

Comparative Raman Study of Carbon Nanotubes Prepared by D.C. Arc Discharge and Catalytic Methods

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The Raman spectra of carbon nanotubes prepared by catalytic (C-CNT) and d.c. arc discharge (D-CNT) methods are reported. A previously unnoticed third-order Raman peak at *ca.* 4248 cm^{-1} was observed in the Raman spectrum of D-CNT. The Raman features of D-CNT and C-CNT are similar to those of highly oriented pyrolytic graphite (HOPG) and active carbon, respectively. The data also suggest that the increase in disorder in D-CNT compared with HOPG is due to structural defects in D-CNT. © 1997 by John Wiley & Sons, Ltd.

INTRODUCTION

Carbon nanotubes were first recognized as a by-product in fullerene production by Iijima.¹ It is a typical one-dimensional material and its multi-faceted structures make it an attractive material for many applications, such as high tensile strength carbon fiber, nanoscale semiconductor material and molecular wires. Recently, it was found that nanotubes can be made into an electron-emitting configuration.^{2–4} Two methods, d.c. arc discharge and catalytic, are commonly used to prepare carbon nanotubes. Raman spectroscopy is a powerful technique for characterizing and analyzing carbon nanotubes and several groups have reported Raman spectra of nanotubes.^{5–9} However, the reports were mostly limited to carbon nanotubes prepared by the d.c. arc discharge method (D-CNT) and, as far as we know, there has been no comparative Raman study of nanotubes prepared by the methods. In this paper, the Raman spectra of carbon nanotubes made by both methods were measured up to 4500 cm^{-1} . The Raman characteristics of these spectra as compared to those of highly oriented pyrolytic graphite (HOPG) and active carbon (A-C) are discussed.

EXPERIMENTAL AND RESULTS

D-CNT and nanotubes made by the catalytic method (C-CNT) were prepared as described previously.¹⁰ The transmission electron microscope (TEM) images of D-CNT and C-CNT used for Raman measurements are shown in Fig. 1(a) and (c). The high-resolution TEM

image of D-CNT is shown in Fig. 1(b). It is estimated that 60% and 90% of D-CNT and C-CNT are nanotubes, respectively. VYH-grade HOPG was purchased from Advanced Ceramics (Cleveland, OH, USA) and used directly. A-C was of analytical grade from Dali Active Carbon Manufacturer (Beijing, China). The Raman spectra of all samples were measured with a Renishaw System 1000 at room temperature. The system consists of holographic notch filters for Rayleigh rejection, a microscope, and a CCD detector. Raman spectra were excited with 632.8 nm radiation from a helium–neon laser. No polarizer was used and Raman signals were measured in back-scattering geometry with a typical laser power of 0.05 mW (8 W cm^{-2}) and a spectral resolution of about 1.0 cm^{-1} . All Raman peak parameters were obtained by least-squares fitting Lorentzian lineshapes to the measured spectra.

Figure 2 shows the Raman spectra of A-C, C-CNT, D-CNT and HOPG between 100 and 4500 cm^{-1} . Table 1 summarizes the wavenumbers, full widths at half maximum (FWHMs) and the integrated intensities relative to that of the peak at *ca.* 1582 cm^{-1} of all the peaks in Fig. 2.

It is well known that three-dimensional crystalline graphite belongs to the point group D_{6h}^+ .^{11,12} At wave-vector $\mathbf{k} = 0$, there are 12 modes. The irreducible representation of the optical modes in the Brillouin zone center is given by

$$\Gamma_{\text{opt}} = 2E_{2g}(\text{R}) + E_{1u}(\text{IR}) + 2B_{2g} + A_{2u}(\text{IR})$$

The doubly degenerate E_{2g} modes are Raman active. One of these is the rigid-layer shear mode at 42 cm^{-1} and the other is the in-plane stretching mode commonly known as the G mode at *ca.* 1582 cm^{-1} . The others are either infrared active or silent. In addition, there is an extra line at *ca.* 1350 cm^{-1} for polycrystalline graphite which has been designated as due to phonons at the M and K points of the hexagonal Brillouin zone.⁸ This

