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The Effect of Temperature on Carbon Nanotubes Synthesized using Trimetallic Catalyst from Waste Cooking Palm Oil Precursor

Kesan Suhu kepada Karbon Nanotiub yang Disintesis daripada Minyak Masak Sawit Terpakai sebagai Prekursor menggunakan Mangkin Trilogam

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Abstract

In this study, we investigate the effects of synthesis temperature ranging from 650-900° C on carbon nanotubes (CNT) morphology. The synthesis was performed using thermal chemical vapor deposition method. Waste cooking palm oil was used as an economical and bio-hydrocarbon precursor. The Fe-Ni-Co catalyst was used as trimetallic catalyst which was deposited using spin coating method. The samples were analyzed using scanning electron microscope, micro-Raman and Fourier transform infrared spectroscopy. The analysis shows that the synthesis temperature significantly affects the density, diameter and quality of the CNT produced. The synthesis temperature of 750° C was considered the optimum temperature for smaller diameter CNT and good crystallinity (I_D/I_G ~0.82).

Keywoods carbon nanotubes (CNT), waste cooking oil, palm oil, bio-hydrocarbon precursor, trimetallic catalyst

Abstrak

Dalam kajian ini, kesan suhu sintesis antara 650-900° C terhadap morfologi nanotiub karbon (CNT) dikaji secara terperinci. Kaedah pemendapan wap kimia haba digunakan untuk tujuan penghasilan CNT. Minyak masak sawit terpakai digunakan sebagai prekursor bio-hidrokarbon yang murah. Mangkin Fe-Ni-Co digunakan sebagai mangkin trilogam yang ditumbuhkan melalui kaedah penyalutan spin. Sampel kemudiaannya dianalisis menggunakan mikroskopi imbasan elektron, spektroskopi-mikro Raman dan spektroskopi inframerah transformasi Fourier. Analisis menunjukkan suhu sintesis memberi kesan yang ketara kepada kepadatan, diameter dan kualiti CNT yang dihasilkan. Suhu sintesis 750° C dianggap sebagai suhu optimum bagi penghasilan CNT yang berdiameter kecil dengan tahap penghabluran yang baik (I_D/I_G ~0.82).

Jurnal Sains dan Matematik Vol.4 No.2 (2012) 87-93
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Kata kunci nanotiub karbon (CNT), minyak masak terpakai, minyak sawit, prekursor bio-hidrokarbon, mangkin trilogam

Introduction

Carbon nanotubes (CNT) were discovered by Ijima in 1991. Since then many researcher have been attracted to CNT due to its good mechanical and electrical properties as well as its potential applications in field electron emission device and biosensors. There are several techniques used to develop the CNT growth such as laser ablation (Guo, 1995), arc discharge (Qin, 2000) and chemical vapor deposition (CVD) methods (Lee *et al*., 2000; Suriani *et al*., 2010-2012 ; Azmina *et al*., 2012). Nowadays the transition metals such as iron (Fe), cobalt (Co) and nickel (Ni) were active catalyst for the growth of CNT. Fe, Ni and Co were normally used as seeded catalysts. Other than the use of single element catalyst, bimetallic or trimetallic mixture of Fe, Ni and Co with element such as molybdenum, yttrium, sulphur, rhodium and bismuth leads to mass production of CNT (Guo *et al*., 1995 ; Zhou *et al*., 2004 ; Braidy *et al*., 2002 ; Bethune *et al*., 2002 ; Osvath *et al*., 2002 ; Christen *et al*., 2004 ; Kataura *et al*., 1999). However, there were very few report on the production of CNT by using trimetallic catalysts from the combination of Fe-Ni-Co. In this work, we demonstrate the combination of Fe-Ni-Co catalyst and investigate the structure of CNT. We synthesize CNT using thermal CVD (TCVD) method from waste cooking palm oil precursor. The synthesis was done at various synthesis temperatures ranging from 650-900° C.

