

Synthesis of Multi-Walled Carbon Nanotubes in an Arc Discharge Using Hydrocarbons Precursor as Carbon Sources

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Abstract: The influence of starting carbon materials on the synthesis of carbon nanotubes (CNTs) is investigated. Comparisons are made between graphite rods and polycyclic aromatic hydrocarbons (PAHs) as carbon sources in helium arc discharge. The major parameters are also evaluated in order to obtain high-yield and high-quality carbon nanotubes. The cathode deposits are examined using scanning electron microscopy (SEM) and scanning probe microscopy (SPM) in AFM mode to determine the microstructure and nanostructure of carbon nanotubes. The SEM investigation of the carbon nanotube deposits formed on the cathode provides evidence that PAHs can serve as building blocks for nanotube formation. The high-temperature graphitization process induced by the arc plasma enables the hydrocarbons to act as carbon sources and changes the aromatic species into the layered graphite structure of CNT. These polycyclic aromatic hydrocarbons not only act as the precursors but also enhance the production rate of carbon nanotubes. The PAH precursors thus play an important role in the mass production of carbon nanotubes.

Key words: Multi-Walled Carbon Nanotube (MWCNT) • Arc Discharge • Precursor • Polycyclic Aromatic Hydrocarbons (PAH) • Field Emission

INTRODUCTION

The fullerenes and carbon nanotubes (CNTs) are both new carbon materials discovered recently. The discovery of fullerene, reported by Kroto *et al.* [1] in 1985, had an strong impact which extended way beyond the restrict of academic chemical physics and marked the beginning of a new era in carbon material science. In 1991, Iijima [2] discovered the carbon nanotube with a diameter of 3-10 nm. This discovery, followed by the large synthesis of CNTs, has generated extraordinary excitement in scientific communities all over the world. A notable progress has been made in CNTs synthesis. These synthesis methods including electric arc discharge [3-6], laser-vaporization [7, 8] and catalytic decomposition of hydrocarbons [9, 10], have been reported to be able to form CNTs. Moreover, experiments have been performed to produce nanowires and nanorods for future potential applications [11-14]. A large volume of research work has been focused on the MWCNTs formed by a dc arc discharge method. Lauerhaas *et al.* [6] have studied the effect of arc parameters on the growth of MWCNT. This

study provides evidence that polycyclic aromatic hydrocarbons (PAHs) can serve as building blocks for nanotube formation and the size of the building blocks are important for nanotube growth. Recently, Liu *et al.* [15] reported a semi-continuous hydrogen arc discharge method, by which CNTs can be synthesized at higher production rate with catalyst together. There have been many reports on the potential applications of MWCNTs since their discovery [16-19]. Chang's research group has demonstrated a nanotube-based fieldemission flat panel display [20]. Further improvement of this technology may lead to easy-to-make and low-cost flat panel display. The CNT has the great potential to replace the microtip emitter of flat panel display due to its high brightness. The CNT can also be used as probe tips for scanning probe microscope (SPM). The MWCNT is produced either by arc discharge or catalytic-CVD currently. The quantity and quality, however, have not reached the expectation. In order to obtain possible large-scale and high-quality CNTs, the MWCNTs are synthesized by using the arc discharge method along with polycyclic aromatic hydrocarbons as precursor.

MATERIALS AND METHODS

The vacuum arc furnace in vertical type was used to produce the MWCNTs. A schematic drawing of the arc discharge apparatus is shown in Fig. 1. The arc was generated by a dc power supply from a welding machine.

The dc voltages were 10-50 V and the currents were 30-90 A. The dynamic flowing of He gas was supplied in the pressure of 300-600 mmHg and at the flow rate of 5-10 l/min. The diameter of anode graphite was 10 mm and those of cathode graphite were 10 and 20 mm. The graphite specimen was cleaned first and the top surface of cathode graphite was then coated with a hydrocarbon compound paste and the PAH precursor. The PAH precursors had two types: xylene (C_8H_{10}) and pyrene ($C_{16}H_{10}$). The gaps between anode and cathode electrodes were 1-3 mm. The major experimental parameters of MWCNT synthesized by arc discharge method are listed in Table 1. After the arcing of anode graphite, the graphite rod started to proceed with the deposition under the stable plasma environment. The CNTs were formed on the surface of cathode graphite. The CNT deposit specimens after suitable cooling were then examined using SEM to determine their microstructure.

