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Rapid growth of well-aligned carbon nanotube arrays

Xianfeng Zhang [a,*], Anyuan Cao [a,b], Bingqing Wei [b], Yanhui Li [a], Jinquan Wei [a], Cailu Xu [a], Dehai Wu [a]

[a] *Department of Mechanical Engineering, State Key Laboratory of Auto. Safety and Energy, Tsinghua University, Beijing 100084, China*
[b] *Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, USA*

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Abstract

Vertically aligned carbon nanotube (CNT) arrays with high density were synthesized on quartz substrates in large areas (100×40 mm^2) by catalytic decomposition of a ferrocene–xylene mixture at 850 °C in a quartz tube reactor. The nanotubes grow at a high growth rate of ~50 μm/min, and reach 1.5 mm in length in 30 min. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) investigations reveal that the nanotubes are high-purity multi-wall CNTs with well-ordered graphene sheets, and about 30–60 nm in diameter. This provides a simple way to synthesize well-aligned CNTs in large areas. A continuous rapid growth model is suggested for the CNTs in high growth rate under our experimental conditions.

1. Introduction

Since the discovery in 1991 [1], carbon nanotubes (CNTs) have shown many unique physical and chemical properties [2–5]. Numerous potential applications, such as flat panel displays [6,7], hydrogen storage [8,9], chemical sensors [10], etc., were proposed. To research their growth mechanism and to realize their potentials controlled growth of well-aligned CNTs is essential. There have been many reports in this field [11–18]. The chemical vapor deposition (CVD) method has attracted much attention because of the advantage that the growth of CNTs can be achieved with high purity, high yield, and vertical alignment. Terrones et al. [11] obtained aligned CNT films at growth rate of about 3.3 μm/min by pyrolysis of organic precursors on laser etched cobalt films. Li et al. obtained aligned CNTs on mesoporous silica embedded with iron nanoparticles by CVD method. The area of aligned nanotubes is limited (5–20 mm^2), and their growth rate is very low (~0.4 μm/min) [12]. Using the same method, Pan et al. [13] obtained 2 mm long aligned nanotubes after 48 h of growth with an average rate of no more than 0.5 μm/min. Ren et al. [14] synthesized arrays of aligned CNTs on nickel-coated glass by plasma-enhance hot filament CVD method. Their growth rate is 2 μm/min, and the maximal length is 50 μm. Bower et al. [15] claimed that the aligned CNTs grow at a surprisingly high rate of ~6 μm/min in their plasma process, which is more than 40 times

* Corresponding author. Fax.: +86-10-6278-9739.
E-mail address: zxfeng99@mails.tsinghua.edu.cn (X. Zhang).

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higher than that without the plasma enhancement. Rao et al. [16] obtained 10 μm long aligned CNTs by pyrolysis of ferrocene at a certain heating rate under a flow of argon and acetylene. In this Letter, we report a rapid growth of well-aligned carbon naotube arrays by catalytic decomposition of a ferrocene–xylene mixture; the growth rate of CNTs can reach ~ 50 μm/min, the length of them reaches 1.5 mm in 30 min.

2. Experimental

The method we used here is similar to that reported in [17,18], but we made some improvements in reaction temperature, Fe/C ratio, flow rate of Ar/H_2, feed rate of solution, and feeding method of solution. The growth rate of CNTs in [17] is ~ 0.4 μm/min. In our experiments we used quartz sheets (100×40 mm^2) as substrates for aligned CNTs growth. Ferrocene was dissolved in xylene to obtain a solution of 0.02 g/ml, which was then fed continuously into a two-stage tubular quartz reactor (50 mm in diameter) by a flux pump at a feeding rate of 0.4 ml/min. Ferrocene acts as a producer for Fe catalyst particles and xylene was selected as carbon source. The temperatures at preheating stage and decomposition stage of the reactor were maintained at 300 °C and 850 °C, respectively. The flowing rates of Ar/H_2 during the reaction were kept at 2000/400 sccm. After the reactor was cooled to room temperature in Ar ambient, uniform black films were formed on the every side of quartz sheets and the walls of quartz tube reactor. The long nanotube films were easily peeled off from the quartz substrates.

