Quantitative Surface Analysis 19 (QSA-19)

Materials Characterization in Multiple Dimensions

September 21, 2025
Charlotte NC

Featuring:

- **Atomic-resolution methods**
- **Depth-profiling advances**
- **Subsurface kinetics**
- **Imaging spectroscopy**

Introduction: Materials Characterization Beyond the Surface

The theme of QSA-19, *Materials Characterization in Multiple Dimensions*, reflects the increasingly urgent need to develop and apply analytical techniques that look beyond the topmost atomic layers of materials. Historically, surface science focused largely on planar structures and static systems. However, modern technological challenges demand more. Devices and materials now operate under complex conditions—high pressure, temperature, strain, and radiation—and are often composed of heterogeneous architectures, interfaces, and buried layers that evolve over time.

Characterizing materials solely at the surface no longer provides a complete picture. Many of the most critical properties—such as catalytic activity, corrosion resistance, charge transport, and mechanical strength—are governed by interactions that span from the atomic surface into the subsurface and bulk. These behaviors are often anisotropic, dynamic, and localized, requiring tools capable of high-resolution measurement in depth, time, energy, and spatial domain.

To address these needs, researchers have begun integrating complementary techniques like X-ray Photoelectron Spectroscopy (XPS), X-ray Absorption Fine Structure (XAFS), Secondary Ion Mass Spectrometry (SIMS), and emerging electron-based methods like MicroED. These tools, when used in conjunction with advanced data analytics and simulation, enable a multidimensional understanding of materials—capturing compositional gradients, oxidation states, lattice distortions, and morphological evolution in operando environments.

Yet, this shift toward multidimensional analysis is not without challenges. As dimensionality increases, so does the complexity of data acquisition, calibration, and interpretation. High-throughput measurements produce large, multidimensional datasets that require machine learning and automated pipelines to extract insight. Moreover, depth resolution, signal attenuation, and sample stability often limit what can be observed, making experimental design and instrumentation crucial.

QSA-19 brings together experts from diverse fields—surface science, chemistry, materials physics, bioengineering, and data science—to share innovations that are pushing the limits of what can be known about the subsurface. Whether through refined imaging methods, novel spectroscopic strategies, or computational corrections for depth profiling, this workshop emphasizes the essential role of multidimensional materials characterization in advancing science and technology.

Through this lens, QSA-19 aims not only to highlight groundbreaking work but also to foster collaborations that bridge disciplines, accelerate discovery, and empower the next generation of researchers to see beyond the surface.

Kinetics and Dynamics of Heterogeneously Catalyzed Oxidation on Silver and Rhodium Surfaces

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Understanding the interaction of oxygen with transition metal surfaces is important in many areas including corrosion and catalysis. Of interest to us is the formation and chemistry of subsurface oxygen (Osub); oxygen atoms dissolved in the near-surface region of catalytically active metals. We seek to understand how incorporation of Osub into the selvedge alters the surface structure and chemistry and use ultra-high vacuum (UHV) based surface science techniques to characterize Ag and Rh surfaces after exposure to atomic oxygen (AO) to obtain O coverages in excess of 1 ML. We have found that the surface temperature during deposition is an important factor for the formation of Osub and the consequent surface structures. Rh surfaces are significantly more reactive towards CO oxidation when Osub is present. This enhanced reactivity is located at the interface between the less reactive RhO2 oxide and O-covered metallic Rh. This leads to question – what are the microscopic steps the reagents take in a surface-catalyzed oxidation reaction? The ability to obtain velocity distributions of molecules desorbing from surfaces with both high temporal precision and angular resolution provides newfound insight into both the kinetics and the dynamics of recombinative desorption and subsurface emergence.

We have recently studied subsurface oxygen emerging from beneath Rh(111) and how the velocity distribution shifts in comparison to the thermally-dominated desorption pathways found for surface-adsorbed oxygen. In addition, it was recently discovered that decomposition of oxygenaceous surface phases on Ag(111) also exhibit pronounced shifts in the energetics of the desorbing oxygen molecules. I will discuss these observations and their potential impacts in oxidation reactions in heterogeneously catalyzed reactions over transition metal surfaces.

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MicroED at the Surface: Atomic-Resolution Structures from Nanocrystals—Proteins to Functional Materials

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Microcrystal Electron Diffraction (MicroED) provides a powerful new route to atomic-resolution structures of nanoscale crystals—materials critical for catalysis, thin-film growth, and functional surface properties but often invisible to conventional crystallographic methods. By merging electron microscopy with crystallographic rotation techniques, MicroED rapidly delivers three-dimensional structures at better than 1 Å resolution from sub-micron crystals, even when traditional X-ray diffraction methods fail. This talk will illustrate how MicroED is used for protein crystallography and a versatile tool for materials, chemistry, and surface science, showcasing examples ranging from pharmaceutical polymorphs to inorganic nanoparticles. Special emphasis will be placed on scenarios where MicroED complements or exceeds synchrotron powder diffraction, revealing polymorph identity, absolute stereochemistry, charge densities from minute samples, and crystallographic orientations directly on surfaces. This presentation aims to inspire cross-disciplinary collaboration by highlighting how existing TEM infrastructure in surface-science labs can harness MicroED to unlock detailed structural insights into nanoscale materials already at hand.

