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ORIGINAL ARTICLE

Synthesis of carbon nanofibers on impregnated powdered activated carbon as cheap substrate

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Abstract The catalysis and characterization of carbon nanofibers (CNFs) composite are reported in this work. Carbon nanofibers were produced on oil palm shell powdered activated carbon (PAC), which was impregnated with nickel. Chemical Vapor Deposition (CVD) of C_2H_2 was used in the presence of hydrogen at ~650 °C. The flow rates of carbon source and hydrogen were fixed. The CNFs formed directly on the surface of the impregnated PAC. Variable weight percentages (1%, 3%, 5%, 7% and 9%) of the catalyst salt (Ni^{+2}) were used for the impregnation. However, the best catalysis was observed on the substrate with 3% Ni^{+2}. The product displayed a relatively high surface area, essentially constituted by the external surface. New functional groups also appeared compared to those in the PAC. Field Emission Scanning Microscopy (FESEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared (FTIR), BET surface area analysis and energy dispersive X-ray (EDX) were used for the characterization of the new carbon nano product, which was produced through a clean novel process.

1. Introduction

Carbon is an important support material used in many heterogeneous catalysis applications (Figueiredo and Pereira, 2010; Nhut et al., 2003; Coq et al., 1998; Rodriguez-Reinoso, 1998). Application of activated carbon produced from various sources and raw materials is well-known. Activated carbon (AC) is a form of carbon that has been treated either physically by steam and carbon dioxide, or chemically using an activating agent at elevated temperatures (Macias-Garcia et al., 2003; Molina-Sabio et al., 1996; Gómez-Serrano et al., 1991). Such treatment results in a carbonaceous material that has high surface area and pore volume (Stiles, 1987; Smisek and Cerny, 1970; Auer et al., 1998). A variety of metal catalysts, such as noble metals (Pt, Pd and Rh) and base metals (Sn, Fe, Mn, Co and Ni), have been used as active catalyst via dispersion on active carbon supports (Molina-Sabio et al., 1996; Stiles,

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1987; Harada et al., 2007; Li et al., 2004). The four primary methods of metal impregnation are: wet impregnation, ion exchange, precipitation, and chemical vapor deposition (Stiles, 1987).

Research on nano or micro-sized carbons has drawn much attention because of their potential uses in a wide range of fields (Hasan et al., 2007; Fu et al., 2007; Zhang et al., 2006; Yu et al., 2005; Qiu et al., 2004). It is possible to tailor the microstructures of CNFs by the selection of a preparation method, including catalyst, carbon source and operating conditions (Tang et al., 2000; Thess et al., 1996; Díaz et al., 2010; Zhou et al., 2006). Various methods can be used to produce CNFs such as arc-discharge, laser ablation, or chemical vapor deposition (CVD). However, synthesis of CNFs on impregnated PAC as a substrate is not reported yet. However, various impregnation techniques are reported to be used for several substrates (other than PAC) in projects related to nanotechnology (Rao et al., 2013; Atkinson et al., 2011; Thiele et al., 2009; Chong et al., 2009; Gallego et al., 2008; Barreca et al., 2007). On the other hand, the effect of temperature on the growth of CNFs was studied by others (Ichi-oka et al., 2007; Huang et al., 2009). Here, we present the modification of powdered activated carbon (PAC) having sizes ranged between 100 and 250 μm by the impregnation of nickel and growth of CNFs.

2. Material and methods

In this study, palm kernel shell PACs were impregnated by using nickel (II) catalyst dissolved in acetone. The powdered activated carbon was immersed into the nickel solution and sonicated for 30 min in ultrasonic bath (Model: JAC 2010P)

