

Vertically aligned carbon nanotube arrays grown on a lamellar catalyst by fluidized bed catalytic chemical vapor deposition

Qiang Zhang, Meng-Qiang Zhao, Jia-Qi Huang, Yi Liu, Yao Wang, Wei-Zhong Qian, 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

Large amount of vertically aligned carbon nanotube (CNT) arrays were grown among the layers of vermiculite in a fluidized bed reactor. The vermiculite, which was 100–300 μ m in diameter and merely 50–100 μ m thick, served as catalyst carrier. The Fe/Mo active phase was randomly distributed among the layers of vermiculite. The catalyst shows good fluidization characteristics, and can easily be fluidized in the reactor within a large range of gas velocities. When ethylene is used as carbon source, CNT arrays with a relatively uniform length and CNT diameter can be synthesized. The CNTs in the arrays are with an inner diameter of 3–6 nm, an outer diameter of 7–12 nm, and a length of up to several tens of micrometers. The as-grown CNTs possess good alignment and exhibit a purity of *ca*. 84%. Unlike CNT arrays grown on a plane or spherical substrate, the CNT arrays grown in the fluidized bed remain their particle morphologies with a size of 50–300 μ m and the good fluidization characteristics were preserved accordingly.

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1. Introduction

The synthesis of vertically aligned carbon nanotube (CNT) arrays has been a flourishing area in carbon material research since 1996 [1]. Their advantages include large aspect ratio, good orientation, and high purity. CNT arrays are attractive for their wide potential applications in field emission devices [2], anisotropic conductive materials, filaments [3], membrane [4], super springs [5], etc. The CNT arrays are with strong shear binding-on and easy normal lifting-off properties [6]. Meanwhile, the nitrogen-doped CNT arrays are with high electrocatalytic activity for oxygen reduction [7]. Compared with agglomerated single-walled CNTs (SWCNTs) and multiwalled CNTs (MWCNTs), CNT arrays are more readily dispersed into fluffy CNTs [8]. They can easily be constructed into CNT network/paper/film by evaporated filtration [9]. Moreover, there have been significant improvements in the

* Corresponding author: Fax: +86 10 6277 2051.

E-mail address: weifei@flotu.org (F. Wei).

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electronic, mechanical, and thermal properties of polymers after CNT reinforcement. Apparently, the mass production of desirable CNT arrays is the stimulus to their applications and commercial uses [10].

Generally, as the main product, CNTs grown on a catalyst are not easily to be separated from catalyst. This is obviously different from most heterogeneous reactions in which the reactants absorbed on the surface of the catalyst, and the products desorbed from the active sites, generating the products in gaseous phase. In the situation for CNTs, the catalyst and product are in solid state. They are continuously transported through the reactor for CNT production. Up to now, vertically aligned CNT arrays are mainly synthesized on a flat substrate packed in a furnace [1,2,11–18]. The quantity of the CNT array is proportional to the surface area of the substrate. The CNT array is obtained in small amounts because of the limited surface area of the flat substrate. Moreover, this kind of substrate is difficult to suspend or move because of the anisotropic morphology, exhibiting poor mobility. These disadvantages made the growth of CNT array over a flat substrate difficult to scale up. Only 1.0 g/h CNT arrays were obtained with a flat quartz plate as substrate [13]. If a substrate with a larger surface area is employed, more CNT arrays can be obtained. Thus, the substrate with a larger surface area and a round shape (i.e., sphere or sphere-liked particles) would be favorable for the radial growth of CNT arrays in large quantities and would facilitate easy collection. Recently, we successfully obtained several grams of CNT arrays per hour using ceramic spheres via floating catalyst process [19-21]. We found many carbon sources including xylene, cyclohexane, benzene, hexane in liquid state, or ethylene, propylene, and liquefied petroleum gas, can be used for large scale synthesis of CNT array [19-21]. This strategy provided a potential way for large scale growth of CNT array on spheres with a low cost.

