Nanostructure and Optical Properties of Fe₃O₄: Effect of Calcination Temperature and Dwelling Time

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Abstract. In this work, we reported the nanostructure and optical properties of the Fe₃O₄ nanoparticles. The Fe₃O₄ have been synthesized from local iron sand Halmahera Utara by using the coprecipitation method at a temperature of 80°C and NaOH concentration of 3M. The nanoparticles were calcined at 150°C and 250°C for 4 hours consecutively, while the calcination dwelling time was 2 hours and 4 hours at a temperature of 250°C. The results show that a formation of Fe₃O₄ nanoparticles with a spinel crystal structure. The lattice parameter of nanoparticles decreases with an increase of calcination temperature and dwelling time due to higher thermal energy driving the atom to move closer to each other. Hence, the crystallite size of the nanoparticles increases due to the expansion process to the grain of the nanoparticles. The optical gap energy of the nanoparticles decreases due to the formation of a larger particle. It also confirms that the existence of Fe³⁺-O and Fe²⁺-O bonds in the nanoparticles which are characteristic functional group bond of Fe₃O₄ in the tetrahedral and octahedral sublattice. This result can prove that a higher calcination temperature and longer dwelling time can improve the nanostructure and optical properties of Fe₃O₄.

1. Introduction

The Fe₃O₄ nanoparticle has widely used in many fields of applications, such as electronic device, sensor technology, magnetic storage media, as well as for organic and inorganic adsorbent in the case of water treatment, biological and environmental treatment based on photocatalysis. Those potentials are caused by the unique physical and chemical properties of Fe₃O₄ nanoparticles. In the case of sensor technology, especially for surface plasmon resonance (SPR) based biosensor that Fe₃O₄ nanoparticle has potential application as an active material which can generate larger SPR signal [1,2]. The Fe₃O₄ nanoparticles layered on the surface of Au film on prims can actively bind the analyte and also takes a role as a ligand.

In other to be able generating larger SPR signal, so the Fe₃O₄ nanoparticle must have a higher degree of crystallinity and nanostructure. Both crystallinity and nanostructure determine the physical and chemical properties of the nanoparticles, especially for their optical properties. Nanostructure, in this case, refers to the crystal structure, particle size, lattice strain, and the X-ray density of the nanoparticles [3]. Due to a quantum confinement effect, the optical properties of Fe₃O₄ nanoparticle depend on their particle size. Therefore, controlling the particles size and the crystallinity can improve the optical properties of Fe₃O₄ nanoparticle.

Many efforts have been done to control particles size and improving the crystallinity of the nanoparticles. JiangLing et al [4] had controlled the molar ratio of iron salt precursors, the order of surfactant, dwelling time, and stirring rate of the solution during the synthesis. Manani et al [5] used chemical synthesis route to prepare high crystallinity sample of Fe₃O₄ nanoparticles for biomedical applications. Yusoff et al [6] had controlled the particle size of FeO⁺ by varying pH solution of the
precursors. The particle size of Fe$_3$O$_4$ strongly depends on the value of the pH solution. The particle size decreases with an increase of the pH up to the critical value of 12.5 and upper this value the particle size increases gradually. This result is in line with the findings of [7]. Other researchers, such as Salviano et al [8], Girija and Vasu [9], and Takai et al [10] employed different synthesis techniques to prepare Fe$_3$O$_4$ nanoparticles. Chemical wet-coprecipitation technique is considered as the most simple procedure and can produce Fe$_3$O$_4$ nanoparticle with larger yield. Unfortunately, the powder Fe$_3$O$_4$ nanoparticle still has a low degree of crystallinity and wider particle size distribution [8, 10]. Therefore, it is needed the addition of heat treatment for the synthesized nanoparticle. Calcination is one type of heat treatment given to the Fe$_3$O$_4$ nanoparticle after synthesis. Calcination plays an important role on the nanostructure as well as the optical properties of the nanoparticle. Calcination can control the particle size of the nanoparticles with narrow size distribution [11]. Besides that, calcination also increases the crystallinity toward removing impurity in the samples [12].

In this work, we have been investigated the effect of calcination temperature and its dwelling time to the nanostructure and optical properties of the Fe$_3$O$_4$ nanoparticles. The optical parameters being investigated are the absorbance profile and the optical gap energy both direct and indirect. These parameters are important to be considered for future application of Fe$_3$O$_4$ as an active material for SPR based biosensor. The recent results show that the particle size of the nanoparticle increased with an increase in the calcination temperature and dwell time. The crystallinity of Fe$_3$O$_4$ also gradually increases.

