The fundamental aspects of carbon nanotube metrology

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The accurate and reproducible measurement of the properties and performance characteristics of nano-scale materials, devices and systems are essential for quality and process control, commercial transactions and effective regulations. Scientists, manufacturers, governments, regulators and health and environmental protection agencies, will need measurement systems and evaluation protocols supported by well founded and robust standards, both physical and documentary. In this paper we discuss some fundamental aspects of the use of the resonance Raman spectroscopy of the radial breathing mode (RBM) of single wall carbon nanotubes (SWNTs) for metrological purposes. The achievements and problems are pointed, hoping for the development of procedures capable of making the promised nanotechnology revolution to become a reality.

1 Introduction

Historically, the diffusion of a coherent measurement system, based on invariant physical properties, was the consequence of a radical transformation in the world [1]. In 1889, as a result of the work of many scientists over many decades, a standardization document was approved at the *Weights and Length General Conference* in Paris [2]. The equations relating national and international standards for the meter and kilogram were within the limits of ± 0.01 mm and ± 1 mg. Even though technology has improved substantially and the international system of units is well established, *nanoscience* promises a revolution in technology. The development of nanotechnology is now bringing us back to the very basic problem of defining metrics and measurement systems, back to the basics of metrology [3–5]. The fast development of carbon nanotube science and applications urged studies on metrology, standardization and industrial quality control.

Development of protocols for the definition of sample parameters like structural metrics, physical properties and stability are important for both research and applications of carbon nanotubes. This paper focuses on the use of the radial breathing mode (RBM) resonance Raman spectroscopy as a characterization tool, discussing the achievements, limitations and directions where further research is needed for the development of standards and protocols for metrology. Although development of standards has a clear applied aspects, it has to be carefully based on fundamental aspects. The importance of the excitonic nature of the optical transitions in carbon nanotubes for the correct description of the diameter dependence and environmental effects on the resonance Raman signal is now evident. Any optically based diameter characterization of a carbon nanotube sample has to take this fundamental aspect into account for an accurate description. This property becomes more important in the low diameter limit (d_t below

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2 nm), where spatial confinement enhances substantially the electron−electron and electron−hole Columbic interactions. These issues will be discussed here.

2 Experimental details

A triple-monochromator Raman spectrometer can be used for resonance Raman spectroscopy studies, since it uses no notch filter, so that the excitation laser line can be tuned continuously. Equipped with a coupled charge device (CCD) detector, a Dilor XY has been used for the experiments. Back-scattering configuration through a microscope is used. The different excitations come from an ArKr laser, a Ti:Sapphire laser and a Dye laser pumped by a 6 W Ar laser. The single-wall carbon nanotube (SWNT) samples used here are carpet-like CVD grown.

3 Basic principles

Optical techniques have been largely used to characterize carbon nanotubes. The advantages of optics rely on both experimental and fundamental aspects. Experimentally, the techniques are readily available, relatively simple to perform, quick, and can be performed at room temperature and under ambient pressure. Fundamentally, the optical techniques are non-destructive and non-invasive because they use the photon, a massless and chargeless particle, as a probe. Furthermore, optical experiments can be carried out at the single nanotube level [6−8] due to the unusually high optical response of nanotubes, which is a consequence of the one-dimensional confinement of their electronic structure [9].

Despite the specificity of each optical technique, the basis for the understanding of the optical responses from carbon nanotubes is common to all optical spectroscopies and can be represented by the so-called *Kataura plot*, proposed by Kataura et al. in 1999 [10], plotting the optical transition energies E_{ii} as a function of tube diameter d_t. An enormous number of experimental and theoretical works have been done in order to establish this plot [11], i.e. to establish the (n, m) dependence for E_{ii}. The first and second optical levels for semiconducting tubes, E_{11}^S and E_{22}^S, respectively, are related to strongly bound excitons, while for the higher lying levels E_{ii}^S, $i > 3$, the electronic continuum might screen the exciton binding energies [12]. E_{11}^M is the lowest set of transition energies for metallic SWNTs. Good agreement between experimental and theoretical values for E_{ii} has been obtained by using an extended (non-orthogonal, symmetry adapted) tight binding model [13, 14] plus diameter dependent many-body corrections [15]. A simple expression for E_{ii}, that can be used to build a Kataura plot, has been introduced recently [12]:

$$E_{ii}(p, d_t, \theta) = \{a(p/d_t)[1 + b \cdot \log(c \cdot p/d_t)] + \beta_p \cos(3\theta)/d_t^2\} + \gamma p/d_t, \qquad (1)$$

with $a = 1.049$ eV nm, $b = 0.456$ and $c = 0.812$ nm^{-1} and $p = 1, 2, 3, 4, 5$ for E_{11}^S, E_{22}^S, E_{11}^M, E_{33}^S, E_{44}^S, respectively, for vertically aligned single-wall carbon nanotubes grown by the chemical vapour deposition method from alcohol [16]. The experimental β_p values for the lower (upper) E_{ii} branches are −0.07(0.05), −0.19(0.14), −0.19 (not observed), −0.42(0.42) and −0.4(0.4) for $p = 1, 2, 3, 4$ and 5, respectively. Each term has its physical origin, as discussed in Ref. [12], and the last term (outside the curly brackets) applies only for the E_{ii} levels with $p > 3$, with $\gamma = (0.305 \pm 0.004)$ eV nm.

