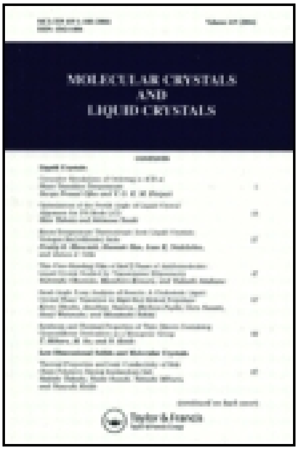

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High Yield Synthesis of Single-Walled Carbon Nanotubes by DC Arc Discharge in High Temperature He Gas

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High yield synthesis of single-walled carbon nanotubes (SWNTs) was realized by DC arc discharge evaporation of Ni 4% – Y 1% composite graphite rodes in high temperature atmospheric gas of He. With the help of scanning electron microscope and transmission electron microscope, SWNTs were confirmed as the web formed in the evaporation chamber. The micro-Raman studies on the specimen indicated that the SWNTs had four breathing mode frequencies corresponding to 1.25 – 1.49 nm diameter of SWNTs.

Keywords: single-walled carbon nanotube; high temperature arc discharge

INTRODUCTION

Carbon nanotubes were first found by Iijima in the cathode deposit obtained by DC arc discharge evaporation of pure graphite electrodes in inert gas [1]. These carbon nanotubes were consisted of many seamless cylindrical shells of graphene sheets, and they were called as multiwalled carbon nanotubes (MWNTs) after the discovery of single-walled carbon nanotubes (SWNTs) made of only one graphene sheet [2,3]. Theoretical calculations predicted that SWNTs were either metallic or semiconducting depending on their diameter and chirality [4,5]. The prediction was confirmed by scanning tunneling spectroscopy on individual SWNTs [6,7].

In order to produce SWNTs, the use of metal composite graphite electrodes [2,3,8] or rods [9] was essentially necessary. High yield synthesis of

SWNTs could be realized by laser ablation[9] or by DC arc discharge evaporation[8]. In this paper, it is shown that the mass production of SWNTs was realized by DC arc discharge evaporation of composite graphite electrodes in high temperature atmospheric gas of He.

EXPERIMENTAL

The schematic diagram of apparatus for DC arc discharge evaporation in high temperature atmospheric gas is shown in Fig. 1. In the center of a chamber, a pure graphite cathode (10 mm diameter, lower side) and Ni 4% - Y 1% composite graphite anode (6 mm diameter, upper side) were installed vertically. A cylindrical carbon heater (30 mm diameter) was inserted surrounding the two electrodes. The carbon heater was covered with carbon wall and carbon felt (60 mm inner diameter × 100 mm height) to maintain high temperature.

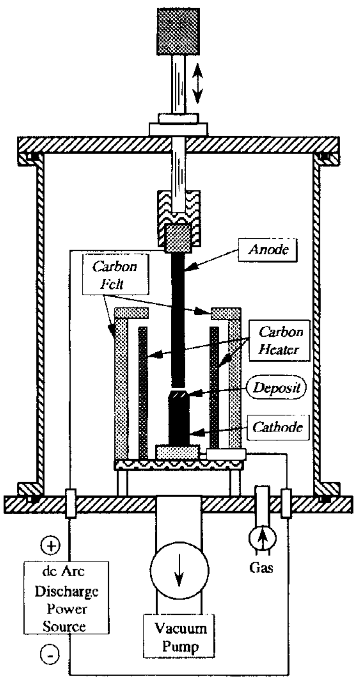

FIGURE 1
The shematic diagram of apparatus for SWNT preparation by DC arc discharge evaporation in high temperature He gas.

After introducing He gas into the working chamber at the pressure of 500 Torr and supplying an electric power to the surrounding carbon heater, a DC arc voltage was applied between the two electrodes. The electric power of carbon heater was varied from 1.5 to 10 kW (the temperature of carbon heater was 700 - 1100℃), and the DC arc current was set in the range of 30 - 80A. The composite graphite anode of Ni - Y was evaporated and a large amount of carbon smoke occurred. During evaporation process, the gap between two electrodes was kept about 2 mm by moving the upper anode with monitoring the DC arc voltage. After the evaporation, a carbon deposit was formed on the surface of lower cathode, and a lot of cottony carbon soot was suspended on the wall of working chamber like a web.

