Apertureless Tip-Enhanced Raman Microscopy with Confocal Bottom Illumination/Collection Optics

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1. Introduction

One of the recent microscopy techniques to overcome Abbe limit on optical resolution is so-called "apertureless" near-field microscopy. Potentially, it could provide chemical fingerprinting with nanomer-size spatial resolution and single molecule sensitivity, which obviously has far-reaching implications. In the case of Raman spectroscopy, the basic idea of such apertureless scattering-type near-field microscopy is to use laser light illumination to generate high concentration of electric field (E) at the tip of antenna. If dimensions of such tip are in nanometer scale, it can act as an effective nanometer-size light source at the near-field region of the tip apex. When sample in placed in this region, the well-known phenomena of surface enhanced Raman scattering (SERS) could be produced.^{1,2} Then, it is possible to collect SERS light by ordinary far-field optics. Depending on the tip to sample separation distance, wavelength of the laser light and its incidence angle, tip apex geometry, and material of the tip and sample, the surface plasmon resonance, lightning rod, image, and chemical enhancement effects could be involved. Since Raman signal intensity is proportional to the E^4 , in principle, it is possible to obtain Raman spectra with single molecule sensitivity³ and tip apex-size spatial resolution.⁴ In addition, if atomic force microscope (AFM) cantilever is used as apertureless probe, both sample surface topography and corresponding chemical composition could be obtained simultaneously.

In recent years, several optical configurations of such apertureless Raman microscopes were tested and described in literature.⁵⁻¹⁰ Our confocal bottom illumination/collection scheme belongs to this family of apertureless Raman microscopes, but has several advantageous points useful for particular applications. First of all, confocal configuration has very small focal volume, which should suppress contribution of unwanted background far-field scattering from sample and tip shaft. At the same time, the position of the focal plane is adjustable to achieve maximum Raman signal enhancements. Also, bottom illumination/collection scheme doesn't generate shadowing from the tip. In addition, apparatus could be based on ready available commercial components, which require minimum user adaptation. However, there is also obvious limitation attributed to this technique such as sample transparency.

2. Experimental

Figure 1 shows basic experimental set-up. Gold-coated AFM (SMENA, NT-MDT) cantilever (<u>N</u>SG 20/Au) is illuminated by 532 nm laser (Coherent DPSS 532) beam. The typical tip radius is 50 nm, cone angle is

less than 22°, and Au film thickness is ~50 nm. The illumination is done through the objective (UMPlanFl, NA=0.95, 100x, WD=0.31 mm) of Olympus IX-70 inverted microscope by using Nanofinder (TII, Inc) confocal unit. The scattered light is collected with the same objective, passed same pinhole (ϕ 60 µm) and directed to the Nanofinder spectrograph and ANDOR CCD for spectral analysis. As a sample material, we used synthetic monocrystalline diamond powder (Sigma-Aldrich, ~1µm, 99.9%) on microscope coverslip surface. The background corrected Raman spectra were measured with 90 s accumulation time for 2 mW laser power at the sample position.

3. Results and Discussion



Figure 1. Confocal experimental set-up for generation and observation of tip-enhanced Raman scattering.

Using the results for intensity ratio, $I_{near field} / I_{far field} \approx 5$, from Fig. 2b and simple cylindrical model

for the size of the confocal light collection volume ($d_{spot} \approx 240$ nm, $h_{far field} \approx 1040/2$ nm) and light scattering near-field volume under the tip ($r_{tip} \approx 50$, $h_{\text{near field}} \approx 20$ nm), the enhancement factor, $EF = (I_{near field} / I_{far field}) (V_{far field} / V_{near field})$, for Raman signal from diamond was about 10^3 . This result can be compared with previously reported experimental EF to be around $10^3 - 10^4$, when other apertureless Raman microscopes were used. Thus, typical electric field enhancements under the AFM cantilever tips were between ~6 and 10. Interesting that various optical configurations, tip apertures, its coating material, and different laser excitation wavelengths produced very similar results experimentally⁵⁻¹⁰ and computationally.⁴ As a result, it seems that lightning rod effect played an important role in observed enhancements. However, the detailed understanding of the contribution of surface plasmon resonance requires future studies. Therefore, without additional involvement of other SERS effects, it seems that principal experimental improvements of apertureless Raman microscopes are in efficiency of light collection, quality of AFM tips, resolution, and scanning function.

It is also worth to mention several complications, which we encountered in our experiments. On one occasion, small diamond nanoparticle, which was incidentally attached to the cantilever tip during AFM scanning (not laser trapped), produced Raman signal comparable in intensity to larger micro-particles. Since particle was in direct contact with tip golden surface, and because main enhancements were from the fixed near-field region of tip apex, it explained the observed similarity. On the other hand, picking up minute amounts of sample on cantilever tip, basically, could be a useful technique for Raman microanalysis. Another complication was aging of the cantilever tip apex. After several tenths of AFM scans, gold-coated cantilever tips stopped to produce measurable enhancements. Also, only fraction of



Figure 2. Surface topography (A) and Raman spectra of diamond micro-particle as a function of different vertical (B) and horizontal (C) positions of golden AFM cantilever. The black spot corresponds to the initial cantilever tip position in semi-contact mode.

commercial gold-coated cantilevers was suitable for apertureless Raman microscopy due to insufficient gold coating on Si surface.

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