

PREPARATION AND CHARACTERIZATION OF SUPERPARAMAGNETIC Fe₃O₄-CHITOAN NANOCOMPOSITES

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Received 6 March 2014

Abstract

In this study, superparamagnetic nanocomposite Fe₃O₄-chitosan has been prepared by two step method. The Fe₃O₄ nanoparticles were prepared by a co-precipitation process and subsequently coated with chitosan. The magnetite nanoparticles and chitosan coated magnetic nanoparticles were characterized by XRD, IR and TEM. The magnetic properties were measured with homemade vibrating sample magnetometer (VSM) and evaluated in terms of saturation magnetization and coercivity. The results revealed that typical iron oxide nanoparticles were Fe₃O₄ with a core diameter of 15-20 nm. Magnetic nanoparticles were formed inside the chitosan matrix through possible binding of iron ions to NH₂ group of chitosan. The Fe₃O₄-chitosan nanoparticles with core-shell structure exhibit superparamagnetic properties and highly dispersed nano magnetite particles with diameters around 15 nm.

Keywords: Fe₃O₄, chitosan, superparamagnetic nanocomposite, two step method.

1. INTRODUCTION

With the rapid development of nanotechnology, it has become possible to fabricate, characterize and specially tailor the functional properties of nanoparticles for biomedical applications and diagnostics. Increased investigations with several types of iron oxides have been carried out in the field of nanosized magnetic particles, among them magnetite (Fe₃O₄) is a very promising candidate since its biocompatibility has already been proven [1-4]. For biomedical applications Fe₃O₄ nanoparticles (NPs) are often treated with surface modification. On the one hand the modification could increase the chemical stability of the Fe₃O₄ NPs; on the other hand it could improve the biocompatibility of the NPs. A variety of materials has been reported to modify Fe₃O₄ NPs, such as precious metals [5], silica [6], carbon [7] and biopolymers [8-10].

Chitosan is a partially acetylated glucosamine biopolymer with many useful features such as hydrophilicity, biocompatibility and biodegradability. In addition, the amino groups on the chitosan can also be used for further functionalization with specific components, such as various drugs, specific binding sites, or other

functional groups. Thus, it is a suitable kind of polymer to be used to modify the Fe₃O₄ NPs. Many investigations into chitosan modified magnetic NPs used for biomedical applications have been reported. Liang et al. [11] prepared superparamagnetic Fe₃O₄ NPs decorated with carboxymethylated chitosan which were used for covalent conjugation of papain. Feng et al. [12] synthesized monodisperse chitosan/polyacrylic acid/Fe₃O₄ NPs which could be used for MRI. Donadel et al [13] prepared iron oxide magnetic particles coated with chitosan used for hyperthermia. However, the saturation magnetization (22 emu/g) of the composite NPs is low and the heating effect is not desirable. Zhao et al. [14] prepared chitosan-Fe₃O₄ NPs in inverse emulsion and investigated their inductive heating property in AC magnetic field. The problem about this method was that the use of organic solvent is not environment friendly and the dispersity of the chitosan-Fe₃O₄ NPs prepared is poor. For biomedical applications such as hyperthermia, it is required that the Fe₃O₄ NPs have high saturation magnetization, uniform particle size and superparamagnetism.

In this paper, chitosan coated Fe₃O₄ NPs of 15-20nm has been prepared by two step method: The Fe₃O₄ nanoparticles were prepared by a

coprecipitation process and subsequently coated with chitosan. To optimize the colloidal stability of Fe₃O₄ NPs modified with chitosan, the adsorption of chitosan onto the Fe₃O₄ NPs has been investigated. Furthermore, the core-shell structure and the magnetic properties of chitosan-coated Fe₃O₄ NPs have been discussed.

2. EXPERIMENTAL

2.1. Materials

All reagents were analytical grade and used as received without further purification. Ferric chloride hexahydrate (FeCl₃.6H₂O, Merck), Ferrous chloride tetrahydrate (FeCl₂.4H₂O, Merck) and chitosan (DD = 94 %, MW = 10.000 Daltons, Quangzi, China) were used as iron and polymer stabilizer sources, respectively. HCl and NaOH (Quangzi, China) were used to adjust pH.

