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Large scale intercalated growth of short aligned carbon nanotubes among vermiculite layers in a fluidized bed reactor

Meng-Qiang Zhao, Qiang Zhang, Jia-Qi Huang, Fei Wei *

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

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ABSTRACT

Short aligned carbon nanotubes (CNTs) were intercalated grown among vermiculite layers from ethylene using a simple fluidized bed chemical vapor deposition (CVD) process. The length of CNTs ranged from 0.5 to 1.5 μm after a synthesizing duration of 1–5 min at 650 °C. The as-grown CNTs vertically aligned to the vermiculite layers were with the mean outer and inner diameter of 6.7 and 3.7 nm, respectively. A CNT yield of 0.22 g/g_{cat} was obtained for a 5-min growth. Those indicated that the fluidized bed CVD was an effective way for mass production of short CNTs.

1. Introduction

Carbon nanotubes (CNTs) are of great interest in nanotechnology due to their unique properties. Some technical obstacles must be overcome before these properties can be fully used, one of which concerns on the length control of CNTs. Some applications, including electronic [1,2], biological and optical devices [3–5], require short individual nanotubes. CNTs with a length of 500–2000 nm are required in field emission displays with the expectation of uniform emission performance. These demands inspirited researchers to explore accessible and efficient methods for producing short CNTs. Until now, most short CNTs were obtained by acid treatment-cutting [6–9], which has several inevitable disadvantages such as loss of materials, increased number of defects, and difficulty in large scale production. Other reported methods to produce short CNTs include ball-milling [10,11], high speed agitation [12], solid-state cutting [13,14] and cryogenic crushing [4]. However, these treatments always suffered from long duration and the destruction of the CNT quality. If CNTs with certain length could be synthesized directly, these tedious of post-treatment and the damage on the pristine CNTs could thus be avoided, which may facilitate the promising applications of short CNTs.

There are many methods to produce CNTs, of which chemical vapor deposition (CVD) is mostly used because of its advantages of high yield and controllable growth conditions. Until now, the agglomerated CNTs and aligned CNTs have been synthesized through the CVD process. In the agglomerated CNTs, CNTs entangled with each other [15]. The length of agglomerated CNTs is believed to be above several micrometers, although the exact length is still unknown. For CNT array, the length is always long [16,17]. For some carbon nanofibers grown from plasma enhanced CVD, the length is always about 1.0 μm [1,18,19]. However, the diameter is always larger than 50 nm and the growth density is low.

Recently, we found that the vertically aligned carbon nanotube (VACNT) can grow among some layered compounds such as vermiculite, mica, and so on [20]. The layered catalysts show good fluidization characteristics and can be used in a fluidized bed for the mass production of VACNT arrays [21]. Based on this process, the yield of CNTs can be dramatically improved due to the large specific surface and the short CNTs in array form could be easily obtained thanks to the confinement of the layered structure. Here, we report large scale production of short CNTs intercalated grown among exfoliated vermiculite from ethylene using a simple chemical vapor deposition in a fluidized bed reactor.

2. Experimental

Vermiculite, a clay mineral formed by the weathering of the mica mineral biotite, was used as the carrier of catalyst. $Fe(NO_3)_3 \cdot 9H_2O$ (>99.0%, 5.0 g) and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (>99.0%, 1.0 g) was dissolved in deionized water (100 ml). Then 20.0 g exfoliated vermiculite powder with a size of around 300–400 μm (bulk density of about 211 kg/m^3), was suspended in solution to form a uniform suspension through strong stirring at 80 °C and kept for 3 h. After filtration and washing, the filtrated

* Corresponding author. Tel.: +86 10 62785464; fax: +86 10 62772051.
E-mail address: wf-dce@tsinghua.edu.cn (F. Wei).

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cake was dried at 110 °C for 12 h and was further calcined at 350 °C for 4 h. Then the Fe/Mo/vermiculite catalyst for short CNT synthesis was obtained.

The synthesis process was operated in a fluidized bed reactor made of quartz glass with an inner diameter of 20 mm and a height of 300 mm. There was a sintered porous plate used as the gas distributor at the bottom of the reactor. About 2.0 g Fe/Mo/vermiculite catalyst was fed into the reactor before reaction. The quartz fluidized bed reactor, mounted in an electrical tube furnace, was then heated to 650 °C in argon and hydrogen atmosphere at a flow rate of 500 and 20 ml/min, respectively. After that, C_2H_4 with a flow rate of 100 ml/min was introduced into the fluidized bed to achieve a short-term growth of CNTs for 1, 3, and 5 min, respectively. Both the catalyst and the CNTs were smoothly fluidized in the reactor. After growth, the fluidized bed reactor was cooled at argon atmosphere. The carbon product was collected and characterized as follows.

