JOURNAL OF MATERIALS SCIENCE **40** (2005) 3635–3638

Synthesis of carbon nanotubes via toluene-thermal reduction process at moderate temperature

YUANZHU MI, YINGLIANG LIU*, DINGSHENG YUAN, JINGXIAN ZHANG, YONG XIAO
Department of Chemistry, Jinan University, Guangzhou, 510632, People's Republic of China
E-mail: tliuyl@jnu.edu.cn

Carbon nanotubes were synthesized with toluene as carbon source and solvent at 350°C under stiring situation. In this process, La/Ni were used as catalyst, which were reduced via $LaCl_3$ and $NiCl_2$ with sodium as reductant. The products were characterized with X-ray powder diffractometer (XRD), transmission electronic microscopy (TEM) and Raman spectroscopy. The carbon nanotubes had diameters ranging from 100–200 nm and lengths ranging from hundreds of nanometers to several micrometers. The yield of carbon nanotubes, in accordance with TEM observations was estimated to be about 70%.

1. Introduction

Carbon nanotubes are known for their unique electronic and physical properties, which are attributed to their nanometer size and pseudo one dimensionality. Since Iijima's discovery [1], Carbon nanotubes have attracted more and more attention from physicists, chemists and engineers [2]. This is because the carbon nanotubes have various potential applications such as electrochemical devices [3], nanotweezers [4], gas storage [5], field emission devices [6], memory devices [7], thermal conduction strain sensors and catalyst supports [8] amongst others.

Various methods have been developed for the synthesis of carbon nanotubes, such as pyrolysis method [9–12], electric arc discharge [13, 14], laser ablation [15, 16], hydrothermal [17], floating catalyst method [18], chemical vapour deposition (CVD) [19–24]. Compared with other high temperature methods such as arc discharge and laser ablation, CVD method is more controllable and cost-efficient. CVD-grown carbon nanotubes, obtained by the decomposition of hydrocarbons in the presence of metal catalysts, are usually longer and can grow aligned if a patterned substrate is used as a catalyst [20–22]. However, toxic and hazardous gases such as C_2H_2, matallocene etc. were used as carbon sources and very often H_2 gas for improving tube graphitization. To explore other alternatives, the Qian's group have applied solvothermal methods to synthesize carbon materials such as carbon nanotubes [25], hollow spheres [26] and cones [27]. Liu and co-workers have synthesized carbon nanotubes on a large scale using the reaction of ethanol with magnesium, and the yield was estimated to be about 80%, but the reaction temperature was as high as 600°C [28]. Recently, Wang *et al.* have successfully synthesized multiwall carbon nanotubes by a low temperature solvothermal approach at 310°C without adding the conventional catalysts such as Fe/Co/Ni, in which the ethoxylated alcohol polyoxyethylene (4) ether ($C_{12}E_4$) was used as a carbon source, and their yield was estimated to be about 20% [29].

In this work, we have used toluene as carbon sources, $LaCl_3$ and $NiCl_2$ as catlyzer precursor which have been reduced by sodium, to synthesize carbon nanotubes via toluene-thermal process at 350°C under stiring situation. The yield was estimated to be about 70% via electron microscope observations.

2. Experimental

All reagents of analytical grade were commercially available. The mixture (wt%2:1) of $LaCl_3{\cdot}nH_2O$ and $NiCl_2{\cdot}6H_2O$ was put into the hard glass tube, and dehydrated at 350°C under vacuum situation. The catalyzer precursor was ground into powder in glove case. Metallic Na was washed with toluene and wiped with filter paper.

In a typical experiment, catalyzer precursor (0.5 g), metallic Na (0.8 g) and toluene (80 ml) were mixed in a stainless steel stiring autoclave of 120 ml capacity. The stiring speed was set at 180 r/min, and the sealed autoclave was heated at 350°C for 24 h and then allowed to cool to room temperature naturally. The dark precipitate was collected and washed with absolute ethanol, and then was dipped in dilute aqueous HCl solution (1:1) about 20 h. After that, it was washed with

*Author to whom all correspondence should be addressed.

