High-Quality Double-Walled Carbon Nanotubes Produced by Catalytic Decomposition of Benzene

Seung Chul Lyu, Bao Chun Liu, and Cheol Jin Lee*

Department of Nanotechnology, Hanyang University, Seoul 133-791, Korea

Hee Kwang Kang and Cheol-Woong Yang

Department of Advanced Materials Engineering, Sungkyunkwan University, Suwon 440-746, Korea

Chong Yun Park

Department of Physics, Sungkyunkwan University, Suwon 440-746, Korea, and Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, Suwon 440-746, Korea

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High-quality double-walled carbon nanotubes (DWNTs) have been produced by catalytic decomposition of benzene over Fe−Mo/Al_2O_3 catalyst at 900 °C. The produced carbon materials are DWNT bundles free of amorphous carbon covering on the surface. DWNTs have inner tube diameters in the range of 0.69−2.53 nm and outer tube diameters in the range of 1.44−3.30 nm. The interlayer spacing between graphene layers ranges from 0.35 to 0.38 nm. Transmission electron microscopy and Raman analysis show that produced carbon materials have a low defect level in the atomic carbon structure, indicating the synthesis of high-quality DWNTs. Our results demonstrate that benzene is an ideal carbon feedstock to synthesize high-purity DWNTs over Fe−Mo/Al_2O_3 catalyst.

Introduction

Since the first discovery of carbon nanotubes (CNTs) in 1991,[1] various methods, including arc discharge, laser ablation, and catalytic chemical vapor deposition (CCVD), have been developed to synthesize CNTs.[2−4] There has been tremendous progress in the synthesis and characterization of CNTs,[5−16] and various applications of CNTs have also been actively studied by many research groups.[17−22] Recently, much attention has been attracted to the synthesis of double-walled carbon nanotubes (DWNTs), which consist of two concentric cylindrical graphene layers. DWNT has some advantages over other types of CNTs such as single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs). For example, the inner tube of a DWNT can maintain the inherent SWNT character after modification of the outer tube of DWNT, and DWNTs can offer excellent field emission properties, compared with those of SWNTs and MWNTs.[23] Theoretical studies indicated that the stability of DWNTs mainly depended on their interlayer spacing, which affected the mechanical properties of the DWNTs.[24] To date, several research groups

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* Corresponding author. E-mail: cjlee@hanyang.ac.kr. Tel: +82-2-2293-4744. Fax: +82-2-2290-0768.

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have studied the electron-transport[25,26] and electronic structure of DWNTs,[27] which could be expected to be used in nanoscale electronic devices. To evaluate the validity of theoretical predictions and explore the possible applications in nanotechnology, high-quality DWNTs are inevitably necessary. There have been several reports for the synthesis of DWNTs by different methods. Hutchison et al.[28] and Saito et al.[29] reported that DWNTs as a dominate component in product mixture were produced by the arc discharge technique in an atmosphere of Ar and H_2 mixture. Bandow et al.[30] obtained DWNTs by the coalescence of C_{60} in SWNTs at high temperature. And also, there have been a few reports on the synthesis of DWNTs by CCVD.[31−34] It is well-known that the CCVD method is an attractive technique because it could be possible to control the growth and the structure of CNTs by controlling reaction parameters (carbon source, catalyst concentration, reaction temperature, and so on) and also be easily scaled up for large-scale synthesis. Although there has been much progress for the synthesis of DWNTs, it is still difficult to obtain high-quality DWNTs products without unwanted forms of carbon material. Recently, our group reported the synthesis of high-quality DWNTs using catalytic decomposition of alcohol over Fe−Mo/Al_2O_3 catalyst.[35] But it is still very desirable to study large-scale synthesis and characterization of high-quality DWNTs using various carbon source materials. Among carbon source materials, benzene can be one candidate for mass production of CNTs because benzene is a cheap carbon source material. Nowadays, benzene has been successfully used to synthesize both SWNTs and MWNTs using CCVD.[36,37] However, there has been no report for the synthesis of DWNTs using benzene as a carbon source.

