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Preparation of MWCNT-Fe_3O_4 Nanocomposites from Iron Sand Using Sonochemical Route

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Abstract: The composites of multi-walled carbon nanotube (MWCNT) and magnetite (Fe_3O_4) nanoparticles from iron sand were successfully prepared via the sonochemical route. In this experiment, the MWCNT-Fe_3O_4 nanocomposites were prepared with different compositions of MWCNT (0.01%, 0.02%, and 0.04%) with the constant composition of Fe_3O_4 particles. The characterizations were performed by means of X-Ray Diffractometry (XRD), Fourier Transform Infra-Red (FTIR) Spectrometer and Scanning Electron Microscopy (SEM) integrated with Energy Dispersive X-Ray (EDX). The XRD data analysis showed that the Fe_3O_4 crystallize in spinel structure in nanometric size. Furthermore, the crystallinity of the samples tended to reduce by increasing the MWCNT compositions. The SEM images showed that Fe_3O_4 tend to agglomerate in nanometric size. The FTIR spectra detected the functional groups of Fe-O bonding that showed the existence of Fe^{2+} and Fe^{3+}. In the composites, the Fe_3O_4 nanoparticles were physically mixed with the MWCNTs constructing a unique structure. The as prepared MWCNT-Fe_3O_4 nanocomposites have the potential for bio-applications.

Keywords: MWCNT, Fe_3O_4, iron sand, nanocomposite, sonochemical route.

1. Introduction

Nowadays, the development of nanomaterials was focused on improvement of properties and function as well as their promising application. So, the fabrication of nanocomposites has been extensively investigated by researchers for exploring the new type of materials with combine of two or more compounds with better performances. By definitions, a nanocomposite consists of a multiphase of solid materials where part(s) or all of the phases with dimensions less than 100 nanometers (nm) [1]. In recent years, nanocomposites of carbon nanotube (CNT) and magnetite (Fe_3O_4) become much attention due to their unique properties owned by these materials, especially in nanoscale. The CNT has great potential in many application since found in 1991 by Iijima [2] due to it has many advantages such as large surface area, high electric conductivity, superior in mechanical and thermal properties [3-4]. Meanwhile, the Fe_3O_4 also has standout properties particularly in magnetic properties,

namely superparamagnetic behaviors in nanoscale [5]. Furthermore, the flexibility of Fe_3O_4 which can be arranged depending on their sizes and structures make it become the fascinating materials.

The nanocomposite of MWCNT-Fe_3O_4 have been applied in many fields such as for removal trace arsenic and chromium [4,6], for magnetic printing ink [7], as adsorbents [8], for enhancing electrochemical performance in Li-ion batteries [9], for immunoscreening [10], for immune sensor [11], for hyperthermia and drug delivery [12], and so forth. There are three general approaches for creating MWCNT-Fe_3O_4 composites i.e. the Fe_3O_4 can be encapsulated, incorporated within the walls and deposited on the outer surface of nanotubes [13]. Various techniques have been conducted by researchers for obtaining the nanocomposite of MWCNT-Fe_3O_4. Pourkhalil [14] successfully synthesized the MWCNT-Fe_3O_4 nanocomposite by using sol-gel methods. The results showed that the Fe_3O_4 distributed on the surface of the MWCNT with superparamagnetic behavior at room temperature and with saturation magnetization of 19 emu/g. Meanwhile, Balacianu et al. [15] reported that the synthesis of MWCNT-Fe_3O_4 was done by coprecipitation method with covalent functionalization of Fe_3O_4. However, this process was not significantly add the amount of MWCNT which attached on the Fe_3O_4. The coprecipitation method was also used by Qu et al. [16] resulting the Fe_3O_4 with average sizes of 10-30 nm found on the surface of MWCNT. Its electrochemical characterization revealed that the nanocomposite of MWCNT-Fe_3O_4 is very appropriate for biosensor applications. Furthermore, Zhou et al. [7] reported that the MWCNT-Fe_3O_4 nanocomposite was successfully prepared by hydrothermal method. The result showed that the Fe_3O_4 with cubic structure attaching to the surface of MWCNT. Its magnetic characterization showed that the nanocomposite has superparamagnetic behavior with saturation magnetization of 38 emu/g.

The various synthesis methods of the MWCNT- Fe_3O_4 nanocomposites and their application were reported by many researchers. However, the synthesis of the MWCNT-Fe_3O_4 with the sonochemical route using a starting material of Fe_3O_4 from iron sand have never been found in the literature. Therefore, this paper will report the effective and simple method to synthesize the MWCNT-Fe_3O_4 nanocomposites from iron sand via sonochemical route. Besides that, the influence of MWCNT composition on the morphology of nanocomposite MWCNT-Fe_3O_4 is also discussed.