Table 1: The major experimental parameters of MWCNT synthesized by arc discharge method

Specimen	Anode diameter (mm)	Cathode diameter (mm)	Precursor	He flow rate (l/min)	Reaction time (min)
A	10	10	non	5	5
B	10	10	xylene	10	1
C	10	20	xylene	5	40
D	10	10	pyrene	5	1

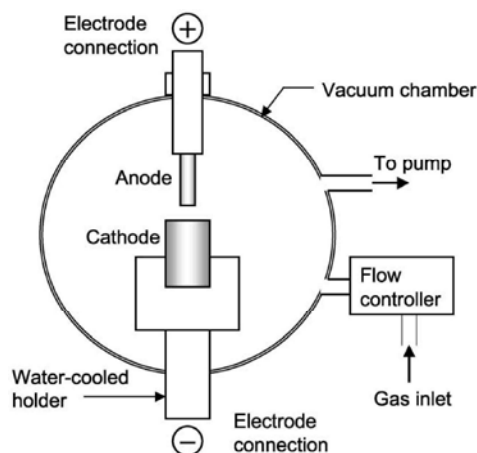


Fig. 1: A schematic diagram of the apparatus used for synthesizing MWCNTs by a dc arc discharge method

RESULTS AND DISCUSSION

The typical SEM micrographs of cathode deposit and AFM images are shown in Figs. 2-8. Fig. 2(a) shows the cross-section of the specimen A. The fine columnar structure consisting of flakes can be observed on the deposit.

The diameter of each MWCNT column is about 10-30 μm . The fiber-like CNTs and carbon nanoparticles distributed randomly were observed on the surface of the fine column, shown in Fig. 3.

Fig. 4 shows the SEM micrograph of specimen B (using xylene) and Fig. 5 shows the AFM image of specimen B. At the top surface, the long fibrous MWCNTs with the length of more than 20 μm can be seen. The particles of hydrocarbon compound paste in the order of micrometer were observed below the MWCNTs. Compared with the precursor-free specimen A, the long but loose CNT could be formed at 1 min.

Fig. 6 shows the center region of top surface of specimen C. The quasi-polygonal structure with dense fiber-like MWCNTs was observed at the top of cathode surface. A typical diameter of CNT bundle is about 20-30 μm . The length of CNT is about 5 μm . From the results of specimens B and C, we can observe that the small amount but long CNTs were formed at 1 min. However, the large number but short CNTs were produced at longer time.

