

The Preparation of Bamboo-Structured Carbon Nanotubes with the Controlled Porosity by CVD of Acetylene on Co-Mo/MCM-41

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ABSTRACT: *Bamboo-structured carbon nanotubes are grown on Co-Mo/MCM-41 catalyst in the temperature range of 873-973 K by thermal chemical vapor deposition of acetylene. This study shows that the purified carbon nanotubes have open tips and the metals of the catalyst are not encapsulated. Thus, the bamboo-structure seems to grow from the base. Pore size distribution of the product is quite narrow and is in the range of 2- 5 nm similar to the catalyst pore size distribution. The results of this study demonstrate that by manipulating the template, the pore size distribution of the final product may be controlled. The so-prepared carbon nanotubes with controlled porosity are better suited for the application in gas adsorption and catalyst synthesis.*

KEY WORDS: *Bamboo-structured, Carbon nanotube, CVD, MCM-41, Porosity.*

INTRODUCTION

Carbon nanotubes CNTs have attracted much attention because of their extraordinary properties and their potential applications in various technologies. In order to suitably make use of the nanotubes for some applications such as gas adsorption and catalyst synthesis, they should be prepared with narrow pore size distribution. This requirement makes the synthesis of carbon nanotube a real challenge [1-4].

There are different ways for synthesis of carbon

nanotubes, e.g., arc discharge [5], laser vaporization [6] and catalytic method [7]. Among these, the catalytic method is simple, cheap and seems to be the proper way for the large-scale production of carbon nanotubes [8]. The bamboo-structured carbon nanotubes, a special morphology of CNTs, are synthesized by DC arc-evaporation [9] and catalytic growth methods [10-13]. Understanding the growth mechanism of CNTs would help in controlled growth and also development of new synthesis methods.

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Different preparation methods and formation mechanisms for bamboo-structured carbon nanotubes have been proposed, e.g., Fe catalytic particles deposited on silicon oxide substrate [14], moving of catalyst particles under the action of the shell stress [15], vapor pressure of the catalyst [10] or surface diffusion with two-particle cooperation [13].

There are several studies reflecting the effects of pore structure of the catalyst on the size of CNTs [14-15]. Wang *et al.* [14] studied the growth of CNTs in the pores of a template catalyst (ALPO-5). This zeolite has an upper limit in channel size of 0.73 nm. Zeolites have micro pores (less than 1.5 nm in diameter) and the channel size cannot be varied without changing the structure and the chemical composition of the final material. This makes zeolites inappropriate for the controlled template growth of carbon nanotubes. Urban *et al.* [15] reported the synthesis of MWNTs using mesoporous MCM-41 silicalites in the absence of any metal as the active phase. Much interests in the fields have been focused on the size control of the nanotubes, by employing different techniques.

This paper presents the experimental results on the preparation of bamboo-structured CNTs with the controlled porosity. We used MCM-41 as a template materials and incorporated cobalt and molybdenum in the silica framework. It enables to control the porosity of CNTs, which corresponds to the pore size of MCM-41. Nanotubes with controlled porosity have a good potential for some applications such as gas adsorption and catalyst synthesis.

EXPERIMENTAL

MCM-41 preparation

The reagents used in this work were sodium silicate containing 25.5-28.5% silica, cetyltrimethyl ammonium bromide (Aldrich), and sodium oleate (Merck). Sodium silicate was used as a silica source and cetyltrimethyl ammonium bromide and sodium oleate as surfactants. The reaction mixture was prepared by mixing of cetyltrimethyl ammonium bromide and sodium oleate and distilled water with proper stoichiometric ratios for 10 minutes. The sodium silicate was then added to the mixture while stirring vigorously for about 30 min. The crystallization was performed in an unagitated closely sealed autoclave system for 7 days at 373 K. Upon the

completion of the reaction, the mixture was immediately cooled and the product was filtered off from the mother liquor and thoroughly washed with distilled water. The product was dried at 263 K overnight and calcined at about 500 K for 5 h.