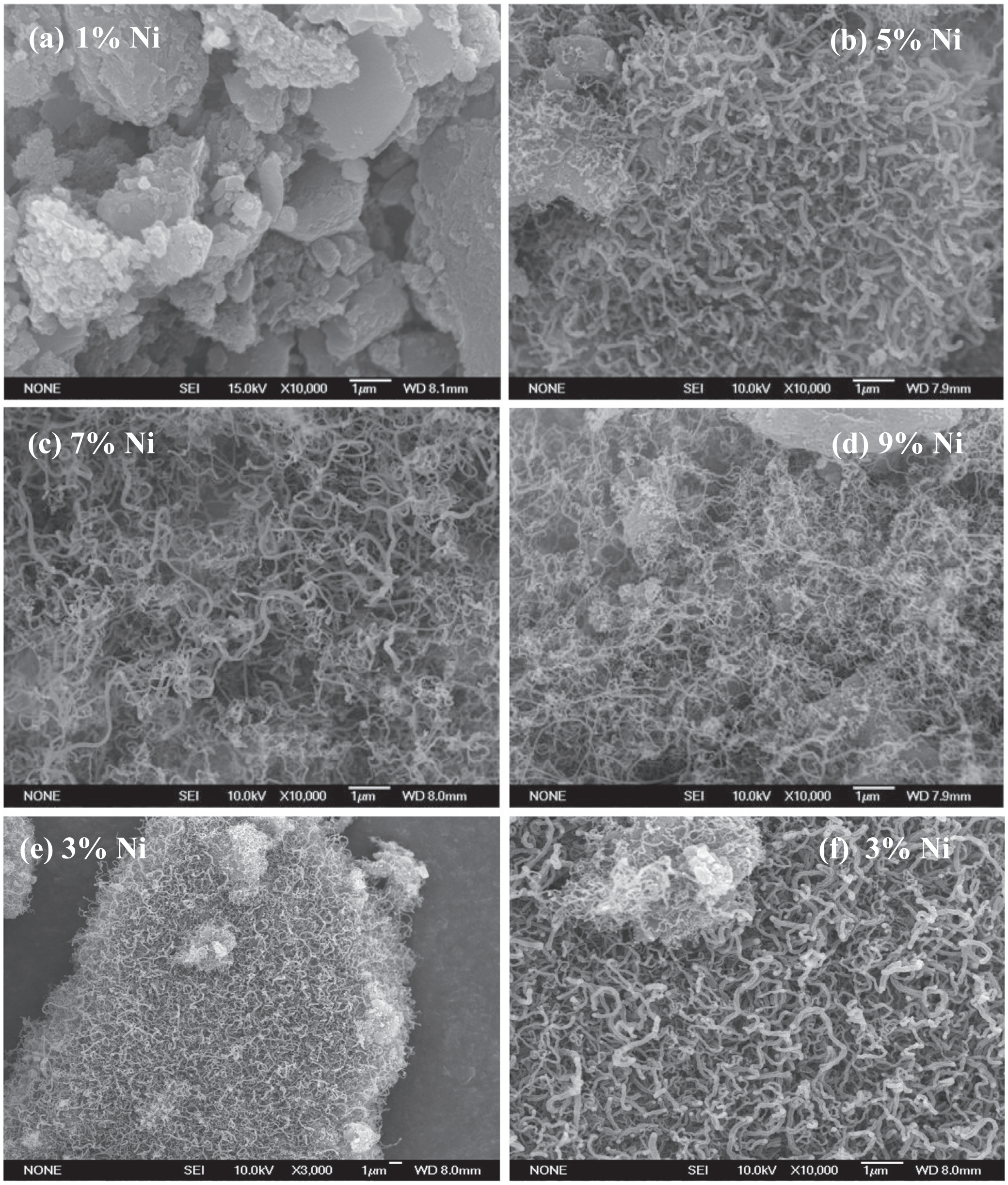


Figure 1 FESEM images of the CNFs.

and dried overnight under sonification in water bath at 56 °C. Five different ratios (1%, 3%, 5%, 7% and 9% w/w) of the catalyst were investigated to achieve production with satisfactory yield of CNFs. The impregnated PAC was "calcined" for 2 h in the presence of commercial grade pure N_2 gas (300 mL min^{-1}) at 350 °C and then "reduced" in situ by flowing pure hydrogen gas (200 mL min^{-1}) at 400 °C for another 2 h. The growth of CNFs was carried out on the reduced catalyst in a tubular ceramic reactor (inner diameter 40 mm and length 1500 mm) at atmospheric pressure in the presence of a mixture of acetylene (30 mL min^{-1} C_2H_2) and hydrogen (140 mL min^{-1} H_2) at 680 °C for 1 h.

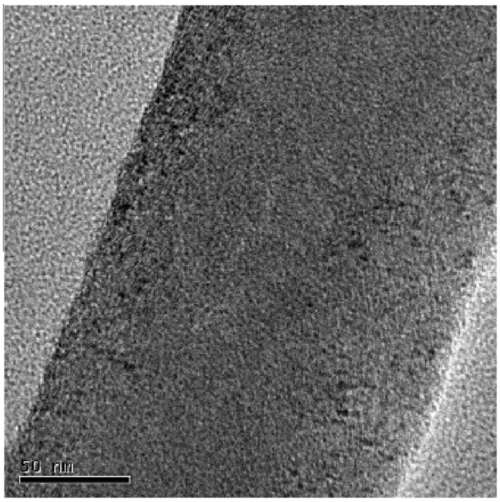


Figure 2 Transmission Electron Microscopy (TEM) Image.

