Design for Biosecurity

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Lecture 20

AFM-Cum-Electrochemistry Workstation

Welcome to the final lecture of this week, Lecture 20, where we will explore the compelling integration of Atomic Force Microscopy (AFM) with electrochemistry workstations. Over the course of this week, we've covered the foundational aspects of AFM, delving into its various operational modes, contact mode, non-contact mode, and intermittent mode. We also discussed how AFM can be synergized with spectroscopic tools like Raman and infrared spectrometers.

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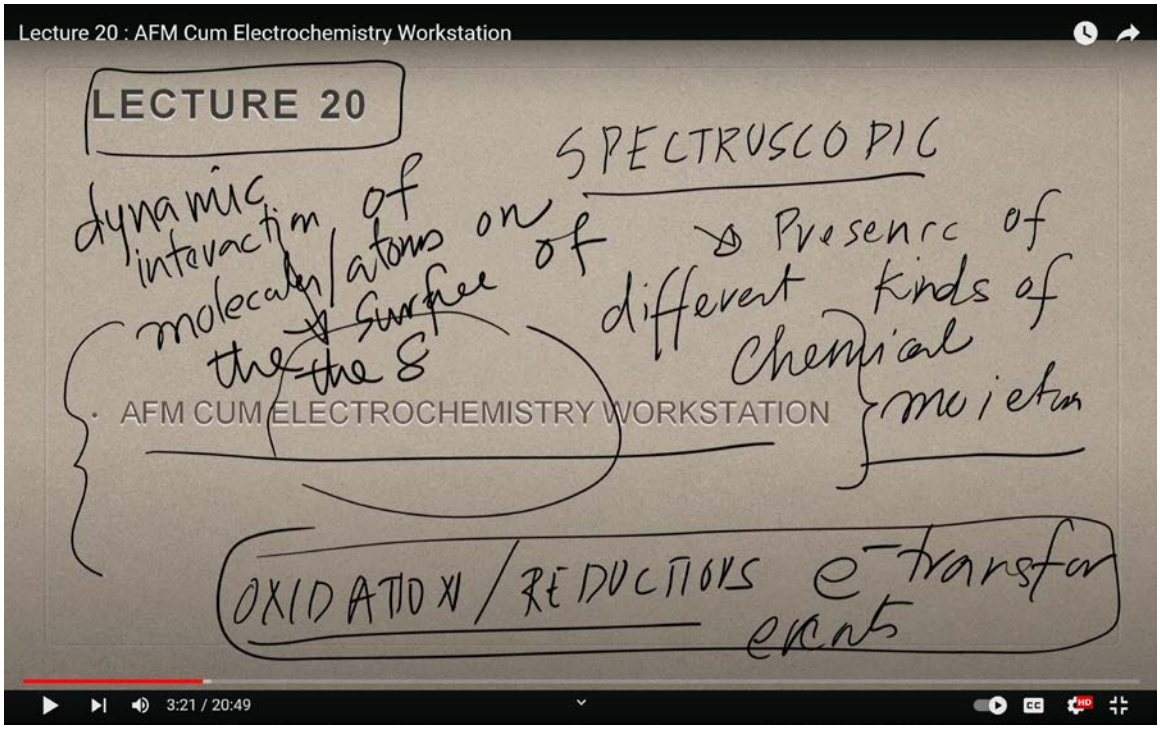

Today, we'll turn our attention to the fascinating combination of AFM with electrochemistry workstations, a particularly intriguing area of study. In earlier discussions

on spectroscopic tools, we examined the presence of different chemical moieties on surfaces. However, surfaces are rarely static; they often host dynamic processes such as oxidation, reduction, and other electron transfer events.

When investigating an electrically active surface, where ions and electrons are constantly in motion, the integration of AFM with electrochemistry workstations is not just beneficial, it's essential. This combination allows us to probe surfaces that are undergoing active electrochemical processes, offering invaluable insights into the behavior of electrically active substrates.

This sophisticated setup is specifically designed to study the real-time dynamic interactions of molecules and atoms on a sample's surface. Up until this point, we've focused on various static properties like the presence of specific functional groups, topography, elasticity, bending, flexibility, and the three-dimensional geometry of surfaces. However, we have not yet ventured into the realm of electron transfer processes.

