Indonesian Journal of Chemical Research

http://ojs3.unpatti.ac.id/index.php/ijcr Indo. J. Chem. Res., 8(3), 167-171, 2021

Study Nanostructure of Fe_3O_4 Modification Using PEG 4000 from Iron Sand at Wari Ino Beach

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Received: September 2020
Received in revised: November 2020
Accepted: December 2020
Available online: January 2021

Abstract

Fe_3O_4 encapsulated PEG from iron sand at Wari Ino beach has been successfully synthesized by co-precipitation method. Fe_3O_4 modification PEG 4000 was successfully encapsulated the samples by the presence C-O-C and CH bonding that were characterized using Fourier Transform Infra Red (FTIR), X-Ray Diffraction (XRD) pattern shows that all samples are formed by single phase cubic spinel magnetite, and Scanning Electron Microscopy (SEM) shows the high dispersion capability while encapsulated process using PEG. The results showed that the Fe_3O_4 nanoparticle successfully encapsulated by PEG 4000. The average particle size of the nanoparticle 11.3 nm was determined by Scherrer formula.

Keywords: Fe_3O_4 Nanoparticles, Fe_3O_4/PEG 4000, biosensor, spinel structure

INTRODUCTION

Halmahera Utara Island-Indonesia has a big natural resources such as gold, nickel, iron sand, and so on. Iron sand material is one of the most materials has a ferromagnetic properties (Kurniawan et al., 2017). The natural resources are raw formmaterial, and need some exploration to reach a new materials such as iron oxide (Fe_3O_4). On the nanometer scale, the Fe_3O_4 magnetic nanoparticle has the unique properties such as super paramagnetic, large surface-to-volume ratio, small size and ability to function at the cellular level that have a wide range of applications such as biosensor, magnetic hyperthermia and drug delivery system (Wu et al., 2010; Patsula et al., 2019; Rusnaenah et al., 2017; Taba et al., 2019; Ren et al., 2005; Estelrich., 2015; Xiong et al., 2018). There have been many reports of Fe_3O_4 coated PEG for applications magnetic fluids as a drugs delivery, contrast agents for magnetic resonance imaging, magnetically guided carriers for drug deliver, or heat mediators for hyperthermia (Guibert et al., 2015; Peng et al., 2008).

These applications needs Fe_3O_4 with the homogeneously particle and particle size less than 100 nm (Gupta and Gupta, 2004). The Fe_3O_4 nanoparticle have large surface energy (100 dyne/cm) make it easily to agglomerate on the fluids. Therefore encapsulated with the polymers (e.g., poly (acrylic acid), chitosan, phosphate, polyethylene glycol were used as a coating agent to avoid the agglomeration of the Fe_3O_4 nanoparticles (Wei et al., 2012; Nurillah et al., 2016). It is really crucial to expand study an effective surface-modification method to synthesize Fe_3O_4 nanoparticles with narrow size distribution and high dispersion on aqueous or in aqueous solution.

In this work we explored iron sand to synthesize Fe_3O_4 nanoparticles using co-precipitation method with narrow size distribution and high dispersion on the fluids and modified with PEG 4000 respectively. The effect of the modifiers on the crystal structure, morphology, dispersion and size distribution of Fe_3O_4 nanoparticles will be investigated. Fe_3O_4 nanoparticles with nanometer scale are promising for biomedical and biosensor application. As a biosensor application, the Fe_3O_4 ought to have a narrow size distribution and well dispersibility at aqueous place. However the pure Fe_3O_4 tend to show the agglomeration because of the heavy specific surface area and strong dipole-dipole interactions. It is a crucial research to combine the Fe_3O_4 with PEG 4000 as a stabilization and functionalization for biosensor application (Anbarasu et al., 2015).

METHODOLOGY

Materials and Instrumentals

The reagent to synthesize the Fe_3O_4 nanoparticle was Fe^{2+} and Fe^{3+} ion from iron sand. Sodium hydroxide and Hydrogen chloride were used as a raw material and PEG 4000 as a coating agent.

Methods

Total of 20 grams pure iron sand added into 19.9 mL HCl that had been heated at the temperature 65 °C and stirrer for one hour under constant magnetic stirring at 250 rpm. The solution added into 3 M HCl solution for one hour at temperature 70 °C under constant magnetic stirring at 400 rpm. The result of the nanoparticle was magnetically separated and washed repeatedly with deionized water until reach pH 7 the resulted particles then dried at 100 °C for 3 hours until get a slurry. The slurry then coated by PEG 4000 with ratio 1:1 (w/w) then dried at room temperature. The product characterized by X-Ray Diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Energy Dispersive X-Ray (EDX), and Scanning Electron Microscope (SEM).

