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# Effect of Temperature on the Growth of Vertically Aligned Carbon Nanotubes from Palm Oil

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**Abstract.** The effects of synthesis temperature on the quality and quantity of vertically aligned carbon nanotubes (VACNT) were studied using high resolution scanning electron microscopy, and micro-Raman spectroscopy. The VACNT was synthesized by Fe catalytic decomposition of palm oil deposited on silicon substrate by thermal chemical vapour deposition method. The analysis shows that the growth rate increases from 3.8 to 5.5 $\mu$m/min as the temperature was increased from 750 to 800°C. The nanotube diameters were observed bigger at low temperature range. Smaller and uniform diameter (~15 nm) was found at 750°C and the increment in diameter size was seen at higher temperature range. Smaller graphite Raman "G" peak width, low $I_D/I_G$ ratio (~0.52) indicated higher crystallinity of the nanotube and moderate $I_{2D1}/ I_{2D2}$ ratio for second order Raman peak was also detected at synthesis temperature of 750°C. These results indicated that the optimum synthesis temperature for higher quality VACNT production was at 750°C.

## Introduction

Carbon nanotubes (CNTs) have attracted worldwide attention since its discovery in 1991 [1]. They have shown distinguished properties like unique physical and chemical behavior which make them useful in numerous applications such as field emission sources, polymer/CNTs nanocomposites, supercapasitor and etc. [2, 3]. CNTs can be classified into two categories, namely single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). A special form of MWCNT is the double-walled CNT (DWCNT). It is of great interest to indentify the factors controlling the nanotubes diameter, number of walls and degree of graphitization during the synthesis process. This is due to the fact that different atomic structure of tubes may cause great changes in their properties. Therefore, the parameter optimization is the important factor during synthesis regardless the method

used either by arc-discharge [4], laser ablation[5], chemical vapor deposition [6] and spray pyrolisis [7]. Among the parameter, the synthesis temperature is the crucial factor in controlling carbon nanotubes formation as well as its degree of graphitization.

In this paper, we describe a study on the effect of synthesis temperature on the formation of VACNT using the thermal catalytic technique utilizing palm oil as the carbon source and ferrocene as the catalyst. The quality of the VACNT formed was evaluated by high resolution scanning electron microscopy (FESEM) and micro-Raman spectroscopy.

## Materials and Methods

The detailed experimental procedures were discussed elsewhere [6]. Briefly, palm oil ("Buruh" brand) manufactured by Lam Soon Sdn. Bhd, Malaysia and ferrocene (Sigma Aldrich, 99.9%) were mixed to form the precursor for VACNT production. The synthesis process was done in a double furnace thermal chemical vapor deposition system. The synthesis temperatures were varied from 700 to 800°C in steps of 25°C for a total time of 30 min. The typical characterizations were done using FESEM (ZEISS Supra 40VP) at 5 kV acceleration voltage and micro-Raman spectroscopy (Horiba Jobin Yvon -DU420A-OE-325) utilizing the 514.5 nm argon laser line.

## Results and Discussions

The effects of synthesis temperature were studied in the range of 700-800°C in steps of 25°C. The FESEM images of the resulting CNT are shown in Fig. 1 (a)-(h) and Fig. 2 (a)-(f). The CNTs were observed to grow within the temperature range, however at temperature below 750°C, not indicating any VACNT growth. Below 750°C, the temperature is not enough to pyrolyse the precursor and at the same time the catalyst activity was weak causes low production of carbon atoms. As a result, only small amount of spaghetti liked nanotubes with amorphous carbon (a-C) were synthesized as detected in 700 and 725$^{o}$C samples (as in Fig. 1(a), (b), (e) and (f)). Meanwhile further reduction in temperature (lower than 700°C) resulted in no CNT deposited on the silicon substrate.

At 750°C and above, vertically aligned carbon nanotubes were produced with growth rate, $R_g$ increased with temperature. The average $R_g$ of VACNT was approximately 3.8 $\mu$m/min for 750$^{o}$C and increased to 4.0 $\mu$m/min for 775$^{o}$C samples. The calculated $R_g$ further increased to 5.5 $\mu$m/min as the synthesis temperature reached 800$^{o}$C. From FESEM analysis (Fig 2(a), (b) and (c)) it was observed that good quality of VACNT array was formed at temperatures between 750-800 $^{o}$C. But the higher degree of lateral alignment which was based on side view image that showed uniform nanotubes orientation, distribution and diameter within the bundle was detected for samples synthesized at 750°C. It is possible that at this temperature the precursor was sufficiently pyrolyzed and good interaction between the hydrocarbon and catalyst facilitated the formation of uniform nanotube diameter and good alignment within the bundle.

