Tip-enhanced Raman spectroscopy with silver-coated optical fiber probe in reflection mode for investigating multiwall carbon nanotubes

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We developed a tip-enhanced Raman spectrometer (TERS) with reflection mode. The instrument, with a scanning shear-force microscope (ShFM) and a side-illumination Raman spectroscope, can overcome the diffraction limit and has high sensitivity. A chemical method to fabricate optical fiber probes with Ag coating is proposed. The local electromagnetic responses of the silver-coated optical fiber probe are numerically analyzed by the finite-difference time-domain method, and the excitation wavelength is optimized to resonate with the localized surface plasmons (LSP) of the probe tip. The instrument is applied to investigate a single multiwall carbon nanotube. The experiment results indicate that our TERS instrument has a spatial resolution better than 70 nm, and the enhancement factor is about 5×10^3. © 2010 Optical Society of America

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1. Introduction

Since the tip-enhanced Raman spectroscopy (TERS) was simultaneously and independently developed by several groups [1–4] in 2000, it has been applied widely in research on nanomaterials, semiconductors, chemical composites, dye molecules, and biological samples due to its ability to overcome the diffraction limit and its high detection sensitivity. However, while lots of research results are obtained by means of TERS in laboratories, it is a long way from being versatile and popular in the field. Research on instrument configuration and tip preparation methods for TERS still continues, and some companies and research groups [5–7] have been making efforts in recent years. A TERS instrument consists of two necessary parts. One is the scanning probe microscope, which is usually one of three types: scanning tunneling microscope (STM), atomic force microscope (AFM), and scanning shear-force microscope (ShFM). To the present, one single molecule has been successfully detected by the STM-based TERS instrument under a ultrahigh vacuum condition [8,9], but the requirements of the conductive samples and an undisturbed environment restrict its application. AFM and ShFM-based TERS instruments are applicable to many kinds of samples, especially biological tissue and semiconductors. Compared with AFM, the tip of ShFM is easier to fabricate and is cheaper. The other necessary part of the TERS instrument is a Raman microscope with two alternative illumination geometries: a reflection mode or a transmission mode. The reflection mode has a wider applicability and feasibility to various samples than the transmission mode.

In this paper, we set up a tilt-reflection mode TERS instrument combined with ShFM, so the application cannot be limited by the transparency and the conductivity of the samples and substrates. A chemical method for preparing the Ag coating on the optical fiber probe is proposed. The local electromagnetic responses of the silver-coated optical fiber probe are

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numerically analyzed by the finite-difference time-domain (FDTD) method, and the excitation wavelength is optimized to resonate with the localized surface plasmons (LSP) of the probe tip. Finally, the topography of single multiwall carbon nanotube (MWCNT) and the TERS spectra are obtained by the home-built TERS instrument.

2. Experimental Setup

The schematic diagram of our home-built TERS instrument is shown in Fig. 1. It consists of a Raman spectrometer (inVia, Renishaw) combined with side-illumination optics for Raman measurements, a scanning ShFM (BL222NNTF, NT-MDT) and three-dimensional piezo stage (P-517.3CL, Physik Instrument) for tip and sample manipulation, respectively. The control software is used to communicate with the Raman spectrometer and the ShFM to obtain Raman spectra and tomography simultaneously. The stability of the entire system is ensured by the use of vibration and sound isolation accessories. The laser beam (532 nm Nd:YAG) is focused on the probe tip by a long work distance objective (50×, NA = 0.42, WD = 20.5 mm, Mitutoyo) at an incident angle of 65° relative to the axis of the probe. The polarization of the incident light is along the axis of the probe by adjusting a half-wave plate to maximize the enhancement of the electric field under the tip. The separation between the silver-coated optical fiber probe tip and the sample is kept constant and less than 5 nm by the shear-force feedback control. The Raman scattering light is collected by the same objective, then is steered into the Raman spectroscope, and detected by a charge-coupled device (CCD) camera. The measured wavenumber range from 4000 to 100 cm^{-1} is determined by the bandwidth of the edge filter.

3. Fabrication of the Silver-Coated Optical Fiber Probe

For extensive utilization, a preparation method is necessary for the tip to be reproducible, easy to fabricate, low cost, strong, and with stable enhancement. Silver is an excellent material for TERS due to its high enhancement performance in the visible region, even though it can be oxidized easily in air. In 2005, Wang *et al.* [10] reported a method of tip preparation for TERS in which the Ag coating is deposited on the AFM probe by a modified Ag mirror reaction, but the reaction is too fast to be controlled easily. In this work, the silver-coated optical fiber probe is prepared by the electroless silver-plating method proposed by Chen *et al.* [11].

