Temperature Dependent Raman Spectra of Carbon Nanobuds

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Carbon nanobuds (CNBs) represent an emerging nanostructure, in which fullerene molecules are covalently bonded to the outer surface of single-walled carbon nanotubes (SWNTs). The Raman spectra of CNBs were systematically investigated and compared to those of SWNTs. The spectra were recorded using a 514 nm laser and evaluating the temperature-dependent Raman frequency shift in CNBs in the range 27–475 °C. The temperature coefficient of the G-mode frequency of the CNBs was much larger than that of the SWNTs. Consequently, the CNBs have lower thermal stability, which is attributed to the fact that the fullerenes are covalently bonded to the sidewall of SWNTs. At the same time, we observed that the radical breathing modes (RBMs) of CNBs downshift ~2–6 cm⁻¹ compared to the RBMs of SWNTs, and this shift can be attributed to the smaller van der Waals (VDWs) interactions between the CNBs. Using a 750 nm laser, a broad G⁻ band, which is an intrinsic character of metallic properties, was clearly observed. This characteristic feature provides evidence that the nanobuds of some nanotubes remain metallic.

Introduction

Both carbon nanotubes and fullerenes are constituents of the new class of carbon nanomaterials.1,2 Owing to their extraordinary electronic, mechanical, optical, and chemical properties, they have attracted a great deal of attention.3–7 Carbon nanotubes and fullerenes have great potential in nanotechnology applications and nanoscale engineering, including building blocks for energy conversion devices,3 nanoelectronic devices,4 sensors,5 field emission,6 and composite materials.7 Their hybrids are supposed to have even more interesting properties which can be tuned.

As already shown by previous experiments, carbon nanotubes and fullerenes can be combined to form hybrid carbon nanostructures.8–10 Smith et al. have demonstrated that during the pulsed laser vaporization of graphite, C60 fullerenes can be trapped inside SWNTs to form the so-called nanotube peapod, where the C60 fullerenes are separated from the SWNT by a graphitic VDWs gap.8 Electrical measurements of the peapod have shown that the encapsulated C60 molecules give rise to a hybrid electronic band and modify the local electronic structure of the nanotube.8 This feature can be utilized in nanoelectronic applications.11

CNBs, where fullerenes are covalently bonded to an SWNT, have successfully been synthesized as an alternative hybrid carbon nanostructure.9,11 Compared to pure SWNTs, CNBs exhibit a rather low field threshold (0.65 V·μm⁻¹) and a much higher current density.9 Thus, it can be expected that CNBs possess other advantageous properties.9 For example, the attached fullerenes may yield more space between the SWNTs and thereby weaken the tendency toward adhesion among the SWNTs and thus prevent the formation of tight bundles of SWNTs. The fullerenes could also be used as molecular anchors to prevent slipping of SWNTs in composites, and thereby greatly enhance the strength of SWNT based composites. In regard to the electronic properties of CNBs, different research groups have performed first-principles studies,12–14 It is expected that the properties of CNBs can be modified by the chemical interaction between C60 and the SWNT in the same way as has been observed in the case of nanotube peapods. Thus, their properties can also be highly tunable by changing the C60 density on the sidewall of SWNT. Meng et al. and He et al. predicted that CNBs of some carbon nanotubes remain metallic,12,13 while Wu et al. concluded that all the CNBs are semiconducting regardless of the original SWNT base being metallic or semiconducting.14 Experimental work is therefore highly desirable to further explore CNB materials.