2. Experimental Method

2.1 Preparation of Fe$_3$O$_4$ Nanoparticles

The Fe$_3$O$_4$ nanoparticles were synthesized from local iron sand at Wari Ino beach, Halmahera Utara. The synthesis was carried out by employing the coprecipitation process. The preparation was started with providing a clean and very smooth iron sand. Iron sand of 2 gram was dissolves in 20 ml HCL 12M and stirrer at room temperature for 10 minutes. The Fe$^{3+}$ and Fe$^{2+}$ solution will be produced from this mixture. The Fe solution was filtered by using a filter sheet. This solution was dropped wisely to the NaOH solution of 3M while stirring at 60 rpm and temperature of 80°C. The mixture of Fe solution and NaOH was kept with an aging time of 60 minutes. During synthesis, the Fe$_3$O$_4$ nanoparticle will form according to the reaction mechanism showed by the chemical reaction in equation 1:

$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8 \text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}. \quad (1)$$

According to the reaction, the excess of OH$^-$ ion will drive the formation of the larger particle due to larger energy provided in the reaction. Furthermore, this condition also causes an excess hydroxyl group on the surface of the nanoparticle that can accelerate the oxidation process of the Fe$_3$O$_4$ nanoparticles.

After the aging process, the slurry of Fe$_3$O$_4$ nanoparticle will be formed. A black slurry will precipitate on the bottom of the beaker glass. These slurry were washed for four times using distilled water and finally were separated by using permanent magnet toward the glass. The slurry was heated at a temperature of 100°C for 4 hours. A black dry chip of Fe$_3$O$_4$ nanoparticles will be obtained. Those chips were ground by using mortar to get black powder of Fe$_3$O$_4$ nanoparticles.

The Fe$_3$O$_4$ nanoparticles were then calcined at a temperature of 150°C (S1) and 250°C (S2) with dwelling time of 4 hours. For dwelling time variation, the nanoparticles were calcined at a temperature of 250°C for 2 hours (S3) and 4 hours (S2) consecutively.

2.2 Characterization of Fe$_3$O$_4$ Nanoparticles

The powder of Fe$_3$O$_4$ nanoparticles was characterized for their nanostructure by using X-Ray Diffraction (XRD) technique. Based on this characterization, the crystal structure, lattice parameter, lattice strain, X-Ray density and the particle size of the nanoparticles can be analyzed. The surface morphology and surface elemental map of the Fe$_3$O$_4$ nanoparticles were characterized by using Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDAX) techniques, respectively. Hence, the function group vibration of the nanoparticles was characterized by using Fourier Transform Infrared Spectroscopy (FTIR) technique. The last, the optical properties of
the nanoparticles was analyzed based on the absorbance vs wavelength data from Specular UV-Visible Spectroscopy (UV-Vis SR) characterization.

3. Result and Discussion

3.1 Nanostructural Properties of Fe$_3$O$_4$ Nanoparticles

The XRD patterns of Fe$_3$O$_4$ nanoparticles can be shown in Figure 1. There are five diffraction peaks successfully identified in the diffraction patterns, such as (220), (311), (400), (511), and (400). Those are the reflection peaks of Fe$_3$O$_4$ nanoparticles according to the Joint Committee on Powder Diffraction Standard (JCPDS) card no. 11-0614. There is no another peak investigated in these patterns which confirm that samples of nanoparticle purely consist of single-phase Fe$_3$O$_4$. Those single-phase Fe$_3$O$_4$ nanoparticles have a face-centered cubic crystal structure. The exclusive FCC structure such as inverse spinel structure of Fe$_3$O$_4$ nanoparticles in this results agrees with the results reported by [6]. According to Figure 1, the diffraction peaks of nanoparticles are sharp and become sharper with increasing calcination temperature (Figure 1a) and calcination dwelling time (Figure 1b). These confirm the formation of the higher crystalline sample of Fe$_3$O$_4$. An increase in the calcination temperature and dwelling time will increase the degree of crystallinity of sample gradually. Quantitatively, the value of crystallinity of samples can be provided in Table 1.

