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Synthesis of single- and double-walled carbon nanotubes by catalytic decomposition of methane

B.C. Liu [a,b], S.C. Lyu [a], T.J. Lee [a], S.K. Choi [a], S.J. Eum [d], C.W. Yang [d], C.Y. Park [b,c], C.J. Lee [a,*]

[a] *Department of Nanotechnology, Hanyang University, 17 Haengdang-dong Seongdong-gu, Seoul 133-791, Korea*
[b] *Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, Suwon 440-746, Korea*
[c] *Department of Physics, Sungkyunkwan University, Suwon 440-746, Korea*
[d] *Department of Advanced Materials Engineering, Sungkyunkwan University, Suwon 440-746, Korea*

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Abstract

Single-walled carbon nanotubes (SWNTs) and double-walled carbon nanotubes (DWNTs) are simultaneously synthesized by catalytic decomposition of CH_4 over Fe–Mo/Al_2O_3 catalyst. High-resolution transmission electron microscopy observation shows that produced carbon materials consist of about 70% SWNTs and about 30% DWNTs. The diameters of SWNTs are in the range of 0.8–1.5 nm while the outer and inner diameters of DWNTs are in the range of 1.75–3.1 and 0.95–2.3 nm, respectively. Raman analysis indicates that the synthesized SWNTs and DWNTs have high-quality graphite structure.

1. Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have been one of the most actively studied materials because of their unique structure and extraordinary physical properties. Many studies have been carried out on their synthesis. A few methods, including arc discharge [1], laser ablation [2] and catalytic chemical vapor deposition (CCVD) [3,4], have been developed to synthesize CNTs. Among them, the CCVD method appears as a promising technique for scaling up the production of CNTs at a relatively low cost. The production of MWNTs with more than five layers by the CCVD method is now on a commercial scale. Currently, many researchers have focused their attention on the production of single-walled carbon nanotubes (SWNTs) and double-walled carbon nanotubes (DWNTs) by the CCVD method. In the CCVD approach, the structure of carbon materials obtained is closely related with the catalyst, carbon source and reaction condition. For example, Resasco and co-workers [5] demonstrated that the ratio of Co and Mo was critical to synthesize SWNTs. Smalley and co-workers [6] reported that the mixture of SWNTs and DWNTs

* Corresponding author. Fax: +82-2-2290-0768.
E-mail address: cjlee@hanyang.ac.kr (C.J. Lee).

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was produced by catalytic decomposition of C_2H_4 over a supported Fe–Mo catalyst and the amount of DWNTs was increased by increasing the reaction temperature. A few carbon-containing molecules such as methane [4,7–14], acetylene [3,15,16], hexane [17], and alcohol [18,19] were used as carbon feedstock to synthesize SWNTs and/or DWNTs. Among the carbon-containing molecules, the methane CVD is a very attractive synthetic method because of high stability at elevated temperature and low cost. In the methane CVD method, the catalysts such as Fe, Co, Ni, Mo or mixtures of these metals are generally supported on Al_2O_3 or MgO powder to synthesize nanotubes.

In this Letter, we report the synthesis of SWNTs and DWNTs by catalytic decomposition of methane over Fe–Mo/Al_2O_3 catalyst. The characterization of produced carbon materials is performed by TEM and Raman analysis.

2. Experimental

The synthesis of nanotubes was carried out by catalytic reaction of CH_4 and Fe–Mo catalyst in a fixed bed reactor. A mixture of $Fe(NO_3)_3 \cdot 9H_2O$ (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. In order to embed the Fe–Mo bimetallic catalyst onto the Al_2O_3 powder, the mixed Fe–Mo solution was introduced to the suspension of Al_2O_3 powder and DI water followed by sonication for 1 h. In our experiment, the molar ratio of catalyst was $Fe:Mo:Al_2O_3 = 1:0.1:13$. After drying, the material was baked at 150 °C for 15 h in a vacuum ambient and then ground in mortar to break the chunks into powder. For each synthesis, ~100 mg Fe–Mo/Al_2O_3 catalyst was placed in the quartz boat that was inserted into the center of a quartz tube (20 mm i.d., and 500 mm long). The quartz tube was then mounted in an electrical tube furnace, and it was heated to 950 °C in Ar atmosphere. Subsequently, the mixture gas of Ar and CH_4 was introduced into the quartz tube for the production of nanotube materials. The synthesis of nanotubes was conducted at 950 °C for 30 min in atmospheric pressure. The flow rate of CH_4 and Ar was 100 and 500 sccm, respectively. The flow of Ar/CH_4 was maintained for 30 min before the furnace was cooled to room temperature in Ar atmosphere.