FE-SEM model 6700F from JEOL Ltd., Japan was used to determine the morphology of CNFs. The diameter of the CNFs was determined using Transmission Electron Microscope – TEM (JEOL JSM-6700F). An energy dispersive X-ray analyzer was attached to the FESEM for the determination of structure of the PAC and CNFs. The surface area of the PAC and CNFs was determined using Quantachrome Autosorb Automated Gas Sorption System from Quantachrome Company, USA surface area analyzer.

3. Results and discussion

It was observed that the PACs impregnated with 3% catalysts (Fig. 1 e and f, showing different magnifications) have produced better yield of CNFs compared to other ratios of catalysts (1%, 5%, 7% and 9% for Fig. 1a–d, respectively) in terms of coverage of the host substrate and density of CNFs growth.

The presence of H_2 (with certain ratio to the carbon source) inside the reactant mixture was essential to obtain uniform sizes of CNFs. In the absence of sufficient H_2, these nanofibers became less homogenous with the appearance of irregular structures and nanoparticles (Pham-Huu et al., 2006).

The Transmission Electron Microscope (TEM) technique was used to show the diameter of the CNFs (Fig. 2). The image

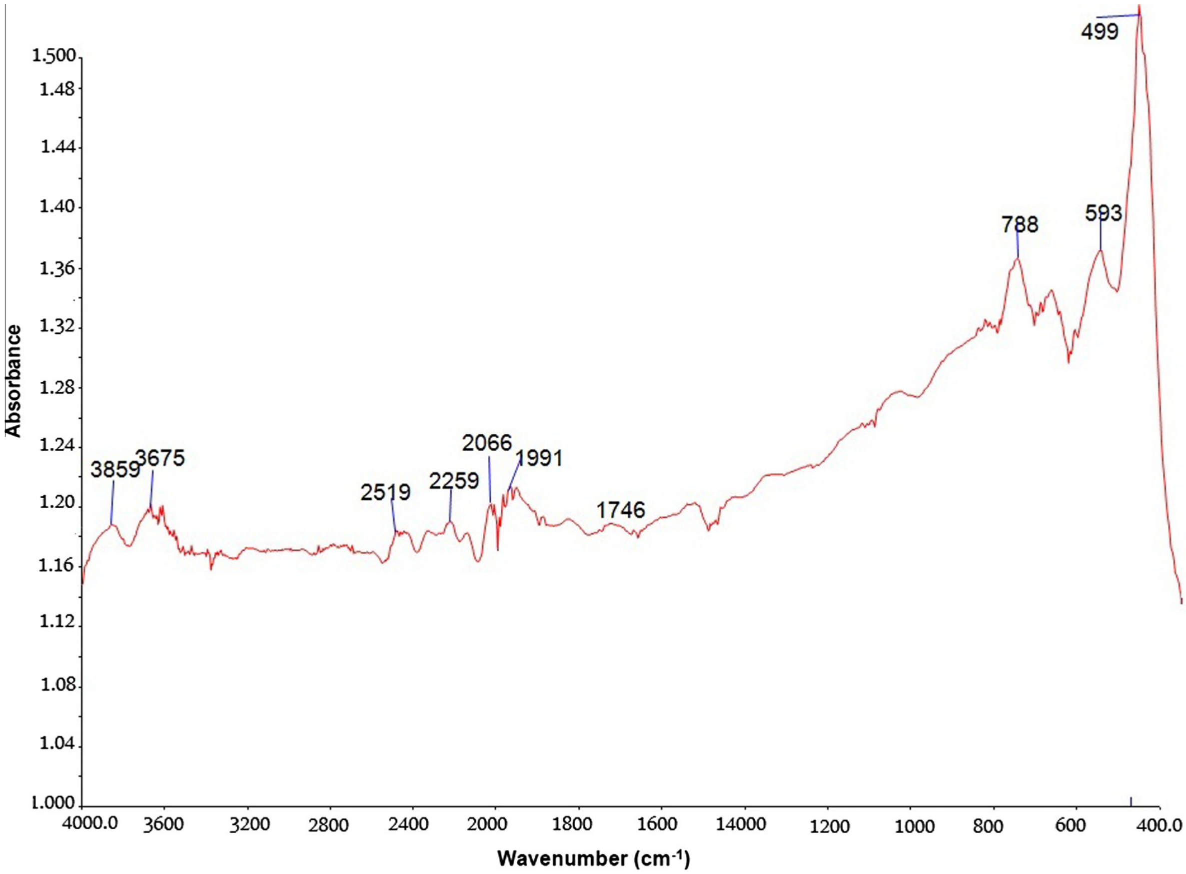
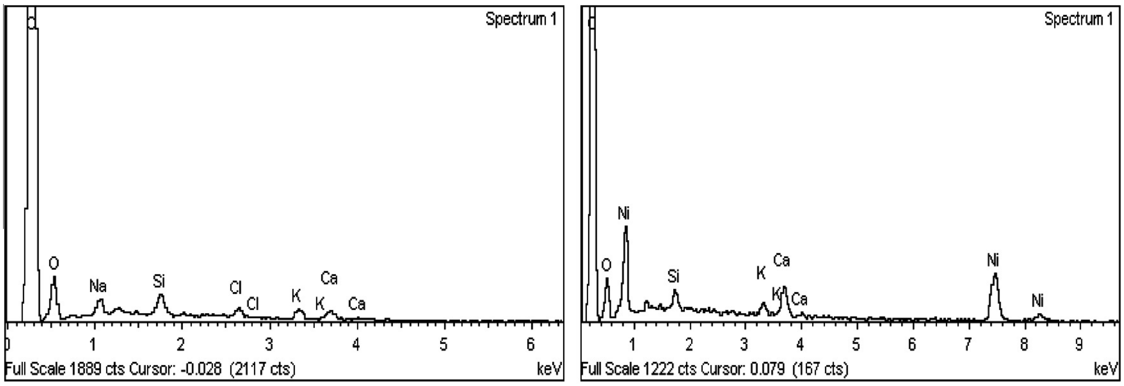


