Tip-enhanced Raman scattering for liquid samples using a Chemically-modified Tip

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Tip-enhanced Raman scattering (TERS) has recently been a matter of great interest because it provides site-specific information on a nano- to subnano-scale, with spatial resolution beyond the diffraction limit of light (1). TERS can be performed in various environments, such as ambient air, ultrahigh vacuum (UHV), solutions, and electrochemical environments.

We proposed chemically modified tips with various probe molecules to improve the sensitivity, selectivity, and stability of TERS tips during liquid phase measurements (2,3). These tips were employed for nanoscale pH measurement in solutions and chirality discrimination using TERS. Using p-mercaptobenzoic acid (pMBA) and p-aminothiophenol (pATP) molecules attached to the tip, we measured the pH profile near an amino-group-modified surface, revealing a local increase in pH due to water dissociation and an exponential decay with distance (2). This technique may allow to probe pH in biological samples and investigate other solution-based properties using various tip-modifying molecules.

Sukmanee et al. introduced a TERS method for enantiomeric discrimination using a para-mercaptopyridine (pMPY)-coated silver tip (3). The asymmetric electric field at the tip apex, arising from the arrangement of silver atoms, interacts differently with enantiomers, leading to distinct changes in pMPY's Raman spectra. For this reason, even if pMPY is an achiral molecule, different spectra from different enantiomers can be obtained, and then enantiomeric discrimination can be achieved.

References

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