The morphology and microscopic structure of CNTs were characterized by scanning electron microscopy (SEM) (Hitachi, S-4700), transmission electron microscopy (TEM) (JEOL, JEM-3011, 300 kV), and Raman spectrometer (Bruker, RFS-100/S).

3. Results and discussion

Fig. 1 shows the SEM images of as-synthesized carbon materials. Fig. 1a shows that large amounts of entangled carbon filaments free of amorphous carbon deposit are covered on Fe–Mo/Al_2O_3 catalyst surface. It demonstrates that our synthesis method is preferable to obtain high-yield production. We observed an average yield of CNTs relative to the weight of Fe–Mo metal in Fe–Mo/Al_2O_3 catalyst. In this work, the yield of nanotubes after synthesis was over 250%. It is worth mentioning that the SEM image shown here is of an as-prepared sample and no purification was conducted before the imaging. The SEM image hence demonstrates that high-purity carbon filaments are synthesized by catalytic decomposition of methane over Fe–Mo/Al_2O_3 catalyst. The diameters of these filaments are in the range of 20–45 nm as shown in Fig. 1b.

Fig. 2 shows the high-resolution TEM (HRTEM) images of the as-synthesized carbon filaments. Fig. 2a reveals that the carbon filaments in the SEM images are only SWNT bundles. On the other hand, the carbon filaments in Fig. 2b indicate two kinds of nanotubes such as SWNTs (1) and DWNTs (2). We could find that the produced carbon filaments consisted of about 70% SWNTs and about 30% DWNTs and most of the nanotubes were organized into bundles due to the van der Waals interaction between the tubes. In this work, we also could understand that the diameter of DWNTs was much larger than that of SWNTs. Fig. 2c shows the HRTEM image of SWNT bundles with a typical rope-like shape, which is similar to the structure obtained by other methods [2,20]. The SWNTs in the bundle are

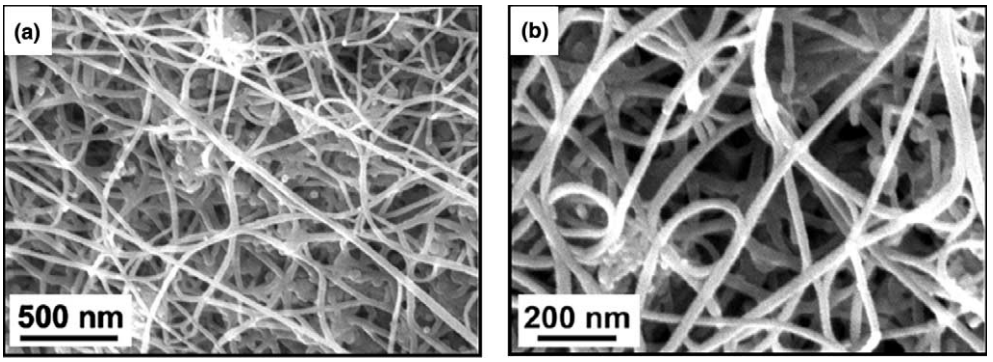

Fig. 1. SEM images of the as-synthesized carbon filament materials by catalytic decomposition of CH_4 over Fe–Mo/Al_2O_3: (a) low-magnification SEM image and (b) high-magnification SEM image.