Increasing the synthesis temperature from 850 to 900°C in steps of 50°C produced nanotubes shown in Fig. 1(c), (d), (g) and (h), all of which showed low degree nanotubes alignment. The tubes seemed to be low in quality and obviously blended with a-C and carbon particles. A possible explanation is chemical reaction between carbon and the iron catalyst to form iron carbide which caused it to loose its catalytic behavior [8]. Also, high hydrocarbon concentrations were expected at high temperatures. This favored the formation of amorphous carbon which may have encapsulated the iron catalyst particles, thus incapacitating its catalytic properties.

The nanotubes diameter were also affected by temperature change. In general, the diameter of the CNTs were seen bigger at lower temperature and decreases to ~15nm at synthesis temperature of 750°C. As temperature increased from 775 to 900$^{o}$C the diameters were seen to increase again.

Above 750°C, the increase in CNT diameter was due to the coalescence of the catalyst particles. The smallest and uniform diameters of nanotubes were detected at 750°C as compared to VACNT samples at 775 and 800°C.

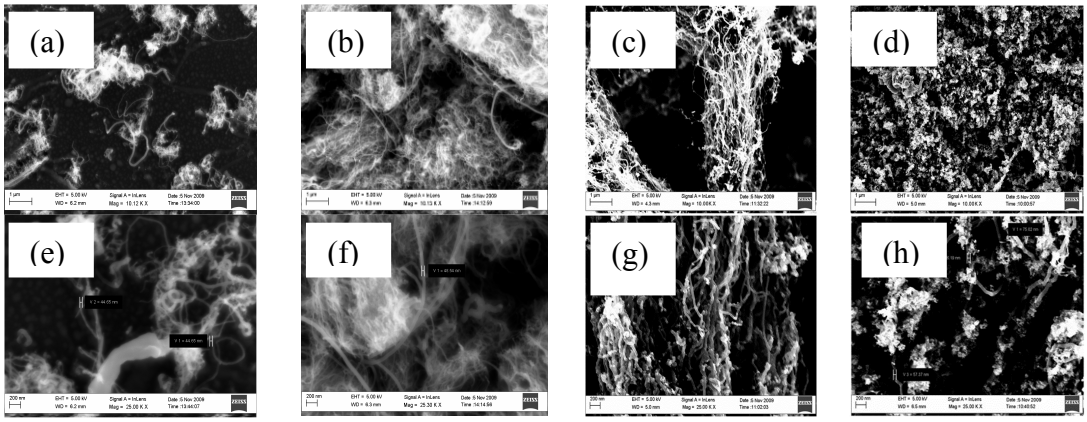


Fig. 1 FESEM images of CNTs synthesized at different synthesis temperatures: (a) 700°C, (b) 725°C, (c) 850°C and (d) 900°C. Fig. 1(e), (f), (g) and (h) are the magnified view of Fig. 1(a), (b), (c) and (d) respectively.

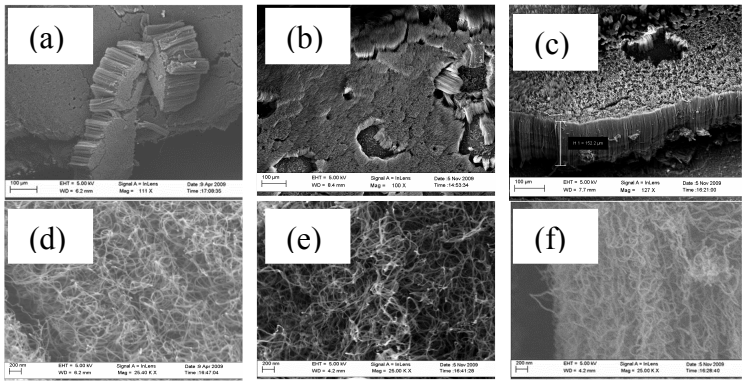


Fig. 2 FESEM images of CNTs synthesized at different synthesis temperatures: (a) 700°C, (b) 725°C, (c) 750°C, (d) 775°C and (e) 800°C. Fig. 2(d), (e) and (f) are the magnified view of Fig. 2(a), (b) and (c) respectively.