![Figure 1](image-url)  
**Figure 1.** XRD patterns of Fe$_3$O$_4$ nanoparticles: (a) calcination temperature variation and (b) calcination dwelling time variation.

| Sample | Calcination Temperature (°C) | Dwelling Time (hour) | Crystallinity (%) | $t_{av}$ (nm) | $a$ (Å) | $\varepsilon \times 10^3$ (line) | $\rho_{x-ray}$ (gr/cm$^3$) |
|--------|-----------------------------|----------------------|-------------------|--------------|--------|------------------------|-------------------|
| AP     | -                           | -                    | 72.85             | 24.90        | 8.3369 | 1.51                   | 5.32              |
| S1     | 150                         | 4                    | 74.04             | 14.84        | 8.3279 | 2.53                   | 5.34              |
| S2     | 250                         | 4                    | 81.52             | 21.58        | 8.3009 | 1.60                   | 5.39              |
| S3     | 250                         | 2                    | 75.42             | 20.09        | 8.3054 | 1.81                   | 5.38              |

According to Table 1, the crystallinity of as-prepared (AP) sample Fe$_3$O$_4$ is smaller than the calcined sample. Calcination can be removing the unnecessary content in the sample of nanoparticles which is produced during the synthesis. For example, the excess of OH$^-$ anion can be reduced via calcination. The existence of large amount OH$^-$ can reduce the crystallinity of the sample. In another hand, the existence of undesired product such as Fe(OH)$_2$ and FeOOH also can be removed toward calcination [4]. Besides that, calcination also facilitates the renucleation process of the nanoparticles due to a thermal diffusion on their surface. A higher calcination temperature produces larger thermal
energy driving the thermal diffusion. Therefore, the surface tension of the nanoparticle will decrease and the nanoparticles will not be agglomerated. Somehow, in this research was found that the Fe$_3$O$_4$ nanoparticles with the highest calcination temperature and the longest dwelling time (S2) have the highest degree of crystallinity.

In the case of the crystallinity, we also analyzed the texture coefficient of each diffraction peaks of the nanoparticles and presented in Figure 2. The texture coefficient explains the preferred orientation of the particles in a polycrystalline material perpendicular to their diffraction planes [13]. In other word, the texture coefficient determines the distribution of the crystallographic orientations of particles. The texture coefficient can be calculated from the intensity of the diffraction peaks by using the equation given by [13]. The texture coefficient of each sample can be presented in Figure 3.

![Figure 2](image.png)

**Figure 2.** Texture coefficient of related diffraction peak of Fe$_3$O$_4$ nanoparticles for each sample.

According to Figure 2, the peak (311) has a texture coefficient value bigger than 1. Peaks (440) of sample S2 (green) and S3 (old red) only has a texture coefficient bigger than 1, others are almost near 1 even smaller than 1. These indicate that the preferential growth orientation of the particle during nucleation in the direction perpendicular to the (311) and (440) planes is greater. These results are in agreement with the diffraction pattern in Figure 1.

Another nanostructural parameter, such as particle size was also presented in Table 1. The average particle size of Fe$_3$O$_4$ nanoparticle increases with an increase of calcination temperature and the dwelling time. The particle size of the nanoparticle was calculated using Scherrer’s equation [11]. These results are in agreement with the result reported by [11,12, 14]. Calcination temperature determines the amount of thermal energy given to the nanoparticles. A higher calcination temperature gives higher thermal energy. A longer dwelling time for the calcination than more thermal energy being absorbed by the nanoparticles. Due to higher thermal energy makes the Fe$_3$O$_4$ nanoparticles lose their surface energy. The thermal energy, in this case, takes a role as a driving force that acts over the surface of nanoparticles to interact with the neighboring particles. Thermodynamically, when two particles are in contact so during calcination between those two particles will occur atomic transport. This is well-known as Oswald ripening process. Those two-particle will interact throughout decreasing their boundary energy. There will happen grain boundary migration from one particle to its neighboring particles through surface diffusion. During this process, one particle will rotate in a direction to another particle in other to their crystal planes are aligned. In the final stage of those process will be produced a new larger particle. These particles are denser than the early particles. This is the reason why Fe$_3$O$_4$ nanoparticles with higher calcination temperature and dwelling time will have larger X-ray density.
An interesting thing about the calcination process is crystallization. During calcination, the Fe$_3$O$_4$ nanoparticle experiences crystallization which means the formation of more crystalline particle. The crystalline particle has longer range order of atoms in their lattice. As explained above, in the calcination process, there might a movement of the atom (atomic transport from one particle to another) if the external thermal energy bigger than the binding energy of the atom with the neighboring atom in the lattice. This movement, of course, will change the position of the atom in the entire crystal lattice. As the effect, a strain will happen to the lattice of the crystal. The atomic movement, in this case, doesn’t mean followed by a change in the crystal structure. Its only effect on the lattice parameter of the nanoparticles. Due to higher thermal energy, the atoms of the Fe$_3$O$_4$ nanoparticles might move closer to each other so that the lattice parameter becomes shorter.

