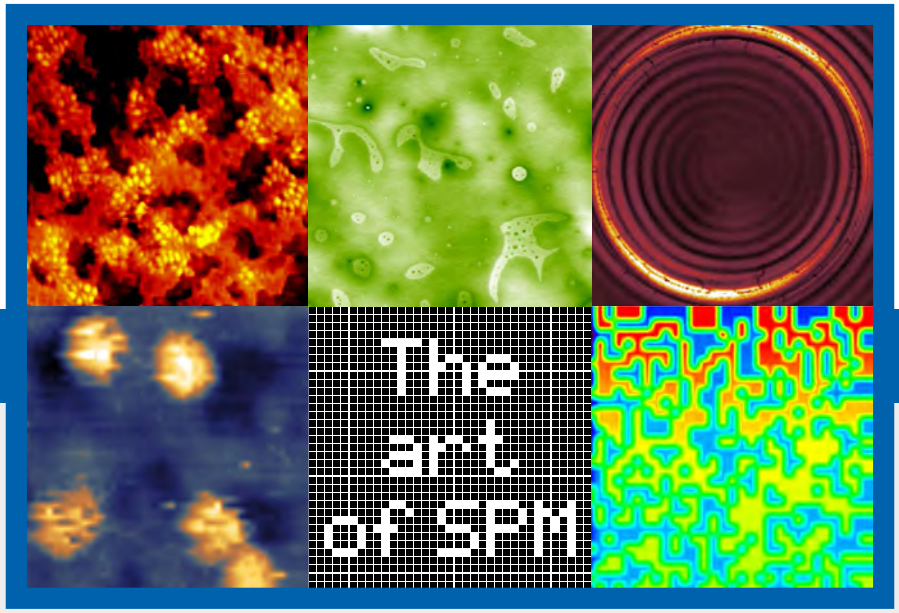
3/2025

BBPCAX 101 (8) 1083-1196 (1998)
ISSN 1611 – 9479

Bunsen-Magazin

Zeitschrift der Deutschen Bunsen-Gesellschaft
für physikalische Chemie



Main topic

Scanning probe microscopy

Editorial

Scanning probe microscopy –
a window into the nanoscale

- Experimental modelling of sustainable (photo)catalysts: Insights from combined *in-situ* scanning tunneling microscopy
- Application of AFM in chemical industry: Insights into materials nanostructure and performance
- AFM with copper-oxide tips: Imaging atoms in real space with elemental selectivity
- Aptamer-modified nanopipettes – towards nanoscale chemical mapping

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IMPRESSUM

Bunsen-Magazin

Heft 3 Jahrgang 27

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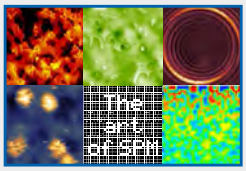
Zum Titelbild:
A curated collage of the six selected works from The Art of SPM - a special feature in this issue celebrating the interplay of scientific precision and visual elegance in scanning probe microscopy. These nanoscale images reveal the hidden beauty of atomic landscapes, where structure meets art.

Copyright: Cover by Florian Schneider, SPM-images by: top left: Lars Mohrhusen and Jeppe Lauritsen, top center: Kim Noelle Dreier, top right: Enrico Baù, Thorsten Gölz and Andreas Tittl, bottom left: Marco Moors and Kirill Monakhov, bottom right: Nelly Nembot and Marius Muhle.



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Das Bunsen-Magazin wurde auf recyceltem Papier gedruckt.

Noah Al-Shamery, Tobias Dickbreder, Florian Schneider

Scanning probe microscopy – a window into the nanoscale

Understanding matter at the nanoscale is one of the fundamental challenges in physical chemistry. The invention of scanning probe microscopy (SPM) at the end of the last century has enabled us to image the structure of surfaces and interfaces, revolutionizing our ability to explore atomic and molecular structures in real space with unprecedented resolution. This issue of the *Bunsen-Magazin* is dedicated to the history and latest advances in SPM techniques, covering techniques including and deriving from scanning tunneling microscopy (STM), atomic force microscopy (AFM), and electrochemical probe microscopy techniques. This issue includes cutting-edge research, methodological innovations, and insightful interviews with leading experts and pioneers in the field.

The SPM Editorial Team – LTR: Dr. Tobias Dickbreder, Noah Al-Shamery, Florian Schneider

The first section of this issue delves into recent advancements in STM techniques and their applications in catalysis, polymer characterization, and quantum science. Dr. Lars Mohrhusen provides insights into the experimental modeling of sustainable (photo)catalysts using *in-situ* STM. Every SPM experimentalist knows that sample preparation is crucial for successful SPM experiments, but can be very challenging. In this regard, Paola Mantegazza and Prof. Dr. Giovanni Costantini push the boundaries of polymer characterization with their electrospray deposition STM technique. Moreover, Dr. Andreas Walz and Dr. Tobias Dickbreder explore the controlled deposition of intact (bio)organic molecules to push the limits of systems explorable by SPM even further. Dr. Dmitriy Borodin provides insights into the role of SPM in quantum science, particularly in studying spins on surfaces. A special feature in this section is an interview with Prof. Dr. Andreas Heinrich, conducted by Noah Al-Shamery, discussing the past, present, and future of electron spin resonance STM, a technique that has opened new doors in spin manipulation and quantum research. Additionally, early career researcher Anna Juliana Kny contributes to the "your Publications: Communicated!" segment, showcasing her STM work on carpet growth of KCl on Ag (111).

The second section shifts focus to AFM, highlighting its diverse applications in industry and fundamental research. Dr. Svetlana Guriyanova, Sebastian Müller, and Dr. Bernhard von Vacano discuss the use of AFM in the chemical industry for analyzing materials at the nanoscale. PD Dr. Harry Mönig presents a study on AFM with copper-oxide tips, demonstrating elemental selectivity in atomic imaging on oxide surfaces. Dr. Tobias Dickbreder discusses a recent article by Prof. Dr. Franz J. Gießibl on the inception of AFM with qPlus sensors. Pascal Niko Rohrbeck, Dr. Yenal Yalcinkaya, and Prof. Dr. Stefan Weber give an introduction to Kelvin probe force microscopy, showcasing its potential as a nanoscale voltmeter. Dr. Ilka Hermes highlights the use of piezoresponse force microscopy for novel computing components. Antonia Köhler reflects on major breakthroughs in 3D atomic force microscopy at solid-liquid interfaces. Dr. Thorsten Gölz, Enrico Baù, and Prof. Dr. Andreas Tittl discuss how nanoscale optical imaging with tip-bound light can push past the diffraction limit, and Dr. Korbinian Kaltenecker presents a multimodal approach integrating scattering-type scanning near field optical microscopy, Raman, and photoluminescence for advanced material characterization.

The final section of this issue covers the latest developments in electrochemical scanning probe techniques. Sandra Hernández Escobar and Prof. Nako Nakatsuka introduce aptamer-modified nanopipettes, a promising approach for nanoscale chemical sensing. Moreover, Prof. Dr. Pat Unwin, the father of scanning electrochemical cell microscopy (SECCM), reflects on the evolution and applications of SECCM in an interview with Noah Al-Shamery. Bethanie Dean presents a unique perspective on how SPM-researchers spend their time during the scans, and Simon Sprengel and Prof. Dr. Dmitry Momotenko explore the versatility of scanning probe methods, from high-resolution imaging to nanoscale additive manufacturing.

Since SPM images are often not only of scientific interest but also highly aesthetic, this issue features the mini section "*The art of SPM*" highlighting Nature's beauty hidden within atomic and molecular structures. "*The art of SPM*" is a visual exploration of stunning nanoscale images captured using a variety of scanning probe techniques. A collage of all submissions can be seen on the front cover, while the individual images are distributed through the issue.

With this issue of the Bunsen-Magazin, we aim to provide an overview of the latest advancements in scanning probe microscopy, offering valuable insights for both early-career researchers and seasoned experts. Whether you are interested in STM, AFM, electrochemical probe techniques, or other variations of SPM, we hope this collection of articles deepens your understanding of these powerful techniques and inspires future research in the field!

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Lars Mohrhusen

Experimental modelling of sustainable (photo)catalysts: Insights from combined *in-situ* scanning tunneling microscopy

Materials and technologies for the energy transition and the sustainable fabrication of chemical products on the industrial scale have attracted increasing interest in recent years. This includes the usage of noncritical and sustainable feedstocks, such as the production of sustainable fuels for aviation or heavy transport from biomass via quick pyrolysis and subsequent hydrotreatments [1, 2]. Moreover, the tolerance to different reactant feeds and impurities, but also the product distribution are heavily influenced by the used catalyst. As another example, sustainable materials for chemical storage of solar energy are highly demanded. However, sustainability includes many aspects in the life cycle of (photo)catalytic processes, and life cycle assessments are of increasing importance. In particular, noble metal catalysts (such as platinum-group metals) suffer from limited abundance and high production footprints (e.g., in CO_2/global warming potential but also ecological and, for some, social or political risks), and thus have to be considered as critical materials. Such metal nanocatalysts often are prone to deactivation via segregation, poisoning, coking or agglomeration, which limits their lifetime. As a result, research towards novel, more sustainable catalytic materials is needed, and strategies for the replacement of noble metals have to be established.

As a possible alternative, we develop nanostructured hybrid materials consisting of well-defined organic or inorganic two-dimensional materials which shall act as replacements for (noble) metal nanoparticles on the surface of (semiconducting) oxides (funded by the BMBF within SINATRA-Su_2nCat-CO_2). As one example, we currently investigate combinations of (semi-metallic) single-layer sulfides (Fig. 1) on titanium dioxide surfaces as novel photocatalysts. Due to their stability, their optical properties (e.g. plasmonic properties, visible light absorption) and lastly due to the robustness against CO poisoning, transition metal nitrides and carbides represent other candidates under investigation. In addition to inorganic-inorganic material combinations, organic 2D materials such as conjugated polymers may be used on oxides surfaces. Similar to graphene, these materials absorb visible light, are relatively robust and can be understood as a highly tailorable platform, for example by chemical functionalization or the controlled introduction of defects. Scanning probe microscopy is an essential tool to understand these materials.

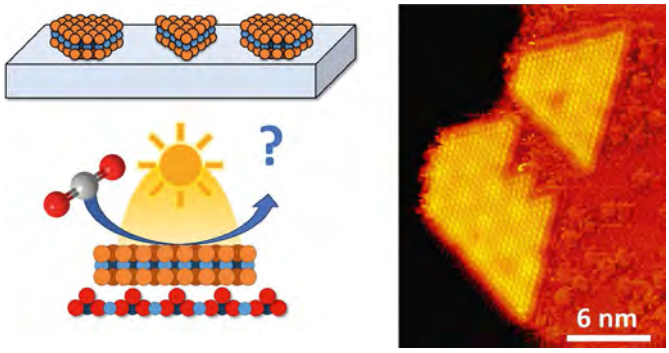

Fig. 1: Single layer titanium sulfide nanoparticles for (photo)catalytic applications. Left: sketch to illustrate the few nm sized TiS_2 particles. Such nanoclusters are investigated as replacements for noble metal nanoparticles in future (photo)catalysts, e.g. for greenhouse gas utilization. Right: atomically resolved STM image of two TiS_2 nanoparticles on Au(111) in UHV (as a model system) [3]. Such model studies allow to identify, locate and probe possible active sites such as corners, edges and individual defects.

Experimental modelling: Insights from a multimethodic approach

The initial design and subsequent material optimization follows a rational design strategy: We aim to establish an atomic level structure-property understanding of the materials and processes on well-defined model systems with different levels of reduced complexity. These findings shall then gradually be transferred to scalable materials and conditions, to eventually enable a systematic material design. For this purpose, well-defined model systems have to be established, usually employing single-crystal surfaces on which defined nanomaterials are fabricated. However, even on the model systems, the catalytically relevant processes often span orders of magnitude in temporal and spatial dimensions. To identify the active phase and gain a comprehensive picture of the relevant processes, it is essential to combine different surface sensitive methods to balance their individual advantages and disadvantages (Fig. 2). For example, several spectroscopy tools such as X-ray spectroscopies (XPS and XAS, EXAFS) or vibrational spectroscopies (FTIRRAS, Raman, HREELS, ...) are highly chemically sensitive and allow to (semi-)quantitatively distinguish different elements and their oxidation states or chemical environment [4, 5]. On the molec-

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DOI-Nr.: 10.26125/szsv-2q91

ular level, even smaller adsorbate-substrate or intermolecular interactions can be detected, but these methods lack relevant spatial/structural resolution (typically few hundred microns at best) and provide only an averaged view of the sampled surface [6]. Similar applies for the evaluation of reactivity and product distribution, most often based on mass spectrometry [7]. Diffraction-based techniques (LEED, SXRD) can partially complement with structural information for ordered and crystalline materials, yet they still produce mainly area-averaged results. Thus, combination with atomic-level microscopy is a promising approach. The latter methods gain structural information even on unordered materials down to the atomic level, and consequently also allow to study formation, location and behavior of individual defects, that are chemically relevant, but otherwise would be hidden in the averaged spectra or patterns [8, 9]. Unfortunately, the interpretation of scanning probe microscopy can be quite complex and is often not intuitive. For instance, scanning tunneling microscopy (STM) images may be challenging to interprete, as they reflect a combination of both topography and electronic structure (or more precisely, the local density of filled or empty states at the given scanning potential) [10]. Thus, combining STM with high resolution elemental and vibrational spectroscopy is a powerful strategy, leveraging the strength of both techniques. Additionally, computational simulations can aid for example in STM contrast interpretation and vibrational spectra analysis, at least for well-defined systems. Traditionally, most of such studies were performed for single crystal surfaces under ultrahigh vacuum (UHV) conditions, in virtue of both, the need for long inelastic mean free path for electrons (XPS, HREELS, LEED) and the need to prepare and conserve clean surfaces [10, 11]. These so-called experimental model studies can gain very deep insights into elementary reaction steps, key intermediates or the role of promotors. However, the results need to be transferred from UHV (~10^{-10} mbar) to technical conditions (~10^{5} mbar; often referred to as the pressure gap), and significant differences between model studies and real-world applications frequently emerge.

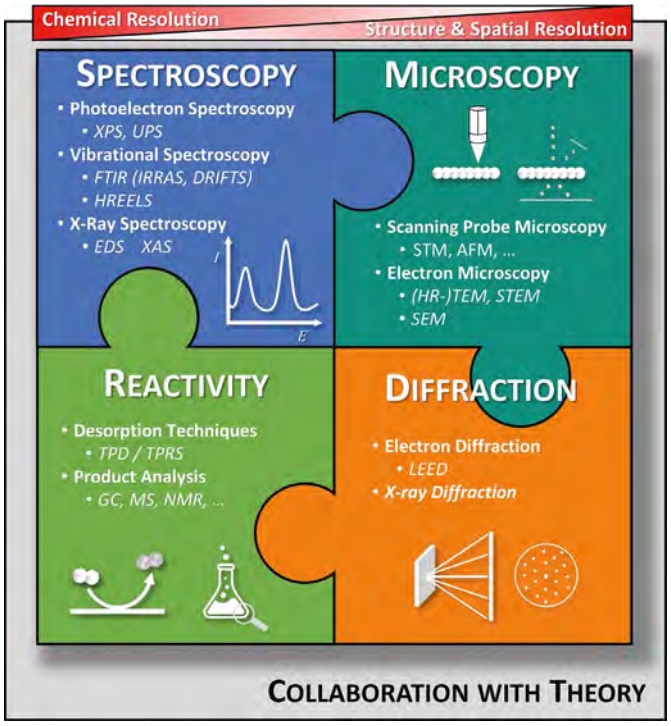

Fig. 2: Illustration on the multimethodic approach for model studies in catalyst design. The methods are placed by their chemical and spatial resolution. Interestingly, especially combinations of high-level microscopy with elemental and vibrational spectroscopy are a specifically powerful combination, as the advantages and disadvantages are balanced. This is especially the case for scanning tunneling microscopy (STM), because the interpretation of STM images can be challenging due to contributions of both, the topography and the electronic structure.

Nevertheless, STM is a technique that allows to probe flat sample surfaces *in situ*, i.e., in reactive gas atmospheres at catalytically relevant temperatures. While vacuum conditions are not specifically required, in practice the application of high-resolution STM under typical thermal catalytic conditions (few bars, >450 K) can be challenging, as outlined by the following examples. Because flat surfaces are a prerequisite for STM, the setups are commonly integrated into UHV chambers that serve for sample preparation. Thus, a leak tight sealing is necessary, and the sealed cell then must be mechanically decoupled from the surroundings for vibrational isolation. Gasses have to be introduced through capillaries to prevent mechanical interference by solid tubing, and in general vibrations introduced by the gas stream, especially for higher flow and pressures, have to be avoided. Chemical reactions with any part of the instrumentation and foremost the metallic scanning tip, such as oxidation for W tips, or hydrogenation reactions triggered by Pt tips, can become serious complications and even lead to tip-induced sample changes. Finally, due to the ultimate surface sensitivity of STM, which usually is of great advantage, even traces of contaminants in the gas feed (ppm level and lower) may cause strong surface contamination and render atomic-resolution imaging impossible. Thus, high efforts must be taken to realize ultra-pure gas supplies. All of this realistically limits the accessible experimental pressure range. On the other hand, thermal drift becomes an increasing problem when the sample is heated in the flow of (cold) feed gas, which leads to relevant thermal gradients in the setups and nonconstant thermal profiles. Lastly, in conventional STM under UHV conditions, low sample temperatures are a relevant experimental tool to decelerate surface dynamics and allow direct imaging of, for example, adsorbate diffusion [12–15] or limit overgrowth phenomena such as SMSI (strong metal support interaction). For *in-situ* experiments, this is often impractical if not impossible, as either surface contamination worsens or the desired reaction is not realized because the necessary activation energy is not reached to light off the catalytic turnover. Consequently, elevated temperatures often lead to fast dynamics at the surfaces resulting in blurry images. Even though this exemplary list of challenges appears huge on the first view, there are already custom-built and even commercial technical realizations that allow *in-situ* STM experiments in reactive gas atmospheres [16–18]. Especially activation and deactivation processes, that often include surface restructuring and segregation or agglomeration processes, have been investigated under operando conditions, along with the identification of the structure of the active phase and adsorption sites. For example, such studies have contributed to the understanding of CO and CO_2 conversion on copper surfaces [19, 20], the oxidation of noble metal surfaces [21, 22], the hydrodesulphurization (HDS) of organic molecules on MoS_2 catalysts [23, 24] and the encapsulation of noble metal particles on reduceable oxides [25].

It is evident, that operando STM has made it into application for thermal catalysis in a number of laboratories worldwide. But what could be potential future directions for operando STM in reactive gas atmospheres, especially from the viewpoint of catalyst design? While pushing the boundaries of temporal and spatial resolution is a constant activity, widening the experimentally accessible thermal and pressure window surely would be beneficial to realize actual technical conditions. Surprisingly, one of the white spots in *in-situ* STM is the imaging of photocatalysts in gas atmospheres under working conditions. While there are several pre-post illumination reports from UHV conditions [11], none of the commercially available AP-STM instruments allows illumination of the sample surface in the reactive atmosphere. Especially the mild reaction conditions (often room temperature) render such experiments attractive, along with the fact that light is a widely contaminant-free reactant (except for photoinduced degassing of parts of the instrumentation). However, photoinduced charge on semiconductors could be a first obstacle in simple imaging, but in reverse a microscopic map of the photogenerated potential would be an important descriptor for the local photocatalytic performance, although STM is not fast enough to catch individual exciton lifetimes without special efforts. Similarly, it could be possible to map plasmonic excitations [26, 27]. Ongoing conversion and product formation (and the connected dynamics) may additionally blur the images, which has been a problem in thermal catalysis as well. Finally, coupling of spectroscopic tools with scanning probe instrumentation is a relevant field of research, and especially tip-enhanced Raman spectroscopy has been realized [27–29]. Enabling such a powerful combination for reactive gas atmospheres (under thermal or photochemical conditions) would have a large impact and boost the understanding especially for the conversion of organic molecules on model catalysts.

Overall, scanning tunneling microscopy remains a fascinating technique, that is often nonintuitive and requires substantial efforts in experiment and data evaluation. But when combined with complementing methods it yields highly impactful information with access to the desired comprehensive atomic-level picture of the activation, deactivation and active state of catalytic materials under operando conditions, finally allowing for novel, tailor-made materials from the derived design principles. Scanning tunneling microscopy is especially appropriate to study two- and low-dimensional materials and defects therein, which eventually could replace critical materials far beyond sustainable catalysis, for example in corrosion protections, electronic devices and other technologies, and thus operando STM should become, if not remain part, of the standard catalogue of operando methods not only in catalysis research.

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Dr. Lars Mohrhusen

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Lars Mohrhusen studied chemistry at the Carl von Ossietzky University of Oldenburg between 2011 and 2016. He completed his PhD (2017–2021) on the topic of point defects in titanium dioxide in bifunctional catalysts and their influence on (photo)catalysis, also at the Carl von Ossietzky University of Oldenburg under the supervision of Prof. K. Al-Shamery with a doctoral scholarship of the German Academic Scholarship Foundation. Subsequently, he undertook a postdoctoral stay (2021–2022) at Harvard University, Cambridge, with Professors C. Friend and R. J. Madix, where he focused on model studies of Pd-based alloy catalysts at the DOE Energy Research Frontier Center (EFRC) "Integrated Mesoscale Architectures for Sustainable Catalysis" (IMASC). This was followed by another postdoctoral stay (2022–2024) at Aarhus University, Denmark, with Prof. J. Lauritsen, characterizing 2D MoS_2 nanoparticles for the hydrodeoxygenation of bio-oils using (operando) STM and XPS. In 2024, he returned to Germany to the Carl von Ossietzky University of Oldenburg to lead an independent research group and the BMBF-funded project "Su_2nCat-CO_2." He was awarded a number of prizes, including a prize for outstanding doctoral work by the Carl von Ossietzky University of Oldenburg, a special mention by the Gian-Paolo-Brivio Award and the Ewald-Wicke prize, jointly conferred by the Bunsen Society and the Ewald-Wicke foundation.

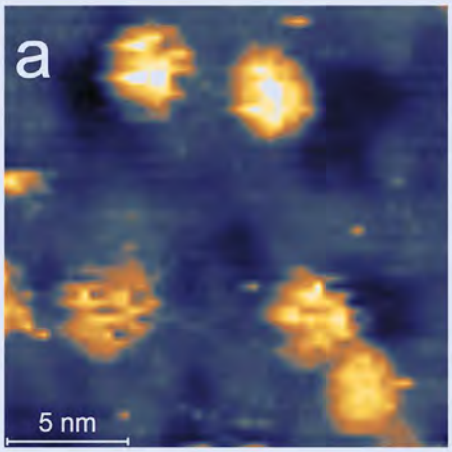
The art of SPM

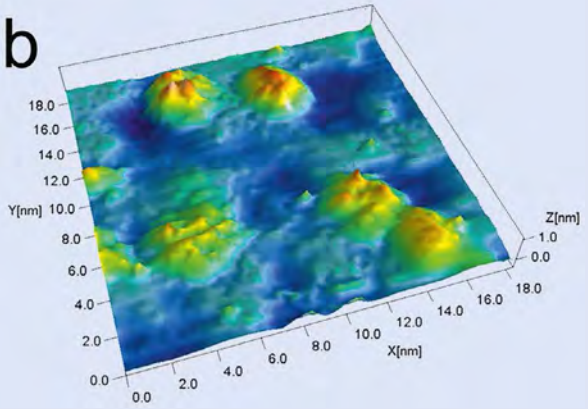
Artist: **Dr. Marco Moors & Dr. Kirill Monakhov – Switchable Molecularly Functionalized Surfaces Group (Leibniz Institute of Surface Engineering (IOM))**

SPM technique: **Scanning tunneling microscopy (STM) (U_B = 1.0 V; I_T = 10 pA)**

Investigated System: **Several groups of single ($n$$Bu_4N)_2[V_6O_{13}((OCH_2)_3CCH_2OH)_2]$ polyoxometalates (MeCN, $c = 10^{-4}$ mol L^{-1}) immobilized on the Au(111) surface at room temperature, showcasing a significant intermolecular interaction of two POMS resembling the conjugation route of genetic information exchange between cells of bacteria.**

Title: "***Life-inspired crosstalk of surface-confined polyoxometalates***"





Paola Mantegazza, Giovanni Costantini

ESD-STM technique pushes the quantitative characterisation of conjugated polymers beyond traditional boundaries

Conjugated polymers are carbon-based macromolecules that have attracted significant attention for their unique ability to combine electronic semiconducting properties essential for advanced (opto)electronic, energy and sensing applications with the mechanical flexibility, low weight, ease of processing and cost-effectiveness characteristic of plastic materials. Their properties can be chemically tailored to specific functions, making conjugated polymers highly promising candidates for a wide range of applications including soft electronics, wearable sensors, thermoelectrics, biosensors and neuromorphic computing.

Despite their great potential, a major challenge in conjugated polymer research stems from the limitations of available structural characterisation techniques. These materials are inherently heterogeneous, polydisperse and prone to aggregation, imposing significant restrictions on conventional analytical methods. As a result, obtaining reliable information on their precise backbone sequence, molecular weight and assembly configurations remains challenging. Traditional techniques commonly used in polymer science, such as gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), mass spectrometry and X-ray diffraction, often struggle to provide a comprehensive and accurate characterisation of conjugated polymers.

GPC, commonly used to determine molecular weight distributions, tends to overestimate values for conjugated polymers due to calibration challenges and aggregation effects. NMR, often employed for sequencing and molecular weight determination, is generally limited to short conjugated polymers, as longer ones exhibit low solubility and cause signal broadening, preventing quantitative analysis. Matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) is the preferred mass spectrometry technique, as other methods fail to generate gas-phase ions from conjugated polymers, but it tends to overrepresent low-mass fractions and is inherently not quantitative. For structural characterisation of polymeric thin films, grazing incidence wide angle X-ray scattering (GIWAXS) can provide information on crystallinity but only in ordered regions, making it less effective for semi-crystalline or amorphous materials, which constitute the majority of conjugated polymers.

Beyond traditional methods, microscopy approaches [1–7] have begun to be explored to overcome the limitations of the techniques mentioned above, which, apart from the specific constraints for conjugated polymers, primarily provide averaged quantities that are insufficient for describing such heterogeneous systems. Among various microscopy techniques, scanning probe microscopy (SPM) in general can achieve extremely high resolution on 2D systems, offering precise molecular-scale insights into the analysed materials at the local level, regardless of the sample's degree of large-range order.

