ADVANCED MATERIALS

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Sustained Growth of Ultralong Carbon Nanotube Arrays for Fiber Spinning**

By *Qingwen Li*, *Xiefei Zhang*, *Raymond F. DePaula*, *Lianxi Zheng*, *Yonghao Zhao*, *Liliana Stan*, *Terry G. Holesinger*, *Paul N. Arendt*, *Dean E. Peterson*, and *Yuntian T. Zhu**

Carbon nanotubes (CNTs) are the strongest materials ever discovered by mankind. With measured tensile strengths as high as 150 GPa and a high modulus of 1 TPa,[1,2] CNTs are very promising for many high-strength, lightweight applications.[3,4] Several approaches have been reported to process micrometer-long CNTs into fibers, including dispersing CNTs into polymer or acid solutions[5–8] and then spinning them into composite or pure CNT fibers. Unfortunately, difficulties in CNT dispersion and alignment have hindered the full utilization of CNT strength.[9] Recently, CNT yarns have been directly spun from CNT arrays.[10–13] This new approach has the advantage of good CNT alignment and high CNT volume fraction, and therefore is very promising for producing higher strength CNT yarns and fibers. So far, CNT fibers can only be spun from CNT arrays that are less than 300 μm long, and this has limited their tensile strengths to only a few hundred MPa.[10,11] Therefore, it is critical to synthesize spinnable long CNT arrays so that higher strength can be obtained in the spun CNT fibers.

Long active growth is the key to growing long CNT arrays. However, during CVD processes using thin Fe catalyst films, the catalysts usually become inactive within several minutes due to either interdiffusion with the substrate[14] or the accumulation of amorphous carbon.[15] In order to achieve sustained growth for long CNT arrays, catalysts like ferrocene have been added continuously or intermittently into the system to nucleate new catalyst particles during the growth.[16,17] This makes individual CNTs much shorter than the array height. In addition, CNTs synthesized in this way are often thick and dirty with undesirable excessive catalytic particles and amorphous carbon. Alternatively, sustained growth was realized by introducing a thin buffer layer, either Al_2O_3[18,19] or MgO,[20] beneath the sputtered Fe film. This strategy has resulted in CNT arrays that are as long as 2.5 mm. However, these long CNT arrays are not conducive to spinning.

In this paper, we report the synthesis of 4.7 mm long CNT arrays with a high-efficiency, long-life catalyst film. A dense Al_2O_3 buffer layer (10 nm) was first deposited on a Si substrate using ion-beam assisted deposition (IBAD), and a Fe film (1 nm) was deposited on the buffer layer. Compared to previous works,[18,19] our approach to grow long (4.7 mm) CNT arrays is simple (no special treatment of catalysts), safe (using a forming gas with 6 % hydrogen), and cost-effective (relatively low gas flow rate). Moreover, our CNT arrays are spinnable in a wide range of lengths (0.5 to 1.5 mm) and much longer than those reported previously.[10–13] Such long arrays have resulted in CNT fibers with superior strength and electrical conductivity.

Figure 1a shows scanning electron microscopy (SEM) images of the longest CNT array (4.7 mm) grown at 750 °C for 2 h with the assistance of water vapor. To our knowledge, this is the longest CNT array grown on a catalyst film without feeding any other catalyst into the furnace. The previous record is 2.5 mm.[18] A close examination of the array (Fig. 1b) reveals that the CNTs are well aligned. Transmission electron microscopy (TEM) revealed that the CNTs are multiwalled, with <8 walls, and that their average diameter is ca. 10 nm (see Fig. S1 in the Supporting Information). Interestingly, without water vapor our CNT arrays grew to 3 mm long in 2 h (not shown here), which is still longer than the previous record. In addition, our process requires low total flow rates of gases (100 sccm ethylene and 100 sccm forming gas with 6 %

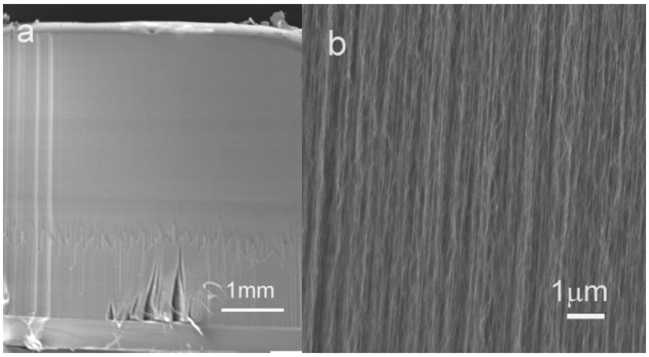

Figure 1. a) 4.7 mm long CNT arrays grown on the catalyst SiO_2/Al_2O_3(10 nm)/Fe(1 nm) with the assistance of water vapor. b) Enlarged SEM image showing well-aligned CNTs.

