Structure Analysis of Fe$_3$O$_4$@SiO$_2$ Core Shells Prepared from Amorphous and Crystalline SiO$_2$ Particles

Munasir$^{1,2}$, A. S. Dewanto$^1$, D. H. Kusumawati$^{1,2}$, N. P. Putri$^{1,2}$, A. Yulianingsih$^1$, I. K. F. Sa’adah$^1$, A. Taufiq$^3$, N. Hidayat$^3$, S. Sunaryono$^3$, Z. A. I. Supardi$^{1,2}$

$^1$Department of Physics, Faculty of Mathematics and Natural Science, Universitas Negeri Surabaya, Jl. Ketintang, Surabaya, 60231, Indonesia
$^2$Research Center for Advanced Materials, Universitas Negeri Surabaya, Jl. Ketintang, Surabaya 60231, Indonesia
$^3$Department of Physics, Faculty of Mathematics and Natural Science, Universitas Negeri Malang, Jl. Semarang 5, Malang 64145, Indonesia

E-mail: munasir.physics@unesa.ac.id

Abstract: This article reports the results synthesis of crystalline (Fe$_3$O$_4$@c-SiO$_2$) and amorphous (Fe$_3$O$_4$@a-SiO$_2$) nanoparticles from natural resources (iron sand and silica sand). The synthesis of Fe$_3$O$_4$ and SiO$_2$ nanoparticles used co-precipitation and hydrothermal-coprecipitation methods with polyethylene glycol (PEG) 4000 as a template. The XRD data analysis presented that the amorphous SiO$_2$ particles were successfully produced using hydrothermal and co-precipitation methods. The XRD data analysis also presented that the crystalline phases were formed in quartz and tridymite phases after calcination process of the amorphous phase. SEM images exhibited that the amorphous phase had different particle size and morphology from the crystalline phase. FTIR spectra presented some absorption peaks of new functional groups indicating the existence of Si-O-Si (silanol), Fe-O, C-N, and Fe-O-Si as new functional groups.

Keywords. Core-shell, crystalline and amorphous structures, Fe$_3$O$_4$@SiO$_2$, iron sand, nanoparticle, and silica sand.

1. Introduction
Iron oxide nanoparticle particle has special superior characteristics comparing to other mineral compounds. Naturally, the iron oxide is easily found in iron sand and andesite [1], [2]. The iron oxide has various applications of technologies such as for data saving [3], sensor, spintronic [4], drug delivery system, medical diagnosis [3]–[6], immobilization of protein and enzyme separations [5], [7], [8], and water absorbent [9]–[14]. Related to these applications, particle size strongly determines the electrical, optical, and magnetic properties of the magnetic nanoparticles. Magnetite (Fe$_3$O$_4$), besides maghemite ($\gamma$-Fe$_2$O$_3$) and hematite ($\alpha$-Fe$_2$O$_3$), is an iron oxide that possesses a strong magnetic property. Fe$_3$O$_4$ is commonly known as black iron oxide, magnetic iron ore, loadstone, ferrous ferrite, or a Hercules stone that shows the strongest magnetic characteristic [15]–[17].

Despite Fe$_3$O$_4$, silica (SiO$_2$) also has special characteristics that superior to be applied in various applications. In general, the SiO$_2$ can be found in rocks [1], [18] of about 60 % for example in source
rocks (diorite, gabbro), silica sand, clay or mud, organic material like rice husk ash, and bagasse ash [19]-[21]. The common forms of the SiO₂ crystal structure are quartz, cristobalite, and tridymite [18]. Typically, the SiO₂ nanoparticle has an amorphous phase, and it can be commercially produced as silica gel, fume-silica, and so forth. Several applications of SiO₂ nanoparticles for examples such as medical purposes [22–24], as additives for rubber and plastics [25–27], as fillers for composite construction concrete [28–30], as stabilizers and agents drug delivery and theranostics [23, 31], and as a heavy metal absorbent material in a water filter [14], [22].

In order to increase the application performance of the Fe₃O₄/SiO₂ particles effectively, it is essential to prepare the particles using the inexpensive method from natural resources as raw materials. Based on the previous reports, various methods have been employed such as hydrolysis, microemulsions, and co-precipitation. Meanwhile, the Fe₃O₄/SiO₂ nanocomposites have been fabricated via coprecipitation method [1], [15], [23], [24]. In this work, we exploited a simple co-precipitation method at room temperature which easier to control the particle size of the samples. The main purpose of this research was the synthesis of Fe₃O₄@SiO₂ core shells based on natural materials using polyethylene glycol (PEG) 4000 as a template, and analyzing their structure both in amorphous phase (a-SiO₂) and crystalline phase (c-SO₂).

