Facile and Economic Method for the Preparation of Core-Shell Magnetic Mesoporous Silica

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ABSTRACT: In this work core-shell structure $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{meso-SiO}_2$ microsphere has been successfully prepared. An inorganic magnetic core has been coated with multi-shell structure, dense nonporous silica as an inner layer and mesoporous silica as an outer layer. The dense silica shell can enhance the stability and minimize the negative effect of acidic condition on the inner core and the porous outer shell can provide high surface area and enhance the loading of a functionalized group. Cetyltrimethylammonium bromide (CTAB) has been used as a pore-forming agent and a modified methodology was adopted to improve the extraction condition of this kind of surfactant. The as-prepared microspheres were characterized by Field Emission Scanning Electron Microscope (FESEM), X-Ray Diffraction (XRD), Fourier Transform InfraRed (FT-IR) spectroscopy, Vibration Sample Magnetometer (VSM), $N_2$ adsorption-desorption, and Particle Size Analyzer (PSA). The resulted materials possessing uniform core-shell structure, and well preserved structural stability. Additionally, they can be collected readily by using an external magnetic field. The prepared material has considerable potential applications in various fields including catalysis, drug delivery, and water treatment.

KEYWORDS: Magnetic $\text{Fe}_3\text{O}_4$; Core-shell structure; Mesoporous silica; Nanoparticles; Solvent extraction.

INTRODUCTION

Core-shell structure materials have recently received much attention due to their great potential applications in catalysis, drug/DNA/gene delivery, water treatment, and so on [1-3]. As a main member of the core-shell family, magnetic nanospheres consisting of a magnetic core and silica shell have been developed for two important reasons. The magnetic character makes iron oxide nanoparticles removable and recyclable by the magnetic field easily. Meanwhile, the coated silica layer can not only prevent the aggregation of a magnetic core, also protect it against oxidization condition. Also, mesoporous silica material has several appealing features, such as

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stable structure, high surface area, low toxicity, controllable pore diameters, and easily incorporated bonding groups which help to improve the performance of this material in different applications [4-7]. Wang et al. prepared a novel amino-functionalized magnetic nanomaterial with a core-shell structure to remove heavy metal ions from aqueous media. The structural, surface and magnetic characteristics of the adsorbent were investigated in detail. Due to the complexation of the metal ions by surface amino groups, this adsorbent exhibited high adsorption affinity for aqueous Cu (II), Pb (II), and Cd (II) ions. The adsorbent could be recovered readily from aqueous solution by magnetic separation and regenerated easily by acid treatment. The obtained mesoporous nanoparticles with magnetic and luminescent features. The obtained magnetic–luminescent composite nanoparticles are characterized by different methodologies to confirm the core-shell-shell structure [9]. Yang et al. have synthesized Fe₃O₄ microspheres encapsulated with nonporous silica and a further layer of mesoporous silica. The surface of the outer silica shell was also functionalized by the deposition of YVO₄: Eu³⁺ phosphors. The material was used as a drug carrier to investigate the storage and release properties using ibuprofen (IBU) as a model drug by the surface modification [10]. Yaung et al. developed a novel multifunctional magnetic mesoporous silica via a novel step sol-gel method. This adsorbent had a large pore size and has shown high adsorption capacity for heavy metal ions such as Cu (II), Pb (II), and Cd (II). After adsorption process, the material has been separated from the solution by the magnet and regenerated by acid treatment. The adsorption capacity of the adsorbent remained almost unchanged after 4 cycles [11].

The core-shell magnetic-mesoporous silica can be prepared by different methodologies [12]. In this paper, it is aimed to adopt the effective, economic and facile method to prepare the mentioned structure. First, the nanoparticle is synthesized through the co-precipitation method and transferred to an ethanol/ammonia mixture. Then silica shell is formed on the surface of magnetic nanoparticle through hydrolysis and condensation of tetraethylorthosilicate (TEOS). Uniform mesoporous silica shell is also coated on the obtained structure through a surfactant-templating agent such as cetyltrimethylammonium bromide (CTAB) [13]. To achieve a mesoporous structure, the surfactant needs to be removed effectively. There are several strategies to remove this template including calcination, supercritical CO₂ extraction and solvent extraction [14, 15]. Each methodology follows specific advantages and disadvantages, however, the solvent extraction can be selected as one of the most common strategies due to several reasons. Firstly, compared to the calcination at a high temperature, solvent extraction can guarantee the stability of the structure during the process. Secondly, in comparison to the supercritical CO₂ method which needs to be performed at high pressure or temperature, extraction by solvent can be performed in a safe condition. However, it should be mentioned that the solvent extraction needs to be carefully developed to avoid the degradation of the material and subsequently ensure long-term reusability [16]. For example, if the extraction takes too much time or the temperature is failed to be controlled during the extraction process, the physical and chemical properties of materials may be changed or deteriorated.

