Synthesis of Carbon Nanotubes using Electric Arc Furnace Slag as a Source of Catalyst

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Abstract

Low-cost productions of high-quality multiwall carbon nanotubes (MWCNTs) have been widely studied. Carbon nanotubes have been synthesized using thermal chemical vapor deposition previously. In this paper, high purity and quality of MWCNTs with about 30 nm in diameter have been successfully produced using catalyst derived

from electric arc furnace slag (EAFS) and acetylene gas (C_2H_2) as a carbon source via chemical vapor deposition. The hematite catalyst was extracted from EAFS using simple reflux and re-precipitation process. Catalyst and CNTs was characterized using field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), thermogravimetric analysis (TGA) and Raman spectroscopy. The carbon nanotubes were highly graphitized (I_D/I_G ratio = 0.36) and have higher purity up to 93 %. Because the catalyst is the unsupported catalyst, they can be removed from carbon nanotubes by simple reflux with a low concentration of hydrochloric acids for only 30 minutes. In a nutshell, the utilization of EAFS not only solve the environmental problem causes by the dumping of EAFS in the landfill, it also produces a value-added product such as MWCNTs.

***Keywords**: carbon nanotubes, hematite, electric arc furnace slag, chemical vapor deposition.*

Introduction

Carbon nanotubes (CNTs) are one of the key materials in nanotechnology and are currently among the most intensively investigated materials since it was first discovered by [1]. CNTs has been used in plethora of application including catalysis, optoelectronic device[2] biotechnology[3], coating [4] and many more[5]. A key parameter in governing the growth of CNTs is the catalyst [6, 7]. Commonly, the catalyst used in the production of CNTs will be supported on various supporting material such as silica, calcium carbonate, zeolites and alumina [1, 6-10]. Eventhough it produces better distribution of CNTs diameter compared to the unsupported catalyst, the inherent disadvantage of supported catalysts is its incorporation into the CNTs formed, which necessitates aggressive purification. The use of unsupported catalyst, on the other hand will minimize the CNTs to aggressive purification treatments that might damage the nanotubes. High purity of CNTs have been reported with the use of unsupported catalyst including hematite [2]. This paper reports on the extraction of nanoparticle hematite catalyst from electric arc furnace slag (EAFS) and the growth of high quality multiwall carbon nanotubes (MWCNTs) via decomposition of acetylene. Hematite was chosen as a catalyst as it is easily available with low cost. Hematite also well known to have good catalytic properties. The use of EAFS as a starting material in catalyst production for synthesis of MWCNTs has never been reported. Elemental composition of slag includes Fe, Ca, Si, Mn, Al and Mg while the minerals are present as gehlenite, larnite and bredigite, magnetite and magnesioferrite and manganese oxide together with anhydrous calcium silicates and silicoaluminates [11, 12]. These elements and minerals normally release to the environment by aging process and leaching which contributes to water and soil pollution[6]. However, the presence of these elements and minerals also makes EAFS as potential catalyst candidate for MWCNTs growth. The extracted nanoparticle hematite catalyst was successfully used as an unsupported catalyst in the growth of MWCNTs using an in-built house CVD reactor. The use of unsupported catalyst has further minimized the purification time as well as defect in the MWCNTs. High density and quality (>90%) of MWCNTs has successfully produced using hematite catalyst extracted from EAFS.

Methodology/ Methods

2.1 Catalyst preparation

The EAFS used in the work was collected from Antara Steel Mills Sdn Bhd, Malaysia. The unsupported nanoparticle hematite catalyst used for the growth of carbon nanotubes was extracted from EAFS by refluxing the grounded slag in 6 M ammonium chloride solution for 4 hours. The resulting mixture was filtered followed by the addition of 0.1 M potassium hydroxide solution and stirred slowly to induce the precipitation of the nanoparticle hematite. After decant the filtrate solution, the solid nanoparticle hematite was collected and annealed at 900 °C, grounded, and sieved.