In particular, scanning tunnelling microscopy (STM), which exploits the tunnelling current between a metallic tip and the sample, has become a well-established technique in surface science for atomic-level imaging of conductive surfaces and small molecules adsorbed on them. However, achieving sub-molecular resolution with STM typically requires ultra-high vacuum (UHV) conditions to prevent contamination from airborne molecules and to enable cooling to cryogenic temperatures, thereby reducing thermal agitation and facilitating scanning operations. For this reason, UHV-STM is commonly limited to the study of pristine solid surfaces or small molecules that can be thermally sublimated onto substrates in UHV, whereas macromolecules, being generally thermolabile and non-volatile, pose significant challenges.

The use of UHV-STM for imaging conjugated polymers was championed by the Costantini Group by employing an electrospray deposition (ESD) system, which enables the intact deposition of macromolecules onto substrate surfaces in UHV conditions [8–10]. Originally conceived at the University of Nottingham in 2007 [11], this apparatus couples an ambient pressure spraying system with a differential pumping vacuum setup. A polymer solution is delivered via a syringe, generating a fine mist of microdroplets as it passes through a needle. A high voltage (generally between 1-2 kV) is applied between the emitter needle and the entrance of the first stage of the pumping system, propelling the droplets into the vacuum manifold, where a beam is defined by the small apertures separating successive vacuum stages. As they traverse these stages, the droplets shrink, ultimately depositing onto an atomically flat and clean metallic single-crystal substrate at pressures of 10^{-7} to 10^{-8} mbar (Figure 1). There, the remaining solvent –

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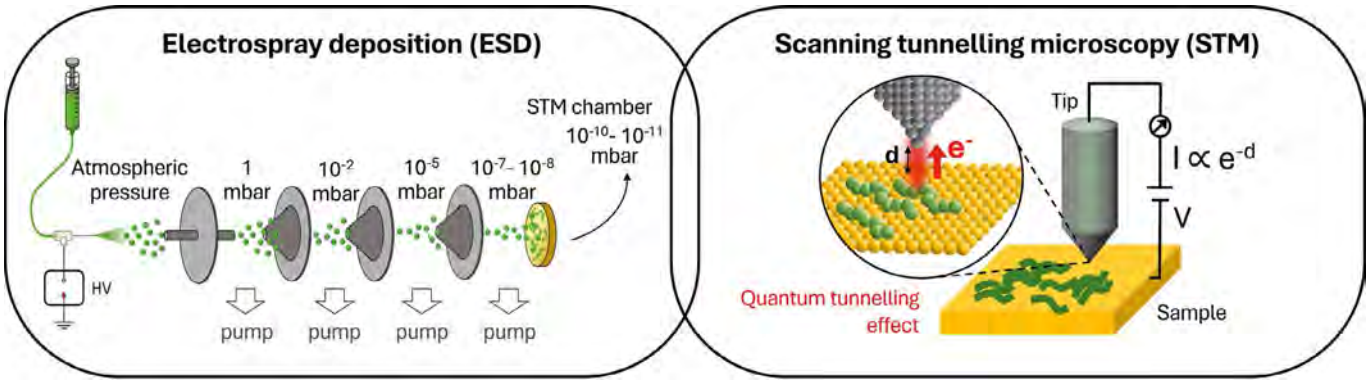

Fig. 1: Scheme of the experimental setup and working principle of electrospray deposition (left) and scanning tunnelling microscopy (right).

typically a volatile organic solvent – evaporates, leaving behind the polymer. The molecular coverage can be precisely regulated by controlling the exposure of the substrate to the ESD beam, with deposition conditions typically chosen to achieve monolayer coverage, as this is optimal for STM imaging.

The straightforward design of this ESD apparatus makes it particularly easy to use, especially when compared to more complex alternatives such as electrospray ion beam deposition (ESIBD) [12]. Moreover, since most molecules reach the substrate while still solvated in microdroplets, this method offers several key advantages, making it particularly well-suited for the quantitative analysis of conjugated polymers.

In fact, while conjugated polymers cannot be deposited by ESIBD because the electrospray process does not ionise them into individual gas-phase molecules, they can still be transported onto surfaces by their carrying microdroplets, allowing their deposition via ESD. Additionally, because the deposition process involves a beam of droplets rather than individual molecules, it is highly non-selective, ensuring that the molecular composition of the sample adsorbed on the surface closely reflects that of the original solution, preserving characteristics such as molecular weight and chemical structure. Furthermore, the rapid solvent evaporation that drives the surface polymer assembly in ESD is analogous to the formation of conjugated polymer films via drop-casting or spin-coating. As a result, the 2D polymer arrangements accessible to STM exhibit significant structural similarities to the microstructure of 3D thin films commonly used in devices.

The main advantage of combining ESD with UHV-STM is that STM imaging gives access to both qualitative and quantitative insights into the structure of conjugated polymers with a level of detail unattainable by any other technique. A thorough analysis of a statistically relevant set of STM images is the key for obtaining reliable and accurate quantitative information on their chemical sequence [8, 13–15], length [10] and local ordering [9, 16–18].

In particular, high-resolution STM images can be fitted with optimised molecular models, enabling precise determination of the sequence of monomers or co-monomers along polymer backbones, including the identification of polymerisation defects and variations in subunit conformations. Figure 2a displays an example of this analysis, performed on the benchmark conjugated polymer pgBTTT, which consists of an alternating sequence of thienotiophenes (TT) and glycolated bithiophenes (gBT) units. In this case, the analysis of STM images revealed different types of homocoupling defects, such as TT-TT and gBT-gBT linkages, with their frequencies quantitatively determined.

On the other hand, large-scale images provide insights into the mass distribution of the polymers, as well as the interactions between different polymer chains, their flexibility and the patterns they form when assembling on the surface. Figure 2b presents an example of the mass distribution analysis, showing the number-average molar mass, M_n, the weight-average molar mass, M_w, and the degree of polymerisation, DP_n of pgBTTT, determined by measuring the length profiles of numerous polymer chains. Figure 2c illustrates the various assembly patterns formed in high-density regions of the sample, along with the interaction modes of the glycolated side chains, which play a key role in mediating this organisation.

Although, in principle, the assembly of polymers in the bulk may differ from their arrangement in two dimensions, the primary constraint imposed by the substrate in 2D assembly is that the molecules lie flat on the surface, without significantly affecting the intermolecular interactions that govern in-plane organisation. For this reason, and given the similarity in molecular assembly driven by rapid solvent evaporation, it is reasonable to expect – an expectation experimentally confirmed through direct comparisons between STM results and GIWAXS measurements – that the microstructure of 2D monolayers of adsorbed conjugated polymers shares several similarities with that of the same materials in bulk-like films.

In summary, ESD-STM measurements of conjugated polymers uniquely provide quantitative evidence of their chemical structure and mass distribution, allowing for the validation of hypotheses on reaction processes by directly revealing the actual products. At the same time, they contribute to understanding the microstructure of these materials in thin films designed for applications.

The development of high-performance devices based on conjugated polymers still faces several challenges. Beyond issues related to batch-to-batch variability, a key difficulty lies in establishing a reliable structure-function relationship for these mate-

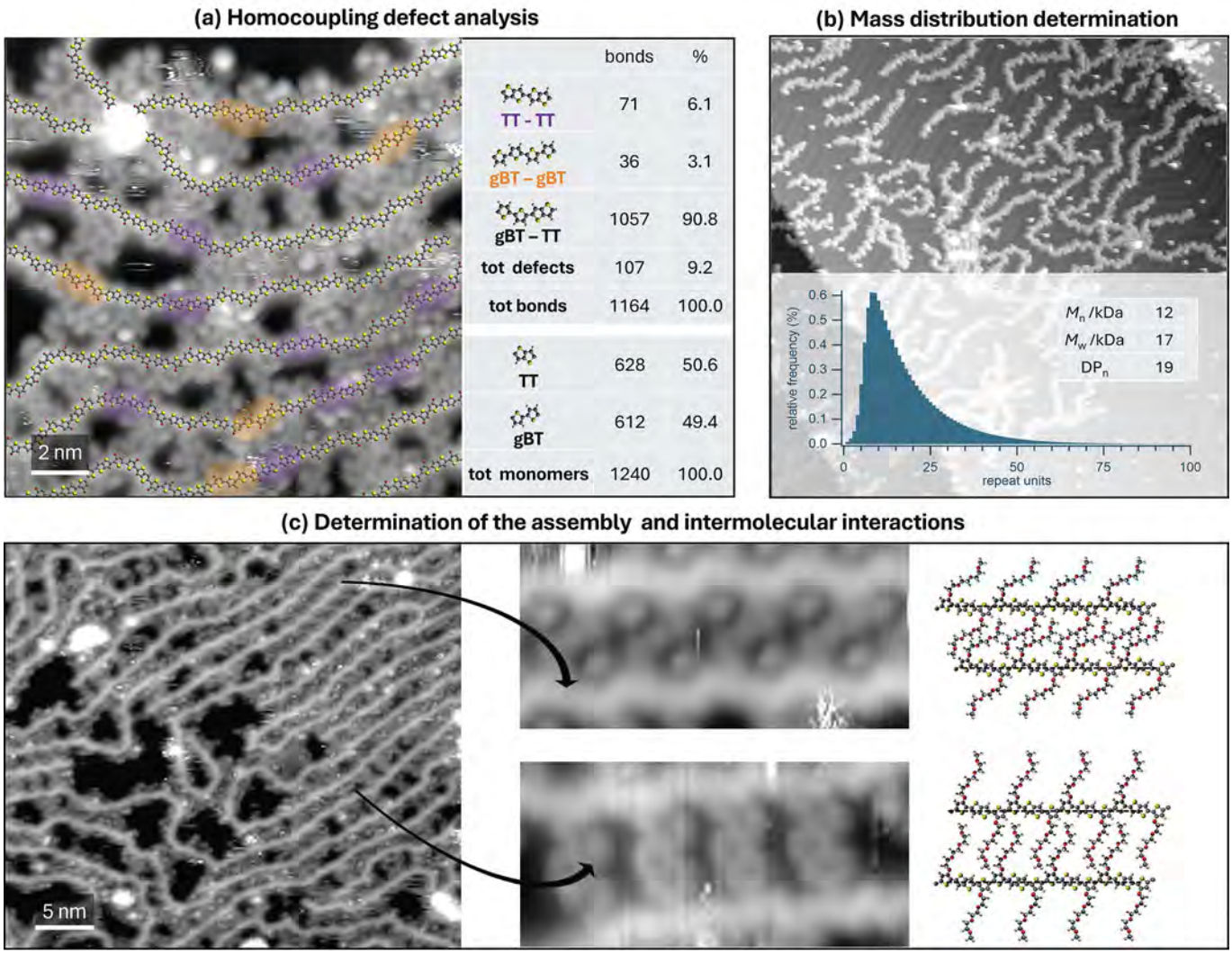

Fig. 2: Examples of information extracted from STM images for the polymer pgBTTT [19]: (a) statistical analysis of defects, (b) experimental mass distribution and key associated parameters, (c) STM image of a high-density region highlighting two distinct assembly types (shown in close-up images). The corresponding molecular models are displayed on the right.

rials. Systematic and rational design for practical applications requires a fully integrated feedback loop between synthetic protocols, analytical characterisation and device performance. Currently, this central and crucial step remains difficult due to the inherent limitations of traditional analytical techniques for conjugated polymers. In this context, we envision that advancing ESD-STM as a powerful analytical tool for structural characterisation could significantly enhance this feedback loop, ultimately accelerating research and progress in the field.

Future developments for this technique will involve both experimental enhancements and analytical advances. One of the key strengths of STM is its ability to investigate not only the morphological characteristics of a surface but also its electronic properties with exceptional spatial resolution. In particular, applying scanning tunnelling spectroscopy (STS) and the related molecular orbital mapping technique (dI/dV imaging) to ESD-deposited conjugated polymers could provide critical insights into their electronic structure near the Fermi level, including the HOMO-LUMO gap and the spatial distribution of molecular orbitals, with sub-molecular precision. Such information would be fundamental for understanding how charge transport properties depend on local features such as polymerisation defects, molecular conformations, inter-polymer interactions and molecular doping.

A further advancement would be the use of non-contact atomic force microscopy (nc-AFM) as the imaging technique, which would significantly increase spatial resolution, as this method has been shown to resolve the position of individual atoms and even chemical bonds within single molecules [20, 21].

However, to establish ESD-STM as a widely adopted and mainstream analytical tool, automation must be implemented for both image acquisition and analysis. Integrating machine learning algorithms into measurement optimisation, combined with advanced image recognition tools for the statistical analysis of acquired images, would streamline and significantly accelerate ESD-STM workflows. This transformation would allow ESD-STM to evolve from an exciting yet still rather specialised technique into a fast, efficient and reliable method for the molecular-scale characterisation of conjugated polymers.

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Paola Mantegazza, M. Sc.

Paola studied physics at the University of Milan (B. Sc.) and at the University of Trieste (M. Sc.). During her studies, she gained experience with synchrotron-based techniques and other surface science characterisation methods. In 2022, she began her PhD in the Costantini Group at the University of Birmingham, UK. Her current project focuses on the molecular imaging of various types of conjugated polymers and other organic macromolecules using electrospray deposition (ESD) combined with scanning tunnelling microscopy (STM).

Prof. Giovanni Costantini

Prof. Giovanni Costantini is chair in physical chemistry at the University of Birmingham, where he leads the Nanoscience@Surfaces group. His research focuses on fundamental interactions and properties of functional molecules on solid surfaces, as well as the development of advanced characterisation methods at the molecular and atomic scale. He studied physics at the University of Genova, obtaining a PhD in surface science in 2000. He then joined the Max Planck Institute for Solid State Research in Stuttgart as a group leader in the Nanoscience Department. In 2007, he became assistant professor in physical chemistry at the University of Warwick, where he was promoted to associate professor in 2010 and full professor in 2016. In 2022, he joined the School of Chemistry at the University of Birmingham.

Andreas Walz, Tobias Dickbreder

Soft-landing (bio)organic molecules for SPM

Organic molecules for scanning probe microscopy experiments in ultrahigh vacuum are commonly deposited via thermal evaporation, which crucially depends on the molecules' vapor pressure upon heating and thermal stability. An interesting alternative, especially for thermally unstable and biological molecules, is soft landing molecules via controlled ion beam deposition (CIBD). In this interview Andreas Walz from the startup company pureions, which develops commercial CIBD devices, discusses with Tobias Dickbreder the capabilities and challenges of controlled ion beam deposition. Moreover, they talk about the transition from a research project to a startup company.

What is controlled ion beam deposition?

Controlled ion beam deposition is a method to gently coat surfaces with ions of organic molecules in an ultra-pure and highly controlled manner. It can be considered a variation of mass spectrometry, however, with a significant modification: CIBD is a versatile and powerful preparative tool, that also bears a mass spectrometer function for both - analytical and selection tasks.

The functionality of the CIBD device is outlined as follows: The device performs four primary steps namely ionization, purification, selection and deposition: Initially, ions are generated by electrospray ionization (ESI) from a fluid containing dissolved organic molecules. These ions are transferred towards cascading vacuum chambers, where unwanted neutral contaminants are removed (solvent, particles from gas atmosphere or other neutral impurities). Subsequently, the pre-cleaned ion beam enters a built-in mass spectrometer, where the target ions undergo fine-selection and enrichment while further remaining ions are removed including fragments, debris, aggregates and synthesis residues. The mass spectrometer employs a mass window to ensure the transmission of exclusively ions with the correct mass (mass-to-charge ratio, to be precise) of the target molecules. Finally, the resulting ion beam, which is distinguished by its homogeneous composition, is delicately deposited on a solid surface (soft-landing). In this juncture, the molecules have the potential to self-assemble into layers or to engage in other configurations. They are accessible to common analytical surface science tools such as SPM.

Ions as charged particles are efficiently guided by alternating electrical radio frequency (RF) fields which are applied via self-developed ion guides during the entire process. Three vacuum pumps ensure a significant pressure drop from ambient (ESI stage) to ultrahigh vacuum (mass spectrometer and landing stage). Both, efficient ion guides and a very low final pressure are key for the high purity that is achieved by CIBD.

In simple words, we build a molecular printer for preparing atomically thin layers of mainly organic molecules under vacuum conditions. Our "ink" is the molecule of interest dissolved in a solvent.

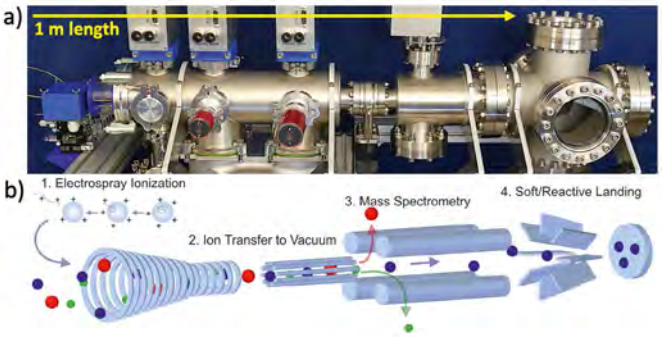

Fig. 1: a) Photograph of the CIBD instrument (left) developed by pureions attached to a small ultrahigh vacuum chamber (right). b) Principle and schematic of a CIBD setup. Shown are the four main steps of CIBD: electrospray ionization of the ions (1), ion transfer into vacuum (2), mass selection of the ions (3) and soft/reactive landing on the sample surface (4). Copyright © 2025 pureions GmbH.

How can CIBD be combined with scanning probe microscopy?

The result of a CIBD process is a layer on a sample surface. This sample can be transferred to a microscope (SPM) either via a vacuum suitcase, or more directly when the system is connected in-line with an SPM. SPM imaging together with mass spectra taken at deposition delivers a quite holistic picture of the objects. Scientist are interested in a number of effects on the surfaces: The soft-landing technique involves the utilization of minimal kinetic energy during the landing process, effectively serving as a parachute for the ions. Another aspect of CIBD is the dose control. Each landing ion induces a charge into the substrate that can be measured as an electric current. The time integral of the current tells you precisely how many ions already landed on the substrate. Typical doses range from sub monolayers to few multilayers. The biggest advantage of CIBD is its flexibility in application. It is possible to process a vast range of molecules that is not accessible via thermal evaporation in vacuum. Additionally, you have a very high degree of control and quite precise information on your layers before any further analysis step.

Which molecules can be deposited with controlled ion beam deposition? Are there limits for instance in terms of stability or size of the molecules?

That is a very good question. First, CIBD enables us to apply all our surface-science and nanotech analysis tools to very clean

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layers of fragile, reactive and very large, including bio relevant molecules. Examples range from thermolabile porphyrin over graphene nanoribbons up to natively folded proteins or micrometer long DNA strands. With respect to limitations: There might be limits to the size and stability of the molecules, as always, but we did not really find them yet. For electrospray ionization, there are many fascinating publications from mass spectrometry showing that you can bring huge molecules such as proteins and even virus assemblies, or at least parts of them, into the ionic gas phase while they still stay native or native-like [1]. This means that they keep their conformation and I would consider a natively folded protein already rather fragile. There are studies that show that you can also land those proteins and investigate them afterwards with electron microscopy and similar techniques [2]. When we asked ourselves the same question, we started to deposit DNA of different sizes because it is readily available in all kinds of lengths and masses. We stopped with pUC19 [3], which is a circular plasmid DNA of roughly 2 MDa in mass and 1 µm circumference, because our scanning tunneling microscope just had a scan range of 2 µm x 2 µm. So even if we measured the whole scan range for one picture, we just saw a few of these huge rings, rods and rackets. We reached the physical limit of the scanning probe instrument before maybe reaching the actual limit of what we can ionize and land. This is where we stopped in terms of size, but we also tried to deposit a variety of molecules with different chemistry. In addition to biologically relevant organic molecules, we also deposited, for example, graphene nanoribbons [4]. These need very different treatment in terms of solvent environment, which was almost non-aqueous in contrast to biological molecules, and it also worked out. There seems to be always a way – maybe after a while of method development – to bring molecules to the surface to finally look at it with the scanning probe microscope. The question is how to dissolve, spray and handle the molecules correctly.

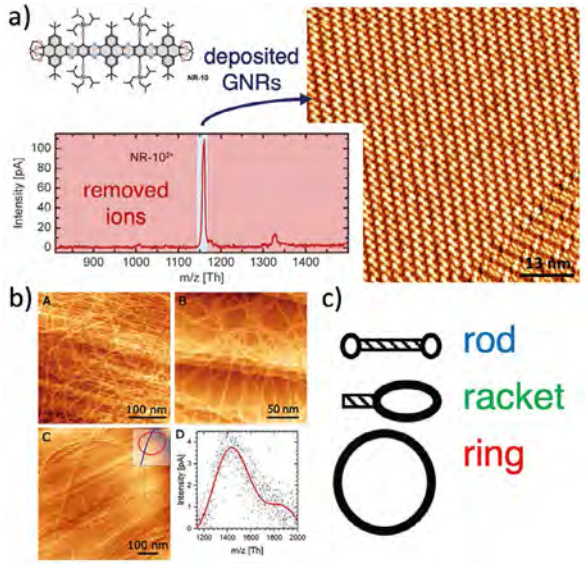

Fig. 2: Examples of organic and biological molecules deposited on surfaces with CIBD and imaged with scanning tunneling microscopy. a) Graphene nanoribbons on Ag (111). Adapted by Andreas Walz from Ran et al. [4]. Copyright © 2022 The Authors. Angewandte Chemie International Edition under CC-BY. b) Plasmid DNA pUC19 on Ag (111) reproduced from [3]. Copyright © 2022 The Authors. Published by American Chemical Society under CC-BY-NC-ND 4.0. c) Shapes of the DNA molecules shown in b. Copyright © 2025 Annette Hüttig (pureions GmbH).

How difficult is it to deposit a new molecule onto the surface safely?

It always depends on the molecule. If you already sprayed a similar molecule or one that dissolves in a very similar environment and behaves rather similar, it is likely not too difficult because you can move forward from what you already know. But if you start with something that is completely unknown, the first thing is to ask your chemist or wherever you got your molecules from "In which solvent does it dissolve?". The solvent you use for your electrospray is more or less given by the molecule. However, not each solvent, which is good for dissolving the molecules, is also good for spraying. The next question is "Do you spray it as positively or negatively charged ions?". It is feasible to implement a duality of polarity; however, it is imperative to assess which polarity proves more efficacious – or is it applicable – in the specific instance under consideration. In most of the cases that is quite obvious from the molecular structure. DNA, for example, has a phosphate backbone, so it is already negatively charged in water. Hence, it is meaningful to try spraying with negative polarity first. Once you figured this out, the trickiest part is to get it sprayed with a high intensity. In a normal analytical mass spectrometer, you do not need high intensities. You are happy when you find the molecules you want, but we need a certain intensity to decorate the surface within a reasonable amount of time. The intensity of course depends on how you spray the molecule: What's the pH value of the solvent that you use? Do you add proton acceptors or donors or other additives to increase conductivity, do you have sufficient volatility and a suitable surface tension? You have to ask yourself these kinds of questions once spraying a new molecule, but the parameter space is already limited by the molecule that you want to spray.

How good is your control of the charge state and kinetic energy of the molecules upon deposition?

Before the landing, the charge state is almost perfectly known from your mass spectrum. The mass spectrum does not give you the mass, it gives you the mass over charge ratio. Since you typically know the mass of the molecule that you want to deposit, you also know the charge state quite precisely. The coverage of your molecule on the surface is then also very well predictable from the deposited charge. You measure the electric current on the sample that you decorate and then, from the integral of the current over the time you get the charge and coverage of your sample. The question is what the charge state of your molecule on the surface is. Does it just induce a mirror charge into the surface and is it still charged on the surface or does it completely discharge? This is actually a very interesting question, and I am sure that there are different things that can happen. Some of the molecules will remain an ion on the surface – at least for some time – and some won't. They will lose their charge instantly and become neutral again. I think both cases are possible and it strongly depends on what you land, where you land it as well as the other conditions like the temperature.

Can you use charged ion beam deposition to deposit molecules on insulating surfaces or is this prevented by surface charging?

That's a very good point. If you land on a bulk insulator in the sense of a thick layer and not just a few monolayers of insulator, you will start to build up a retarding field once you start landing ions. Similar effects may appear in case of a molecule that stays an ion after landing on a surface. This retarding field will probably build up rather quickly until no ion will land anymore. The question is what the potential of the surface is and how to control it. One of the solutions might be alternating deposition of positively and negatively charged ions [5]. When switching polarities back and forth with a certain frequency, the charge balances out. With this it seems possible to land full monolayers or thicker layers of charged species on the surface and most probably also to land on bulk insulators.

In addition to these scientific questions, I also have some questions on the development and commercialization of your setup. Your controlled ion beam deposition setup started as a research project at the TU Munich before it transitioned into a business idea. When did you realize that your idea can be commercialized and how did it develop into a startup company?

The vision to commercialize this machine did not come from one moment to the next, it was more of a process. First commercialization thoughts can be dated back to 2016 already, when two of us consulted the TU Munich's founder's bureau for the first time for advice. Later, when we had the machine running as a demonstrator at the TU Munich, we always got very good response from other scientists when they visited us, and when we meet them on conferences. We realized that there is quite a bit of interest in the community to get such a deposition tool for conducting all the experiments that do not work for example with thermal evaporation. The idea to commercialize the machine did really manifest at this point and then we asked ourselves questions like: Is it possible to build these machines for a reasonable price and how long does it take to develop such a machine? What is the size of the market? After some time, we then got EXIST funding, which is a funding dedicated for technologies that were developed at universities to be commercialized. With this funding the specific activity started to build up a startup and to develop this demonstrator further to a commercially available system. It is one thing to build a demonstrator that does in principle work and another to get it to a status that's sellable.

Did you get some help in developing your business idea and applying for the EXIST funding or did you manage that on your own?

You always get some assistance from different parties, but the main driving force must be you and the people that do it together with you. Our startup has been founded by four persons and all of them need to participate and put in all their effort to get such a project running. To get the funding, to get the machine running, to get the technology ready, to found the company and to get all the bureaucracy done in parallel is quite a big effort which is heavily underestimated in many cases. You don't only have to get your technology running but you also need to get the rest of this economic structure and also the infrastructure established. Especially at the very beginning.

Thank you very much for the interview!

