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The Effect of Substrate Positioning on the Growth of Carbon Nanotubes from Palm Oil Precursor

Kesan Kedudukan Substrat kepada Pertumbuhan Tiub Nanokarbon daripada Pelopor Minyak Sawit

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Abstract

The effect of substrate positioning inside a thermal chemical vapour deposition furnace on diameter, quality and purity of the grown carbon nanotube (CNT) were reported. The CNT was synthesized using bio-hydrocarbon precursor, palm oil at 750°C synthesis temperature. The substrates were positioned at six different places where the distance between the subsequent substrate was fixed at 1 cm. Field emission scanning electron microscope, Raman spectroscopy and thermogravimetric analysis were employed for CNT morphology, quality and purity characterization. Samples deposited on substrate positioned at 3.0 cm showed good morphology of dense CNT distribution with higher quality and purity.

Keywords carbon nanotube (CNT), palm oil, chemical vapour deposition, morphology

Abstrak

Artikel ini adalah berkaitan kesan kedudukan substrat di dalam relau pengenapan wap kimia terma terhadap diameter, kualiti dan ketulenan karbon nano tiub (CNT) yang dihasilkan. CNT tersebut disintesis pada suhu 750° C menggunakan pelopor biohidrokarbon, iaitu minyak sawit. Beberapa substrat diletakkan pada enam kedudukan berturutan dengan jarak pemisah 1 cm di antara satu sama lain. Pencirian morfologi, kualiti dan ketulenan CNT dilakukan dengan menggunakan mikroskop elektron pengimbas pancaran medan, spektroskopi Raman dan analisis termogravimetri. CNT yang dienapkan pada kedudukan 3.0 cm menunjukkan morfologi taburan ketumpatan CNT yang baik dengan kualiti dan ketulenan yang lebih tinggi.

Kata kunci karbon nano tiub (CNT), minyak sawit, pengenapan wap kimia, morfologi

Introduction

Carbon nanotubes (CNT) are an established material in the field of nanotechnology research.

This is due to its unique electrical properties, incredible mechanical strength, extraordinary chemical and thermal behaviour. The uniqueness of CNT make them suitable in diverse applications such as in field electron emission (Robertson, 2004), nanoelectronics (Wang, 2011), supercapacitors (Zhou *et al*., 2006) and conductive composites (Robertson, 2004; Yu *et al*., 2007).

Currently, research are being carried out which involves parameters that controls the growth of CNT such as temperature (Arfe *et al*., 2006; Bai *et al*., 2005; Azmina *et al*., 2012), time (Niu *et al*., 2008), catalyst effect (Bai *et al*., 2005; Azmina *et al*., 2012) and substrate positioning (Li *et al*., 2010). It is highly important to produce CNT of controlled, uniform and smaller diameter, higher structural quality and purity to meet the requirement for specific applications at high capacity. Among the mentioned parameters, the substrate positioning effect was the least studied (Li *et al*., 2009; Pitayapiboonpong *et al*., 2010) even though this parameter is an important factor in determining the final properties of CNT. Comprehensive study on substrate position was also needed particularly to scale up the CNT production. Specifically for floated catalyst approach whereas the catalyst distribution were not uniform throughout the furnace, then the substrate position is one of the crucial factor to determine the possibility of getting single-walled CNT. Therefore, in this paper, the effect of substrate positions on the synthesized CNT from palm oil was investigated for the first time. The synthesis was carried out using thermal chemical vapour deposition method which utilizes ferrocene as catalyst.

Experimental Method

The experimental procedures done in this work are similar with the one reported previously (Suriani, Nor & Rusop, 2010; Suriani *et al*., 2009). The difference was only the amount of the palm oil and ferrocene mixture introduced in the synthesis furnace which was 20 ml. For the effect of substrate positioning, the substrates were placed at six different positions in the deposition furnace which were labelled as P1, P2, P3, P4, P5 and P6 in Figure 1. The distance between subsequent substrate was 1 cm. The P2, P3 and P4 samples were placed on effective heating area, while P1, P5 and P6 were placed away from the effective heating area which was closer to tube end. The CNT images were taken with JOEL-JSM 7600F field emission scanning electron microscope (FESEM). A micro-Raman analysis was carried out in a Horiba Jobin Yvon-DU420A-OE-325 instrument. The CNT purity identification was done using Thermogravimetric analysis TGA-Perkin Elmer Pyris 1.

