

IMAGING BEYOND THE PLASMONICS: NEW ASPECTS IN TIP-ENHANCED RAMAN MICROSCOPY

Satoshi Kawata

Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan
RIKEN, Wako, Saitama 351-0198, Japan.
E-mail: kawata@skawata.com

KEY WORDS: Near-field Raman microscopy, High-resolution microscopy, Chemical effects, Plasmonic enhancement.

The utilization of metallic tip in near-field optical microscopy [1] opened the doors for high resolution optical microscopy through plasmonic enhancement at the apex of a metallic tip, which was latter utilized in tip-enhanced Raman scattering (TERS) [2]. With the advances of this technique, we demonstrated that tip-enhanced Raman microscopy can image a sample with extremely high spatial resolution much beyond the diffraction limits of the probing light. In particular, the spatial resolution for tip-enhanced CARS microscopy was demonstrated to be as high as 15 nm [3]. The primary mechanism of tip-sample interaction in tip-enhanced Raman microscopy is electromagnetic, which is based on the excitation of localized surface plasmon polaritons. However, when the tip is close enough to the sample, typically at molecular distances, the mechanical and chemical interactions between the tip and the sample become important. These interactions add new interesting phenomena in tip-enhanced Raman microscopy, which goes beyond the simple plasmonic effects. When a sample is pressurized in a controlled manner by the tip apex [4], highly localized structural deformation of the sample perturbs Raman modes at a much higher spatial resolution. This can potentially enable TERS to achieve extremely high spatial resolution. On the other hand, chemical interactions between tip molecules and sample molecules can even indicate the possibilities of single molecule imaging [5]. We have demonstrated that, when a sample molecule gets adsorbed at the tip molecule, strong temporal fluctuations of Raman scattering could be observed. Sensing this temporal fluctuation, tip-enhanced Raman microscopy can achieve very high spatial resolution, ideally, single molecule imaging. This would open new doors for TERS microscopy with super resolving capabilities beyond the limits of plasmonic enhancements.

- [1] Y. Inouye and S. Kawata, "Near-field optical microscopy with metallic probe tip", *Opt. Lett.* **19**, 159 (1994).
- [2] N. Hayazawa, Y. Inouye, Z. Sekkat and S. Kawata, "Metallized tip amplification of near-field Raman scattering", *Opt. Commun.* **183**, 333 (2000).
- [3] T. Ichimura, N. Hayazawa, M. Hashimoto, Y. Inouye and S. Kawata, "Tip-Enhanced Coherent Anti-Stokes Raman Scattering for Vibrational Nanoimaging", *Phys. Rev. Lett.* **92**, 220801 (2004).
- [4] T. Yano, Y. Inouye and S. Kawata, "Nanoscale uniaxial pressure effect of a carbon nanotube bundle on tip-enhanced near-field Raman spectra", *Nano Lett.* **6**, 1269 (2006).
- [5] T. Ichimura, H. Watanabe, Y. Morita, P. Verma, S. Kawata and Y. Inouye, "Temporal fluctuation of tip-enhanced Raman spectra of adenine molecules", *J. Phys. Chem. C*, **111**, 9460 (2007)