Large-Scale Synthesis of High-Quality Single-Walled Carbon Nanotubes by Catalytic Decomposition of Ethylene

S. C. Lyu,[†] B. C. Liu,[†,‡] S. H. Lee,[†] C. Y. Park,[‡,§] H. K. Kang,[||] C. W. Yang,[||] and C. J. Lee*[,†]

Department of Nanotechnology, Hanyang University, Seoul 133-791, Korea, Department of Physics, Sungkyunkwan University, Suwon 440-746, Korea, Department of Advanced Materials Engineering, Sungkyunkwan University, Suwon 440-746, Korea, and Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, Suwon 440-746, Korea.

Received: May 28, 2003; In Final Form: October 21, 2003

High-quality single-walled carbon nanotubes (SWNTs) have been synthesized over Fe−Mo/MgO catalyst by catalytic decomposition of ethylene at 800 °C. The produced carbon material primarily consists of a SWNT bundle with few defects and a very small amount of amorphous carbon coating. The diameter of an individual SWNT is in the range of 0.7−2.8 nm. The as-synthesized SWNTs have a high yield of over 550% relative to the weight of Fe−Mo metal in the Fe−Mo/MgO catalyst. Our results show that ethylene can be a very ideal carbon source for the synthesis of SWNTs. We suggest that catalytic decomposition of ethylene over Fe−Mo/MgO catalyst can promise a large-scale production of high-quality SWNTs.

Introduction

Since their discovery in 1993,[1,2] single-walled carbon nanotubes (SWNTs) have attracted considerable attention due to many unique physical and chemical properties.[3−6] Based on SWNTs as active components, many potential applications such as field emitters,[7] nanoscale transistors,[8] supercapacitors,[9] and sensors[10] have been demonstrated. To realize various applications of SWNT, large quantities of high-quality SWNTs are inevitably necessary. Much effort has been devoted to synthesize SWNTs over the past few years. Various techniques, including arc discharge,[11] laser ablation,[12] and chemical vapor deposition (CVD)[13−15] have been developed for the synthesis of SWNTs aiming to producing SWNTs at high quality, high yield, and low cost.

Recently, many research groups have studied the synthesis of SWNTs by the CVD method because the CVD method is of benefit to achieve high purity and high yield of SWNTs and easily scale-up the synthesis of SWNTs at low cost. To achieve a large-scale synthesis of high-quality SWNTs, several carbon-containing molecules such as methane,[13,16−21] carbon monoxide,[14,22,23] ethylene,[22,24,25] acetylene,[15,26,27] hexane,[28] alcohol,[29] and benzene[30] have been studied as carbon sources. Among many carbon sources, ethylene is a useful candidate for the synthesis of CNTs because ethylene is a common and cheap carbon source. Today, large-scale production of multiwalled carbon nanotubes (MWNTs) has been reported by catalytic decomposition of ethylene over a supported catalyst.[31] However, there were only a few reports on the synthesis of SWNTs using ethylene as a carbon source. Hafner et al.[22] reported the synthesis of SWNT materials using ethylene over the alumina supported bimetallic catalyst, but in their results, the carbon product contained about 30−70% double-walled carbon nanotubes (DWNTs). Colomer et al.[24] announced the synthesis of SWNTs from ethylene over the alumina or silica supported metal catalyst at a high temperature of 1080 °C. In their carbon products, a lot of amorphous carbon materials appeared. Cheung et al.[25] investigated the synthesis of SWNTs by catalytic decomposition of ethylene over Fe nanoparticles. Their experimental results showed that the produced nanotubes contained about 30% DWNTs. After the synthesis of SWNTs on the Al_2O_3 or MgO supported metal catalyst, the used support material must be removed by acid treatment. In general, MgO can be readily removed by mild acid treatment compared with Al_2O_3, promising various applications with high-purity SWNTs. It is still difficult to realize a large-scale synthesis of high-quality SWNTs, even though there has been some progress for the synthesis of SWNTs by catalytic decomposition of ethylene.

