Growth of Conical Carbon Nanotubes by Chemical Reduction of MgCO₃

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Received: October 10, 2004; In Final Form: April 1, 2005

Carbon nanotubes were synthesized by chemical reduction of magnesium carbonate with metallic lithium at 600 °C. The nanotubes with an average length of 13 μ m and diameter of 60 nm are made of short coaxial conical cylinder tubular graphite sheets with their cone axis parallel to the tube axis, different from the ordinary carbon nanotubes, composed of concentric cylindrical graphite layers with their normal perpendicular to the tube axis. It is suggested that nanoscale rough surface of lithium formed at the interface between supercritical carbon dioxide and liquid lithium takes the roles of both the reductant for reduction of carbon dioxide to carbon and the template for growth of carbon nanotubes.

Introduction

Carbon nanotubes (CNTs) have attracted much attention from the fields of physics, chemistry, and materials science and from some high-tech firms because carbon nanotubes possess remarkable physical and chemical properties such as metallic or semiconductor performance, excellent mechanical strength, capability of storing H₂, adsorptive ability, and good adsorption of microwaves.¹⁻³ Various commercial applications including carbon nanotube electronics,⁴⁻⁵ high-strength polymer composites,^{6,7} and hydrogen storage⁸ have been demonstrated. So far, fabrication methods developed involve arc discharge,⁹ laser vaporization of graphite,^{10,11} pyrolysis,¹² and metal-catalyzed chemical vapor deposition (CVD) of hydrocarbons.¹³⁻¹⁴ All these methods produce CNTs in milligram to gram quantities. For example, CVD can produce carbon nanotubes by catalytic pyrolysis of hydrocarbons with a quantity of 0.5 g per day. However, a lot of potential applications require kilogram to ton quantities of CNTs in high purity and at low cost if they are to achieve industrial viability. For example, a practical approach to producing CNT composites is by shear mixing of CNTs into polymer matrixes followed by extrusion or injection molding. Sufficient dispersion has been found to be the key in realizing the potential of these unique nano reinforcements.¹⁵ Therefore, a simple and effective chemical process is expected for mass production of such a material.^{16,17}

On the other hand, graphite consists of two-dimensional sheets of graphite, arranged in a hexagonal lattice. An ordinary carbon nanotube is formed by rolling up such a sheet. We believe that other types of pure carbon nanotubes are feasible. For example, rolling of trapezoidal or conical graphite sheets could lead to the formation of conical carbon nanotubes, which would enrich families of carbon nanotubes.

The aim of the present work is to develop a method for preparation of carbon nanotubes in large quantities using carbonate as the carbon source, which is easily handed for industrial CNT production. Carbon nanotubes with novel structure are also expected to be produced by this approach.

Experimental Section

Magnesium carbonate was used as the carbon source and metallic Li as the reductant to synthesize CNTs. The reaction was carried out in a stainless steel autoclave (10 mL). A typical reaction used 5.0 g of magnesium carbonate and 0.5 g of metallic Li; they were placed in a cell at room temperature. The vessel was then immediately closed tightly and heated to 600 °C, and kept at this temperature for 10 h. The reaction took place at an autogenic pressure depending on the amount of reactant added. After cooling to room temperature, solid product was collected and treated in 6.0 mol/L HCl aqueous solution at 70 °C for 6 h. A microfilter was used to collect the precipitate that was then washed with ethanol and dried in air, yielding about 0.16 g of product.

X-ray diffraction (XRD) analysis was performed on a Rigaku (Japan) D/max-rA X-ray diffraction meter equipped with graphite monochromatized Cu K α radiation ($\lambda = 0.154$ 178 nm). The morphology of the samples was observed on a field emission scanning electron microscope (FESEM) (JEOL-6300F, 15 kV). Transmission electron microscopic (TEM) images and electron diffraction (ED) patterns were taken on a Hitachi H-800 transmission electron microscope. The microstructure of carbon nanotubes was analyzed by high-resolution transmission electron microscopy (HRTEM), which was performed on a JEOL-2010 transmission electron microscopic analysis was carried out on a LABRAM-HR confocal laser micro-Raman spectrometer at room temperature.

Results and Discussion

The solid product, weighing 0.16 g, was confirmed containing CNTs, graphite, and amorphous carbon. CNTs accounted for

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Figure 1. FESEM image of the product produced at 600 °C. The boxed areas depict tubular structure.



Figure 2. TEM image of typical carbon nanotube of sample before washing. The inset is the electron diffraction pattern of the nanotube. The nanotube at the end contains lithium as verified by EDS.

about 75% of the product, and the other products were graphite and amorphous carbon, estimated from the images of FESEM.