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Dr. Andreas Walz

Dr. Andreas Walz from Munich (Germany) is a co-founder of the startup company pureions. He is a physicist by training and graduated from the Technical University Munich. In 2020, Andreas Walz completed his doctoral thesis at the chair of surface and interface physics under the supervision of Prof. Dr. Johannes Barth at the Technical University of Munich with *summa cum laude*. Afterwards, he continued his scientific work on ion beam deposition methods as a post-doctoral researcher in the same group. Andreas Walz works on the development of powerful ion beam deposition devices, which enable the deposition of non-volatile and fragile building blocks for functional nanostructures in UHV. This innovative and promising technology overlaps a variety of facets in physics, chemistry and engineering. Major parts of his work deal with the physics, manufacturing and electric control of deposition devices, ion guides and mass spectrometers. Together with his colleagues, Andreas Walz raised public grants to develop versatile and user-friendly tools for controlled ion beam deposition experiments. In 2023, Andreas Walz co-founded the startup company pureions GmbH aiming to provide the CIBD technology to the nanotech and surface science community.

BUNSEN-MAGAZIN · 27. JAHRGANG · 3/2025

Dmitriy Borodin

Scanning probe microscopy for quantum science with spins on surfaces

Introduction

What we know today as scanning probe microscopy (SPM) encompasses two primary techniques: Scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Both were pioneered in the 1980s and revolutionized surface science by enabling the visualization of atomic-scale structures. While structural imaging remains an important application of SPM, truly fascinating things become possible when microscopes are engineered for mechanically stable operation at cryogenic temperatures of just a few kelvins.

At low temperatures, *random* motion of atoms and molecules on the surface (thermal diffusion) will not occur on experimental timescales. However, *controlled* manipulation of individual atoms and rupture of chemical bonds with a SPM tip can create atomic arrangements and new molecules that do not occur in nature by itself [1]. While this is an exciting aspect, the possibility to simultaneously gain insights into the electronic structure of such arrangements is the true power of low-temperature SPM.

For conductive samples, the primary spectroscopic technique is inelastic electron tunneling spectroscopy (IETS) [2]. Here, tunneling electrons lose energy to electronic transitions, vibrations, or spin excitations in atoms and molecules, which is reflected as step-wise increase of differential conductance (dI/dV). For non-conductive surfaces, force spectroscopy is the primary diagnostics tool. By measuring tip-adsorbate interactions, we can infer details about the electronic structure of adsorbed species. For example, electrostatic forces between the tip and individual atoms can be quantified, revealing the sub-atomic electron density distribution that is responsible for the formation of certain crystal structures [3]. Alternatively, the magnitude of tip-sample forces is used directly to evaluate the acidity of catalytic binding sites [4].

The increased interest in quantum technology has also sparked interest to use individual atoms and molecules as quantum resources, i.e., two-level systems that can be individually addressed and coherently controlled. For quantum science, electron and nuclear spins are a convenient degree of freedom for coherent operations as resonance frequencies can be "adjusted" by external magnetic fields. Furthermore, spins in atoms and molecules on surfaces can be easily coupled together and read out individually with SPM. Unfortunately, established spectroscopic techniques in SPM are incoherent, limiting their resolution and their use for coherent control of spins. A big leap in this regard came around 10 years ago, when for the first time, electron spin resonance (ESR) was demonstrated on a single atom with STM [5].

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Single atom and molecule electron spin resonance

Electron spin resonance scanning tunneling microscopy (ESR-STM) combines the atomic-scale spatial resolution of SPM with single-spin sensitivity through ESR spectroscopy. The realization of ESR-STM typically requires temperatures close to 1 kelvin and magnetic fields on the order of 1 tesla. The external (static) magnetic field (B_0) is needed to split the energy between two magnetic states of the electron, while the low temperature ensures an increased Boltzmann population difference between these states. To enable spin transitions and their detection via STM, spin-polarized tips are required. These tips can be easily created by transferring a few magnetic atoms from the surface to the tip apex. In conventional ESR, an oscillating magnetic field (B_1), applied perpendicular to the static magnetic field, induces magnetic transitions. However, in ESR-STM, this approach is not feasible. Instead, strong oscillating electric fields generated in the STM junction modulate the exchange coupling between the spin-polarized tip and the electron spin target. With a spin-polarized tip, ESR can be detected from time-averaged changes in the electron spin population of the target spin. When the frequency of the AC electric field matches the spin transition, the time-averaged population between the "spin-up" and "spin-down" states deviates from its thermal population. Due to tunneling-magnetoresistance between the tip and sample, ESR appears as a small change in the tunneling current, on the order of ~100 fA.

Figure 1(a) shows a typical set of continuous wave ESR-STM spectra for a Ti atom adsorbed on two layers of MgO on an Ag(100) surface [6]. In this case, Ti atoms undergo charge transfer to the substrate and retain only one unpaired electron (S = 1/2). Although the ESR spectra of three Ti atoms in Figure 1(a) differ, they are indistinguishable in topography or IETS. The spectral differences arise because the three atoms are different isotopes of Ti, each with a unique nuclear spin that interacts with the electron spin via hyperfine coupling, as reflected in the ESR spectra. In Figure 1(b), three ESR spectra are shown, with the Ti atom manipulated into a different binding site between measurements (follow the first column in Figure 1(c)). Spectra (1) and (3) correspond to Ti in a bridge binding site on MgO, while spectrum (2) corresponds to Ti on an oxygen

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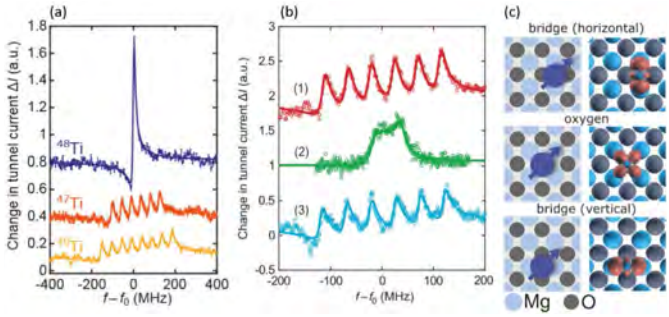

Fig. 1: (a) ESR-STM spectra on three different Ti-isotopes. (b) and (c) ESR spectra of a Ti atom at different binding sites with its calculated ground state orbital. Adopted from [6].

binding site. Clearly, the binding site determines the electronic structure of the adsorbate, as evidenced by the strong changes in the hyperfine coupling of the Ti atom – see Figure 1(c).

A key limitation of ESR-STM is that its detection mechanism relies on electron tunneling, restricting its application to thin insulators. Additionally, spin lifetimes and phase coherence times in this system are typically as short as ~100 nanoseconds. However, a recent study demonstrated how single-molecule ESR can be performed on insulators [7]. Certain organic molecules, such as pentacene, can be excited into their first excited triplet state via sequential electron transfer events between a metallic tip and the molecule [8]. In this triplet state, the energy levels split (zero-field splitting), enabling coherent spin manipulation using AC magnetic fields. In this experiment, time-dependent magnetic fields were generated by a device beneath the sample surface, while state readout was achieved via electron transfer from the molecule and AFM detection. Since the excited molecule on the insulator has a lifetime on the order of ~100 microseconds, its phase coherence time was shown to exceed several tens of microseconds. This work provides valuable insight into how single-atom and single-molecule ESR could be implemented on thick insulators using AFM.

While more ESR-AFM examples remain to be explored, ESR-STM has already been applied to diverse atomic arrangements [9] and molecules [10]. Pulsed ESR-STM techniques have also been developed, enabling coherent spin manipulation [11]. Remarkably, a qubit device capable of executing simple quantum logic operations was demonstrated using only five atoms with coherent electron spin manipulation achieved via ESR-STM [12]. Although the future role of ESR-STM in quantum computing remains to be determined, one exciting avenue is quantum sensing. Since atomic-scale resolution is inherent to SPM, combining it with ESR spectroscopy opens exciting possibilities for achieving truly atomic-scale quantum sensing.

Atomic-scale quantum sensing

Quantum sensing relies on sharp (spin) transitions that are sensitive to weak external magnetic and electric fields. Most commonly, Nitrogen-vacancy (NV-)centers in diamond are used for this purpose [13]. Unfortunately, NV-centers function only when embedded within the diamond lattice, preventing true atomic-resolution (~angstrom scale) quantum sensing.

Since the first demonstration of ESR-STM, it did not take long to realize that atoms on a surface can “sense” each other’s presence at appreciable distances of several nanometers [14]. Moving two atoms closer together leads to a shift in the ESR frequency characteristic of magnetic dipolar interactions – providing a true demonstration of atomic-scale quantum sensing. While this example confirmed ESR-STM’s capability for atomic-scale quantum sensing, using atoms bound to a thin insulating layer as sensors significantly limits its applicability. An insulating substrate remains crucial, however, to effectively decouple the atomic electron spin from metal electrons, which would otherwise hybridize and cause spin relaxation. This dilemma has driven research into molecules with atomic-scale sensing properties that remain intact when attached to the tip of an SPM.

Two excellent examples of electrostatic and spin sensing at the atomic scale are PTCDA and nickelocene molecules attached to an SPM tip. The PTCDA molecule exhibits quantum dot behavior, allowing it to be charged when an appropriate gating voltage is applied. The required gating voltage is highly sensitive to the electrostatic potential of the adsorbate. Since quantum dot charging is detected via AFM, no tunneling current between tip and sample is required, enabling electric field quantification at distances of several nanometers from the surface. This technique, often referred to as scanning quantum dot microscopy (SQDM), provides sub-nanometer spatial resolution [15]. More recently, nickelocene (Nc) molecules have gained popularity for studying surface-bound spins using SPM [16, 17]. Nc has a triplet ground state with axial anisotropy, favoring the $m_S = 0$ state over $m_S = \pm 1$ states, which are lifted by a few meV. Transitions within the triplet state produce intense signals in IETS, which remain observable even when Nc is attached to the apex of a metallic tip. When an Nc-functionalized tip is brought close to an atom or molecule with a finite electron spin, the IETS transitions of Nc are altered due to exchange coupling between the adsorbate and Nc spin. From these IETS changes, the spin state of the adsorbate can be determined. This method works even in the absence of an external magnetic field, and an increasing number of laboratories are adopting it as an atomic-scale tool for characterizing and localizing electron spins in atoms and molecules on surfaces.

While SQDM and Nc-based techniques offer accessible atomic-scale sensing methods, they are not strictly quantum sensing techniques. The group of Wilson Ho provided the first demonstration of a “mobile” atomic-scale quantum sensor [18]. They utilized a hydrogen molecule trapped in an STM junction as a two-level system. The interaction of H_2 with the tip and surface forms a double-well potential, where a superposition between bound states in each well is created by THz femtosecond laser pulses. The phase coherence of this superposition state was measured in a pump-probe fashion as a function of lateral position on a Cu_2N island on a Cu surface. The phase coherence and energy gap of the two-level system were found to be sensitive to the local environment. While this is an impressive demonstration of space- and time-resolved atomic-scale quantum sensing, the experiment primarily maps the potential energy surface of the hydrogen molecule and its environmental coupling. However, in many cases, more quantitative conclusions on electrostatic and magnetic fields are of interest, necessitating alternative approaches.

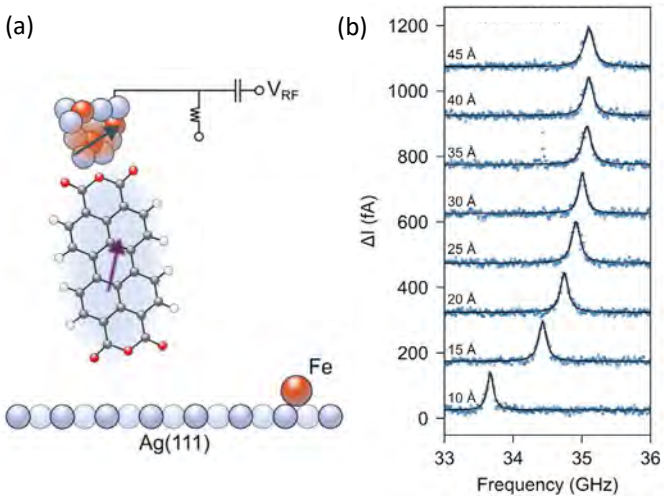

Fig. 2: (a) Schematics of the PTCDA-based atomic-scale quantum sensor. (b) ESR-STM spectra at a decreasing distance from the Fe atom on the surface (indicated). Adopted from [19].

Recently we have demonstrated an advanced form of atomic-scale quantum sensing [19]. We constructed the sensor on an STM tip using Fe atoms and a PTCDA molecule. When PTCDA is bound to a metallic tip, it acquires an unpaired electron that is sufficiently decoupled from the substrate and can be addressed in an ESR-STM experiment. Fe atoms at the tip facilitate spin transitions via AC electric fields and ensure that the current needed for ESR readout is spin-polarized. When the tip-bound PTCDA molecule approaches an Fe atom on a metal surface, we observe a shift in the ESR frequency, which corresponds to a response from electrostatic and magnetic interactions. By varying the direction of the external magnetic field, we disentangled these contributions and quantified the associated magnetic and electric dipole moments of a surface bound Fe atom. Our sensor achieves an energy resolution of ~100 neV, with detectable resonance frequency shifts on a sub-angstrom scale. In the future, this or a similar quantum sensor could be applied to study catalytically active sites or biomolecules on surfaces.

Outlook

The development of ESR-STM has pushed the boundaries of low temperature scanning probe techniques, making quantum coherent manipulations of spins on surfaces possible. It would certainly be desirable to combine SPM with optical spectroscopy to study spins on surfaces in greater depth in the future. Furthermore, the continuous development of molecular quantum sensors may make their handling more controlled and broadly applicable to open problems in chemistry and physics – so far, most studies remain at the proof-of-concept stage. It would also be interesting to explore whether ESR and coherent spin manipulations can be more generally applied to insulators. For example, magnetic exchange force microscopy [20] may be a tool that allows the spin state of atoms and molecules to be read out without the need for tunneling current. The advancements in the field of spins on surfaces over the past years have been accelerating, and more exciting findings are to be expected in the years to come.

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Dr. Dmitriy Borodin

Dmitriy Borodin obtained his PhD in physical chemistry from the University of Göttingen, where he worked with Alec M. Wodtke on the reaction kinetics and dynamics of surface reactions. For his doctoral research, he was awarded, among others, the 2023 Otto Hahn Award of the Max Planck Society. He is currently a Feodor Lynen Fellow at the IBS Center for Quantum Nanoscience in South Korea, where he works with Andreas J. Heinrich on atomic-scale quantum sensing of individual spins on surfaces using advanced low-temperature scanning probe techniques.

Andreas J. Heinrich, Noah Al-Shamery

Exploring the evolution and future of ESR-STM: An interview with Andreas Heinrich

Professor Andreas Heinrich is a pioneer in the field of scanning probe microscopy and a leading figure in the development of Electron Spin Resonance Scanning Tunneling Microscopy (ESR-STM). His groundbreaking work has enabled researchers to probe and manipulate individual spins with unprecedented precision. In this interview, Andreas shares insights into the origins, challenges, and future directions of ESR-STM, offering a glimpse into the next frontiers of atomic-scale magnetic measurements.

Could you share how the idea of combining ESR with STM first emerged? What was the motivation behind this approach?

For my postdoc, I went to the U.S. to work with Don Eigler, who was at the time the premier expert in working with individual atoms on surfaces. My task was to extend this technique to spins – building an STM that operated at lower temperatures and in magnetic fields so we could observe spin behavior.

The key idea behind ESR-STM came later, in 2007, at a winter physics conference in Aspen, Colorado. There, I met Arzhang Ardavan, a professor at Oxford and an expert in ensemble-based ESR, particularly in molecular qubits. As we were both avid skiers, we bonded over that, and during our discussions, we realized that it should, in principle, be possible to combine STM's spatial resolution with the energy resolution and control offered by ESR. That moment marked the conceptual birth of ESR-STM – but it would take another seven years of work before we successfully demonstrated it in 2015 [1].

What were some of the major technical challenges in implementing ESR-STM, and how were they overcome?

Back in 2007, STM was already capable of probing single spins using inelastic tunneling spectroscopy. Other researchers, primarily the group of Roland Wiesendanger in Hamburg, had developed spin-polarized STM, which was another way of accessing spin properties. However, STM inherently lacks time resolution, which made combining it with ESR a challenge.

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One major hurdle was achieving the necessary gigahertz frequency control. STM traditionally works with steady-state tunneling currents, so we had to modify the wiring and electronics to introduce fast electrical pulses. Sebastian Loth, a postdoc in my group at the time, played a key role in this effort, successfully implementing the infrastructure needed for ESR-STM. Another challenge was finding the right system where we could reliably drive ESR transitions with STM's localized electric fields. Once those steps were completed, we had a functional ESR-STM setup, but it took years of incremental progress to get there.

Your team developed a comprehensive ESR-STM tutorial available online. What inspired you to create this resource, and how do you see it benefiting the scientific community?

When you develop a new technique, you have two options: you can either keep it to yourself, limiting competition, or you can share it openly to build a research community. I've always preferred the latter approach.

We wanted to make sure that other groups didn't waste time on technical details like choosing the right cables or assembling the right circuit components. Initially, we invited researchers to visit our lab in Korea to learn ESR-STM firsthand. However, when COVID-19 prevented travel, we pivoted to creating a YouTube tutorial. This turned out to be a highly effective way to share knowledge with minimal effort on our part. Our students and postdocs contributed their expertise, making it a collaborative and successful outreach effort [2].

What do you see as the most exciting open questions in ESR-STM, and where is the field headed in the next five to ten years?

Predicting a decade ahead is difficult, but over the next two to three years, several key directions are emerging. Since the first ESR-STM paper, about 14 groups worldwide have successfully implemented the technique, with at least 10 more actively working on it.

Currently, most ESR-STM studies are conducted on a single material – a thin film of magnesium oxide (MgO) grown on silver. About 98% of results use this system, which means we need to expand to different insulators and spin systems, including molecular spins. Another breakthrough is the development of ESR sensors that are attached to the STM tip rather than the sample. This "lab-on-a-tip" approach, developed in collabora-

tion with the group of Stefan Tautz from Forschungszentrum Jülich, allows us to measure magnetic and electric fields with atomic-scale spatial resolution and ESR sensitivity [3]. It also frees us from being limited to specific sample materials, opening doors to studying complex surfaces like 2D magnetic materials, and other exotic quantum systems.

Can ESR-STM eventually be used to study more complex systems, such as biological molecules or buried interfaces?

I personally prefer working with "dead things": well-defined, static systems like atoms on surfaces. In biological systems, complexity increases exponentially, making them more challenging to analyze.

That said, our new tip-based ESR sensor provides a way to investigate more complex systems. One promising direction involves studying endohedral fullerenes – carbon cages that encapsulate magnetic atoms. These systems are ideal because the encapsulated spins are shielded from their environment, making them stable and well-defined, yet challenging to probe directly with STM.

Going further, applying ESR-STM to buried interfaces, where interesting quantum phenomena often occur, is a goal for the next several years. This will require overcoming technical barriers, such as operating with multiple samples in the same system, but it's an exciting avenue for future research.

The future of ESR-STM seems incredibly promising. Thank you for sharing your insights, Andreas. The Bunsen Society community will surely appreciate learning more about this technique.

My pleasure! I look forward to seeing more researchers engage with ESR-STM and take it in new directions.

ESR-STM has already revolutionized our ability to study and manipulate individual spins at the atomic scale, but its full potential is still unfolding. As researchers continue to push the boundaries of this technique, new materials, novel applications, and unexpected discoveries are sure to emerge. With ongoing advancements in instrumentation and methodology, ESR-STM will remain at the forefront of nanoscale science, providing deeper insights into quantum phenomena and expanding our understanding of the microscopic world.

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Prof. Dr. Andreas J. Heinrich

Professor Andreas Heinrich is a world-leading researcher in quantum measurements at the atomic scale. He pioneered spin excitation and single-atom spin resonance spectroscopy with scanning tunneling microscopes, enabling high-resolution access to quantum states. Currently, he is the director of the Center for Quantum Nanoscience at the Institute for Basic Science in South Korea and a distinguished professor at Ewha Womans University. His contributions to the field have been recognized with numerous awards, including the 2024 Honorary Citizen of Seoul title, the 2023 Humboldt Research Award, and the 2020 Heinrich Rohrer Medal.

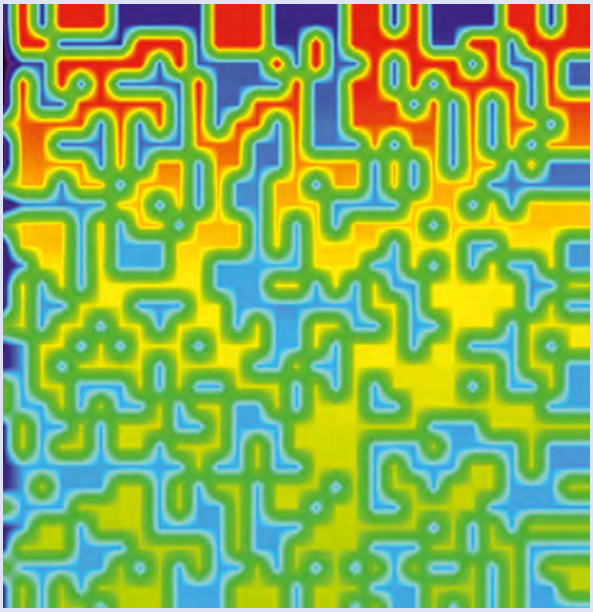
The art of SPM

Artist: **Nelly Nembot & Marius Muhle (Carl von Ossietzky University Oldenburg)**

SPM technique: **Substrate-generation/tip collection mode of scanning electrochemical microscopy (SG/TC-SECM) using pulsed amperometric detection.**

Investigated System: **Gas-diffusion electrode for Li-air battery. The color scale highlights the noise to create the impression of a decorative maze.**

Title: ***"The maze of gas diffusion electrodes"***



your Publications: Communicated!

Welcome to "*your Publications: Communicated!*", the new Bunsen-Magazin category in which we invite early career researchers to briefly summarize their newest research paper. Below, you can find a contribution we selected for this issue covering the atomistic analysis of the layer distortions in the carpet growth region of KCl layers at Ag(111) step edges.

If you are also interested in sharing your research with the Bunsen-community, just send us a short one paragraph summary of your paper as well as a meaningful figure to ypc@go.bunsen.de and we will share the best ones here in the Bunsen-Magazin and across our yPC social media channels!

yPC Editorial Team

Anna Juliana Kny

The carpet growth of KCl across Ag(111) step edges: An atomistic analysis

Anna J. Kny, Adam Sweetman, Moritz Sokolowski, An Atomistic Analysis of the Carpet Growth of KCl Across Step Edges on the Ag(111) Surface, Journal of Physical Chemistry Letters 2025, 16, 696-702 doi: https://doi.org/10.1021/acs.jpclett.4c02809

Thin alkali halide (AH) films of 2-3 atomic layer thickness, grown on metal substrates, are widely used for studying decoupled molecules by scanning tunneling microscopy. For many combinations of AH and metal surfaces, a continuous growth of the AH layer across step edges of the substrate is observed, which is called *carpet growth*.

Here, we report a first atomistic analysis of the layer distortions in the carpet growth region of KCl layers at Ag(111) step edges. STM measurements performed at room temperature and with Cl^- decorated W-tips provided the necessary atomic resolution on the terraces and, most importantly, in the regions of the step edges. We find that the AH layer distorts locally and in a non-uniform manner within a short lateral distance of four unit cells when it grows across the Ag step. Furthermore, we find that the Ag(111) surface adapts to the AH layer, as the carpet growth is accompanied by a straightening of the Ag steps. In addition, the carpet growth induces a splitting of higher Ag steps into multiple mono-atomic ones. These mono-atomic Ag steps allow for the carpet growth if the distance between them is larger than 13 Å, while a carpet growth across higher or closer Ag steps is not observed. Thus, we can show that the interactions of the AH layer with the surface drive a rearrangement of the Ag steps. This rearrangement allows the KCl film to minimize the area of distortion, i.e., the area of the carpet growth region, when overgrowing the steps and to increase the contact area of the AH film with the surface.

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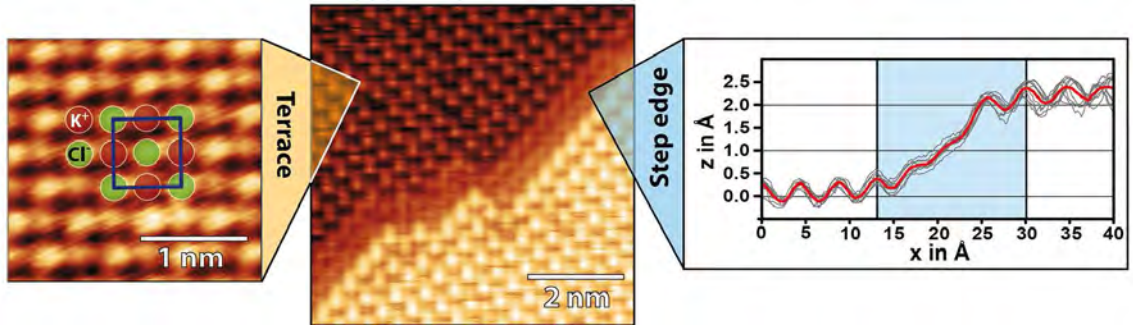

Fig. 1: Carpet growth of a 3 ML KCl layer across a monatomic Ag(111) step investigated by STM (middle, right). The ionic arrangement of the terrace (left) was imaged for a 2 ML KCl layer. Adapted from 2025 ACS.

BUNSEN-MAGAZIN · 27. JAHRGANG · 3/2025

Svetlana Guriyanova, Sebastian Müller, Bernhard von Vacano

Application of AFM in chemical industry: Insights into materials nanostructure and performance

Structures and surfaces at the nanometer scale, along with the interaction forces present at these dimensions, play a crucial role in determining material properties across countless industrial applications. These properties include friction, which is significant for tribological layers and anti-scratch coatings, as well as gloss, adhesion, and the adsorption of various species from surrounding media or their prevention. Barrier properties, corrosion behavior, the functionality of layers applied to semiconductors, and the mesophase morphologies of advanced materials and polymers all necessitate a comprehensive understanding of the relevant length scales, as well as the surfaces and interfaces involved. BASF has a rich history of utilizing Scanning probe microscopy (SPM) techniques since the 1990s [1, 2]. Currently, the company maintains specialized laboratories in its global research and development (R&D) and technical hubs located in Germany, Asia, and the United States.

Atomic force microscopy (AFM) is particularly adept at addressing technical and industrial challenges by relying on the interaction forces between the resolution-determining probe and the sample being analyzed. These forces can include mechanical contact for topographical mapping, elastic or plastic deformation to identify localized differences in mechanical properties, adhesive forces, charge interactions, and more. Unlike electron microscopy, AFM does not require sample staining, which makes it a more versatile option.

