Synthesis and Characterization of Fe₃O₄/SiO₂ nanocomposites

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Abstract. Fe₃O₄@SiO₂ nanocomposites have been synthesized using the Stöber method. X-ray diffraction data analysis showed the addition of SiO₂ changed the diffraction pattern peak which represented the existence of Fe₃O₄ and SiO₂ nanoparticles. Based on the elemental analysis, it can be seen that Si compositions on the samples were 14.7% (S1), 19.8% (S2), and 20.4% (S3). It strengthens the existence of Fe₃O₄ and SiO₂ nanoparticles on the sample. Furthermore, the infrared spectrum showed that Fe₃O₄ and SiO₂ molecular functional groups were recorded at the wavenumber of 548 cm⁻¹ with Fe-O-Si bond. Furthermore, Fe-O bond was recorded at the wavenumber of 461 cm⁻¹. Meanwhile, Si-O-Si and Si-O bonds were detected at the wavenumbers of 1102 cm⁻¹ and 949 cm⁻¹ respectively. Furthermore, the data from UV-Vis characterization presented the peak shifted towards a higher angle of the wavelength which indicated that there is a phenomenon of changes in band gap particle size along with increased content of SiO₂.

Keywords: Fe₃O₄, SiO₂, structure, nanocomposite, Stöber.

1. Introduction
Thus far, magnetic nanoparticles especially Fe₃O₄ becomes the study focus of material scientists due to its unique physicochemical and high application potentials. Several applications have been reported, among them are for magnetic data storage [1], environmental remediation [2], catalyst [3], sensor [4] and biomedical field [5–7]. To support its application potentials, the study on shape, size, structure, and synthesis method becomes essential to be conducted. In general, Fe₃O₄ was synthesized using relatively expensive commercial materials. In this study, the raw material used to synthesize Fe₃O₄ was a natural material namely iron sand. This was performed as an effort to utilize the abundant amount of iron sand in Indonesia. The use of iron sand as a raw material has been proven to be able to generate high purity and relatively affordable Fe₃O₄ [8,9]. Therefore, the use of iron sand as the raw material is considered more efficient.

Based on the previous work, the Fe₃O₄ nanoparticles have a large surface volume ration which is around 20 nm [10]. The large surface volume ratio causes high surface energy which leads to the occurrence of particle aggregation. Besides that, Fe₃O₄ has high chemical activity on its surface, so it is susceptible to air oxidation to take place which then causing its magnetic properties and dispersibility to decline [11,12]. This becomes a challenge for the researchers; therefore, it is necessary to modify the functionalization of Fe₃O₄ with various materials such as polymer, silica, carbon, oxide absorber, metal oxide, or luminescent material [13]. Based on the previously mentioned
materials, an inorganic material such as silica (SiO$_2$) is valued to fulfill the requirement to overcome the problems.

Silica has more stable properties towards acidic condition, has hydroxyl groups which enable the functionalization of Fe$_3$O$_4$ to bind diverse biological ligands. Another excellence related to the properties of SiO$_2$ is having a nanometer particle size with interface energy and adequate bounds to connect with the core. Besides, SiO$_2$ particle in nontoxic, biocompatible, and often used as the component of vitamin supplement and food additives [14]. SiO$_2$ nanoparticles also have hydrophilic properties due to the existence of a silanol group on the surface. Furthermore, SiO$_2$ is considered as one of the promising materials for high-performance drug delivery [15]. According to several previous works, SiO$_2$ particles have been proven to be able to give protection to Fe$_3$O$_4$, moreover to the high toxicity properties [11,16–18].

The combination of Fe$_3$O$_4$ and SiO$_2$ in the nanocomposite system has more advantages such as having biocompatibility, high biostability, and excellent response in drug delivery. Therefore, the selection of materials and the synthesis method become critical to improving the performance of Fe$_3$O$_4$/SiO$_2$ nanocomposites. In this research, we exploited the Stöber method at room temperature in which it is more effortless to control the particle size. Practically, Stöber method is the least complicated method which has easy control from SiO$_2$ thickness and to produce an excellent product shape [19].