Here, we demonstrate a large-scale synthesis of high-quality SWNTs with high yield over a Fe−Mo/MgO catalyst using ethylene. The produced carbon materials indicate high-purity carbon nanotubes consisting of almost only SWNTs with few amorphous carbon products. Our results show that ethylene could be a very ideal carbon source for mass production of high-quality SWNTs in high yield.

Experimental Section

The preparation of the Fe−Mo/MgO catalyst was conducted 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 DI water for 1 h. To embed the Fe−Mo bimetallic catalyst onto the MgO powder, the mixed Fe−Mo solution was introduced to the suspension of MgO powder and DI water followed by sonication for 1 h. In our experiment, the weight ratio of Fe:Mo:MgO = 1:0.1:12 was used to fabricate the catalyst embedded on the support material. After drying, the material was baked at 150 °C for 15 h in a vacuum ambient and then ground in a mortar to break the chunks into powder. The ground catalyst material was calcined in a quartz furnace at 700 °C for 7 h in

* To whom correspondence should be addressed. E-mail: cjlee@hanyang.ac.kr.
[†] Hanyang University.
[‡] Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University.
[§] Department of Physics, Sungkyunkwan University.
[||] Department of Advanced Materials Engineering, Sungkyunkwan University.

10.1021/jp030661t CCC: $27.50
Published on Web 01/13/2004

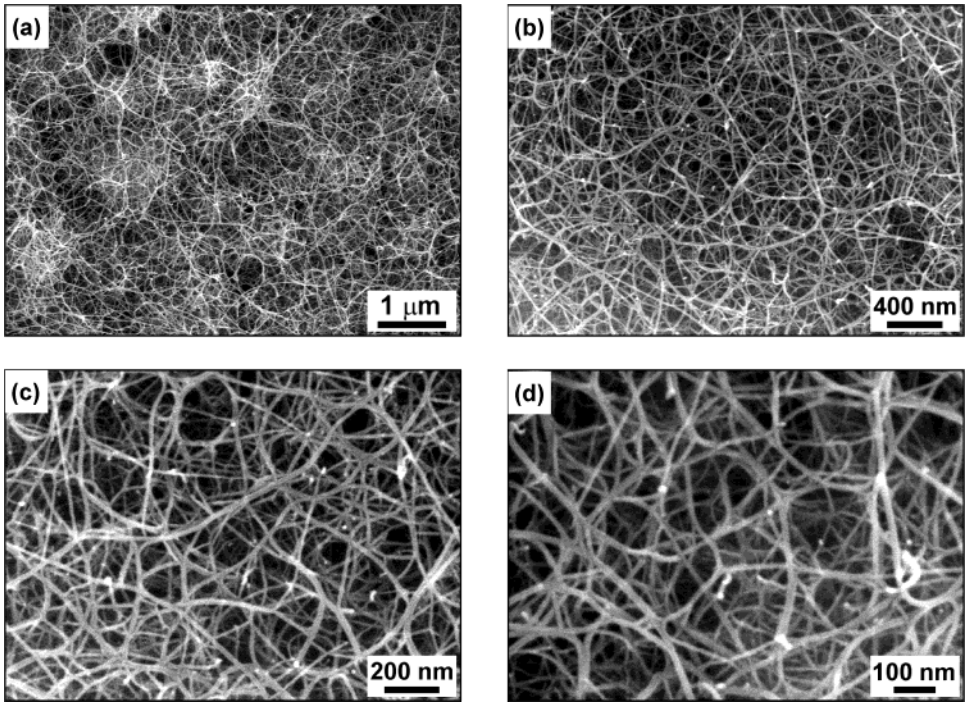

Figure 1. SEM images of the as-synthesized carbon filaments over the Fe−Mo/MgO catalyst by catalytic decomposition of ethylene. (a and b) Low-magnification SEM images and (c and d) high-magnification SEM images.

