SYNTHESIS AND CHARACTERIZATION OF Fe₃O₄@SiO₂ SUB-NANO CORE/ SHELL WITH SiO₂ DERIVED FROM RICE HUSK ASH

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Abstract - This study aims to synthesize and characterize Fe₃O₄@SiO₂ sub-nanoparticles (SNPs) with high saturation magnetization (SM). The research process was conducted in simple and environmentally friendly conditions. The results of ultraviolet-visible (UV-Vis) spectroscopy and X-ray diffraction (XRD) analysis presented that the Fe₃O₄@SiO₂ SNPs were well formed and the phase change of Fe₃O₄ NPs did not happen in Fe₃O₄@SiO₂ SNPs. Transmission electron microscope (TEM) analysis showed that the Fe₃O₄@SiO₂ SNPs are in a fairly spherical shape with a core/shell structure and a diameter in a range of 100 nm to 500 nm. Fourier transform infrared spectroscopy (FT-IR) spectra of Fe₃O₄@SiO₂ SNPs presented some absorption peaks indicating the existence of Si-O-Si, O-Si-O, Fe-O and Fe-O-Si. The SM of Fe₃O₄ particles and Fe₃O₄@SiO₂ SNPs determined via vibrating sample magnetometer (VSM) were 50.9 emu.g⁻¹ and 19.5 emu.g⁻¹, respectively. All the above results provide clear evidence that the Fe₃O₄ particles were coated by SiO₂ to form sub-nanocore/shell with great SM.

Key words - Fe₃O₄@SiO₂; core-shell structure; saturation magnetization; rice husk ash

1. Introduction

Nowadays, Fe₃O₄ nano particles (NPs) have attracted much research interest for application in biomedical fields which consist of targeted drug delivery and immunoassays [1-3], carrier for enzyme immobilization for different uses [4-6]. Fe₃O₄ NPs with chemically stable, biocompatible and highly dispersible in various pH liquid media are mostly required for biomedical applications [7-9]. Methods for preparing magnetic nanoparticles including solid state reaction [10], sol–gel [11], co-precipitation [12], hydrothermal processes [13], and ultrasonic method [14] have been reported widely in literature. However, the bare Fe₃O₄ NPs are highly sensitive to acidic and oxidative conditions; thus, coating of Fe₃O₄ NPs with SiO₂ will also avoid the agglomeration and protect them from dissolution in acidic solution.

Polymer [15], noble metals [16] and silica [17, 18] have been discovered in recent years for use as the coating materials. Among those materials, silica is considered as one of the most promising candidates because it not only protects Fe₃O₄ NPs from oxidation and agglomeration, but also can be compatible with various chemicals and molecules for bio-conjugations due to its unique surface chemistry [19]. The silica shell in the Stöber method [20] is formed through the hydrolysis and condensation of silane precursor, namely tetraethyl orthosilicate (TEOs). The formation of large aggregates and polydispersed products is inevitable due to the high and uncontainable hydrolysis rate of TEOs and the quite low critical concentration for homogeneous nucleation of silica [21]. Although the above method is normally used for silica coating, it involves alcohol–water–ammonia as the media and TEOs as the silane monomers, resulting in a complex and expensive coating process. Silica that may be produced by treating rice husk ash (RHA) with sodium hydroxide and chloric acid has been repord for preparation of the shell coated Fe₃O₄ NPs. RHA is a solid waste of agricultural products and can be potentially used as raw material for preparation of new silica-based materials due to high content of silica (80-90%) [22]. In this work, synthesis of Fe₃O₄@SiO₂ sub-nanoparticles (SNPs) with SiO₂ from RHA is reported in a non-alcohol solution and without any expensive precursors and organic solvents.

2. Experiment

2.1. Materials

Ferric chloride hexahydrate (FeCl₃.6H₂O), sodium hydroxide (NaOH), chloric acid (HCl), and ammonium hydroxide (NH₄OH) are reagent-grade and purchased from Xilong Chemicals. Sodium borohydride (NaBH₄) and poly vinyl pyrrolidone (PVP) were obtained from Sigma-Aldrich. All chemicals were used without further purification. For the coating experiment, SiO₂ extracted from RHA purchased at Can Tho city, Vietnam was used.

