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Re-growth of single-walled carbon nanotube by hot-wall and cold-wall chemical vapor deposition



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ABSTRACT

Single-walled carbon nanotube (SWCNT) was synthesized from short nanotubes using chemical vapor deposition (CVD) and the associated factors affecting the re-growth of the SWCNT were both investigated and optimized. Long, dense nanotubes were prepared from a mixture of acetylene and ethanol on airannealed ST-cut quartz substrates by hot-wall CVD. Raman and photoluminescence analyses of the resulting material demonstrated that SWCNT was generated from the initial seeds since the chiralities of the seeds were maintained in the re-grown SWCNT. The re-growth of SWCNT was also achieved by coldwall CVD. In both CVD systems, the efficiency of SWCNT re-growth was largely determined by the pretreatment conditions and growth parameters. By varying these factors, the growth of SWCNT from seeds was controlled. The re-growth mechanism is discussed based on experimental observations.

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1. Introduction

The synthesis of single-walled carbon nanotube (SWCNT) with well-defined structures has become an important issue because the electronic properties of carbon nanotubes are primarily determined by their chirality [1-3]. In addition, to allow for applications in microelectronic devices, both growth control and the separation of metallic species from semiconducting SWCNT is required. To achieve this, there have been many studies concerning the growth of SWCNT by chemical vapor deposition (CVD) and separation techniques [4-12]. Using metal catalysts, high purity semiconducting SWCNT has been selectively grown by controlling various experimental parameters [13]. Recently, synthesis of SWCNT with specific chiralities has also been achieved through the use of alloy metal catalysts, which may suggest a potential direction for nanotube growth [6,8]. As an alternative to metal catalysts, the growth of SWCNT can also be accomplished using predefined carbon structures, such as fullerenes, nanotubes or even organic

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carbon rings, as "seeds," thus generating a product that does not contain residual catalyst [7,14–19]. Among these potential seed structures, the use of nanotubes offers a straightforward means of directly obtaining SWCNT with specific chiralities [7,16,20]. In contrast to metal catalysts, it has been shown that pretreatment to activate the surfaces of carbon structure seeds is a crucial step for the re-growth of the SWCNT, and this is normally performed by air oxidation or treatment with water [16]. However, further research is needed to investigate the various conditions under which this method can be applied, as well as to ascertain the effects of experimental parameters on the re-growth of SWCNT from seeds. Considering the potential applications of this material, optimization of the growth conditions to achieve mass production of chiralspecific SWCNT is an important goal.

In this study, we optimized the growth conditions and increased the re-growth efficiency of SWCNT from short nanotubes via chemical vapor deposition (CVD). Raman and photoluminescence (PL) analyses suggested that the re-grown SWCNT was in fact produced from the original nanotube seeds. In addition, the regrowth of SWCNT was also realized by cold-wall CVD. The mechanism by which the SWCNT was generated from the seeds is discussed based on comparing the growth conditions of these two CVD systems.





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2. Experimental

Substrates incorporating SWCNT seeds were prepared by a drop deposition technique. Briefly, as-grown High-Pressure CO Conversion (HiPCO) SWCNT was shortened and purified as an initial step, after which they were dispersed in a deoxyribonucleic acid (DNA) and water solution with a SWCNT concentration of 0.5 µg/ml [21]. SWCNT was transferred onto SiO₂/Si or quartz substrates by depositing drops of the solution onto the substrates. The substrates were subsequently dried under air. A hot-wall thermal furnace was used to pretreat the seeds. Typically, a two-step pretreatment was employed to activate nanotube seeds, consisting of air oxidation and water treatment. The substrates with SWCNT seeds were first loaded into a silica tube furnace and oxidized in air at 500 °C for 8 min, following which water vapor (0.1 sccm) was introduced into the furnace at 2.9 \times 10³ Pa for a span of 4 min.

During conventional hot-wall CVD, the re-growth of the SWCNT was typically performed using a carrier gas consisting of $Ar/H_2(3\%)$ at a flow rate of 600 sccm along with a bubbled ethanol at 10 sccm, at 850 °C for 20 min. Cold-wall CVD was conducted in the chamber of a scanning electron microscope (SEM, Carl Zeiss LEO 1530VP), by which SWCNT re-growth and in situ SEM observation without air exposure were realized at a low vacuum mode and a high vacuum mode, respectively. The set-up of cold-wall CVD is illustrated in supporting information. Reaction gases such as ethanol or acetylene were typically introduced into the chamber for the purposes of re-growth, at pressures below 2.0 Pa. The temperature of the substrate, consisting of a silicon ribbon with a 100 nm oxidized layer, was increased by resistive heating and monitored by an infrared optical pyrometer. For this cold-wall CVD system, the growth process was conducted at approximately 750 °C. Following the regrowth of the nanotubes, Raman scattering was also employed to characterize the diameter distribution and quality, using a Raman microscope (Nano Photon RAMAN-11) with a 785 nm laser.

