Growth of Large-Diameter Single-Walled Carbon Nanotubes

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Single-walled carbon nanotubes (SWNTs) give every indication that they will make a major impact on science and technology. Their unusual physical and chemical properties, which depend on nanotube diameter and helicity, make them particularly attractive for future molecular nanotechnology applications. Production of a variety of nanotubes will be necessary to explore novel properties arising from a variety of detailed atomic structures. We have synthesized large-diameter SWNTs by adding catalyst promoters, using either Co or Fe as primary catalyst. SWNTs produced by transition metal catalysts alone have a diameter distribution between 1 and 2 nm. Adding catalyst promoter alters the diameter distribution to a much wider range, with a variety of helicities, and dramatically increases the nanotube yields. The results indicate the need for a general growth mechanism that accounts for the effect of catalyst promoters.

Introduction

Since the discovery of single-walled carbon nanotubes (SWNTs) in 1993,[1,2] numerous studies have shown that they are stable and possess many useful chemical, electrical, and mechanical properties.[3−7] Many applications, ranging from hydrogen storage in fuel cells to molecular electronic devices, would benefit from the availability of SWNTs of varying diameters and helicities. SWNTs with a variety of diameters in significant quantities is advantageous for testing many theoretical predictions and for practical applications such as hydrogen storage,[3] molecular electronics,[6] nanoelectrical machines,[4,5,8] and gas separations.[9] For example, a 3 nm diameter nanotube may achieve the goal as hydrogen storage medium for practical vehicular fuel-cell applications.[3] Since several purification and separation techniques have been developed,[10,11] one may soon be able to separate SWNTs according to their sizes. Here we describe an efficient method for producing large quantities of large-diameter SWNTs in high yields. Many of the electrical, mechanical, and chemical properties[3,12] that depend on the diameters may now be tested. A growth model explaining the effect of catalyst promoter is provided.

Experimental Methods and Results

SWNTs were produced by an electric arc generated with a 65−95 A DC current under 200−500 Torr of helium.[1,13−15] The electrodes were 6 mm diameter graphite rods, with the anode cored by a 4 mm cylinder filled in with mixtures of graphite powder, varying amounts of Co or Fe catalyst, and promoter (S, Y, Bi, or Pb). A supply voltage of 25 V between the electrodes was kept constant by gradually advancing the cathode toward the anode to maintain a constant voltage drop as the anode was consumed and a cathode deposit was built up. Promoters were used to improve the catalytic properties of primary catalyst to produce high-yield, large-diameter SWNTs.

As in a typical arc reactor for catalytic synthesis of nanotubes, weblike material forms as the rod is consumed. With the addition of promoter, weblike material quickly filled the reaction chamber within seconds of the arc initiation. The composition of the deposit depends on its location within the reaction chamber.
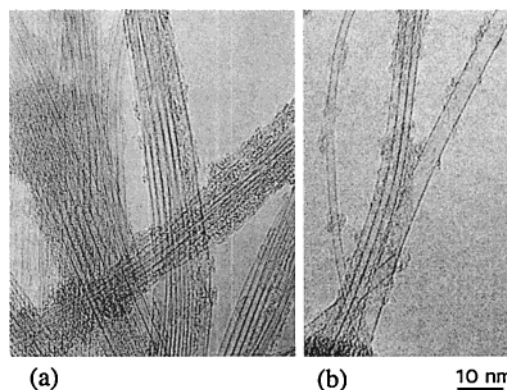

Figure 1. High-resolution transmission electron microscopy images of single-walled carbon nanotubes (SWNTs): (a) high content of SWNTs throughout the soot materials; (b) SWNTs with a wide range of diameters produced in large quantities with catalyst promoter.

Most of the soot (including the weblike material) deposits on the chamber walls with small amounts of collarette deposited around the cathode tip. Soot collected from different regions of the chamber was sonicated in ethanol, and a drop containing the suspended materials was placed on a lacey carbon grid for transmission electron microscopy (TEM) examinations. The microscope (TOPCON 002B) was operated at 120 or 200 kV accelerating voltage.