RESULT AND DISCUSSION

The XRD characterization is used to identify the crystalline structure, particle size, microstrain of the Fe_3O_4 nanoparticles. Figure 1 shows the pattern of peak before and after modification surface by PEG 4000 confirms that the characteristic peak of invers cubic spinel structure with JCPDS No. 19-0629. The size of the nanoparticle was calculated by Debye-Scherrer equation about 11.36 nm without encapsulation.

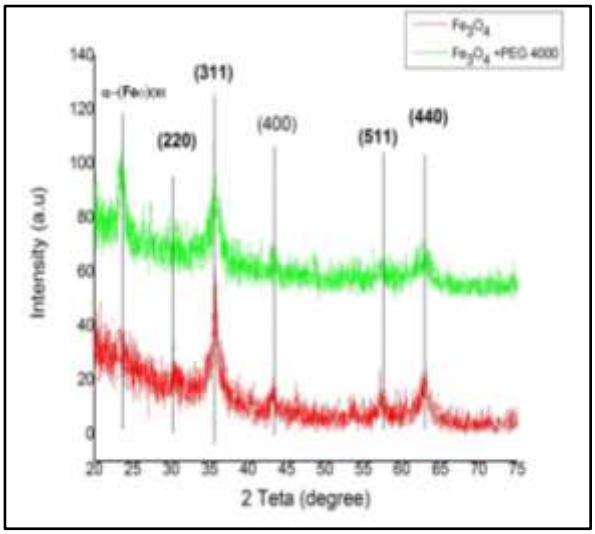


Figure 1. Diffraction peaks of the nanoparticle Fe_3O_4 and Fe_3O_4 modified by PEG 4000.

The analysis shows that all samples are formed by single-phase magnetic Fe_3O_4 with the cubic spinel crystalline structure according to diffraction pattern (220), (311), (400), (442), (511), and (440) plane diffraction. We can infer that the modification by PEG 4000 does not change the crystalline structure of Fe_3O_4 nanoparticle.

Fe_3O_4 modification by PEG 4000 shows there is peak $\alpha-$(FeO)OH that indicates H_2O molecule interact with the Fe_3O_4 nanoparticles while encapsulation process. The peak confirmed that the Fe_3O_4 was successfully modified by PEG 4000 (Heriansyah, 2015). Fe_3O_4 encapsulation using PEG 4000 enhance dispersion capability to reduce the agglomeration of the Fe_3O_4 nanoparticle as shown in Figure 4.

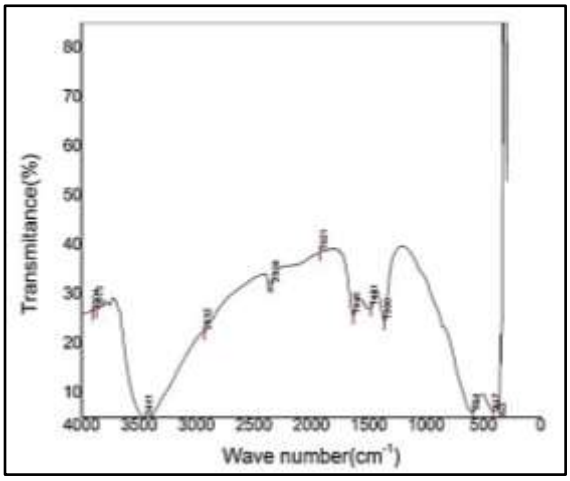


Figure 2. FTIR Spectra of Fe_3O_4 nanoparticles

Figure 2 shows there is vibration occurs between 586 to 600 cm^{-1}. It characteristics absorption of Fe-O bonding that confirmed Fe_3O_4 nanoparticles was successfully synthesized (Wei et al., 2012). The similar characteristics peaks are found in Figure 3. Table 1 shows the vibration that occurs on Fe_3O_4/PEG 4000 nanoparticles. We find some new vibration as shown in the Table 1 which is the characteristics of PEG 4000. It indicates that PEG 4000 has been successfully grafted into Fe_3O_4 nanoparticles.

In Figure 3 shows a new few absorptions of ether bond symmetric and asymmetric at the 1102 and 1361 cm^{-1}. The vibration make the presence of the PEG 4000 (Chandra Mohanta et al., 2018). The C-O-C vibration occurs at 1031 cm^{-1}, it peaks also contributed form PEG bonding as shown in Figure 3 (Kurniawan et al., 2017). FeO bonding occurs at 594 and 580 cm^{-1} (Wei et al., 2012).

