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Atomic force and shear force based tip-enhanced Raman spectroscopy and imaging

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Abstract

Underlying near-field optical effects on the nanoscale have stimulated the development of apertureless vibrational spectroscopy and imaging with ultrahigh spatial resolution. We demonstrate tip-enhanced Raman spectra of single-walled carbon nanotubes (SWCNTs), recorded with a scanning near-field optical spectrometer using both atomic force (AF) and shear force (SF) feedback lock-in regulation, and critically discuss the advantages and drawbacks of both operation modes. For accurate calculation of the enhancement factor obtained, we have analysed the tip shape and diameter by means of scanning electron and transmission electron microscopy (SEM and TEM). In our experiments we reproducibly attain diameter-corrected and area-corrected enhancement factors of up to $\sim 10^4$ and $\sim 10^5$, respectively, estimated as the linear ratio of near- and far-field intensities, and we are able to demonstrate near-field Raman imaging of SWCNTs with spatial resolution better than 50 nm.

1. Introduction

Optical spectroscopy, including infrared (IR) absorption, Raman scattering, coherent anti-Stokes Raman spectroscopy, higher harmonics generation, and single- and two-photon excited fluorescence, is of fundamental importance in exploring the physical and chemical properties of matter. However, the Abbé diffraction limit does not allow us to extend these methods for visualization and local chemical nondestructive analysis of nanometre-sized materials. There have been several ways to overcome the diffraction limit and, therefore, to improve the spatial resolution

$$d \sim \lambda / \text{NA}$$
 (1)

 $(\lambda$ is the wavelength, NA is the numerical aperture).

Traditionally, one can shorten the wavelength by either choosing a proper laser source or using oil immersion optics (typically, n = 1.5). Alternatively, spectral features can be spatially resolved with frequency mixing (moiré effect) or second harmonics generation.

On the other hand, the concept of evanescent waves existing in the near field (<100 nm) allows us to extend a range of optical measurements beyond the diffraction limit and, therefore, to attain ultrahigh resolution in optical spectroscopy. A practical implementation of that has become possible by combining optical spectroscopy and scanning probe microscopy (SPM) as reported recently [1-6]. According to Novotny et al [1] this approach-often referred to as apertureless near-field optical microscopy-can be divided into scattering-based and local excitation-based techniques. The crucial role in both these techniques is played by the SPM tip as a nanoscopic scatterer and/or lighting source. In the first case, the tip disturbs a confined non-radiating electromagnetic field in the proximity of a nanometre-sized specimen and converts it to a radiating one, which can then be detected by standard diffraction-limited optics. In the second case, a tip localizes and enhances the scattered optical radiation over the incident one due to the coupled excitation of free electrons and the electromagnetic field present (called the localized surface plasmon) in the metal of the tip. The latter is caused by the fact that metals, due to their small skin effect,

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provide the highest enhancement and scattering efficiency. An additional contribution to the field enhancement, known as the quasi-static lighting rod effect, comes from a purely geometrical factor of the tip resulting in a quasi-singularity of the electromagnetic field near its apex. The material composition of the tip, its geometry and the polarization state of the incident light in the local excitation-based scheme are of the greatest importance for efficient enhancements. The highest field enhancement in the visible wavelength region is provided by copper, gold, and silver probes with sizes of 10-100 nm, as reported elsewhere [1-10].

Generally speaking, both the schemes considered above can be simultaneously implemented in practice. This is because an initial laser beam can excite both a localized surface plasmon in the tip and generate the evanescent near field around fine structures of a specimen. Thus, the optical image detected in the far field is a result of interference of a tipinduced evanescent field scattering and tip-enhanced near-field transmission, and its interpretation can be challenging. In the case of a specimen deposited on a rough noble metal substrate, additional electromagnetic resonances may occur due to the nonlinear interaction of the localized surface plasmons and the travelling surface plasmons, and, as a consequence, sub-tip resolution is possible [11]. In addition to the electromagnetic field enhancement, there is a contribution to the enhancement from chemical effects relating to the presence of adsorbed chemical species. These are coupled with molecules of interest in close proximity and provide an effective pathway to transfer energy to their molecular vibrational modes (in the case of Raman scattering this effect is known as surfaceenhanced Raman scattering, SERS). Discrimination between the electromagnetic and chemical enhancements and their relative contributions are still in discussion [10, 12, 13].

