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A Study on the Effect of Calcination Temperature on the Graphitization of Carbon Nanotubes Synthesized by the Decomposition of Methane

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Abstract. The effect of calcination temperature for Fe_2O_3/MgO catalysts on the formation of carbon nanotubes (CNTs) was examined. CNTs were synthesized over Fe_2O_3/MgO catalysts calcined at different temperatures by catalytic decomposition of methane at 1000^oC. The synthesized CNTs were investigated by a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman spectroscopy. The results show that the effect of calcination temperatures greatly governed the diameter and the quality of the SWCNTs formed. The catalysts calcined at 500, 600 and 700^oC produced CNTs with the diameters of 1.53, 1.95 and 2.97nm, respectively. Generally, an increase in the calcination temperature increases the average diameter and decreases the quality of the CNTs produced.

Introduction

Earlier, Iijima [1] had demonstrated that the filamentous carbon synthesized from the arc-discharge method appeared in nano-scale tubular structure, consisting of two or more tubular graphene (multi-walled carbon nanotubes, MWCNTs). The real breakthrough in SWCNTs synthesis was after the discovery of Bethune [2] and Iijima [3] in 1993. Since then, SWCNTs have attracted a lot of attentions as a new material in this century due to their unique physical and chemical properties [4,5]. SWCNTs have been proven to have great potential applications, including hydrogen storage [6], field emission devices [7], and others. Several techniques such as the electric arc-discharge [1,8], the laser evaporation [8], and the chemical vapor deposition (CVD) [9–11] had been reported for synthesizing SWCNTs. Among these methods, CVD is considered suitable for large-scale and low cost synthesis of SWCNTs [12]. Previously, we had reported the importance of catalyst calcination temperature on the diameter of produced CNTs [13]. We had also synthesized SWCNTs using alumina supported nickel oxide catalyst [14]. There are very few papers reported the effect of calcination temperature for catalyst on the synthesis of SWCNTs. Since calcination temperature is one of the crucial factors affecting the quality of SWCNTs as well as the diameters, the main objective of this study is aimed at investigating the effect of calcination temperature for Fe_2O_3/MgO catalyst on the quality and diameters of synthesized SWCNTs.

Experimental

Preparation of Catalyst. The right amount of $Fe(NO_3)_3 \cdot 9H_2O$ (supplied by Merck) and MgO (supplied by Fluka) were dissolved in distilled water and then mixed stoichiometrically. The mole ratio of Fe_2O_3:MgO was set to 1:9. The mixtures were dried at 100^oC for 12 hours. The catalysts were ground thoroughly into fine powder and then calcined in air at 500^{o}C, 600^{o}C, and 700^{o}C for 3 hours. The powdered materials obtained were used for CNT synthesis.

CNT Synthesis. The synthesis of SWCNTs were carried out at atmospheric pressure in a quartz reactor which was placed vertically in a stainless-steel housing (length and diameter of the reactor are 700 and 20mm, respectively). For synthesizing SWCNTs, 0.2g of catalyst was distributed in the middle part of the quartz tube. The stainless steel reactor was then mounted in an electrical furnace. The catalyst was heated to 1000^{o}C in flowing N_2 (99.999% purity, supplied by Sitt Tatt Industrial Gases Sdn. Bhd.) with a flow rate of 40ml/min. Subsequently, high purity methane (99.999% purity, supplied by Malaysian Oxygen Bhd.) mixed with nitrogen with 1:1 (v/v) was introduced into the reactor once the temperature was stable. The reaction was maintained for 30 min at this process condition, after that the furnace was allowed to cool to room temperature under nitrogen flow at 40ml/min. The CNT in black powder form were finally collected from the quartz reactor for characterization.

Characterization. The structure and morphology of the synthesized CNTs were characterized using a scanning electron microscope (SEM) system (Supra 35VP-24-58) and transmission electron microscope (TEM) system (Philips CM12). X-ray diffraction (XRD) patterns of the fresh catalysts were measured by Siemens D-5000 diffractometer, using Cu Ka radiation and a graphite secondary beam monochromator. Intensity was measured by step scanning in the 2θ range of 10–90^o with a step of 0.02^o and a measuring time of 2s per point. The average size of magnetite crystallites was obtained by Scherrer equation. Raman spectra were recorded using a Raman spectrometer (Jobin Yvon HR 800 UV) with Ar^+ laser excitation with wavelength 514.5nm.

