The effect of silica mass ratio on pore structure and magnetic characteristics of Fe₃O₄@SiO₂ core-shell nanoparticles

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Abstract

The fabrication of Fe₃O₄@SiO₂ core-shell was prepared from natural iron sand as Fe₃O₄ core resource and in situ SiO₂-coating method. The Fe₃O₄@SiO₂ was synthesized via an ultrasonic route with various ratios of tetraethyl orthosilicate (TEOS) to evaluate the core-shell's morphological, pore structure, and magnetic properties. XRD and FTIR were used to characterize the prepared Fe₃O₄ and Fe₃O₄@SiO₂. SEM analyzed the effect of the TEOS on the particle size, and TEM observed the morphology of core-shell and shell thickness. The BET data revealed that Fe₃O₄@SiO₂(65) exhibited a larger diameter pore size of 88.17 nm and eight times higher BET surface area (80.23 m²/g) than Fe₃O₄@SiO₂(55) and Fe₃O₄@SiO₂(45) (27.69 nm; 10.5 m²/g). The VSM data indicated that the more TEOS addition on Fe₃O₄@SiO₂ caused the decrease of magnetization value but still gave good magnetic properties from 95.32 emu/g for Fe₃O₄@SiO₂(45) to 17.02 emu/g for Fe₃O₄@SiO₂(65). The study found that the higher content of SiO₂ reduced the agglomeration of the Fe₃O₄ core indicated by no hysteresis loop on the N2 adsorption-desorption curve of Fe₃O₄@SiO₂(65), resulting in core-shell material with better properties in higher specific surface area, average pore size and volume for further application.

Keywords: Fe₃O₄@SiO₂ Core-Shell, Nanoparticles, TEOS, Magnetic Nanoparticle
Introduction

Recently, Fe₃O₄ nanoparticles have provided unique material properties and have a significant role in various applications due to their essential superparamagnetic properties, which show high saturation magnetization but remnant magnetism and low coercivity[1]. For example, the Fe₃O₄ magnetic feature eases the separation of material from the mixed system, such as for the adsorption application[2], catalyst in the reaction[3], and drug delivery system[4]. Indonesia has abundant iron sand that can be used as a Fe₃O₄ source. This iron sand has been reported to produce Fe₃O₄, replacing the Fe₃O₄ synthetics route from expensive FeCl₃ material [5,6]. Many research attempts are related to studying chemical stability, structure, magnetic properties, and synthesis methods to support its Fe₃O₄ magnetic application[7,8]. The problem with using Fe₃O₄ in the direct application is that it is chemically unstable due to the high surface energy of Fe₃O₄ nanoparticles, causing particle agglomeration[9]. One of the most effective methods to cope with the problem is to incorporate/combine amorphous silica material with Fe₃O₄ NPs. Amorphous mesoporous silica material has a non-toxic nature, a highly specific surface, an ordered mesoporous structure, tunable pore size, and volumes with abundant Si-OH bonds on the pore surface[10].

Core-shell nanomaterials with magnetic Fe₃O₄ nanoparticles as the core have been successfully synthesized previously, such as Fe₃O₄@TiO₂[11], Fe₃O₄@Ag[12], and Fe₃O₄@ZnO[13] using hydrothermal techniques; Fe₃O₄@SiO₂ was carried out using the Stöber method[14]. The core-shell nanoparticles showed superparamagnetic behavior at room temperature, and their toxicity was evaluated using hepatocellular carcinoma liver tumor cells. Furthermore, it has potential applications in biomedical and pharmaceutical fields thanks to its excellent properties, such as increased thermal and chemical stability, dispersibility, low toxicity [6,15], pH-responsive drug release, and biocompatibility[15,16]. Core-shell Fe₃O₄@SiO₂ and its modification with Ag doping, Fe₃O₄@SiO₂-Ag is very effective as an anti-bacterial agent (E. Coli and S. Aureus) and an anticancer drug carrier[17], also helpful in designing thermal seeds in magnetic hyperthermia therapy[18], and for environmental applications[15–22].