Only one X-ray diffraction peak was assigned to graphitic (002) at $2\theta = 26.2^{\circ}$. Detected for the product after digestion with HCl, the peak exhibits a relatively broadening feature (not shown). It is known that the separation of the interlayer in CNTs is about 3.40 Å, larger than the 3.35 Å of graphite,¹⁸ which would move the diffraction peak to a lower angle; there also exists a distribution of the separation between the interlayer due to CNTs with different diameters.¹⁹ Therefore, the broadening of the diffraction peak indicates the formation of CNTs in the reaction. This can be confirmed by FESEM and TEM analysis.

Figure 1 shows that large amounts of CNTs were formed. They are uniform with an average diameter of 55 nm. The boxed areas of Figure 1 depict clearly the tubular structure with opened caps. A TEM image of a typical nanotube reveals that the diameter and the length of it are about 60 nm and >13 μ m, respectively [Figure 2], resulting in an aspect length-to-diameter ratio of more than 200. Unlike the straight feature of those produced by the arc/plasma technique,⁹ the nanotubes in our product tend to form loops. The electron diffraction pattern for the nanotubes shows a diffraction ring corresponding to (002) (inset of Figure 2); the broadening of the diffraction ring is obvious due to the rolling of graphitic layers, which agrees well with XRD results.

The Raman spectrum for the sample is shown in Figure 3. Two peaks around 1350 cm⁻¹ (D-band) and 1580 cm⁻¹ (G-band) were detected. The peak at 1580 cm⁻¹ (G-band) corresponds to an E_{2g} mode of graphite and is related to the vibration of sp²-bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphitic layer.¹⁸ The D-band around 1350 cm⁻¹ is associated with the presence of defects in the hexagonal graphitic layers. The intensity of the D-band is known to be



Figure 3. Raman spectrum of as-prepared carbon nanotubes.

high for badly graphitized materials. The inverse of the I_D/I_G intensity ratio between the G- and D-bands serves as a measure of the graphitic ordering and indicates the approximate crystalline size in the hexagonal plane, L_a ,^{20–22} which is related to the length of pristine graphitic multiwalls in the CNTs. The calculation using the formula $L_a = 44(I_D/I_G)^{-1}$ yields values of around 1.2 μ m, much shorter than the maximum length of the carbon nanotubes observed in the TEM and SEM images. The conical structure of the carbon nanotubes should be responsible for this difference, which will be discussed later in this paper.

At 600 °C, magnesium carbonate rapidly decomposes to give off MgO and CO₂. The pressure at 600 °C is about 780 atm, which indicates CO₂ being in supercritical state (31 °C, 73 atm). To examine the effects of the type of carbon source on the products, (NH₄)₂CO₃, MnCO₃, or NiC₂O₄ was selected to substitute for MgCO₃. It was found that well-crystallized carbon nanotubes were also formed. It is reasonable to suggest that other carbonates or oxalate, whatever can decompose and give off CO₂ gas at relatively low temperatures, can be used as the carbon source to prepare CNTs by this approach. To further examine the catalytic role of the stainless steel wall, a reaction was also carried out in a copper cell. CNTs were also observed by TEM. Independent of CNT formation on the wall, the materials of the reaction cell make us rule out the possibility that metal atoms of the cell wall catalyzed the formation of CNTs. Energy dispersive spectroscopic (EDS) analysis on the composition of these nanotubes shows that they contain only carbon. However, Li was detected at the end (boxed area in Figure 2) of the nanotubes, which indicates that nanoparticles of metallic Li play a critical role in the one-dimensional growth of CNTs.

Figure 4 gives the HRTEM image of a typical carbon nanotube. The nanotube is imaged to have nearly parallel lines, which are graphite atomic planes separated by 0.34 nm (bottom insets of Figure 4). This is almost the same as that in ordinary carbon nanotubes. However, it is found that the graphite layers are not arranged parallel to the axis of the nanotube, which is different from that in ordinary carbon nanotubes: the graphite layers are arranged along the axis of the nanotubes. It is known that the result of a diffraction experiment depends very much on the orientation of the nanotube in the area of the diffraction. However, it seems that the above HRTEM image shows the intrinsic structure of the carbon nanotubes because it is found that the inner surface is coarse due to the length difference of graphite sheets, which is not identical to common carbon



Figure 4. HRTEM image of one typical nanotube grown on the nanoprotrudent. The bottom insets show the enlargement of the boxed regions of both sides of wall, showing that the graphite layers are not arranged parallel to the axis of the nanotube. The center inset shows the structure model of the nanotubes consisting of coaxial conical cylinder tubular graphite sheets.