Catalyst Preparation

The Co-Mo catalysts were prepared by incipient-wetness impregnation of MCM-41 support with aqueous solution of cobalt nitrate and ammonium heptamolybdate. The molar ratio of Co/Mo in the catalyst was 1:2. The catalyst was first dried in air at room temperature, then in an oven at 393 K, and finally calcined at 773 K for 3 h. The CNTs were synthesized by decomposition of acetylene over catalyst at 973 K. A horizontal tube furnace was employed for the acetylene decomposition. Typically, 200 mg of catalyst was placed in the center of a quartz tube located in the tube furnace and acetylene decomposition reaction was conducted at ambient pressure. A gas mixture of acetylene and hydrogen with molar ratio of $C_2H_2: H_2=1:4$ and total flow rate of 100-150 cm^3/min was introduced into the reactor. The temperature was raised from room temperature to 973 K with a ramp rate of 5 K/min and maintained for 30 min at the final temperature. The acetylene flow was then stopped and sample was cooled down under hydrogen flow.

In order to produce pure carbon nanotubes, the catalyst materials were removed by dissolving the sample in 2 M NaOH for 24 h. Afterwards, the mixtures of 2.5% of NaOH and ETOH/ H_2O with volume ratio of 50:50 were applied for complete removal of the catalyst materials.

The purified samples were characterized by TEM, SEM, XRD and BET surface area techniques. TEM was performed on a CM 120 Philips with a tension voltage of 120 kV. PHILIPS X-Ray diffraction model "PW1840" with APO Software package was used for qualitative phase analysis of the products. SEM micrographs were taken using a "Cambridge stereo scan" SEM model 360. The BET surface area was measured on ASAP2010, Micromeritics Co., using N_2 as the adsorbate at 77 K.

RESULTS AND DISCUSSION

The XRD patterns of the purified CNTs samples grown on Co-Mo/MCM-41 are presented in Fig. 1.

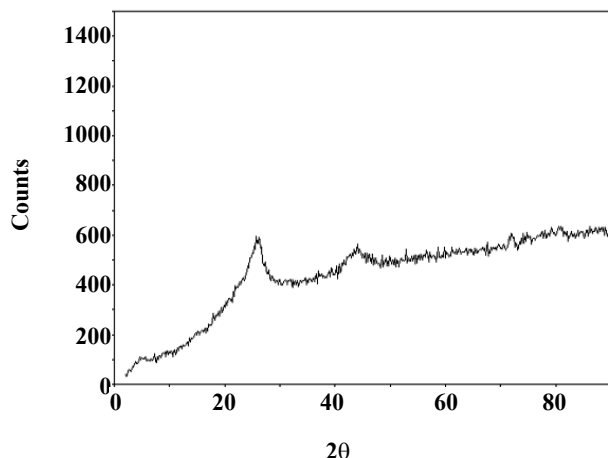


Fig. 1: XRD pattern of bamboo-structured carbon nanotubes grown on Co-Mo/MCM-41 at 973 K.



Fig. 2: SEM micrographs of bamboo-structured carbon nanotubes grown on Co-Mo/MCM-41 at 973 K.

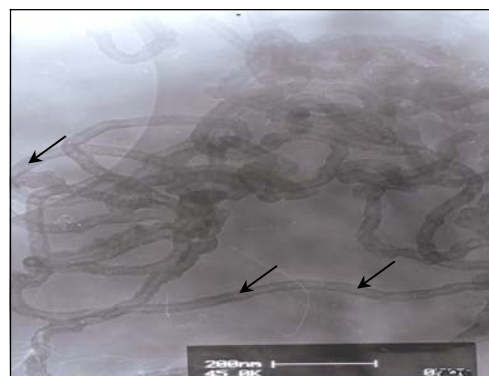
Two peaks appeared at $2\theta=25^\circ$ and $2\theta=43^\circ$ represent the carbon nanotubes which are consistent with the results reported by other research groups [16].

Fig. 2 shows a SEM micrograph of bamboo-structured CNTs grown on Co-Mo/MCM-41. For this synthesis a flow of 50 mL/min of C_2H_2 was passed over the catalyst for 30 min. The bed temperature was kept constant at 973 K.

The TEM images of the purified sample are shown in Fig. 3a and 3b. In the Fig. 3a the image reveal the open tip of the nanotubes without any encapsulated metal particles as marked by the arrow sign on the image. As discussed before, the purification method was employed to remove mostly the MCM-41. Having observed no metal particles in the openings of the tubes, it may be concluded that the base-growth mechanism is the dominant mechanism for this synthesis. Also, given the



(a)



(b)

Fig. 3: TEM images of bamboo-structured carbon nanotubes on Co-Mo/MCM-41 at 973 K.

