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Technology

Raman
Spectroscopy

Application
Note

Nanotechnology
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SWNTs, Quality Control by Raman Spectroscopy

Abstract

Carbon NanoTubes (CNT) form a new class of materials that have attracted interest for a variety of engineering applications. Structurally they are related to graphitic carbon. One can conceptualise the structure of a Single-Walled Carbon Nanotube (SWNT) by imagining a single layer of graphite that is rolled into a tube (Figure 1). The orientation of the graphite plane relative to the axis of the tube, as well as the diameter of the tube, will determine many physical properties; tubes can be insulating, semiconducting, or metallic. When multiple layers of graphite are rolled into a single tube, the resulting structure is called a Multi-Walled Carbon Nanotube (MWNT).

Keywords

Raman Spectroscopy, nanotechnology characterization, SWNT, CNT, Ultra Low Frequency (ULF)
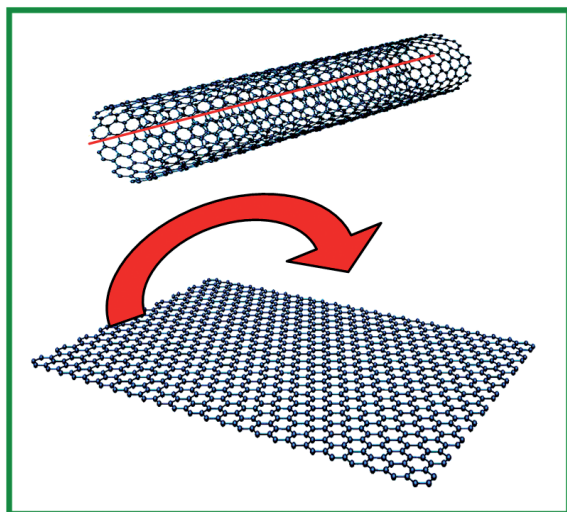

Fig.1: Illustration of the structure of a single walled carbon nanotube from a graphite sheet.

These materials have provided fertile ground for solid state calculations that predict the electronic and vibrational properties [1] of these structures. In addition, there are limitless ideas of how to take advantage of the tubes' properties in engineered materials. For instance, composites will take advantage of the tensile strength of the tubes and Metallic tubes have already been used in integrated circuits [9].

Raman spectra of these tubes are quite interesting because of resonance phenomena and sensitivity to tube structure. That is, there is very strong excitation wavelength dependence of the spectra resulting from the electronic and structure. And features in the Raman spectra are diagnostic of the CNT type [8].

The large variety of SWNTs is defined by a pair of integers (n,m) from which their diameter, Chirality and Semiconducting / metallic behaviour can be determined. Chirality defines the orientation of the rolled Graphite sheet relative to the main axis of the tube.

The characteristic Raman spectrum of SWNT

The most important feature in the Raman spectrum of CNT's is the Radial Breathing Mode (RBM), which is often observed between 100 and 250 cm^{-1}. The frequency of the RBM (ω in cm^{-1}) is directly linked to the reciprocal of the nanotube diameter (d_t). In the case of an isolated Single Wall NanoTube (SWNT) this relation is [1]:

$$\omega_r = 224/d_t$$

However, non isolated SWNT's are subject to inter-tube interactions which increase the frequency of the RBM.

The D mode (the disorder band is well-known in disordered graphitic materials and located between 1330-1360 cm^{-1} when excited with a visible laser) is expected to be observed in Multi Wall NanoTubes (MWNT). However when it is observed in SWNT's, one assumes that it is due to defects in the tubes.

The G mode or (TM- Tangential Mode) corresponds to the stretching mode of the -C-C- bond in the graphite plane. This mode is located near 1580 cm^{-1}.

Exciting at several wavelengths- WHY ?

