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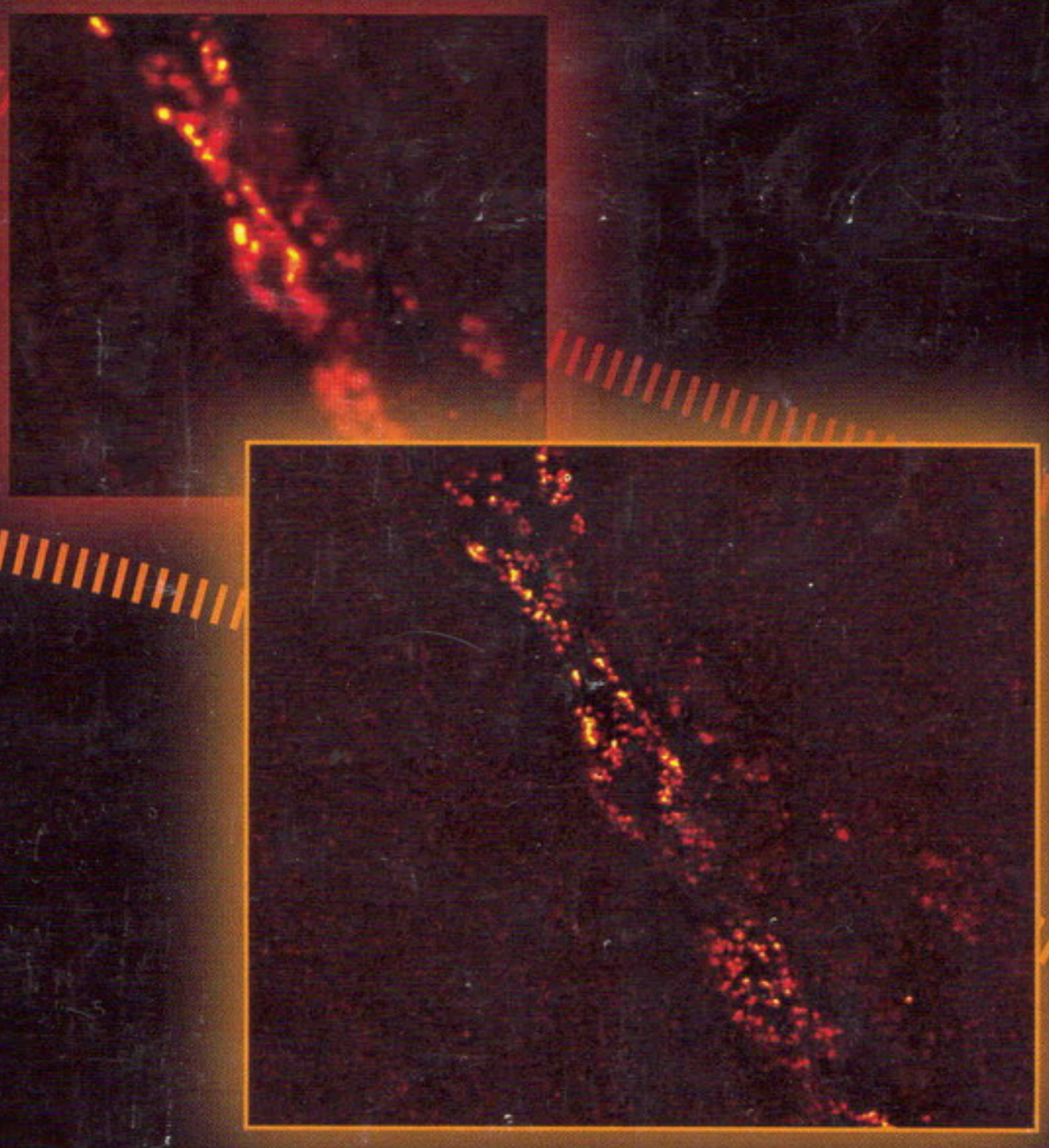

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Tip-enhanced Raman Spectroscopy and Imaging

Nanoscopic Imaging of Single-walled Carbon Nanotubes

A possibility to not only visualize but to locally probe a chemical structure, composition, conformational state and stresses on the nanoscale has stimulated the development of apertureless near-field vibrational spectroscopy and imaging with ultrahigh spatial resolution laying beyond the diffraction limit [1–3]. It has become possible due to the delocalization of evanescent waves (near-field) existing in the proximity of nano-sized objects with a sharp metal probe.