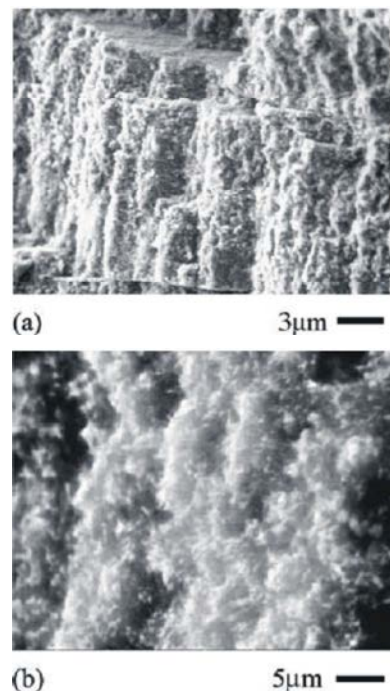


Fig. 2: (a) SEM micrograph of specimen A, (b) high magnification

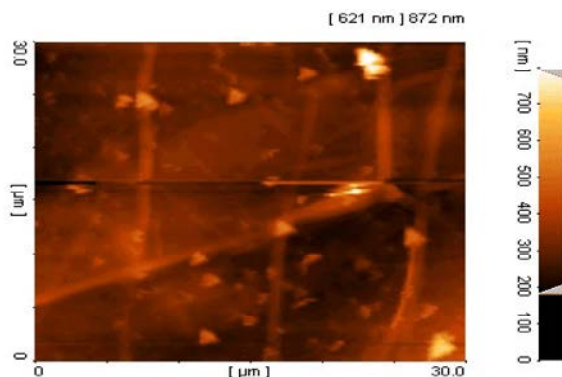


Fig. 3: AFM image of MWCNTs distributed randomly

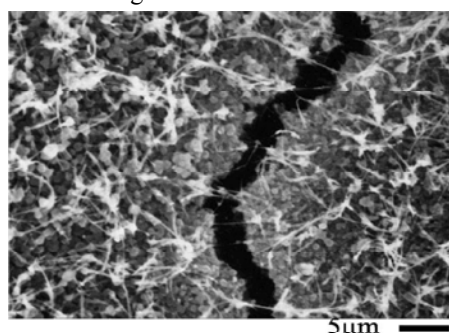


Fig. 4: SEM micrograph of specimen B

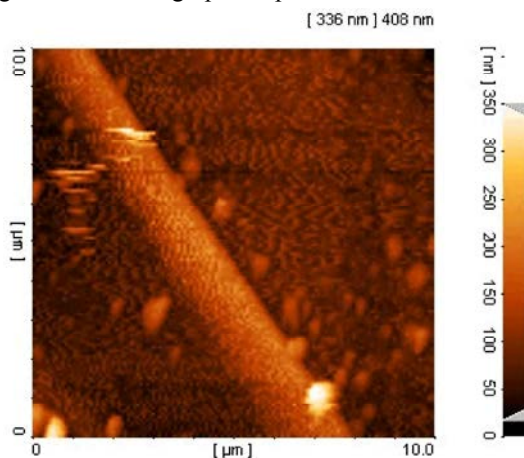


Fig. 5: AFM image of specimen B

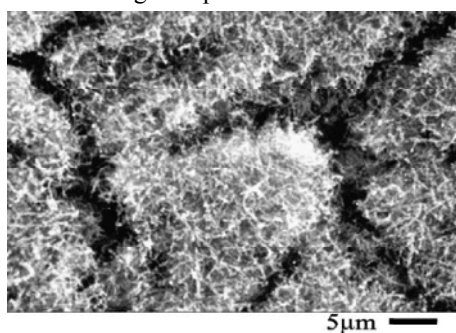


Fig. 6: SEM micrograph of specimen C

The SEM micrographs of specimen D (using pyrene) are shown in Fig. 7(a) and (b). The fine MWCNT columns are seen at the cross-section of center region and the coarse columns are observed at the rim region. For the coarse columnar structure, the bud-like crystal grows upward along the vertical direction and becomes a stone-like tree. On the other hand, the fine columnar structure consists of quasi-scale carbon flake. The height of the fine column is about 0.7-1.1 mm. The length of MWCNT is estimated to be about 10-50 μm .

The MWCNT columns were observed on the cross-section of graphite deposit. These parallel MWCNT columns grow approximately along the deposit axis. The electric field accordingly has an effect on the formation of CNT [21, 22]. The diameter of each MWCNT column is in the range of 10-50 μm . From the SEM and AFM results, the columnar structure can be formed for the pure graphite and graphite coated with precursor in the arcing process. Furthermore, the column includes two primary structures. The fine column structure is located in the center region and the coarse column structure is found in the rim region typically. The microstructure of deposit mainly depends on the cooling condition.

The formation of MWCNT from graphite can be performed at both low temperature ($\sim 1000^\circ\text{C}$) and high temperature ($\sim 3000^\circ\text{C}$). At low temperature, the vapor-grown CNT is nucleated at the active spot. On the contrary, at higher temperature, the MWCNT growth and the graphitization of the thickening deposit take place at the same time. Consequently, all the coaxial CNTs grow immediately. The disordered carbon structure gradually changes towards an ordered graphite structure during the graphitization process.