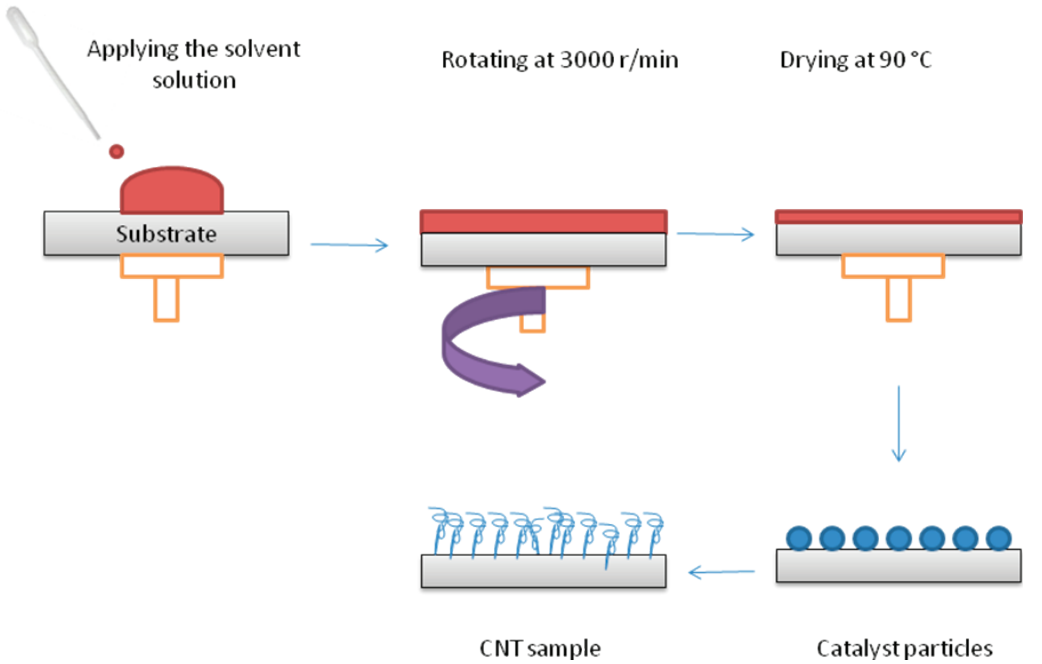

Figure 1 Catalyst preparation procedures which involves spin coating of trimetallic solution on silicon substrate and drying at 90°C. Stirring rate was fixed at 3000 rpm

Experimental Method

For the preparation of Fe-Ni-Co catalyst, the iron ($Fe(NO_3)_3.6H_2O$), nickel ($Ni(NO_3)_2.6H_2O$) and cobalt nitrate ($Co(NO_3)_2.6H_2O$) with ratio of 1:1:1 were used. The mixture was dissolved in ethanol solution. The catalyst solution was then stirred for 20 minutes and 3 drops of the catalyst were spin coated on the substrate at speed of 3000 rpm. The catalyst preparation procedures are illustrated in Figure 1. Then the catalyst was dried at 90° C for 24 hours before being loaded into synthesis furnace. Prior to the synthesis process, argon gas were flowed into the furnace in order to create inert ambient (see Figure 2). The temperature of the first furnace was fixed at 450° C. For the second furnace, the temperature was varied from 650 to 900° C with increment rate of 50° C. The synthesis period was fixed at 15 mins. *After* the synthesis process, *the furnace was cooled down to room temperature.* The morphology and crystallinity of the as-synthesized *samples were characterized* using scanning electron microscope (SEM- JSM JEOL-6360LA), micro-Raman (Yvon Horiba Jobin-DU420A-OE-325) and Fourier transform infrared spectroscopy (FTIR-Nexus).

