Research Article

Raman Spectroscopic Study of Carbon Nanotubes Prepared Using Fe/ZnO-Palm Olein-Chemical Vapour Deposition

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Multiwalled carbon nanotubes (MWCNTs) were synthesized using Fe/ZnO catalyst by a dual-furnace thermal chemical vapor deposition (CVD) method at 800–1000°C using nitrogen gas with a constant flow rate of 150 sccm/min as a gas carrier. Palm olein (PO), ferrocene in the presence of 0.05 M zinc nitrate, and a p-type silicon wafer were used as carbon source, catalyst precursor, and sample target, respectively. D, G, and G' bands were observed at 1336–1364, 1559–1680, and 2667–2682 cm⁻¹, respectively. Carbon nanotubes (CNTs) with the highest degree of crystallinity were obtained at around 8000°C, and the smallest diameter of about 2 nm was deposited on the silicon substrate at 1000°C.

1. Introduction

Carbon nanotubes (CNTs) were first reported by Iijima as multiwall nanotubes (MWCNTs) [1] and as single-wall nanotubes (SWCNTs) 2 years later. Since then, CNTs have attracted a lot of attention due to their superiority, particularly with regard to mechanical and electrical properties, and consequent suitability for a wide range of high-end applications in various fields. Generally, there are three main common techniques for synthesizing CNTs, namely, arc discharge, laser ablation, and thermal chemical vapor deposition (CVD).

Catalysts play an important role in synthesizing CNTs, and there are three main common catalysts that are widely used for the preparation of CNTs, namely, nickel (Ni), iron

(Fe), and cobalt (Co) and their combinations [2]. It has been reported that vertically aligned carbon nanotubes (VACNTs) were synthesized using PO as a carbon precursor by thermal CVD [3]. Similarly, MWCNTs were also synthesized using ZnO cold wall radio-frequency catalytic CVD [4]. The results show that the presence of ZnO narrows down the size distribution of the MWCNTs.

In this work, a palm-oil-based cooking oil, in particular, palm olein (PO), was used as a carbon precursor. The significant advantages of the precursor are that it is a very cheap, renewable biomaterial, green, and abundantly available. Owing to these factors, it has a huge potential to be used as the carbon source for the synthesis of CNTs, and therefore, the resulting product can be commercialized at a lower cost.

2. Experimental Setup

Zinc nitrate hexahydrate, hexamethylenetetramine, and ferrocene purchased from Systerm, Riedel-de-Haen, and Acros Organics, respectively, were used without further purification. A (100) p-type silicon wafer with a resistivity of 0–10 Ω/cm was purchased from Polishing Corp of America.

The substrate was prepared by cutting the silicon wafer into an area of 1 cm^2 , cleaned with acetone, ethanol and hydrofluoric acid, and finally dried. PO was mixed with different weight percentages of ferrocene and left for a day. The mixture solution was further mixed with 0.05 M zinc nitrate solution for another 30 minutes, so that the ratio of 30 PO (2% Fe) to 20 zinc nitrate was obtained. The MWCNTs were prepared using a dual furnace system with Furnace 1 and Furnace 2 placed in parallel. The prepared substrate was placed at the center of Furnace 2, and the mixture solution was placed in Furnace 1, in a quartz tube. Stoppers were inserted at both the ends of the quartz tube. A gas carrier, namely, nitrogen, with a flow rate of 150 sccm/min, was flushed into the tube to create an inert atmosphere. Furnace 2 was first switched on and heated to 750–1000°C, and then, Furnace 1 was heated to 500°C. The deposition time was set at 1 h, followed by an annealing process for 30 min. Characterizations were done on the resulting MWCNTs using a field-emission scanning electron microscope (Zeiss, Supra 40VP) and a Raman spectrophotometer with a laser of 514 nm wavelength (Horiba Jobin Yvon, LabRam HR800). X-ray diffraction (XRD) patterns of the MWCNTs were recorded on a Shimadzu XRD-6000 diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 30 mA at the scan rate of 2° min^{-1} . HRTEM analysis was done using a Philips, Tecnai 2 G.