Until now, it is commonly believed that the most efficient way for mass production of CNTs is fluidized bed catalytic chemical vapor deposition (CVD) [22-24]. In a fluidized bed, the solid particles (such as catalyst and the as-grown products) transformed into a fluid-like state through suspension in gas or liquid [24]. The fluidized bed reactor has great advantages in terms of enough growth space, excellent diffusion and heat transfer, easiness in scaling up and continuous operation for CNT production. A pilot mass production of agglomerated MWCNTs with high yield (15 kg/h) was realized in a fluidized bed reactor in 2002 [25]. The CNTs entangled together and formed agglomerates with a size of $10-200 \,\mu m$, which could be considered as A particles according to Geldart particles classification [26]. The powders in group A exhibit dense phase expansion after minimum fluidization velocity, and this state can be maintained over large velocity range. After then, fluidized bed catalytic CVD was widely used for agglomerated CNT production [27-47]. Agglomerated MWCNTs [26-42], double walled CNTs [43,44], and SWCNTs [45–47] can also be mass produced in a fluidized bed reactor. Recently, some companies have commercialized CNTs production with fluidized bed process. However, it should be noticed that all the products of the present fluidized bed process are agglomerated CNT products [22-47]. A fluidizable catalyst was necessary for the synthesis of CNTs in fluidized bed. Although radial growth on spheres was a good strategy for the mass production of CNT arrays [19-21], the diameter of the spheres was too large to be fluidized. The spherical substrates were with a size of about 0.6~1.2 mm, which can be classified into D particles according to Geldart particle classification [26]. They can be fluidized in spouted bed with strong collisions, which may disturb the growth of CNT array in fluidized state. If the CNTs can be grown within a single particle, then the collusions among CNT arrays during growth can be avoided. Recently, we found that the CNT array could grow among some lamellar compounds such as vermiculite and mica [48]. It can be used in a fluidized bed for the mass production of the CNT array if the lamellar catalyst were with good fluidization characteristics.

In the current article, we report a lamellar catalyst with a size of $100-300 \,\mu\text{m}$ obtained by traditional impregnating methods using lamellar structure compounds as carrier. The

CNT array can easily be synthesized among the layers of the catalyst. Both the catalyst and the product are with a size of $80-200 \ \mu\text{m}$ and can be easily fluidized. Therefore, fluidized bed catalytic CVD used for CNT array production can be achieved, which will significantly facilitate the mass production of CNT arrays. The as-grown CNT arrays are with high purity, which can be easily obtained by further purification.

2. Experimental

2.1. Catalyst preparation

The vermiculite is a kind of limited expansion clay with 2 tetrahedral sheets for every one octahedral sheet. It has a high cation exchange capacity of 100-150 meq/100 g. Vermiculite clays are weathered micas in which the K⁺ ions between the molecular sheets are replaced by Mg²⁺ and Fe²⁺ cations. In this contribution, vermiculite was used as carrier of the catalyst. The vermiculite (SiO₂, 42%, Al₂O₃, 12%, MgO 28%, Fe₂O₃ 13%, K₂O 4.0%, CaO 0.5%, H₂O 0.5%) used in our experiment was mined in Lingshou, Hebei Province of China. In brief, vermiculite powder with a size of $10-100 \,\mu\text{m}$ (bulk density of about 160 kg/m³) was suspended in distilled water to form a uniform suspension through strong stirring at 80 °C for 6.0 h. Subsequently, a solution of Fe(NO₃)₃·9H₂O and (NH₄)₆Mo₇O₂₄·4H₂O was added slowly into the suspension while stirring. The mass ratio of Fe:Mo:vermiculite was 5:5:90. After filtration, the filtrated cake was dried at 110 °C for 12 h and was further calcined at 300 °C for another 4 h. Then the lamellar Fe/Mo/vermiculite catalyst for CNT array production was obtained.

2.2. Vertically aligned CNT array synthesis

The schematic representation of the apparatus used in the experiment is shown in Fig. 1. The main body was a fluidized bed reactor made of quartz glass with an inner diameter of 50 mm and a height of 1300 mm. A sintered porous plate is used as the gas distributor at the bottom of the reactor. The gas distributor also acts as the floor, which supports the solids in the reactor before they are suspended in fluid flow. Here, the lamellar Fe/Mo/vermiculite was used as catalyst. About 5.0 g catalyst was fed into the reactor before reaction. The gas mixture containing a carbon source reactant enters the bottom vessel of the reactor and then passes through the gas distributor, the fluidized bed units, and finally flows out into the atmosphere. The quartz fluidized bed reactor, mounted in an electrical tube furnace, was heated to 650 °C in argon atmosphere at a flow rate of 1800 ml/min. The catalyst particles were pushed apart from one another by the upflow of the gas at a sufficient velocity. When a mixture of C_2H_4/H_2 (300/20 ml/min, v/v) was introduced into the fluidized bed, reaction occurs within the catalyst particles which were the sites of growing CNT array. Both the catalyst and the CNTs were smoothly fluidized in the reactor. After growth, the fluidized bed reactor was cooled down at argon atmosphere. The carbon product was then collected and characterized. The carbon product can be transferred out of the reactor in fast fluidization state for continuous production.



Fig. 1 – Schematic representation of the fluidized bed for synthesis of CNT arrays. 1-Gas chromatogram; 2-Mass flow controller; 3-Cyclone; 4-Fluidized-bed reactor; 5-Gas distributor; 6-thermocouple; 7-Heat controller.

