

Preparation and Characteristics of Carbon Nanotubes Filled with Cobalt

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Carbon nanotubes filled with long continuous cobalt nanorods or nanoparticles were synthesized by a simple catalytic process. $\text{Co}(\text{CO})_3\text{NO}$ was used as the precursor and served as both the source for the carbon nanotubes and for the cobalt, the catalyst. Some nanotubes filled with nanorods have big heads. The Co-filled nanotubes can be separated easily from the products by using a permanent magnet. The average diameter of the multiwalled nanotubes is about 40 nm. The cobalt nanorods are a few micrometers long with a diameter of 20 nm. In addition, some long, ribbonlike structures of flattened nanotubes were also observed in the product mixture. After sonication of the product mixture, a small number of nanotube rings with cobalt nanoparticles were found. X-ray diffraction analysis shows the cobalt nanorods encapsulated in the carbon nanotubes as having an fcc and not the stable hexagonal structure. A growth mechanism for these filled nanotubes is proposed. XPS and Raman spectrum were also employed to analyze the products. The dc magnetic measurements were conducted to test for its magnetic properties.

Introduction

Since the discovery of carbon nanotubes, interest was sparked by the possibility of inserting materials into the core volume of nanotubes¹ in order to produce nanorods (or nanowires), composite fibers, and microcrystals in a confined configuration. This interest has been driven chiefly by the potential applications of filled nanoparticles in areas as diverse as magnetic recording, nuclear medicine, and environmental protection.^{2–4} Different methods of synthesis have been attempted and various materials encapsulated have been tested,⁵ in particular those involving magnetic or ferromagnetic materials.

Cobalt-filled carbon nanoparticles or nanotubes were recently prepared and studied by several groups.^{6–10} However, all of the above studies were based on the materials prepared by the conventional arc or modified

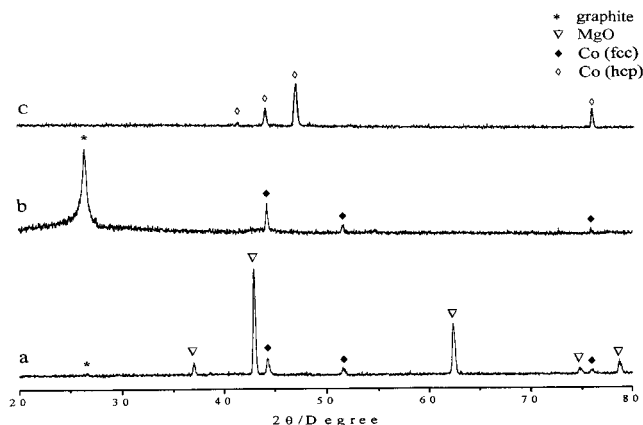


Figure 1. X-ray diffraction pattern of the sample: (a) as-prepared sample and (b) after treatment with concentrated HCl. (c) Co was separated from the products after aging for 4 days at room temperature.

arc method. Guerret-Plecourt and co-workers were the only group to report the preparation of cobalt nanorods encapsulated in nanotubes.⁶ They used the arc-discharge method for their fabrication. Their cobalt nanorods, however, were short, having only a 200 nm length. Chemical methods to synthesize cobalt-filled carbon nanoparticles or nanotubes were also recently attempted.^{11,12} Organometallic precursors were success-