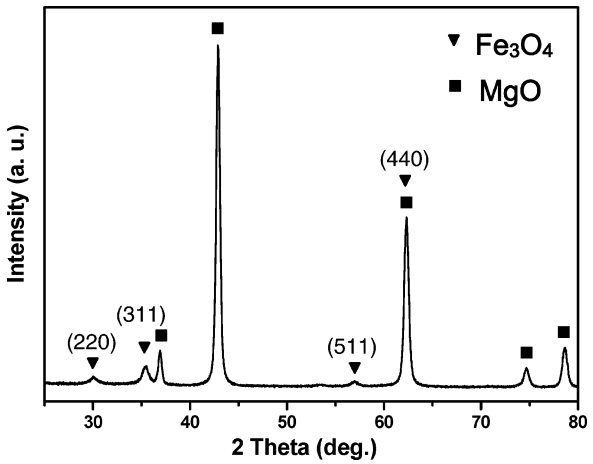

Figure 2. XRD pattern of the Fe−Mo/MgO catalyst after calcination at 700 °C for 7 h in air ambient.

air ambient. The synthesis of SWNTs was carried out in a quartz tube reactor. For each synthesis, ∼1 g of the Fe−Mo/MgO catalyst was put into a quartz boat. The quartz boat was inserted into the center of the quartz tube mounted in an electrical tube furnace. Subsequently, the reactor was heated to 800 °C in Ar atmosphere. Then a mixture of ethylene and Ar was introduced into the reactor maintained at 800−900 °C for the synthesis of SWNTs. The flow rates of ethylene and Ar were 40 and 2000 sccm, respectively. After 20 min, the reactor was cooled to room temperature in Ar atmosphere.

The as-synthesized CNT materials were characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and Raman spectroscopy. SEM was conducted using a Hitachi (S-4700) SEM by placing the as-prepared samples on conductive carbon tape. HRTEM is one of the most useful techniques to evaluate nanostructured materials. For HRTEM studies, the sample was prepared by sonication of the obtained product in ethanol alcohol and a few drops of resulting suspension were put onto a holey carbon TEM grid. HRTEM was performed at 300 kV using a JEOL (JEM-3011) TEM. To obtain overall information about the configuration of CNT samples, Raman spectrum was taken with a Bruker (RFS-100/S) spectrometer using a 1064 nm Nd:YAG laser excitation wavelength.

Results and Discussion

Typical low-magnification SEM images (Figure 1, parts a and b) for the as-synthesized product show extremely abundant carbon filaments, being over tens of microns in length. It is noteworthy mentioning that the SEM images are obtained from the as-synthesized carbon material without purification. They indicate that significant quantities of carbon filaments have been produced over the Fe−Mo/MgO catalyst by catalytic decomposition of ethylene at 800 °C. The produced carbon filaments fully cover the entire surface of the catalyst, indicating a large-scale synthesis of carbon filaments in high yield using our method. SEM observation only gives qualitative results of the carbon filament yield. So a quantitative measurement of the as-synthesized carbon filament yield was further conducted. A weight gain measurement for the as-synthesized carbon filaments indicates a high carbon filament yield of over 550 wt % relative to the weight of Fe−Mo metal in the MgO supported Fe−Mo bimetallic catalyst. Figure 1, parts c and d, shows high-magnification SEM images of the as-synthesized carbon filaments. They show that the produced carbon filaments have a smooth and clean surface without amorphous carbon deposits and have a diameter ranging from 11 to 29 nm.

