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Effect of Iron and Cobalt Catalysts on The Growth of Carbon Nanotubes from Palm Oil Precursor

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Abstract. Catalysts which are typically a transition metal is mandatory and plays an important role in the production of CNT. In this work, the effect of iron (Fe) and cobalt (Co) nitrate catalyst on the growth of carbon nanotubes (CNT) were systematically studied. Green bio-hydrocarbon precursor namely palm oil was used as a precursor. The synthesis was done using thermal chemical vapour deposition method at temperature of 750°C for 15 min synthesis time. The Fe and Co solution were spin-coated separately on silicon substrate at speed of 3000 rev.min-1. The CNT characteristics were analyzed using field emission scanning electron microscopy and micro-Raman spectroscopy. The experimental results revealed that CNT properties were strongly affected by the catalyst type. CNT catalyzed by Co yields large diameter, crooked tube and lower quality, whereas CNT produced by Fe catalyst results in the smallest diameter and reasonably good graphitization. As a conclusion, Fe was considered as the optimum catalyst for better CNT structure and crystallinity. This was due to efficient, uniform and stable Fe catalytic activity as compared to Co catalyst in producing CNT.

1. Introduction

Carbon nanotubes (CNT) were discovered in 1991 [1], since then many studies have been performed on their synthesis [2-6]. The synthesis of CNT can be classified into catalytic and non-catalytic methods. As for the catalytic method, nickel (Ni), iron (Fe) and cobalt (Co) are common transition metal utilized as pure-metal to catalyze the CNT growth [7-12]. The catalyst particles essentially serve as seeds for the growth of CNT. The main challenge in CNT production is to mass produce at low cost. In this regard, the catalytic method has been claimed to be the best approach due to its capability in lowering the reaction temperatures and cost. Between Ni, Fe and Co as a catalyst, Fe was reported to be the most efficient catalyst [13]. CNT produced from Fe catalyst were found to have higher degree crystallinity character, high density and small diameter tubes. However in term of growth rate Ni and Co catalysts have demonstrated better growth rate which outperformed Fe catalyst [13]. The ability of those catalyst were related to its catalytic activity for the decomposition and diffusion of hydrocarbon precursor on the active site, the formation of C-hexagon as well as the catalyst deactivation and the formation of meta-stable carbides [14, 15]. The catalyst itself can be used either separately or combined together to form bi or tri-catalyst combination [4]. Each single catalyst has its own role, a synergistic effect was expected when the catalyst were combined. Although the effect of catalyst on the growth of CNT have been extensively study but the decomposition of palm oil precursor over Fe and Co surface for the production of CNT have not been clearly discussed.

Here we report a systematic study of the effect of Fe and Co-nitrate on the growth of CNT using palm oil precursor. The synthesis was done in double furnace thermal chemical vapor deposition (TCVD) system. The results clearly revealed that the catalysts were not only affecting the diameter and growth rate but also the morphology and microstructure of CNT. The structural properties of CNT were analyzed using field emission scanning electron microscope (FESEM) and micro-Raman spectroscopy.

2. Experimental

First, the Fe and Co-nitrate catalyst were diluted separately with ethanol and stirred for 20 min. The catalyst films *were* prepared by dropping 3 drops of catalyst on Si substrates using a spin coater at speed of 3000 rev.min^{-1}. The catalyst coated substrate was dried at 90 ℃ for 24 hours before loaded into deposition furnace of TCVD system. 3 mL of palm oil was used as carbon source and loaded into *precursor* furnace. The deposition furnace was then heated to 750°C with argon gas supplied continuously. When the temperature was stable at 750°C, precursor furnace was turned-on at temperature of 450°C. The CNT synthesis was carried out for 15 min followed by 10 min of annealing time. When the growth completed, a Zeiss Supra 40VP FESEM and Jobin-Yvon, Horiba miro-Raman spectrometer were used to characterize the samples.

3. Results and Discussion

3.1. Morphological features

The CNT synthesis was done using two different catalysts namely Fe and Co-nitrate at synthesis temperature of 750°C. Figure 1 shows the morphologies of CNT synthesized using (a) Fe and (c) Co catalyst. The magnified images of CNT are shown in Figure 1 (b) and (c) for Fe and Co catalyst respectively. For comparison purposes, the FESEM images for 700°C samples are also shown in Figure 2 (a)-(d). Both catalysts gave a dense distribution of nanotubes growth with the presence number of un-reacted catalyst particles. In term of diameter, CNT catalyzed by Fe produced smaller and uniform diameter ranged at 31.2 nm. The tubes were longer as compared to Co catalyst. The diameter of CNT produced by Co catalyst were in range of 80-100 nm. The nanotubes were also severely crooked, obviously mixed with impurities namely amorphous carbon (a-C) and non-tubular carbon structures. A synthesis temperature of 700°C gave less CNT population particularly for Fe catalyst where large catalyst particles that remained un-reacted amidst the nanotubes were seen. For Co catalyst, it was clearly seen that the nanotubes diameter were getting smaller (42.2 nm) as

compared to 750°C synthesis temperature. In contrast to CNT catalyzed by Fe at 750 °C the tubes diameter greatly increases when it was synthesized at 700°C to 83.3 nm. From FESEM images in Figure 2 (e) and (f) it showed that better and smooth morphology CNT have been repeatedly demonstrated by CNT catalyzed by Fe catalyst which was regardless of the temperature utilized during the synthesis process.