In recent years, a few groups have developed apertureless near-field optical spectrometers based on top-down or bottomup axial illumination (back-scattering geometry) and sideillumination optics [2, 14-19]. The basic idea in these set-ups is to bring an apertureless probe in direct contact with a sample of interest (a z-distance from the sample surface to the probe of about a few nanometres) in order to establish the near-field optical interaction between them. Scanning with the probe over the sample might provide high spatial resolution due to delocalization of evanescent (near-field) waves and/or nanoscopic lighting coming from the probe. In contrast to widely used techniques reaching a high spatial resolution (for example, scanning electron microscopy (SEM) and transmission electron microscopy (TEM)), the near-field optical technique provides in situ chemical structural information on a specimen while scanning, which has stimulated the development of tip-enhanced Raman spectroscopy (TERS). TERS has been proven to be a powerful analytical tool for investigation of the chemical structure, composition, conformational state and stresses on the nanoscale [1, 2, 20-22]. Unfortunately, so far most of the nearfield techniques are still far from any routine applications in nanosciences, and spatial resolution is low.

In the present work we perform TERS experiments on single-walled carbon nanotubes (SWCNTs) to demonstrate high enhancement factors and spatial resolution of a few tens of nanometres. The choice for SWCNTs primarily is dictated by the fact that the nearly ideal one-dimensional structure of SWCNTs can be viewed as a rolled-up segment of a graphite sheet with diameter of 0.5-3 nm and several micrometres in length, and that the electron-phonon coupling under resonance conditions in SWCNTs results in well-defined strong Raman spectra. The observation of Raman spectra from SWCNTs is possible because of the very large density of electronic states close to the van Hove singularities of this one-dimensional structure [23-25]. The resonance Raman effect yields structural information through identification of the (n, m) indices (describing the type of wrapping of the graphite sheet) for isolated SWCNTs since every nanotube is in resonance with an unique interband energy E_{ii} (n, m). Thus, SWCNTs offer the possibility to test the spatial resolution beyond the diffraction limit and, simultaneously, to study some features of the Raman spectra obtained giving information on their diameter, chirality, excitation energy, polarization and local defects.

2. Experimental details

The back-scattering geometry based configuration of the scanning optical spectrometer NTEGRA SPECTRATM (NT-MDT) for analysing a specimen on transparent substrates allows us to record atomic force microscopy (AFM) or shear force microscopy (SFM) images (topography, phase contrast, etc), confocal far-field Raman and tip-enhanced near-field Raman spectra and images (figure 1). A continuous wave (cw) linearly polarized laser light from a He-Ne laser operating at 632.8 nm (E = 1.96 eV, transverse electromagnetic mode: TEM_{00}) enters the spectrometer through a single-mode optical fibre. The laser output passing through the laser line filter is expanded and converted to a mode with a given polarization (linear, circular, radial, azimuthal). After that it is reflected by the edge filter and goes into an inverted optical microscope (Olympus IX70) through a beam-splitter cube (10/90) and a pinhole. A $100 \times$ oil immersion objective (Olympus, NA = 1.3, refractive index n = 1.516) focuses the laser beam into a spot with size of less than 300 nm and with a power at the sample of $\sim 100 \ \mu W$.

For TERS experiments, the metal tip is positioned into one of the two longitudinal lobes near the rims of the diffractionlimited laser spot to locally enhance the electromagnetic field beneath its apex. This system allows one to lock the tip position inside the laser spot to maintain optimum illumination conditions. A near-field Raman image is established by scanning the sample with an x, y stage equipped with a closeloop operation system. Scattered and/or reflected light is collected with the same objective and directed back into the spectrometer through the pinhole. An additional Kaiser notch filter is installed into the optical path to further suppress the Rayleigh scattering. In the laser confocal and spectral modes the light transmitted by the beam-splitter cube is detected with a photomultiplier (Hamamatsu, PMT943-02) and/or a thermoelectrically cooled charge-coupled detector (ANDOR, DV420), respectively. All Raman spectra were recorded within a spectral range 150-2800 cm⁻¹. A 200 lines mm⁻¹ grating provides spectral resolution better than 15 cm^{-1} . The pinhole size was equal to 40 μ m because of making use of the 100× oil immersion objective (NA = 1.3).