In this work, we used mixed catalyst of Fe and Mo to obtain a high yield of SWNTs, but there was no success of a high yield of SWNTs with Fe-only or Mo-only catalysts at the same process conditions. Further study is necessary to understand why the mixed catalyst of Fe and Mo is much more effective in obtaining a high yield of SWNTs in our experiments. Before loading the mixed catalyst into the quartz tube, the Fe−Mo catalyst embedded on MgO support material was calcined at 700 °C for 7 h in air ambient. During the calcination process,

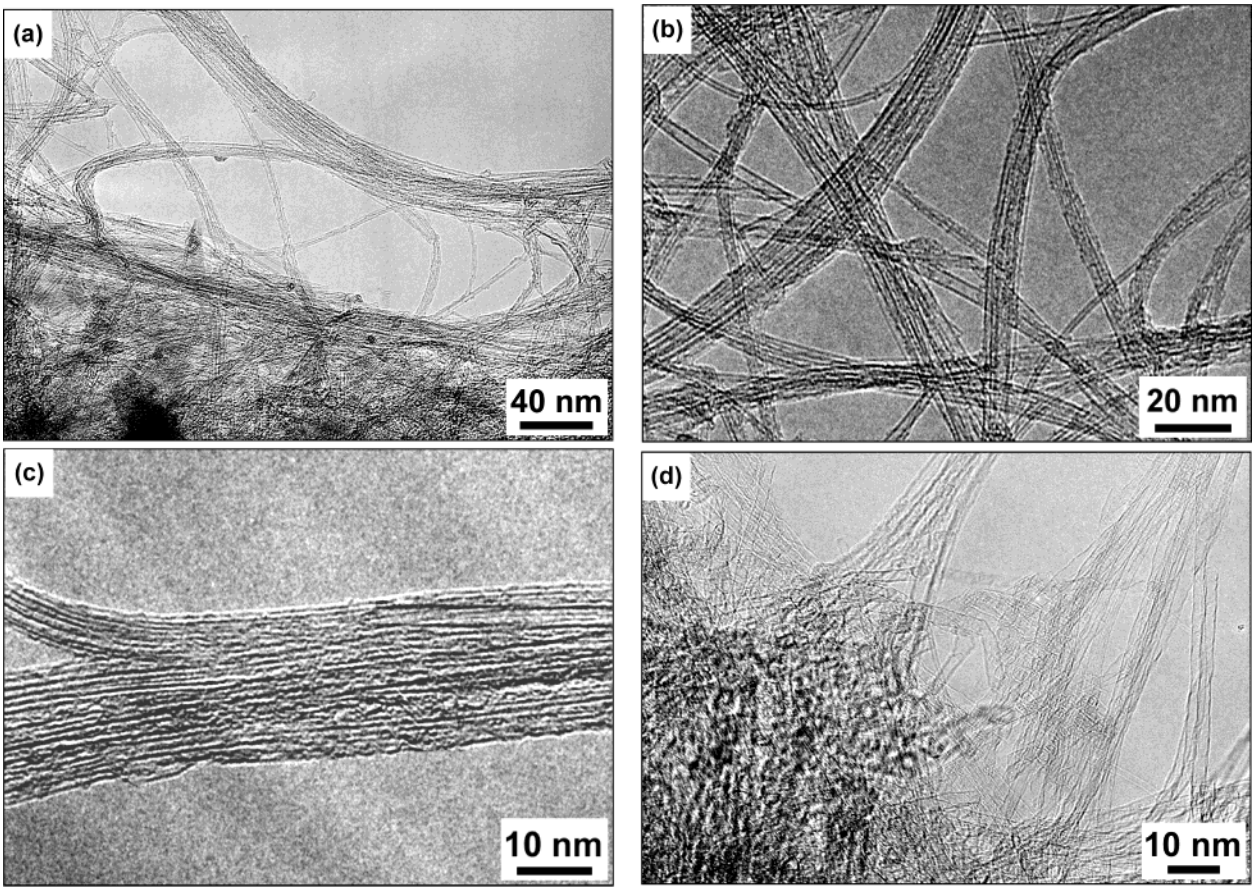

Figure 3. TEM images of the as-synthesized SWNTs over the Fe−Mo/MgO catalyst (a and b) Low-magnification TEM images, (c) a high-magnification TEM image of a SWNT bundle, and (d) a high-magnification TEM image of isolated SWNTs with large diameters of 2.2−2.8 nm.

