**Tip-enhanced Raman Spectroscopy for Nanoscale**

**Chemical Analysis of Sensitive 2-Dimensional Materials**

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Tip-enhanced Raman Spectroscopy (TERS) is a nanoscale chemical analysis and imaging method with a spatial resolution of <10 nm, even at ambient conditions [1]. TERS relies on the enhancement of the local electromagnetic field by a plasmonic metal nanostructure that is scanned over the sample by means of a scanning probe microscope, using either AFM or STM feedback. Analogous to SERS, the local electromagnetic field of Raman scattered light is enhanced by many orders of magnitude in TERS, large enough to render monomolecular films and 2D materials spectroscopically visible that would otherwise be optically too thin to be analyzed with conventional vibrational spectroscopy. However, the study of sensitive samples (e.g., biological membranes) and organic materials with TERS has been quite problematic so far, partially due to sample degradation.

The working principle, experimental realization, and capabilities of TERS will first be presented [1]. Several practical aspects will be discussed, including interpretation (and misinterpretation) of TERS spectra due to issues such as tip contamination and sample decomposition triggered by the very high local field under the TERS tip. Recent data from our lab shows that this is due not primarily a thermal effect, but rather due to plasmon-driven, photocatalytic reactions [2]. I will also present strategies to mitigate sample decomposition, for imaging studies of fragile samples over extended periods of time, and strategies to improve the reproducibility of TERS, especially for investigation of biological samples.

In the second part of this presentation, applications of TERS to the spatially resolved chemical analysis and imaging of molecular nanomaterials will be discussed. Examples from recent TERS studies in our laboratory will be chosen, such as two-dimensional polymers (2DPs) [3], self-assembled monolayers and model membranes [4], biological nanostructures such as amyloid forming proteins [5], and catalysts [6].

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