic molecular vibrations, revealing their chemical composition. However, TERS advances this analysis a step further by allowing the study of individual mEVs and specific locations on their surfaces with nanometer lateral resolution. AFM and Transmission Electron Microscopy (TEM) provide critical data on the size, distribution and morphology of the mEVs, confirming their spherical shape and structural integrity. In particular, AFM analysis provided detailed topographical images, while TEM confirmed the average size of 86 ± 34 nm. The characteristic peaks obtained in the Raman spectra indicated the presence of various molecular components such as proteins, lipids and nucleic acids [1]. These analyses provided a comprehensive chemical profile of the mEVs, which served as a reference for the subsequent TERS analysis. TERS characterisation was then carried out to obtain Raman spectra of isolated mEVs and specific locations on their surfaces. The TERS technique uses a silver-coated AFM tip to amplify the Raman signal through plasmonic effects, enabling the acquisition of spectra from nano-sized volumes [2]. This study focused on the 600-1800 cm^{-1} and 2600-3200 cm^{-1} spectral ranges typical of biological structures. TERS spectra showed distinct peaks correlating with chemical bonds identified in standard Raman spectra, with additional peaks and improved resolution, demonstrating the superior sensitivity and spatial resolution of the technique. The potential of TERS for nanoscale chemical mapping was further demonstrated by probing different locations on the surface of a single mEV. In particular, the analysis focused on the CH stretching region (2750-3050 cm^{-1}) due to the high intensity of the peaks in this region. By collecting spectra from multiple points on the mEV surface, it was possible to detect variations in the intensity of the CH_2 and CH_3 stretching peaks, indicating compositional heterogeneity at the nanoscale [3]. This ability to perform detailed chemical mapping of individual mEVs highlights the value of TERS for advanced studies at the molecular level, such as investigating the mechanisms of mEV loading and their functional properties in drug delivery.

In conclusion, this work highlights the power of TERS to provide a comprehensive nanoscale characterisation of mEVs, integrating morphological and chemical information. The ability to perform chemical analysis at the level of individual vesicles and specific surface locations paves the way for more detailed studies of the composition and functionality of extracellular vesicles, enhancing their potential applications in biotechnology and medicine.

Keywords: Extracellular vesicle, tip enhanced Raman spectroscopy, microscopy, characterization, drug delivery



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