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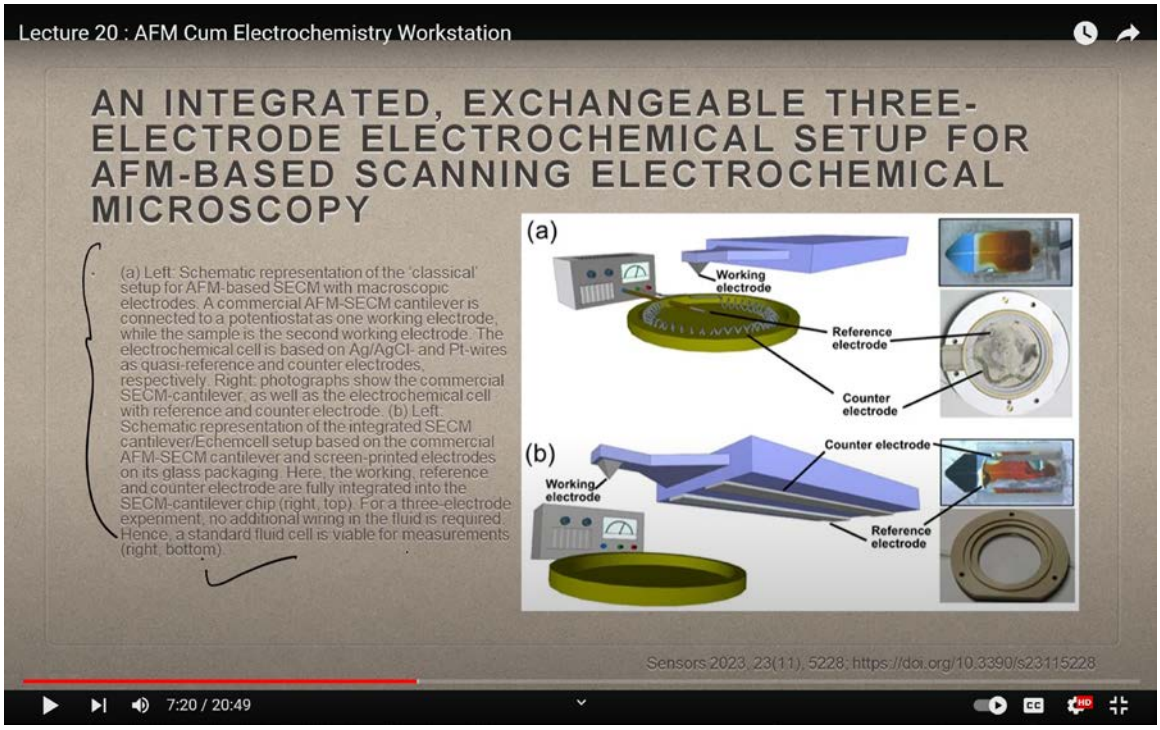

In this lecture, we will shift our focus to electron transfer processes, which leads us to the discussion of the most advanced models, those involving an integrated three-electrode electrochemical setup for AFM-based scanning electrochemical microscopy (SECM).

To revisit the basics, those of you familiar with the bioelectrochemistry course will recall that an electrochemical setup typically employs three electrodes: the working electrode, the reference electrode, and the counter electrode. The reference electrode, such as a hydrogen or platinum electrode, serves as a universal reference point, much like a pH reference electrode provides a baseline for acidity or basicity. The working electrode is the primary measurement electrode, while the counter electrode completes the circuit. Measurements are conducted between the working and counter electrodes, with the reference electrode providing a baseline for comparison.

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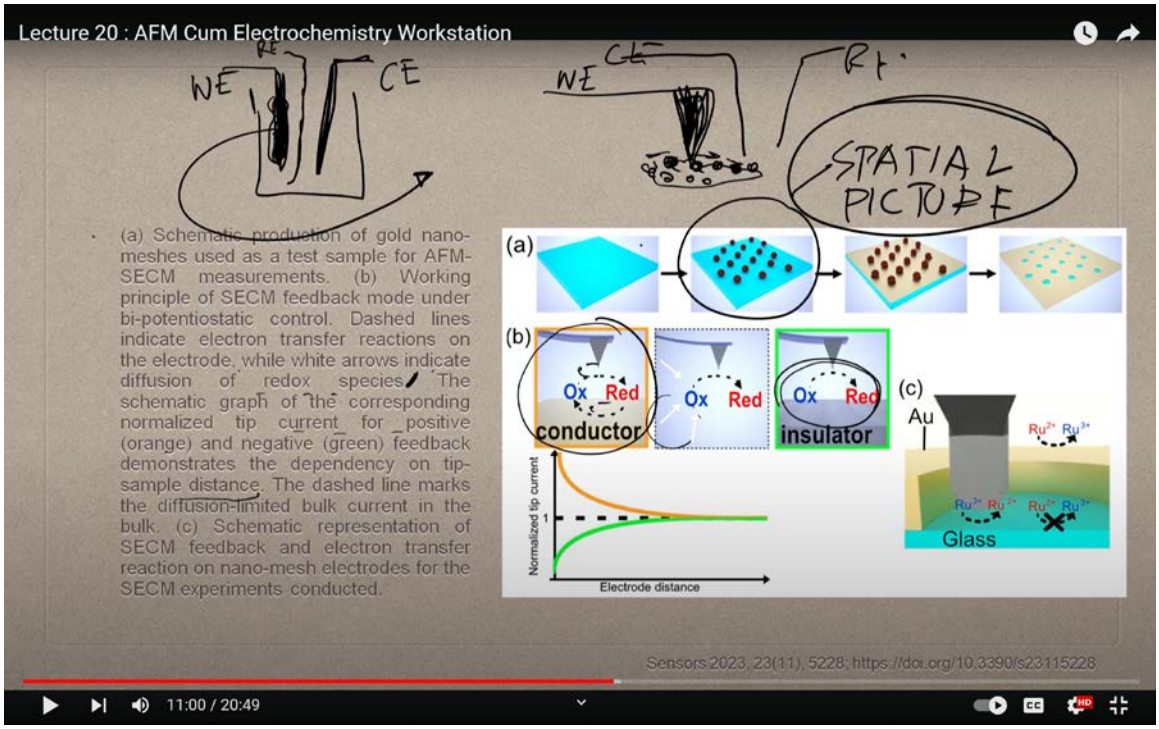

