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SCIENCE DIRECT
Solid State Communications 133 (2005) 527–529
solid state communications
www.elsevier.com/locate/ssc

Synthesis of Y-junction carbon nanotubes within porous anodic aluminum oxide template

Ling-Bin Kong*

State Key Laboratory of Advanced Non-ferrous Materials, Lanzhou University of Technology, Lanzhou 730050, P.R. China

Received 12 September 2004; received in revised form 18 September 2004; accepted 9 December 2004 by H. Akai
Available online 5 January 2005

Abstract

Y-junction carbon nanotubes with the average diameter about 200 nm were successfully synthesized within porous anodic aluminum oxide template, which was prepared by anodic anodizing aluminum sheet in 1.0 mol/l H_3PO_4 solution at a constant anodization voltage 90 V.

PACS: 81.40.Cz; 81.15.Pq; 82.45.Cc; 82.45.Qr

Keywords: A. Y-junction carbon nanotubes; A. Anodic aluminum oxide

1. Introduction

There has been increasing interest in carbon nanotubes (CNTs) due to the many potential applications such as electron emitters [1], probes for electrochemistry devices and scanning probe microscopy [2,3], single electron transistors [4], quantum wires [5], hydrogen storage media [6], chemical sensors [7], nanotweezers [8], and so on. For these purposes, both the development of new manipulation techniques and alternative synthetic routes must be found. There has been increasingly interest on the synthesis of Y-junction CNTs, which might provide nanoelectronics community with a new material for electronic devices [9–12]. Recently, it is still a researching focus to find a simple and cheap method for preparation of Y-junction CNTs.

In relation with the synthetic routes, special attention is being paid to the production of CNTs confined in a template. The growth in anodic aluminum oxide (AAO) template is one of the more promising approaches owing to the possibility of tailoring the size, density and shape of their pores [13–15]. Templates of porous AAO are relatively easy to produce and there is no practical limitation to their size. CNTs confined in AAO have been obtained by the pyrolysis of some polymeric materials such as polyacrylonitrile or propylene and by the catalytic pyrolysis of acetylene within the pores [16,17].

Recent work shows that Y-junction CNTs can be grown within Y-shaped AAO nanochannels when the voltage conditions are adjusted in a specific way along a double step template growth process [18]. Compared with the complex branching phenomena observed in CNTs produced under specific arc-discharge condition [19], the Y-shaped CNTs produced by AAO template are well-aligned and similar in shape and size. Sui et al. [20] have also prepared CNTs junctions with the average diameter less than 100 nm by AAO template. However, Y-junction CNTs with relatively large diameters have not been investigated. In this paper, we successfully synthesized Y-junction CNTs with the average diameter about 200 nm, which may be used as a novel base material for the development of nanoelectronic devices.

2. Experiment

High-purity aluminum sheets (99.99%, 35×10×

* Tel.: +86 931 297 6363; fax: +86 931 280 6962.
E-mail address: konglb@lut.cn.

0038-1098/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2004.12.009

$0.15\ mm^3$) were employed in this experiment. Prior to anodization, the metal surfaces were degreased, etched in ethanol by sonicating. After rinsed in distilled water, the aluminum sheets were electropolished in C_2H_5OH and $HClO_4$ solution [$V(C_2H_5OH):V(HClO_4)=4:1$] in order to achieve a smooth surface. It was necessary to immerse the samples in concentrated acid or alkaline solution for several minutes to remove the oxide layer formed during the electropolishing process. All samples were rinsed in distilled water and then transferred to a nitrogen environment. The resultant clean aluminum samples were anodic anodized in 1.0 mol/l H_3PO_4 solution at 20 °C, with the aluminum sheets as the counter electrodes.

In order to obtain several AAO films with different pore structures, different anodization conditions were used. For the first set of samples, a single step anodization process was used. An initial anodization voltage of 50 V of DC was applied for 1 h and then it was abruptly jumped up to 90 V and maintained for 1 h. For comparative purpose, the constant voltage of 50 and 90 V were applied to obtain template with straight and branched channels, respectively.