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Contribution of X-Rays Photon-Electron Spectroscopy (XPS) Imaging to XPS Spectroscopy Characterization on Spatial Heterogeneous Samples

Vincent Fernandez, Jonas Baltrusaitis and Neal Fairley

The XPS of heterogeneous samples is made difficult by lateral and in-depth distribution of disparate chemistry. Spectra measured from heterogeneous samples tend to mix signal from locations on the sample that might have distinct chemistry. Collecting spectra targeting specific chemistry requires knowledge about the location of the chemistry of interest. The alternative to spectroscopy is imaging XPS[1], where prior knowledge of sample chemistry is less important. Imaging XPS gathers signal from a larger area with the view to constructing spectra representative of these disparate chemistries[2], where spectra are formed that target pseudo-homogeneous locations on the sample. Spectra obtained by imaging XPS may be further enhanced by applying the approach described previously as the informed amorphous sample model[3], which aims to manipulate spectra by linear algebraic means to obtain spectral constructs more representative of distinct chemistries in a heterogeneous sample[4], but were not available in the recorded data. These spectral constructs allow chemistry to be assess using quantification steps typically used for XPS and fitting these spectral constructs to imaging XPS data, expressed as spectra-at-pixels, allows chemical state images to be computed. By these means, the chemistry of heterogeneous samples can be classified and the location of the classes presented in image form. Quantification by XPS is dependent on uniformity of response of signal to electron energy. Imaging XPS offers the possibility to calibrate a spectrometer [5] to ensure minimal variation in instrumental transmission response to energy. Interpreting imaging XPS quantification is then limited by signal variation caused by escape depth variation influenced by in-depth distribution of chemistry and the availability of appropriate relative sensitivity factors that describe the physics of collecting photoelectrons for a given instrument geometry and photoionization cross-sections.

References:

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[2] N. Fairley et al., ‘Systematic and collaborative approach to problem solving using X-ray photoelectron spectroscopy’, APPLIED SURFACE SCIENCE ADVANCES, vol. 5, Sep. 2021, doi: 10.1016/j.apsadv.2021.100112.

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[4] R. Ettouri et al., ‘Combined analysis methods for investigating titanium and nickel surface contamination after plasma deep etching’, Surface and Interface Analysis, vol. 54, no. 2, pp. 134–147, Feb. 2022, doi: 10.1002/sia.7030.

[5] V. Fernandez, O. Renault, N. Fairley, and J. Baltrusaitis, ‘Surface science insight note: Optimizing XPS instrument performance for quantification of spectra’, Surface and Interface Analysis, vol. n/a, no. n/a, Mar. 2024, doi: 10.1002/sia.7296.

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Computational Depth Correction of 3D SIMS Depth Profiling Images

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We have developed a computational strategy that is implemented in MATLAB for correcting the distortion in the z-direction that occurs in 3D SIMS depth profiling images acquired from contoured samples. This strategy does not require characterization of the sample's topology (e.g., AFM measurements) or knowledge of sputter rate. The secondary ion or secondary electron images that are acquired during SIMS depth profiling are used to generate a 3D model of the sample's surface at the time each depth profiling image was acquired. These 3D models of the sample's surface are used to adjust the z-position and height of every voxel in the 3D SIMS depth profiling images. To assess the accuracy of the 3D models that are used for depth correction in the absence of topographic data, each 3D model is compared to the corresponding secondary electron or secondary ion depth profiling image. Quantitative metrics for how well each surface model matches the morphology of the sample shown in the SIMS images have been developed. These metrics indicate the 3D models of the sample, and thus the depth corrected SIMS images, are most accurate when the secondary ion or secondary electron images used for model construction have high signal intensities. Nonetheless, even 3D SIMS images that were depth corrected using secondary ions with relatively low intensities are more accurate than uncorrected 3D SIMS depth profiling images. This computational depth correction strategy for 3D SIMS depth profiling images of contoured samples may improve the interpretation of SIMS depth profiling data.

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Beyond the Surface: Multidimensional Probing with XPS and XAFS—Experimental Frontiers and Data Challenges Across Synchrotron and Laboratory Platforms

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X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Fine Structure (XAFS) are foundational techniques for probing the electronic structure, chemical environment, and local atomic arrangements in materials. With the increasing demand to understand materials under operando, in situ, and extreme conditions, these techniques have evolved into sophisticated multidimensional probes that span not just energy, but also depth, pressure, temperature, spatial resolution, and chemical state dynamics.

This presentation explores the expanding landscape of multidimensional XPS and XAFS experimentation, encompassing both synchrotron-based and advanced laboratory-based systems. We will describe innovations in laboratory setups—such as time-of-flight and high-throughput XPS systems, high-resolution lab-based X-ray absorption instruments using crystal analyzers or von Hamos geometries, and integrated in situ reactors—alongside the powerful but logistically demanding synchrotron configurations. Emphasis will be placed on comparative capabilities, throughput, and practical accessibility, particularly as lab-based instruments increasingly enable meaningful time-resolved and environmental studies once reserved for large-scale facilities.

We will examine the challenges of designing experimental setups to achieve high dimensional resolution: from aligning grazing incidence optics and depth profiling in XPS, to managing high-temperature, high-pressure cells for operando XAFS. A significant portion of the talk will also address the data challenges posed by such experiments. As experimental dimensionality increases, data size and complexity scale rapidly—introducing bottlenecks in calibration, deconvolution, normalization, and interpretation. Strategies for managing these challenges—including multivariate analysis, machine learning, automated pipelines, and cloud-based data infrastructure—will be discussed in detail.

This presentation aims to be of interest to those using equipment ranging from large-scale synchrotron techniques to the emerging lab-based capabilities. It will emphasize their complementary roles in tackling grand challenges in catalysis, energy materials, corrosion, biomaterials, and nanostructured systems. It is particularly suited for researchers, instrumentation scientists, and data analysts seeking a holistic view of the evolving capabilities and computational needs of modern materials characterization workflows.