In this advanced setup, the AFM tip itself can function as the reference electrode. As the AFM tip scans the surface, it detects various properties. If the surface is conductive, the AFM tip, which can be modified to act as a conducting electrode, can sense and measure

the electrochemical activities occurring at the surface. This integration allows for a detailed exploration of the dynamic interactions between the surface and the AFM tip.

Now, let's examine the schematic representation of a classical AFM-based scanning electrochemical microscopy (SECM) setup equipped with microscopic electrodes. In this configuration, a commercial AFM-SECM cantilever is connected to a potentiostat, serving as one of the working electrodes, while the sample itself acts as the second working electrode. The electrochemical cell is equipped with an Ag-AgCl reference electrode and a platinum wire counter electrode, which serve as the quasi-reference and counter electrodes, respectively.

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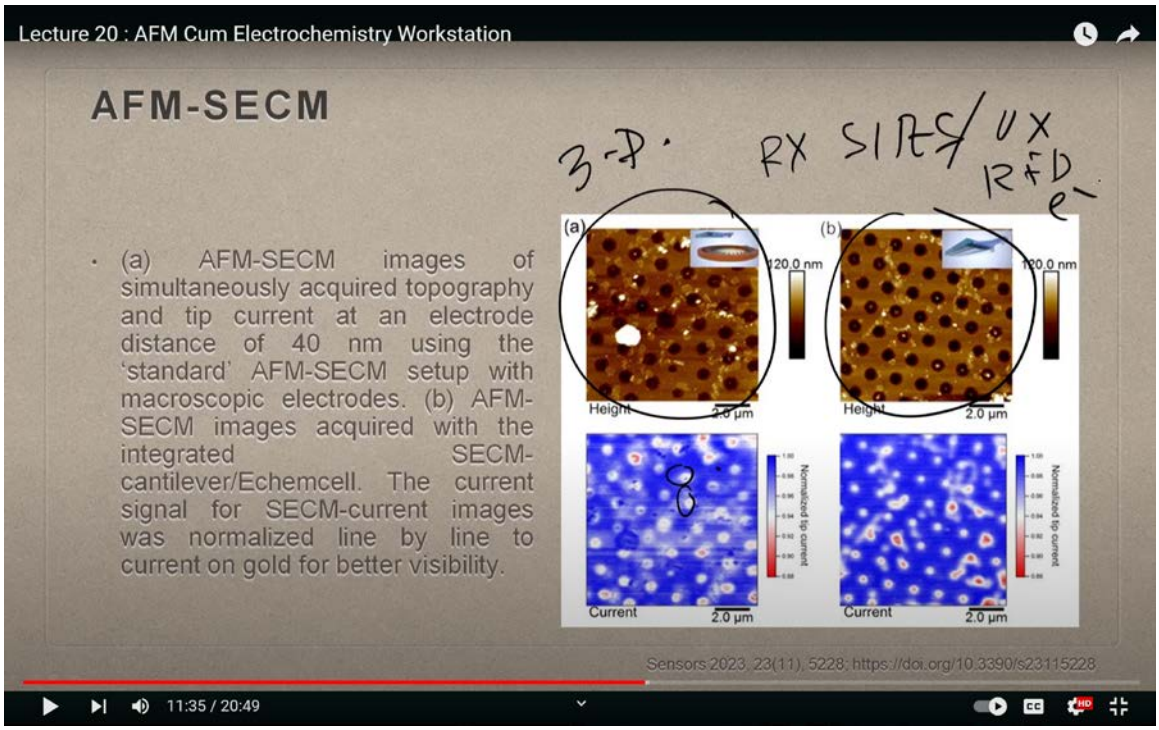

The photograph on the right depicts a commercial SECM cantilever along with the electrochemical cell, clearly highlighting the reference and counter electrodes. On the left, the schematic illustrates a cantilever designed with a commercial AFM-SECM setup, featuring a screen-printed electrode embedded in its glass packaging. In this design, the working, reference, and counter electrodes are seamlessly integrated into the SECM

cantilever chip. This allows for a three-electrode experiment without requiring additional wiring within the fluid. As a result, this configuration enables the use of a standard fluid cell for measurements, making it one of the most compact models available, with the tip incorporating printed electronics.

