EFFECT OF PYROLYSIS TEMPERATURE ON THE MORPHOLOGICALQUALITY OF CARBON NANOTUBES SYNTHESIZED VIA CHEMICAL VAPOR DEPOSITION METHOD

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Abstract

Among all reaction parameters involved in the chemical vapor deposition (CVD) method of carbon nanotubes (CNTs) synthesis, the working temperature is regarded as the most influential determinant of the morphological quality of the as-grown materials. To investigate this effect, Fe_2O_3/Al_2O_3 catalyst nano-particles were prepared by the impregnation and calcination of $Fe(NO_3)_3.9H_2O/Al(NO_3)_3.9H_2O$ precursor salts, respectively, at 450^oC. Samples of multi walled carbon nanotubes were grown via CVD pyrolysis of C_6H_{14}/N_2 feedstock on the prepared catalyst. The CVD catalyst loading, gas flow-rate and pyrolysis time were kept constant at 1 g, 100 mL/m and 1 hour, respectively, while the working temperatures were varied at 650^oC, 750^oC and 850^oC. Field Emission Scanning Electron Microscopy (FESEM), transmission electron microscopy (TEM) and Raman analyses of the as-grown sample CNTs showed increasing morphological quality with increasing temperature. This may suggest good experimental control and validity.

Keywords: CVD; Catalyst; CNTs; Working Temperature; CNT morphology.

1. Introduction

Carbon nanotubes (CNTs) are formed by rolling graphene sheet into a seamless cylinder. They are called single walled carbon nanotubes (SWCNTs) when only one single graphene sheet is used, and multi-walled carbon nanotubes (MWCNTs) when more than two sheets are used. These carbon materials are reported to possess excellent thermal, mechanical, optical and electronic properties that enabled them find applications in the nano technology industries, where they are used in the fabrication of electronic devices, composite materials, sensors and probes, energy storage devise and biological materials (Liu et al. 2017). However, the excellent characteristics of CNTs were dependent on their surface morphologies, making it necessary for researchers to focus their attention towards enhancing the production of quality as-grown materials, especially when using chemical vapor deposition (CVD) method, which was known for its mass production out-put but low quality out-put. Kumar & Ando, (2010) investigated the effect of growth temperature on the morphological quality of CNTs, within the temperature range 500-1000^{o}C. The authors observed very short-length tubes at 550^{o}C and at 600-650^{o}C, there was enormous increase in growth rate increases at the expense of quality. Clean CNTs were obtained at 750^{o}C; above 750^{o}C onward, both the diameter and the diameter-distribution range increased drastically. At 850^{o}C and above, SWCNTs began to form besides MWCNTs and the volume of SWCNTs increased with the increasing temperature.

In the current report, reaction temperature effect on the quality of CNTs is investigated from 650-850ºC CVD working temperatures, with 100ºC interval; CNTs synthesis was achieved via CVD pyrolysis of C_6H_{14}/N_2 carbon feedstock on Fe_2O_3/Al_2O_3 catalyst matrix, while keeping other parameters fixed. External morphologies of the as-grown CNTs were evaluated using field emission electron microscopy (FESEM), while their internal structures were investigated using transmission electron microscopy (TEM). Raman analysis was conducted to compliment these analyses.

2. Materials and Methods

2.1. Catalyst Preparation

$Fe(NO_3)_3.9H_2O$ and $Al(NO_3)_3.9H_2O$ (98%; Fisher) were used as precursor salts for the preparation of the corresponding Fe_2O_3/Al_2O_3 oxide catalyst matrix, respectively, and were estimated using equation (1)

$$M_s = \frac{W_s \times O_m}{w_o \times p_s} \quad (1)$$

where M_s, W_s, O_m, w_o and p_s are the amounts of precursor salt, molecular weight of precursor salt, amount of metal or support oxide needed to obtain the desired SWCNT, molecular weight of metal or support oxide and percentage purity of precursor salt, respectively. Hence, appropriate amount of $Fe(NO_3)_3.9H_2O$ and $Al(NO_3)_3.9H_2O$ were dissolved in 100 mL distilled water in a conical flask and stirred for stirred for two hours, then left for another 24 hours, in order to achieve homogeneity. The nitrate solution was then dried for 48 hours at an adjusted temperature of 90˚C. Calcination was performed in a Vulcan furnace at 450˚C under air circulation for two hours, at a heating rate of 5˚C/min. Solid products were finally cooled to room temperature, manually grounded and stored in sample bottle.

