Large-Scale Synthesis of High-Quality Double-Walled Carbon Nanotubes by Catalytic Decomposition of *n*-Hexane

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Large quantities of high-quality double-walled carbon nanotubes (DWNTs) with very small amounts of amorphous carbon deposits have been produced by catalytic decomposition of *n*-hexane over Fe−Mo/MgO catalyst. More than 90% of the as-synthesized carbon nanotubes was DWNTs. Raman analysis indicated that the outer tube diameter and inner tube diameter of DWNTs were in the range of 1.44−2.53 nm and 0.70−1.82 nm, respectively, and the interlayer spacing ranged from 0.35 to 0.42 nm. Both Raman analysis and HRTEM observation indicated that the as-synthesized DWNTs were of high quality.

Introduction

Since their discovery in 1991,[1] the studies on carbon nanotubes (CNTs) have attracted much attention due to their unique structure and a wide range of potential applications.[2] Recently, much attention has been focused on double-walled carbon nanotubes (DWNTs) because DWNTs, which consist of two concentric cylindrical graphene layers, are interesting geometries for numerous structural and electrical studies.[3] Recent study indicated that DWNTs possess excellent field emission properties, having both merits of single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs), namely, low threshold voltage for electron emission as SWNTs and good emission stability similar to that of MWNTs.[4] Moreover, an inner tube of DWNT can maintain inherent SWNT characteristics after the modification of an outer tube. Large quantities of high-quality DWNTs have been required for fundamental studies and practical applications. There have been some reports on the synthesis of DWNTs by several methods.[5−14] The arc discharge method has been employed to synthesize DWNTs.[5−7] However, it is still difficult to scale up the production of DWNTs using the arc discharge method. The coalescence of C_{60} molecules inside SWNTs has also been used to prepare DWNTs at the temperature of 1200 °C.[8] In this case, the inner walls of DWNTs are not continuous over the entire length of nanotubes. It has been well-known that a chemical vapor deposition (CVD) method is a promising way for the CNT production.[15,16] Recently, the CVD technique using methane and acetylene as carbon sources has been used to synthesize DWNTs by several groups.[9−14] However, most of them showed low yields of DWNTs or low selectivities toward DWNTs. More recently, our group reported the catalytic synthesis of high-quality DWNTs using alcohol (ethanol) and benzene, respectively, as the carbon source over an alumina-supported bimetallic catalyst.[17,18]

There have been a few reports on the synthesis of SWNTs and DWNTs using *n*-hexane as a carbon source in a floating catalyst method.[19,20] In their results, however, ∼20% of synthesized carbon products consisted of various kinds of unwanted forms of carbon materials such as SWNTs, MWNTs, and carbon nanofibers.[20] In addition, a high reaction temperature and a special promoter such as thiophene were used in their experiments.

Here, we report a large-scale synthesis of high-quality DWNTs over an Fe−Mo/MgO catalyst by catalytic decomposition of *n*-hexane. In many applications, it is desirable to remove a support material after the growth of DWNTs. We consider that the removal of MgO support material is much easier than that of Al_2O_3 or zeolite support material in the acid treatment. We obtained an over 900% high yield of CNTs relative to the weight of Fe−Mo in the Fe−Mo/MgO catalyst. Especially, more than 90% of CNTs was DWNTs in this work. Our result indicates that *n*-hexane can be an ideal carbon source for a large-scale synthesis of high-quality DWNTs.

Experimental Section

The synthesis of DWNTs was conducted by the catalytic reaction of *n*-hexane and Fe−Mo catalyst. Fe−Mo/MgO catalyst was prepared according to the following procedure. A mixture of $Fe(NO_3)_3 \cdot 9H_2O$ (99.99%, Aldrich) and Mo solution (Aldrich, ICP/DCP standard solution, 9.8 mg/mL of Mo in H_2O) was dissolved in deionized water for 1 h. The mixed Fe−Mo solution was then introduced to the suspension of MgO powder and deionized water, followed by sonication for 1 h. In our experiment, we used the weight ratio of Fe/Mo/MgO = 1:0.1:12. After drying, the material was baked at 150 °C for

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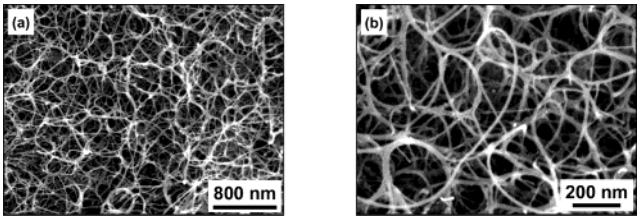

Figure 1. SEM images of the as-synthesized carbon materials by catalytic decomposition of *n*-hexane. (a) Low-magnification SEM image. (b) High-magnification SEM image.

