



Imaging Carbon Nanotubes and Graphene with a High-Speed, High-Resolution Raman Microscope.

Application Note R547

Carbon nanomaterials, particularly carbon nanotubes (CNT) and graphene, are renowned for their exceptional strength and electrical conductivity. Their unique properties make them valuable in various applications, including electronics, energy storage, and advanced hybrid materials. As the significance of these materials grows, there is an increasing demand for efficient visualization of multiple samples.

In the research and development of carbon nanomaterials represented by carbon nanotubes (CNT) and graphene, Raman spectroscopy and microscopy is an indispensable analytical tool. That is because the Raman spectra of carbon nanomaterials contain a wealth of information, such as the number of defects in the material, the diameter of CNTs, or the number of layers in graphene. The RAMANtouch laser Raman microscope from Nanophoton - a Bruker company is equipped with ultra-fast imaging capabilities through line illumination and offers a spatial resolution of 350 nm, approaching the diffraction limit, making it an ideal instrument for imaging analysis of the local structure and microscopic distribution of nano-carbon materials. Here, we present examples of observations of CNTs and graphene using the RAMANtouch.



■ Semiconductor SWNT (146 cm^{-1})
■ Semiconductor SWNT (179 cm^{-1})

■ Semiconductor SWNT (192 cm^{-1})
■ Metallic SWNT (232 cm^{-1})

Fig. 1

Raman image of a carbon nanotube field-effect transistor (CNT-FET). It captures the distribution of various types of Radial Breathing Mode (RBM) in the synthesized CNT between the electrodes. Measurement parameters: Excitation wavelength: 532nm, Number of spectra: 13,200, Objective lens: 100x (NA=0.90), Measurement time: 16 minutes. The sample was provided by Professor Shigeo Maruyama of the University of Tokyo.

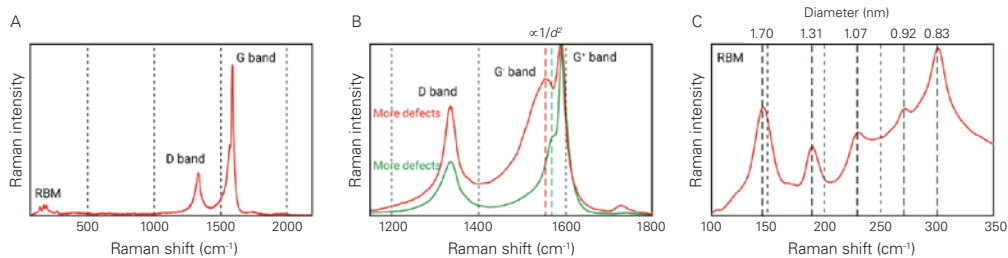


Fig. 2
Raman spectra of carbon nanotubes.

A: Spontaneous Raman spectrum of a CNT, containing the radial breathing mode (RBM), G- and D-band.

B: Comparison of a carbon sample with more and less defects.

C: Zoom-in to the radial breathing modes and display of corresponding wall diameters.

G Band

This peak around 1590 cm^{-1} originates from the in-plane vibrations of six-membered rings common to carbon-based materials (Fig. 2A). In the case of CNTs, the degeneracy of the G band is lifted, splitting into G+ and G- (Fig. 2B). G+ corresponds to the longitudinal optical (LO) mode along the CNT axis, while G- corresponds to the transverse optical (TO) mode perpendicular to the axis. The frequency of G+ appears around 1590 cm^{-1} regardless of the diameter of the CNT, whereas the frequency of G- varies inversely with the square of the diameter.

D Band

This peak around 1350 cm^{-1} is attributed to defects. The intensity ratio of the G band to the D band (G/D ratio) is used as an indicator of the number of defects in the CNT (Fig. 2A). A larger G/D ratio suggests fewer defects in the CNT, while a smaller ratio indicates a higher number of defects.

RBM (Radial Breathing Mode)

This mode involves the radial expansion and contraction of single-walled carbon nanotubes (SWNTs) (Fig. 2C). A peak appears on the low-frequency side ($\sim 300 \text{ cm}^{-1}$), and the peak position ω_{RBM} (cm^{-1}) has the following relationship with the diameter d (nm) of the SWNT:

$$d = 248/\omega_{\text{RBM}}$$

By utilizing this relationship, the diameter of the SWNTs contained in the sample can be evaluated, as shown in the Figure 2.

In CNTs, we observe resonant Raman scattering that occurs when the excitation wavelength matches the optical transition energy of the material. Therefore, to comprehensively observe SWNTs with different chiralities, it is necessary to perform measurements using multiple excitation wavelengths.

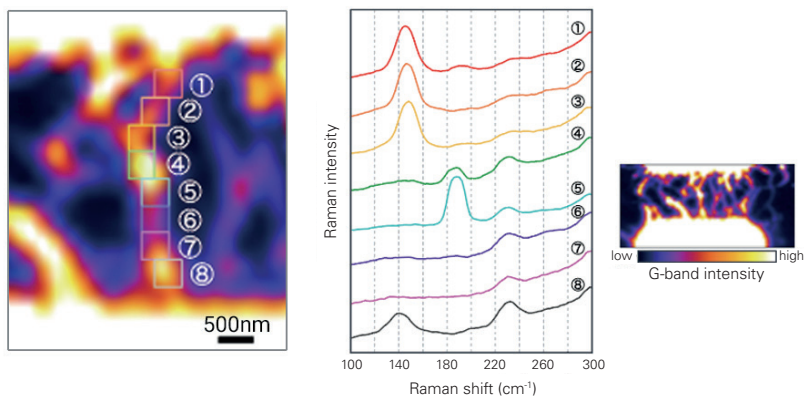


Fig. 3
Analysis of the spatial distribution of the RBM peak

Left: Zoom-in to one CNT.