In addition to the graphite fragment, the aromatic hydrocarbon can be used as a feasible material for the formation of MWCNT as shown in Figs. 4-8. The xylene contains one aromatic ring and the pyrene also contains four aromatic rings. The PAH structure is changed into nanotube in the graphitization process and the rearrangement of aromatic ring system then can lead to an increase in the formation and growth of MWCNT. Pyrene and xylene both have the ability to form carbon nanostructure and can be used as the building blocks for the formation and growth of MWCNT. The formation of MWCNT is thus much easier. The yield of MWCNT per unit area is relatively high as shown in specimens C and D. This gives strong evidence that PAHs not only act as the precursors but also enhance the growth rate of MWCNT. Therefore, the PAH precursors thus play an important role in the mass production of carbon nanotubes.

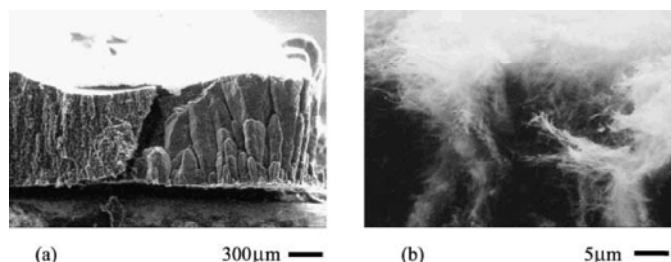


Fig. 7: SEM micrographs of specimen D (using pyrene precursor): (a) edge of cathode surface, (b) high magnification of MWCNT column

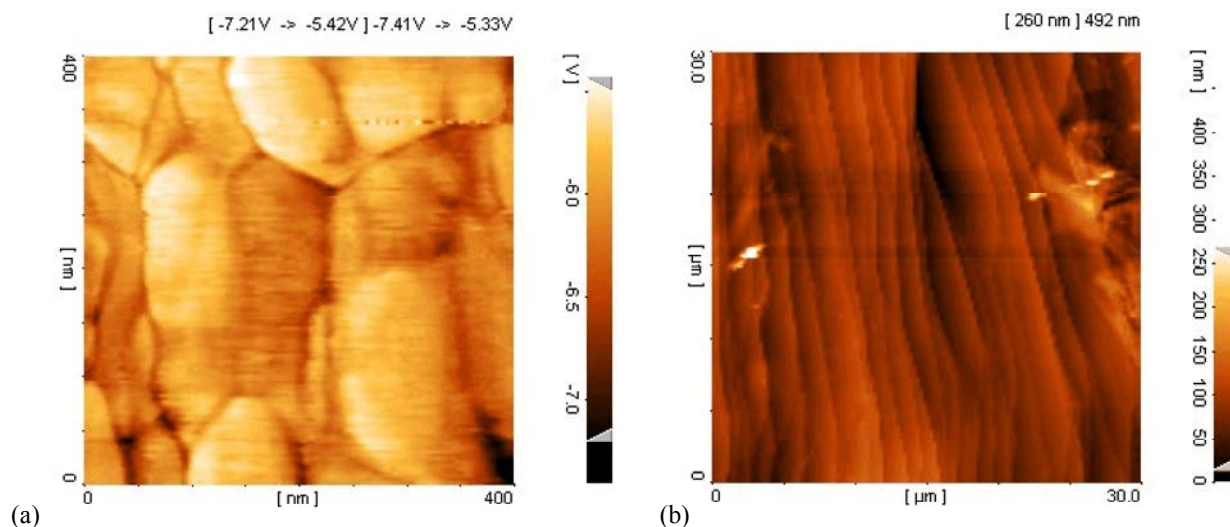


Fig. 8: AFM images of specimen D: (a) edge of cathode surface, (b) high magnification of MWCNT column

CONCLUSIONS

The MWCNT columns were observed on the surface of cathode deposits in the arc discharge. The fine columns composed of the fiber-like CNTs were observed on the cross section of graphite deposit for pure graphite and graphite coated with PAH precursor. These parallel MWCNT columns grow approximately along the deposit axis. The diameter of each MWCNT column is in the range of 10-50 μ m. The aromatic hydrocarbons, including pyrene and xylene, were suggested to not only act as precursors but also enhance the growth rate of carbon nanotubes.

