OXIDANT DURING ALIGNED CARBON NANOTUBE GROWTH: A POWERFUL TOOL IN STRUCTURE MODULATION AND RELEASE OF ARRAYS

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Introduction

In carbon science, the oxidation atmosphere (such as O_2, H_2O and CO_2) is widely used as a powerful tool in produce activated carbons. The mechanism of the reaction between the oxidants and the carbon materials have also been widely investigated by Walker Jr's group [1] and other groups [2]. However, the exploration of the applications oxidant in the field of carbon nanotubes (CNTs) was still limited.

Though extensively studied, the synthesis of CNT arrays faced some difficulties. For example, the facile wall-number modulation of CNTs in array for certain applications and the release of the arrays for applications still remained obstacle. It was noticed that under high temperature, the oxidants may react with the solid carbon. Importantly, different kinds of carbon materials (graphite carbon, amorphous carbon, etc) may possess different stabilities under oxidation atmosphere, which provided the possibility of selective etching of carbon material under oxidation atmosphere. The ability of selective etching may promote the synthesis of CNTs and CNT arrays in above mentioned fields.

Herein, we reported the application of weak oxidant (CO_2) in the synthesis of CNT arrays. The selective etching of the unstable carbon was realized, and the modulation of wall-number distribution [3], clearance of amorphous carbon and the release of CNT arrays from the substrate [4] were achieved simultaneously.

Experimental

Modulation of wall number: Electron beam evaporation was employed to deposit Al_2O_3 (10.0 nm), Fe (1.0 nm) and MgO (1.0 nm) sequentially on a silicon wafer with SiO_2 of 600 nm thickness as catalyst. The silicon wafer was then cut into small pieces (5.0 mm × 5.0 mm) and put in a quartz tube for CVD growth. In a typical growth process, the quartz tube was positioned in the tube furnace and the temperature was risen under the protection of Ar and H_2. When the temperature reached 750 ^oC, CO_2 and C_2H_4 was introduced into the quartz tube to start the synthesis of CNT arrays. The concentration of CO_2 was varied to modulate the growth of CNT arrays. After a one-hour growth, the supply of C_2H_4 and CO_2 was shut off and the reaction chamber was cooled down under Ar protection.

Release of CNT arrays: The CNT arrays were synthesized on quartz plates (size: 30×10×2.0 mm) using ferrocene as the catalyst precursor and xylene as the carbon source. The xylene solution was injected into the reactor with a feed rate of 6.0 ml/h using a motorized syringe pump after the react temperature reached 800 ^oC under carrier gas. After the growth of CNT array, the feed of xylene solution and hydrogen were terminated. Then, the temperature of the reaction zone was left to be cooled down to 700 ^oC and the oxidative reagent (CO_2) was introduced into the reactor. The oxidation atmosphere lasted for half an hour, after which the furnace was cooled down to room temperature under Ar protection. For a typical experiment, the concentration of CO_2 was 4000 ppm for oxidation.

The morphology of the CNT forests was characterized by a JSM 7401F high resolution scanning electron microscope (SEM) operated at 5.0 kV and a JEM 2010 high resolution transmission electron microscope (TEM) operated at 120.0 kV. Raman experiments were performed with a Renishaw RM2000 Raman spectrophotometer with 633 nm excitation.

Results and Discussion

Modulation of wall number: After the synthesis of CNT arrays on silicon wafer under different CO_2 concentration, TEM images were taken to analyze the wall number distribution of CNTs in the sample. Fig. 1a illustrated the wall number distribution of as-grown CNTs. As indicated by the stack bars, the content of double-walled CNTs was near 50% and the content of single-walled CNTs was below 20% without CO_2 addition. While for CNTs grown with the assistance of CO_2, the content of single-walled CNTs gradually increased from 20% to 71%. Together with the increasing of single walled CNT content, CNTs with large wall numbers (triple- and multi-walled) were eliminated. Besides modulating the wall number distribution, the presence of CO_2 in the growth atmosphere can also change the diameter of CNTs. The mean diameters of CNTs in the forest were negatively correlated with the concentration of CO_2. By introducing CO_2 with the concentration of 36.8 mol%, the average outer diameter decreased from 4.30 to 3.83 nm. The mean diameters of the inner shell of CNTs did not differ a lot with the changing of CO_2 concentration, indicating the addition of CO_2 did not obviously alter the inner diameter.

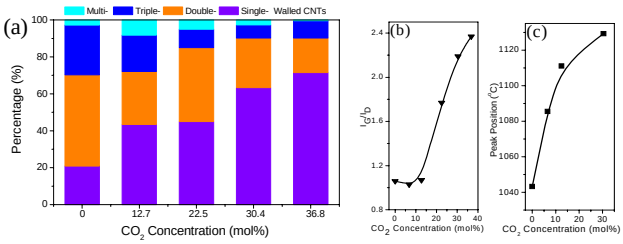

Fig. 1 (a) Changes in wall number distribution; (b) the curve of I_G/I_D ratio of the CNT forests, (c) the position of the weight loss peak (TG under CO_2 atmosphere).