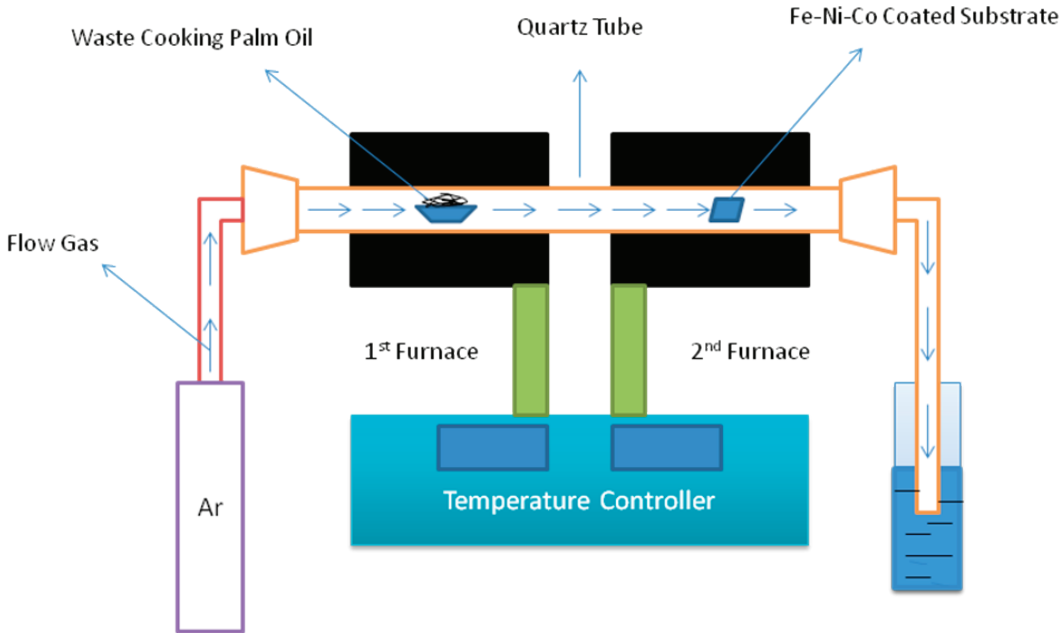

Figure 2 Schematic diagram of TCVD method used in the preparation of CNT

Results and Discussions

Figure 3 (a)-(f) shows the FESEM images of CNT synthesized at synthesis temperature of 650-900°C using trimetallic catalyst. The CNT sample synthesized at 650° C shows low CNT density with only short tube emerging from the catalyst surface. This was believed due to insufficient temperature for pyrolysis and catalytic activity (Ando, 2010). This led to low carbon atoms production which resulted in low CNT production. Higher CNT density were detected at samples synthesize between 700 to 750° C. The possible explanation for the higher CNT formation at these temperature range was due to good reaction between trimetallic catalyst and hydrocarbon vapour. At the same time at these temperature, the waste cooking palm oil vapour was sufficiently pyrolyzed (Ando, 2010).

Jurnal Sains dan Matematik Vol.4 No.2 (2012) 87-93
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Increasing the synthesis temperature from 800 to 900° C in step of 50° C, produced non-tubular structure as shown in Figure 3 (d)-(f). The substrates surfaces were occupied with carbon particles and nano-microspheres with the size of around 0.86 to 186 µm as well as amorphous carbon (a-C) coating. This demonstrated that the deposited samples were low in quality. This was believed due to the creation of metal carbide which was more favourable to occur at high synthesis temperature between 800-900° C (Ando, 2010). The formation of metal carbide tends to reduce the catalytic behaviour of the trimetallic catalyst. In addition, higher hydrocarbon vapours were expected at high synthesis temperatures due to faster rate of pyrolysis reaction (Ando, 2010). This most likely favoured the formation of carbon spheres and a-C coating. The a-C coating may have encapsulated the metal catalyst particles, thus weaken its catalytic behaviour.

In term of diameter, the CNT with lowest diameter were detected at samples synthesized at 700 and 750° C (140 nm). However the sample synthesized at 750° C showed wider range of CNT diameter from 140 to 180 nm, where bigger CNT tube can be easily seen from the FESEM image. For sample synthesized at 700° C the tubes size seem to be more uniform where the CNT diameter were approximately the same size. Wider diameter range detected at CNT-750° C sample was due to the catalyst particles that start and tend to agglomerate at 750° C, thus increasing the metal particles size. The widening of metal catalyst size promote bigger tubes diameter as catalysts were the nucleation site for CNT growth. For carbon spheres the smaller diameter were detected at CNT-800° C sample (0.86-1.22 µm) then the diameter increases to 1.07-1.58 µm as temperature increases at 850° C. The biggest carbon spheres diameter were measured at CNT-900° C sample of 1.86 µm. Again, the agglomeration of the catalyst was believed to be the cause for bigger carbon spheres detected at 900° C.