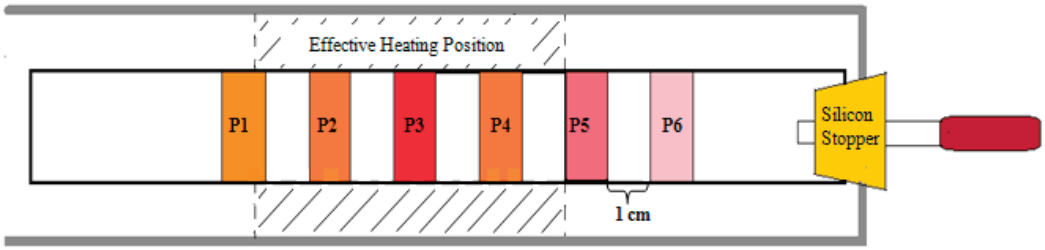

Figure 1 The schematic diagram of 6 identical substrates positioned on the platform inside the deposition furnace.

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Results and Discussions

Fig. 2 (a)-(f) show FESEM images of the CNT synthesized at position P1 until P6 in the deposition furnace. It was obvious that the samples deposited at position P2 and P3 demonstrated the best CNT morphology. At positions P2 and P3, the CNT have smooth surface and nearly uniform diameters which were around 35.6-37.5 nm. However, the smallest CNT diameter was measured at sample deposited at P3 (25.2 nm) with less impurities and amorphous carbon (a-C). The CNT grown at P1 have lower quality and density as compared to the samples deposited at P2 and P3 position. Bigger and non-uniform CNT diameters were also detected in the range of 46.9-61.9 nm.

At P4 position the CNT diameter were found to be bigger in the range of 34.6-46.9 nm and the decreased in CNT morphology quality were also detected. The CNT were no longer uniform in diameter and it starts to show more crooked shape. Meanwhile, the CNT grown at P5 to P6 showed poor CNT quality with bigger diameter which were around 41.3-77.7 nm. This occurred because the substrates lie outside the heating areas where temperature was believed to be less than 750^{o}C. In the meantime, a relatively lower in-situ Fe catalyst deposition can be observed as it approaches downstream particularly toward outlet point. The deposition catalyst was not sufficient to catalyze the nanotubes growth as it has already deposited on position P1 until P3. Therefore, it can be said that the position near to outlet point were less favourable for higher quality nanotubes growth.