3.2 Surface Morphology and Electron Diffraction
The surface morphology of the nanoparticle was characterized by using SEM. The surface morphology image of the Fe$_3$O$_4$ nanoparticles calcined at a temperature of 250°C for 4 hours can be presented in Figure 3a. Furthermore, the elemental map of the surface of this sample can be presented in Figure 3b.

The morphology of the nanoparticle is irregular in shape. There is still agglomeration occur due to the magnetic interaction of the nanoparticles. Some research also reported that pure Fe$_3$O$_4$ nanoparticle tend to be agglomerated due to their magnetic properties in nature and the strong inter-particles Van der Waals force acts over the surface of the nanoparticles [10,15,16]. The image obtained from EDAX spectra confirmed that the formation of Fe$_3$O$_4$ nanoparticle by the existence of Fe (56.29 wt%) and O (30.16 wt%). These two elements bind to each other and make Fe-O functional group bond. The existence of this bond will be proved by using FTIR spectra.

3.3 Vibrational Spectra of the Functional Group Bonds
The vibration of functional group bonds of the nanoparticles can be shown from the FTIR spectra in Figure 4. The spectra confirm that the formation of four functional groups in the sample. The vibration region of O-H bending occurs at the frequency range of 1759 cm$^{-1}$ – 1206 cm$^{-1}$ and O-H stretching vibration occur at the frequency range of 3713 cm$^{-1}$ – 2258 cm$^{-1}$. These are in agreement with the result reported by [10,17,18,19]. The appearance of these groups indicates that the existence of water molecule which is not fully evaporated on the surface of the Fe$_3$O$_4$ nanoparticles during calcination. Hence, Fe$_3$O$_4$ nanoparticles are hygroscopic. The nanoparticles can bind easily with water molecules in the air. Increasing calcination temperature then the water content decreases. This is justified by the narrower and shallower dives in the vibration region of O-H bending and O-H stretching (Figure 4b).
The characteristic bonds vibration of Fe$^{3+}$-O and Fe$^{2+}$-O were also successfully investigated in the samples. These vibrations occur at the frequency range of 850 cm$^{-1}$ – 488 cm$^{-1}$ and 480 cm$^{-1}$–370 cm$^{-1}$, consecutively. The appearance of these functional group bonds justifies the formation of Fe$_3$O$_4$ nanoparticles with an inverse spinel crystal structure. The Fe$^{3+}$-O vibration occurs in the tetrahedral site, while Fe$^{2+}$-O vibration occurs in the octahedral site. Increasing the calcination temperature causes a shift in the vibrational frequency to a higher value for both Fe$^{3+}$-O and Fe$^{2+}$-O groups. This means that the stiffness of bond between Fe and O species enhanced.

![Figure 4](image1.png)

**Figure 4.** (a) Complete FTIR spectra of the Fe$_3$O$_4$ nanoparticles with variation in calcination temperature and calcination dwelling time; (b) Zoom of the spectra in the region of 1450 cm$^{-1}$ – 350 cm$^{-1}$.

### 3.4 Optical Properties

The optical absorbance of the nanoparticle has been characterized by using UV-Vis SR. The absorbance curve versus photon wavelength for all samples is shown in Figure 5. The absorbance spectra contain one broad peak at its related maximum wavelength ($\lambda_{\text{max}}$). Increasing the calcination temperature and dwelling time causes absorbance peaks broader. This can be affected by two factors, i.e., the particles size and the distribution of the particle size. Larger particles size and larger particles distribution cause a broader range of photon energy being absorbed by the particles. Each particle needs a different amount of photon energy to excite their electrons from valence band to the conduction band. In another hand, nonuniform of the morphology of the particles also takes a role in determining the shape of the absorbance peak [20].

![Figure 5](image2.png)

**Figure 5.** UV-Vis SR spectra of all samples Fe$_3$O$_4$ nanoparticle.
Form UV-Vis spectra, we also observe that increasing the calcination temperature and dwelling time causes an increase in the absorbance intensity. The absorbance spectra decrease exponentially along with the photon wavelength increases from 320 nm to 800 nm. This is due to various reasons, such as perfection of the crystal structure because of the deformation of the lattice, the inelastic of charge carriers by phonons, and larger particles size of the nanoparticles with larger particle size distribution [11]. The absorbance edge in the region of 200 nm to 300 nm might be due to a structural disorder of the nanoparticles [20]. The most interesting information is the occurrence of the redshift to the maximum absorbance peak of the Fe$_3$O$_4$ nanoparticles. The maximum wavelength is shifted to the higher value with an increase of the calcination temperature and dwelling time. This indicates that smaller energy needed by electrons of the particle to excite from valence band to the conduction band.