15 h in a vacuum ambient and then ground in a mortar to break the chunk into powder. Then, the ground catalyst material was calcined in a quartz furnace at 700 °C for 7 h in air ambient. The synthesis of DWNTs was carried out in a quartz tube reactor (70 mm i.d., and 700 mm long) mounted in a tube furnace. An amount of 1 g of the supported Fe−Mo catalyst was put into a quartz boat at the center of the reactor tube. The liquid *n*-hexane was placed in a stainless steel bubbler at room temperature. Argon gas purged the reactor while the reactor was heated to 900 °C. Once the temperature reached 900 °C, a mixture gas of Ar (200 sccm) passing through *n*-hexane and Ar/H_2 (2000 sccm/100 sccm) was introduced into the reactor for 10 min in order to synthesize DWNTs. Finally the reactor was cooled to room temperature in Ar atmosphere.

The morphologies and microstructures of the as-synthesized carbon materials were characterized by scanning electron microscopy (SEM, Hitachi, S-4700) and transmission electron microscopy (TEM, JEOL, JEM-3011, 300 kV). For TEM studies, the sample was prepared by sonication of the as-synthesized product in ethanol alcohol, and a few drops of the resultant suspension were put onto a holey carbon TEM grid. To obtain the overall information of the as-synthesized carbon materials, the product was further characterized by Raman spectroscopy (Bruker, RFS-100/S, Nd: YAG laser excitation, laser beam wavelength: 1064 nm).

Results and Discussion

A low-magnification SEM image of the as-synthesized product is shown in Figure 1a. It shows that abundant carbon filaments, having lengths of over tens of micrometers, have been produced by catalytic decomposition of *n*-hexane. The tangled carbon filaments fully cover the entire catalyst surface. It is noteworthy mentioning that no purification was conducted before imaging. Thus, SEM observation qualitatively indicates that the produced carbon filaments have a high yield. To quantify the yield of carbon filaments, a weight gain measurement was done on the as-synthesized carbon filaments. An over 900% high yield of the carbon filaments was obtained relative to the weight of Fe−Mo in the Fe−Mo/MgO catalyst, revealing a significantly high yield of carbon filaments. A high-magnification SEM image (Figure 1b) shows that the as-synthesized carbon filaments have uniform diameters ranging from 14 to 27 nm and have clean surfaces without carbon particle deposits.

Figure 2a shows a typical TEM image of the as-synthesized carbon filament materials. It clearly shows that most of the produced carbon filaments are nanotube bundles even though a few isolated nanotubes appear in the TEM image (see arrows). Figure 2b shows a HRTEM image of a DWNT bundle, indicating that the as-synthesized DWNTs have well-resolved walls and no amorphous carbon deposits on the surface of DWNTs. Moreover, in this work, catalyst particles are seldom observed in nanotube bundles. These results indicate that the as-synthesized DWNTs are of high quality. From HRTEM

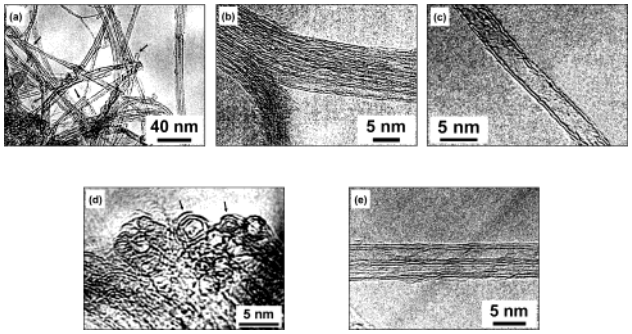

Figure 2. TEM images of the as-synthesized DWNT materials by catalytic decomposition of *n*-hexane. (a) A typical TEM image. (b) HRTEM image of a DWNT bundle. (c) HRTEM image of an isolated DWNT. (d) HRTEM image of cross-section view of a DWNT bundle. (e) HRTEM image of two TWNTs.