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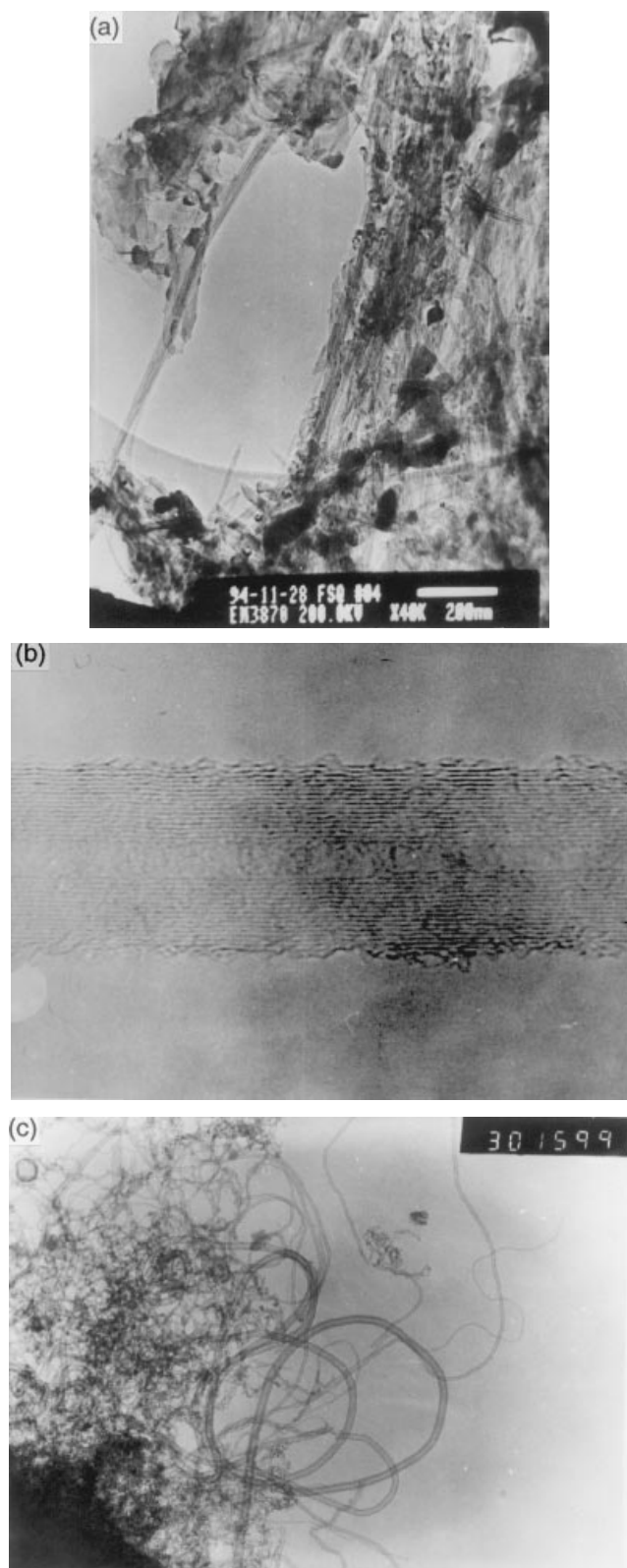


Figure 1. TEM image of nanotubes prepared by (a) the d.c. arc discharge method (D-CNT) and (c) the catalytic method (C-CNT). (b) Higher-resolution TEM image of D-CNT.

mode is often designated as the D mode and its first overtone as D*. Since the selection rule at $k = 0$ does not apply to high-order Raman scattering, it is possible to observe the D* peak even though the D peak is normally unobservable for single-crystal graphite. HOPG is a two-dimensional graphite. Since the interlayer inter-

action in the three-dimensional crystalline graphite is very weak, the mode analysis of single-crystal graphite can apply to HOPG. It is known that single layer or multi-layer nanotubes are formed by rolling two-dimensional graphite sheet(s) into a hollow tube(s).¹ The interaction between layers of graphite in nanotubes is also weak. Thus the Raman spectrum of perfect nanotubes should be similar to that of HOPG theoretically and HOPG can be used as a reference in analyzing the structure and the degree of disorder in nanotubes. On the other hand, even though the major structural component of A-C is still the same hexagonal carbon ring of HOPG, the planar structure of the graphite sheet and the interlayer arrangement of the graphite sheets of A-C are relatively disordered. The Raman spectrum of A-C can be used as a reference of disordered carbon structure to indicate the degree of disorder in nanotubes.