2. Experimental Method

2.1. Materials

In this work, the materials were multiwall carbon nanotubes (~ 50 nm in diameter, and ~ 1 μm in length), iron sand from the southern coast of Indonesia, HCl (molarity 12 M), NH_4OH (molarity 6.5 M), HNO_3 (65 %), ethanol, and distilled water.

2.2. Functionalization of MWCNT

The MWCNTs (1 g) were functionalized by treating nitric acid (1: 100 w/v) and sonicated at frequency of 40 kHz for 120 minutes at 50 °C. The functionalized MWCNTs were filtered by the paper filter and repeatedly washed with ethanol and distilled water until pH neutral. After that, the samples were dried in an oven at 100 °C for 5 hours.

2.3. MWCNT-Fe_3O_4 nanocomposite fabrication

The first step, the iron sand that had been extracted by a magnet permanent was dissolved in HCl and stirred 900 rpm for 30 minutes until to obtain the iron salts solutions. Later, 10 mL the solutions were added into 0.1 g of MWCNTs (0.01 % of the total composite) and sonicated (40 kHz) for 10 minutes. The next process was the dropping of 12 mL NH_4OH to get the black precipitate, sonication process continued for 20 minutes. The resulted precipitate was washed extensively with the distilled water, and the MWCNT-Fe_3O_4 was collected by a strong magnet. The as-prepared MWCNT-Fe_3O_4 was dried in an oven at 100 °C for 5 hours. This process was repeated with various MWCNT contents, i.e. 0.02% and 0.04%.

2.4. Characterizations

The samples were characterized by XRD for find out their crystalline size and crystal structure. Meanwhile, the functional groups of the nanocomposites were investigated by FTIR. Furthermore, the morphology and composition of the samples were observed by SEM-EDX.

3. Results and discussion

Figure 1 shows the XRD patterns of the samples. From the figure, the peaks of the Fe_3O_4 nanoparticles and MWCNT of all samples were clearly identified. The peak of MWCNT as shown in figure 1c for 0.04 % MWCNT at 2θ = 25.9° on the plane (0 0 2), is in good agreement with the JCPDS 76-1651, and the MWCNT was identified as the hexagonal graphite structure [7]. The appearance peaks of MWCNT proves that the structure of MWCNT is not change due to the sonochemical process. Meanwhile, the peak of the Fe_3O_4 at 30.1°, 35.5°, 43.2°, 53.6°, 57.2°, and 62.7° well matched with the planes of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) of the cubic spinel phase of Fe_3O_4 (JCPDS No 19-0629) [14]. Furthermore, the XRD pattern revealed that the peaks of MWCNT disappear along with the decreasing MWCNT composition in the composite. Related to the result, Zhou et al. [7], reported that the lowering of the MWCNT peaks for XRD patterns caused by the Fe_3O_4 particles with good crystalline structure that covered the e surface of the MWCNT. In this work, the crystallite size of the Fe_3O_4 particles was determined using Debye Scherer's formula [17]. The data analysis using the formula showed that the Fe_3O_4 particles have crystallite size in the range of 10-20 nm.

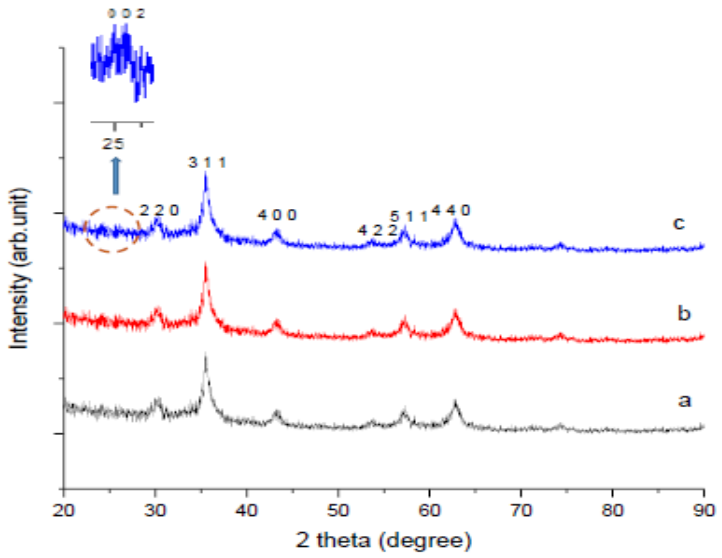

Figure. 1 The patterns of X-Ray diffraction of MWCNT-Fe_3O_4, (a) 0.01% MWCNT, (b) 0.02% MWCNT, and (c) 0.04% MWCNT.

