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Comparison of Sol-Gel And Hydrothermal Synthesis Of Zinc Ferrite ($ZnFe_2O_4$) Nanoparticles.

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ABSTRACT

Two solution-based techniques (sol-gel and hydrothermal synthesis methods) for the preparation of $ZnFe_2O_4$ nanoparticles have been investigated. In sol-gel method, ethanol is used as thesolvent, while citric acid as thechelating agent. The hydrothermal process used NaOH solution as the precipitator and controlling alkaline conditions. The synthesized nanoparticles are characterized by X-ray diffraction analysis, Scanning Electron Microscopy and Transmission Electron Microscopy. Spherical of $ZnFe_2O_4$ nanoparticle with a size of 10 nm can be obtained using hydrothermal method, which is smaller than nanoparticle resulted from sol gel method (35 nm). The results depict that formation methods play an important role on the particle size and quality of the $ZnFe_2O_4$nanoparticles.

Keywords: $ZnFe_2O_4$, solgel, hydrothermal, nanoparticles

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INTRODUCTION

Ferrite compounds (MFe_2O_4) where M = transition metal or alkaline earth is a magnetic material with spinel structure. Recently, ferrite compounds has attracted the attention of researchers for potential applications such as data storage, biosensors, drug delivery and diagnosis of the disease, gas sensors, electronic devices, catalysts and others [1-2]. In the photocatalytic process MFe_2O_4 particles have been used to degrade some of the volatile organic compounds in the water[3-4]. MFe_2O_4 with a narrow band gap can be used to enhance the ability of ZnO in the photocatalytic process, because this material can narrow band gap of ZnO and expanding absorption area in the visible light region. In addition, ferrite with magnetic properties can be separated easily from the liquid by using the influence of the external magnetic field [5-6].

On the other hand, some spinel material such as $ZnFe_2O_4$known as semiconductorcompound withrelatively smallenergy gap (about 2 eV). The semiconductor properties show a very good response to the visible light, good photochemical stability, as well as magnetic profitable. Until now, $ZnFe_2O_4$nanoparticles has been synthesized using various methods, such as co-precipitation [7], sol-gel [8], the reaction of solid-state [9], the combustion reaction using glycine [10] and urea as a reducing agent [11], hydrothermal synthesis [12], solvothermal and microwave solvothermal synthesis [13], a high-energy ball-milling [14], microwave combustion method [15]. Most of the research was done independently. The current study made and compared between solgel and hydrothermal methodson the preparation of $ZnFe_2O_4$nanoparticles. The use of sol-gel and hydrothermal methods on the structural, morphological and magnetic properties of the prepared $ZnFe_2O_4$ nanoparticle is presented.

MATERIALS AND METHODS

The materials used in this study was zinc nitrate tetra hydrate $Zn(NO_3)_2.\ 4H_2O$ (Merck), $Fe(NO_3)_3.9H_2O$(Merck), citric acid $C_6H_8O_7$ (Merck), NaOH (Merck), ethanol p.a (Merck), ethanol, and distilled water. Equipment used in the form of glassware, Teflon autoclave, furnace and spectrophotometers. Characterization of the samples was done by means of X-ray diffraction (XRD), Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX), and Transmission Electron Microscopy (TEM).

Synthesis by sol-gel method:

A total of 10 mmol of $Zn(NO_3)_2.4H_2O$ and 20 mmol $Fe(NO_3)_3.9H_2O$ mixed in 40 mL ethanol p.a, then 30 mmol of citric acid was dissolved in 40 mL ethanol P.A. All of the solution is mixed with a mole ratio of Zn + 2: Fe + 3: citric acid is 1: 2: 3. The mixture was stirred at 500 rpm for 1 hour at 70°C to form a wet gel. The gel formed is dried in an oven at a temperature of 120°C for 24 hours to form a dry gel. Then, dry gel is crushed with a mortar to form more fine powders. The resulting powder heated in a furnace at a temperature of 600°C for 2 hours, and then characterized by XRD equipment, SEM-EDX, and TEM.