This functional is consistent with experimental results on CoMoCAT and HiPco tubes in SDS aqueous solution, alcohol assisted and water assisted CVD grown aligned SWNT samples, and isolated SWNTs suspended on Si trenches, measured by resonance Raman spectroscopy, photoluminescence-excitation and Rayleigh scattering, as discussed in Refs. [12, 17−19]. In the water assisted CVD grown SWNT samples, Eq. (1) was shown to apply up to the sixth optical level in semiconducting SWNTs, and up to the fourth optical level in metallic SWNTs. However, the E_{ii} values are expected to change with changes in environment (within 1−10% for bundling, temperature and pressure dependent effects [17−19]). Environmental effects is a big challenge for metrology, and advances are obtained by taking the same tube and putting it in different environments. Controlled and systematic experiments are needed.

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# 4 Resonance Raman spectroscopy of the RBMs in SWNTs

The RBM is unique to carbon nanotubes and it is not observed in other carbon materials. It has the very important property of being proportional to the inverse tube diameter. By considering that common Raman instruments have a spectral accuracy of about 1 cm^{-1}, and that the RBM frequencies (ω_{RBM}) from typical samples (diameters d_t around 0.5–5.0 nm) range from 500–50 cm^{-1}, Raman spectra can determine the tube diameter with 1 angstrom accuracy for a $d_t = 5.0$ nm tube, the accuracy increasing with decreasing diameter, reaching 1pm accuracy for a $d_t = 0.5$ nm tube. The use of a triple-monochromator in additive mode can get this resolution to 0.1 cm^{-1} in frequency, i.e. up to 0.1 pm resolution in the diameter determination.

The big problem is the determination of the precise relation between ω_{RBM} and d_t [9, 15, 17–19]. Although the RBM frequency has been shown to be weakly dependent on doping (charge transfer) or laser heating (temperature-dependent effects), there are many different ω_{RBM} vs. d_t relations in the literature, probably due to the different environmental conditions on each particular measurement. While very small diameter tube may exhibit a chiral angle dependent curvature effects, ideally the intrinsic relation should converge to $\omega_{RBM} = 227/d_t$ for larger diameter tubes, consistent with the elastic properties of graphite [15].

Figure 1 shows three resonance Raman spectroscopy maps for three different SWNT samples (see caption). The RBM spectral profiles clearly show the different (n, m) populations. Direct inspection of the intensity distributions, however, lead to a wrong description of the SWNT contents.

Figure 2 shows a comparison of the tube diameter distribution obtained for the alcohol assisted CVD sample (right panel in Fig. 1) as obtained by resonance Raman spectroscopy and high resolution transmission electron microscopy (HRTEM). Each bullet in Fig. 2 represents the RBM Raman intensity for an specific (n, m) SWNT in full resonance with a given E_{ii} optical transition. The RBM frequency was converted to diameter using the relation $\omega_{RBM} = 219/d_t + 14$ [12]. The solid line represents the result of counting tube diameters from HRTEM, with a d_t distribution from 0.8 nm to 3.0 nm, average 2.0 nm, standard deviation 0.4 nm [16]. The two results are clearly different.