In the present work, we demonstrate the synthesis of high-quality DWNTs by catalytic decomposition of benzene over Fe−Mo/Al_2O_3 catalyst. We also investigate the diameter and the structure of DWNTs using transmission electron microscopy (TEM) and Raman analysis. Our results indicate that benzene can be an ideal carbon source to synthesize high-purity DWNTs over Fe−Mo/Al_2O_3 catalyst using CCVD method.

Experimental Section

Fe−Mo/Al_2O_3 catalyst was prepared according to the following procedure.[38] A mixture of $Fe(NO_3)_3 \cdot 9H_2O$ (99%, Aldrich) and molybdenum solution (Aldrich, ICP/DCP standard, 9.8 mg/mL in H_2O) was dissolved in DI water for 1 h. The mixed Fe−Mo solution was then introduced to the suspension of Al_2O_3 powder and DI water followed by sonication for 1 h. The average particle size and surface area of the Al_2O_3 powder (Degussa) is 13 nm and 100 m^2/g, respectively. In our experiment, the molar ratio of catalyst was $Fe/Mo/Al_2O_3 = 1:0.1:13$. After drying, the material was baked in a vacuum at 150 °C for 15 h and then ground in a mortar to break the chunks into fine powder.

The synthesis of CNTs was conducted in a quartz tube reactor (20 mm i.d., and 500 mm long) mounted in a tube furnace. Supported Fe−Mo catalyst (~200 mg) was placed into a quartz boat at the center of the reactor tube. Liquid benzene was placed in a stainless steel bubbler at room temperature. The quartz tube was heated to 900 °C in Ar atmosphere. Subsequently, Ar (200 sccm) passing through benzene and a mixture of Ar (1000 sccm) and H_2 (20 sccm) were introduced into the reactor. Benzene was carried into the reactor maintained at 900 °C. After 10 min, the reactor was cooled to room temperature in Ar atmosphere.

The morphologies and microscopic structure of CNTs were characterized by scanning electron microscopy (SEM) (Hitachi, S-4700) and high-resolution TEM (HRTEM) (JEOL, JEM-3011, 300 kV). The diameter and crystallinity of CNTs were evaluated by Raman spectrometer (Bruker, RFS-100/S) using Nd:YAG laser excitation (laser beam wavelength 1064 nm).

Results and Discussion

Figure 1a is the low resolution SEM image of the as-synthesized sample. It shows large amounts of tangled carbon filaments, indicating that the lengths of carbon filaments are over several tens of micrometers. These filaments seem to be in a layer network and cover the overall catalyst surface as shown in Figure 1a. It is worthwhile to mention that the SEM image shown here is of as-prepared sample and no purification was conducted before the imaging. This result demonstrates that the carbon filaments synthesized by catalytic decomposition of benzene have fairly high yield. Figure 1b shows the magnified SEM image of the as-synthesized sample. This image shows that abundant carbon filaments are produced by catalytic decomposition of benzene even though some catalyst particles such as a white spot appear in the carbon filaments. Figure 1c is the high-resolution SEM image of the as-synthesized sample, showing that the diameter of carbon filaments is in the range of 11−25 nm.

Figure 2 is the HRTEM images of as-synthesized carbon filaments. Figure 2a shows that the carbon filaments observed in the SEM are actually bundles of DWNTs consisting of two concentric graphene sheets. In addition to DWNTs, one can find some Al_2O_3 particles because as-synthesized carbon materials have not been