Figure 1. Layout of the scanning near-field optical spectrometer (inverted configuration). (This figure is in colour only in the electronic version)

The AFM head (SFC050NTF, NT-MDT) operates in the intermittent-contact mode with commercial gold-coated cantilevers (NSC18/Cr–Au, MikroMasch) with apex radius of less than 50 nm (according to the producer's data sheet), cone angle of less than 30°, and tip height of 20 μ m. To prevent interference of the cantilever deflection control laser with the Raman scattering, a 830 nm diode laser mounted inside the AFM head was used.

A scanning near-field optical microscopy (SNOM) head (SNLG101NTF, NT-MDT) was used for TERS experiments with self-made gold-pointed probes. According to Ren *et al* [26] a less than 50 nm in radius gold tip with a smooth surface can be reproducibly produced by dc electrochemical etching in a mixture of 37% HCl (Merck, p.A.) and absolute ethanol in a proportion of 1:1 with an applied voltage of 2.4 V. For etching we have used a 99.999% pure gold wire of 200 μ m in diameter as drawn and flame annealed before use. After etching, the probes were immediately rinsed with distilled water and dried with nitrogen. Subsequently, the probes were glued to a tuning fork that showed a *Q*-factor value of ~1000 at a resonant frequency of ~190 kHz.

Gold-coated AFM tips and self-made gold probes for SFM were investigated by a JSM-840A scanning electron microscope (JEOL) operated at 10 kV, and a TECNAI G^2 20 (FEI) transmission electron microscope operated at 200 kV, respectively.

We utilized purified single-walled carbon nanotubes (HiPCo, Carbon Nanotechnology Inc.) as a proper onedimensional object with strong Raman-active spectral lines for testing the ultrahigh spatial resolution. A dispersion was prepared by mixing 0.05 g SWCNTs with 20 g dichloromethane in a flask and then sonicating the resulting dispersion for about 1 h. The sonication was carried out using a horn sonicator (Sonic Vibracell VC750) with a cylindrical tip (10 mm end cap in diameter). The output power was 20 W and, therefore, the delivering energy was 1100–1200 J min⁻¹. The flask was placed inside a bath with ice water during sonication in order to prevent rising of the temperature. A droplet of this dispersion was spin coated at 300 rpm for 2 min on a microscopy cover glass slide. The glass slide was preliminarily cleaned in a piranha solution ($H_2SO_4:H_2O_2$) at ambient conditions for 30 min, then rinsed in CH₃OH and finally dried under a continuous N₂-gas flow.

3. Results and discussion

3.1. AFM and SFM probes

Unlike silver and copper used in near-field optical experiments, gold is a more stable metal in ambient conditions. Gold tips are often used as a nanoscopic light sources at 632.8 nm excitation wavelength, because gold provides the highest enhancement in the near-infrared region [3, 6, 7]. Indeed, when we deal with nanometre-sized (non-bulk) gold material slight spectral shifts in absorption spectra are observed due to changes in the size-dependent dielectric constant (permittivity). For example, for gold we have $\varepsilon = -2.2 + i3.8$ (488 nm), $\varepsilon = -6.3 + i2.0$ (540 nm), $\varepsilon = -26.6 + i1.6$ (830 nm). Because the excitation strength of surface plasmons is determined by the ratio of imaginary and real parts of the dielectric constant, gold has an optimal excitation of surface plasmons that takes place in the near-infrared region.