The curve for I_G/I_D value under various CO_2 concentrations was given in Fig. 1b to show the graphite crystallization degree of the samples. The I_G/I_D value increased dramatically under high CO_2 concentration. The I_G/I_D value of CNT forest derived under CO_2 concentration of 36.8 mol% reached 2.37, indicating a relatively low content of carbonaceous impurities.

To identify the stability of CNT forests obtained under different CO_2 concentrations, the TG test under CO_2 atmosphere was employed. The peak position of the weight loss appeared to increase with higher CO_2 concentration during the synthesis process, indicating the enhanced stability of CNTs in CO_2 because of the selective oxidation (Fig. 1c).

Release of CNT arrays: The structures of the separated CNT array with and without the oxidation process were shown in Fig. 2a and 2b. The post oxidation of CO_2 significantly reduced the interaction between CNT arrays and the substrate by selectively etching the carbon around the catalyst particles. Consequently, the arrays can be easily separated from the substrate with the pristine structure maintained. No evidence of damage can be observed due to the avoidance of strong mechanical force in the release process. The morphologies of CNT roots were also well preserved. Some CNTs were with catalyst particles, while others were free of catalyst particles (Fig. 2a). Comparatively, the mechanical separation of CNT arrays without CO_2 oxidation caused severe damage to the CNTs. The roots of CNTs in the arrays exhibited clear orientation, which was caused by the strong array-substrate interaction and the damage of blades. The CNTs on the root ruptured due to the shear strength during the blade peeling process and few catalyst particles can be found at the root of CNTs (Fig. 2b).

The oxidation can also improve the purity of the CNT arrays. The TGA results under CO_2 atmosphere (Fig. 2c) confirmed the elimination of amorphous carbon, in which the weight loss peak corresponded to the amorphous carbon (near 770 ^{o}C) disappeared for the samples with CO_2 oxidation. This result consisted well with the Raman data, which showed an obvious improvement of I_G/I_D value in all positions (Fig. 2d). Besides, it was found that the top part of CNT arrays showed higher crystallization degree compared with the bottom part, which may be attributed to the concentration gradient and reaction consumption of CO_2 in this process.

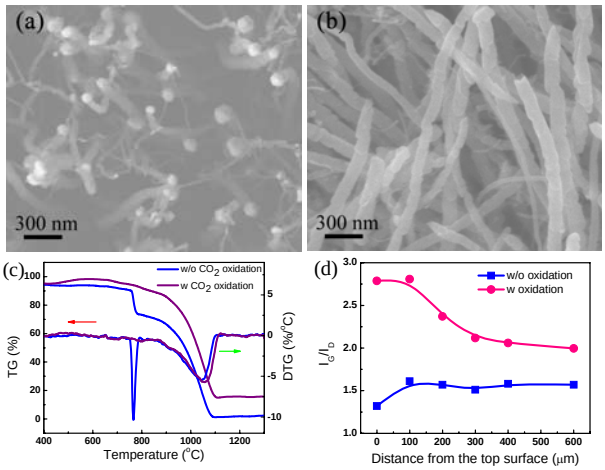

Fig. 2 SEM image on the bottom of released CNT arrays (a) with CO_2 oxidation and (b) without CO_2 oxidation; (c) TGA curve of CNT arrays with CO_2 oxidation; (f) I_G/I_D values at different positions on side walls of pristine and oxidized arrays.

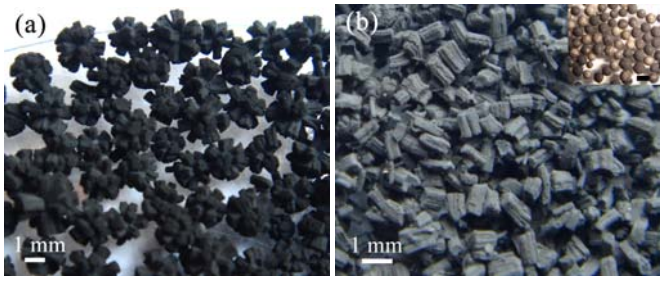

Fig. 3 (a) The as grown CNT arrays on ceramic spheres; (b) The released CNT arrays by simple mechanical vibration after the CO_2 oxidation. The insert shows the bare ceramic spheres after the detachment of CNT arrays, the scale bar was 1 mm.

Finally, it should be noticed that this presented simple oxidation approach was suitable to release free standing CNT arrays from various substrates of various compositions. As shown in Fig. 3, free standing CNT arrays can be easily released from spherical ceramic substrates [5] with CO2 oxidation. With the oxidation, the connection between CNT pillars and the substrate was weakened and the mechanical force can be applied to realize the separation. This oxidation strategy can be easily scaled up to obtain large quantity of free standing CNT arrays on irregular substrates.

Conclusions

CO_2 was used as weak oxidant to modulate the wall number distribution and assist the release process of CNT arrays from the substrates. By controlling the concentration of CO_2, the content of single-wall CNTs can be varied between 20% and 70%. The introduction of CO_2 may also reduce the interaction between CNTs and the substrate, which facilitate the easy separation without damage the pristine structure of arrays. Meanwhile, in the oxidation process, the amorphous carbon can be selectively etched, which greatly improve the quality of CNT arrays. The application of CO_2 was promising in the controllable synthesis and separation of CNT arrays.

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