Figure 5. Polarized Raman spectrum of as-prepared carbon nanotubes. The polarization direction of the incident and scattered light is (A) parallel and (B) perpendicular.

nanotubes, indicating the formation of CNTs with a novel structure instead of common carbon nanotubes. To further confirm this structure, the CNTs were characterized by Raman scattering with polarized light. It almost always achieves the same result that the signal intensity is larger when the polarization directions of the incident and scattered light are parallel than when they are perpendicular [Figure 5]. Indeed, polarization of the incident and scattered light is not an important issue for a sample of misaligned carbon nanotubes. In other words, there should be no difference in the signal intensity for different polarization directions of the incident and scattered light as scattered light because of the random orientation of CNTs in the sample, which might also be explained by the formation of such a kind of novel structure.

HRTEM reveals that the nanotubes are made of short coaxial cylinder tubular graphite sheets with cone-shaped structure. The apex angle of coaxial cylinders is about 25.2°, which is schematically shown in the center inset of Figure 4. In this structure, the length of graphite sheets is not equal in length to that of nanotubes. This can explain well why the length of the nanotubes calculated using the formula $L_a = 44(I_D/I_G)^{-1}$ from Raman results is much shorter than that observed in FESEM



Figure 6. Schematic diagram of the growth process. In this process, coexistence of dense carbon dioxide and liquid lithium with a nanoscale rough interface, the growth of nanotubes occurred on the nanoprotrudents on the rough interface.

and TEM images. However, a uniform nanotube rather than a cone-shaped appearance is observed because the nanotube consists of conical tubular cylinders rather than elementary cones and the lengths of the graphite conical cylinders remain almost constant, which is different from formerly fabricated coneshaped or bamboo-mode carbon nanotubes.^{23,24} Otherwise, a cone-shaped structure will be caused by a gradual shortening of the length of the graphite sheets along the axial direction from the inner to the outer layer.²⁵ The novel structure of this material would lead to considerable interest in its hydrogen storage and electronic properties, and in the development of advanced nanotube devices for future applications as well. For example, in terms of gas adsorption properties, the carbon nanotube is expected to have improved properties in catalytic and adsorbent materials, because foreign substances might become more easily incorporated into the nanotubes not only by the capillary phenomenon but also due to the stepwise structure in the inner surface of nanotubes acting as active adsorption sites.

High-quality cubic diamond particles as large as $510 \,\mu$ m were synthesized by the reduction of magnesium carbonate with metallic sodium at 500 °C.²⁶ However, in this reaction system, no diamond was detected by XRD analysis and TEM, but a large amount of CNTs was found present in the as-synthesized sample, as shown in Figure 1. Recently we found that using metallic Li as reductant could also lead to the generation of small diamonds.²⁷ Therefore, it is suggested that a higher temperature is not favorable for the diamond but is favorable for CNT formation.

Metallic lithium melts at 180.5 °C, its normal boiling temperature is 1342 °C, the vapor pressure of Li at 600 °C is about 2.4×10^{-2} mmHg. In the supercritical carbon dioxide system, liquid Li might form a nanoscale rough surface with nanoprotrusions (we call nanoprotrusions nanodroplets) at the growth temperature, from which CNTs might grow. A possible growth mechanism is schematically shown in Figure 6. Because the nanodroplets have a continued liquid lithium background and multiwall carbon nanotubes as long as 13 μ m were produced, we think a root-growth process was involved. Li nanodroplets take the roles of both the reductant for CO2 reduction to carbon and the growth templates. It is suggested that CO₂ molecules were adsorbed and reduced on Li droplets. The growth occurred on the slope surfaces of lithium droplets, resulting in the formation of cylinder tubular graphite sheets with the diameter a small increase along the axis of the nanotubes from the root to the top, as illustrated in Figure 6.

This research demonstrates that the complex structure of graphitic concentric shells can be grown by a simple chemical reduction approach starting from magnesium carbonate. Compared with conventional arc discharge and laser vaporization of graphite, and metal-catalyzed CVD process using CO/CH_4 as the carbon source, our approach for the preparation of large quantities of CNTs was carried out by a simple chemical reduction process using carbonate as the carbon source. Carbonate is a quite common industry raw material, easily available and cheap. It is believed that further work could lead to the development of this process to be a carbon nanotube industry production method.

Conclusions

In summary, large amounts of carbon nanotubes with dimensions of 13 μ m × 60 nm were fabricated by reduction of magnesium carbonate with metallic Li at 600 °C. The nanotubes were found to be made of short coaxial conical cylinder tubular graphite sheets, arranged to align along the axis of carbon nanotubes, different from the structure of conventional carbon nanotubes by rolling of graphite sheets. The carbon source is carbonate, which is quite common and easily available in industry. Combined with the fact that the operation process is simple, it is believed that the process could be scaled up for industry production of carbon nanotubes with novel structure. Moreover, the novel structure of this material would create considerable interest in its hydrogen storage and electronic properties, and in the development of advanced nanotube devices for future applications as well.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (20321101, 20125103 and 90206034).

