Production of Carbon Nanotubes over Pre-reduced $LaCoO_3$ by Using Fluidized-bed Catalytic Reactor

LIU, Bao-Chun[a,b](刘宝春) **TANG, Shui-Hua**[a](唐水花) **LIANG, Qi**[a](梁奇)
GAO, Li-Zhen[a](高利珍) **ZHANG, Bo-Lan**[a](张伯兰) **QU, Mei-Zhen**[a](瞿美臻)
YU, Zuo-Long *,[a](于作龙)
[a] *Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, Sichuan 610041, China*
[b] *Department of Applied Chemistry, Nanjing University of Chemical Technology, Nanjing, Jiangsu 210009, China*

A technique has been developed to grow carbon nanotubes by flowing acetylene over pre-reduced $LaCoO_3$ catalyst in a fluidized-bed catalytic reactor. Carbon nanotubes were characterized by means of SEM and TEM. The pre-reduced $LaCoO_3$ catalyst was found to be effective in producing carbon nanotubes with even diameter. The effects of reduction temperature of $LaCoO_3$ on the growth of carbon nanotubes were investigated. This process can easily be scaled up.

Keywords Carbon nanotubes, $LaCoO_3$, fluidized-bed

Introduction

A great amount of research on carbon nanotubes has been carried out since its discovery in 1991.[1] Mechanical measurement of the axial Young's modulus of multi-walled carbon nanotubes[2] obtained extremely high values of about 1800 GPa, suggesting that carbon nannotubes are the stiffest material known to date. Measurements on carbon nanotubes,[3] individual multi-walled carbon nanotubes[4,5] and ropes of single-walled carbon nanotubes[6] have revealed that their conducting properties depend markedly on the degree of graphitisation, diameter and helicity. This unique electronic property makes carbon nanotubes a novel material and suggests that there will be a wide range of potential applications in the future.

Carbon nanotubes can now be produced by various techniques, including arc discharge,[7,8] laser vaporization[9,10] and hydrocarbon catalytic pyrolysis.[11,12] In order to make carbon nanotubes of practical importance, the criteria for assessing any synthesis technique must base on the feasibility and potentiality to scale-up production at low cost as well as the ability to control the structure of carbon nanotubes. Among the current methods employed, the catalytic method is simple, cheap and productive. In the catalytic method, it is crucial to select and prepare an effective catalyst with appropriate size of active metal particles, usually Fe, Co and Ni. Among them, cobalt was claimed to give rise to the best quality carbon nanotubes.[13] It has been known that if the particle size of the metals is large, carbon filaments or fibers rather than the Iijima-type carbon nanotubes are generally obtained.[14,15] In addition, Dai *et al*. found that the diameter of carbon nanotubes could be determined by the size of transition metal particles.[16] However, most methods used, to date, to generate carbon nanotubes suffer from the drawback of low productivity or the highly variable dimensions.

In this paper, we report an effective method to produce large quantities of carbon nanotubes. In our method, there are mainly two important innovations. (1) A fluidized-bed catalytic reactor was used to produce carbon nanotubes. In the fluidized-bed catalytic reactor, a large quantity of catalyst was loaded and the feed gas kept in good touch with the catalyst. This process could be easily scaled up. (2) $LaCoO_3$ was employed as the catalyst precursor. The presence of La_2O_3

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* E-mail: yzuolong@mail.sc.cninfo.net

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can prevent Co° from agglomerating during reduction, benefiting the growth of evenly sized carbon nanotubes.

Experimental

The catalyst precursor ($LaCoO_3$) was prepared by dissolving a stoichiometric mixture of cobalt nitrate and lanthanum nitrate in water and then mixing them with citric acid. The solution was evaporated with vigorous stirring at 80℃. When it got dense, the evaporation temperature was increased to 100℃, and then the slurry burned and turned into a black powder. Then the black powder obtained was calcined at 600℃ for 1.0 h, subsequently at 800℃ for 3.0 h. Finally, a black and fluffy sample of catalyst precursor was obtained. XRD pattern of the catalyst precursor $LaCoO_3$ identified that it is a single phase with a ABO_3 perovskite structure, wherein Co^{3+} and La^{3+} ions are evenly distributed.

The synthesis of carbon nanotubes was carried out in a fluidized-bed catalytic reactor. The reactor is illustrated schematically in Fig. 1.