Dr. S. S. Kharintsev, Eindhoven University of Technology, The Netherlands

Keywords:

near-field, enhancement, tip-enhanced Raman spectroscopy

A considerable progress in nanoscopic imaging has been achieved with a laser-illuminated pointed metal tip allowing us to improve spatial resolution and increase the field-enhancement [4–7]. This is caused by the geometric singularity of sharply pointed metal probes (lightning rod effect) and surface plasmon resonances, which depend on both the excitation wavelength and tip geometry. In this respect, highly confined electromagnetic fields at the tip apex can be used to locally explore light-matter interactions. This paper demonstrates some advances of tip-enhanced Raman spectroscopy and nanoscopic imaging of single-walled carbon nanotubes (SWCNTs).

Experimental Details

In our studies we used a commercial available scanning near-field optical nanoscope NTEGRA SPECTRA (NT-MDT, Russia), whose general view is schemati-

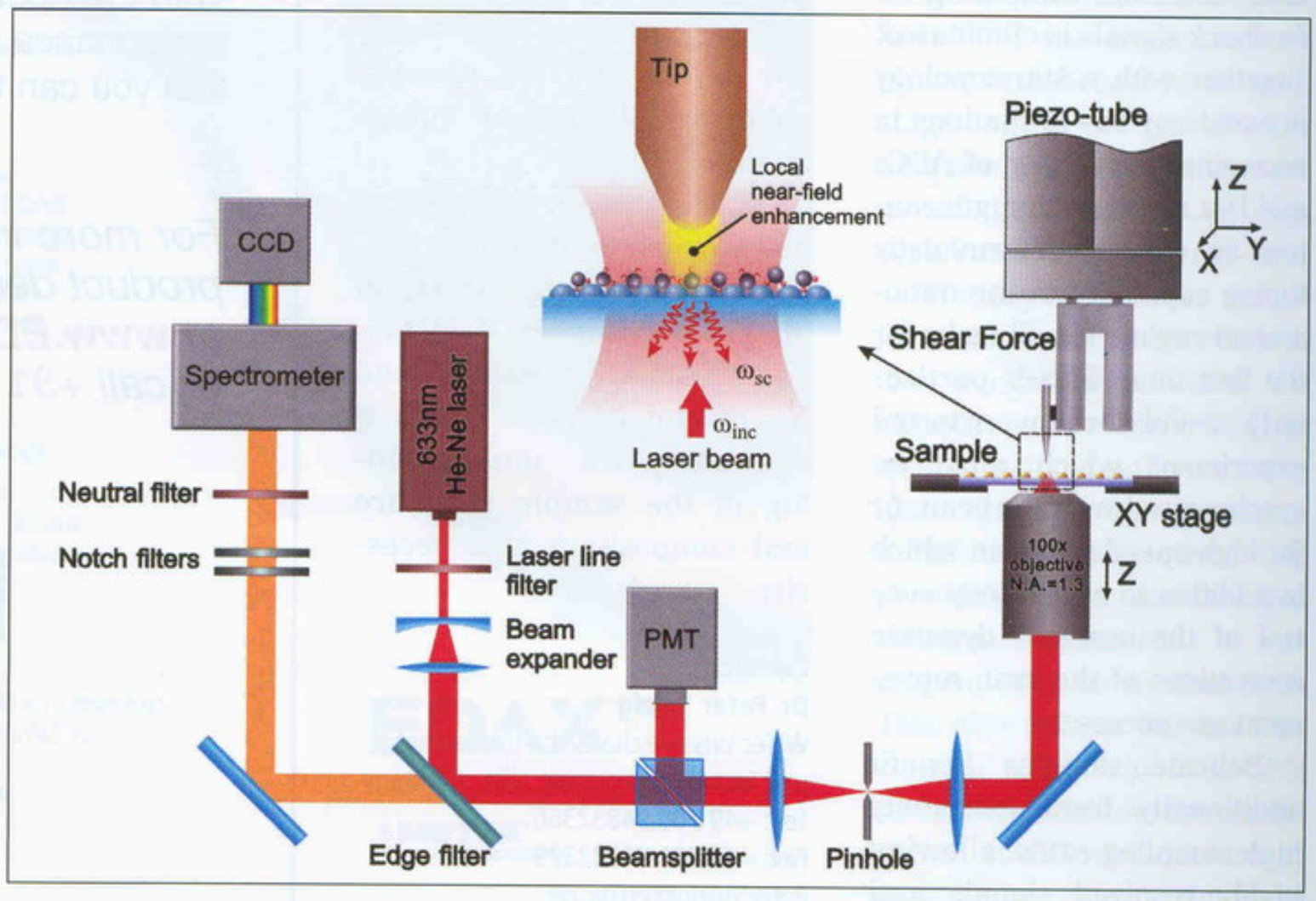

Fig. 1: A schematic layout of the scanning near-field optical spectrometer.

cally shown in figure 1. A 632.8 nm linearly-polarized laser light is transmitted by a laser line filter and a beam expander, reflected by an edge-filter and goes into the inverted optical microscope through a beamsplitter and a pinhole. A 100 x oil immersion objective (N.A.=1.3) focuses the laser beam into a spot with the size of less than 300 nm and with a power of ~100 μW at a sample. A gold tip is held in the constant height mode of ~3 nm by means of the shear-force feedback mechanism. In order to produce the desired field enhancement at the tip apex, one should couple the tip with one of two longitudinal field lobes (for a Gaussian beam) located at rims of the diffraction limited laser spot. A near-field optical image is produced by raster scanning the sample with x, y stage and maintaining the tip fixed in respect to the longitudinal lobe. Scattered and reflected light is collected with the same objective and directed back, through the pinhole and the beamsplitter, into a photomultiplier