The deposit on the chamber walls, which accounts for most of the product, contains the highest density of SWNTs, as shown in Figure 1a. Product yields vary with catalyst compositions. When using Co as primary catalyst, the best results were obtained from the soot produced under 400 Torr helium flow with a catalyst composition of, in atomic percentage, 3.5% Co and 3.5% S. In the presence of S, Bi, or Pb, sheets of nanotubes form abundantly, with an apparent yield of 70% (judging by the nanotube to amorphous carbon ratio obtained from the TEM micrographs), increasing the yield by 3-fold compared to the product generated by using Co alone.[1,16,17] More importantly, large-diameter ($D > 2$ nm) SWNTs, which are not produced with iron group metal catalysts (Fe, Co, and Ni) alone, form abundantly, as shown in Figure 1b.
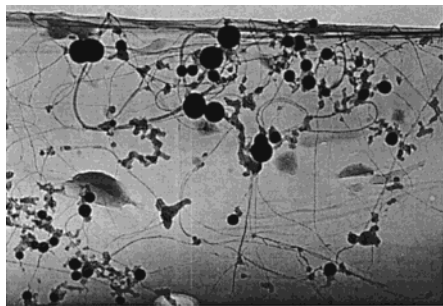
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Figure 2. High-resolution transmission electron microscopy images of single-walled carbon nanotubes (SWNTs) produced by Fe and Bi. Adding catalyst promoter to Fe dramatically increased SWNT yield.

Promoter has a more dramatic effect on Fe catalyst. Figure 2 is a typical low-magnification TEM image of soot produced from 3% Fe and 3% Bi, which demonstrates that Fe can be a good catalyst for high-yield synthesis of SWNTs. Unlike Co and Ni, Fe alone produces SWNTs in very low yields[2] and, therefore, has had a limited role in SWNT production. Fe has been widely adopted in industrial production of vapor grown carbon nanofibers[18] because of its nontoxicity and low cost, and use of promoter allows one to replace Co and Ni with Fe, which is essential for large-scale production of SWNTs.

A more interesting effect of promoter is that both metal (Bi and Pb) and nonmetal (S) promoters not only improve Fe and Co catalytic activities, but also co-catalyze the formation of large-diameter SWNTs. This is evidenced by the fact that no SWNTs formed without primary catalyst, and large-diameter SWNTs were produced only in the presence of a promoter. Single-walled nanotubes of diameter as large as 7 nm were observed, and electron diffractions indicated that these nanotubes have a variety of helical structures.

Different promoters appeared to have similar effect on Co catalyst, as determined by the improvement in yields and the change in diameter distributions. Since all promoters have similar effect on diameter distribution, we have combined the data from different promoters to increase the statistical significance. The results, shown in Figure 3a, is similar to that from sulfur promoter.[13] We have observed that adding promoter to Co catalyst broadens the SWNT diameter distribution with a slight shift in peak position (from 1.3 to 1.5 nm). On the other hand, adding Bi promoter to Fe catalyst has a minor broadening effect in the distribution while resulting in larger shift in peak position (from 1 to 2 nm), as shown in Figure 3b.

Large-diameter SWNTs appear to be more stable, as predicted by the energetics argument that the strain energy per carbon varies with $1/R^2$.[19] They are also less susceptible to chemical reaction and oxidation and, hence, would be better for incorporating foreign materials.[20] The possibility of manipulating and modifying nanotubes for specific functionality is greatly improved due to the stability of large-diameter nanotubes. For example, by taking advantage of the mechanical strength of large-diameter SWNTs, we have aligned SWNTs by stretching the nanotube containing soot, as shown in Figure 4. Large diameter nanotubes also have stronger van der Waals surface forces,[12] and this larger binding energy is advantageous for applications such as scanning probe microscope tips. A fullerene physically bonded to a SWNT in vacuum is demonstrated in Figure 5.

Discussion

The catalytic properties possessed by various elements naturally suggest that tuning the growth conditions should allow
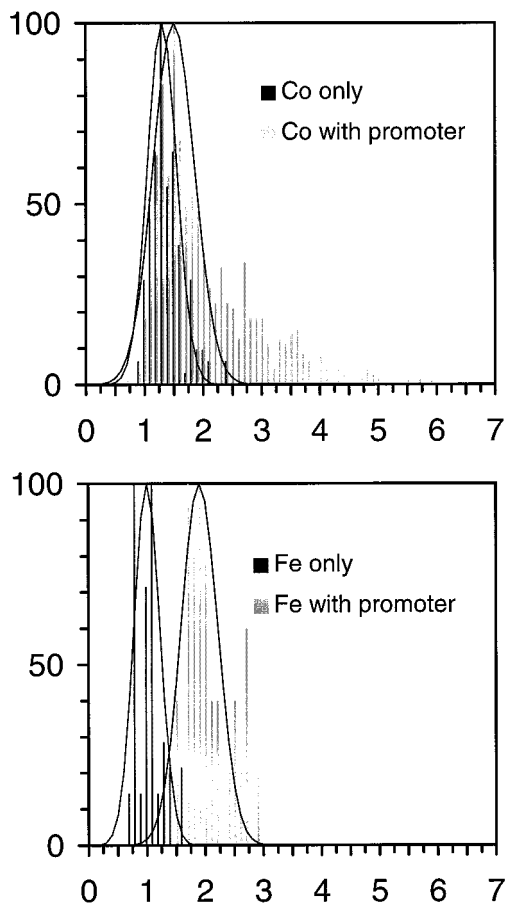

