Journal of Magnetism and Magnetic Materials 410 (2016) 27–33

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Green synthesis of magnetic chitosan nanocomposites by a new sol–gel auto-combustion method

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ARTICLE INFO

Article history:
Received 23 March 2015
Received in revised form
21 February 2016
Accepted 3 March 2016
Available online 4 March 2016

Keywords:
Nanocomposites
Chitosan
Sol–gel
Auto-combustion process
Copper ferrite
Magnetic properties

ABSTRACT

The $Fe_2O_3/CuFe_2O_4$/chitosan nanocomposites have been successfully synthesized via a new sol–gel auto-combustion route. To prepare the nanocomposites, copper ferrite ($CuFe_2O_4$) and iron (II) oxide (Fe_2O_3) nanostructures were first prepared utilizing onion as a green reductant for the first time, and characterized by SEM, TEM, XRD, IR and VSM. Then chitosan was added into the nanostructures dispersed in water. Chitosan was used to functionalize and modify the nanostructures and also to improve surface properties. The nanocomposites were also characterized by several techniques including SEM, TEM, XRD, IR and VSM. The effects of amount of onion and chitosan on the morphology and particle size of nanocomposites were evaluated.

1. Introduction

Chitosan is a low-cost and effective adsorbent compared with activated carbons and other adsorbents used in treatment organic or inorganic contaminated water [1,2]. In recent years, extensive attention has been paid to the performance of chitosan as an adsorbent for pollutants from water [3,4]. This is due to the unique polycationic structure, selectivity and cationic behavior of chitosan. Chitosan, as a natural polysaccharide, has reactive amino and hydroxyl groups in its linear polyglucosamine chains that can be used to functionalize and modify ferrite nanoparticles [5,6]. In general, chitosan itself does not exhibit magnetic properties. With adding a magnetic component to chitosan, including Fe_3O_4, Fe_2O_3, $NiFe_2O_4$, $CoFe_2O_4$, $CuFe_2O_4$ and $ZnFe_2O_4$, the magnetic nanocomposites are obtained [6–9]. Magnetic chitosan composites have a fast adsorption rate and high adsorption efficiency, efficient to remove various pollutants and they are easy to recover and reuse. Significant interests have been generated in preparing magnetic chitosan nanocomposites for their exceptional electromagnetic properties in many applications ranging from metal ions adsorption to drug delivery [10,11].

It is well known that properties of powders depend on their particle size and morphology [12–16]. Therefore, exploring appropriate methods to synthesize nanomaterials and controlling their particle morphology and size is crucially important. Herein, we develop the sol–gel auto-combustion route to prepare $CuFe_2O_4$ and Fe_2O_3 nanostructures. This is a novel way with a unique combination of the chemical sol–gel process and the auto-combustion process based on the gelling and subsequent auto-combustion [17]. Then the nanostructures are coated with the chitosan to improve surface properties and enhance loading capacity when used in magnetic targeted delivery and metal ions adsorption [18]. This approach is simple, low-cost and friendly to the environment. We have used nontoxic reactants and solvent. Water is an interminable, cheap, available solvent. At the first time, we have used onion as reductant for green synthesis of magnetic nanocomposites and also it is the first time that $Fe_2O_3/CuFe_2O_4$/chitosan nanocomposites are synthesized. Onion contains vitamin C as one of its constituents. The vitamin C is responsible for the reduction.

2. Experimental

2.1. Materials and experiments

All the chemicals used in our experiments were of analytical grade, were purchased from Merck and used as received without further purification. XRD patterns were collected from a diffractometer of Philips Company with X'PertPro monochromatized Cu Kα radiation ($\lambda = 1.54$ Å). FE-SEM images were obtained on MIRA3 FEG-SEM. TEM images were obtained on a Philips EM208S transmission electron microscope with an

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http://dx.doi.org/10.1016/j.jmmm.2016.03.014
0304-8853/

accelerating voltage of 100 kV. FT-IR spectrum was recorded with Shimadzu Varian 4300 spectrophotometer in KBr pellets. The magnetic properties of the samples were detected at room temperature using a vibrating sample magnetometer (VSM, Meghnatis Kavir Kashan Co., Kashan, Iran).

2.2. Synthesis of Fe_2O_3 and $CuFe_2O_4$

Fe_2O_3 and $CuFe_2O_4$ nanostructures were prepared by the sol–gel auto-combustion process. First, $Cu(NO_3)_2$ was dissolved in distilled water to form a clear solution. Then an aqueous solution containing onion was added into the copper nitrate solution dropwise under strong magnetic stirring at room temperature. The onion aqueous was prepared by finely cutting onion and then taking its water. The experiments were carried out with three different amounts of onion that including 0, 20 and 40 ml. The solution was heated by stirring at 60 °C. After stirring the solution for 30 min, an aqueous solution containing $Fe(NO_3)_3 \cdot 9H_2O$ was added to the above solution and was heated at 120 °C by stirring for 1 h. Evaporation of the mixed solution caused formation of a highly viscous gel. The gel then was dried in an oven at 100 °C. The final residue was calcined at 900 °C for 3 h to form the Fe_2O_3 and $CuFe_2O_4$ nanostructures.

2.3. Synthesis of Fe_2O_3/$CuFe_2O_4$/chitosan nanocomposites

To prepare the Fe_2O_3/$CuFe_2O_4$/chitosan nanocomposites, chitosan was dissolved in distilled water and acetic acid. The molecular weight of chitosan used was 100,000–300,000 and the volume ratio of water and acid used was 10:1. Then Fe_2O_3 and $CuFe_2O_4$ nanostructures dispersed in distilled water, were added into the solution under strong magnetic stirring. The mixture was stirred for 24 h until the water was vapored. The nanocomposites were washed with distilled water and ethanol several times, and dried under vacuum at 60 °C for 4 h. Table 1 lists the reaction terms for the synthesis of the products in this work.