2.3. Characterizations

The morphology of the CNT array was characterized using a JSM 7401F scanning electron microscope (SEM) operated at 5.0 kV, and a JEM 2010 high-resolution transmission electron microscope (TEM) operated at 120.0 kV. The sample for TEM observation was prepared using a common sonication method. 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 on the CNT array kept at ambient temperature. The purity of CNTs in the as-grown product was obtained through thermalgravimetric analysis (TGA) by Q500.

The size distributions of the suspended catalysts were measured by a laser particle size instrument. The reliability of the agglomerate size was further confirmed by SEM observations. The SEM photographs of the results from such analyses offer the most direct data of the catalyst and CNT agglomerates in the liquid phase, although the field of vision was limited. The fluidization characteristic of the lamellar Fe/ Mo/vermiculite catalyst and CNT array powder was investigated under ambient condition in an experimental apparatus as reported in Wang et al. [49].

3. Results and discussion

3.1. Fluidization behavior of the catalyst and as-grown products

The vermiculite consists of layers of mica plates with water and exchangeable ions between the layers. In this contribution, the vermiculite particles were soaked in Fe(NO₃)₃·9H₂O and (NH₄)₆Mo₇O₂₄·4H₂O solution. During the soaking process, the exchangeable ion among the layers of vermiculite, such as Ca²⁺, Mg²⁺, K⁺, can be replaced by Fe³⁺ (Fig. 2a and b). Meanwhile, the lamellar structure was preserved, and the morphology was also well maintained. From the SEM images as shown in Fig. 3, it can be noticed that the catalyst was still in a multilayer structure with a thickness of 50–100 μ m and a diameter of 100–300 µm. The Fe/Mo/vermiculite catalysts are lamellar in structure, as indicated in Fig. 3b and c. There are a lot of large pores in the catalyst, which was produced by the exfoliation process of vermiculite during drying and calcination. With regard to the axis direction of each layer, the interactions among layers were weak. After calcinations and reduction, active phases such as Fe particles were formed on each layer of the vermiculite for further CNT growth (Figs. 2 and 3d).

The fluidization properties of the catalyst were studied as follows. The pristine density of the vermiculite is 2300 kg/m³, while the bulk density of the as-obtained catalyst was 160 kg/m³. According to the density and size distribution, we believe that the irregular Fe/Mo/vermiculite catalyst particles belong to A particles according to Geldart particles classification. Fig. 4 shows the fluidization characteristic of the lamellar Fe/Mo/vermiculite catalyst. Typical bed expansion and pressure drop varied with superficial gas velocity were tested under a condition without reaction. These indicate that when the catalyst is exposed to an increasing up-flow of gas, the pressure drop and bed expansion will increase with higher gas flow. The point where the pressure drop is balanced with the weight of the bed is shown in Fig. 4. At this point, well fluidized state for this bed was established. The minimal fluidization velocity (u_{mf}) of the lamellar catalyst and the CNT product is 1.6 cm/s. The catalysts will be in fluidized state while the gas velocity was over u_{mf}. The mass behaves like a fluid that tends to establish a level and flows in response to pressure gradients. With an increasing gas velocity, several flow patterns or regimes were identified as particulate fluidization, bubbling fluidization, and turbulent fluidization. The pressure drop was kept almost constant in the turbulent fluidization stage, while height of the bed kept increasing. If the gas velocity is also further increased, fast fluidization and the pneumatic conveying regimes will be achieved. This indicates that the lamellar catalyst can be in stable fluidization state with a large domain. In our experiment, the gas velocity was kept at about 7.0 cm/s.



Fig. 2 – Schematic representation of the catalyst particle formation process. The Fe³⁺ can exchange with Ca²⁺, Mg²⁺, K⁺ in the vermiculite. After reduction, iron catalyst particles were formed on the surface of vermiculite layers.



Fig. 3 – SEM images of the fluidizable Fe/Mo/vermiculite catalyst. (a) Bird view of the catalyst particles. (b) and (c) Cross section of multi-layered structure of the catalyst. (d) Iron catalyst particles distributed on vermiculite layers after calcinations and reduction.



Fig. 4 – The fluidization characteristic of the lamellar Fe/Mo/ vermiculite catalyst.

