Communication

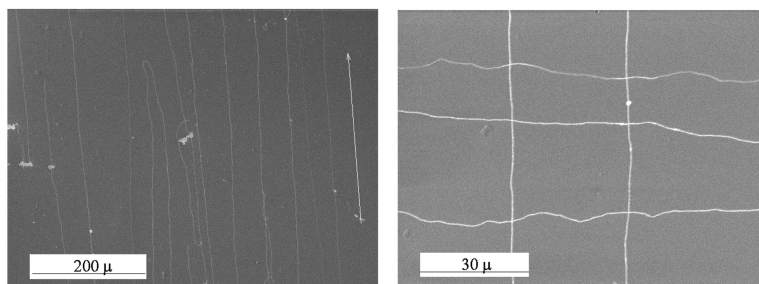# Growth of Millimeter-Long and Horizontally Aligned Single-Walled Carbon Nanotubes on Flat Substrates

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Growth of Millimeter-Long and Horizontally Aligned Single-Walled Carbon Nanotubes on Flat Substrates

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Single-walled carbon nanotubes (SWNTs) have attracted much attention due to their unique structural, mechanical, and electrical properties.[1] They are generally considered as promising building blocks for nanoscale electronics. Several nanoelectronic devices based on individual SWNTs such as quantum wires,[2] field-effect transistors,[3] logic gates,[4] field emitters,[5] diodes,[6] and inverters,[7] etc., have been demonstrated. Other applications such as sensors[8] and scanning microscope probes[9] were also reported in the literature. These devices were generally prepared by either depositing a suspension of purified bulk nanotube samples on substrates or using individual nanotubes directly grown on substrates using the chemical vapor deposition (CVD) method. The CVD method has great advantages in terms of low temperature, large-scale production, and controllability. Many efforts have been made to grow SWNTs on surface by using isolated catalytic nanoparticles or identical clusters.[10] However, there still exist some major obstacles for the development of nanotube-based nanoelectronics. One of them is the control of location and orientation for large array of SWNTs on substrates, which is required for the development of a reliable and scalable process for making a large number of devices. Over the last year, some progress has been made in controlling the orientation of nanotubes. For example, Dai et al. reported electric field-induced orientated growth of suspended SWNTs or SWNTs on flat surfaces.[11] Vectorial growth of SWNT arrays on a surface by an electric field based on the CVD of ethylene was also reported recently.[12] However, the introduction of a strong electric field during growth of nanotubes is not an easy task. Furthermore, organizing SWNTs arrays into multidimensional crossed-network structures in a controllable manner was not demonstrated. In our experiments, we have directly grown millimeter-long, well-aligned SWNTs in large areas on flat substrate using monodispersed Fe/Mo nanoparticles as catalysts and CO as feeding gas. The lengths of the SWNTs can be more than 2 mm. The orientation of nanotubes is directly controlled by the direction of gas flow in the CVD system. More importantly, we can easily fabricate 2D nanotube networks with controlled geometry. These results present a breakthrough in controlling the orientation of the produced SWNTs and will have a great impact on the production of organized SWNT arrays for large-scale carbon nanotube-based nanodevice fabrication.

The growth of SWNTs was carried out by CO-CVD in a two-furnace system described previously.[10a] The feeding gas was a CO/H_2 mixture, and the catalysts were monodispersed Fe/Mo nanoparticles dispersed or patterned on SiO_2/Si wafers using photolithography (see Supporting Information). All samples described in this report were grown at 900 °C for 10 min. The monodispersed Fe/Mo nanoparticles were synthesized by thermal decomposition of $Fe(CO)_5$/$Mo(CO)_6$ under the protection of surfactant according to the reference.[13] A silicon wafer with 600 nm thick silica on top was used as substrate. Catalysts were either directly deposited on the substrate from their hexane solution or patterned by the photolithographic technique. Normally, only short and randomly
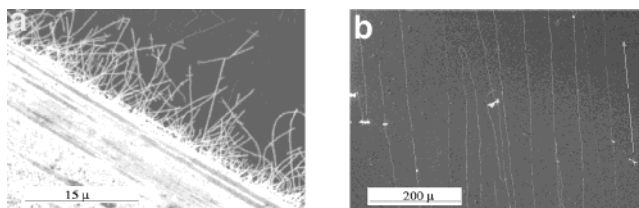

Figure 1. SEM image of SWNTs prepared using (a) normal heating and (b) fast heating processes.
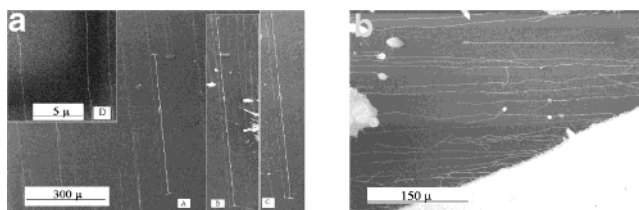

Figure 2. (a) SEM image of a >2 mm long nanotube (sections A, B, and C show the same nanotube highlighted with a white line) and (b) SWNTs along controlled angle with respect to the edge of the catalyst island. Inset: Higher magnification SEM images of aligned SWNTs.