As mentioned earlier there is strong excitation wavelength dependence on the Raman intensity of SWNT's resulting from the proximity of the laser wavelength to the transitions between electronic states (DOS) which determine the transition energies and intensities can be calculated and are quite sensitive to the tube structure [1].
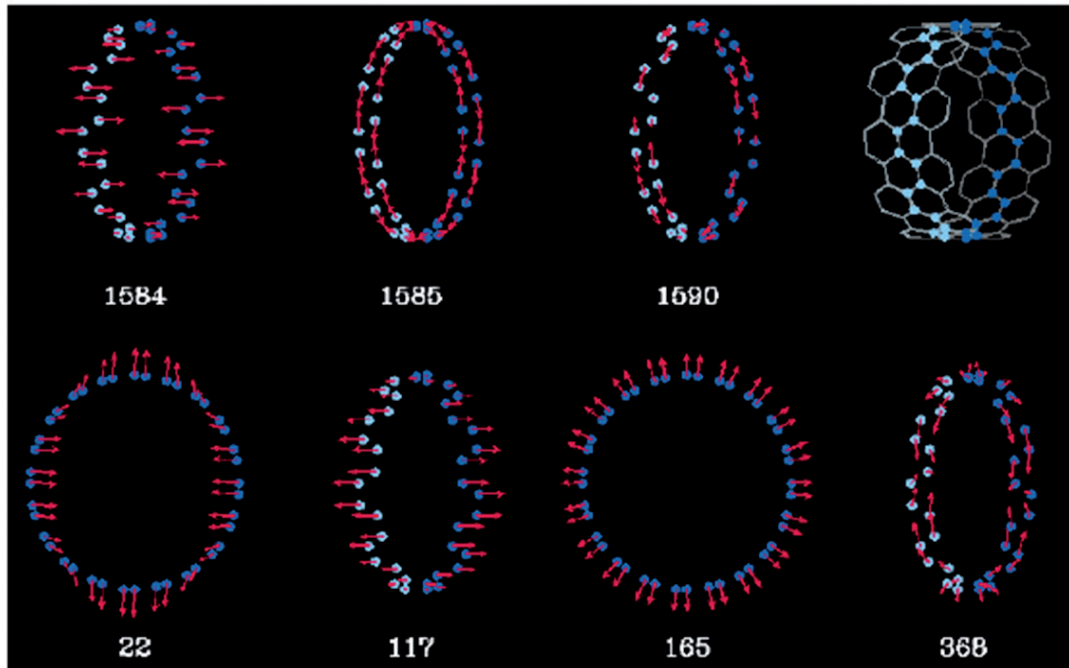
Fig. 2. Raman-active normal mode eigenvectors and frequencies for a (10,10) nanotube. The red arrows indicate the magnitude and direction of the appropriate C-atom displacements, and the eigenvectors shown correspond to the seven most intense modes (see Fig, 1). The unit cell (blue atoms) is shown schematically in the upper right-hand corner.
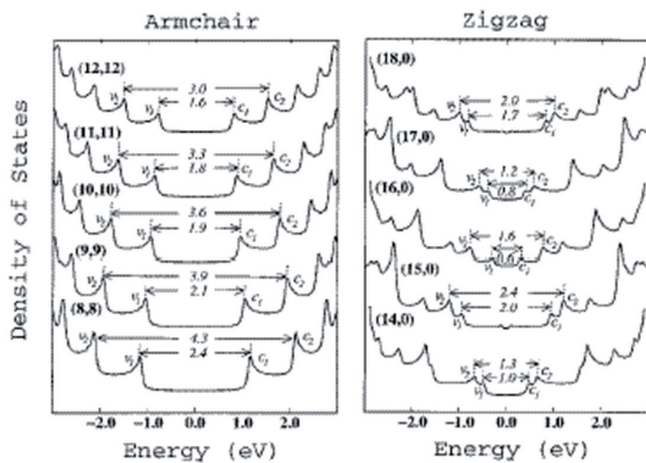

Fig. 3: Kataura plots based on the energy of the C-C nearest neighbour interaction of 2.9eV – From Prof. Maruyama's home page [12]. The energy gaps between the electronic states is plotted as a function of the tube diameters (figure a) and Raman shift (figure b).