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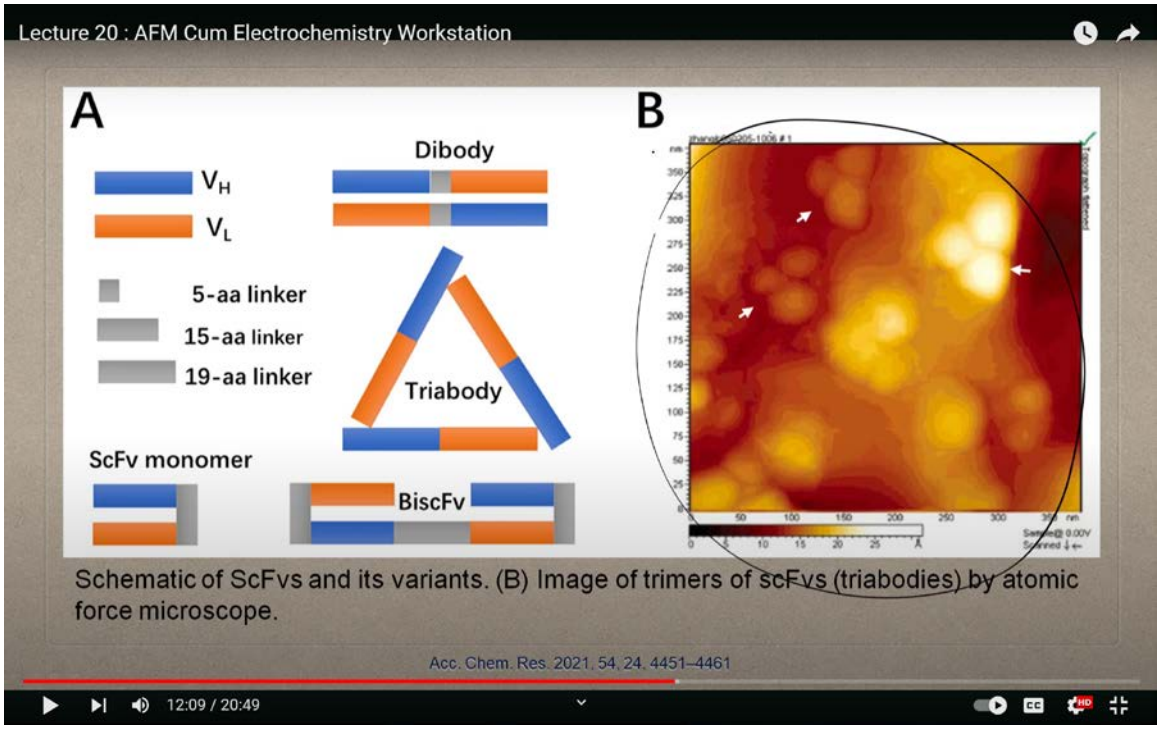

In the example shown, a gold nanomesh substrate is employed as the test sample within the AFM-SECM setup. The operating principle involves feedback mode under bipotentiostatic control. The dashed lines in the schematic represent electron transfer reactions occurring at the electrode, while the white arrows illustrate the diffusion of redox species. This setup effectively demonstrates electron transport phenomena, where electrons are either gained or lost at the electrode surface. In contrast, on the insulating surface, such electron transfer phenomena are not observed.

The corresponding graph illustrates the normalized tip current as a function of distance, ranging from positive to negative feedback, showing how the sample's distance influences

the current. The dashed line indicates the diffusion limits of the bulk current, underscoring the variations in conductivity across different regions of the sample surface.

As the AFM tip traverses the surface, it can detect where oxidation or reduction reactions are taking place or pinpoint areas with no detectable activity. This capability enables the spatial mapping of a substrate's potential or electrical activity with high precision.

In contrast, a traditional electrochemical setup provides only limited spatial information. For example, in a conventional setup, you typically have a working electrode (WE), a counter electrode (CE), and a reference electrode (RE). While you measure the compound's response on the working electrode, this setup does not offer insight into the distribution of the compound across the electrode surface.

Now, imagine transforming the working electrode into a dynamic scanning tool. With the AFM tip traversing the sample, it can detect and map the distribution of reaction sites and their associated activities. This setup delivers a dynamic and detailed spatial representation of the substrate, showing where reactions occur and how they are distributed, capabilities that traditional electrochemical setups lack.

The advantage of integrating AFM with electrochemical techniques lies in this real-time visualization of electron transport phenomena. While traditional imaging captures a broad view of the entire substrate, the AFM-SECM approach provides a more detailed perspective. It reveals three-dimensional features and allows for the precise identification of specific zones where reaction sites, such as oxidation or reduction, are located. This enhanced resolution facilitates accurate pinpointing of exact locations of electron transfer and reaction activity.

When comparing static electrochemical measurements to dynamic AFM-based approaches, the distinction is evident. Traditional electrochemical measurements offer a snapshot of data but fall short in providing the detailed spatial and temporal insights that AFM techniques offer.

Reflecting on our exploration, we began by delving into the diverse applications of AFM. For instance, we discussed its role in detecting various antibodies for pathogen

identification. Each image or schematic we examined tells a broader story of the technology's development and its diverse applications. To wrap up, let's revisit the foundational concepts we have covered.

