Hot wire chemical vapor deposition of isolated carbon single-walled nanotubes

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Hot wire chemical vapor deposition (HWCVD) has been employed for the continuous generation of carbon single-walled nanotube (SWNT) materials. Interestingly, transmission electron microscopy analyses revealed only the presence of isolated SWNTs, rather than nanotubes existing in bundles. An analysis of the growth mechanism explaining the production of isolated SWNTs is provided. Also, the Raman radial breathing modes (RBMs) of the isolated HWCVD-generated nanotubes are compared to the RBMs of small bundles of nanotubes deposited by a conventional CVD technique having a similar diameter distribution. © *2002 American Institute of Physics.*
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Carbon single-walled nanotubes (SWNTs) hold great promise for a wide variety of applications. The development of a low-cost scalable production method has therefore been a major research priority. In 1996, SWNT growth employing chemical vapor deposition (CVD) on a supported catalyst was demonstrated as a promising route to nanotube production.[1] Multiple reports quickly followed, further establishing CVD as a viable large-scale production process.[2–10] CVD techniques have also been used to make SWNT scanning probe microscopy tips[11] and nano-scale devices.[12,13] The production of isolated nanotubes with specific diameters has been achieved by varying supported catalyst particle sizes in the range of 1 to 5 nm.[14]

Plasma-enhanced hot wire chemical vapor deposition (HWCVD) has been successfully employed for the deposition of well-aligned carbon multiwall nanotubes on nickel-coated glass substrates.[15] In the hope of simplifying the process, HWCVD of carbon nanotubes was attempted without a plasma on nickel-coated single-crystalline Si and amorphous SiO_2 substrates. Unfortunately, nanotube formation was not confirmed.[16] More recently, HWCVD was employed to grow bundles of SWNTs between metallic contacts, forming a nanoscale conducting network. Electron transport measurements were then employed to show that the device was fully operational.[17]

This letter demonstrates HWCVD synthesis of SWNT materials in a continuous fashion with the catalyst supplied in the gas phase. Using methane as a carbon source and ferrocene as the metal catalyst, a hot filament operating at $\sim 2000 \, °C$ is sufficient to decompose the gas-phase precursors without an additional plasma. Although no attempt was made to control the catalyst particle size, extensive transmission electron microscopy (TEM) analyses showed all the nanotubes to be isolated. Raman spectra of the SWNT radial breathing modes (RBMs) for the isolated HWCVD tubes are compared to those of nanotubes in small bundles generated by a conventional CVD technique[10] having a similar diameter distribution. Contrary to theoretical predictions, no shift

in RBM frequency is observed for the bundled SWNTs.

The deposition chamber has been described previously.[18] A 0.5 mm tungsten filament was operated at 29 A, 20 V, and $\sim 2000 \, °C$ in a static gas atmosphere of 1:5 CH_4:H_2 at 150 Torr. Several Torr of ferrocene were introduced into the chamber and decomposed on the hot filament, providing a gas-phase metal catalyst. SWNT-containing material was deposited on a glass substrate, heated to $450 \, °C$ and located approximately one in. from the filament. Samples were prepared for TEM by suspending ~ 0.2 mg of the material in 10 ml of acetone. The solutions were sonicated for 5 min, and ~ 6 drops were placed on Ted Pella Ultra-thin Carbon Type-A 400 mesh grids. To confirm that the sample preparation process did not effect the SWNT bundling, small pieces of dry sample extracted from the glass substrate were mounted directly on grids. A total of eight samples from different areas of the deposited film were analyzed. Eight to ten images were then taken at random from different places on each grid at a magnification that resolved isolated tubes. Raman spectroscopy was performed with a resolution of $2–4 \, cm^{-1}$ using ~ 7 mW of the 488 nm line of an Ar ion laser. For comparison, identical TEM and Raman analyses were performed on a material made in our lab by a conventional CVD technique.[10]

