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Growth of Super Long Aligned Brush-Like Carbon Nanotubes

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Efficient chemical vapor deposition (CVD) synthesis of super long (7 mm) aligned carbon nanotubes (CNTs) with high-density is reported here. Activity of catalyst nanoparticles has been achieved for very long time periods (*ca.* 12 h) by optimization of experimental parameters. The relative levels of ethylene and water, as well as those of ethylene and H_2, were found to be most important for achieving extended-time activity of the catalyst. Transmission electron microscope (TEM) images revealed that the nanotubes were mainly double-walled, but very few single-walled and multi-walled nanotubes were also present in the sample. [DOI: 10.1143/JJAP.45.L720]

KEYWORDS: carbon nanotube, super long, vertically aligned, thermal chemical vapor deposition, double-walled nanotubes

Nanotechnologies based on carbon nanotubes (CNTs) are developing very rapidly because of their outstanding mechanical, electrical, and optical properties.[1–5)] Intense research efforts have been undertaken to synthesize aligned long CNTs;[6–9)] nevertheless, many limitations to synthesis of very long aligned CNTs remain. Recently, the Iijima group succeeded in growing 2.5-mm-long aligned single-walled CNTs with high purity using water-assisted chemical vapor deposition (CVD) technique.[10)] Research into the synthesis of long aligned CNTs is of great interest because of its possible applications by which their properties are coupled with extended lengths that will enable new technological developments. The long aligned nanotubes can be spun into fibers and sheets[5,11,12)] that are vastly stronger than any existing structural material, which will engender revolutionary advances in lightweight and high-strength applications. In light of the requirements and possible research trends of CNTs for the development of advanced technologies described above, we have synthesized super-long aligned brush-like CNTs with high density.

Here we report the synthesis of 7-mm-long aligned brush-like CNTs with high density using a thermal catalytic CVD process. The long time (*ca.* 12 h) catalyst activity was achieved by balancing the relative levels of ethylene and water with those of ethylene and H_2, which is also reported here. A sharp optimum CVD condition was achieved for growth of super long aligned CNTs.

The super long aligned CNTs were synthesized using a conventional thermal catalytic CVD technique. High-purity ethylene was used as the source gas of carbon. Helium (99.9999%) was used with H_2 (99.9999%) as a carrier gas at one atmosphere of pressure. A controlled amount of water vapor with different concentration (150–500 ppm) was also introduced with the carrier gas during the deposition process. The total gas flow rate throughout the deposition process was maintained at 200 sccm. The ethylene flow rate was varied from 5 to 25% of the total flow rate (200 sccm) to obtain the optimum flow rate of the source gas for growing super long CNTs. Results showed that the optimum flow rate of ethylene (15 sccm) was 7.5% of the total flow rate, which can produce super long aligned CNTs with high density. Thin (1 nm thick) layers of Fe were used as the catalyst and an Al_2O_3 (10 nm) buffer layer was used between the Si/SiO_2 substrate and the Fe catalyst. Typical CVD growth was carried out at 750 °C for 30 min as the standard growth time. During the heating process of the reactor, a steady flow of helium (120 sccm) and H_2 (80 sccm) was maintained. The helium gases at 105 and 15 sccm were introduced separately into the reactor during reactor heating. After attaining the growth temperature (750 °C), ethylene was introduced at 15 sccm by replacing the helium gas at 15 sccm. This quick exchange of helium gas by ethylene rapidly increased the concentration of the source gas reaching the substrate and produced a very high growth rate of CNTs during the first few seconds of deposition.[13)]

Results showed that the synthesis of super long aligned CNTs is very sensitive to experimental parameters like the flow rate of the source gas ethylene, the water concentration, and the H_2 flow rate. Balancing the relative levels of ethylene and water, as well as those of ethylene and H_2, was crucial for achieving long-time activity of the catalyst. In our experiments, we studied the dependence of CNTs' height on ethylene-to-water and ethylene-to-H_2 ratios to determine the best possible conditions for easy synthesis of super long CNTs with good reproducibility. A sharp optimum condition was achieved in our experiments for the growth of super long aligned brush-like CNTs. The variation of growth time of the CNTs showed a continuous increase in height up to 12 h of deposition. The longest aligned CNTs of about 7 mm after 12 h of deposition, as shown in Fig. 1(a), were achieved by optimizing the experimental parameters.

