Structural Characterizations of Magnetite/Zinc Oxide Nanocomposites Prepared by Co-precipitation Method

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Abstract. Magnetite/zinc oxide nanocomposites were synthesized by a co-precipitation method. The mass compositions of the nanocomposites (ratio of magnetite: zinc oxide) were 1.5:0, 1:0.5, 0.75:0.75, 0.5:1, and 0:1.5. The ratios were given the respective codes of NC1, NC2, NC3, NC4, NC5. The data analysis of the x-ray diffraction data showed that the magnetite had a spinel configuration and sized 11 nm. Meanwhile, the zinc oxide had a particle size of 40 nm. However, the zinc oxide constructed any impurities. In this work, all samples formed agglomerations in nanometric size with various shapes. The functional groups of the magnetite and zinc oxide were detected in the respective wavenumber of about 470 cm\(^{-1}\) and 575 cm\(^{-1}\).

Keywords: Zinc oxide, nanoparticle, structure, optical band gap energy, antifungal agent.

1. Introduction
Magnetite in the chemical formula of Fe\(_3\)O\(_4\) is one of the types of magnetic material having interesting characteristics. Such characteristics include stable thermal character, a unique magnetic character based on the particle size and high spin polarization at room temperature [1]. Based on such characteristics, many experts utilize the magnetite material for any kinds of application. As a description, the application in the medical field uses the magnetite material as a drug delivery system [2], magnetic resonance imaging [3], and magnetic fluid for hyperthermia [4]. Meanwhile, the application in the industrial field utilizes magnetite material in producing load speakers and as enhanced oil recovery [5]. Thereby, the relatively broad application in various fields enables the magnetite function has a bigger opportunity to be modified and improved through, for example, nanocomposite engineering. In another side, this material is easily accessible since it exists in the main component of iron sand.

The improvement of magnetite function through nanocomposite engineering, zinc oxide (ZnO) with its character excellence is one of the primary material candidates to be developed. This material is preeminent since it can absorb UV radiation well like titanium dioxide material [6]. Moreover, zinc dioxide has more economic benefit than titanium dioxide so that this material becomes one of the study-focuses carried out by some researchers in some recent decades. Furthermore, in the nanometer order, zinc oxide has a broad application in some nanotechnology fields such as a sensor selectivity [7], drug delivery [8], solar cells [9], and photocatalytic and gas sensing [10]. Thereby, since some applications need a material with specific criteria, the development of new material based on magnetite/zinc oxide nanocomposite is urgently required.
In some recent years, the study on magnetite/zinc oxide nanocomposites is intensively conducted for it is interesting where both materials have different characters yet if it is composited it will result in material that has superior physical characteristic [11]. The physical characteristic is in the forms of high Curie temperature and high spin polarization of the nano magnetite particles while the high electrical and optical characteristics are expected to appear from nano zinc oxide particles [1]. The previous research reported that magnetite/zinc oxide nanocomposites could be applied as an agent to remove toxic of metal ion and become an anti-bacterial [12], gate dielectric [13], media cancer cells [14] and wastewater treatment [15]. Therefore, to reach the excellent development of the current application, the study of some important factors especially the structural characteristics of magnetite/zinc oxide nanocomposites is principal to be undertaken.

Some key factors influence the characters of specific material such as crystal structure, particle size, and good homogeneity. That is why this research conducted a simple method development to result in such characteristics using a coprecipitation method. Some popular methods in the synthesis process of magnetite/zinc oxide nanocomposites are sol-gel method [16, 17], hydrothermal [18], and solid-state [1]. Generally, those methods have several weaknesses and benefits. However, the coprecipitation method offers particular excellence, such as a simple chemical reaction process and it can be done in at low temperature [19]. Therefore, this research prepared the samples using a coprecipitation method.