Raman spectroscopy is an exceedingly powerful tool for characterizing fullerenes,15 SWNTs,16 nanotube peapods,17 and CNBs.9,18 Nevertheless, it is rather difficult to attribute specific features of Raman spectra to the fullerenes due to the high weight distribution of fullerenes and polymerization of fullerenes in bulk CNBs.9 Still, some valuable information concerning the structures (diameters, purity, etc.) can be obtained. For example, the radical breathing mode (RBM) is especially important, not only for determining SWNT diameters but also for understanding the effect of tube–tube interaction.19–21 In addition, the electron–phonon coupling (EPC) in SWNTs is a key coupling parameter in the electronic band structure.22 EPC has a major impact on the electronic and phonon transport properties23 as well as on Raman scattering.16 Raman spectroscopy also allows direct measurement of Γ-centered phonons and therefore G mode broadening due to strong EPC should be observable in metallic SWNTs.24 Hence, G mode broadening has been

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assigned to metallic tubes and can be used as a tool to identify whether an SWNT is metallic or semiconducting.25

The temperature-dependent Raman frequency shift of carbon nanomaterials is more informative than room temperature data and has therefore been investigated widely.26–31 For example, the temperature coefficients of Raman frequencies that are deduced from the Raman spectra obtained at different temperatures can be used as a measure of the thermal stability of SWNTs.28

Herein, we report a study related to the temperature-dependent Raman spectra of CNBs. The experiments were conducted in an argon (Ar) atmosphere to avoid the adsorption of O2 in ambient air. The temperature dependent Raman spectra of both SWNTs and CNBs were obtained with 514 nm laser excitation, the thermal coefficients of G bands were calculated and compared following their frequency change. In addition, the RBM frequencies of CNBs were compared to those of SWNTs, and the reasons for this change were considered carefully. Furthermore, Raman spectra produced with 750 nm laser excitation were used to assess whether some CNBs in the sample were metallic or not.

Experimental Section

SWNTs were synthesized in an experimental setup based on ferrocene vapor decomposition in a carbon monoxide (CO) atmosphere at 1000 °C, as has been reported elsewhere.3,11 Briefly, CO with a flow rate of 300 cm3/min passes through a cartridge filled with ferrocene powder at ambient temperature. The vapor flow containing ferrocene was then introduced into the high temperature zone of a ceramic tube reactor through a water-cooled probe and mixed with an additional 100 cm3/min CO. To produce CNBs, a small amount of H2O (145 ppm) was introduced to the system through an H2O saturation vessel. The products were collected downstream of the reactor, either by filtering on nitrocellulose disk filters or by depositing on TEM grids using an electrostatic precipitator. The morphology of the as-obtained product was investigated with a Philips CM-200 FEG transmission electron microscope (TEM) operating at 200 kV.

Raman scattering measurements were carried out with a JY LabRam HR 300 using 2.41 eV (514 nm) Ar ion laser excitation source with ×50 air objective (laser spot diameter of 2 µm). Laser power was kept at ~10 µW for all measurements. Samples were placed in the controlled environment chamber equipped with an optical window and a heating stage (programmable hot-stage TS 1500, Linkam Scientific Instruments Ltd.) that was used for in situ Raman measurements. Before characterization, samples were first annealed under a continuous air flow (50 cm3/min) at 380 °C for 30 min to burn off amorphous carbon and thereafter annealed in Ar flow at 450 °C to remove O2 adsorbed on the samples. Spectra were taken in steps of 25 °C from room temperature to 475 °C in Ar flow (50 cm3/min). After reaching the desired temperature, the samples were cooled at a rate of 20 °C/min to 27 °C. All the Raman spectra were fitted to Lorentzian peak shapes to obtain the peak frequencies.

Raman measurements using a 750 nm (1.65 eV) laser excitation source were performed with a tunable continuous-wave Ti/sapphire laser source in air. The laser beam was focused on the sample surface by an objective lens (×50). The diameter of the laser spot was ~2 µm.