Synthesis by hydrothermal method:

Some of 10 mmol$Zn(NO_3)_2.4H_2O$ and 20 mmol $Fe(NO_3)_3.9H_2O$ dissolved in 100 mL of distilled water and stirred until homogeneous. 2 M NaOH was then added to the solution gradually and keep stirring until pH 12. The result was a mixture of suspension. The mixture was poured into tube autoclave and heated in an oven at a temperature of 180°C for 3 hours. The nanoparticles were filtered then rinsed with distilled water until pH 7-8 and dried. The resulting powders were characterized by means of XRD equipment, SEM-EDX, andTEM.

RESULTS AND DISCUSSION

In general, the powder resulted from the two methods were slightly different in terms of its color, whichwas blackish brown color. However, there was a difference in fineness or size of the particles produced, as shown in Fig 1. In visualization regular, powder obtained from sol-gel method was more rugged than the powder obtained fromhydrothermal method.

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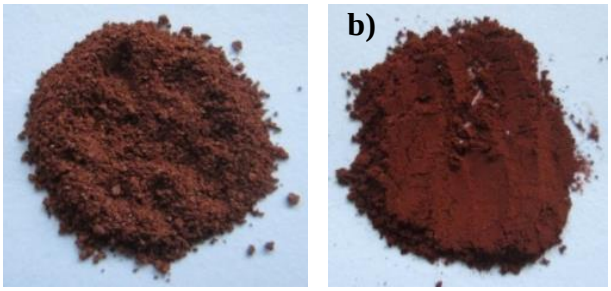

Fig 1: The photograph of $ZnFe_2O_4$ powders which were synthesized by a) sol-gel and b) hydrothermal methods

XRD samples were prepared by the method $ZnFe_2O_4$ solgel (a) and hydrothermal (b) as can be seen in Figure 2. The diffractograms for both samples showed that every sample has a cubic spinel structure according to the standard JCPDS No. 89-1012. Diffraction peaks at 2θ of 30.05°, 35.36°, 42.78°, 52.96°, 56.78° and 62.20° can be ascribed to the reflection spinel $ZnFe_2O_4$field at (220), (311), (400), (422), (511) and (440). On the other hand, the difference in this preparation method gives different peak sharpness and heights. Peaks obtained formsolgel method weresharper and higher than hidrotemal method. Based on the equation Scherer, a sharp and heightpeak give crystal size was larger than the width and low peak. This can be proved later by SEM and TEM.

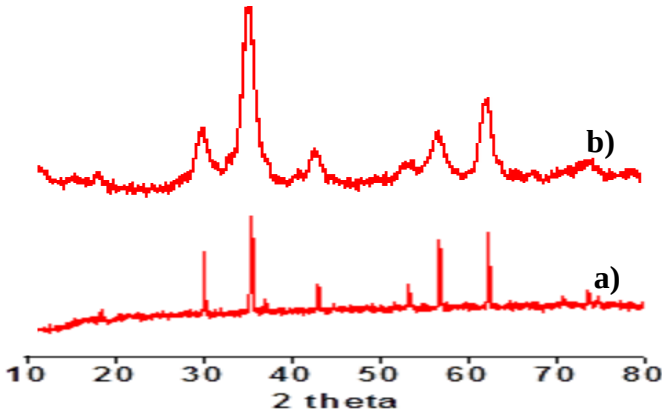

Fig 2: XRD pattern of $ZnFe_2O_4$ which are synthesized by a) sol-gel process and b) Hydrothermal

The results of the SEM image (see Fig. 3) showed that the sample $ZnFe_2O_4$ with solgel method (a) and hydrothermal (b) formed by the agglomeration of the particles. Smaller particle size was obtained from $ZnFe_2O_4$prepared by solgel method. This data is matched with the visualization of the powder before and approved also agreed by the XRD data. The fine particles obtained by using hydrothermal, since this methodsused lower temperature during processing. The use ofsolgel method to get a good ofcrystallinitymust be done at temperatures above 500°C. When the temperature is raised, in general, the growth of crystallinity will also increase.