The pore bottom of as-obtained AAO film was opened by chemical etching in 0.3 mol/l H_3PO_4 aqueous solution at 60 °C for 10 min, and the catalyzer-iron nanoparticles were deposited on the inner wall of the AAO template pores before the CVD. This process was accomplished by immersion of the alumina membrane into a solution of the 0.1 mol/l $Fe(NO_3)_3\cdot 9H_2O$ for 10–15 min. After immersion, the template was dried and placed in a quartz boat and then inserted into the center of a 40 cm long quartz tube reactor winded with heating tungsten filament. Atmosphere in the reactor was purged with a mechanical vacuum pump. And the Fe ions were reduced to iron by a 1.5 h exposure to flowing H_2 gas (20 ml/min) under vacuum ($\sim$150 Pa) at 800 °C. Subsequently, the heating temperature was adjusted to 700 °C, and a flow of acetylene was initiated at 15 ml/min, then the CNTs were synthesized in the pores of the AAO template by deposition of carbon atoms from decomposition of acetylene. After deposition, the acetylene and hydrogen flows were terminated, then the heating was turned off and the reactor was cooled to room temperature.

The aluminum oxide template was dissolved by immersion in a 6 mol/l NaOH solution for several hours at room temperature to release the CNTs. The washed and dried nanotubes were dispersed in toluene by sonication. A drop of toluene suspension of the nanotubes was placed on a transmission electron microscope (TEM, Philips CM120) grid for structure observation.

3. Results and discussion

Fig. 1 shows the TEM image of CNTs grown with the single step electrochemical oxidization method described above. When the AAO template anodized at 50 V, the CNTs with a uniform diameter of 100 mm is observed. However, when the anodizating voltage increase to 90 V, the diameter of the CNTs increased to 200 nm, and Y-junction nanotubes were observed.

It cannot be expected that Y-junction CNTs, such as those shown in Fig. 1(B), could be formed in a straight hole. So it is reasonable to conclude that the porous AAO template has a complex channel structure and the CNTs perfectly copy this three-dimensional structure of the AAO template. In the previously described method, a single step anodization process was used, starting at 50 V and then changing abruptly to 90 V, with the branched pores being formed when the higher voltage conditions were used [20].

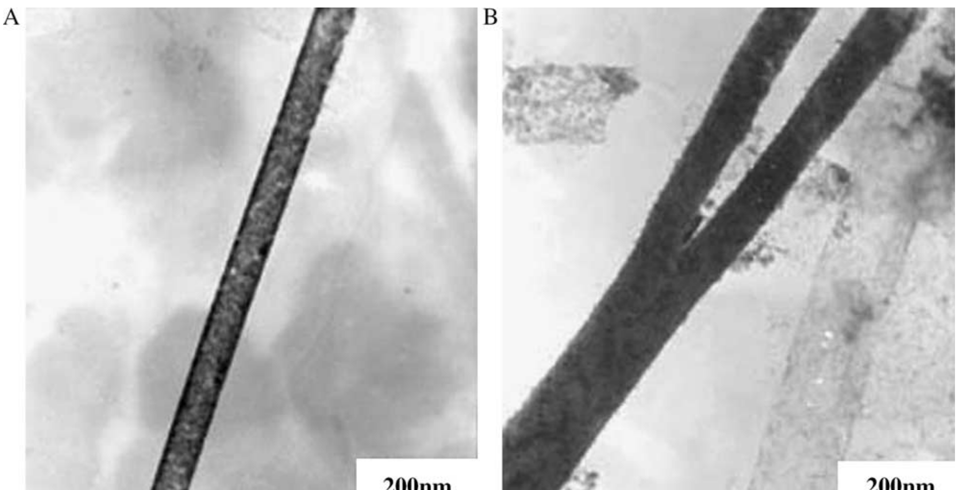

Fig. 1. TEM images of CNTs released from AAO template which was anodized at (A) 50 V and (B) 90 V.

In order to know if this abrupt change of the operating voltage plays some role in the formation of the branched pore templates, a new anodization test was performed using a constant working voltage of 90 V. No differences were observed either in the CNTs structure grown into AAO templates produced at a constant 90 V operation when single or double step approaches were used. On the contrary, when the AAO templates were produced at a constant operating voltage of 50 V, the CNTs grown in such templates were straight, in accordance with other reports [14]. From these results, it is possible to conclude that the formation of the branches is not caused by the abrupt increase of the voltage. It is only a characteristic of the high anodization voltage.