CNTs will grow from the active sites among the layers of the Fe/Mo/vermiculite catalyst once the carbon source is introduced into the fluidized bed reactor. A good fluidization state was maintained during the whole reaction process. The typical products of the CNT arrays grown from ethylene on the lamellar catalyst are shown in Fig. 5a. It can be noticed that unlike other as-grown CNT arrays on plates or spheres with filmy morphologies, the CNT arrays synthesized here are still in loose powder form. A typical product size distribution from 50 to 300 μ m was obtained by laser particle size instrument as can be found in Fig. 5b. This is exactly one of the important reasons why they can be fluidized smoothly through the entire synthesis process. A typical fluidization characteristic of the Group A particle was shown for as-grown CNT on the Fe/Mo/vermiculite catalyst. Meanwhile, the CNT arrays grown among vermiculite exhibited a bulk density below 200 kg/m³. The u_{mf} of the as-grown product increased to 2.6 cm/s, which can be illustrated by traditional predictions as follows [50]:

$$u_{\rm mf} = \frac{d_p^2 (\rho_p - \rho) g}{1650 \mu} \tag{1}$$

where ρ and μ are the density and viscosity of air, d_p and ρ_p are the mean size and native density of the particles, and *g* is the acceleration of gravity. Using Eq. (1), the u_{mf} for the



Fig. 5 – (a) Typical morphology and (b) size distribution of the CNT arrays grown among the lamellar Fe/Mo/vermiculite catalysts in the fluidized bed CVD at 650 °C.

products was calculated to be about 2.5 cm/s. The catalysts were with lamellar morphology, which is beyond the assumption of Eq. (1). For the CNT array particles, the error between the predictions and experimental results was just 4.0%, indicating that the as-grown particle was similar to the traditional particle, which can be in stable fluidization in a large domain. From Fig. 6, several flow patterns or regimes have been identified as particulate fluidization, bubbling fluidization, and turbulent fluidization with increasing gas velocity. The pressure drop and the bed expansion ratio also showed similar trends as the Fe/Mo/vermiculite catalyst. In our experiment, the gas velocity was kept at about 7.0 cm/s, which was much larger than u_{mf}, indicating that the CNT products were still in stable fluidization state. Also, some large particles broke into pieces in the violent flow due to the weak connections between vermiculite layers. Thus, if the products can be



Fig. 6 – The typical fluidization characteristic of the CNT array powders. The powder was obtained by a half-hour growth in the fluidized bed CVD.

limited within the scope of A particles according to Geldart particle classification [26], we can keep the fluidized state stable.

3.2. Evolution of CNT arrays in the fluidized bed reactor

The evolution of CNT arrays in the fluidized bed were illustrated by the SEM images as shown in Fig. 7. When the catalysts were exposed to the ethylene for 10 min under growth condition, CNT array can be synthesized between the lamellar structures (Fig. 7a and b). The arrays pushed the layers of the vermiculite and expanded the distance between layers uniformly. After a 10 min growth process, the length of the array reached 2 μ m. The thickness of a single layer of the vermiculite layer was just 10-40 nm, indicating that the vermiculite has been cleaved. After the reaction, the length of vermiculite particle expanded to over 200 μ m with the diameter almost kept constant. It can be noticed as well that the CNT array with similar height could grow on both sides of the vermiculite as indicated by the arrow points in Fig. 7b. The layers of the vermiculite maintained their large size. With the CNT arrays further growing, it will push the opposite arrays in the vermiculite. There was stress distributed among CNT array during growth. The junction of CNT arrays growth from the opposite surface of vermiculite can be found in Figs. 7b and f and 8. When the growth time reached 30 min, the length of CNT became 6-8 µm as shown in Fig. 7c. High magnification SEM images indicated that the CNTs in the array possessed good alignment (Fig. 7d), and they are perpendicular oriented to the vermiculite layer (Fig. 7e). With the CNT array growing, the stress among the layers of vermiculite and arrays will also increase, leading to the breakage of the vermiculite layer. As shown in Fig. 7f, the arrow points the interface where the CNTs in the array pushed each other, and the layers of the vermiculite were crushed into small pieces. The small vermiculite pieces were with a size of 5–30 μ m as shown in Fig. 7g. Although the vermiculite was crushed into small pieces, the CNTs were still perpendicular to the plane of vermiculite layer (Fig. 7g and h). Meanwhile, the CNTs grown on the vermiculite layer showed good alignment in a large area as shown in Fig. 7d-i.

The growth behavior of the CNT array among vermiculite layers is obviously different from that of most agglomerated

CNTs grown from powder catalyst. For most of the catalysts used in fluidized bed, they were agglomerate nanoparticles



Fig. 7 – The morphology of the CNT array grown among Fe/Mo/vermiculite catalyst layers at 650 °C in a fluidized bed reactor for (a, b) 10 min, (c–e) 30 min, and (f–i) 60 min. The arrows in (a) and (f) indicate the junction during growth, and the arrow in (g) indicated the crushed vermiculite layers.



