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The Effect of Precursor Vaporization Temperature on the Growth of Vertically Aligned Carbon Nanotubes using Palm Oil

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Abstract. Carbon nanotubes (CNTs) were fabricated from palm oil using the thermal chemical vapor deposition technique utilizing a two furnace system. The effect of precursor vaporization temperature of the first furnace, in the range of 300-600°C was systematically studied with the synthesis temperature (second furnace) fixed at 750°C for a total time of 30 min. The samples were characterized using field emission scanning electron microscopy and micro-Raman spectroscopy. CNTs of various packing densities and diameters were synthesized with the varying precursor vaporization temperature. Based on micro-Raman measurements nanotube defect level and the presence of SWCNT were dependent on the vaporization temperature. Vertically aligned CNTs (VACNTs) were found to grow within the vaporization temperature range of 400-500°C, with well graphitized and higher yield obtained at 450°C with excellent lateral alignment, uniform nanotubes diameter (~15 nm), orientation and distribution within the CNT bundles. At vaporization temperatures of 300-350°C and 500-600°C, lower growth rate, bigger nanotubes diameter and higher I_D/I_G ratio were observed which indicated lower nanotubes quality that produced at both temperature ranges.

Introduction

The production of carbon based material namely fullerene and glassy carbon using camphor which was first demonstrated by Mukhopadhyay et al. [1, 2] has inspired further exploration of carbon nanostructure material fabrication utilizing bio-hydrocarbon source. In recent years, camphor [3-7], turpentine [8-11] and eucalyptus oil [12] were used for the production of carbon nanotubes (CNT). In our laboratory palm oil [13] and palm-based dihyrostearic acids (DHSA) [14] has been employed as starting material to grow CNT. At a synthesis temperature 750°C using ferrocene as the catalyst, vertically aligned CNTs (VACNTs) were grown on silicon substrates using palm oil at precursor temperature of 450°C at atmospheric pressure. As an extension of this work we present a correlation of the palm oil vaporization temperature on the formation of vertically aligned carbon nanotubes (VACNTs). Distinct structural differences between the nanotubes produced were presented and discussed based on imaging from field emission scanning electron microscopy (FESEM) and Raman spectra of CNT. Thermogravimetry analysis (TGA) was performed on precursor, catalyst and their mixture for further analysis and comparison.

Materials and Methods

The details of experimental set-up, synthesis process and characterization of the CNT obtained from palm oil were reported elsewhere [13]. Briefly, VACNT was fabricated using the thermal chemical vapor deposition technique utilizing a two furnace system by catalytic decomposition of palm oil in ferrocene catalyst (Sigma Aldrich, 99.9%). The effect of vaporization temperature at first furnace, 300°C, 350°C, 400°C, 450°C, 500°C 550°C and 600°C was systematically studied with fixed synthesis temperature of 750°C for a total time of 30 min. The characteristics of CNT were analyzed using FESEM (ZEISS Supra 40VP) at 5 kV acceleration voltage with the in lens mode and micro-Raman spectroscopy (Horiba Jobin Yvon -DU420A-OE-325) using the Ar+ laser line at 514.5 nm wavelength and power of 20 mW. TGA analysis (Pyris 1 TGA, Perkin Elmer) was carried out in an oxidative ambient at a heating rate of 10^{o}C/min up to 650^{o}C.

Results and Discussions

The effect of palm oil vaporization temperatures on nanotubes formation were investigated in the range of 300 to 600°C in steps of 50°C. Fig. 3 shows the FESEM images of CNT for precursor temperatures of (a) 300°C, (b) 350°C, (c) 400°C, (d) 450°C, (e) 500°C (f) 550°C and (g) 600°C. Low magnification of VACNT arrays are shown at the top right of the images. Apparently, small amount and bigger diameter (100 nm) nanotubes were synthesized at vaporization temperature of 300 and 350°C. The nanotubes were also found to be poor in quality and higher amorphous carbon (a-C) content as evident from Fig. 3 (a) and (b). The image of the sample for vaporization temperature of 400°C (Fig.3(c)), showed well formed VACNT with length of about 64 nm and diameters between 35-45 nm. This gave an average growth rate, R_g, of 2.1 μm/min. The value of R_g was found to increase to 3.8 μm/min at 450°C and to 4.3 μm/min at 500°C. In the 500°C sample, an appreciable amount of amorphous carbon (a-C) growth was noticeable as evident from Fig. 2(e). The reduction of R_g value to 0.57 μm/min was seen at further elevation of palm oil vaporization temperature from 550 to 600°C. The nanotubes array was covered with heap of the a-C layer at thickness of 4.50 to 5.67 nm.