Figure 3 FTIR spectra for CNFs show different surface functional groups.



(a) Impregnated PAC

(b) CNFs

Figure 4 The EDX spectrum.

showed that the fibers have an average diameter range between 100 and 200 nm which are matched with images of FESEM above.

The FTIR spectrum of the selected batch of CNFs was scanned by using Perkin Elmer PE 1600 FTIR. Fig. 3 shows the absorbance peaks of the CNFs. In the recorded spectra, 4000–3000 cm^{-1} the bands of stretching O–H vibrations are revealed which can be attributed to surface hydroxylic groups and physically adsorbed water from the atmosphere (Chen and Wu, 2004). The weak absorption peaks in 2250–2400 cm^{-1} can be assigned to double bonded carbon oxygen groups (Nadeem et al., 2009). The characteristic bands at 878 and 834 cm^{-1} are assigned to aromatic C–H out of the plane bending vibrations (El-Hendawy, 2006). Absorption peaks at 766 and 702 cm^{-1} represent NO_2 bending vibrations (out of plane) in aromatic nitro groups. These functional groups would control the use of the CNFs for various purposes (e.g. as adsorbent for gas or liquid).

Physical characterization of the PAC and CNFs samples was analyzed with fully automated analyzer (model Quantachrome). The selected samples were analyzed by N_2 adsorption and the surface area of the samples was measured based on the Brunauer–Emmert–Teller (BET) equation (Brunauer et al., 1938). The results showed that the BET surface area of the PAC was increased from 101.1 m^2/g to 836.7 m^2/g after the growth of CNFs.

The energy dispersive X-ray (EDX) was used for the determination of the PAC and CNFs structures (Fig. 4).

4. Conclusions

Various methods, substrates and reagents can be used to synthesize CNFs. Many methods are costly (such as arc-discharge and laser ablation), and few methods used hazardous gasses such as C_6H_6. The growth of CNFs on impregnated PAC was successfully conducted using a cheap substrate and less hazardous gas (C_2H_2). The characterization of CNFs showed that, besides temperature, gas ratios and carbon source, w/w percentage of the impregnation of nickel was a decisive factor in the growth of CNFs. The FTIR spectra showed the presence of various functional groups that are important for the applications of the CNFs, for various purposes.

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References

Atkinson, J.D., Fortunato, M.E., Dastgheib, S.A., Abadi, M.R., Rood, M.J., Suslick, K.S., 2011. Carbon 49 (2), 587–598.

Auer, E., Freund, A., Pietsch, J., Tacke, T., 1998. Appl. Catal. A 173, 259–271.

Barreca, D., Blau, W.J., Croke, G.M., Deeney, F.A., Dillon, F.C., Holmes, J.D., Kufazvinei, C., Morris, M.A., Spalding, T.R., Tondello, E., 2007. Microporous Mesoporous Mater. 103 (1–3), 142–149.

Brunauer, S., Emmet, P.H., Teller, E., 1938. J. Am. Chem. Soc. 60, 309–319.

