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**Raman Spectroscopy**

## Characterization of Carbon Nanotubes using Tip-Enhanced Raman Spectroscopy (TERS)

Application Note

Nanotechnology
RA64

8 nm

20 nm
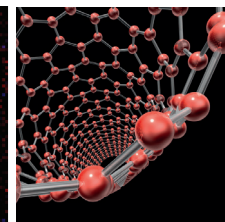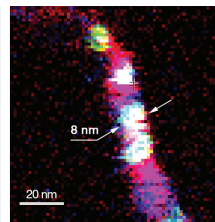
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Carbon nanotubes (CNTs) - Nanomaterials - Tip-Enhanced Raman Spectroscopy

## Context and issues

Carbon nanotubes are now manufactured in large volumes (several thousand tons per year) and are present in many daily life products ranging from car parts, batteries, and sports equipment, to water filtration systems and boat equipment.

Nevertheless, there is still a long way to go to produce SWCNT (single wall carbon nanotube) in large scale devices with exceptional theoretical electrical and thermal conductivities and mechanical resistance. Additional knowledge is essential for boosting CNT integration into thin film microelectronics, optoelectronics, and medical devices.

## Potential / Input from technique

Raman spectroscopy is the technique of choice to characterize CNTs and related nano-objects in terms of chirality, diameter, density, length, and presence of defects. Because conventional Raman is a far-field optical technique (the spot size is diffraction-limited), its applications are restricted to the micro- and macro-worlds. TERS bridges the gap to NanoRaman and offers nanometric spatial resolution down to the single tube level for those characteristics provided by the rich Raman spectra.

## Starting point, what is known?

Carbon nanotubes exhibit several strong Raman peaks: (i) the radial breathing mode in the range of 100-400 cm$^{-1}$ has a frequency related to nanotube diameter and chirality through a simple known function; (ii) the G-band peak (at ~1590 cm$^{-1}$) can distinguish SWNT as metallic or semiconducting; and (iii) the disorder-induced D band (~1350 cm-$^{1}$)

provides information about the presence of defects in the nanotube structure. The 2D band (a two-phonon band at ~2700 cm$^{-1}$ associated with the disorder-induced D band) indicates changes in the electron energy dispersion of CNT and thereby is informative about the presence of dopants in their 1D structure.

## Description of sample and measurement

This application note presents TERS data obtained on CVD-grown SWCNTs deposited on Au substrate using spin-coating. TERS measurements were performed using a NanoRaman™ system from HORIBA Scientific combining an Atomic Force Microscope (SmartSPM, AIST-NT) with a Raman spectrometer (XploRA) with a ×100 LWD objective tilted at 60° with respect to the sample plane. A 638 nm *p*-polarized laser is focused onto the cantilever-based silver TERS tip with a 0.13 mW power on the sample. An AFM topography map is first recorded to locate one or several CNTs. Then a high resolution Raman map focusing on two SWCNTs (300 × 160 nm (100 × 60 points)) is collected with a 100 ms integration time for the Raman spectrum (200-3600 cm$^{-1}$) of each pixel (3 nm step). The Raman image (Figure 1) is generated from the integration of the three D, G, 2D band intensities using blue, green, red color scales respectively. The integration windows for the D, G, 2D bands are visible in figure 1 (b) showing two TER spectra detected at two different locations in the CNT. The intensity of the D band (blue pixels) is showing the imperfection in the structure of the latter and thus the location of the defects. In contrast, the areas in red correspond to the pure graphitic arrangement of the CNT through the intensity of the 2D band.
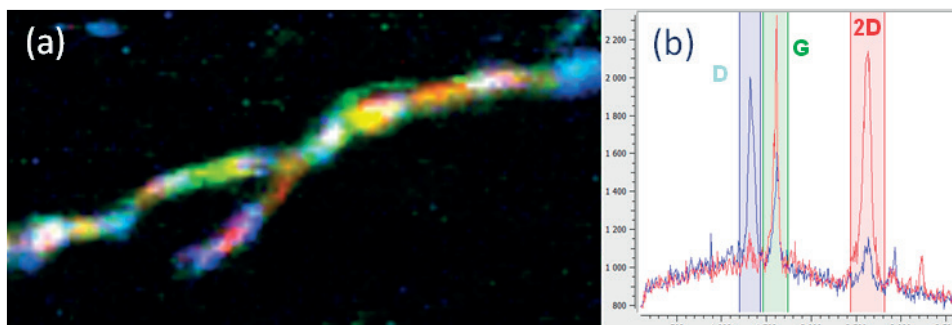


Figure 1. (a) TERS chemical mapping of two SWCNTs, (b) typical TER spectra from the tubes.