Modifications of the Fe₃O₄ magnetic surface with SiO₂ enable selective targeting by forming functional groups on the surface through chemical bonds (covalent, ionic, or hydrogen). Due to their hydrophilic properties, this silica coating feature possesses excellent dispersibility and chemical stability in aqueous solutions[23]. However, the fabrication of Fe₃O₄@SiO₂ core-shell is still challenging due to the aggregation of multiple Fe₃O₄ magnets during surface coating. The aggregation of the Fe₃O₄ core
impacts the decrease of the surface area and limits their applications, such as in adsorption and bioimmobilization[24]. Fe$_3$O$_4$@SiO$_2$, as a drug carrier or adsorbent, needs a high surface-to-volume (S/V) ratio, which can lead to more robustness in their application[25,26]. The surface-to-volume ratio of nanomaterial plays a vital role because the high S/V increases the biomolecule or dye molecule density that can be adsorbed in the Fe$_3$O$_4$@SiO$_2$ surface[27]. Therefore, the additional silica ratio and the thickness of the silica shell on the Fe$_3$O$_4$@SiO$_2$ significantly affect the aggregation of Fe$_3$O$_4$, the pore structure, and the characteristics of the core shell[26,28]. The Fe$_3$O$_4$ with uniform and controlled thickness silica coating is still being challenged. Therefore, adjusting silica content is needed to tailor the end properties of the material.

In this study, we report the facile synthesis of Fe$_3$O$_4$@SiO$_2$ with the in-situ method. The Fe$_3$O$_4$ core was prepared from iron sand by the co-precipitation method. The incorporation of SiO$_2$ to Fe$_3$O$_4$ was adjusted according to the silica ratio on the Fe$_3$O$_4$@SiO$_2$. Silica coating parameters are used to tune this silica layer's thickness and minimize the Fe$_3$O$_4$ particle agglomeration. The magnetic incorporation of SiO$_2$ into Fe$_3$O$_4$ is tailored to particle size, pore, surface area, and magnetic properties, which are discussed in this paper. By adjusting the silica ratio on the Fe$_3$O$_4$@SiO$_2$, the thickness of the Fe$_3$O$_4$@SiO$_2$ shell can be controlled and significantly impact the increment of the core shell's surface area and pore diameter. This feature of silica microspheres with magnetic properties is an available prospect for the wide potential application of iron sand as raw material for better uses.

**Materials and methods**

2.1. Materials

All chemicals were in analytical grade and used without any further purification. Iron sand (98% Fe$_3$O$_4$), hydrochloric acid (HCl, Pro Analysis (37%)), ammonium hydroxide (NH$_4$OH), ethanol (C$_2$H$_5$OH, 96%), ammonia (NH$_3$.H$_2$O,25%), tetraethyl orthosilicate (TEOS, 97%) were purchased from Sigma Aldrich, distilled water, and filter paper (Whatman, 60mm).

2.2. Synthesis Method

2.2.1. Synthesis of Fe$_3$O$_4$ Magnetic

The synthesis of Fe$_3$O$_4$ nanoparticles was prepared and extracted from iron sand using the co-precipitation method, as done in the previous research[29]. A mass of 20 g of iron sand was dissolved in
38 mL of HCl (2M) and stirred for 10-12 min at 60 °C. When the color changed to yellow, 24 mL of NH₄OH (6M) was added and stirred until the color became dark black. The solution was separated and washed with distilled water several times. The Fe₃O₄ was dried in an oven at 70 °C for 12 h. The chemical reaction proceeds as follows [16–18]:

\[
\begin{align*}
\text{Fe}_3\text{O}_4(s) + 8\text{HCl}(l) & \rightarrow 2\text{FeCl}_3(l) + \text{FeCl}_2(l) + 4\text{H}_2\text{O}(l) \\
2\text{FeCl}_3(l) + \text{FeCl}_2(l) + 8\text{NH}_4\text{OH} \cdot \text{H}_2\text{O}(l) & \rightarrow \text{Fe}_3\text{O}_4(s) + 8\text{NH}_4\text{Cl}(l) + 5\text{H}_2\text{O}(l)
\end{align*}
\]

2.2.2. Synthesis of Fe₃O₄@SiO₂ Core-Shell

The synthesis process of Fe₃O₄@SiO₂ core-shell was carried out using the in-situ coating method as done according to previous reports with a little change[19]. A mass of 1 g of Fe₃O₄ nanoparticle powder was mixed with 24 mL distilled water and dispersed in ultra-sonification for 30 min. Furthermore, 240 mL of ethanol was added to the mixture while stirring until it was interpreted as evenly mixed. Next, 4 mL of ammonia and a variation of mass ratio TEOS addition (4.5, 5.5, and 6.5 mL) were added. The mass variation of TEOS addition in Fe₃O₄ were subsequently denoted as Fe₃O₄@SiO₂(45), as Fe₃O₄@SiO₂(55), and as Fe₃O₄@SiO₂(65). The mixture was stirred for eight hours at room temperature. The resulting solution was brownish-black and washed with distilled water until it reached a pH of 7. The final stage of the resulting precipitate was dried at 60°C for 24 h; these are the chemical reactions of the prepared SiO₂ shell from TEOS:

\[
\begin{align*}
\text{Si}(\text{OC}_2\text{H}_5)_4(aq) + 4\text{H}_2\text{O}(l) & \rightarrow \text{Si}(\text{OH})_4(s) + 4\text{C}_2\text{H}_5\text{OH}(g) \\
\text{Si}(\text{OH})_4(s) + \text{Si}(\text{OH})_4(s) & \rightarrow (\text{OH})_3\text{Si} - \text{O} - \text{Si}(\text{OH})_3(s) + \text{H}_2\text{O}(l)
\end{align*}
\]

2.2.3. Mechanism of Fe₃O₄@SiO₂ core-shell formation

Figure 1 shows the mechanism for the formation of core-shell Fe₃O₄@SiO₂. Tetraethyl orthosilicate (TEOS) was used as a silica precursor to make a SiO₂ layer on the surface of Fe₃O₄ nanoparticles. This reaction proceeds through hydrolysis and condensation reaction through the ionization of Si(OC₂H₅)₄. Si(OC₂H₅)₄ reacts with H₂O and is converted through ionization to form orthosilicic acid Si(OH)₄, which can be used as a silicon oxide precursor and ethanol gas (C₂H₅OH). The orthosilicic acid formed binds to the OH group on the surface of the Fe₃O₄ nanoparticles, and the condensation reaction is then repeated to form a SiO₂ layer while forming a network structure around the particles. The dense silica coating factors affecting the mesoporous shell formation are ethanol and ammonia concentrations.
The modification of the surface of Fe$_3$O$_4$ nanoparticles can be conducted with appropriate ligands or functional groups. This modification is believed to increase its stability and prevent agglomeration. Silane coupling agents, for example, can be used to modify the surface chemistry of Fe$_3$O$_4$ nanoparticles. The use of ultrasonication or other dispersion techniques during the synthesis process is to break up lumps. However, be careful in increasing the temperature during ultrasonication, as excessive heat can cause further caking. Optimizing the strength and duration of ultrasonication and mechanical stirring during ultrasonication can help distribute the heat generated by ultrasonication and prevent local overheating.

2.3. Characterizations

All materials preparation was characterized by X-ray diffraction (Paan Analytical, Type: Expert Pro) and scanned at a range of 5°-75°. Fourier Transform infrared spectroscopy (FTIR, Shimadzu, Type: IRPrestige) analyzed functional groups at 400 to 4000 cm$^{-1}$ wavenumbers. The material morphological structure and particle size were conducted using scanning electron microscopy (SEM, Zeiss Evo MA 10), and the formation of the core-shell structure was monitored using a transmission electron microscope (TEM) (Hitachi HT7700, USA). The magnetic properties were recorded at room temperature using a vibrating sample magnetometer (VSM; 7404, Lakeshore, USA).

Results and discussion

3.1 Structure Analysis of Fe$_3$O$_4$@SiO$_2$ magnetic

The XRD patterns of Fe$_3$O$_4$, TEOS, and Fe$_3$O$_4$@SiO$_2$ with different amounts of TEOS are shown in Figure 2. In all synthesized Fe$_3$O$_4$@SiO$_2$ core-shell, five major 20 diffraction peaks at 30.2°, 35.5°, 43.1°, 57.1°, and 62.8° observed, which represent (220), (311), (400), (422) and (511) planes of standard Fe$_3$O$_4$ magnetic pattern, respectively[29]. The characteristic of amorphous silica SiO$_2$ was showed in broad diffraction peak at 24°. This peak of silica is weak in all synthesized materials, which might be due to a small signal-to-noise ratio[5]. The obtained Fe$_3$O$_4$@SiO$_2$ XRD patterns showed that the addition of SiO$_2$ did not significantly change the structure of Fe$_3$O$_4$ and revealed that after coating silica, the core still persevered its crystallinity. Furthermore, as the loading amount of SiO$_2$ increased, the intensity peak at 35.5° was decreased, revealing the reduction of Fe$_3$O$_4$ crystallinity. In addition, the peak width at 35° of all synthesized material is broader than that of Fe$_3$O$_4$ magnetic. This is because the Fe$_3$O$_4$ magnetic surface was under stress between the Fe$_3$O$_4$ core and SiO$_2$ shell due to the slight increment of inter-planar distance[10]. The crystallite size of the Fe$_3$O$_4$ cores calculated by the Debye Scherrer equation reveals 1.6 nm while the Fe$_3$O$_4$@SiO$_2$ (45), Fe$_3$O$_4$@SiO$_2$ (55), Fe$_3$O$_4$@SiO$_2$ (65) have 8.47, 14.12, and 22.59 nm, respectively. These results reveal that adding silica content increased the crystallite size of the Fe$_3$O$_4$@SiO$_2$. This examination of XRD results verifies that the Fe$_3$O$_4$@SiO$_2$ are constructed of Fe$_3$O$_4$ and SiO$_2$ (shown in Table 1) [30–32].
3.3. Functional Analysis by FTIR of Fe$_3$O$_4$@SiO$_2$ magnetic