Following the extensive TEM analysis of the HWCVD-generated materials, it was possible to find only isolated nanotubes. Measurements of all images of the isolated tubes showed the SWNT diameter range to be 1.1 to 1.5 nm. Figure 1 displays TEM images of the isolated SWNTs found in a HWCVD deposited film. The figure contains images from both solution and dry preparation techniques. In general, SWNTs form bundles of nanotubes during synthesis that are stabilized by tube/tube van der Waals interactions. Especially large bundles (tens to hundreds of tubes) are generated by laser-vaporization of a metal-doped graphite target in a furnace between 850 and $1200 \, °C$.[19] Laser-generated catalyst particles grow to diameters of $\sim 10–60$ nm, and nanotube growth occurs as particles are transported out of the hot zone of the furnace by flowing argon. Conventional CVD production generally employs the pyrolysis of a gas phase carbon
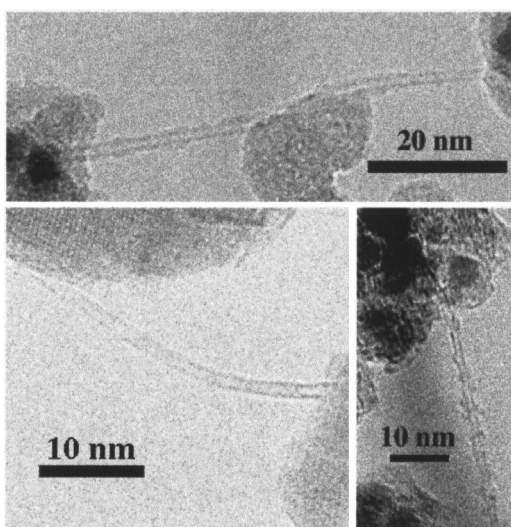
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FIG. 1. TEM images of isolated SWNTs produced by the hot wire technique. The lower left image is a tube from the dry preparation technique. Images were obtained on a Phillips CM-30 TEM/STEM operating at 200 kV with a 50 μm objective aperture for improved contrast.
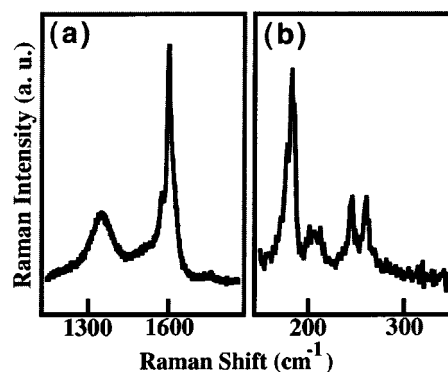

FIG. 2. Raman spectra of HWCVD SWNT material for (a) the nanotube tangential vibrational modes and (b) the radial breathing modes using 488 nm excitation.

precursor on supported catalyst particles, and results in smaller nanotube bundles containing <20 tubes.[2,3,10] Synthesis temperatures vary between ~700 and 1200 °C, and catalyst particles are typically 5–20 nm in diameter. Isolated SWNTs have been grown via CVD on small catalyst particles with diameters of only a few nms.[1,14]

It is reasonable to assume that nanotube bundles reach sizes similar to the diameter of the catalyst used in the synthesis. The production of larger bundles of SWNTs by laser vaporization may then be partially explained by the growth of catalyst particles larger than those typically employed in CVD processes. However, many laser-generated bundles have diameters significantly bigger than the catalyst particles. It therefore seems likely that as the nanotubes are freely transported through the hot growth zone, multiple smaller bundles collide and agglomerate resulting in nanotube bundles up to several hundred nanometers in diameter. Conversely, since growing CVD tubes remain anchored to their catalyst particles, bundles approximately the size of the catalyst particles are formed. For very small metal particles, it is then possible to form isolated tubes.[1,14]

In this HWCVD process the catalyst particle sizes as observed by TEM are ~5–25 nm in diameter. Based on these sizes, it is surprising that all SWNTs are observed to be isolated. However, in this deposition, the nanotube growth zone is very short, as the SWNTs are deposited approximately 1 in. from the filament on a glass substrate at 450 °C. This very short hot zone does not allow for a significant growth time and may reduce the number of carbon atoms in contact with the catalyst such that only a single SWNT is formed on a given particle. In addition, although the nanotube species are produced in a mobile vapor phase with a higher catalyst density than used in the typical laser process, the individual tubes do not have time to collide and produce bundles. An alternate explanation could be that HWCVD species are generally negatively charged due to the high electron flux emitted from the filament.[20] As the charged nanotubes grow in length a buildup of negative charge accrues.

The long charged tubes would tend to repel each other rather than form cohesive bundles. Future studies performed inside an external furnace will provide a much longer SWNT formation period. It should then be possible to differentiate between limited growth time and charging effects as reasons for the production of exclusively isolated SWNTs.

