Radial growth of vertically aligned carbon nanotube arrays from ethylene on ceramic spheres

Qiang Zhang, Jia-Qi Huang, Meng-Qiang Zhao, Wei-Zhong Qian, Yao Wang, Fei Wei*

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

ARTICLE INFO

Article history:
Received 22 January 2008
Accepted 10 April 2008
Available online 16 April 2008

ABSTRACT

Vertically aligned carbon nanotube (VACNT) arrays grown on ceramic spheres are obtained from ethylene using a floating catalysis process. The exhaust gas mainly contains light gaseous hydrocarbons, which decreases the contamination at the outlet of the reactor. Linear synchronous growth of the VACNT arrays is demonstrated and the morphology evolution of VACNT array grown on spheres is shown. The VACNT arrays on the spheres crack radially into a flower-like structure when the length of CNT is above 400 μm. The VACNT arrays grown on spheres still possess good flowability even when the length of the array reaches 1100 μm after a 2-h growth at 800 °C. The arrays on the spheres show good alignment, high purity and good graphitization. Meanwhile, with a decrease in temperature, the diameter of CNTs in the array correspondingly decreases, the distribution becomes narrower, and the growth rate decreases. The apparent activation energy is 180 ± 8 kJ/mol, indicating that ethylene is a good carbon source for fast and continuous radial growth of millimeter VACNT arrays on ceramic spheres.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Vertically aligned carbon nanotube (VACNT) arrays have been a topic in carbon materials research since they were first synthesized in 1996 [1]. Since then, various structures of VACNT arrays have been obtained [2–7]. VACNT arrays grown into small bundles can be used as a field emission display [2]. They can also be grown on a fiber to produce a CNT bush to clean the surface of nanoparticles [4] or to enhance the texture of cloth [5]. The structure of VACNT array can display amazing architecture for various applications [7]. Aligned CNTs have many attractive properties such as identical tube length, uniform orientation, extra high purity, and can be easily spun into macroscopic fibers. Therefore, the as-grown arrays can be used to construct field emission devices, anisotropic conductive materials, multi-functional membranes and super strong yarn. Even with the loss of the original alignment, longer and straighter multi-walled CNTs (MWCNTs) from the VACNT arrays are found to be better than randomly aggregated multi-walled or even single-walled CNTs (SWCNTs) in improving the electronic, mechanical and thermal properties of a polymer. These applications will become feasible if VACNT arrays can be produced at a low cost on a large scale.

It is commonly reported that VACNT arrays can be synthesized on a flat surface [1–3,8–11]. However, the surface area of the flat substrate is often limited and its mobility is poor. Only 1 g/h VACNT array can be obtained with flat silica as substrate [11]. The quantity of the VACNT array is proportional to the surface area of the substrate. If a substrate with a larger surface area is used, more VACNT arrays can be produced. Spherical particles have the largest surface area. Specifically, when spheres with diameters of around 0.8 mm and a total volume of 1 dm³ are used as the growth substrates, the surface area increases by as much as 7.5 m² (equivalent to the surface area...
of 14,500 pieces of 1-in. wafer). These spheres exhibit good flowability and can be transferred easily in the reactor. We have recently synthesized VACNT arrays from cyclohexane on ceramic spheres [12]. However, cyclohexane is in liquid state at room temperature, so a delicate pump is needed to quantitatively feed it into the reactor. Cyclohexane is a chemical reactant with a high price and limited supply, and the cracking mechanism is complex. Some heavy hydrocarbons are deposited on the walls of the reactor. If a gas phase hydrocarbon, such as methane, ethylene, or propylene, is used as the carbon source, the process will be more efficient. Liquefied petroleum gas (LPG) can be used as carbon source for CNT growth on spheres, but the growth rate of the array is slow and the length of the CNTs is limited [13]. In this study, vertically aligned CNT arrays on ceramic spheres are successfully obtained using the floating catalyst process with ethylene as the carbon source.