The characterization of the synthesized Fe$_3$O$_4$@SiO$_2$ core-shell with mass ratio variation of SiO$_2$ is obtained through the FTIR spectrum, represented in Figure 3. The Fe$_3$O$_4$ magnetic have adsorption characteristic peaks at 582 and 456 cm$^{-1}$ assigned to the stretching vibration of Fe in the tetrahedral and octahedral region[30], in which these peaks also appear in the magnetic nanoparticles spectrums after TEOS addition. The FTIR spectrum of TEOS showed the adsorption band of Si-O-Si asymmetric vibration, Si-O stretching vibration, and Si-O-Si symmetric at 1130, 960, and 800 cm$^{-1}$, respectively[28,32]. This absorption peak is present in all synthesized Fe$_3$O$_4$@SiO$_2$ core-shell materials, and Si-O-Si asymmetric vibration intensity increases with increasing silica ratio (TEOS) of Fe$_3$O$_4$ magnetic particles. Moreover, the silanol group (Si-OH) on the surface of SiO$_2$ at 1629 cm$^{-1}$[14] is present in all synthesized materials. This confirms that the raw material's functional groups and chemical bondings indicate that the SiO$_2$ (the shell) was successfully incorporated in Fe$_3$O$_4$ (the core).

The remanent magnetization (Mr), field coercivity (Hc), and saturation (Ms) data obtained by the magnetic hysteresis loop are essential in determining the magnetic properties of the material. The coercivity is a magnetic field described as material's resistance to make zero magnetism. This coercivity value determined the nature of paramagnetic. The higher Hc value indicates stronger paramagnetic nature properties[33]. The remanent magnetization is the magnetization residue after removing the external magnetic field. Table 2 compares the magnetic properties of the Fe$_3$O$_4$ and Fe$_3$O$_4$ after TEOS coating. Fe$_3$O$_4$ has the highest Hc value, 0.067 tesla, which exhibited a superparamagnetic nature. The addition of TEOS contributes to lowering the Hc and remanent values along with the larger crystal size obtained by the Debye Scherrer formula from XRD data. A detailed investigation by Li et al. for Fe$_3$O$_4$ NPs envisages a decrease of both remanent magnetization and coercivity with an increase in size even when the saturation magnetization increases[34]. This data revealed that the smaller crystal size tended to have a higher value of Hc and Mr. The coercivity field was further discussed in Figure 4. The coercive field of Fe$_3$O$_4$ was smaller than the others. Fe$_3$O$_4$@SiO$_2$(45) has a coercivity field similar to Fe$_3$O$_4$. After the addition of more TEOS content on the Fe$_3$O$_4$, the coercivity became larger. By designing the Fe$_3$O$_4$@SiO$_2$ core-shell structure, the Fe$_3$O$_4$ core acts as a soft magnetic (weak magnetic anisotropy which easily magnetized and demagnetized), and the SiO$_2$ acts as the shell of a hard magnetic (large magnetic anisotropy)[35]. The Ms value, obtained by applying the law of approach to saturation[36], increases with increasing crystal size for all samples. Meanwhile, Hc and remanent magnetization (Mr) are also affected by crystallite size. The high Hc value may be caused by the strong spin interactions in the highly crystalline Fe$_3$O$_4$ NPs during spin alignment. The crystalline properties of Fe$_3$O$_4$ NPs affect their magnetic properties, especially Hc. This trend is consistent with that found in the previous work[38].