However, gold suffers from the disadvantage of its low hardness, and in particular gold tips can easily be destroyed in the AFM-based feedback mechanism. SEM images of a gold-coated AFM cantilever tip before and after scanning over a sample surface are depicted in figure 2. The damage of the apex tip is clearly observed. This is caused by landing of the tip below the near-field threshold during scanning. Apex damage of the tip can be *in situ* detected by a Raman signal coming from the Si/SiO₂-based cantilever support if the gold coating is removed. Other drawbacks of Au-coated AFM cantilevers are the lack of preferable crystallographic orientation in the Au film and a large curvature radius that is of order of 50 nm, because of the presence of an intermediate Cr layer of ~20 nm



Figure 2. SEM images of a gold-coated AFM cantilever tip before (A) and after (B) scanning in tapping mode.



Figure 3. SEM image of a gold probe (A) and the corresponding TEM image of its apex (B).

in thickness improving the adhesion properties between the Au deposit and Si cantilever.

Figure 3 shows images of apex size and shape of a selfmade SFM Au probe recorded with both SEM and TEM, respectively. The curvature radius of the tip is about 16 nm. We observe a uniform shell around the tip apex arising from carbon contamination in the SEM chamber. It is uncertain whether this carbon layer is of advantage or not for TERS experiments; this issue is currently under investigation. Since the SFM probes are prepared from pure Au wires, mechanical adhesion problems as for gold-coated AFM cantilevers do not exist. Moreover, depending on production history of the initial Au wire and etching procedure applied, ultimately, crystalline orientation and sharpness of the apex tip can be controlled. Consequently, such Au tips hold a promise to be the optimal nanoscopic light probe for the implementation of TERS. However, a main drawback of Au is still its weak mechanical performance, which may cause apex damage during scanning.

To attain the maximal near-field (plasmonic) effect the polarization of the incident laser light should be parallel to the tip axis (p-polarization) [27, 28]. In this case the charge density oscillating with the external field frequency is rotationally symmetric in respect to the tip apex axis and results in the constructive interference of the electric field (the *z*-component of the electric field has axial symmetry). Both longitudinal and azimuthal field modes are very sensitive to surface gradients.

From a physical viewpoint, surface charges produce a standing wave with a wavelength less than that of incident light. If the polarization direction is perpendicular to the tip axis, destructive interference of the electric field at the tip apex takes place, and the surface charge density at the tip apex is negligible (s-polarization). However, longitudinal field lobes are spatially shifted from the core of the laser beam and their strength is \sim 5 times weaker than the transverse field strength at the centre of the focus. Tightly focused higher-order laser modes (e.g. TEM_{10}) can be used to intensify a longitudinal field component to be comparable or even exceed the strength of a transverse field component. In particular, the radially polarized light produced with a four-section polarizer $(0^{\circ},$ $+45^{\circ}, +90^{\circ}$ and -45°), generates the longitudinal mode at the core of the laser focus with the strength being about two times larger than that of the transverse mode. Alternatively, the longitudinal field component can be enhanced by changing the tip orientation with respect to the incident light direction in the bottom-up axis illumination scheme [29].

Consequently, one of the important steps in TERS experiments is to guarantee the coincidence of the apex of a tip and the diffraction-limited laser spot. In the top- or bottomup axial illumination schemes, the reflection pattern consists of two longitudinal lobes; in one of them a metal probe is positioned. This means that we displace the tip from the centre of the laser beam in the direction of its polarization into one



Figure 4. Optical reflection images of a gold-coated AFM cantilever tip (A), a self-made gold SFM tip (C) and their corresponding intensity cross sections ((B) and (D)), respectively. The white bar shows the different scale in the figures and is a measure of the tip scanning distance.

of the two longitudinal field lobes near rims of the diffractionlimited laser spot. Optical reflection images of a gold-coated AFM cantilever tip and a self-made SFM gold probe glued to a tuning fork and their cross sections taken along the white solid lines are shown in figure 4. In case of the AFM cantilever we observe feebly marked longitudinal lobes (figure 4(B)), whereas in case of the SFM probe the two-lobe pattern clearly can be seen (figure 4(D)). In our experiments, noticeable field enhancement appeared only in one of the longitudinal lobes, indicated with an arrow in figure 4(D). This asymmetric behaviour in the distribution of the radiation energy is most likely explained by a slight tilt of the probe in respect to the optical axis and is not related to the quality of the probe itself. This observation confirms the possibility of changing the tip orientation relative to the incidence of linearly polarized light to enhance the longitudinal field component.

