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Study of Effect of Temperature on the Synthesis of Carbon Nanotubes by Floating Catalyst Method

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Abstract

Carbon nanotubes (CNTs) were grown by floating catalyst method using acetylene as carbon precursor and ferrocene as catalyst precursor. The CNTs were grown in the temperature range of 700 - 1150°C. The prepared CNTs were purified by acid treatment and air oxidation methods. The purified CNTs were characterized by scanning electron microscopy, transmission electron microscopy and Raman spectroscopy. The purity of CNTs was determined by thermal analysis and X-ray diffraction method. The yield, diameter and length of grown CNTs were same at all temperatures. The crystalline perfection of CNTs increases as the temperature increases. Our results indicated that the synthesis temperature could affect the degree of graphitization of CNTs.

Keywords: Carbon nanotubes, Floating catalyst method, Double stage CVD, Effect of temperature

Introduction

Since the discovery by Iijima,[1] carbon nanotubes (CNTs) have drawn much attention and intensive research has been carried out. This great interest is due to CNTs unique microstructure, low density and they posses excellent mechanical and electrical properties, that enable them to be applied in many promising fields, such as; mechanical reinforcements in polymer composites,[2] nanoelectronics devices,[3] hydrogen storage,[4] biosensors,[5] fuel cells,[6] field emitters[7] and as catalyst supports.[8]

Until now various synthesis methods have been developed for the production of CNTs, including are arc discharge,[1] laser ablation,[9] chemical vapor deposition (CVD)[10] and so on. The main disadvantage of arc discharge and laser ablation method is that they are uncontrolled in the process parameters. Compared with arc discharge and laser ablation method, CVD is simple, cheap and parameters are easily controlled. The CVD method requires both the metal catalyst (Ni, Co and Fe) and a carbon source to produce CNTs. The introduction of a catalyst divides CVD methods into floating catalyst methods group, using a catalyst in the gas phase and fixed catalyst methods group with supported catalyst. The main advantage of floating catalyst method is that it does not require the stage of catalyst preparation as in the case of fixed catalyst method because the catalyst particles are continuously formed in the reactor and catalyst deactivation problem is avoided. Generally, organometallic compounds formed by transition metal (Ni, Co or Fe) are mainly used as precursors in the floating catalyst method.

In this paper, we investigated the CNT synthesis by floating catalyst method by using ferrocene as catalyst precursor and acetylene as carbon precursor. The effect of temperature on the synthesis of CNTs was also studied. The CNTs synthesised were characterised by using scanning electron microscopy, transmission electron microscopy and Raman spectroscopy. The purity of CNTs was determined by thermal analysis and X-ray diffraction studies.

Materials and Experimental Procedures

In order to synthesise CNTs, the apparatus (Figure 1) consists of two stage furnace system fitted with quartz tube (25 mm Inner Diameter, 1200mm Length). Argon gas was used as carrier gas and acetylene gas was used as carbon precursor. The amount of carbon deposit was studied at different flow rates at 850°C for better yield. We investigated the effect of temperature on the quality of CNTs synthesised at gas flow rates of acetylene (15 sccm)

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and argon (500 sccm). 100 mg of ferrocene was taken in the quartz boat and placed inside the quartz reactor. The preheater furnace was heated to 230°C, after the temperature in the second furnace reached to desired temperature (700-1150°C). Acetylene gas flow was allowed for 10 min. Finally, the furnace was cooled to room temperature in the argon flow. Carbonaceous material was deposited as a black film onto the walls of quartz tube, which was collected.

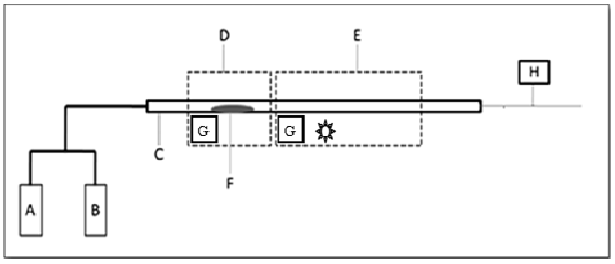

Figure 1. Schematic representation of CVD set-up. A-Argon gas cylinder. B-Acetylene gas cylinder. C-Quartz tube. D-Pre heater. E-Reaction zone. F-Quartz boat. G-Controller. H-Water bubbler.