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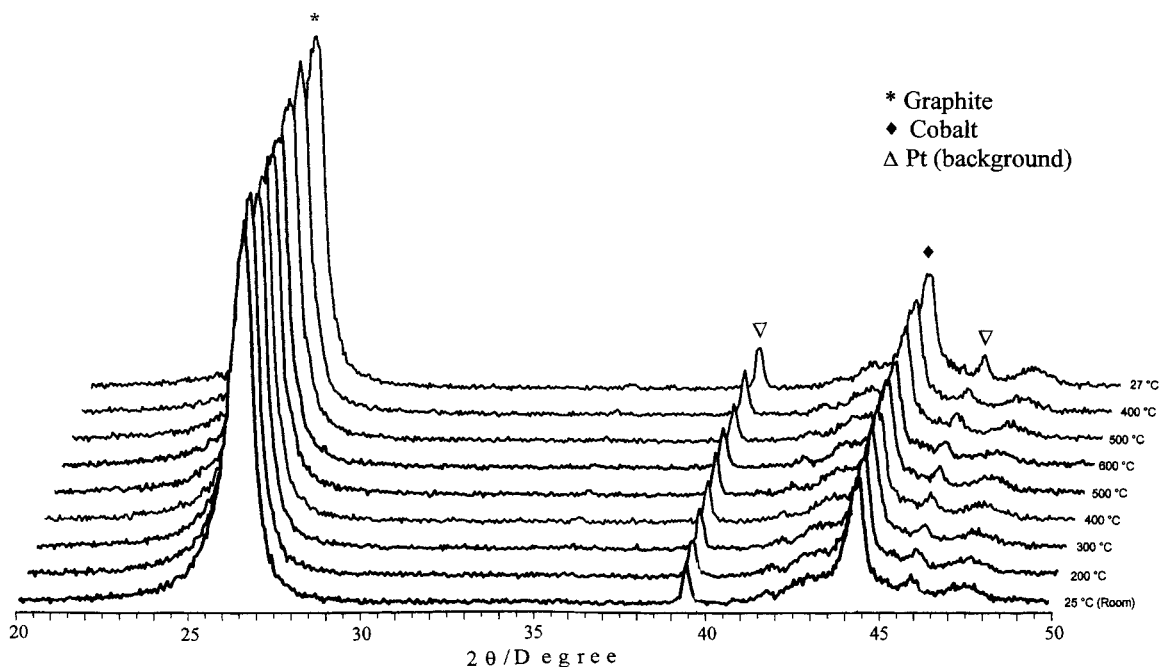


Figure 2. X-ray diffraction patterns of the sample treated with HCl, as a function of temperature. The two Pt peaks found in the spectra are due to a Pt plate that was used as the sample holder.

fully used as sources for the carbon and the metal and yielded carbon nanotubes, some of them filled with materials.^{12,13} Up until now, we have not found a report in which long continuous cobalt nanorods inside carbon nanotubes were synthesized.

In the current paper, we report a simple method to synthesize multiwalled carbon nanotubes (MWNTs) filled with long continuous cobalt nanorods. The 3d transition metals are known for their efficient production of single-walled and multiwalled nanotubes.¹⁴ For this reason, we chose $\text{Co}(\text{CO})_3\text{NO}$ as our precursor. These molecules, on decomposition, not only act as a source of carbon, but also give rise to small metal clusters or particles which act as catalysts in the formation of the nanotubes. The average diameter of the tubes is 40 nm. Both tubes filled with cobalt nanorods and tubes filled with cobalt nanoparticles were found in our experiments.

Experimental Section

The synthesis was carried out in a 2 mL closed vessel cell which was assembled from stainless steel Swagelok parts. A $\frac{3}{8}$ in. union part was capped from one side by a standard plug. For this synthesis, 400 mg of magnesium powder and 700 mg of $\text{Co}(\text{CO})_3\text{NO}$ were placed in a cell at room temperature. The vessel was then immediately closed tightly, because $\text{Co}(\text{CO})_3\text{NO}$ is an air-sensitive material, and heated at 900 °C for 3 h. The reaction takes place at the autogenic pressure of the precursors. After cooling to room temperature, there was no pressure inside the vessel. The products were treated with 50 mL of 8 M HCl at 70 °C for 1 h and then left overnight at room temperature. Finally, a black, sootlike product was obtained after filtering and washing processes. The cobalt-filled nanotubes can be easily separated from the products by using a magnet.

MWNT rings were prepared by ultrasonic irradiation. The as-prepared sample was suspended in 2-propanol, using 2 h of sonication with low-power ultrasound (~ 150 W).

Transmission electron microscopy (TEM) was performed using a JEOL JEM-1220. High-resolution transmission electron microscopy (HRTEM) was also carried out using a Phillips CM-120 microscope operating at 120 kV. Specimens for TEM and HRTEM were dispersed in ethanol in an ultrasonic bath for a period of 10 min and then loaded onto copper grids (200 mesh).

Raman spectroscopy was carried out at room temperature using a Renishaw Raman spectrometer equipped with a 514.5 nm He/Ne laser. The measurements were carried out in a standard backscattering geometry, with a laser power of 2.5 nW focused on a spot of ca. 1 mm in diameter. Several locations of each sample surface were probed to ensure the reproducibility of the data. X-ray photoelectron spectroscopy (XPS) was recorded using an AXIS, HIS, 160, ULTRA (KRRATOS ANALYTICAL).