In order to push the limit of the optical resolution through TERS, figure 2 presents a high resolution TERS hyperspectral image of an individual SWCNT, 100 x 100 nm scanning area, obtained with a pixel step size of 1.3 nm, in a total acquisition time < 9 min, 100 ms per pixel. The Full Width at Half Maximum (FWHM) of the TER intensity profile along the line across the CNT clearly demonstrates 8 nm spatial resolution. In addition, the TERS map (Figure 2 a in which D band is shown in white and green pixels and 2D band in red) also demonstrates a chemical sensitivity down to the pixel size (1.3 nm): e.g. the intensity of the D peak in the red circle marked area close to the local lattice defects rises drastically from one pixel to the adjacent one (Figure 2 c).

## Conclusion and perspectives

The use of TERS to reveal the defects density in the structure of CNTs is of interest for a better understanding of the electrical properties of the devices made with such nano-objects. Not only defects concentration but also local chirality changes from the different radial breathing modes,

pressure effect and strain distribution can be studied at the single carbon nanotube level through TERS. The TERS characterization of both 1D carbon nanotubes and 2D graphene (another very promising form of carbon for a wide range of applications) is likely to contribute to further deployment of these carbon materials into general consumer products.

## Bibliography

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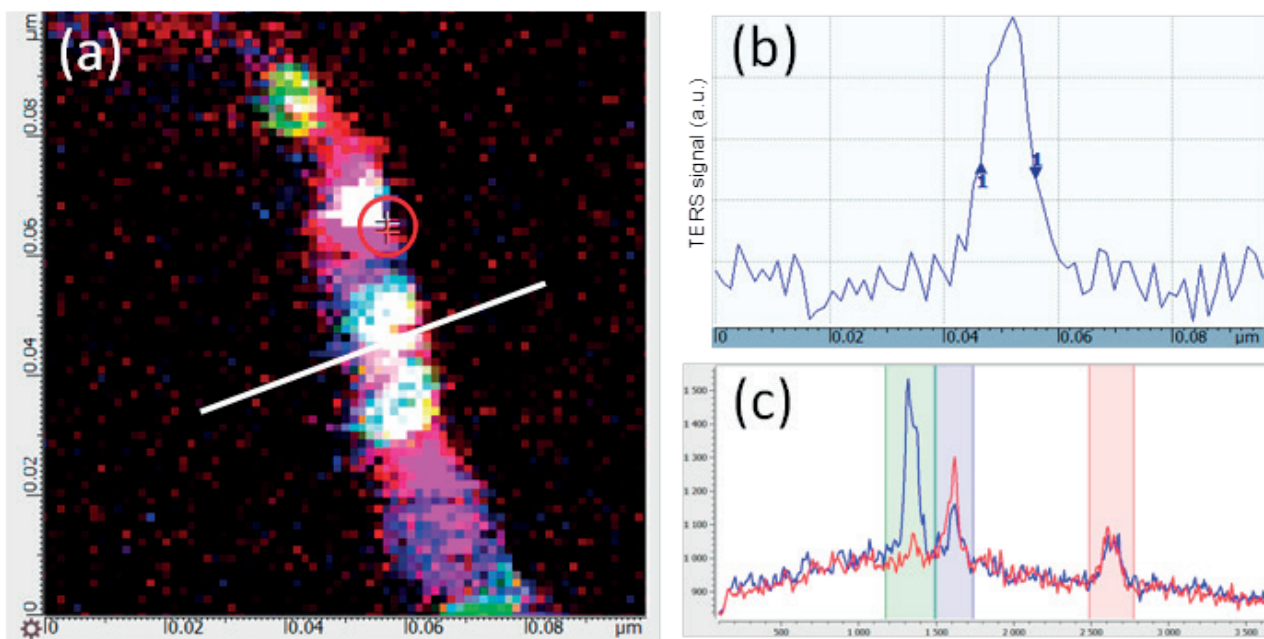
Figure 2: (a) Hyperspectral TERS map (100 nm x 100 nm, 1.3 nm step size) of an isolated CNT, (b) section analysis of the TERS signal (G band) showing <10 nm Raman resolution, (c) TER spectra from the area located by the red circle. The two Raman spectra are from two adjacent pixels (separated by only 1.3 nm).

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