2.2 *Carbon nanotubes growth and purification*

In an in-house-built TCVD reactor, MWCNTs were synthesized using acetylene as a carbon precursor [6, 13]. First, around 0.5 g of the unsupported hematite catalyst was spread evenly on a 150 mm length quartz boat. By supplying nitrogen gas at 0.1 L/min, the horizontal tube furnace was heated in an inert environment. Acetylene gas was added into the system for 30 minutes once the reactor temperature reached 700 °C. The MWCNTs were synthesized and allowed to cool in an inert environment for 2 hours before being removed for characterisation and purification. The as-synthesized MWCNTs was purify by refluxing it in 5 M hydrochloric acid for 30 minutes[6, 14].

2.3.Catalyst and carbon nanotubes characterization

Field Emission Scanning Electron Microscopy (FESEM-Hitachi SU8020), High Resolution Transmission Electron Microscopy (HRTEM-JEOL JEM 2100), micro-Raman spectroscopy (Renishaw InVia microRaman System), and thermogravimetric analysis (Perkin-Elmer Pyris 1) were used to examine the properties of catalyst and MWCNTs in terms of the physical structure, crystallinity and thermogravimetric analysis.

Results and Discussion

3.1 Catalyst preparation

Figure 1 shows the XRD and FESEM image of the nanoparticle hematite catalyst extracted from EAFS. Figure 1a depicted all the diffraction lines were fitted to rhombohedral crystalline phases of iron oxide. The XRD pattern has good agreement with the reference pattern (ASTM Card No. 33-0664) of hematite (α-Fe_2O_3). The estimation average crystallite sizes of α-Fe_2O_3 through three most intense indexed peaks of (104), (110) and (116) and the d values were 57.5, 60.0, and 53.5 nm respectively, with the average size of 57.0 nm. Fig. 1b shows the FESEM micrograph for α-Fe_2O_3 nanoparticles annealed at 900 °C. The α-Fe_2O_3 nanoparticles have flower-like densely porous nanoarchitectures composed of ultra-thin nanoflakes[15]. The diameter of this nanostructure was between 50 – 60 nm thus confirming that the nanosized of α-Fe_2O_3 was extracted from the EAFS. This is in agreement with the results obtained from the Debye-Scherrer equation from XRD analysis. Thus, the method employed has successfully synthesized α-Fe_2O_3 nanoparticles with a narrow size distribution.
Refer to Figure 1

3.2 Carbon nanotubes growth

High density MWCNTs was successfully synthesized using the nanoparticle hematite catalyst. The diameters of MWCNTs obtained are in a range of 10.6 nm- 42.1 nm. FESEM image shown in Figure 2a reveals the MWCNTs are formed in bundles scheme instead of isolated. The presence of these bundles structure was attributed to the formation of weak interaction force (van der Waals forces) between nanotubes[16]. TEM image in Figures 2b and 2c exhibits the thread-like structure of MWCNTs that were successfully synthesized and purified using hydrochloric acids. The well-graphitized of MWCNTs were clearly seen; MWCNTs is very well-graphitized with an internal diameter in the range of ~ 5-30 nm. Hence, TEM image had demonstrated the existence of uniform and narrow diameter of MWCNTs.

Refer to Figure 2

The TGA and Raman spectra of MWCNTs are shown in Figure 3. The thermal stability of MWCNTs was assessed using TGA to identify the percentage of deposited carbon in the product. In general, the oxidation of MWCNTs synthesised by TCVD

technique results in two significant weight losses: amorphous carbon (300-400 °C), carbon nanotubes (400-700 °C) [17]. Figure 3a shows that 93% of weight loss occurred between 400 and 700 °C, indicating that carbon was predominantly deposited in the form of MWCNTs. In addition, during the synthesis process, only a limited amount of amorphous and graphitic carbon is formed [18]. The ID/IG ratio was 0.36, according to Raman spectroscopy. The D band (1380 cm^{-1}) is associated with carbon disorder or defect, while the G band (1580 cm^{-1}) is associated with MWCNTs graphitization. As a result, the low I D/I G ratio, which corresponds to a weak D band and a strong G band, suggests that the product contains a few defects which proposed the synthesis of high quality MWCNTs.

