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Catalytic growth of single-walled carbon nanotubes with a narrow distribution of diameters over Fe nanoparticles prepared in situ by the reduction of $LaFeO_3$

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Abstract

Bundles of single-walled carbon nanotubes (SWNTs) with a narrower distribution of diameter have been produced by catalytic decomposition of methane at 1010 °C on a newly developed catalyst $LaFeO_3$. The SWNTs were characterized by means of transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy. The diameter of the SWNTs is in the range of 0.8–1.8 nm. This result shows for the first time that SWNTs could be produced by catalytic decomposition of hydrocarbons without Al_2O_3, or SiO_2 or MgO support. © 2002 Published by Elsevier Science B.V.

1. Introduction

Since their discovery in 1993 [1,2], single-walled carbon nanotubes (SWNTs) have attracted intense interest because of their unique physical, mechanical, and chemical properties. It is well known that the electronic structures of SWNTs depend strongly on diameter and chirality [3]. Thus, the diameter control technique is very important for the investigation of physical properties and future application. Demonstrated methods for producing SWNTs involve the electric arc discharge [4], the laser ablation [5], and catalytic pyrolysis [6]. Both the laser ablation method and the arc discharge method yield high-quality SWNTs. However, both techniques suffer from the problem that it is hard to scale up the production of the nanotubes material to industrial scale. Many previous reports have shown that the catalytic way could be a possibility to produce nanotubes on a large scale at a very low cost [6–13]. Clearly, a method of making high-quality SWNTs by catalytic decomposition could lead to economic production of SWNTs in bulk.

In recent years, several researchers have focused their attention to the production of SWNTs by

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catalytic decomposition of carbon-containing molecules. In the catalytic method, it is crucial to select and prepare an effective catalyst with appropriate size of active metal particles, usually Fe, Co, Ni. Catalytic metal nanoparticles are closely linked to the SWNTs. Dai et al. [7] found that the diameter of nanotubes could be determined by the size of transition metal particle. Therefore, the size of metal particles seems to be very important. Most catalyst used, to date, to generate SWNTs were supported pre-formed nanoparticles catalysts. Thus, the dimension of the catalytic particles dispersed on the support was not easy to control precisely. Hence the diameter distribution of SWNTs obtained is large, commonly in the range of 1–5 nm [7–11]. In addition, the separation and purification of SWNTs is difficult because the supports generally used in the catalyst preparation are Al_2O_3, SiO_2 or Al_2O_3–SiO_2 hybrid materials [6–10,12,13].

In the present work, a new catalyst $LaFeO_3$ was developed to synthesize high-quality SWNTs. With respect to other catalysts reported in the literature, it can result in a narrower size distribution of the prepared nanotubes materials. In addition, it can be readily dissolved in acids.

2. Experimental

$LaFeO_3$ was synthesized by citric acid complexing method described previously [14]. In brief, excess of citric solution was added to a mixed aqueous solution of iron and lanthanum nitrates with appropriate stoichiometry. The solution was evaporated with vigorously stirring at 80 °C. When it got dense, the evaporation temperature was increased to 100 °C, and gradually, the slurry burned and turned into a brown power. The brown power obtained was calcined at 600 °C for 1.0 h, subsequently at 800 °C for 3.0 h. Finally, a brown material was obtained. XRD pattern of the catalyst precursor identified that it is single phase of $LaFeO_3$ with an orthorhombic ABO_3 perovskite structure.

The SWNTs was synthesized by using fixed-bed catalytic reactor. 50 mg catalyst precursor was placed in the quartz boat and heated to 1010 °C in N_2 gas flowing through a quartz tube in an electrical furnace. Once the temperature reached 1010 °C, the N_2 flow was shut off and the mixture of methane/hydrogen was introduced at a flow rate of 210 sccm (CH_4/H_2, 100/110), The flow of methane/hydrogen was maintained for 8 min and was replaced by N_2 before the furnace was cooled to room temperature. The purification of samples collected was conducted with hydrochloric acid.

The morphologies and microscopic structure of carbon nanotubes were characterized by the transmission electron microscopy (TEM) (JEOL JEM-100CX), high-resolution transmission electron microscopy (HRTEM) (JEOL2010), and Raman spectrometer (Renishaw UV–Vis Raman System 1000R). The oxidation of carbon nanotubes in air were performed over thermogravimetry (TG) (Perkin–Elmer TGA 7) (scanning rate = 10 °C/min).

3. Results and discussion

Fig. 1 shows a low magnification TEM image of as-prepared SWNTs material with this catalyst. One can find that only bundles of SWNTs are synthesized. The SWNTs bundles which seem to be similar to those produced by arc discharge or laser evaporation techniques have diameters between 25 and 50 nm and lengths up to 1 μm. The oxidation of obtained SWNTs materials in air has been studied over thermogravimetry. The results show that the oxidation of the SWNTs occurred at

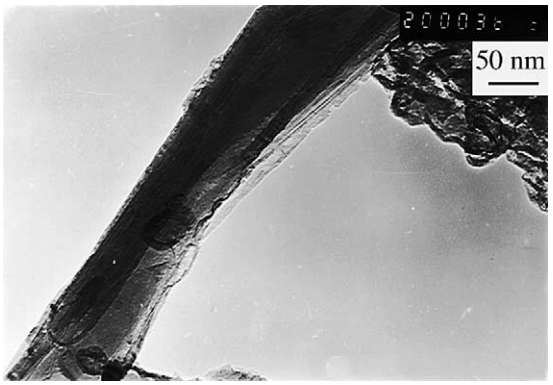

Fig. 1. Low magnification TEM image of as-synthesized SWNTs.

a temperature of ca. 509.1 °C, which is in agreement with that reported in the literature [6].

