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Raman characterization of aligned carbon nanotubes produced by thermal decomposition of hydrocarbon vapor

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Raman characterization of aligned carbon nanotubes of average diameter 10–15 nm, produced by chemical vapor deposition on a mesoporous substrate, has been carried out. The resonance behavior and higher-order Raman bands up to fourth order have been observed and compared with those of carbon nanotubes produced by arc discharge and highly oriented pyrolytic graphite, as well as pyrolytic graphite. The phonon properties have been analyzed with the help of high-resolution transmission electron microscope studies. © *1997 American Institute of Physics*. [S0003-6951(97)02520-5]

The discovery of carbon nanotubes (CNTs)¹ has generated remarkable excitement in scientific communities.²⁻⁶ Large quantities of CNTs can now be produced by either arc discharge^{1,2,4,5} or thermal decomposition of hydrocarbon vapor.^{3,6} However, CNTs produced by these methods are of disordered orientation and mixed with carbon nanoparticles or amorphous carbon, which restricts their experimental characterization and applications. Recently, Ajayan et al.⁴ and de Heer et al.⁵ have successfully produced aligned CNTs by orienting the as-formed arc-discharge CNTs (DCNTs). We have developed a new method to produce a pure, high density, and aligned array of carbon nanotubes,⁷ which is favorable for its property analysis. Raman characterization is very sensitive to the breakdown in translational symmetry of carbon materials and can provide detailed information about the microstructure, hence, it offers a relatively easy and unique tool to characterize the structure of CNTs without destroying the sample. A considerable number of papers on the Raman spectra and resonance behavior of DCNTs have already been published,⁸⁻¹³ revealing that this material has unique Raman spectral features. Recently, single wall CNTs have been studied by using a Raman scattering technique with laser excitation wavelengths in the range from 514.5 to 1320 nm, numerous Raman peaks were observed and identified with vibrational modes of armchair symmetry (n,n)CNTs.¹⁴ However, Raman spectra of CNTs are often disturbed by their disorder distribution and very low density, so Raman studies of aligned and dense carbon nanotubes are helpful in understanding the vibrational spectra and microstructure of the carbon nanotubes.

In this letter, the first- and higher-order Raman scattering of an aligned array of carbon nanotubes produced by chemical vapor deposition (CVD) of hydrocarbon gas (CCNTs) (Ref. 7) are studied and compared to that of DCNTs and highly oriented pyrolytic graphite (HOPG) as well as pyrolytic graphite (PG). Higher-order Raman bands up to fourth order of the CCNTs have been observed and assigned to the corresponding fundamental frequencies, then the phonon properties of CCNTs may be discussed with the help of highresolution transmission electron microscope (HRTEM) results.

The aligned CCNTs were fabricated by chemical vapor deposition of acetylene at 700 °C.³ The main feature of our method is to use mesoporous silica embedded by iron nanoparticles as a substrate to produce aligned carbon nanotubes. A more detailed process of the method has been described elsewhere.⁷ Because the CCNTs were formed on the surface of the silica substrate, we can, using a scanning electron microscope (SEM) (S-4200, Hitachi), observe the original morphology and distribution of the CCNTs without damaging the samples. The HRTEM (JEM 200-cx) specimen was prepared by grinding the sample in mortar and suspending in ethanol before being dropped on a hole carbon copper grid.

Raman studies were performed directly on the as-formed large area aligned CCNTs. A Renishaw Raman spectrometer equipped with a charge coupled device detector (CCD) was employed. A 25 mW, 514.5 nm, Argon ion (Ar⁺) laser was used as a light source, typically with 0.2 mW at the sample. A 50× objective was employed, giving an illuminated spot of about 2 μ m in diameter. The incident light was polarized perpendicular to the orienting direction of the CCNTs. Typical acquisition times for the spectra were 90 s. The spectral resolution was better than 2 cm⁻¹, and no smoothing was applied to the spectra.