2.2. Synthesis

2.2.1. SiO₂ particles preparation

The SiO₂ particles were synthesized by chemical reduction technique [23]. The initial step is extraction of SiO₂ from RHA as Na₂SiO₃ using aqueous NaOH. Ten gram of RHA was first stirred with 100 mL of NaOH 3 M at 200°C for 2 h. A yellow viscous solution was obtained after filtration of the reacted slurry. The second step of the process is SiO₂ precipitation. The SiO₂ particles were precipitated from Na₂SiO₃ solution by acidification using HCl 2.5 M. The addition of the acid was done very slowly till pH of solution reached 6.0. The white SiO₂ precipitates were obtained. This SiO₂ was subjected to a successive washing with distilled water. Finally, the wet precipitates were dried at 60°C in an oven for 24 h.

2.2.2. Fe₃O₄@SiO₂ SNPs synthesis

Firstly, 0.054 g FeCl₃.6H₂O was dissolved in 50 mL of PVP 1% with stirring, and then 50 mL of NaBH₄ 0.5 M was added to the obtained solution. In the meantime, temperature was increased to 80°C for 15 min. The color of solution changed from bright to dark bright after that. In sequence, 0.02 g of SiO₂ was added to the obtained solution and pH was maintained during the synthesis, around 12.0 by adding NH₄OH 25%.
The Fe₃O₄@SiO₂ NPs were synthesized for 2h at the above temperature, sequently cooled down to room temperature and then given multiple washing with distilled water and absolute ethanol. The product was dried in vacuum condition of 50°C and 0.5 atm for 6h.

2.2.3. Synthesized material characterization

The as-synthesized materials were subsequently characterized by UV-Vis spectroscopy measured by UV-1800 Shimadzu. The size and morphologic analyses of Fe₃O₄ NPs and Fe₃O₄@SiO₂ NPs were obtained using an Instrument Jem 1400 transmission electron microscope (TEM). The crystalline structures of Fe₃O₄ NPs and Fe₃O₄@SiO₂ NPs were investigated by XRD measured by a D8-Advance using Cu-Kα radiation (λ=0.15405 nm). The Nicolet 6700 Fourier transform infrared (FT-IR) spectroscopy were employed to analyze the functional groups, as well as the interaction between SiO₂ and Fe₃O₄ NPs. Magnetic properties of the Fe₃O₄ NPs and Fe₃O₄@SiO₂ NPs were studied by using the vibrating sample magnetometer (VSM), quantum design 14 T PPMS.

3. Results and discussion

3.1. Preparation of Fe₃O₄@SiO₂ SNPs

The process for synthesizing Fe₃O₄@SiO₂ SNPs with SiO₂ derived from RHA is shown in Figure 1. The PVP-grafted Fe₃O₄ NPs were synthesized by web chemical reduction of FeCl₃ and reducting agent NaBH₄. Poly vinyl pyrrolidone molecules attached to the surface of Fe₃O₄ NPs prevented random agglomeration of particles and facilitated the cluster formation. The PVP-grafted Fe₃O₄ NPs prepared via this method has a number of hydroxyl groups on the surface. The silica shell coated Fe₃O₄ NPs was achieved by the reaction between silicon element and the hydroxyl groups on the surface of magnetite.

3.2. Ultra Violet – Visible

The UV-Vis absorption spectra of different samples in water are illustrated in Figure 2. The absorption spectra of SiO₂ showed no significant peaks. No obvious peaks appeared in the spectra of Fe₃O₄ NPs and SiO₂. However, a board featureless peak can be observed at 380 nm in the spectrum of Fe₃O₄@SiO₂ SNPs. The broad peak indicated the core-shell structure of Fe₃O₄@SiO₂ SNPs [24, 25], and this peak may come from the changes of band gap caused by the quantum size effect and surface effect of macrostructure, indicating that SiO₂-coated Fe₃O₄ NPs were successfully synthesized.

Figure 2. Preparation of silica coated magnetic nanoparticles

Figure 3a presented a typical yellow solution of Fe(III). As soon as the reducing agent (NaBH₄) was added to the solution, a black precipitate was formed (Figure 3b). A similar phenomenon was also observed in the study of Basavegowda, N. et al. [26]. However, the color of the solution was slightly changed from a dark black to a light black (Figure 3c) when SiO₂ coated on the surface of the Fe₃O₄ core. This color change is caused by an increase in the particle size due to coating SiO₂ around the Fe₃O₄ NPs.