Refer to Figure 3

Conclusion

In summary, we have synthesised good crystallinity (I_D/I_G ratio of 0.36) and high-purity (93 %) MWCNTs with a minimal defect or carbonaceous particle on their surface layers using hematite unsupported catalyst derived from EAFS. The production of MWCNTs from EAFS was simple, low cost and easy implement for industrial production. Furthermore, EAFS as industrial residue was an alternative budget-free catalyst source to the conventional available catalyst. This project provide solution to tackle issues of EAFS as an environmental pollution and enlighten new application of EAFS in the nanotechnology field. Hence, with low production cost, high high-quality MWCNTs can be produced with catalyst extracted from EAFS.

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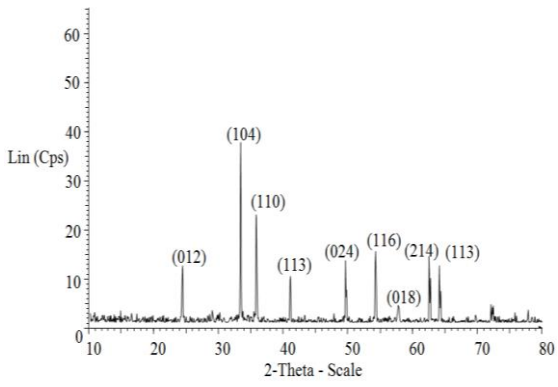
Figure Captions

Fig. 1. (a) XRD pattern, (b) FESEM micrograph of α-Fe_2O_3 nanoparticles catalyst after annealed at 900 °C.

Fig. 2. (a) FESEM images of MWCNTs grown from EAFS, (b) and (c) TEM images of MWCNTs grown from EAFS.

Fig. 3. (a) The TGA and DTGA curves of CNT grown from EAFS, (b) Micro-Raman spectrum showing the D and G line of MWCNTs.