The FTIR spectra of the MWCNT-Fe_3O_4 nanocomposites were given in Figure 2. The spectra revealed that there are several peaks presenting the functional groups of the MWCNT and the Fe_3O_4. The peaks covered at 3321 cm^{-1} (O-H stretching), 1720 cm^{-1} (C=O stretching), 1574 cm^{-1} (C=C stretching, 1310 cm^{-1} (O-H bending) and 588 cm^{-1} (F-O stretching and bending mode) [8,10]. Based on this characterization, it can be stated that the sonication process with nitric acid was successfully generated carboxyl groups on the surface of the MWCNTs. The carboxyl groups attached the Fe_3O_4 nanoparticles with occur electrostatic interaction between negative charge from carboxyl groups and positive charge from Fe_3O_4. Huang et al. [18] reported that the carboxyl groups could be attached to micro molecules that open potential opportunity for biomedical applications. According to Zhuo et al. [7], the functional groups of the MWCNT-Fe_3O_4 nanocomposites are easily to be homogeneous by

dispersing in a liquid medium. The XRD result presented that Fe_3O_4 has a spinel cubic structure which corresponds to result from the FTIR spectra which confirm the existence of Fe-O stretching. Figure 2 also shows that the absorption bands of Fe-O become greater with increasing MWCNT composition in the nanocomposites. Moreover, Ghazanfari et al. [19] investigated that the addition of the amount of MWCNT in the composite increase the oxidation rate of Fe^{2+} to Fe^{3+}.

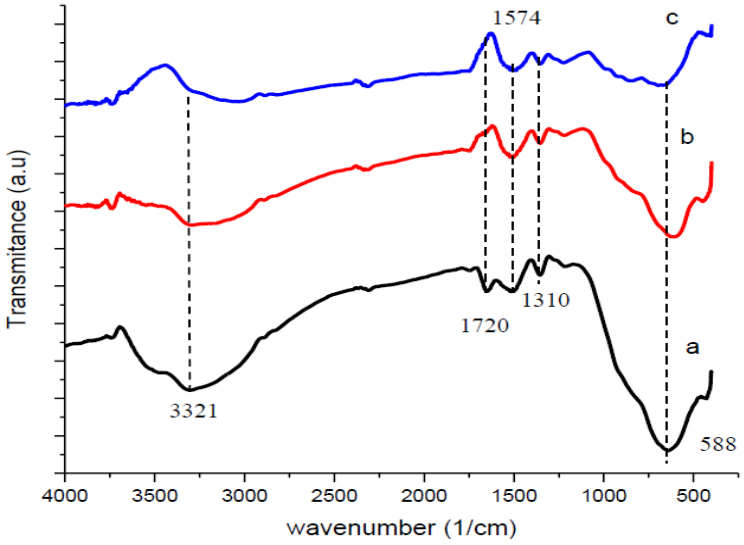

Figure 2. FTIR spectra of MWCNT-Fe_3O_4, (a) 0.01 % MWCNT, (b) 0.02 % MWCNT and (c) 0.04 % MWCNT

The morphology of the MWCNTs, Fe_3O_4 nanoparticles, and nanocomposites of MWCNT-Fe_3O_4 was investigated by SEM. As shown in Figure 3, the MWCNT was functionalized by nitric acid having particle size in diameter ranging from 39 to 63 nm. The decrease of the size of MWCNT if compared before functionalization process due to defect in the wall of MWCNT by the acid reaction. According to Samouhos et al. [13], the defect on the MWCNT surface become the nucleation sites for Fe_3O_4. As shown in Figure 1a, it can be seen that the MWCNT forms the bundles due to the strong Van der Waals attractions. Meanwhile, the morphology of the Fe_3O_4 synthesized by sonochemical methods (in Figure 3b) presents clusters of the Fe_3O_4 that cling together and form aggregates in spherical shapes with individual sizes ranging from 10 to 20 nm. The clusters of the Fe_3O_4 are originated from the magnetostatic coupling between particles [19]. The SEM images of the MWCNT-Fe_3O_4 nanocomposites are described in Figure 3c-3e. Based on the figure, it can be seen that network of MWCNTs is interwoven among the Fe_3O_4 nanoparticles. The morphology of the nanocomposite with 0.01 % MWCNT appears that the Fe_3O_4 adhered on the surface of MWCNT as well as form the large agglomeration as free particles. It can be explained that the amount of the MWCNT is less for nucleation and growth of Fe_3O_4. However, the agglomeration of the Fe_3O_4 decreased with increasing the MWCNT contents as shown in Figure 3d and 3e. Even, when utilization of 0.04 % MWCNT in the nanocomposite, the Fe_3O_4 attached uniformly on the surface of MWCNT. It can be indicated that the nanocomposite of MWCNT-Fe_3O_4 was successfully synthesized by sonochemical route.