Results and Discussion

Characterization of CNTs. Fig. 1 shows the SEM images of the as-prepared materials produced at temperature of 1000^{o}C using catalyst calcined at 500, 600 and 700^{o}C. Those images show that CNTs were grown on almost all catalyst samples, as shown in Figs. 1a-c. As the calcination temperatures increased, the diameters of CNTs also increased as observed at the SEM images. For Fe_2O_3/MgO catalyst calcined at the 700^{o}C, CNTs with large diameter of 51.36nm were observed, as shown in Fig. 1c.

Figs. 2a-c show the TEM images of the as-synthesized CNTs produced from the catalyst calcined at 500, 600, and 700^{o}C. TEM observation reveals that SWCNT bundles with smaller and uniform diameter were formed by Fe_2O_3/MgO catalyst calcined at 500^{o}C. A mixture of SWCNTs and MWCNTs were synthesized by Fe_2O_3/MgO catalyst calcined at 600^{o}C and 700^{o}C. More than 30 CNTs per sample were taken into account for drawing the diameter distribution histogram as presented in Figs. 2a-c. The solid lines correspond to the Gaussian fits. The results show that SWCNTs with narrower diameters and smaller diameter distributions were grown on the catalysts calcined at lower calcination temperature. It can be summarized that SWCNTs produced by catalyst calcined at 500, 600, and 700^{o}C possessed the diameter of 1.53±0.31, 1.95±0.74, and 2.97±0.86nm, respectively.

In Fig. 2a, the diameter distribution of the SWCNTs grown on the catalyst calcined at 500^{o}C was relatively narrow. These SWCNTs had diameter distributed over a small range of 0.86–2.32nm and with an average diameter of 1.53nm. The corresponding TEM image shows that the diameter distribution of bundles SWCNT was relatively uniform. The corresponding Raman spectrum shows the existence of the strong G-Band at 1589cm^{-1} and weak D-band at 1347cm^{-1}, indicated high degree of graphitization of SWCNTs were synthesized by the catalyst calcined at 500^{o}C. The D-band is known as

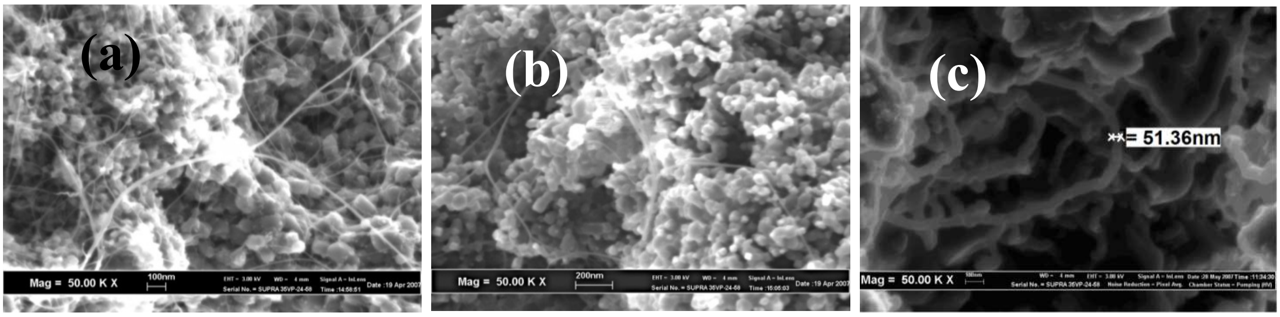


Fig. 1: SEM images of the SWCNTs grown on Fe_2O_3/MgO catalysts calcined at (a) 500^oC, (b) 600^oC and (c) 700^oC, respectively.

the disorder induced due to either the wall disorder or the presence of amorphous carbon deposited on the outer surface of nanotubes. The G-band can be attributed to the degree of graphitization of carbon nanotubes and the ratio of I_D/I_G of the D- and G-band can be regarded as an index for the crystalline order of carbon nanotubes [15]. The obtained I_D/I_G ratio was 0.32 for this carbon sample, indicating the defect level in the nanotubes level is very low. Fig. 2b shows the TEM image of CNTs produced by catalyst calcined at 600^oC. The TEM image shows that these CNTs had larger diameter distribution (marked by arrows) as compared to those CNTs grown on the catalyst calcined at 500^oC. The average diameter calculated was 1.95nm with a standard deviation of 0.74nm. The I_D/I_G ratio calculated was 0.78, indicated the quality of CNTs decreased. Catalyst calcined at 700^oC produced CNTs with diameter ranging from 1.66 to 5.23nm with an average diameter of 2.97nm and standard deviation of 0.86nm. The low degree of graphitization and diameter uniformity of the produced CNTs can be seen clearly in the TEM image in Fig. 2c. The highest I_D/I_G ratio was obtained at 1.10. This result shows that the structures of the produced CNTs contain more defects as compared to the CNTs produced by former two catalysts. The carbon sample contains more MWCNTs as compared to the SWCNTs as observed in the TEM images. The I_G/I_D ratio for CNTs produced by catalyst calcined at 500, 600, and 700^oC was plotted in Fig. 3. This shows that an increase of calcination temperature increases the I_D/I_G ratio and reduces the quality of produced CNTs. This may be due to the poor-crystalline nanotubes structures formed by the larger sizes of catalyst particles. The results obtained were in agreement with the works by Dai et al. [16] and Pérez-Cabero et al. [17] that the larger catalyst particles lead to the formation of other forms of carbon than nanotubes.