In Figure 5, the results of the measurements of the hysteresis curve for the sample Fe$_3$O$_4$@SiO$_2$ core-shell, prepared by the in-situ method, show a trend of decreasing magnetization value with the
addition of layers of SiO$_2$ particle as a covering for the Fe$_3$O$_4$ particles. The magnetization saturation values of Fe$_3$O$_4$, Fe$_7$O$_{14}$@SiO$_2$ (45, 55, and 65) were 95.32, 80.58, 23.62, and 17.02 emu/g [29][37]. The magnitude of magnetization decreased from approximately 95.32 emu/g to 17.02 emu/g, along with an increase in the ratio mass of TEOS (46, 55, and 65) (see Figure 5a (b-d)), and the shell thicknesses increased from 142 to 161 nm.

3.5. Morphology of Fe$_3$O$_4$@SiO$_2$ magnetic

The morphology of Fe$_3$O$_4$@SiO$_2$ with different Silica ratios was investigated by SEM image. Figure 6 shows the spherical-like morphology of both synthesized Fe$_3$O$_4$@SiO$_2$ materials. The Fe$_3$O$_4$@SiO$_2$ with an addition ratio of 45 of TEOS has a slightly rough surface, whereas the surface of the Fe$_3$O$_4$@SiO$_2$ with an addition ratio of 65 of TEOS appears to be relatively smooth. The TEM images of Fe$_3$O$_4$ and synthesized Fe$_3$O$_4$@SiO$_2$ are presented in Figure 7. The Fe$_3$O$_4$ nanoparticles have spherical shapes and showed an increment of particle size after coating with SiO$_2$. The particle size was estimated at 150 nm and 161 nm for Fe$_3$O$_4$@SiO$_2$(45) and Fe$_3$O$_4$@SiO$_2$(65). Meanwhile, the Fe3O4, before coating, has an estimated particle size of 120 nm. Meanwhile, the average particle size observed from SEM and TEM indicates the size of the Fe$_3$O$_4$ NPs. The size of the Fe$_3$O$_4$ core we obtained exceeds 100 nm because it is probably caused by the Fe$_3$O$_4$ NPs synthesis method we used. As reported, the formation of Fe$_3$O$_4$ follows the nucleation growth mechanism via the oxidation-precipitation method. Nucleation of magnetite particles occurs when the molar ratio of Fe(OH)$_2$/Fe(OH)$_3$ approaches 1:2, a characteristic value of magnetite structure. Then, Fe$_3$O$_4$ nuclei begin to grow. Therefore, the product size highly depends on reaction conditions such as reaction time, molar ratio of FeSO$_4$ and oxidizing agent, and concentration of FeSO$_4$, etc. [21,38]

From the TEM image, it can be seen that the core-shell formation is identified by two different contrasts observed: the dark contrasts of the Fe$_3$O$_4$ core and the light contrast of the SiO$_2$ shell. The layer of SiO$_2$ was estimated to be around 3 nm for Fe$_3$O$_4$@SiO$_2$(45) and 6 nm for Fe$_3$O$_4$@SiO$_2$(65). The existence of SiO$_2$ in Fe$_3$O$_4$ aligns with previous FTIR and XRD results. Furthermore, this SEM and TEM result showed that the additional SiO$_2$ ratio exhibits different layers, surface roughness, and particle size. The more TEOS addition results in a thicker and smoother layer of SiO$_2$ and larger particles of Fe$_3$O$_4$@SiO$_2$ [39,40].

The more TEOS addition results in a thicker and smoother layer of SiO$_2$ and larger particles of Fe$_3$O$_4$@SiO$_2$[9]. TEOS acts as a silica layer maker on the Fe$_3$O$_4$@SiO$_2$. It started from the corporation of the SiO$_2$ layer via Fe-O-Si chemical bonding on the surface Fe$_3$O$_4$. The addition of TEOS subsequently will construct Si-O-Si silica chain polymers that grow layer by layer, corresponding to shell thickness increment of Fe$_3$O$_4$@SiO$_2$. These chemical bonds were identified in previous FTIR data. Adding TEOS to Fe$_3$O$_4$ contributes to the size increment of nanoparticles and the core shell. This finding also aligns with the research result of Prado et al., (2012)[35], which revealed that the higher TEOS/Fe$_3$O$_4$ molar ratio would lead to a thicker silica shell.

The Fe$_3$O$_4$ nanoparticles obtained by co-precipitation due to the large surface-to-volume ratio, high surface energy, and magnetic dipole-dipole attractions between the particles, and magnetic nanostructures
are highly prone to aggregation. Therefore, controlling the core size is necessary by choosing the correct method, solvent, and precursor to obtain the desired core size. To synthesize well-dispersed silica-coated Fe$_3$O$_4$ NPs, the sol–gel method, the Stöber method, and microemulsion are the most common methods for coating the surface of Fe$_3$O$_4$ nanoparticles with silica. Silica coating on the surface of Fe$_3$O$_4$ with various layers cannot completely change the size of the morphology formed.

