



Contents lists available at ScienceDirect

## Advanced Powder Technology

journal homepage: [www.elsevier.com/locate/apt](http://www.elsevier.com/locate/apt)

# Superparamagnetic maghemite/polyrhodanine core/shell nanoparticles: Synthesis and characterization

Somaye Seraj, Behruz Mirzayi\*, Ali Nematollahzadeh

Chemical Engineering Department, University of Mohaghegh Ardabili, P.O. Box 179, Ardabil, Iran

## ARTICLE INFO

## Article history:

Received 24 February 2014  
 Received in revised form 20 April 2014  
 Accepted 24 April 2014  
 Available online xxxxx

## Keywords:

Maghemite  
 Polyrhodanine  
 Core/shell nanoparticles  
 Synthesis  
 Characterization

## ABSTRACT

Maghemite nanoparticles (MNPs) with a thin layer of polyrhodanine (PRd) at the surface were synthesized via chemical oxidative polymerization of rhodanine monomer at the MNPs surface in the presence of ferric chloride as oxidant. X-ray diffraction (XRD) pattern gave direct evidence that the synthesized nanoparticles are crystalline maghemite of about 8 nm in size. Magnetization of the particles versus an applied magnetic field exhibited no hysteresis loop, indicated superparamagnetic behavior in the particles. Transmission electron microscopy (TEM) together with Fourier-transform infrared (FT-IR) spectroscopy were used to determine the morphology and the chemical structure of the magnetic core and the polymeric shell. Through the microscopy analysis the shell thickness was estimated to be about 1.5 nm, whereas through thermogravimetric analysis (TGA) it was estimated to be about 0.6 nm. Moreover inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements revealed that the oxidant residue in the polymer backbone is ca. 4 wt.%.

© 2014 The Society of Powder Technology Japan. Published by Elsevier B.V. All rights reserved.

## 1. Introduction

Nowadays, magnetic nanoparticles offer promising applications in verity of areas such as environmental, catalyst and chemical reactions, biomedical, coatings and pigments, data storage, tribology, hygiene and cosmetics, separation and purification sciences [1–5]. Their appeal originates not only from their size and high specific surface area, but also from their magnetic property which makes them to be unique among the other non-magnetic nanoparticles. Among the three main oxides of iron, namely maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), maghemite nanoparticles (MNPs) especially due to their non-toxicity, biocompatibility, eco-friendly performance, relatively low cost and thermal and chemical stability have become one of the most promising product [6]. Moreover, maghemite nanoparticles due to desorption of  $\text{Fe}^{2+}$  ion from their crystalline structure bear vacancies which are mainly located in the surface layer of MNPs. This vacancies can be used in many applications such as heavy metal ion removal from water [7]. So far, various techniques, such as coprecipitation [8], microemulsion [6], thermal decomposition [9], hydrothermal [10], sol–gel [11], sonochemical [12] and electrochemical [13], have been used for the production of MNPs.

The most commonly used method for the synthesis of MNPs is the coprecipitation of iron salts in the presence of a base [8]. However, tendency of MNPs to aggregate and to decompose or lose their integrity in a harsh medium (e.g. in a strong acid) has been addressed as main issues in their use [14–16]. To overcome the aforementioned problems, several types of polymers have been investigated for the surface coating of the MNPs. Surface modification of MNPs can be carried out either during their synthesis in an *in situ* process [16] or in an *ex situ* process [17]. While the *in situ* method refers to the fabrication of nanoparticles from precursors with the presence of another phase material which leads to composite MNPs, *ex situ* or post-synthesis method coats pre-synthesized nanoparticles with polymer using specific processing and therefore results in core/shell MNPs [18–20].