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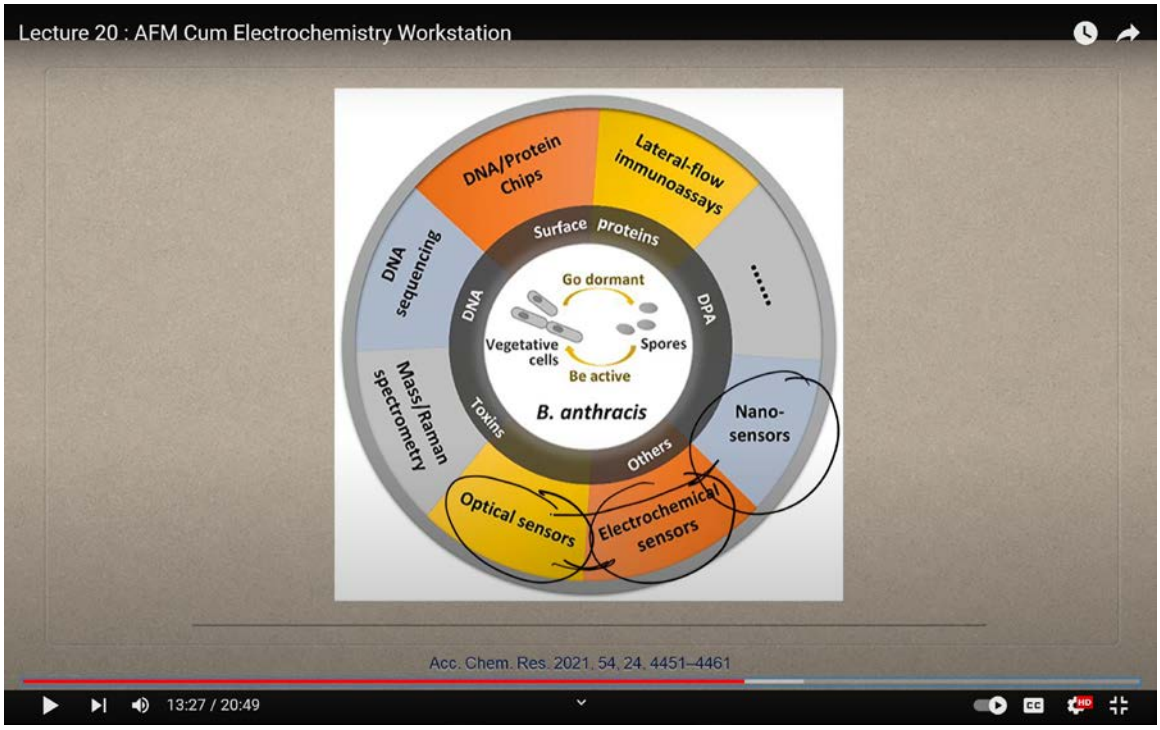

We began our exploration with quartz crystal microbalances (QCM) and piezoelectric sensors, setting the stage for our deeper dive into impedance analysis. Our initial discussions concentrated on the sensitivity of piezoelectric crystals. This foundation was crucial as we transitioned into exploring electrochemical and optical sensors, which prepared us to understand their integration with nanoscale technologies.

We subsequently investigated nanomaterials and a variety of sensing techniques, including Raman spectroscopy, infrared (IR) spectroscopy, piezoelectricity, electrochemistry, and AFM signatures. Our discussions focused on how these techniques can be applied to detect specific phenomena, highlighting the importance of a comprehensive approach. Each technique provides unique insights, and grasping their interactions is essential for a thorough understanding of the subject.

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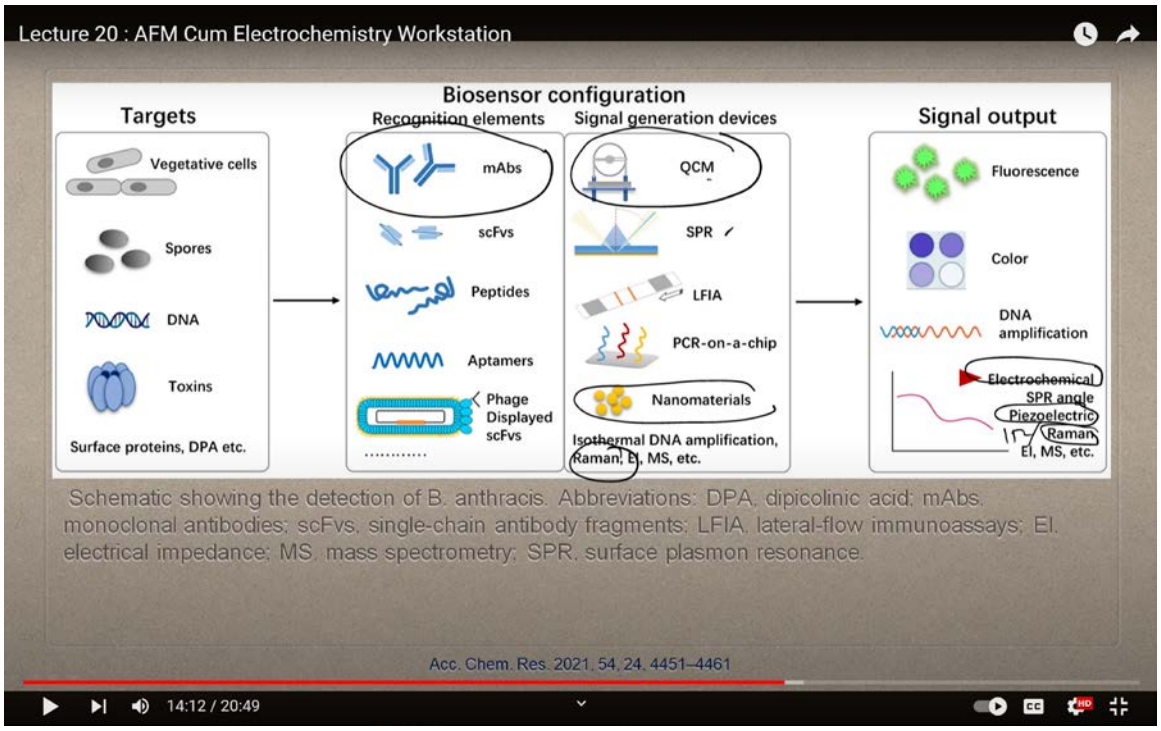