The dc magnetic measurements in the range of 5–300 K were performed using a commercial (Quantum Design) superconducting quantum interference device magnetometer (SQUID).

Results and Discussion

XRD. The as-prepared powder was characterized by X-ray powder diffraction (Figure 1a), and the main peaks were identified as those of MgO (JCPDS 45-946) and fcc metallic cobalt (JCPDS 15-806). After dissolving the powder in concentrated HCl (8 M), MgO and most of the metallic cobalt features disappeared. Therefore, the graphite peaks became the dominant peak (Figure 1b), while the fcc cobalt patterns revealed weaker diffraction peaks. On the basis of the XRD patterns, the following mechanism is proposed. In the first step, $\text{Co}(\text{CO})_3\text{NO}$ is decomposed into Co, CO, and NO. Subsequently, CO reacts with Mg to yield MgO and carbon.

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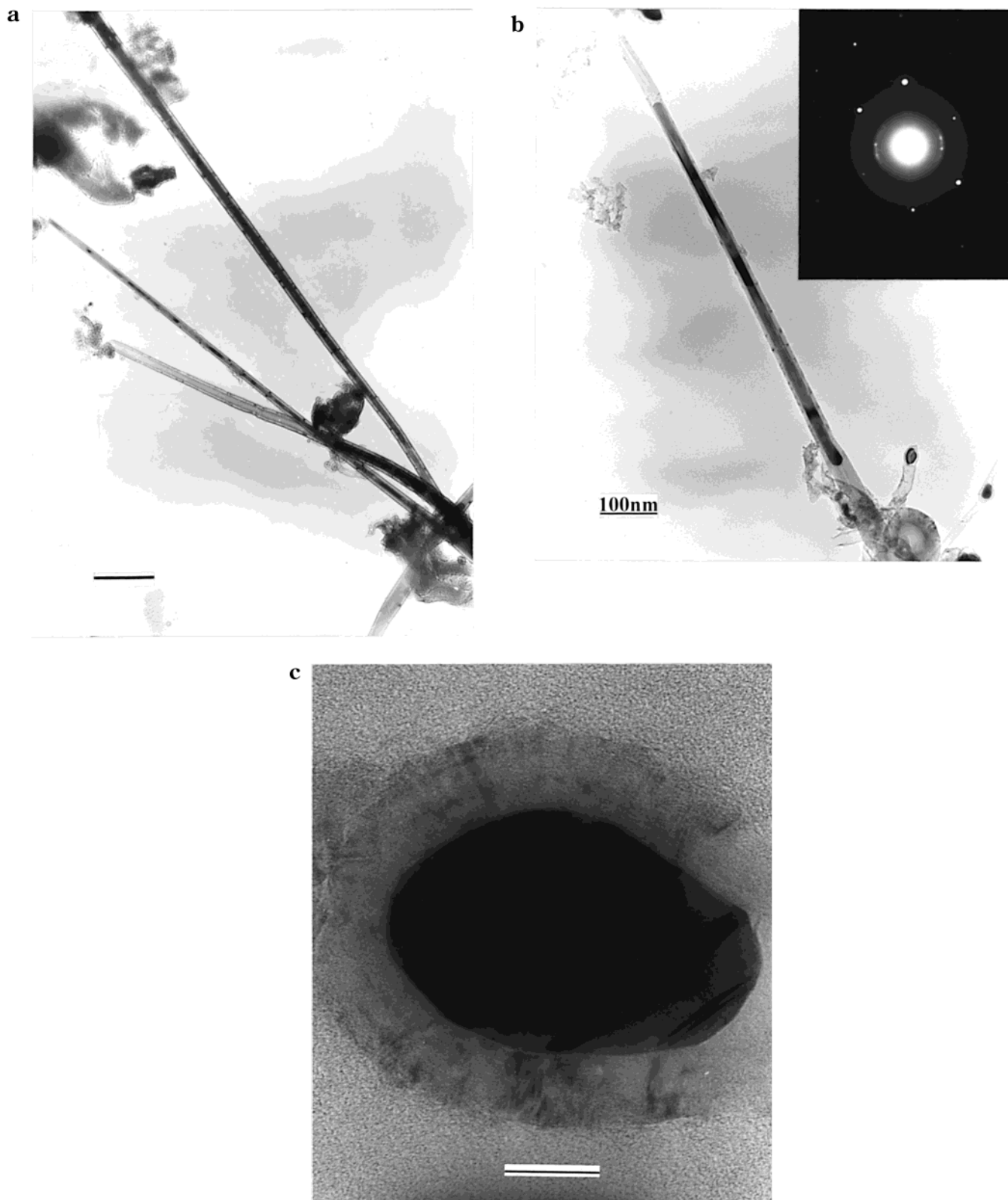
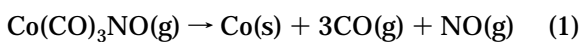