2. Experimental

Typical experiments are performed in a horizontal quartz tube, 25 mm in diameter and 1200 mm in length using a two-stage furnace. Ferrocene is used as the catalyst precursor and ethylene is used as the carbon source. The substrates were commercially available ball-milling spheres consisting of 50% SiO2, 30% Al2O3, and 20% ZrO2. They were about 700 μm in diameter. The spheres were rinsed with ethanol for 5 min and then placed in the second stage of the quartz tube. The ferrocene was placed in a ceramic boat and was evaporated in the first stage of the furnace at 80 °C. The second stage was heated to 800 °C in an atmosphere of 95% Ar (99.999%) and 5% H2 (99.999%) with a flow rate of 800 sccm. Then the ethylene (99.95%) was introduced into the reactor with a flow rate of 100 sccm. The growth continued for a specific time at 800 °C, after which the product was removed from the reactor for further analysis. The gas product compositions were analyzed using an on-line gas chromatograph (Shimazu 14B) with a 50 m Al2O3 capillary column and a flame ionization detector. The morphology of the VACNT array was visualized using a JEOL JSM 7400F scanning electron microscope (SEM) operated at 5.0 kV and a JEM 2010 transmission electron microscope (TEM) operated at 120.0 kV. The sample for the TEM observation was prepared using a commonsonication method. Raman experiments were performed using a Renishaw RM2000 Raman spectrophotometer. The spectra were recorded using a He–Ne laser excitation line at 633.0 nm. The purity of the CNTs in the as-grown product was measured using thermal gravimetric analysis by TGA Q500.

3. Results and discussion

Ethylene was used as carbon source for VACNT arrays grown on spheres using the floating catalysis process. One part of ethylene was converted into VACNT arrays, while the other part was kept as gaseous hydrocarbon in the exhaust gas. Table 1 shows a typical composition of hydrocarbon products in the exhaust of the floating catalysis process using ethylene, LPG, and cyclohexane as carbon sources. When ethylene was used, the hydrocarbons in the exhaust were mainly ethylene, ethane and methane. LPG was mainly composed of C3 and C4 alkanes and alkenes. When it was used as carbon source, not only ethylene, ethane and methane were found in the exhaust, but also hydrocarbons above C5 were present at specific concentrations. For the liquid phase carbon source, such as cyclohexane, the main compositions of the exhaust were hydrocarbons above C6. The differences among the exhaust were mainly dependent on the carbon atom number in the initial hydrocarbons. For ethylene, the gaseous cracking products were mostly methane and ethane. Some of ethylene can be combined into C4, while for the LPG, more heavy hydrocarbons were present. This is because LPG consists of heavier hydrocarbons. For cyclohexane, apart from solid carbon products, heavier hydrocarbons were produced. The hydrocarbons above C6 in the exhaust were liquid or solid at room temperature and deposit easily on the reactor when the temperature was low. The outlet of the reactors thus became seriously contaminated. The coagulation on the wall of the reactor was sticky, making the continuous transfer of as-grown VACNT array out of reactor difficult. For ethylene, few heavy hydrocarbons existed in the exhaust, and the wall of reactor was kept clean. Thus, continuous delivering as-grown VACNT array on spheres became easier when ethylene served as a carbon source.

In another aspect, VACNT arrays were deposited during the floating catalysis process (Fig. 1, Figs. S1 and S2 in the supplementary material). The arrangement of CNTs is dependent on the size of the catalyst carriers. If the sphere or particles had a size of several to tens nanometers (such as CNTs growth on Fe/Mo/Al2O3 powders, Fe/MgO powders [14,15]) as the catalyst carrier, the CNTs grown were in a random tangled state. When spheres of a diameter similar to the diameter of CNTs were used, CNT mats were always deposited [16]. In this study, the diameter of the sphere was about 700 μm, which is larger than that of the CNTs. Thus, the surface of the sphere is almost flat relative to the scale of CNT growth. After the floating catalysis process which lasted for 2 h, all of the spheres had a flower-like structure, with 15–25 mats of long VACNT arrays oriented perpendicular to the surface of the sphere (Fig. 1a, Fig. 52b). The CNTs in each array were in good alignment (Fig. 1b). Some of the CNTs in the array were straight (Type 1), while the others were curved (Type 2) with a tortuosity factor of 1.13 ± 0.05 [17,18]. They displayed a structure similar to the VACNT arrays grown on a flat substrate in a synchronous growth [18]. Because the curvature of the spheres was almost flat at the scale of a single CNT, VACNT arrays showed a fast linear growth time on the spheres as shown in Fig. 2.