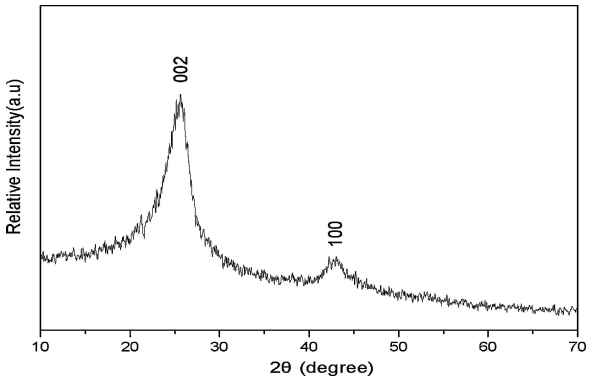

Figure 1 XRD pattern of the products.

distilled water, absolute ethanol, respectively. The obtained sample was dried in a vacuum at 60°C for 4 h.

Structure characterization was performed by X-ray diffraction (XRD) on a MSAL-XD2 X-ray diffractometer using Cu-K_α radiation (40 kV, 20 mA, λ = 1.54051 Å). The morphologies of the sample were characterized with Philips TECNAI-10 transmission electron microscopy. The Raman spectrum of as-prepared samples was recorded at room temperature on a Renishaw RM2000 Raman microspectronmeter with an argon-ion laser at an excitation wavelength of 514.5 nm.

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared products. A scanning rate of 0.08° s^{-1} has been used to record the pattern in the range of 10–70°. Two intense peaks can be indexed to a hexagonal graphite lattice with cell constant $a = 2.4308$ Å and $c = 6.8104$ Å. The deviation was lower than 2% compared with the reported values $a = 2.4704$ Å and $c = 6.7244$ Å (JCPDS 41-1487).

Fig. 2a depicts a typical TEM image of carbon nanotubes. These carbon nanotubes have diameters ranging