2.2. Synthesis of CNTs

Pyrolysis of C_6H_{14}/N_2 feedstock on Fe_2O_3/Al_2O_3catalyst was carried out in a split type horizontal furnace (LT Furnace STF-30-1200 model) at 650^{o}C, 750^{o}C and 850^{o}C under nitrogen gas flow rate of 100 mL/min. About 1.0 gram of catalyst was loaded in an alumina boat and the pyrolysis time was set for 60 min. at 0.06 mL/min., resulting products were then cooled and scraped into sample bottles.

2.3. Catalyst and CNT Characterization

Morphologies of the catalyst and CNT samples were analyzed using a field-emission-scanning electron microscope (FESEM) (FEI Nova Nanosem 230), operated at 15 kV.

3. Results and Discussion

Figure 1 (a and b) shows the FESEM images of the catalyst before and after calcination, respectively. The surface morphologies of the figures indicated an enhanced increase in the particle surface area of the calcined sample which was recorded in a nanometer scale, as compared with the same sample before calcination which was recorded at the micrometer level.

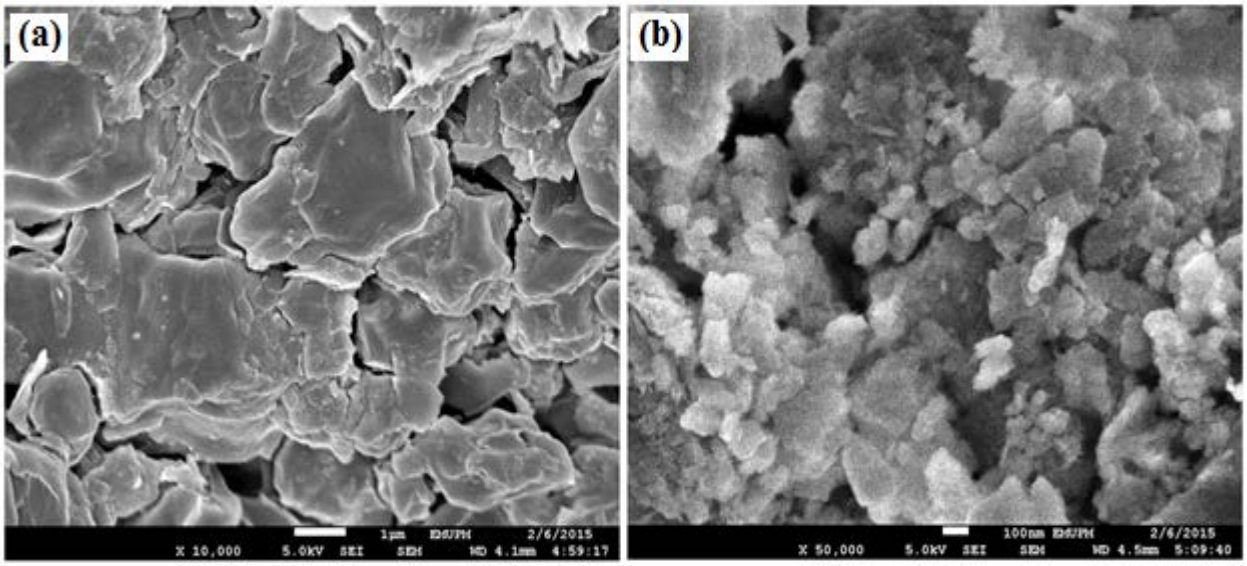

Figure 1: FESEM images of the catalyst matrix (a) before calcination and (b) after calcination showing increase in surface area from micrometer to nanometer scales, respectively.