Fig. 3b (arrow sign), in the compartment layers the curvature is directed towards the tip of the tubes, which is another indication of the base-growth mechanism. TEM images indicate that the carbon nanotubes have diameter in the range of 20-30 nm and length of several micrometers.

The nitrogen physisorption test results are presented in Fig. 4 for both the MCM-41 catalyst and the carbon nanotubes grown on the catalyst. According to the figure, the pore size distribution for both carbon nanotubes and the MCM-41 is quite narrow and follow the same trends. Therefore, by employing the method applied in this work for the catalyst preparation, it is possible to control the pore size distribution of the carbon nanotubes, i.e. the guest, according to the pore size distribution of the MCM-41 host.

Fig. 5 presents the adsorption isotherms for the catalyst

and the purified carbon nanotubes. According to this figure, the isotherms of MCM-41 and carbon nanotube follow the same trend, which indicates that the use of the template imposes a control on porosity of the carbon nanotubes.

Fig. 6 is the schematic growth model of carbon nanotubes. The growth model of bamboo-structure of carbon nanotube in this study seems to be more consistent with the base growth mode proposed by *Cheol Jin Lee* [17]. Carbons produced from the decomposition of C_2H_2 on the active metal particles diffuse via surface and bulk of the metals to form the graphitic sheets as a cap on the metal particles (Fig. 6a). As the cap lifts off the catalytic particle, a closed tip with inside hollow is produced (Fig. 6b). The size of catalytic particles limits the diameter of the growing tubes. The carbons accumulated at the inside surface of the catalytic particle, probably via bulk diffusion, can form the compartment graphitic sheets. This layer will depart from the catalytic particle due to the stress (Fig. 6c). While the wall grows upward, the next compartment layer is formed on the catalytic particle and will be combined with the wall (Fig. 6d). If the carbons are supplied under steady-state conditions, the layers can appear periodically (Fig. 6e). However, non-uniform carbon supply would result in an irregular appearance of the compartment layers with various thicknesses and shapes.

CONCLUSIONS

We have reported the bamboo-structured CNTs grown on Co-Mo/MCM-41 in the temperature range of 873-973 K by catalytic decomposition of C_2H_2 . All of the CNTs produced have bamboo-structure in which the curvature of the compartment layers is directed to the tip. The CNTs grown have diameters in the range of 20-30 nm. Base growth model seemed to be possible for the synthesis based on the TEM images of the sample. According to the results, the porosity of the carbon nanotubes was controlled by Co-Mo/MCM-41 as a template.

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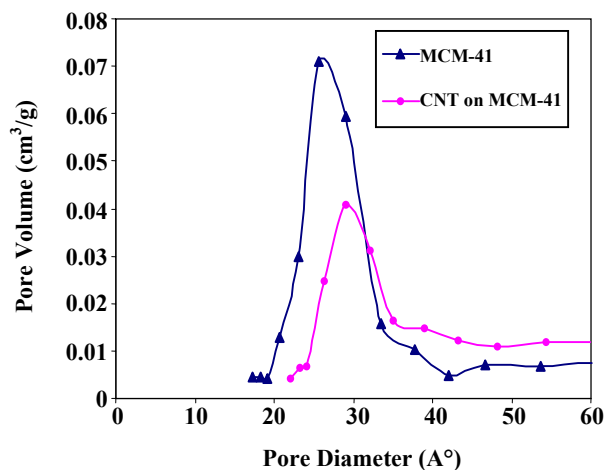


Fig. 4: Pore size distribution curves for (a) MCM-41, and (b) bamboo-structured carbon nanotubes in MCM-41.

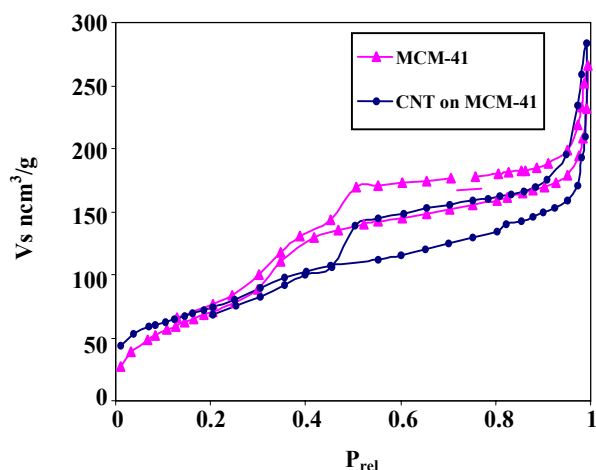


Fig. 5: Nitrogen adsorption isotherm at 77 K for (a) MCM-41, and (b) bamboo-structured carbon nanotubes within MCM-41.

