

Nanowire-based AFM vibrational nano-spectroscopy

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Vibrational spectroscopy, such as Raman and infrared (IR) spectroscopy, is a powerful tool for acquiring chemical information about samples. These techniques are widely used across various fields, including plastics, semiconductors, and biomaterials. However, as advanced materials and devices increasingly demand nanoscale structural control, analytical techniques with nanometer-level spatial resolution are required. Conventional vibrational spectroscopy is limited to $\sim 1\ \mu\text{m}$ spatial resolution due to the diffraction limit of light, making it inadequate for detailed nanoscale chemical characterization.

To overcome this limitation, near-field vibrational spectroscopy, which integrates atomic force microscopy (AFM) with vibrational spectroscopy, has been developed. Key methods include tip-enhanced Raman scattering (TERS) microscopy, which achieves $<10\ \text{nm}$ resolution via plasmonic enhancement, and AFM-based mid-infrared (AFM-IR) microscopy, which detects pulsed IR-induced thermal or dipole responses of a tip/sample system with spatial resolution below $50\ \text{nm}$. AFM-IR microscopy, in particular, supports a broader range of sample systems, including polymers, inorganics, biomaterials, and industrial samples, making it a standard for nanoscale chemical analysis.

A crucial component in these techniques is the quality of the AFM probe, which functions as an optical antenna. Conventional metal-coated AFM probes (e.g., Au, Ag) suffer from non-uniform coatings and mechanical degradation, leading to poor reproducibility and durability. To address these issues, we have developed a novel type of AFM probes by immobilizing chemically synthesized noble metal nanowires onto AFM cantilever apices. These nanowires offer excellent structural uniformity and high crystallinity, enabling reproducible, highly sensitive, and stable near-field vibrational spectroscopy. We applied this nanowire probe to TERS microscopy, which we referred to as nanowire-based TERS microscopy, and demonstrated sub- $10\ \text{nm}$ structural analysis of nanocarbon materials [1,2]. More recently, we have extended this approach to IR spectroscopy. Current AFM-IR microscopy utilizes thick coated metallic probes, which limit spatial resolution to $\sim 50\ \text{nm}$. In contrast, our nanowire-based AFM-IR microscopy utilizes Fabry-Pérot resonance-active plasmonic nanowires that generate strong localized near-fields at the nanowire ends [3], enhancing both spatial resolution and sensitivity.

In this presentation, I will provide an overview of the nanowire-based AFM vibrational spectroscopy techniques and highlight recent progress.

Reference

- [1] P. Walke, et al. *Nanoscale* **10**, 7556-7565 (2018).
- [2] T. Inose, et al. *Small* **20**, 2301841 (2023).
- [3] N. Baden, et al. *Nanoscale Horiz.* **9**, 1311-1317 (2024).