

Challenge of spatial resolution by STM based near-field nanophotonics

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TERS (tip enhanced Raman spectroscopy) opens a new horizon for nanoscale characterization. A scanning tunneling microscope (STM) based near field optics system was established for exploring photonic and spectroscopic phenomena of single molecules and nanoscale objects. Till now, single wall carbon nanotubes (CNT) have been successfully imaged by this STM-TERS system with resolution about 3 nm. This is nearly one order improvement than typical AFM-TERS experiments. With this tool, we can have better TERS resolution to look into the detail of compositions in nanoscale.

1. Introduction

This STM based TERS is an alternative way from AFM -TERS developed previously in our group. By utilizing the gap mode plasmons (tip dipole and image dipole due to metallic surface), the enhancement effect is expected to be much stronger than simply AFM tip plasmon configuration. The other advantage for STM-TERS is the better spatial resolution provided by STM to resolve finer structures. By this way, it becomes possible to determine the intrinsic TERS resolution as well as the detail relation between structure and Raman shift.

2. System configuration

STM itself is a widely used analytical tool but it does not provide any chemical information about the surface adsorbates. Combining optics may open a new way for chemical identification. However, there is a limitation of photon collection solid angle in commercial STM scanners. To overcome this problem, from 2012, a new STM allowing N. A. = 0.7 collection was constructed for TERS experiments. The objective lens, collection optics, and all filters are integrated into one unit which can be precisely controlled by piezo motors. The photon collection efficiency is satisfactory in the current setup. Furthermore, to avoid the tunneling junction instabilities in the ambient environment, a stainless steel chamber for dry nitrogen purge was added to the system (Fig. 1). After the accomplishment of the environmental chamber, the overall stability has been improved a lot and ultra-high resolution (~ 3 nm) in Raman imaging has been achieved.

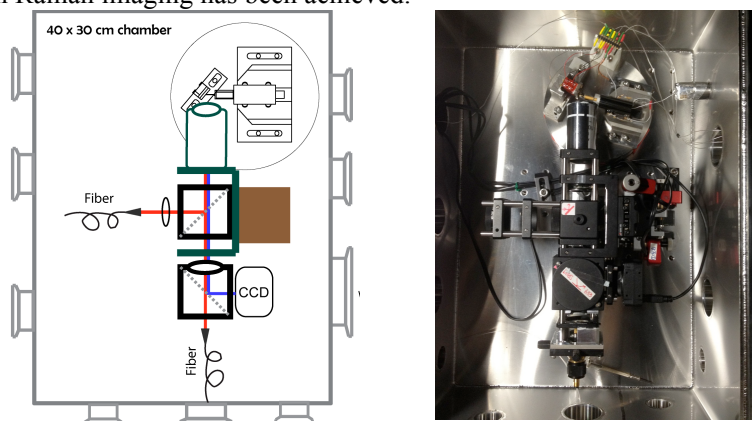


Fig. 1. (Left) Schematic and (Right) Photos of STM and the optical collection inside an environmental chamber. The Raman signal is collected through back scattering scheme. The collection objective has 0.7 in N. A. and 6.5 mm working distance.

3. Experimental results

Carbon nanotube has been characterized by AFM-TERS systems in a few groups around the world. We want to get better images of fine structure in CNT by STM and its corresponding Raman spectra locally. For imaging purpose, CNT is a very good sample for TERS because it has very strong Raman signal as well as clear

morphology. Fig. 2 shows the STM topography, near field imaging, and spectroscopy of CNT taken simultaneously. The TERS signal is spatially confined only within CNTs.

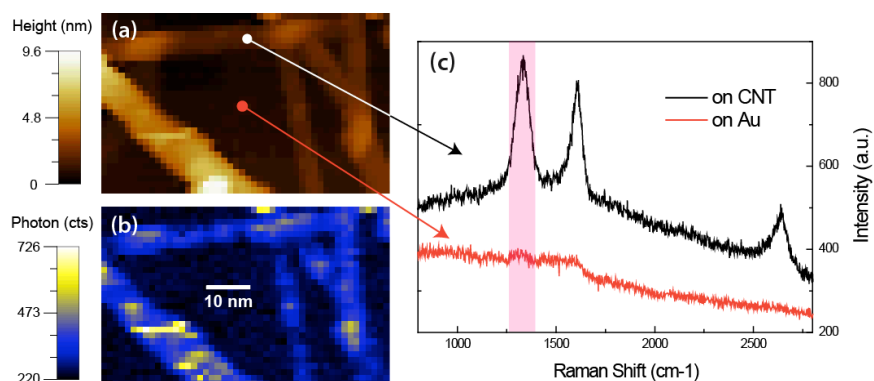


Fig. 2. STM topography, near field imaging, and spectroscopy of CNT. (a) Topographic image of CNT resolves some CNT bundles and one single CNT. (b) Raman imaging of d band signal taken simultaneously with the topographic scan. The integration time per pixel is 40 ms under 0.5 mW, 633nm laser illumination. (c) Comparison of near field Raman on CNT and on Au substrate (1sec).

In case of AFM-TERS, the best resolution is reported as 15 nm but usually it is around 20-50 nm. In our case, due to the gap mode enhancement, the near field Raman signal has much faster decay with respect to the gap distance. The TERS signal intensity drops to 1/10 within 5 nm of tip retraction. This also improves its x-y resolution to be almost one order better than AFM-TERS. Here we achieved very high resolution around 2-3 nm estimated from the FWHM of the Raman image.

While STM scanning, sometimes it will get the sample molecules attached to the tip. Such a molecule-modified tip has dramatic effects in AFM or STM imaging such as presenting finer details in topography. In our case, carbon nanotube could be attached to the STM tip easily while scanning but very difficult to remove. Such carbon nanotube-modified tip shows strong Raman signal originates from the attached carbon nanotube (surface-enhanced Raman effect, SERS). When this CNT-modified tip is used for imaging the surface, a reversed TERS contrast is found (Fig. 3). This is a very interesting phenomenon and still we are not sure this is simply due to gap distance change or some other reasons. Such reversed contrast also shows good spatial resolution around 3 nm.

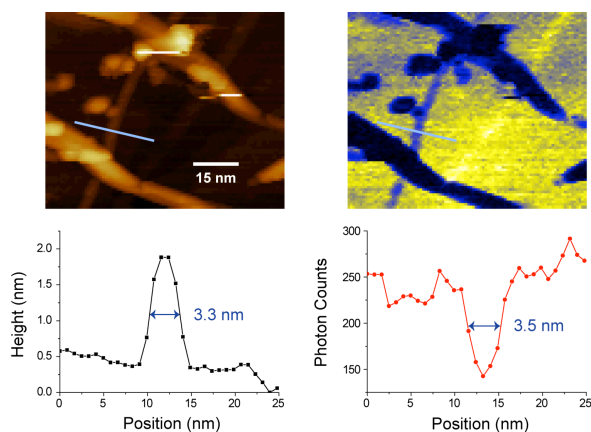


Fig. 3. (Left) STM topography of CNT and its line cut across a single tube. (Right) Near-field Raman imaging shows reversed contrast from usual TERS. The Raman imaging shows high spatial resolution as the STM topography.

4. Conclusion

TERS is a difficult experiment, which requires sophisticated techniques from both optics and scanning probe microscope. However, now it is possible to make it a more practical research tool for chemical recognition and imaging with spatial resolution around 3 nm. This may change the views and ways of analytical chemistry as well as optics and spectroscopy. There are some new possibilities in the nanoscale playground.