Figure 3. TEM image of carbon nanotubes filled with cobalt nanorods and nanoparticles. (a) The nanotubes filled with long continuous nanorods and partial filled nanotubes. Scale bar: 500 nm. (b) Nanotubes filled with nanoparticles or nanorods, and carbon onion filled with a nanoparticle. The inset is a selected area electron diffraction pattern of a Co wire. (c) HRTEM image of a nanoparticle in the top of a nanotube. Scale bar: 20 nm.

The reactions are as follows:



During carbon formation, Co plays the role of catalyst for the creation of nanotubes. At the same time, part of the metallic Co produced by the decomposition of the precursor is encapsulated in the carbon shells. The cobalt which is not encapsulated in the carbon shells

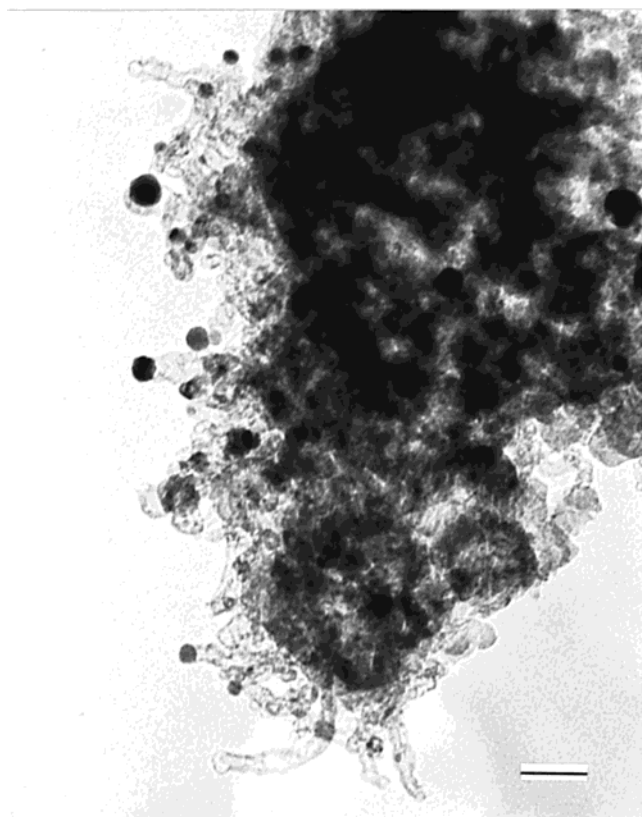


Figure 4. The sample produced from $\text{Fe}(\text{CO})_5$ precursor is just beginning to form the nanotubes at 900°C . Scale bar: 50 nm.

and which exists as metallic-colored beads can be easily separated from the other components, depending on the densities. When the gray-black product is put into HCl solution, several Co beads can be seen and separated by decantation. Using a pair of tweezers, one can even pick up the larger ones, which are on the scale of a millimeter. Co–MgO or Ni–MgO mixtures are known to catalyze carbon nanotubes formation in the decomposition of CH_4 or CO .^{10,11} It is therefore suggested that MgO is also reacting as a catalyst in the carbon nanotube formation. The X-ray diffraction patterns (Figure 1a,b) show that the sample contains small amounts of Co, even after protracted treatment with concentrated HCl. This implies that Co is encapsulated inside the carbon shells. From X-ray diffraction patterns a mean interlayer spacing of 0.338 nm is measured. This value is slightly smaller than that of previous reports (0.34 nm),¹² but slightly larger than the single-crystal graphite value (0.335 nm).