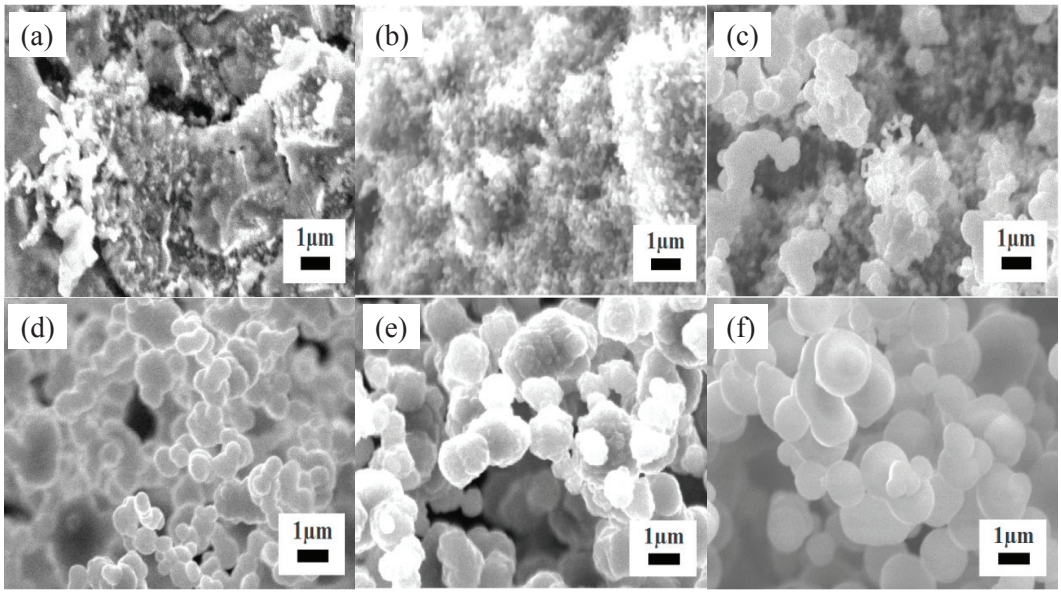

Figure 3 FESEM images of CNT synthesized at different synthesis temperature: (a) 650° C, (b) 700° C, (c) 750° C, (d) 800° C, (e) 850° C and (f) 900° C

The Raman spectra of CNT synthesized at different temperature 650-900° C are shown in Figure 4. The D or disorder mode which was originated from structural defects can

be clearly seen at 1343.18-1365.82 cm^{-1}. The G or graphite mode corresponds to planar vibrations of carbon atoms were seen at 1583.83-1610.29 cm^{-1}. Therefore, from the D and G mode, the I_D/I_G ratio can be calculated which represents the degree of disorder in CNT structures. From Table 1, the values of I_D/I_G ratio was found to be the lowest at CNT synthesized at 750° C (0.82). The I_D/I_G ratio value then increases from 0.83 to 1.00 when the CNT samples were synthesized at higher and lower than 750° C. The highest I_D/I_G ratio was detected at CNT synthesized at 900° C synthesis temperature. This reveals that the trend of CNT crystallinity varies with temperature during the synthesis process. The results indicated that the best crystallinity was shown by CNT synthesized at 750° C.

