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To cite this article: F.I. A. Bakar *et al* 2018 *J. Phys.: Conf. Ser.* **1082** 012048

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Synthesis of α -Fe₂O₃ Nanowires/MWCNTs Composite for Photocatalyst

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Abstract. Multi-walled carbon nanotube (MWCNTs) was decorated on nanowires iron oxide (α -Fe₂O₃) thin film (α -Fe₂O₃/MWCNTs) by spin coating method. Nanowires hematite was produced by thermal oxidation of Fe substrate at 400 °C for 120 minutes. The aim of this nanocomposite α -Fe₂O₃/MWCNT is to improve the photocatalytic efficiency of the α -Fe₂O₃ nanowires. The structural characterization of the as-prepared composites were analyzed by x-ray diffraction (XRD), raman spectra, and photoluminescence spectra (PL) to identify the structure of pure α -Fe₂O₃ and decorated of MWCNTs. While, the morphological observation, interaction of MWCNTs and nanowires structure on hematite phase was done by scanning electron microscopy (FESEM). It was found that, the optimization dispersion of MWCNTs in the dimethyl form amide (DMF) solvent through acid treatment with 3 Molar nitric acid (HNO₃), shows the homogenized well-decorated MWCNTs on the surface of the nanowires structure, which can eliminate the limitation of iron oxide and help in electron transfer from α -Fe₂O₃ to MWCNTs.

1. Introduction

Over the past several decades, exponential population, rapid development of industrialization have been accompanied by a sharp modernization and metropolitan growth. The industrial activities leading to deleterious interferences of the vast generation, such as food processing, textiles, leather, paper, synthetic dyes have accounted for causing water pollution.

Therefore, developing advanced methods for purification of water is important for monitoring the environmental and human health. According Jantawasu et al., advanced oxidation processes (AOPs) are one of the promising methods for this issue due to its competency in degrading and mineralizing organic pollutant rather than other methods [1]. α -Fe₂O₃ is one of the challenging materials in this case that has a suitable properties to be one of the attractive semiconductor in such application compared to other semiconductor such as ZnO and TiO₂. This is due to low cost, most stable phases and narrow band gap of 2-2.2 eV [2]. Furthermore, it can absorb in the red light of the visible range, solar light up 620 nm, which is around 43% in the solar spectrum [3]. The photoactivity α -Fe₂O₃ is generally hampered by poor charge transportation, short holes diffusion length of 2-4 nm and its leading to high recombination photogenerated electron-hole pairs [4].



To overcome the limitation of α -Fe₂O₃ nanostructure, a relatively new method was created to minimize the recombination of charge pairs and improved the charge transportation in nanostructured. Thus, the properties of α -Fe₂O₃ is modified by formation of composite by combining with carbon nanomaterial's such as carbon nanotube (CNT) [5-6]. This composite sample have fascinating properties such as large surface area, inert chemical properties, one-dimension structure and strength that has not been shown by any known materials. Recently, CNT have drawn much attention because of their unique characteristics such as excellent stability, small size, high porosity, higher surface area and layered structure provide enough adsorption sites as well as good support catalytic assistant materials [6]. Furthermore, CNT has excellent electrical, mechanical, and thermal properties. This effect is believed to originate either from the favourable adsorption properties of MWCNTs. Their ability to trap electrons and thus reduce the electron-hole recombination. However, good combination between α -Fe₂O₃ and MWCNTs has become the challenge. Where, problems faced in transferring the MWCNTs to the application. The MWCNT had very strong van der wall interaction, thus it's very easy to agglomeration and entanglements. Therefore, this work is to propose a good solvent for MWCNT dispersion and functionalize the CNT in the carboxyl group to provide extra oxygen so that more hydrophilic surface structure can be generated [7]. This would help to increase the ion-exchange which leads to a well decorated CNT on the α -Fe₂O₃.

Nowadays, many researchers studied on focus on attachment of α -Fe₂O₃ nanoparticle to the MWCNT in various applications [8-10]. However, this study is focusing on nanocomposite of α -Fe₂O₃ nanowires/MWCNTs by convenient method is proposed.

2. Methodology

High-purity iron foil (99.99 %) was used with a thickness of 0.25 cm. The substrate was subjected to an ultrasonic cleaning in ethanol for 10 minutes and rinsed with distilled water. Then, the cleaned Fe substrate is dried in an air stream and placed on a substrate heater in chamber furnace at 400 °C and oxidation for 120 minutes. The heating rate around rate $\sim 10^{\circ}\text{C min}^{-1}$ and cooled down at room temperature to consist of scarlet layer homogeneously. This work was conducted under ambient environment.