Finding a lobe in which the strongest field enhancement takes place is practically implemented in the experimental setup by scanning a probe over a uniform substrate with Ramanactive spectral lines (e.g. Si/SiO₂) and detecting tip-enhanced Raman scattering from the latter. Unlike the confocal laser mode, the spectral mode is more sensitive to the longitudinal fields due to the chemical specificity and therefore provides exact positioning of the probe.

3.2. Field-enhancement factor

The actual field-enhancement factor realized in a TERS experiment is a crucial issue in near-field apertureless optical microscopy. Presently, there are several methods for estimating the enhancement effect in the near field [3, 7, 16–18]. In order to detect the plasmonic effect and therefore to estimate the enhancement while taking into account a near-field interaction zone the following expression might be used:

$$F = \frac{(I_{\text{near}} - B_{\text{near}}) - (I_{\text{far}} - B_{\text{far}})}{I_{\text{far}} - B_{\text{far}}} \frac{d_{\text{spot}}}{d_{\text{tip}}},$$
 (2)

where I_{near} , B_{near} and I_{far} , B_{far} are intensity and background in the near and far field, respectively, and d_{spot} is the laser spot size (approximately $\lambda/2$), d_{tip} is the lateral dimension of the 0



40

50

10 20 30 Tip-sample distance / nm

Figure 5. A plot of the enhancement factor of a Raman signal, taken from an SWCNT bundle at $\Delta v = 1594 \text{ cm}^{-1}$, versus tip–sample distance for both AF and SF regulation. To show the exponential behaviour of both curves, two different *y*-scales have been used.

near-field interaction zone $(d_{tip} = \sqrt{2Rh})$, where h is the tipsample distance, R is the radius of the tip).

This equation describes the signal enhancement obtained; however, it also provides a rough estimate for the field enhancement. It is important to note that for $h \ll R$, $d_{\rm tip}$ is less than the tip radius ($d_{\rm tip} < R$) and, therefore, a sub-tip size spatial resolution can be attainable [11]. The subtraction of the near-field background $B_{\rm near}$ allows one to suppress the irradiation reflected from a tip ('mirror' effect) and, thus, to improve the signal-to-noise ratio. One should emphasize that the expression considered above gives a rough estimate for the field-enhancement factor, since neither Landau damping nor size and shape effects are taken into account, respectively. This can lead to a substantial overestimation of theoretically determined enhancement factors compared with the experimentally observed ones. In addition, the proper choice of the wavelength for the excitation of localized surface plasmons and the polarization of incident photons are very important. One should keep in mind that, if the size-dependent dielectric constant of the probe is not experimentally measured, the experimental determined enhancement factor cannot be compared with the theoretical one.

Figure 5 demonstrates the calculated field-enhancement factor of the Raman signal at $\Delta \nu = 1594 \text{ cm}^{-1}$ taken from SWCNTs versus tip–sample distance for both AF and SF feedback lock-in techniques according to equation (2), in which the geometrical form factor was not taken into account. Both data sets were fitted with exponential curves (shown as solid lines). Decay lengths of ~4 nm (SFM) and ~12 nm (AFM) determine a near-field threshold to maintain, i.e. the maximum tip–sample distance for reasonable enhancement. They depend on resonance properties of a probe that can be controlled by its spring constant (AFM) and mass (SFM). In the latter case the heavier tip glued to a tuning fork shows only low-frequency eigenmode but has the smaller decay rate, and thus a well-pronounced threshold for enhancement.

3.3. Nanoscale spectroscopy and imaging of SWCNTs

In order to investigate the nanoscale structural details of SWCNT samples and to demonstrate the spatial resolution capabilities of our experimental set-up we analyse the main Raman-active vibrational modes of SWCNTs: the radial breathing mode (RBM) (100–300 cm⁻¹), associated with a symmetric movement of all carbon atoms in the radial direction; the disorder-induced D band (~1300 cm⁻¹), caused by the presence of in-plane substitutional heteroatoms, vacancies, grain boundaries and other defects; and the G⁺ (~1594 cm⁻¹) and G⁻ (~1557 cm⁻¹) bands, assigned to the tangential stretching C–C vibrations along the axis of the nanotube and its circumference [30–32]. Figure 6 shows a topographic image of a SWCNT bundle deposed on glass (A) and the corresponding cross section (B) along the white solid line indicated in figure 6(A). As seen from the figure



Figure 6. AFM image of an SWCNT bundle (A) and the corresponding cross section (B).



