One pot and sonically assisted synthesis of Fe₃O₄ and SiO₂@Fe₃O₄

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Abstract. Magnetite (Fe₃O₄) and core-shell SiO₂@Fe₃O₄ nanoparticles were successfully synthesized through a one pot assisted by sonication method. The products were morphologically, physically and chemically characterized using Transmission Electron Microscopy (TEM), N₂ adsorption-desorption, and Fourier Transform Infra-red (FTIR). In this research, concentration of tetraethyl orthosilicate (TEOS), a precursor of SiO₂, was varied by 1, 3 and 5 mmol in order to control the SiO₂ shell thickness. The FTIR measurements showed that the increasing of TEOS concentration was parallel with the increasing of Si-O stretching vibration peak intensity revealing an enlargement of SiO₂ shell thickness. It was proved by morphological study where the addition of 1 mmol of TEOS has approximately 2 nm of shell thickness while by using 5 mmol was ~10 nm of shell thickness. Magnetite nanoparticle has 80.43 m² g⁻¹ of BET surface area but dramatically decreased to 55.74 m² g⁻¹ after incorporating of SiO₂ (TEOS 5 mmol) caused by the presence of CTAB in pore channel.

1. Introduction
Magnetite (Fe₃O₄), in nature, is deposited in rocks and naturally arising material contained 1:2 stoichiometric ratio of Fe²⁺ and Fe³⁺ ions. Generally, magnetite is a crystalline material with bravis crystal structure of face-centered cubic (FCC) close-packing of oxide ions, where Fe²⁺ occupied octahedral site and Fe³⁺ engaged half of octahedral and tetrahedral sites [1]. The synthesis of magnetite nanoparticle was firstly introduced by Massart [2] by a simplest method called co-precipitation. Briefly, the co-precipitation of magnetite nanoparticle involves Fe²⁺ and Fe³⁺ ions with molar ratio by 1:2 catalysed by alkaline (OH⁻). The formation of Fe₃O₄ is relatively fast if the solution reached pH between 8 and 14. This method, however, have a minor obstacles, i.e. difficult to control the size of Fe₃O₄ nanoparticles and produce an aggregate of particles [3]. To control the particle size of magnetite nanoparticle, researchers usually introduce coating or template agent. For example, Petcharoen and Sirivat [4] synthesized magnetite nanoparticle through co-precipitation method and added oleic acid and hexanoic acid resulting a good particle size distribution. Si et al. [5] controlled the particle size of magnetite nanoparticle by incorporating of polyelectrolyte. Sun et al. [6] synthesized of biocompatible Fe₃O₄ nanoparticle in addition of polyethylene glycol (PEG-6000) and oleic acid, a class of surfactant,
to control the dispersion and size of magnetite nanoparticle. In this study, we used cationic surfactant, hexadecyl trimethyl ammonium bromide (also known as cetyl trimethyl ammonium bromide, CTAB) to synthesize magnetite nanoparticle. This surfactant is often used as pore structure directing agent in synthesis of mesoporous silica nanoparticle.

In order to protect the magnetite nanoparticle from instability in acid environment, the formation of SiO$_2$ shell is introduced. The SiO$_2$ shell was often post-fabricated after obtaining Fe$_3$O$_4$ nanoparticle [7,8]. However, there are limited article reporting a one pot synthesis of core-shell SiO$_2$@Fe$_3$O$_4$ nanoparticle. Thus, in this paper, we reported a facile synthesis of core-shell SiO$_2$@Fe$_3$O$_4$ through one pot method.

2. Experimental

2.1. Materials
Iron(II) sulphate heptahydrate (FeSO$_4$.7H$_2$O), iron(III) chloride hexahydrate (FeCl$_3$.6H$_2$O), hexadecyltrimethylammonium bromide (CTAB), ethanol, were purchased from Merck. Tetraethyl orthosilicate (TEOS) and ammonium hydroxide (NH$_4$OH, 25-28%) were commercially available in Sigma-Aldrich. Ultrapure distilled water was obtained from MIPA Terpadu laboratory. All chemicals were used as received without further purification.

2.2. Synthesis of Magnetite Nanoparticles (MNPs)
Iron(III) chloride hexahydrate (2 mmol) and Iron (II) sulphate heptahydrate (1 mmol) was dissolved in 50 mL of distilled water with and without CTAB. After completely dissolved, ammonium hydroxide (32%, 5 mL) was wisely dropped to the solution. The dark brown precipitate was observed after first drop of ammonium hydroxide addition and turned to be black precipitate after several minutes. The precipitate was stirred for 1 h for equilibrium, separated using external magnetic field, washed several times using distilled water and ethanol until reaching neutral pH, and dried using freeze drying machine (freeze for 1 h at -49 °C, freeze drying 12 h). The obtained MNPs with and without CTAB (with CTAB noted as MNPs+CTAB) were characterized using FTIR, TEM and N$_2$ adsorption desorption.