DISCUSSION

We first discuss the Raman spectra of HOPG and A-C. The number of observed Raman lines below 3500 cm^{-1} in our measurement (Fig. 2 and Table 1) agrees with the most recent result on HOPG.⁷ Thus, with the exception of the double peaks at 2457 and 2474 cm^{-1} , the designations of the observed peaks of HOPG in Fig. 2 and Table 1 follow those of Refs 7 and 12. We assign the double peaks at *ca.* 2460 cm^{-1} as due to $(G + A_{2u})$ from the wavenumber match of these combination modes. In addition, it is important to note that we observe a previously unnoticed line at 4265 cm^{-1} . This new line is assigned to the third-order combination mode of $(G + D^*)$ from wavenumber considerations. In contrast, only four modes were observed for A-C in Fig. 2. These peaks are designated D, G, D* and $(D + G)$ in Table 1. Note that the FWHMs of the D, G and D* peaks of A-C are much broader than the corresponding ones of HOPG, by factors of 4.1, 4.0 and 16 respectively. In addition, the intensity ratio of the D to G line, I_D/I_G , of A-C is 65 times that of HOPG. This ratio has been shown to correlate with the amount of disorder.⁸ The broader FWHMs and the larger I_D/I_G clearly indicate the higher degree of disorder in the structure of A-C.

It is easy to see in Fig. 2 that the Raman characteristics of D-CNT are very similar to those of HOPG but differ from those of A-C. In contrast, those of C-CNT are similar to those of A-C. Below, we compare and contrast the Raman spectral features of D-CNT and HOPG. Likewise, we discuss the similarities and differences of C-CNT and A-C and their consequences as related to the structure of the nanotubes.

We first note that the newly observed third-order combination mode of $(G + D^*)$ in HOPG can also be seen in the spectrum of D-CNT. We note further that the FWHMs of the D and G lines of D-CNT are only slightly larger (by about 20%) than those of HOPG. In contrast, the I_D/I_G ratio of D-CNT is more than eight times that of HOPG, indicating an increase in disorder in D-CNT. Furthermore, two lines at *ca.* 1619 and 2931 cm^{-1} are observed in D-CNT but not in HOPG (see Fig. 2). These lines can be assigned to the $E'_{2g}(R, \perp)$ and $(D + G)$ modes, respectively, and can also be observed

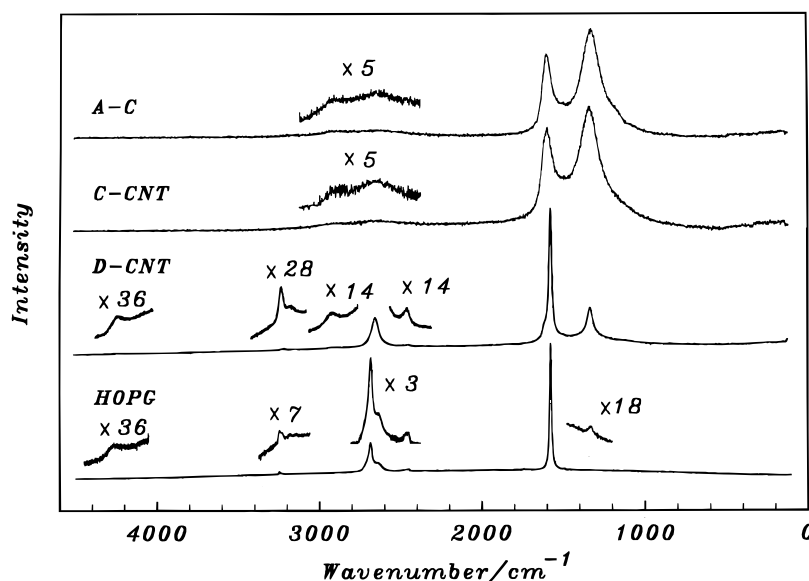


Figure 2. Unpolarized Raman spectra of active carbon (A-C), nanotubes prepared by the catalytic method (C-CNT), nanotubes prepared by the d.c. arc discharge method (D-CNT) and highly oriented pyrolytic graphite (HOPG), with excitation at 632.8 nm.