Acetone is highly recommended as an effective solvent in this respect since it is more economical, has low toxicity and is widely available, however, it poses some problems. In one hand, the significant amount of acetone is required to extract surfactant from the structure to reach mesoporous material. On the other hand, it takes too much time to complete the extraction process, (at least 48h) [17]. Minimization and selection of the solvent can be considered as an important sustainability aspect which has been taken into account by some scientists. For instance, the optimal design of solvent blends for environmental impact minimization has been investigated by Buxton et al. They proposed a systematic procedure based on the optimal solvent blends for nonreactive, multicomponent absorption processes accounting for plant-wide point source environmental interactions. This methodology involves the selection of an optimal solvent blend candidate based on the global plant-wide process and environmental constraints [18]. Slater et al. suggested the greener process that uses a continuous adsorption system, composed of a more efficient adsorbent, consuming less organic solvent and rinse water, which leads to less waste disposal. The approach is also more energy and cost-efficient from an operational perspective since the carbon footprint reduces to 94% compared with the latest method [19].
Interestingly, the solvent used in the extraction process can be also sustainably recovered through membranes which is so useful from an environmental and economic point of view [20, 21]. Therefore, preparing material in a short time and via less amount of solvent can be highly beneficial from an economic and environmental perspective. It can pave the way to produce this kind of material on an industrial scale, effectively. Therefore, the main purpose of this paper is to offer a specific solvent for the solvent extraction which needs the lower required time and solvent than those reported in the latest works (see Table 1).

**EXPERIMENTAL SECTION**

**Material used**

Ferric chloride (FeCl₃·6H₂O), ferrous chloride (FeCl₂·7H₂O), tetraethylorthosilicate (TEOS), NH₃OH(28%wt.), cetyltrimethylammonium bromide (CTAB), absolute alcohol (EtOH) and toluene from Merck company. All chemical reagents and solvents were of analytical grades and used without further purification.

**Methods**

**Preparation of Fe₃O₄**

The chemical co-precipitation method was employed to synthesize the Magnetic NanoParticles (MNPs) with some modification [27] using FeCl₃·4H₂O and FeCl₂·6H₂O (molar ratio, 1:2) in deionized water. At 75 °C, about 75 mL of NH₃OH solution was added under vigorous stirring (1000 rpm) in the presence of nitrogen. The resulted in dark-colored precipitate turned black by heating at 80 °C for 20 min and 70 °C for 5 h and pH solution ± 12. The precipitation of Fe₃O₄ was completed at pH between 8 and 14. Then the particles were washed several times with water and aqueous ethanol (volume ratio 2:1). At last, the obtained MNPs were dried in a vacuum oven overnight at 60 °C.

**Synthesis of Fe₃O₄@SiO₂**

The interlayer of SiO₂ was prepared through a simple sol-gel process [28]. Briefly, 0.1 g Fe₃O₄ microspheres were homogeneously dispersed in a mixture of ethanol (30 mL) and deionized water (10 mL) under ultrasonic vibration for 10 min, then the concentrated ammonia aqueous solution (2 mL, 28 wt%) was added to this solution with the help of ultra-sonication for 10 min under the frequency of 40 kHz and power of 150 W, and followed by the addition of tetraethoxysilane dropwise until the total amount of TEOS reached 0.05 mL. After stirring for 8 h, at room temperature and mild stirring (500 rpm), the product was collected with the help of a magnet and washed with ethanol and water (volume ratio 2:1) for 3 times, and then vacuum dried at 80 °C for 12 h.

**Synthesis of Fe₃O₄@SiO₂@meso-SiO₂ microspheres**

The core-shell magnetic mesoporous Fe₃O₄@SiO₂@meso-SiO₂ was prepared by adopting the mentioned method in the literature [29] with some modification. The suspension of the as-prepared core-shell magnetic Fe₃O₄@SiO₂ nanosphere (0.1 g) was diluted by a mixture of absolute alcohol (30 mL) and deionized water (20 mL) with the aid of sonication for 15 min. Subsequently, 1.5 mL of NH₃OH (28 wt%, A. R.), 0.4 g CTAB and 0.4 mL TEOS were added and the suspension was stirred (500 rpm) at room temperature for 7 h. Finally, the resultant product was collected by an external magnetic field and washed several times with ethanol and deionized water (volume ratio 1:2).