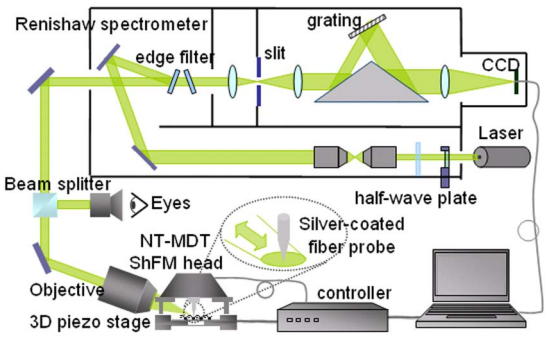

Fig. 1. (Color online) Schematic diagram of a home-built TERS instrument.

The uncovered optical fiber probe was fabricated from a standard single-mode fiber by the chemical-etching method invented by Turner in 1983 [12], subsequently rinsed thoroughly with an NaOH-in-ethanol cleaning solution, and then the fiber probe was immersed in 5% tin dichloride solution for sensitization of the surface for 2 h. After that, it was washed with distilled water to remove the excess Sn^{2+} ions. A 10 μl 1wt.% NaOH solution was added into 1 ml of 0.2 wt. % silver nitrate aqueous solution, and the pale brown precipitate of Ag_2O was observed. Then it was followed by adding a triethanolamine (TEA) water solution (7.5 mol l^{-1}) drop by drop until the solution became clear and colorless. The sensitized uncovered optical fiber probe was immersed into the complex solution of TEA and silver ion. After 30 min of growth, the color of the surface of the optical fiber probe changed to brown black, which meant Ag particles had been deposited on the optical fiber probe. Finally, the silver-coated optical fiber probe was washed with distilled water and preserved in the N_2 gas. The scanning electron microscope images and photomicrographs of the probe tip before and after coating by the electroless silver plating are shown in Fig. 2. A single-layer silver film was formed on the surface of the optical fiber probe, which is composed of Ag particles with a diameter of about 20 nm.

4. Simulation and Instrument Optimization

The performance of the TERS instrument is determined by the local electromagnetic enhancement of the probe tip. It is influenced by many factors,

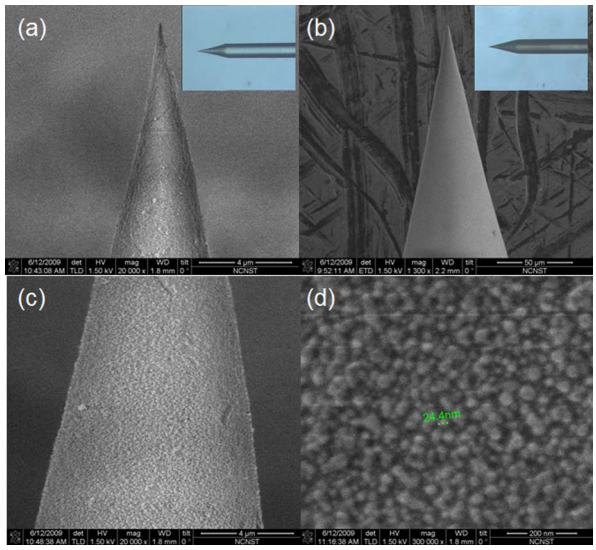

Fig. 2. (Color online) SEM images and photomicrographs of the optical fiber probe tip (a) before the coating process and (b) after the coating process. (c) and (d) are the partial enlargements of (b) and indicate a deposited film composed of Ag particles with a diameter of about 20 nm was formed.

including the material of the probe, and the wavelength and the polarization of the incident light. In the visible region, there is the most remarkable enhancement with the gold probe and the silver probe. In addition, the local electromagnetic enhancement below the probe tip is maximized when the following two conditions are satisfied: a) the incident wavelength matches the resonant wavelength of the LSP of the metallic structure on the probe tip, and b) the polarization direction of the incident beam is along the probe tip axial. These conditions must be taken in account in the design to make the TERS instrument in the optimal operation.

To find the conditions for matching the plasmon resonance of the silver-coated optical fiber probe with the incident wavelength and to obtain the optimal performance of the instrument, the FDTD method was used to simulate the local electromagnetic response of the silver-coated optical fiber probes with different sizes. The inset in Fig. 3 is a sketch of the silver-coated optical fiber probe. R_1 (30–40 nm) and R_2 (10–20 nm) denote the curvature radius of the silver-coated probe tip and the inner optical fiber probe tip, respectively. The silver layer thickness was 20 nm. The wavelength of the incident light was changing from 400 to 750 nm, with the polarization along the axial direction of the probe. The electromagnetic responses of the different probes are shown in Fig. 3. The resonance peaks are kept within the scope of 500–550 nm, and, with the probe size increasing, the peak reduces a little and shows a red-shift tendency. Thus, the incident wavelength of 532 nm is chosen to excite the silver-coated optical fiber probe in the experiment and high-sensitivity detection is consequently realized.