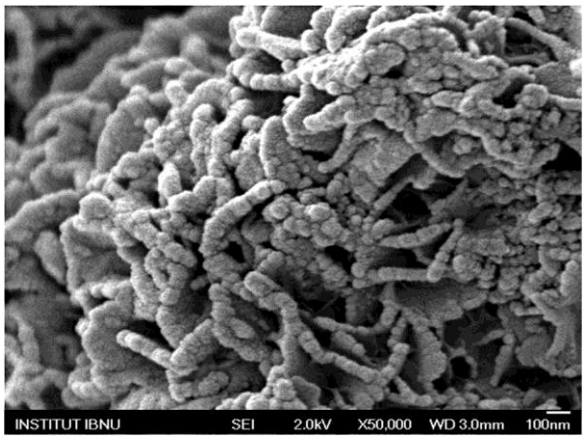


Figure 1

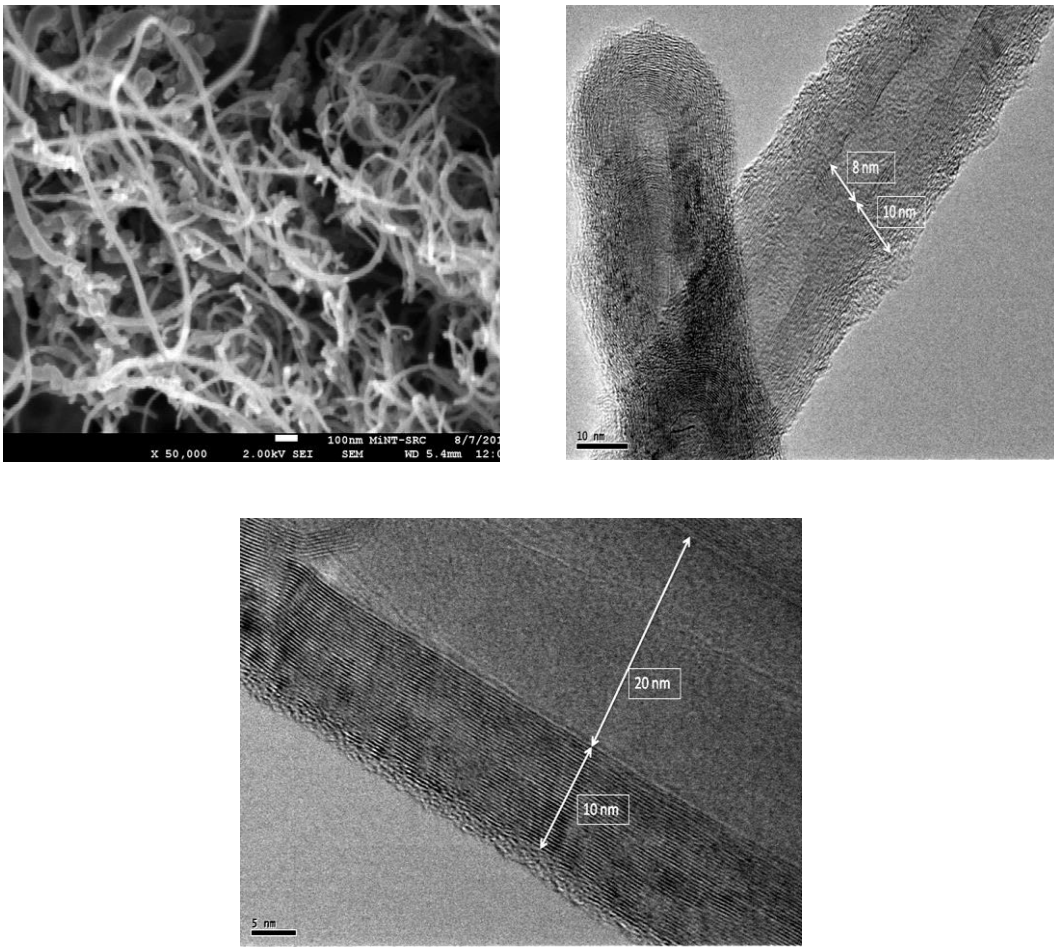


Figure 2

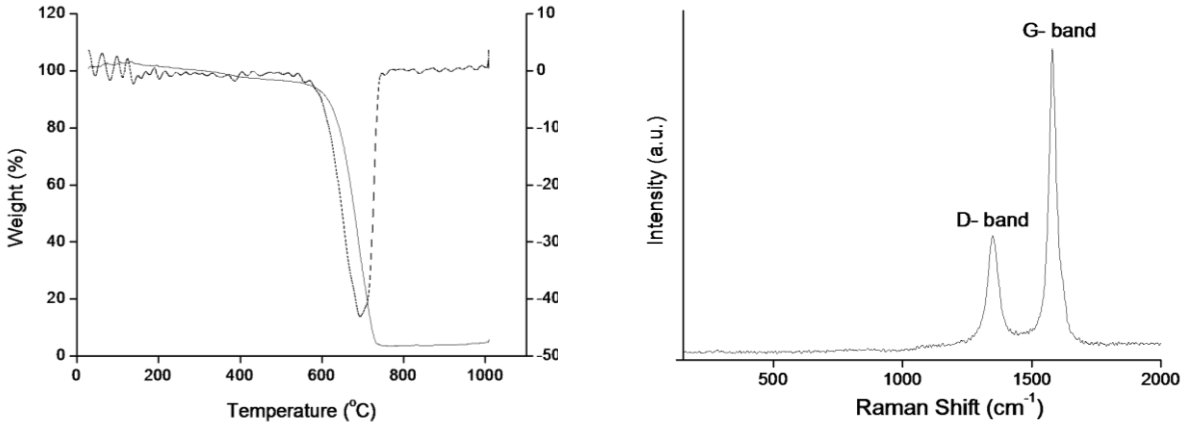


Figure 3