Figure 1(a) depicts a photograph of 7-mm-long aligned brush-like CNTs on the substrate. A scanning electron microscope (SEM) image of the top surface of the 7-mm-long aligned CNTs is shown in Fig. 1(b); it reveals a very smooth and flat surface. This image shows that all the nanotubes are of uniform length, indicating very uniform growth over the entire substrate surface. Close examination of the different parts (upper and lower) of the CNTs was done using SEM. Low-magnification SEM images of the upper and lower parts of the nanotubes are shown respectively in Figs. 1(c) and 1(e), which reveal that the nanotubes are packed densely and aligned vertically. Figures 1(d) and 1(f) show high-magnification images of upper and lower parts of the nanotubes. High-magnification SEM images

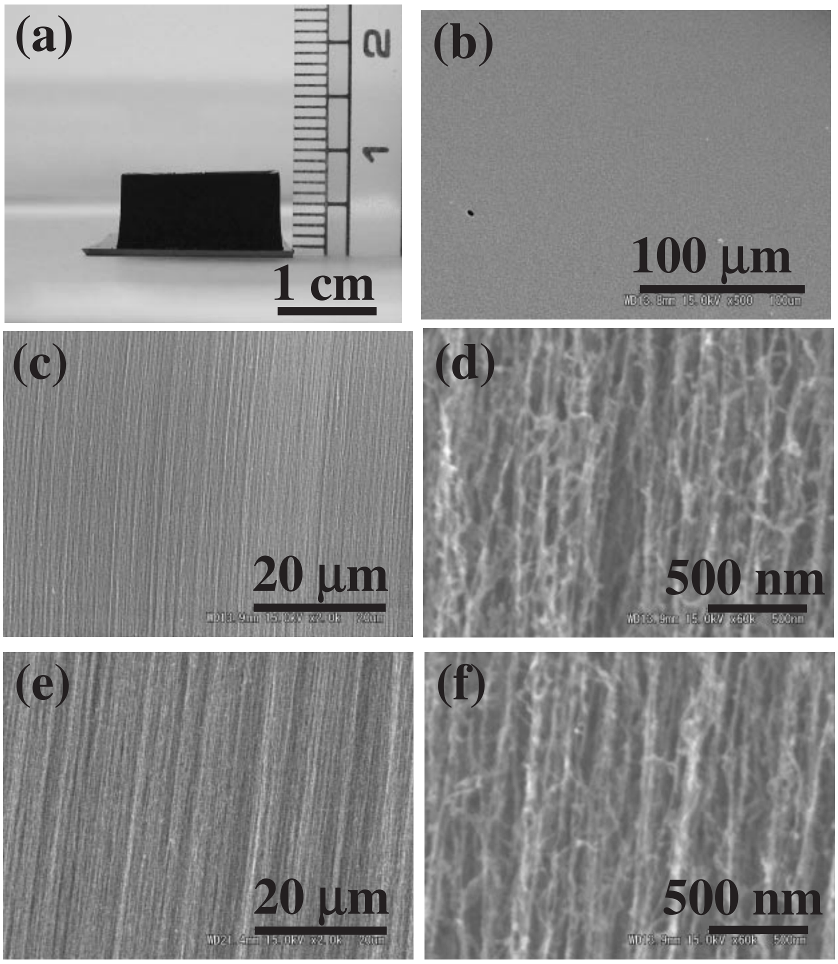

Fig. 1. Images of a super long aligned brush-like CNTs: (a) digital photographic image of 7-mm-long aligned CNTs, (b) a SEM image of the top surface of the 7-mm-long aligned CNTs, (c) a low-magnification SEM image of the upper part of the aligned nanotubes, (d) a high-magnification SEM image of the upper part, (e) a low-magnification SEM image of the lower part of the aligned nanotubes, and (f) a high-magnification SEM image of the nanotubes.

clearly portray that the nanotubes are curved and mutually interconnected on a nanoscale. The morphology of the middle part of the nanotubes was almost identical to that of the upper and lower parts of the nanotubes.