To understand why the fcc Co can exist in the nanotubes, we separated the cobalt which is not inserted in the carbon shells and measured its XRD diffraction. It was found that these samples are easily converted into hexagonal Co after aging for few days at room temperature. In Figure 1C we present the XRD diffraction pattern of the Co which was removed from the CNT and aged for 4 days. The fcc Co encapsulated in the nanotubes, however, exists unchanged for a few months. Furthermore, the results of temperature-dependent XRD measurements show that there is no hexagonal Co, even in the process of cooling (see Figure 2). There are considerable differences in the dimensions of the unit cells of the hexagonal and fcc Co. The length of the

cube edge in the fcc phase is 3.5447 \AA (JCPDS 15-806), while the dimensions of the hexagonal cell are $a = b = 2.5031 \text{ \AA}$, $c = 4.0605 \text{ \AA}$ (JCPDS 5-727). The changes from the fcc to the hexagonal phase would require space. These changes are hindered by the walls of the CNT. Probably the nanospace in the tubes is too narrow for such a phase transition. In other words, the nanotube walls may hinder the conversion of the fcc Co to the stable hexagonal phase. We anticipate that carbon nanotubes may be used in the future to store some unstable materials at room temperature.

TEM. A typical electron micrograph (Figure 3) of the HCl-treated product shows nanotubes filled with long cobalt nanorods or small cobalt nanoparticles. Part of the nanorods are successively connected and have a length of up to several microns (see Figure 3a). The distribution of the Co content is such that roughly 10–20% of the Co is found inside the CNT, while the other 80–90% is outside the tubes. After HCl treatment all the Co is found inside the CNT. The percentage of the Co-filled CNT out of the total number of nanotubes is estimated at about 7%. The average diameter of the multiwalled nanotubes is about 40 nm. The cobalt nanorods are a few micrometers long with a diameter of 20 nm. The average number of the layers of the multiwalled nanotubes is about 30–40. Inside those nanotubes we also observe Co nanoparticles. Their sizes vary from several to tens of nanometers. They can be found either in the center of tubes or at the ends of the tubes. Figure 3c is a high-resolution TEM image of a nanoparticle at the end of a nanotube. There are about 30 layers in the tube. A SAED (selected area electron diffraction) of a nanorod encapsulated in the center of the carbon nanotubes is presented as an inset in Figure 3b. Surprisingly, the dots in the electron diffraction picture correspond to hexagonal Co rather than to the fcc phase detected in the XRD. We have also found that when the electron beam was focused on the cobalt nanorods, sometimes the image density of the nanotubes changed. The driving force for the change of the as-prepared fcc Co to the more stable hexagonal phase is probably due to the irradiation by the electron beam during the TEM measurement. In addition, the majority of the structures imaged by TEM are shown in Figure 3. We also have observed some long, ribbonlike structures of flattened nanotubes¹⁵ as part of our product.

Cobalt is a more effective catalyst than iron in the formation of carbon nanotubes. As a comparative test, we did a similar experiment, using $\text{Fe}(\text{CO})_5$ at the same temperature. We observed shapes which look like nanotubes at the early stages of their formation (see Figure 4). The ends of these nanotubes were decorated with iron nanoparticles. Even at 1000°C , the graphitization of nanotubes is not completed.

Ring Formation. Single-walled and multiwall nanotube rings were fabricated recently by several groups.^{16–18} We also prepared a small number of MWNT rings by