As part of our journey, we examined the application of quartz crystal microbalances and piezoelectric resonators, noting their integration into AFM applications. This week's emphasis was on AFM as a sensing tool, encompassing its various forms, from surface profiling to its integration with electrochemical and spectroscopic setups. We explored a range of topics including atomic topography, nanomechanics, electromechanics, nanoelectronics, nanospectroscopy, and nanoelectrochemistry, showcasing the versatility and scope of AFM in scientific research.

In our recent discussions, we covered an extensive array of techniques and concepts. We began by exploring different tip-sample interactions, including contact forces, and examined various AFM modes: contact mode, non-contact mode, and intermittent mode. Additionally, we delved into Scanning Near-Field Optical Microscopy (SNOM), discussing both its scattering and infrared variants.

We then delved into Near-Field Raman Imaging and harnessed the capabilities of Tapping AFM IR mode, which has proven to be an exceptionally robust tool.

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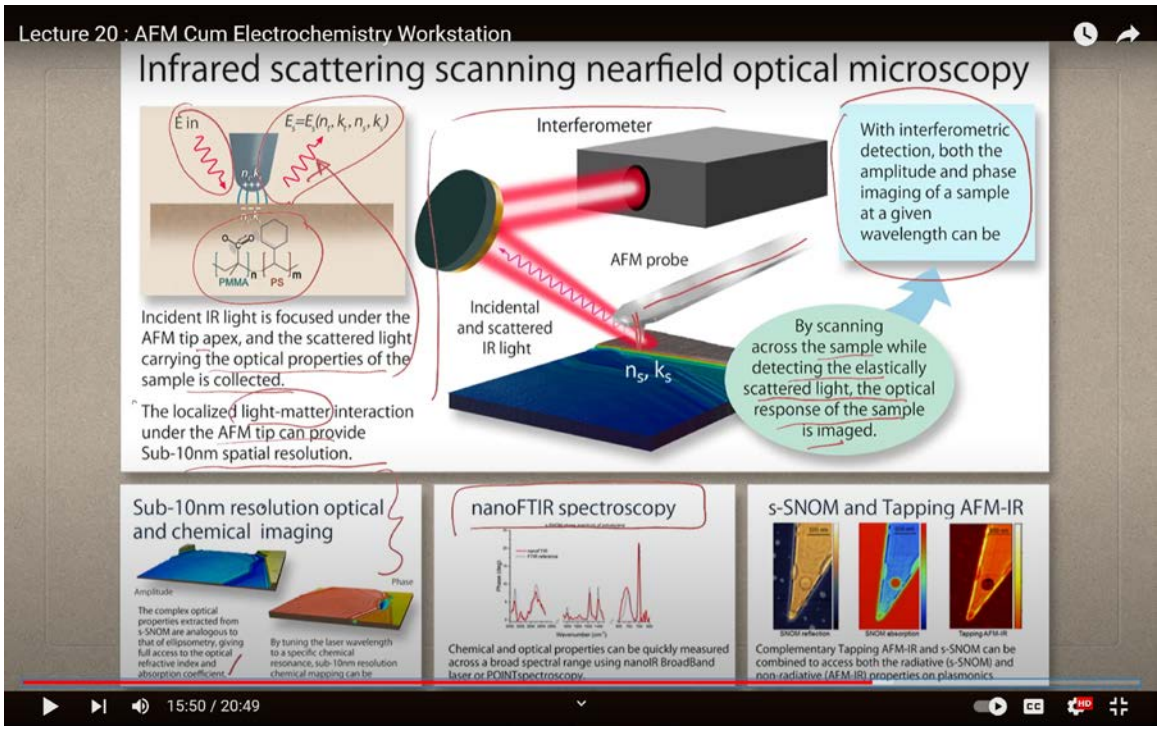