Fig. 8 – High magnification SEM images of junctions during CNT array growth. The growth time is (a) 15 min and (b) 60 min.

with the active phases supported on the carriers, which were mainly nanoparticles [24,27–47]. In the initial growth period, the growing CNTs crushed the catalyst particles, disrupted the structure, and formed separated catalytic sites. With the carbon deposition increasing, the catalysts will be crushed as much as they can, and the CNTs will grow all around the catalyst sites [51]. The growing CNTs will then push away and separate the sites from one another, leading to an increase in agglomerate size and a decrease in density until fragmentation by ablation dominates the growing process. In the case reported in this work, the lamellar catalyst was an anisotropic material with a slice vertical to the axial plane with a strong connection at the radial directions and weak connection at the axis directions (Fig. 2a). After ion-exchange and calcination, the catalyst phases intercalated among the catalyst layers with a high density (Fig. 2b and c). During the reaction process, the carbon source diffused into the layers, adsorbed, and decomposed at the active sites on the vermiculite layers (Fig. 9a). Furthermore, the catalysts are with a high density, causing the crowded growth of CNTs among the layers. As the CNTs grew longer, space resistance developed especially in the radial direction (Fig. 9b). Thus, they were prone to grow in the axis direction to form CNT arrays [52]. With length of CNTs increasing, the layers of vermiculites



Fig. 9 – Schematic representation of the synchronous growth of CNT array among lamellar catalyst: (a) CNT nucleation and CNT random growth on the substrate and as-grown CNT push off the layer a period of growth, (b) CNT array grown synchronously among the layers. (c) The growth rate of the array did not match, thus the layer was crushed into small pieces and the length of CNT array increased.



Fig. 10 – (a) TEM and (b) high resolution TEM images of the as-grown CNT array; distribution of the (c) inner diameter, (d) outer diameter, and (e) wall number of the CNT grown among Fe/Mo/vermiculite catalysts.



Fig. 11 – Raman spectrum of the CNT arrays.

were crushed into small pieces. However, the as-grown CNTs still showed good alignment (Fig. 9c). Even in a fluidized bed, the synchronous growth mode with internal stress was maintained [52], leading to the formation of CNT arrays among the vermiculite layers. Furthermore, the collisions among large particles during the fluidization were released by the out layers of particles, preventing the growth of intercalated CNT arrays from disturbance.

3.3. Vertically aligned CNT array products grown in the fluidized bed reactor

After growth for an hour at 650 °C, the length of the CNT arrays reached 10–20 $\mu m.$ In addition, the CNT arrays grown among the layers were of high quality. The TEM images showed that they were tubular-structured and with high purity (Fig. 10a and b). No other impurities, including the carbon spheres and Fe catalyst encapsulated in carbon can be found in the asgrown product. The diameter of the CNT was a key factor to evaluate the quality. The CNTs in array form obtained by the floating catalyst process are always with a diameter ranging from 10 to 60 nm [5,11-13,17-21]. And for most products prepared by thermal CVD and plasma-enhanced CVD, the size of CNTs mainly depends on the thickness of the metal film and annealing procedures and the diameters commonly range from 1 to 80 nm [1,2,14-16]. CNT arrays composed with fewwalled CNTs can be only obtained in small scale of 10-1000 mg per piece of wafer by thermal CVD in previous studies. Here, as shown in Fig. 10c-e, the inner diameter of the CNTs was about 3-6 nm, while the outer diameter showed a wide dis-



Fig. 12 – (a) Large amount of CNT arrays grown on Fe/Mo/vermiculite catalyst; (b) Morphology of the as purified CNT array by impregnation of HF and HCl solution; (c) TGA curves of the as-grown and purified CNT array.

tribution of 7–12 nm. This indicated that small catalyst particles were distributed among the layers of vermiculites.

The HRTEM image (Fig. 10b) shows that CNTs are mainly composed of clear graphite fringe with some defects co-existed. A typical Raman spectrum of the CNT array with D and G peak was recorded (Fig. 11), of which the I_D/I_G ratio was about 1.06. The low I_D/I_G ratio indicated relatively high defect density in the consisting CNTs, which was mainly caused by strong stress during the growth of CNTs. Meanwhile, the K-containing vermiculite will slightly poison the catalyst, making the inner diameter increasing as compared to the Fe/Mo phase in MgO particles [44]. Besides, the carbon precipitation rate is still uninformed, leading to more defects in CNTs. The yields of CNT among the vermiculites are high. The TGA results (Fig. 12) revealed the CNT arrays grown had a purity of about 84% in the as-grown products. After a one-hour reaction, we obtained 26 g of CNT arrays among the catalyst layers, which is equivalent to the productivity of 10⁶ spheres [19–21] or about 1500 1 inch wafers as substrate [1,2,14–16] using ethylene as carbon source (assuming that the density of the CNT array on wafer is 40 g/L and the length is 3.0 mm for 1 h growth). However, it was noticed that the CNT arrays grown among the vermiculite layers were still short and contained a number of defects, which was to be improved in further studies.