3. Results and discussion

Fig. 1 shows an as-grown nanotube film with a growth time of 30 min. This film exhibits a good elasticity, when pressed by tweezers and then released, it recovered to its original thickness. The thickness of the film, i.e. the CNT length is about 1.5 mm, as shown in Fig. 1a. Fig. 1b is an enlarged image of Fig. 1a, showing that the film consists of well-aligned CNTs with high density (estimated about 100–200 μm^{-2}). The CNTs in the arrays are very clean with a uniform diameter of about 30–60 nm. The average growth rate calculated is about 50 μm/min, which is almost 1–2 orders higher than that of other CVD methods reported [11–20]. Such a high growth speed is important for successful commercialization of nanotube applications.

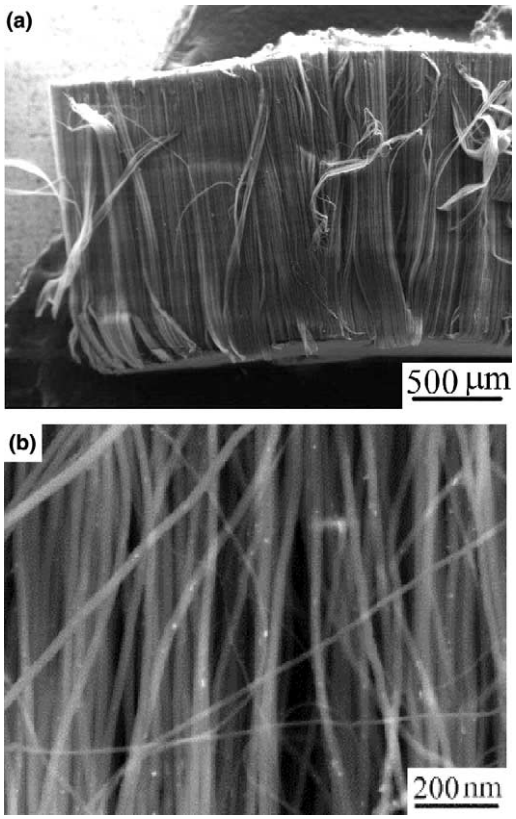

Fig. 1. (a) Low magnification SEM image of as-grown film of CNTs with growth time of 30 min. The thickness of the film is about 1.5 mm. So the caculated average growth rate of CNTs is ~ 50 μm/min. (b) High-magnification SEM of (a), showing that the CNTs are well-aligned, closely contacted, and clean.

Surprisingly, the aligned CNTs can grow at such high speed by a common CVD method. SEM examinations show that the dense-aligned CNTs become straight only in few microns from their start positions (Fig. 2a). Fig 2b is a TEM image of the roots of two nanotubes, which have horn-like hollows with Fe catalyst particles sitting at the horn tops (indicated by arrows). We suggest that the initial parts of CNTs may mainly be formed in

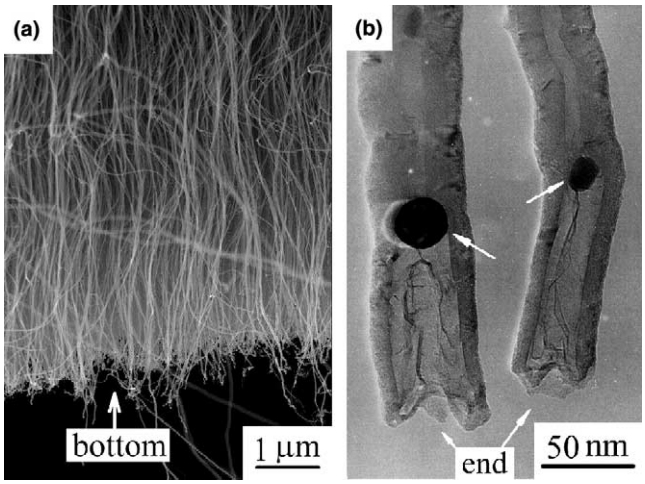

Fig. 2. (a) SEM image of the roots of aligned CNTs, showing that the dense-aligned CNTs become straight only in few microns from the bottom of the array. (b) TEM image of the roots of two nanotubes, showing that the hollows of the roots are like horns with Fe catalyst particles sitting at their tops (indicated by two arrows).