The semiconducting nanotubes generally have resonance between 457.9 nm (2.7 eV) and 514.5 nm (2.4 eV) and at 1064nm (1.17 eV) whereas the metallic nanotubes have resonance in the UV (< 3 eV) and around 1064 nm [7]. In resonance conditions, the Raman signal is highly enhanced and it is even possible to record the Raman spectrum of an isolated Carbon Nanotube from which one can determine its structural and electronic (n,m) properties [4].

The RBM is the feature in the spectrum which is most characteristic of the structure of the tube. Consequently the Kataura plot summarizes all the information contained in the Raman spectrum.

When the Resonant Raman spectrum of one/several SWNT has been recorded, the Kataura plot allows one to determine its/their semiconducting or metallic behaviour, to estimate its/their diameter and (n,m) integers [4].

Each SWNT exhibits a Resonance Raman spectrum in a certain range of excitation wavelengths (i.e. when the excitation wavelength matches the energy gap between the DOS). Figure 3 shows the Kataura plot that correlates the frequency of the Raman shift of the RBM to the energy separation of the peaks in the DOS for each type of tube characterized by (n,m). In resonance conditions, the Raman signal is highly enhanced and it is even possible to record the Raman spectrum of an isolated Carbon Nanotube from which one can determine its structural and electronic properties (n,m).
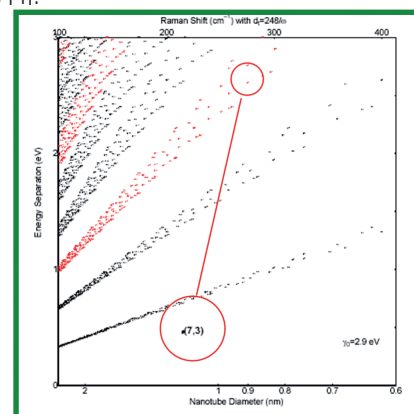

Fig. 3: Kataura plot based on an energy of the C-C nearest neighbour interaction of 2.9 eV. Black points stand for semiconducting SWNTs and Red for Metallic.

There is currently no way to synthesize selectively one kind of SWNT with a fixed diameter d and orientation (n,m). Exciting at several wavelengths allows to sweep several resonance conditions in order to point out selectively the existence of various carbon nanotubes in the sample. Figure 4 clearly demonstrates that this procedure is a good way to enhance selectively the Raman spectrum of different SWNTs [6].
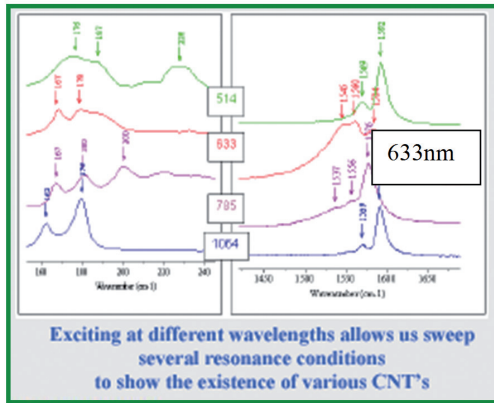

Fig. 4: Spectra recorded on the surface of a powder of SWNTs

Need of spectral resolution- WHY ?