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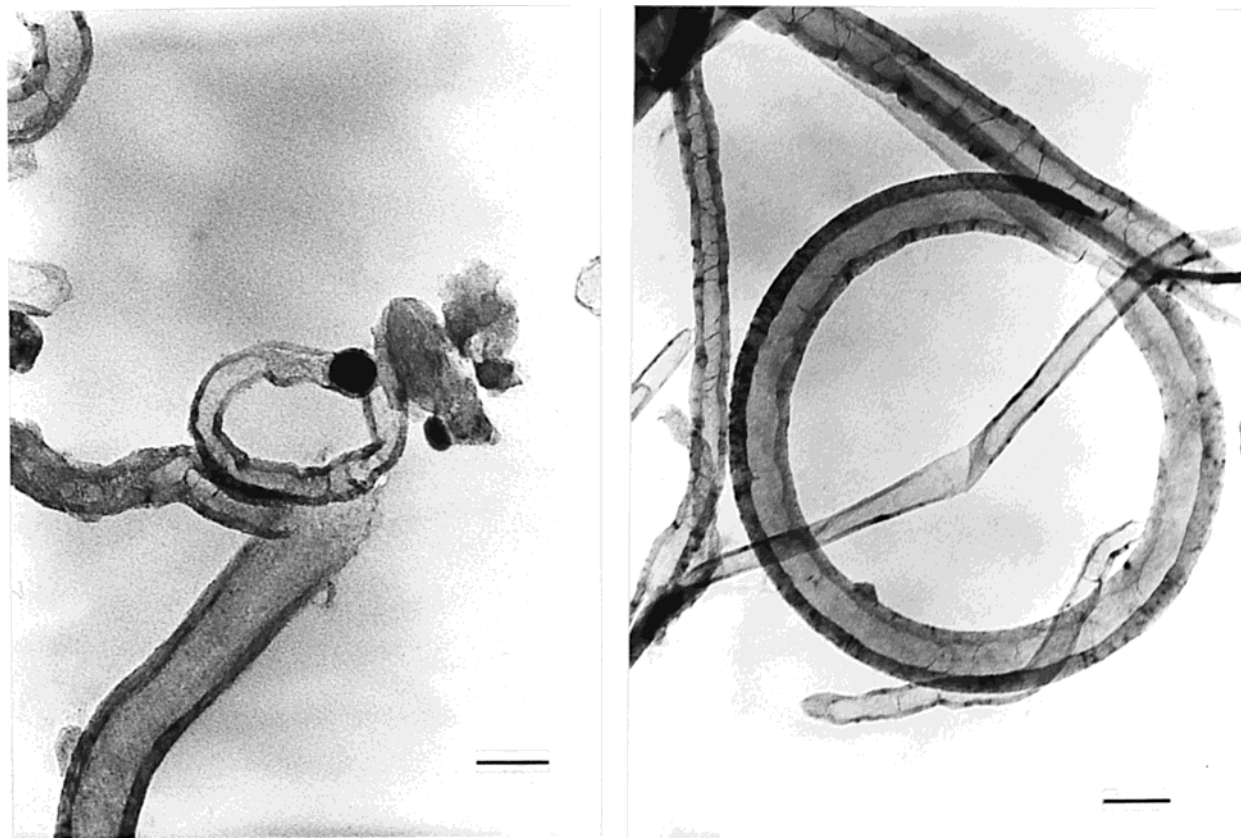


Figure 5. (a) A nanotube filled with a Co nanoparticle was folded into a ring after sonication for 2 h. Scale bar: 50 nm. (b) A TEM image of an almost perfect coil formed from an empty and opened nanotube. Scale bar: 50 nm.

sonication. However, we failed to obtain the rings with cobalt nanorods. This is probably because the nanotubes filled with nanorods are too stiff to be bent. We only find nanotube rings which are empty or filled with nanoparticles. Figure 5 shows two TEM images of carbon nanotube rings. Figure 5a shows a ring with a diameter of 150 nm; in the tube there is a cobalt nanoparticle. In Figure 5b we present a TEM image of an almost perfect coil with a diameter of 400 nm. The precursor for the formation of this coil is an empty nanotube. It is easy to see that the ends of the tube are obviously open. The rings resulting from the actions of bubbles generated by ultrasound waves, which cause carbon nanotubes to curl up spontaneously into rings and form weak van der Waals interactions, which keep the tubes from folding onto themselves.¹⁶ In Figure 5b, however, there are not such van der Waals interactions between the two ends of the tube. This result supports the proposal that twisting pair defects must be present in the MWNTs.^{16,17}

XPS and Raman Spectra. The XPS spectrum detected for the carbon nanotubes identified only pure carbon (no Co signal). This result is not consistent with the TEM results, indicating that metallic Co is contained within the carbon nanotubes or encapsulated by Graphotec shells. Furthermore, XPS measurements show that the C-1s electron binding energy in the carbon nanotubes is 284.6 eV, which is slightly higher than that of graphite, 284.3 eV (see Figure 6), and the peak width is much narrower, when compared with graphite. The obvious reason for the absence of the cobalt spectrum is due to the fact that the XPS mostly monitors the surface area. The outer cobalt layer can be found as deep

as 10 nm from the surface, and therefore, it is not observed in the XPS spectrum.