2. Materials and methods
The materials used in this research were silica sand, iron sand, sodium hydroxide (NaOH, 7 M, PA), chloride acid (HCl, 2 M, PA), distilled water, ammonium hydroxide (NH₄OH, 6.5 M, PA), and polyethylene glycol (PEG-4000, PA). The SiO₂ particle formation from silica sand followed equations (1-3), while the fabrication of the Fe₃O₄ particle from iron sand followed equation 4. The preparation process of the SiO₂ particle was initiated by an extraction process to form Na₂O.xSiO₃ and Si(OH)₄ silica gel with NaCl as a compound of the remaining product.

\[
x\text{SiO}_2(s) + 2\text{NaOH}(l) \rightarrow \text{Na}_2\text{OxSiO}_3(aq) + \text{H}_2\text{O}(l)
\]

\[
\text{Na}_2\text{OxSiO}_3(aq) + \text{H}_2\text{O}(l) + 2\text{HCl}(aq) \rightarrow \text{Si(OH)}_4(aq) + 2\text{NaCl}(aq)
\]

\[
\text{Si(OH)}_4(aq) \quad \text{(Drying) \rightarrow SiO}_2(s) + 2\text{H}_2\text{O}(g)
\]

\[
2\text{FeCl}_3(l) + \text{FeCl}_2(l) + \text{H}_2\text{O}(l) + 8\text{NH}_4\text{OH}(l) \rightarrow \text{Fe}_3\text{O}_4(s) + 8\text{NH}_4\text{Cl}(l) + 5\text{H}_2\text{O}(l)
\]

The Fe₃O₄ powder from iron sand was reacted with HCl and followed by NH₄OH to form a Fe₃O₄ particle. Furthermore, the preparation of the Fe₃O₄@SiO₂ core shells was conducted using PEG-4000 as a template, and then it will be removed after calcination at (50 to 60) °C. The Fe₃O₄, SiO₂, and PEG were set based on their respective mass composition by comparison of 2:3:3 before draining process at below 60 °C. The crystal structure characterization of the samples was performed using XRD (based on Cu-Kα), while identification of a special functional group of SiO₂ (amorphous and crystalline phases), Fe₃O₄ and Fe₃O₄@SiO₂ employed FTIR. The profile analysis of the samples (morphology and particle size) was done using SEM-EDX.

3. Results and discussion
The diffraction patterns are presented in Figure 1, while the data analysis is presented in Table 1. The figure reveals the existence of a Fe₃O₄ phase with the characteristic peaks (at 2θ): 30.20°, 35.51°, 37.23°, 43.16°, 53.51°, 57.01°, 62.60° and 74.18°. These peaks are by their respective crystalline indices of (220), (311), (222), (400), (422), (511), (440), and (533) originating from an inverse cubic spinel [17]. In Table 1, the crystal field or peaks (hkl) of the experimental sample characteristics are not significantly different from the previous research and shows a similar pattern to the PDF database 00-019-0629 (shown in Table 1). From the results of quantitative analysis using Reitica software with Rietveld method, and modeling referring to suitable the crystallographic database. Moreover, the
sample had a particle diameter of about \( (25 \pm 3.5) \) nm \((d < 100 \text{ nm})\), and was identified as a cubic structure.

**Figure 1.** XRD patterns of \( \text{Fe}_3\text{O}_4@c\)-SiO\(_2\) and \( \text{Fe}_3\text{O}_4@a\)-SiO\(_2\) particles: c and a represent the crystalline and amorphous phases.

From Figure 1, it is also found a broad peak at \( 2\theta \approx 20^\circ \) to \( 24^\circ \) presenting a peak of the amorphous silica. Therefore, the figure proves a combination of the \( \text{Fe}_3\text{O}_4 \) particle and the c-SiO\(_2\) particle. \( \text{Fe}_3\text{O}_4 \) particles that added to the SiO\(_2\) particle as a matrix for crystal or amorphous phase affected the size of the \( \text{Fe}_3\text{O}_4@\text{SiO}_2 \). This phenomenon can be predicted by the growth of finite particles by a large number of Si-O-Si chains on amorphous phase. The diffraction patterns among the \( \text{Fe}_3\text{O}_4@c\)-SiO\(_2\) and \( \text{Fe}_3\text{O}_4@a\)-SiO\(_2\) particles could also be seen. On the wave number of 1130 cm\(^{-1}\) represents the asymmetric vibration of the Si-O-Si and...
SiO$_2$ bonds and a Si-OH bond is found at 900 cm$^{-1}$. The 3014-3498 cm$^{-1}$ wavenumbers show O-H (water molecule) bond stretching in SiO$_2$. Such functional groups have similarities with the characteristics of the Fe$_3$O$_4$@c-SiO$_2$ particles obtained from the previous research [25], [26].