observation (Figure 2b), the outer tube diameters of the as-synthesized DWNTs mostly range from 1.5 to 2.6 nm, and inner tube diameters are primarily in the range of 0.75 to 1.8 nm. The interlayer spacing is about 0.38 nm, which is consistent with the results reported by another group.[10] We could find that the diameters of isolated DWNTs were larger than those of individual DWNTs in a bundle. Figure 2c shows a HRTEM image of an isolated DWNT having an outer diameter of about 3.6 nm. Besides DWNTs, we could occasionally find SWNTs and triple-walled carbon nanotubes (TWNTs) in the HRTEM images. Figure 2d shows a HRTEM image of a cross-section view of a nanotube bundle, indicating the presence of DWNTs and TWNTs (see arrow) with different diameters. Figure 2e shows a HRTEM image of two TWNTs, which have an outer diameter of 3.2 nm, an inner diameter of 1.8 nm, and an interlayer spacing of 0.36 nm, respectively. But the amount of SWNTs and TWNTs is less than 10%, which indicates that our method is preferable to the highly selective synthesis toward DWNTs. In this work, TWNTs have a larger outer and inner diameters compared with DWNTs in the bundle. It has been well-known that the diameters of CNTs are dependent upon the size of catalytic metal particle.[21] Moreover, it is considered that a catalytic metal particle with a large size favors the growth of CNT with more walls. According to HRTEM images, our work showed that DWNTs were selectively produced with a high yield. We consider that the reason can be mostly attributed to large quantities of highly dispersed catalytic metal particles with an uniform size suitable for the growth of DWNTs. Moreover, the optimized process condition such as composition of catalyst and a carbon feed gas also can contribute to the high selectivity of DWNT in our product. For a better understanding of the growth of DWNT, more work is underway in our group.

Raman spectroscopy was used to further characterize diameters and crystallinities of the as-synthesized DWNT materials. It has been well-known that the radial breathing mode (RBM) of DWNTs with a small size can be detected.[8,10,17] Figure 3 shows the Raman spectrum of the as-synthesized DWNTs. In low-frequency domain, there are twelve components at 94.9, 114.2, 129.6, 147, 162.4, 175.9, 216.4, 235.7, 262.7, 278.1, 312.8, and 328.2 cm^{-1}, respectively. The expression: $\omega = 6.5 + 223.75/d$, was used to calculated the diameters of the outer tubes and inner tubes because the DWNTs were aggregated into bundles.[17] Table 1 summarizes Raman peak positions and the calculated diameters of the produced DWNTs. From Table 1, the outer tube diameters are in the range of 1.44−2.53 nm and the inner tube diameters are in the range of 0.7−1.82 nm. Also, DWNTs with the same outer tube diameter can have different inner tube diameters due to the difference of chirality.[8] The

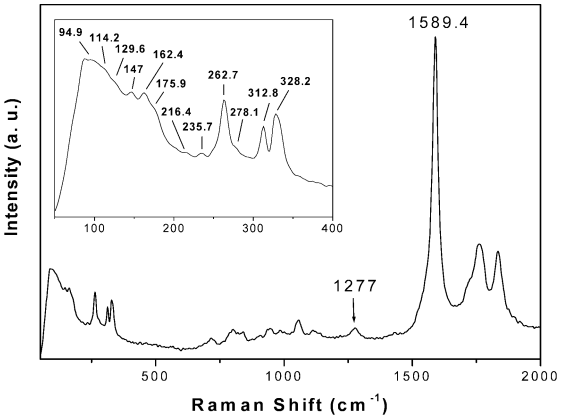

Figure 3. Raman spectrum of the as-synthesized DWNTs by catalytic decomposition of *n*-hexane.

TABLE 1: Raman Peak Positions and the Calculated Diameters of the Produced DWNTs

outer tube, ω (d) cm^{-1} (nm)	inner tube, ω (d) cm^{-1} (nm)
94.9 (2.53)	129.6 (1.82)
114.2 (2.08)	175.9 (1.32)
129.6 (1.82)	216.4 (1.07)
129.6 (1.82)	235.7 (0.98)
147.0 (1.59)	262.7 (0.87)
147.0 (1.59)	278.1 (0.82)
162.4 (1.44)	312.8 (0.73)
162.4 (1.44)	328.2 (0.70)

interlayer spacings of DWNTs range from 0.35 to 0.42 nm, which is in agreement with that from HRTEM observation. In comparisons with Raman data of DWNTs produced by catalytic decomposition of CH_4 reported by other groups, our DWNTs exhibit larger inner diameters and outer diameters but similar interlayer spacings.[14,22] The peak centered at 1589.4 cm^{-1} (G-band) is narrow and strong in this spectrum, indicating a good arrangement of hexagonal lattice of graphite. The peak centered at 1277 cm^{-1} (D-band) is weak, revealing that the amount of disorder carbon is small in the as-synthesized DWNT materials. The small ratio of I(D)/I(G) indicates that the as-synthesized DWNTs have low defect levels in atomic carbon structures.[17] The HRTEM observation and the Raman analysis indicate that the produced DWNTs are of high quality.