The CNTs junctions grown in this kind of AAO template may be compared with the Y-shaped CNTs obtained by Li et al. [18]. It seems clear that, the reported Y-shaped nanotubes may be superior to the junction structure reported in this work in relation with shape controllability. Nevertheless, the two-step method used by Li et al. is time- and energy-consuming and requires a careful control of voltage. On the other hand, the present approach for making a template with branched nanochannels can be easily accomplished and has a high efficiency. At the same time, compared with the CNTs junctions obtained by Sui et al. [20], which obtained CNTs junctions grown at AAO template anodized in $H_2C_2O_4$ solution with average diameters smaller than 100 nm, the Y-junction CNTs we have obtained in this experiment have relatively large diameters.

In summary, we have synthesized Y-junction CNTs with diameters about 200 nm by pyrolyzing of acetylene in a AAO obtained under anodic voltages as high as 90 V in phosphoric acid. At the same time, straight CNTs can also be produced in AAO templates with straight nanochannels working at lower anodization voltages. The formation of the branched pore structure is due to the unstable growth of the AAO film at high anodizating voltage. By using the present method, it is possible to obtain a large number of branched CNTs with large diameters, which might provide the community with a new material for nanoelectronic devices.

Acknowledgements

The author is grateful for the financial support by the Doctorial Foundation, Lanzhou University of Technology, P.R. China.

References

[1] A.G. Rinzler, J.H. Hafner, P. Nikolaev, L. Lou, S.G. Kim, D. Tomanek, P. Nordlander, D.T. Colbert, R.E. Smalley, Science 269 (1995) 1550.
[2] H. Dai, J.H. Hafner, A.G. Rinzler, D.T. Colbert, R.E. Smalley, Nature 384 (1996) 147.
[3] G. Che, B.B. Lakshmi, E.R. Fissher, C.R. Martin, Nature 393 (1998) 346.
[4] M. Bockrath, D.H. Cobden, P.L. McEuen, N.G. Chopra, A. Zettl, A. Thess, R.E. Smalley, Science 275 (1997) 1922.
[5] S.L. Tans, M.H. Devoret, H. Dai, A. Thess, R.E. Smally, L.J. Geerligs, C. Dekker, Nature 386 (1997) 474.
[6] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, Nature 386 (1997) 377.
[7] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, Science 287 (2000) 622.
[8] P. Kim, C.M. Lieber, Science 286 (1999) 2148.
[9] B. Gan, J. Ahn, Q. Zhang, Rusli, S.F. Yoon, J. Yu, Q.F. Huang, K. Chew, V.A. Ligatchev, X.B. Zhang, W.Z. Li, Chem. Phys. Lett. 333 (2001) 23.
[10] F.L. Deepak, A. Govindaraj, C.N.R. Rao, Chem. Phys. Lett. 345 (2001) 5.
[11] H. Zhu, L. Ci, C. Xu, J. Liang, D. Wu, Diamond Relat. Mater. 11 (2002) 1349.
[12] Z. Klusek, S. Datta, P. Byszewski, P. Kowalczyk, W. Kozlowski, Surf. Sci. 507–510 (2002) 577.
[13] T. Iwasaki, T. Motoi, T. Den, Appl. Phys. Lett. 75 (1999) 2044.
[14] J. Li, C. Papadopoulos, J.M. Xu, Appl. Phys. Lett. 75 (1999) 367.
[15] C.W. Wang, M.K. Li, S.L. Pan, H.L. Li, Chin. Sci. Bull. 45 (2000) 1373.
[16] C.R. Martin, Science 266 (1994) 1961.
[17] T. Kyotani, L. Tsai, A. Tomita, Chem. Mater. 8 (1996) 2190.
[18] J. Li, C. Papadopoulos, J.M. Xu, Nature 402 (1999) 253.
[19] D. Zhou, S. Seraphin, Chem. Phys. Lett. 238 (1995) 286.
[20] Y.C. Sui, J.A. Gonzalez-Leon, A. Bermudez, J.M. Saniger, Carbon 39 (2001) 1709.