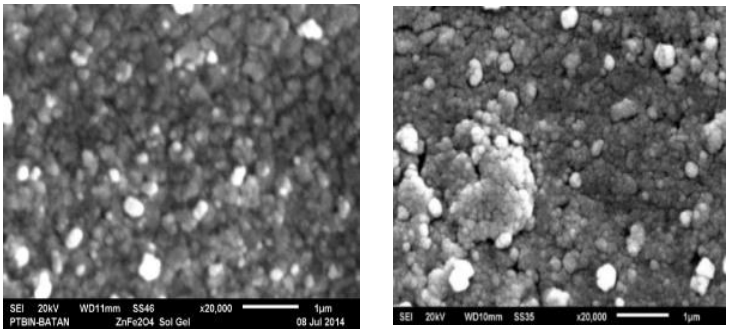

Fig 3: SEM images of $ZnFe_2O4$ which are synthesized by a) sol-gel process and b) Hydrothermal

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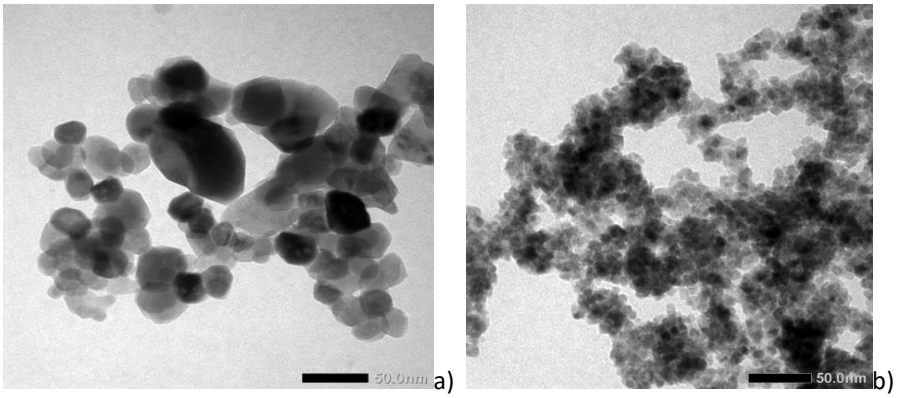
Representative of TEM pictures of solgel and hydrothermal samples are shown in Fig. 4. Most of the $ZnFe_2O_4$ nanoparticles are spherical in these pictures. It can be seen that differences in the shape and size of $ZnFe_2O_4$nanoparticles were synthesized via sol-gel method (Fig.4a) and hydrothermal (Fig. 4b). Particles prepared by sol gel method have a larger size with an average size of about 35 nm. This may be caused by high temperatures in the formation of $ZnFe_2O_4$ crystals (calcination at 600^oC). This condition has caused the incorporation of particles or small crystals to form a larger particles.While particles prepared by hydrothermal method has a smaller size that is below 10 nm. Moreover, particles obtained by hydrothermal method has a size that is much more refined and homogeneous



a) b)

Fig 4: TEM images of $ZnFe_2O4$ which are synthesized by a) sol-gel process and b) Hydrothermal

CONCLUSION

Two solution-based techniques for the preparation of $ZnFe_2O_4$ nanoparticles have been presented: sol-gel and hydrothermal synthesis methods. The physical and chemical properties of the powders obtained from both methods have been compared by using a range of techniques. Comparison of these two methods showed that the powder obtained by hydrothermal process is much smaller than solgel method.The sol-gel synthesis method produced $ZnFe_2O_4$ nano-particles which were spherical particles with average of 35 nm in size. Whereas by using hydrothermal synthesis produced a very fine powder with an average of 10 nm.

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