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Growth Mechanism of Oriented Long Single Walled Carbon Nanotubes Using "Fast-Heating" Chemical Vapor Deposition Process

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ABSTRACT

The growth mechanism of long and aligned single walled carbon nanotubes using a recently reported "fast heating" chemical vapor deposition (CVD) method is discussed. The effect of heating speed at the initial stage of the CVD process has been systematically studied, and a "kite-mechanism" for the nanotube growth is proposed. The understanding of the growth mechanism would enable us to design future experiments to obtain better control of the morphology of the produced nanotubes.

The growth of long (mm to cm scale) individual single walled carbon nanotubes (SWNTs) with controlled orientations using the "fast-heating" chemical vapor deposition (CVD) method[1,2] will have important impacts for future applications in both nanoelectronics and high strength composite materials. The results not only demonstrated the control of orientations of individual nanotubes on a substrate simply using the flow of the feeding gas, they also showed that nanotubes could be grown into macroscopic length under appropriate conditions. For applications in nanoelectronics, the capability to control the locations and orientations of individual nanotubes is a requirement for large-scale fabrications of devices, while for high strength composite materials, the long length of each individual nanotube would improve the load transfer between the nanotubes and the matrices. However, in previous reports,[1,2] the origin of the alignment and long length was not clearly identified. Obtaining insights into the growth mechanism of such long nanotubes is of both scientific and technical importance for designing future experiments to achieve better control of the nanotube growth. Compared with conventional chemical vapor deposition methods that produce shorter and randomly oriented nanotubes,[3−7] the feeding gas, catalysts and many other experimental conditions in "fast-heating" CVD are similar. The only major difference between these two methods is the heating speed of the sample at the initial stage of the growth process. In this article, we demonstrate how the heating speed difference can alter the growth mechanism of the nanotubes. A new "kite-mechanism" is proposed to explain the growth of these long nanotubes. Additionally, we demonstrate that "fast-heating" effect is not limited to the CO CVD method as previously reported. Long and oriented nanotubes can be grown from several feeding gases and catalysts.

In our previous reports,[1,2] we have described the use of Fe/Mo nanoparticles as catalysts and a mixture of CO and H_2 as feeding gas to grow long and oriented SWNTs. Subsequent experiments have shown that the choices of catalysts and feeding gas are more flexible. Similar results were obtained using four different catalysts (Fe/Mo nanoparticles, Fe nanoparticles, Fe/Pt nanoparticles, and molecular clusters containing Fe and Mo)[8] and three kinds of feeding gases (CO, hydrocarbons, and alcohols) (Figure 1). All experiments were performed on oxidized Si wafers with the catalysts patterned on the surface using photolithography or by simple deposition (Supporting Information). The key step in the growth of these long SWNTs was the step of "fast-heating" when the Si wafer with the catalyst was transferred into the center of the heated furnace. This step is usually carried out by either transferring the whole quartz tube containing the sample or by moving the furnace in the opposite direction so that the sample is relocated at the center of the heating zone. The samples were characterized by scanning electron microscope (SEM), atomic force microscope (AFM), and transmission electron microscope (TEM). SEM images were recorded by the SEM (XL-30 FEG from Philips) at 1 or 30 kV. AFM images were taken with a

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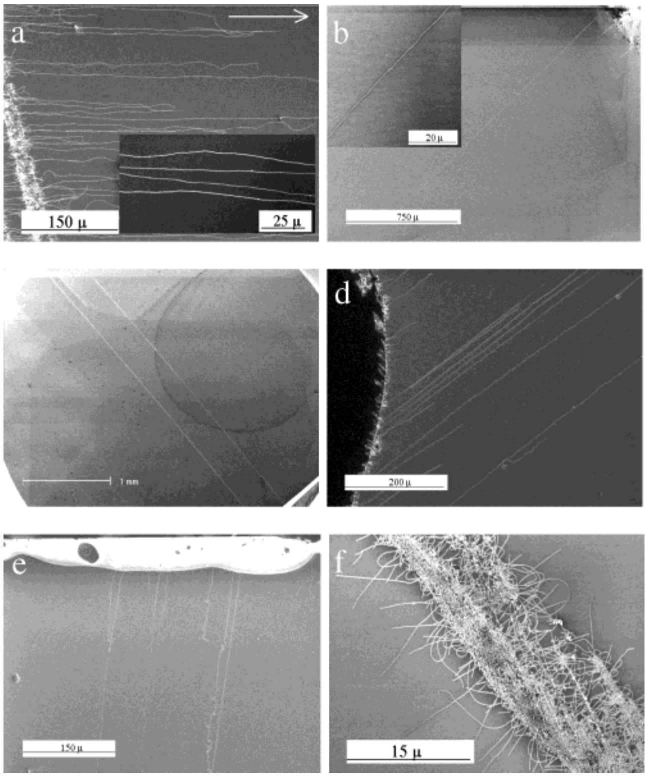