MWCNTs were supplied by CNano Technology. MWCNTs had an average length and a diameter of 10 μm and 11 nm with ~ 95 % purity. In order to improve their solubility and remove residual catalyst, the nanotubes were functionalization with -COOH group and carried out using HNO₃ by chemical technique. For the oxidation treatment, 0.3 g MWCNTs were treated into 3 molar HNO₃ with 100 ml solution followed by distilled water. The mixture were sonication using the sonicating bath (100w, 50Hz) for 2 hours at 70 °C. Thus, was promotes MWCNTs disentanglement within acid solution. The purified MWCNTs were obtained after filtering and thoroughly rinsed with distilled water until reaching pH 7. Finally, the slurry is dried in drying oven at 80 °C for 24 hours.

In a composite sample, there have two different solutions for dissolution of the MWCNTs, which are organic solvent such as acetone, DMF and aqueous solvent using surfactant is sodium dodecylbenzenesulfonate (SDBS) with distilled water with amount of 9 mg/ml. The MWCNTs suspension was prepared using UP 100H ultrasonic horn with 0.25 mg/ml for 45 minutes. The deposition of MWCNTs on the α -Fe₂O₃ thin film were carried out by spin coating method. The spinning time and speed was set for 30 sec, 4000 rpm/s for acetone and SDBS. While, DMF solvent was set for 120 sec and 3000 rpm/s. The finally, the sample was contain SDBS solvent was immersed in the Deionized water (DI water) for 1 hours to assist the removal of the surfactant.

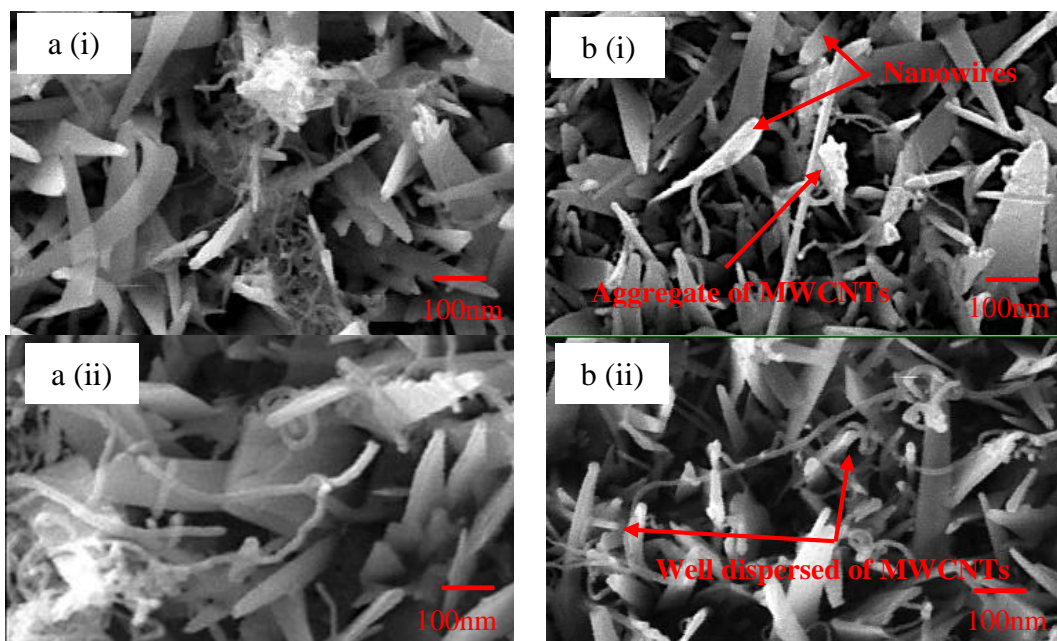
Then, to evaluate the incorporation of α -Fe₂O₃/MWCNTs composite, surface morphologies were characterized by FE-SEM S4800, Hitachi. While, the crystalline structure of α -Fe₂O₃/MWCNTs composite was characterized by XRD, Cu K α radiation, $\lambda = 1.5406\text{\AA}$ in the range 20 ° to 80 ° and Raman spectra were recorded at room temperature using the UniRAM-3500 performed at a laser wavelength of 523 nm. Besides, PL spectra were measured on FLS920 Edinburgh instrument, with Xenon lamp 450Watt.