This was a suggestion that the dispersion of Fe_2O_3/Al_2O_3 catalyst matrix was enhanced at the set temperature of 450ºC. The average crystallite size of the calcined catalyst sample was estimated as 100 nm which was a suggestion that their pore sizes were mesoporous (Liu et al., 2015; Gulshan & Okada, 2013). Figure 2 (a, b and c) shows the FESEM morphological images of as-grown CNT samples synthesized at 650ºC, 750ºC and 850ºC, respectively.

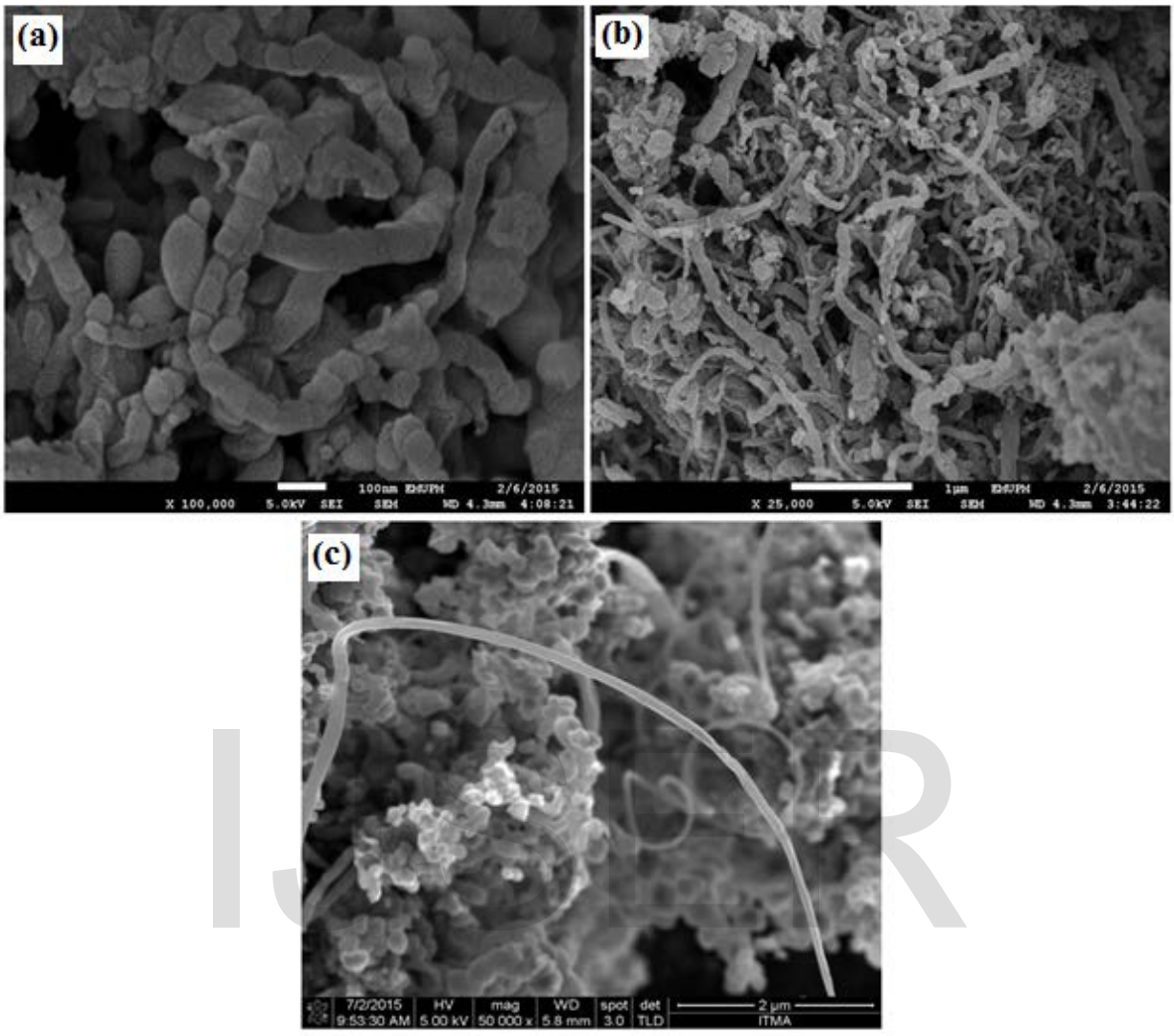

Figure 2: FESEM images of as-grown CNTs (a) synthesized at 650ºC (b) synthesized at 750ºC and (c) synthesized at 850ºC showing enhanced morphological quality with increasing temperature.

Figure 2a morphology appears to be composed of broken tubes with low length to diameter ratio. The cup-like edges may be attributed to the etching effect of nitrogen at specific positions on the hexagonal matrix of the CNT network due to low working temperature (Dong et al., 2015). At 750ºC, the CNTs appeared to compose of fairly long tubes with an average length to diameter ratio, as shown in Figure 2b. The image of CNTs in Figure 2c synthesized at 850ºC shows long tube with a high length to diameter ratio. The TEM images in Figure 3 (a, b and c) were those of

CNTs synthesized at 650^{o}C, 750^{o}C and 850^{o}C, respectively. Figure 3a indicated the presence of internal impurities and poor graphitization; Figure 3b shows clean internal morphology, however, the graphitization was still not very much enhanced. Figure 3c shows a clean and well graphitized CNT. These results also shows enhancement of morphological quality with