Length characterization of DNA-wrapped carbon nanotubes using Raman spectroscopy

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A systematic resonance Raman study has been carried out on DNA-wrapped single walled carbon nanotubes (SWCNTs) of three different average lengths $\langle L_{\text{tube}} \rangle$ using seven different values of laser excitation energy E_{laser}. The dependence of the intensity ratio of the *D*-band and *G*-band Raman features (I_D/I_G) on $\langle L_{\text{tube}} \rangle$ indicates that nanotube length can be used as an important structural parameter for Raman characterization. By systematically varying E_{laser}, the ratio I_D/I_G is found to be much stronger for metallic than for semiconducting SWCNTs but appears to have the same functional dependence on E_{laser} and $\langle L_{\text{tube}} \rangle$ or crystallite size as does nanographite. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2713121]

Raman spectroscopy is widely utilized as a structural characterization tool for graphitic materials, and one of the most informative parameters in the Raman characterization of carbon materials is the ratio between the integrated intensities of the *D* and *G* bands, I_D/I_G.[1–3] Since the *D*-band scattering process involves broken in-plane translational symmetry, the *D*-band peak appears for sp^2 samples containing structural disorder.[3,4] The I_D/I_G ratio can thus be used as a gauge for determining the crystallite size L_a.[1,5] Although I_D/I_G ratios have been studied for different graphitic material systems since 1970,[1] it is only recently that systematic studies have been made to understand the correlation between I_D/I_G and both L_a and laser excitation energy E_{laser}.[5,6]

Over the past 13 years, single walled carbon nanotubes (SWCNTs) have arisen as a new class of highly confined carbon materials with properties that both mirror and contrast the parent material graphite.[7] Even though I_D/I_G is used qualitatively to characterize the relative defect concentration in SWCNTs, no systematic study has been carried out to understand the correlation between the I_D/I_G ratio and the crystalline size L_a or the tube length L_{tube} which are both important parameters for SWCNT device performance. In addition to L_a and L_{tube}, the one dimensional (1D) resonance enhancement in SWCNTs, as well as the intrinsically different electronic structure associated with the semiconducting SWCNTs (S-SWCNTs) or metallic SWCNTs (M-SWCNTs), is expected to affect I_D/I_G and its dependence on E_{laser} and L_a or L_{tube} compared to other graphitic materials.[8–14]

In this study, a systematic resonance Raman investigation is carried out for DNA-wrapped CoMoCAT (cobalt Molybdenum catalyst) SWCNT samples[15] using three different average nanotube lengths $\langle L_{\text{tube}} \rangle$ and seven values of E_{laser} and the results are compared with the behavior of the I_D/I_G ratio in two dimensional (2D) nanographite samples.[5] In contrast to 2D nanographite, the crystallite size L_a for 1D systems such as SWCNTs can be conceptualized by two independent parameters: the diameter (d_t) and length (L_{tube}). We further consider the effect of the special 1D resonance Raman phenomenon of SWCNTs as different SWCNTs come into resonance with different values of E_{laser}. The effects of d_t and SWCNT metallicity on I_D/I_G are also studied.

Three samples of DNA-wrapped CoMoCAT SWCNTs with average lengths $\langle L_{\text{tube}} \rangle$ equal to ~50, ~70, and ~100 nm were prepared using size exclusion chromatography, following previously established procedures.[16,17] $\langle L_{\text{tube}} \rangle$

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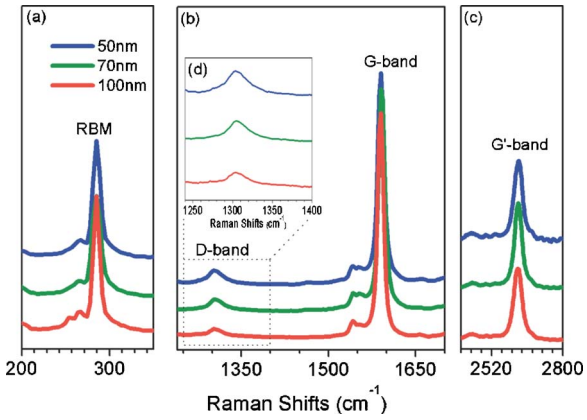

FIG. 1. (Color online) Raman spectra for the (a) RBM, (b) *D* and *G* bands, and (c) *G'* regions for three samples of different average lengths $\langle L_{\text{tube}}\rangle$ excited at $E_{\text{laser}}=1.937$ eV (640 nm). (d) (inset) the *D*-band region on an expanded scale. All spectra are normalized to their *G*-band intensities. The RBM spectra show that only one dominant SWCNT species is resonant for all samples.