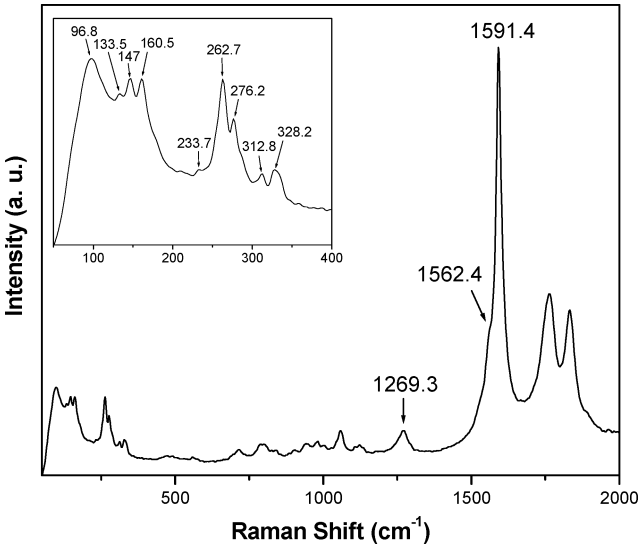

Figure 4. Raman spectrum of the as-synthesized carbon materials over the Fe−Mo/MgO catalyst.

Fe and Mo must be oxidized, resulting in a metal oxide structure on the MgO support material.

XRD analysis indicates that Fe was changed to Fe_3O_4, but there were no molybdenum oxide peaks as shown in Figure 2. In this work, we used the weight ratio of Fe:Mo = 1:0.1 to fabricate the mixed Fe−Mo catalyst. We consider that that amount of Mo was too small to detect the molybdenum oxide peaks in XRD analysis. From the XRD pattern, we suggest that metal oxide catalysts play a key role in yielding a large-scale synthesis of SWNTs in our work.

TEM studies give further information about the morphology and microstructure of the as-synthesized carbon filaments over the Fe−Mo/MgO catalyst by catalytic decomposition of ethylene. In Figure 3, parts a and b, typical TEM images of the as-synthesized carbon filaments illustrate that the carbon filaments primarily consist of nanotube bundles even though occasionally a few isolated SWNTs are observed in the carbon product. Figure 3c shows the HRTEM image of one SWNT bundle, which indicates clear graphene layers. The SWNT in a bundle have a diameter of about 0.9 nm. From TEM observation, the SWNTs produced by catalytic CVD indicate the diameters in the range of 0.7−2.8 nm, showing a wide diameter distribution compared with SWNTs by the arc discharge method. Interestingly, isolated SWNTs have large diameters of 2.2−2.8 nm compared with SWNTs in a bundle as shown in Figure 3d. In this work, a very small amount of amorphous carbon materials cover the surface of the SWNTs, indicating that the as-synthesized SWNT materials are of high purity. Moreover, we could find that the produced nanotubes indicate mainly SWNT bundles even though a few DWNTs appear in the as-synthesized product, which are similar to that synthesized by other techniques.[11,12]

It has been well-known that Raman spectroscopy is a useful tool for the characterization of SWNTs. A Raman spectrum can provide the molecule fingerprint of SWNT. Figure 4 shows a typical Raman spectrum obtained with an excitation source of 1064 nm on the CNTs produced on the Fe−Mo/MgO catalyst by catalytic decomposition of ethylene. It clearly exhibits the characteristic frequency of SWNTs. Generally, the frequency is strongly dependent on the diameter of SWNTs. The high-resolution spectrum in the low-frequency region shows nine