3. Results

Typically, the SWCNT re-growth procedure includes pretreatment and a CVD growth process. Thus, to optimize the re-growth of SWCNT, both the pretreatment and growth conditions were systematically studied, and the length and number of SWCNT generated in a given area were summarized in the form of histograms to illustrate the effects of these factors.

3.1. Effects of pretreatment

Experimental observations showed that the re-growth of SWCNT was very sensitive to the pretreatment conditions. During these trials, we varied the air oxidation and water treatment parameters, including the temperature and time, as well as the carrier gas and water vapor flow rates, to ascertain their influences. We found that both treatments were indispensable since there was almost no re-growth of nanotubes when applying solely air oxidation or solely water treatment. The effects of air oxidation parameters were initially investigated, and the temperature during oxidation was varied from 200 to 600 °C while applying different reaction times. When the temperature was overly high (>500 °C) or overly low (<400 °C), no re-growth was observed, and the optimal condition was found to be 8 min of oxidation at 500 °C. The water treatment was typically performed by introducing water vapor and carrier gas (Ar/H₂ (3%)) together into the reaction chamber following air oxidation. In the case of the water treatment, there were three parameters; water flow rate, treatment time and temperature. The results demonstrated that the optimum ranges for the water flow rate and treatment time were rather narrow, and values of 0.1 sccm for the water flow at a rate of 450 sccm Ar/H₂ (3%) over a 4 min time span were found to be optimal for our CVD system. Slight deviations from these conditions resulted in essentially no re-growth. Thus, we varied the water treatment temperature from 400 to 900 °C using these optimized conditions, and found that the best re-growth results were obtained at 500 °C, and the re-growth efficiency was greatly decreased at higher or lower temperatures. The effects of temperature on the re-growth of SWCNT during water treatment are summarized in Fig. 1. At 500 °C, both the yield and length of the nanotubes were improved. The average length of the SWCNT was increased from 17 μ m at 700 °C to 38 μ m at 500 °C. Furthermore, the active edges of the original nanotube seeds were found to be stable in air, since contact with air following the pretreatment did not affect the re-growth results.

3.2. Effects of substrate

The effects of the substrate on the re-growth of nanotubes were also prominent. On SiO₂/Si substrates, curved SWCNT with wide distributions of both length and density was synthesized. In contrast, long, well-aligned SWCNT was obtained on quartz substrates. The length distributions of the re-grown SWCNT were, however, similar when using either substrate, as shown in Fig. 2. When the substrate was replaced by ST-cut quartz annealed in air at 1000 °C for 1 h, substantial improvements were seen in both yield and length, such that the nanotube density was enhanced and the average length was increased to 40 µm. It has previously been demonstrated that, when using the ST-cut quartz substrate, the surface morphology can be effectively modified by annealing in air. by which the surface of the ST-cut substrate is made smooth and uniform, with a surface roughness less than 1 nm [22,23]. Our results suggest that this smooth, clean surface was helpful to the regrowth process, possibly because it favors the diffusion of carbon radicals on the surface. Therefore, the nanotube re-growth was significantly improved on this substrate.

3.3. Effects of carbon source

The carbon source was also an important parameter since the carbon radicals that assemble the nanotube structures represent the decomposition products of this source. In order to optimize the re-growth, two carbon sources were assessed: ethanol and acetylene. As shown in Fig. 3, the re-growth of SWCNT could be realized using either ethanol or acetylene after proper pretreatment. To obtain the best growth conditions, we varied the associated reaction parameters, including the growth temperature, the carrier gas ratio and the carbon source. The optimal growth temperature was found to be 850 °C for both carbon sources. In addition, the regrowth of nanotubes was found to require only a small amount of the carbon supply since otherwise the formation of amorphous carbon hampered the re-growth. For ethanol, it was introduced into the furnace through the bubbler (10 sccm) with a 600 sccm flow of the carrier gas (Ar/H_2) together. In the case of acetylene, the carbon source was diluted to a concentration of approximately 0.5% by Ar, and the optimal ratio between the carrier gas and Ar with acetylene was found to be 400/8 sccm. Under these optimized conditions, the average nanotube length was around 40 µm with both carbon sources. It is also evident from Fig. 3 that the SWCNT yield obtained from ethanol was higher than from acetylene. Interestingly, the yield and average length of the nanotubes were both considerably enhanced when a mixture of ethanol and acetylene was used as the carbon source. To obtain the best result, the same flow rate of 4 sccm was applied to both ethanol and acetylene in the mixed process and the flow of the carrier gas was set to 400 sccm. As