Results and Discussion

1. Evolution of the G Band at Different Temperatures in an Ar Atmosphere. Parts a and b of Figure 1 show the typical high-resolution transmission electron microscope (HRTEM) images of the as-produced SWNTs and CNBs, respectively. The outside walls of both samples are not quite “clean”, and fullerene-like materials can be observed. Before the samples were characterized by Raman spectroscopy, they were annealed in air at 380 °C for 30 min. The data shown in Figure 1c,d imply that the heat treatment did not damage the samples. Similarly, amorphous carbon that was deposited on both samples during the growth process could be burned away easily by heat treatment in air.32

Due to the high specific surface areas of SWNTs and CNBs, their electronic properties are extremely sensitive to their chemical environment.33–35 Transport measurements and scanning tunneling spectroscopy have shown that the SWNTs’ electrical resistance, thermoelectric power, and local density of states are dramatically influenced when SWNTs are exposed to air.33 As a result, the SWNT field effect transistor (FET) demonstrates p-character in air.34,35 At the same time, O2 adsorption also leads to an actual increase in the physical disorder of SWNT, which complicates the Raman active mode’s line shape and causes the frequency shift of the Raman spectrum.36–38 To avoid the deviation of the real peak position of Raman spectroscopy due to the interaction with O2, both SWNTs and CNBs were annealed at 450 °C in flowing argon to remove the O2.37,38

After annealing in argon, Raman scattering was obtained with Eλaser = 2.41 eV from the degassed samples in a temperature range from 300 to 748 K in an Ar atmosphere. The Raman spectra of SWNTs and CNBs at ambient temperature are displayed in Figure 2a. Both Raman spectra show very high G/D ratios, which prove the high quality of our samples. Following ref 28, each spectrum was fitted to three Lorentzians for the G band. Figure 2b demonstrates the fitting results of the G band at ambient temperature. Both of the fittings include one main peak (ωG1) at ~1594 cm−1 and two second-strongest peaks on both sides. There is no obvious peak shift in the ωG1 of CNBs when compared to that for SWNTs, although this shift was expected because of the charge transfer from SWNTs to fullerenes in CNBs.14

Figure 1. TEM images of the as-produced (a) SWNTs and (b) CNBs. TEM images of (c) SWNTs and (d) CNBs after annealing in air at 380 °C for 30 min. The scale bars in all the figures are 10 nm.
Parts c and d of Figure 2 display the G band evolutions of SWNTs and CNBs, respectively, at different selected temperatures during the heating and cooling processes. The spectra measured in the cooling and heating process are reversible. The frequency of the G band downshifted with increasing temperature in both samples. This observation is consistent with the previous reports on temperature dependent Raman spectra of SWNTs. The Raman frequency downshift with increasing temperature can be readily understood considering the softening of the C–C bond: the C–C bond stretching force consistently decreases with increasing temperature.

For simplicity, only $\omega_G$, the main peak in the G band was followed as a function of temperature because it shows little diameter/purity dependences. Obviously, the temperature variations of the G frequency fit well in a straight line (Figure 2e). The temperature dependence of the frequency in terms of $d\omega/dT$ was obtained from the slope of the linear fitting. The value obtained for SWNTs, $-0.0196$ cm$^{-1}$ K$^{-1}$, is similar to that obtained for HiPco SWNTs ($-0.0189$ cm$^{-1}$ K$^{-1}$). On the other hand, for CNBs, the value of $d\omega/dT$ is $-0.0273$ cm$^{-1}$ K$^{-1}$. The temperature coefficient of Raman frequency has been defined as $\alpha_\omega = (d\omega/dT)/\omega (T = 300$ K), and it has been widely studied for various carbon nanomaterials. The different slope values in Figure 2e clearly show that the temperature coefficients of G mode in Raman spectra differ. For SWNTs, $\alpha_{\omega G}$ is $-1.23 \times 10^{-5}$ K$^{-1}$, deduced from the temperature dependent Raman spectra of SWNTs. This value is much smaller than that of CNBs ($-1.71 \times 10^{-5}$ K$^{-1}$). For clarity, it should be noted that the $\omega_G$ of CNBs at 475 °C is $\sim 3$ cm$^{-1}$ lower relative to that of SWNTs (Figure 2f).