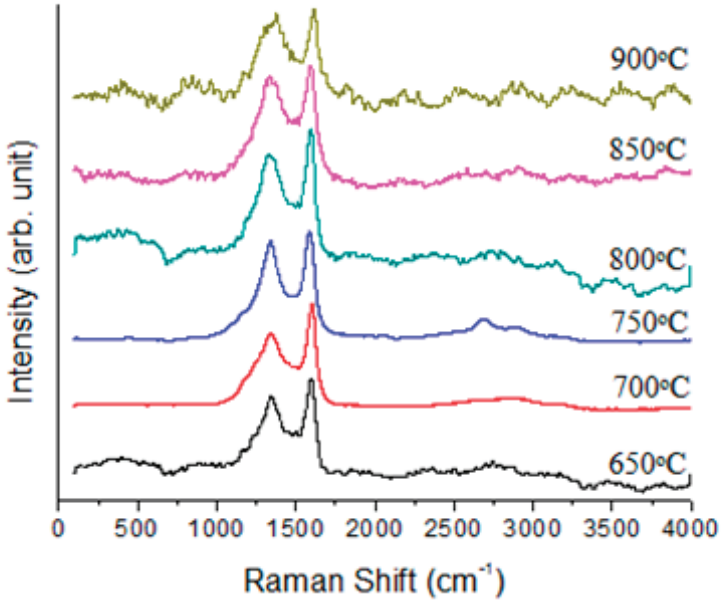

Figure 4 Raman spectra of CNT synthesized at different synthesis temperature of 650-900° C

Table 1 Raman peaks position and intensity ratios of D and G peaks for CNT synthesized at 600 to 800° C

Sample (° C)	G peak (cm^{-1})	G width (cm^{-1})	D peak (cm^{-1})	D width (cm^{-1})	I_D/I_G
650	1583.83	71.45	1343.18	205.10	0.84
700	1603.94	82.48	1365.82	194.70	0.94
750	1584.87	76.64	1340.15	208.73	0.82
800	1590.72	63.80	1347.99	252.73	0.83
850	1590.71	83.17	1350.00	229.69	0.97
900	1610.29	79.14	1357.85	214.63	1.00

Figure 5 shows FTIR spectra in the range of 500-4000 cm^{-1} for CNT synthesized between 650-900° C. Generally the samples shows peak at 1150, 1459, 1550, 1650, 1700, 1740, 2336 and 2366 cm^{-1} which corresponds to Si-O-Si stretching vibration, multi-walled CNT

Jurnal Sains dan Matematik Vol.4 No.2 (2012) 87-93
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and C=C vibration mode which were due to carbon skeleton and C-O respectively (Misra, 2006). It can be seen that the degree of absorption at 1740 cm^{-1} reduces at samples with less CNT density. Peaks were rather difficult to identify due to broader trend particularly for samples synthesized at lower (650° C) and higher synthesis temperature (800, 850 and 900° C). The clearest and strongest absorption at 1740 cm^{-1} was detected at samples deposited at 750° C. The peaks in the range of 2800-3000 cm^{-1} were the characteristic of C-H stretching mode which indicates the existence of a-C in the sample. The absorption peaks at 2956, 2927, 2860 cm^{-1} corresponds to sp^3 CH_3 (asymmetric), sp^3 CH_2 (asymmetric) or sp^3 CH, and sp^3 CH_3 (symmetric) stretches.

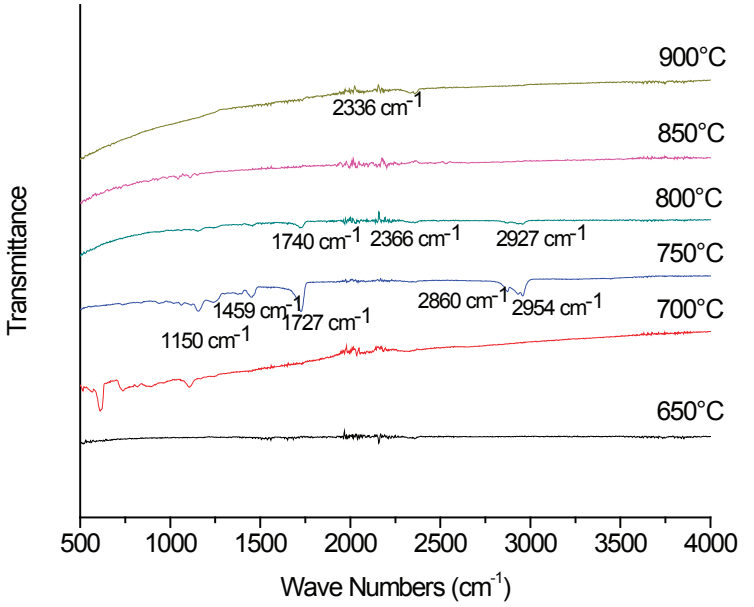

Figure 5 FTIR results of CNT synthesized at different temperature of 650-900 °C

Conclusion

In conclusion, the synthesis temperature of 750° C was considered the optimum temperature for CNT production based on small nanotubes diameter as well as low I_D/I_G ratio of 0.82. The FTIR spectra showed different absorption peak in the range of 500-4000 cm^{-1}. The degree of absorption at 1740 cm^{-1} which corresponds to CNT density, reduces at lower and higher than 750° C of synthesis temperature.

