Oxidation and Opening of Well-Aligned Carbon Nanotube Tips

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We report here that well-aligned carbon nanotubes with open tips can be directly obtained by introducing carbon dioxide during the chemical vapor deposition process. In-situ oxidation of carbon nanotubes by carbon dioxide results in the strip off of nanotube tips, however, without damaging the nanotube alignment. Such oxidation of aligned nanotube arrays, whose tips are all on the array surface, is more efficient than the oxidation of disordered nanotubes. Aligned carbon nanotube arrays with open tips have potential applications in field emission, filter membrane, and energy storage.

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1. Introduction

Since the discovery in 1991, 1) carbon nanotubes (CNTs) have shown many unique physical and chemical properties. 2,3) Many potential applications, such as flat panel displays, 4,5) hydrogen storage, 6) chemical sensors, 7) etc., have been proposed. Synthesis of aligned CNTs is important for further study on the properties and applications of CNTs. There have been many reports in this field. Li et al. obtained aligned CNTs on mesoporous silica embedded with iron nanoparticles by chemical vapor deposition (CVD) method. 8) Ren et al. synthesized arrays of aligned CNTs on nickel-coated glass by a plasma-enhanced hot filament CVD method. 9) Andrews et al. produced amount of pure aligned CNTs on quartz substrates through the catalytic decomposition of a ferrocene-xylene mixture. 10) However, for aligned CNTs prepared by most of the CVD methods, the nanotube tips are generally closed or caped with catalyst particles. 11,12) Various approaches have been reported to open the nanotube tips for further applications such as, oxidation using oxygen, 13,14) oxidation using carbon dioxide (CO2), 15) oxidation using oxidizing acid solution, 16,17) bromination, 18) etc. But these post-treatments are not suitable for aligned CNTs, since the nanotube alignment would be destroyed inevitably. Here, we describe the direct growth of well-aligned CNTs with open tips by in-situ oxidation of CO2 during the CNT growth process. In-situ oxidation may also apply to synthesize defective CNTs.

2. Experimental

The experimental equipment and process is similar to that described elsewhere. 12,13) Quartz sheets were used as the growth substrates for aligned CNTs. Ferrocene was dissolved in xylene to obtain a solution of 0.02 kg/L, which was then fed continuously into a two-stage tubular quartz reactor for 30 min. Ferrocene (decomposition temperature, ∼190°C) was used to produce Fe catalytic particles, and xylene (boiling point, ∼140°C) was selected as the hydrocarbon source. The temperature at the preheating stage and the decomposition stage of the reactor was maintained at 180°C and 820°C, respectively. The flowing rate of Ar during the reaction was kept at 1000 sccm. As soon as the feeding of solution was stopped, CO2 was introduced into the reactor at 100 sccm, and the flow rate for different oxidation times. CO2 gas was used because of its mild effect for oxidation, 18) so the oxidation of CNTs is more easily controlled than using O2. After the reactor was cooled to room temperature in flowing Ar, the quartz sheets were taken out of the reactor. The sheets were covered with uniform black films, which were easily stripped off.

3. Results and Discussion

Field emission scanning electronic microscopy (FESEM) was used to examine the effects of CO2 on the morphology of the aligned CNT films. Figure 1(a) is the SEM image of an as-grown CNT film without CO2 oxidation. The CNTs in the film are well-aligned with their tips pointing upward unanimously. The roof of the film is uniform and clean. Figure 1(b) is the section image of a CNT film that has been oxidized by CO2 for 10 minutes. The CNTs are still in good alignment, and there are only small amount of impurity on the roof of the film. Figure 1(b) is the section image of a CNT film that has been oxidized by CO2 for 10 minutes. The CNTs are still in good alignment, and there are only small amount of impurity on the roof of the film. To observe the tips in more detail, an enlarged view on the roof of the film is shown in Fig. 1(b). We can see that most of the tips of the nanotubes are broken or/and tapered. The inside hollow of some of the nanotubes can be observed clearly due to the strip off of the nanotube tips. Figure 1(c) is the roof image of a CNT film oxidized by CO2 for 15 min. The CNTs in the film are still in alignment, but there are more impurities on them, which come from the oxidized graphite sheets and drop-out catalyst particles.