orientated SWNTs were observed on substrate surfaces (Figure 1a) if the samples were heated slowly from room temperature. These nanotubes are normally less than 20 μm long with occasionally longer SWNTs of several tens micrometers and have been shown to be SWNTs.[10a] However, when the substrate with the catalysts was heated using a quick heating process (see Supporting Information) in CO/H_2 flow to the desired reaction temperature (900 °C), ultralong and well-aligned SWNTs arrays were produced. Figure 1b is the typical SEM image of the as-grown SWNT arrays on the surface. Under these magnification and imaging conditions, nanotubes were shown as bright lines under SEM. The inset in Figure 2a shows a high magnification image of the aligned nanotubes. In addition, AFM measurements (see Supporting Information) have shown that the heights of the nanotubes were between 1 and 2.5 nm, in good agreement with previous results of SWNT growth under similar growth conditions.[10a] As shown in Figures 1b and 2, the majority of the SWNTs grew along one direction, which was later determined as the direction of the gas flow. These nanotubes normally have one of their ends embedded within the island of catalysts and the other (free ends) extended several hundreds of micrometers to a few millimeters along the growth direction. Occasionally, we observed a few ultralong nanotubes having a U-turn structure (Figure 1b) with both of their ends embedded within the catalyst islands, which may be caused by the pinning of the free ends within the catalyst islands due to local turbulent flow during the early stage of growth when the nanotube was still short. The continuing growth of the tube with both of its ends pinned

into the catalyst island produced the U-shaped nanotubes as seen in the figure. Most of the as-grown SWNTs are relatively straight and have the lengths of several hundreds micrometers after 10 min of growth (Figure 1b). The longest one we have observed is longer than 2 mm (Figure 2a). The growth rate is estimated to be more than 200 μm/min. Such long nanotubes make the evaporation of multiple metal electrodes on a single nanotube a relatively easy task. Thus, multiple devices can be created on the same nanotube along its length. This added processibility is desirable for large-scale device fabrications.

Recently, electric field was employed to control the growth directions of suspended SWNTs or nanotubes on a surface.[11] The alignment effect is believed to originate from the high polarizability of SWNTs. It was also reported that heating silicon carbide at 1500 °C under high vacuum produced a SWNT network with preferential orientation.[14] In our case, no external field was applied. The orientation force of the long SWNT arrays is from the gas flow because we have found the alignment direction is always along the direction of gas flow. To further prove this, we have used the edge of the catalyst island as a reference. The wafer was placed in the furnace with a predetermined angle between the island edge and the gas flow direction. As shown in Figure 2b, SEM observation clearly showed that the nanotube arrays were along the same direction of the gas flow and had the same angle with the catalyst island edge.

Comparing the nanotubes in Figure 1a and 1b, we found that the major differences are the lengths and orientations of the nanotubes. The lengths, as well as the growth rates, of nanotubes are 100 times different. What causes such huge differences in the SWNTs growth? We have noted that the main difference between the two procedures is the heating process. Clearly, the fast heating is favored for the growth of long and well-aligned nanotubes. From Figure 1a, we have noticed that most of the nanotubes are shorter than 20 μm and the aligned nanotubes in Figure 1b are much longer. We speculate that the length of the nanotubes plays a very important role in their alignment. We believe that the extremely quick growth (more than 3.3 μm/s) at the initial stage is the key factor for the length and alignment of the nanotubes. Such a high growth rate ensures that the nanotubes are "sliding" along the substrate without strong interaction with the underlying substrate. On the other hand, when the growth rate is slow, not only are the nanotubes shorter, but they also have more tendency to maximize their interaction with the substrate, making it harder for the nanotubes to align along the gas flow. Clearly, more experimental and theoretical works are needed (and are underway in our group) for a better understanding of the mechanism. Nevertheless, the capability to grow long and well-aligned nanotubes with controlled orientations represents a major step in controlling the arrangements of the nanotubes and has solved one of the main obstacles for the fabrication of nanotube devices.

More importantly, such a capability also enables us to grow more complicated two-dimensional nanotube frameworks on substrates that cannot be produced otherwise. Assembling SWNTs and other nanowires into multiterminal devices and complex circuits is an important and difficult challenge for many applications.[3,4] Some progress has been made to self-assemble nanowires into functional networks.[15] Yet less success for SWNT has been reported,[16] and no report of the direct growth of multidimensional nanotube networks exists. Our successful growth of long isolated nanotubes on a surface with controllable direction and location makes it possible to fabricate such multidimensional and multilayer crossed-
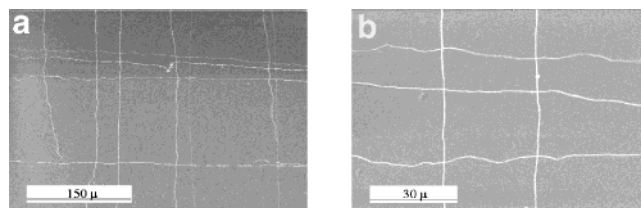

Figure 3. SEM images of directly grown 2D network of SWNTs.

networks (see methods for details). As shown in Figure 3a, we have fabricated well-defined crossed-network structures of SWNTs on a large scale by a two-step growth process. Figure 3b is a higher magnification image of a smaller area. These images showed that we could easily fabricate crossed nanotubes by orientating the Si wafers along different directions during the two growth steps. Basically, two-dimensional crossed-networks with any angle can be easily fabricated using such a process.

In summary, we have presented a simple method to produce millimeter-long, isolated, and well-orientated SWNT arrays on a large scale on a flat surface without the use of any external force like electric and magnetic fields. The length of the nanotubes can be a few millimeters. Their orientations can be easily controlled by changing the orientations of the substrates with respect to the gas flow directions. Two-dimensional crossed-networks of nanotubes can be fabricated using a two-step process. These results have shown that we have gained much more control, including the control of orientations and locations, in the synthesis of SWNTs.

Supporting Information Available: Detailed experimental procedure and AFM characterization of the samples (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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