5. Results and Discussions

Carbon nanotubes are typical one-dimensional nanomaterials, and their novel properties in mechanics, thermotics, electronics, and chemistry lead to potential applications. Recently, the TERS method has been applied in the characterization of single-wall carbon nanotubes (SWCNTs), such as the structure and defects [13–16]. However, investigation of the single MWCNT by TERS is rarely reported [17].

In our research, the samples under test were water dispersible MWCNTs (Shenzhen Nanotech Port Co. Ltd), with tube diameters of 20–40 nm. After further dilution with deionized water and dispersion with ultrasonics, the sample solution (~0.2 wt. %) was dropped on the surface of the silicon wafer and dried.

By use of our TERS instrument, a topographic image of a single MWCNT was obtained, as shown in Fig. 4(a). A cross section along the dashed-dotted line in Fig. 4(a) is shown in Fig. 4(b). It is clearly indicated that the height of the MWCNT is about 40 nm. The diameter of the single MWCNT is markedly broadened to 100 nm due to the geometry of the tip. Three points, A1, A2, and A3, with intervals of ~70 nm are chosen on the cross line and the TERS information on the three points is detected.

The near-field TERS spectra with the tip and far-field Raman spectrum without the tip are displayed in Fig. 4(c). The two peaks (around 1300 cm^{-1} and 1600 cm^{-1}) correspond to the defect-related mode (D mode) and graphitelike mode (G mode), respectively. Among the near-field Raman spectra at A1, A2, and A3, distinct differences can be observed. Points A1 and A3 locate brims of the tube and lead to barely apparent Raman peaks. Point A2 locates only on the carbon tube and there is a stronger Raman peak in the TERS spectrum. It demonstrates experimentally that the spatial resolution is better than 70 nm with the instrument.

The comparison between the near-field Raman intensity at point A2 and the far-field Raman intensity shows that the former had 5–6 times more intensity than the latter. Considering the radius of the tip and the size of the laser focused spot [18], the tip-enhancement factor is about 5×10^3. Although both tip-enhanced Raman spectra and far-field Raman spectra show the inherent Raman peaks of the MWCNT, the spectrum at A2 appears with more fine features. This is probably from a structure defect or the interaction between the tip and the MWCNT.

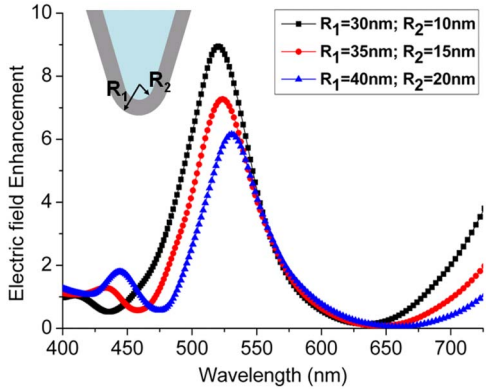

Fig. 3. (Color online) Local electromagnetic response of the silver-coated optical fiber probes with various tip sizes by FDTD simulation.

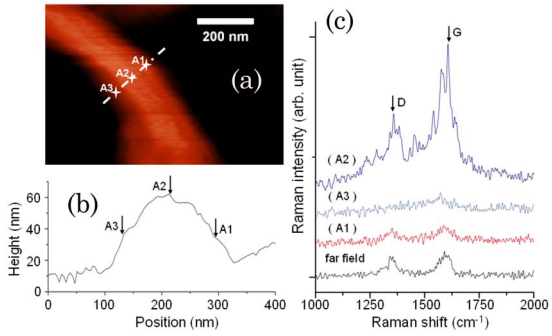

Fig. 4. (Color online) TERS experiment on the single MWCNT. (a) The topography image of the single MWCNT, (b) the corresponding height cross sections along the measuring points marked in (a), and (c) the tip-enhanced Raman spectra of the MWCNT at different points and the far-field micro-Raman spectrum of the whole area. (Integration time is 10 s at each point; the laser power is around 1 mW on the sample surface).

6. Conclusion

In conclusion, a TERS instrument working in the reflection mode and with side-illumination optics is set up. The instrument has a significant advantage in its applicability in various samples, regardless of the sample's conductivity and transparency, which is attributed to the shear-force distance regulation and tilt-reflection mode. A chemical method to prepare the high-performance tip for TERS based on the electroless silver-plating process is proposed, which is low cost and easy to self-fabricate and use. The local electromagnetic responses of the silver-coated optical fiber probe are analyzed by the FDTD simulation, and the optimal excitation resonance condition for plasmon enhancement is deduced. Finally, the remarkably enhanced Raman spectra of a single MWCNT are obtained by our home-built TERS instrument, which indicates a spatial resolution of better than 70 nm.