Fig. 4 shows the Raman spectra of the CNTs sample measured in the radial breathing mode (RBM) range. It is clear that the band shape is quite different from one line to another. This is because the sample contains CNTs with different diameter distribution. The shapes of the RBM bands depend on the relative population of each nanotube type that is in resonance with the laser excitation frequency. RBM modes arise from the symmetrical expansion and contraction of the tubes around the tube axis by the carbon atoms moving radially, and they are unique to carbon nanotubes. These features are occurred with frequencies ω_{RBM} between 120 and 350cm^{-1}. These RBM frequencies are therefore very useful for identifying whether a given carbon material contains SWCNTs, through the presence of RBM modes, and for characterizing the nanotube diameter distribution in the sample through the use of the relation d_t /nm = 248/ ω_{RBM}/cm^{-1} [18,19]. In this work, the Raman spectra obtained in the low-frequency domain show several components between 120 and 350 cm^{-1} (Fig. 4). According to above expression, the diameters of nanotubes were calculated, as shown in Fig. 4. It is important to note that two significant peaks with high intensity at Raman shift 170cm^{-1} and 185cm^{-1} were observed in Fig. 4a. The presence of the two high intensity peaks in RBM tells us that most of the synthesized SWCNTs appeared to be almost uniform in diameter with majority SWCNTs possessed diameters of 1.46 and 1.34nm.

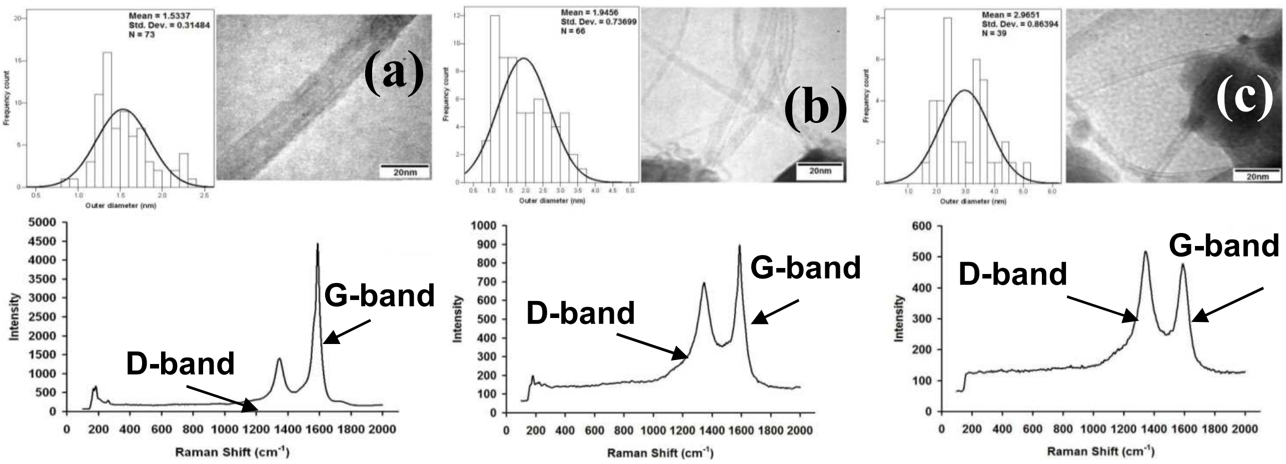


Fig. 2: (Left) Histogram of SWCNT diameter distributions; (Right) TEM image of SWCNTs; (Bottom) Raman spectra of SWCNTs grown on Fe_2O_3/MgO catalysts calcined at (a) 500°C, (b) 600°C and (c) 700°C, respectively.

