SYNTHESIS AND CHARACTERIZATION OF MAGNETIC Fe₃O₄ NANOPARTICLES USING OLEIC ACID AS STABILIZING AGENT

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ABSTRACT

Magnetic iron oxide nanoparticles (Fe₃O₄) provide multiple advantages for drug delivery application due to their inertness, non-toxicity, biocompatibility, and ease of detection as the diagnostic tool for contrast imaging in the human body. To protect against oxidation, preferably covalently bonded a surfactant for coating Fe₃O₄ is required. For this purpose, in the present study, oleic acid (OA) was applied to stabilize Fe₃O₄ magnetic nanoparticles via one-pot-three-component reaction. Mild conditions as well as simple reaction could be attributed to this method in producing Fe₃O₄-OA nanoparticles. The amount of oleic acid (OA) was studied to explore properties of the resulted nanoparticles. Infrared spectroscopy revealed that OA is chemisorbed via a carboxyl group onto the surface of the iron oxide nanoparticle and is coordinated symmetrically to the oxide atoms. Furthermore, there is a ligand exchange between –OH groups and –COO groups on the Fe₃O₄ nanoparticle surfaces. X-ray diffraction (XRD) spectra indicated that Fe₃O₄ phase was predominantly obtained beside small amount of γ-Fe₂O₃ phase. The average crystallite size of the synthesized Fe₃O₄ nanoparticles at different amount of OA was found in the range of 6.60 nm to 9.48 nm. Magnetic properties of the nanoparticles were determined by electron spin resonance (ESR). The gradient curve of ESR spectra revealed that Fe₃O₄ and OA-coated Fe₃O₄ nanoparticles possess significantly different magnetic properties.

Keywords: Iron oxide, Nanoparticles, Oleic acid, Magnetite, Maghemite.

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INTRODUCTION

Magnetic nanoparticles are very useful materials in many fields such as a magnetic recording, biological research, and medical science applications.¹ One of the most magnetic nanoparticles is iron oxide. Among iron oxides, magnetite (Fe₃O₄) has many unique properties such as superparamagnetism², biocompatible, low toxicity, biodegradable.³ The size, shape, size distribution and magnetic properties of magnetite nanoparticles generally depend on the method of synthesis. Several methods for the Fe₃O₄ nanoparticles synthesis are coprecipitation of iron salts, microemulsions, hydrothermal synthesis, and thermal decomposition of the iron precursor.³ Among them, the coprecipitation method is mostly applied for the synthesis magnetite nanoparticles from an aqueous mixture of Fe²⁺ + Fe³⁺ salts solution in the presence of a base under an inert environment at room temperature.⁴

Fe₃O₄ nanoparticles are unstable and easily oxidize to form another phase such as maghemite (γ-Fe₂O₃) and hematite (α-Fe₂O₃). Furthermore, Fe₃O₄ nanoparticles are easily to form aggregate as a result of interactions among nanoscale particles. To improve stability as well as prevent particle aggregations, surface modification of Fe₃O₄ nanoparticles are absolutely required. Therefore, coating technology by using polymer, metal or non-metal, and the surfactant has been studied previously.^{5,6}

Oleic acid (OA) is a surfactant which is commonly employed to stabilize the magnetite nanoparticles. Oleic acid can form a strong chemical bond through the interaction of its carboxyl group with magnetite nanoparticles.⁷ Wang et al⁸ produced Fe₃O₄ nanoparticles that stable in organic solvents by using DMSO

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to oxidize Fe^{2+} and oleic acid as surfactant. Masur *et al*⁹ produced monodisperse magnetite nanoparticles by using thermal decomposition method and study their magnetic properties by using electron spin resonances (ESR). Electron spin resonance (ESR) is a very sensitive technique for examining unpaired electron species such as superparamagnetic Fe_3O_4 nanoparticles. This method stands on the interaction of external magnetic fields with magnetic moments of unpaired electron species in the sample, which leads to the separation of electron energy levels.¹⁰ Furthermore, the ESR provides additional information about the magnetism evolution from magnetic nanoparticles with various layers and suspension fluids.¹¹

The purpose of this work is to synthesis Fe_3O_4 nanoparticles by varying the amount of oleic acid via coprecipitation method. The phase composition, crystallite size, size distribution, lattice parameter, magnetic properties, and interaction between oleic acid and Fe_3O_4 nanoparticles were investigated.

