Growth Conditions of Double-Walled Carbon Nanotubes in Arc Discharge

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Preparation conditions for large-scale synthesis of double-walled carbon nanotubes (DWCNTs) by using electric arc discharge were examined. Iron, cobalt and nickel were used as catalysts, and sulfur was added as a promoter. Hydrogen and rare gases were used as buffer gases of the arc discharge. The yield of DWCNTs was sensitively dependent on the catalytic metal and the atmosphere gas, and it was deduced that the addition of sulfur into an electrode and the presence of hydrogen in atmosphere are indispensable for the selective formation of DWCNTs. In the optimal condition, DWCNTs occupied more than 90% of the synthesized nanotubes, though trace amounts of single-walled carbon nanotubes are also grown. The diameters of DWCNTs are in a range from 2 to 5 nm, and the spacings between the inner and the outer walls are about 0.38 nm wider than those usually observed for multiwall carbon nanotubes.

1. Introduction

Carbon nanotubes (CNTs) are now attracting considerable attention because of their potential applications from nanoelectronics to energy storage.[1] CNTs produced in large quantities so far are classified typically into two groups: i.e., single-walled and multiwalled CNTs. Diameters of single-walled carbon nanotubes (SWCNTs) can be controlled from 1 to 3 nm by varying synthesis conditions,[2−4] and relatively narrow distributions of SWCNT diameters are obtained. For multiwalled carbon nanotubes (MWCNTs), on the other hand, it has so far been impossible to control the number of walls comprising them. Electric arc discharge between carbon electrodes produces MWCNTs with a wide range of wall thicknesses (ranging from two to ca. 50 walls).[5,6] Recently, Hutchison et al.[7] succeeded in preparing double-walled carbon nanotube (DWCNTs) in large quantities by arc discharge using a mixture of Fe, Co, Ni, and S powders as catalyst in an atmosphere of argon and hydrogen mixture. DWCNTs offer a new class of CNTs that will widen the research field of CNTs and provide versatility to CNTs for their applications. In fact, a recent study on field emission has shown that DWCNTs possess both merits of SWCNTs and MWCNTs;[8] i.e., threshold voltage for electron emission of DWCNTs is as low as that for SWCNTs and the lifetime (long-term emission stability) of DWCNTs is excellent as that of MWCNTs.

In the present study, DWCNT production experiments were carried out systematically under various synthesis conditions. It was found that the purity and yield depend sensitively on catalysts and atmosphere gases, and under certain conditions DWCNTs were selectively obtained in weblike carbon soot formed by arc discharge.

It is revealed that the addition of sulfur to iron-group metals as catalysts and the presence of hydrogen in atmosphere are indispensable for the selective formation of DWCNTs. Structural characterization of DWCNTs was also performed by transmission electron microscopy (TEM).

2. Experimental Section

Direct current (DC) arc discharge experiments were carried out in a stainless steel chamber that was filled with hydrogen, helium, or their mixture at 300 Torr. Sulfides of ion group metals (FeS, NiS, and CoS) or mixtures of the sulfides and elements of Fe, Ni, and Co were used as catalysts for producing DWCNTs. A mixture of sulfides, elemental metals, and graphite powders was packed into a hole (4 mm diameter and 40 mm deep) of a graphite rod (6 mm diameter and 50 mm long), which was used as an anode. The mixing ratios of sulfides, elemental metals, and graphite powders are summarized in Table 1, together with the observed yield of DWCNTs. The cathode was a pure graphite rod (13 mm diameter and 30 mm long). The purity of the graphite rod and powder was 99.998%, and the purity of the metal and sulfide powders was more than 99%. The discharge current was typically 50 A, and the voltage, about 20 V. Soot materials with weblike appearance were formed on the inner walls of the reaction chamber and around the cathode after the evaporation. The weblike materials were examined by transmission electron microscopes operated at 120 and 200 kV (JEM2010). TEM Samples were prepared by sonicating soot materials in ethanol and putting a drop of the suspension onto a copper grid covered with a perforated carbon film.