2. Methods

The materials used in this research were iron sand, hydrochloric acid (HCl, 38%), ammonium hydroxide (NH$_4$OH, 25%), distilled water, ethanol and tetraethyl orthosilicate (TEOS). Fe$_3$O$_4$ nanoparticles were synthesized via previous works [20,21]. The Fe$_3$O$_4$ nanoparticles were added with deionized water and then stirred using the ultrasonic machine at room temperature. The solution generated was added with and stirred until homogeneous. NH$_4$OH and TEOS were added by titration. The yielded solution was washed using H$_2$O until neutral pH then washed using ethanol eliminate empty SiO$_2$ nanoparticles. The solution generated from the reaction was filtered and put in the oven at the temperature of 80 °C for two hours. In this study, three variations of TEOS compositions were performed. S1 with 2 ml TEOS composition, S2 with 4 ml TEOS composition and S3 with 6 ml TEOS composition. This research used the XRD, XRF, FTIR, and UV-Vis characterization instruments. The XRD characterization was conducted to discover the particle size and lattice parameter. The XRF testing was performed to explore the element compositions contained in a specific material. FTIR was used to find out the functional group of the material. Meanwhile, UV-Vis was performed to reveal the band gap of the material.

3. Results and Discussion

Figure 1 shows the XRD patterns of Fe$_3$O$_4$/SiO$_2$ from various samples. Based on the figure, the peaks yielded from XRD characterization were identified at the angles of 30.3°; 35.6°; 43.2°; 53.1°; 57 °, and 62.8° with the hkl fields of (022), (113), (004), (224), (115), and (044) respectively on all samples. The characteristic peaks from the results showed that the magnetic nanoparticles appeared in all of the reaction process [14]. Based on the XRF testing results portrayed in Table 1, it is proven that the formation of dominant Fe compound was around 85.3% (S1), 80.2% (S2), and 79.6% (S3). The difference of Fe compound content in the three samples was stimulated by the addition of different TEOS contents.

Based on the figure, it can be observed that there is a wide peak around the angle of 22.3°. The peak represented there was a bread peak which showed a characterized feature from SiO$_2$ amorphous properties. This peak identified that SiO$_2$ was successfully synthesized using the Stöber method at room temperature [22]. This is also strengthened with the results of XRF testing which signified the existence of Si compound composition on the sample as much as 14.7% (S1), 19.8 % (S2), and 20.4% (S3). In this research, the addition of around 2-4 ml TEOS, the SiO$_2$ peak was not significantly visible because the silica layer formed due to the addition of TEOS was fragile. However, in S3 with the
addition of 6 ml TEOS, Si amorphous peak was slightly visible. Munasir et al. state that the higher amount of TEOS added to SiO₂ amorphous peak will be more significantly visible [23].

The highest intensity of diffraction peak (311) was analyzed using the Scherer equation (as shown in Equation 1) generated the particle sizes of 10.1 nm, 13.7, and 14.2 nm.

$$D = \frac{k \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where variable $D$ is crystal size (nm), $K$ is lattice constant (0.98), $\lambda$ is wavelength (0.154 nm), $\beta$ is full width half maximum (FWHM) of the maximum intensity, and $\theta$ is Bragg peak angle. The higher the TEOS content added, the bigger the particle size of Fe₃O₄/SiO₂ [24]. The particle size yielded from this research was significantly smaller compared to the previous research by Neena et al. [25] using a sol-gel method which was 15 nm. Based on the analysis results using Rietica, several parameter values were obtained as presented in Table 2.

![Figure 1](image-url). Diffraction patterns of Fe₃O₄/SiO₂ nanocomposites and their refinement results
Table 1. Elemental composition of Fe₃O₄/SiO₂ nanocomposites

| Compound | S1   | S2   | S3   |
|----------|------|------|------|
| Si       | 14.7%| 19.8%| 20.4%|
| Fe       | 85.3%| 80.2%| 79.6%|

Table 2. Refinement results of Fe₃O₄/SiO₂ nanocomposites

| Parameter | S1    | S2    | S3    |
|-----------|-------|-------|-------|
| a = b = c (Å) | 8.36  | 8.37  | 8.37  |
| α = β = γ    | 90.0  | 90.0  | 90.0  |
| Rp          | 20.06 | 23.27 | 20.32 |
| Rwp         | 27.61 | 31.74 | 26.84 |
| χ           | 1.241 | 1.360 | 1.359 |

Besides conducting the above calculation analysis, 3D crystal model visualization was also performed. This step was conducted using Vesta software. The imaging yielded in this research is presented in Figure 2. Based on Figure 2 (a), two types of Fe atom have different sites. The first site is tetragonal site and the second site is the octahedral site. The red-colored atom represents the O atom. The Fe₃O₄ crystal structure was spinel inverse cubic [26]. The chemical reaction from magnetic nanoparticle can be written as [Fe³⁺]₄M[Fe³⁺, Fe²⁺]₄O₄. The M letter in the equation symbolizes tetrahedral site of iron oxide (8 cell units), and the letter N symbolizes the octahedral site (16 cell units). In the magnetite, octahedral and tetrahedral sites formed two magnetic sublattices with an antiparallel moment spin between M sublattice and N sublattice.