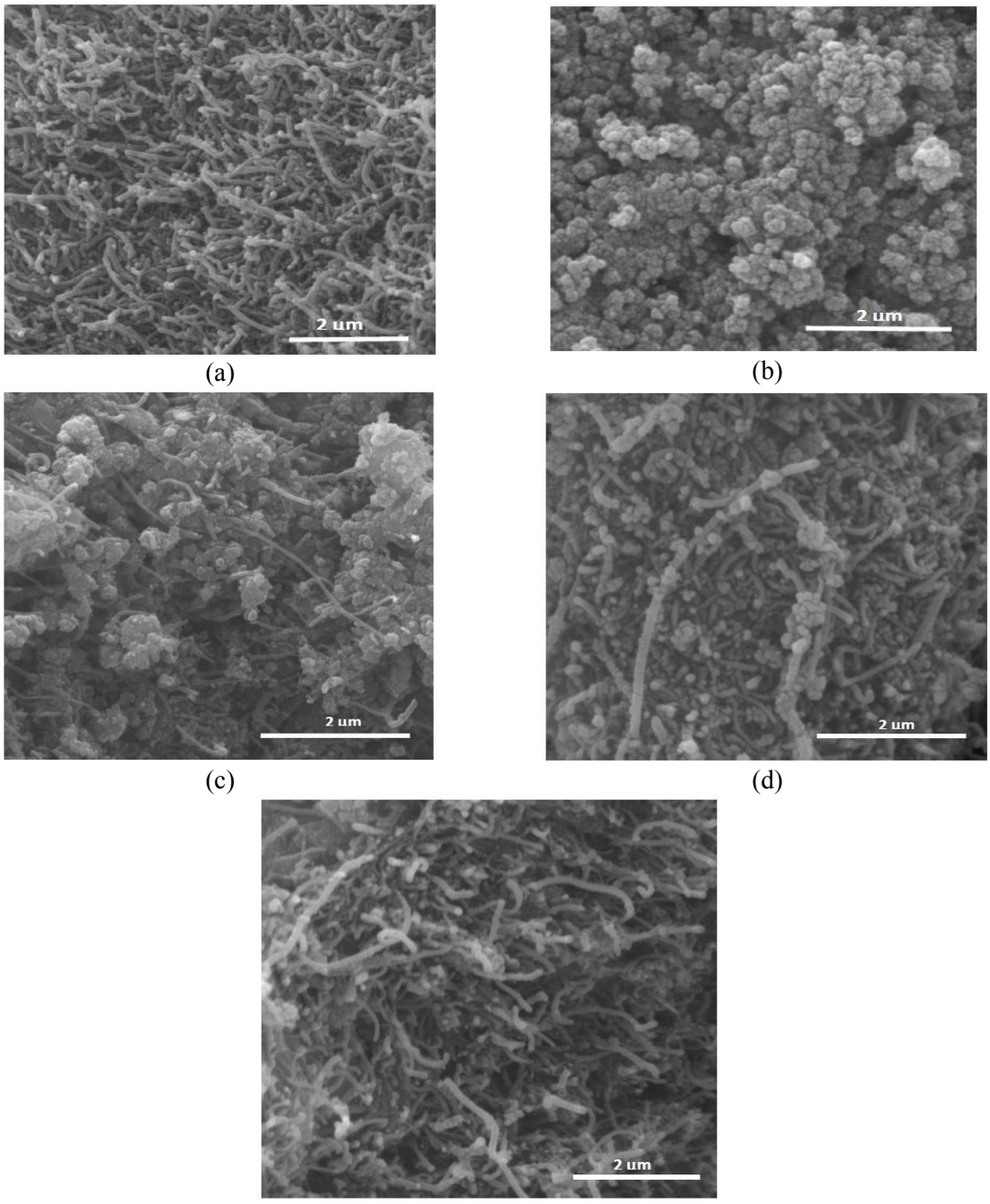

Figure 3. SEM images of (a) MWCNTs, (b) Fe_3O_4, (c) MWCNT-Fe_3O_4 with 0.01 % MWCNT, (d) MWCNT-Fe_3O_4 with 0.02 % MWCNT, (e) MWCNT-Fe_3O_4 with 0.04 % MWCNT.