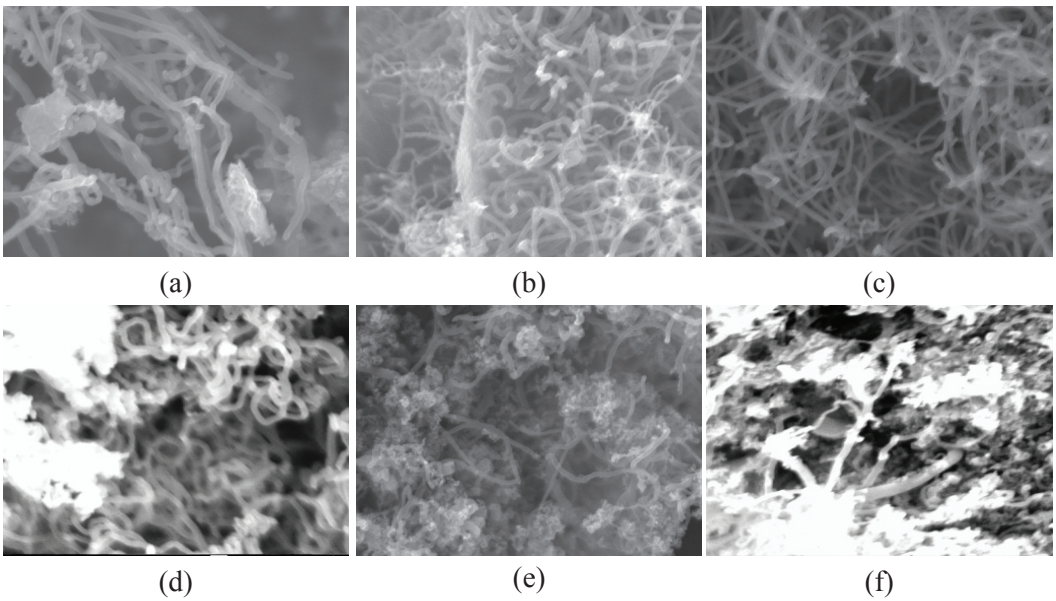

Figure 2 FESEM images of the CNT synthesized at position: (a) P1, (b) P2, (c) P3, (d) P4, (e) P5 and (f) P6

Vibrational spectroscopic analysis of the samples deposited at P1 until P6 were recorded using micro-Raman spectroscopy. The spectra show two Raman peaks at 1585.0-1593.9 cm^{-1} for G peaks and at 1345.9-1369.1 cm^{-1} for D peaks (Figure 3). The I_D/I_G ratios were calculated to estimate the variation of CNT crystallinity from P1-P6 position where the lowest I_D/I_G ratio points out greater crystallinity. The I_D/I_G value was found to be lower for

sample synthesized at P3 position which was 0.83. The ratios were found slightly higher when CNT was synthesized at other substrate positions. The I_D/I_G ratio gave the following ratio; 0.90 for P1, 0.89 for P2, 0.85 for P4, 0.95 for P5 and 1.08 for P6. With this, it was evident that CNT crystallinity was improved when the sample were deposited at P3 position. Raman spectra and I_D/I_G ratios of CNT at different substrate position are shown in Table 1.

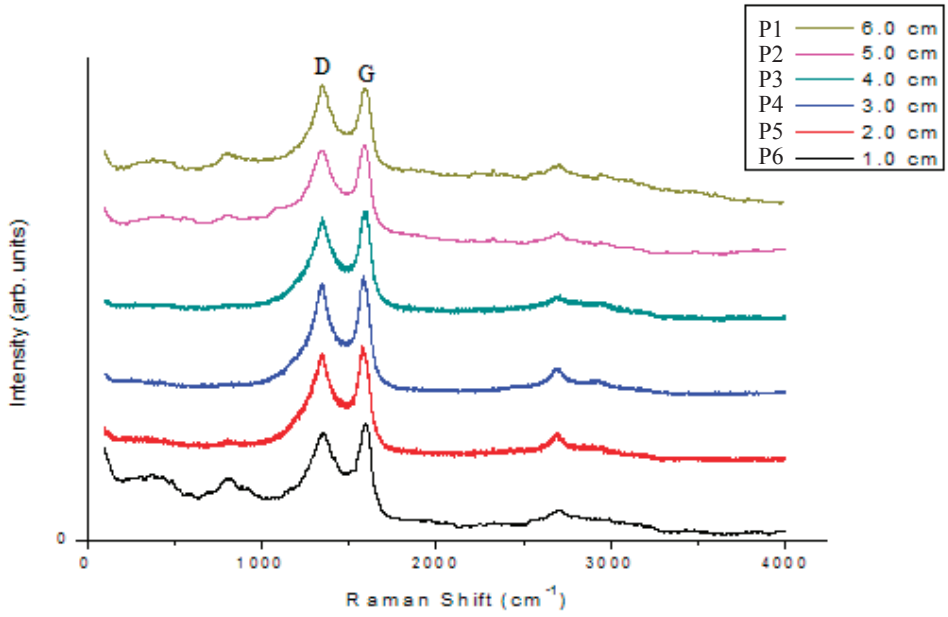

Figure 3 Raman pattern at different substrate position, P1 until P6

Table 1 Raman peaks position and D & G intensity ratios for all substrate position (P1-P6)

Sample	D-Peak (cm^{-1})	D-Width (cm^{-1})	G-Peak (cm^{-1})	G-Width (cm^{-1})	I_D/I_G Ratio
P1	1356.6	252.1	1588.4	78.2	0.90
P2	1347.0	241.2	1584.7	76.0	0.89
P3	1345.9	214.8	1585.0	76.6	0.83
P4	1352.3	229.6	1592.7	76.7	0.85
P5	1355.2	385.8	1593.7	80.2	0.95
P6	1369.1	440.9	1593.9	52.8	1.08