High Spectral Resolution is needed to separate very close modes in the spectrum of a single nanotube or in the spectrum of a bundle of nanotubes. Figure 5 shows a RBM spectrum that represents tubes with at least 3 different properties:
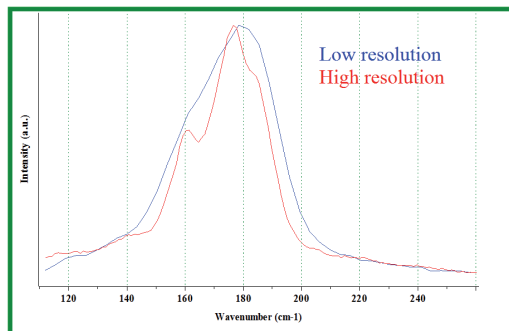

Fig. 5: Sample bundle of SWNTs 600 gr/mm and 1800 gr/mm on a Labram at 633 nm with power of 0.08 mW. NB: even better spectral resolution can be reached on a Labram HR

Need of spatial resolution- WHY ?

Using resonant conditions in Raman micro-spectroscopy, the spectrum of a single isolated SWNT can be detected. The difficulty for those experiments is to localise the nanotube on the surface. Probing a large area of the substrate by the mean of a map is often the only way to find the "hot spot" [2, 5].

Figure 6: On the map, the RB mode appears at 3 distinct frequencies (a). The intensity at these frequencies is plotted on the 3 maps (b) and the range of the RBM frequencies are displayed in red.

Single SWCNT islands are pointed out allowing to isolate different d_t . (c) For the 3 classes of SWCNTs, the G band is also different.
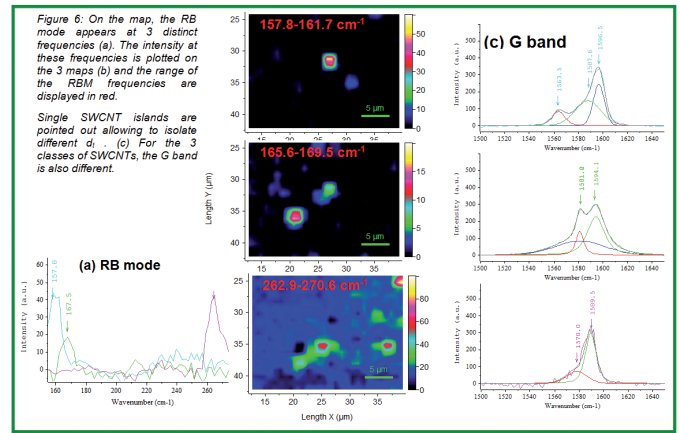
Fig 6: In the map of Figure 6, three RBM frequencies positions are plotted to see the distribution of the different tube diameters. The tubes in this work are scattered on a silicon substrate and are around 0.8 nm to 1.5 nm in diameter.
Despite the fact that the laser spot is much larger than the tube diameter the resonance behaviour of the tubes allows the spectra to be recorded.

The effect of increasing temperature

The light absorption coefficient of the sample depends on the wavelength of the excitation source. If the light absorption coefficient is high, this may lead to an increase of the temperature in the material and sometimes to damage of the sample. Therefore, it is necessary to reduce the power density at the sample. It is very easy to monitor whether a frequency shift occurs. The temperature changes in carbon nanotube induce frequency down shifts. The amplitude of the shift varies for each mode. For example, the G band follows a downshift of 0.026 $cm^{-1}.K^{-1}$ in a MultiWall NanoTube.

An experiment has been performed by measuring a spectrum first at low power density and then at high power density. Dramatic spectral changes occur when the laser power increases and those modifications can be partially reversible. The effect is mainly due to a decrease in the quantity of defects, as shown in figure 7; the D band clearly disappears after the heat treatment. For samples that are particularly sensitive to laser power a line-scan feature can be employed. This feature can also be employed to decrease the time required to map a sample.
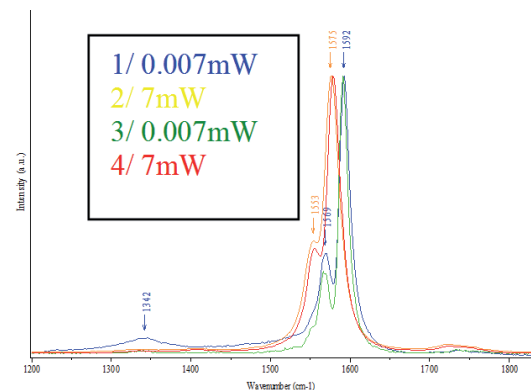