Micro-Raman spectroscopy was used to characterize the quality of the samples synthesized at different temperatures and the spectrums are shown in Fig. 2(a). Two major peaks associated with graphite G peak (~ 1574.58-1584.74 $cm^{-1}$) and the D peak (~1346.05-1356.22 $cm^{-1}$) were observed in all samples. The G and D peak at 700°C were observed at 1584.74 and 1356.22 $cm^{-1}$ whereas both peak shifted to slightly lower wave number of 1581.54 and 1350.18 $cm^{-1}$ at 725°C temperature. Meanwhile the lowest wave number of G and D peak were detected at a temperature of 750°C at 1574.58 and 1346.05 $cm^{-1}$. The wave numbers were then shifted back to higher value of 1579.97 and 1350.92 $cm^{-1}$ at elevated temperature (775 and 800°C). This frequency shift of the G and D peak might be due to defects in the tube such as pentagons and curvatures [9]. From Fig. 2 (a) it was also observed that the smaller G peak width was from the reaction temperature of 750°C, this indicated good crystallinity nanotubes. The integrated intensity ratio of the D and G peak ($I_D/I_G$) was used as a parameter to evaluate the crystallinity of CNT. It was evident that the CNT synthesized at 750°C showed much lower $I_D/I_G$ ratio (~0.52) than that of the CNT synthesized at the other temperature (~0.59-0.67). This was another indicator that the CNT synthesized at 750°C were more crystalline as compared to the rest of the samples. At low synthesis temperature range (700-725°C) low catalyst-precursor activity attributed to low graphitization of the nanotubes produced.

Meanwhile, at high synthesis temperature range (775-800°C) low graphitization of the nanotubes was suggested from higher carbon concentration produced.

From micro-Raman analysis (Fig. 2 (b)), it was also evident that the samples synthesized at temperatures of 700-800°C consisted of a mixture of SWCNTs and MWCNTs. The presence of the lower frequency radial breathing modes (RBM) at wavenumber < 500cm$^{-1}$ indicated the presence of SWCNTs as shown in Fig. 2(b). The diameter, d, of the SWCNTs can be estimated from the RBM peak position, ω, as d = 248 (cm$^{-1}$ nm)/ω(cm$^{-1}$) [10], which yielded diameters in the range of 0.58-1.14 nm. At low temperature (700°C) the RBM peak were detected at higher wave number, 430 cm$^{-1}$ which gave a smaller SWCNT diameter, while the steps at 225 cm$^{-1}$ and the peaks at 300.6 cm$^{-1}$ came from the silicon substrate [11]. As the temperature was increased (725-750°C) the peak position shifted to a lower wavenumber of around 214.9-395.5 cm$^{-1}$ which gave larger SWCNT diameters. It is speculated that the catalyst particles coalesced more at higher temperatures which contributed to larger SWCNT diameter. At the same time, smaller number of carbon atom produced at 700°C might also be the reason for the smaller SWCNT diameter observed. The faint RBM peak detected at 775 and 800°C samples was due to the abundance of carbon produced at this temperature which promoted the growth of MWCNT, thus suppressed the growth of SWCNT. The detailed Raman analysis results which included the positions of the G, D and RBM lines, G and D width and intensity ratios and SWCNT diameter for synthesis temperature from 700 to 800$^{o}$C are tabulated in Table 1. The analysis from FESEM and micro-Raman spectroscopy was consistent in that the appropriated temperature for preparing VACNT with higher yield and good quality was at 750°C.

The Raman peak at around 2700 cm$^{-1}$ known as the G' line is the second order of zone-boundary phonons which is sensitive to the three dimensional stacking of graphene layer which has nothing to do with G peak [12]. As the CNT produced in this study were mainly MWCNT, the G' peak were found to be broad and increase in number of layer leads to a significant decrease of the G' peak intensity [12]. Consistent with the smaller diameter observed with the sample at 750°C the highest intensity of G' peak with lowest FWHM were detected. Notably, the low intensity of the G' peak was detected with the bigger diameter nanotubes at lower and higher temperature range. The fitting results of G' peak using the Lorentzian distribution show that the peak can be deconvoluted into 2 major peaks which is around ~2680 ($2D_1$) and 2700 cm$^{-1}$ ($2D_2$). The $I_{2D1}$/ $I_{2D2}$ were calculated and it gave ratio values of 0.82-0.95 for the VACNT samples synthesized from 750 to 800$^{o}$C temperature range. On the other hand the spaghetti-like samples synthesized at temperatures of 700 to 725$^{o}$C showed slightly higher ratio of 0.97-1.04. This indicated that well aligned 3D stacking of graphene layer were detected from samples synthesized at temperatures of 750 to 800$^{o}$C with the lowest ratio value were seen at 775$^{o}$C. However, the difference between $2D_2$-$2D_1$ did not show any clear pattern and the larger difference was found at 775$^{o}$C, 28.81cm$^{-1}$. The Raman spectroscopy parameter for G' peak are reported in Table 2.