The web was collected with a pair of tweezers and observed by a scanning electron microscope (SEM; Topcon ABT-150) and a transmission electron microscope (TEM; Hitachi HU-12A). The micro-Raman spectra were recorded by Raman spectrometer (Jobin Yvon; RAMANOR T64000) at 514.5 nm (Ar-laser) in a low power of 10 mW. Then, an objective lens (100×) was used, giving an illuminated spot size of 1 μm on the surface of specimen. Typical acquisition time to obtain spectra was 90s, and non-polarized light was used.

EXPERIMENTAL RESULTS

Figure 2 shows a typical SEM micrograph of collected cottony carbon soot. The specimen was prepared by DC arc current 50A, and the electric power of carbon heater was 2.5 kW. A large amount of entangled carbon filaments with diameter ranging from 10 to 35 nm can be observed. It was considered that these carbon filaments consisted of the bundle of SWNTs.

The TEM observation on cottony carbon soot showed that some metal particles (20-30 nm in diameter) were existing with the bundle of SWNTs, and usually covered by carbon materials. Figure 3 shows a typical TEM micrograph of SWNTs, which were prepared in the same condition as that used to take the SEM micrographs of Fig. 2.

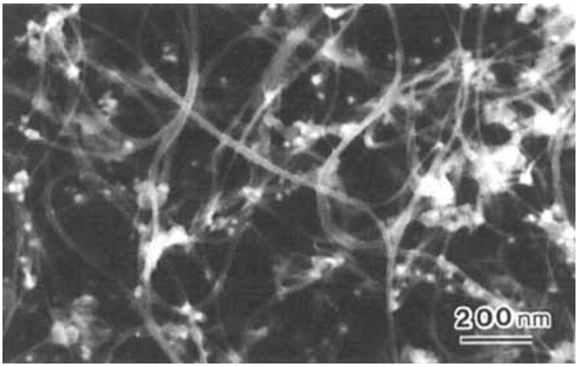

FIGURE 2 A characteristic SEM micrograph of collected web.

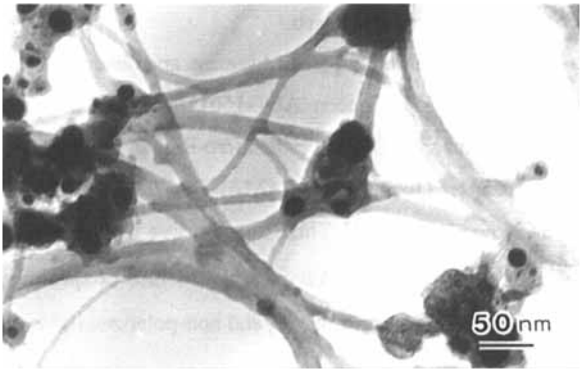

FIGURE 3 A typical TEM micrograph of SWNTs.

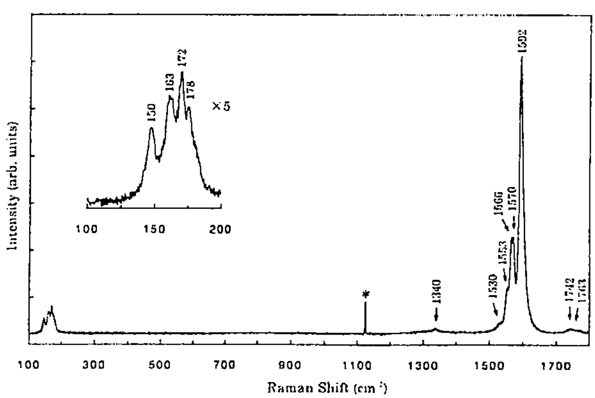

FIGURE 4 The micro-Raman spectra covering the frequency range from 100 to 1800 cm^{-1}.

The micro-Raman spectrum covering the frequency range from 100 to 1800 cm^{-1} of SWNTs is shown in Fig. 4, and its inset shows the breathing modes of SWNTs (four peaks at 150, 163, 172 and 178 cm^{-1}). In the high frequency range from 1500 to 1600 cm^{-1}, five peaks (1530, 1553, 1566, 1570 and 1592 cm^{-1}) can be observed, and they are characteristic of SWNTs [8,10,11]. All of these peaks should be assigned to a splitting of the E_{2g} mode of graphite. In addition, the peaks at 1742 and 1763 cm^{-1} can be attributed to a combination of the peak at 1592 cm^{-1} and the breathing modes. The peak at 1340 cm^{-1} corresponds to the disorder-induced phonon mode of graphite [12,13], and the sharp peak at 1121 cm^{-1} indicated by * was from the fluorescent lamp line.