increasing CVD working temperature. Raman profiles for the CNTs were displayed in Figure 4 (a, b and c) synthesized at 650^{o}C, 750^{o}C and 850^{o}C, respectively. Figure 4 (a and b) indicated that both CNTs samples shows very strong bands at 1353 cm^{-1} and 1355 cm^{-1}, respectively, known as the D-band, which is attributed to presence of amorphous carbon impurities in the samples. The peaks at 1588 cm^{-1} and 1587 cm^{-1}, respectively, called the G-band, are attributed to tangential vibrations of carbon atoms and its intensity is a measure of degree of graphitization in a sample. The ID/IG ratios of the two samples were estimated as ≈ 0.98, which suggested low graphitization and high levels of impurities in the samples (Lehman et al., 2011). The accumulation and diffusion of more carbon atoms due to one hour pyrolysis of the hexane hydrocarbons and the reaction temperature might have resulted in the formation of more amorphous carbon impurities. Figure 4c showed weak D-bands at 1351 cm^{-1}, while the G-band has very strong appearance at 1582 cm^{-1}. From the analysis of this profile, an estimated ID/IG ratio of 0.2 was recorded, indicating high level of graphitization or low impurities in the sample. This sample also showed very strong intensity peaks of G'-bands at 2697 cm^{-1} which according to Lehman et al (2011) was an indication of high degree of long range order in the samples. Another interesting observation on this profile was the weak peak appearing at 2472cm^{-1} which according to Dresselhaus et al (2005), requires good quality and long experimental observation time to detect.

