Synthesis and Properties of Iron Oxide Particles Prepared by Hidrothermal Method

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Abstract. Iron oxide of hematite (α-Fe₂O₃) has been successfully synthesized by hydrothermal method. The starting materials were Fe(NO₃)₃·9H₂O, 2-methoxyethanol, diethanolamine and n-hexane. The optical, morphology and crystal structure were measured by UV-VIS, TEM and XRD, respectively. From UV-VIS measurement, it was found that the band-gap of sample was 4.17 eV. The morphology of particle was plate-like form. The sample which sintered at 1100°C has high quality crystal with hexagonal structure of α-Fe₂O₃ phase.

1. Introduction
Iron oxides are the most industrially important iron ores. It is well known that there are three iron oxides in Fe-O system, namely, iron (II) oxide (FeO), iron (II,III) oxide or magnetite (Fe₃O₄) and hematite (α-Fe₂O₃) or maghemite (γ-Fe₂O₃) which is ferromagnetic mineral with the spinel group. Hematite is most stable iron oxide under ambient conditions with rhombohedral structure and antiferromagnetic below its Morin transition (Tₘ) of about 260 K. Magnetic properties of hematite depend on pressure, particle size, and magnetic intensity. Hematite is also n-type semiconductor with Eₑ = 2.1 eV. Maghemite can be change to be hematite phase at high temperature. Maghemite with spherical nanoparticles (NPs) and diameters less than 20 nm has advantages properties, such as chemical stability, biocompatibility and can be used for biomedical applications due to their ability to affect the relaxation rate of water proton. The relaxation rate can be decreased signal intensity resulting darkening effect in magnetic resonance image [1,2].

Various of chemical methods have been done to synthesize magnetic nanostructure including the precipitation method [3], sol–gel process [4], hydrothermal synthesis [5], high temperature reaction [6], microwave irradiation synthesis [7], polyl methods [8] and seed mediated growth method [9,10]. To control the size and morphology of nanostructure, all the methods manipulate various experimental parameters such as the pH of the solution, ionic strength, capping agent, reaction temperature, composition and pressure. However, research to obtain nanoparticles with controlled size and morphology is still open wide challenges. Recently, Kazeminezhad and Mosivand [1] have been synthesized iron oxide by electro-oxidation method and explored the sintering effect to produce magnetite, maghemit and hematite. However the sintering temperatures are limited in the range of 100°C – 1000°C. The sintering temperature above 1000°C is still attracting much interest to find other structure properties of iron oxide. In this paper, we reported the synthesis of iron oxide prepared by hydrothermal method and explored the crystal structure of iron oxide on the sintering temperature at 1100°C.
2. Experimental Method
Iron oxide prepared by hydrothermal method. This method is a simple, reliable and cheap process for small and large scale laboratory. The starting materials were Fe(NO$_3$)$_3$.9H$_2$O, 2-methoxyethanol and diethanolamine. The raw materials were dissolved in 2-methoxyethanol and diethanolamine (DEA) was dropped wisely to control the value of pH at 10. The solutions were reacted in hydrothermal chamber at 100°C for 72 hours, following by washing with n-hexane. The NH$_4$OH added to the solution until reaching a pH value of 5, and resulting precipitate particles. Particles were then re-dispersed in 2-methoxyethanol solution. The sample was characterized by UV-VIS and TEM to observe the optical and morphological particle, respectively. The value of band-gap was calculated from UV-VIS data by using simple equation of $E_g = \frac{hc}{\lambda_{cut-off}}$. To study structure and magnetic properties, sample was dried at 200°C for 6 hours, pre-sintered at 400°C for 4 hours, and sintered at 1100°C for 6 hours, then characterized by XRD and VSM measurement.

3. Result and Discussion
Figure 1 shows the wavelength dependent of absorbtion from UV-Vis measurements. From the graphics, it was found that $\lambda_{cut-off}$ is 297.36 nm. Using the equation of $E_g$, the band-gap of the sample was 4.17 eV. The large value of band-gap in this sample indicated the magnetite characteristic. This indication is also supported by the black colour of particles [1,11].

![Figure 1. UV-Vis spectra of magnetite (Fe$_3$O$_4$) prepared by hydrothermal.](image)

Figure 2 shows TEM image of iron oxides with the bar scale of 100 nm. The morphology of sample is mainly plate-like particles. The average size of particle has been calculated at 115 nm × 47 nm. The particles of iron oxide were still in submicron size and need to be optimized to obtain magnetite nanoparticles.
Figure 2. TEM image of sample iron oxides prepared by hydrothermal.

Figure 3 shows the XRD pattern of iron oxide sample sintered at 1100°C for 6 hours. For comparison, the XRD patterns of Fe$_3$O$_4$ (JCPDS#75-0033) and α-Fe$_2$O$_3$ (JCPDS#86-0550) are also displayed. It was found that the sample has high quality crystal with hexagonal structure of hematite α-Fe$_2$O$_3$ phase without impurity peaks. Compared with the experimental result reported by Kazeminezhad and Mosivand [1], the crystal structure sintered at temperature in the range of 800°C – 1000°C was rhombohedral. However, in our experiment, we observed the hexagonal phase structure when it was sintered at 1100°C. The changes of structure from rhombohedral to hexagonal phase probably due to the arrangement of oxygen position during sintering process. The hexagonal phase of α-Fe$_2$O$_3$ has more advantages and potential in drug delivery system. It can also provide a slow drug release matrix and protect protein from chemical degradation [12]. The lattice parameter a and c are 5.0356 Å and 13.7489 Å, respectively, which is similar with the lattice parameter observed in JCPDS#86-0550.

Figure 3. XRD pattern of powder α-Fe$_2$O$_3$ sintered at 1100°C for 6 hours.
From XRD data, the average crystallite size can also be calculated using the Scherrer equation below [13]:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where $D$ is the average size of the crystallites, $K$ is the Scherrer constant (0.9) [14], $\lambda$ is the wavelength of radiation (1.54186 Å), $\beta$ is full width at half maximum (FWHM) of diffraction lines and $\theta$ corresponds to the peak position. The average size of crystallite is about 15.79 nm.

4. Conclusion
Iron oxide of hematite ($\alpha$-Fe$_2$O$_3$) has been successfully synthesized by hydrothermal method. It was found that the band-gap of sample was 4.17 eV with the plate-like form of 115 nm $\times$ 47 nm, in dimension. The sample sintered at 1100°C for 6 hours has high quality crystal with hexagonal structure of $\alpha$-Fe$_2$O$_3$ phase with lattice parameter of 5.035 Å and 13.7489 Å, for $a$-axis and $c$-axis, respectively. The average size of crystallite is about 15.79 nm. The present result gave a good information to develop a research in drug delivery system.

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