3. Results

Figure 1 shows a typical TEM image of DWCNTs obtained using FeS−NiS−CoS catalysts in a hydrogen gas atmosphere of 300 Torr (preparation condition (PC) no. 1 in Table 1), which is one of the best conditions for preparing DWCNTs in large quantity. A pair of dark fringes with a spacing of 0.38 nm is observed on both sides of nanotubes, showing that each tube comprises of two walls and is hollow inside. The dark, spherical particles covered with carbon layers are catalyst metals. Other tubular products such as single-walled carbon nanotubes (SWCNTs) were also found as minor product, as revealed by

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TABLE 1: Preparation Conditions and Yield of DWCNTs

			chamber soot		cathode soot	
no.	catalysts and wt. ratio	gas (pressure in Torr)	yield of CNTs[a]	fraction of DWCNT[b]	yield of CNTs[a]	fraction of DWCNT[b]
1	FeS:NiS:CoS = 1:1:1	H_2 (300)	H	~90%	H	~90%
2	FeS:NiS:CoS = 1:1:1	H_2 (150) + He (150)	VL	>80%	L	>80%
3	FeS:NiS:CoS = 1:1:1	H_2 (50) + He (250)	VL	~60%	VL	~60%
4	FeS:NiS:CoS = 1:1:1	He (300)	VH	none	H	none
5	FeS:Ni:Co = 1:1:1	H_2 (300)	H	~30%	H	~30%
6	Fe:Ni:Co:S = 1:1:1:2	H_2 (300)	H	~60%	H	~60%
7	FeS:NiS = 1:1	H_2 (300)	M	>80%	L	>80%
8	FeS:CoS = 1:1	H_2 (300)	M	>80%	M	>80%
9	CoS:NiS = 1:1	H_2 (300)	L	>80%	L	>80%
10	FeS	H_2 (300)	M	>80%	L	>80%
11	CoS	H_2 (300)	M	~30%	M	>80%
12	NiS	H_2 (300)	L	>80%	VL	>80%
13	FeS	He (300)	VL	none	VL	none
14	CoS	He (300)	H	none	VH	none
15	NiS	He (300)	VL	none	M	none
16	Fe	H_2 (300)	none	none	none	none
17	Co	H_2 (300)	L	none	L	none
18	Ni	H_2 (300)	none	none	VL	none

[a] Yield of CNTs, which means the amount of carbon atoms comprising DWCNT and SWCNT against the whole amount of carbon in the soot, is graded into six ranks: VH (more than 30%), H (~20%), M (~10%), L (several %), VL (less than 1%), and none (0%). [b] Fraction of DWCNT means the ratio of number of DWCNT to the total number of DWCNT and SWCNT.

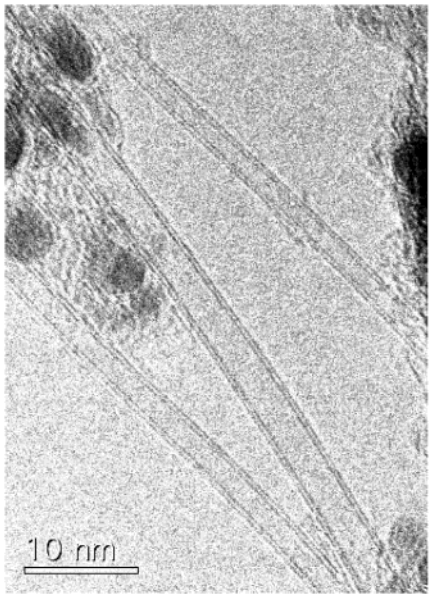

Figure 1. TEM picture of DWCNTs grown in a hydrogen arc with FeS−NiS−CoS catalyst.

TEM. One of such TEM pictures is shown in Figure 2 where SWCNTs, as indicated by an arrow, are observed together with DWCNTs. The relative amount of DWCNTs against the whole tubular products (DWCNTs + SWCNTs) depends on the preparation condition as summarized in Table 1.

The length of DWCNTs exceeds 1 μm. Outer diameter of DWCNTs ranges from 2 to 5 nm, and the diameter distribution is relatively wide compared with that for SWCNTs prepared from Ni−Y[9] and Rh−Pt catalysts[2] or even those prepared from Co−Bi and Co−Pb catalysts[10] in helium. Distributions of outer diameters of DWCNTs in the chamber and the cathode soot, prepared under the optimum condition for DWCNT growth (PC no. 1), are shown in Figures 3a and 3b, respectively. Diameters of SWCNTs coexisting with DWCNTs in each soot are also shown in the respective figures. The numbers of DWCNTs and SWCNTs shown in the histograms approximately reflect the relative population of the two types of CNTs. DWCNTs are the major CNTs in the both soot (i.e., chamber and cathode soot); DWCNTs occupy about 90% of the CNTs in the soot.

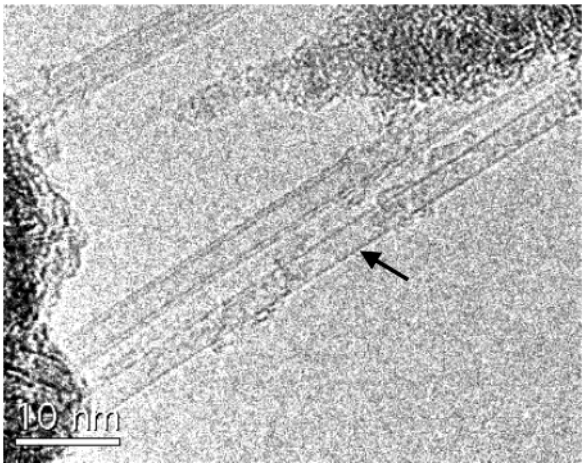

Figure 2. TEM picture of a SWCNT (indicated by arrow) coexisting with DWCNTs.