Moreover, this technique can conduct measurements in various modes under ambient conditions, even on hydrated soft matter samples, within the liquid cell, or temperature-controlled investigations that replicate real-world application scenarios. The interaction between probe and sample enables the possibility of conducting localized mechanical or spectroscopical analysis, which can provide additional chemical information up to the nanoscale level. Given these diverse capabilities, the potential applications in industry are equally varied. Scientists and SPM experts collaborate with application testing laboratories, R&D teams, technical marketing departments, and customer representatives to design SPM studies that yield the desired insights within specified time and budget constraints. Here, we present examples that illustrate some of the range of capabilities, along with their application context and the associated scientific and technical questions.

A long-standing application of AFM is the study of the structure of film-forming polymer dispersions. In these dispersions, polymer particles are suspended in water, and as the water evaporates upon drying, the particles coalesce to form a continuous film. Polymer dispersions find application in a variety of formulations, including adhesives, sealants, architectural coatings, paper coatings, construction materials, and fiber bonding agents. Each application field requires different compositions, morphologies, and properties tailored to meet specific performance criteria. The quality of the resulting film is significantly influenced by the extent of particle interdiffusion and the bonding strength between particles [3]. These factors can be optimized by adjusting the core-shell structure of the dispersion particles, which typically combines hard and soft components. In tapping mode AFM, topography images provide valuable insights into the roughness of the film surface (see Figure 1). To gain a deeper understanding of the bulk morphology, it is necessary to prepare an ultra-microtomy cross-section of the

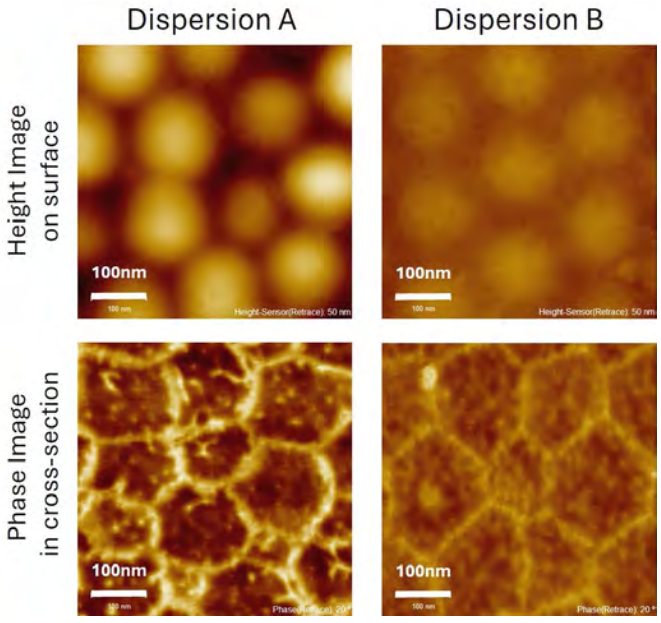

Fig. 1: Polymer dispersion films A and B measured in AFM tapping mode: Topography image on film surface and phase image in cross-section to visualize the bulk morphology.

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polymer film. Additionally, phase images obtained through AFM allow for the visualization of material contrast between hard (bright color) and soft (dark color) domains within the film. These images reveal the core-shell structure of the dispersions in cross-section. Notably, a thinner shell around the core of the particles tends to enhance film formation and results in a smoother film surface, as demonstrated by the example of dispersion B in Figure 1.

The properties of polymeric materials are directly influenced by their internal structure, which spans the nano- to micrometer scale. In particular, soft phases within an optimal particle size range play a significant role in enhancing the toughness of materials by effectively dissipating stress concentrations. However, if these particles are too large, they can act as defects within the polymer matrix, resulting in a reduction of the overall material strength. This challenge is particularly common when different types of plastics are mixed during recycling processes, leading to undesirable mechanical properties. To mitigate this issue, the incorporation of compatibilizers can be beneficial. Compatibilizers facilitate the creation of appropriate morphologies within the material, which can enhance compatibility between different polymer phases and improve the overall performance of the composite. The effectiveness of these modifications can be validated through peakforce quantitative nanomechanical mapping (PF-QNM®) of the elastic modulus using AFM, as illustrated in Figure 2. This technique provides detailed insights into the mechanical properties at the nanoscale, allowing for a better understanding of how internal structures influence the performance of polymeric materials.

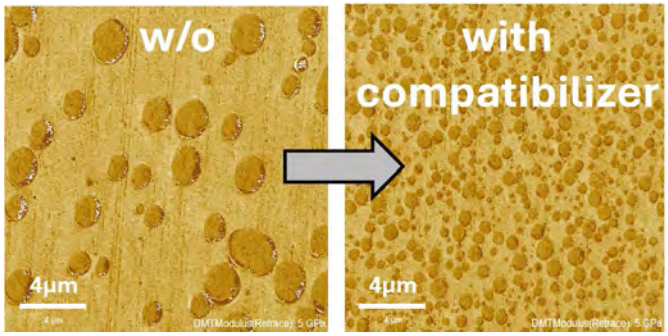

Fig. 2: Quantitative E-modulus mapping in a mixed recycled polymer blend without compatibilizer (left) and with compatibilizer (right).

In other scenarios, such as with polyurethane elastomers used across various application fields, semicrystalline spherulite structures with varying sizes and properties can be observed, depending on the composition and processing parameters (see Figure 3). The AFM PF-QNM technique allows for quantitative comparisons of the elastic modulus of different phases within the same material, as well as direct comparisons between different materials. The hard and soft phase separation in polyurethanes materials plays an important role in determining their mechanical properties, including tensile strength, hardness, flexural strength, and impact resistance [4]. This understanding allows for the design and formulation of polyurethanes that meet specific performance requirements across various industries like construction, automotive, footwear, textiles, and medical devices.

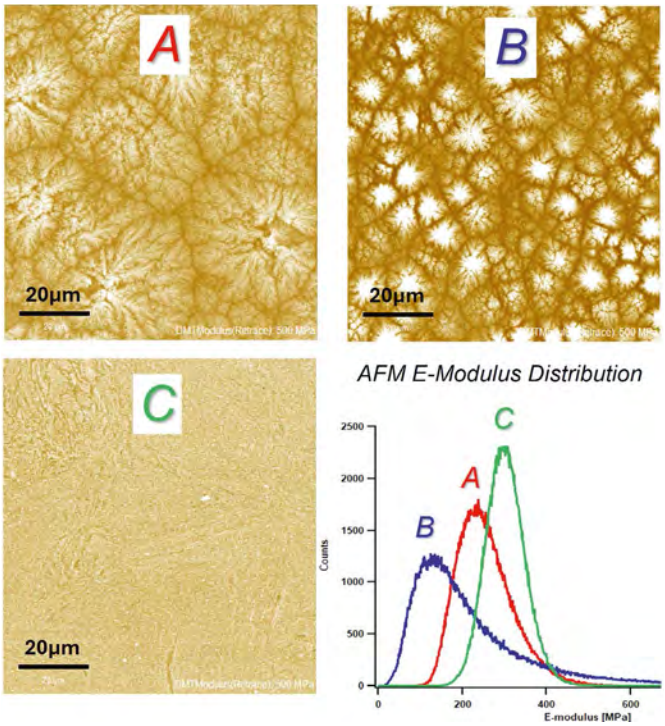

Fig. 3: Quantitative E-modulus mapping of different polyurethane elastomers, and the histogram with the corresponding E-Modulus distributions.

In the case of foam structures, an intriguing nanoscale morphology can be observed within the micrometer-sized foam struts of the polymer foam. The behavior of the foam at elevated temperatures correlates with changes in the elasticity of the hard domains present within these foam struts. To investigate this phenomenon, a single foam strut was prepared as a thin slice using a microtome and placed on the AFM heating stage (as shown in Figure 4). The tests at various temperatures

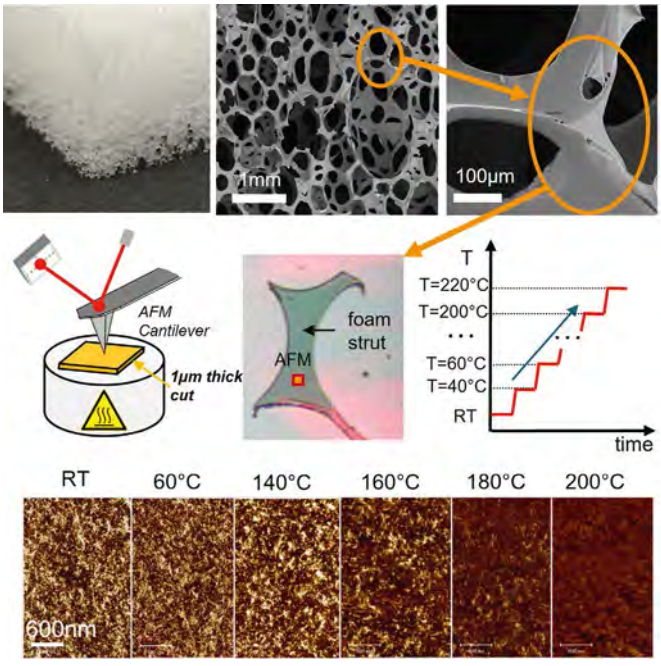

Fig. 4: Exemplary PU foam sample preparation of a single foam strut lamella, which was then mapped at different temperatures. The contrast between hard and soft phase vanishes at >180 °C.

revealed that the contrast between the hard and soft phases disappears at temperatures exceeding 180 °C. This observation provides valuable insights into the melting properties of the foam and the interactions between different hard and soft domains within the material.

Finally, using AFM, intermolecular forces are measured to understand and optimize surface modifications with functional polymers. This approach is employed, for example, to enhance the adhesion properties of adhesives or to reduce adhesion through surface modification, which can lead to anti-stain effects in laundry detergents or antifouling applications, as illustrated in Figure 5.

Force spectroscopy measurements can be conducted in air or in a fluid medium, allowing for the study of various factors such as pH, concentration variations, or the type of surfactant on interaction forces. As a probe, a standard AFM tip can be used, either with or without specific functionality on its surface. Alternatively, a colloidal probe made from different materials such as silica or polymers can be attached to a cantilever for these measurements [5].

This versatility in probing techniques enables detailed investigations into the interactions at the surface level, facilitating the development of more effective functional polymer applications.

In conclusion, the application of AFM in the chemical industry offers important insights into the nanostructure and performance of materials, making it a powerful tool for material characterization and optimization. The versatility of SPM techniques allows scientists and engineers to investigate the detailed interactions and forces that affect material properties at the nanoscale. This capability is crucial for enhancing various applications, including adhesives, coatings, and polymers, where understanding the structural and mechanical properties can lead to improved product performance. The collaboration between SPM experts and application testing laboratories fosters a comprehensive approach to tackling industry-specific challenges, ensuring that the insights gained align with the practical requirements. As the chemical industry continues to develop, leveraging advanced SPM techniques will be essential for driving innovation and staying competitive through the development of next-generation materials.

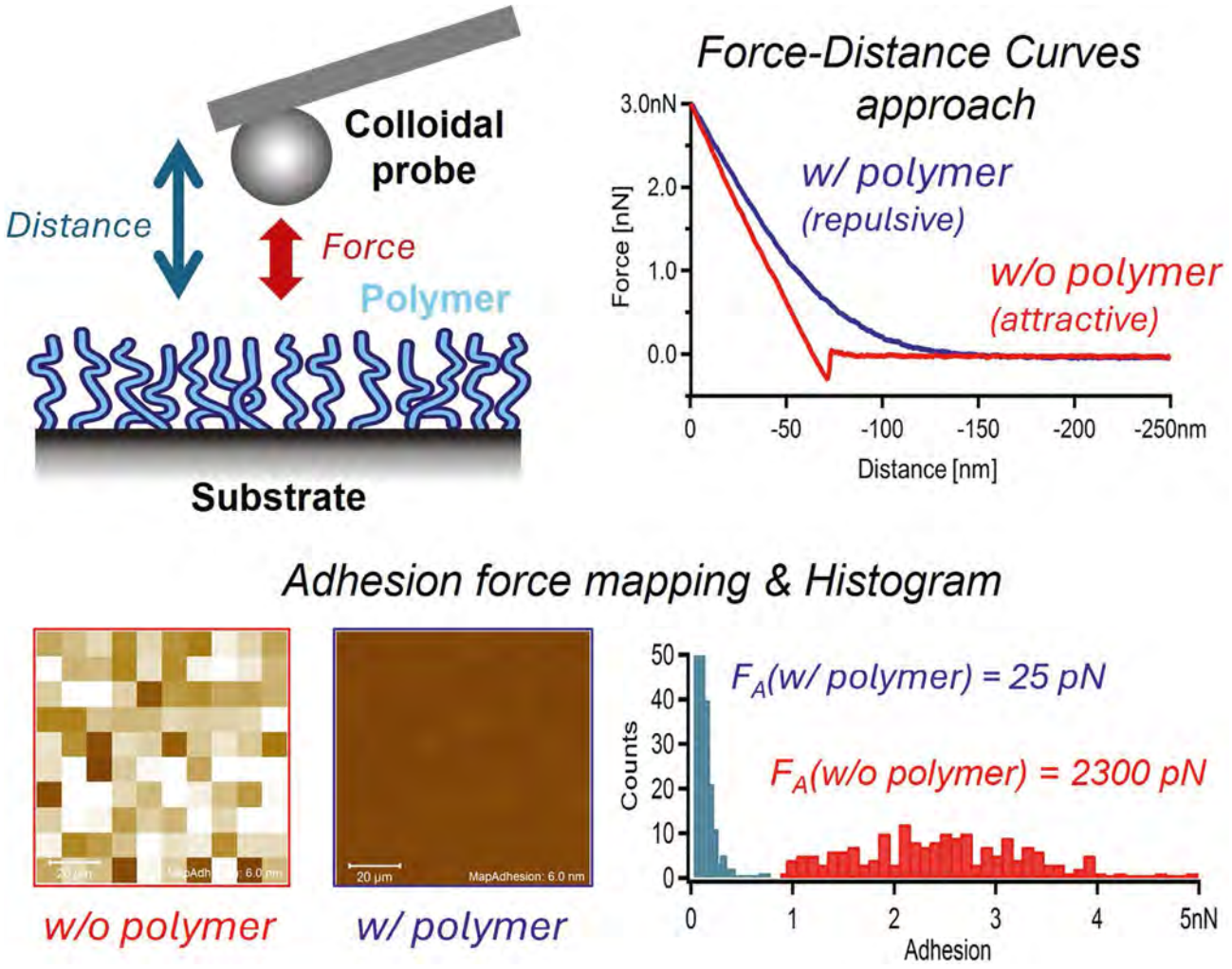

Fig. 5: Colloidal probe force spectroscopy - characterization of polymer surface modification. The mean adhesion force with the adsorbed polymer is nearly a factor of 100 smaller than that on the uncoated surface.

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Dr. Bernhard von Vacano

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Harry Mönig

AFM with copper-oxide tips: Imaging atoms in real space with elemental selectivity

In scanning probe microscopy experiments, the identity of the tip-terminating atom and its bonding configuration at the apex can drastically affect the image contrast [1-3]. In particular, in the field of noncontact atomic force microscopy (nc-AFM), considerable progress has been made through the implementation of different tip functionalization approaches, which, in combination with the ultra-small oscillation amplitudes of qPlus-type force sensors, have led to a new era in surface chemistry [4, 5]. By far the most established probes used in nc-AFM experiments are CO-functionalized tips. They are prepared by first co-adsorbing a low density of CO molecules on the surface under study and then picking up a single molecule by a sharp metallic tip apex leading to a configuration where the O-atom points to the surface [1, 4, 5]. This significantly reduces chemical interactions within the tip-sample junction allowing for constant-height nc-AFM imaging in the repulsive force regime where organic nanostructures can be imaged with sub-molecular resolution [4, 5]. However, a major problem of using such probe particles for nc-AFM experiments is their lateral flexibility at the apex. It can lead to image distortions, a systematic overestimation of bond lengths, and even artificial contrast features [6-8]. The latter particularly concern surface sites with a strongly varying tip-sample potential where tip flexibility affects the contrast the most.

In the following, an alternative approach based on so called copper-oxide tips (CuOx-tips) is discussed. These tips consist of a Cu-apex terminated by a single O-atom, which is covalently bound in a tetrahedral configuration to its upper Cu-atoms (Fig. 1a). With this structure, CuOx-tips allow for stable constant-height imaging in the repulsive force regime and to resolve single bonds in organic nano-structures (Fig. 1b). At the same time, CuOx-tips are extremely rigid, which allows to largely neglect artefacts due to tip flexibility [3, 6, 7].

CuOx-tips can be prepared by controlled tip indentations and voltage pulses on a slightly oxidized single crystalline Cu substrate. Figure 1c shows a scanning tunneling microscopy (STM) image of a partially oxidized Cu(110) surface showing the typical (2x1)O-reconstructed oxide stripes, which is acquired during such tip forming procedures [9]. While recording the lower part of the image, the tip is terminated in a pure metallic apex where frequent tip indentations and voltage pulses below the horizontal scan line result in instabilities. Due to the reduced density of states, the topographically elevated oxide stripes appear as deep trenches in the STM contrast at feedback settings of -0.1 V/50 pA (see also black line profile in Fig. 1d). Only when the tip picks up copper-oxide material from the sur-

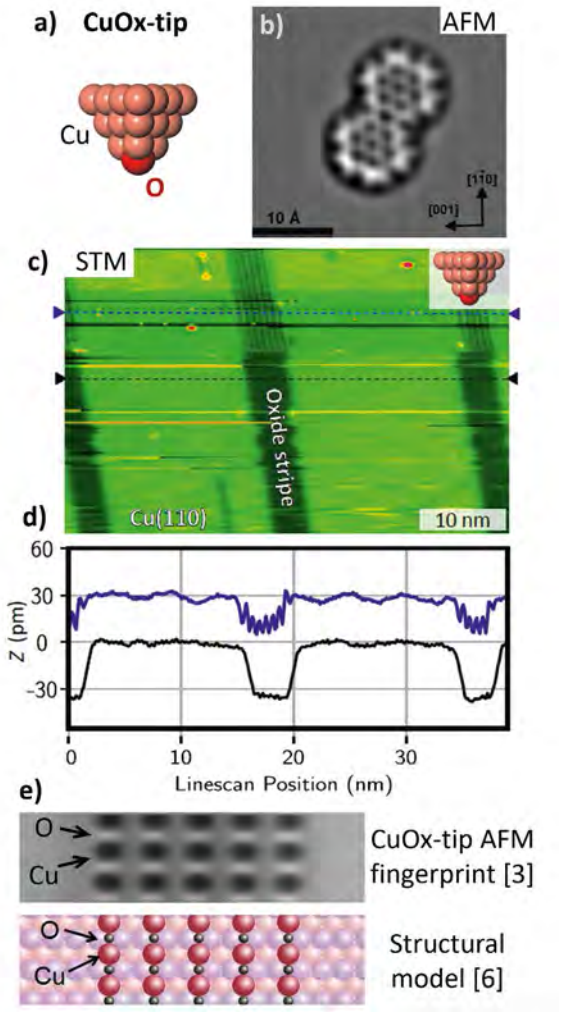

Fig. 1: a) DFT-optimized model of a CuOx-tip. b) Constant-height nc-AFM image of dicoronylene on Cu(110) recorded with a CuOx-tip (reprinted from ref. [6] with permission from Springer Nature). c) Constant-current STM image of a partially oxidized Cu(110) surface recorded during tip forming procedures [9]. d) Line profiles from c for a pure metallic apex (black) and after successful CuOx-tip functionalization (blue). e) Constant-height nc-AFM on an oxide stripe (adapted from ref. [3] with permission from Royal Society of Chemistry). Such a contrast serves as a fingerprint allowing to unambiguously verify a CuOx-tip. Structural model reprinted from ref. [6] with permission from Springer Nature.

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DOI-Nr.: 10.26125/z3pa-7387

face leading to an O termination at the apex, the STM contrast changes significantly (upper part of Fig. 1d). This not only increases the resolution, but also reduces the apparent depth of the trenches (blue line profile in Fig. 1d). Yet, it is important to note that such a change in the STM contrast alone does not prove a CuOx-tip termination. In principle, any passivated tip could show such a contrast. To unambiguously verify a CuOx-tip termination, the recording of an nc-AFM image above one of the oxide stripes is required. As demonstrated by systematic DFT simulations, only a contrast as shown in Fig. 1e allows to confirm the formation of a CuOx-tip. In fact, a constant-height nc-AFM contrast as shown in Fig. 1e serves as fingerprint for a CuOx-tip [3, 6, 7]. Here, single Cu-atoms within the (2x1)O-reconstruction appear as dark ellipsoidal depressions, while the O-atoms are imaged as bright contrast features (dominated by repulsive forces) in between (Fig. 1d). As shown in the following, this remarkable chemical selectivity for metal- and oxygen atoms is a specific property of CuOx-tips, which can even be generalized for the whole class of metal-oxide surfaces.

As a first step for this generalization, the role of the tip termination was investigated by comparing the contrast of four commonly used probe tips. The upper panels in Fig. 2 show constant-height nc-AFM images of (2x1)O-reconstructed oxide stripes recorded with four atomically defined tip-terminations at tip-heights of maximum contrast [3]. It was found that the high reactivity of pure Cu-tips (Fig. 2a) leads to atomic relaxations within the tip-sample junction already in the attractive force regime. Therefore, imaging at even more reduced tip-sample distances leads to unstable imaging conditions and sudden tip changes. For the case of Xe- and CO-passivated tips, it is possible to enter the repulsive force regime (Fig. 2b, c). However, the observed contrast does not allow to clearly identify specific atomic surface sites, rather the images appear strongly distorted and show emphasized contrast signatures at inter-atomic sites (i.e. between the O-Cu-O rows). Mechanistic simulations allowed to explain these findings by dynamic tip bending effects, which are particularly emphasized due to the strongly varying tip-sample potential between Cu- and O-sites [3]. On the contrary, the data recorded with a CuOx-tip show a pronounced site-specific interaction and shape distinction for the Cu- and O atoms within the (2x1)O-reconstructed oxide stripes (Fig. 2d). Therefore, the identification of Cu- and O-sites is straight forward. As demonstrated by height-dependent imaging in combination with force-distance spectroscopy, the observed elemental selectivity is obtained over an extended range of tip-heights [3].

Force-distance *(F(Z))* simulations based on density functional theory (DFT) provide a more detailed view on the contrast mechanism. The lower panels in Fig. 2 show corresponding *F(Z)* curves from O- and Cu-sites for all four tips, plotted on identical force scales to facilitate comparability. As the contrast is solely based on lateral differences in the chemical interaction, the simulated data are plotted without van der Waals contributions, which add only a background without any lateral variation for each tip. On both atomic sites, the Cu-tip shows pronounced minima at Z < 3 Å, which can be associated with a strong attraction and related high chemical reactivity, especially on the O-site. With the differing force interaction of the Cu- and O sites, such force curves indicate a strong contrast at Z < 3 Å, which in principle would allow to clearly distinguish the atoms within this force regime. However, the high chemical forces in combination

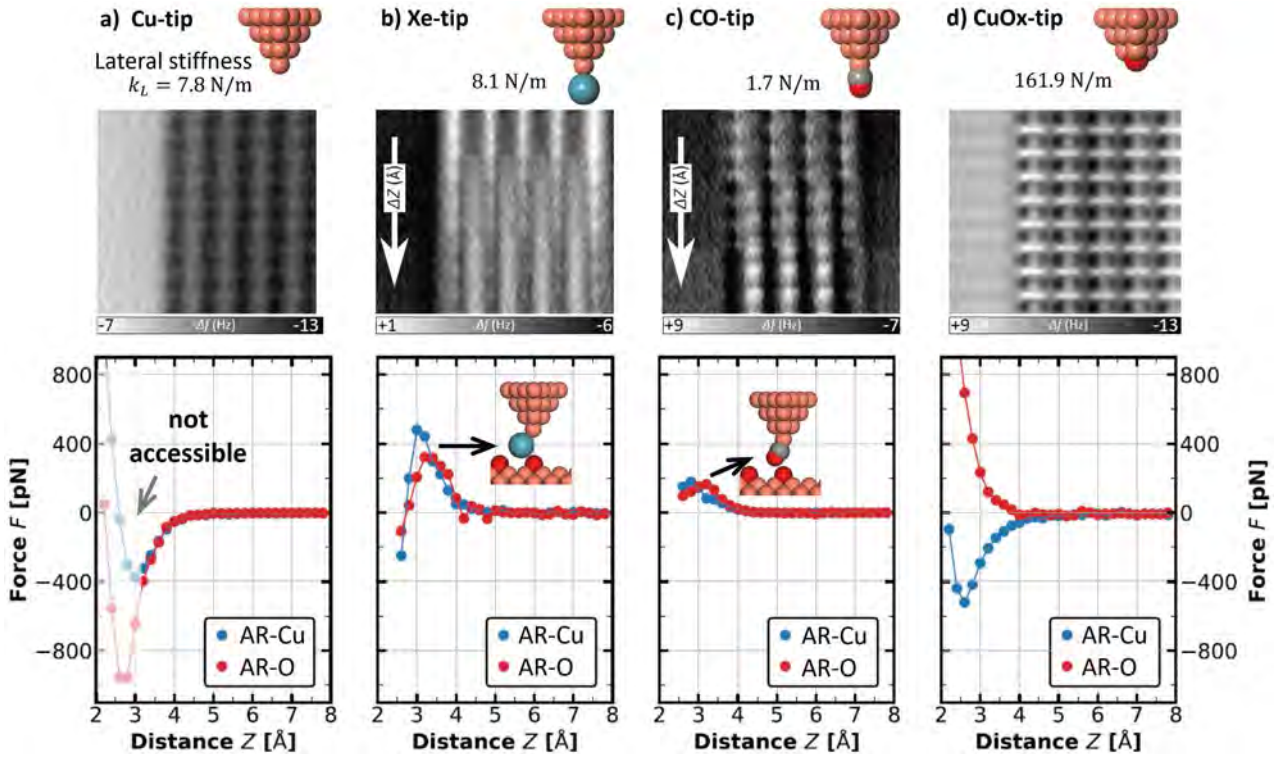

Fig. 2: (Upper panels) Comparison of nc-AFM images for various atomically defined tip terminations, recorded in constant-height mode above (2x1)O-reconstructed oxide stripes of a partially oxidized Cu(110) surface. The DFT-derived lateral spring constants given next to the tip models allow to quantify tip flexibility. (Lower panels) DFT-simulated *F(Z)* force-distance spectra where the vdW components have been subtracted to assess the chemical interactions for O- and Cu sites. Adapted from ref. [3] with permission from Royal Society of Chemistry.

with a weak stiffness of the Cu-tip leads to atomic relaxations within the tip-sample junction. Therefore, the tip-height regime in which a strong contrast could be expected is not accessible without the metallic tip reacting with surface oxygen [3, 7]. On the contrary, the Xe- and CO-tip both hardly show any attraction, which confirms the chemical passivation of these two tips. At the same time, the force-distance curves show nearly no separation, which explains the experimentally observed weak contrast between the O- and Cu-sites. In addition, both show kink-like maxima around Z = 3 Å, which are typical for lateral bending effects of the Xe- and CO probe particles [3, 8]. In comparison, the curves for the CuOx-tip show a largely inert interaction on the O-site and a moderate attraction (i.e. reactivity) on the Cu-site. This leads to a distinct separation of the F(z) curves at Z < 4 Å (Fig. 2d), which is in agreement with the experimentally observed strong contrast. Furthermore, due to the high stiffness of the CuOx-tips, artefacts due to tip bending effects are absent. The differences in tip flexibility are demonstrated by a quantitative comparison of the DFT-derived lateral spring constants, given in the top row of Fig. 2 [3].