Rhodanine ( $\text{C}_3\text{H}_3\text{NOS}_2$ ) is an organic monomer derived from thiazolidine and is used in the synthesis of phenylalanine. Rhodanine based compounds seem to have antibacterial [16,21], antimicrobial [22,23] and corrosion inhibition effects [24], pharmacological properties [25–28] and capability as an adsorbent in the separation processes [29]. Recently, polyrhodanine (PRd) as a new type of conducting polymer have been widely studied. Kong et al. reported the fabrication and antibacterial properties of silver/polyrhodanine nanofibers [22] and composite  $\gamma\text{-Fe}_2\text{O}_3$ /polyrhodanine nanoparticles [16]. Song et al. [30] used polyrhodanine-encapsulated  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles for the removal of heavy metal ions from

\* Corresponding author. Tel.: +98 451 5517374; fax: +98 451 5512904.  
 E-mail address: [mirzayib@uma.ac.ir](mailto:mirzayib@uma.ac.ir) (B. Mirzayi).

aqueous solution. In another study they fabricated silica/polyrhodanine core/shell nanoparticles and studied antibacterial effect of the particles [21], as well. Nonetheless, according to the best of our knowledge there is no report on the synthesis of the magnetic core/shell nanoparticles by the post-synthesis method.

The main purpose of this work is, therefore, to prepare maghemite and maghemite/polyrhodanine core/shell nanoparticles (MNP@PRd) via a post-synthesis process and to investigate the products in terms of morphology, chemical structure, magnetic property and thermal stability. To the best of our knowledge this is the first report on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles coating with polyrhodanine in a post-synthesis process.

## 2. Experimental

### 2.1. Synthesis methodology

All the chemical reagents used in this work were of analytical grade and used as received without further purification. Maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles were synthesized by chemical coprecipitation of Fe (III) and Fe (II) ions with a 2:1 molar ratio of [Fe<sup>3+</sup>]/[Fe<sup>2+</sup>]. Hydrochloric acid aqueous solution (2 M) was added to the mixture. Then the solution was gradually added into ammonia solution (2 M) under agitation by a mechanical overhead stirrer (Fanavaran Sahand Azar Co., Iran). The synthesis process continued for 20 min at room temperature. The obtained MNPs were washed with deionized water five times and with ethanol three times, respectively. In each washing step the MNPs were separated by a magnet. Finally, the MNPs were dispersed in 40 mL ethanol and stored under refrigeration until their use.

The surface of MNPs was coated with polyrhodanine by a modified method. The coating was performed via oxidative polymerization of rhodanine monomer using FeCl<sub>3</sub> as oxidant. In order to obtain MNP@PRd, 1 g of the MNPs was first dispersed in 50 mL rhodanine monomer solution (0.03 M) and stirred for 30 min by mechanical overhead stirrer. Afterwards, 50 mL of FeCl<sub>3</sub> solution (0.1 M) was added dropwise to the mixture under stirring at room temperature for 24 h. The product was collected by magnetic separation and washed repeatedly with deionized water until the wash solution reached neutral pH. Then the product was dried under vacuum at 40 °C for 24 h.

### 2.2. Characterization of nanoparticles

The XRD pattern of freshly prepared sample was taken using a Siemens D5000 X-ray diffractometer operating in the reflection mode with Cu K $\alpha$  radiation ( $\lambda = 0.1542$  nm). The scanning range was between  $2\theta = 20$ – $80^\circ$  with a step size of  $0.04^\circ$  and a dwell time of 6 s. The size and morphology of the synthesized MNPs and the resultant core/shell were determined by transmission electron microscope (TEM, EM10C). Prior to the TEM observation, the nanoparticles were deposited on a commercial carbon coated copper grid by immersion the grid in a suspension of the nanoparticles in ethanol and allowed to air dry. Images were taken at an acceleration voltage of 80 KV. The nanoparticles were investigated by Fourier-transform infrared (FT-IR) spectroscopy (Perkin-Elmer) in the frequency range of  $4000$ – $400$  cm<sup>-1</sup> by pelletizing a homogenized powder of the synthesized particles and KBr. The spectra were corrected by subtracting the spectrum of a KBr blank pellet and were presented in the transmittance mode. Room temperature isothermal magnetization between  $-100$  and  $100$  kOe was carried out using a vibrating sample magnetometer (VSM, MDK6). Thermal stability and coating thickness of MNP@PRd were investigated by thermogravimetric analysis (NETZSCH, IRIS-209-F1). The samples were heated up to  $800$  °C at a heating rate of  $10$  °C min<sup>-1</sup> under oxygen

atmosphere. The relative weight-loss for the whole event was calculated by subtracting the weights between minima in the derivative plot and correcting these from the oxidant (i.e. Fe(III) ion) content of the shell. To determine the Fe(III) ion content of the polymers, two samples with different quantities of the oxidant (i.e. 4 and 5 mass ratio) were prepared. Besides the TGA, the oxidant content of the synthesized polymers was determined by ICP-OES instrument (VISTA-PRO, Varian Co.), as well. For the ICP-OES experiment, first the organic constituent of the polymer was ignited by air at a relatively elevated temperature ( $800$  °C) in a muffle furnace. Then the ash residue was dissolved in concentrated hydrochloric acid at  $80$  °C. After cooling the solution, the vessel content was filtered to separate the supernatant for the ICP analysis.