VACNT diameters of 15 nm and less were observed for 450°C sample which showed excellent lateral alignment, uniform nanotubes diameter, orientation and distribution within the bundle as compared to other samples. The average diameter of nanotube was found to increase from about 44 to 90 nm with the increased in precursor temperature of 500-600°C. The presence of a-C that covered-up some part of the nanotubes can be obviously seen for the 600°C sample as shown by the arrow in Fig. 3(g). Lateral alignment also affected by precursor temperature where over 450°C the VACNT lateral alignment was no longer visible.

The observed results can be discussed as follows. Below 450°C, the temperature was not enough to completely vaporize the palm oil precursor. By heating up the precursor at temperature of 300, 350 and 400°C only 4.6, 6.3 and 18.0 % of palm oil were vaporized into a concoction of hydrocarbons for CNT production as shown by thermogravimetric analysis (TGA) (Fig. 4). This is the main reason for the thin layered and poor quality CNT produced. Therefore, the temperatures lower than 450°C were not favourable for high productivity nanotube synthesis. TGA analysis was done on natural palm oil, palm oil- ferrocene mixture and ferrocene which showed that palm oil completely vaporized at ~460°C. The existence of 5.33 wt% of ferrocene in palm oil slightly shifted the vaporization temperature of palm oil to a low value of ~450°C. A step at 220°C was due to the vaporization of ferrocene catalyst which was about 5 % of the total weight. Ferrocene was entirely vaporized at ~190°C. The suitable vaporization for high quality and large scale VACNT was found to be 450°C where only 8% of palm oil remains unvaporized. Meanwhile, due to more energy supply to the palm oil at over 450°C yielded low quality CNTs. The increase in temperature causes the thermal cracking rate of palm oil to become higher. As a result, it is expected that much more hydrocarbon radicals were present at the silicon substrate and caused the catalyst to be deactivated quicker and this condition was most severe at 600°C where only short array of nanotube were observed.