3. Results and Discussion

The microstructure of the MWCNTs was studied by Raman spectroscopy. Raman spectra of the MWCNTs (Figure 1(a)) showed three prominent bands at around 1331–1366 cm^{-1} , 1569–1584 cm^{-1} , and 2667–2682 cm^{-1} , corresponding to the D, G, and 2D or G' bands, respectively (Table 1). The D band corresponds to the defects that are associated with the vacancies and the presence of other carbonaceous impurities that destroy the graphitic symmetry of the G band [5, 6]. On the other hand, the G and 2D bands represent the splitting of the E_{2g} stretching mode for the graphite and overtone of the D band, respectively.

Previous studies have shown that SWCNTs exhibit a radial breathing mode (RBM) with a wavenumber at 100–200 cm^{-1} [7, 8]. The nonexistence of RBM mode in the Raman spectrum (Figure 1(a)) indicates that the presence of SWCNTs can be ruled out, and therefore, the product of the synthesized material is dominated by MWCNTs. The wavenumbers of MWCNTs are summarized in Table 1.

Generally, the ratio of I_G/I_D can be used to show the presence of structural defects of the noncrystalline carbonaceous products [9]. A plot of I_G/I_D against deposition temperature (Figure 1(b)) showed that the crystallinity generally decreases as the deposition temperature increases from 800

TABLE 1: Properties of D, G, and 2D bands of MWCNTs synthesized at 750–1000°C studied by Raman Spectroscopy.

Temperature (°C)	Wavenumber (cm^{-1})			I_G/I_D ratio	I_{2D}/I_G ratio
	D band	G band	2D band		
750	1364	1569	2682	1.42	0.50
800	1361	1571	2685	1.79	0.37
850	1364	1576	2680	1.36	0.56
900	1350	1577	2675	1.10	0.52
950	1343	1584	2671	1.01	0.57
1000	1336	1680	2667	1.32	0.61

to 950°C. However, it was found that the crystallinity was improved as the temperature was increased from 950 to 1000°C with the I_G/I_D value of 1.79–1.01. Furthermore, the red shift of the G band indicated the reduction in graphitization of the resulting material.

The results obtained in this work were compared with MWCNTs prepared from other natural resources such as turpentine and coconut oil. MWCNTs prepared using both turpentine and coconut oil as the carbon sources were found to have a lower I_G/I_D value when compared with that of PO. This reveals that the microstructural quality of MWCNTs synthesized using PO is much better than that of turpentine and coconut oil under our experimental conditions. From the microstructure analysis, it can be concluded that the PO has resulted in MWCNTs with better crystallinity and has the potential to be used as a good carbon precursor. This is towards the use of renewable bioresources as the carbon source for CNTs production.

The overtone of the D band, usually labeled as the 2D or G' band, can be associated with the degree of crystallinity of the CNTs. The ratio of I_{2D}/I_G , given in Table 1 and plotted in Figure 1(c), shows that the wavenumbers of the G band are red-shifted from 1571 to 1686 cm^{-1} as the deposition temperature increased from 750 to 1000°C, in parallel with a finding from previous works that the degree of graphitization decreased as the wavenumbers of the G band increased [10]. At the same time, it can be noted that the D and G bands are blue-shifted. This shows that the deposition temperature also affects the graphitization degree of the resulting MWCNTs.

A more uniform size of MWCNTs was observed under our experimental method, when compared with the dense bundles of mixed MWCNTs and SWCNTs obtained by previous study [3], and the introduction of ZnO as a supported catalyst used in this work was found to reduce the size distribution of MWCNTs. In addition, the method of preparation is relatively simple, that is, only mixing of the PO with 0.05 M zinc nitrate and 2% ferrocene (w/w), followed by pyrolysis.

Figure 2 shows the morphology of MWCNTs deposited on a silicon substrate at different temperatures. Linear and helical structures [11] were observed at a lower deposition temperature of 850°C (Figure 2(a)). When the temperature was increased to 950°C, a necklace-like MWCNTs [12, 13] became dominant, with a smaller diameter of around 3–4 nm (Figure 2(b)). At 1000°C, a more uniform distribution of

FIGURE 1: (a) Typical Raman spectrum of MWCNTs showing the absence of RBM at around $100\text{--}200\text{ cm}^{-1}$; (b) plot of deposition temperature of the MWCNTs against I_G/I_D ; (c) plot of deposition temperature of the MWCNTs against I_{2D}/I_G .

