Growing 20 cm Long DWNTs/TWNTs at a Rapid Growth Rate of 80–90 μm/s

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Carbon nanotubes (CNTs) of centimeters long1,2 are important because they would allow easy fabrication of multiple FET devices using an individual tube3,4 and they offer the potential for direct dry-spinning a super high strength fiber with the longer tubes available.5,6 To date, the only effective method to prepare these materials is gas-flow-directed chemical vapor deposition (CVD) on a Si substrate. In this method, catalyst particles catalyze the decomposition of the carbon source to provide carbon flow-directed chemical vapor deposition (CVD) on a Si substrate. In this method, catalyst particles catalyze the decomposition of the carbon source to provide carbon atoms and the gas flow provide the buoyancy for suspended tubes to grow without resistance. This method has shown growth rates of 10–24 μm/s (with a reported rate reached 50 μm/s).7,8,9 The longest CNT reported was 18.5 cm for single-walled CNTs (SWNTs)9 and 10 cm for triple-walled CNTs (TWNTs).9 Despite all the efforts, it is still difficult to get long CNTs with a high efficiency and at low cost. This is due to the narrow condition window and long time for the growth, and the serious depending on the use of

Figure 1. (a) Optical picture of the 20 cm long Si substrate. (b) Optical picture of the substrate connected by Si (dark substrates) and SiO2 (white substrates) substrates. (c, d) TEM pictures of DWNT and TWNT. (e) Raman spectra of DWNT.

Si substrate. In this work, we proposed gas-flow-directed CH4–H2O CVD to increase the growth efficiency of centimeters long CNTs. Water served to maintain the catalyst activity. With an optimized concentration of water feed and manner of water addition, the average growth rate of 10–20 cm CNTs was increased from 20 to 80–90 μm/s. Raman characterization showed the long tubes had a nearly perfect structure. In addition, it was shown that these long tubes could be grown without the use of long Si substrates. Instead, many short Si and SiO2 substrates put together in line could be used. Thus, our results showed a highly efficient and cheap method for the large scale up preparation of centimeters-long CNTs.

The growth of the 20 cm long CNTs was carried out in a horizontal quartz tube reactor using the CH4–H2O CVD method. Twenty cm long substrate was obtained by connecting two 10 cm long Si substrates (each with a 700 nm thick SiO2 layer on the surface, Figure 1a) or connecting many short Si and SiO2 substrates in sequence (Figure 1b). Iron catalyst was prepared by first spouting FeCl3 solution (0.03 mol FeCl3 in 1 L ethanol) onto the left edge of Si substrate, evaporation of the ethanol, and then the reduction under H2 for 10 min at 900 °C. For the growth of CNTs, gas reactants of 20–30 sccm CH4, 40–80 sccm H2, and 0.02–1.2 vol. % H2O in small amounts (obtained by bubbling H2 through a water container) were fed into the reactor at 1000 °C for 10–40 min. The obtained long CNTs on the Si substrate were directly observed by SEM (JSM7401F, 1 kV). The detailed CNT structure was determined by TEM (JEOL 2010, 120 kV) by a transfer method reported elsewhere.9

Images a and b in Figure 1 showed the substrates after the growth of very long CNTs (the 20 cm long CNTs grown on them are shown in Figure 2). It is observed that CNTs can grow across the slot between two Si substrates or the slots between Si and SiO2 substrates, which is
SEM pictures of long CNTs grown on Si substrates with water (left) and without water (right). The white lines in the left column are CNTs. The white areas in the right column are amorphous carbon, which is shown in g.

0.05–0.1 mm wide. The density and straightness of the long tubes on the SiO2 substrate were similar to those on the Si substrate (see the Supporting Information, SI-3). When considering that the SiO2 substrate was far from flat and clean compared to the Si substrate, this result suggested that the Si substrate can be used only for the catalyst part for the initial growth period, and other parts of the long substrate can be replaced by less expensive SiO2 substrate. Our result confirmed the kite growth mechanism, where most of the CNTs were floating in the gas flow and only sink down onto the substrate when the gas flow was stopped.12 Thus, the further growth of super long tubes longer than Si substrate size become possible and at low cost.

High-resolution TEM revealed that the centimeters long CNTs (longer than 3 cm) were mostly TWNTs (diameter from about 3 to 5 nm and selectivity >90%) in the reaction without adding water,9 and were mixture of 49% double-walled CNTs (DWNTs) (outer diameter of 2.5–3.3 nm) and 11% SWNTs (outer diameter of 2.4–3.3 nm) when water was added (Figure 1c,d). It is obvious that water addition changed the state of the reduced Fe nanoparticles and made their size smaller, in agreement with previous reports.13–15 TEM also indicated that most CNTs longer than 3 cm existed as individual tubes and did not form bundles.

Raman spectra of a DWNT growing across the trenches (cut by laser on the Si substrate, about 100 μm wide, inner picture in Figure 1e), characterized by a Horiba JY instrument (excited at 633 nm), showed no D band but rather a very strong G band in Figure 1e. The G band included a strong peak at 1568 cm⁻¹ and a relative weak peak at 1580 cm⁻¹. Since the CNT section subjected to Raman spectroscopic analysis was not in contact with the Si substrate, the Raman response in the present work reflected the nature of the CNT structure. This result indicated that the long tubes with nearly perfect structure would be ideal for the fabrication of quantum conductive devices.

