

## **TIME EVOLUTION OF THE GROWTH OF VERTICALLY ALIGNED CARBON NANOTUBES USING PALM OIL**

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### **ABSTRACT**

We studied the change in morphology and microstructure of carbon nanotubes (CNT) grown for 5, 10, 15, 20, 25, 30, 35 and 40 mins respectively. The CNT was fabricated from palm oil using thermal chemical vapor deposition method at fixed synthesis temperature of 750°C in argon ambient. The samples were analyzed using field emission scanning electron microscopy and micro-Raman spectroscopy. At 5 min of growing time, a very thin layer of CNT was produced without any vertical growth of CNT. The tube walls were also defective and coated with amorphous carbon. The vertically aligned CNT (VACNT) was initially observed at 10 min synthesis time and the length increases with prolonged synthesis time at various growth rate. It should also be highlighted that as the nanotubes get longer and thickens with time, the development of secondary growth structures was also spotted particularly for synthesis time more than 30 min. From Energy-dispersive X-ray spectroscopy analysis, it is justifiable that the generation of secondary growth came from the raised catalyst. As a conclusion, it can be said that, the optimum synthesis time for higher growth rate VACNT, smaller diameter and mix with single-walled CNT, low  $I_D/I_G$  ratio was identified at 30 min time.

**Key words:** Nanotubes, Chemical synthesis method, Scanning electron microscopy (SEM) and Raman spectra.

### **ABSTRAK**

Kami mengkaji perubahan morfologi dan struktur mikro tabung nano karbon (CNT) yang ditumbuhkan selama 5, 10, 15, 20, 25, 30, 35 dan 40 menit. CNT difabrikasi dari minyak sawit menggunakan metode deposisi uap kimia termal pada suhu sintesis 750 °C dalam lingkungan argon. Sampel dianalisis menggunakan mikroskop elektron dan spektroskopi mikro-Raman. Pada waktu pertumbuhan 5 menit, diperoleh lapisan CNT yang sangat tipis tanpa pertumbuhan vertikal CNT. Dinding tabung juga rusak dan dilapisi dengan karbon amorf. Pertumbuhan CNT vertikal sejajar (VACNT) pada awalnya teramati pada waktu sintesis 10 menit dan panjangnya bertambah seiring dengan perpanjangan waktu sintesis di berbagai tingkat pertumbuhan. Harus digaribawahi pula bahwa semakin panjang dan tebal tabung nano seiring bertambahnya waktu, perkembangan struktur pertumbuhan sekunder juga terlihat terutama untuk waktu sintesis lebih dari 30 menit. Dari analisis spektroskopi energi dispersif sinar-X, terlihat bahwa generasi pertumbuhan sekunder berasal dari katalis yang terangkat. Sebagai kesimpulan, dapat dikatakan bahwa waktu sintesis optimal

untuk tingkat pertumbuhan VACNT yang lebih tinggi, diameter lebih kecil, bercampur dengan CNT berdingding tunggal, dan rasio  $I_D/I_G$  rendah diidentifikasi pada 30 waktu menit.

**Kata Kunci:** tabung nano karbon, metode sintesis kimiawi, mikroskop electron (SEM), spectrum Raman

## INTRODUCTION

Carbon nanotubes (CNT) have gained worldwide attention due to their outstanding physical properties and extensive future applications. Vertically aligned CNT (VACNT) towers could be utilized in applications such as field emission displays, which would require a scalable production method. Using chemical vapour deposition (CVD) as a synthesis method for VACNT production allows for mass production with simpler setup and lower operating temperature compared to arc-discharge (Wang, *et al*, 2005) and laser ablation (Rode, *et al*, 2005). Control over the CVD growth process is crucial as this affects the dimension and structural characteristic of CNT for their integration into practical devices. Variation in CVD parameter has been explored such as synthesis temperature (Suriani, *et al*, 2011a; Suriani, *et al*, 2011b) and time (Niu and Yang, 2006) and substrate positioning (Li, *et al*, 2010). Although much can be deduced based on published data, no comprehensive investigation on the effect of time evolution on the growth of VACNT array has yet been reported.