Conclusions

High-quality DWNTs have been massively produced by catalytic decomposition of *n*-hexane over Fe−Mo/MgO catalyst. An over 900% high yield of CNTs is obtained using our experimental conditions. More than 90% of produced CNTs was DWNTs. The outer tube and inner tube diameters of the as-synthesized DWNTs were in the range of 1.44−2.53 nm and 0.70−1.82 nm, respectively. Large quantities of highly dispersed catalytic metal particles with a uniform size mainly contribute to the synthesis of highly selective DWNTs with the high yield. Our results indicate that *n*-hexane can be a very ideal carbon source for the synthesis of DWNTs. We suggest that this method can promise a large-scale synthesis of high-quality DWNTs.

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References and Notes

(1) Iijima, S. *Nature* **1991**, *354*, 56.
(2) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787.
(3) (a) Tanaka, K.; Aoki, H.; Ago, H.; Yamabe, T.; Okahara, K. *Carbon* **1997**, *35*, 121. (b) Kociak, M.; Suenaga, K.; Hirahara, K.; Saito, Y.; Nakahira, T.; Iijima, S. *Phys. Rev. Lett.* **2002**, *89*, 155501. (c) Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. *J. Appl. Phys.* **1993**, *73*, 494.
(4) Kurachi, H.; Uemura, S.; Yotani, J.; Nagasako, T.; Yamada, H.; Ezaki, T.; Maesoba, T.; Loutfy, R.; Moravsky, A.; Nakagawa, T.; Katagiri, S.; Saito, Y. *Proceedings of 21st International Display Research Conference/ 8th International Display Workshops* **2001**, pp 1245−1245.
(5) Hutchison, J. L.; Kiselev, N. A.; Krinichnaya, E. P.; Krestinin, A. V.; Loutfy, R. O.; Morawsky, A. P.; Muradyan, V. E.; Obraztsova, E. D.; Sloan, J.; Terekhov, S. V.; Zakharov, D. N. *Carbon* **2001**, *39*, 761.
(6) Saito, Y.; Nakahira, T.; Uemura, S. *J. Phys. Chem. B* **2003**, *107*, 931.
(7) Sugai, T.; Yoshida, H.; Shimada, T.; Okazaki, T.; Shinohara, H. *Nano Lett.* **2003**, *3*, 769.
(8) Bandow, S.; Takizawa, M.; Hirahara, K.; Yudasaka, M.; Iijima, S. *Chem. Phys. Lett.* **2001**, *337*, 48.
(9) Ci, L.; Rao, Z.; Zhou, Z.; Tang, D.; Yan, X.; Liang, Y.; Liu, D.; Yuan, H.; Zhou, W.; Wang, G.; Liu, W.; Xie, S. *Chem. Phys. Lett.* **2002**, *359*, 63.
(10) Ren, W.; Li, F.; Chen, J.; Bai, S.; Cheng, H. M. *Chem. Phys. Lett.* **2002**, *359*, 196.
(11) Li, W. Z.; Wen, J. G.; Sennett, M.; Ren, Z. F. *Chem. Phys. Lett.* **2003**, *368*, 299.
(12) (a) Flahaut, E.; Peigney, A.; Laurent, Ch.; Rousset, A. *J. Mater. Chem.* **2000**, *10*, 249. (b) Flahaut, E.; Bacsa, R.; Peigney, A.; Laurent, Ch. *Chem. Commun.* **2003**, 1442.
(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) Wei, J.; Ci, L.; Jiang, B.; Li, Y.; Zhang, X.; Zhu, H.; Xu, C.; Wu, D. *J. Mater. Chem.* **2003**, *13*, 1340.
(15) Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, *313*, 91.
(16) Cassell, A. M.; Raymakers, J. A.; Kong, J.; Dai, H. *J. Phys. Chem. B* **1999**, *103*, 6484.
(17) Lyu, S. C.; Lee, T. J.; Yang, C. W.; Lee, C. J. *Chem. Commun.* **2003**, 1404.
(18) Lyu, S. C.; Liu, B. C.; Lee, C. J.; Kang, H. K.; Yang, C.-W.; Park, C. Y. *Chem. Mater.* **2003**, *15*, 3951.
(19) Zhu, H. W.; Xu, C. J.; Wu, D. H.; Wei, B. Q.; Vajtai, R.; Ajayan, P. M. *Science* **2002**, *296*, 884.
(20) Zhu, H.; Xu, C.; Wei, B.; Wu, D. *Carbon* **2002**, *40*, 2021.
(21) Dai, H.; Rinzler, A. G.; Nikolaev, P.; Thess, A.; Colbert, D. T.; Smalley, R. E. *Chem. Phys. Lett.* **1996**, *260*, 471.
(22) Bacsa, R. R.; Peigney, A.; Laurent, Ch.; Puech, P.; Bacsa, W. S. *Phys. Rev. B* **2002**, *65*, 161404(R).