2.3. Synthesis of SiO$_2$@Fe$_3$O$_4$ Nanoparticle
Synthesis of SiO$_2$@Fe$_3$O$_4$ nanoparticles were conducted in one pot approached assisted by sonication techniques. After obtaining MNPs by following the previous procedure in the presence of CTAB, amount of TEOS (1, 3, and 5 mmol) was added and sonicated for 30 minutes. Afterward, the mixture was stirred for 1 h, separated by external magnetic field, washed with distilled water and ethanol, and dried using freeze drying machine. The final products marked as 1SiO$_2$@Fe$_3$O$_4$, 3SiO$_2$@Fe$_3$O$_4$ and 5SiO$_2$@Fe$_3$O$_4$ were characterized using FTIR, TEM, and N$_2$ adsorption-desorption.

3. Result and Discussion

3.1. Synthesis of Magnetite and SiO$_2$@Fe$_3$O$_4$ Nanoparticles
Precipitation of Fe$^{3+}$:Fe$^{2+}$ 2:1 in basic condition (pH ~11) is a conventional method to synthesize MNPs. This method is relatively easy to perform and yielding high amount of precipitate of MNPs. Briefly, MNPs is constructed by mixing Fe$^{2+}$ ion and Fe$^{3+}$ ion with 1:2 molar ratio catalyzed by base. In this research, we used FeSO$_4$.7H$_2$O and FeCl$_3$.6H$_2$O as Fe$^{2+}$ and Fe$^{3+}$ ions sources, respectively. According to Petcharoen and Sirivat [4], Fe$^{2+}$ ion forms Fe(OH)$_2$ after addition of base (OH$^-$) with molar ratio 2:1 to Fe$^{2+}$ ion. However, Fe$^{3+}$ ion forms Fe(OH)$_3$ in basic solution (3 mol of OH$^-$). Magnetite (Fe$_3$O$_4$) is a result of Fe(OH)$_2$ and 2Fe(OH)$_3$ reaction. The base (ammonium hydroxide) plays important role in the formation of MNPs, especially in the size of MNPs. Sun et al. [6] reported that the addition of ammonium hydroxide until reaching pH ~11 produced MNPs with average particle size below 10 nm, but it turn to bigger than by increasing or decreasing the pH value (~ 10 nm at pH 10 or 12, but >20 nm at pH 9 or 13). The size of MNPs influences the magnetic properties where superparamagnetic is obtained if the size of MNPs below 20 nm, but the size 20-100 nm is categorized
as stable single-domain ferrimagnetic [1]. In our investigation, we adjusted the pH of solution around 10 concerning the green chemistry principle, use as small amount chemical as possible.

Synthesis of SiO$_2$@Fe$_3$O$_4$ was performed by directly adding TEOS as silica precursor into a same pot of MNPs with the presence of CTAB. The concentration of TEOS was varied in order to evaluate the shell thickness of SiO$_2$ toward Fe$_3$O$_4$ as core. The role of CTAB is to direct the pore structure of SiO$_2$ shell by forming a micelle structure in proper concentration. In our study, the concentration of CTAB was slightly more than its critical micelle concentration. According to Figure 1, the TEOS as SiO$_2$ precursor, covered the Fe$_3$O$_4$. The proposed mechanism is as follow: TEOS is adsorbed in the surface of Fe$_3$O$_4$ then hydrolyzed to form silanol group, and finally polymerized to form SiO$_2$ while the pore structure directed by CTAB.

![Figure 1. Schematic illustration of synthesis of MNPs and SiO$_2$@Fe$_3$O$_4$](image)

3.2. Functional Group Analysis

Functional group analysis is one of the simple techniques to chemically characterize the materials in term of their functional group using FTIR spectroscopy. Figure 2 shows the FTIR spectrums of MNPs, 1SiO$_2$@Fe$_3$O$_4$, 3SiO$_2$@Fe$_3$O$_4$, and 5SiO$_2$@Fe$_3$O$_4$. Briefly, the MNPs have characteristic peaks around 3400 cm$^{-1}$ and 570 cm$^{-1}$ assigned as stretching vibration of O-H and Fe-O, respectively. Coating of Fe$_3$O$_4$ by SiO$_2$ shell was evaluated by FTIR showing an increasing of Si-O absorbance band at around 1052 cm$^{-1}$ following an increasing of TEOS concentration. This indicates that the shell thickness of SiO$_2$ becomes thicker.