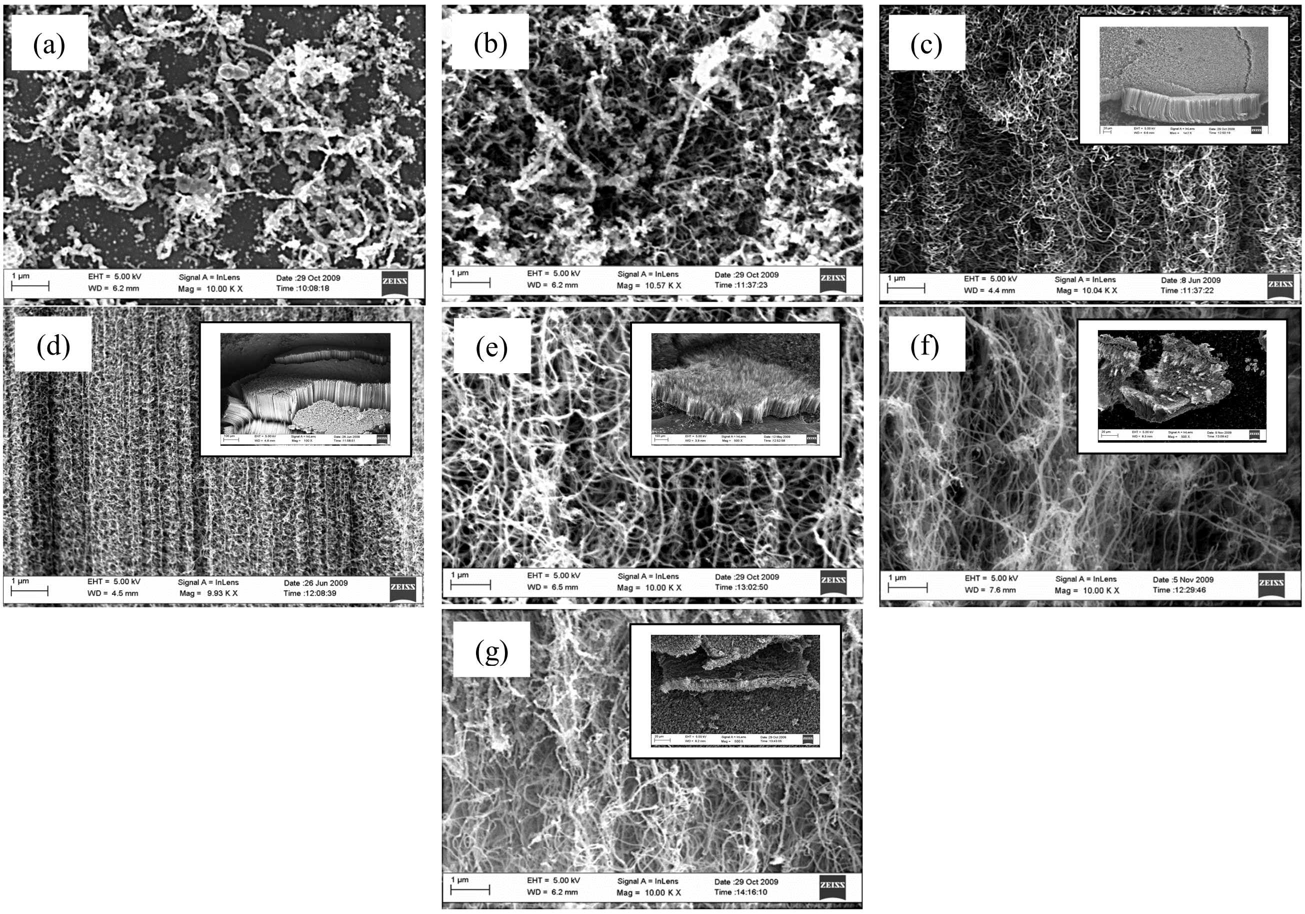

Fig. 1. FESEM images of CNTs synthesized at different precursor temperatures: (a) 300°C, (b) 350°C, (c) 400°C, (d) 450°C, (e) 500°C, (f) 550°C and (g) 600°C.

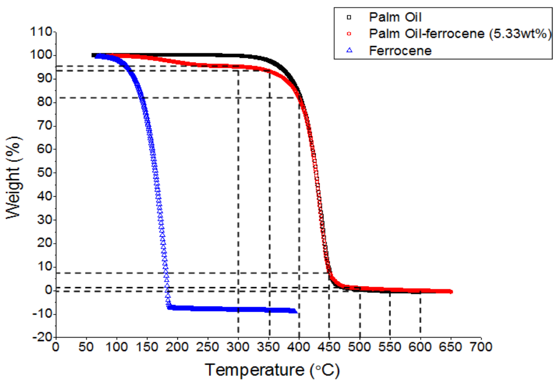

Fig. 2. TGA curves of natural palm oil, palm oil-ferrocene mixture and ferrocene. The dotted line shows the precursor temperature and remaining weight percentage of palm oil.

The Raman spectra obtained at different precursor temperature are shown in Fig. 4(a). Intensity data are tabulated in Table 1. The peaks intensity at ~1574.58-1587.55 cm^{-1} were attributed with the graphitic "G" line and the peak ~1341.16-1352.28 cm^{-1} associates to the disordered "D" line and the "2D" line at ~2700 cm^{-1} were detected at all samples. Small changes in the Raman shift, intensity and full-width half-maximum (FWHM) were observed with the nanotubes produced at different precursor temperature indicating difference in crystallinity. A shoulder at ~1604 cm^{-1} was detected in the Raman spectra of the samples synthesized at 500 to 600°C which may be associated to the disordered induced "D'" line. The ratios, I_D/I_G, were calculated to estimate the variation of CNT quality with precursor temperature. The results obtained were 0.88 for 300°C, 0.75 for 350°C, 0.62 for 400°C and further reduced to a lowest value of 0.52 for 450°C, which clearly showed a trend of increasing CNT crystallinity with increase in temperature. Beyond this temperature, the I_D/I_G ratio increased to a value of 0.69 for 500°C, 0.85 for 550°C and the highest value of 1.23 was found at 600°C sample. Our results indicated that the best crystallinity was obtained at 450°C. The results were found to be consistent when the widths of the 2D Raman peaks were examined. The nanotubes with higher defects at low precursor temperature (300-400°C) and also at high precursor temperature (500-600°C) showed FWHM of 33.94-46.27 cm^{-1}, compared to that of the 450°C sample of 32.07cm^{-1}. As mentioned before, high hydrocarbon concentration resulting from overheating at 500°C and 600°C was the main factor attributing to lower quality CNT.