Variation of the relative levels of ethylene and H_2 was found to be very effective for growing super long aligned CNTs. Figure 2(a) shows the variation of CNT height according to the ethylene-to-H_2 ratio where the total flow rate of 200 sccm, the deposition temperature of 750 °C for 30 min and water concentration 350 ppm were kept constant. The plot indicates that the relative levels of ethylene and H_2 are crucial for producing super long CNTs. The maximum height of the aligned brush-like CNTs was achieved for the ethylene-to-H_2 ratio of 0.188, which means that the H_2 flow rate was about five times the ethylene flow rate. A slight change in the ethylene-to-H_2 ratio caused a significant decrease in the CNT height. Figure 2(a) shows that the CNT height decreases with increasing ethylene-to-H_2 ratio. The CNT height decreased continuously for the ethylene-to-H_2 ratio beyond 0.1875 – 0.65: again when the ratio was 0.125, the height decreased. This experimental observation indicates clearly that a sharp optimum relative level of ethylene and H_2 for the growth of super long aligned CNTs. Without H_2 flow, the nanotube growth yield decreased rapidly and no long aligned CNTs were produced. Generally, H_2 can increase the activity of the metal catalyst for cracking hydrocarbons. It can also clean the catalytic surface by etching polycyclic hydrocarbon species, which tend to encapsulate metal surfaces.[14,15] Reduction of the catalyst to metallic Fe by H_2 might improve CNT nucleation,[16] but prolonged treatment with H_2 might suppress growth, thereby engendering sintering of metal particles or altering metal–support interactions.[17]

The dependence of CNT height with the relative levels of ethylene and water was also studied; it is shown in Fig. 2(b). During this variation, the total flow rate of 200 sccm, H_2 flow rate 80 sccm (40% of the total flow rate), and deposition temperature of 750 °C for 30 min were kept constant. The plot in Fig. 2(b) shows that, here also, an optimum condition was obtained for growing aligned CNTs with maximum height. A small amount of water vapor functioned as a weak oxidizer[10] which helped to maintain catalyst activity by oxidizing the amorphous carbon layer deposited on the catalyst particle surface.

The CNT deposition time was varied from 10 min to 12 h and the corresponding results are shown in Fig. 2(c). An increase in the CNT height was observed even up to 12 h of deposition time. Until now, our best achievement is the synthesis of 7-mm-long aligned CNTs after 12 h of deposition. The great advantage in this experiment is the activity of catalyst nanoparticles for a long time. In contrast to the results reported by Hata *et al.*,[10] in which the catalyst was found to be active for about 30 min, our results indicated a remarkably long time (12 h) of activity of the catalyst nanoparticles, which is an important achievement. Apparently, such a long time activity of the catalyst nanoparticles