The as grown products contain iron nanoparticles which were removed by an acid treatment with 5N HCl at 80°C for 30min. To eliminate the acid, finally the samples were washed with distilled water. The samples were dried in an oven at 100°C. This was followed by air oxidation to remove the amorphous carbon.

The as grown and purified samples were analysed by Thermogravimetry (TGA, SDT Q600 TA) to determine the amount of metal present and purity of sample after purification. The samples were again characterised by using X-ray diffraction method (XRD, JEOL JDX 8P diffractometer with Cu Kα radiation, λ=1.5418A˚) to determine the purity of sample. The microstructure of the samples were obtained by using scanning electron microscope (SEM, SUPRA 40VP Carl Zeiss) and transmission electron microscope (TEM, CM200 Philips). The relative intensities of D-band and G-band were obtained by Raman spectroscopy (Renishaw, RM 1000, He-Ne laser excitation line at 633.0 nm).

Results and Discussion

In order to estimate the purity of the sample, TGA was performed in air. Figure 2 shows the TGA profiles of as grown product at 850°C and its purified sample by acid treatment and air oxidation method. The as grown sample shows the little or no weight loss before 500°C indicating the presence of negligible amount of amorphous carbon and major weight loss after 500°C. The as grown CNTs contain iron particles of 24% in weight. The purified sample shows loss only after 500°C indicates the absence of amorphous carbon and only 1% of iron content was present which was unable to remove from acid treatment. The purity of the sample was again analysed by XRD. The XRD pattern (Figure 3) contains characteristic peaks at 26.0°, 43.5° and 53.5°, indexed with (002), (101) and (004) diffraction planes of hexagonal graphite (JCPDS card files, no 41-1487), respectively.[11] No other noticeable peaks induced by catalyst can be observed in the XRD pattern.

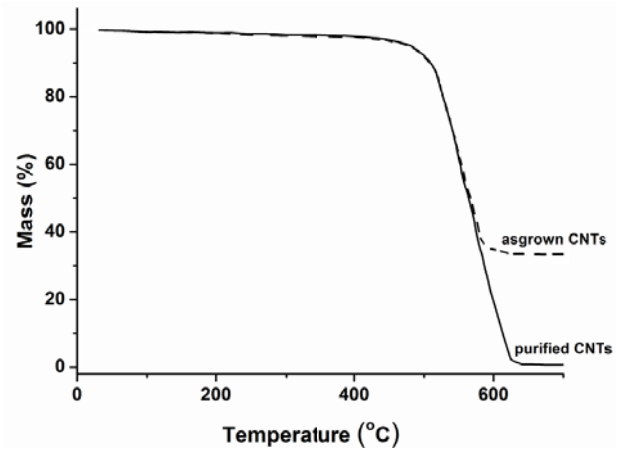

Figure 2. TGA analyses of as grown and purified carbon deposits grown at 850°C

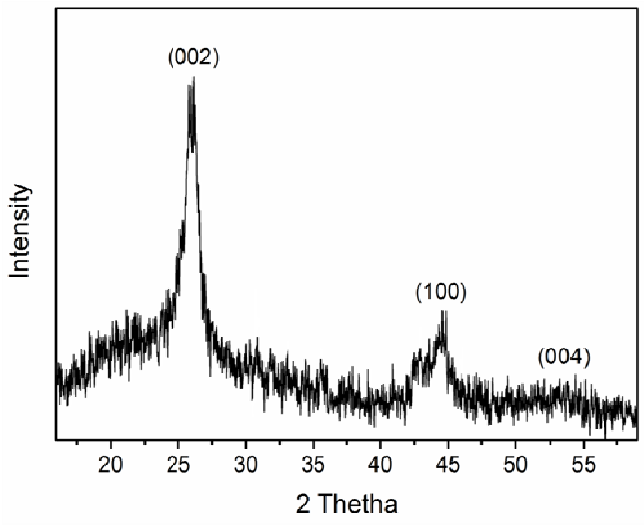

Figure 3. XRD pattern of purified product grown at 850°C

Figure 4 shows SEM images of the purified CNTs grown at 700°C, 850°C, 1000°C and 1150°C

for 10 min. The length and diameter of CNTs remained almost same at all the growth temperatures. The diameter of CNTs was 20-40nm, because of their twisting morphology it is difficult to measure the length of the CNT from the SEM micrographs, but the length can be estimated to be more than several tens of micrometers. The formation of CNTs was further confirmed by TEM. It can be observed from TEM that as temperature increases the crystallization perfection of the graphitic walls of CNTs also increases (Figure 5).