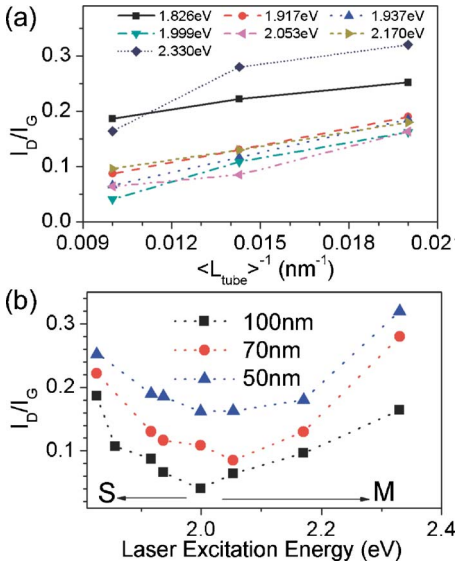

FIG. 2. (Color online) (a) I_D/I_G as a function of $\langle L_{\text{tube}}\rangle^{-1}$, excited at different values of E_{laser}. (b) I_D/I_G ratio vs E_{laser} for DNA-wrapped SWCNTs of different $\langle L_{\text{tube}}\rangle$ values. The ranges where S-SWCNTs and M-SWCNTs are resonant are indicated.

for each sample was previously determined by atomic force microscopy measurements,[17] and the variation in L_{tube} for each sample was estimated to be 10%.[17] The dried samples used for optical characterization were deposited onto sapphire substrates as previously described.[18] Resonance Raman measurements were carried out using a micro-Raman system in a backscattering geometry and the intensity of each spectrum was normalized to its *G*-band intensity. The seven E_{laser} values used in this study were generated by a Kr^+ ion laser and a dye laser (using DCM [4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran] and rhodamine 6*G* dyes), pumped by an Ar^+ ion laser. A thermoelectrically cooled Si charge coupled device detector was used in conjunction with the dye laser. The laser power level on the SWCNT sample was kept below 0.45 mW through a 50× microscope objective in the backscattering geometry to prevent overheating the sample.

Figures 1(a)–1(c) show the Raman spectra for the three samples, each with a different $\langle L_{\text{tube}}\rangle$, excited at 640 nm (1.937 eV). The relative intensities (I_{RBM}/I_G) for the radial breathing modes (RBMs) shown in Fig. 1(a) remain unchanged as $\langle L_{\text{tube}}\rangle$ is decreased from 100 to 50 nm. Since the RBM and *G* band are both first-order scattering processes associated with totally symmetric vibrations, we expect I_{RBM}/I_G to be independent of $\langle L_{\text{tube}}\rangle$.

As $\langle L_{\text{tube}}\rangle$ becomes shorter, the intensity ratio (I_D/I_G) increases, as in Fig. 1(d). This is expected since the fraction of the total surface associated with the end caps increases as $\langle L_{\text{tube}}\rangle$ decreases. However, the relative *G'* band intensities ($I_{G'}/I_G$), shown in Fig. 1(c), remain relatively unchanged with decreasing $\langle L_{\text{tube}}\rangle$. In contrast to the *D* band, the scattering process for the second harmonic of the *D* band (the *G'* band) is symmetry allowed by momentum conservation.[19] Thus, the broken translational symmetry in short nanotubes (short compared to λ, the laser wavelength) is not expected to change ($I_{G'}/I_G$), in agreement with our observations.

To clarify the effect of $\langle L_{\text{tube}}\rangle$ on the increase in I_D/I_G, Fig. 2(a) shows I_D/I_G as a function of $\langle L_{\text{tube}}\rangle^{-1}$ at seven values of E_{laser}. Table I lists the observed RBM frequency (ω_{RBM}) and the corresponding metallicity (M or S) for resonant SWCNTs for each E_{laser}. With decreasing $\langle L_{\text{tube}}\rangle$, a larger I_D/I_G is observed for all values of E_{laser}. From Fig. 2(a), a clear correlation is also seen between I_D/I_G and the $\langle L_{\text{tube}}\rangle^{-1}$ for each set of SWCNTs, excited at a particular E_{laser}. Thus, for the same E_{laser}, where similar d_t SWCNTs are in resonance, I_D/I_G can be used as an indicator to estimate $\langle L_{\text{tube}}\rangle$ of the SWCNT sample when $\langle L_{\text{tube}}\rangle < \lambda/4$, where λ is the wave length of light. *ID/IG*. The I_D/I_G ratio is seen to be larger for M-SWCNTs ($E_{\text{laser}}=2.330$ eV) than for S-SWCNTs, of the same $\langle L_{\text{tube}}\rangle$. Figure 2(a) also shows that in the limit of long SWCNTs, $\langle L_{\text{tube}}\rangle \geqslant 100$ nm, the I_D/I_G ratio does not go to zero. These finite residual values of I_D/I_G likely arise from defect-induced scattering introduced within the tube walls, as for example, by the sample preparation method used to produce short tubes.