We chose various CO2 oxidation times during the CVD process and the remaining lengths of aligned CNTs were measured by SEM (Fig. 2). For comparison, the length of as-grown CNTs without CO2 oxidation is also presented in Fig. 2, which is about 120 µm. The length of aligned CNTs has no obvious change within the oxidation time of 5 min. For the oxidation time of 10 min, the length of carbon nanotubes reduces to 110 µm. With longer oxidation time, the nanotube length decreases continuously. The alignment of
CNTs was kept well within the oxidation time of 20 min, but destroyed obviously after that time. After 30 min of CO$_2$ oxidation, the nanotubes were no longer aligned and the length of them could not be measured directly. The length of aligned CNTs oxidized for 20 min was only about one third of their original size, so that the weight loss of the CNTs due to the CO$_2$ oxidation is about two third. The weight loss of disordered CNTs oxidized by CO$_2$ at 850°C for 5 h was reported to be only 10%. So it seems that aligned CNTs are more sensitive to the oxidation of CO$_2$ than disordered CNTs. The reason may be that the tips of CNTs are much more easily to be oxidized than the nanotube walls due to the large curvature and crystal defects of nanotube tips. Furthermore, the nanotube tips are gathered in the surface of aligned CNT arrays. They face CO$_2$ directly that is flowing over the arrays, while the nanotube walls hide inside the arrays where CO$_2$ can not access easily. For disordered CNTs, as most of nanotube tips are covered by each other, the etching of them by CO$_2$ should be less efficient. The average diameter of the aligned CNTs has no obvious change within 15 min, but became smaller after an oxidation of 20 min. We suppose that after 20 min, CO$_2$ start to oxidize and etch away the nanotube walls as well as the tips because the CNTs in the arrays become much shorter and disordered.

As mentioned above, the oxidation mainly took place at the surface of the CNTs films at the initial stages. Firstly, the tips of aligned CNTs were oxidized and open. The catalyst particles covered on the nanotube tips may drop out at this time. Subsequently, CNTs were shaven by CO$_2$ from the tips step by step. When the flowing CO$_2$ passed over the surface of aligned CNT arrays, only a very small mount of the CO$_2$ could get into the interior of the films because the aligned CNTs are densely packed. So the average diameter of the aligned CNTs shows no obvious change and the good alignment of nanotubes maintains until 15 min. During the first
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15 min of CO₂ oxidation, only the length of CNTs decreases. For a longer time of oxidation (after 20 min), more CO₂ entered the interior of the aligned CNTs films and can access and oxidize the nanotube walls. Thus the diameter of CNTs became smaller with the alignment degree of them decreasing, but the decrease of their length becomes slow after the oxidation time of 20 min.

Transmission electronic microscopy (TEM) was used to examine the oxidation effects of CO₂ on nanotube tips. Figure 3 shows four TEM images of the oxidized carbon nanotube tips with different oxidation extent. Figure 3(a) shows a nanotube tip oxidized for 5 min, it is partially open and the catalytic particle just drops out of it, leaving a spherical hollow cavity in the nanotube tip. Figure 3(b) is an image of a CNT tip oxidized for 7 min, which is almost open. Figure 3(c) shows a nanotube oxidized for 15 min, whose tip has been completely open due to the longer time oxidation by CO₂. Some carbonaceous debris has been sucked into the inside hollow (indicated by an arrow). The CNTs in Figure 3(d) are oxidized for 30 min. Their tips stick together by the carbonaceous debris (indicated by an arrow), which come from the oxidation of the graphitic sheets of CNTs. So it is difficult to distinguish them. In the TEM examination we also found that some CNTs still have close tips. These CNTs may be covered by other longer ones in the aligned CNT array so that CO₂ could not arrive at their tips.

4. Conclusion

In conclusion, well-aligned CNTs can be easily oxidized by CO₂ during the CVD synthesis process comparing to disordered CNTs, and they are oxidized step by step from their tips down to their bodies as oxidation continues. As a result, most of the nanotube tips in the aligned CNT arrays are open. At the same time, the alignment of them can be maintained within the oxidation time of 15 min. Other conventional oxidation or purification methods, such as acid treatment, centrifugation or filtration, could not maintain the original alignment of carbon nanotubes. Thus, the field emission properties of CNT arrays may be improved by this method, and the doping of other elements (such as N) from the nanotube tips and the storage of foreign molecules (such as H₂) in the nanotube

![TEM images of the as-grown carbon nanotube tips with different oxidation times.](image-url)
inner cavities can be easier.

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