JOURNAL OF MATERIALS SCIENCE **39** (2004) 283–284

Synthesis of carbon nanowires using dc pulsed corona discharge plasma reaction

MING-WEI LI
Department of Chemistry, Tianjin University, Tianjin 300072, People's Republic of China
E-mail: mweilee@sohu.com

ZHENG HU, XI-ZHANG WANG, QIANG WU, YI CHEN
Department of Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

Carbon nanotubes grown on the cathode by arc discharge method were first observed in 1991 [1]. From then on, one-dimensional (1D) carbon nanostructures including carbon nanotubes and carbon nanowires have drawn much attention because of their unique physical properties and many potential applications. For example, carbon nanotubes possess excellent field emission properties and well-aligned carbon nanotube arrays have being considered to manufacture flat panel displays [2]. The outstanding properties exhibited by nanomaterials are determined by their microstructure. Recently, it is reported that carbon nanowires, which are solid and thus are different from hollow carbon nanotubes, have field emission properties comparable to or even better than those of carbon nanotubes [3–6].

Carbon nanowires can be synthesized by arc discharge method [3], chemical vapor deposition (CVD) [4, 7–9] and plasma enhanced-CVD [5, 6, 10]. As they have functioned in synthesizing nanotube, porous anodic aluminum oxide (AAO) template and nonequilibrium plasma are respectively used to produce aligned carbon nanowires [7, 9] and to lower the synthesis temperature [5, 6, 10]. It is important to synthesize 1D carbon nanostructures at lower temperature either for scientific research or for practical applications. A few kinds of nonequilibrium plasma such as hot filament plasma [11], microwave plasma [12] and glow plasma [13], have been successfully employed to synthesize carbon nanotubes and/or carbon nanowires by plasma enhanced-CVD method. However, the plasma enhanced-CVD method is usually operated at low gas pressure using a vacuum system. This is inconvenient and costly for large-scale synthesis of nanomaterials. Recently, we have successfully synthesized carbon nanotubes using ac corona discharge plasma reaction at atmospheric pressure [14]. In this letter, we report the synthesis of aligned carbon nanowires using dc pulsed corona discharge plasma reaction at atmospheric pressure and low temperature.

The setup used here is similar to that described previously [14]. The quartz tube reactor consists of two axially centered electrodes, an upper needle-like tungsten wire acting as anode and a lower circular stainless steel plate acting as cathode. A dc pulsed high voltage generator operating at 3000 V and 50 kpps with the power of 20 W was used to initiate the corona discharge plasma. A piece of AAO template was put onto the plate cathode and the wire anode was positioned with its top 5 mm above the template surface. The average diameter of template pores is about 80 nm. A small amount of Fe/Co catalytic particles were dc-electrodeposited into the template pores from a mixture solution of $FeSO_4$, $CoSO_4$ and H_3BO_3. The carbon nanowires were synthesized using methane (2 sccm) as carbon source together with hydrogen (20 sccm). The experiment was started at atmospheric pressure and room temperature and lasted for 10 min. The temperature within the reactor is estimated to be below 200 ° according to a thermocouple measuring method [14]. The product was characterized by a transmission electron microscope (TEM) (Jeol JEM-100S) and a scanning electron microscope (SEM) (Jeol JSM-6300) equipped energy dispersive X-ray (EDX) spectroscopy.

The SEM image of the as-prepared sample surface is shown in Fig. 1. It is seen that many carbon nanowires grew out from the template. Most of the nanowires have diameters of less than 100 nm, while only a few of them more than 200 nm. When the nanowires grew out from the template, they became curved due to the absence of the space restriction of the template channels.

When the AAO template was completely dissolved in a hydrochloric acid solution and then the nanowires were dispersed by ultrasonic treatment. As shown in Fig. 2, TEM image of the paralleled nanowires shows that they have diameters about 80 nm. Note that the nanowires are not hollow but solid at their cores. The inset of Fig. 2 shows the selected-area electron diffraction pattern of the nanowires. The diffuse diffraction ring implies that the carbon nanowires are mainly amorphous. Moreover, the friable characteristic of the carbon nanowires shown in Fig. 2 means that the strength of these nanowires is not high enough. This is in good agreement with the characteristic of carbon nanowires reported in the literatures [7–9].

To clarify whether or not the catalyst was at the template surface, EDX was used to analyze the chemical composition of the sample (see Fig. 3). The spectrum of the surface layer contains the co-existing signals corresponding to the elements of Al, O, S, C and W. The intense signals of Al, O come from the alumina template, and C indicates the carbon nanowires or other carbon species deposited at the template. The S is from the residue of sulfuric acid used during the template preparation. The element W comes from the tungsten anode

0022–2461

Figure 1 SEM image of carbon nanowires growing from the AAO template pores.