REFERENCES

1. Kroto, H.W. and J.R. Heath, 1985. S.c. O'Brien, R.F. Curl, R.E. Smaller, Nature, 318: 162.
2. Lijima, S., 1991. Nature, 354: 56.
3. Wang, X.K., X.W. Lin, V.P. David, J.T. Ketterson and R.P.H. Chang, 1993. Appl. Phys. Lett., 60: 1881.
4. Lin, X., X.K. Wang, V.P. Dravid, R.P.H. Chang, J.T. Ketterson, 1994. Appl. Phys. Lett., 64: 181.
5. Jones, J.M., R.P. Malcolm, K.M. Thomas and S.H. Bottrell, 1996. Carbon, 34: 231.
6. Lauerhaas, J.M., J.Y. Dai, A.A. Setlur and R.P.H. Chang, 1997. J. Mater. Res., 12(6): 1536.
7. Colbert, D.T., J. Zhang, S.M. McClure, P. Nikolaev, Z. Chen, J.H. Hafner, D.W. Owens, P.G. Kotula, C.T. Carter, J.H. Weaver, A.G. Rinzler and R.E. Smaller, 1994. Science, 266: 1218.
8. Thess, A., 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. Tomanek, J.E. Fischer and R.E. Smaller, Science, 273: 483.
9. Li, W.Z., S.S. Xie, L.X. Qian, R.H. Chang, S.S. Zou, W.Y. Zhou, R.A. Zhao and G. Wang, Science, 1996. 274: 1701.
10. Huang, S. and L. Dai, 1999. AWH. Mau., J. Phys. Chem., 8 103(21): 4223.
11. Dai, J.Y., J.M. Lauerhaas, A.A. Setlur and R.P.H. Chang, 1996. Chem. Phys. Lett., 258: 547.
12. Setlur, A.A., J.M. Lauerhaas, J.Y. Dai and R.P.H. Chang, 1996. Appl. Phys. Lett., 69(3): 345.

13. Setlur, A.A., J.Y. Dai, J.M. Lauerhaas, R.P.H. Chang, 1998. Carbon, 36: 721.
14. Han, W., S. Fan, Q. Li and Y. Hu, 1997. Science, 277: 1287.
15. Liu, C., H.T. Cong, F. Li, P.H. Tan, H.M. Cheng, K. Lu and S.L. Zhou, 1999. Carbon, 37: 1865.
16. Wang, Q.H., T.D. Corrigan, J.Y. Dai, R.P.H. Chang and A.R. Krauss, 1997. Appl. Phys. Lett., 70: 3308.
17. Fan, S., M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassel and H. Dai, 1999. Science, 283: 512.
18. Harris, P.J.F., 1999. Carbon Nanotubes and Related Structures. Cambridge Univ. Press, Cambridge, UK, pp: 266-271.
19. Ebbesen, T.W., 1997. Carbon Nanotubes: Preparation and Properties. CRC Press, Florida, pp: 277-290.
20. Wang, Q.H., A.A. Setlur, J.M. Lauerhaas, J.Y. Dai, E.W. See Ling and R.P.H. Chang, 1998. Appl. Phys. Lett., 72: 2912.
21. Lai, H.J., M.C.C. Lin, M.H. Yang, A.J.C. Win and S.J. Li, 2000. Nano-structured and Amorphous Materials Symposium, PCCU, Taiwan, pp: 702.
22. Shi, Z., X. Zhou, Z. Jin, Z. Gu, J. Wang, S. Feng, X. Xu, Z. Liu, 1996. Solid State Commun., 97: 371.