In this work, the nanocomposite photocatalyst $\alpha\text{-Fe}_2\text{O}_3/\text{MWCNTs}$ was verified by the degradation of 10 ppm methyl orange. The degradation was done under UV-light irradiation. During the experiment, $\alpha\text{-Fe}_2\text{O}_3/\text{MWCNTs}$ photocatalyst film were put in 20 ml of methyl orange containing beaker. The solution of MO with photocatalyst is then kept in the dark for 1 hours for the adsorption and desorption equilibrium. Then, exposed to UV light for 5 hours and the solution were taking out every 2 hours during irradiation for analyzing the absorbance change of MO by UV-VIS spectroscopy (UV-1700).

3. Results and discussion

3.1 Electron microscopy analysis

Nanocomposite sample with the pristine MWCNTs and functionalized MWCNTs with COOH is shown in Figure 1 (a) and (b) respectively. From Figure 1(a) i- 1(a) iii, it is seen that, samples with pristine MWCNTs leads to the agglomeration of MWCNTs on the nanowires structure composite for all solvents. This is due to the strong van der wall interaction of MWCNTs that contributed to the clustering of MWCNTs on the $\alpha\text{-Fe}_2\text{O}_3$. While for functionalized MWCNTs (Figure 1(b) i - 1(b) iii), surface reactivity of MWCNTs is significantly enhanced, given the better decorated composite. It showed that, metal catalyst and amorphous carbon were removed and wettability of MWCNTs was enhanced. In Figure 1 b (i), shows the coverage of MWCNTs in acetone are non-uniform and has a small aggregate of MWCNTs on nanowire structure. But the combined effect of surfactant with SDBS in water-soluble (Figure 1 b (iii)) and dispersion in DMF solvent (Figure 1 b (ii)) has given the well-dispersed and decorated of MWCNTs on the nanowires structure. This is because SDBS surfactant has a benzene rings that could contribute to increase the dispersion power of surfactant by interaction of π - π , thus leading MWCNTs prolongs the slurry suspension time [11]. Furthermore, the tail of the surfactant work as hydrophobic properties and it react to attach on the surface of MWCNTs to overcome bundled of MWCNTs, thus stabilized nanotubes. While, dispersion in DMF solvent shows almost a fully covered MWCNTs with a fairly thin film due to the availability free electron pair and high solvatochromic parameter [12]. It has made this solvent as one of the best solvent in the dispersion of MWCNTs. The high polar wettability of DMF offers the fast and all directional solution spread-out during spinning. Thus, the low surface tension of DMF solvent at the liquid/solid interface contributed to the improved uniformity of the layer and boost the coverage of thin film [13].



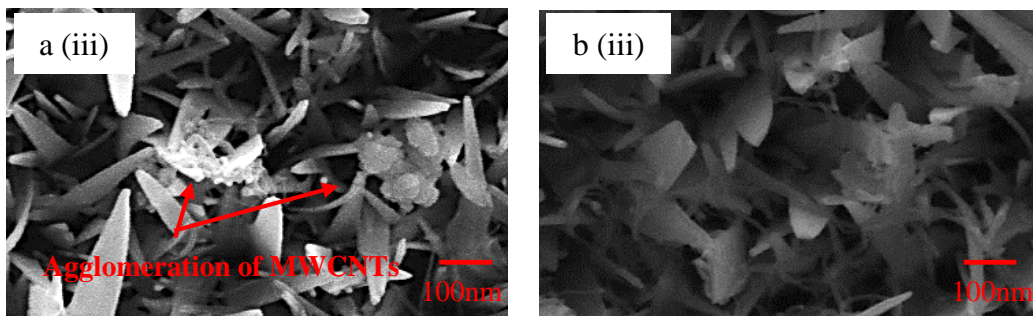


Figure 1. SEM micrographs of (a) α -Fe₂O₃/MWCNTs nanocomposite with untreated MWCNTs and (b) α -Fe₂O₃/MWCNTs nanocomposite with treated MWCNTs. Different solvent used is for WMCNTs dispersion: i) acetone, ii) DMF, iii) aqueous solvent (SDBS)

3.2 XRD analysis

Figure 2 indicates XRD patterns of pristine α -Fe₂O₃ and α -Fe₂O₃/MWCNTs thin film. The pristine α -Fe₂O₃ and nanocomposite of α -Fe₂O₃/MWCNTs in various solvent exhibited dominant peaks of α -Fe₂O₃ phase at 33.3, 35.8, 41.1, 43.8, 49.8, 54.5, 57.8, 62.8, 64.4 which corresponds to (104), (110), (113), (202), (024), (116), (122), (214) and (300) planes. These standard peaks attributed to α -Fe₂O₃ phase for pure rhombohedral, space group: R3c with lattice constant, $a = 5.0082\text{\AA}$ and $c = 13.6467\text{\AA}$ (JCPDS No. 01-072-6226). Therefore, the crystal structure of [110] showing the favorable growth of nanostructured on the hematite phases. In nanocomposite, no diffraction peak of MWCNTs was observed even in functionalized of MWCNTs, due to the low content of MWCNTs and low diffraction pattern intensity [14]. Furthermore, no significant changes occur between the pristine α -Fe₂O₃ and MWCNTs. The phase purity of α -Fe₂O₃ in composite structure is maintained and MWCNTs are not incorporated into the lattice of α -Fe₂O₃.