MWCNTs was observed with a diameter of around 80 nm, but the presence of small diameter of 2 nm could still be observed (Figure 2(c) on the right).

Recently, Paul and Samdarshi [14] reported that the diameters of a random-orientation CNTs of around 80–90 nm were obtained when coconut oil was used as the carbon precursor. Similarly, turpentine oil was also used by Ghosh et al. to synthesize VACNTs with a diameter of 7–30 nm [15]. In this work, the surface morphology study showed that the smallest diameter obtained was around 2 nm when PO was used as the carbon precursor, and that it possessed a higher graphitic-to-defect ratio, when compared with other methods previously reported.

Figure 3 shows the high-resolution transmission electron microscope (HRTEM) images of MWCNTs at lower and higher magnifications. Carbon of nanotubes type can be clearly observed (Figure 3(a)) and a bamboo-like multi-walled structure is clearly visible in Figure 3(b) with a thickness of around 20–25 nm. This is in agreement with the absence of RBM wavenumbers at $100\text{--}200\text{ cm}^{-1}$ in the Raman spectrum, as shown in Figure 1(a), indicating that the product of the synthesis is exclusively MWCNTs without any presence of SWCNTs.

Energy dispersive X-ray spectroscopy (EDX) was also used to identify the elements existing in the samples. Several elements were detected, such as carbon, oxygen, iron, zinc,

FIGURE 2: Surface morphology of MWCNTs synthesized using PO as the carbon source at (a) 850, (b) 950, and (c) 1000°C. Higher magnification is given on the right.

and silicon, as shown in Figure 4. Carbon is the main element of the CNTs, while zinc and iron are present due to the catalysts. On the other hand, the silicon detected is due to the substrate used to deposit the MWCNTs.

X-ray diffraction (XRD) technique was used to determine the phases that exist on the resulting synthesized products (Figure 5). As shown in the figure, there are three phases coexisted namely zinc oxide [16], graphitic carbon [17] and iron oxide [18]. The presence of crystalline graphitic carbon instead of the amorphous phase clearly indicates that no coformation of amorphous carbon phase exists in the resulting product, and the carbon product is generally of MWCNTs type.

4. Conclusions

This study shows that MWCNTs can be synthesized by CVD method using PO as the carbon source. The smallest diameter of MWCNTs of about 2 nm was deposited on the silicon substrate at 1000°C. The highest crystallinity of carbon, I_G/I_D , was formed at 800°C. As the deposition temperature increased, the degree of crystallinity of the CNTs decreased due to more defects being introduced, possibly as a result of the coformation of nongraphitic carbons. The product of the synthesis exhibited a non-RBM of Raman Spectra and the HRTEM showed that the thickness of the walls was about 20–25 nm, indicating MWCNTs were formed. EDX, together with XRD analyses, proved that ZnO

(a)

(b)

FIGURE 3: HRTEM images of the MWCNT synthesis at 1000°C; at (a) lower magnification and (b) higher magnification.

FIGURE 4: A typical EDX of CNTs.

phase was also formed during the formation of MWCNTs from PO.

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FIGURE 5: A typical XRD pattern of MWCNTs showing the presence of graphitic carbon (a) and zinc oxide (b) and iron oxide phases (c), ghost peak (*).