In the present contribution, we studied the change in morphology and microstructure of CNT synthesis for 5 to 45 mins at increment rate of 5 mins. Over 45 mins, the synthesis was carried out at 60, 75 and 90 mins. This parameter seems to be one of the critical parameter for the possibility of VACNT growth. In our early attempt the

VACNT growth was unsuccessful due to the reaction process which was done within just 5 mins synthesis time. The density, growth rate, diameter uniformity and the quality of the CNT produced was qualitatively determined from Raman spectroscopy which was greatly affected by the growth duration. The synthesis of VACNT was done using an alternative precursor namely palm oil in CVD reactor.

## MATERIALS AND METHODS

The synthesis of CNT was carried out in the double furnace thermal chemical vapour deposition (TCVD) system at synthesis temperature of 750°C, palm oil vaporization temperature of 450°C and 5.33 wt% of ferrocene concentrations. The synthesis time were varied up to 45 mins at a rate of 5 mins. Over 45 min the synthesis time were increased at a rate of 15 mins; giving a synthesis time of 60, 75 and 90 mins. The precursor furnace was turned off when the desired time was reached and the system was then cooled to room temperature. The morphology and microstructure change upon synthesis time were investigated using field electron field emission scanning electron microscopy, FESEM (ZEISS Supra 40VP), micro-Raman spectroscopy (Horiba Jobin Yvon - DU420A-OE-325) and Thermogravimetric analysis, TGA (Perkin Elmer Pyris 1 TGA).

## RESULTS AND DISCUSSIONS

Figure 1(a)-(j) and 2(a)-(u) shows the FESEM images of CNT synthesized from 5 to 90 mins. Generally, VACNT length increases with prolonged synthesis time at various growth rates. The same situation was observed in nanotubes diameter for synthesis time more than 30 mins where the increase in diameter was clearly observed. Within the first 5 mins of growth, a thin layer of CNT was produced without any VACNT (see Figure 1 (a)-(b)). The CNT were always short with bigger diameter in the range of 47.2-61.3  $\mu\text{m}$ . The tubes walls were also defective and coated with amorphous carbon (a-C) material. The cross-section of a sample grown at 10 mins exhibited the growth of VACNT at 10.9  $\mu\text{m}$  long giving the growth rate of 1.1  $\mu\text{mmin}^{-1}$ . Smaller tubes diameters of 17.4-27.6 nm were also observed. At the same time, the top layer of the sample was covered with 2.5  $\mu\text{m}$  of a-C layer which was believed due to incomplete decomposition and pyrolysis of hydrocarbon within a short reaction time. Figure 3 shows the dependence of VACNT length on the synthesis time. From the analysis, a log curve fit of  $y = 84.90 \ln(x) - 198.2$  was obtained, where  $y$  was the VACNT length and  $x$  was the synthesis time, describes the initial nucleation and growth of nanotubes. From the graph, a prominent increase of VACNT length was observed for the synthesis time less or equal to 30 mins. After the initial growth of VACNT at 10 mins, the tubes grew more perfectly and had length of 19.3-31.2  $\mu\text{m}$  for 15 and 20 mins sample respectively. Then, the length reaches about 115.0  $\mu\text{m}$  at 30 mins synthesis time. This demonstrates an increase in VACNT growth rate. Starting with zero growth rates at 5 mins synthesis time, the rate increases

to a maximum value of 3.8  $\mu\text{mmin}^{-1}$  at 30 mins synthesis time.

However, the synthesis done at longer time (more than 30 mins) was not capable in producing the same increase rate of nanotubes length. It was expected to see double growth in nanotubes length at 60 mins time, but at 90 mins synthesis time the length only reached 181.8 nm. This implies that the growth rate got slower. In synthesis time more than 30 mins the growth rate decreased with synthesis time from 3.8 to 2.0  $\mu\text{mmin}^{-1}$  at 90 mins. This situation was presumably due to the catalyst becoming inactive (Niu and Yang, 2006) and most of the VACNT growth had taken place in the first 30 mins. In the mean time, slower VACNT growth observed at synthesis time less than 30 mins was due to the carbon atom just being recently adsorbed on the catalyst surface and begins to form hexagonal ring. Other possible explanation was due to the short decomposition time given, produces low amount of hydrocarbon vapour occupies the catalytic sites. This was less favourable for high VACNT growth rate. However, once carbon atom got sufficiently saturated onto the catalyst surface, the VACNT growth increase rapidly as shown in the sample synthesized at 30 mins time.