The outer diameter of DWCNTs is in average thicker than that of simultaneously grown SWCNTs. The by-produced SWCNTs have larger diameters than those commonly prepared without sulfur additive.[2−4,9]

The interlayer spacing between graphene layers forming the wall of DWCNTs was about 0.38 nm in average, which is about 12% larger than that usually observed for MWCNTs (0.34 nm).[11]

The growth and the yield of DWCNTs are very sensitive against the preparation condition as revealed in Table 1. In an atmosphere of helium even with the sulfur additive, no DWCNTs in the present experiment (see PC no. 4 and nos. 13−15) or very few DWCNTs in the previous study[12] were observed. On the other hand, when the atmosphere of arc discharge was pure hydrogen or a mixture of hydrogen and rare gases (He or Ar), DWCNTs were formed (see PC nos. 1−3 and nos. 5−12). These observations suggest that hydrogen gas is indispensable for DWCNT growth. However, even an arc discharge in hydrogen did not produce any DWCNTs without sulfur additive (see PC nos. 16−18). Moreover, no DWCNT was obtained when the iron group metals were replaced by other metals such as yttrium and lanthanum. Summarizing these observations, we can conclude that the iron-group metal catalyst,

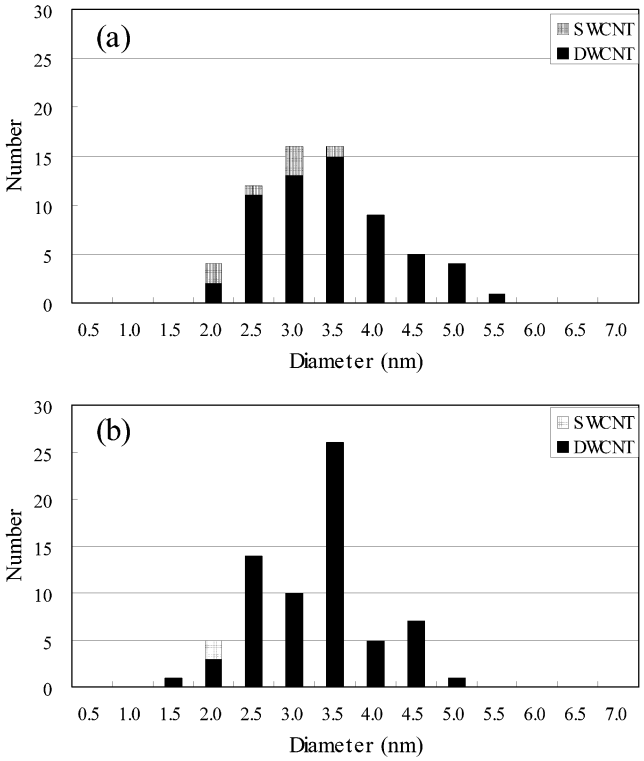

Figure 3. Diameter distribution of DWCNTs and SWCNTs found in (a) chamber soot and (b) cathode soot. Catalyst used was FeS−NiS−CoS, and buffer gas, 300 Torr hydrogen. The numbers of DWCNTs and SWCNTs in the histogram reflect the relative population of the respective nanotubes.

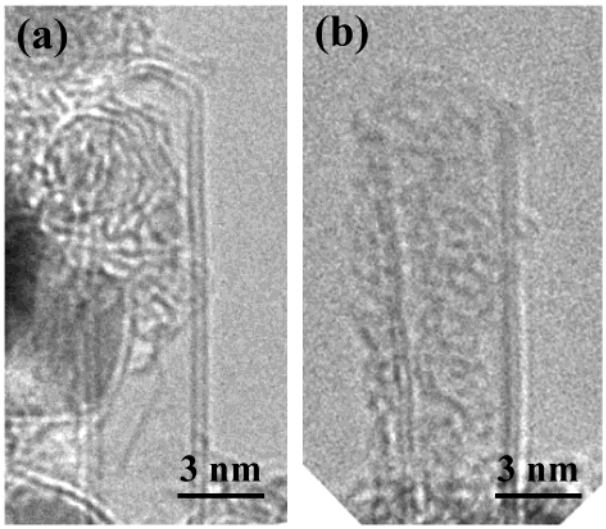

Figure 4. TEM pictures of tips of DWCNTs. (a) Capped tip with two layers and (b) open tip.

sulfur additive, and hydrogen gas are indispensable for the DWCNT production.