Figure 7. Raman spectra of SWCNT bundles when a gold-coated AFM tip (A) and a self-made gold SFM tip (B) is brought close to and withdrawn from a sample, respectively; data presented are original data without applying smoothening procedures.

Table 1. The field-enhancement values for characteristic vibrational modes. An asterisk indicates that a correction factor $d_{\text{spot}}/d_{\text{tip}}$ or $A_{\text{spot}}/A_{\text{tip}}$ (from $R_{\text{spot}} = 150 \text{ nm}$, R_{tip} (AFM) = 25 nm, and R_{tip} (SFM) = 8 nm) is not taken into account.

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Mode	RBM	D	G^-	G^+	
$\Delta v \ (\text{cm}^{-1})$	263	1313	1557	1594	Correction factor
AFM	4* 70	12* 214	9* 160	6* 118	None $d_{\rm spot}/d_{\rm tip}$
	144	432	324	216	$A_{\rm spot}/A_{\rm tip}$
SFM	457* 27 420 182 800	190* 11 400 76 000	263* 15 780 105 200	254* 15 240 101 600	None $d_{ m spot}/d_{ m tip}$ $A_{ m spot}/A_{ m tip}$

the SWCNT bundle has a width of about 100 nm (neglecting deconvolution of the image) and a height of 2-2.5 nm.

Raman spectra of the same SWCNT bundle when a tip is brought close to (tip-on mode) and withdrawn from (tip-off mode) the sample for both AFM (A) and SFM (B) feedback regulations are shown in figure 7; data presented are original data without applying smoothening procedures. Shadowed bars correspond to the predefined spectral windows in which scattered photons are detected.

From the recorded spectra we can estimate the fieldenhancement factors for the above-mentioned bands. These values obtained with and without taking into account the correction factor $d_{\text{spot}}/d_{\text{tip}}$ or $A_{\text{spot}}/A_{\text{tip}}$ are given in table 1. In the case of quasi-2D objects (SWCNTs), the correction factor $d_{\text{spot}}/d_{\text{tip}}$ provides the most reliable enhancement factor. The Raman enhancement factors are non-uniform for various spectral lines as reported earlier [1, 31]. Most probably, these enhancement variations reflect different near-field interaction strengths, but also sample heterogeneity or technical factors such as tip orientation with respect to the sample might be the reason for these variations. Weak intensities of the RBM bands observed in case of AF feedback when compared with SF feedback may be caused by direct tip-sample contact and poor quality of the tip used. In the present experimental setup, tip-sample contact is most likely since the free oscillation amplitude of the cantilever used is about 20 nm, and the mean

tip–sample distance is about 12 nm, respectively. External stresses, as forced by such tip–sample contact, can lead to the damping of symmetric vibrations of carbon atoms in the radial direction and/or the changes (e.g. local defects) in the molecular structure of an SWCNT. Further, additional features with Raman shifts of 521 and 960 cm⁻¹ are observed in the spectrum of figure 7(A), which are assigned to the first- and second-order Raman bands that originate from the Si core of the AFM cantilever. This observation indicates that gold is partly removed from the tip apex, so that Raman lines from the Si core of the tip can be generated. In the spectrum shown in figure 7(A) the silicon signal is much smaller than that generated by pure silicon and the enhancement factors for the TERS signals are still those of table 1, indicating that the gold loss by mechanical wear is still tolerably low.

The increase of the near-field background in the wavenumber region of 2000 cm⁻¹ and higher (figure 7(A)) is explained by the stray light coming from the 830 nm laser diode as mentioned above. It might be noticeably decreased with the help of the pinhole or fully deleted with a double monochromator. In our case the pinhole size was optimized to get a high signal-to-noise ratio.