EXPERIMENTAL

Materials

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%, b/b), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (99%, b/b) and oleic acid (OA, 90%, v/v) as main reagents for the synthesis of Fe_3O_4 -OA nanoparticles were purchased from Sigma-Aldrich (Singapore). Ammonia solution (25%, v/v) from Merck (Indonesia) was used as the precipitating agent. All of the reagents were used without further purification.

Synthesis of Fe_3O_4 Nanoparticles Coated with Oleic Acid

The Fe_3O_4 nanoparticles were formed via co-precipitation method in the environment of nitrogen gas. Such amounts of 0.125 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 0.350 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 mL deionized water with vigorous stirring at room temperature. A 10 mL of 25% ammonia solution was dropped slowly using a syringe pump at the flow rate of 10 mL/h. The solution color changed from yellow to black rapidly. The varying amounts of oleic acid (OA) such as 25, 50, 75, 100, 125, and 150 μL were added to the solutions followed by vigorous stirring for 15 min. The resulted OA-coated magnetite (Fe_3O_4) nanoparticles were washed several times with deionized water until $\text{pH} \pm 7$, then suspended in 5 mL water, and finally dried by the mean of the freeze-drying method. Figure-1 describe the synthesis procedure of Fe_3O_4 -OA nanoparticles with a color change in every step. The pristine Fe_3O_4 nanoparticles were prepared by a similar procedure without OA as a coating agent. Fe_3O_4 with different amount of oleic acid (OA) was labeled such as Fe_3O_4 -OA (25), Fe_3O_4 -OA (50), Fe_3O_4 -OA (75), Fe_3O_4 -OA (100), Fe_3O_4 -OA (125), and Fe_3O_4 -OA (150). The number in parenthesis shows the amount (μL) of oleic acid (OA) added. For the Fe_3O_4 nanoparticles without oleic acid was labeled as Fe_3O_4 only.

Characterization of Oleic Acid-Coated Fe_3O_4 Nanoparticles

The resulted Fe_3O_4 -OA nanoparticles were firstly characterized by an FT-IR spectrometer (Shimadzu) at a wavenumber range of 400-4000 cm^{-1} to examine the interaction between the nanoparticles and functional groups of OA. The KBr optical gradewasemployed as background material. The resulted in nanoparticles and dried KBr were mixed at the ration of nanoparticles : KBr = 0.075:0.0002, then they were compressed into pellets.

Crystallite size for Fe_3O_4 dan Fe_3O_4 -OA nanoparticles was determined by using XRD at angle $2\theta = 15-65^\circ$, then calculated by using Scherrer formula:¹²

$$D = \frac{K\lambda}{\beta \sin \theta} \quad (1)$$

D, K, λ , and β represented crystallite size, a constant with value 0.9, the wavelength for X-ray, and full width at half maximum (FWHM), respectively. $\text{CuK}\alpha 1$ was applied as a radiation source with the wavelength 0.15406 nm. The phases composition was identified by comparison with the Joint Committee Powder Diffraction Standards (JCPDS). Magnetic properties of the resulted Fe_3O_4 -OA nanoparticles were assessed by the ESR. There are two approximate to analyze their magnetic properties. First, by using slope value to identify the Zeeman splitting pattern. ESR slope value was determined by using formula (2):

$$\text{Slope} = \frac{Y_2 - Y_1}{X_2 - X_1} \quad (2)$$

Second, by using g-Lande factor to study their magnetic character. a g-Lande factor was determined by using formula (3).^{13, 14}

$$\Delta E = h \nu = g \mu_B B_0 \quad (3)$$

Fig.- 1: Synthesis procedure of Fe₃O₄-OA nanoparticles and color change phenomenon in the synthesis of Fe₃O₄ nanoparticles

RESULTS AND DISCUSSION

FTIR and Fe₃O₄ nanoparticles Coated with Oleic Acid (Fe₃O₄-OA)

The synthesis of Fe₃O₄ by mixing Fe²⁺ and Fe³⁺ solution in the presence of ammonia solution showed the color change phenomenon from bright yellow to brown, dark brown, and black color sequentially as illustrated in Fig.-1. These colors indicate the phase transformation of iron oxide as previously studied by Ahn et al.⁴. The transformation process of iron oxide consists of two different steps. The first step is started with the formation of akageneite followed by the formation of goethite, hematite, maghemite, and magnetite, respectively. The second step is started with the formation of ferrous hydroxide which was further transformed into lepidocrite, maghemite, and magnetite.