Up to this point, elemental selectivity was observed only for the (2x1)O-reconstructed Cu(110) surface. Consequently, the next steps in this research addressed the question if this finding applies to other reconstructions and other metal oxide surfaces as well. For a systematic investigation of this issue, CuOx-tip nc-AFM imaging was applied to various O-induced reconstructions, namely Cu(110) (6x2)O, Cu(100) $(2\sqrt{2}x\sqrt{2})R45°$O, and Ag(111) p(4x4)O. Even for these surfaces where metal and oxygen atoms occupy sites with a variety of different relative heights, the distinct elemental selectivity of the contrast allowed to directly identify atomic sites and defect structures [10].

To further understand the origin of this contrast, theoretical simulations based on DFT were employed. In Fig. 3a, b, experimental CuOx-tip images of the Cu(100) $(2\sqrt{2}x\sqrt{2})R45°$O surface and an OH defect on (magnetite) $Fe_3O_4(001)$ are compared to corresponding maps of the local electrostatic potential E^{el}_{pot}. These simulated potential maps were derived from DFT-optimized structures of these well-known surfaces and do not consider any tip interaction. Therefore, the remarkable agreement of the experimental data and the E^{el}_{pot}-maps reveals that the elemental selectivity of CuOx-tips is mainly based on electrostatic interactions [10]. In this simple picture, the tip-terminating O atom of the CuOx-tip can be regarded as a single point charge e^-, which is scanned above the strongly varying charge density between metal- and oxygen sites (Fig. 3c). In fact, considering the charge density accumulation at the apex of a CuOx-tip by Bader charge analysis, leads to a partial charge similar to CO-tips of roughly 1 e^- [6].

By extending this methodology to surfaces with highly complex, a priori unknown surface structures, and to surfaces of bulk metal-oxide materials, demonstrates the powerful capability of this approach [10, 12]. Figure 4a shows data of a titanium oxide (TiO_x) thin film grown on a Pt(111) substrate where the arrangement of 4-fold and 3-fold coordinated titanium atoms leads to a surface structure with a high degree of complexity [10]. Similarly, Figure 4b shows CuOx-tip measurements of an $Al_2O_3(0001)$ surface which forms a $(\sqrt{31}x\sqrt{31})R\pm9°$ reconstruc-

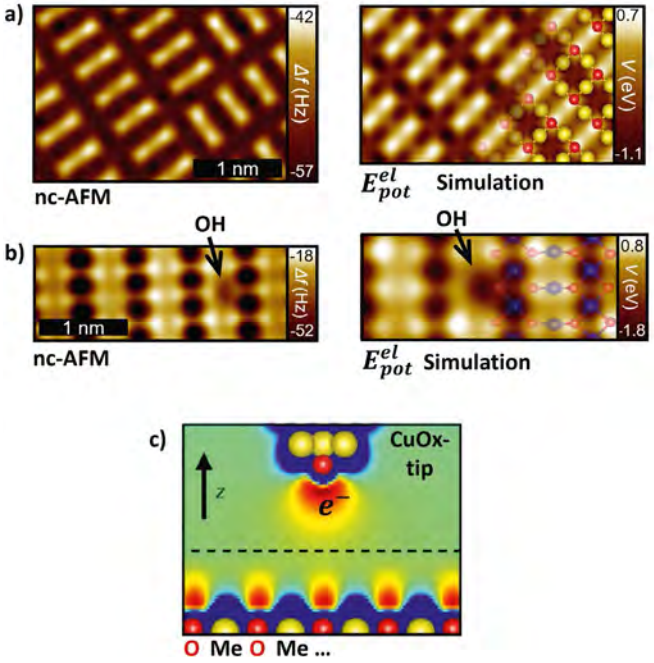

Fig. 3: a) and b) Comparison of experimental CuOx-tip nc-AFM data from the Cu(100) $(2\sqrt{2}x\sqrt{2})R45°$O- and $Fe_3O_4(001)$ surfaces (left) with electrostatic potential maps (right) derived from DFT optimized surface models. c) Cross section of the electrostatic potential of the CuOx-tip and a metal oxide surface. The O-termination of the tip leads to an increased electron density at the apex dominating the interaction with the surface. Reprinted with permission from ref. [10]. Copyright 2014 American Chemical Society.

tion exhibiting a stochiometric composition and emphasizing the applicability also to insulating surfaces [12]. In these experiments, the distinct contrast obtained with the CuOx-tip provided immediate access to the metal- and oxygen sublattices. Beyond that, imaging with such an elemental selectivity provides access to a direct structural characterization of atomic-scale point defects (Fig. 3b) [10, 12], which play an important role

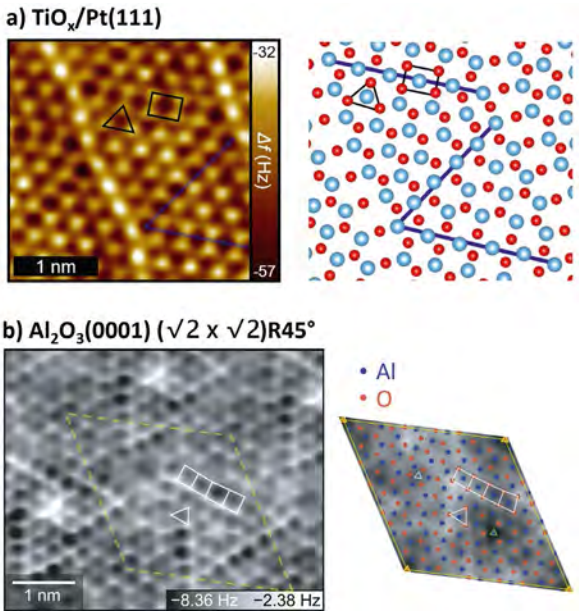

Fig. 4: a) nc-AFM data of a titanium oxide thin film grown on Pt(111). The elemental selectivity of the CuOx-tip allows to directly obtain the surface structure (shown on the right). b) CuOx-tip nc-AFM image recorded on the bulk insulator Al_2O_3 (left). The surface structure can be directly derived from the experiment (right). Reprinted from ref. [12], with permission from AAAS.

in the fundamental understanding of the catalytic, optical, and electronic properties of metal-oxide materials [10, 11, 13].

With their universal elemental selectivity on metal-oxide surfaces, CuOx-tip functionalization constitutes a powerful methodology for the atomic-scale characterization of this technologically relevant class of materials. The successful application to even highly complex surfaces and defects where conclusive structural models had been missing so far, must be set in context to the longstanding dream for scanning probe microscopy to directly determine the elemental identity of single atoms [14-16]. Our approach allows to drastically reduce the theoretical efforts and related indirect structural considerations and assumptions (e.g. for tip terminations and atomic positions) for the development of structural surface models. Moreover, CuOx-tips allow neglecting imaging artefacts due to tip-flexibility [6, 7] and can be routinely used at liquid nitrogen temperatures (e.g. nc-AFM data in Fig. 3a, b and Fig. 4a) [10, 17]. These highly desired properties make these probes unique for standardized scanning probe microscopy experiments.

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PD Dr. Harry Mönig

Harry Mönig, leader of the Nanoscale Interface Analytics group at the University of Münster, received his diploma in physics from the University of Kassel in 2005. After that, he continued his research with a doctorate on synchrotron-based interface analytics of chalcopyrite thin film solar cells at the Helmholtz Zentrum Berlin / BESSY. After completing his PhD in 2009, Harry Mönig worked as a postdoc at Yale University on simultaneous STM/nc-AFM measurements and force spectroscopy on metal oxide surfaces, before starting his current role in 2012. In 2019, he was appointed Privatdozent after finishing his habilitation thesis on correlating macroscopic and nanoscale phenomena in interface science.

Harry Mönig's current research focuses on nanoscale chemistry, single atom catalysis, electrocatalysis and interface analytics for solar cells. He made important contributions to the field of high-resolution nc-AFM by developing a new technique to image surfaces with copper-oxide terminated AFM/STM tips. Due to the rigidity of the copper-oxide tip, this technique is especially suited to study oxide and insulator surfaces.

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Tobias Dickbreder

Literature discussion: Atomic force microscopy with qPlus sensors

High-resolution atomic force microscopy is known for producing fascinating images with sub-molecular and sometimes even sub-atomic resolution. For instance, it has been possible to resolve the internal structure of aromatic molecules [1] and small iron clusters [2] adsorbed on a supporting surface. Many of these remarkable images were taken with AFM setups using so-called qPlus sensors to detect the force between tip and sample. These qPlus sensors combine a very high stiffness with the sensitivity to detect atomic size oscillation amplitudes, which allows for imaging close to reactive surfaces with high spatial resolution without snapping into contact. In his recent article, Prof. Dr. Franz Gießibl, the inventor of the qPlus sensor, reports on the development of this sensor. He intertwines scientific and technological aspects with his personal scientific journey, giving the reader insights into the history of AFM as well as the thought process behind his invention.

Franz Gießibl describes how he developed the first AFM capable of achieving true atomic resolution as a PhD student with G. Binnig and how he later achieved true atomic resolution on Si (111) – (7x7) during his time at Park Scientific Instruments (California). After these achievements, he felt like the hard problems were solved, while simultaneously being confused that solving such a hard problem did not automatically lead to financial success of his newly developed microscope. To learn more about adapting ideas to the world, Franz Gießibl decided to join a management consulting firm. Inspired by his experiences in consulting, he started to wonder whether cantilevers are the most efficient way to measure the force in an AFM experiment. He subsequently identified quartz tuning forks from watches as a prospective force sensor and started experiments during paid and unpaid vacation in his “quickly established home laboratory”. After successful completion of these first experiments, he decided to change back to academia, where he could pursue the development of the qPlus sensor full time. After describing the last steps towards the realization of AFM with qPlus sensors, Franz Gießibl closes with some current and future research pursued in his own research group and other leading groups in the field.

Franz Gießibl’s article provides interesting and inspiring insights into his professional journey and the developments leading to the invention of the qPlus sensor. It is especially capturing to follow the vivid descriptions of his experiments and to read how the benchmarking skills he gained in the seemingly unrelated consulting industry contributed to identifying quartz tuning forks as powerful force sensors for AFM experiments.

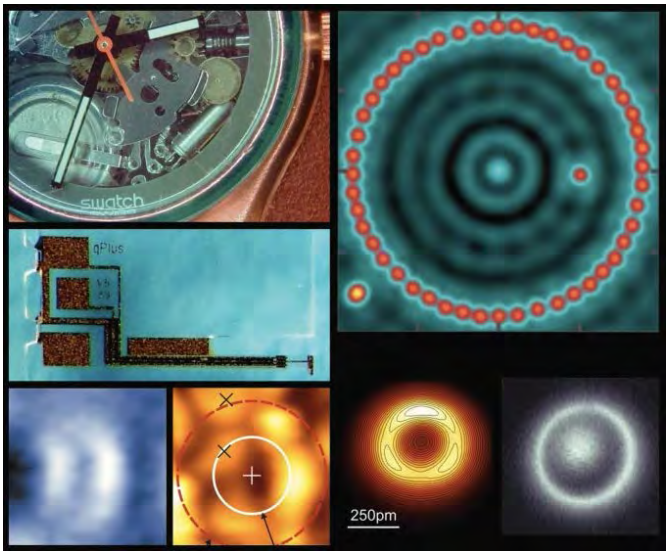

Fig. 1: Graphical abstract reproduced from Franz J. Gießibl: Atomic force microscopy with qPlus sensors, MRS Bulletin 49 (2024), 492 – 502. https://doi.org/10.1557/s43577-023-00654-w. Copyright © 2024 F. J. Gießibl. Licensed under Creative Commons CC-BY 4.0.

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Kelvin probe force microscopy: The nanoscale voltmeter

Kelvin probe force microscopy (KPFM) is a scanning probe microscopy (SPM) method for mapping electrical surface potentials with nanometer resolution. In this article, we will explain the fundamentals of KPFM and discuss some applications from the field of energy materials. Nevertheless, the applications for KPFM are manyfold, so we will be merely scratching the surface if you will.

KPFM is an extension of atomic force microscopy (AFM), where a sharp conductive probe scans a material's surface while detecting variations in its electrostatic tip-sample force. By compensating these electrostatic interactions with an external bias voltage, KPFM can quantify the local surface potential – a nanoscale voltmeter! In equilibrium, this potential corresponds to the contact potential difference (CPD) between the tip material and the sample surface. KPFM can be performed in various ways. In amplitude modulation (AM) KPFM, the electrostatic force is detected directly. This is the most commonly used method on commercial AFMs, as it is straight-forward to implement. Nevertheless, AM-KPFM is prone to cross talk, e.g., from non-local electrostatic interactions with topographic features and thus, it is difficult to get quantitative results [1]. Frequency-modulation (FM) KPFM detects the force gradient via the resonance frequency shift or by sideband signals induced by the electrostatic tip-sample interaction. For quantitative CPD measurements in ambient environments, FM heterodyne KPFM (H-KPFM) provides the most quantitative results [1]. In H-KPFM, the topography is measured at the first eigenmode, while the electrical excitation is performed at the difference between the eigenmodes, which leads to the sideband frequency appearing at the second eigenmode. This approach enables fast measurements at higher SNR [3]. Apart from CPD contrast, KPFM can also

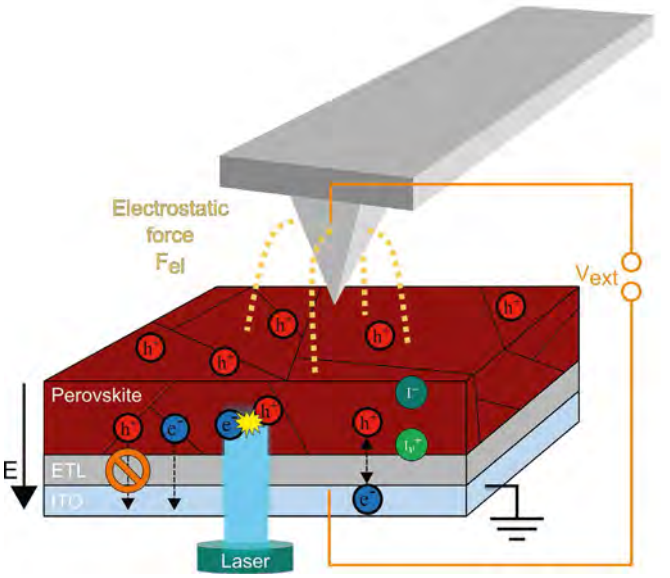

Fig. 1: Illustration of KPFM working principle. Adapted from [2] 2023 John Wiley and Sons ©.

study non-equilibrium states, such as photoexcitation or ion migration in photovoltaic perovskites (see Fig. 1). Moreover, KPFM can provide information about material composition, electronic behavior, and surface charge distribution, making it essential in fields such as semiconductor research, material science, and nanotechnology.

A big strength of AFM/KPFM is that the surface potential can be correlated to the topography. The CPD/topography overlay of a halide perovskite surface reveals that the different crystal facets show different CPD values, indicating crystal anisotropy (Fig. 2). Moreover, the darker CPD contrast observed on the rod-shaped structure on the left clearly identifies it as a defect structure – most likely leftover lead iodide from the sample preparation or as a result of sample degradation. This example demonstrates the power of KPFM for studying the quality of surfaces. In practice, KPFM is widely used to study effects like corrosion on nanostructures, thin films and coatings, enabling a deeper understanding of the interaction of different materials on the microscopic level. In organic electronics, such as transistors, OLEDs, and flexible displays, KPFM can help evaluating the microscopic charge transport properties and their influence on the macroscopic device efficiency. The technique's versatility extends to biological studies as well, where it helps analyzing cell membranes and biomolecular interactions.

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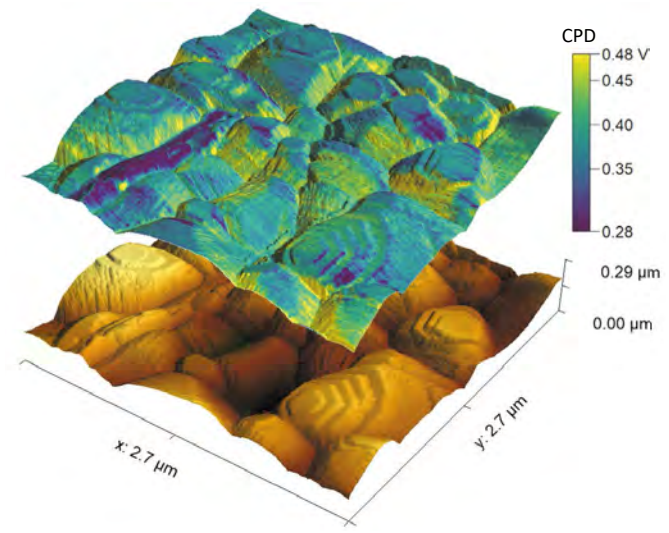

Fig. 2: 3D Topography (bottom) and CPD (top) images obtained via KPFM from a triple cation halide perovskite film (unpublished data).

Semiconductor device measurements

In the field of semiconductors, KPFM helps investigating charge distribution, defects and performance variations in microelectronic devices. By measuring electrical potentials directly on nanostructures and devices, researchers can optimize the design and efficiency of transistors, solar cells, and other electronic components. The technique also finds use in energy storage research, where it helps improve the performance of batteries and supercapacitors. Our team has used KPFM to map the potential distribution across the different layers of perovskite solar cells. Using time-resolved (tr-) KPFM, we were able to investigate the response of the potential distribution to light- or voltage pulses, revealing a stabilized charge layers at the electrode interfaces (Fig. 3).

Applying tr-KPFM to photovoltaic thin films allows nanoscale surface photovoltage (nano-SPV) spectroscopy [2]. Here, we can record the local SPV response to light pulses to study the steady-state SPV as well as the saturation kinetics. From the kinetics, we can distinguish between different charging mechanisms such as charge trapping, ion migration and charge extraction and recombination (see Fig. 1). By studying the response of the SPV to changing light intensities, we can furthermore map the local ideality factor of the charge separating pn junction to the substrate. Deviations from an ideality factor of one are commonly linked to the presence of defects. We performed a combined SPV/ideality factor mapping study on a methylamine-treated triple cation perovskite thin film sample (Fig. 4). In the topography, we are able to identify the position of grain

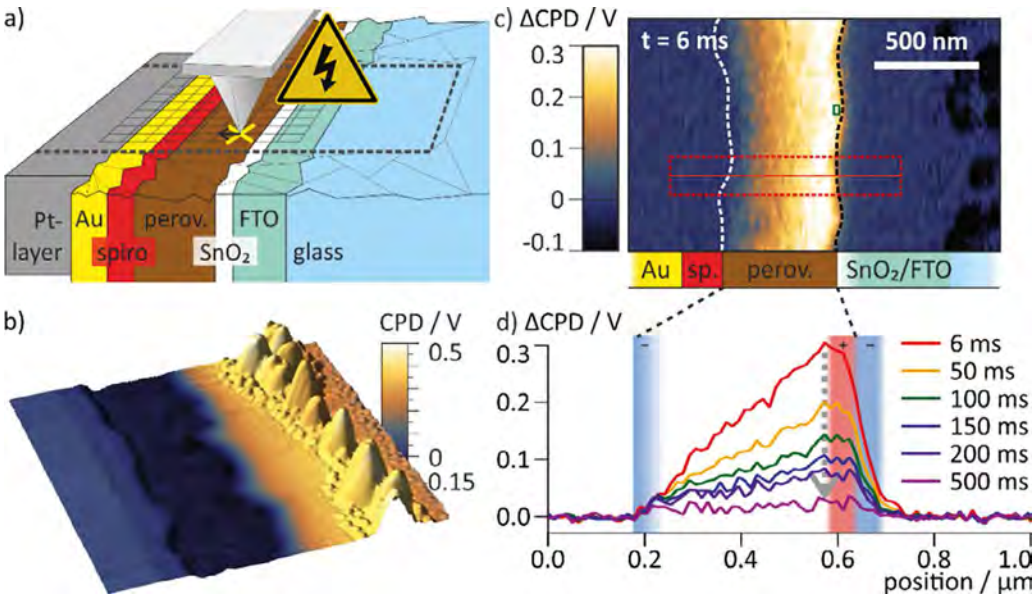

Fig. 3: a) Cross sections through operating devices enable potential measurements under operating conditions; b) overlay of topography and CPD map measured on a MHP solar cell (2x2) µm²; c) and d) time-resolved KPFM maps of the potential change after applying a 0.5V voltage pulse, revealing a remnant ionic polarization within the device that remains for up to 500 ms. Reproduced and adapted from Ref. [3] with permission from the Royal Society of Chemistry.

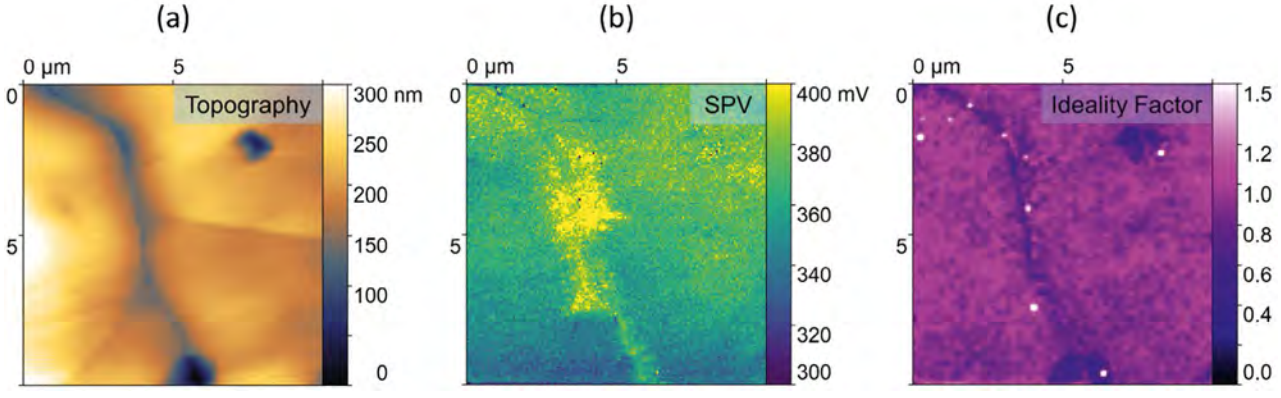

Fig. 4: Obtained topography, SPV, and ideality factor images obtained from nano-SPV measurement. Copied from [2] 2023 John Wiley and Sons ©.

boundaries. The SPV map shows increased SPV values in the proximity of the central grain boundary. Interestingly, the ideality factor map showed a different contrast, indicating that SPV and ideality factor provide complementary information about the photovoltaic thin film [2].

KPFM is a versatile tool with applications from nanotechnology over material science and corrosion studies to biology. KPFM can provide fundamental insights into the material physics in quantum structures, 2D materials, organic molecules, and energy materials. The possibility of studying functional nanostructures both *in situ* and *in operando* at high lateral resolution makes KPFM the method of choice for identifying loss mechanisms and performance bottlenecks, thus providing pivotal insights for device development and optimization.

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Pascal N. Rohrbeck studied chemistry in Mainz at the Johannes Gutenberg University (2014–2021). Since 2021, he is a Ph.D. student in chemistry at Johannes Gutenberg University Mainz and the Max Planck Institute for Polymer Research (MPIP) in Mainz (with Prof. Dr. Stefan A. L. Weber). His research focuses on developing new atomic force microscopy (AFM) methods to study interfaces of energy materials.

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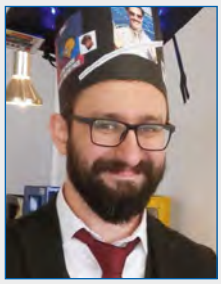

Yenal Yalcinkaya obtained his master's degree in materials science and engineering from Gebze Technical University in 2018. He joined Prof. Dr. Stefan A. L. Weber's group at the Max Planck Institute for Polymer Research in 2020 and obtained his Ph.D. in chemistry in 2024. The focus of his Ph.D. was electrical characterization of halide perovskite materials via electrical atomic force microscopy (AFM) methods. Since 2024, he is a postdoctoral researcher at the University of Konstanz.

Prof. Dr. Stefan A. L. Weber

Prof. Dr. Stefan A. L. Weber studied physics at the University of Konstanz. Already as an undergrad student he started to work with an SFM in the group of Prof. Leiderer. For his diploma thesis under the supervision of Prof. Dr. Johannes Boneberg he studied the interaction of gold nanoparticles with pulsed laser light. In 2007, he joined the group of Prof. H.-J. Butt at the Max Planck Institute for Polymer Reaearch (MPI-P), Mainz. During his PhD, he spent six months at Seoul National University, Korea, in the groups of Prof. K. Char and Prof. C. Lee. In 2010 he received a joint doctoral degree from Mainz University and SNU. In 2011 he went to University College Dublin as a Feodor Lynen Fellow (Alexander von Humboldt Foundation) to join Prof. B. Rodriguez and Prof. S. Jarvis. In 2012 he became a group leader in the Physics of Interfaces group in the department of Prof. H.-J. Butt at the Max Planck Institute for Polymer Research (MPI-P), Mainz. From 2015 to 2023 he held a junior professor postition in the physics department of Mainz University. Since June 2023, he is a permament group leader at the Institute for Photovoltaics at University Stuttgart, where he heads the Nanoscale Microscopy and Characterization group. In 2024, he won an ERC Consolidator grant for the development of a photovoltaic microscope that combines nanoscale electrical imaging with high-resolution optical microscopy and ultrafast spectroscopy.