For the four E_{laser} values below 2 eV, where the values of E_{laser} are predominantly in resonance with S-SWCNTs, the I_D/I_G ratio decreases with increasing values of E_{laser}. This observation is qualitatively consistent with the general *D*-band behavior observed for sp^2 carbon materials.[1,5,8,20] The very low value of I_D/I_G for $1.95 < E_{\text{laser}} < 2.05$ eV in Fig. 2(b) corresponds to the range where there are few resonant SWCNTs for the incident photons from the Kataura plot,[19] and the smaller value of ω_D relative to ω_G also contributes to a weak double resonance effect for scattered photons. On the other hand, I_D/I_G in Fig. 2(b) again increases with E_{laser} when $E_{\text{laser}} > 2$ eV, as a larger fraction of

TABLE I. Observed resonant ω_{RBM} at each E_{laser} and the corresponding metallicity for the resonant SWCNTs.

E_{laser} (eV)	ω_{RBM} (cm^{-1})	Metallicity
1.826	299	S
1.917	290	S
1.937	290	S
1.999	260, 280	S
2.053	211, 251, 280	S, M
2.171	223, 245, 312	S, M
2.330	275	M

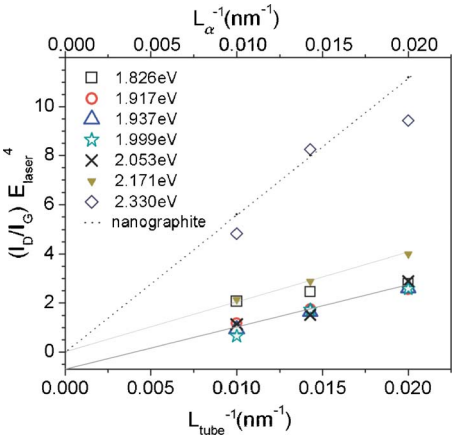

FIG. 3. (Color online) Comparison of the length dependence of I_D/I_G for short SWCNT samples, excited at different E_{laser}, plotted in terms of the variables in Eq. (1) for nanographite (where the dotted line is for nanographite and the solid line is qualitatively for S-SWCNTs) (Ref. 5).

M-SWCNTs comes into resonance with E_{11}^M transitions. For these M-SWCNTs ($d_t > 1$ nm), the electron-phonon matrix element of the TO phonon mode at the K point is larger than that for S-SWCNTs.[21] As a result the I_D/I_G ratio becomes larger when E_{laser} is strongly resonant with M-SWCNTs.[8,20]

The I_D/I_G ratio has been a commonly used parameter for sp^2 carbon materials characterization to qualitatively determine L_a and the amount of structural disorder.[1,5] The combined studies of crystallography, microscopy, and spectroscopy of nanographite have further established the following universal relation:[5]

$$\left(\frac{I_D}{I_G}\right)E_{\text{laser}}^4 = \frac{560}{L_a}. \tag{1}$$

To further compare the 1D SWCNT system with Eq. (1) for 2D nanographite,[5] we use $\langle L_{\text{tube}}\rangle^{-1}$ as an analog of $1/L_a$ in Eq. (1), and we plot in Fig. 3 the calculated $(I_D/I_G)\ E_{\text{laser}}^4$ values versus $\langle L_{\text{tube}}\rangle^{-1}$. The results show that the I_D/I_G ratios of the special M-SWCNTs that are in resonance with the 2.33 eV excitation do follow a similar dependence as Eq. (1) for nanographite.

If we consider all data points from the S-SWCNTs in Fig. 3, then the fit to the data is consistent with the solid line in Fig. 3 coming from the data in Fig. 1 for S-SWCNTs. These results suggest that an $(I_D/I_G)\ E_{\text{laser}}^4$ vs $\langle L_{\text{tube}}\rangle^{-1}$ dependence might also apply to SWCNTs, with a coefficient of proportionality for S-SWCNTs that is much smaller (by perhaps a factor of ~4) than for M-SWCNTs, for which the proportionality constant may be of a similar magnitude as that for nanographite.[5]

In summary, a systematic resonance Raman study has been carried out on DNA-wrapped SWCNTs of three different lengths using seven different values of E_{laser}. The correlation observed between the I_D/I_D ratio and $\langle L_{\text{tube}}\rangle^{-1}$ indicates that nanotube length can be used as the dominant structural parameter for the Raman characterization of SWCNTs with $\langle L_{\text{tube}}\rangle < \lambda/4$, and that I_D/I_G can be used for estimating the average nanotube length when a single laser excitation energy is used. More systematic studies of the $(I_D/I_G)\ E_{\text{laser}}^4$ vs $\langle L_{\text{tube}}\rangle^{-1}$ for both S-SWCNTs and M-SWCNTs are needed to establish conditions under which these relations are valid and the value of the relevant proportionality constants for S-SWCNTs and M-SWCNTs. Such results will guide future theoretical work which will advance the use of Raman spectroscopy to distinguish the characteristics of specific defect types from one another in graphitic systems.

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