Figure 7 : All the spectra are recorded on the same point on a powder of SWNTs. Source 532 nm. Objective 100x (NA= 0.9). Blue: spectrum recorded with a 0.007mW. Orange: spectrum recorded with a power of 7mW. Green: spectrum recorded at 0.007 mW after a 30mn cooling. Red: spectrum recorded at 7mW.

Band gap Photo Luminescence / Fluorescence can be collected from SWCNT

In addition to Raman diffusion, Photoluminescence emission of the excited sample can bring information on the Nanotubes' structure [10]. Figure 8 shows the principle of Band gap Photoluminescence / Fluorescence using the typical density of state diagram already displayed figure 2.

This new approach is revealed to be a complementary tool to study the nanotube chemical and physical properties which are affected by their structure.
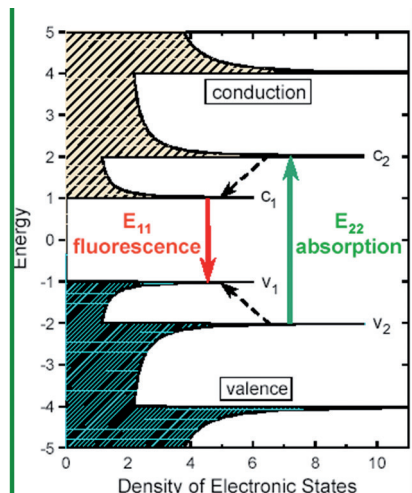

Fig. 8: Schematic density of electronic states for a single nanotube structure. Solid arrows depict the optical excitation and emission transitions of interest; dashed arrows denote nonradiative relaxation of the electron (in conduction band) and hole (in valence band) prior to emission – from ref 10.

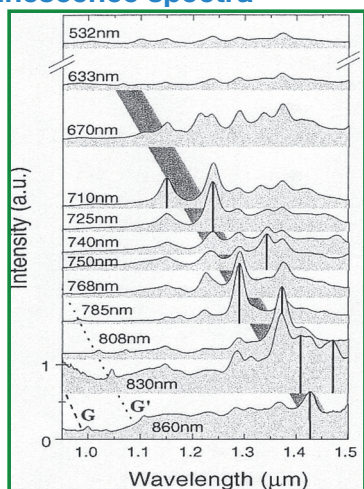## Excitation wavelength dependence of photoluminescence spectra

Figure 9: J.Lefebvre, Y. Homma, and P.Finnie, Phys. Lett. 90,217401,(2003). Photoluminescence spectra are shown for a series of excitation wavelength. Spectra were taken at room temperature in air using various lasers). A 100μm spot diameter and an average power of 1.7mW was used in all cases. Each spectrum is offset along the y axis by an amount proportional to the excitation wavelength. The same laser power and collection optics were used for all spectra so the intensity can be compared for different curves. The thick gray band highlights the expected PL resonance. The black vertical lines highlights PL peaks which are resonant. The dotted and dashed lines trace the G' and G Raman modes, respectively.

Conclusion

This note demonstrates that depending on the configuration of the Raman system used, one can extract different types of information about Carbon Nanotubes. A multiexcitation, low frequency, high spectral and spatial resolution Raman system is the best solution to collect the maximum information.

Raman has shown a high potential in characterising the SWCNTs ' structure. The correlation between knowledge about structure with physical and chemical properties about the tubes make the technique extremely powerful to control the quality of the SWCNTs for specific applications. Raman spectrometer capabilities like spatial resolution, spectral resolution and excitation wavelength versatility have been examined. Beside Raman, preliminary fluorescence studies are describing the potential of the technique.

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