2. Methods
The primary materials used in the synthesis of magnetite/zinc oxide nanocomposites were iron sand, zinc chloride (ZnCl₂), ammonia solution (NH₄OH Merck 25%), and hydrochloric acid fuming (HCl Merck 37%). The magnetite particles were synthesized begun by the process of iron sand and HCl dissolution at the temperature of 70 °C to form a solution in accordance with Equation 1.

\[
\text{Fe}_3\text{O}_4 + 8 \text{HCl} \rightarrow 2\text{FeCl}_3 + \text{FeCl}_2 + 4\text{H}_2\text{O} \tag{1}
\]

The solution of the reaction product was then stirred on a magnetic stirrer. At the same time, the NH₄OH solution was dropped continually to produce a deposition. After that, the deposition of reaction result was leached by H₂O repeatedly until the pH of the solution was neutral. Subsequently, the deposition as the reaction result was filtered and calcinated at the temperature of 100 °C for one hour. The zinc oxide synthesized using coprecipitation method was then prepared through the dissolution process oh ZnCl₂ and distilled water stirred on the magnetic stirrer at room temperature. The formed solution was titrated with an NH₄OH solution so that it formed zinc dioxide deposition. After that, the deposition as the reaction result was also filtered and calcinated at the temperature of 100 °C for one hour. Moreover, the sequence of magnetite/ zinc oxide nanocomposite samples were prepared via coprecipitation process with the ratios of magnetite mass and zinc dioxide were 1.5:0, 1:0.5, 0.75:0.75, 0.5:1, 0:1.5. Each sample was coded with NC1, NC2, NC3, NC4, and NC5. Subsequently, the samples were stirred for 10 minutes at the ambient temperature. They were then filtered and dried at the temperature of 100 °C for one hour. The last step was testing the material including XRD characterization to study the crystal structure and particle size. SEM characterization was done to know the distribution of particle size and material morphology, and FTIR to know the characteristic of the functional group in the material.

3. Results and Discussion
Figure 1 shows the diffraction pattern of magnetite/zinc oxide nanocomposite. The peak is the magnetite characteristic appearing at the angle of 2-theta = 30.554°, 35.728°, 43.347°, 53.839°, 57.577°, and 63.03°coinciding with Miller section of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0). Such results were successfully confirmed based on a crystal model of AMSCD No. 0000945. Besides the peaks of the magnetite phase characteristics, there were also the characteristic of zinc oxide appearing with Miller of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (2 0 0), (1 1 2), and (2 0 1) based on the AMSCD No. 005203 model.
Figure 1. The diffraction pattern of X-Ray of magnetite/zinc oxide nanocomposite

The peaks of the characteristic of NC1, NC2, and NC3 dominantly at miller section of (3 1 1) identified were the characteristic peaks of magnetite. Meanwhile, in NC4 and NC5 samples, the peaks of characteristics dominantly on the miller section of (1 0 1) identified were the peaks of the characteristic of zinc oxide. This case could be related to the treatment of magnetite composition and zinc oxide ratios given to each sample. Based on Figure 1, NC1 consisted of magnetite phase without the impurity or appearing new phase. This case could be confirmed by the absence of the peaks appearing beside the characteristic of magnetite phase. In line with the increase in the mass composition, the zinc oxide resulted in the appearing new phase. In this case, the magnetite phase was signed with (∆) symbol, and zinc oxide was indicated with (*) symbol. Interestingly, in the NC3, NC4, and NC5 samples, there was a new phase besides the magnetite phase, or zinc oxide indicated as the impurity formed in the synthesis process.

Subsequently, the results of data analysis used the Rietveld method showed that the magnetite particle sizes were about 10.89 nm with the crystal structure in the form of cubic spinel as illustrated in Figure 2. The crystal structure of magnetite consists of 32 ions of oxygen. There were Fe$^{2+}$ and Fe$^{3+}$ ions in the gaps of oxygen in the tetrahedral and octahedral sub-room. Meanwhile, the zinc oxide particles (NC5 sample) have the size about 40 nm with wurtzite hexagonal structural model. Figure 3 shows the crystal structure of zinc oxide. Based on Figure 3, the wurtzite hexagonal structure has two sub-lattices namely Zn$^{2+}$ and O$^{2-}$ with the space group of P6$_3$mc.
Figure 2. Crystal structure of magnetite