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[*] Dr. Y. T. Zhu, Dr. Q. W. Li, Dr. X. F. Zhang, R. DePaula,
Dr. L. X. Zheng, Dr. Y. H. Zhao, Dr. L. Stan, Dr. T. G. Holesinger,
Dr. P. N. Arendt, Dr. D. E. Peterson
Materials Physics & Applications, Los Alamos National Laboratory
Los Alamos, NM 87545 (USA)
E-mail: yzhu@lanl.gov

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H_2), which makes the process safer and cheaper for industrial production.

In order to understand the behavior of our catalyst, we investigated the CNT growth kinetics. Figure 2 shows the CNT array length as a function of growth time at 750 °C without the assistance of water vapor. As shown, in the first 20 min the CNT arrays grew at a rate of ca. 60 µm min^{-1}. Afterwards, the growth slowed down gradually and terminated at 90 min with a final array length of 3 mm. This is in sharp contrast with previous reports[18,21] where CNT arrays started growing at ca. 300 µm min^{-1}, but growth then slowed down quickly and stopped at 20 min.

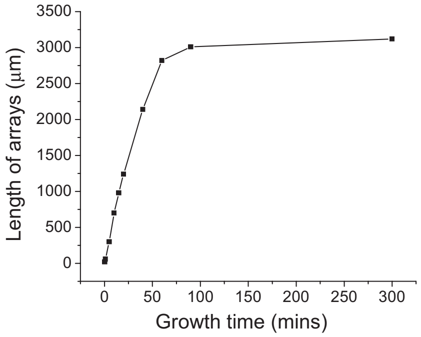

Figure 2. Evolution of CNT array length with time at 750 °C with no water vapor and with ethylene and carrier-gas flow rates at 100 sccm.

Moreover, although water vapor, as a weak oxidant, has been reported to promote CNT growth,[18,22] we did not observe any significant effect of water vapor on CNT growth during the first 30 min at 750 °C. However, the water vapor prolonged the growth of CNT arrays. Under an optimal amount of water vapor (bubbling by Ar at 8 sccm), the growth of the CNT arrays lasted for 2 h, which produced 4.7 mm CNT arrays. This indicates that our catalyst can maintain its activity during the CNT growth for a much longer time than previously reported catalysts.[18–21] The long catalyst life is responsible for growing such long CNT arrays.

The long catalyst life in this study could be due to the unique method used to deposit the Al_2O_3 buffer layer. It has been found that the Al_2O_3 layer deposited by the IBAD technique was mostly amorphous and denser than those deposited by other techniques.[23,24] This dense buffer layer may help with the deposition of a more uniform Fe film by increasing the wettability of Fe on its surface,[25] preventing the interdiffusion between the Fe film and the substrate,[18,26] and controlling the formation of catalyst particles during the CNT growth.[27]

In order to achieve a high growth rate while maintaining a long catalyst lifetime, we investigated the effect of the temperature on CNT growth rate of arrays. Normally, CNT growth can be accelerated by either supplying more carbon or increasing the temperature. However, both approaches may lead to catalyst deactivation caused by the formation of amorphous carbon. Water vapor might provide for a way to promote CNT growth while avoiding this problem. In this study, we used a combination of 100 sccm ethylene with 100 sccm forming gas (Ar + 6 % H_2), and a fixed growth time of 15 min, while varying the temperature from 730 to 780 °C. The water vapor, when used, was introduced into the furnace by bubbling 8 sccm Ar gas through water. As shown in Figure 3a, water vapor did not have a great influence on the CNT growth rate in the lower temperature range of 730 to 750 °C. However, at the higher temperature of 780 °C it significantly enhanced the growth rate. Without water vapor the growth rate increased with temperature in the lower temperature range of 730 to 750 °C, but increased only slightly when the temperature went up to 780 °C. In contrast, with water vapor the growth was accelerated remarkably at higher temperatures.

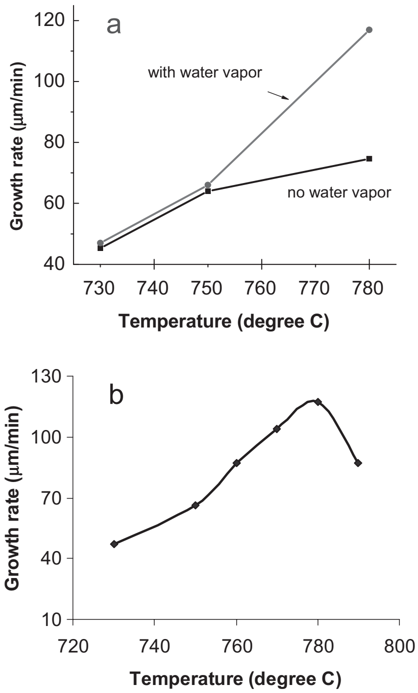

Figure 3. a) Effect of water vapor on the growth rate of CNT arrays at different temperatures. b) Temperature dependence of the growth rate of CNT arrays.