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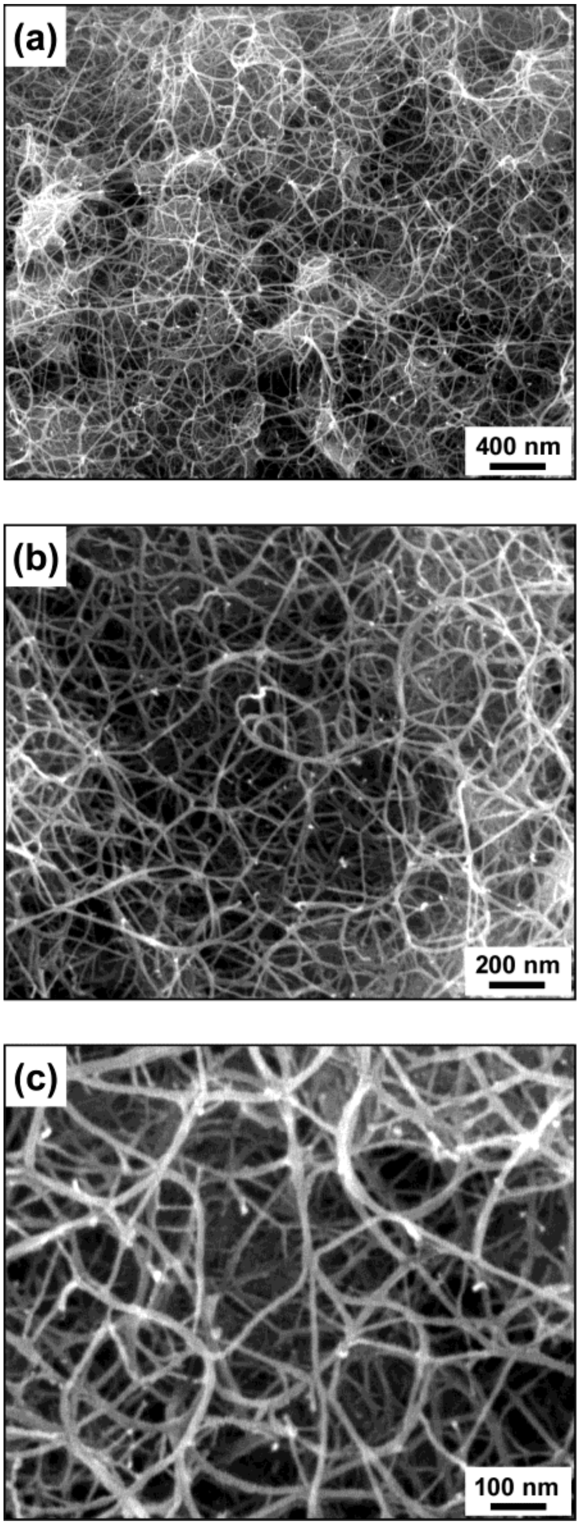

Figure 1. SEM images of as-synthesized carbon filaments by catalytic decomposition of benzene at 900 °C over Fe−Mo/Al_2O_3 catalyst: (a) low-resolution SEM image, (b) magnified SEM image, and (c) high-resolution SEM image.

purified before TEM imaging. In Figure 2b, the DWNTs have clearly resolved graphene layers and no amorphous carbon covering on the surface, indicating the synthesis of high-quality DWNTs. But all the graphene layers indicate the waving structure in a short range, which reveals degradation of graphene layers due to a high acceleration voltage of electron beam (300 kV) during HRTEM observation. We found that the graphene layers were severely destroyed after TEM observation time was over 10 s. Figure 2c is the magnified HRTEM image of a cross-section of the DWNTs shown in Figure 2a. DWNTs within the bundle have the structure of concentric circles and different diameters, unlike SWNTs. From HRTEM observation, the outer diameter and inner diameter of DWNTs are in the range of 1.46−3.30 nm and 0.72−2.59 nm, respectively. It is well-known that the diameters of DWNTs produced by CCVD are smaller than those of DWNTs produced by the arc discharge method.[28,29] In addition, HRTEM observation