the method of top growth mechanism. With the growth of CNTs, the Fe catalyst particles detach from quartz substrate, and rise at the tips of the growing nanotubes. Finally, these particles are encircled by carbon layers, and kept in the cavities of CNTs. However, the CNTs have not stopped growing with the stop of Fe catalyst particles. With the continuous giving of Fe catalyst and carbon source, CNTs grow into a few millimeter long CNTs. From Fig. 2b we can also see that the initial parts of nanotubes are not very straight, and not with uniform inner and outer diameters. The reason may be that the nanotubes are at the nucleation stage from disorder to order. The competitive growth among them may result in the same growth direction and uniform inner and outer diameters.

Further TEM examinations reveal that there are large numbers of long column-like Fe catalyst particles in the cavities of CNTs (Fig. 3a, indicated by arrows). The length of them is usually more than 100 nm. The number of them is much larger than that in our previous experiments [9,18,19]. This might be due to the higher temperature at preheating stage (300 °C, 125 °C higher than that in [17]), the higher feed rate of solution (0.4 ml/min, 0.32–0.38 ml/min higher than that in [17]), and the continuous feeding method of solution (by a precision flux pump, an injector in [17–19]). The higher temperature is favorable to the decomposition of ferrocene to Fe catalyst particles (the decomposition temperature of ferrocene $\sim$190 °C). The higher feed rate provides abundant Fe catalyst particles and carbon source. The continuous feeding method secures the continuous providing of Fe catalyst particles and carbon source during the continuous growth process of aligned CNTs. These trapped particles may maintain a rapid continuous growth of CNTs. The distance between two adjacent particles is usually less than 1 μm, so the growth time between two adjacent particles is less than 1 s. This may be favorable to maintain the high catalytic activity of Fe particles. Fig. 3b is a high-magnification TEM image of a tip in Fig. 3a. The wall of CNT has not formed completely, and some layers of graphite are precipitating from Fe catalyst particle (indicated by two arrows). This conforms that CNTs grow in the method of top growth mechanism when there are Fe catalyst particles at the tips of nanotubes. From Fig. 3b we can also see that the shape of catalyst particle is an approximate column, not a sphere. The reason may be that the wall of nanotube produces large pressure to the catalyst particle when the layers of graphite precipitate from it. Consequently, the Fe catalyst particle is deformed from a sphere to a