## 3. Results and discussion

The overall synthetic procedure of the polyrhodanine coated maghemite nanoparticles is illustrated in Fig. 1. As it can be seen in the scheme, Fe(III) ions attach to the surface of the MNPs due to electrostatic interactions between the cationic Fe(III) ions and the negatively charged maghemite surface. Subsequently, Fe(III) ions reduce to Fe(II), coordinate with sulfur or oxygen atoms of two rhodanine molecules and consequently lead to induced chemical oxidative polymerization of rhodanine [21].

Identification and crystal structure investigation of the synthesized MNP and MNP@PRd were based on the position of characteristic peaks in the diffractogram of the samples using the JCPDS data card 39-1346 [31]. Intensity signals appeared at defined scattering angles  $2\theta$  with the most prominent ones at  $30.32^\circ$ ,  $35.58^\circ$ ,  $43.22^\circ$ ,  $57.1^\circ$  and  $62.76^\circ$  for MNP and  $30.4^\circ$ ,  $35.62^\circ$ ,  $43.32^\circ$ ,  $57.2^\circ$  and  $63.16^\circ$  for MNP@PRd. The Bragg peaks could be assigned to specific diffraction planes inside the maghemite lattice (shown in Fig. 2) were (220), (311), (400), (511) and (440) [32].

Table 1 presents the five most intensive reflections of the synthesized MNP@PRd in comparison with JCPDS data for magnetite (No. 19-0629) and maghemite (No. 39-1346). The XRD pattern of the synthesized materials matches well with standard  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> reflections [33]. Therefore, it can be concluded that the MNP@PRd is composed of maghemite cores.

The assembly of the diffraction peaks is indicative for a cubic defect spinel structure. Broadening of the peaks is caused by crystallite size and, to a minor extent, lattice strain. The crystallite size of the synthesized particles was estimated by the Scherrer equation [11]. The formula is given by:

$$D = \frac{K\lambda}{B \cos \theta} \quad (1)$$

where  $D$  is the diameter,  $\lambda$  is the X-ray wavelength ( $\lambda = 0.1542$  nm),  $K$  is the shape factor (set to 0.9–1),  $\theta$  is the Bragg angle (in radian) and  $B$  is the full width at half maximum (FWHM), i.e. line broadening measured at half-height and expressed in radian. In the X-ray diffraction pattern (Fig. 2) the peak at  $2\theta = 35.58^\circ$  for MNP and  $2\theta = 35.62^\circ$  for MNP@PRd is assigned to the (311) crystal plane of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. As it can be seen in Fig. 3, XRD patterns show almost the same FWHM for the both samples (MNP and MNP@PRd). Hence, it was inferred that the average crystallite size of both of the synthesized MNP and MNP@PRd are the same and it was calculated to be 8 nm. This can be due to the fact that ultrathin coating thickness does not significantly affect XRD pattern [34].

The chemical oxidative polymerization of rhodanine monomer at the surface of the MNPs was characterized by Fourier transform infrared (FT-IR) spectroscopy. Fig. 4 shows the FT-IR spectra for the pristine MNP, PRd and MNP@PRd. FT-IR spectra of iron oxide exhibited strong bands in the low-frequency region ( $1000$ – $500$  cm<sup>-1</sup>) due to the iron oxide skeleton. In Fig. 4, the characteristic peaks of the maghemite particles at  $440$  and  $640$  cm<sup>-1</sup> were

Download English Version:

<https://daneshyari.com/en/article/10260441>

Download Persian Version:

<https://daneshyari.com/article/10260441>

[Daneshyari.com](https://daneshyari.com)