and a thermoelectrically cooled charge-coupled detector. Raman spectra were recorded within a spectral range of 150–3000 cm^{-1} with the spectral resolution better than 15 cm^{-1}. Acquisition time was 500 ms per image pixel. As a probe we used a high-purity (99.998%) gold drawn wire electrochemically etched in a mixture of HCl/Ethanol to an end diameter of ~20 nm [8]. Figure 2 shows a data set acquired from the sample containing a dispersion of large SWCNTs bundles: A – atomic force microscopy (AFM) image, B – confocal optical image, C – confocal far-field Raman image (~1587cm^{-1}).

Enhanced Spectroscopy and Nanoscopic Imaging

In this section we consider the main characteristics of tip-based nanoscopic imaging such as spatial resolution and field-enhancement factor by means of Raman active modes along carbon nanotubes, namely: the radial breathing mode (RBM) (100–300 cm^{-1}); disorder-induced D band (~1310 cm^{-1}) and its first overtone D* (~2606 cm^{-1}); G^+ (~1587 cm^{-1}) and G^- band (~1559 cm^{-1}). Raman spectra of a small SWCNTs bundle when a tip is landed to and retracted from the sample are depicted in figure 3. From the data acquired we can estimate the field enhancement factor, calculated as an area-corrected ratio of near- and far-field intensities, for mentioned above bands: ~9750 (RBM), ~7500 (D band) and ~9750 (D* band), ~9000 (G^+ band) and ~10500 (G^- band). Thus, Raman enhancements are non-uniform for various spectral lines as reported earlier [9,10]. A noticeable pedestal within the range of 200–2200 cm^{-1} is caused by back-scattered light from the tip. A topographic AFM image of a SWCNTs bundle on glass and its cross section, taken along a white solid straight are shown in figure 4 (a,b). As seen from the figure, the lateral resolution is of ~90 nm which is obviously caused by the convolution of the ~50 nm tip apex with the SWCNTs bundle under study. By height of the cross section of the latter (fig. 4b), we can presume that this bundle is composed of at least two carbon nanotubes. The same is followed by the complex structure of the