Figures 8(A-I), (B-I) and (C-I) shows confocal farfield Raman spectroscopy intensity distribution images of the SWCNT bundle as discussed in figure 6(A) for the characteristic Raman modes. As expected, in the confocal mode the spatial resolution is about 250 nm. It follows from figures 6(A) and 8 that topographic and optical images are closely correlated and SWCNTs can be easily identified. However, the intensity distribution of the observable Raman signals does not scale with the topographic height distribution of the bundle under consideration. For the Raman spectroscopy intensity distribution images acquired in TERS mode we use a self-made gold tip and scan in SF mode (figures 8(A-II), (B-II) and (C-II)). The non-uniform intensity of observable features indicates that the SWCNTs are either twisted in the bundle or, more probably, intensity variations indicate the presence of defects and other heterogeneities along the SWCNTs (figures 8(A-III), (B-III) and (C-III)). Comparing the far- and near-field Raman intensity distribution images, obviously the TERS technique avoids averaging of the Raman



Figure 8. Confocal far-field Raman images ((A-I), (B-I) and (C-I)) and tip-enhanced near-field Raman intensity distribution images acquired by a self-made gold tip in SFM mode ((A-II), (B-II) and (C-II)) of an SWCNT bundle for characteristic vibrational modes: RBM at 290 cm⁻¹ (A), D-line at 1390 cm⁻¹ (B), G⁺-line at 1594 cm⁻¹ (C), and their corresponding cross sections ((A-III) (B-III) and (C-III)), original data).

spectrum along the SWCNT bundle, and thus allows us to locally analyse fine features with ultrahigh spatial resolution.

Tip-enhanced spectra exhibit strong Raman peaks in the bottom part of the bundle, whereas the Raman intensity is negligible at the top and drops down to zero at the middle of the SWCNT bundle (figures 8(A-II), (B-II) and (C-II)). On the one hand, topographically detected carbon nanotubes can be non-resonant at 632.8 nm and therefore do not appear in the optical image. In other words, the Raman scattering strength of SWCNTs is strongly dependent on the energy difference between photon energies and their electronic energies. On the other hand, as seen in figure 6(A), there are three bumps in close proximity of the bundle that are invisible in tip-enhanced Raman maps due to the chemical specificity of the method. A central bump can affect the molecular structure and also changes locally resonant properties of the nanotube bundle.

A strong correlation between tip-enhanced Raman images taken for different Raman active bands establishes that the

non-uniformity is caused by the polarization direction of the incident beam that is perpendicular to the tube axis at this place. Indeed we can observe that the Raman intensity of all modes decreases monotonically on increasing the angle between the bundle axis and the polarization direction. From the cross-sectional plots taken along the white solid lines in figures 8(A-II), (B-II) and (C-II) the spatial resolution attained with the optical method is better than 50 nm (figures 8(A-III), (B-III)); a Gaussian fit of the original data as presented would result in an even better spatial resolution of about 30 nm. Such resolution allows, for example, for the detection of local defects along the long axis of SWCNTs.

4. Conclusions

In the present study we have investigated tip-enhanced nearfield Raman scattering from single-walled carbon nanotubes deposited on transparent substrates with both atomic force and shear force feedback lock-in regulations. A comparative analysis of confocal diffraction-limited far-field and tipenhanced near-field Raman spectra and intensity distribution images of SWCNTs has been performed. The experimental enhancement factors for different vibrational modes of SWCNTs are up to $\sim 4 \times 10^2$ for AF mode and up to $\sim 10^5$ for SF mode, calculated as a ratio of near- and far-field intensities using the approximated sizes of the incident laser spot and the curvature of the tip apex as determined by TEM. The optically achievable spatial resolution is better than 50 nm applying SF mode with a self-made gold probe having a 16 nm apex radius. Such performance allows, for example, for the detection of defects along individual SWCNTs.

In future studies, we would like to understand the significance of crystallographic orientations at the probe apex on the field enhancement and the role of texture and defect structure (e.g. dislocation density, etc) present in bulk material on the quality (sharpness, hardness) of the probe produced by the electrochemical etching procedure. Optimization of the probe seems for us the key towards TERS imaging with ultimate spatial resolution.

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