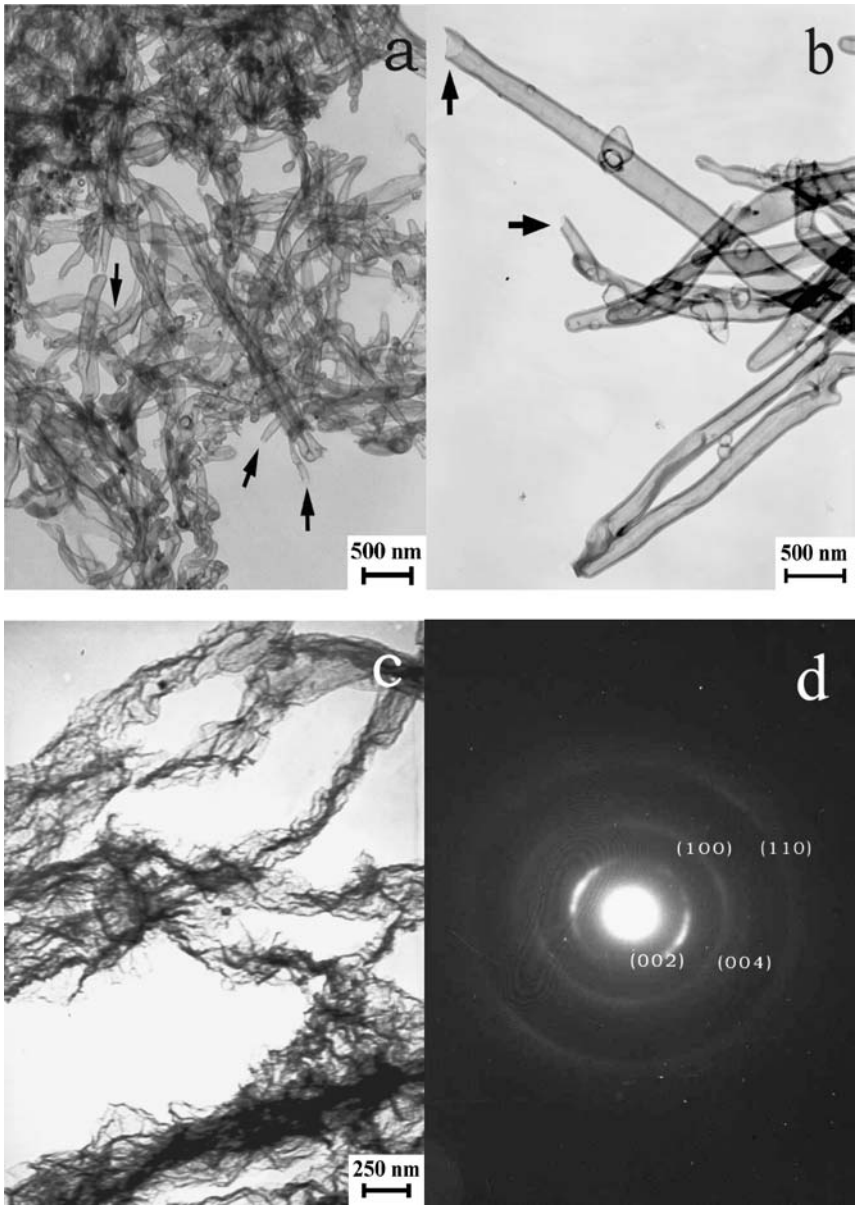

Figure 2 TEM image of as-prepared sample: (a) carbon nanotubes, (b) enlarged image of carbon nanotubes (c) carbon nanoribbons, (d) selected-area electron diffraction pattern of a carbon nanotube.

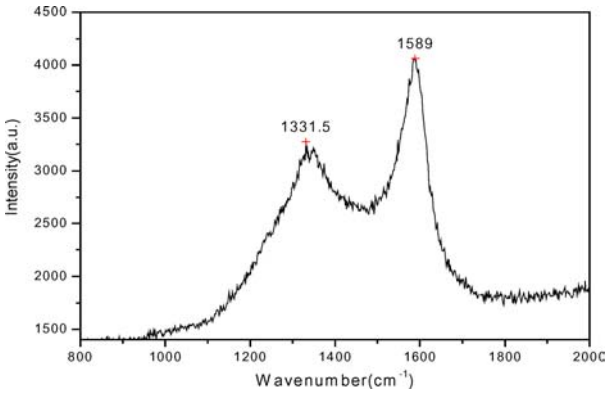

Figure 3 Raman spectrum of the as-prepared products which shows two graphite peaks at 1331.5 and 1589 cm^{-1}.

from 100–200 nm and lengths ranging from hundreds of nanometers to several micrometers. There is no encapsulated solid particle at the closed carbon nanotubes tips. Our observations are consistent with that of Liu and co-workers [28], who demonstrated that there was no encapsulated solid particle at the closed tip. What's more, the carbon nanotubes have open-end structure indicated by the headed arrow (Fig. 2a and b). The yield of carbon nanotubes was estimated through TEM observations of the as-prepared samples to be about 70%. Meanwhile, carbon nanoribbons were observed in the as-prepared sample, too. Fig. 2c depicts a TEM image of the carbon ribbons, of which, the widths range from hundreds of nanometers to several micrometers. The selected area electron diffraction (SAED) pattern (Fig. 2d) exhibits a pair of strong arc for 002 and a pair of weak arc for 004, together with a ring for 100 and a ring for 110 diffractions. The appearance of 002 and 004 diffraction as a pair of arcs indicates some orientation of the 001 planes in the carbon tubes.

The carbonous products have been used directly to record the Raman spectrum (Fig. 3) at ambient temperature at an excitation wavelength of 514.5 nm. There exists two peaks at 1331.5 and 1589 cm^{-1}, corresponding to the typical Raman peaks of carbon nanotubes [30]. The peak at 1589 cm^{-1} corresponds to an E_{2g} mode of graphite and is related to the vibration of sp^2-bonded carbon atoms in a two–dimensions hexagonal lattice, such as in a graphite layer. The peaks at 1331.5 cm^{-1} is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite [31, 32].