Figure 4 shows the combination peaks of the nanoparticle Fe_3O_4 and Fe_3O_4/PEG 4000 to compare the vibration between Fe_3O_4 and Fe_3O_4/PEG 4000. The result of the peak absorption of FeO bonding shows that there is shifted absorption from 594 to 580. It is indicating the PEG 4000 was successfully grafted into the surface of Fe_3O_4 nanoparticles is due to the

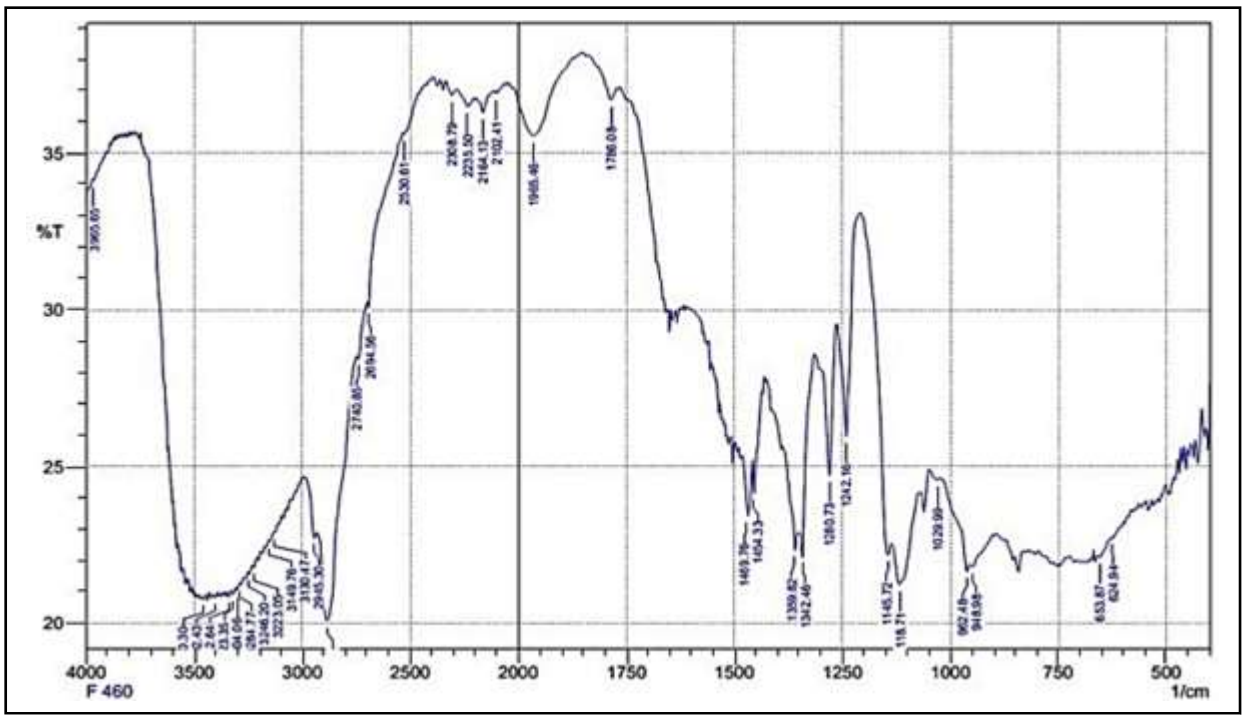


Figure 3. FTIR Spectra of Fe_3O_4 nanoparticles encapsulated PEG 4000

fact that the enhancing vibration energy of FeO bonding as the result of Fe_3O_4 and PEG bonding. In the Table 3 there is no arrow to show the vibration but the fact that there is the vibration after analyze peak using software of the Origin Pro 9, 32 Bit. Base on the Figure 5, the surface and distribution of the Fe_3O_4 encapsulated by PEG 4000 has been characterized by SEM Micrographs.

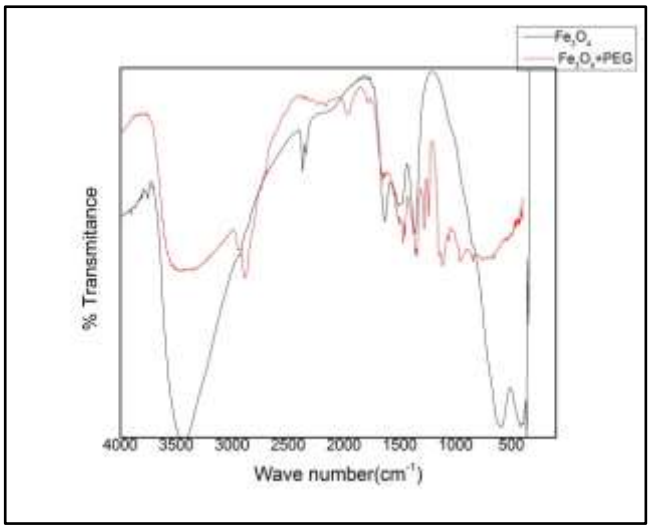


Figure 4. FTIR combination of Fe_3O_4 and Fe_3O_4 nanoparticles encapsulated PEG 4000

It shows the high dispersion capability while encapsulated process using PEG 4000, that could be because the fact that the PEG as a stabilizer and dipersant (Anbarasu et al., 2015). The high surface energy also dipolar attraction of the nanoparticle Fe_3O_4 successfully reduced after encapsulated by PEG 4000 (Wei et al., 2012). The elemental compositions were analyzed by energy dispersive spectroscopy (EDS) as shown in Figure 6.