BUNSEN-MAGAZIN · 27. JAHRGANG · 3/2025

Ilka Hermes

Piezoresponse force microscopy for novel computing components

In the future, ferroelectric components, such as ferroelectric field-effect transistors or tunnel junctions, could act as building blocks in novel computing concepts including neuromorphic computing. These applications require an in-depth understanding of the used ferroelectric materials, from domain structure to polarization switching behavior. Piezoresponse force microscopy, a functional atomic force microscopy technique, can access this information with a nanoscale resolution and even manipulate or tailor customized domain patterns.

In their native form, ferroelectrics have no macroscopic polarization. Instead, the materials form many small domains of opposite polarization orientation that compensate the overall polarization to lower the energy. However, if you subject ferroelectrics to an external electric field, you can switch the polarization orientation either globally or locally, and even draw images or tailored patterns of domains with different polarization orientations (Figure 1b) [1]. This adaptability is what makes ferroelectrics so interesting for modern computing technologies: Ferroelectric random access memories (FeRAMs) store information by inscribing information into the ferroelectric storage medium via local polarization switching [2]; Ferroelectric field-effect transistors (FeFETs) use ferroelectric materials in their gate stack to adjust the threshold voltage via the local polarization direction [3]; Ferroelectric tunnel junctions (FTJs) change the tunneling resistance based on the polarization and could serve as building bock in artificial synapses for neuromorphic computing [4].

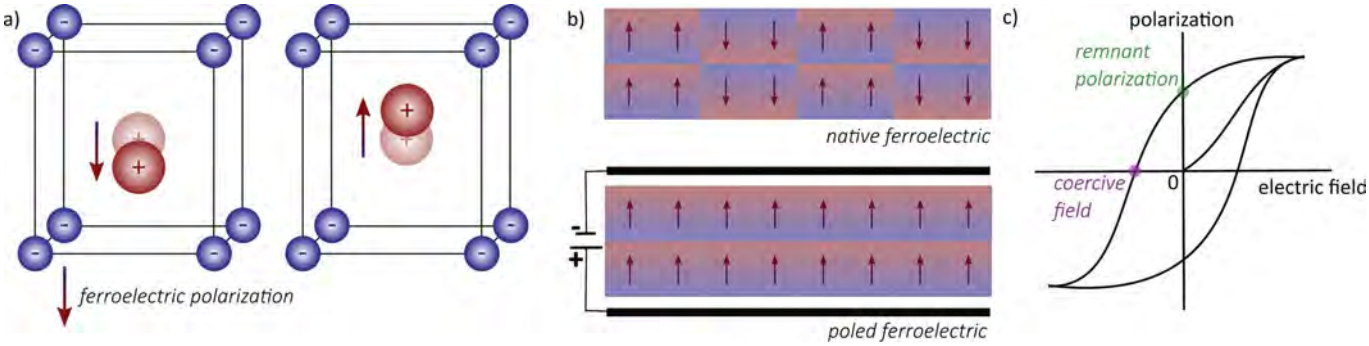

Fig. 1: a) Upwards or downward ferroelectric polarization state in a tetragonal unit cell, due to off-centering of a positive center-ion with respect to negative counter ions. b) Compensation of macroscopic polarization due to domains with opposite polarization orientation in the native state of ferroelectrics and poled state after external field application. c) Ferroelectric hysteresis.

Ferroelectric materials feature an intrinsic electrical polarization that is stable in two or more orientations: Imagine a crystalline material with a tetragonal unit cell, in which a positively charged center-ion experiences a directional electrostatic pull from some of the coordinating negative counterions or a steric hindrance due to a size mismatch between center-ion and counterions. These electrostatic interactions or steric effects can force the center-ion off its original position – for example by moving it a little bit up or down. The off-centering consequently induces a spatial misbalance between the negative and positive charges in the unit cell which leads to an electrical polarization pointing either upwards or downwards, depending on the shift of the center-ion (Figure 1a). If the center-ion has the same energy in its upward and downward shifted state, you now have two oppositely oriented, but equally stable ferroelectric polarization states [1].

To push these potential applications into commercialization, we have to understand ferroelectric domain structures and their switching behavior precisely and down to the nanoscale. Here, piezoresponse force microscopy (PFM) comes into play. PFM is a functional atomic force microscopy (AFM) method, which means simultaneous to the surface structure (topography), it can deliver functional information on local ferroelectric properties. In a PFM measurement, an electrically conductive tip attached to a cantilever scans the surface in contact mode with a constant interaction force (Figure 2). This constant force is enabled by a height feedback that keeps the cantilever deflection constant by adjusting the tip-sample distance at each pixel of the scan. At the same time, an AC voltage is applied between the tip and the back electrode *below* the ferroelectric sample.

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Since all ferroelectrics are piezoelectric [1], this AC voltage induces a mechanical oscillation in the material at the same frequency as the applied AC voltage. The oscillating material piezoresponse can be monitored in the cantilever deflection and decoupled from the topography using a lock-in amplifier [5].

Although difficult to quantify, the amplitude of the oscillating piezoresponse – the PFM amplitude – can give us information on the piezoelectric coefficient of the ferroelectric, i.e., how much the material extends or contracts in a given direction per applied Volt. In addition, the PFM amplitude shows the positions of domain walls as local minima. The phase of the piezoresponse – the PFM phase – captures the polarization orientation of the domains. For example, domains with opposite out-of-plane polarization would result in a 180° PFM phase contrast [5].

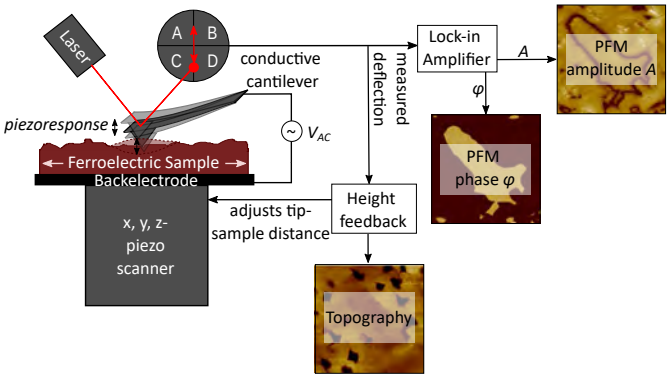

Fig. 2: Experimental setup of PFM, capturing the sample's topography and ferroelectric domains from the local piezoresponse induced by the AC voltage V_{AC}. The PFM amplitude shows the positions of domain walls as local minima and the PFM phase the polarization orientation in the domains. The exemplary images were measured on a bismuth ferrite thin film.

Since the piezoresponse per applied Volt is often times only a few tens of picometers or even below, we can enhance the signal by moving the AC excitation to the contact resonance of the cantilever and thereby use the natural amplification of oscillating systems. However, particularly for rough material surfaces, the contact resonance is not very stable. In fact, we have observed shifts in the contact resonance of up to 10 kHz on the same sample, in dependence of the local topography [6]. The resulting changes in PFM amplitude and phase can be easily mistaken for real sample responses. In order to avoid this topographic crosstalk, it is best practice to either measure far from the resonance for those sample with sufficiently large piezoresponse, or to employ dual amplitude resonance tracking (DART). DART PFM introduces an additional frequency feedback that adjusts the frequency of the AC excitation on each pixel of the scan to match the contact resonance [7]. Since its implementation requires additional lock-in amplifiers, DART is only offered on a few commercial AFMs or in combination with additional external electronics.

Besides domain imaging, PFM also allows insights on the local polarization switching behavior of ferroelectrics, which are important for their application in modern computing as FeRAM, FeFETs as well FTJs. In general, the polarization switching in ferroelectrics is described by the ferroelectric hysteresis (Figure 1c). A DC voltage is swept back and forth while the polarization is monitored. The polarization will switch, once the applied voltage exceeds the coercive field, positive and negative. Macroscopically, the polarization is measured via a reference capacitor; Microscopically, we can detect the polarization in the PFM phase in PFM switching spectroscopy. In order to do so, we stop the AFM scan at the position of interest and alternatingly apply DC voltages of increasing magnitude and AC voltages for PFM detection between tip and sample. The reason why we are alternating between excitation and detection is to minimize electrostatic crosstalk during the PFM detection. In a more recent development, researchers were able to automatize PFM switching spectroscopy using machine learning approaches for higher throughput material characterization. In the future this high throughput characterization may aid to fine-tune material composition to required ferroelectric properties for certain applications [8].

An innovative PFM approach for polarization switching and domain customization has just been presented by a group of researchers from the US (Figure 3). They combined the local writing of domain patterns via a conductive AFM tip with unusual scan trajectories: Instead of scanning back-and forth in a rectangular pattern as common in AFM, they were able to move the tip in a spiral motion or in a flower-like pattern, while applying a DC voltage to the tip. These scan trajectories together with the DC voltage allowed them to tailor nanodomains with controlled polarization orientations, that, among others, introduced charged ferroelectric domain walls [9]. Charged domain walls occur, when positive ends of the polarization ("head") of two neighboring domains point towards each other or the negative ends ("tails"), respectively. This polarization orientation leads to an energetically instable configuration with an absolute charge at the domain walls. Charged domain walls can serve as two-dimensional electronic conduction pathways through otherwise insulating ferroelectric materials and carry

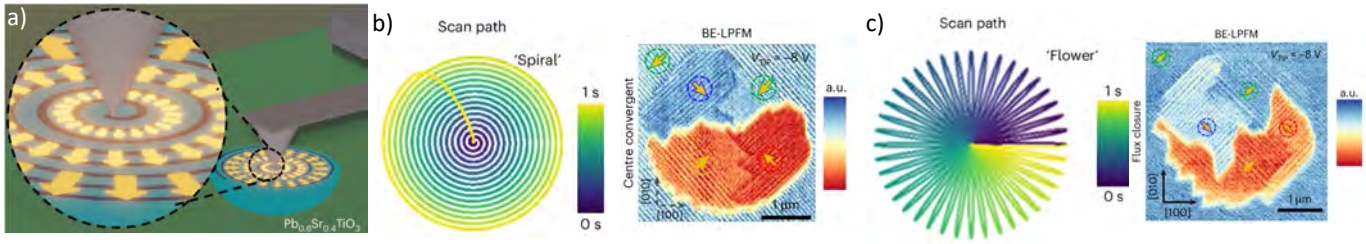

Fig. 3: a) Illustration of experimental PFM setup with customized scan trajectories. b) "Spiral" writing trajectory and corresponding in-plane PFM measurements after writing with +8 V demonstrating convergent polarization states in a head-to-head orientation. c) "Flower" writing trajectory and corresponding in-plane PFM measurements after writing with -8 V demonstrating flux-closure polarization states. The polarization orientations of the domains are shown with the orange arrows in b and c [9]. Copyright © 2024, UT-Battelle, LLC, 2024

a variety of other unique physical properties. In particular, the mobile nature of ferroelectric domain walls makes themselves intriguing candidates for nanoelectronic components such as artificial synapses for neuromorphic computing [10].

To summarize, PFM can further deepen the knowledge on ferroelectric properties such as domain formation, structure and switching behavior. Researchers have demonstrated that PFM can even be applied to customize domain patters that could find future application in novel computing concepts.

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Dr. Ilka Hermes

Ilka Hermes studied chemistry at the Johannes Gutenberg University in Mainz and began her work on scanning probe microscopy (SPM) in 2013 to resolve the arrangement of water molecules on mineral surfaces. For her dissertation, she moved to the Max Planck Institute for Polymer Research, where she used electrical and electromechanical SPM to understand the impact of different structural interfaces on charge carriers in perovskite solar cells. After a three-year stint in industry at the SPM manufacturer Park Systems Europe GmbH, Ilka started a junior research group for advanced correlative SPM at the Leibniz Institute of Polymer Research in Dresden, where her group is investigating the impact of the nanostructure on charge transport in perovskite solar cells and novel 2D materials.

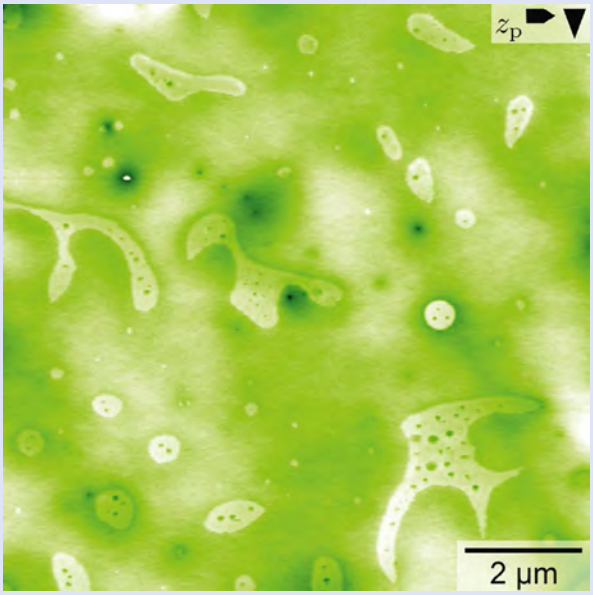
The art of SPM

Artist: **Kim Noelle Dreier (Bielefeld University)**

SPM technique: **Dynamic Atomic Force Microscopy (amplitude modulation mode)**

Investigated System: **silver iodide AgI (0001) plane in n-heptane**

Title: ***"The organic-inorganic aquarium"***



Antonia Köhler

Solid-liquid interfaces: Reflecting on the major breakthroughs in 3D atomic force microscopy

As early as 1988, solid-liquid interfaces have been studied using contact atomic force microscopy (AFM) [1]. After the invention of the dynamic AFM modes, using 'amplitude modulation' (AM) [2], 'phase modulation' (PM) [3] and 'frequency modulation' (FM) [4], T. Fukuma et al. [5] have demonstrated for the first time true atomic resolution on a mica (001) surface achieved with dynamic FM-AFM in 2005. These AFM data are typically referred to as two-dimensional (2D) AFM data, originating from the basic AFM principle where a sharp tip is laterally scanned in *XY*-direction over the sample surface while measuring the force acting between tip and sample [Fig 1(a) (here, AFM is referred to as scanning force microscopy (SFM)]. Figure 1 is taken from the original literature by T. Fukuma et al., therefore the term AFM, which is commonly used today, is not utilized in the figure.

However, at the interface between a solid surface and a liquid, the interfacial structure expands into the liquid solution. For a comprehensive description, it is thus necessary to probe a whole three-dimensional (3D) volume at the surface to study local distributions of solvent molecules. Therefore, T. Fukuma *et al.* first presented 3D-FM-AFM data at the mica-water interface in 2010 [6]. Before the invention of 3D-AFM, 1D-AFM force-distance curves have been recorded, first presented by J. H. Hoh et al. in 1992 [7]. This type of measurement will not be the subject of this article. In 3D-AFM, the tip is simultaneously scanned in *XY*- and *Z*-direction resulting in a 3D data set typically referred to as a 3D map [Fig. 1(b)]. In the early days of 3D-AFM measurements the tip has been excited with a piezo actuator and modulated with a sine wave via the piezo scanner to perform the *Z*-movement. During measurement, the frequency shift is recorded with respect to the tip position, while the average tip height is regulated to keep the frequency shift value constant [Fig. 1(c)]. The 3D frequency shift map can be further evaluated to obtain the 3D force map [8, 9]. From this 3D volume, lateral and vertical slices can be extracted to obtain information about the local distribution of solvent molecules.

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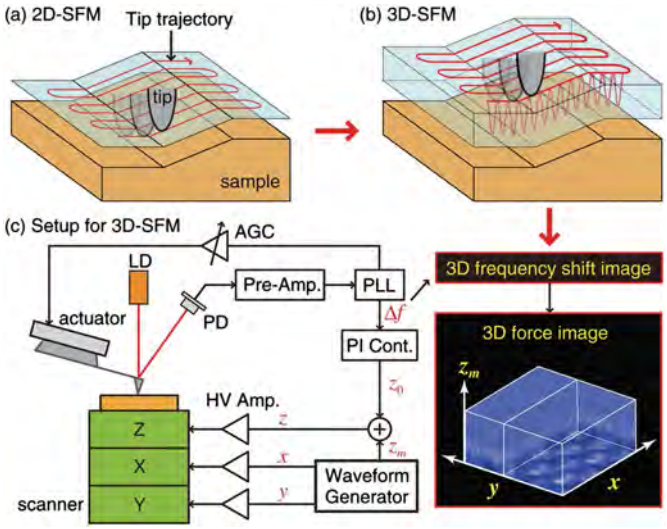

Fig. 1: Schematic illustrations of the basic 2D-AFM principle (a) (here referred to as scanning force microscopy (SFM)) and 3D-AFM principle (b). (c) Experimental setup for 3D-AFM using a piezo actuator to excite the cantilever and a phase-locked loop (PLL) circuit to detect the cantilever frequency. An automatic gain control (AGC) circuit is used to keep the cantilever amplitude constant. The 3D force image has been obtained at the mica-water interface (2 x 2 x 0.78 nm^3). Reprinted from: Takeshi Fukuma, Yasumasa Ueda, Shunsuke Yoshioka and Hitoshi Asakawa, *PRL* 2010 104, 016101, Copyright © 2010, Physical Review Letters.

Shortly after, A. Labuda et al. [10] improved the 3D-AFM setup by replacing the piezoacoustic excitation of the cantilever with photothermal excitation. Photothermal cantilever excitation in liquids, originally introduced by Ratcliff et al. in 1998 [11], has the advantage of directly exciting the cantilever without evoking vibrations in the surrounding liquid. Therefore, measurement artefacts are reduced. This is why photothermal excitation advanced to the method of choice when performing 3D-AFM in liquids.

Subsequently, questions have arisen on how the obtained contrast in 3D maps can be interpreted and, directly correlated, how the tip state influences the contrast [12]. In 2013, M. Watkins and B. Reischl introduced a simple model where the force, acting between tip and sample, is directly related to the local water density (today known as the solvent-tip approximation (STA)) [13]. The model incorporates a single water molecule at the tip apex directly probing the water density on top of the surface. At that time, 3D measurements have been collected at different surfaces including mica [6, 12], calcite [14, 15], α-Al_2O_3 [16], graphite [17], alkanethiol films [18, 19]

and organic crystals [20]. What all these investigations have in common is that the liquid phase is structured at the interface. Comparison of experimental results and molecular dynamics (MD) simulations, e.g., at the calcite-water interface support the existence of structured solvent layers in agreement with the STA [21]. In the case of water, these layers are referred to as hydration layers. Furthermore, 3D mapping has been used to obtain surface charge distributions on biological molecules, highlighting the applicability in biological systems [22]. In addition, 3D mapping has opened up the possibility to distinguish between anionic and cationic surface species and, more challenging, between interfacial atoms with the same net charge. This has been first demonstrated by T. Fukuma et al. in 2015 [21] and further on by H. Söngen et al. in 2016 [23] at the calcite- and dolomite-water interface.

The ubiquity of solid-liquid interfaces initially led to the investigation of systems with a relative ease in preparation, in particular hydrophilic mineral-water interfaces. Over time, however, more complex systems such as hydrophobic surfaces have come into focus [24, 25]. Investigations, e.g., at the graphite-water interface with 2D-AFM have revealed the presence of airborne hydrocarbons at the graphite surface [26, 27]. These experimental findings are corroborated by 3D-AFM data showing larger interlayer distances of solvation layers that do not match those of hydration layers.

Recently, experimental and theoretical work has often focused on the characterization of tips in terms of geometry, chemical properties and charge. In a combined experimental and theoretical work by K. Miyazawa et al. from 2020 [28], the correlation between different terminated tips and the contrast obtained is analyzed. They conclude that by comparing experimental data with atomistic MD simulations of different tip models, it is possible to determine the hydration structure of the tip apex. Knowledge of the hydration structure of the experimentally used tip is crucial in order to be able to compare different measurements. This study has been supported and investigated further by E. Nakouzi et al. in 2021 [29] highlighting the effect of tip properties for data interpretation.

Lately, interest in carrying out 3D-AFM measurements in electrochemical systems has increased. This combined technique, introduced by T. Utsunomiya et al. in 2015 [30] is named electrochemical (EC) 3D-AFM. The combination of an electrochemical setup with 3D-AFM enables the investigation of potential-dependent structures at electrode-electrolyte interfaces, as demonstrated, e.g. by S. Zhou et al. in 2020 [31].

In summary, the further development from 2D- to 3D-AFM has fundamentally changed the understanding of the interfacial structure at solid-liquid interfaces. The ongoing combination of 3D-AFM and theoretical work will continue to better understand phenomena at solid-liquid interfaces down to the molecular level.

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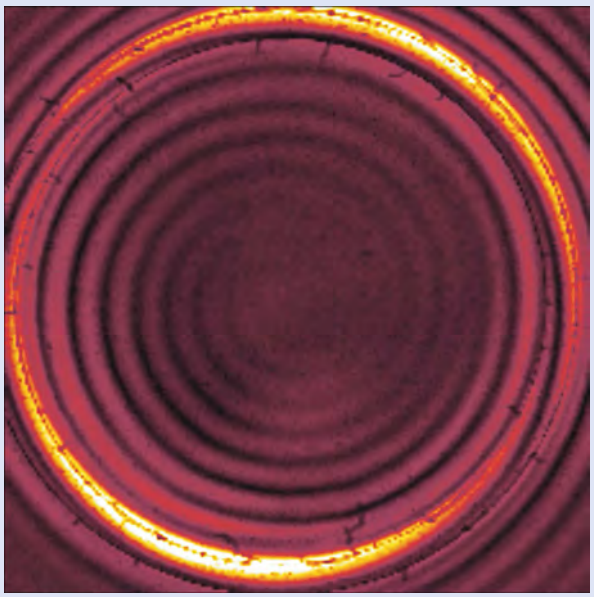
The art of SPM

Artist: **Enrico Baù, Thorsten Gölz & Andreas Tittl (Ludwig Maximilians Universität München)**

SPM technique: **Pseudo-heterodyne imaging by scattering scanning near-field optical microscopy (s-SNOM) with infrared light**

Investigated System: **Through engineered constructive and destructive interference, surface phonon polaritons in silicon carbide can form vortices of light, which is imaged by s-SNOM with nanoscale resolution.**

Titel: "***Light vortex odyssey***"



BUNSEN-MAGAZIN · 27. JAHRGANG · 3/2025

Thorsten Gölz, Enrico Baù, Andreas Tittl

Beyond the diffraction limit: *In-situ* nanoscale optical imaging and spectroscopy with tip-bound light

Optical microscopy and spectroscopy spanning the visible to terahertz spectral ranges is a foundational scientific tool in modern science, enabling advancements across diverse fields such as biomedical research, materials science, and fundamental physics. However, the spatial resolution of conventional optical techniques is inherently limited to approximately half the wavelength of light due to the diffraction limit of light [1]. This limitation hinders the direct optical investigation of nanoscale structures and their dynamic properties, which increasingly govern technological innovations and material functionalities in everyday life. To overcome this fundamental barrier, various super-resolution methodologies have been developed over the last few decades. Among these techniques, scattering-type scanning near-field optical microscopy (s-SNOM) has emerged as a particularly powerful approach due to its label-free nature [2, 3]. In s-SNOM, a sharp metallic tip, which is typically integrated into an atomic force microscope (AFM) setup, is illuminated by a tightly focused laser beam, generating a highly localized optical near-field at the tip apex. These strongly enhanced fields are created due to the achromatic lightning rod effect present around high curvature nanostructures, shown conceptually in Figure 1a. The near-field interaction between the tip and sample contains the nanoscale optical response of the sample below the tip apex. The near-field response is extracted from the detected light scattered from the tip containing both near-field and far-field response of the sample through interferometric processing on the basis of an asymmetric Michelson interferometry setup as displayed in Figure 1b and higher harmonics signal demodulation nΩ of the AFM tapping frequency Ω [3]. This methodology enables label-free spatially resolved optical probing with exceptional resolution only limited by the tip radius reaching down to 10–20 nm [4], far surpassing the diffraction limit. Furthermore, the optical response is recorded in correlation with the AFM response of the sample obtained through standard AFM-tapping mode operation. S-SNOM has been applied for the investigation of a wide range of materials such as 2D materials, doped semiconductors and phase change materials, as well as their intrinsic properties like charge carrier concentration [5], chemical composition [4] and refractive index [4].

In the last decade, s-SNOM has demonstrated its utility in the field of biology and biophysics by enabling infrared spectroscopic analysis and imaging of single proteins and fibrils [6], lipid monolayers [7], and fixed cellular structures [8] with nanoscale resolution. Yet, until recently, the exploration of dynamic biological and chemical processes and the study of biomolecules and cells in their native aqueous environment remained largely unfeasible. This limitation arose from the technical challenges associated with operating a near-field microscope in liquid, where the strong infrared absorption of the liquid and the mechanical instability of the tip hinder effective signal acquisition and stable measurements over a prolonged period.

Recent advancements, however, have begun to push the boundaries of this frontier, enabling hour-long stable near-field nanoscopy of complex liquid samples. In particular, nanometre thin membranes as shown in Figure 1c can act as a protective capping layer separating the liquid sample compartment from the delicate near-field tip. This method has proven itself to be a successful technique to enable stable operation, easy optical alignment and protection of both the delicate tip and the sample space [9, 10]. Importantly, the technique allows for the detection of both the optical and mechanical properties of the liquid-immersed sample adhering to the membrane [11].