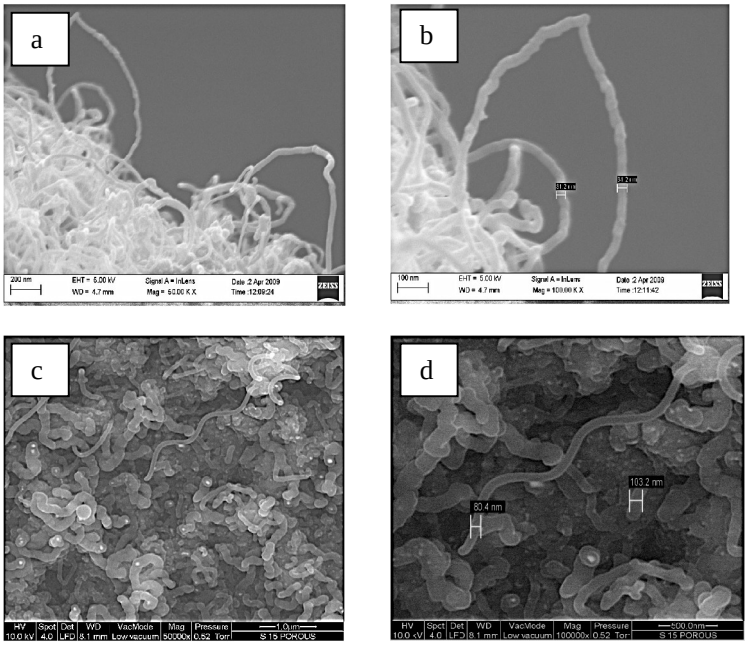
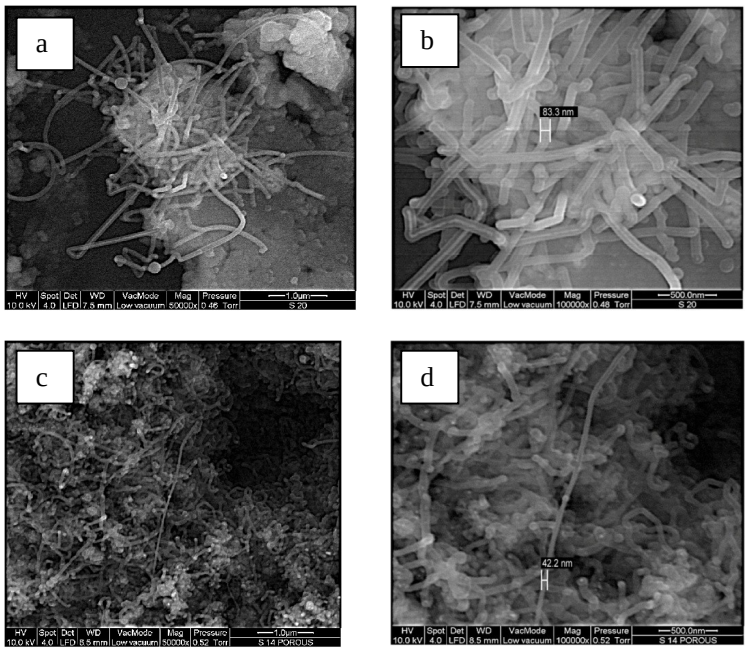


Figure 1. FESEM images of CNT synthesized at 750°C using (a)-(b) Fe and (c)-(d) Co-nitrate catalyst.



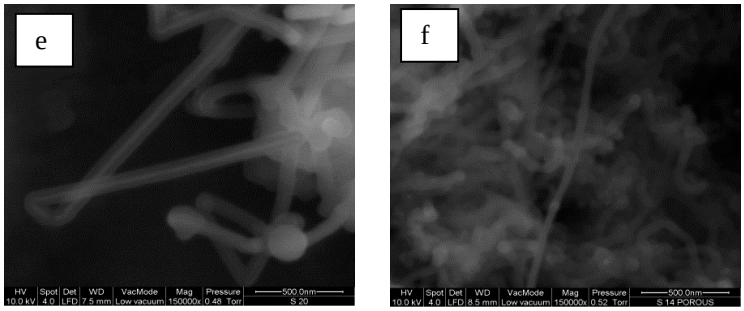


Figure 2. FESEM images of CNT synthesized at 700°C using (a),(b),(e) Fe-nitrate catalyst and (c),(d),(f) Co-nitrate.