It is interesting to note that at temperatures lower and equal to 450°C the A_{1g} radial breathing mode (RBM) peak at low wave number region between 100 to 500 cm^{-1} were detected indicating the presence of single-walled CNTs. The possibility of single-walled CNT was due to limited number of carbon which came from insufficient heat supplied at low range temperature of 300-400°C. However, problem with low precursor temperature is that the nanotubes produced were lower in quality as shown by higher I_D/I_G ratio. From the Raman spectrum represented in Fig. 4 (b) there were eleven RBM peaks identified at 212.0, 276.8, 386.5 for 300°C, 225.0, 291.8, 406.9 for 350°C, 216.2, 280.2 for 400°C and 214.9, 277.2, 395.5 for 450°C samples. This corresponds to the tubes diameter of (calculated from [15]) 1.17, 0.90, 0.64 for 300°C, 1.10, 0.85, 0.61 for 350°C, 1.15, 0.89 for 400°C, 1.15, 0.89, 0.63 for 450°C, respectively. Since higher amount of hydrocarbon has been produced at absolutely faster rate at higher temperature range (500-600°C), this enable the formation of larger diameter tubes, vanishing the RBM intensity. The broader 2D Raman peak was also evidence for multi-walled CNTs (MWCNTs) at 500-600°C samples.

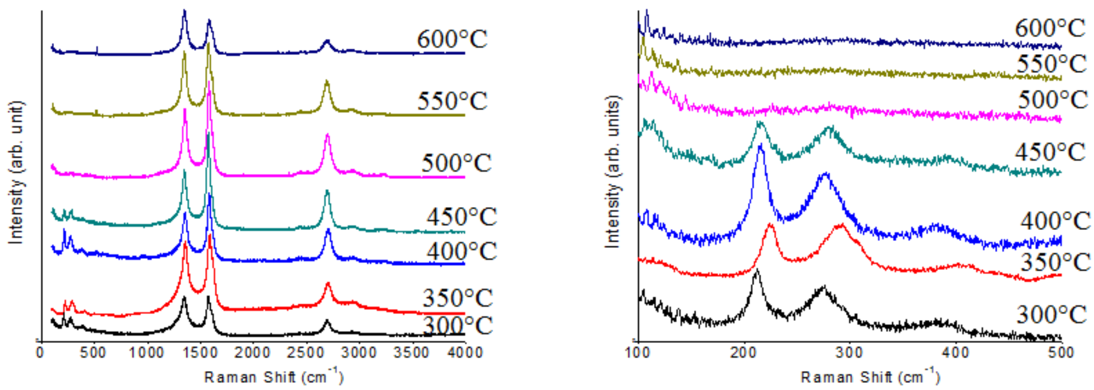

Fig. 3. (a) Typical Raman spectra of palm oil based CNTs synthesized at precursor temperature 300 to 600°C with increment rate of 50°C (b) multiple low frequency peaks associated with radial breathing mode (RBM) appeared at synthesis temperature 300 to 450°C.