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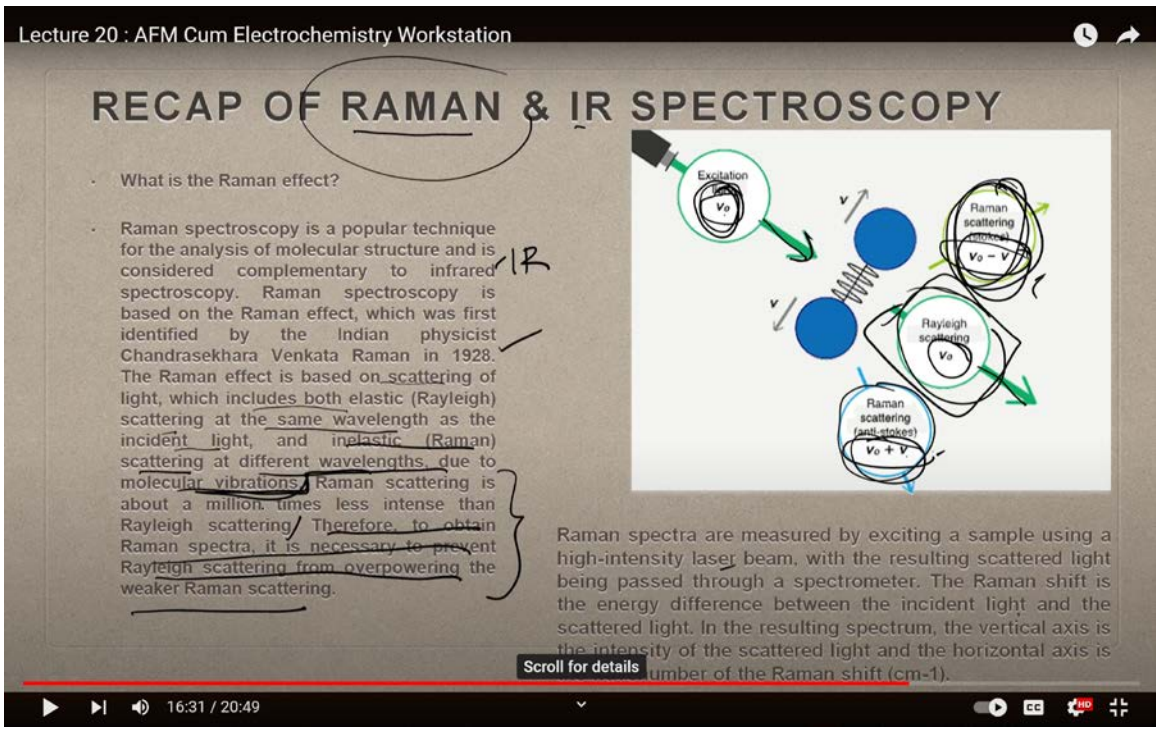

Our attention subsequently turned to Contact Resonance AFM, where we explored its underlying principles and practical applications.

In the field of spectroscopy, we reviewed the essential principles of Raman and Infrared (IR) spectroscopy. We discussed the concept of polarizability in Raman spectra and the influence of dipole moments in IR measurements. Additionally, we examined the Raman shift, addressing the importance of Rayleigh scattering and techniques for its suppression to achieve clearer Raman spectra, as well as distinguishing between Stokes and Anti-Stokes shifts.

As we progressed, we compared IR and Raman spectra, highlighting the differences between homonuclear and heteronuclear distributions in these spectra. We also emphasized the complementary nature of Raman and IR spectroscopy. Our discussions extended to the practical applications of Raman spectroscopy across various industries, including pharmaceuticals, food, and biological materials, such as biopolymers.

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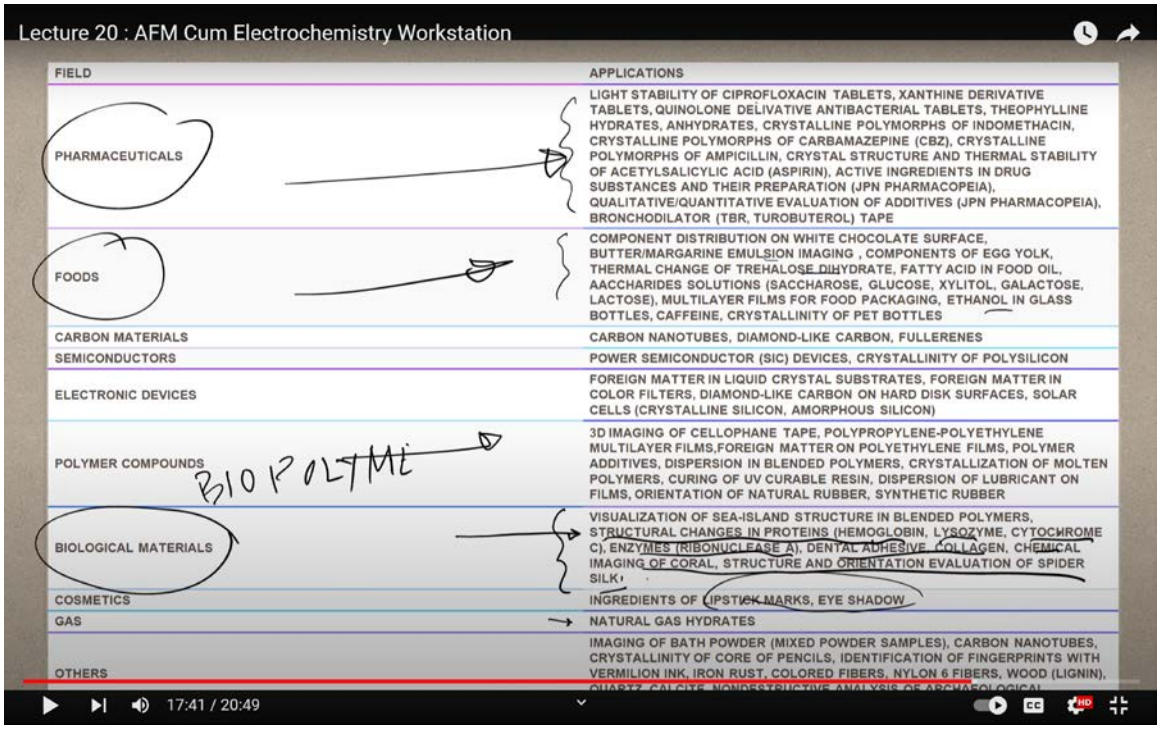