The synthesis time also affected the tubes diameter. The synthesis done below and above 30 mins show an increment in nanotubes diameter to a maximum range of 55.9-61.3 nm at lowest (5 mins) and highest (90 mins) synthesis time respectively (see Table 1). The nanotubes with reduced and uniform diameter (less or equal to 15.0 nm) were detected at 30 mins synthesis time as shown in Figure 2 (c). It should also be highlighted that as the nanotubes

got longer and thickens with time, the development of secondary growth structures was also spotted. This phenomenon was always observed due to interval of the feed injection as reported by Zhang *et al.* (2003). The initiation of secondary growth was observed at sample synthesized at 35 mins with 0.6  $\mu\text{m}$  length as revealed by Figure 2 (f). It then continues developing to 6.6  $\mu\text{m}$  length where a boundary which separates the array into two layers was clearly noticed. The secondary growth kept on progressing until the highest length of 22.7  $\mu\text{m}$  at 90 mins times. In spite of the development on the secondary growth, it was believed that lower part continues to grow with a somewhat lower growth rate. This was because, the incoming hydrocarbon were used in upper part for secondary growth development.

This condition can be speculated as follows: after some time, when the length reached more than 100  $\mu\text{m}$ , it was believed that the encapsulated catalysts in the tubes were brought to a certain height due to capillary effect. Then it catalyzes the second generation

of CNT. The secondary growth layer of VACNT used the existing nanotubes array as a substrate. To clarify this, EDX analysis was carried out on different part of the VACNT. First the scan was done on the boundary line either along or point scan which noted as spectrum 1 and 2 in Figure 4.25. Next the scan was performed on the lower part of the boundary which covers large CNT population (spectrum 3). The analysis from EDX shows that the weight percentage of Fe catalyst was higher at boundary line in the range of 2.29 wt% in comparison to Fe distribution on large CNT surface of 0.88 wt% (Table 4.6). This justifies that the generation of secondary growth came from the raised catalyst. The secondary growth was also observed on VACNT produced at less than 30 mins growth, however it show no clear trend. Meanwhile, at sample synthesized at 30 mins, the secondary growth on the primary VACNT layer was almost not visible, whereby the VACNT continue to grow in bundle and stop afterwards. Therefore, this synthesis time can be considered as suitable time as less secondary growth was detected.

Table 1: The average VACNT length, secondary growth, diameter and growth rate of CNT synthesized from 5 to 90 mins.

Synthesis (mins)	Average Nanotubes Length ( $\mu\text{m}$ )	Average Secondary Growth Length ( $\mu\text{m}$ )	Growth rate of VACNT	Diameter (nm)
5	0	0	0	47.2-61.3
10	10.9	2.5 (a-C)	1.1	17.4-27.6
15	19.3	0.5	1.3	17.2-26.8
20	31.2	3.0	1.6	15.3-25.1
25	62.3	5.2	2.5	15.0-19.6
30	115.0	0	3.8	13.3-15.0
35	119.5	0.6	3.4	18.0-21.8
40	121.8	6.6	3.0	21.6-30.2
45	127.5	11.5	2.8	29.2-35.4
60	144.4	13.3	2.4	33.2-41.0
75	162.0	22.0	2.1	39.3-49.1
90	181.8	22.7	2.0	46.0-55.9