Chen, J.P., Wu, S., 2004. Langmuir 20, 2233–2242.

Chong, M.N., Lei, S., Jin, B., Saint, C., Chow, C.W.K., 2009. Sep. Purif. Technol. 67 (3), 355–363.

Coq, B., Planeix, M.J., Brotons, V., 1998. Appl. Catal. A 173 (2), 175–183.

Díaz, E., León, M., Ordóñez, S., 2010. Int. J. Hydrogen Energy 35, 4576–4581.

El-Hendawy, A.N.A., 2006. J. Anal. Appl. Pyrol. 75, 159–166.

Figueiredo, J.L., Pereira, M.F.R., 2010. Catal. Today 150, 2–7.

Fu, X.B., Yu, H., Peng, F., Wang, H.J., Qian, Y., 2007. Appl. Catal. A 321, 190–197.

Gallego, V., Giraldo, L.F., López, B.L., Sierra, L., 2008. Stud. Surf. Sci. Catal. B 174, 961–964.

Gómez-Serrano, V., Sánchez-Iñiguez, F., Valenzuela-Calahorro, C., 1991. Fuel 70, 1083–1090.

Harada, T., Ikeda, S., Miyazaki, M., Sakata, T., Mori, H., Matsumura, M., 2007. J. Mol. Catal. A: Chem. 268, 59–64.

Hasan, M.M., Zhou, Y.X., Jeelani, S., 2007. Mater. Lett. 61, 1134–1136.

Huang, C.W., Wu, H.C., Lin, W.H., Li, Y.Y., 2009. Carbon 47, 795–803.

Ichi-oka, H., Higashi, N., Yamada, Y., Miyake, T., Suzuki, T., 2007. Diam. Relat. Mater. 16, 1121–1125.

Li, X., Zhang, Y., Smith, K.J., 2004. Appl. Catal. A 264, 81–91.

Macias-Garcia, A., Gomez-Serrano, V., Alexandre-Franco, M.F., Valenzuela-Calahorro, C., 2003. J. Hazard. Mater. B 103, 141–152.

Molina-Sabio, M., Gonzalez, M.T., Rodriguez-Reinoso, F., Sepúlveda-Escribano, A., 1996. Carbon 34, 505–509.

Nadeem, R., Ansari, T.M., Akhtar, K., Khalid, M., 2009. Chem. Eng. J. 152, 54–63.

Nhut, J., Pesant, L., Tessonnier, J., Winé, G., Guille, J., Pham-Huu, C., Ledoux, M., 2003. Appl. Catal. A 254, 345–363.

Pham-Huu, C., Vieira, R., Louis, B., Carvalho, A., Amadou, J., Dintzer, T., 2006. J. Catal. 240, 194–202.

Qiu, J.S., Li, Y.F., Wang, Y.P., 2004. Carbon 42, 2359–2362.

Rao, V.M., Castano, C.H., Rojas, J., Abdulghani, A.J., 2013. Radiat. Phys. Chem. 89, 51–56.

Rodriguez-Reinoso, F., 1998. Carbon 36, 159–175.

Smisek, M., Cerny, S., 1970. Active Carbon; Manufacture, Properties and Applications. Elsevier, New York (pp. 1–32).

Stiles, A., 1987. Catalyst Supports and Supported Catalysts: Theoretical and Applied Concepts. Butterworth Publishers, Stoneham (pp. 110–117).

Tang, D.S., Xie, S.S., Liu, W., Chang, B.H., Sun, L.F., Liu, Z.Q., Wan, G., Zhou, W.Y., 2000. Carbon 38, 480–483.

Thess, A., Lee, R., Nikolaev, P., Dai, H., Petit, P., Robert, J., Xu, C., Lee, Y.H., Kim, S.G., Rinzler, A.G., Colbert, D.T., Scuseria, G.E., Tománek, D., Fischer, J.E., Smalley, R.E., 1996. Science 26, 483–487.

Thiele, D., Colmenarejo, E.L., Grobety, B., Züttel, A., 2009. Diam. Relat. Mater. 18 (1), 34–38.

Yu, Z., Chen, D., Tøtdal, B., Holmen, A., 2005. Mater. Chem. Phys. 92, 71–81.

Zhang, H.L., Zhang, Y., Zhang, X.G., Li, F., Liu, C., Tan, J., 2006. Carbon 44, 2778–2784.

Zhou, J.H., Sui, Z.J., Li, P., Chen, D., Dai, Y.C., Yuan, W.K., 2006. Carbon 44, 3255–3266.