

## Tip-applied pressure: A step forward in near-field Raman microscopy

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When Raman microscopy is combined with the near-field techniques, it achieves new and exciting features as it goes beyond the conventional limits of optical microscopy, in terms of both the spatial resolution and the sensitivity. This is done by so called tip-enhanced Raman scattering (TERS) technique, which utilizes a metallic nano-tip for characterizing and imaging samples at molecular level. Interesting near-field effects could be observed, which could be analyzed through Raman scattering process, as the tip molecules interact with the sample molecules. This interaction, which results in photon confinement and signal enhancement, occurring near the tip apex due to the plasmonic resonance of the metallic tip and due to the charge transfer in the complex made between the tip molecules and the sample molecules, are usually classified into two categories, namely, electromagnetic and chemical. Experimentally, it results into huge field enhancement along with extremely high spatial resolution, which makes this technique an ideal tool for experimental analysis of nano-materials. We have utilized this technique to study several samples, such as carbon nanotubes, carbon-60 molecules and adenine molecules, and were able to optically map them with a resolution better than 25 nm in linear and 15 nm in nonlinear TERS experiments, far beyond the diffraction limits of the probing light. Also, a signal enhancement by a factor as high as one million was observed. In addition to the electromagnetic and chemical interactions, if the tip is pressed against the sample molecules, the tip can also interact with the sample molecules mechanically by applying a controlled pressure on the sample molecules. Unlike the isotropic hydraulic pressure that is often used by researchers to investigate the pressure effects in conventional Raman scattering, here the pressure applied by the tip apex is uniaxial and hence the bond lengths of the sample change anisotropically. This effect shows up in interesting spectral changes, such as peak shift, peak broadening and new peak rising, as the AFM-controlled tip-applied pressure is sequentially changed. Due to extremely localized nature of the tip-applied pressure, this technique further advances the nano-imaging capabilities of TERS.

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