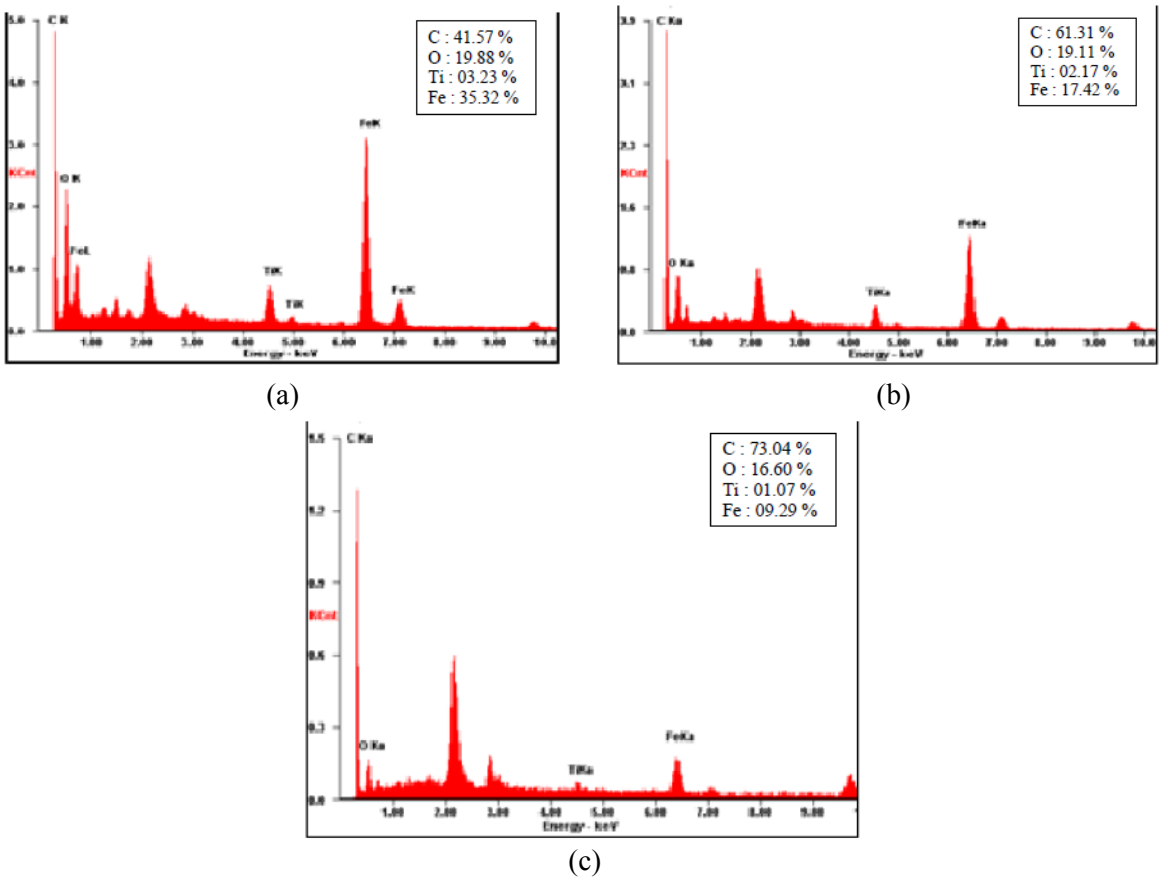

Figure 4. EDX spectra of MWMWCNT-Fe_3O_4 nanocomposites, (a) 0.01 % MWCNT, (b) 0.02 % MWCNT and (c) 0.04 % MWCNT

To compare the element content of nanocomposite, EDX characterization was carried out and the result is shown in Figure 4. The figure confirms the presence of C, O, and Fe element in the nanocomposites. These results are consistent with the result of XRD, FTIR, and SEM data. For more details, the C signal was generated by MWCNT. Meanwhile, the O signal appeared due to the functionalization process of MWCNT, and the Fe signal was generated by Fe_3O_4. However, in EDX appears the Ti element as impurity regarding to the iron sand as a starting material. From the EDX result. It also can be concluded that the percentage of Fe element (in wt%) decreases with increasing the amount of MWCNT.

4. Conclusion

A simple sonochemical route was employed to synthesize MWCNT-Fe_3O_4 nanocomposites. The Fe_3O_4 produced from iron sand as a starting material can be attached uniformly on the surface of the MWCNT. The agglomeration of the Fe_3O_4 in nanocomposite decreased with increasing the MWCNT composition. Based on the result of characterizations, the MWCNT-Fe_3O_4 nanocomposites are very recommended for many application, especially in bioapplication. This simple method can be extended for other metals, alloys or oxides nanoparticles which compatible with properties of CNT.

5. References

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