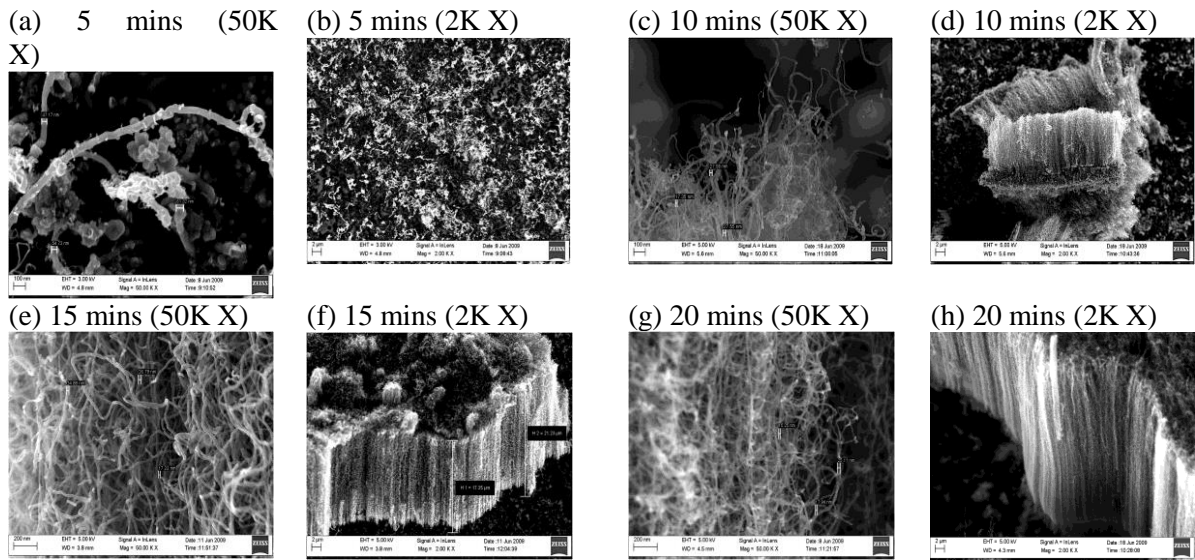
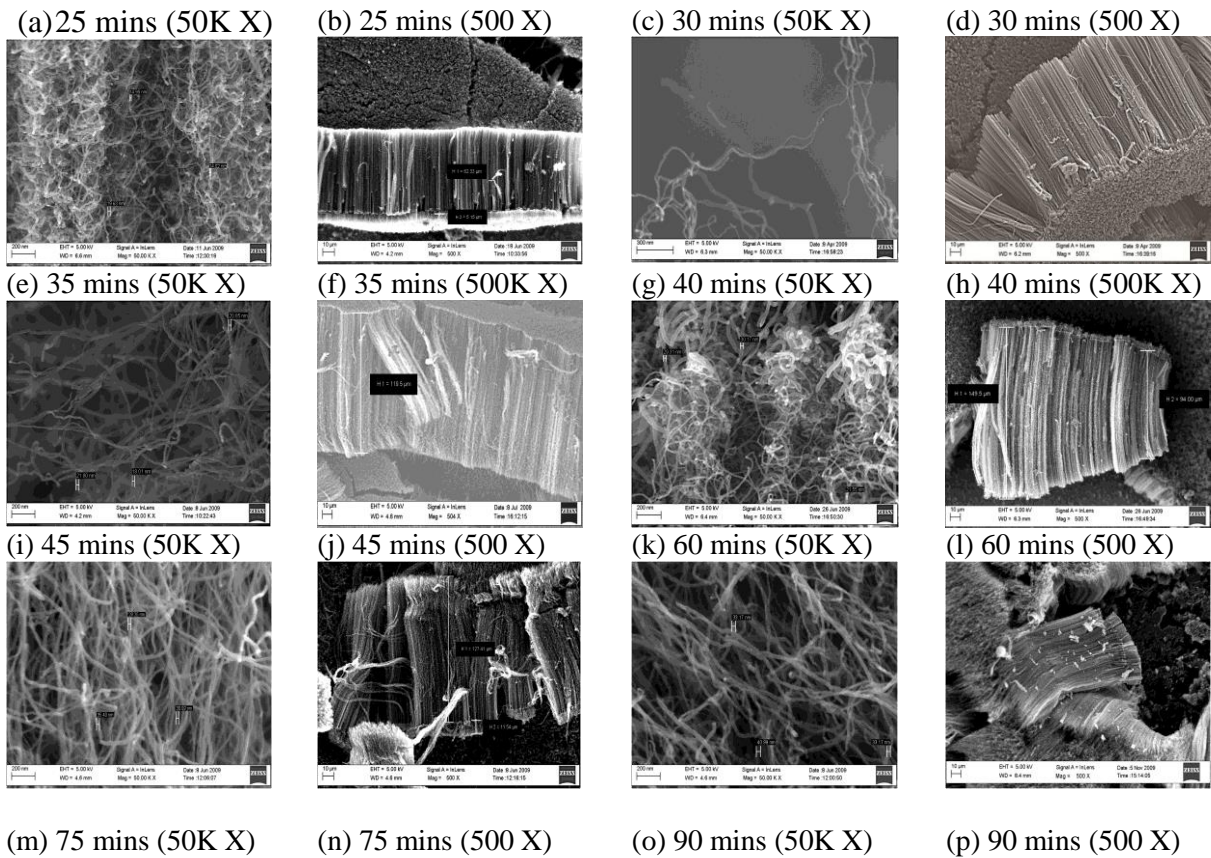