peaks at 96.8, 133.5, 147, 160.5, 233.7, 262.7, 276.2, 312.8, and 328.2 cm^{-1}. This frequency region is associated with the radial breathing mode (RBM). We consider that van der Waals forces exist between the tubes because individual SWNTs are packed into bundles in the as-synthesized SWNT samples. By considering the interaction effect due to the aggregation of individual SWNT in bundles, the expression $\omega = 6.5 + 223.75/d$ is used to calculate the diameter of SWNTs, where ω is the RBM frequency in cm^{-1} and d is the diameter of the SWNTs in nm.[27] According to the above formula, these peaks at 96.8, 133.5, 147, 160.5, 233.7, 262.7, 276.2, 312.8, and 328.2 cm^{-1} correspond to the SWNTs with a diameter of 2.48, 1.76, 1.59, 1.45, 0.98, 0.87, 0.83, 0.73, and 0.70 nm, respectively. The diameter distribution of SWNTs from Raman spectrum analysis is in the range of 0.7−2.5 nm. By the way, besides SWNTs, we could find a few DWNTs in the synthesized carbon products from HRTEM observation. Therefore, it is considered that the Raman spectrum also reveals the existence of DWNTs in this work. Possibly, in the Raman spectrum, the peaks centered at 96.8, 133.5, 160.5, 233.7, and 312.8 cm^{-1} are partly from DWNTs based upon both the analysis of the combination (2.48−1.76, 1.76−0.98, and 1.45−0.73 nm) of the corresponding diameter from these peaks and HRTEM observation. Between 1500 and 1600 cm^{-1}, the peak centered at 1591.4 cm^{-1} was referred as the G band. In this work, the G band has a narrow and strong spectrum peak, indicating a good arrangement of the hexagonal lattice of graphite, whereas the other peak at 1562.4 cm^{-1}, appearing at the left of the G band, was considered to be a characteristic of Raman spectrum for SWNTs.[32] The peak at 1269.3 cm^{-1} (D band) gives an indication of the level of disorder carbon. The D band has a small and weak spectrum peak, indicating that the amount of amorphous carbon in the as-synthesized SWNT sample is very small. The small ratio of I_D/I_G indicates that the prepared nanotubes have a low defect level in the atomic carbon structure. Both Raman analysis and TEM observation demonstrate that the as-synthesized SWNTs are of high quality.

Conclusions

High-quality SWNTs have been produced over an Fe−Mo/MgO catalyst by catalytic decomposition of ethylene. The as-synthesized SWNTs have a high yield of over 550% relative to the weight of Fe−Mo metal in the MgO supported Fe−Mo bimetallic catalyst. A very small amount of amorphous carbon materials cover the surface of the synthesized SWNTs. Besides SWNTs, the synthesized carbon products by the catalytic CVD of ethylene contain a few DWNTs. The SWNTs have the diameters in the range of 0.7−2.8 nm. The isolated SWNTs have a larger diameter than SWNTs in a bundle. Our results demonstrate that ethylene is a very ideal carbon source for a large-scale synthesis of high-quality SWNTs.

Acknowledgment. This work was supported by Center for Nanotubes and Nanostructured Composites at SKKU and by National R&D Project for Nano Science and Technology of MOST.

References and Notes

(1) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603.

(2) Bethune, D. S.; Kiang, C. H.; de Vries, M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature* **1993**, *363*, 605.

(3) Treacy, M. M. J.; Ebbesen, T. W.; Gibson, J. K. *Nature* **1996**, *381*, 678.

(4) Delaney, P.; Choi, H. J.; Ihm, J.; Louie, S. G.; Cohen, M. L. *Nature* **1998**, *391*, 466.

(5) Ouyang, M.; Huang, J.-L.; Lieber, C. M. *Acc. Chem. Res.* **2002**, *35*, 1018.

(6) Sun, Y.-P.; Fu, K.; Lin, Y.; Huang, W. *Acc. Chem. Res.* **2002**, *35*, 1096.

(7) Bonard, J. M.; Salvetat, J. P.; Stockli, T.; de Heer, W. A.; Forro, L.; Chatelain, A. *Appl. Phys. Lett.* **1998**, *73*, 918.

(8) Bachtold, A.; Hadley, P.; Nakanishi, T.; Dekker, C. *Science* **2001**, *294*, 1317.