Table 1 Raman and RBM peak position, G & D intensity ratios and SWCNT diameter for precursor temperature from 300 to 600°C

Samples/Peak		Peak Position (cm^{-1})	FWHM (cm^{-1})/ SWCNT diameter (nm)	Integrated Intensity Ratio of D, G Bands, I_D/I_G Ratio
300°C	G	1577.65	52.65	0.88
	D	1341.16	97.28	
	2D	2684.81	75.97	
	D’	1604.34		
	RBM	212.0, 276.8, 386.5	1.17, 0.90, 0.64	
350°C	G	1587.55	76.04	0.75
	D	1351.60	128.88	
	2D	2697.72	79.50	
	D’	1607.65		
	RBM	225.0, 291.8, 406.9	1.10, 0.85, 0.61	
400°C	G	1583.35	51.31	0.62
	D	1350.12	87.72	
	2D	2686.37	33.94	
	D’	1609.49		
	RBM	216.2, 280.2	1.15, 0.89	
450°C	G	1574.58	42.51	0.52
	D	1346.05	74.09	
	2D	2679.33	32.07	
	D’	1610.38		
	RBM	214.9, 277.2, 395.5	1.15, 0.89, 0.63	
500°C	G	1582.052	54.19	0.69
	D	1352.28	69.57	
	2D	2681.12	46.27	
	D’	1615.22		
550°C	G	1578.64	60.26	0.85
	D	1346.50	64.29	
	2D	2673.62	45.49	
	D’	1606.58		
600°C	G	1584.77	61.65	1.23
	D	1348.15	63.10	
	2D	2670.94	40.51	
	D’	1606.98		

Conclusions

By varying the precursor vaporization temperature from 300-600°C, nanotubes of various packing density and diameter were synthesized. The nanotube graphitic defect and formation of SWCNTs were found to be dependent on the vaporization temperature. At lower and higher vaporization temperature, both range produced low R_g values with bigger nanotubes diameter and lower qualities which were based on higher I_D/I_G ratio. However, from Raman spectroscopy it was found that at low vaporization temperatures the samples contained SWCNTs. Well formed VACNTs were found to grow within the temperature range of 400-500°C, with a well graphitized and the best yield were observed at 450°C which showed excellent lateral alignment, uniform nanotubes diameter (~15 nm), orientation and distribution within the bundle when compared to other samples.

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References

[1] K. Mukhopadhyay and M. Sharon: Materials Chemistry and Physics Vol. 49 (1997), p. 105

[2] K. Mukhopadhyay, K. M. Krishna and M. Sharon: Physical Review Letters Vol. 72 (1994), p. 3182

[3] M. Kumar, K. Kakamu, T. Okazaki and Y. Ando: Chemical Physics Letters Vol. 385 (2004), p. 161

[4] M. Kumar and Y. Ando: Diamond and Related Materials Vol. 12 (2003), p. 1845

[5] M. Kumar and Y. Ando: Diamond and Related Materials Vol. 12 (2003), p. 998

[6] M. Kumar and Y. Ando: Chemical Physics Letters Vol. 374 (2003), p. 521

[7] M. Kumar and Y. Ando: Carbon Vol. 43 (2005), p. 533

[8] P. Ghosh, T. Soga, R. A. Afre and T. Jimbo: Journal of Alloys and Compounds Vol. 462 (2008), p. 289

[9] R. A. Afre, T. Soga, T. Jimbo, M. Kumar, Y. Ando and M. Sharon, Chemical Physics Letters Vol. 414 (2005), p. 6

[10] R. A. Afre, T. Soga, T. Jimbo, M. Kumar, Y. Ando, M. Sharon, P. R. Somani and M. Umeno: Microporous and Mesoporous Materials Vol. 96 (2006), p. 184

[11] P. Ghosh, T. Soga, K. Ghosh, R. A. Afre, T. Jimbo and Y. Ando: Journal of Non-Crystalline Solids Vol. 354 (2008), p. 4101

[12] P. Ghosh, R. A. Afre, T. Soga and T. Jimbo: Materials Letters Vol. 61 (2007), p. 3768

[13] A. B. Suriani, A. A. Azira, S. F. Nik, R. Md Nor and M. Rusop: Materials Letters Vol. 63 (2009), p. 2704

[14] N. F. A. Zainal, T. I. T. Kudin, A. Azira, A. Z. Ahmed, S. Abdullah, and M. Rusop: American Institute of Physics (AIP) Vol. 1017 (2008), p.112

[15] W. Huang, Y. Wang, G. Luo and F. Wei: Carbon Vol. 41 (2003), p. 2585.

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