2.2. Preparation of Fe₃O₄ particles and Fe₃O₄-chitosan

In this paper, superparamagnetic iron oxide nanoparticles-chitosan was prepared by two-step coprecipitation method. In brief, for first step, Fe₃O₄ NPs were synthesized by the coprecipitation of ferric and ferrous ion with sodium hydroxide (NaOH). The ferric chlorides (2 mmol) and ferrous chlorides (1 mmol) (molar ratio of 2:1) were dissolved in 100 mL HCl (pH = 2) and chemical precipitation was achieved by slow adding 0.1 mol.L⁻¹ NaOH solution at 80 °C with stirred vigorously for 30 min. The products were recovered by filtering, washing, drying at 60 °C. As for second step, obtained Fe₃O₄ powder was dispersed in distilled water (1 g/100 mL), the Fe₃O₄ suspension was added slowly chitosan solution (1 g/100 mL) with vigorous stirring at 50 °C for 30 min. The mixture was recovered by filtering, washing, drying at room temperature.

2.3. Material characterization

X-ray diffraction was performed to identify the structure of Fe₃O₄ and nanocomposite chitosan-Fe₃O₄ using D8 Advance, Bruker, Germany. Thermal behaviors were investigated by SETARAM. The morphology was studied with a transmission electron microscope (TEM) using Jeole-3432. Magnetic property was analyzed using a Vibrating Sample Magnetometer (VSM). IR spectra were recorded with Nicolet 6700 FTIR Spectrometer.

3. RESULTS AND DISCUSSION

The phase investigation of chitosan-Fe₃O₄ and Fe₃O₄ was performed by XRD as shown in Fig. 1. The XRD pattern of Fe₃O₄ is also shown for the sake of comparison. All of the observed characterized peaks with the diffractions of (220), (311), (400), (422), (511) and (440) which are indexed by the cubic structure of Fe₃O₄ (JCPDS No. 19-0629). Weak diffraction lines of composite pattern indicated that Fe₃O₄ particles have been coated by amorphous chitosan. Furthermore, this coating did not result in phase change of Fe₃O₄. Lines broadening in the pattern can be quantitatively evaluated using Debye-Scherrer equation $d = (k\lambda / \beta \cos \theta)$ where d is the thickness of the crystal; k the Dbye-Scherrer constant (0.89); λ the X-ray wavelength (0.15406 nm) and β the line broadening in radian obtained from the full width at half maximum; θ the Bragg angle. According to Dbye-Scherrer equation, particle sizes of uncoated Fe₃O₄ and chitosan-coated Fe₃O₄ is estimated to be 15.4 and 13.2 nm, respectively.

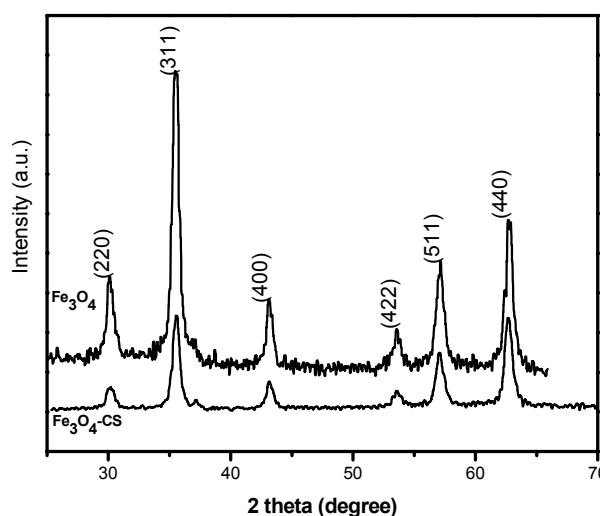


Figure 1: XRD pattern of Fe₃O₄ and Fe₃O₄-chitosan nanocomposites

TEM micrographs for pure Fe₃O₄ and chitosan-coated Fe₃O₄ were demonstrated on Fig. 2. It is clear that pure Fe₃O₄ NPs were quite agglomerated with mean diameter in the range 15-20 nm, while the morphology of chitosan-coated magnetite nanoparticles exhibits highly dispersed particles with diameters around 15 nm. The results are consistent with those obtained by sizes calculated from XRD.

Magnetic properties of Fe₃O₄-chitosan NPs were characterized by vibrating sample magnetometer (VSM). The magnetic hysteresis curves for pristine Fe₃O₄ and Fe₃O₄-chitosan nanoparticles was shown in Fig. 3. It can be seen that

no coercivity or remanence could be observed for all of the two samples, suggesting the superparamagnetic properties of the Fe₃O₄ NPs. This can be ascribed to the small size of nanoparticles which were smaller than the superparamagnetic critical size (25 nm) [15]. The saturation magnetization of the pristine Fe₃O₄ NPs was high

saturation magnetization indicated the good crystal structure. The saturation magnetization of the Fe₃O₄-chitosan nanoparticles was 60 (emu/g) which was lower than the pristine Fe₃O₄ (76.68 emu/g). This was due to the existence of the large amount of diamagnetic chitosan in the Fe₃O₄-chitosan nanoparticles.