(9) An, K. H.; Kim, W. S.; Park, Y. S.; Choi, Y. C.; Lee, S. M.; Chung, D. C.; Bae, D. J.; Lim, S. C.; Lee, Y. H. *Adv. Mater.* **2001**, *13*, 497.

(10) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622.

(11) Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; Lamy de la Chapelle, M.; Lefrant, S.; Deniard, P.; Lee, R.; Fischer, J. E. *Nature* **1997**, *388*, 756.

(12) 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.

(13) Kong, J.; Soh, H. T.; Cassell, A. M.; Quate, C. F.; Dai, H. *Nature* **1998**, *395*, 878.

(14) 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.

(15) Satishkumar, B. C.; Govindaraj, A.; Rahul, S.; Rao, C. N. R. *Chem. Phys. Lett.* **1998**, *293*, 47.

(16) Flahaut, E.; Govindaraj, A.; Peigney, A.; Laurent, Ch.; Rousset, A.; Rao, C. N. R. *Chem. Phys. Lett.* **1999**, *300*, 236.

(17) Liu, B. C.; Lyu, S. C.; Lee, T. J.; Choi, S. K.; Eum, S. J.; Yang, C. W.; Park, C. Y.; Lee, C. J. *Chem. Phys. Lett.* **2003**, 373, 475.

(18) Cassell, A. M.; Raymakers, J. A.; Kong, J.; Dai, H. *J. Phys. Chem. B* **1999**, *103*, 6484.

(19) Flahaut, E.; Peigney, A.; Laurent, Ch.; Rousset, A. *J. Mater. Chem.* **2000**, *10*, 249.

(20) Colomer, J. F.; Stephan, C.; Lefrant, S.; Van Tendeloo, G.; Willems, I.; Konya, Z.; Fonseca, A.; Laurent, Ch.; Nagy, J. B. *Chem. Phys. Lett.* **2000**, *317*, 83.

(21) Su, M.; Zheng, B.; Liu, J. *Chem. Phys. Lett.* **2000**, *322*, 321.

(22) 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.

(23) Kitiyanan, B.; Alvarez, W. E.; Harwell, J. H.; Resasco, D. E. *Chem. Phys. Lett.* **2000**, *317*, 497.

(24) Colomer, J. F.; Bister, G.; Willems, I.; Konya, Z.; Fonseca, A.; Van Tendeloo, G.; Nagy, J. B. *Chem. Commun.* **1999**, 1343.

(25) Cheung, C. L.; Kurtz, A.; Park, H.; Lieber, C. M. *J. Phys. Chem. B* **2002**, *106*, 2429.

(26) Ci, L.; Xie, S.; Tang, D.; Yan, X.; Li, Y.; Liu, Z.; Zou, X.; Zhou, W.; Wang, G. *Chem. Phys. Lett.* **2001**, *349*, 191.

(27) Lyu, S. C.; Liu, B. C.; Lee, T. J.; Liu, Z. Y.; Yang, C. W.; Park, C. Y.; Lee, C. J. *Chem. Commun.* **2003**, 734.

(28) Zhu, H. W.; Xu, C. L.; Wu, D. H.; Wei, B. Q.; Vajtai, R.; Ajayan, P. M. *Science* **2002**, *296*, 884.

(29) Maruyama, S.; Kojima, R.; Miyauchi, Y.; Chiashi, S.; Kohno, M. *Chem. Phys. Lett.* **2002**, *360*, 229.

(30) Cheng, H. M.; Li, F.; Su, G.; Pan, H. Y.; He, L. L.; Sun, X.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1998**, *72*, 3282.

(31) Hernadi, K.; Fonseca, A.; Nagy, J. B.; Siska, A.; Kiricsi, I. *Appl. Catal. A* **2000**, *199*, 245.

(32) Kasuya, A.; Sasaki, Y.; Saito, Y.; Tohji, K.; Nishina, Y. *Phys. Rew. Lett.* **1997**, *78*, 4434.