In our experiment, the chlorides of La and Ni were reduced to La/Ni catalyzer by metallic Na. Toluene played a manifold role in the formation of the carbon nanotubes. It was used as carbon resource and solvent simultaneously. In the presence of La/Ni catlyzer, Na reacts with toluene to produce carbon, The freshly formed carbon atoms assemble into hexagonal carbon clusters, which may grow into nanotubes at the surface of the catalyst particles. The catalyst played an important role in the process of nanotube growth. In order to prove this, we conducted another experiment for the sake of comparison, in which, the same condition was maintained; however, carbon nanotubes cannot be observed in the as-prepared sample unless the mixture of $LaCl_3$ and $NiCl_2$ was used. A detailed study of the growth mechanism of the carbon nanotubes and nanoribbons is underway.

4. Conclusions

In summary, a catalytic-assembly toluene-thermal route to carbon nanotubes using reduction of toluene by metallic Na in the presence of La/Ni catalyzer at 350°C has been developed. The carbon nanotubes obtained from our experiment are well graphited. The catalytic metal particles may play an important role in the nucleation of the nanotubes. The carbon nanotubes have diameters ranging from 100–200 nm and lengths ranging from hundreds of nanometers to several micrometers. The yield of carbon nanotubes, based on TEM observations of the as-prepared samples was estimated to be about 70%.

Acknowledgement

This work was financially supported by the Science and Technology Project of Guangdong Province (2KM02304G).

References

1. S. IIJIMA, *Nature* **354** (1991) 56.
2. G. BENEDEK, P. MILANI and V. G. RALCHENKO, in "Nanostructured Carbon for Advanced Appilications" (Kluwer Academic Publishers, Dordrecht, The Netherlands, 2001).
3. R. H. BAUGHMAN, C. X. CUI, A. A. ZAKHIDOV, Z. IQBAL, J. N. BARISCI, G. M. SPINKS, G. G. WALLLACE, A. MAZZOLDI, D. DE ROSSI, A. G. RINZLER, O. JASCHINSKI, S. ROTH and M. KERTESZ, *Science* **284** (1999) 1340.
4. P. KIM and C. M. LIEBER, *ibid.* **286** (1999) 2148.
5. C. LIU, Y. Y. FAN, M. LIU, H. T. CONG, H. M. CHENG and M. S. DRESSELHAUS, *ibid.* **286** (1999) 1127.
6. M. SHIM, A. JAVEY, N. W. S. KAM and H. J. DAI, *J. Am. Chem. Soc.* **123** (2001) 11512.
7. N. GROBERT, M. TERRONES, PH. REDLICH, H. TERRONES, R. ESCUDERO, F. MORALES, W. K. HSU, Y. Q. ZHU and J. P. HARE, *Appl. Phys. Lett.* **75** (1999) 3366.
8. L. P. BIRO, C. A. BERNARDO, G. G. TIBBETTS and P. H. LARNBIN (eds.), in "Carbon Filaments and Nanotubes: Common Origins, Differing Application" (Kluwer Academic Publishers Dordrecht, The Netherlands, 2001).
9. Z. J. JIA, Z. Y. WANG, J. LIANG, B. Q. WEI and D. H. WU, *Carbon* **37** (1999) 903.
10. A. KUKOVECZ, Z. KONYA, N. NAGARAJU, I. WILLEMS, A. TAMASI, A. FONSECA, J. B. NAGY and I. KIRICSI, *Phys. Chem. Chem. Phys.* **2** (2000) 3071.
11. R. SEN, A. GOVINDARAJ and C. N. R. RAO, *Chem. Mater.* **9** (1997) 2078.
12. R. KAMALAKARAN, M. TERRONES, T. SEEGER, P. KOHLER-REDLICH and M. RUHLE, *Appl. Phys. Lett.* **77** (2000) 3385.
13. A. HUCZKO, H. LANGE and T. SOGABE, *J. Phys. Chem. A.* **104** (2000) 10708.
14. D. S. BETHUNE, G. H. KIANG, M. S. DEVRIES, G. GORMAN, R. SAVOY and J. VAZQUEZ, *Nature* **363** (1993) 605.
15. H. ZHANG, K. CHEN, Y. HE, Y. ZHU, Y. CHEN, C. WU, J. WANG, J. H. LIAO and S. H. LIU, *J. Phys. Chem. Solids* **62** (2001) 2007.
16. C. D. SCOTT, S. AREPALLI, P. NIKOLAEV and R. E. SMALLEY, *Appl. Phys. A.* **72** (2001) 573.
17. J. M. C. MORENO and M. YOSHIMURA, *J. Am. Chem. Soc.* **123** (2001) 741.