Figure-2 showed the spectra of Fe₃O₄ and Fe₃O₄-OA nanoparticles. In the Fe₃O₄ bare, peaks at 3420 cm⁻¹ and 1632 cm⁻¹ were associated with O-H vibrations, indicating that the surface of Fe₃O₄ nanoparticles was covered with hydroxyl groups. The peak at 634 and 565 cm⁻¹ represented the vibration of the Fe-O lattice. In the spectrum of the Fe₃O₄-OA sample, the C=O band at 1710 cm⁻¹, and the O-H bands at 1464 and 937 cm⁻¹ for the OA group (-COO⁻) were not found. Two new bands, which correspond to the asymmetric $\nu_{as}(\text{COO}^-)$ and symmetric $\nu_s(\text{COO}^-)$ stretching vibrations, were found at 1464, 1521 cm⁻¹, respectively. So, OA existed as a carboxyl group when it chemically interacted with the Fe₃O₄ nanoparticles.

The interaction between carboxyl groups and metal atoms can exist as monodentate, bridging bidentate, chelating bidentate, and ionic. The types of interactions can be distinguished by the separation of wavenumber (Δ) of the $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ bands. Δ values of 200-320 cm⁻¹ were attributed to monodentate, whereas bridging bidentate and chelating bidentate interaction were represented by Δ values of 140-190 cm⁻¹ and <110 cm⁻¹, respectively.^{7,9} Therefore, the existence Δ of 145 was due to the bridging bidentate interaction, where a covalent bond could be attributed to the COO⁻ group and Fe interaction. The coating-replacing group process at the nano-magnetite surface was briefly described on Figure-3. The oleic acid (OA) can form single-, double-, or multilayer-coated structures on the Fe₃O₄ nanoparticles surface. For the formation of the bilayer structure of OA-coated Fe₃O₄ nanoparticles, the first layer of OA

covered the nanoparticle surface through the chemical bonding of COO⁻ group with Fe. Then, a second layer is formed through the hydrophobic interaction of aliphatic chains of the inner (first layer) with outer OA layer.^{15,16,17} The presence of the C=O band at 1710 cm⁻¹ is a key point to distinguish the existence of single and bilayer OA-coated structures. Because of this band was not found in the spectra of all Fe₃O₄-OA samples, the single layer-coated structure formation could be addressed to these samples. From the IR spectra, the presence of Fe₃O₄ and γ -Fe₂O₃ can be distinguished. For magnetite (Fe₃O₄), there was a significant peak at 530 cm⁻¹ while for maghemite (γ -Fe₂O₃) on 620 cm⁻¹. This result similar to the previous study.^{16,18}

Fig.-2: IR spectra for pure OA, bare Fe₃O₄ and oleic acid-coated Fe₃O₄ (Fe₃O₄-OA)

XRD Patterns, ESR Analysis, and Crystallite Size of Fe₃O₄-OA Nanoparticles

Figure-4 shows the XRD results of bare Fe₃O₄ and Fe₃O₄ coated with different amount of oleic acid (OA). The sharp peaks of different samples reveal that the nanoparticles have high crystallinity. After surface modification by using OA, the crystal structure of Fe₃O₄ is well-maintained. The diffraction peaks of (220), (311), (400), (422), and (511) reflect the magnetite crystal with a cubic spinel structure.¹ Based on FT-IR measurement, there are two phases of iron oxide in sample bare Fe₃O₄ and OA-coated Fe₃O₄, which is magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃). The XRD crystal structure for maghemite similar to magnetite, so it is difficult to distinguish both of them. In order to identify the dominant phase of nanoparticles, we used some calculation to identify the unit cell parameter and the phase composition of iron oxide in nanoparticles. The results were summarized in Figure-5 and Table-1.