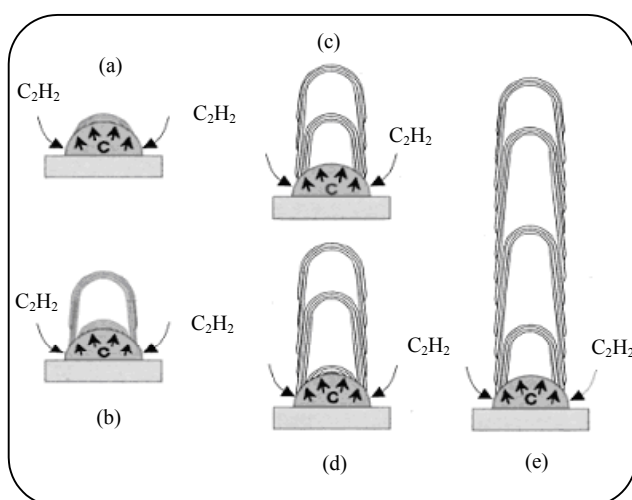


Fig. 6: Schematic diagrams of a base growth model of bamboo-structured carbon nanotubes.

REFERENCES

- [1] Iijima, S., *Nature*, **56**, 354 (1991).
- [2] Subramoney, S., *Interface*, **34**, 8 (1999).
- [3] Chen, P., Wu, X., Lin, J. and Tan, K.L., *Science*, **285**, 91(1999).
- [4] Dai, H., Rinzer, A., Nikolaev, P., Theses, A., Colbert, D.T. and Smalley, R.E., *Chem. Phys. Lett.*, **471**, 260 (1999).
- [5] Iijima, S. and Ichihashi, T., *Nature*, **603**, 363 (1993).
- [6] Kong, J., Cassell, A.M., and Dai, H., *Chem. Phys. Lett.*, **4**, 292 (1998).
- [7] Nikolaev, T., Guo, P., Thess, A., Colbert, D.T., and Smalley, R.E., *Chem. Phys. Lett.*, **49**, 243 (1995).
- [8] Colomer, J.F., Stephan, C., Lefrant, S., Tendeloo, G.V., Willems, I., Konya, Z., Fonseca, A., Laurent, Ch., and Nagy, J.B., *Chem. Phys. Lett.*, **83**, 317 (2000).
- [9] Saito, Y., and Yoshikawa, T., *J. Cryst. Growth*, **154**, 134 (1993).
- [10] Kovalevski, V.V. and Safronov, A.N., *Carbon*, **96**, 336 (1998).
- [11] Kiselev, N.A., Slaoan, J., Zakharov, D.N., Kukovitskii, E.F., Hutchison, J.L., Hammer, J., Kotosonov, A.S., *Carbon*, **36**, 1149 (1998).
- [12] Li, Y.D., Chen, J.L, Ma, Y.M., Zhao, J.B., Qin, and Chang, N., L., *Chem. Commun*, **12**, 1141, (1999).
- [13] Li, D.C., Dai, L.M., Huang, S.M., Mau, A.W.H. and Wang, Z.L., *Chem. Phys. Lett.*, **349**, 316 (2000).
- [14] Wang, N., Tang, Z.K., Li, G.D. and Chen, J.S., *Nature*, **50**, 408 (2000).
- [15] Urban, M., Mehn, D., Konya, Z. and Kiricsi, I., *Chem. Phys. Lett.*, **95**, 359 (2002).
- [16] Liu, B. C., Gao, L. Z., Liang, Q., Tang, S.H., Qu, M.Z. and Yu, Z.L., *Catalyst Letters*, **225**, 71 (2001).
- [17] Lee, C.J. and Park, J., *J. Phys. Chem., B*, **105**, 365 (2001).