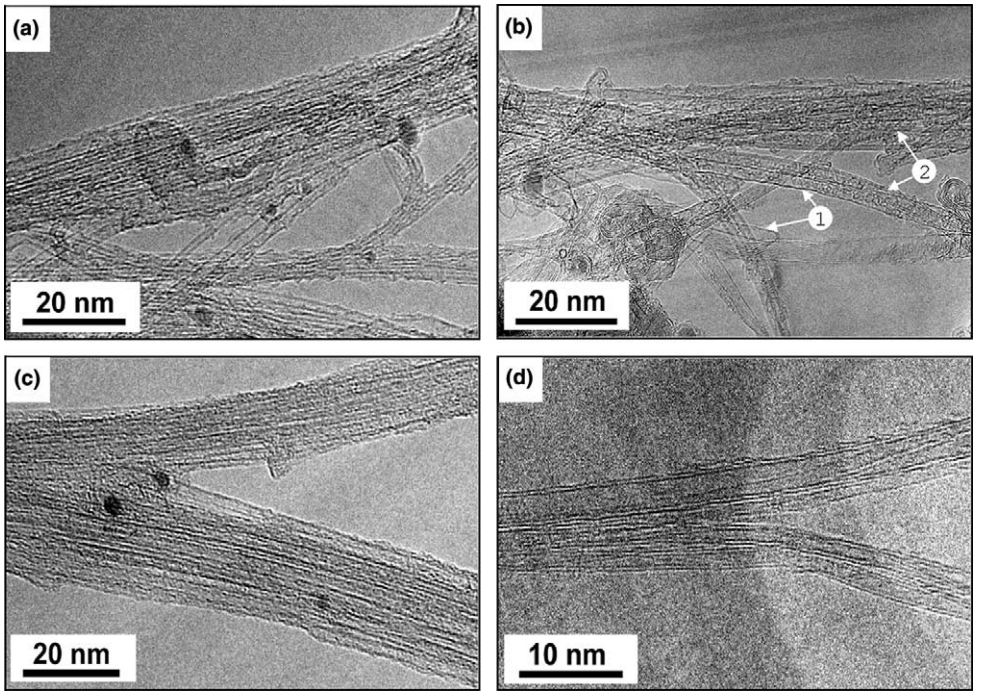

Fig. 2. TEM images of the as-synthesized single-walled and double-walled carbon nanotubes: (a) HRTEM image of SWNTs; (b) HRTEM image of SWNTs (1) and DWNTs (2); (c) HRTEM image of a SWNT bundle; and (d) HRTEM image of a DWNT bundle.

degraded due to the damage of the SWNTs under electron beam irradiation during TEM observation. HRTEM observation indicates that the diameter of SWNTs is in the range of 0.8–1.5 nm even though the diameter of some isolated SWNTs indicates over 3 nm. Fig. 2d shows the HRTEM image of DWNT bundles, in which the walls of nanotubes are clearly resolved. No amorphous carbon product could be detected on the nanotubes' exterior. Individual DWNTs within one bundle have different diameters. One DWNT has an outer diameter of 3.1 nm and an inner diameter of 2.3 nm while another DWNT has an outer diameter of about 1.75 nm and an inner diameter of

0.95 nm. The distance between the outer and the inner graphene layers is about 0.4 nm in the DWNTs.

The as-grown nanotube materials have been further characterized by Raman spectroscopy. In this work, Nd–YAG laser with wavelength of 1064 nm was used. Fig. 3 shows Raman spectrum of the carbon nanotube materials. The spectrum obtained in the low-frequency domain shows five components at 95.6, 134.2, 146.8, 172.2, 263.6 cm^{-1}. It has been well known that the frequency range is strongly dependent on the diameter of SWNTs. In the case of carbon nanotube bundles, we can use same formula to calculate the diameters of SWNTs and DWNTs, even though DWNTs, which consist of two concentric cylindrical graphene layers, can be considered as two coaxial SWNTs [7]. In our experiment, synthesized SWNTs and DWNTs are bundle structures in which van der Waals interaction exists between the tubes. Therefore, the expression $w\ (cm^{-1}) = 6.5 + 223.75/d$ (nm) can be used to calculate the diameter of SWNT and DWNT [21]. According to this expression, the radial breathing mode (RBM) frequencies of 95.6, 134.2, 146.8, 172.2, and 263.6 cm^{-1} correspond to CNTs with the diameter of 2.41, 1.72, 1.57, 1.34, and 0.87 nm, respectively. HRTEM observation shows that the diameter of SWNTs is in the range of 0.8–1.5 nm. Based on