Figure 2 (b) is the crystal structure of SiO₂. Si atom shows the tetrahedral coordination with 4 oxygen atoms surrounding the center Si atom. SiO₂ has several different crystal structures (polymorph) besides amorphous structures. In general, Silica which has polymorph crystal are quartz, cristobalite and tridymite, stishovite, and coesite [27,28]. Macro-size silica has a crystalline structure, while nano-size silica has an amorphous structure [29].

![Figure 2](image-url)
stretched in SiO$_2$. This is also strengthened by previous studies in which O-H bond vibration at the wavenumbers ranged between 3200 – 3650 cm$^{-1}$ [23] [30]. There was H-O-H group around the SiO$_2$ surface which appeared at the wave vibration of 1647 cm$^{-1}$. Besides that, the vibration peaks at 2310 and 1865 were C-O stretching and CO$_2$ vibrations.

![Figure 3. FTIR spectrum of Fe$_3$O$_4$/SiO$_2$ nanocomposites](image)

Based on the data analysis, the characteristic peak between Fe$_3$O$_4$ and SiO$_2$ molecules appeared at the wavenumber of 548 cm$^{-1}$. This kind of functional group was also found in previous research [14,23]. The wave vibration value identified there was a stereotype of Si-O-Fe bond, and at the wavenumber value of 461 cm$^{-1}$, there was Fe-O bond. Therefore, the Fe$_3$O$_4$/SiO$_2$ nanocomposites process took place. On another peak, precisely at 1132 cm$^{-1}$, there was Si-O-Si bound, and SiO bound at the wavenumber of 949 cm$^{-1}$. This reflected that there were siloxane bond and silanol bond in the silica [23]. The previous research also stated that the bond is an asymmetrical bond related to the existence of oxygen transfer [27]. Based on the data above, the addition of TEOS content in the sample causes a stronger Si-O bond which was signified with the higher peak intensity [24].

The optical properties of Fe$_3$O$_4$/SiO$_2$ nanocomposites were generated using UV-Vis spectroscopy as shown in Figure 5. From the figure, there is a wide peak at the wavelengths around 400-600 nm. It can be observed that the absorbance peak on the S1 was at the wavelength value of 460 nm. The absorbance peak on S2 was at the wavelength value around 590 nm, and the absorbance peak of S3

| Functional Group | Wavenumber (cm$^{-1}$) | Reference wavenumber (cm$^{-1}$) | Reference |
|------------------|------------------------|---------------------------------|-----------|
| O-H              | 3280                   | 3650 – 3200                     | [23,30]   |
| H-O-H            | 1641                   | 1640-3483                       | [14,30]   |
| C-O-O            | 1516                   | 1630 and 1385                   | [31]      |
| C-O              | 2310                   | 2346 and 1122                   | [31]      |
| Si-O-Si          | 1102                   | 1094                            | [32]      |
| Fe-O-Si          | 548                    | 569                             | [14]      |
| Si-O             | 949                    | 949                             | [14]      |
| Fe-O             | 461                    | 461 and 468                     | [23]      |

The optical properties of Fe$_3$O$_4$/SiO$_2$ nanocomposites were generated using UV-Vis spectroscopy as shown in Figure 5. From the figure, there is a wide peak at the wavelengths around 400-600 nm. It can be observed that the absorbance peak on the S1 was at the wavelength value of 460 nm. The absorbance peak on S2 was at the wavelength value around 590 nm, and the absorbance peak of S3
was at the wavelength around 624 nm. The peak identified that there was a change in the band gap caused by the quantum size effect and surface effect of Fe₃O₄ nanoparticle structure [16]. Based on the graphic, the increase in TEOS content causes the absorbance peak to shift towards a higher wavelength. Sachin et al. state that the increase in the particle size causes the band gap value of the sample to decline so that the absorbance peak shifted towards a higher wavelength [24].