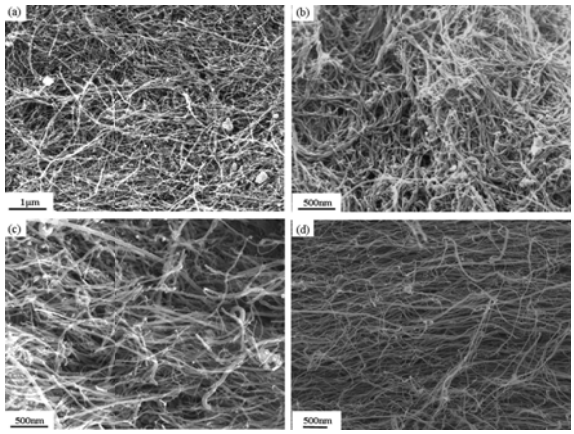

Figure. 4. SEM images of purified products grown at (a) 700°C (b) 850°C (c) 1000°C (d) 1150°C

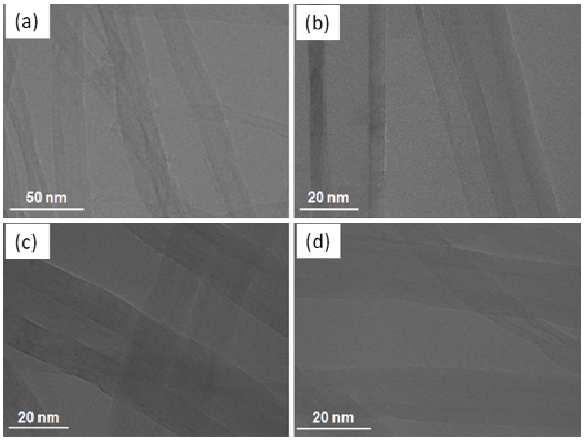

Figure. 5. TEM images of purified products grown at (a) 700°C (b) 850°C (c) 1000°C (d) 1150°C

The Raman spectra obtained from CNTs have shown in the figure 6. All spectra show 2 bands at around 1325cm^{-1} (D-band) and 1575cm^{-1} (G-band). The D-band is due to disordered structure and the G-band is due to the graphitic structure of CNTs. The quality of CNTs can be identified by using the peak intensity ratio of the D-peak to G-peak.[12] The value of I_D/I_G ratio decreases as temperature increases from 700°C to 1150°C. The I_D/I_G value was plotted versus temperature as shown in the figure 7. The plot shows that the crystalline perfection increases linearly with the temperature. The table 1 gives summary of reaction temperature, diameters of CNTs and I_D/I_G values.

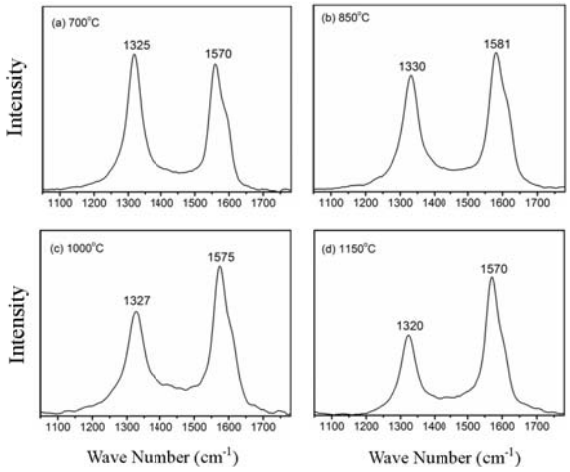

Figure 6. Raman spectra of purified products grown at (a) 700°C (b) 850°C (c) 1000°C (d) 1150°C