By fluidized bed catalytic CVD, large amount of CNT arrays can be obtained as shown in Fig. 12a. By impregnation in 3.0 mol/l HCl solution for 1.0 h, and 1.0 mol/l HCl solution subsequently, the vermiculite can be removed. Fig. 12b shows a typical SEM micrograph of the as purified product, in which the vermiculite layers had been removed by acid treatment. The CNT arrays still possessed good alignment after acid treatment and the interface among CNT arrays is clearly shown in Fig. 12b. The purity of CNT arrays was increased from 84.0% to 97.5% (Fig. 12c) by the purification process. It can be further improved by high temperature treatment in vacuum atmosphere in future.

In final, compared with fixed bed reactor used in CNT growth on plane or spherical substrate, fluidized reactor used for intercalated growth in lamellar catalyst is a preferred process for the large-scale production of CNT arrays because the reactors involved provide a large, effective surface area and plenty of space for the growth of CNTs [24]. Good heat and mass transfer ensure the uniform temperature and reactant concentration in the entire fluidized bed, which is important for the controlled growth of CNT arrays among the vermiculite layers. The well-mixed solids avoid rapid temperature and concentration changes, as well as the abrupt changes in operating conditions. Thus, the operation can be controlled easily and reliably. This assures the rapid diffusion of carbon atoms over and through the metal to a location where they assemble into an ordered structure. The collisions took place among particles while the CNT arrays synchronously grew among the vermiculite layers. Thus, a process of this nature can be easily scaled up from several thousand kilograms to tons per year, which will open up new opportunities for the industrial application of CNT arrays. Although these arrays have been successfully synthesized on a large scale via fluidized bed CVD, further investigations are certainly needed in order to delicately control the array structure, including its length, diameter, defects density.

4. Conclusions

When lamellar Fe/Mo/vermiculites with a thickness of 50–100 μ m and a diameter of 100–300 μ m were used as catalyst carriers, they can easily be fluidized in the reactor. CNT arrays can grow among the layers of vermiculites. Unlike other CNT arrays grown on a plane or spherical substrate, the as-grown CNT arrays are still in powder form and can easily be fluidized in the reactor. The CNTs grown among vermiculites possess good alignment. They are with an inner diameter of 3–6 nm, an outside diameter of 7–12 nm, a length of several tens micrometers, a purity of 84.0%, and the purity can be increased to 97.5% by simple purification. Large amounts of CNT array can be produced using this fluidized CVD.

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REFERENCES

- Li WZ, Xie SS, Qian LX, Chang BH, Zou BS, Zhou WY, et al. Large-scale synthesis of aligned carbon nanotubes. Science 1996;274(5293):1701–3.
- [2] Fan SS, Chapline MG, Franklin NR, Tombler TW, Cassell AM, Dai HJ. Self-oriented regular arrays of carbon nanotubes and their field emission properties. Science 1999;283(5401):512–4.
- [3] Jiang KL, Li QQ, Fan SS. Nanotechnology: spinning continuous carbon nanotube yarns – Carbon nanotubes weave their way into a range of imaginative macroscopic applications. Nature 2002;419(6909):801.
- [4] Hinds BJ, Chopra N, Rantell T, Andrews R, Gavalas V, Bachas LG. Aligned multiwalled carbon nanotube membranes. Science 2004;303(5654):62–5.
- [5] Cao AY, Dickrell PL, Sawyer WG, Ghasemi-Nejhad MN, Ajayan PM. Super-compressible foamlike carbon nanotube films. Science 2005;310(5752):1307–10.
- [6] Qu LT, Dai LM, Stone M, Xia ZH, Wang ZL. Carbon nanotube arrays with strong shear binding-on and easy normal liftingoff. Science 2008;322(5899):238–42.
- [7] Gong KP, Du F, Xia ZH, Durstock M, Dai LM. Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction. Science 2009;323(5915):760–4.
- [8] Zhang Q, Xu GH, Huang JQ, Zhou WP, Zhao MQ, Wang Y, et al. Fluffy carbon nanotubes produced by shearing vertically aligned carbon nanotube arrays. Carbon 2009;47(2):538–41.
- [9] Xu GH, Zhang Q, Zhou WP, Huang JQ, Wei F. The feasibility of producing MWCNT paper and strong MWCNT film from VACNT array. Appl Phys A 2008;92(3):531–9.
- [10] Wei F, Zhang Q, Qian WZ, Xu GH, Xiang R, Wen Q, et al. Progress on aligned carbon nanotube arrays. New Carbon Mater 2007;22(3):271–82.
- [11] Andrews R, Jacques D, Rao AM, Derbyshire F, Qian D, Fan X, et al. Continuous production of aligned carbon nanotubes: a step closer to commercial realization. Chem Phys Lett 1999;303(5–6):467–74.