The morphology of the short CNTs was characterized using a JSM 7401F scanning electron microscope (SEM) operated at 3.0 kV, and a JEM 2010 high-resolution transmission electron microscope (TEM) operated at 120.0 kV. Raman experiments were performed with a Renishaw RM2000 Raman spectrophotometer. The spectra were recorded using a He–Ne laser excitation line at 632.8 nm with a spot size of about 20 μm^2. The purity of CNTs in the as-grown product was obtained through thermalgravimetric analysis (TGA) by TGA Q500.

3. Results and discussion

The as-obtained Fe/Mo/vermiculite catalyst is lamellar in structure and the distance between two layers is shown from tens of nanometer to several micrometers (Fig. 1(a) and (b)). They are with a size of about 300 μm and the bulk density is measured to be 211 m^3/kg. According to Geldart particles classification [22], the Fe/Mo/vermiculite catalyst particles belong to A particles. The minimal fluidization velocity (u_{mf}) of the lamellar catalyst was about 1.5 cm/s. They exhibited dense phase expansion after minimum fluidization velocity. After CNT growth, the color of catalyst particles turned from golden to black. However, the size and bulk density of the particles did not change a lot. The u_{mf} of the as-obtained products was still about 1.5 cm/s. The gas velocity in the reactor was fixed at about 9.0 cm/s to maintain a good bubbling fluidization during the whole reaction process. The typical morphology of the as-grown product was shown in Fig. 1(c) and (d). Short CNTs were intercalated grown in the inter spaces of the catalyst layers, as is shown in Fig. 1d. Detailed information can be observed from Fig. 1e–g. One can see clearly from Fig. 1e that well aligned CNTs with a length of around 500 nm grew vertically on the flat surface of the vermiculite layers after a 1-min growth. With the reaction time increasing to 3 min, the length of the obtained aligned CNTs increased to ca. 1 μm. Furthermore, aligned CNTs with a length of around 1.5 μm could be obtained after a 5-min reaction. It should be noticed that the alignment of CNTs was obviously improved when the length of CNTs increased, which can be explained by the pristine stress among CNTs during the heterogeneous catalysis process [23]. The array pushed the layer of the vermiculite away uniformly from the other layers. It also can be observed that the aligned CNTs grew on both sides of the vermiculite layer as indicated in Fig. 1h.

The structure of CNTs was characterized by TEM. As shown in Fig. 2a, all of the nanotubes are with hollow structure, with no catalyst particles encapsulated in the nanotube. Compared with floating catalyst process [24,25], the catalyst particles were loaded on the vermiculite layers and reduced by hydrogen, and they showed a strong metal–support interaction.

The HRTEM image shown in Fig. 2b indicates that CNTs are with clear graphite fringe. Based on statistics of 400 CNTs, the outer diameter shows a narrow distribution of 4–9 nm, while the inner diameter of the CNTs is about 2–5 nm (Fig. 2c). A typical Raman spectrum of the CNT array with D and G peak was recorded (Fig. 3a), of which the I_D/I_G ratio was about 1.54. The yield of the short aligned CNTs was analyzed by TGA. From Fig. 3b, there were about 18 wt% CNTs in the as grown products, and the ignition temperature of CNTs was 580 °C. This indicated that a CNT yield of 0.22 g/g_{cat} was obtained after a 5-min growth in the fluidized bed reactor.

Finally, it is worth mentioning that compared with plate substrate (surface area ~8 cm^2/g) [16–18] or spheres (~200 cm^2/g) [26], the layered vermiculites are with a huge surface area (about 40,000 cm^2/g). The vermiculite provides huge area of substrate for large scale growth of short CNTs. Furthermore, intercalated growth of CNTs prevented the CNT arrays from damage of collisions among large particles. The advantages of