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References

Iijima, S. (1991). Helical microtubules of graphitic carbon. *Nature, 354*(6348), 56-58.

Guo T., P. N., Thess A., Colbert D.T., Smalley R.E. (1995). Catalytic growth of single-walled nanotubes by laser vaporization. *Chem. Phys. Lett., 243*, 49-54.

Qin L.H., X. Z., Hirahara K., Ando Y. and Ijima S., ((2000) .). Single-walled 4 Å carbon nanotube arrays. *Nature, 408*(50).

Lee C.J., J. H. P., Park J.H., (2000). Synthesis of bamboo-shaped multiwalled carbon nanotubes using thermal chemical vapor deposition. *chem. Phys. Lett., 323*, 560.

Suriani A.B., M. N. R. (2010). Vertically aligned carbon nanotubes synthesized from waste cooking palm oil, *Journal of the Ceramic Society, 65-66*, 963-968.

Suriani A.B., M. S., Sarah M.S.P., (2011). Effect of Temperature on the Growth of Vertically Aligned Carbon Nanotubes from Palm Oil. *Defect and Diffusion Forum, 312-315*, 906-911.

Suriani A.B., Azmina M.S., Falina A.N., Salina M., Rosly J., and Rusop M. "Preparation of Palm Oil Based Carbon Nanotubes at Various Ferrocene Concentrations," *Advanced Materials Research,* vol. 364, pp. 408-411, 2012.

Azmina M.S., Suriani A.B., Falina A.N., Salina M. and Rusop M., (2012). Temperature Effects on The Production of Carbon Nanotubes from Palm Oil by Thermal Chemical Vapor Deposition Method. *Advanced Materials Research 364*, 359-362.

Zhou W.J., W. Z. L., Song S.Q., Zhou Z.H., Jiang L.H., Sun G.Q., Xin Q., Poulianitis K., Kontou S., Tsiakaras P. (2004). Bi- and tri-metallic Pt-based anode catalysts for direct ethanol fuel cells. *Journal of Power Sources, 131*, 217-223.

Braidy. N, M. A. E. K., and Botton G.A. (2002). Effect of laser intensity on yield and physical characteristics of single wall carbon nanotubes produced by the Nd:YAG laser vaporization method *Carbon, 40* 2835-2842.

Bethune, D. S. (2002). Carbon and metals: a path to single-wall carbon nanotubes *Physica B: Condensed Matter, 323*, 90-96.

Osváth Z., A. A. K., Z. E. Horváth, Gyulai J., Benito A.M., Martínez M.T., Maser W.K., and Biró L.P., (2002). Arc-grown Y-branched carbon nanotubes observed by scanning tunneling microscopy (STM). *Chemical Physics Letters, 365*, 338-342.

H. M. Christen, A. A. P., H. Cui, K. Belay, P. H. Fleming, D. B. Geohegan, and D. H. Lowndes (2004). Rapid Growth of Long, VerticallyAligned Carbon Nanotubes through Efficient Catalyst Optimization Using Metal Film Gradients. *Nano Letters, 4* 1939-1942.

Kataura, H., Kumazawa, Y., Maniwa, Y., Umezu, I., Suzuki, S., Ohtsuka, Y., *et al*. (1999). Optical properties of single-wall carbon nanotubes. *Synthetic Metals, 103*, 2555-2558.

Ando, M. K. a. Y. (2010). Chemical vapor deposition of carbon nanotubes: a review on growth mechanism and mass production. *Nanoscience and Nanotechnology,, 10*, 3739-3758.

Misra, A., Tyagi, P. K., Singh, M. K., & Misra, D. S. (2006). FTIR studies of nitrogen doped carbon nanotubes. *Diamond and Related Materials, 15*(2-3), 385-388.