Figure 3. Crystal structure of zinc oxide

Figure 4 is an FTIR curve of magnetite/zinc oxide nanocomposites showing the relationship between intensity and wave number. The peaks resulted were the realization of interaction between the atoms in the material. Such peaks appeared at the range of wavenumber of 470.35, 494.84, 574.79, 723.31, 1090.20, 1680.49, and 3448.72 cm\(^{-1}\). Moreover, the peaks at the wavenumber of 3448.72 cm\(^{-1}\) and 1680.49 cm\(^{-1}\) were produced by the vibration of the O-H atom from H\(_2\)O as reported by Hasanpour et al. [11]. The vibration of the O-H atom from the H\(_2\)O molecule indicated the existence of water absorbed at the surface of the magnetite/zinc oxide samples. The peaks of absorption were at the range of wavenumber of 723.31 cm\(^{-1}\) and 1090.20 cm\(^{-1}\). They were the characteristics of the O-C-O peak. The absorption peak at the wavenumber about 800 cm\(^{-1}\) associated with the characteristics of Zn-O-Zn atom indicating the existence of the hexagonal phase of ZnO. The characteristics of Zn-O-Zn atom could be found in the NC3, NC4, and NC5 samples. Meanwhile, the peaks at the range of 470.35 cm\(^{-1}\) and 574.79 cm\(^{-1}\) were the characteristics of Fe – O atom bonding at the tetrahedral and octahedral parts [19, 20]. The vibration of metal atom and oxygen in tetrahedral and octahedral parts confirmed that that sample
had a cubic spinel structure. Moreover, the peak of 494.84 cm\(^{-1}\) was the stretching vibration of Zn-O as reported by Nikazar et al. [20]. Meanwhile, the vibration of Zn – O atom showed that zinc oxide had been coated at the magnetite. This case is in line with the results of XRD characterization which signify that there was a phase of zinc oxide in the NC3, NC4, and NC3 samples.

![Figure 4. FTIR pattern of magnetite/zinc oxide nanocomposite](image)

Figure 4. FTIR pattern of magnetite/zinc oxide nanocomposite

Figure 5 presents the morphology of magnetite/zinc oxide nanocomposite particles. Visually, the magnetite/zinc oxide nanocomposite particles were successfully formed. The morphology of magnetite particles could be well read. It was in the form of a ball and equally distributed. Meanwhile, the morphology of zinc oxide particles tended to be less homogeneity. Based on Figure 5, NC1 and NC2 samples qualitatively had the tendency of having a rough surface. In line with the increase in the composition of zinc oxide mass, the particles showed a smoother morphology surface. This enhancement also showed an increase in particle size. We can see that the visualized NC5 sample had the greater particle size compared to NC1 until NC4 samples. This case corresponds to the result of the previous XRD characterization. This phenomenon could be related to the thickness of the zinc oxide layer on the magnetite surface resulted in bigger particle size and some particles grouping and forming new particles having a greater size due to the agglomeration.

Figure 6 is the histogram of particle size distribution from magnetite/zinc oxide nanocomposites. The data analysis showed that the distribution of particle size means of magnetite/zinc oxide nanocomposites was at the range between 17.45 – 58.14 nm. Such results were close to the previous research results showing that magnetite/zinc oxide nanocomposites as the synthesis result using a sol-gel method exhibited the range of 40-50 nm particle size [13]. Besides, the particle size tended to increase as the enhancement of zinc oxide composition influenced by the distribution of the getting bigger zinc oxide particles distribution. Moreover, the difference in particle size between the results of SEM data analysis and the results of XRD analysis was caused by agglomeration in magnetite/zinc oxide nanocomposite particles so that SEM tended to read them as big.
Figure 5. SEM of magnetite/zinc oxide nanocomposites with the code of: NC1 (a), NC2 (b), NC3 (c), NC4 (d), NC5 (e)

Figure 6. Particle size distribution of magnetite/zinc oxide nanocomposites
4. Conclusion
Magnetite/zinc oxide nanocomposites were synthesized and formed a cubic spinel and wurtzite hexagonal structures. The particle size enhanced from about 11 nm to 40 nm as the increase ratio of zinc oxide mass composition to zinc oxide. Meanwhile, the mean sizes of Magnetite/Zinc oxide particles resulted from SEM characterization were insignificantly different from the results of the XRD characterization namely at the range of 17.45 – 58.14 nm. This case was possible because of the agglomeration at the magnetite/zinc oxide nanocomposite particles. FTIR characterization confirmed the Fe–O functional group at the range of 470 cm\(^{-1}\) and 575 cm\(^{-1}\) in tetrahedral and octahedral parts and the Zn-O functional group about 495 cm\(^{-1}\) showing the special characteristic of cubic spinel structure and wurtzite hexagonal.

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