Figure 1. SEM images of SWNTs on surface. (a) Oriented long SWNT arrays from "fast-heating" growth process. Catalyst: Fe/Mo nanoparticles; CO/H_2 900 °C, 10 min. Inset is the enlarged image. (b) A 2.1 mm individual straight SWNT. Catalyst: Fe/Mo nanoparticles; CH_4/H_2 900 °C, 10 min. (c) Individual parallel straight SWNTs having 3.9 mm in length. Catalysts: Fe/Pt nanoparticles; CO/H_2 900 °C, 20 min. (d) SWNT arrays. Catalysts: identical Fe/Mo molecular cluster, CO/H_2 900 °C, 10 min. (e) Long SWNTs. Catalysts: Fe/Mo nanoparticles; CH_3OH/H_2/Ar, 900 °C, 20 min. (f) Random short SWNTs from conventional growth process using Fe/Mo nanoparticles as catalysts and CO/H_2 as feeding gas at 900 °C for 10 min.

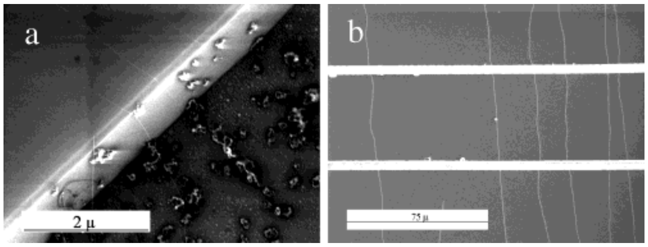

Figure 2. (a) SEM image showing that the nanotubes started growing from the catalyst in the trench and grow over a barrier 800 nm high; (b) SEM image of nanotube arrays cross over the trench.

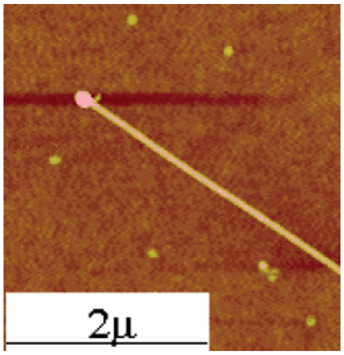

Figure 3. AFM image of the oriented long nanotubes with particle on the tip.

Nanoscope IIIA system (Vecco Inc. CA) in tapping mode. TEM image was taken by a Philips TEM.

Comparing the SWNTs obtained using "fast heating" CVD process (Figure 1a–e) with those from conventional CVD processes (Figure 1f), it is obvious that as-grown SWNTs by conventional process are shorter (normally shorter than several tens of microns) and randomly oriented, while the SWNTs grown using the "fast-heating" process are several hundreds microns to millimeters long and well oriented along the direction of the gas flow. As we demonstrated in our previous reports, the average diameter of the nanotubes is 1.25 nm from Raman measurements.[2] The length of the nanotubes can be as long as 1.5 cm obtained from a 20 min growth using methane as feeding gas (see Supporting Information for SEM image of a 1.1 cm long nanotube array). To understand the growth mechanism of these long and oriented nanotubes, we need to understand what kind of effect was caused by the fast-heating step.

For nanotube growth in the CVD process, two main mechanisms were proposed previously, with the "tip-growth" mechanism well demonstrated for certain multiwalled carbon nanotubes (MWNTs)[9−12] and "base-growth" for both MWNTs and SWNTs.[6] Previous reports have demonstrated that the "base-growth" mechanism is most likely the mechanism for SWNTs grown in the conventional CVD process.[6] In the "fast heating" CVD process, the experimental results have shown that the orientation of the nanotubes is determined by the direction of the gas flow, which implies that the nanotubes have to be floating in the gas flow during growth rather than growing on the surface of the substrates and sliding along the direction of growth. Figure 2 shows SEM images of nanotubes grown over a barrier on the substrate and across trenches. The catalysts were deposited in the trench with a depth of 800 nm fabricated on a Si wafer. Several nanotubes shown in the figure were observed to grow over the barrier with a height of 800 nm. If nanotubes grew along the surface, they would be stopped by the vertical barrier on the surface. Additionally, the nanotubes have to be floating to grow across a trench as shown in Figure 2b. These results demonstrated that at the initial stage of the growth, the nanotubes grew up from the surface. Additionally, the results also suggested that the "base-growth" mechanism may not be appropriate for the growth of these long nanotubes since the entire nanotube, up to a centimeter long, has to be floating in order to remain relatively straight. Based on such a hypothesis, these nanotubes should be grown by a "tip-growth" mechanism with the active catalysts on the tips of the growing nanotubes. Direct evidence for the "tip-growth" mechanism under fast heating conditions also came from the AFM observations. It was found that every tip of the long nanotubes had a nanoparticle as indicated in Figure 3. The size of the particles on the tip of the nanotubes was normally larger than the nanotube diameter. We believe this is due to the amorphous carbon formation around the catalyst during the cooling process.