### Table 1: Needed time and solvents for the preparation of core-shell magnetic mesoporous silica in recent works.

<table>
<thead>
<tr>
<th>Methodology to remove the surfactant</th>
<th>Type of solvent</th>
<th>Required solvent (mL)</th>
<th>Required time (h)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent extraction</td>
<td>Ethanol</td>
<td>180</td>
<td>36</td>
<td>[22]</td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>Ethanol</td>
<td>180</td>
<td>36</td>
<td>[23]</td>
</tr>
<tr>
<td>Calcination at high temperature</td>
<td>-</td>
<td>-</td>
<td>6</td>
<td>[24]</td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>Acetone</td>
<td>250</td>
<td>48</td>
<td>[25]</td>
</tr>
<tr>
<td>Calcination at high temperature</td>
<td>Acetone</td>
<td>-</td>
<td>48</td>
<td>[1]</td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>Acetone</td>
<td>300</td>
<td>144</td>
<td>[17]</td>
</tr>
</tbody>
</table>

The product was dried in a vacuum oven for 9 h. Finally, the obtained sample was re-dispersed in 100 ml ethanol solution containing 2% NH₄NO₃ and stirred at 70 °C for 15 min to remove the surfactant. The resulted powder was washed with water and dried overnight at 60 °C. The synthesis reactor can be seen in Fig.1. It consists of a three-neck glass reactor with 250 ml capacity which is equipped with a thermometer, inlet pipe of nitrogen gas and a magnetic stirrer and this reactor should be placed in an oil bath to achieve constant temperature during sample preparation.

**Characterization**

The size and morphology of the core-shell magnetic mesoporous structure were characterized by field emission scanning electron microscope (FESEM, Hitachi 1460, Japan). The surface modification and pectinase binding were confirmed by FT-IR spectroscopy (Perkin Elmer spectrum) using the potassium bromide (KBr) pellet method in the range of 400–2400 cm⁻¹. The crystalline structures of the sample would be assessed by XRD analysis on a Bruker AXS D8-Advance X-ray diffractometer with CuKα radiation. Magnetization measurement was performed on a Superconducting Quantum Interference Device (SQUID) magnetometer at 300 K (VSM; Kavir Magnet Company, Iran). The average particle size was determined by Mettle-Toledo thermal instrument. The specific surface area and pore diameter of the magnetic microspheres was measured at 77 K on a PHS-1020 (PHS, China) analyzer by the Brunauer–Emmett–Teller (BET) method. The ThermoGravimetric Analysis (TGA) curve was conducted using a Perkin–Elmer Pyris 1 TGA instrument (Perkin–Elmer, USA) from 25 °C to 700 °C under N₂ at a heating rate of 15 °C/min.

**RESULTS AND DISCUSSIONS**

**Characterization of magnetic mesoporous silica**

**Morphology analysis**

Morphology of the Fe₃O₄ @SiO₂ and Fe₃O₄@SiO₂@meso-SiO₂ samples were investigated by FE-SEM. The spherical morphology and solid Fe₃O₄ @SiO₂ nanoparticles with an average diameter of 34 nm were illustrated in Fig. 2a. Interestingly, the magnetic core-silica shell nanoparticles seem to be aggregated due to dipole-dipole interaction, but as it is shown in Fig. 2b, Fe₃O₄@SiO₂@meso-SiO₂ looks good dispersal due to the repulsion of MNPs. It should also be mentioned that the proposed extraction process has not any adverse effect on the Fe₃O₄@SiO₂ and the morphological properties of this structure was kept unchanged after adopting this methodology. Furthermore, the mean diameter of Fe₃O₄@SiO₂@meso-SiO₂ was reported to be about 684 nm.

**Particle size analyzer**

The PSA images of Fe₃O₄ @SiO₂ and Fe₃O₄@SiO₂@meso-SiO₂ samples are shown in Fig. 3. It is seen that Fe₃O₄ @SiO₂ and Fe₃O₄@SiO₂ @meso-SiO₂ have a narrow size distribution and their mean diameters were obtained to be 36.7, 682 nm, which are in good agreement with the FESEM results.