Middle: Averaged spectra corresponding to the regions indicated in the Raman image (left).

Right: Full Raman image showing the G band intensity.

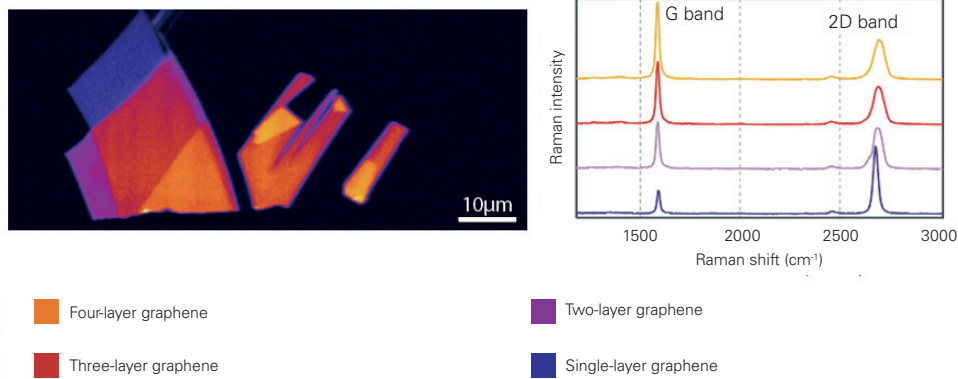


Fig. 4
Raman imaging analysis
of the layer number
distribution of graphene.

Left: Raman image of multilayer graphene. The color represents different numbers of layers. Right: Raman spectra of 1 - 4 layers of graphene, showing the different ratios of the G and 2D band. Measurement parameters: Excitation wavelength: 532nm, Number of spectra: 67,600 (400x169), Objective lens: 100x (NA=0.90), Measurement time: 5 minutes 30 seconds. The sample was provided by Daiki Tsugaya from the National Institute for Materials Science.

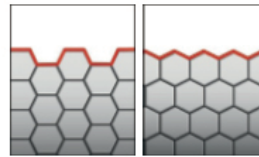
From the analysis of the Raman image, where each pixel consists of a full Raman spectrum, four different types of RBMs were detected. Figure 3 displays the peak intensity distributions of four different modes (mode 1: 1 - 3; mode 2: 4 + 5, mode 3: 6 + 7; mode 4: 8) and classifies the carbon nanotubes into semiconductor SWNT (single-walled carbon nanotube) and metallic SWNT based on the Kataura plot. The average Raman spectra originate from the eight selected rectangular areas within the Raman image, with each rectangle having a side length of 400 nm. By observing the transition of the RBM peaks from region 1 to region 8, it is evident that CNTs with different chiralities are distributed in an entangled manner between the electrodes. Utilizing RAMANtouch, which boasts spatial resolution approaching the diffraction limit, allows for clear observation of the microscopic spatial distribution of various RBM peaks.

Raman Imaging Analysis of Graphene

Figure 4 shows Raman imaging of a graphene thin film distributed on a thermally oxidized silicon substrate, completed in approximately five minutes. In this measurement, the number of graphene layers was identified by the intensity ratio of the G band to the 2D band ($G/2D$) within the Raman spectrum. This $G/2D$ ratio is about 0.3 for single-layer graphene, increases linearly up to around five layers, and saturates beyond six layers. For single-layer graphene, the peak position of the 2D band appears at approximately $2678.8 \pm 1.0 \text{ cm}^{-1}$; however, for two or more layers, the peak position of the 2D band shifts to the higher wavenumber side, and the full width at half maximum also broadens. The 2D band of single-layer graphene can be fitted with a single Lorentzian, but for two or more layers, it consists of a sum of multiple sub-peaks. The slight distortion observed in the low-wavenumber tail of the 2D band for bilayer graphene is due to this. Thus, the Raman spectrum of graphene contains information suggesting its layer number.

In addition to the number of layers, controlling the edge structure of graphene is also one of the important challenges for device applications. There are two types of edge structures: armchair and zigzag. The former shows the D band, while the latter does not. The Raman image in Figure 5 reveals that, based on the intensity distribution of the D band, the edge on the right side of the graphene is of the armchair type.

In this way, using the high-speed and high-resolution imaging capabilities of the laser Raman microscope RAMANtouch enables the clear capture of the spatial distribution of structures and properties of nanocarbon materials with sub-micron resolution in about ten minutes.



Armchair type

Zigzag type

Graphene

Armchair Edge

Fig. 5 Analysis of the Edge Structure of Graphene.

Left: Raman image of an edge structure of graphene.

Right: Scheme of an armchair and zigzag edge structure. Measurement parameters: Excitation wavelength: 532nm, Objective lens: 100x (NA=0.90), Measurement time: 8 minutes. The sample was provided by Professor Yoshihiro Kobayashi of Osaka University.

Conclusion

Carbon nanomaterials such as carbon nanotubes (CNT) and graphene exhibit remarkable properties that make them indispensable in various advanced applications. The use of Raman spectroscopy and microscopy, particularly with instruments like the RAMANtouch laser Raman microscope, is crucial for the detailed analysis of these materials. The ability to visualize and analyze the local structure and distribution of CNTs and graphene with high spatial resolution provides valuable insights into their properties and potential defects. This advanced imaging capability not only enhances our understanding of these nanomaterials but also supports their development and integration into innovative technologies. As research progresses, the precise and efficient characterization of carbon nanomaterials will continue to play a pivotal role in unlocking their full potential.