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References

1. M. S. Anderson, "Locally enhanced Raman spectroscopy with an atomic force microscope," Appl. Phys. Lett. **76**, 3130–3132 (2000).
2. N. Hayazawa, Y. Inouye, Z. Sekkat, and S. Kawata, "Metallized tip amplification of near-field Raman scattering," Opt. Commun. **183**, 333–336 (2000).
3. R. M. Stockle, Y. D. Suh, V. Deckert, and R. Zenobi, "Nanoscale chemical analysis by tip-enhanced Raman spectroscopy," Chem. Phys. Lett. **318**, 131–136 (2000).
4. B. Pettinger, G. Picardi, R. Schuster, and G. Ertl, "Surface enhanced Raman spectroscopy: towards single molecular spectroscopy," Electrochemistry **68**, 942–949 (2000).
5. X. Wang, Z. Liu, M. D. Zhuang, H. M. Zhang, Z. X. Xie, D. Y. Wu, B. Ren, and Z. Q. Tian, "Tip-enhanced Raman spectroscopy for investigating adsorbed species on a single-crystal surface using electrochemically prepared Au tips," Appl. Phys. Lett. **91**, 101105 (2007).
6. L. Zhu, C. Georgi, M. Hecker, J. Rinderknecht, A. Mai, Y. Ritz, and E. Zschech, "Nano-Raman spectroscopy with metallized atomic force microscopy tips on strained silicon structures," J. Appl. Phys. **101**, 104305 (2007).
7. W. X. Sun and Z. X. Shen, "Optimizing the near field around silver tips," J. Opt. Soc. Am. A **20**, 2254–2259 (2003).
8. J. Steidtner and B. Pettinger, "High-resolution microscope for tip-enhanced optical processes in ultrahigh vacuum," Rev. Sci. Instrum. **78**, 103104 (2007).
9. J. Steidtner and B. Pettinger, "Tip-enhanced Raman spectroscopy and microscopy on single dye molecules with 15 nm resolution," Phys. Rev. Lett. **100**, 236101 (2008).
10. J. J. Wang, Y. Saito, D. N. Batchelder, J. Kirkham, C. Robinson, and D. A. Smith, "Controllable method for the preparation of metalized probes for efficient scanning near-field optical Raman microscopy," Appl. Phys. Lett. **86**, 263111 (2005).
11. D. Chen, H.-Y. Liu, J.-S. Liu, X.-L. Ren, X.-W. Meng, W. Wu, and F.-Q. Tang, "A general method for synthesis continuous silver nanoshells on dielectric colloids," Thin Solid Films, 6371–6376 (2008).
12. D. R. Turner, "Etch procedure for optical fibers," U.S. patent 4,469,554 (4 Sept. 1984).
13. N. Hayazawa, T. Yano, H. Watanabe, Y. Inouye, and S. Kawata, "Detection of an individual single-wall carbon nanotube by tip-enhanced near-field Raman spectroscopy," Chem. Phys. Lett. **376**, 174–180 (2003).
14. Y. Saito, N. Hayazawa, H. Kataura, T. Murakami, K. Tsukagoshi, Y. Inouye, and S. Kawata, "Polarization measurements in tip-enhanced Raman spectroscopy applied to single-walled carbon nanotubes," Chem. Phys. Lett. **410**, 136–141 (2005).
15. N. Anderson, A. Hartschuh, S. Cronin, and L. Novotny, "Nanoscale vibrational analysis of single-walled carbon nanotubes," J. Am. Chem. Soc. **127**, 2533–2537 (2005).
16. T. Yano, P. Verma, S. Kawata, and Y. Inouye, "Diameter-selective near-field Raman analysis and imaging of isolated carbon nanotube bundles," Appl. Phys. Lett. **88**, 093125 (2006).
17. G. Picardi, M. Chaigneau, and R. Ossikovski, "High resolution probing of multi wall carbon nanotubes by tip enhanced Raman spectroscopy in gap-mode," Chem. Phys. Lett. **469**, 161–165 (2009).
18. T. Schmid, B. S. Yeo, W. Zhang, and R. Zenobi, "Use of tip-enhanced vibrational spectroscopy for analytical applications in chemistry, biology, and materials science," in *Tip Enhancement*, S. Kawata and V. M. Shalaev, eds. (Elsevier, 2007), pp. 115–155.