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Synthesis of magnetic mesoporous nanocomposites: A promising candidate for diagnostic and therapeutic biomedical applications

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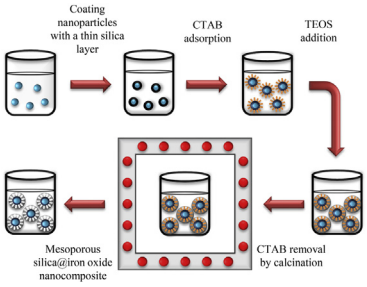
HIGHLIGHTS

- 42 nm sized 3-layered mesoporous silica-iron oxide nanocomposite were synthesized.
- The hydrothermal treatment of iron oxide nanoparticles improved their purity.
- The nanocomposite possessed 212–295 m^2/g surface area.
- The nanocomposite has a relatively high saturation magnetization of 30 emu/g.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present research, iron oxide nanoparticles were synthesized through the hydrothermal method, and the influence of processing parameters such as pH of the initial coprecipitation reaction, time and temperature of hydrothermal treatment was studied. The magnetic iron oxide nanoparticles were coated with a negatively charged, thin layer of silica. The product is then coated with a layer of mesoporous silica. As a result of the electrostatic attraction between the cationic CTAB and the primary silica coating, the formation of mesoporous silica would be mainly localized on the surface of nanoparticles. Calcination was performed in an argon atmosphere tube furnace at 550 °C, through which CTAB was decomposed and eliminated thoroughly from the structure, thereby leaving the oriented pore structure behind. The effects of synthesis parameters such as the ethanol/water volume ratio, the amount of catalyst needed for the sol–gel reaction, and the molar ratio of TEOS/CTAB on the synthesized nanocomposite were investigated. FESEM observations were used to define the morphology and approximate particle size of the product. The FTIR analysis confirmed the formation of Si–O–Fe bonds as a proof for the core/shell morphology of the nanocomposite particles. The nitrogen adsorption behavior through the BET method proved the presence of mesopores in the magnetic nanocomposite. The specific surface area of the nanocomposite varied with the amount of CTAB in the range of 212–295 m^2/g. The magnetic mesoporous nanocomposite possessed a considerable magnetic saturation of 30 emu/g, while the final mean diameter of the nanoparticles was about 42 nm.

1. Introduction

In recent years, the investigation of novel nanomaterials based on porous structures has become an interesting field of research.

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Among these kinds of material, mesoporous silica has extensive applications in the fields of catalysis, absorbance and biomedical engineering. Integrating the surface characteristics of mesoporous silica with the remarkable magnetic properties of iron oxide nanoparticles would lead to the production of new nanocomposites with unique properties. In this regard, preserving the spherical morphology of the nanocomposite particles is vital. There has always been a great deal of interest in acquiring novel magnetic nanomaterials following the goal to reach a combination of certain physical and chemical properties. As a consequence, many investigations have so far been carried out to prepare the qualified superparamagnetic iron oxide nanoparticles applicable in a broad range of applications, including: the separation of environmental contaminants [1], catalysis [2] and biomedical applications [3–5]. All these applications can be achieved by using several organic (polyethylene glycol [3], dextran [6], polyacrylic acid [7]) and inorganic (silica [8], titanium dioxide [9], gold [10]) materials as coatings, as well as different synthesizing routes (coprecipitation [6], hydrothermal [11,12], microemulsion [10]) to modify the ultimate properties; however, there is still a long way ahead to properly optimize their characterization. Biomedical applications are probably the most important ones as they directly deal with the health care of human beings. Regarding this field of interest, silica is best known for its biocompatibility and the ability to be easily modified by chemical bonds for further conjugation to other molecular sieves or the selective sorption of compounds [13,14]. Besides, its mesoporous types provide a high surface area and a 3D pore network with adjustable pore size varying in the range of 2–50 nm [15]. There were also some attempts to synthesize porous iron oxide nanoparticles to increase the available surface area for further drug loading, but the ultimate surface area is entirely incomparable to that of mesoporous silica-iron oxide nanocomposites [16]. The magnetic mesoporous nanocomposite is considered to be a superb potential candidate for both targeted drug delivery and magnetic resonance imaging, and is an attractive issue in research and development.