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References

- [1] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, no. 6348, pp. 56–58, 1991.
- [2] A. A. Azira, N. F. A. Zainal, S. F. Nik et al., "Properties of carbon nanotubes synthesised using fluidized floating catalyst method from camphor oil," *Malaysian Journal of Science*, vol. 28, pp. 123–128, 2009.
- [3] A. B. Suriani, A. A. Azira, S. F. Nik, R. Md Nor, and M. Rusop, "Synthesis of vertically aligned carbon nanotubes using natural palm oil as carbon precursor," *Materials Letters*, vol. 63, no. 30, pp. 2704–2706, 2009.
- [4] D. Lupu, A. R. Biris, F. Watanabe et al., "Synthesis of narrow diameter distribution carbon nanotubes on ZnO supported catalysts," *Chemical Physics Letters*, vol. 473, no. 4–6, pp. 299–304, 2009.
- [5] S. Lefrant, M. Baibarac, I. Baltog, J. Y. Mevellec, C. Godon, and O. Chauvet, "Functionalization of single-walled carbon nanotubes with conducting polymers evidenced by Raman and FTIR spectroscopy," *Diamond and Related Materials*, vol. 14, no. 3–7, pp. 867–872, 2005.
- [6] S. Kamikura, T. Uchida, K. Naka, T. Asaji, H. Uchiyama, and Y. Yoshida, "Single-walled carbon nanotube growth using cobalt nanoparticles prepared by vacuum deposition on a surface-active liquid," *Diamond and Related Materials*, vol. 20, no. 7, pp. 863–865, 2011.
- [7] K. Kobayashi, R. Kitaura, Y. Kumai, Y. Goto, S. Inagaki, and H. Shinohara, "Synthesis of single-wall carbon nanotubes grown from size-controlled Rh/Pd nanoparticles by catalyst-supported chemical vapor deposition," *Chemical Physics Letters*, vol. 458, no. 4–6, pp. 346–350, 2008.

- [8] Y. Wang, Z. Zhang, H. Liu et al., "The effect of catalyst concentration on the synthesis of single-wall carbon nanotubes," *Spectrochimica Acta*, vol. 58, no. 10, pp. 2089–2095, 2002.
- [9] G. Zou, D. Zhang, C. Dong et al., "Carbon nanofibers: synthesis, characterization, and electrochemical properties," *Carbon*, vol. 44, no. 5, pp. 828–832, 2006.
- [10] J. Liu, Y. Zhang, M. I. Ionescu, R. Li, and X. Sun, "Nitrogen-doped carbon nanotubes with tunable structure and high yield produced by ultrasonic spray pyrolysis," *Applied Surface Science*, vol. 257, no. 17, pp. 7837–7844, 2011.
- [11] T. Luo, J. Liu, L. Chen, S. Zeng, and Y. Qian, "Synthesis of helically coiled carbon nanotubes by reducing ethyl ether with metallic zinc," *Carbon*, vol. 43, no. 4, pp. 755–759, 2005.
- [12] D. Zhang, C. Pan, J. Zhang, and L. Shi, "Solvothermal synthesis of necklace-like carbon nanotube/ceria composites," *Materials Letters*, vol. 62, no. 23, pp. 3821–3823, 2008.
- [13] A. Aguilar-Elguézabal, D. Lardizábal, W. Antúnez-Flores, and F. Paraguay-Delgado, "A novel necklace like structure assembled with MCM-41 and carbon nanotubes," *Journal of Alloys and Compounds*, vol. 466, no. 1-2, pp. 521–524, 2008.
- [14] S. Paul and S. Samdarshi, "A green precursor for carbon nanotube synthesis," *New Carbon Materials*, vol. 26, no. 2, pp. 85–88, 2011.
- [15] P. Ghosh, T. Soga, K. Ghosh, R. A. Afre, T. Jimbo, and Y. Ando, "Vertically aligned N-doped carbon nanotubes by spray pyrolysis of turpentine oil and pyridine derivative with dissolved ferrocene," *Journal of Non-Crystalline Solids*, vol. 354, no. 34, pp. 4101–4106, 2008.
- [16] S. Kumar, Y. J. Kim, B. H. Koo et al., "Room temperature ferromagnetism in chemically synthesized ZnO rods," *Materials Letters*, vol. 63, no. 2, pp. 194–196, 2009.
- [17] T. Takamura, K. Endo, L. Fu, Y. Wu, K. J. Lee, and T. Matsumoto, "Identification of nano-sized holes by TEM in the graphene layer of graphite and the high rate discharge capability of Li-ion battery anodes," *Electrochimica Acta*, vol. 53, no. 3, pp. 1055–1061, 2007.
- [18] J. Zieliński, I. Zglinicka, L. Znak, and Z. Kaszkur, "Reduction of Fe_2O_3 with hydrogen," *Applied Catalysis A*, vol. 381, no. 1-2, pp. 191–196, 2010.