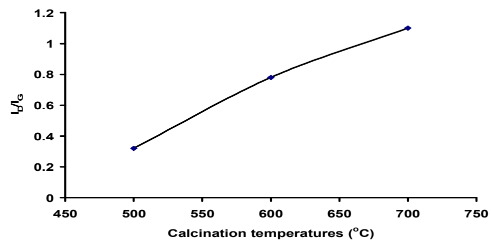
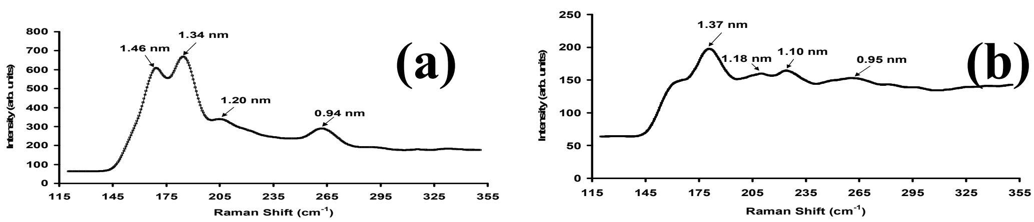


Fig. 3: Variation of I_D/I_G ratios with increasing calcination temperatures.

In Fig. 4b, a significant peak at 182cm^{-1} was observed. This result indicates that some of the SWCNTs with diameter of 1.36nm were formed by catalyst calcined at 600°C. However, no significant peak at RBM range was found in Fig. 4c due to very low amount of SWCNTs were produced by the catalyst calcined at 700°C in various diameters.

Characterization of Catalyst. Fig. 5 is the powder XRD patterns of the freshly prepared Fe_2O_3/MgO catalysts calcined at 500, 600 and 700°C. The representative peaks for magnetite ($Fe+2Fe_2+3O_4$) is denoted in the XRD spectra. It is noticeable that the width of the diffraction peak at 43° and 62.5° decreased with increasing calcination temperatures from 500°C to 700°C. This result shows that the lower calcination temperature resulted in formation of smaller crystallites sizes of magnetite. The crystallite sizes of magnetite for the catalyst calcined at 500, 600, and 700°C are tabulated in Table 1. At calcination temperature of 600 and 700°C, high mobility of materials was expected to exist. This mobility led to a ripening of the catalyst particles. Crystals grew by absorbing material from the vicinity and larger crystallites continued growing at the expense of smaller ones nearby, known as Ostwald ripening [20]. Therefore, the increase in calcination temperature to 700°C caused magnetite to be sintered from smaller crystallites sizes of 23.09nm to bigger crystallites sizes of 29.28nm. We speculate that the larger crystallites resulted in formation of larger magnetite cluster which formed the larger diameters of CNTs and wider diameters distributions.



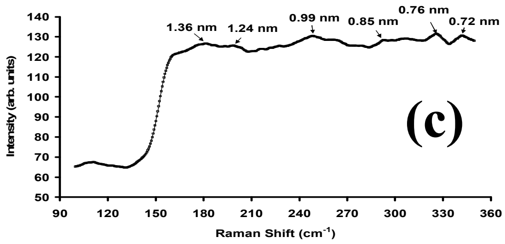


Fig. 4: Radial breathing mode (RBM) of Raman spectra for SWCNTs grown on Fe_2O_3/MgO catalysts calcined at (a) 500°C, (b) 600°C and (c) 700°C, respectively.

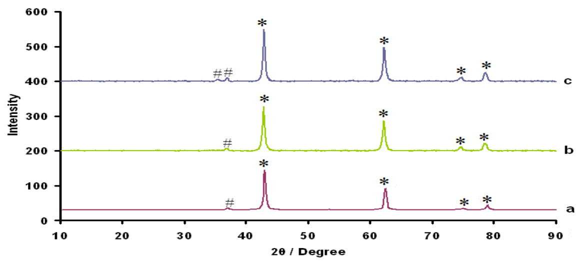


Fig. 5: XRD patterns of Fe_2O_3/MgO catalysts calcined at (a) 500°C (b) 600°C, (c) 700°C. The peaks marked by # and * are correspond to magnetite and MgO, respectively.

Summary

SWCNTs were synthesized at 1000°C by catalytic decomposition of methane over Fe_2O_3/MgO catalyst. SWCNTs with narrower diameter distribution and good quality were synthesized by catalyst calcined at 500°C. Those catalysts calcined at 600°C and 700°C formed larger diameter distribution and lower quality of CNTs. TEM observation reveals that nanotubes synthesized by catalyst calcined at 500°C consisted of SWCNT bundles and had better morphology. We had found that the proportion of diameter of CNTs increases with increasing calcination temperature. Raman analysis further reveals that increase in calcination temperature increase the I_D/I_G ratio and reduce the quality of the produced CNTs.

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