The correlation between band gap energy and the absorbance \( \alpha \) coefficient is explained in Tauc’s relation as shown in Equation 2 [33]:

\[
(\alpha h\nu)^n = A(h\nu - E_g)^n
\]

where \( A \) is the constant proportion of energy, \( n \) shows the transition type \((n = 1/2, 3/2, 2 \text{ and } 3)\) for the transition types of direct allowed, direct forbidden, indirect forbidden or indirect forbidden, \( h\nu \) is energy photon, \( E_g \) is the optical band gap. The photon absorption can take place is the electron from the valence band is excited to the conduction band, therefore in the conduction band, free electron existed; and in the valence band, the hole existed. The value of the phonon energy is the quantized value whose value can only be determined by Equation 3 [34]:

\[
E = \frac{hc}{\lambda}
\]

Based on Equation 3, the information on the band gap value was obtained using Tauc’s plot method as presented in Figure 4.

![Figure 4. UV-Vis spectrum of Fe₃O₄/SiO₂ nanocomposites](image_url)

Based on Figure 5, Fe₃O₄/SiO₂ nanocomposites have the band gap energy value as much as 2.047 eV (S1), 1.750 eV (S2), and 1.453 eV (S3). The increase in TEOS content causes the energy gap in the sample became smaller. The band gap energy of the sample is inversely proportional with the particle size. In physics, it is due to the existence of the condition density change in the conduction band. The value of band gap energy illustrates the amount of energy needed for electron excitation from the valence band to conduction band. The high band gap value needs more energy for electron excitation, so the high light frequency and low wavelength will be absorbed [33].
Figure 5. Band gap energy of Fe$_3$O$_4$/SiO$_2$ nanocomposites

Besides energy gap, there were several other parameters of the material properties which can be identified through the results of UV-Vis spectrum testing, among them are the value of absorption index, optical conductivity, dielectric constant, and refractive index. Refractive index is one of the fundamental properties of the materials related to ion electronic polarization on a material. Several theories have been proposed by scientists on the formulation of optical refractive index value theoretically. Moss proposed a simple correlation to calculate the optical refractive index value through Equation 4 [35].

\[ \frac{n_0^4}{\lambda_g} = 77 \mu m^{-1} \]  

Such equation is equivalent to the Equation 5.

\[ n_0^4E_g = 95 eV \]  

This is based on the fact where the energy level of the electron in the dense crystal was minimized by the factor $1/\varepsilon^2$ where \( \varepsilon \) is the dielectric constant. However, the equation is considered to have limited validity; therefore, Ravindra and Gupta [36] proposed a new theory on the refractive index. They proposed that there is a linear correlation between the energy gap and the optical refractive index through Equation 6.
4.084 – 0.63E_g \quad (6)

Alternatively, it can be stated using Equation 7.

n_0^2E_g = 108eV \quad (7)

By applying Equations 4-5, the calculated refractive index of the samples were 2.610, 2.714, and 2.843 for the respective S1, S2, and S3. Such values were quite similar to the refractive index calculated by Equations 6-7 having the values of 2.695, 2.802, and 2.936 for S1, S2, and S3, respectively. In general, the refractive index value tends to increase by increasing TEOS composition. However, the band gap energy value tends to decrease by increasing TEOS composition. The lower band gap energy, the higher the refractive index of the sample. Theoretically, lower band gap energy needs lower energy to transfer electrons from the valence band to the conduction band that increases the refractive index of the samples [37].

4. Conclusion

In this work, the XRD patterns confirmed the existence of SiO₂ and Fe₃O₄ phases in all samples indicating that the Fe₃O₄/SiO₂ nanocomposites were successfully synthesized. It was also strengthened by the elemental analysis showing the addition of Si content by the increase in the TEOS content added. Based on the FTIR results, the functional groups of Fe₃O₄ and SiO₂ molecules were detected at the wavenumber of 461, 548, 948, and 1102 cm⁻¹. Interestingly, the addition of TEOS content on the sample caused the Si-O bond to get stronger signified with the higher peak intensity. UV-vis spectrum showed a wavelength shift with the increase in SiO₂.

Acknowledgments

We would like to thank the KEMENRISTEKDIKTI RI for providing financial support for AT in 2019.

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