Tabel 1. The Vibration Group of Fe_3O_4/PEG 4000

Wave number	Vibration Group	Interpretation
457	Fe O	Stretching (Octahedral)
580	Fe-O	
626	Fe-O	
950	CH	
1031	C-O-C	
1062	Fe-O-H	Bending
1102	Ether	
1344	O-H	Bending
1361	C-O-C	Ether asymetric
1471	CH_2	
1622	C=O	
1635	O-H	
2889	CH_2	

According to the area electron diffraction pattern shows the Fe_3O_4/PEG 4000 is polycrystalline of cubic spinel crystal structure (Anbarasu et al. 2015), that is based on the XRD result and SEM image as shown in Figure 5. The SEM images shows the roughly spherical shape, these have been reported that spherical shape is formed due to the nucleation rate per unit areas are isotopic at the interface between the Fe_3O_4 magnetic nanoparticles.

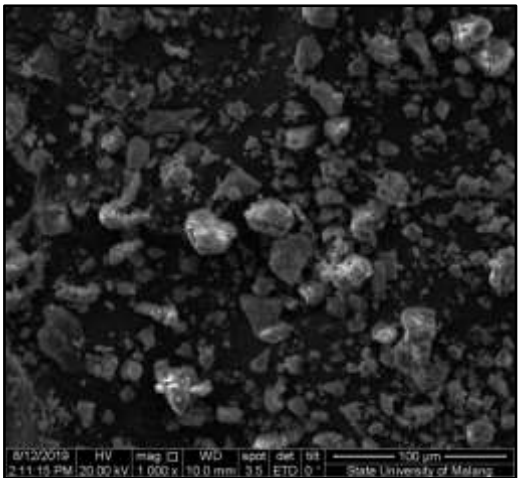
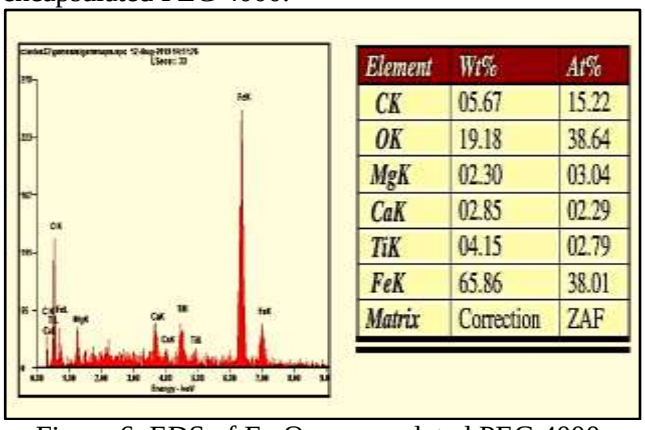


Figure 5. SEM of Fe_3O_4 encapsulated PEG 4000

Figure 6 shows the EDX results to show the elementary analysis of the nanoparticle Fe_3O_4 encapsulated PEG 4000.



Element	Wt%	At%
CK	05.67	15.22
OK	19.18	38.64
MgK	02.30	03.04
CaK	02.85	02.29
TiK	04.15	02.79
FeK	65.86	38.01
Matrix	Correction	ZAF

Figure 6. EDS of Fe_3O_4 encapsulated PEG 4000

The result of energy spectra as shown in figure 6 shows that the most dominant element of the nanoparticle is oxygen (O) and iron (Fe) which were consecutively in 0.5 keV and 6.4 keV energy with K-wavelength. It means that the extraction of Fe_3O_4 nanoparticle has successfully separatedd the iron Fe from other impurities and successfully coated using PEG 4000 (Gunanto et al., 2018).

CONCLUSIONS

Fe_3O_4 encapsulated PEG 4000 was successfully synthesized by co-precipitation method. The XRD Characterization shows that the characteristic of peak is spinel ferrite. The size of the nanoparticle was calculated by Debye-Scherrer equation that is about 11.36 nm without encapsulation. The C-O-C vibration occurs at 1031 cm^{-1}, we believed that it peaks also contributed form PEG bonding and SEM micrographs shows that the encapsulated make the nanoparticle have the good distribution and low dipolar attraction of the nanoparticles.

ACKNOWLEDGMENT

The author would like to thank DRPM RISTEK DIKTI 2019 that full funded this research.

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