It is true that one has to be careful with the counting procedure on HRTEM experiments. A careful statistical analysis has to be performed rather than a "looking for good image" procedure, since "finding" larger diameter tubes is easier than finding smaller diameter tubes. However, the responsible for the large difference between the results obtained with Raman and HRTEM is the strong dependence of the Raman cross-section on the tube diameter. This effect has been calculated recently by Jiang et al. [21]. The authors show that the dependence of the optical absorption of SWNTs increase substantially when considering the exciton nature of the excited states. Consequently, the resonance Raman intensity increases
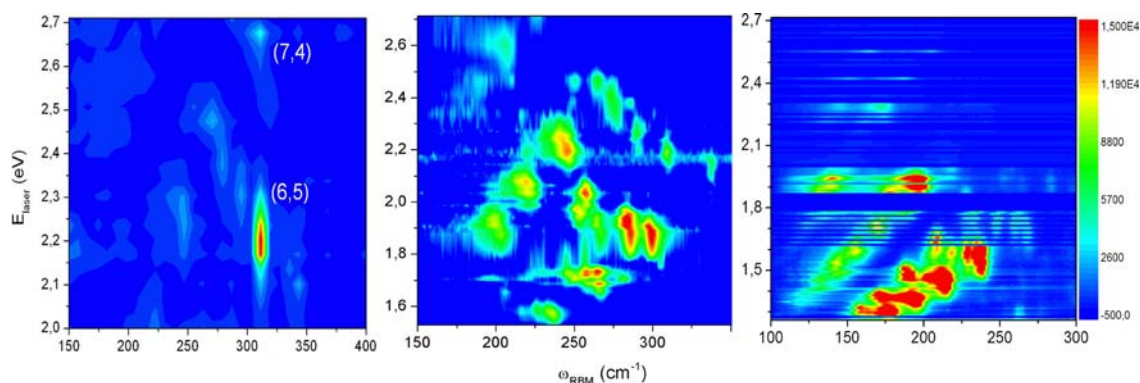
Fig. 1 (online colour at: www.pss-b.com)   Resonance Raman maps for three different SWNT samples: (left) DNA wrapped CoMoCAT sample dispersed in aqueous solution [20], (center) HiPco sample dispersed in aqueous solution with SDS [17], (right) carpet-like alcohol assisted CVD [12].
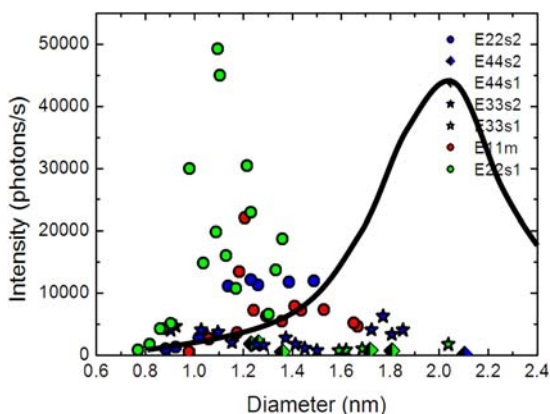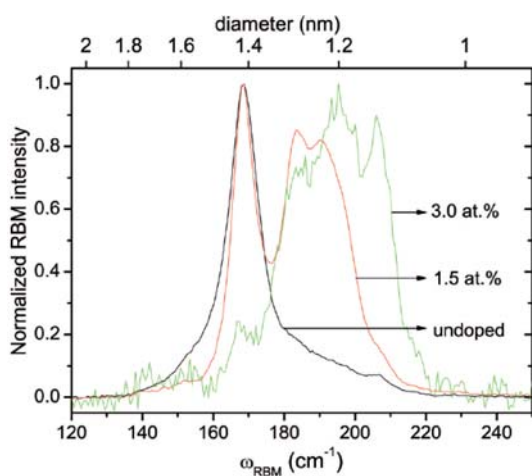
Fig. 2 (online colour at: www.pss-b.com) Diameter distribution of the alcohol assistet CVD SWNT sample obtained by RBM resonance Raman spectroscopy (dots). Each symbol represents RBM information obtained from a specific E_{ii} resonance (see legend). The solid curve shows the diameter distribution that is obtained by directly measuring the diameter distribution in the sample using high resolution transmission electron microscopy [16].

strongly when decreasing the tube diameter, changing by one order of magnitude when going from a SWNT with $d_t = 1.6$ nm to a tube with $d_t = 0.6$ nm.

The use of optics to determine SWNT population is also perturbed by tube-environmental interactions. A clear effect has been observed when the resonance profiles are obtained for the RBMs in the bundled sample and compared with the SWNTs dispersed in solution [22]. While as-grown samples show a broad profile of RBM frequencies (i.e. large diameter distribution), when the sample is dispersed in SDS aqueous solution, a narrower frequency (diameter) distribution is observed, shifting towards higher frequencies (lower diameters). However, when the sample is dried and measured again, the low frequency RBMs are observed again, showing that there was no real change in tube diameter distribution, but rather a change in the diameter dependence of the Raman cross-section. This result is probably related to the excitonic nature of the optical transitions, since the Culomb interactions and the presence of trap states should depend strongly on the environmental conditions.

A different example is shown in Fig. 3, that plots the RBM (diameter) distribution of three SWNT samples grown by laser ablation, with and without the presence of boron in the graphite target [23]. The RBM frequency distribution clearly shifts toward higher frequencies (lower tube diameters) when adding boron. However, it is not yet clear if the influence of boron happens in the diameter of the tubes during formation, or in their optical properties, or in both. More work is needed to understand the effect of boron in the RBM results.

Fig. 3 (online colour at: www.pss-b.com) Diameter distribution of SWNTs grown by laser ablation of a graphite target, with and without boron in the target. The profiles are obtained by summing up 66 Raman spectra obtained with different excitation laser lines from 1.6 eV to 2.7 eV, thus representing well the diameter ditribution in the sample [23].

5　Summary

The resonance Raman spectroscopy is a powerful tool for carbon nanotube metrology. However, the development of fundamental understanding of the optical phenomena in SWNTs, mainly with respect to environmental effects, relaxation and light emission processes, are required for an accurate description of carbon nanotube samples by using optics.

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