EDX analysis results obtained for Fe$_3$O$_4$@SiO$_2$-core-shell showed that the elemental composition of Si and Fe with the corresponding mass percentage of 4.0% and 51.0% (Fe$_3$O$_4$@SiO$_2$(45)) then 26.0% and 28.0% (Fe$_3$O$_4$@SiO$_2$(65)), respectively. The elemental mapping (Figure 8) of Fe$_3$O$_4$@SiO$_2$-core-shell morphology shows that Si is more dominant on the surface than Fe with an increase in the ratio mass of TEOS. This indicates the successful preparation of Fe$_3$O$_4$@SiO$_2$-core-shell in the ratio mass of TEOS, as evidenced by other characterizations.

3.6. N$_2$ Adsorption-desorption of Fe$_3$O$_4$@SiO$_2$ magnetic

The type of porous structure of synthesized Fe$_3$O$_4$@SiO$_2$ was further analyzed by the N$_2$ adsorption-desorption experiment in Figure 9 and summarized in Table 3. The hysteresis loop of obtained synthesized material was classified as a type IV pattern for all materials microspheres, which show mesoporous characteristics[40]. The isotherm of Fe$_3$O$_4$ with a lower Si amount (ratio 45) showed a notable hysteresis loop in the relative pressure range of 0.3-0.9, which indicates the mesopores formation due to agglomeration[41]. Furthermore, the agglomeration of Fe$_3$O$_4$@SiO$_2$ with lower Si content caused the smaller specific surface area, average pore size, and volume. It can be seen that the histogram of the Fe$_3$O$_4$@SiO$_2$ composite with Si content between the two other materials has a pattern that is almost similar to 45. The average pore diameter of Fe$_3$O$_4$@SiO$_2$(45), Fe$_3$O$_4$@SiO$_2$(55), and Fe$_3$O$_4$@SiO$_2$(65) were 27.69, 33.04, and 88.17 nm, respectively. In addition, the Fe$_3$O$_4$ with a ratio of 65 of TEOS addition has a BET surface area of 80.23 m$^2$/g, which is eight times higher than the Fe$_3$O$_4$ with a ratio of 45 of TEOS addition (10.5 m$^2$/g). Interestingly, from Figure 9, it was seen that Fe$_3$O$_4$ with a higher Si amount (ratio 65) has no hysteresis loop. This result indicates that more content of the SiO$_2$ layer helps reduce the agglomeration, which releases the void space among particles and reflects in higher specific surface area, average pore size, and volume.

The porosity analysis was done by simulating the adsorption curve using density functional theory (DFT). The obtained porosity curve is shown in Figure 10. Fe$_3$O$_4$@SiO$_2$(45) has a pores size of 27.691 Å (2.7691 nm), Fe$_3$O$_4$@SiO$_2$(55) has a pores size of 33.041 Å (3.3041 nm), and Fe$_3$O$_4$@SiO$_2$(65) is 88.171 Å (8.8171 nm). The results indicated that adding SiO$_2$ to the surface of the Fe$_3$O$_4$ nanoparticles would make the pores more mesoporous.

In the core-shell synthesis, Fe$_3$O$_4$@SiO$_2$ may be linked to Janus nanofluids through the formation of a unique nanoparticle structure that combines the different properties of the core (Fe$_3$O$_4$ nanoparticles) and the shell (SiO$_2$) [42]. The agglomeration process of core-shell particles with TEOS precursor media can be related to nanofluids, and it can be considered whether the core-shell structure influences the agglomeration of these particles and the morphology of the aggregates formed [42,43].
For further studies, the influence of aggregation morphology on thermal conductivity provides a basis for understanding how Janus nanofluid aggregates are structured, which may be influenced by core-shell synthesis. Moreover, the image analysis modeling approach on Janus nanofluids can provide a deep understanding of particle morphology. It is necessary to consider whether this modeling approach can be applied to nanofluids resulting from core-shell synthesis to describe and predict the distribution of particle morphology in more detail [42–45].