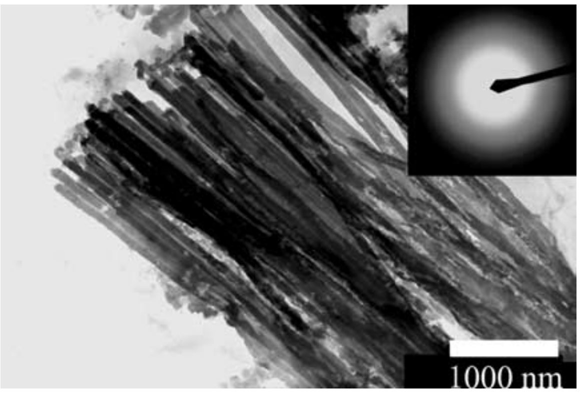
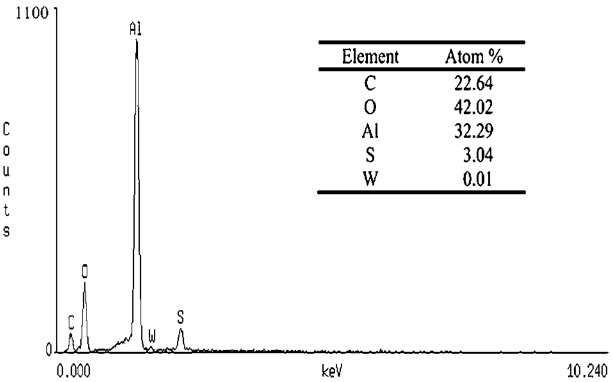


Figure 2 TEM image of carbon nanowires after removing the template, the inset is the selected-area electron diffraction pattern of the carbon nanowires.



Element	Atom %
C	22.64
O	42.02
Al	32.29
S	3.04
W	0.01

Figure 3 EDX spectrum of the surface layer of the sample shown in Fig. 1. The inset shows the quantitative composition of the materials.

due to sputtering during the plasma reaction. Note that neither Fe nor Co signal was detected, indicating a tip growth mechanism cannot be entirely responsible for the carbon nanowire growth [11]. The role that catalyst played is unclear at present, and the situation is complicated by the presence of metal sulfide that may also act as catalyst in the nanowires formation [15].

We have reported that carbon nanotubes were synthesized by ac discharge plasma reaction [14]. How does the electric field affect the formation of different carbon nanostructures, i.e., nanotubes and nanowires? A possible explanation is as follows. When the reactant discharged in the high voltage electric field, various species were formed within the corona plasma. These species include radicals (H, C, CH_3, C_6H_5, etc.), ions (C^+, CH_3^+, $C_6H_5^+$, etc.), and other species (CH_4, H_2, electron, etc.). The radicals move in random directions, whereas the ions moved under the governing of electrostatic force. When ac discharge plasma was formed within high frequency electric field, such as 25 kHz, most of the carbon-containing ions cannot directionally move to the template due to the alternating electric field effect. Then only carbon-containing radicals moved into the template pores and formed stronger carbon nanotubes through radical reactions. In contrast, within dc pulsed electric field, both carbon-containing radicals and ions moved to the template located on the anode and formed looser carbon nanowires. In any case, the exact synthesis mechanism may be quite complex and will require further detailed study.

In conclusion, carbon nanowires arrays can be synthesized by a new method which combines dc pulsed corona discharge plasma reaction with template-controlled growth technology. We think that the plasma reaction that occurred within the dc pulsed electric field favors synthesizing solid carbon nanowires rather than hollow carbon nanotubes. One outstanding advantage of this method is that the experiment could be carried out under ambient condition, i.e., atmospheric pressure and low temperature, which is promising for scale-up production of carbon nanowires.

Acknowledgment

The financial support from the National Natural Science Foundation of China is greatly acknowledged.

References

1. S. IIJIMA, *Nature* **354** (1991) 56.
2. S.-H. JEONG, H.-Y. HWANG, K.-H. LEE and Y. JEONG, *Appl. Phys. Lett.* **78** (2001) 2052.
3. J.-L. KWO, M. YOKOYAMA and I.-N. LIN, *J. Vac. Sci. Technol.* B **19** (2001) 1040.
4. A. Y. CAO, X. F. ZHANG, X. XIAO, M. Q. DING, D. M. ZHUANG, C. L. XU, B. Q. WEI, J. LIANG and D. H. WU, *Mater. Lett.* **51** (2001) 371.
5. F. HOSHI, K. TSUGAWA, A. GOTO, T. ISHIKURA, S. YAMASHITA, M. YUMURA, T. HIRAO, K. OURA and Y. KOGA, *Diam. Relat. Mater.* **10** (2001) 254.
6. T. IKUNO, J.-T. RYU, T. OYAMA, S. OHKURA, Y.-G. BAEK, S. HONDA, M. KATAYAMA, T. HIRAO and K. OURA, *Vacuum* **66** (2002) 341.
7. G. CHE, B. B. LAKSHMI, C. R. MARTIN, E. R. FISHER and R. S. RUOFF, *Chem. Mater.* **10** (1998) 260.
8. Y. H. TANG, N. WANG, Y. F. ZHANG, C. S. LEE, I. BELLO and S. T. LEE, *Appl. Phys. Lett.* **75** (1999) 2921.
9. J. P. TU, L. P. ZHU, K. HOU and S. Y. GUO, *Carbon* **41** (2003) 1257.
10. J.-M. TING and R. M. LIU, *ibid.* **41** (2003) 601.
11. Z. F. REN, Z. P. HUANG, J. W. XU, J. H. WANG, P. BUSH, M. P. SIEGAL and P. N. PROVENCIO, *Science* **282** (1998) 1105.
12. M. OKAI, T. MUNEYOSHI, T. YAGUCHI and S. SASAKI, *Appl. Phys. Lett.* **77** (2000) 3468.
13. V. I. MERKULOV, A. V. MELECHKO, M. A. GUILLORN, D. H. LOWNDES and M. L. SIMPSON, *ibid.* **79** (2001) 2970.
14. M.-W. LI, Z. HU, X.-Z. WANG, Q. WU and Y. CHEN, *J. Mater. Sci. Lett.* **22** (2003) 1223.
15. H. HUANG, H. KAJIURA, Y. MURAKAMI and M. ATA, *Carbon* **41** (2003) 615.

Received 19 June
and accepted 12 August 2003