The CVD process was manipulated under optimal conditions;⁷ after reacting for about 2 h, a black layer of CCNTs was formed on the substrate surface. The SEM image [Fig. 1(a)] shows that the thickness of the tube layers is about 50 μ m. A high-magnification SEM image [Fig. 1(b)] illustrates that the layer is composed of aligned CCNTs about 10–15 nm in diameter, most of which are approximately perpendicular to the substrate surface while a few are slightly tilted. These CCNTs are isolated with spacings about 100 nm, and neither bundles of CCNTs,¹⁵ nor carbon nanoparticles,¹⁶ have been detected in the array of aligned CCNTs.

HRTEM images (Fig. 2) display the well-graphitized CCNTs and only a little bit of carbonaceous material attached to the surface of the CCNTs. These CCNTs consist of more than ten concentric carbon shells with a spacing of 0.34 nm, which is consistent with that of graphite. Most aligned

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FIG. 1. SEM images of aligned CCNTs formed on the substrate. (a) Lowmagnification image reveals that the aligned CCNTs are about 50 μ m long, (b) high-magnification SEM image of aligned CCNTs shows that most nanotubes are approximately perpendicular to the surface of the substrate. The diameter of the CCNTs are of about 10–15 nm. These nanotubes are separated and very pure.

CCNTs are very straight, as displayed in Fig. 2(a), while some slightly curved tubes caused by kinks or defects^{17,18} are shown in Fig. 2(b). The formation of the kinks and defects is attributed to the low temperature (700 °C) of the CVD process.

The first-order Raman spectrum of aligned CCNTs shows a strong sharp peak at 1581 cm^{-1} (G line), which is the high-frequency E_{2g} first-order mode. One of the most unusual properties of aligned CCNTs is that the Raman spectrum shows an additional strong band at 1348 cm^{-1} (D line) and a weak band at around 1617 cm^{-1} (D' line), as shown in Fig. 3(a). It is worth noting that the strong peak at 1348 cm^{-1} is similar to that of PG and is not observed in the spectra of HOPG.^{8–13} The origin of the D and D' lines in other forms of carbon materials has been explained as disorder-induced features due to the finite particle size effect or lattice distortion.^{19–21} In other words, the relative intensity



FIG. 2. HRTEM images of the well-graphitized nanotubes. The nanotube consists of ten concentric graphene shells with a spacing of 0.34 nm. (a) Perfectly graphitized straight carbon nanotube, and (b) curved carbon nanotube resulting from kinks or defects.



FIG. 3. Micro-Raman spectra of aligned CCNTs excited by 514.5 nm. (a) Fundamental and second-order part, and (b) third- and fourth-order part.

of the 1348 cm^{-1} mode with respect to the 1581 cm^{-1} mode depends on the crystal planar domain size of graphite. In our case, SEM and HRTEM images of the present aligned CCNTs reveal that the CCNTs only consist of many isolated and well-graphitized tubes, and contain no carbon nanoparticles at all. Therefore, it is reasonable that the 1348 cm^{-1} mode origination may be attributed to defects in the curved graphene sheets, tube ends, and finite size crystalline do-mains of the tubes.²²⁻²⁴ Compared with the weak line at 1350 cm^{-1} of DCNTs,⁸⁻¹³ the appearance of the strong D line of CCNTs can be interpreted as being due to: (1) the turbostratic structure of carbon sheets in tubes, namely the finite size (nanometer order) of the crystalline domains; and (2) the high density of the aligned tubes. Thus, the large amount of crystalline domains on the nanometer scale and the surfaces of the tubes must account for the enhancement of the D line at 1348 cm⁻¹. In principle, the position of the G line at 1581 cm⁻¹ is slightly dependent on domain size, but the shift to high frequency is not observed within our experimental accuracy, although the G line at 1581 cm^{-1} appears to be a doublet due to the finite size effect. The D line (at 1348 cm⁻¹) has also been attributed to first-order scattering

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TABLE I. Fundamental and higher-order bands of aligned CCNTs recorded on a Renishaw Raman system with 514.5 nm laser line $I_D/I_G = 1.3 \pm 0.02$.