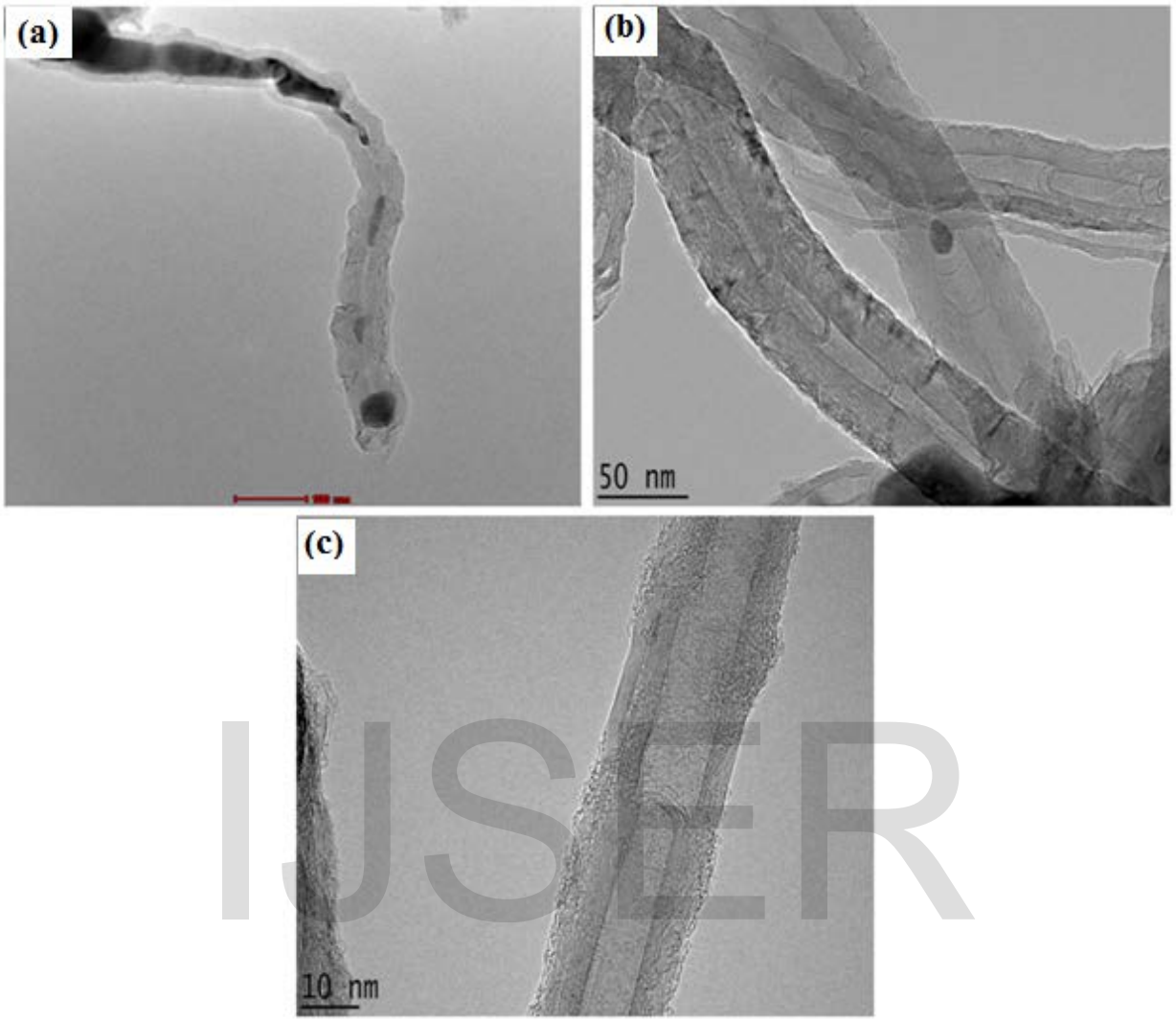

Figure 3: TEM images of CNTs synthesized at (a) 650ºC showing internal impurities and poor graphitization (b) 750ºC showing clean internal morphology but poor graphitization (c) 850ºC showing clean internal structure and good graphitization.