18. C. SINGH, M. S. P. SHAFFER, K. K. K. KOZIOL, I. A. KINLOCH and A. H. WINDLE, *Chem. Phys. Lett.* **372** (2003) 860.
19. H. YOKOMICHI, F. SAKAI, M. ICHIHARA and N. KISHIMOTO, *Thin Solid Films* **395** (2001) 253.
20. W. Z. LI, S. S. XIE, L. X. QIAN, B. H. CHANG, B. S. ZOU, W. Y. ZHOU, R. A. ZHAO and G. WANG, *Science* **274** (1996) 1701.
21. M. TERRONES, N. GROBERT, J. OLIVARES, J. P. ZHANG, H. TERRONES, K. KORDATOS, W. K. HSU, J. P. HARE, P. D. TOWNSEND, K. PRASSIDES, A. K. CHEETHAM, H. W. KROTO and D. R. M. WALTON, *Nature* **388** (1997) 52.
22. S. S. FAN, M. G. CHAPLINE, N. R. FRANKLIN, T. W. TOMBLER, A. M. CASSELL and H. DAI, *Science* **283** (1999) 512.
23. H. W. ZHU, C. L. XU, D. H. WU, B. Q. WEI, R. VAJTAI and P. M. AJAYAN, *ibid.* **296** (2002) 884.
24. A. FONSECA1, K. HERNADI, P. PIEDIGROSSO, J. F. COLOMER, K. MUKHOPADHYAY, R. DOOME, S. LAZARESCU, L. P. BIRO, PH. LAMBIN, P. A. THIRY, D. BERNAERTS and J. B. NAGY, *Appl. Phys. A.* **67** (1998) 11.
25. Y. JIANG, Y. WU, S. Y. ZHANG, C. Y. XU, W. C. YU, Y. XIE and Y. T. QIAN, *J. Am. Chem. Soc.* **122** (2000) 12383.
26. J. W. LIU, M. W. SHAO, Q. TANG, X. Y. CHEN, Z. P. LIU and Y. T. QIAN, *Carbon* **411** (2002) 1682.
27. J. W. LIU, W. J. LIN, X. Y. CHEN, S. Y. ZHANG, F. Q. LI and Y. T. QIAN, *ibid.* **42** (2004) 669.
28. J. W. LIU, M. W. SHAO, X. Y. CHEN, W. C. YU, X. M. LIU and Y. T. QIAN, *J. Am. Chem. Soc.* **125** (2003) 8088.
29. W. Z. WANG, S. KUNWAR, J. Y. HUANG, D. Z. WANG and Z. F. REN, *Nanotechnology* **16** (2005) 21.
30. M. W. SHAO, D. B. WANG, G. H. YU, B. HU, W. C. YU and Y. T. QIAN, *Carbon* **42** (2004) 183.
31. A. M. BENITO, Y. MANIETTE, E. MUNOZ and M. T. MARTINEZ, *ibid.* **36** (1998) 681.
32. M. JOSE-YACAMAN, M. MIKI-YOSHIDA, L. RENDON and J. G. SANTIESTEBAN, *Appl. Phys. Lett.* **62** (1993) 657.

Received 5 November 2004
and accepted 14 February 2005