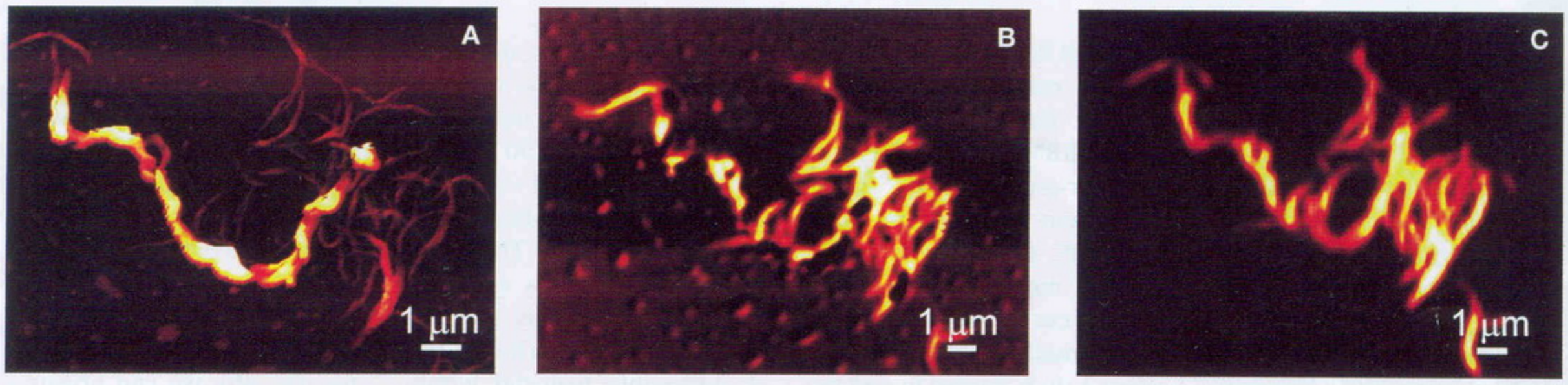

Fig. 2: SWNTs bundle: a) AFM image b) confocal optical image, c) confocal Raman image taken at $\Delta\nu$ = 1587 cm^{-1}.