The morphology evolution of the arrays with the reaction time is shown in the inserted SEM images of Fig. 2. When
the arrays were short, they were in the form of films similar to CNT arrays grown on a plate. When the length reached 300 μm, the woven structure on the top broke and the film began to crack through large CNT bundles with a diameter of a few hundred micrometers. When the length of a VACNT array reached the millimeter scale, VACNT bundles with a diameter of several hundred micrometers grew radially from the sphere. The morphology changes led to a reduction in the flowability of the spheres. The static repose angle (SRA), which can be measured using the methods proposed by Santomaso et al. [19], quantitatively reflects the flowability of the VACNT sphere arrays. The ceramic spheres were round and slippery and had an SRA of 17° (Fig. 3), indicating an excellent flowability, and could roll in the reactor easily [20,21]. During the floating catalyst process, the SRA of the sphere gradually increased due to the coarse surface of the CNT spheres. It is
believed that when the SRA is below 30°, the particles will still have excellent flow and when the SRA is in the range of 30°–45°, the particles will be free-flowing. Here, when the length of as-grown VACNT arrays was less than 400 μm, the VACNT array held together and the SRA was less than 30°. As the length of the array increased, the VACNT arrays cracked into the CNT bundles. There was more interaction among CNT bundles when they crossed each other during flow. Fortu-

<table>
<thead>
<tr>
<th>Growth rate (μm/min)</th>
<th>Amount of array on single sphere (μg/h)</th>
<th>Tortuosity factor</th>
<th>Typical I_D/I_G ratio</th>
<th>Purity (%)</th>
<th>Inner diameter (nm)</th>
<th>Outer diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_2H_4</td>
<td>~8.9</td>
<td>1.13 ± 0.05</td>
<td>0.66</td>
<td>~98</td>
<td>~10</td>
<td>~23</td>
</tr>
<tr>
<td>LPG</td>
<td>~1.5</td>
<td>1.41 ± 0.08</td>
<td>0.72</td>
<td>~97.5</td>
<td>~10</td>
<td>~35</td>
</tr>
<tr>
<td>C_6H_12</td>
<td>~8</td>
<td>1.15 ± 0.04</td>
<td>0.46</td>
<td>~93.7</td>
<td>~9</td>
<td>~35</td>
</tr>
</tbody>
</table>

a The amount of VACNT array was calculated from the volume with the assumption of the density is 25 g/L.

b The tortuosity factor of the Type 2 (curved) nanotube [18], which is defined as the ratio of the length of the curved line between two points to linear distance between the two points [17,18], was obtained at a calculated scale of 10 μm.

c Typical I_D/I_G ratios were obtained from the related Raman spectra.

d The purity were obtained using TGA test.

e The diameter is a mean value. The original distribution of CNTs in the array from LPG and C_6H_12 can be found in Refs. [12,13].
nately, even when the length of the CNT arrays reached 1100 \( \mu \)m, the SRA was just 35° (Fig. 3), indicating that the spheres can still flow freely in the reactor. Thus, millimeter-sized VACNT arrays can be transferred in the reactor easily.

In this study, long VACNT arrays can be grown on the spheres from ethylene. After a 2-h growth at 800 °C, the length reached 1100 \( \mu \)m. The length was 1.1 times and 5.9 times of arrays grown from cyclohexane and LPG, respectively (Table 2). Also, the VACNT array grown from ethylene on the sphere showed the highest yield, at 21 \( \mu \)g/h on a single sphere. Meanwhile, as shown in Table 2, the VACNT arrays grown on the sphere from ethylene were of high quality. A typical MWCNT Raman spectrum of the VACNT array with D and G peaks is shown in Fig. S3 and the \( I_D/I_G \) ratio are about 0.66. From the TGA results, the VACNTs in the array grown from ethylene were of high purity, which was about 98% (Fig S4). TEM images (Fig. 4a and b) showed that the VACNT arrays on the spheres at 800 °C were tubular in structure with a high purity. No other impurities, including the amorphous carbon, iron catalyst encapsulated with carbon, could be found in the as-grown product. The inner diameter of the CNTs was about 10 nm, while the outer diameter showed a wide distribution (Fig. 5c) with a mean value of 23 nm, which could be modulated further by growth temperature. VACNT array can still be grown on ceramic spheres at 700 °C with a growth rate of 1.0 \( \mu \)m/min. As shown in Fig. 5a and b, the CNTs produced will still have a high level of purity and good graphitization. However, the outer diameter decreased to 19 nm, the diameter distribution was narrow, and the number of graphite layer decreased. The ratio of inner to outer diameter was increased. For VACNT array growth via floating catalysis process, the in situ formed Fe nanoparticles were sitting at the bottom of the array [22]. The diameter of the CNTs was noted to be mainly proportional to the size of catalyst particle [23]. At low temperatures, the sintering of the in situ formed Fe nanoparticles was apparently lowered, leading to the formation of small diameter CNTs with narrow distribution in low temperature floating catalysis process. This is similar to the VACNT array grown on plate substrate. The modulation techniques of VACNT arrays on the plate, including lithography to design