The temperature coefficient of Raman frequency has been used to define the thermal stability of ring-shaped SWNTs. Due to the high bending strain energy along the nanotube rings, as induced by the sidewall in the ring-shaped SWNTs, the temperature coefficients of both the RBMs and the G mode frequencies are smaller compared to those for straight SWNTs. In other words, the thermal stability is higher for ring-shaped SWNTs than for straight SWNTs. In our case, the temperature coefficient of Raman frequency of CNBs is larger than that of SWNTs. This means that the thermal stability of CNBs is lower than that of SWNTs.
than that of pure SWNTs. This result can be interpreted when considering that the fullerenes covalently bonded to the sidewall of SWNTs induce a local distortion on the SWNT surface. As a result, some carbon atoms are pulled outward from the wall surface of SWNT, and thus destroy the original perfect structure of SWNTs and thereby decrease their thermal stability.

2. Downshift in Frequencies of RBM. The RBMs of SWNTs and CNBs in an Ar atmosphere have also been compared. Figure 3a displays an obvious downshift of RBMs in CNBs. The Lorentzian fittings in Figure 3b show that the RBMs of CNBs downshift \( \sim 2-6 \text{ cm}^{-1} \) compared to those of SWNTs. Similarly, the nanotube peapods have also shown \( \sim 2-5 \text{ cm}^{-1} \) downshift in their RBMs,\(^{40}\) and no downshift in their G band. In the case of the nanotube peapods, the downshift in RBMs was interpreted by the small charge transfer from fullerenes to SWNTs. This charge transfer can be detected from the RBM frequency even though no change was observed in the stretching mode frequency.\(^{40}\) However, in the case of stable CNBs configurations, electrons are transferred from SWNTs to fullerenes,\(^{9}\) and this certainly induces the hardening of C–C bonds and should thus cause an upshift of the RBMs.

Several other factors may cause the Raman spectrum shifts in the RBM modes. One possibility is the diameter change of CNBs during growth influenced by the addition of H\(_2\)O. As reported in other literature,\(^{41,42}\) the addition of H\(_2\)O in the synthesis of SWNTs not only plays a cleaning role by removing amorphous carbon species but also plays an additional indirect role in growth promotion.\(^{42}\) However, a small amount of H\(_2\)O will change neither the diameter of the catalytic nanoparticles nor the diameters of the SWNTs grown on the catalyst.\(^{42}\) Another possibility for the downshift of RBMs is the change of band gap; the cycloadDITION of fullerenes in CNBs induces numerous impurity states near the Fermi level and narrows the band gap.\(^{14}\) According to the theoretical predictions,\(^{43,44}\) the band gap of SWNTs varies inversely with their diameters. Keeping this point in mind and taking into account the resonant effect, which is sensitive to the matching between the exciting (scattered) energy and allowed transitions between two van Hove singularities, the Raman scattering should be resonant with smaller diameter SWNTs in CNBs and the RBM frequencies should upshift.

Besides the above factors, the interactions between SWNTs should be taken into account. Because of the space restrictions imposed by the presence of neighboring SWNTs, the interactions within a bundle have been predicted to cause a \( \sim 6-20 \text{ cm}^{-1} \) upshift in RBMs with respect to isolated SWNTs.\(^{20}\) Bandow et al. calculated the relation between the RBM wavenumber \( (\omega) \) and the diameter \( (d) \) of isolated tubes using a force constant model, which includes interactions to the fourth neighbor \( (\omega \text{ (cm}^{-1}) = 224 \text{ (cm}^{-1}\text{·nm)/d (nm)}) \).\(^{45}\) However, most of the tubes produced have a tendency to form bundles. Therefore, when the RBM frequency is calculated, an additional Lennard-Jones potential must be considered to account for the VDWs interaction between the tubes, since this interaction causes about 10% shift upward in the RBM of the bundled SWNTs.\(^{21}\) In other words, the presence of VDWs interaction between the SWNTs can cause an upshift of RBMs. Thus, we can expect that the VDWs interaction also induced differences in the RBMs between CNBs and SWNTs. In the case of CNBs, the attached fullerenes yield more spaces between SWNTs,\(^{9}\) these spaces prevent the formation of tight bundles between SWNTs and therefore weaken the VDWs interaction between them. On the basis of the analysis above, we tentatively attribute the frequencies downshift of RBMs to the smaller VDWs interactions between CNBs, as schematically illustrated in Figure 3c.