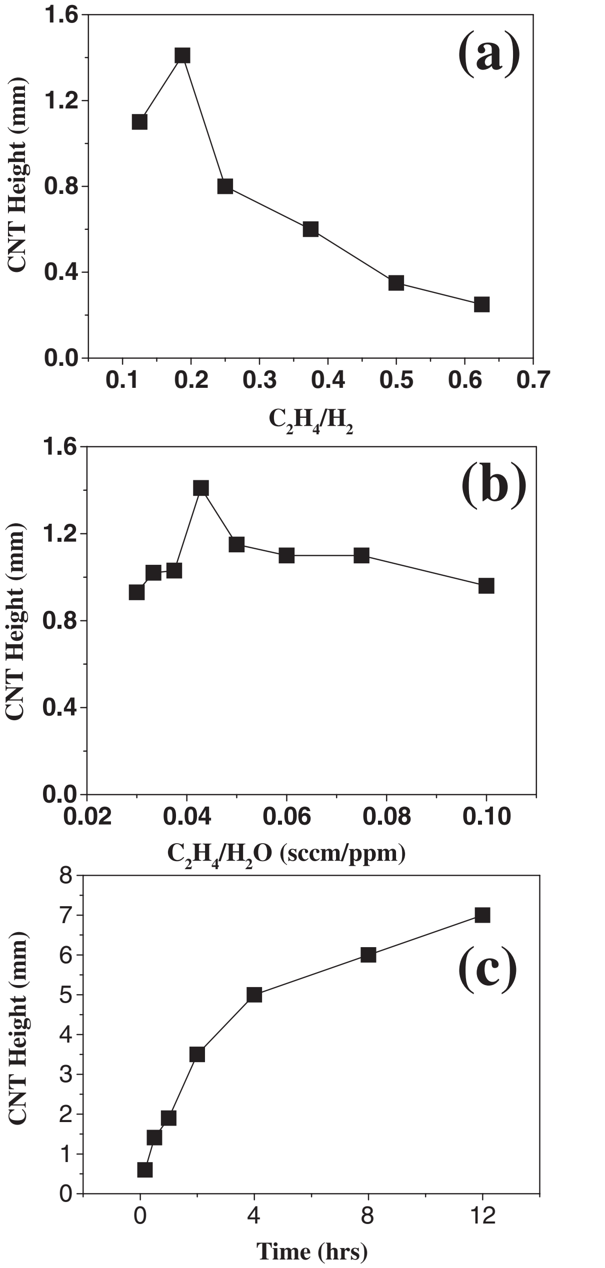

Fig. 2. Plots of CNT height dependence: (a) variation of CNT height according to the C_2H_4/H_2 ratio, (b) variation of CNT height with the C_2H_4/H_2O ratio, and (c) variation of CNT height with the growth time.

was achieved only because of perfect optimization of the relative levels of ethylene–H_2 and ethylene–water during the CVD growth of CNTs. Here, we achieved a sharp optimum CVD condition to keep the catalyst active for such a long period.

Transmission electron microscope (TEM) images of the 7-mm-long aligned brush-like CNTs are shown in Figs. 3(a) and 3(b). They confirm the absence of metallic nanoparticles. High-resolution TEM images also showed that the nanotubes were mainly double-walled. One representative image is shown in Fig. 3(b). In addition, a very low percentage of single-walled and multi-walled (three or four walls) nanotubes were present in the sample.

In summary, super long (7 mm) aligned high-density CNTs were synthesized with high reproducibility using CVD technique. The relative levels of ethylene and water, as well as ethylene and H_2 during the CVD, were found to be the most important factor for the growth of such super long aligned CNTs. A narrow optimum CVD condition was achieved for growth of a super long aligned brush-like CNTs. The optimized experimental conditions maintained the catalyst activity for a very long time (*ca.* 12 h), which is a remarkable achievement. The nanotubes were mainly double-walled, which is also an important achievement. This synthesis of super long high-purity brush-like aligned CNTs will greatly advance nanotechnology based on CNTs.

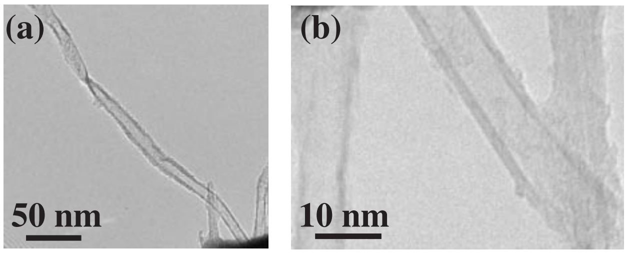

Fig. 3. TEM images of 7-mm-long aligned CNTs: (a) a low-resolution image and (b) a high-resolution image.

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