3.3. X-ray powder diffraction

In terms of nano-material synthesis, phase identification and crystalline structures of NPs is one of key uses of XRD. The XRD patterns of SiO₂, Fe₃O₄ and
Fe₂O₃@SiO₂ are shown in Figure 4. As shown in Figure 4a, an amorphous peak of precipitated SiO₂ with the equivalent Bragg angle at 2θ = 22° – 23° was recorded [27, 28]. In the meantime, the crystallinity and structures of Fe₃O₄ NPs and Fe₂O₃@SiO₂ SNPs were determined via their XRD patterns in Figure 4b. The main peaks at 2θ = 30.3°; 35.7°; 43.4°; 53.8°; 57.3°; 62.9° refer to (200); (311); (400); (422); (511); (440) plane of cubic inverse spinel Fe₃O₄ NPs [19, 29], respectively. The lattice parameter is in good agreement to the standard data (JCPDS No. 00-001-1111). No other significant peaks of FeOOH, Fe₂O₃ can be observed in the XRD pattern of Fe₂O₃@SiO₂ SNPs.

Additionally, the XRD results of the coated magnetite material reveal comparatively broad diffraction peak at 2θ = 22° – 23° and lower peak intensity in comparison to peak intensity of non-coating one, which proves SiO₂ coating on surface of the magnetite material. Similar result was found in the study of Nuryono et al. (2014) when the crystallite was coated by silica from RHA [30]. Thus, XRD further confirmed the formation of Fe₂O₃@SiO₂ SNPs. This also revealed that the phase change of Fe₃O₄ NPs did not take place in Fe₂O₃@SiO₂ SNPs.

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D = \frac{k \cdot \lambda}{\beta \cdot \cos(\theta)} \text{ (Å)}
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Figure 4. XRD patterns of (a) SiO₂ and (b) Fe₂O₃ NPs and Fe₂O₃@SiO₂ NPs

The particles’ size was calculated from the XRD data using Scherrer’s equation, where D is particles’ size, k is the grain shape factor taken as unity contemplating that the particles are spherical in shape, \( \lambda \) is the incident X-ray wavelength of Cu-Kα radiation and \( \theta \) is the Bragg’s angle, \( \beta \) is the broadening of diffraction line measured at half maximum intensity (radians).

Different Bragg’s angles of Fe₂O₃@SiO₂ SNPs had been employed to calculate crystallite size, and the result is presented in Table 1. With six Bragg’s angle used to calculate crystallite size, the obtained crystallite size varied from 16.4 nm to 38.3 nm, and the average crystallite size was determined at 26.04 nm.

**Table 1. X-ray diffraction measurements of Fe₂O₃@SiO₂ NPs for evaluating average crystallite size**

| Peak | 2θ (deg) | hkl | FWHM (radians) | D (nm) |
|------|----------|-----|----------------|--------|
| 1    | 30.3     | (200) | 0.00462       | 31.1   |
| 2    | 35.7     | (311) | 0.00614       | 23.7   |
| 3    | 43.4     | (400) | 0.00567       | 26.3   |
| 4    | 53.8     | (422) | 0.00406       | 38.3   |
| 5    | 57.3     | (511) | 0.00770       | 20.5   |
| 6    | 62.9     | (440) | 0.00993       | 16.4   |

3.4. Fourier transform infrared

Fourier transform infrared analysis was proved to be useful to characteristic of Fe₂O₃@SiO₂ NPs. Pure Fe₂O₃ NPs and Fe₂O₃@SiO₂ SNPs were analyzed by FT-IR and their IR spectra were compared and presented in Figure 5. Typical bondings of these two materials were also summarized and shown in Table 2. The characteristic vibration of Fe-O at 570cm⁻¹ and 571cm⁻¹ were respectively observed at IR spectrum of Fe₂O₃ NPs and Fe₂O₃@SiO₂ SNPs. It proves that the Fe₂O₃@SiO₂ SNPs contained Fe₂O₃ NPs [29]. However, the vibration of Si-O-Si or O-Si-O can be only observed in IR spectrum of Fe₂O₃@SiO₂ NPs. In fact, the absorption band with high-intensity at 1075.4 cm⁻¹ is due to the asymmetric stretching bonds of Si-O-Si. The band at 450 cm⁻¹ is consistent with Si-O-Si or O-Si-O [31]. These above results confirm that Fe₂O₃ NPs were coated by SiO₂ to form Fe₂O₃@SiO₂ SNPs. Besides those characteristic vibration, some other vibrations such as O-H bending vibration, O-H stretching vibration appeared at 1654.9 cm⁻¹, 3382.6 cm⁻¹ and 1643.9 cm⁻¹, 3404.3 cm⁻¹ in both IR spectra of Fe₂O₃ NPs and Fe₂O₃@SiO₂ SNPs respectively [31, 32].