$\frac{\Delta\nu}{(\mathrm{cm}^{-1})}$	Designation	$\frac{\Delta \nu}{(\mathrm{cm}^{-1})}$	Designation
1094		3233	$2\omega_{\mathrm{D}'}$
1348	$\omega_{\rm D}$	4043	$3\omega_{\rm D}$
1581	ω _G	4274	$2\omega_{\rm D} + \omega_{\rm G}$
1617	$\omega_{\mathrm{D}'}$	4511	$\omega_{\rm D} + 2\omega_{\rm G}$
2453	_	4819	$\omega_{\rm G} + 2\omega_{\rm D'}$
2697	$2\omega_{\rm D}$	5385	$4\omega_{\rm D}$
2930	$\omega_{ m D} + \omega_{ m G}$	5861	$2\omega_{\rm D} + 2\omega_{\rm G}$

from a zone-boundary phonon activated by the disorder associated with finite crystalline size. This assignment is corroborated with the strong peak at $\sim 2697 \text{ cm}^{-1}$ (i.e., ~ 2 $\times 1348 \text{ cm}^{-1}$) in the second-order Raman spectrum and the weak peak at \sim 5385 cm⁻¹ (i.e., \sim 4 × 1348 cm⁻¹) in the fourth-order Raman spectrum. While the D line at 1348 cm⁻¹ has a counterpart in the second-order spectrum, if its presence results from the finite crystalline size of nanometer order, it might be expected that the peak at 1617 cm^{-1} also has a counterpart in the second-order spectrum of CCNTs, namely, 3233 cm^{-1} . It is important to note that the differences in frequency between the observed first-order modes and half the frequency of the corresponding secondorder modes could be due to matrix element effects or to the region of the k space strongly sampled by the breakdown of wave-vector conservation.

The second-order Raman spectrum of CCNTs is shown in Fig. 3(a). As mentioned above, the peak at 2697 cm⁻¹ (D*) is the overtone of the D line, and the peak at 2930 cm⁻¹ is attributed to the combination of the D and G lines. In addition, the second-order scattering at 2453 and 3233 cm⁻¹ has also been observed very clearly and attributed to the corresponding fundamental bands, as summarized in Table I. The observation of the line at 3233 cm⁻¹ is strong evidence for overtone scattering from the highest-frequency line at ~1617 cm⁻¹ in the density of states.

The third- and fourth-order Raman spectra are shown in Fig. 3(b). To our knowledge, this is the first report on the detection of such higher-order Raman spectra of carbon nanotubes. The very clear and strong third-order peak at 4274 cm^{-1} can be safely attributed to a combination of 2 $\times 1348 + 1581$ cm⁻¹. However, this peak shows a large downshift in frequency with respect to both the 4320 cm^{-1} peak of HOPG and the 4305 cm⁻¹ peak of PG.²⁵ Furthermore, the third-order peaks at 4043, 4511, and 4819 cm^{-1} have also been observed and assigned to $3 \times 1348 \text{ cm}^{-1}$, $1348 + 2 \times 1581 \text{ cm}^{-1}$, and $1581 + 2 \times 1617 \text{ cm}^{-1}$, respectively. The fourth-order Raman band at 5861 cm⁻¹ is also observed clearly in Fig. 3(b) and can be assigned to the combination of $2 \times 1348 + 2 \times 1581$ cm⁻¹, while the fourth-order Raman spectrum at 5392 cm^{-1} seems to appear and can be assigned to 4×1348 cm⁻¹.

Basically, all the Raman features of aligned CCNTs are similar to those of PG.²⁵ This indicates that the microstructure of individual tubes of CCNTs is composed of many crystalline domains, which possess a high degree of crystalline order, as shown by the appearance of high-order Raman spectra. Undoubtedly, the high density of the aligned CCNTs helps detection of the higher-order Raman spectra.

In summary, we have successfully synthesized large area aligned CCNTs, which are perpendicular to the surface of the substrate. The tubes are around 10–15 nm in diameter and 50 μ m long. Raman spectra up to fourth order of the aligned CCNTs have been collected, indicating that CCNTs are highly graphitized. The appearance of a strong D band shows that a nanometer scale turbostratic structure may be formed in carbon nanotubes due to the relatively low growth temperature. The Raman studies are consistent with the results from SEM and HRTEM. Resonance behavior shows that the lattice properties of the aligned CCNTs are different from that of other forms of carbon. Third- and fourth-order Raman spectra have been detected.

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