Figure 2(a) displays the Raman spectrum of the characteristic SWNT tangential bands at 1593 and 1571 cm^{-1} for the HWCVD film. At 488 nm, Raman excitation almost exclusively probes semiconducting SWNTs.[21] No evidence of the Breit–Wigner–Fano line shape in the G-band that would be associated with scattering from metallic SWNTs is observed. A broad disorder band at 1350 cm^{-1} is apparent, indicating the presence of amorphous carbon and nanocrystalline graphite impurities.[22] The concentration of impurities is expected to decrease dramatically upon further process optimization that includes the use of mixed catalysts and a longer high temperature growth zone. Figure 2(b) displays the Raman spectrum of the material between 150 and 350 cm^{-1}. The features in this region are attributed to the SWNT RBMs, and their frequencies are diameter dependent.[23] Assuming that the RBMs for all SWNTs fall on the line $\omega(d) = 223.75/d$ (ω is in units of cm^{-1}, d corresponds to the tube diameter in nm),[24] the spectral features in Fig. 2(b) are consistent with a diameter distribution of ~0.9–1.4 nm. In addition, the spacing of the peak frequencies of the RBMs is consistent with the production of exclusively zigzag SWNTs.[25]

Since TEM analysis showed all HWCVD tubes to be isolated, it is interesting to compare the Raman spectra of the RBMs of these isolated tubes to those of similar SWNTs in bundles. Figure 3 displays a Raman RBM comparison for the HWCVD isolated SWNTs and conventional CVD nanotubes[10] bundled in several to tens of nanotubes. The high correlation between the Raman RBM spectra for the CVD and HWCVD samples strongly suggests that for Raman excitation at 488 nm these samples have highly similar diameter distributions. These two samples therefore provide an opportunity to look for a difference between the RBM frequencies of SWNTs of similar diameter that exist in bundles versus isolated SWNTs.

Theoretical investigations predict that the SWNT Raman RBM frequencies are strongly effected by nanotube bundling.[26–28] However, an experimental confirmation of

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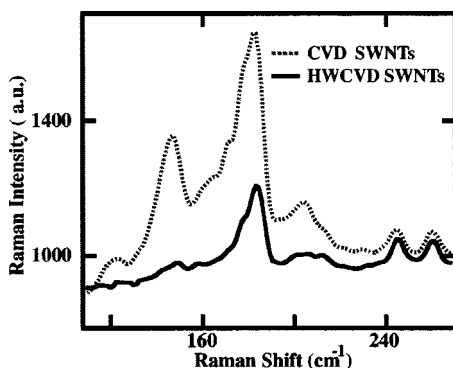
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FIG. 3. Comparison of the Raman spectra of the radial breathing modes of isolated HWCVD-generated single-wall carbon nanotubes and small SWNT bundles of conventional CVD-generated tubes.

such an effect has not been established. The theoretical works have shown that for bundled SWNTs, tube/tube interactions can result in shifts of the RBM frequencies between ~ 1 and $15\ cm^{-1}$.[26–28] In particular, Kahn *et al.*[26] and Venkateswaran *et al.*[27] predict blue shifts for RBM frequencies of bundled SWNTs of $\sim 6\ cm^{-1}$ for a (10,10) tube and $\sim 14\ cm^{-1}$ for a (9,9) tube. In a detailed analysis Henrad *et al.*[28] predict two hybrid breathing modes (BM1 and BM2) for infinite SWNT bundles. However, for small diameter SWNTs, only BM1 has a significant intensity.[28] For tubes with a diameter <2 nm this BM1 is blue shifted between 1 and $15\ cm^{-1}$; the degree of the shift increases with decreasing SWNT diameter.

In view of these theoretical predictions, it is especially interesting to compare the spectral features at 246 and $260\ cm^{-1}$ (Fig. 3) corresponding to the RBMs of SWNTs with diameters of 0.91 and 0.86 nm, respectively. Since these features are well resolved from each other due to the decreasing number of tubes with smaller diameters, it is possible to examine peaks attributed to only two distinct diameters. The frequencies of these two peaks are the same for both the small bundled CVD tubes and the isolated HWCVD tubes and show no signs of the blue shift predicted for bundled SWNTs.[26–28] Thus, these experimental results suggest that bundling does not result in a significant change in SWNT RBM Raman frequencies.

It is possible that some population of bundled SWNTs was undetected by TEM in the HWCVD material and that a significant population of isolated SWNTs exists in the CVD material. Were these both to occur, the features at $246\ cm^{-1}$ could be consistent with the RBM of isolated tubes, and the features at $260\ cm^{-1}$ consistent with BM1 for bundled SWNTs. The shift predicted for bundled tubes of ~ 0.9 nm diameter is $15\ cm^{-1}$.[28] However, since the RBMs at lower frequencies do not display a similar trend, this interpretation does not seem likely. Alternately, the small bundles produced by conventional CVD are still too small to produce bundling effects.

In summary, a simple, scalable, continuous HWCVD process for the deposition of SWNT materials has been demonstrated. Interestingly, the SWNTs were found to be iso- lated, yet no significant changes were observed in the Raman spectra when compared to similar bundled SWNTs. Further development of this process could have profound impact on SWNT production technology.

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