3.2. Raman spectroscopy

The grown CNT were then characterized by Raman spectroscopy as shown in Figure 3. The well separated two Raman peaks at ~1592.67-1600.12 cm^{-1} for G peaks and at ~1346.30-1353.23 cm^{-1} for D peaks was observed for all samples. The I_D/I_G ratios were calculated to estimate the variation of CNT crystallinity with Fe and Co catalyst. The I_D/I_G value was found to be lower at Fe-750°C sample which was 0.65 and slightly higher using Co-nitrate (0.78). Irrespective of the type of catalyst used, the ratio values increases at 700°C synthesis temperature (Table 1). This reveals that the trend of CNT crystallinity varies with catalyst and synthesis temperature. Our results indicated that the best crystallinity was shown by CNT grown on Fe catalyst at synthesis temperature of 750°C. There was no lower frequency radial breathing mode (RBM) peaks detected for all samples which indicate no single-walled CNT (SWCNT) was produced [16].

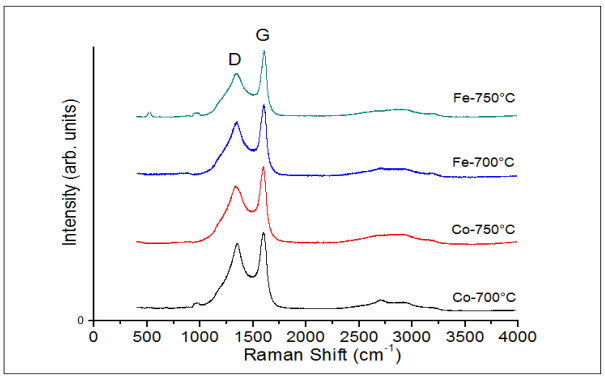


Figure 3. Typical Raman spectra of palm oil based CNT catalyzed by Fe and Co-nitrate at 750 and 700°C synthesis temperatures

Table 1. The Summary of Raman Scattering Data of CNT Catalyzed by Fe and Co-Nitrate at 750 and 700°C Synthesis Temperatures.

Samples	G peak (cm^{-1})	G-Width (cm^{-1})	D peak (cm^{-1})	D-Width (cm^{-1})	I_D/I_G ratio
Fe-750°C	1600.12	59.76	1353.23	236.93	0.65
Fe-700°C	1596.50	64.60	1346.30	237.54	0.72
Co-750°C	1592.67	69.91	1350.32	243.21	0.78
Co-700°C	1594.79	72.71	1352.42	232.69	0.81

Analyzing the efficiencies of Fe and Co-nitrate on the morphology and microstructure quality of CNT synthesized at 700 and 750°C, it was observed that good graphitization nanotubes (from ID/IG ratio) was best catalyzed by Fe and followed by Co catalyst. Co catalyst results in crooked, biggest diameter and impurities-rich tubes. This deduced that Co catalyst exhibit inefficient, less uniform and instable catalytic activity as compared to Fe which was much more efficient, uniform and stable across catalyst surface [4]. Figure 4 (a)-(b) shows FESEM images of Fe and Co-nitrate catalyst. From the images it can be seen that the Co particles have much bigger particles size distribution as compared to Fe. The catalyst particles size distribution were greatly affecting the efficacy of the catalytic activity and the size of the tubes itself. High surface area to volume ratio of small particles size of Fe catalyst was a crucial factor for faster and better catalytic reaction as compared to Co catalyst. This was because more surface area were involved in the reaction. As a result, the CNT catalyzed by Fe show better microstructure and less crooked. Therefore, the growth optimization with low I_D/I_G ratio and low nanotubes diameter were obtained when Fe-nitrate was used as catalyst at synthesis temperature of 750°C. However, the common features shown either by Fe or Co-nitrate catalyst was that there was no vertically aligned carbon nanotubes (VACNT) successfully produced and overall entangle, bigger diameter with moderate quality and quantity CNT were synthesized. In addition, this catalyst preparation method (through spin coating) produces non-continuous nanotube growth due to catalyst driven growth which would be a drawback, for some characterization [17] particularly for the application in nanoelectronic devices. For this reason, this creates the need to seek for better catalyst preparation method which able to produce densely packed CNT-bundle that cover the entire sample area.

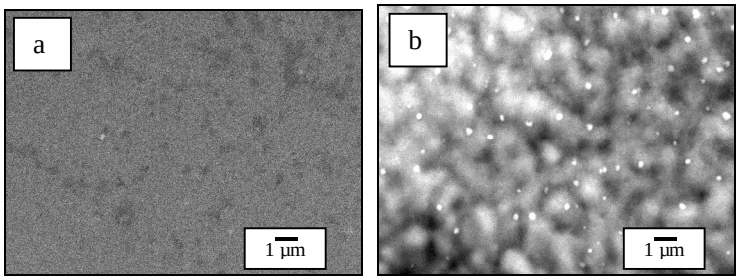


Figure 4. FESEM images of (a) Fe and (b) Co-nitrate catalyst.

4. Conclusion

In this study, the effect of Fe and Co-nitrate on the morphology and microstructure of CNT were investigated. The finding here suggest that Fe catalyst was an effective catalyst in obtaining the optimal CNT graphitization with lower diameter. Crooked, bigger diameter and impurities tubes were produced by Co catalyst. Due to low surface area to volume ratio of Co catalyst yielded inefficient, less uniform and instable catalytic activity in comparison to Fe catalyst. Through this catalyst preparation method there was no VACNT and SWCNT produced and the CNT population did not cover the entire substrate surface.

Acknowledgement

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