The optical gap energy of Fe$_3$O$_4$ nanoparticles has been calculated by using Tauch’s plot method provided in [20,21,22]. In this research, we have been successful to analyze the direct and indirect optical gap energy of the nanoparticles. The direct optical gap energy can be shown in Figure 6 and the indirect optical gap energy shown in Figure 7.

![Figure 6](image-url). Tauch’s plot for determining the direct optical gap energy of Fe$_3$O$_4$ nanoparticles.

The direct optical gap energy of Fe$_3$O$_4$ means energy needed by electrons of the nanoparticle to directly transition from valence band to conduction band with the same wave vector $k$ at the Brillouin zone. In this case, the direct optical gap energy of the nanoparticle becomes smaller as increasing the calcination temperature and dwelling time, as reported by [11,23]. This is a consequence of increasing particle size of the nanoparticles. Calcination facilitates the occurrence of atomic displacement in the entire particle, further the atomic transport between particles. This may generate a small deformation to the crystal structure of the nanoparticles depend on the amount of thermal energy. This phenomenon is considered able to generate new energy level to reduce the optical band gap energy [11]. Another reason by [23] might be considered that increasing calcination temperature can trigger the formation of
new localized level which potentially to generate localized energy inside the optical gap energy of the Fe$_3$O$_4$ nanoparticles and decrease the energy gap.

Here, we also analyzed the indirect optical gap energy, as shown in Figure 7. Indirect optical gap energy of the nanoparticle is the energy needed by electrons to displace from valence band to conduction band with different wave vector $k$ at the Brillouin zone. In this research, it was found that the indirect optical gap energy of Fe$_3$O$_4$ becomes smaller as increasing calcination temperature and dwelling time. The reason might be the same as the particle growth experienced by Fe$_3$O$_4$ nanoparticle when the calcination temperature and dwelling time increase. Somehow, the most interesting phenomena are the value of indirect optical gap energy smaller than direct gap energy.

**Figure 7.** Tauch’s plot for determining the indirect optical gap energy of Fe$_3$O$_4$ nanoparticles.

There are two reasons can be offered to address this phenomenon. First, mathematically, the Tauch’s equation given in [22] informs that $n = 2$ for indirect allowed transition and $n = 1/2$ for a direct allowed transition. If $n = 2$, the plot between $(\alpha h \nu)^{1/n}$ vs $(h \nu)$ is well fit for lower photon energy range, while $n = 1/2$ is well fit for higher photon energy range. Therefore, the direct optical gap energy will bigger than indirect gap energy. Second, indirect gap energy is the narrowest gap in the energy between the valence band and the conduction band. It also requires the interaction of phonon to absorb or emit the photon energy in other electron arrives in the purposed point in the conduction band. In certain materials, the electron might excite from the highest valence band energy to the lowest conduction band energy via phonon interaction. This case may be considered as the factor causing lower energy of the indirect bandgap than the direct gap.
4. Conclusion
The Fe$_3$O$_4$ samples nanoparticle with various calcination temperature and dwelling time have been successfully synthesized. The nanostructure and optical properties of the nanoparticles have been successfully investigated. Both calcination temperature and dwelling time affecting nanostucture and optical properties of the Fe$_3$O$_4$. The crystallinity of Fe$_3$O$_4$ increases as increasing calcination temperature and dwelling time. The crystallite size becomes larger due to grain growth caused by thermal energy. The lattice parameter of the Fe$_3$O$_4$ nanoparticle change to be shorter due to the crystal deformation and the strain on the entire lattice of Fe$_3$O$_4$. The density of the nanoparticles increases due to densification process experienced by the particle under calcination. The optical properties of Fe$_3$O$_4$ significantly affected by a change of the calcination temperature and dwelling time. Both direct and indirect optical gap energy tend to be bigger as increasing the calcination temperature and dwelling time. Further, controlling the calcination temperature and dwelling time can facilitate to improve the physical properties of Fe$_3$O$_4$ nanoparticle for more potential applications.

Acknowledgments
The authors grateful to the Government of Indonesia throughout the Ministry of Research, Technology and Higher Education of Republik Indonesia for PDP Research Grant 2018-2019 to funded this work under contract grant of 0.36/uniera.H/PM/2019. The authors also would like thanks to the LPPMP Universitas Halmahera for facilitating the administration of this grant.

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