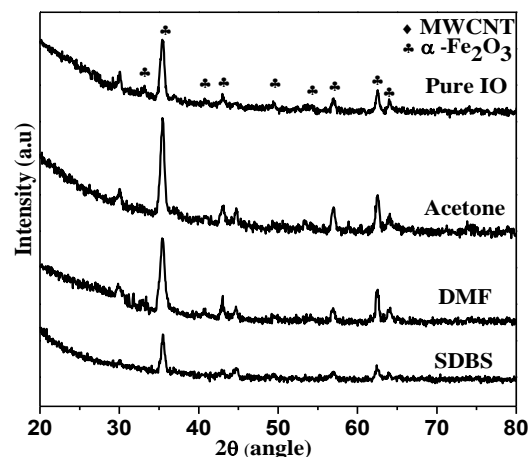


Figure 2. XRD patterns for pristine α -Fe₂O₃ and α -Fe₂O₃/MWCNTs nanocomposite with, treated MWCNTs in various solvent

3.3 Raman spectra analysis

Raman spectroscopy was carried out to confirm presence of carbon nanotube in the α -Fe₂O₃/MWCNTs sample. Figure 3 shows the Raman spectra of α -Fe₂O₃ and α -Fe₂O₃/MWCNTs. In the case of a modified sample of α -Fe₂O₃/MWCNTs, two peaks of MWCNTs at 1339 cm⁻¹ and 1580 cm⁻¹ can be attributed to the D and G band respectively (Figure 3 (a)). This Raman analysis of functionalized MWCNTs shows the intensity of D band become higher compared to G bands, it's due to the presence of more defects on the surface of MWCNTs in functionalization process and good interaction in composite sample. While, another five peaks rise in the composite sample for hematite phase was detected due vibration modes of

Fe-O bonds for α -Fe₂O₃ at lower Raman shift (218, 277, 393, 483 and 592 cm⁻¹). This is classified as “internal mode” (2A_{1g} + 3E_g). This results aligned with Wang et al., [15]. In composite, it can also be observed that the average I_G/I_D ratio in DMF solvent are 0.91, which are higher compared to the other solvent. This has caused the dispersion and decorated of MWCNTs on the nanowires structure in DMF solvent is in better condition and quality. Furthermore, in the case of nanocomposite α -Fe₂O₃/MWCNTs as shows in Figure 3 (b), small shift indicating a weak shift compared to pure α -Fe₂O₃. It is reported, that a good contact and direct interaction between α -Fe₂O₃ nanowires structure and MWCNTs is created.

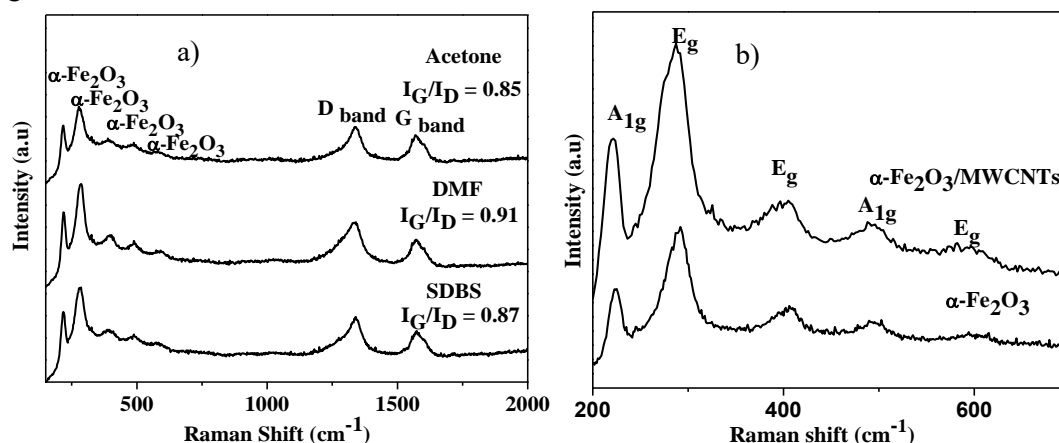


Figure 3. The Raman spectra of α -Fe₂O₃ and α -Fe₂O₃/MWCNTs (a- showing full range in composite and b – showing low range)