![Fig. 5 – (a) and (b) TEM images of the as-grown VACNT array on the ceramic sphere at 700 °C for 2 h. (c) Diameter distribution of the CNTs in the array.](image-url)
The activation energy of the VACNT array grown on ceramic spheres using ethylene as carbon source.

Fig. 6 – The activation energy of the VACNT array grown on ceramic spheres using ethylene as carbon source.

When ethylene is used as carbon source, radially aligned VACNT arrays on ceramic spheres are produced, and only light gaseous hydrocarbons exist in the exhaust. The VACNT array on the sphere grows at a linear rate of 8.9 μm/min at 800 °C, showing a faster growth rate as compared to that of cyclohexane and LPG. The VACNT arrays on the spheres are noted to crack radially into a flower-like structure; the arrays are of high quality. The inner diameter of the CNTs is about 10 nm, while the outer diameter shows a wide distribution with a mean value of 23 nm. The VACNTs in the array have a 98% purity level. When the growth temperature is decreased to 700 °C, the distribution of the outer diameter becomes narrow with a mean value of 19 nm. The SRA of particle increases from 17° to 35° with the growth of the VACNT arrays, but the spheres can still move freely even if the length of the arrays reaches 1100 μm. The VACNT array will grow fast at high temperature, with the activation energy of array growth on spheres at 180 ± 8 kJ/mol. Compared to LPG and cyclohexane, ethylene is an optimized carbon source for continuous radial growth of high quality VACNT arrays on ceramic spheres.

4. Conclusion

When ethylene is used as carbon source, radially aligned VACNT arrays on ceramic spheres are produced, and only light gaseous hydrocarbons exist in the exhaust. The VACNT array on the sphere grows at a linear rate of 8.9 μm/min at 800 °C, showing a faster growth rate as compared to that of cyclohexane and LPG. The VACNT arrays on the spheres are noted to crack radially into a flower-like structure; the arrays are of high quality. The inner diameter of the CNTs is about 10 nm, while the outer diameter shows a wide distribution with a mean value of 23 nm. The VACNTs in the array have a 98% purity level. When the growth temperature is decreased to 700 °C, the distribution of the outer diameter becomes narrow with a mean value of 19 nm. The SRA of particle increases from 17° to 35° with the growth of the VACNT arrays, but the spheres can still move freely even if the length of the arrays reaches 1100 μm. The VACNT array will grow fast at high temperature, with the activation energy of array growth on spheres at 180 ± 8 kJ/mol. Compared to LPG and cyclohexane, ethylene is an optimized carbon source for continuous radial growth of high quality VACNT arrays on ceramic spheres.

Acknowledgements

We thank Prof. Peter A. Thrower for the helpful discussion, suggestion and touching up of the article. The work was supported by the Foundation for Natural Scientific Foundation of China (Nos. 20606020 and 20736007), China National program (No. 2006CB932702), Key Project of Chinese Ministry of Education (No. 106011), the Author of National Excellent Doctoral Dissertation of PR China (No. 200548).

Appendix A. Supplementary data

The online version of this article contains additional supplementary material. The quality of CNT array grown from ethylene on the ceramic sphere, the morphology of VACNT arrays on spheres (Fig. S1, S2), Raman spectra (Fig. S3), TGA evaluation (Fig. S4) of the as-grown VACNT arrays are provided. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2008.04.017.

References