To obtain an efficient structure, the nanocomposite demands narrow particle size distribution, high magnetic saturation, as well as the low coercivity to preserve its colloidal stability. Moreover, the high surface area and fully protected magnetic cores with the least probability of leaching into the medium are required. There are two approaches to the fabrication of mesoporous silica nanocomposites: 1. Fabrication of nanocmposite in the form of embedded magnetic nanoparticles in mesoporous silica matrix. 2. The deposition of a mesoporous silica shell on the surface of magnetic cores. Most researches in this area resulted in the former morphology [14,15,17,19]. In contrast, researches dealing with core–shell nanocomposites are scarcer [18,20]. The core–shell structure of the magnetic mesoporous nanocomposite was first reported by Wu et al., who suggested employing an initial layer of thin amorphous silica prior to the mesoporous shell [20]. However, the resultant magnetic composite particles were irregular in shape, and had a wide size distribution from a few hundreds of nanometers to several microns. Since then, some researchers have attempted to improve the structure in several aspects: from physical properties such as the size, shape and pore diameter to its different applications [1,21–24], but there is still a great deficiency in the successful preparation of nanocomposite particles that keep the properties of magnetic nanoparticles basically intact. In the present study, the synthesis of the magnetic mesoporous nanocomposite on the basis of core–shell structures, with a particle diameter of less than 50 nm, a high surface area and a relatively high magnetic saturation, has been reported.

2. Materials and methods

2.1. Reactants

Ferrous sulfate ($FeSO_4.7H_2O$), ferric chloride ($FeCl_3.6H_2O$), sodium hydroxide, tetraethoxysilane (TEOS), cetyltrimethyl ammonium bromide (CTAB) and concentrated ammonium aqueous solution (32 wt% NH_3) were all purchased from MERCK company and utilized without further purification. Distilled water and absolute ethanol (99.8%) were used in all experiments for synthesis and washing purposes.

2.2. Preparation of magnetic mesoporous nanocomposite

The whole procedure of producing the nanocomposite can be summarized in three individual steps.

2.2.1. Synthesis of iron oxide nanoparticles

This process consists of the coprecipitation of iron salts in an alkaline medium followed by a hydrothermal treatment. An aqueous solution of ferric and ferrous salts with the molar ratio of 2:1 in 25 ml distilled water was prepared under exposure to ultrasonic waves and argon bubbling. After 30 min, 2.5 M sodium hydroxide was abruptly added to the mixture and its pH value was maintained in the range of 11–12. To perform hydrothermal treatment, the black mixture was immediately transmitted into a Teflon-lined stainless steel autoclave and placed in an oven set at temperatures of 150 °C, 175 °C and 200 °C for 1, 3 and 5 h (Details can be found in Table 1). After cooling to room temperature, a permanent magnet was used to immobilize the precipitate and the supernatant was removed by decantation.

2.2.2. Deposition of amorphous silica onto the surface of iron oxide nanoparticles

Since iron oxide nanoparticles have strong native affinity toward silica [13], the coating process can be carried out by making some modifications to the conventional Stöber method. Iron oxide nanoparticles were first resuspended in a mixture of water, ethanol and ammonia solution using an ultrasonic probe in its pulsed mode. Subsequently, TEOS was added abruptly to the mixture in order to form a 3–5 nm thick silica layer on the surface of iron oxide nanoparticles. The volume ratio of water: ethanol and ammonia solution: TEOS is crucial and were kept at 1:4 and 5:1, respectively [25]. The reaction was allowed to proceed for further 6 h. Magnetic nanoparticles were then isolated from the reaction medium using an external magnetic field and washed thoroughly with ethanol and water for several times.

2.2.3. Synthesis of mesoporous silica-iron oxide nanocomposite

The final nanocomposite was synthesized, utilizing CTAB as structure directing agent, ammonia solution as a catalyst in the reaction medium and TEOS as silica precursor. A quite stable suspension of magnetic cores was redispersed in absolute ethanol and sonicated for 35 min to shatter all existing aggregations. PH of the

Table 1
Different experimental conditions for synthesis of iron oxide nanoparticles.

Sample	pH	Temperature (°C)	Time (h)	d_{av} (nm)
M1	11	175	3	24
M2	11	200	3	22
M3	11	200	5	26
M4	12	175	5	18
M5	11	150	1	27
M6	12	150	3	22