Figure 5. FT-IR spectra of (a) Fe₂O₃ NPs and (b) Fe₂O₃@SiO₂ NPs

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when SiO2 was coated on Fe3O4 nanoparticles through sodium silicate hydrolyzing under acid condition [38]. This again confirms that the outer part of the core-shell structure decreases the Ms. In other words, the thinner the outer part thickness is, the higher the Ms is. In terms of green chemistry, the Fe3O4@SiO2 SNPs with well-defined core-shell structure and high Ms in this study were obtained without adding any TEOs.

3.5. Transmission electron microscope

TEM analysis was employed to determine surface morphology, size and dispersion of the as-prepared Fe3O4@SiO2 SNPs. It also helps to illustrate the core-shell structure of a material. Figure 6 shows the TEM images of the as-synthesized Fe3O4@SiO2 SNPs at various resolutions. The result indicates that the as-prepared Fe3O4@SiO2 SNPs are almost spherical in shape. The diameter of the particles mainly ranged from 100 nm to 500 nm, which is similar to the studies of Subhan et al. (2019) and Rahman et al. (2015), although the synthesis of core-shell Fe3O4@SiO2 SNPs was not performed by the Stober method [33, 34]. The Fe3O4@SiO2 SNPs in this investigation formed a well-defined core-shell structure with dark contrast of the crystalline nature of Fe3O4 and light contrast of SiO2. This well-defined core-shell structure was proved to be highly defensive for avoiding the corrosion, keeping a stable dispersion and making the magnetic core stable.

3.6. Vibrating sample magnetometer

The investigation of the magnetic property was conducted through the analysis of VSM. Figure 7 revealed that no hysteresis in the magnetization curves can be observed. The remnant magnetization and coercivity field cannot be found from these curves as well. It confirms that Fe3O4@SiO2 core/shell SNPs are super-paramagnetic. Both curves demonstrated super-paramagnetic property with a saturation magnetization (Ms) of 50.9 emu.g
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for Fe3O4 and 19.5 emu.g
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for Fe3O4@SiO2 NPs. As Fe3O4@SiO2 SNPs were synthesized, SiO2 shells would shield the magnetism of Fe3O4 NPs that led to a decrease in Ms of Fe3O4@SiO2 SNPs [35, 36]. In the study of Gao et al. (2011), the Ms of Fe3O4@SiO2 SNPs changed from 12.7 to 6.3, 4.3, 3.1 and 2.4 emu.g
1
with variation of TEOs adding from 1 to 2, 3, 5 and 8 mL [37]. Similarly, the study of Shengxiao et al. (2013) showed that the Ms of Fe3O4 and Fe3O4@SiO2 SNPs changed from 55.05 emu.g
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to 25.45 when SiO2 was coated on Fe3O4 nanoparticles through sodium silicate hydrolyzing under acid condition [38]. This again confirms that the outer part of the core-shell structure decreases the Ms. In other words, the thinner the outer part thickness is, the higher the Ms is. In terms of green chemistry, the Fe3O4@SiO2 SNPs with well-defined core-shell structure and high Ms in this study were obtained without adding any TEOs.

4. Conclusions

The Fe3O4@SiO2 SNPs with a core-shell structure in this study were well prepared via a simple, efficient and inexpensive process. The supporting agent – SiO2 extracted from RHA was to work in forming the shell of Fe3O4@SiO2 SNPs. The analyses of TEM, FTIR and XRD showed that the obtained NPs are in a fairly spherical shape and its size is about 100-500 nm. The well-defined core-shell structure of Fe3O4@SiO2 SNPs was successfully synthesized without any phase change of Fe3O4 NPs. The Fe3O4@SiO2 SNPs presented super-paramagnetic property with high saturation magnetization of 19.5 emu.g
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. These core-shell Fe3O4@SiO2 SNPs are highly promising for much needed bio-conjugation applications.
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