in boron-doped HOPG.⁷ Boron doping is known to introduce structural defects in HOPG. Thus, the appearance of these peaks in the spectrum of D-CNT suggests that the increase in disorder in D-CNT is mainly due to structural defects, in agreement with Bacsa *et al.*⁹ Bacsa *et al.* also suggested that the rolling of graphite sheets into hollow tubes in nanotubes does not result in mode softening and subsequent lowering of wavenumber. On the contrary, a slight increase in wavenumber is expected. The G peak of D-CNT was observed to be 1 cm^{-1} higher than that of HOPG (Table 1), supporting the assertion of Bacsa *et al.* Finally, the two double peaks at *ca.* 2460 cm^{-1} (G + A_{2u}) and *ca.* 2660 cm^{-1} (D*) in HOPG are observed as single peaks in D-CNT. The simplistic reason is an increase in symmetry in D-CNT compared with HOPG, resulting in the degeneracy of these modes. However, D* is also a single peak in A-C (see Fig. 2). It is also possible that a single D* (and G + A_{2u}) peak is an indication of an increase in disorder. We favor the latter interpretation.

The similarities between the Raman spectra of C-CNT and A-C are striking (Fig. 2). The number of

observable peaks and their assignments are the same. The FWHMs of these peaks and the I_D/I_G ratio are in the same range, indicating similar degrees of disorder. The only difference is in the wavenumbers of the D peak and the higher order peaks involving the D mode. The wavenumbers of the D, D* and (D + G) peaks of C-CNT are higher than the corresponding peaks of A-C by 9, 16 and 23 cm^{-1} , respectively. These similarities strongly suggest that the structure of C-CNT is very similar to that of A-C.

Finally, we compare the Raman features of nanotubes prepared by the two different methods, D-CNT and C-CNT. Several differences can be discerned. First, the number of observable modes in C-CNT is clearly less than that in D-CNT. In particular, the third-order combination peak of (G + D*) can only be observed in D-CNT. Second, the FWHMs of the four observable peaks of D, G, D* and (D + G) in C-CNT are all broader than the corresponding ones in D-CNT. The increase in FWHM is 3.9, 2.9, 7.2 and 1.9-fold, respectively. In particular, it is significant that the FWHMs of the disorder-related D and D* peaks are much broader in C-CNT, indicating a much higher degree of disorder

Table 1. Wavenumbers ($\tilde{\nu}$), full widths at half maximum (FWHM) and relative integrated intensities (I) of the Raman peaks of highly oriented pyrolytic graphite (HOPG), carbon nanotubes prepared by the d.c. arc discharge method (D-CNT), carbon nanotubes prepared by the catalytic method (C-CNT) and active carbon (A-C)

Material	Parameter	D(\perp), D	E_{2g}^{\perp} (\perp), G	E_{2g}^{\parallel} (\perp)	G + A_{2u}	2 × D, D*	D + G	2 × G	2 × E_{2g}^{\perp}	G + D*
HOPG	$\tilde{\nu}/\text{cm}^{-1}$	1332	1583		2457 2474	2640 2689		3175	3243	4265
	FWHM/ cm^{-1}	34	14		12 32	66 24		108	42	92
	$I/\text{a.u.}$	0.051	1.000		0.010 0.025	0.288 0.312		0.069	0.051	0.013
D-CNT	$\tilde{\nu}/\text{cm}^{-1}$	1336	1584	1619	2468	2669	2931	3186	3242	4248
	FWHM/ cm^{-1}	42	22	22	40	48	92	80	32	98
	$I/\text{a.u.}$	0.430	1.000	0.070	0.016	0.489	0.025	0.011	0.015	0.013
C-CNT	$\tilde{\nu}/\text{cm}^{-1}$	1337	1604			2667	2944			
	FWHM/ cm^{-1}	164	64			344	170			
	$I/\text{a.u.}$	3.564	1.000			0.349	0.082			
A-C	$\tilde{\nu}/\text{cm}^{-1}$	1328	1605			2651	2921			
	FWHM/ cm^{-1}	138	56			380	198			
	$I/\text{a.u.}$	3.324	1.000			0.482	0.170			

in C-CNT. This is also supported by the third difference. The I_D/I_G ratio in C-CNT is eight times larger than that in D-CNT. Thus, even though the catalytic method gives a better yield of nanotubes, the current Raman measurements indicate that the resulting nanotubes have more disorder and their structures are less uniform. Studies with electron microscopy and x-ray diffraction¹³ have also suggested that the nanotubes

prepared by the d.c. arc discharge method are of better quality.

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