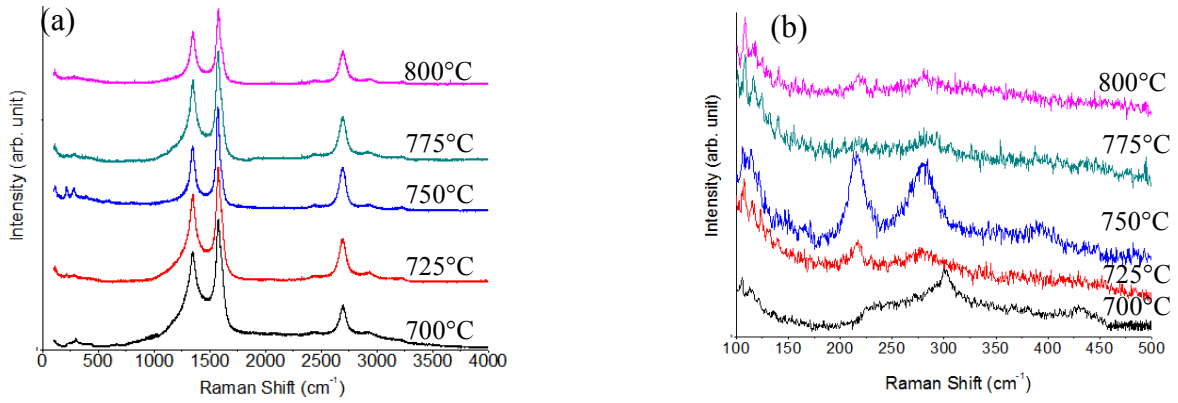


Fig. 2 (a) Typical Raman spectra of palm oil based CNTs synthesized at 700 to 800°C with increment rate of 25°C (b) multiple low frequency peaks associated with radial breathing mode (RBM) appeared at entire synthesis temperature where the intense peaks were noticed at 750°C.

**Table 1** Raman and RBM peak position, G and D intensity ratios and SWCNT diameter for synthesis temperature from 700 to 800°C

| **Samples** | **G peak** ($cm^{-1}$) | **G-Width** ($cm^{-1}$) | **D peak** ($cm^{-1}$) | **D-Width** ($cm^{-1}$) | **$I_D/I_G$ ratio** | **RBM peaks** ($cm^{-1}$) | **SWCNT diameter (nm) (calculated from d=248 ($cm^{-1}$ nm)/ω($cm^{-1}$))** |
|---|---|---|---|---|---|---|---|
| 700°C | 1584.74 | 78.06 | 1356.22 | 172.47 | 0.67 | 300.6, 430.1 | 0.83, 0.58 |
| 725°C | 1581.54 | 61.53 | 1350.18 | 129.05 | 0.63 | 217.2, 278.1 | 1.14, 0.89 |
| 750°C | 1574.58 | 42.51 | 1346.05 | 74.09 | 0.52 | 214.9, 277.2, 395.5 | 1.15, 0.89, 0.63 |
| 775°C | 1578.51 | 56.07 | 1350.92 | 108.16 | 0.59 | 218.2, 281.5 | 1.14,0.88 |
| 800°C | 1579.97 | 48.57 | 1350.34 | 73.03 | 0.62 | 219.5, 281.5 | 1.12, 0.88 |

**Table 2** The fitting results for Second Order Raman peak Using the Lorentzian Distribution Function

| **Samples** | **$2D_1$** | | **$2D_2$** | | **$I_{2D1}/I_{2D2}$** | **$2D_2$-$2D_1$** ($cm^{-1}$) |
|---|---|---|---|---|---|---|
| | **Frequency** ($cm^{-1}$) | **FWHM** ($cm^{-1}$) | **Frequency** ($cm^{-1}$) | **FWHM** ($cm^{-1}$) | | |
| 700°C | 2682.72 | 43.03 | 2709.18 | 40.04 | 1.04 | 26.46 |
| 725°C | 2679.36 | 38.08 | 2707.47 | 39.37 | 0.97 | 28.11 |
| 750°C | 2679.33 | 32.07 | 2704.59 | 30.27 | 0.95 | 25.25 |
| 775°C | 2677.57 | 41.09 | 2706.38 | 44.19 | 0.82 | 28.81 |
| 800°C | 2681.09 | 37.28 | 2708.21 | 38.83 | 0.93 | 27.12 |

## Conclusions

In conclusion, VACNT arrays were successfully produced at a temperature range of 750-800$^{o}$C with growth rates ranging from 3.8 to 5.5 $\mu$m/min. The nanotube diameters were affected by temperature change where at low temperature the diameter were found to be bigger and was greatly reduced at 750$^{o}$C (~15 nm). The diameter increased further as temperature elevated to 900$^{o}$C. The synthesis temperature of 750°C was considered the optimum temperature for VACNT production based on the smaller graphite Raman G peak width, low $I_D/I_G$ ratio (~0.52) that indicated higher crystallinity of the nanotube and moderate $I_{2D1}/ I_{2D2}$ ratio for second order Raman peak. The sample also has uniform nanotubes orientation, distribution and diameter which contribute for better lateral nanotubes alignment within the bundle.

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