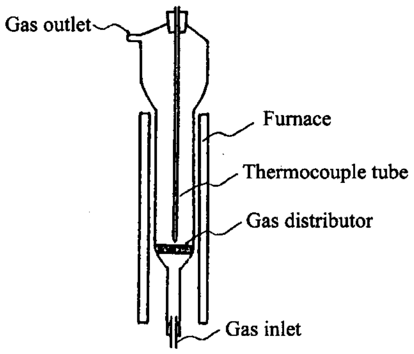

Fig. 1 Schematic of fluidized-bed catalytic reactor used for carbon nanotube synthesis.

The $LaCoO_3$ catalyst precursor (100 mg) was packed into the reactor, followed by heating in a flow of purified N_2 (flow rate 30 mL/min) from room temperature to the desired reduction temperature. Then purified H_2 (flow rate 25 mL/min) was introduced at the same temperature for 1.0 h to reduce $LaCoO_3$. After reduction, the feed gas C_2H_2 ($C_2H_2/N_2 = 1/9$, V/V, flow rate = 700 mL/min) was passed through the reactor at the temperatures of 675—700℃ for 30 min or more. After the scheduled time, the reactor was cooled to room temperature by the passage of nitrogen gas. The carbon nanotubes produced were purified by washing with nitric acid. In this way, the production of carbon nanotubes is very high, for example, over the 650℃-reduced $LaCoO_3$, ~22.0 g of nanotubes were synthesized with a purity of 96% per gram catalyst in one hour.

Scanning electron microscopy (SEM) (KYKY-AMRAY-1000B) and transmission electron microscopy (TEM) (JEOL JEM-100CX) were employed to characterize the morphologies of carbon nanotubes. The structure of catalysts was analyzed by X-ray diffraction (XRD) (D/max-rA).

Results and discussion

XRD pattern reveals that after reduction there are Co° and La_2O_3 in the catalyst. Cobalt exists chiefly as Co° after reduction of $LaCoO_3$. Rare earth oxide, La_2O_3, can prevent Co° from agglomerating and promote dispersion of nano-scale Co° particles, which is very advantageous to the growth of carbon nanotubes. The average diameter of Co° particles calculated from the linewidth in the XRD pattern using Scherrer equation is 20—30 nm.

It was found that the dimension of the cobalt particles was important in controlling the amount and the shape of the carbon nanotubes.

Fig. 2 shows the SEM images of as-synthesized carbon nanotube samples. It clearly illustrates the purity and homogeneity of the tubes, in which graphitic particles and nano-capsules are completely absent.

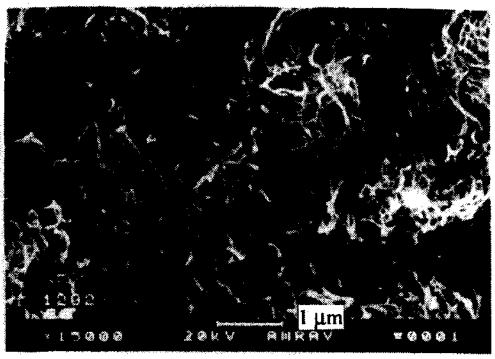

Fig. 2 SEM image of carbon nanotubes grown over the reduced $LaCoO_3$ by using fluidized-bed reactor.

Fig. 3 is the TEM image of carbon nanotubes generated over $LaCoO_3$ pre-reduced at 650℃. It shows that the tubes are quite even, having an inner diameter of 5—10 nm and an external diameter of 10—35 nm. Fig.

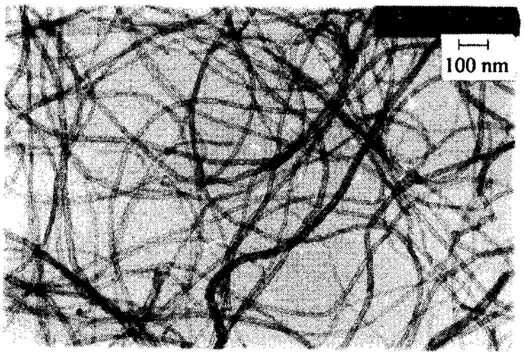

Fig. 3 TEM image of carbon nanotubes of uniform diameter grown over $LaCoO_3$ pre-reduced at 650℃ by using fluidized-bed reactor. Typical diameters of the shown carbon nanotubes are 10—35 nm.