Figure 3. Histograms of diameter distributions of SWNTs produced by (a) Co and Co with promoters (S, Bi, and Pb) and (b) Fe and Fe with promoter (Bi). Solid lines are Gaussian curves fitted to the distributions. Adding catalyst promoter increases the yield and results in formation of large-diameter SWNTs.
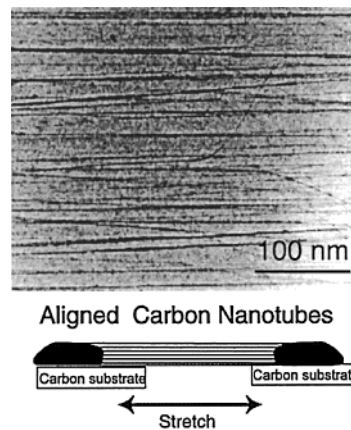

Figure 4. (a, top) Single-walled carbon nanotubes aligned by stretching the nanotube containing soot as depicted in (bottom). Isolated and bundled SWNTs are supported at both ends while hanging across a micrometer-wide space.

one to optimize the production of SWNTs. In contrast to laser ablation[21] and other arc methods,[22] our method produces large amounts of SWNTs with a variety of diameters and helicities. For example, the method reported by Journet et al. using Ni and Y to synthesize SWNTs in an arc[22] produces a high percentage of SWNTs only in the soot deposited around the cathode, which constitutes less than 5% of the total product. Mixtures of single-walled and multiwalled carbon nanotubes in the soot produced by the CVD method[23] imposes difficulty
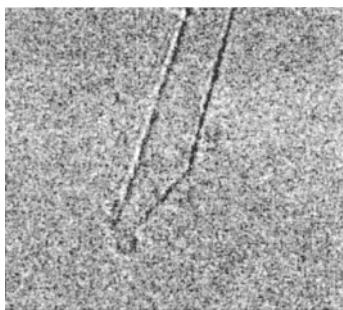
Figure 5. C_{60} molecule attached to a 2 nm diameter SWNT by van der Waals forces.

when studying the properties of these materials since there is no technique for separating single-walled from multiwalled nanotubes to date. Moreover, catalytic synthesis with different elements produced SWNTs with considerably larger diameters, in contrast to a relatively small change in diameter distribution achieved by altering oven temperatures using laser vaporization. In addition, our robust arc method produces high yields of SWNTs, and the setup can easily be scaled up for cost reduction.

The effect of different chemical elements on the growth of SWNTs should provide opportunities for both optimizing the synthetic process and understanding the growth mechanism. Different promoters having similar catalytic effect suggests that growth of SWNTs is dominated by factors that are intrinsic to the mechanism. Thus only modifying the reaction pathway can significantly alter the distribution, whereas changing reaction environment may only fine-tune the distribution. According to the polyyne nuclear growth model,[24] SWNTs grow in the gas phase, where planner carbon rings are the nuclei for tube formation. Low-yield SWNTs produced by Fe may be the result of a high reaction barrier of tubes growing from small carbon rings, and larger rings face the increased reaction probability of forming fullerenes. The effect of promoter is to obstruct the competing reaction pathways, perhaps by preventing rings from assembling into cages, thereby facilitating tube growth.

Large-scale production of exclusively single-walled carbon nanotubes in high yields is a crucial step toward future advances in carbon nanotube research. A credible growth model should be able to explain the effect of catalyst promoters and allow the formation of a wide range of SWNT structures. We hope the present research results lead to a better understanding of the SWNT growth mechanism and further development of a chemical route to a controlled synthesis of single-walled carbon nanotubes.

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