Taking these experimental observations into account, we have proposed a "kite-mechanism" with the catalyst nanoparticle having a long nanotube tail floating in the gas flow. The kite-mechanism contains several important stages. The most important stage is the initial stage of the growth. In "fast-heating" CVD, the samples were heated to reaction temperature (900 °C for most cases) over a very short period. As the result of fast heating, the solid sample and the surrounding gas were heated at different speeds and had different temperatures during the heating. A convection flow was formed due to such temperature difference. Such a convection flow could lift some of the nanotubes up with the catalysts on their tips. The nanotubes grew up, leaving the surface region where the flow velocity of the feeding gas was slow. Then the horizontal laminar flow of the feeding gas above the substrate surface carried the nanotubes while they were growing and aligned the nanotubes along the direction of gas flow. During growth, the active ends of the nanotubes were always floating while the sections close to the original sites where the catalyst was deposited might form van der Waals contacts with the substrate. The nanotubes kept growing until they lay down onto the surface or until termination of the carbon source.

This kite-mechanism can satisfactorily explain the growth of long and oriented nanotubes. It provides reasonable explanations to the observed length of the nanotubes, their morphology, and their yield. The difference in lengths between nanotubes grown using different CVD processes can be explained by taking into account of the difference between "tip-growth" and "base-growth" mechanisms. In the base-growth mechanism, the catalysts stay on the substrate throughout the growth process. Two possible reasons limited the growth of nanotubes. One is the termination of nanotube growth because of the strong van der Waals interaction between the nanotubes and the substrate surface when the nanotubes reach certain length. For the base growth mechanism, since the whole nanotube needs to slide on the surface, once they rest on the surface, the nanotube/substrate interaction would increase as a function of the length. The growth would eventually stop when the force needed to move the whole nanotube becomes energetically unfavorable. For the tip-growth mechanism, this would not present a problem since the catalysts were on the tip of the nanotubes. The other reason for the length difference between the two growth methods may be the diffusion of the feeding gas to the surface of the catalysts. The flow rate of feeding gas on the substrate surface is much lower than above the surface.

If the proposed mechanism is correct, the key requirement to grow long and aligned SWNTs is to make the nanotubes grow away from the substrate surface at the nucleation stage. Since it was reported previously that electric field can be used to align nanotubes on the surface along the direction of the electric field,[13,14] we could envision that the application of a vertical electric field would make more nanotubes grow vertically, thus more long and aligned nanotubes can be grown even without the fast-heating step. Preliminary results described in the attached Supporting Information clearly show that such a hypothesis is correct. We did observe the growth of aligned nanotubes along the direction of the gas flow using an applied vertical electric field rather than the fast heating CVD method. Such an observation further proved the validity of the proposed mechanism.

In conclusion, we have demonstrated that the fast-heating process is a general method to grow long and oriented SWNTs on surface. We have also proven that the growth of long SWNTs by the fast-heating process is through a tip-growth mechanism rather than the previously demonstrated base-growth mechanism for SWNT growth. Although both growth mechanisms coexist in our experiments, only the tip-growth mechanism produces long and oriented nanotubes. The key steep in the proposed mechanism is that nanotubes grew up at the initial stage of the growth. Once the nanotube grew up into a fast-flow region above the surface, they were caught by the wind of the flowing gas, resulting in the alignment and continuous growth. The growth rate for nanotube in a CO/H_2 system could be as high as 3 μ/s and 20 μ/s in a CH_4/H_2 system. The growth efficiency of the long nanotube is still very low. The challenge for future research is to improve the growth efficiency and precisely control the location and orientation of these long nanotubes. Such a capability will have a tremendous impact for the future of nanotube-based electronics, providing a possibility to fabricate a large amount of nanotube devices in a parallel fashion. Additionally, the results have demonstrated that the growth rate of nanotubes can be very high under the right growth conditions. With better understanding of the growth mechanism and higher growth efficiency, long nanotubes would be available for many other applications, including high strength composite materials.

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Supporting Information Available: Detailed experimental procedure, SEM image of 1.1 cm long nanotubes, and the growth of horizontally aligned nanotubes under vertical electric field without "fast-heating" CVD. These materials are available free of charge via the Internet at http://pubs.acs.org.

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