Figure 1: FESEM images of the CNT synthesized at different synthesis time (a)-(b) 5, (c)-(d) 10, (e)-(f) 15 and (g)-(h) 20 mins.



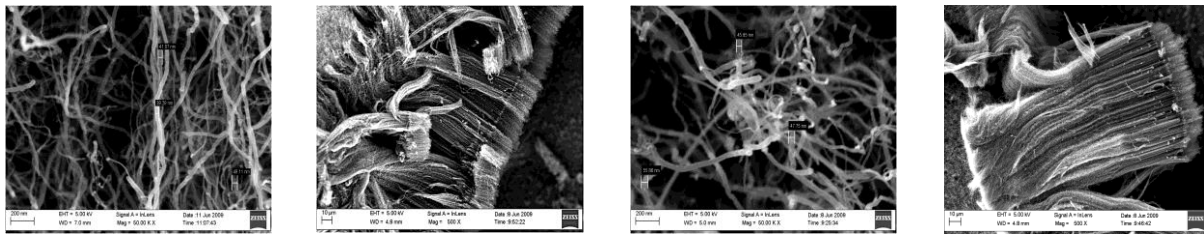


Figure 2: FESEM images of the CNT synthesized at different synthesis time (a)-(c) 25, (c)-(d) 30, (e)-(f) 35, (g)-(h) 40, (i)-(j) 45, (k)-(l) 60, (m)-(n) 75 and (o)-(p) 90 mins.

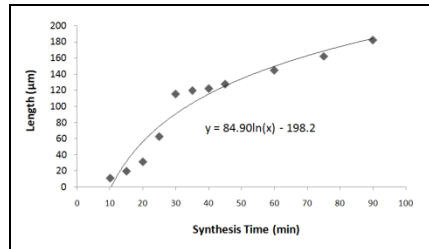


Figure 3: The VACNT length versus synthesis time, keeping other synthesis parameters constant.