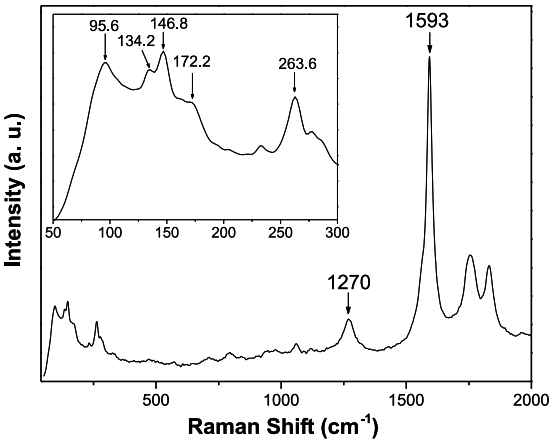

Fig. 3. Raman spectrum of the as-synthesized carbon nanotube materials by catalytic decomposition of CH_4 over Fe–Mo/Al_2O_3.

HRTEM observation, we can consider that the three peaks at 146.8, 172.2, and 263.6 cm^{-1} mainly result from SWNTs having diameters of 1.57, 1.34, and 0.87 nm. We can also consider that the two peaks at 134.2 and 263.6 cm^{-1} mainly result from DWNTs. In Fig. 2d, we can actually find two kinds of DWNTs, which have different diameters (the outer diameter of 3.1 nm/the inner diameter of 2.3 nm and the outer diameter of 1.75 nm/the inner diameter of 0.95 nm). We observed that the distance between graphene layers was 0.4 nm in the DWNTs. We suggest that the RBM peak of 134.2 cm^{-1} indicates the outer diameter (1.75 nm) of DWNTs, but the RBM peak corresponding to the inner diameter (0.95 nm) of those DWNTs is not clear in Raman spectrum. Moreover, the peak at 95.6 cm^{-1} results from the inner graphene layer of DWNTs with the inner diameter of 2.3 nm. The DWNTs may have the outer layer with a diameter of 3.1 nm even though there is no peak appearance in Raman spectrum. It is well known that CNTs with larger diameter over 3.0 nm exhibit a weak Raman cross-section, so their band in low-frequency domain is difficult to detect. In this work, Raman analysis for the diameter of nanotubes indicates good agreement with HRTEM observation. The band at 1270 cm^{-1} usually refers to as the 'D band' due to various forms of disordered sp^2 carbon. The tangential mode 'G band' at 1593 cm^{-1} provides an indication of ordered carbon. Raman analysis shows that D band is weak but G band is strong as shown in Fig. 3. The small ratio of I_D/I_G indicates that the produced nanotubes have low defect level in the atomic carbon structure. The characterization of Raman and TEM reveals that high-quality SWNTs and DWNTs can be synthesized by catalytic decomposition of methane. We consider that the controllable synthesis of SWNTs and DWNTs may be realized by adjusting the reaction parameters. Further work to control the synthesis of nanotubes is in progress.

In summary, SWNTs and DWNTs have been simultaneously synthesized by catalytic decomposition of CH_4 over Fe–Mo/Al_2O_3 catalyst. The yield of carbon nanotubes relative to the weight of Fe–Mo metal in Fe–Mo/Al_2O_3 catalyst after synthesis was over 250%. HRTEM observation reveals that carbon nanotube materials obtained are

about 70% SWNTs and about 30% DWNTs. The SWNTs have diameters in the range of 0.8–1.5 nm while DWNTs have two kinds of diameters, which indicate the outer diameter of 3.1 and 1.75 nm and the inner diameter of 2.3 and 0.95 nm, respectively. The produced carbon nanotube materials indicate a high-quality graphite structure.

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