3. Results and discussion

To investigate the effect of different parameters on the morphology and particle size of the products, the various experiments were performed. All of the preparation terms have been illustrated in Table 1. It is suggested that the following reactions occur during the calcination process. The $Fe(NO_3)_3$ and $Cu(NO_3)_2$ salts are decomposed (Eqs. (1) and (2)). Reaction of the Fe_2O_3 with the CuO is caused to formation of $CuFe_2O_4$ (Eq. (3)). The $CuFe_2O_4$, Fe_2O_3 and chitosan are combined together to form the Fe_2O_3/$CuFe_2O_4$/chitosan nanocomposites (Eq. (4)):

$$2Fe(NO_3)_3 \rightarrow Fe_2O_3 + NO_x \quad (1)$$

$$Cu(NO_3)_2 \rightarrow CuO + NO_x \quad (2)$$

$$CuO + Fe_2O_3 \rightarrow CuFe_2O_4 \quad (3)$$

$$Fe_2O_3 + CuFe_2O_4 + \text{chitosan} \rightarrow Fe_2O_3/CuFe_2O_4/\text{chitosan} \quad (4)$$

The morphologies of the obtained nanostructures and corresponded nanocomposites were investigated by SEM and TEM. Fig. 1 shows SEM images of samples no. 1, 2 and 3. Fig. 1a and b show that coalesced particles and bulk structures were obtained in the absence of onion. Whereas, in case of samples obtained in the presence of 20 ml (sample no. 2, Fig. 1c and d) and 40 ml onion (sample no. 3, Fig. 1e and f), irregular prisms and layer hexagonal plates are formed, respectively. The SEM images in Fig. 1c–f clearly show that the surface of the prisms and plates are not smooth and have been covered with nanoparticles with a diameter lower than 10 nm. The SEM images reveal that, in our experimental conditions, the ideal amount of the onion for the synthesis of Fe_2O_3 and $CuFe_2O_4$ nanostructures is 40 ml.

Fig. 2a–f shows the SEM images of nanocomposites prepared in the presence of 40 ml onion, with different amounts of chitosan involving 0.5, 1, 2, 5, 10 and 50% W/W, respectively. According to the SEM images, it is found that the morphology and crystallinity of the nanocomposites depend on the amount of the chitosan. When the amount of chitosan is low (0.5, 1 and 2% W/W), spherical nanoparticles with nearly even size distribution are formed, as shown in Fig. 2a–c. With increasing the amount of chitosan from 0.5 to 1 and then 2% W/W, the size of the nanoparticles were increased and their agglomeration were decreased. With increasing amount of the chitosan to 5% W/W, rectangular structures are formed, the directional linkage of the rectangles is observed in Fig. 2d. In sample no. 8 obtained in the presence of 10% chitosan, aggregated structures are formed. Whereas, in case of sample no. 9 which was obtained in the presence of 50% chitosan, agglomerated nanoparticles are formed.

Fig. 3 shows TEM images of two samples obtained in the presence of 40 ml onion, one without (sample no. 3) and the other with 1% chitosan (sample no. 5). The TEM images reveal that spherical nanoparticles are formed in both samples. The nanoparticles in Fig. 3a have nearly even size distribution with an average size of ~5 nm. These nanoparticles have been formed on surfaces of hexagonal plates, as shown in Fig. 1e and f. TEM images of the nanocomposites obtained in the presence of 1% chitosan (Fig. 3b, c) show formation of nanoparticles with size of 5–45 nm.

In other side, the crystal structure and composition of the as-prepared samples were determined by XRD. Fig. 4a and b shows the XRD patterns of the samples no. 3 and 5, respectively. The product obtained in the presence of 40 ml onion and without chitosan (sample no. 3) is a mixture of $CuFe_2O_4$ and Fe_2O_3 (Fig. 4a). The peaks which have been indexed with green (or star) and blue colors in Fig. 4a indicate the Fe_2O_3 and $CuFe_2O_4$, respectively. Five characteristic peaks for Fe_2O_3 marked by their indices ((111), (220),

Table 1
The reaction conditions of the nanocomposites synthesized in this work.

Sample no.	Fe Source	Cu Source	Cu:Fe	Onion (ml)	Temperature (°C)	Time (h)	Chitosan (% W/W)
1	$Fe(NO_3)_3 \cdot 9H_2O$	$Cu(NO_3)_2$	1:12	–	900	3	–
2	$Fe(NO_3)_3 \cdot 9H_2O$	$Cu(NO_3)_2$	1:12	20	900	3	–
3	$Fe(NO_3)_3 \cdot 9H_2O$	$Cu(NO_3)_2$	1:12	40	900	3	–
4	$Fe(NO_3)_3 \cdot 9H_2O$	$Cu(NO_3)_2$	1:12	40	900	3	0.5
5	$Fe(NO_3)_3 \cdot 9H_2O$	$Cu(NO_3)_2$	1:12	40	900	3	1
6	$Fe(NO_3)_3 \cdot 9H_2O$	$Cu(NO_3)_2$	1:12	40	900	3	2
7	$Fe(NO_3)_3 \cdot 9H_2O$	$Cu(NO_3)_2$	1:12	40	900	3	5
8	$Fe(NO_3)_3 \cdot 9H_2O$	$Cu(NO_3)_2$	1:12	40	900	3	10
9	$Fe(NO_3)_3 \cdot 9H_2O$	$Cu(NO_3)_2$	1:12	40	900	3	50