Figure 2. FTIR spectra of Fe$_3$O$_4$@c-SiO$_2$ and Fe$_3$O$_4$@a-SiO$_2$ particles

| No | Wave Number (cm$^{-1}$) | Functional group | Wave Number (cm$^{-1}$) | Reference |
|----|--------------------------|------------------|--------------------------|------------|
| 1  | 3465                     | O-H stretching   | 3650-3200                | [27]       |
| 2  | 2870                     | O-H              | 1640-3483                | [28]       |
| 3  | 1386                     | Fe-O             | 1390                     | [27]       |
| 4  | 1097                     | Si-O-Si stretching vibration | 1070-1080 | [27], [29] |
|    |                          |                  |                          |            |
| 5  | 950                      | Si-O             | 964                      | [18], [30] |
| 6  | 800                      | Si-O-Si          | 798                      | [18], [31] |
| 7  | 569                      | Si-O-Fe          | 570                      | [1], [32]  |
| 8  | 468                      | Si-O             | 461                      | [18], [31] |

According to the results of functional groups adjustment of the Fe$_3$O$_4$@a-SiO$_2$ particles as shown in Table 2, there is a bending vibration on the Si-O bond at the wave number of 468 cm$^{-1}$. The characteristic peaks between Fe$_3$O$_4$ and SiO$_2$ molecules can be observed as follows: at 569 cm$^{-1}$ and 1097 cm$^{-1}$ wavenumbers identified as stereo types of Fe-O-Si bonds, and wave number 1386 cm$^{-1}$ that identify as the Fe-O group vibration. Thus the process of formation of the Fe$_3$O$_4$@SiO$_2$ composite has successfully produced. At the same time, the presence of Fe-O group indicates Fe$_3$O$_4$ particles have an interface bond with the SiO$_2$ matrix. As shown in Figure 2, there are three arrows showing vibration waves on Fe-O (1386 cm$^{-1}$) and Fe-O-Si (569 cm$^{-1}$ and 1097 cm$^{-1}$). On the other hand, the peaks at 468, 800, 950, and 1097 cm$^{-1}$ present asymmetrical vibrations and symmetrical stretching of Si-O-Si siloxane and silanol bonds on silica. Therefore, it indicates that the Fe$_3$O$_4$ particles can succeed to form a core formation shell with SiO$_2$ as a layer [1, 18, 40, 41]. The stretching and bending vibration of the H-O-H bond are found at wave numbers of 1641-3465 cm$^{-1}$. Such functional groups have almost similar characteristics with the Fe$_3$O$_4$@a-SiO$_2$ particles obtained from the references [27], [28].
Figure 3. SEM-EDX profiles of Fe$_3$O$_4$@SiO$_2$, with: (a) a-SiO$_2$ and (b) c-SiO$_2$ particles

Table 3. Atomic elements of Fe$_3$O$_4$@SiO$_2$ particles

| Element | Fe$_3$O$_4$@a-SiO$_2$ | Fe$_3$O$_4$@c-SiO$_2$ |
|---------|----------------------|----------------------|
| O       | 40.75                | 46.15                |
|         | 57.15                | 56.21                |
| Si      | 47.94                | 42.50                |
|         | 38.30                | 39.22                |
| Fe      | 11.31                | 11.35                |
|         | 0.55                 | 0.57                 |

Figure 3a Fe$_3$O$_4$@a-SiO$_2$ (for SiO$_2$ amorphous phase) and Figure 3b Fe$_3$O$_4$@c-SiO$_2$ (for SiO$_2$ crystalline phase) are the results of the elective analysis (EDX) for different samples. It appears that the dominant elements of the constituent atom are Si, Fe, and O. The detailed quantitative analysis of the atomic element is presented in Table 3. The elemental atomic content: (i) O Oxygen is 57.15 (At%) and 56.21 (At%); (ii) Si is 38.30 (At%) and 39.22 (At%); (iii) Fe is 4.55 (At%) and 4.57 (At%) respectively. The Fe$_3$O$_4$@a-SiO$_2$ and Fe$_3$O$_4$@c-SiO$_2$ samples show the composition of the constituent elements of the same atom. Morphologically, however, the two samples are different. The Fe$_3$O$_4$@a-SiO$_2$ sample tends to form amorphous formations as shown in Figure 3a comparing to the crystal formation for Fe$_3$O$_4$@c-SiO$_2$ as shown in Figure 3b. The Fe$_3$O$_4$@a-SiO$_2$ sample tends to form an amorphous phase whereas for Fe$_3$O$_4$@c-SiO$_2$ samples tend to have a crystal phase. Furthermore, Figure 4 represented SEM images with different magnification for all samples show that the crystalline sample has different shape and size of the amorphous sample. The amorphous sample tends to form irregular shape comparing to the crystalline phase. Interestingly, using TEM experiment as shown in Figure 5, the Fe$_3$O$_4$@a-SiO$_2$ sample has successfully produced core-shell structure. Based on the data analysis, it was found that Fe$_3$O$_4$ particles presented as core and the a-SiO$_2$ particles presented shell.
4. Conclusions

The Fe$_3$O$_4$@a-SiO$_2$ and Fe$_3$O$_4$@c-SiO$_2$ particles have successfully prepared in crystalline and amorphous phases, respectively. The XRD and SEM data analysis showed that the Fe$_3$O$_4$ particles had a particle size below 100 nm and served as core covered by SiO$_2$ particles. The functional groups of the samples exhibited the formation of the SiO$_2$ and Fe$_3$O$_4$ particles.

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