The TGA curves for samples obtained from palm oil-ferrocene mixture at different substrate position are shown in Figure 4. A summary of the data obtained from the TGA curves for all samples are tabulated in Table 2. Clearly, P1 and P2 show weight percentage loss at about 110 and 210°C. This was due to the decomposition of trace hydrocarbon impurities which constituted about 1.0% of the total weight. The weight loss at about

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250 to 550°C was attributed to the burning of a-C coating which was around 1.3-5.0 %. The prominent weight loss which occurred between 613 and 902°C was due to the decomposition of CNT. From the TGA results it can be seen that the sample deposited at positioned P3 have shown the highest purity of 81.9 % with lowest a-C content of 1.3%. The initial burning of the sample (P3) started at highest value of 658°C which indicates higher quality of produced CNT.

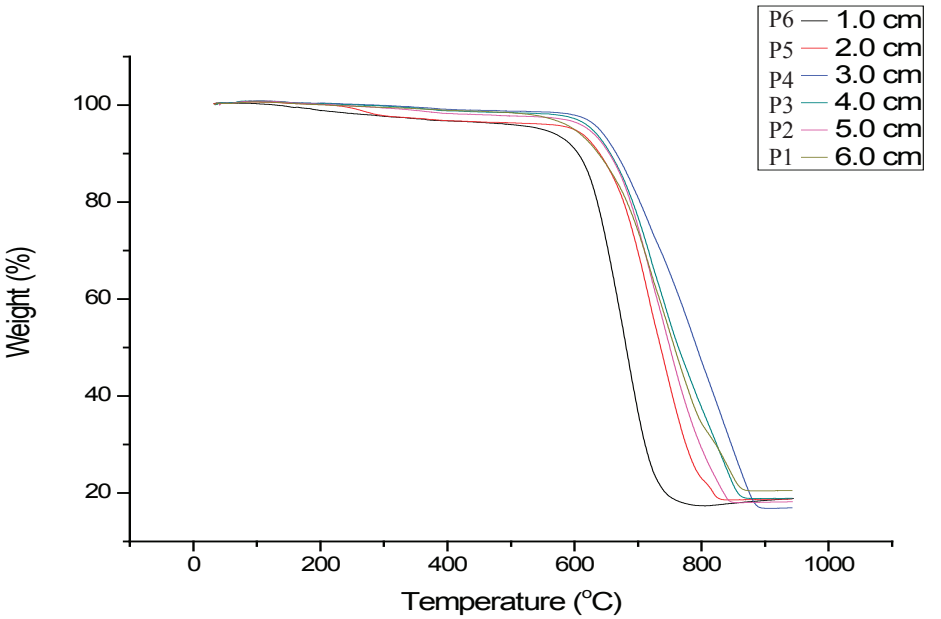

Figure 4 TGA curves for products synthesized at various location of Si multiple stacking in argon ambient

Table 2 Summary of TGA results

Sample	Temperature Onset (°C)	Fully Decomposition Temperature (°C)	Impurities Weight (%) burn at 550°C	Residual Weight (%)	Yield of CNT (%)
P1	613.17	783.39	5.01	18.76	76.23
P2	650.33	848.19	3.89	18.76	77.35
P3	657.70	902.01	1.25	16.90	81.85
P4	653.13	866.32	1.63	18.01	80.36
P5	655.01	848.19	2.37	18.79	78.84
P6	646.75	877.03	2.41	20.28	77.31

Conclusion

The yield of CNT depends strongly on the substrate positioning within the TCVD furnace. The sample deposited at P3 has shown the best CNT morphology with the lowest I_D/I_G ratio of 0.83. The sample also gave the highest CNT purity of about 81.9% with minimal

a-C content. Therefore, the P3 position was considered as the optimum location for higher quality and purity CNT. The location lies outside the effective heating area particularly for sample deposited at position P5 and P6 demonstrated poor quality CNT with bigger diameter. These were believed due to the synthesis temperature which was less than 750°C and relatively lower in-situ Fe catalyst deposition as they moves downstream.

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