References and Notes

- (1) Iijima, S. Nature 1991, 354, 56.
- (2) Ajayan, P. M. Chem. Rev. 1999, 99, 1787.

(3) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. Science 2002, 297, 787.

(4) Tans, S. J.; Verschueren, A. R.; Dekker, C. *Nature* 1998, *393*, 49.
(5) Tans, S. J.; Devoret, M. H.; Dai, H.; Thess, A.; Smalley, R. E.;

Geerlings, L. J.; Dekker, C. *Nature* **1997**, *386*, 474.

(6) Calvert, P. Nature 1999, 399, 210.

(7) Wagner, H. D.; Lourie, O.; Feldman, Y.; Tenne, R. Appl. Phys. Lett. 1998, 72, 188.

(8) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune, D. S.; Heben, M. J. *Nature* **1997**, *386*, 377.

(9) Ebbesen, T. W.; Ajayan, P. M. Nature 1992, 358, 220.

(10) Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.; Petit, P.; Robert, J.; Xu, C.; Lee, Y. H.; Kim, S. G.; Rinzler, A. G.; Colbert, D. T.; Scuseria, G. E.; Tomanek, D.; Fischer, J. E.; Smalley, R. E. *Science* **1996**, *273*, 483.

(11) Rao, A. M.; Richter, E.; Bandow, S.; Chase, B.; Eklund, P. C.; Williams, K. A.; Fang, S.; Subbaswamy, K. R.; Menon, M.; Thess, A.;

Smalley, R. E.; Dresselhaus, G.; Dresselhaus, M. S. Science 1997, 275, 187.

(12) Amelinckx, S.; Zhang, X. B.; Bernaerts, D.; Zhang, X. F.; Ivanov, V.; Nagy, J. B. *Science* **1994**, 265, 635.

(13) Hafner, J. H.; Bronikowski, M. J.; Azamian, B. R.; Nikolaev, P.; Rinzler, A. G.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett.* **1998**, *296*, 195.

(14) Liu, S. W.; Tang, X. H.; Yin, L. X.; Koltypin, Y.; Gedanken, A. J. Mater. Chem. 2000, 10, 1271.

(15) Andrews, R.; Jacques, D.; Rantell, T.; Qian, D.; Anthony, J.; Bom, D. Presented at the 10th Foresight Conference on Molecular Nanotechnology, October 2002, Bethesda, MD.

(16) Motiei, M.; Hacohen, Y. R.; Calderon-Moreno, J.; Gedanken, A. J. Am. Chem. Soc. 2001, 123, 8624.

(17) Lou, Z. S.; Chen, Q. W.; Wang, W.; Zhang, Y. F. Carbon 2003, 41, 3063.

(18) Reznik, D.; Olk, C. H.; Neumann, D. A.; Copley, J. R. D. Phys. Rev. B 1995, 52, 116.

(19) Kiang, C. H.; Endo, M.; Ajayan, P. M.; Dresselhaus, G.; Dresselhaus, M. S. *Phys. Rev. Lett.* **1998**, *81*, 1869.

(20) Tuinstra, F.; Koenig, J. L. J. Chem. Phys. 1970, 53, 1126.

(21) Kasuya, A.; Sasaki, Y.; Saito, Y.; Tohji, K.; Nishina, Y. Phys. Rev. Lett. 1997, 78, 4434.

(22) Moreno, J. M. C.; Swamy, S. S.; Fujino, T.; Yoshimura, M. *Chem. Phys. Lett.* **2000**, *329*, 317.

(23) Shimizu, Y.; Sasaki, T.; Kodaira, T.; Kawaguchi, K.; Terashima, K.; Koshizaki, N. Chem. Phys. Lett. 2003, 370, 774.

(24) Wang, Y. Y.; Tang, G. Y.; Koeck, F. A. M.; Brown, B.; Garguilo,

J. M.; Nemanich, R. J. Diamond Relat. Mater. 2004, 13, 1287.

(25) Zhang, G.; Jiang, X.; Wang, E. Science 2003, 300, 472.

(26) Lou, Z. S.; Chen, Q. W.; Wang, W.; Qian, Y. T.; Zhang, Y. F. Angew. Chem., Int. Ed. 2003, 42, 4501.

(27) Lou, Z. S.; Chen, Q. W.; Zhang, Y. F.; Qian, Y. T.; Wang, W. J. Phys. Chem. B 2004, 108, 4239.