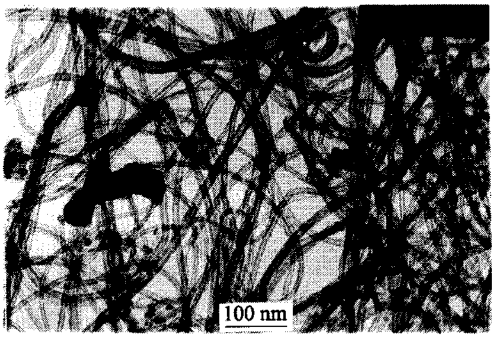

Fig. 4 TEM image of carbon nanotubes of uniform diameter grown over $LaCoO_3$ pre-reduced at 700℃ by using fluidized-bed reactor.

4 is the TEM image of carbon nanotubes formed over $LaCoO_3$ pre-reduced at 700℃. Fig. 4 showed that the tubes were also quite even but the average diameter of tubes was larger than that shown in Fig. 3. Moreover, long and regular helix-shaped carbon nanotubes appeared. This difference results mainly from increasing the reduction temperature of $LaCoO_3$ from 650℃ to 700℃. XRD patterns demonstrated that increasing the reduction temperature resulted in the formation of large Co particles in the catalyst. It seems that the larger the Co particles, the larger the diameter of carbon nanotubes formed. Based on this observation, the reduction temperature was increased to 800℃ in an ensuing experiment. Fig. 5 is a TEM image of the carbon nanotubes formed at the reduction temperature of 800℃. From Fig. 5 it can be seen that the carbon nanotubes were quite even, but increasing reduction temperature resulted in two structural changes, *i.e.*, (i) increasing the average diameter of tube; and (ii) increasing the amount of regular helix-shaped carbon nanotubes (ca. 5%). The average diameters of carbon nanotubes are 21, 22 and 23 nm at 650, 700 and 800℃, respectively. Comparing the results of XRD patterns of reduced catalysts, it can be found that the average diameters of carbon nanotubes are approximate to the sizes of cobalt metal particles which are 23, 25 and 30 nm when reduced at 650, 700 and 800℃ respectively. So, by controlling the reduction temperature of $LaCoO_3$ one can control the size of cobalt particle, and therefore control the amount of regular helix-shaped carbon nanotubes and the average diameter of tubes.

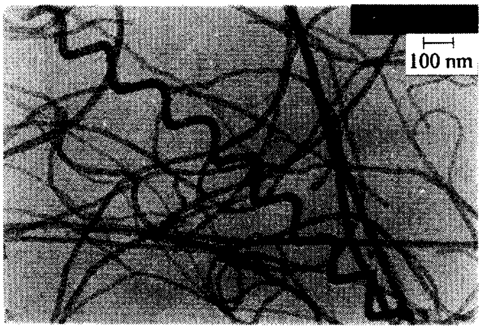

Fig. 5 TEM image of carbon nanotubes of uniform diameter grown over $LaCoO_3$ pre-reduced at 800℃ by using fluidized-bed catalytic reactor.

Helix-shaped carbon nanotubes have only been observed in the catalytically grown fibres, often among the products obtained by pyrolysis of acetylene over a cobalt catalyst.[12,17] In stead of the feed gas of C_2H_2 and N_2, the experiment was conducted over 700℃-reduced $LaCoO_3$ by passing 100% C_2H_2, and almost no straight carbon nanotubes appeared, but fiber helices were produced (Fig. 6). So, the composition of feed gas also plays an important role in the growth of helix-shaped carbon nanotubes. Recent calculations on architypical helices suggested that they might possess metallic properties.[18,19] Regular helix-shaped carbon nanotubes might be a very important type of nanotubes. By controlling the growth conditions, large quantities of regular helix-shaped carbon nanotubes could be synthesized. The synthesis of regular helix-shaped carbon nanotubes and their use in nano-scale engineering and electronics represent an exciting challenge for the future. So far, an acceptable explanation of the growth of regular helix-shaped carbon nanotubes is lacking.[12] It could be considered that the growth of regular helix-shaped carbon nanotubes is due to the helical disorder and special structure of $LaCoO_3$. Further investigation of the regular helix-shaped carbon nanotubes is in progress.

Fig. 6 TEM image of carbon filament grown over $LaCoO_3$ pre-reduced at 700℃.

Conclusion

This work has established a processing route to synthesize carbon nanotubes over pre-reduced $LaCoO_3$ by using a fluidized-bed catalytic reactor. This method could be scaled up easily and produces carbon nanotubes including helix-shaped with quite even diameter.

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