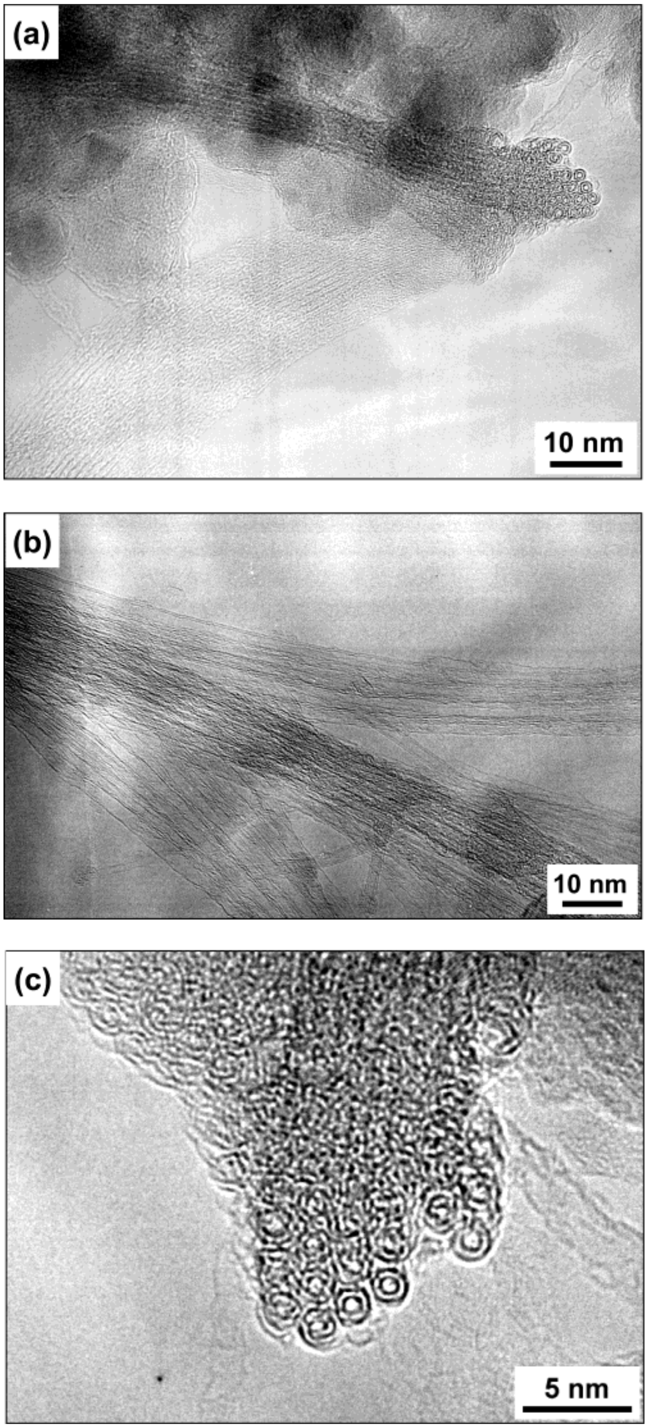

Figure 2. HRTEM images of as-synthesized DWNTs; (a) typical DWNT bundle consisting of nanotubes of two concentric graphene sheets, (b) DWNTs with clearly resolved graphitic layers, and (c) magnified HRTEM image of cross-section of the DWNT bundle shown in (a).

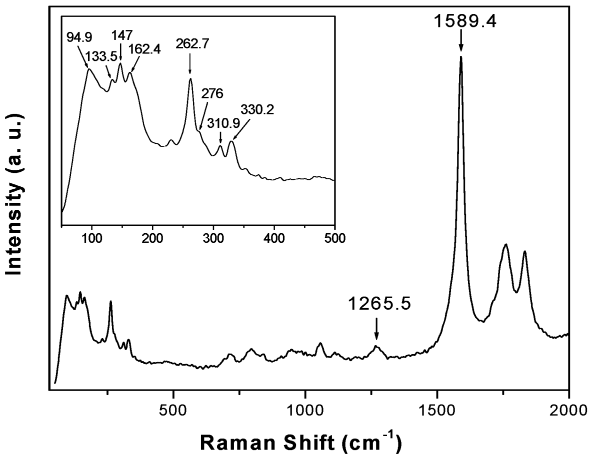

Figure 3. Raman spectrum of as-synthesized DWNTs.

indicates that the interlayer spacing of DWNT is not a constant, it ranges from 0.35 to 0.38 nm. We consider that the increased interlayer distance, compared with MWNTs (> 5 layers) of 0.34 nm spacing, could result from the high curvature due to small diameter of DWNTs.[39] Our results show that the DWNTs synthesized by catalytic decomposition of benzene have almost the same diameters and interlayer spacing as other DWNTs synthesized by methane or acetylene using CCVD method.[31−33]