- [12] Zhang XF, Cao AY, Wei BQ, Li YH, Wei JQ, Xu CL, et al. Rapid growth of well-aligned carbon nanotube arrays. Chem Phys Lett 2002;362(3–4):285–90.
- [13] Singh C, Shaffer MSP, Koziol KKK, Kinloch IA, Windle AH. Towards the production of large-scale aligned carbon nanotubes. Chem Phys Lett 2003;372(5–6):860–5.
- [14] Hata K, Futaba DN, Mizuno K, Namai T, Yumura M, Iijima S. Water-assisted highly efficient synthesis of impurity-free single-waited carbon nanotubes. Science 2004;306(5700):1362–4.
- [15] Bronikowski MJ. CVD growth of carbon nanotube bundle arrays. Carbon 2006;44(13):2822–32.
- [16] Hart AJ, Slocum AH, Royer L. Growth of conformal singlewalled carbon nanotube films from Mo/Fe/Al₂O₃ deposited by electron beam evaporation. Carbon 2006;44(2):348–59.
- [17] Zhang H, Cao GP, Wang ZY, Yang YS, Gu ZN. Electrochemical capacitive properties of carbon nanotube arrays directly grown on glassy carbon and tantalum foils. Carbon 2008;46(5):822–4.
- [18] Kunadian I, Andrews R, Qian DL, Menguc MP. Growth kinetics of MWCNTs synthesized by a continuous-feed CVD method. Carbon 2009;47(2):384–95.
- [19] Xiang R, Luo GH, Qian WZ, Wang Y, Wei F, Li Q. Large area growth of aligned CNT arrays on spheres: towards large scale and continuous production. Chem Vapor Depos 2007;13(10):533–6.
- [20] Zhang Q, Huang JQ, Wei F, Xu GH, Wang Y, Qian WZ, et al. Large scale production of carbon nanotube arrays on the sphere surface from liquefied petroleum gas at low cost. Chinese Sci Bull 2007;52(21):2896–902.
- [21] Zhang Q, Huang JQ, Zhao MQ, Qian WZ, Wang Y, Wei F. Radial growth of vertically aligned carbon nanotube arrays from ethylene on ceramic spheres. Carbon 2008;46(8):1152–8.
- [22] See CH, Harris AT. A review of carbon nanotube synthesis via fluidized bed chemical vapor deposition. Ind Eng Chem Res 2007;46(4):997–1012.
- [23] Philippe R, Moranqais A, Corrias M, Caussat B, Kihn Y, Kalck P, et al. Catalytic production of carbon nanotubes by fluidized-bed CVD. Chem Vapor Depos 2007;13(9):447–57.
- [24] Wei F, Zhang Q, Qian WZ, Yu H, Wang Y, Luo GH, et al. The mass production of carbon nanotubes using a nanoagglomerate fluidized bed reactor: a multiscale space-time analysis. Powder Technol 2008;183(1):10–20.
- [25] Wang Y, Wei F, Luo GH, Yu H, Gu GS. The large-scale production of carbon nanotubes in a nano-agglomerate fluidized bed reactor. Chem Phys Lett 2002;364(5–6):568–72.
- [26] Geldart D. Types of gas fluidization. Powder Technol 1973;7(5):285–92.
- [27] Venegoni D, Serp P, Feurer R, Kihn Y, Vahlas C, Kalck P. Parametric study for the growth of carbon nanotubes by catalytic chemical vapor deposition in a fluidized bed reactor. Carbon 2002;40(10):1799–807.
- [28] Corrias M, Caussat B, Ayral A, Durand J, Kihn Y, Kalck P, et al. Carbon nanotubes produced by fluidized bed catalytic CVD: first approach of the process. Chem Eng Sci 2003;58(19):4475–82.
- [29] Qian WZ, Wei F, Wang ZW, Liu T, Yu H, Luo GH, et al. Production of carbon nanotubes in a packed bed and a fluidized bed. AIChE J 2003;49(3):619–25.
- [30] Xu CB, Zhu J. One-step preparation of highly dispersed metalsupported catalysts by fluidized-bed MOCVD for carbon nanotube synthesis. Nanotechnology 2004;15(11):1671–81.
- [31] Rakov EG, Blinov SN, Ivanov IG, Rakova EV, Digurov NG. Continuous process for obtaining carbon nanofibers. Russian J Appl Chem 2004;77(2):187–91.