**FT-IR spectra**

The FT-IR spectra of Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@SiO₂@meso-SiO₂ are given in Fig. 4. For Fe₃O₄ the peak at 578 cm⁻¹ corresponds to FeO stretching vibration and it can be proved that MNP has been successfully synthesized. The new peaks at 1087 and 786 cm⁻¹ can be ascribed to the antisymmetric and symmetric stretching vibration of Si-O-Si bond in oxygen-silica tetrahedron, respectively. It can confirm that SiO₂ is successfully coated on the surface of the superparamagnetic Fe₃O₄ nanoparticle [30].

The absorption peak of 3448 cm⁻¹ corresponding to the stretching vibration of OH group of water respectively [31].
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Fig. 2: FE-SEM images of (a) Fe₃O₄@SiO₂ and (b) Fe₃O₄@SiO₂@meso-SiO₂.

Fig. 3: PSA images of the Fe₃O₄@SiO₂ (a) and Fe₃O₄@SiO₂@meso-SiO₂ (b).

XRD
The XRD patterns of Fe₃O₄ and Fe₃O₄@SiO₂@meso-SiO₂ samples shown in Fig. 5. The characteristic diffraction peaks at 30.1°, 35.4°, 43.1°, 53.4°, 56.9°, and 62.5° could be the index to the cubic structure of Fe₃O₄ powder diffraction data, which indicates that the crystalline structure of Fe₃O₄ was pure and there was no phase change in MNPs before and after surface coating and modification [32].

TGA analysis
TGA analyses of the Fe₃O₄@SiO₂@meso-SiO₂ were used to determine the heat endurance of the sample (Fig. 6). Fe₃O₄@SiO₂@meso-SiO₂ microsphere indicated three distinct weight loss stages: the first region is characterized by rather a small weight loss below 180 °C as a result of the evaporation of surface adsorbed alcohol and water. In the second region, a large weight loss in the range of 200–600 °C can be attributed to the decomposition of organic substances. Whereas in the third region, a minor weight loss above 550 °C is associated with the release of structured water [8].

Vibrating sample magnetization
The hysteresis loop for Fe₃O₄@SiO₂@meso-SiO₂ microspheres is shown in Fig. 7. The magnetic saturation value of this sample is 24 emu/g. Due to the high magnetization, the Fe₃O₄@SiO₂@meso-SiO₂ microspheres show a fast response to the external magnet and can be separated from the dispersion within the 50s (Fig. 8), which makes them favorable in diverse applications and its suitability for magnetic separation and targeting [33]. These particles can be also redispersed quickly with a slight shake when the magnetic field is removed.

N₂ adsorption-desorption isotherm
N₂ adsorption-desorption isotherm of Fe₃O₄@SiO₂@meso-SiO₂ microsphere is presented.
in Fig.9 (a). This test also proves that Fe₃O₄@SiO₂@meso-SiO₂ microsphere has a porous framework. The isotherm of Fe₃O₄@SiO₂@meso-SiO₂ microsphere is identified as type IV curves with H1-type hysteresis loops, which reveals the formation of well-uniform mesoporous structure. The BET surface area and BJH pore volume of Fe₃O₄@SiO₂@meso-SiO₂ are calculated to be 230 m²/g and 0.547 cm³/g, respectively. The average mesopore size of Fe₃O₄@SiO₂@meso-SiO₂ is also reported to be 2.85 nm (Fig.9 (b)).

CONCLUSION

In this study, magnetic nanoparticle coated with a dense nonporous silica layer and a mesoporous silica shell was prepared successfully by applying the facile, economic and prompt methodology. The required time and solvent for extraction of surfactant have decreased significantly which can offer a unique synthesis approach for the large-scale production. The as-prepared core-shell structured material was characterized by FT-IR spectroscopy, XRD analysis, electron microscopy, TGA and nitrogen adsorption and desorption, which confirmed the successful formation of core-shell-shell structure. The resulted materials possessing uniform core-shell structure (~648 nm), (BET) surface area of 230 m²/g, the pore volume of 0.547 cm³/g and well preserved structural stability. This multifunctional structure also shows good sustained properties and possesses a magnetization saturation of 24 emu/g. The prepared particles have great potential applications in various processes such as drug delivery, water purification, and catalysis. Therefore by adopting the proposed methodology, this kind of material can be easily provided on a large scale.
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Fig. 8: Separation of Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$ from water by a magnetic field

Fig. 9: (a) Nitrogen adsorption-desorption of Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$, (b) Pore size distribution of Fe$_3$O$_4$@SiO$_2$@meso-SiO$_2$.

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