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# Facile fabrication and characterization of amino-functionalized $Fe_3O_4$ cluster@$SiO_2$ core/shell nanocomposite spheres

Mohammad Kalantari [a,b], Mohammad Kazemeini [b,*], Ayyoob Arpanaei [a,**]

[a] Department of Industrial and Environmental Biotechnology, National Institute of Genetic Engineering and Biotechnology, P.O. Box: 14965/161, Tehran, Iran
[b] Department of Chemical and Petroleum Engineering, Sharif University of Technology, P.O. Box: 9465-11365, Tehran, Iran

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ABSTRACT

We developed a modified straightforward method for the fabrication of uniformly sized silica-coated magnetite clusters core/shell type nanocomposite particles. Proposed simple one-step processing method permits quick production of materials in high yield. The structural, surface, and magnetic characteristics of the nanocomposite particles were investigated by transmission electron microscopy (TEM), scanning electron microscope (SEM), powder X-ray diffraction (XRD), vibrating sample magnetometer (VSM), and Fourier-transform infrared (FTIR). The sphere-shaped particles almost have the average diameter of 120 nm, with a magnetic cluster core of 80 ± 15 nm, and a silica shell of 25 ± 10 nm thickness. The particles are superparamagnetic and present strong magnetization (18 emu/g) due to the fact that they possess core of the magnetic clusters. Subsequently, the silica surface of core/shell particles was amino-functionalized via N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (EDS). Findings of the present work highlight the potential for using amino-functionalized magnetic silica core/shell nanocomposite particles in biological applications since they possess useful magnetic properties and proper structure.

## 1. Introduction

In recent years, the fabrication of monodisperse nanoparticles has received a great deal of attention due to the fact that they possess extraordinary technological and fundamental scientific importance. Numerous novel properties and possible applications have developed from uniformly sized materials with small dimensions [1,2]. Compared to other different classes of nanoparticles, composite particles came into being on account of their application in a wide range of fields. Core/shell structured nanocomposite particles have been comprehensively investigated since they are very advantageous from the point of view of presenting the combined functionalities of cores and shells endowing them with potentially very useful applications in various fields [3–6].

As an important family of advanced nanomaterials, the core/shell nanocomposite particles consisting of an iron oxide core and a silica shell have found many promising applications especially in bio-related fields such as bioseparation [7], enzyme immobilization [8], magnetic resonance imaging (MRI) [9], environmental technology [10] and targeted drug delivery [11] for their unique properties. First, silica-coated magnetic nanocomposite particles present the advantage of being conveniently separated from aqueous phase through applying an external magnetic field [12–14]. Another advantage for the magnetic silica hybrid particles is that the silica coating shell has an abundance of surface hydroxyl groups which offers ease of following functionalization of magnetic particles [12–14]. In addition, the magnetic dipolar attraction between magnetic nanoparticles may be screened to avoid their aggregation and improve their chemical stability by coating silica as a shell on the magnetic core [12–14]. Finally, the most important advantage is that the silica coating provides magnetic nanocomposite particles with a chemically inert surface which is especially important in biological applications [12–14].

Currently, there are a great number of examples which have been developed to prepare silica-coated magnetite particles. Vogt and co-workers, for example, report on the production of single core iron oxide–silica shell nanoparticles with tuneable shell thickness by a carefully optimized inverse microemulsion method [15]. Ma et al. provided a facile method to prepare multifunctional core–shell nanocomposite particles with a magnetic core and a silica shell [16]. Pellison et al. prepared silica-coated magnetite nanocomposite particles and used core/shell particles to increase the handling properties of the obtained nanoheterogeneous catalyst [17]. In another study, Mohammad-Beigi et al. synthesized amino-functionalized silica-coated iron oxide nanocomposite

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* Corresponding author. Tel.: +98 9121305309; fax: +98 2166022853.
** Corresponding author. Tel.: +98 2144585463; fax: +98 2144580395.
*E-mail addresses:* kazemini@sharif.edu (M. Kazemeini), arpanaei@yahoo.com (A. Arpanaei).

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particles via the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) [18].

However, despite their effectiveness, the decreased saturation magnetization of the resultant particles which rose from the preventing effects of nonmagnetic silica shell is the major shortcoming of the magnetic silica core/shell nanocomposite particles. Hence, it is desirable to synthesize magnetic silica nanocomposite particles which respond sufficiently strongly or quickly to magnetic fields to be useful in their intended application areas. An alternative strategy to achieve this purpose while maintaining the advantages of the primary magnetic nanoparticles is using clusters composed of multiple primary nanoparticles [19,20]. To the best of these authors' knowledge, there are a very few reports concerning the preparation of magnetic silica core/shell nanocomposite particles with appropriate saturation magnetization. One such work was that of Taboada et al.'s [9] in which a novel one-pot method as a combination of sol–gel chemistry and clean supercritical fluid technology to fabricate particles around 100 nm in diameter was reported. But, some problems such as the specific operating conditions still remained unresolved.

In this work, the method described by Taboada et al. [9] was modified to provide a simple and relatively inexpensive method for preparing amino-functionalized magnetic silica core/shell nanocomposite particles with a core consisting of magnetite nanoparticle clusters. In this modified process, ammonia solution was utilized as a catalyst for the hydrolysis and condensation of silica precursor in the sol–gel as opposed to the supercritical fluid technology in Taboada's method. Small particle size, narrow size distribution, high saturation magnetization and super paramagnetic characteristics obtained in this research may make these particles useful in biological and medical applications.