Finally, we investigated the integration of Raman spectroscopy with multimodal platforms, demonstrating how it can be effectively combined with imaging techniques like AFM and microscopy to enhance analytical capabilities.

We then examined the selection of lasers, emphasizing how different choices can offer distinct advantages and challenges. A significant hurdle is the elimination of fluorescence, which can be effectively managed using low-energy lasers, very narrow apertures, or sophisticated algorithms. I also addressed the complexities associated with using algorithms for removing fluorescence.

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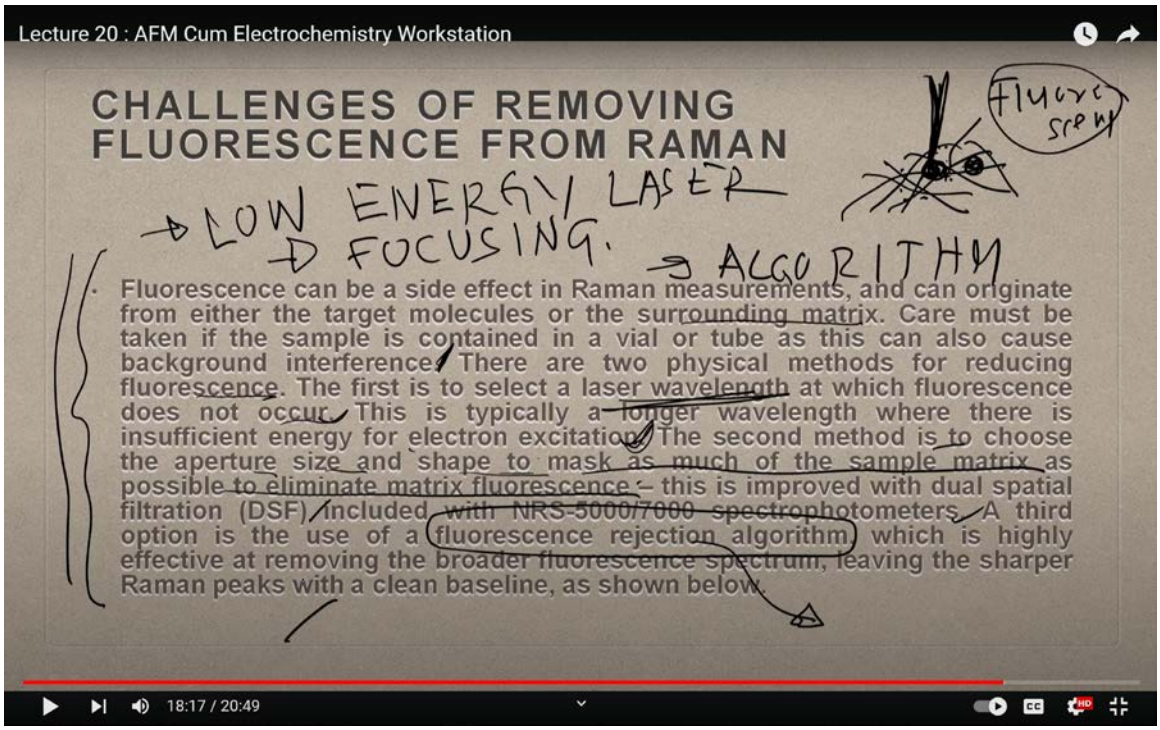

Next, we discussed how to refine Raman spectra to ensure accuracy in results. We explored how combining an electrochemical setup with an AFM tip can form a powerful tool for observing the dynamic movement of electrons on a surface. This concludes our discussions for this week.

Looking ahead to next week, we will delve deeper into the interactions between materials and light, and explore advanced techniques for identifying chemical moieties in pathogens.

Our focus will continue on multimodal modeling and instrumentation, with a strong emphasis on detection systems. We will also revisit and expand upon what we have studied so far through additional case studies. With that, I conclude this week’s lectures. Thank you, and I look forward to exploring new topics with you next week.