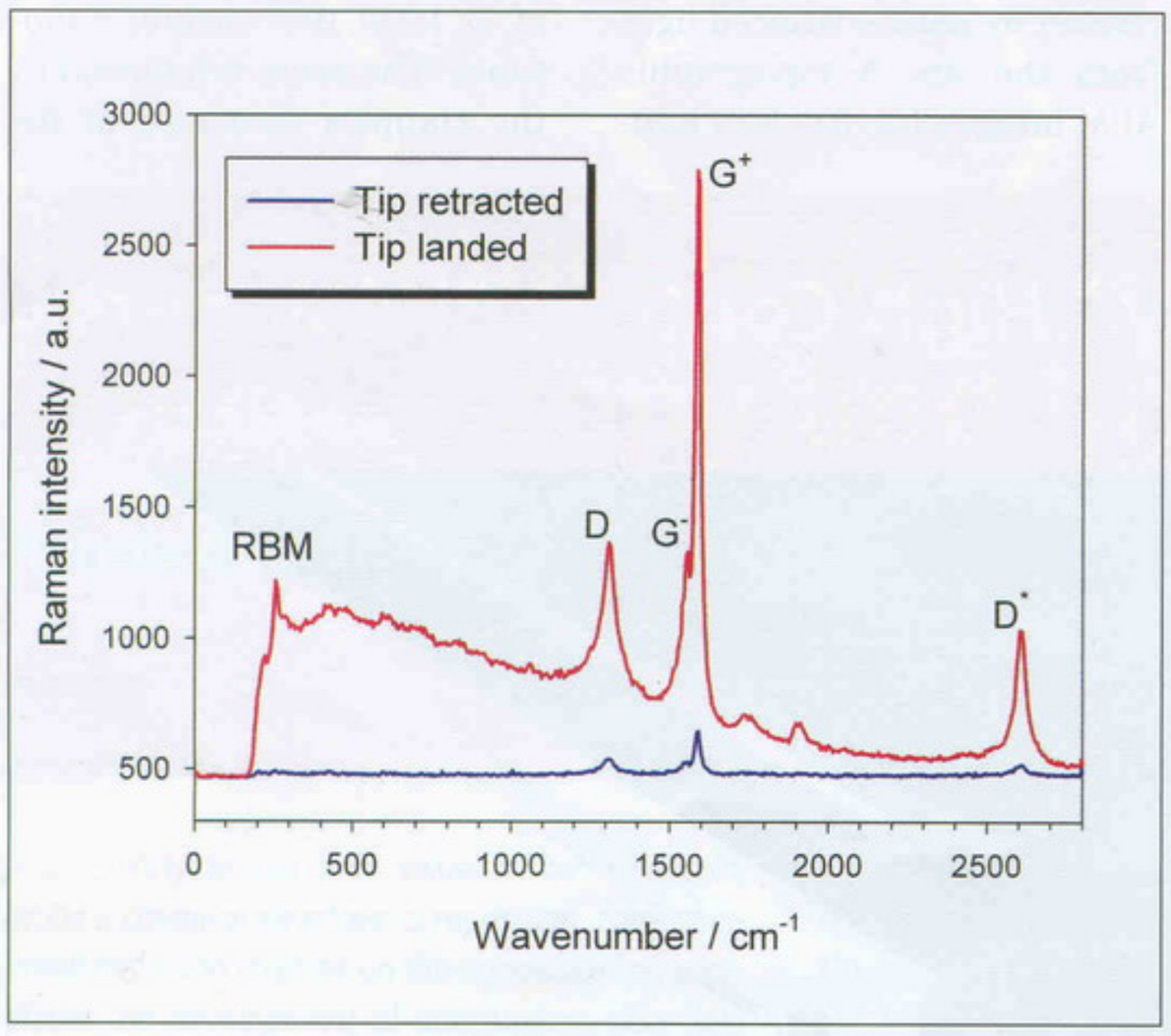

Fig. 3: Raman spectra of a SWCNTs bundle when the gold tip is landed and retracted to and from the sample.