The average crystallite size Fe₃O₄ decreased after modification with OA. Oleic acid could minimize the magnetic attraction between nano-sized particles that could lead to the decrement of crystallite size. The unit cell parameter for bare Fe₃O₄ is 8.370 Å while OA-coated Fe₃O₄ in the range of 8.380 Å- 8.4055 Å. For bare Fe₃O₄, the unit cell parameter is lower than bulk magnetite, 8.390 Å¹², due to small oxidation of Fe²⁺ ions at the surface of nanoparticles. While for OA-coated Fe₃O₄ the unit cell parameter was varying due to the presence of capping ligand at the surface.¹⁹

Figure-5 shows the percentage phase of iron oxide nanoparticles for bare and OA-coated Fe₃O₄. It could be concluded that the presence of OA was succeeded to protect Fe²⁺ ions from the oxidation process. However, above 100 μ L OA the percentage of maghemite was rising due to the incomplete covering of OA to Fe₃O₄ nanoparticle. It may be there is a region at nanoparticle surface that not covering by OA. Furthermore, this region becomes sensitive to Fe²⁺ ion to diffuse from inner to outside crystal plane to form maghemite.

Fig.-3: Coating and group-replacing process in the synthesis of oleic acid-coated Fe_3O_4 nanoparticlesTable-1: Average crystallite size and unit cell parameter of bare Fe_3O_4 and OA-coated Fe_3O_4

Sample	Average Crystallite size (nm)	Unit cell parameter (Å)
Fe_3O_4	8.64	8.3701
Fe_3O_4 -AO (25)	8.36	8.3852
Fe_3O_4 -AO (50)	8.13	8.3909
Fe_3O_4 -AO (75)	7.75	8.4054
Fe_3O_4 -AO (100)	6.59	8.4055
Fe_3O_4 -AO (125)	7.58	8.3950
Fe_3O_4 -AO (150)	9.43	8.3873

Based on Fig.-6, the crystallite size distribution for bare Fe_3O_4 is wide, due to the magnetic attraction phenomenon between nanoparticles that led to non-uniform crystallite size of nanoparticles. In contrast, OA-coated Fe_3O_4 show narrow crystallite size distribution. The presence of capping ligand on the surface of nanoparticles could prevent the interaction between nanoparticles and then keep the crystal growth of nanoparticle uniformly. The crystallite size distribution becomes wider for OA >100 μL , due to the incomplete covering of OA so they could affect the crystal growth.

Table-2: Crystallite size, the slope of ESR curve and g-Lande factor

Sample	Average Crystallite size (nm)	m (Slope)	g-Lande
Fe_3O_4	8.64	1.1	1.98
Fe_3O_4 -AO (25)	8.36	1.5	1.96
Fe_3O_4 -AO (50)	8.13	1.5	1.93
Fe_3O_4 -AO (75)	7.75	2.4	1.90
Fe_3O_4 -AO (100)	6.59	3.2	1.88
Fe_3O_4 -AO (125)	7.58	2.1	1.91
Fe_3O_4 -AO (150)	9.43	1.3	1.95

Table-2 shows the relation among average crystallite size, slope ESR curve, and g-Lande factor. It can be found that Fe_3O_4 and Fe_3O_4 -OA had different magnetic properties. Decreasing in crystallite size and the

g-Lande factor was followed by increasing slope value. This phenomenon happens because of finite-size effect while for the sample $\text{Fe}_3\text{O}_4\text{-AO}$ (125) and $\text{Fe}_3\text{O}_4\text{-AO}$ (150), their g-Lande factors increased with the crystallite size. This phenomenon related to surface-size effect.^{20,21}

Fig.-4: XRD diffractogram of bare Fe_3O_4 and Oleic acid-coated Fe_3O_4 nanoparticles

Fig.-5: Percentage of Fe_3O_4 (magnetite) and $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) phases

Fig.-6: Size distribution of Fe_3O_4 Oleic acid-coated Fe_3O_4 nanoparticles

CONCLUSION

Synthesis of Fe_3O_4 nanoparticles coated with oleic acid was successfully conducted. According to FT-IR, ligand exchange between the hydroxyl group and carboxylate group was identified. The average crystallite size of the synthesized Fe_3O_4 nanoparticles was 8.64 nm, whereas the size of OA-coated Fe_3O_4 nanoparticles at different amounts OA was found in the range of 6.60 nm to 9.48 nm. Magnetic properties of the nanoparticles were determined by electron spin resonances (ESR). The gradient curve of ESR spectra revealed that Fe_3O_4 and OA-coated Fe_3O_4 nanoparticles possess significantly different magnetic properties.

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