To understand the details of the long CNTs grown without or with the addition of water, we compared the growth on a relatively macroscopic scale (Figure 2). Usually, long tubes were grown from a mass of short CNTs near the catalyst source, which is a growth mode similar to many previous reports.10,16 However, water addition caused some differences in the CNT growth. Both the Si substrate and area around CNTs are very clean (left column in Figure 2), although amorphous carbon was found in large amounts adhering to the outer wall of tubes (right column in Figure 2) when no water was added. This was a sharp contrast between the two types of reaction conditions, especially when the growth time was long (more than 1 h). Clearly, water was effective in removing or inhibiting the formation of amorphous carbon from the thermal decomposition of CH4 and provided a good condition for growing long CNTs. Second, the amorphous carbon around the catalyst particles from the thermal decomposition of CH4 was effectively removed by water. This was similar to the effect in other CNT synthesis processes with the addition of oxygen gases.17,18 The result of addition of water was that the amount of active catalyst seeds that could grow long tubes was significantly increased, and these CNTs were grown with a high density. The average parallel distance between grown tubes was decreased from 500 to 100 μm with the addition of water. Thus, the yield of 10–20 cm tubes with the addition of water was 3–5 times that without the addition of water.

The measurement of CNT length was taken under SEM, where the horizontally CNTs are in white lines, since there is obvious color contrast between the substrate and CNTs excited by electron beam (Figure 2). The average growth rate of several longest tubes on a substrate were calculated after a definite reaction time. From the measurement of 150 CNT samples on 50 Si substrates grown for different times and water concentrations, the average growth rate of several longest tubes on a substrate were calculated after a definite reaction time. From the measurement of 150 CNT samples on 50 Si substrates grown for different times and water concentrations,
we determined the condition that would give the highest growth rate of the long tubes. The quantitative measurement of the growth rate of the long tubes showed that the growth rate depended on the water content. In the experiment with the cofeeding of water and \( \text{CH}_4 \), the growth rate of the long CNTs increased from 16 to \( > 80 \) \( \mu \text{m/s} \) as the water content was increased from 0 to 0.43%. However, a further increase of the water content from 0.43 to 1.2% resulted in the gradual decrease of the growth rate, which finally approached to that of CNT growth without the addition of water (Figure 3a). Thus, a low content of water was ineffective in removing all amorphous carbon around the catalyst particles; excess water would not only remove amorphous carbon but also remove other kinds of carbon, which would decrease the carbon supply for CNT growth and cause a slowdown of the growth rate of CNTs. In the experiment, each growth condition was repeated several times and the tube length was measured at least 6 times for different growth times (such as 8, 10, and 20 min for the blue dots in Figure 3b) to get reliable calculation of the CNT growth rates. The data suggested that the growth rate of 1–10 cm long CNTs was faster than 90 \( \mu \text{m/s} \) and the average growth rate for 20 cm long tubes was about 80–90 \( \mu \text{m/s} \). This result also suggested that there was slightly lower catalyst activity in the final growth period, but the difference was not much. In general, the \( \text{V}−\text{L}−\text{S} \) growth model\(^\text{19} \) indicates that the growth rate of CNTs depends on the metal size and its carbon solubility, and SWNTs often grow faster than DWNTs, TWNTs, or MWNTs. Therefore, our method of using water to achieve a 80–90 \( \mu \text{m/s} \) growth rate for DWNTs/TWNTs is more significant because it was compared to the SWNT growth rate of 50 \( \mu \text{m/s} \) in ref 3 and other centimeter long CNTs (Figure 3b).

To better understand the enhancement effect of water, we also changed the manner of water addition (Figure 3c). The cofeeding of water and methane at the beginning of the reaction was more favorable for increasing the growth rate to 80 \( \mu \text{m/s} \), whereas the delayed addition of water resulted in a gradual decreasing of the growth rate of CNTs (to 20 \( \mu \text{m/s} \) when water was added 2 min after feeding methane). It appeared that the deposition of the undesirable amorphous carbon (disordered structure) occurred simultaneously with the nucleation of the CNT ordered structure on the metal at the beginning of the reaction. In the well-established reaction to produce synthesis-gas from steam reforming of \( \text{CH}_4 \), the breaking of the first C–H bond of \( \text{CH}_4 \) is considered the rate-determination step (slowest step) and water reacts rapidly with the reaction intermediates, like \( \text{CH}_3, \text{CH}_2, \text{CH}, \) and \( \text{C} \), at high temperatures.\(^\text{20} \) A rapid deactivation of the metal catalyst by carbon encapsulation occurs at a low ratio of steam to methane. Using this result, the enhancement effect of water in the present work would be to provide more effective surface areas for the decomposition reaction and not by increasing the reaction rate of breaking the C–H bond of \( \text{CH}_4 \). If it is assumed that the activity of a metal nanoparticle is proportional to its effective surface area not covered by carbon, the result suggested that in the absence of water, amorphous carbon would cover about 75% of the surface area of the initial active metal particles within 2 min. Then, after 2 min, there would be a balance between carbon production on the surface (on the active sites by exposure to the bulk gas phase) of the nanosized metal and carbon precipitation on the other surface side of the metal to form ordered CNTs, considering CNTs can grow steadily, although relatively slowly, to centimeters long without water.\(^\text{9} \) Thus, we propose the qualitative model in Figure 3c to describe the metal catalyst state covered by small and large amounts of amorphous carbon with the different manners of feeding water.

In summary, adding 0.43% water was effective in increasing the growth rate of centimeters long CNTs to 80–90 \( \mu \text{m/s} \). This was five times faster than without the addition of water. The role of water was to remove the amorphous carbon that covered the active metal catalyst in CVD method. The replacement of part of Si substrate by \( \text{SiO}_2 \) substrates would solve the length limitation set by the substrates and also decrease the manufacturing cost of centimeters long DWNTs and TWNTs. A future challenge could be the synthesis of superlong CNTs on cheaper supports such as silicate or nature materials.\(^\text{21,22} \)

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**Supporting Information Available:** Experimental details and suspended CNTs grown across trenches (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.