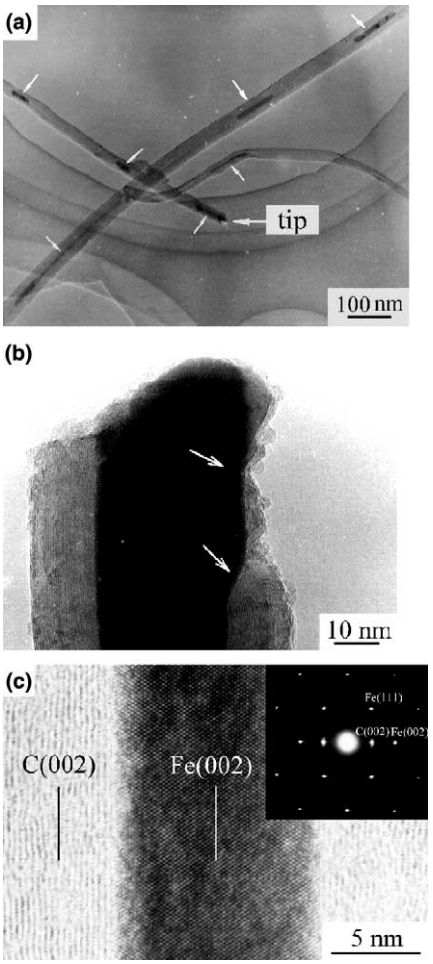

Fig. 3. (a) TEM image of the as-grown CNTs, showing that there are many long column-like catalyst particles in their cavities (indicated by arrows). (b) High-magnification TEM image of a nanotube tip in (a) with a column-like catalyst particle at it, showing that the wall of carbon nanotube has not formed completely, and some layers of graphite are precipitating from the particle (indicated by two arrows). (c) High-resolution TEM image of a Fe catalyst particle encapsulated in a CNT and the corresponding electron diffraction pattern (top right inset), showing that the catalyst particle is a γ-Fe single crystal and the (0 0 2) lattice planes of Fe are parallel to the tube axis.

column with the same diameter as inner cavity of nanotube. This pressure may induce large force of friction between the particle and the wall of nanotube. So the particle stops rising when its long section is circled by the wall of nanotube. Fig. 3c is a high-resolution TEM image of a Fe catalyst particle encapsulated in a CNT and the corresponding electron diffraction pattern (top right inset). The indexed diffraction pattern and the spacing of the planes correspond to γ-Fe single crystal. In most cases the (0 0 2) lattice planes of Fe are parallel or nearly parallel to the tube axis, and the (1 1 1) lattice planes have an angle with the tube axis. This kind of configuration may be favorable to the rapid growth of CNTs.

When the catalyst particle is rising at the tip of nanotube during its growth process, there might be a second and more Fe catalyst particles falling on it. So the long column-like particles in the cavities of CNTs could extend much longer, even more than 600 nm long (Fig. 4a), leading to a formation of very straight and rigid CNTs. Thereby, the CNTs could grow in the same direction, maintain good alignment, and keep high growth speed even after they have reached a millimeter order long. Fig. 4b is a high-magnification TEM image of a nanotube tip in Fig. 4a, showing that there is a hollow (about 30 nm long) above the catalyst particle in the tip. This reveals that the nanotube could grow even without a catalyst particle on the tip. Because the catalyst particle is circled with nanotube wall, the carbon source for the further growth of nanotube must not come from the precipitation of Fe catalyst particles in the tip, but from the direct deposition of carbon cluster (C_n) on the open tip. Fig. 4c is a high-magnification TEM image of a tip with a Fe catalyst particle just falling on it (indicated by a black arrow). The distance between this particle and the adjacent particle (indicated by a white arrow) is very short (about 20 nm). However, the distance between two adjacent particles in a nanotube body is usually more than 200 nm (Figs. 3a, 4a). We conclude that nanotubes grow slowly without catalyst particles on the tips, but grow very fast with catalyst particles on the tips.

The large amounts of Fe catalyst particles trapped in the cavities of CNTs must be an important reason for rapid growth of nanotube arrays. We proposed a continuous rapid growth model shown in Fig. 5. We suggest that CNTs could grow with their tips open during their growth process (Fig. 5a). If the tips are closed, CNTs could

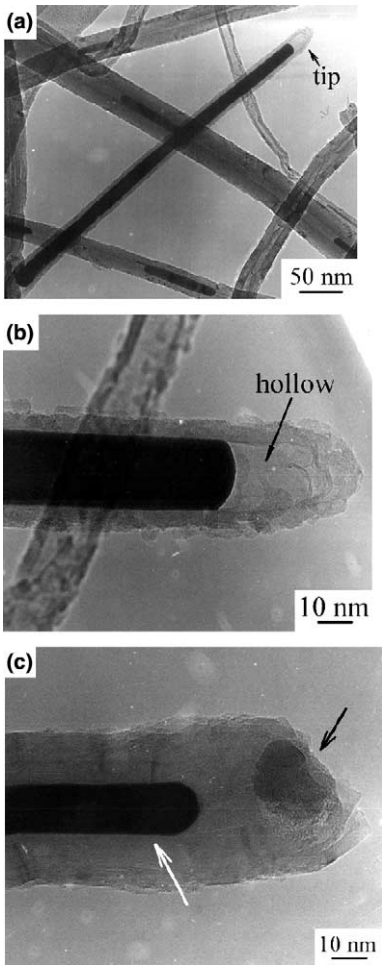

Fig. 4. (a) TEM image of aligned CNTs, showing that the long column-like catalyst particle in their cavities can reach 650 nm long. (b) High-magnification TEM image of a nanotube tip in (a), showing that there is a hollow (about 30 nm long) above the catalyst particle in the tip. (c) High-magnification TEM image of a tip with a catalyst particle just falls on it (indicated by a black arrow). The distance between this particle and the adjacent particle (indicated by a white arrow) is about 20 nm.