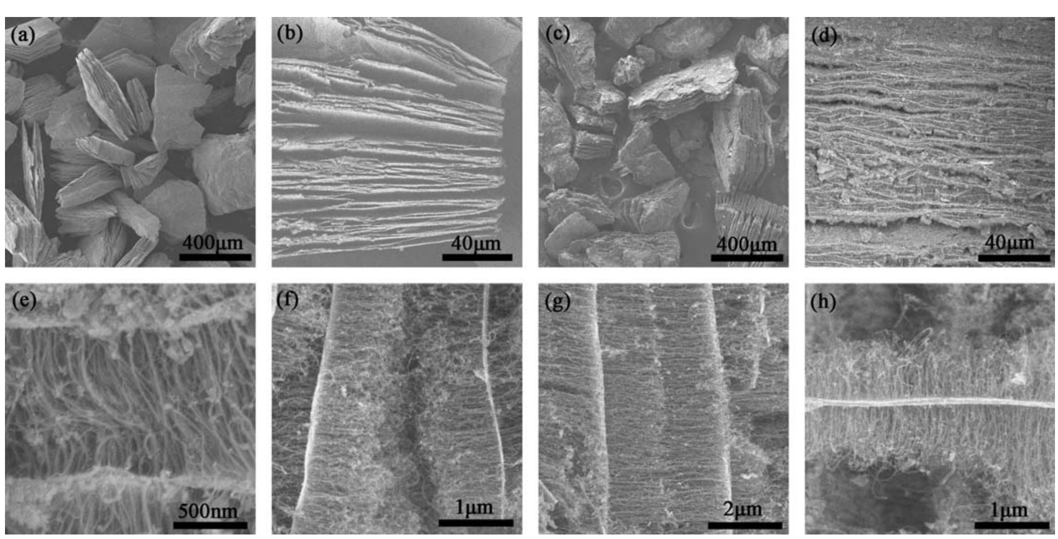

Fig. 1. (a), (b) The morphology of Fe/Mo/vermiculite catalyst; (c), (d) the morphology of short aligned CNTs intercalated among the catalyst layers at 650 °C in a fluidized bed reactor for 5 min; High resolution SEM images of aligned CNTs with a length of around (e) 0.5 μm, (f) 1 μm, (g) 1.5 μm grown between two vermiculite layers after a 1-min, 3-min, and 5-min reaction, respectively; (h) High resolution SEM images of short aligned CNTs grown on both sides of one vermiculite layer.

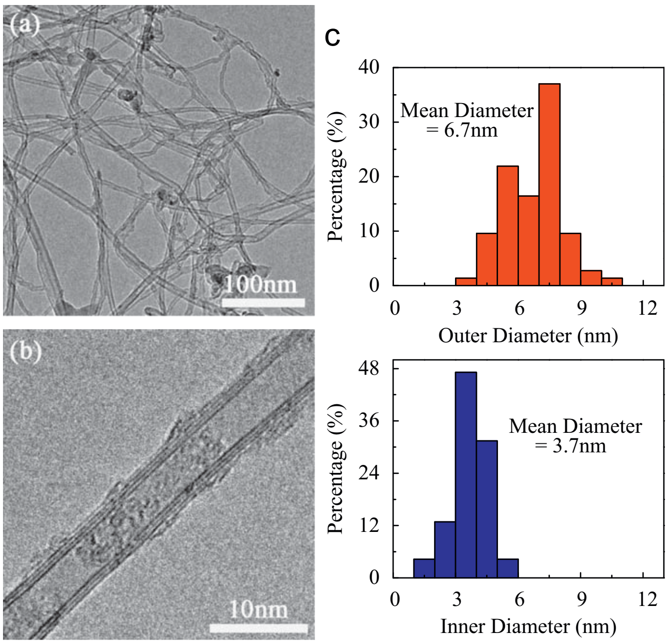

Fig. 2. (a) TEM and (b) high resolution TEM images of the as-obtained CNTs; (c) the outer and inner diameter distribution of the CNTs.

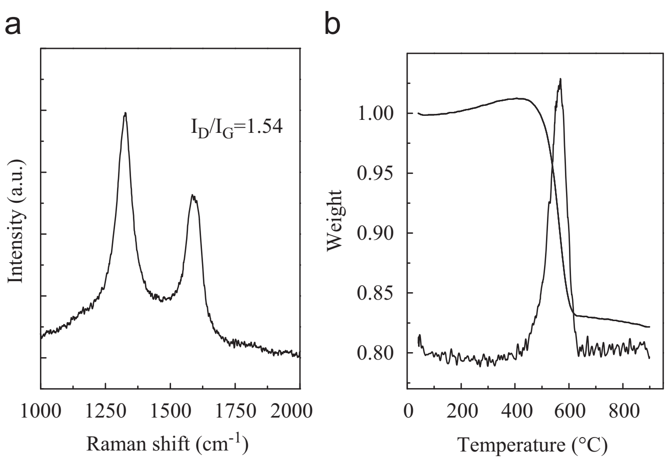

Fig. 3. (a) Raman spectrum of the short aligned CNTs; (b) TGA curves of the as-grown short aligned CNTs.

fluidized bed CVD process for CNT growth, such as plenty of space for CNT growth, good heat and mass transfer, well-mixed solids, are still effective for short CNT production.

4. Conclusions

Short aligned CNTs with a length of around 1 μm grown among the vermiculite layers can be produced via a typical fluidized bed CVD process using layered Fe/Mo/vermiculite catalyst. The CNTs synthesized are of good alignment and small diameter, the mean outer and inner diameter of which are 6.7 and 3.7 nm, respectively. The length of CNT array can be modulated by the growth time. A CNT yield of 0.22 g/g_{cat} was obtained for a 5-min growth, indicating fluidized bed CVD to be an effective way for mass production of short CNTs.

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