In this work, there were few MWNTs in our product, SWNTs (less than 10%) were rarely observed by HRTEM, and the appropriate proportion of DWNTs was over 90% based on HRTEM observation. This result indicates that our method can promise high selectivity toward the growth of DWNTs in the product. It has been well-known that the diameter of carbon nanotubes is dependent upon the size of catalytic metal particles in the chemical vapor deposition process over the supported catalyst. Moreover, the size of catalyst particles can be controlled by reaction parameters such as the pore size of support materials, composition and concentration of catalyst, carbon source material, and reaction temperature. In this work, we suggest that several variables in our chemical vapor deposition process are key to the success of obtaining highly selective DWNTs. First, our catalyst preparation has produced highly dispersed Fe−Mo catalyst particle over the Al_2O_3 support material with a very uniform size suitable for the growth of DWNTs. Second, the suitable combination of reaction parameters (composition and concentration of Fe−Mo catalyst, benzene carbon source content, reactant gas flow rate and reaction temperature) has an important role on the growth of highly selective DWNTs.

Raman spectroscopy was further used to characterize the structure of nanotubes and study in detail the diameter of DWNTs. Figure 3 is the Raman spectrum of as-synthesized sample, showing a weak D-band at 1265.5 cm^{-1} and a strong G-band at 1589.4 cm^{-1}. The weak D-band reveals that as-synthesized sample is high-purity nanotube material. Generally, a ratio of *I* (D)/*I* (G) can be used as an indicator of extent of disorder within the nanotubes. The small ratio of *I* (D)/*I* (G) displayed in Figure 3 demonstrates that the defect level in the atomic carbon structure is low, indicating that high-quality DWNTs are synthesized in our method. It has been known that radial breathing mode (RBM) can be detected for DWNTs.[30] In previous works, the diameter of SWNTs was calculated by the expression $\omega = 6.5 + 223.75/d$.[40] Moreover, it was also reported that same formula used in a SWNT bundle could be applied to calculate the diameter of DWNTs within a bundle.[31,35] In this work, we adopted the expression $\omega = 6.5 + 223.75/d$ to calculate the diameter of DWNT because the synthesized DWNTs have a bundle shape. Table 1 summarizes Raman peak positions and calculated tube diameters of as-synthesized DWNTs.

Table 1. Raman Peak Positions and Tube Diameters of DWNTs

outer tube, ω (d) cm^{-1} (nm)	inner tube, ω (d) cm^{-1} (nm)
–	94.9 (2.53)
94.9 (2.53)	133.5 (1.76)
133.5 (1.76)	229.9 (1.00)
147.0 (1.59)	262.7 (0.87)
147.0 (1.59)	276.0 (0.83)
162.4 (1.44)	310.9 (0.74)
162.4 (1.44)	330.2 (0.69)

From Table 1, we can understand that DWNT can have different inner tube diameters for one outer tube diameter, resulting from the effect of chirality.[30] Generally, nanotubes with large diameters (> 3 nm) exhibit a weak Raman cross-section; as a result, their band in low-frequency domain is difficult to detect. But, we can deduce that the outer tube diameter of DWNTs with an inner tube diameter of 2.53 nm is about 3.27 nm according to the mean interlayer spacing of DWNTs (about 0.37 nm) from HRTEM observation. One can find that the diameter of DWNTs from Raman analysis is in good agreement with HRTEM observation.

Conclusion

We have synthesized high-quality DWNTs by catalytic decomposition of benzene over Fe−Mo/Al_2O_3 catalyst. The outer tube and the inner tube diameters of DWNTs are in the ranges of 1.44−3.30 nm and 0.69−2.53 nm, respectively. The interlayer spacing between graphene layers is in the range of 0.35−0.38 nm. DWNTs can have different inner tube diameters for one outer tube diameter. Both HRTEM and Raman analysis indicate that the synthesized DWNTs have high quality. Our result also demonstrates that benzene can be an ideal carbon feedstock to produce DWNTs over alumina supported Fe−Mo bimetallic catalyst.

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