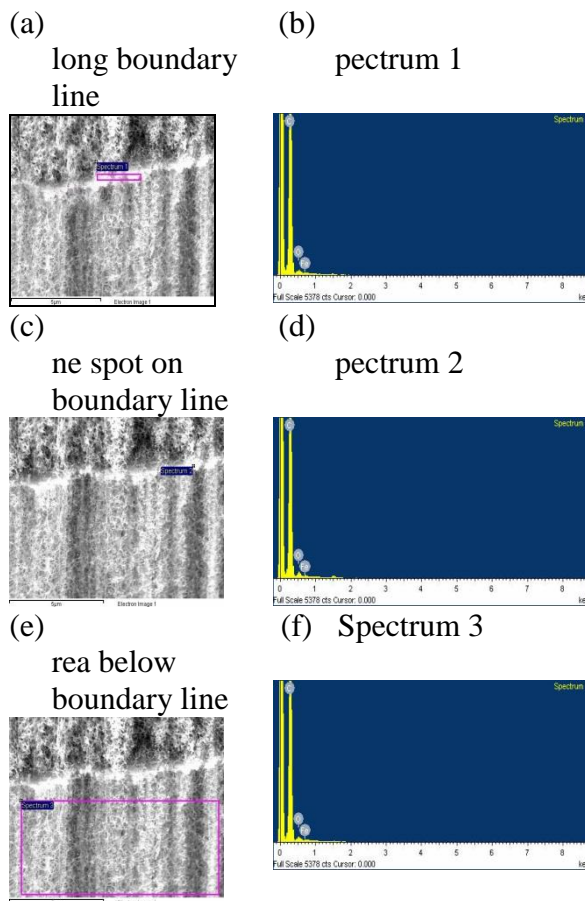


Table 2: The wt% of element content at different part of VACNT.

Area	Element	Weight %
Spectrum 1 – boundary line	Carbon	96.51
	Oxygen	2.29
	Ferum	1.20
	Total	100.00
Spectrum 2- point scan on boundary line	Carbon	93.90
	Oxygen	3.79
	Ferum	2.31
	Total	100.00
Spectrum 3- large scan on lower part of boundary	Carbon	96.47
	Oxygen	2.66

Figure 4: The FESEM images with EDX analysis done at different part of the VACNT (a)-(b) on the boundary line (c)-(d) one spot on boundary line and (e)-(f) on the lower part of the boundary which covers large VACNT population.

line	Ferum	0.88
	Total	100.00

The effect of synthesis time on the morphology of the tubes was investigated using Raman spectroscopic measurement (Figure 4.26 (a) and (b)). Typical G and D peaks were noticeable for all samples centred at 1574.6-1611.6 and 1344.7-1379.4  $\text{cm}^{-1}$  respectively (Table 4.7). Although these two peaks were present in all samples, the variation in the intensity ratio of these two bands ( $I_D/I_G$ ) as a function of synthesis time was identified. In the first 5 mins of growth, the ratio was observed to be higher at around 1.02. The value decline as synthesis time increases, implying that longer time was needed to treat the defect in nanotubes structure. Ratio as low as 0.52 was observed for synthesis time of 30 mins, indicating a very good graphitization of VACNT sample. The  $I_D/I_G$  value then increases again from 0.56 to 0.69 for the synthesis time of 35-90 mins. The rise in  $I_D/I_G$  ratio observed in the present study implies that the deposition of by product such as a-C and introduction of structure defect were more likely at higher synthesis time. This was probably due to the difficulty of the coming hydrocarbon to diffuse the catalyst–nanotubes interface, which resulted in carbon stack-up on the

nanotubes wall which later turn into a-C coating (defects) as also observed by Kwok *et al.* (2010). Other plausible explanation was the reduction in catalytic activity with the increase of synthesis time. This phenomenon was referred to as catalyst poisoning which was usually observed at longer synthesis time, promoting the formation of defect. The clear resonant RBM peaks in 100-400  $\text{cm}^{-1}$  were observed at 15, 20, 25, 30 and 35 mins sample. This shows the existence of SWCNT (Figure 4.26 (b)). In the 15 mins sample, a RBM peak appear at 216.9, 276.7 corresponding to a SWCNT diameter of 1.14 and 0.89 nm based on the equation reported by Saito *et al.* (2000). At 20-25 mins, the RBM peak appeared at 228.9, 288.2, 242.4 and 299.5  $\text{cm}^{-1}$  corresponding to diameter of 1.08, 0.86 nm and 1.02, 0.82 nm respectively. At 30 mins, one new RBM peak appeared at 395.5  $\text{cm}^{-1}$  gave a diameter of 0.63 nm other than 214.9 and 277.2  $\text{cm}^{-1}$  peaks. Meanwhile the RBM peaks almost vanish at 35 mins synthesis time. The disappearance of RBM peak at synthesis time higher than 30 mins was due to the accumulation of more walls on the tubes as proved in the FESEM image.