Raman spectroscopy revealed that CNT arrays grown with water vapor had less amorphous carbon than those grown without water vapor, indicating that water vapor enhanced the CNT growth by reducing the formation of amorphous carbon and thus keeping the catalyst particles cleaner. We also found that even at a lower temperature, for example, 750 °C, the CNT arrays grown for over 1 h were stiff and looked grayish on the top without water vapor, due to the formation of amorphous carbon. In contrast, CNT arrays grown under the same conditions but with the assistance of water vapor remained soft and black.

As shown in Figure 3b, the highest growth rate (ca. 120 µm min^{-1}) was achieved at 780 °C with the assistance of water vapor. Under these conditions the CNT growth lasted for 40 min, resulting in 3 mm CNT arrays. Using the Arrhenius equation, $k = A \exp(-E_a/RT)$, where k is the growth rate, A is a constant, E_a is the apparent activation energy, R is the universal gas constant (8.3144 J mol^{-1} K^{-1}), and T is the temperature, a very good linear relationship was observed when we plotted ln k versus $1/T$ in the temperature range of 730 to 780 °C (see Fig. S2a, Supporting Information), and the activation energy calculated from the slope is 158 kJ. Combined with the fact that the array height increased linearly with time during the initial growth period (20 min) for the entire temperature range of 730 to 780 °C (see Fig. S2b, Supporting Information), we conclude that the CNT growth rate is not controlled by the diffusion of carbon precursors to the catalysts. We also found that at a fixed total flow rate (200 sccm) at 750 °C, the CNT growth rates increased linearly with ethylene concentration in a range of 0 to 50 %, indicating that this is a first-order reaction and the rate-limiting step is the catalytic decomposition of ethylene,[28] which is different from other reports.[29,30]

CNT arrays preferred to grow in the base-growth mode in this study. Growth marks generated by pulsed injection of hydrocarbons can be used as indirect and simple evidence to understand the growth mode of CNT arrays.[31,32] Figure 4a and b show CNT arrays grown with and without water vapor by sequential pulsed injections of ethylene for 1, 2, 3, 4, and 5 min with a 1 min break between adjacent injections. Figure 4a and b show growth marks formed during the injection break. The distance between two adjacent marks is proportional to the injection/growth duration used to grow that segment. For base growth, the distance between two adjacent growth marks should decrease from the substrate to the array top, which is apparently the case in this study. Surprisingly, despite the base-growth mode CNT arrays were still able to grow to 4.7 mm long with uniform length over the entire substrate (0.5 cm × 0.5 cm), in sharp contrast to a report that hydrocarbon diffusion limited the CNT array length to 1 mm.[28,29]

It is worth mentioning that the thickness of the Fe catalyst film significantly affects the structure and diameter of as-formed CNTs. CNTs grown with a 1 nm thick Fe film are multiwalled with an average diameter of 10 nm. In contrast, when the Fe film thickness was reduced to 0.3 nm, the average diameter of the CNTs was decreased to 6 nm and the CNTs are mostly double walled. This observation suggests that it is possible to control the structures and diameters of CNTs by adjusting the thickness of the Fe film.

We found that 0.5 to 1.5 mm long CNT arrays grown at temperatures ≤ 750 °C for 10–15 min without water vapor are favorable for spinning. CNT arrays longer than 1.5 mm were not conducive to spinning because of their relatively high content of amorphous carbon. However, CNT arrays grown with the assistance of water vapor are not conducive to spinning, as the spinnability of CNT arrays depends on several factors such as purity, density, alignment, and the straightness of the CNTs. Their correlations are under investigation. We found that good CNT alignment in the array was critical to spinning. Arrays with curved, intertwined CNTs are not conducive to spinning.