Structural details of DWCNTs may render some information on their growth mechanism. Tips of DWCNTs were sometimes observed as shown in Figure 4, though it was difficult to find tips because DWCNTs were entangled with each other and their tips were often buried in agglomerates of amorphous carbon and catalyst particles. Not only capped but also open-ended DWCNTs were found as shown in Figures 4a and 4b, respectively. The cap in Figure 4a consists of two layers, while the open end in Figure 4b is clogged with carbon debris (amorphous carbon).

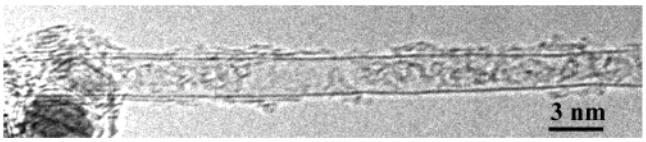

Figure 5. TEM picture of an imperfect DWCNT, in which the outer layer is partially peeled off.

Imperfect DWCNTs, i.e., partially single-walled CNTs, were occasionally observed, as shown in Figure 5. Triple-walled CNTs (TWCNTs) were also found, though they were rare as reported previously.[7]

4. Discussion

4.1. Effect of Sulfur and Hydrogen. The observation of partially doubled SWCNTs (Figure 5) and TWCNTs suggest layer-by-layer growth of DWCNTs, i.e., the inner layer is first formed and then the outer layer grown on it, though the growth mechanism is still an open question like that for SWCNTs. Alternatively, the presence of open-ended DWCNTs (Figure 4b) and the partially peeled DWNTs (Figure 5) may result from the etching effect of reactive hydrogen radicals formed in arc plasma. Sulfur additive is known to have an effect to promote the formation of CNTs and widen the diameter of SWNTs.[12] Moreover, we believe that sulfur enhances the growth of graphitic carbon consisting of multiple layers and thus assists to make thick CNTs. The balance between the thickening of layers by the sulfur and the etching of the layers by hydrogen may be important for the growth of DWCNTs.

4.2. Interlayer Spacing in Double-Layered Graphite. DWCNTs prepared in the present experiment have a wide interlayer spacing (0.38 nm in average) compared to that of ordinal MWCNTs and that of turbostratic carbon (typically 0.34 nm). The present result is consistent with that previously reported by Hutchison et al. who produced DWCNTs by arc discharge.[7] Methods other than the arc discharge can also produce DWCNTs; one such methods is the heat treatment of SWCNTs encapsulating C_{60} fullerenes (so-called "peapods"). Bandow et al. reported that DWCNTs made from peapods also have wide interlayer spacings (0.36 nm),[13] which are about 7% larger than those of normal graphitic carbon. Irrespective of the preparation methods, the interlayer spacings in DWCNTs are distinctly wide compared to those in thick MWCNTs. However, thin MWCNTs with diameters less than about 5 nm are reported to have wide interlayer spacings (ca. 0.35−0.38 nm).[14] These thin MWCNTs are expected to be comprised of a small number of layers, for example, of two to three layers, though the numbers of layers were not explicitly described in the report.[14]

This wide spacing in double-layered graphenes is not limited to the tubular form of carbon. In 1978, Iijima[15] reported wide spacings in planar carbon that consists of only two to four graphene layers. According to his results, the interlayer spacing converged steeply to that of bulk graphite with the increase of the layer number: about 15% larger for the two-layer graphite, and about 5% for the three-layered one. For four-layered graphite, the spacing was almost the same as the normal bulk value.

The significant expansion of the interlayer spacing has been theoretically analyzed by Yoshizawa et al.[16] with the use of the frontier orbital ideas and orbital symmetry. They showed that the highest occupied crystal orbital (HOCO) in the double-layered graphite is out of phase with respect to the interlayer coupling and thus the HOCO has a nodal plane (zero amplitude of wave function) at the center of the two graphene sheets.

Therefore, the two sheets would experience repulsive force if this orbital was occupied. This brings about a large spacing in the double-layered graphite.

5. Conclusion

Carbon arc experiments were carried out under various conditions in order to reveal the growth condition for DWCNTs. Sulfur additive and hydrogen gas, in addition to the iron-group metal catalysts, are indispensable for the selective production of DWCNTs. Under the optimum preparation condition, the majority (more than 90%) of CNTs were DWCNTs with a minor amount of SWCNTs. The outer diameter of DWCNTs was 3.5 nm in average, and the interlayer spacing was about 0.38 nm, which was about 12% larger than that usually observed for MWCNTs.

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