Fig. 1. SEM images of SWCNT grown using water pretreatment at (a) 500 and (b) 700 °C. (c) Histogram of SWCNT length distributions obtained using various pretreatments. The length of the SEM scale bars is 25 μ m. A colour version of this figure can be viewed online.



Fig. 2. SEM images of SWCNT grown on (a) SiO₂/Si, (b) quartz and (c) air-oxidized quartz substrates. (d) Histogram of length distributions of SWCNT on various substrates. The length of the SEM scale bars is 15 μ m. A colour version of this figure can be viewed online.

shown in Fig. 3d, many long nanotubes were generated under this condition, with an average length of 130 $\mu m.$

3.4. Characterizations of SWCNT by Raman

Raman has been proved to be an effective technique to characterize the chirality of SWCNT. To verify whether these CVD-grown nanotubes actually originated from the initial seeds, Raman analyses with a wavelength of 785 nm laser were employed to check the samples at every growth stage. For comparison, the typical SEM images of nanotube seeds and re-grown SWCNT are also demonstrated in Fig. 4a and b, respectively. Accordingly, the average length of nanotube seeds is about 1 µm, whereas longer nanotubes are observed after CVD growth. On the Raman spectrum of asdeposited nanotube seeds (Fig. 4c), a clear G-band peak at high frequency range and several radical breathing mode (RBM) peaks at low frequency range are found. The RBM peaks at 229, 237 and 268 cm^{-1} can be tentatively assigned to (10, 5), (11, 3) and (7, 6), respectively [24–26]. To ensure the Raman signal originate from the grown nanotubes, suspended SWCNT is prepared and its Raman spectra were taken. It is evident in the Raman spectra (Fig. 4c) that almost identical profiles and peak positions were obtained from the as-deposited nanotube seeds, seeds after pretreatments and CVD-grown SWCNT. This Raman analyses clearly prove that the nanotube seeds survive the harsh pretreatment and the CVD-grown SWCNT really comes from the seeds.

3.5. Cold-wall CVD grown SWCNT

To further evaluate the effectiveness of this procedure, the regrowth of SWCNT was also performed in the chamber of the SEM. In this case, SWCNT with (6,5) chirality was used as nanotube seeds. Similarly, ethanol, acetylene and their mixture were used as the carbon sources. Despite varying the experimental conditions, no nanotubes could be synthesized using solely ethanol. In contrast, numerous SWCNT was obtained from acetylene, as shown in Fig. 5a. Most of these SWCNT was short (<2 μ m), although there were also a few long nanotubes (>10 μ m). In the case of using the mixture of ethanol and acetylene as shown in Fig. 5c, many SWCNT was found, in which several nanotubes were longer than 30 μ m. The average length of the SWCNT was about 8 μ m, a value that was significantly greater than that obtained using solely acetylene.

To control the growth condition more precisely and to study the influences of the carbon source on the growth process, another



Fig. 3. SEM images of SWCNT grown using (a) acetylene, (b) ethanol and (c) a mixture of acetylene and ethanol as carbon sources. (d) Histogram of length distributions of SWCNT obtained when using various carbon sources. The length of the SEM scale bars is 25 μ m. A colour version of this figure can be viewed online.



Fig. 4. Identification of nanotube seeds and re-grown SWCNT on SiO₂/Si substrate: (a) SEM image of nanotube seeds, (b) SEM image of re-grown SWCNT, and (c) Raman analyses of as-deposited nanotube seeds, seeds treated in air at 500 °C, seeds treated in air and water at 500 °C and re-grown SWCNT. The length of SEM scale bar is 2 µm. A colour version of this figure can be viewed online.

heater (a filament) was installed into the SEM chamber. The results are summarized in Fig. 5d. The nanotube growth was greatly affected by the temperature of this heater when using only ethanol as the carbon source, such that SWCNT was only obtained when employing the high-temperature filament (Fig. 5d). On the contrary, when using acetylene as the carbon source, SWCNT could be synthesized when the filament was switched off. In the case of the mixture of ethanol and acetylene, SWCNT was formed when using a low filament temperature or when it was off.