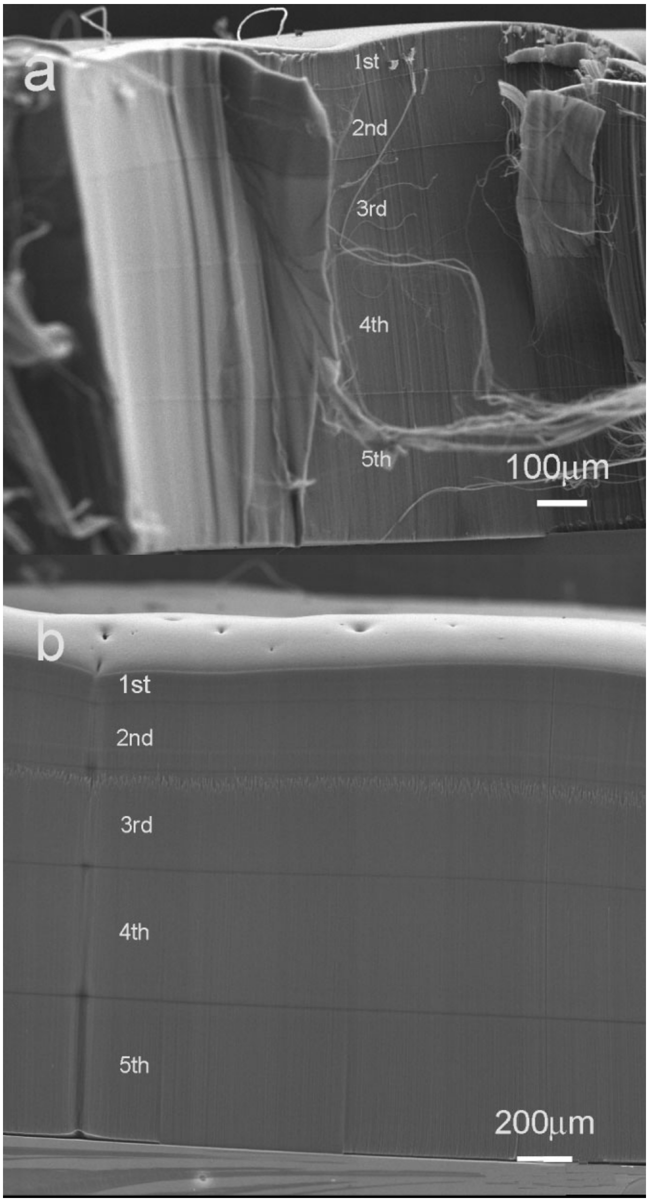

Figure 4. a) SEM image showing growth marks formed at 750 °C, without water vapor. b) Growth marks formed at 780 °C, with water vapor. The presence of growth marks on both samples indicates a base growth mode on this catalyst. The numbers indicate the sequence of the injections.

Long CNT arrays may serve as good precursors for spinning strong fibers. We have spun CNT fibers with diameters in the range of 2 to 10 µm from 0.5 mm and 1 mm CNT arrays using the same spinning parameters. The highest tensile strength of the CNT fibers spun from the 1 mm array is 3.3 GPa, much higher than that of CNT fibers from the 0.65 mm array (1.91 GPa). Both values are higher than previously reported strength values of CNT fibers spun from 0.3 mm arrays.[10] These observations demonstrate the advantage of long CNT arrays in spinning high-quality CNT fibers. We also found that our CNT fibers are more conductive than other reported CNT fibers.[10,27] More details on these CNT fibers will be reported later.[33]

In summary, we have developed a catalyst structure consisting of a thin Fe film on a dense Al_2O_3 buffer layer that was deposited on a Si substrate by IBAD. This catalyst structure enabled fast growth of CNT arrays for a prolonged time (> 90 min), resulting in CNT arrays that are 4.7 mm long with water vapor and 3 mm long without water vapor. These CNT lengths are much longer than the 2.5 mm CNT arrays reported previously. Water vapor was found to reduce the formation of amorphous carbon and to extend the catalyst life. Our synthesis of long CNT arrays requires a very low fraction of hydrogen, which makes the synthesis much safer and more cost-effective. CNT arrays with lengths in the range of 0.5 to 1.5 mm are conducive to spinning CNT fibers. The fibers spun from these long CNT arrays show much higher strength and electrical conductivity than previously reported CNT fibers spun from shorter CNT arrays.

Experimental

Long CNT arrays were synthesized in a 1 inch diameter (1 inch = 2.54 cm) quartz tube furnace. Forming gas (Ar with 6 % H_2) was used as a carrier gas, and pure ethylene served as the carbon source. To study the effect of water vapor on the CNT growth, some CNT arrays were grown with water vapor, which was introduced into the furnace by passing a small fraction of Ar gas through a bubbler. The catalysts used in this study were Al_2O_3 (10 nm)/Fe(0.3–1.0 nm) on Si wafers with a 1 μm SiO_2 layer. The Fe and Al_2O_3 films were deposited by sputtering and IBAD techniques, respectively. Typically, CNT growth was carried out at 750 °C with 100 sccm ethylene and 100 sccm Ar + 6 % H_2 for 15 min. Unless specified otherwise, Al_2O_3(10 nm)/Fe(1 nm) catalyst was used for the growth. CNT fibers were spun from CNT arrays with a spindle rotating at 2500 rpm and drawing at 5 cm min^{-1}. Mechanical tests were carried out on a Rheometrics RSAIII solids analyzer. Electrical measurements were conducted using the four-probe method from 300 K down to 75.4 K with a sampling interval of 0.02 K.

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