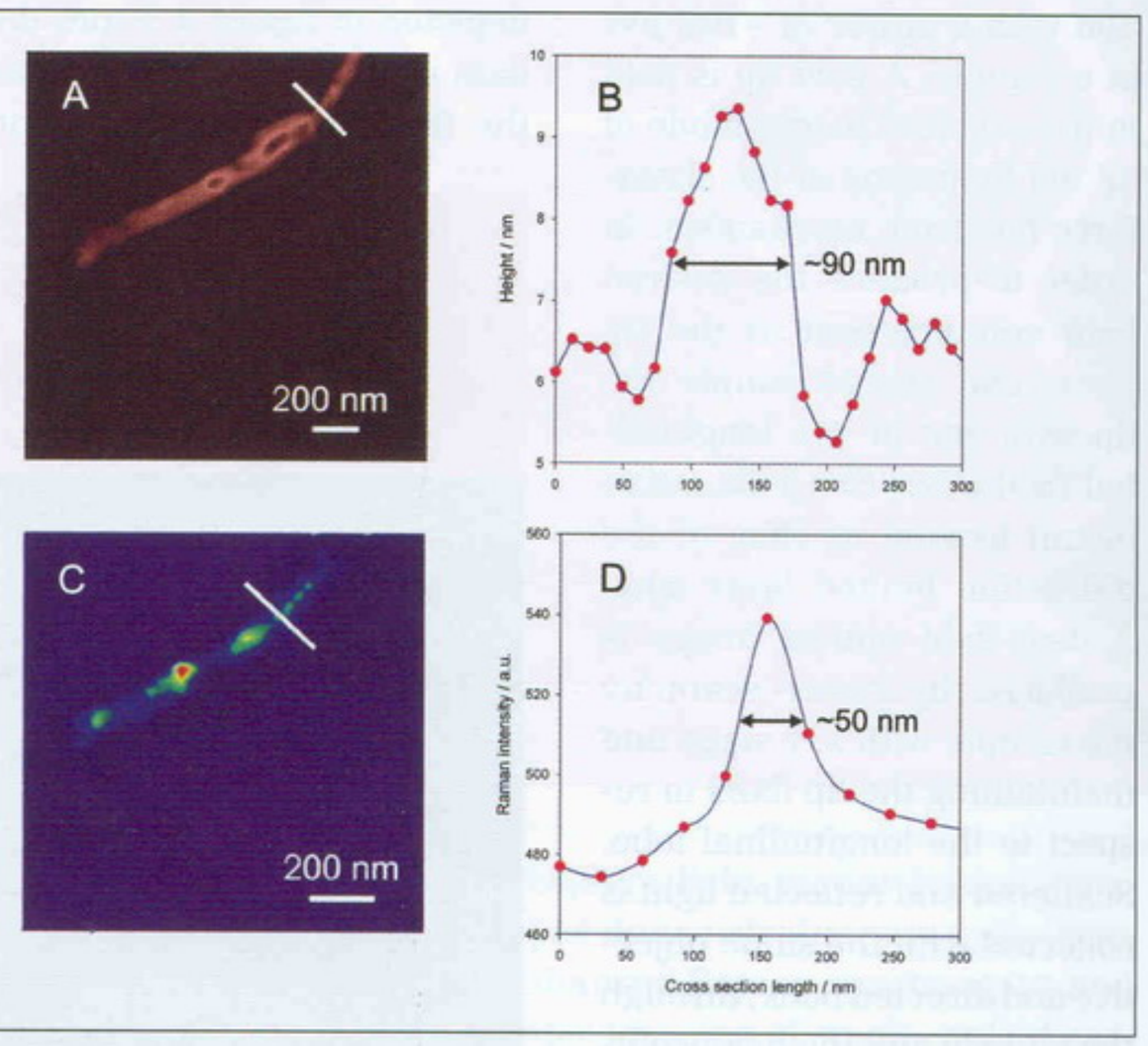

Fig. 4: AFM image (a) and tip-enhanced Raman image of the SWCNTs bundle (c) (1594 cm^{-1}). (b) and (d) are their cross sections taken along a white straight lines, respectively.

RBM band around ~258 cm^{-1} (fig. 3) by which we can identify the carbon nanotubes and then determine their structure. In figure 4c we show a tip-enhanced near-field Raman mapping of the same carbon nanotubes bundle made with the ~20 nm end diameter tip driven by the shear-force regulation. The cross section along the white solid straight on this map indicates the spatial resolution attained with the optical method to be ~50 nm (fig. 4d). It follows from figure 4 that topographic and near-field images are closely correlated and carbon nanotubes can be easily identified due to chemically specific feature of the optical method. However, the distribution of intensity of the tip-enhanced Raman signal along the carbon nanotubes bundle does not scale with its topographic height. This is explained by the fact that carbon nanotubes are twisted and form a bundle consisting of a varying number of single nanotubes. On the other hand, this might be understood in terms of resonance Raman scattering, since some nanotubes are non-resonant at 632.8 nm. Finally, we can see that the tip-based near-field technique allows one to avoid averaging of the Raman spectrum originating from the whole SWCNTs bundle and, therefore, locally probe fine structural features with ultrahigh spatial resolution in a nondestructive way.

Conclusion

In this paper we have illustrated power of tip-enhanced Raman spectroscopy and nanoscopic imaging of carbon nanotubes by achieving the field-enhancement factor up to ~10^4 and the spatial resolution down to ~50 nm, respectively. In further development of the tip-based near-field technique, a special attention should be given to the production of nanoscale probes that not only can produce highly enhanced electromagnetic fields, but could also be used in a wide variety of sample environments.

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Further references are available from the author.

Contacts:
Dr. P. S. Dorozhkin
Institute of Solid State Physics, Chernogolovka, Russia

Dr. G. G. Hoffmann
Dr. J. Loos
Prof. G. de With
Eindhoven University of Technology, The Netherlands
Tel.: +31402473331
S.Kharintsev@tue.nl, www.tue.nl