3.4 Photoluminescence spectra analysis

Figure 4 shows the PL analysis of pure α -Fe₂O₃ and α -Fe₂O₃/MWCNTs composite using the DMF solvent. PL analysis can be used to evaluate the mobility of the charge carriers to the surface and also its recombination process involving the electron-hole pairs [14]. As seen in Figure 4, the intensity of α -Fe₂O₃/MWCNTs nanocomposites were significantly decreased compared the pure α -Fe₂O₃ indicating that, there is inhibition of electron charge recombination with the presence of MWCNTs. The weak intensity of the composite becomes rise due to the well-decorated MWCNTs on the nanowires structure and amount of MWCNTs was added. It is believed that, MWCNTs could be as electron storage to trap part of the electron generated from the photoexcitation of the α -Fe₂O₃ nanowires due to the defect structure and it contained more oxygen during the functionalized of MWCNTs.

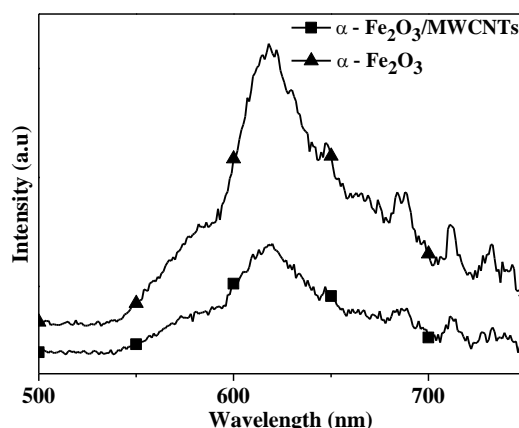


Figure 4. Photoluminescence spectra of α -Fe₂O₃ and α -Fe₂O₃/MWCNTs composite

3.5 Photocatalytic reaction analysis

In the photocatalytic part, degradation of methyl orange is carried out to establish the photocatalytic activity of the pristine α -Fe₂O₃ and α -Fe₂O₃/MWCNTs nanocomposite as shown in Figure 6. The pure

α -Fe₂O₃, has a poor photocatalytic indicated only 28 % degradation efficiency through 5 hours of UV irradiation. While after adding MWCNTs, α -Fe₂O₃/MWCNTs composite with DMF solvent shows dramatic enhancement of degradation efficiency compared to pristine α -Fe₂O₃. This is caused, the usage of MWCNTs tends to reduce the recombination process and effective in accepting, and storing of electron.

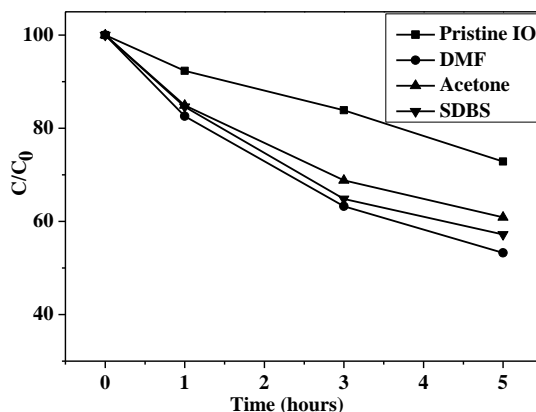


Figure 5. Photocatalytic degradation of methyl orange in 5 hours

4. Conclusions

In summary, the study of α -Fe₂O₃/MWCNTs were successfully prepared by thermal oxidation and spin coating. From this study, photodegradation of the dye and efficiency of composite attribute to a good transfer charge in α -Fe₂O₃ nanowires due to the presence of MWCNTs. Thus, minimized the recombination of electron-hole pairs and MWCNTs were found to be efficient assistant for photocatalyst as it help to create a trap region in α -Fe₂O₃ band gap. The photocatalytic activity of α -Fe₂O₃ can be improved up to 50 % by having a low content of MWCNTs compared pure iron oxide. The higher adsorption capacity by α -Fe₂O₃/MWCNTs is mainly attributed to adsorption sites and defect from the functionalization of MWCNTs in HNO₃.

Acknowledgement

The authors would like to thank Universiti Teknikal Malaysia Melaka for financial (PJP/2016/FKP-AMC/S01499) and facility support.

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