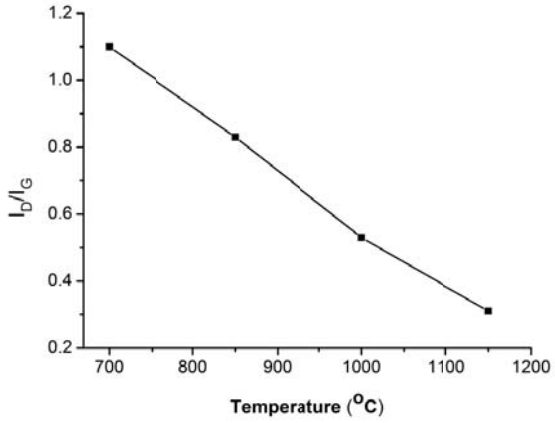

Figure 7. Plot of I_D/I_G ratio versus reaction temperature

Table 1. Summary of reaction temperature, diameters of CNTs and I_D/I_G values

Reaction Temperature (°C)	Diameter of CNTs (nm)	I_D/I_G ratio
700	20-30	1.10
850	25-35	0.83
1000	20-25	0.53
1150	20-30	0.31

The catalytic growth of CNTs has been explained based on vapour-liquid-solid (VLS) model. The VLS model consists of the following steps: (i)

a carbon source is decomposed on the surface of transition metal nanoparticles (ii) liquidised metal carbide is formed by diffusion of carbon atoms into the nanoparticles (iii) after over saturation; the carbon precipitates to form CNTs.

Vaporised ferrocene molecules undergo decomposition in the gas phase or on the surface of the quartz tube in the reaction zone, iron nanoparticles deposit on the quartz tube wall which acts as catalyst. Carbons resulted from the decomposition of acetylene, adsorb on the iron nanoparticles and dissolves to form a miscible alloy. In catalytic iron nanoparticles, as the carbons saturate, they start to precipitate to form the CNTs. Figure 8 shows the supporting TEM image for the carbon nanotube growth model. Initially, they form the graphitic sheets on the catalytic particle (Figure 9a and 9b). As the graphite sheets lifts off the catalytic particle, a closed tip with the inside hollow is produced (Figure 9c and 9d). The diameter of the growing tube was limited by size of the catalytic particle. Probably mainly via bulk diffusion, the carbons accumulated on the surface of catalytic particle dissolves inside the tube. As the temperature increases, carbons can arrive at the reaction site of the growing tube with a higher diffusion rate. Consequently the growth rate of nanotubes increases and the graphitic sheets build up with a less defect. Therefore at the higher temperature, the nanotubes can align better during growth.

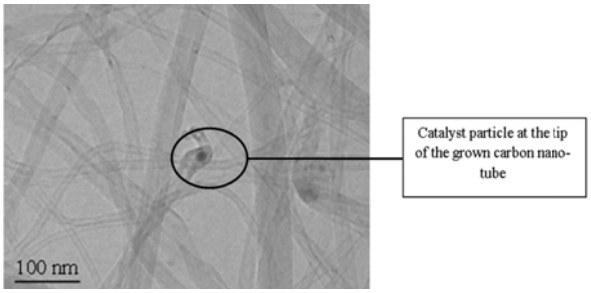

Figure 8. Supporting TEM image for the carbon nanotube growth model

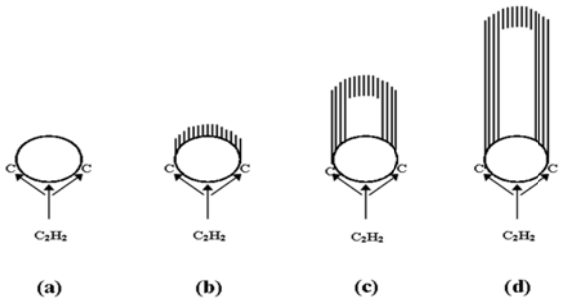

Figure 9. Growth model of CNTs

Conclusions

The CNTs were successfully synthesised by using floating catalyst method. We investigated the effect of temperature on the quality of the grown CNTs. The diameter and yield remained same at all the growth temperature. The purity of CNTs was up to 99%. The I_D/I_G value and TEM results indicates that quality of CNTs increases as temperature increases.

Acknowledgements

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