Figure 7 is the Raman spectra of the product. The first-order Raman spectrum shows a strong Raman band at 1577 cm^{-1} , which is located between the value for highly oriented pyrolytic graphite (1580 cm^{-1}) and that of carbon nanotubes and nanoparticles (1574 cm^{-1}).¹⁹ This difference probably arises because the products are different than those of Ebbesen's measured sample.^{19,20} This can also support the idea that the carbon nanotubes have a nearly perfect crystalline structure. An additional strong Raman band appears at 1315 cm^{-1} , which is shifted considerably from the 1346 cm^{-1} observed for carbon nanotubes.¹⁹ The explanation for this shift is not clear yet. In the second-order Raman spectrum, the band located at 2637 cm^{-1} can be assigned as an overtone of the first-order mode at 1315 cm^{-1} .

Growth Mechanism. There is widespread agreement about how a nanotube lengthens, once it has nucleated from a metal particle. It seems to be generally accepted that metallic particles act as catalysts for the graphitization of carbon present in the vapor phase. The carbon then forms a hemispherical graphene cap on the metal particle and the nanotubes grow from such a graphene cap.²¹

Usually, catalytic particles have certain sizes which do not increase when carbon nanotubes are forming. In

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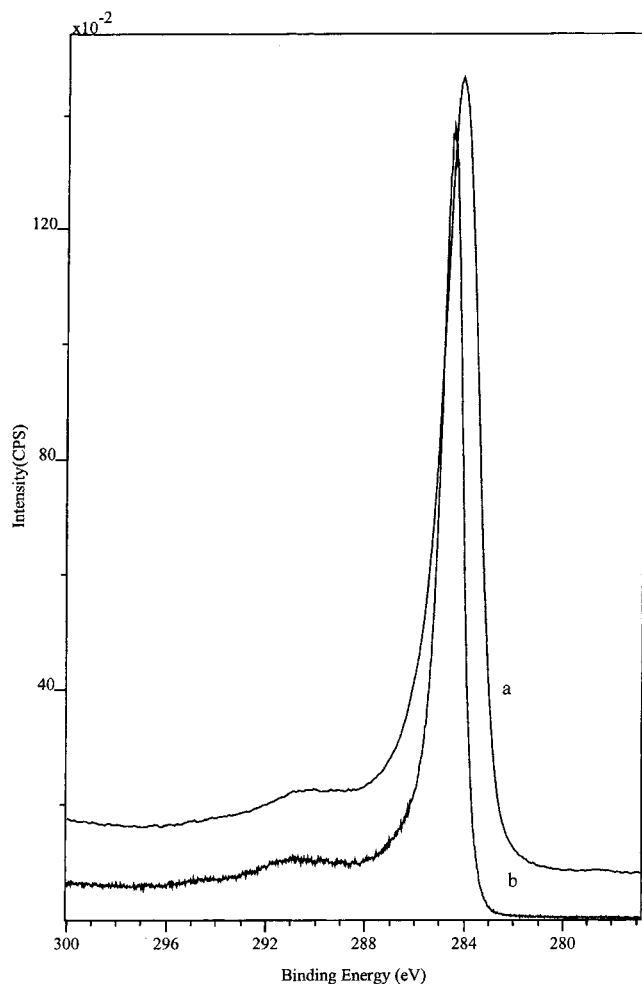


Figure 6. XPS spectra of C-1s electron binding energy peaks in (a) pure graphite and (b) as-prepared nanotubes.

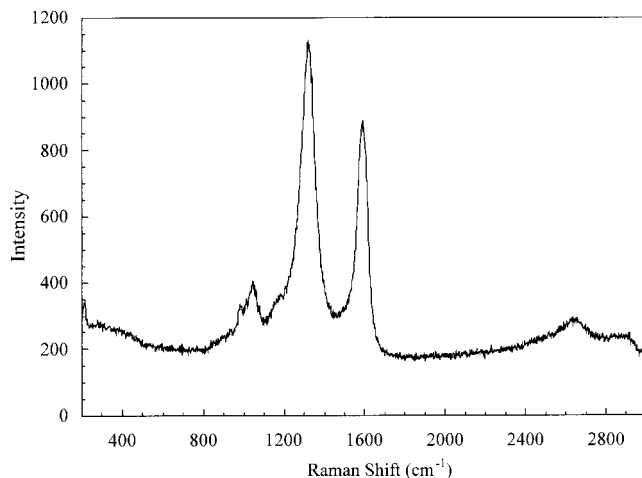


Figure 7. Raman spectrum of the as-prepared sample (laser excitation at 514.5 nm).

