PHOTONS, ELECTRONS, AND PHONONS AT THE NANOSCALE WITH TIP-ENHANCED RAMAN SPECTROSCOPY AND PHOTOTHERMAL IMAGING

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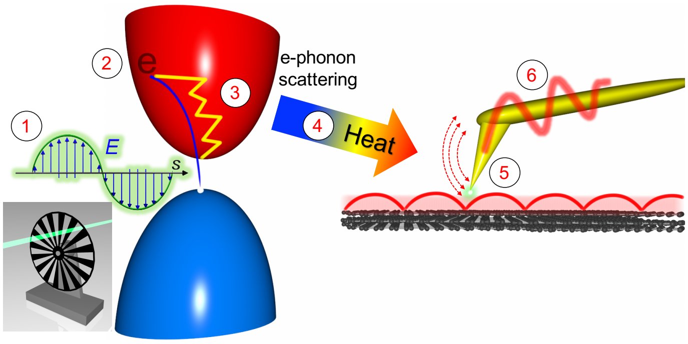

Figure 1: (a) Physical schematics behind nano-vis: (1) a chopper allows the intermittent passage of photons with energy high enough to excite an electron from the valence band to a high energy level (2) in the conduction band, non-radiative relaxation (3) mediated by e-phonon scattering induces (4) heat increase that results in the thermal expansion of the sample (5) and the cantilever deflection (6).

The diffraction limit of light was regarded as a fundamental unbreakable barrier that prevented the visualization of objects with size smaller than half the light wavelength, until super resolution optical methods and near-field optics allowed overcoming that constraint [1,2]. We report on a new approach based on tracking the photo-thermal expansion (nano-vis) in combination with tip-enhanced Raman spectroscopy (TERS). A commercial TERS system based on atomic force microscopy is coupled to a mechanical switch for intermittent visible light excitation. This simple configuration allows detecting small changes in the nano-object volume. Contrary to nano-IR that is based on the detection of molecular and lattice vibrations [3], the principle behind nano-vis involves tracking the heat generated from electronic transitions and scattering during the relaxation in the sample material that occurs due to optical absorption in the visible spectral range. The sensitivity and spatial resolution are further improved by the combined effect of electric field enhancement obtained by excitation of localized surface plasmons, and the synchronization of mechanical resonance of the tip-cantilever system with the intermittent light excitation. Our concept is demonstrated by the TERS and nano-vis analysis of a two-dimensional material (GaSe) on graphite and by an array of multi-walled carbon nanotubes lithographically designed in a silicon oxide matrix. In addition to TERS, an unprecedented spatial resolution for optical absorption below 10 nm is reported.

Keywords: nano-optics, photo-thermal imaging, tip-enhanced Raman spectroscopy, TERS, plasmonics, atomic force microscopy, optical absorption

References

[1] Langelüddecke, L., Singh, P. & Deckert, V. Applied spectroscopy69, (2015), 1357-1371.
[2] Katzenmeyer, A. M., Holland, G., Kjoller, K. & Centrone, A. Analytical Chemistry 87, (2015), 3154-3159.
[3] Dazzi, A., Prazeres, R., Glotin, F. & Ortega, J. Optics Letters 30, (2005), 2388-2390.