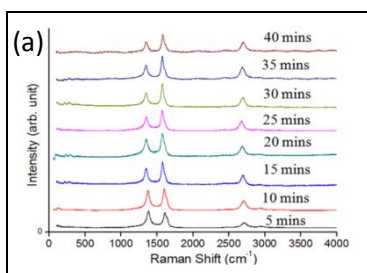


Figure 5: (a) Typical Raman spectra of as-prepared CNT

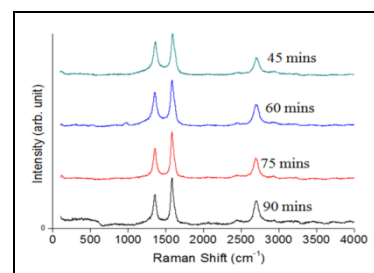
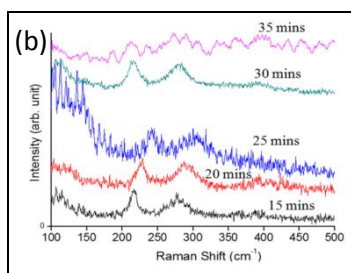


Figure 6: Typical Raman

synthesized at synthesis time of 5-40 mins with increment rate of 5 mins (b) multiple low frequency peaks associated with radial breathing mode (RBM) appeared at 15, 20, 25, 30 and 35 mins.

spectra of as-prepared VACNT synthesized at longer synthesis time of 45, 60, 75 and 90 mins with increment rate of 15 mins.

Table 3: Raman and RBM peak position, G and D intensity ratios and SWCNT diameter for as-prepared CNT synthesized at synthesis time of 5-40 mins with increment rate of 5 mins at longer synthesis time of 45, 60, 75 and 90 mins with increment rate of 15 mins.

Samples (mins)	G peak (cm <sup>-1</sup> )	G-Width (cm <sup>-1</sup> )	D peak (cm <sup>-1</sup> )	D-Width (cm <sup>-1</sup> )	I <sub>D</sub> /I <sub>G</sub> ratio	RBM peaks (cm <sup>-1</sup> )	SWCNT diameter (nm) (calculated from d=248 (cm <sup>-1</sup> nm) /ω(cm <sup>-1</sup> ))
5	1611.6	71.0	1379.4	82.8	1.02		
10	1603.1	65.8	1373.7	79.1	0.86		
15	1579.8	54.2	1348.3	71.9	0.68	216.9, 276.7	1.14, 0.89
20	1576.5	62.9	1350.6	96.4	0.67	228.9, 288.2	1.08, 0.86
25	1374.7	57.4	1351.0	96.9	0.59	242.4, 299.5	1.02, 0.82
30	1574.6	42.5	1346.1	74.1	0.52	214.9, 277.2, 395.5	1.15, 0.89, 0.63
35	1575.8	51.8	1344.7	75.0	0.56	212.5, 273.1, 391.2	1.17, 0.91, 0.63
40	1583.7	49.6	1350.4	49.0	0.60		
45	1584.0	45.5	1353.4	51.5	0.61		
60	1585.2	50.8	1355.4	58.6	0.63		
75	1585.7	63.1	1354.5	92.3	0.64		
90	1593.2	67.2	1362.2	102.3	0.69		

### CONCLUSIONS

As a conclusion, it has been confirmed that the growth rate, diameter and the quality of VACNT depend strongly on the synthesis time. A very thin layer of CNT film without any aligned growth, poor quality and high defect level were obtained at 5 mins synthesis time. The VACNT growth begins at growth time of 10 mins. As the synthesis time increases up to 30 mins, the growth rate of VACNT increases, nanotubes diameter decreases and as well as graphitization degree. After 30 mins, the growth rate became slower, the diameter of nanotubes increases and higher defect level of CNT were observed. This was due to catalyst poisoning and it was believed that most

of the VACNT growth had taken place in the first 30 mins. The RBM peaks were observed at sample synthesized within 15 to 35 mins time which gave the diameters of the SWCNT to be between 0.63 to 1.15 nm. The secondary growth generation was seen starting at 35 mins which was due to the raised catalyst. From the analysis, it can be said that, the optimum synthesis time for higher growth rate VACNT, smaller diameter and mixed with SWCNT, low defect level was identified at 30 mins time.



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