## 2. Material and methods

### 2.1. Materials

Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), oleic acid ($C1_8H_{34}O_2$), ammonia solution (28–30%), anhydrous ethanol (99.99%), hexane (95%), acetone (98%), tetraethyl orthosilicate (TEOS, 99%), N-(2-aminoethyl)-3-aminopropyltrimethoxy silane (EDS) and acetic acid (100%) were purchased from Merck Chemicals Co. All reagents were used as-received without further purification. In all experiments, Millipure water with a resistivity of greater than 18.0 MO cm was deoxygenated first in an ultrasonic bath and then purging $N_2$ gas through for 30 min before using it.

### 2.2. Synthesis

#### 2.2.1. Preparation of oleic acid coated magnetite nanoparticles

Oleic acid-coated magnetic nanoparticles were prepared via the co-precipitation method as described previously [21]. Briefly, $FeCl_3{\cdot}6H_2O$ (0.540 g) and $FeCl_2{\cdot}4H_2O$ (0.199 g) were dissolved in deionized water (60 ml) under a nitrogen atmosphere with vigorous stirring at 1000 rpm. After addition of the oleic acid (0.1 ml), ammonia aqueous solution (7.5 ml) was added all at once. Oleic acid (0.1 ml) was added to the solution at every 5 min intervals with continued stirring at 80 °C for four times. The reaction was then allowed to proceed at 1000 rpm and room temperature for 30 min. The resulting dark brown suspension was cooled to room temperature and the product was collected with a magnet and washed repeatedly with water to remove nonmagnetic by-products.

#### 2.2.2. Preparation of magnetite cluster@silica

Magnetic silica core/shell nanocomposite particles were prepared via a modification of the method first described by Taboada et al. [9]. Briefly, oleic acid-coated magnetic nanoparticles (20 mg) were dispersed in hexane (2.5 ml) then re-dispersed in acetone (60 ml). After rigorous mechanical mixing for 5 min at 1000 rpm and room temperature, ammonium aqueous solution (3 ml) was added to the above mixture. Then, TEOS (0.5 ml) was added to the mixture by drop wise addition for 15 min. After stirring at 350 rpm and room temperature for 24 h, the product was separated using a magnet and washed repeatedly with ethanol and water to remove nonmagnetic by-products.

#### 2.2.3. Functionalization of silica surface with EDS

Amino-functionalized particles were prepared by surface functionalization of core/shell particles using EDS [18]. For this purpose, nanocomposite particles (5 mg) were dispersed in ethanol (4.6 ml). Then, deionised water (0.2 ml), acetic acid (0.1 ml), and EDS (0.1 ml) were all added to this dispersion under continuous stirring. After 1 h of reaction, the product was collected with a magnet and dispersed in the deionized water.

### 2.3. Material characterization

Particles size, morphology and structure of obtained particles were studied using TEM (Philips CM 200, 200 kV TEM, ATM 2k*2k CCD Camera). SEM images were obtained on a scanning electron Philips XL30 microscope. The magnetic properties of particles were analysed using Vibrating Sample Magnetometer (VSM, Meghnatis Daghigh Kavir Co., Iran) equipment ($I_{max}$ = 150 A, $P \leq 9$ kW) at room temperature. The samples were characterized by X-ray diffraction with a Bruker D8 advance X-ray powder Diffractometer. Fourier-transform infrared (FTIR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer using KBr pellets.

## 3. Result and discussion

### 3.1. Magnetite nanoparticles

A widely used method to prevent aggregation of individual particles, might have led to formation of larger particles resulting in deviation from superparamagnetism, and also to produce highly uniform and nearly monodisperse magnetite nanoparticles is to cover the surface of magnetite nanoparticles with amphiphilic capping molecules like oleic acid [22]. The corresponding TEM image of the magnetite nanoparticles is presented in Fig. 1a. As seen in this figure, magnetite nanoparticles are quasi-spherical. Additionally, the size distribution of magnetite nanoparticles (inset of Fig. 1a) reveals that nanoparticles are uniform in size with an average size of 7.8 ± 0.9 nm. Fig. 1b presents the high-resolution TEM (HR-TEM) of the magnetite nanoparticles. As shown in Fig. 1b, the lattice spacing between two neighboring planes is 0.3 nm, corresponding to the distance between two (2 2 0) planes of $Fe_3O_4$ crystals. In the following, electron diffraction (ED) and XRD analysis proved that the nanoparticles are highly crystalline magnetite nanoparticles.

Furthermore, ED pattern (inset of Fig. 1b) of particles displays spotty diffraction rings confirming a polycrystalline nature of the magnetite nanoparticles. Moreover, existence of the six planes (*i.e.*, (2 0 0), (3 1 1), (4 0 0), (5 1 1), (4 2 2) and (4 4 0)) reveals the face centered cubic (FCC) structure of the resultant magnetite nanoparticles.

Fig. 2a presents the energy dispersive X-ray (EDX) spectra of magnetite nanoparticles. The EDX analysis displays the Fe and O peaks for prepared nanoparticles.

The composition of the obtained nanoparticles was determined by powder XRD analysis. Fig. 3a displays the XRD patterns of the magnetite nanoparticles. The six wide diffraction peaks observed at 30°, 36°, 43°, 54°, 58° and 63° of the particles are well-matched