DISCUSSION AND CONCLUSIONS

The synthesis of SWNTs by DC arc discharge with the catalystic bimetal (Ni-Y) composite graphite electrodes was first carried out by Journet *et al.*[8]. They could obtain a high yield of SWNTs more than 50% in a narrow area of collar deposit on the side of the cathode, but the yield of SWNTs was little in the web produced in the whole chamber. However, such collar deposit was not obtained in the present high temperature DC arc discharge. On the contrary, a large amount of web was formed in a wide space of the chamber and a high yield of SWNTs more than 50% in the web was comfirmed by the Raman spectrum. Thus, the quantity of the web including SWNTs was remarkably increased.

Around the E_{2g} mode of graphite (about 1580 cm^{-1}), the characteristic patterns [8, 10, 11] of SWNTs were observed in the micro-Raman spectra of the web. With the help of theoretical calculation for breathing modes [10,14,15], the diameter and chirality of SWNTs can be worked out as shown in Table 1. The chiral SWNT (14,4) with 1.30 nm diameter is semiconducting, and others are metallic. From this table, the diameter distribution of SWNTs is very sharp (1.25 - 1.49 nm), and the experimental data can be explained theoretically.

In conclusion, SWNTs were produced by Ni 4% - Y 1% composite graphite electrodes evaporation using DC arc discharge current of 50A in high temperature He gas. The yield of SWNTs in the web could reach to more than

50%, and the diameters of SWNTs ranged from 1.25 to 1.49 nm.

TABLE 1 Measured Raman shift of breathing mode of SWNTs

Experiment	Chiral indexes	Dia. of SWNTs	Theory	Ref.
178.4 cm^{-1}	(12, 6) chiral	1.25 nm	178 cm^{-1}	[a]
172.2	(14, 4) chiral	1.30	172	[a]
163.2	(10,10) armchair	1.37	163	[a]
149.9	(11,11) armchair	1.49	150	[b]

[a.]; J. Yu, R. K. Kalia and P. Vashista, *J. Chem. Phys*, **103**, 6697 (1995).
[b.]; A. M. Rao et al., *Science*, **273**, 187 (1996).

Acknowledgments

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References

[1] S. Iijima, *Nature*, **354**, 56 (1991).
[2] S. Iijima and T. Ichihashi, *Nature*, **363**, 603 (1993).
[3] D. S. Bethune, C. H. Kiang, M. S. de Vries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers, *Nature*, **363**, 605 (1993).
[4] N. Hamada, S. Sawada and A. Oshiyama, *Phys. Rev. Lett.*, **68**, 1579 (1992).
[5] R. Saito, M. Fujita, G. Dresselhaus and M. S. Dresselhaus, *Phys. Rev. B*, **46**, 1804 (1992).
[6] J. W. Wildöer, L. C. Venema, A. G. Rinzler, R. E. Smalley and C. Dekker, *Nature*, **391**, 59 (1998).
[7] T. W. Odom, J. Huang, P. Kim and C. M. Lieber, *Nature*, **391**, 62 (1998).
[8] C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. L. de la Chapelle, S. Lefrant, P. Deniard, R. Lee and J. E. Fischer, *Nature*, **388**, 756 (1997).
[9] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D.T. Colbert, G. E. Scuseria, D. Tománek, J. E. Fischer and R. E. Smalley, *Science*, **273**, 483 (1996).
[10] A. M. Rao, E. Richter, S. Bandow, B. Chase, P. C. Eklund, K. A. Williams, S. Fang, K. R. Subbaswamy, M. Menon, A. Thess, R. E. Smalley, G. Dresselhaus and M. S. Dresselhaus, *Science*, **275**, 187 (1997).
[11] A. Kasuya, Y. Sasaki, Y. Saito, K. Tohji and Y. Nishina, *Phys. Rev. Lett.*, **78**, 4434 (1997).
[12] R. J. Nemanich and S. A. Solin, *Phys. Rev. B*, **20**, 392 (1979).
[13] X. Zhao and Y. Ando, *Jpn. J. Appl. Phys.*, **37**, 4846 (1998).
[14] J. Yu, R. K. Kalia and P. Vashishta, *J. Chem. Phys.*, **103**, 6697 (1995).
[15] R. Saito, T. Takeya, T. Kimura, G. Dresselhaus and M. S. Dresselhaus, *Phys. Rev. B*, **57**, 4145 (1998).