our experiments, however, the carbon and the catalyst are almost formed simultaneously. At the beginning, the metal particle is only a few nanometers in diameter. Such a particle contains a very high percentage of surface atoms, creating a tremendous surface energy per atom. There are two ways to decrease this surface energy. One of them is when carbon assembles as a graphene cap on the particle surface, with its edges strongly chemisorbed to the metal. The other way is



Figure 8. The cobalt nanorods with "heads" were found in the nanotubes. Scale bar: 1000 nm.

when an excess of cobalt continues to grow onto the particle. This growth is prepared in the longitudinal mode and involves the simultaneous growth of the carbon in the same direction.

The mechanism by which the cobalt-embedded nanotubes are synthesized is as follows: the decomposition of the gas-phase cobalt precursor occurs at the elevated temperature. It leads to the formation of a small nanoparticle of cobalt. This cobalt cluster serves as a nucleation center for the carbon, which is formed by the reduction of the CO residue by the magnesium atoms. The carbon wraps around the cobalt clusters, forming a cylinder around them. A slight edge of the cobalt cluster protrudes from the coated particle, so that when the cobalt is further deposited, it causes the wire to grow in a specific direction. The carbon thus follows, and the tube continues growing along the cylindrical axis.

The formation of a nanotube seems to require a suitable diameter of catalytic particles. Only when the diameter is smaller than a certain value, can the nanotubes be formed. Figure 8 supports such a view. This photo shows some interesting nanorods with big "heads" encapsulated in carbon nanotubes.

Magnetic Properties. Figure 9 shows the low-field magnetization measured in the zero-field-cooled process. The rise in the $M(T)$ curve proves unequivocally that no magnetic transition is observed in this temperature range. Thus the sample is ordered at much higher temperature. Since we did not reach the magnetic transition, the field-cooled aspect was not measured. The inset shows the isotherm magnetization of up to 2.5 T, measured at 275 K. The rise in the low applied field and the saturation achieved around 1 T is typical for a ferromagnetic material. The saturation moment obtained is 8.4 emu/g, a value which is ~5% of the

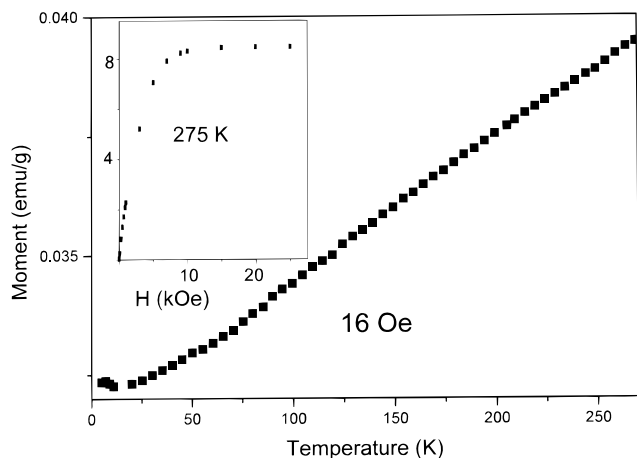


Figure 9. The results of the dc magnetic measurements in the range of 5–300K.

saturation moment for pure Co at 300 K. This is consistent with our determination that the percentage of the Co in the carbon nanotubes is about 7% only.

Conclusion

We have found that Co catalyzes the formation of

multiwall carbon nanotubes filled with long continuous nanorods or nanoparticles of Co. This is obtained by using $\text{Co}(\text{CO})_3\text{NO}$ as a precursor. The synthetic method is very simple, and the catalyst is generated in situ. The restriction imposed by the walls of the nanotubes is responsible for the fcc cobalt existing inside the nanotubes as a stable state. The nanotube with a head filled with cobalt was also found in the products. It has been found that nanotubes filled with cobalt nanorods are difficult to fold into rings by sonication. This synthetic method may be applicable to the synthesis of carbon nanotubes in large quantities and also of cobalt-filled carbon nanotubes, which might be used as special magnetic materials in the future.

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