3. EPC in the G Band of CNBs. In contrast to the G band of graphite, which only exhibits one single Lorenzian peak at \( \sim 1582 \text{ cm}^{-1} \), the G band of SWNTs is composed of several
peaks due to the phonon wave vector confinement and symmetry breaking effects associated with SWNT curvature. The G band features, in particular for metallic SWNTs, consist of two main components, $G'$ ($\sim 1580 \text{ cm}^{-1}$) and $G$ ($\sim 1540 \text{ cm}^{-1}$) peaks, which are due to TO and LO modes. Because of the EPC interaction, the G’ line width is usually broad and can be used for distinguishing metallic SWNTs. However, the EPC interaction, which can be reflected by the Raman spectrum in the broad G’ peak, is very sensitive to the position of the Fermi level. In some cases, even when CVD growth is the very last step, the EPC of SWNTs can be weakened by unintentional doping or O2 adsorption that leads to charge transfer. Therefore, sometimes the G’ band of metallic SWNTs is not broad and obvious, compared to the G’ band of semiconducting ones. However, it is rather safe to determine metallic SWNTs from their broad G’ band.

The Kataura plot predicts that the energy of 750 nm excitation ($E_{\text{exc}} = 1.65 \text{ eV}$) coincides with the energy gap of some metallic SWNTs with a diameter in the range 1.3—1.8 nm. The mean diameters of both SWNTs and CNBs are in this range. Therefore, the 750 nm excitation couples predominantly with the presence of metallic SWNTs in the sample. Figure 3d is a typical Raman spectrum of CNBs obtained from a 750 nm laser; a broad and softened G band is clearly shown. These data provide clear evidence that at least some of the CNBs are still metallic. The result is consistent with the predictions of Meng et al. and He et al. who claimed that some of the CNBs should still be metallic but are contrary to the result depicted in ref 14, where Wu et al. calculate that all the CNBs should be semiconducting, because the attachment of C60 opens up a small band gap in metallic SWNTs.

This divergence of conclusions is due to the difference of contact between the bud and defective SWNT in the CNBs’ geometries. For example, in the model of Meng et al., imperfect C60 connect SWNT via sp3-hybridized [6 + 6] cycloaddition. Moreover, the necks connecting the fullerences and SWNTs are simulated by one or two periods of (6,0) SWNTs. It is thus different from the model simulated for the formation of CNBs by [2 + 2] cycloaddition, wherein the CNBs do not have any period of SWNT in the neck and fullerences can possess a complete spherical structure and can be covalently bonded to SWNTs via sp3-hybridized carbon atoms.

Apparently, the differences between the prepared CNBs structure features and theoretical models may also cause some deviation of their electric structures. Statistical measurements of the buds on the surface of SWNTs have shown a wide distribution of fullerences, such as C$_{20}$, C$_{42}$, C$_{60}$, C$_{70}$, etc., while in all theory models, only C60 fullerences were taken into account as buds. To clarify the metallicity dependence of a CNB on its SWNT’s chirality, further improvements on synthesis process and electrical measurements on individual CNBs are proposed.

Conclusions

Raman spectroscopic characterization has given clear evidence for some open questions about CNBs. In summary, the main results presented in the article are as follows: (1) The temperature dependence of CNBs Raman spectra has shown that the thermal coefficient of the G-band of CNBs is larger than that of SWNTs. In other words, CNBs have lower thermal stability than SWNTs, and consequently we suggest that, in CNBs, the fullerences are covalently bonded to the sidewall of SWNTs. (2) A downshift of RBMs with respect to the case of pure SWNTs is attributed to the smaller VDWs interactions between CNBs. (3) The observation of broad G’ band provides evidence that some tubes in CNBs are still metallic, although some further work is required.