![Figure 2. FTIR spectrum of (a) MNPs, (b) 1SiO$_2$@Fe$_3$O$_4$, (c) 3SiO$_2$@Fe$_3$O$_4$ and (d) 5SiO$_2$@Fe$_3$O$_4$](image)
3.3. Morphological Analysis
The morphology of MNPs was observed by TEM measurement. Figure 3 reveals the TEM pictures of MNP and MNP in the presence of CTAB. MNP have irregular shapes and tend to sticking together to form agglomerate. However, after incorporating CTAB, the particles of MNP was dispersed but still in irregular form. The role of CTAB in the formation of MNP is to prevent agglomeration through coating the surface of MNP thus they are not attached each other.

![Figure 3. TEM pictures of (a) MNPs and (b) MNPs+CTAB](image)

Figure 4 displays TEM images of SiO$_2$@Fe$_3$O$_4$ nanoparticles. It was mentioned before that the addition of high concentration of TEOS as SiO$_2$ precursor caused increasing of SiO$_2$ shell thickness. Figure 4a reveals the TEM image of 1SiO$_2$@Fe$_3$O$_4$ (1 mmol TEOS) having very thin SiO$_2$ shell approximately ~2 nm. However, by incorporating high concentration of TEOS (5 mmol), the SiO$_2$ shell thickness increased to around 10 nm as seen in Figure 4b. The SiO$_2$ shell in both 1SiO$_2$@Fe$_3$O$_4$ and 5SiO$_2$@Fe$_3$O$_4$ not covered a single particle of MNP but group particles of MNP. This is due to the MNP tend to stick together preventing the SiO$_2$ shell covering a single nanoparticle.

![Figure 4. TEM pictures of (a) 1SiO$_2$@Fe$_3$O$_4$ and (b) 5SiO$_2$@Fe$_3$O$_4$](image)

3.4. $N_2$ Adsorption-Desorption
The surface area of MNP and SiO$_2$@Fe$_3$O$_4$ was evaluated using $N_2$ adsorption-desorption. Figure 5 tells hysteresis loop of both MNP and SiO$_2$@Fe$_3$O$_4$. According to IUPAC classification [9], the porous structure type of both was type IV, a class of mesoporous having a pore diameter between 2-50 nm.
The pore size distribution was calculated using Barrett-Joyner-Halenda (BJH) method [10], and found that the average pore size of MNP was 8.34 nm while 5SiO$_2$@Fe$_3$O$_4$ was 1.69 nm. The decreasing of pore size of MNP after covering by SiO$_2$ shell due to there are still CTAB remaining in the pore channel proved by the FTIR data (the presence of C-H stretching absorbance band). The blocking of pore channel by CTAB was not only decrease the average pore size but also decrease the surface area of the nanoparticle calculated by Brunauer-Emment- Teller (BET) method. The MNP has 80.43 m$^2$ g$^{-1}$ of surface area while 5SiO$_2$@Fe$_3$O$_4$ was 55.74 m$^2$ g$^{-1}$.

The decreasing of surface area of 5SiO$_2$@Fe$_3$O$_4$, in fact, is due to the presence of CTAB in pore system of SiO$_2$ pore channels. In this research, we also measured the N$_2$ adsorption-desorption of Fe$_3$O$_4$ with the presence of CTAB and found that the BET surface area is 43.68 m$^2$ g$^{-1}$. Comparing to the Fe$_3$O$_4$ with the presence of CTAB, the 5SiO$_2$@Fe$_3$O$_4$ has higher BET surface area by 27.61%.

![Figure 5](image.png)

**Figure 5.** Hysteresis loop of N$_2$ adsorption-desorption of MNPs and 5SiO$_2$@Fe$_3$O$_4$

4. Conclusion
The MNP and SiO$_2$@Fe$_3$O$_4$ were successfully synthesized through one pot assisted by sonication treatment. Functional group analysis revealed that the increasing of TEOS concentration induced the increasing of Si-O intensity showing an increasing of SiO$_2$ shell thickness. It was supported by TEM measurement, where 1SiO$_2$@Fe$_3$O$_4$ has around 2 nm of SiO$_2$ thickness while 5SiO$_2$@Fe$_3$O$_4$ was 10 nm of SiO$_2$ thickness. The MNP has 8.34 nm of average pore size and 80.43 m$^2$ g$^{-1}$ of surface area. However, after covering by SiO$_2$, the pore size and surface area decreased.

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