Conclusions

This research successfully synthesized the Fe₃O₄@SiO₂ core-shell from natural iron sand using the in-situ SiO₂ coating method. The silica thickness ranging from 3 to 6 nm could be controlled by changing the TEOS mass ratio from 5.5 mL to 6.5 mL. The surface area tended to follow the same pattern as the thickness increased. Increasing the percentage of TEOS resulted in an increase in surface area and a decrease in magnetization of Fe₃O₄@SiO₂. The study found that adding TEOS content (SiO₂) reduced the agglomeration of Fe₃O₄-core. This Fe₃O₄@SiO₂ magnetic material with higher specific surface area, average pore size, volume, and good magnetic properties could make promising materials for further application.

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Abbreviations

SiO₂ : Silicon dioxide (or silica)
Fe₃O₄ : Iron (II) oxide or magnetite
NPs : Nanoparticles
TEOS : Tetraethyl orthosilicate
XRD : X-Ray diffraction
FTIR : Fourier Transform Infra-Red
Mr : Remanent magnetic field
Hc : Coercivity magnetic field
Ms : Saturation magnetic field
VSM : Vibrating sample magnetometer
EDX : Energy Dispersive X-ray
SEM : Scanning Electron Microscope
TEM : Transmission Electron Microscopy
nm : Nanometer
BET : Brunauer-Emmett-Teller
SBET : Specific surface area (of porous material by BET method)
VSM : Vibrating sample magnetometer
\( \text{N}_2 \): Gas of Nitrogen

\( \text{DFT} \): Density functional theory

\( \text{D} \): Crystal size (by Debye Scherrer formula)

\( \beta \): full width at half maximum of peak X-ray diffraction

\( \lambda \): X-ray wavelength (Cu K\text{a})

\( \text{Å} \): Angstrom (1 Å = 10^{-10} meter = 10 nm)

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**Figure 1.** A Schematic illustration of the fabrication of a core-shell structure Fe$_3$O$_4$@SiO$_2$ NPs[10,15].

**Figure 2.** Pattern Diffraction of: (a) SiO$_2$, (b) Fe$_3$O$_4$, and (c-e) Fe$_3$O$_4$@SiO$_2$ core-shell: 45, 55, and 65
Figure 3. The infrared spectra of (a) Fe₃O₄, (b) SiO₂, and (c-d) Fe₃O₄@SiO₂ were synthesized by in-situ method with a ratio of TEOS 45 (c), 55 (d), and 65 (e).
**Figure 4.** The coercivity field of (a) Fe₃O₄ (red line), (b) Fe₃O₄@SiO₂ with TEOS ratio 45 (black line), (c) TEOS ratio 55 (green line), and (d) TEOS ratio 65 (blue line)

![Coercivity field graph](image)

**Figure 5.** The curve of hysteresis of (a) Fe₃O₄ (red line), (b) Fe₃O₄@SiO₂ with TEOS ratio 45 (black line), (c) TEOS ratio 55 (green line), and (d) TEOS ratio 65 (blue line)

![Hysteresis curve](image)

**Figure 6.** SEM Images of Fe₃O₄@SiO₂ core-shells, for TEOS ratio 45 (a) and 65 (b)

![SEM images](image)
Figure 7. TEM images of Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$ (core-shell): Fe$_3$O$_4$ particles (a-b) and SiO$_2$ shell thickness for core-shell with TEOS ratios of 45 (c) and 65 (d).
Figure 8. EDX Mapping of Fe₃O₄@SiO₂ core-shells nanoparticles with TEOS ratio: 45 (a) and 65 (b)

Figure 9. N₂ Adsorption-desorption of Fe₃O₄@SiO₂-core-shells ratio TEOS: (a) 45, (b) 55, and (c) 65

Figure 10. Pore size distribution by DFT method of Fe₃O₄@SiO₂-core-shells ratio TEOS: (a) 45, (b) 55, and (c) 65
Table 1. Pattern X-ray of Fe₃O₄@SiO₂ core-shell nanoparticles

<table>
<thead>
<tr>
<th>Peak (2 theta), samples of Core@Shell (Fe₃O₄@SiO₂)</th>
<th>Crystal Field (hkl)</th>
<th>Average Crystallite Size (Debye Scherrer) (nm)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>45  55  65</td>
<td></td>
<td>D = (0.9λ/β cosθ) hkl (311)</td>
<td></td>
</tr>
<tr>
<td>29.98° 29.07° 30.01°</td>
<td></td>
<td>(220)</td>
<td>[19]</td>
</tr>
<tr>
<td>35.39° 35.34° 35.35°</td>
<td>(311)</td>
<td>8.47 14.12 22.59</td>
<td>[7]</td>
</tr>
<tr>
<td>43.02° 42.99° 43.00°</td>
<td>(400)</td>
<td></td>
<td>[30]</td>
</tr>
<tr>
<td>53.51° 53.44° 53.47°</td>
<td>(422)</td>
<td></td>
<td>[31]</td>
</tr>
<tr>
<td>56.96° 56.89° 56.95°</td>
<td>(511)</td>
<td></td>
<td>[29]</td>
</tr>
<tr>
<td>62.49° 62.46° 62.49°</td>
<td>(440)</td>
<td></td>
<td>[6]</td>
</tr>
</tbody>
</table>