New proof-of-concept studies have demonstrated the significant potential of this technique for the field of biophysics, showing its capability for the investigation of proteins, polymers and living biological samples in the form of E. Coli bacteria and eukaryotic tumour cells with infrared nanoscopy [9]. Furthermore, the technique has been successfully applied to study photoswitchable phospholipid vesicles in their native aqueous environment [12]. These photolipid vesicles are promising candidates for a new form of active targeted drug delivery for cancer therapy [13, 14]. Significantly, it could be shown that the active dynamic morphological modulation of lipid vesicles, driven by the photoisomeric switching of their constituent phospholipid molecules, could be imaged based

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DOI-Nr.: 10.26125/n3p9-kw29

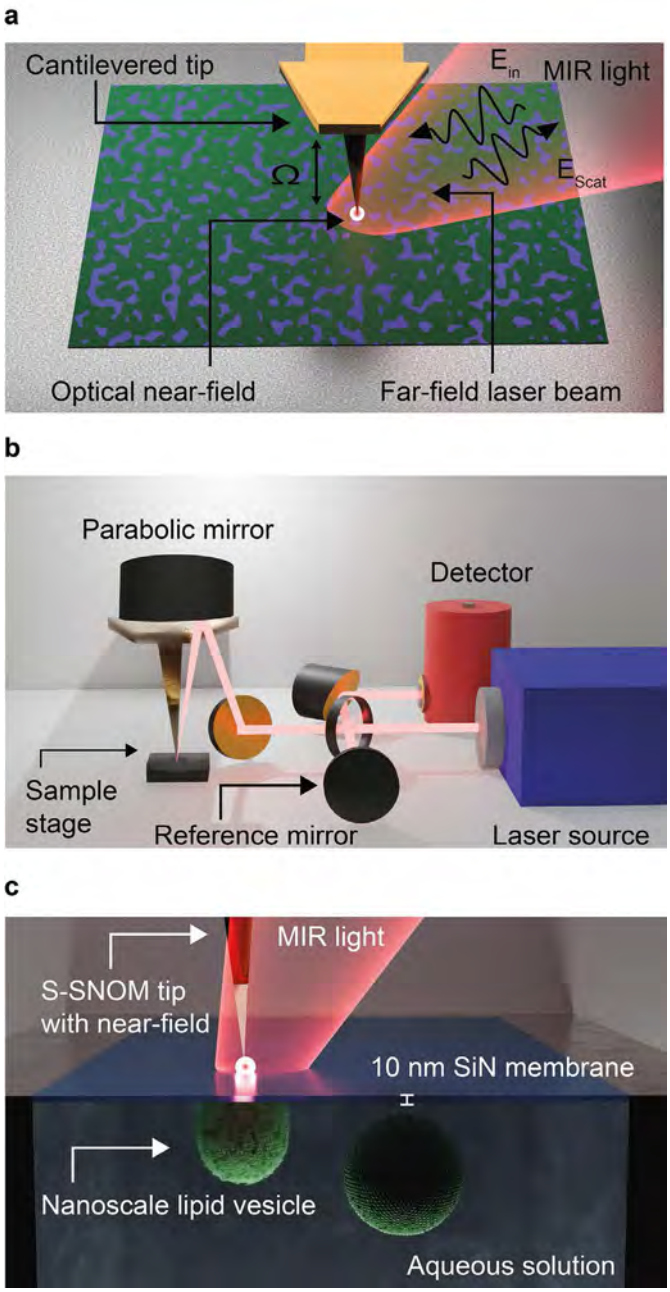

Fig. 1: Scattering scanning near-field optical microscopy (s-SNOM). **a.** s-SNOM cantilever with tip is scanning a sample in tapping mode while being illuminated by a far-field laser spot creating a highly confined near-field at the apex of the tip. The near-field enables the subdiffraction nanoscale resolved optical investigation of the surface of the sample. **b.** Optical setup with the laser beam being focused onto the tip by a parabolic mirror, which recollects the backscattering from the tip. The tip scattered light is modulated by a reference beam, detected by a detector and demodulated based on the tapping frequency Ω to attain the near-field from the far-field background. **c.** ***In-situ*** liquid s-SNOM method based on an ultra-thin SiN membrane allowing the near-field to penetrate through the membrane into the liquid compartment to investigate nanoscale objects located in close proximity to the membrane.

on their intrinsic IR scattering intensity. *In-situ* infrared near-field spectroscopy has also enabled the differentiation of two distinct photoisomeric states within a single lipid vesicle. Finally, the transient photoswitching dynamics of an individual photolipid vesicle, with dimensions well below the diffraction limit of MIR light, were temporally resolved with millisecond precision by monitoring its MIR response at a wavelength sensitive to the switching-induced perturbation.

The road ahead for *in-situ* optical nanoscopy

Based on these initial studies, *in-situ* near-field nanoscopy emerges as a highly promising technique for investigating various biological and chemical phenomena, such as the nature of lipid domains, drug release processes associated with lipid nanoparticles, cellular membrane chemistry, and degradation of heterogeneous catalysts. Furthermore, the recent development of a microfluidic cell module for *in-situ* s-SNOM by Attocube Systems AG and Norcada Inc. will help the broader scientific s-SNOM community to conduct liquid-phase experiments through dynamic exchange of the surrounding medium. This module enables nanoscopic investigations of the sample while simultaneously inducing precise variations in pH, osmolarity, solvent composition, or introducing specific chemical compounds. This capability could unlock entirely new experimental possibilities previously unattainable like the optical investigation of crystallisation and self-assembly processes on the nanoscale or the pH-induced change in secondary structure of single neurotoxic protein fibrils. Further progress in environmental control, such as temperature modulation (heating, cooling) or electrical biasing, as well as the integration of complementary measurement modalities like correlative fluorescence or Raman microscopy, could further expand the potential of *in-situ* s-SNOM. These correlative measurements would allow to compare conventional imaging modalities, such as fluorescence microscopy of cellular samples, with the enhanced spatial resolution and novel contrast mechanisms afforded by near-field microscopy. This integrated approach will provide deeper insights into the sample's nanoscale architecture and molecular organization, surpassing the information content accessible through standard techniques alone. In conclusion, the advancements outlined above underscore the growing applicability of optical nanoscopy to liquid-phase systems and highlight its transformative power for enabling nanoscale optical imaging of samples with spatial resolution well beyond the diffraction limit.

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Multimodal nanoimaging: Integrating s-SNOM, Raman and PL for advanced material characterization

Introduction

Advances in modern materials science, nanotechnology, and biology increasingly depend on precise characterization at the nanoscale, where subtle variations in chemical composition, electronic structure, and morphology profoundly influence material performance and properties. Optical microscopy remains an indispensable tool for characterization in these diverse fields. However, conventional far-field optical methods face a fundamental limitation – the diffraction limit – which restricts their spatial resolution to roughly half the wavelength of illumination [1].

In the infrared (IR) spectral regime – where wavelengths are on the order of 3–20 µm – this diffraction limit restricts resolution to several micrometers, making it challenging to probe nanoscale features in polymers, complex biological molecules, and quantum materials. Nonetheless, IR spectroscopy remains widely used due to its unique capability of identifying chemical species through characteristic vibrational modes associated with changes in molecular dipole moments (IR-active vibrations), providing highly specific chemical fingerprints for diverse materials [2].

Complementing IR spectroscopy, Raman spectroscopy is sensitive to variations in polarizability (Raman-active vibrations) [3]. Accordingly, these two techniques frequently provide complementary molecular information. Far-field Raman microscopy typically reaches spatial resolutions of about 0.5–1 µm – better than traditional IR microscopy but still limited when probing structures at the nanoscale. Moreover, high excitation powers in Raman imaging can cause sample heating or induce unwanted fluorescence, restricting its use in certain samples.

Photoluminescence (PL) spectroscopy, on the other hand, provides insight into electronic and excitonic processes, critical for understanding semiconductors, quantum dots, and emerging two-dimensional (2D) materials such as transition-metal dichalcogenides (TMDs). Nonetheless, conventional PL microscopy also remains subject to the same diffraction limit as IR and Raman, restricting their usefulness when investigating nanoscale phenomena.

Thus, to fully harness the potential of optical spectroscopy at the nanoscale, alternative approaches that surpass these far-field diffraction limits are essential. Scattering-type scanning near-field optical microscopy (s-SNOM) and related tip-enhanced spectroscopic methods have emerged as powerful solutions, overcoming traditional resolution constraints and enabling comprehensive nanoscale characterization.

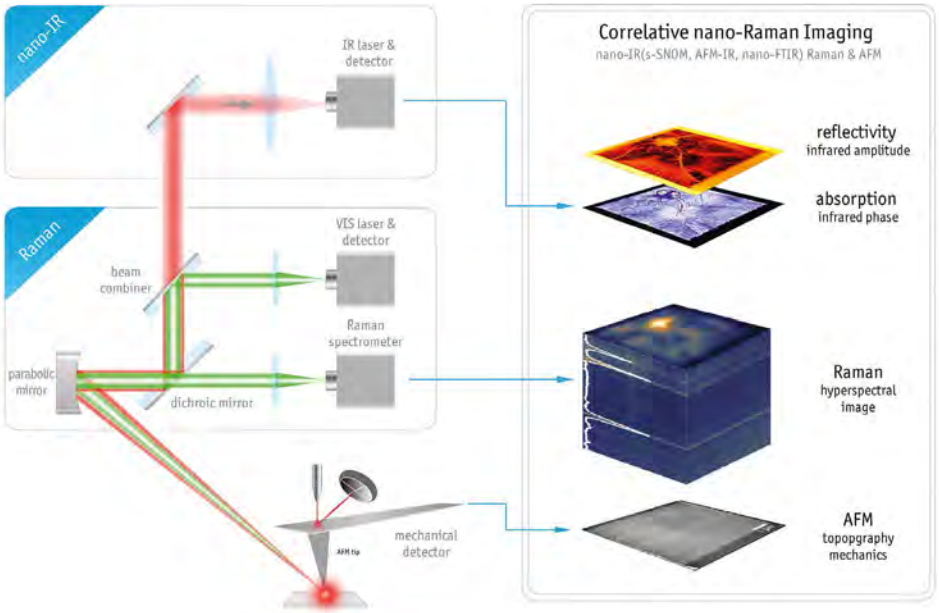

Fig. 1: Correlative nano-Raman integrates Raman and photoluminescence spectroscopy with AFM and nano-IR imaging in a single instrument, enabling nanoscale characterization of Raman- and IR-active vibrational modes. The instrumental setup (left) shows combined optical pathways for infrared (nano-IR) and visible (Raman) spectroscopy, focused onto the sample and AFM tip via a parabolic mirror. The example measurement (right) illustrates nano-IR images of reflectivity and absorption in CVD-grown graphene, along with a Raman hyperspectral data cube with the 2D band distribution on top and complementary AFM topography.

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Overcoming the diffraction limit: Scattering-type scanning near-field optical microscopy

Scattering-type scanning near-field optical microscopy (s-SNOM) addresses the diffraction limit by integrating atomic force microscopy (AFM) with broadband or monochromatic optical excitation from visible to terahertz (THz) frequencies. In s-SNOM, a metalized AFM tip is illuminated while tapping above the sample surface. Acting as a nanoantenna, the tip strongly localizes the electromagnetic field beneath its apex. The elastically scattered near-field signal encodes nanoscale details about local material properties, including vibrational resonances, electronic excitations, or carrier densities, achieving resolutions as fine as 10–50 nm [4, 5].

A critical aspect of s-SNOM is effectively distinguishing the genuine near-field signals from a large far-field background. This is commonly achieved by mechanically tapping the tip and employing higher-harmonic demodulation of the scattered signal, which efficiently isolates the near-field component due to its rapid decay with increasing tip-sample distance. Additionally, interferometric detection methods, such as pseudo-heterodyne detection [6] or broadband nano-FTIR [7], can measure both amplitude and phase, further enhancing the chemical and structural specificity.

While these strategies involve tip-scattered detection, it is worth noting that other IR nanospectroscopy methods also exist, most prominently AFM-IR [8]. In AFM-IR, photothermal expansion of the sample – triggered by IR absorption – drives the cantilever, enabling local chemical imaging with a spatial resolution of roughly 100 nm. As such, AFM-IR serves as an alternative to s-SNOM's tip-scattering–based detection, broadening the range of approaches for nanoscale IR characterization.

Overall, s-SNOM is an exceptionally versatile technique for nanoimaging and nanospectroscopy across the visible–THz spectrum. Its ability to map localized excitations – such as phonons in the IR [9], plasmons at visible [10] and IR [11] frequencies, molecular vibrations [7], or excitons [12] – and to function in a variety of conditions (e.g., cryogenic temperatures [13], electrical currents [14], or in liquids [15]) makes s-SNOM crucial for analyzing quantum materials, polymers, biomolecules, and more.

Tip-enhanced spectroscopies: TERS and TEPL

While s-SNOM typically relies on elastically scattered near fields for nanoscale imaging and spectroscopy, tip-enhanced Raman spectroscopy (TERS) and tip-enhanced photoluminescence (TEPL) take advantage of plasmonically amplified fields at the apex of metallic AFM tips to probe nanoscale chemical and electronic information through inelastic scattering and emission processes, respectively. In TERS, a plasmonically active tip – commonly silver or gold, precisely optimized for a particular excitation wavelength – significantly amplifies the Raman-scattered signals from molecular vibrations, making it possible to reveal chemical composition and molecular structure at resolutions down to a few nanometers or even beyond the single-molecule level [16]. TEPL, similarly, leverages the strong localized fields generated at the tip apex to intensify electronic emission, allowing detailed mapping of excitons, quantum emitters, and defect states at the nanoscale [17, 18]. The strong field enhancement inherent to these techniques provides unmatched sensitivity and specificity, facilitating studies on biological molecules, catalytic reactions, or intrinsic physical properties of 2D materials.

Despite their potential, TERS and TEPL experiments introduce additional technical complexity compared to standard s-SNOM. Tip fabrication is particularly demanding, requiring highly reproducible production of tips with optimal plasmonic properties, minimal contamination, and sustained stability under illumination. Moreover, precise optical alignment is crucial to ensure the necessary signal amplification while carefully controlling excitation power to avoid unwanted effects such as photodamage, thermal degradation, or spurious fluorescence. Consequently, TERS and TEPL often demand considerable expertise and meticulous experimental planning. Nevertheless, when successfully implemented, these methods greatly enhance the analytical depth provided by s-SNOM alone, revealing rich, complementary nanoscale information.

Multimodal approaches: s-SNOM, Raman, and PL together

When integrated into a single platform, s-SNOM, Raman, and PL spectroscopy form a uniquely powerful toolkit for nanometer-scale characterization. On one level, atomic force microscopy delivers high-resolution topographical images, precisely pinpointing structural features. Simultaneously, s-SNOM efficiently yields near-field optical images. When employing visible excitation lasers, the strong elastically scattered near-field signals further facilitate rapid initial alignment and precise localization of optical hotspots at the tip apex, significantly simplifying subsequent TERS and TEPL experiments. These tip-enhanced methods provide complementary chemical and electronic insights. Additionally, researchers can leverage these distinct yet synergistic spectroscopic contrasts by rapidly identifying regions of interest through far-field Raman or PL mapping before conducting deeper near-field IR or tip-enhanced analyses – all without the need to transfer samples between different systems. Moreover, such integrated platforms offer the possibility to simultaneously record s-SNOM and Raman or PL signals, enabling truly correlative measurements. This streamlined multimodal workflow accelerates nanoscale investigations across diverse research areas, including quantum technologies, photonics, materials science, chemistry, and biology – highlighting the broad applicability and versatility of this integrated spectroscopy platform.

Recent advancements in multimodal nanoscale spectroscopy

Following such a complementary approach, Kusch et al. first introduced a unified setup merging TERS and s-SNOM. By correlating tip-enhanced elastically scattered near-field signals with TERS data, they demonstrated more efficient sample alignment and hotspot localization, enabling in-depth morphological and

chemical analyses at the nanoscale – particularly relevant for interfaces, reaction sites, and localized heterogeneities in advanced materials [19]. In a follow-up study, a "double-tip" geometry for in-plane polarized near-field excitation was demonstrated. Because many 2D materials (such as graphene and TMDs) benefit from in-plane fields for optimal detection of vibrational modes and excitons, this dual-tip approach extends the polarization range accessible in near-field experiments, facilitating deeper explorations of anisotropic vibrational modes, localized excitons, and directionally dependent plasmon or polariton phenomena [20].

Turning toward quantum emitter studies, Niehues and coauthors integrated TEPL with s-SNOM, enabling nanoscale mapping of color centers in hexagonal boron nitride (hBN). By harnessing intense near-field nanofocusing and local field enhancements, they revealed the intrinsic dipole orientations and emission characteristics of individual emitters in ultrathin hBN layers. This work highlights the ability of TEPL to resolve spatial and spectral features of single-photon emitters beyond the reach of conventional far-field optics, a significant stride for quantum photonics research [21].

Recently, Roelli et al. harnessed simultaneous IR and visible illumination in plasmonic nanocavities to drive sum-frequency generation (SFG), while concurrently detecting the Raman and IR signals. By placing a metallic scanning probe tip above nanoparticle-on-mirror constructs, they created a "nanolens" that upconverts mid-infrared photons to the visible range with ultrahigh spatial confinement. This dual-excitation scheme not only shows potential for single-molecule–level vibrational spectroscopy but also allows *in-operando* control of local field enhancements – opening new avenues for ultrasensitive chemical and structural characterization [22].

Outlook and impact

Looking ahead, multimodal nanoimaging that combines s-SNOM, (tip-enhanced) Raman and PL spectroscopy promises to drive innovation in a broad range of scientific fields spanning materials science, chemistry, physics, and biology. In soft and polymeric materials, for instance, combining nanometer-resolved IR fingerprinting with Raman imaging reveals intricate morphologies and interfacial phenomena at the nanoscale. In quantum materials, advanced near-field spectroscopies offer a route to visualizing localized excitons or color centers in 2D platforms like TMDs and graphene, accelerating the development of next-generation photonic devices. These techniques also hold transformative potential in bionanotechnology, where proteins, membranes, and other biomolecular assemblies can be scrutinized with complementary spectroscopic contrasts at ultrahigh resolution. By overcoming the diffraction limit and fusing multiple analysis modes within a single platform, these multimodal approaches furnish deeper, more comprehensive insights into nanoscale phenomena than any single technique alone. As the underlying instrumentation and methodologies continue to evolve, this synergy of s-SNOM, TERS, and TEPL will almost certainly spark new discoveries in advanced functional materials – and beyond.

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Sandra Hernández Escobar, Nako Nakatsuka

Aptamer-modified nanopipettes – towards nanoscale chemical mapping

Scanning probe technologies have enabled surface profiling at unprecedented spatial resolutions, providing insight into the structure-property relationships of materials and biological systems [1-3]. But what if we could extend these techniques beyond topography – to mapping chemical dynamics with the same level of precision?

This capability would be particularly valuable for studying the complex communication between brain cells or neurons, driven by the electrically triggered release of neurotransmitters at nanoscale synapses [4]. While there are tools to monitor electrical signaling at high resolution *in vitro (e.g.*, complementary metal oxide semiconductor microelectrode arrays), there are limited analytical techniques that can probe the chemical activity at the resolution at which these interactions occur [5].

One promising approach to fill this technological gap, is adapting nanopipettes – used in scanning ion conductance microscopy (SICM) with nanoscale positional accuracy – into chemical biosensors (Fig. 1). This strategy could facilitate simultaneous topographic and chemical mapping at the nanoscale, providing new opportunities to investigate the complex chemical landscape of biological processes such as neuronal communication.

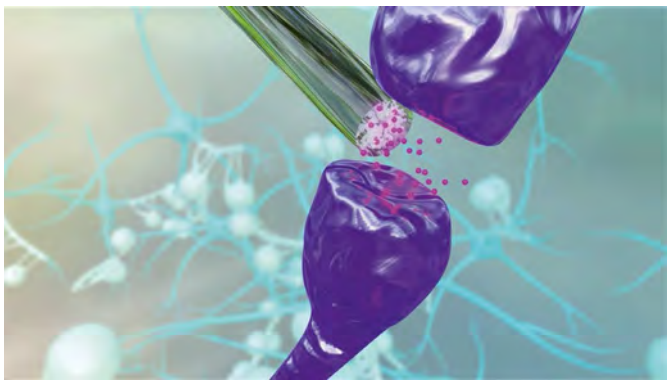

Fig. 1: Artistic rendering of aptamer-modified nanopipettes as nanoscale probes capable of approaching the spatial scale of synapses, where neuronal communication occurs. When integrated with SICM, these sensors may enable mapping of neurotransmitter dynamics with unprecedented spatial resolution. Figure credit: Hanna Grothe and Kevin Roost.

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DOI-Nr.: 10.26125/j2e1-rk52

Chemical biosensing at the nanoscale

A bare quartz nanopipette can be transformed into a chemical biosensor by functionalizing the inner surface with aptamers, artificially engineered, single-stranded oligonucleotides that bind selectively to target molecules (Fig. 2a). Aptamers are generated through an iterative *in vitro* selection process called systematic evolution of ligands by exponential enrichment (SELEX) [6, 7]. The SELEX conditions can be tailored to the intended application. For example, to ensure selectivity against structurally similar interferents, candidate sequences can be exposed to these molecules during counter-SELEX, ensuring only highly specific aptamers for the target analyte are selected [8].

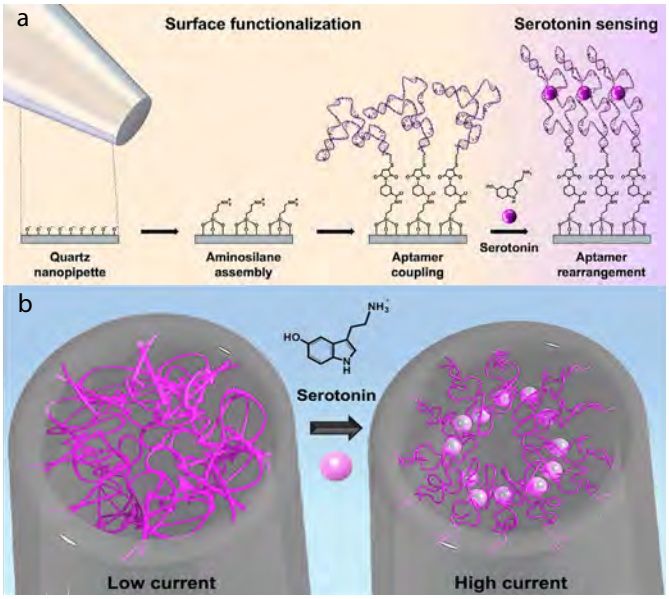

Fig. 2: a. Schematic of the multi-step surface functionalization process, where the inner wall of quartz nanopipettes are functionalized with aptamers. First, aminosilanes are deposited on the quartz surface through controlled chemical vapor deposition. The exposed amine groups (NH_3^+) are then covalently coupled to thiolated serotonin aptamers, which undergo conformational changes upon target binding. b. Artistic rendering of a nanopore modified with aptamers, illustrating their structural rearrangement upon target (serotonin) binding. Both figures reproduced with permission from [9], copyright American Chemical Society.

An additional layer of selectivity can be built into aptamers by designing them during SELEX, to undergo conformational rearrangements upon target binding [10]. As DNA or RNA-based molecules, aptamers are negatively charged, and structural switching upon target recognition redistributes these charges and associated counterions, generating a change in the electronic signal when integrated with nanopores (Fig. 2b). In conical nanopores, ion current rectification arises from asymmet-

ric ion flow, generating distinct responses under positive and negative voltage biases [11]. This effect depends on parameters such as the nanopore size, conical geometry, and charge density inside the sensitive area within the nanopore [12, 13]. Binding of the target to the aptamers induces charge redistribution within the confined nanopore, altering the measured ionic current in a target-specific manner with high sensitivity [9].

Effective gating of ionic flux requires the aptamer size to match the nanopore dimensions. For serotonin- and dopamine-specific aptamers (~ 5 nm), confinement within a ~ 10 nm pore was necessary [14]. As the structure-switching behavior of aptamers drives the measured signal, characterizing their conformational dynamics is crucial. To this end, we use a range of complementary tools. For example, single-molecule techniques such as Förster resonance energy transfer enable the analysis of aptamer backbone movements in solution [10]. In contrast, methods such as quartz crystal microbalance provide a surface-tethered readout, mimicking the nanopore sensor in an ensemble measurement [9, 14, 15]. Molecular dynamics simulations are used to corroborate experimental findings [16].

Our characterization results indicated that dopamine binding compresses the dopamine-specific aptamer backbone while serotonin recognition elongates the serotonin-specific aptamer (Fig. 3a). For the dopamine aptamer, this structural change decreases the measured ionic current through the nanopore upon dopamine binding (Fig. 3b, left). In contrast, serotonin binding increases the measured ionic current as serotonin levels rise (Fig. 3b, right). Similar divergent behavior has been observed in other biosensing platforms that rely on electrical readouts, such as field-effect transistors [10, 17]. Understanding these aptamer-specific conformational dynamics is crucial for designing nanopipette-based biosensors capable of detecting a wide range of analytes.

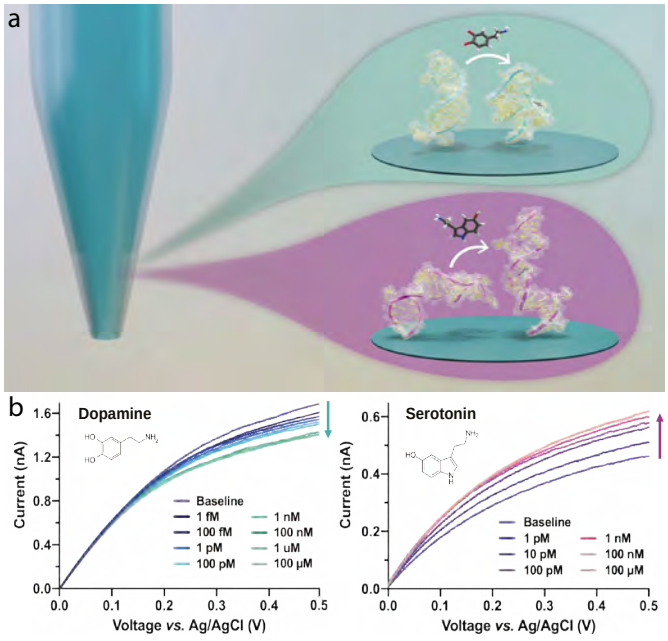

Fig. 3: a. Illustration of aptamer-modified nanopipettes, highlighting conformational changes in the dopamine (top) and serotonin (bottom) aptamers, as extracted from molecular dynamics simulations. b. Ionic current measurements from dopamine (left) and serotonin (right) aptamer-modified nanopipettes, demonstrating distinct opposite responses upon specific target recognition. Figures reproduced with permission from [5, 14], copyright American Chemical Society.

Nanopores tackle nonspecific binding

Aptamer-modified nanopipettes overcome key challenges in small-molecule biosensing, particularly for selective detection in biological environments. A major bottleneck in complex milieus is the non-specific binding of interferents, which can cause false positives, sensor biofouling, and signal degradation [18]. Nanopipettes mitigate this issue by confining aptamer-target interactions inside the ~ 10 nm nanopore pre-filled with aptamers, naturally excluding larger interfering molecules. This strategy has led to the development of highly selective serotonin and dopamine sensors that have been translated to *in vitro* and *ex vivo* settings.

For example, serotonin aptamer-modified nanopipettes enabled direct quantification of serotonin release from human induced pluripotent stem cell-derived neurons [19]. The sensors detected nanomolar changes in serotonin levels following treatment with an antidepressant that modulated neurotransmitter release. Similarly, dopamine aptamer-modified nanopipettes enabled real-time tracking of endogenous dopamine release upon electrical stimulation in the striatum, highlighting their potential for tissue implantation [20].

Nanopipettes are among the smallest implantable small-molecule biosensors available, operating label-free and directly in complex biofluids such as neurobasal medium and serum, without requiring sample pre-treatment or dilution. Their nanoscale dimensions and compatibility with live tissue make them a promising tool for monitoring neurochemical flux at localized positions when coupled to SICM in the future.