- [32] Chen F, Zhang XB, Sun YL, Cheng JP, Li Y. Continuous mass production of carbon nanotube using secondary fluidized bed. J Inorg Mater 2004;19(4):931–4.
- [33] Son SY, Lee DH, Kim SD, Sung SW, Park YS, Han JH. Synthesis of multi-walled carbon nanotube in a gas–solid fluidized bed. Korean J Chem Eng 2006;23(5):838–41.
- [34] Morancais A, Caussat B, Kihn Y, Kalck P, Plee D, Gaillard P, et al. A parametric study of the large scale production of multi-walled carbon nanotubes by fluidized bed catalytic chemical vapor deposition. Carbon 2007;45(3):624–35.
- [35] Shah N, Ma SK, Wang YG, Huffman GP. Semi-continuous hydrogen production from catalytic methane decomposition using a fluidized-bed reactor. Int J Hydrogen Energ 2007;32(15):3315–9.
- [36] Bierdel M, Buchholz S, Michele V, Mleczko L, Rudolf R, Voetz M, et al. Industrial production of multiwalled carbon nanotubes. Phys Status Solidi B 2007;244(11):3939–43.
- [37] See CH, Dunens OM, MacKenzie KJ, Harris AT. Process parameter interaction effects during carbon nanotube synthesis in fluidized beds. Ind Eng Chem Res 2008;47(20):7686–92.
- [38] Yen YW, Huang MD, Lin FJ. Synthesize carbon nanotubes by a novel method using chemical vapor deposition-fluidized bed reactor from solid-stated polymers. Diam Relat Mater 2008;17(4–5):567–70.
- [39] See CH, Harris AT. $CaCO_3$ supported Co–Fe catalysts for carbon nanotube synthesis in fluidized bed reactors. AIChE J 2008;54(3):657–64.
- [40] Son SY, Lee Y, Won S, Lee DH, Kim SD, Sung SW. High-quality multiwalled carbon nanotubes from catalytic decomposition of carboneous materials in gas–solid fluidized beds. Ind Eng Chem Res 2008;47(7):2166–75.
- [41] Hsieh CT, Lin YT, Chen WY, Wei JL. Parameter setting on growth of carbon nanotubes over transition metal/alumina catalysts in a fluidized bed reactor. Powder Technol 2009;192(1):16–22.
- [42] García-García RF, Pérez-Cabero M, Nevskaia DM, Rodríguez-Ramos I, Guerrero-Ruiz A. Improving the synthesis of high purity carbon nanotubes in a catalytic fluidized bed reactor and their comparative test for hydrogen adsorption capacity. Catal Today 2009;133–135:815–21.
- [43] Liu Y, Qian WZ, Zhang Q, Ning GQ, Luo GH, Wang Y, et al. Synthesis of high-quality, double-walled carbon nanotubes in a fluidized bed reactor. Chem Eng Technol 2009;32(1): 73–9.
- [44] Zhang Q, Yu H, Liu Y, Qian WZ, Wang Y, Luo GH, et al. Few walled carbon nanotube production in large-scale by nano-agglomerate fluidized-bed process. Nano 2008;3(1):45–50.
- [45] Li YL, Kinloch IA, Shaffer MSP, Geng JF, Johnson B, Windle AH. Synthesis of single-walled carbon nanotubes by a fluidizedbed method. Chem Phys Lett 2004;384(1–3):98–102.
- [46] Zhang QF, Yu H, Luo GH, Qian WZ, Wei F. Synthesis of singlewalled carbon nanotubes by chemical vapor deposition of methane in a fluidized bed reactor: temperature and reaction time effects. New Carbon Mater 2006;21(4):349–54.
- [47] Liu XB, Sun H, Chen Y, Lau R, Yang YH. Preparation of large particle MCM-41 and investigation on its fluidization behavior and application in single-walled carbon nanotube production in a fluidized-bed reactor. Chem Eng J 2008;142(3):331–6.
- [48] Zhang Q, Zhao MQ, Liu Y, Cao AY, Qian WZ, Lu YF, et al. Energy-absorbing hybrid composites based on alternate carbon nanotube and inorganic layers. Adv Mater 2009. <u>doi:10.1002/adma.200900123</u>.

- [49] Wang Y, Gu GS, Wei F, Wu J. Fluidization and agglomerate structure of SiO₂ nanoparticles. Powder Technol 2002;124(1–2):152–9.
- [50] Bin AK. Prediction of the minimum fluidization velocity. Powder Technol 1994;81(2):197–9.
- [51] Hao Y, Zhang QF, Wei F, Qian WZ, Luo GH. Agglomerated CNTs synthesized in a fluidized bed reactor: agglomerate

structure and formation mechanism. Carbon 2003;41(14):2855–63.

[52] Zhang Q, Zhou WP, Qian WZ, Xiang R, Huang JQ, Wang DZ, et al. Synchronous growth of vertically aligned carbon nanotubes with pristine stress in the heterogeneous catalysis process. J Phys Chem C 2007;111(40):14638–43.