A typical HRTEM image of the purified SWNTs is shown in Fig. 2, which provides structure details of the purified SWNTs sample. It shows the presence of individual SWNTs. The diameter of the tubes measured from HRTEM observation is around 0.9–1.8 nm. We did not obtain clearer TEM image of SWNTs lattice fringes because of the coverage of the amorphous carbon on the bundles.

It is difficult to determine the SWNTs diameter accurately from HRTEM, but the tube configuration can be studied in detail using Raman spectroscopy. Fig. 3 is the Raman spectrum of purified SWNTs. The spectrum exhibits unambiguously the characteristic frequencies of SWNTs. The spectrum obtained in the low-frequency domain shows three components at 126, 198, 262 cm^{-1}. Raman results show that the spectrum in this frequency domain is very sensitive to the sample area investigated. This frequency is related to the curvature of the nanotubes and therefore to the tube diameter, the lower the diameter, the higher the frequency. As a consequence, our results

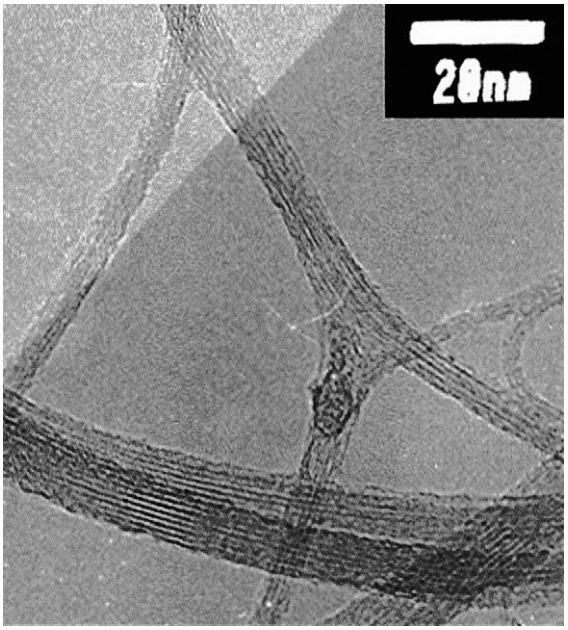

Fig. 2. High-resolution TEM image of purified SWNTs.

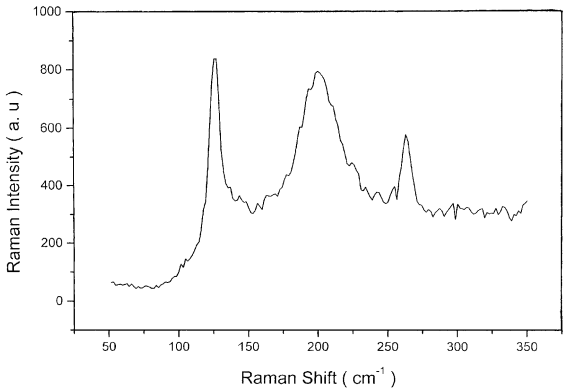

Fig. 3. Raman spectrum of purified SWNTs.

clearly reflect a distribution in diameters which can vary from one location to the other in the sample. Because individual SWNTs were packed into bundles in sample, van der Waals interaction existed between the tubes. Alvarez [15] proposed the expression between the tubes diameter and the low Raman frequency $w\ (cm^{-1}) = 6.5 + 223.75/d$ (nm) by taking into accounts interaction effects due to aggregation of individual tubes in the bundles. According to this formula, the RBM frequencies of 126, 198 and 262 cm^{-1} correspond to SWNTs with diameters of 1.82, 1.16 and 0.88 nm, respectively. The average diameter of SWNTs is 1.29 nm. This value is in agreement with that measured from HRTEM. This narrow distribution of diameter of SWNTs can be mostly attributed to the uniform Fe nanoparticles prepared in situ by the reduction of $LaFeO_3$. In ABO_3 perovskite lattice, the Fe^{3+} and La^{3+} ions were evenly distributed each other. Comparing with $LaCoO_3$ and $LaNiO_3$, $LaFeO_3$ is a less active oxide [16]. XRD pattern reveals that La_2O_3 and $LaFeO_{3-x}$ were only detected when H_2 was only introduced at present reaction temperature. This suggested that the size of Fe nanoparticles (responsible for nucleating SWNTs) anchored on the surface of $LaFeO_{3-x}$ is smaller than 2 nm. Compared with the results from Raman, this may imply that the diameter of the SWNTs obtained is dependent on the size of the Fe nanoparticles. The diameter of the nanotubes will reflect the size of the catalytic particle. Fe nanoparticles were in situ prepared. However, we have not found the SWNTs with the diameter

of <0.7 nm. This suggests that active metallic particles for the formation of SWNTs have a critical size due to instability of smaller SWNTs [17]. These very fine iron nanoparticles appropriate for the growth of SWNTs are uniformly and closely distributed on $LaFeO_{3-x}$. Therefore, the distribution of the diameter of SWNTs was narrow, and SWNTs nucleated on the close-by Fe nanoparticles site grow into bundles to maximize the van der Waals interactions between the walls of the nanotubes.

The effect on the reaction temperature was investigated. No SWNTs was obtained when the synthesis of SWNTs was carried out at either 1000 or 1020 °C. This suggest that the reaction temperature must play an important role in the growth of SWNTs. This is consistent with the result reported in the literature [11].

4. Conclusions

In conclusion, a new catalyst was developed to synthesize SWNTs. It presents the advantage over other catalysts reported in the literature that it can result in SWNT with a narrower distribution of diameter. The diameters of individual SWNT obtained in the present study are in the range of 0.8–1.8 nm. In addition, it can be readily dissolved in acids.

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