Remaining challenges for chemical mapping

Despite significant progress in developing and validating aptamer-modified nanopipettes, several challenges must be overcome to improve their performance and facilitate integration with SICM. These limitations primarily relate to sensor fabrication and reproducibility, real-time operation, and localization within complex biosystems.

One key hurdle is ensuring the reproducibility of the silanization process, the first step in the sequential surface chemistry inside the nanopipette (Fig. 2a), which is critical for sensor performance. We have made significant progress in optimizing silanization protocols by carefully controlling environmental factors to achieve consistent results across different nanopipettes and experimental conditions. However, further improvements are needed to enhance reliability and scalability.

Another fabrication challenge is precise control over the nanopore size, which is essential for adapting the sensor to different aptamers. The ~ 10 nm pore size was optimized for aptamers ~ 5 nm in their folded conformation. However, expanding the range of aptamer-modified nanopipettes to diverse targets re-

quires refining nanopore dimensions to accommodate aptamers of varying sizes. While interface nanopores enable size-tunable pores [21], they are static and cannot be placed in specific locations or interfaced with SICM, limiting their applicability.

Beyond fabrication, an important operational challenge is resetting the nanopipette after analyte binding inside the nanopore. To enable real-time quantification of unknown concentrations, the sensor must first be calibrated with known analyte amounts and then reset to its original state, ensuring free, unbound aptamers are available for subsequent measurements. For charged molecules like serotonin and dopamine, applying an electric field by sweeping voltages can effectively reset the sensor. However, this method is ineffective for neutral molecules, which do not respond to electric fields in the same way.

Beyond resetting, controlling the temporal dynamics of the aptamer-modified nanopipettes is crucial for enabling fast measurements. This capability is particularly important for applications requiring high-speed detection and continuous monitoring, such as capturing neurotransmitter fluctuations from neurons at millisecond resolution. Achieving rapid response times without compromising sensor stability remains a key technical challenge.

Finally, a challenging aspect of interfacing nanopipettes in complex environments, such as brain tissue, is precisely determining the location of the nanopore. As the nanoscale tip cannot be directly visualized, accurately pinpointing its exact placement remains difficult. Coupling nanopipettes with SICM offers a potential solution by enabling positional tracking, but simultaneously monitoring ionic currents for both topographical mapping and chemical sensing presents technical hurdles that must be addressed to ensure accurate and reliable measurements.

Overcoming these challenges will unlock the full potential of aptamer-modified nanopipettes for chemical mapping. Advancing high-speed measurements and real-time spatial tracking will be key for seamless SICM integration and broader translational use [22]. These innovations will pave the way for nanoscale biosensing technologies that enable precise interactions with biological systems, opening new avenues for studying intricate molecular processes in complex environments.

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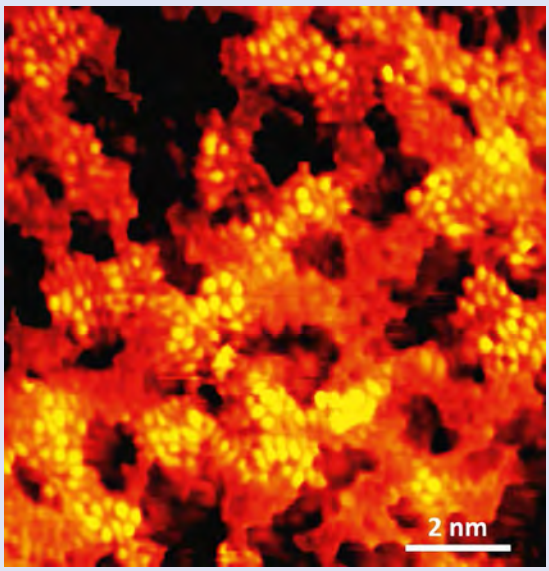
The art of SPM

Artist: **Lars Mohrhusen (Carl von Ossietzky Universität Oldenburg), Jeppe V. Lauritsen (Aarhus University)**

SPM technique: **Scanning tunneling microscope (STM)**

Investigated System: **Carbonaceous contaminants on a Au(111) surface (after a NAP treatment, scanned in UHV).**

Titel: „***Carbon disorder***"



Prof. Nako Nakatsuka

Prof. Nako Nakatsuka leads the Laboratory of Chemical Nanotechnology (CHEMINA) at the Neuro-X Institute, EPFL, since January 2024. Her research lies at the intersection of chemistry, engineering, and neuroscience, focusing on developing innovative technologies for human health. Born and raised in Tokyo, Japan, she moved to the U.S. for her bachelor's degree in chemistry at Fordham University (Bronx, NY). She then earned her Ph.D. at UCLA (Los Angeles, CA), where she developed transistor-based biosensors for neurochemical detection in the brain. After receiving the ETH Zürich Postdoctoral Fellowship, she moved to Switzerland and later became a senior scientist at the Laboratory of Biosensors and Bioelectronics. During this time, she pioneered aptamer-modified nanopipettes with the long-term vision of probing synapses at the nanoscale. For this work, she was named an MIT Under 35 Pioneer (2021), received the iCanX Young Scientist award (2022), the ACS Nano Lectureship Award (2023), and the C&EN Talented 12 Award (2024). Beyond research, Prof. Nakatsuka is passionate about science communication. She illustrated the children's chemistry book "A is for Atom: ABCs for Aspiring Chemists" to inspire future generations of scientists.

Patrick R. Unwin, Noah Al-Shamery

Scanning electrochemical cell microscopy: An interview with Pat Unwin

Professor Pat Unwin, a leading electrochemist at the University of Warwick, has played a pivotal role in the development of scanning electrochemical cell microscopy (SECCM). This technique has revolutionized nanoscale electrochemical imaging, offering new insights into material surfaces and electrochemical processes. In this interview with Noah Al-Shamery, he discusses the origins of SECCM, its challenges, and its promising future.

What initially inspired you to develop SECCM?

Well, we had a long history of working with scanning electrochemical microscopy (SECM), a powerful technique utilizing micro- or ultramicroelectrodes. However, SECM faced significant challenges at the nanoscale. It became clear that a different approach was needed to achieve high-resolution electrochemical imaging. We had also been exploring scanning ion conductance microscopy, which has its own advantages, but we needed a technique that confined electrochemical measurements in a more controlled way. That's where SECCM came in – using a pipette to confine an electrolyte solution to a tiny area of a surface, enabling high-resolution mapping of electrochemical activity. Pipettes are relatively easy to fabricate at the nanoscale, drawing inspiration from techniques like patch-clamp methods in electrophysiology. SECCM provided a way to tackle nanoscale electrochemistry problems that other techniques simply couldn't address.

Were there any early challenges that nearly made you abandon the idea?

Certainly. Our initial approach involved single-channel pipettes in what we called the scanning micro-pipette contact method. The pipettes were around a micron in size, down to a few hundred nanometers. While effective, this method required a conducting substrate, limiting its application to certain materials. We quickly realized that a new approach was necessary to position the pipette reliably. That's when we introduced the *theta pipette* dual-channel probes that incorporated ion-conductance feedback to allow positioning on any surface. Initially, landing the pipette on the surface with precision was a challenge, but I had an excellent student, Neil Ebejer, who played a crucial role in refining the technique. His work demonstrated that we could reliably position the pipette and obtain high-quality images [1].

SECCM is known for its versatility. What are some of the more unusual materials you've analyzed?

Early on, we focused on carbon-based materials, particularly graphene and carbon nanotubes. There was considerable debate in the literature about their intrinsic electrochemical activity. We wanted to investigate whether single-layer graphene was more or less active than graphite and to determine the reactivity of carbon nanotubes – whether it was primarily at the ends or along the sidewalls [2]. One particularly unusual experiment involved imaging individual platinum nanoparticles supported on a carbon nanotube. This was an extremely challenging substrate, but we managed to map the electrochemical activity at the nanoscale [3]. Another fascinating study involved using SECCM combined with SECM in a four-channel probe to explore static charge effects on insulating materials, demonstrating that electrochemical reactions could be driven by static charge – a controversial topic at the time [4]. Over the years, we've attempted even more unconventional applications, including scanning plant leaves and other biological samples, showcasing SECCM's adaptability.

Do you see increasing industry adoption of SECCM and similar scanning probe techniques?

Academia and industry often collaborate on electrochemical imaging projects, and we've worked with companies to investigate various processes. However, whether SECCM will be widely adopted in industry depends on several factors. Industries that heavily rely on surface characterization, such as semiconductors, have incorporated techniques like atomic force microscopy into their workflows and this provides some confidence that other industries could adopt SECCM. SECCM has great potential in industries where understanding electrochemical properties at the nanoscale is crucial, such as battery development, corrosion studies, and catalysis. However, widespread adoption requires not just investment in the equipment but also in skilled personnel who can effectively operate the instrument and interpret the data. Automation will likely play a key role in making SECCM more accessible to industry.

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With advancements in AI and automation, where do you see SECCM heading in the next decade?

SECCM is already more user-friendly than many other electrochemical scanning probe techniques, but automation will further enhance its accessibility. We've demonstrated semi-autonomous scanning, where the system identifies regions of interest via optical microscopy and then performs localized electrochemical analysis [5]. The next step is achieving full automation, where the instrument can analyze data in real-time and adapt its scanning strategy dynamically. In the future, I envision SECCM becoming highly autonomous, reducing the need for manual intervention. Additionally, we're likely to see more integration with complementary *in-situ* techniques, such as Raman spectroscopy, mass spectrometry, and other spectroelectrochemical methods. These advances will open up entirely new possibilities for understanding material properties at the nanoscale.

Looking back on your career, where does SECCM rank among your proudest achievements?

SECCM is right at the top. It's not just about the technique itself but how it integrates with other microscopies to provide a more comprehensive understanding of structure-function relationships. When we first obtained results with dual-channel SECCM, it was clear that this was a breakthrough – enabling nanoscale electrochemical imaging in a way that had never been done before. At that moment, we decided to focus all our efforts on developing SECCM further, demonstrating its versatility across a wide range of applications. To gain traction, a new technique needs strong proof-of-concept studies, and we put in a lot of work to ensure that SECCM was robust and broadly applicable. Seeing other researchers adopt and expand upon SECCM has been incredibly rewarding, and I look forward to its continued evolution.

Pat Unwin's insights highlight the remarkable journey of SECCM from its inception to its current role in nanoscale electrochemistry. With ongoing advancements in automation and integration with other analytical techniques, SECCM is poised to become even more powerful and widely used in both academia and industry.

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Prof. Dr. Patrick R. Unwin

Professor Patrick Unwin studied at the University of Liverpool and the University of Oxford before holding research positions at Balliol College, Oxford, and the University of Texas at Austin. Since 1991, he has been a professor at the University of Warwick, where he founded the Warwick Electrochemistry & Interfaces Group and led the EPSRC-Warwick Centre for Analytical Sciences. His groundbreaking work has been recognized with major awards, including the ACS Award in Electrochemistry, the Society of Electroanalytical Chemistry Charles N. Reilley Award, and multiple honors from the Royal Society of Chemistry and the International Society of Electrochemistry. In 2024, he was elected Fellow of the Royal Society (FRS), the UK's national academy of science.

Bethanie Dean

Brewing success

Waiting for a scanning electrochemical cell microscopy (SECCM) experiment to finish requires patience – and a touch of superstition. Data collection is slow, and slight disturbances can cause major disruption.

Experience has unfortunately taught me that if I stand too close, watch too intently or expectedly, something will go wrong. A droplet will burst, a false landing will occur, a tip will block. So, I step away to make a cup of tea. English breakfast. I brew it slowly, ensuring a strong full-bodied flavour. Milk and two sugars. A rushed cup of tea, made without care, never results in a satisfying cup. I ground myself in the steam, pretending that the outcome of this experiment does not define the rest of my day – or my week. Only then, will the experiment run smoothly.

A cup of tea is more than a drink. It brings calm to an otherwise stressful day, inviting an overlooked aspect of science – a good conversation. Whilst the experiment continues undisturbed, tea sparks office discussions: interesting stories, ongoing research, scientific debates. It's a space where perspectives can be challenged, ideas flow freely, and new insights emerge.

This habit has earned me a reputation for drinking ridiculous amounts of tea – an unintended consequence of (not) monitoring my experiments. But science is not just data collection. Some of the most productive days do not yield quantifiable results. Instead, they give us room to breathe, step back, and think to gain the perspective needed to generate weeks of meaningful progress.

When I return, I check the results, hoping my superstition holds true. More often than not, the experiment has behaved in my absence. And if it hasn't? At least I have a warm cup of tea to enjoy while I figure out the next step.

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Bethanie Dean M. Sc.

I joined as a member of the AS CDT at the University of Warwick in 2022 and began my PhD project with the Wilson Group utilising nanoscale electrochemistry through the use of modified scanning electrochemical cell microscopy (SECCM). The project aims to focus on the development and application of dual-barrel scanning probe microscopy techniques for the electrosynthesis of polymeric materials. I am interested in the physical and chemical properties of synthesis at the nanoscale to improve current technologies for things such as health monitoring and drug delivery.

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Simon Sprengel, Dmitry Momotenko

Scanning probe methods: From high-resolution imaging to nanoscale additive manufacturing

Scanning probe microscopy (SPM) is a family of powerful techniques for structural and functional imaging of interfaces using a (solid) probe. Starting with the pioneering development of scanning tunneling microscopy (STM) in 1982, the fundament for high resolution localized surface interaction was laid [1]. Already from the early age of SPM it became clear that the way the probe interacts with the surface could be adjusted to also allow local surface modification. Quickly, SPM became a tool for high resolution maskless patterning. Nowadays, SPM makes another leap in nanotechnology by extending microfabrication into the third dimension.

Manipulating molecules with high resolution

Since the introduction of SPM there has been a plethora of examples of local surface modification with high resolution. Among the most impressive ones is a stunning demonstration shown by IBM in 2011 in form of a Stop-Motion Movie called "A Boy And His Atom", published on the video platform YouTube (Fig. 1a). An STM tip was employed to precisely manipulate CO molecules on a copper substrate. The experiment was conducted at 5 K operating temperature to ensure stationarity of adsorbed CO, which was imaged by STM after each re-organization of the surface thus creating the movie frames [2]. Another elegant example was shown by recreating a painting "Degas Dancers" by Gina Candelori (Fig. 1b) and the University of Cambridge coat of arms on a microscale (Fig. 1c). The images were patterned by red and green fluorescently labeled DNA molecules on a streptavidin-coated glass surface [3]. Evidently, read-write capabilities of many SPMs provide a vast playground for creating functional interfaces. Scanning electrochemical microscopy (SECM) is particularly suited for these tasks, as, for instance, in creating cell adhesive and repellant coatings. A microelectrode tip was used to locally etch a oligo(ethylene glycol)-terminated self-assembled monolayer (OEG-SAM) forming a pixelated portrait, which has then been visualized by electrochemical imaging (Fig. 1d-f) [4].

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A journey into the third dimension

Until recently the bulk of the progress in surface modification with SPM has been made on planar interfaces and in 2D arrangement. At the same time, the demand for 3D micro- and nanostructures has grown tremendously. While 3D printing or additive manufacturing (AM) is already enjoying success across various industries, 3D-approaches in microfabrication only now start to get traction. For SPM-based techniques the trend is somewhat similar, since transitioning from 2D to 3D is not trivial and requires tight control of instrumental and materials aspects in all three dimensions.

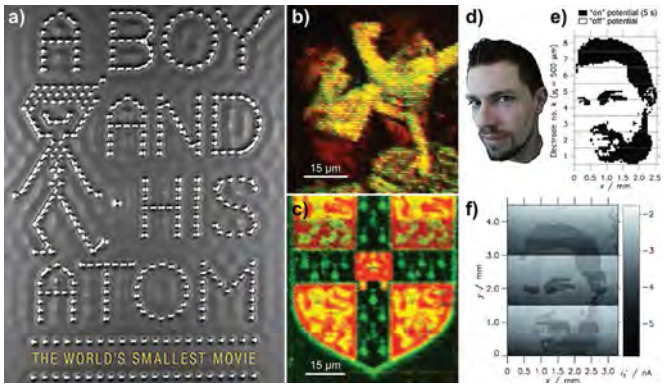

Fig. 1: Surface modification examples by SPMs. (a) IBM's stop-motion film "A Boy and His Atom", (b) a recreation of "Degas Dancers" by Gina Candelori and (c) The University of Cambridge emblem, formed by arranging fluorescently labeled DNA biomolecules on a streptavidin-coated glass surface. (d-f) Chemical surface modification via SECM by local etching of an OEG-SAM. © Angewandte Chemie International Edition [3, 4]. Reproduced by permission of John Wiley & Sons Ltd. and IBM/ YouTube "Fair-Use" [2]. All rights reserved.

Some examples of out-of-plane fabrication with SPMs, however, have been known for quite a while already. Electrochemical deposition using a microelectrode in SECM configuration achieved a 100 µm diameter copper pillar (Fig. 2 SECM) [5]. Also, more recently a major step towards 3D metal AM was achieved via meniscus-confined electrodeposition (MCED) that produced copper-structures with <1 µm diameter [6]. The current development of AM for microfabrication relies on similar principles but is equipped with a whole range of additional features to ensure reliable and reproducible operation even at the nanoscale, which remained unattainable for a long time.

Zurück zum Inhaltsverzeichnis

Emerging techniques for small-scale AM

The recent advances in SPM for high resolution 3D printing are made by implementing AM-specific adjustments in SPM instrumentation. For example, FluidFM, which is based on conventional atomic force microscopy (AFM), uses a hollow cantilever filled with electrolyte solution. When the cantilever delivers precursor metal ions into the electrolyte bath, electrochemical reduction at the substrate drives the deposition of the solid metal. The AFM feedback allows tracking metal growth at individual voxel level, ensuring full automation for the fabrication of complex 3D structures with microscale resolution (Fig. 2 FluidFM) [7].

The recent breakthroughs in AM in terms of feature size have been achieved by introducing an intermittent meniscus formation as feedback in MCED. This boosted the level of automation, allowing to monitor metal growth with kHz bandwidths, opening the way to achieve 25 nm voxel size (Fig. 2 MCED) [8]. At larger dimensions, MCED has also demonstrated for printing complex structures. Several other important advances in small scale SPM-based AM have been achieved using electrohydrodynamic redox printing (EHD-RP) (which shares many similarities with SPM-based AM without strictly being an SPM). EHD-RP utilizes electric field induced nanodroplet ejection from electrolyte-filled nozzles. As the droplets land on the biased substrate, the metal ion content gets converted into solid metal via electroreduction. As shown recently, a tight droplet control can allow metal structures with diameters down to 50 nm, with a complexity level approaching that somewhat between FluidFM and MCED (Fig. 2 EHD-RP) [9].

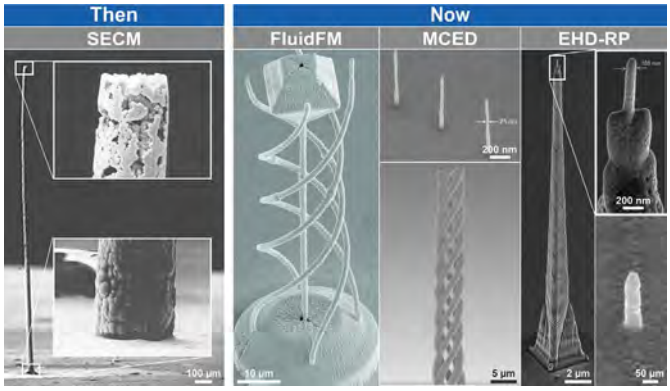

Fig. 2: Advances of 3D SPM Then vs Now. A comparison of early SECM copper deposition vs current techniques of FluidFM, MCED, and EHD-RP techniques. © The Electrochemical Society [5], © Advanced Engineering Materials [7], © Small [9]. Reproduced by permission of IOP Publishing Ltd., John Wiley & Sons Ltd., and under CC-BY-NC-ND 4.0 [8]. All rights reserved.

Challenges and future directions of SPM-based 3D printing techniques

The rising interest to small scale AM has led to significant advances in SPM-based 3D printing, but further development is yet restricted by various challenges. One remains within fundamental aspects that govern many functional SPMs – mass-transport. The limitations of ion transport at the nanoscale, typical for techniques like FluidFM, limit the available range of printing rates and resolution. Mass-transport-related broadening in liquid is difficult to take control of by simply reducing the nozzle opening. Similar limitations apply for EHD-RP where the resolution is linked to the droplet size, which becomes independent of the nozzle diameter at the nanoscale. For MCED, which currently champions the resolution, fabrication of more complex structures remains challenging. Despite success in printing overhangs and coils (Fig. 3a) reliable printing of more complex shapes and making connections between structures is still difficult (see missing part of "H" in Fig. 3a) [8].

Further advances also require extensive understanding of materials growth and microstructure control. Electrochemical AM offers fully dense as well as porous materials (like shown in Fig. 3b-c) [8, 10]. For advanced nanoscale applications, varying porosity could become very beneficial. Further progress in materials design needs means of surface structure engineering, as well as understanding of nanoscale mechanics (which for small scale AM becomes its own playground [11]). Electrical properties of the additively manufactured nanostructures are also a focus of current research activities. This requires extensive combination of high-resolution techniques, including electron microscopy, nanomechanical characterization, as well as advanced sample preparation techniques.

Additionally, macroscopic electrodeposition chemistries are not always directly transferrable to nanoscale AM. Although chemical composition of the printed features is typically given by the purity of the metal precursor (see EDX of the pure copper structures shown in Fig. 3d-e) [8], chemical composition control is often needed for new materials and processes. An extension of the material library is central for advanced applications along with the development of techniques to combine multiple materials into a single design.

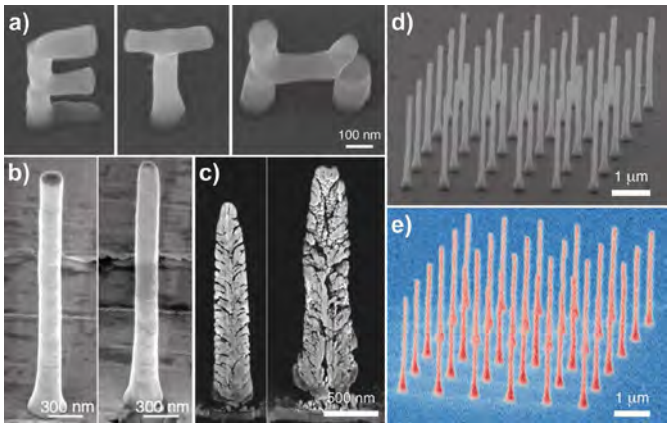

Fig. 3: Microstructure and chemical composition of additively manufactured metals. (a) Advances in MCED towards printing overhangs, focused ion beam (FIB) milling of (b) MCED- and (c) EHD-RP-fabricated Cu pillar porosity comparison, and (d-e) SEM/EDX analysis of MCED-printed structures, confirming high copper purity. Reproduced from [8] and [10] under CC-BY-NC-ND 4.0.

SPM has come a long way from its origins as a purely imaging approach to a powerful tool for surface modification and nanofabrication. The transition from 2D to 3D structures has opened new frontiers, but significant challenges remain. While recent advancements in SPM-based techniques such as FluidFM, MCED, and EHD-RP have enabled higher resolu-

tion and wider material library, technical issues and questions about material properties require further research. The immense opportunities that these techniques are yet to offer in micro- and nanofabrication fuel the growing interest in these developments.

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Simon Sprengel, M.Sc.

Simon Sprengel studied chemistry at the Carl von Ossietzky Universität Oldenburg, Germany. With the focus on technical electrochemistry he joined the group of Dmitry Momotenko at the Department of Chemistry. During his master's thesis he started the development of a microfluidic printing platform for single cell bioprinting technology for biomedical applications. Continuing his journey in Prof. Dmitry Momotenko's working group, he started as PhD candidate performing research on the development of micro- and nanoscale electrochemical additive manufacturing processes.

Prof. Dr. Dmitry Momotenko

Dmitry Momotenko studied analytical chemistry at the M. V. Lomonosov Moscow State University, Russia, and obtained his PhD at École Polytechnique Fédérale de Lausanne (EPFL, Switzerland) in 2013 in the Group of Prof. Hubert H. Girault. Main focus of his thesis was on electrochemistry for local chemical analysis. After the PhD studies, he received a Marie Curie Fellowship at the University of Warwick (UK) with the project on nanoscale ion sensing with glass nanopores to track heterogeneous chemical reactions. In 2017 he joined ETH Zürich (Switzerland) as an independent group leader with an Ambizione Grant from the Swiss National Science Foundation to work on new nanoparticle manipulation methods. In 2020 he obtained an ERC Starting Grant and in 2021 he joined the Carl von Ossietzky University of Oldenburg, Germany, where he is currently leading the Electrochemical Nanotechnology Group with research centered on nanoscale 3D printing, chemical sensing, scanning probe microscopy and electrocatalysis.

Auszeichnungen und Ehrungen

Marius David Gerlach, Dr., Radboud University, NL: Agnes-Pockels-Promotionspreis 2025 der DBG in recognition of the characterization of the photo ionization and photo fragmentation of HCNO towards the understanding of interstellar chemistry. Die Auszeichnung ist mit 1.000 Euro dotiert.

Lars Mohrhusen, Dr., Carl von Ossietzky Universität Oldenburg: Ewald Wicke-Preis 2025 der Ewald Wicke-Stiftung und der DBG für seine herausragenden wissenschaftlichen Leistungen zum Thema: Experimental studies of the role of defects, single atoms and two-dimensional systems on the (photo)catalytic activity and selectivity of heterogeneous catalysts for hydration reactions and for C1-chemistry. Die Auszeichnung ist mit 2.500 Euro dotiert.

Jacek Kozuch, Dr, Freie Universität Berlin: Nernst-Haber-Bodenstein-Preis 2025 der DBG für seine herausragenden wissenschaftlichen Leistungen zum Thema: In the development of vibrational spectroscopic methods for the molecular understanding of electrostatic effects in mechanisms of antibiotic resistance and viral infection. Die Auszeichnung ist mit 2.000 Euro dotiert.

Paola Bertucci, Prof., Yale University: Paul-Bunge-Preis 2025 der Hans-R.-Jenemann-Stiftung für ihre Monographie „In the Land of Marvels. Science, Fabricated Realities, and Industrial Espionage in the Age of the Grand Tour“. Die Auszeichnung ist mit 7.500 Euro dotiert.

Helmut Schwarz, Prof. Dr., Technische Universität Berlin: 2025 Wolf Prize Laureate in Chemistry der Wolf Foundation für seine herausragenden wissenschaftlichen Leistungen zum Thema: “For quantifying reactive species in the gas phase to solve fundamental problems in catalysis”. Die Auszeichnung ist mit 100.000 USD dotiert.

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für physikalische Chemie

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