Table 2. Magnetic data of Fe₃O₄@SiO₂ core-shell nanoparticles by VSM

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal Size (nm)</th>
<th>Ms (emu/g)</th>
<th>Hc (Tesla)</th>
<th>Mr (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄</td>
<td>1.6</td>
<td>95.01</td>
<td>0.067</td>
<td>19.86</td>
</tr>
<tr>
<td>Fe₃O₄@SiO₂(45)</td>
<td>8.47</td>
<td>80.14</td>
<td>0.040</td>
<td>18.67</td>
</tr>
<tr>
<td>Fe₃O₄@SiO₂(55)</td>
<td>14.12</td>
<td>23.73</td>
<td>0.014</td>
<td>7.226</td>
</tr>
<tr>
<td>Fe₃O₄@SiO₂(65)</td>
<td>22.59</td>
<td>17.13</td>
<td>0.013</td>
<td>4.27</td>
</tr>
</tbody>
</table>
Table 3. Surface area, pore volume, and pore diameter of Fe$_3$O$_4$@SiO$_2$-core-shell nanoparticles

<table>
<thead>
<tr>
<th>Materials</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>Pore volume (cc/g)</th>
<th>Pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$@SiO$_2$ (45)</td>
<td>10.50</td>
<td>0.02</td>
<td>27.69</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@SiO$_2$ (55)</td>
<td>21.04</td>
<td>0.03</td>
<td>33.04</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@SiO$_2$ (65)</td>
<td>80.23</td>
<td>0.83</td>
<td>88.17</td>
</tr>
</tbody>
</table>

Biographies:

**Munasir Nasir** received his PhD from the Institut Teknologi Sepuluh Nopember (ITS), Surabaya, Indonesia. He is a Professor and Head of Physics Department at Universitas Negeri Surabaya (Unesa), Indonesia. He has numerous publications (more than 50) in international conferences and journals with impact and patents. He is actively involved in studies of natural materials, nanomaterials, and their applications. Recently, He has developed materials for drug delivery systems, graphene-based membrane materials for desalination and filtration of water contaminated with pollutants, ZnO/rGO and TiO$_2$/rGO nanomaterials for photocatalysts, and ZnO as a quantum dot. His research interests include green synthesis of nanomaterials, materials for medicine, and materials for energy.

**Ahmad Taufiq** is a Professor and Head of Physics Department at Universitas Negeri Malang (UM), Indonesia. He is also a Vice President of Materials Research Society of Indonesia (MRS-id) and a Head of Scientific Committee of Indonesian Magnetic Society (IMS). His research interests include synthesis and characterization of nanomaterials for advanced applications. He has hundreds of published articles in reputable international journals with impact and dozens of patents. More than one hundred research grants were funded from the university and several national and international institutions. He also received several prestigious awards and most recently was named National Academic Leader in the Science Sector from the Indonesian Government at the end of 2023.

**Nuhaa Faaizatunnisa** received her B.S. degree in Chemistry from Sebelas Maret University (UNS) Surakarta, Indonesia, in 2019 and received an M.Sc. degree in Chemistry from Institut Teknologi Sepuluh Nopember (ITS) Surabaya, Indonesia in 2022. He is a doctoral candidate (Ph.D.) in Inorganic Chemistry at Sepuluh Nopember Institut Teknologi Sepuluh Nopember (ITS). His research interests focus on Metal-Organic Frameworks (MOFs), inorganic materials, photocatalysis, drug delivery systems, and adsorption.

**Lydia Rohmawati** received B.S. and M.Sc. degrees in Materials Physics from Institut Teknologi Sepuluh Nopember (ITS), Surabaya, Indonesia. She is working as an Assistant Professor at Department of Physics at Universitas Negeri Surabaya (Unesa). Her research interests focus on the fabrication and implementation of nanomaterials in the medical field, waste processing of organic dyes, sensors and materials energy.