4. Discussion

The influences of various factors on the re-growth of nanotubes have been carefully investigated and the associated conditions have been optimized. As a result, the yield and the length of the SWCNT were both considerably improved. There are two important aspects of this re-growth process: an indispensable pretreatment and a narrow growth window. In fact, similar procedures were used for the pretreatment of SWCNT seeds in previous studies, in which the SWCNT seeds were annealed at 200 °C in air followed by water treatment at 400 °C [16,20]. In comparison, pretreatment in the present study was relatively harsh since the air oxidation and water treatment were performed at 500 °C. Using this pretreatment, high yields of long re-grown nanotubes were obtained from seeds under optimized growth conditions. Moreover, the re-growth of SWCNT could also be performed using a cold-wall CVD system. These results further confirmed that this re-growth procedure is robust since it can be reproduced in different situations. The overall SWCNT re-growth process is illustrated in Fig. 6. The pretreatment, including air oxidation and water treatment, likely generates certain chemical groups on the edges of the nanotube seeds and these initiate the SWCNT growth. During growth, reactive carbon species generated by the decomposition of the carbon source may directly attach on the seed surfaces to assemble nanotube structures. Therefore, the formation of a clean, smooth surface is essential to promote efficient SWCNT growth since it favors the

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Fig. 5. SEM images of SWCNT obtained from cold-wall CVD using (a) acetylene, (b) ethanol and (c) a mixture of acetylene and ethanol. (d) Summary of the cold-wall CVD grown SWCNT. A colour version of this figure can be viewed online.



Fig. 6. The growth process of SWCNT from nanotube seeds. A colour version of this figure can be viewed online.

diffusion of these carbon species on the surface and hence the elongation of the nanotubes. The balance between the generation of reactive species and their assembly on the edges of the nanotubes must also be carefully maintained. Otherwise, the formation of extensive carbon radicals may result in the synthesis of amorphous-like carbon and terminate the growth process.

In the re-growth of nanotubes from seeds, there are some points in common for these two CVD systems. Firstly, the pretreatment is indispensable for both systems. Without proper pretreatment, almost no re-growth of nanotubes could be achieved. Another common factor is the carbon source; the mixture of acetylene and ethanol proved to be very effective for these two CVD systems. Unlike conventional hot-wall CVD, only the substrate was heated in the cold-wall CVD. In this case, re-growth could be realized using acetylene or a mixture of ethanol and acetylene when the secondary heater (a filament) was switched off. In contrast, when the temperature of filament was set to high temperature, the re-growth of SWCNT became possible from ethanol source. Thus, it is reasonable to conclude that the pyrolysis products of ethanol including C₂H₄, H₂O, C₂H₂, CH₄, CO and H₂ [27,28], actually supply the reactive carbon species for the elongation of nanotube seeds. In the case of acetylene source, its pyrolysis products such as H_2 , C_6H_6 , C_4H_4 , C_2H_4 and CH_4 , may not be responsible for this growth process, as has been demonstrated previously [29,30]. Therefore, acetylene itself is likely to be the direct carbon species for the elongation of nanotubes since acetylene is an active precursor [31,32] and its pyrolysis actually hampered the re-growth of SWCNT. The promotional effects of ethanol on the re-growth of nanotubes may be due to the formation of H₂O after its decomposition, by which the attached amorphous carbon on the growth edge can be effectively removed. As the result, the growth of SWCNT using mixture of acetylene and ethanol is largely promoted. Although the exact growth mechanisms during re-growth of the SWCNT are still not clear, it is reasonable to surmise that the cloning of SWCNT follows the same reaction mode as Diels-Alder cycloaddition, where acetylene is incorporated into the structure edges [16,33].

5. Conclusion

In summary, we have demonstrated the re-growth of SWCNT from seeds, both in hot-wall and cold-wall CVD systems. By comparing the results of these two CVD systems, a re-growth process and growth mechanism have been proposed. The parameters affecting the re-growth of SWCNT were comprehensively investigated and optimized. Long, dense SWCNT was synthesized with a mixture of ethanol and acetylene on an air-annealed quartz substrate. The research provides an experimental evidence to show that acetylene is a direct carbon species for the elongation of SWCNT, which suggests that the re-growth of SWCNT follows the mode of Diels—Alder cycloaddition. The systematically studies deepen our understanding on the re-growth of SWCNT and promote the research on the mass production of chirality-defined SWCNT.

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