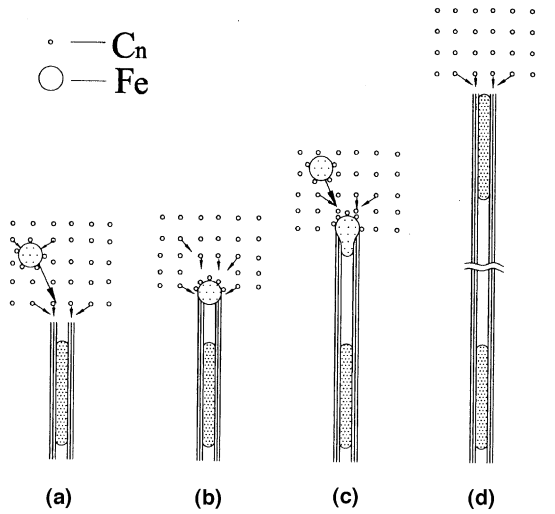

Fig. 5. Proposed continuous rapid growth model of aligned CNTs. (a) Slow growth state. The tip of nanotube is open. (b) Start of the rapid growth stage. A Fe catalyst particle just falls on the tip. (c) Rapid growth state. The particle is deformed due to the squeeze of the tip, and a new particle may fall on it. (d) End of the rapid growth stage (that is, the start of the slow growth stage). The particle stop rising and is circled by the wall of nanotube.

not grow a millimeter order long under our experimental conditions. The higher hydrogen flux (400 sccm, no more than 200 sccm in [17–19]) may be favorable in keeping the tips open. Only a small number of carbon clusters (C_n) deposit directly on the open tip and transform into graphite layers. Most of the C_n pass above the arrays of CNTs. Once a Fe catalyst particle falls on the tip, the nanotube begin to grow rapidly (Fig. 5b). At the rapid growth state of nanotube (Fig. 5c), the Fe catalyst particle has high catalytic activity, and more C_n are transformed into the graphite layers of nanotube. During the rapid growth stage (b → c → d), the Fe particle is deformed due to the squeeze of the nanotube tip. Finally the particle stops rising and is circled by the nanotube wall (Fig. 5d). The reason may be that the Fe catalyst particle loses its catalytic activity, and/or the adherence strength between the particle and the wall is higher than the push force of the nanotube tip. The nanotube grows very slowly with its tip open (d → a → b). Until one new Fe catalyst particle falls on the open tip, a new circulation starts. Therefore, the existence of the large number of Fe catalyst particles shortens the slow growth stage of nanotube, and makes it at the rapid growth state during their growth process.

It should be pointed out that the growth rate is not linear, which decreases with the increase of growth time. The length of aligned CNTs with the growth time of 240 min is about 6 mm, so the average rate is about 25 μm/min. While the

average growth rate might be higher than 50 μm/min with a short growth time. In addition, the diameter of the aligned CNTs increases slightly with the increase of growth time.

4. Conclusion

In conclusion, we obtained arrays of well-aligned CNTs in large areas by common CVD method. The nanotubes grow at a high average rate of ~ 50 μm/min, and can reach 1.5 mm in 30 min. The reason may be related with the large number of long column-like Fe catalyst particles in the cavities of CNTs. A continuous rapid growth model is suggested to explain the high growth rate under our experimental conditions. This provides a simple way to synthesize rapidly macroscopic aligned CNT arrays, thus will be helpful for their successful commercial applications.

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