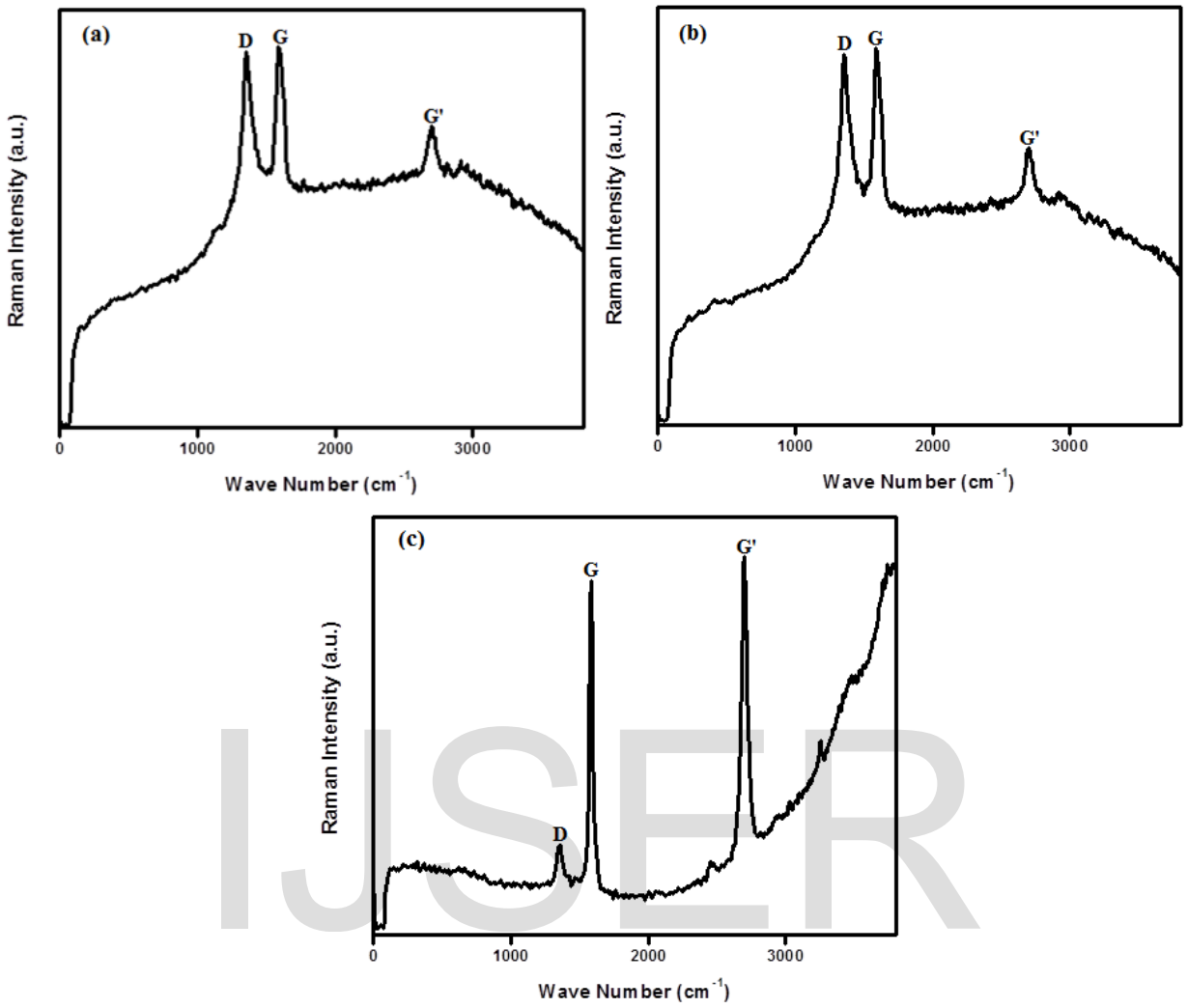

Figure 4: Plots of Raman profiles for CNTs synthesized at (a) 650ºC and (b) 750ºC showing strong intensity of D-band which was an indication of presence of impurities and poor graphitization (c) 850ºC showing weak intensity of D-band and strong G-band suggesting high quality and high degree of graphitization.

Absence of the Radial breathing mode (RBM) frequency peak (< 300 cm^{-1}) in all the sample profiles was an indication that the samples did not contain any SWCNT, and are therefore composed of only MWNTs (Dresselhaus et al., 2005). Results of this finding suggested an overall increase in the morphological quality of the as-grown CNTs with corresponding increase in temperature.

4. Conclusion

Effect of temperature on the quality of CNTs were investigated and the outcome revealed increase in quality of the order 650^{o}C < 750^{o}C < 850^{o}C, suggesting good agreement with experimental facts.

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