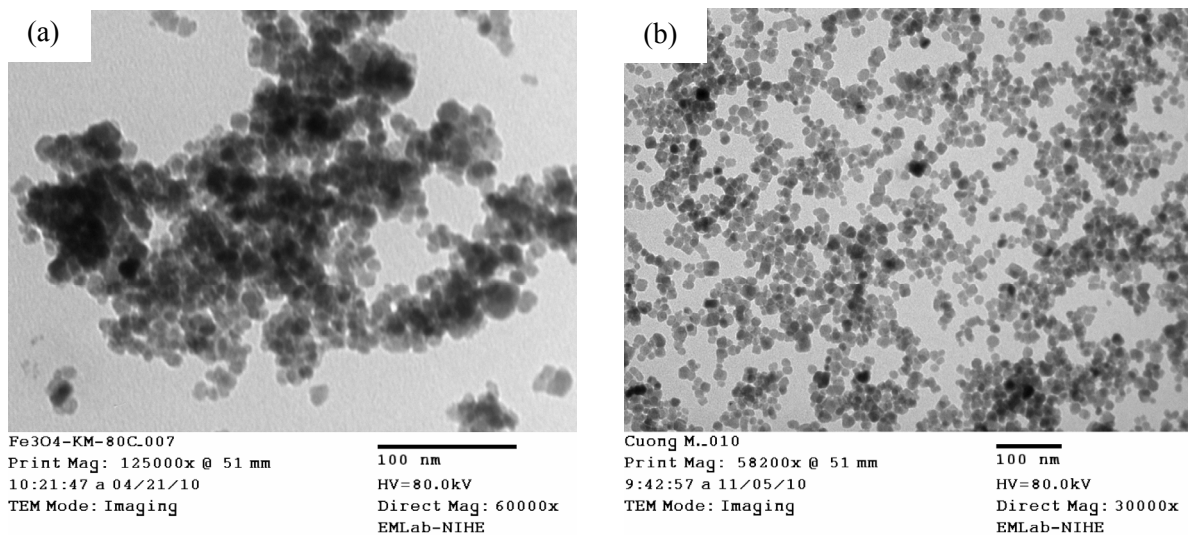


Figure 2: TEM images of pristine Fe₃O₄ nanoparticles (a) and Fe₃O₄-chitosan (b)

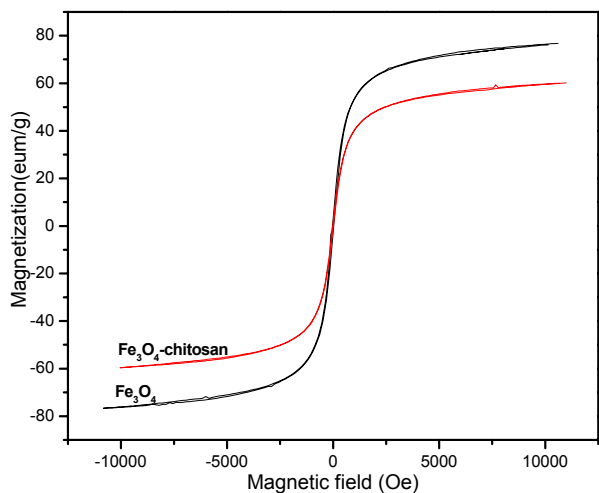


Figure 3: Magnetic hysteresis curves of Fe₃O₄ and Fe₃O₄-chitosan

Fig. 4 shows the FT-IR of spectra of pristine Fe₃O₄ NPs (a), and Fe₃O₄-chitosan (b), and chitosan (c). The characteristic peaks of Fe₃O₄ at 580 cm⁻¹ could be observed in both of (a) and (b) which indicated that the nanoparticles were Fe₃O₄. IR spectrum of chitosan is characterized by the following absorption bands ν (C-H) of backbone polymer appeared at: 2905, 2881 cm⁻¹, ν (C₃-O) of primary alcoholic group: 1421 cm⁻¹, ν (C-O), amide I at 1084 and 1033 cm⁻¹, δ (N-H), amide II of

primary amine: 1655 cm⁻¹. In comparison with IR spectra of a, b and c samples it can be noted that the presence of chitosan did shift vibration of Fe₃O₄ but did not alter them very much. Especially, the band shift of Fe-O stretching (from 580 to 5568 cm⁻¹) and that of N-H bending vibration from 1655 to 1628 cm⁻¹ is most significant. The data indicated possible binding of iron ions to NH₂ group of chitosan. Besides, electrostatic interaction between surface negative charged Fe₃O₄ and positively protonated chitosan can also contribute to this IR change. The results suggested the integration of Fe₃O₄ NPs and chitosan in the Fe₃O₄-chitosan NPs.

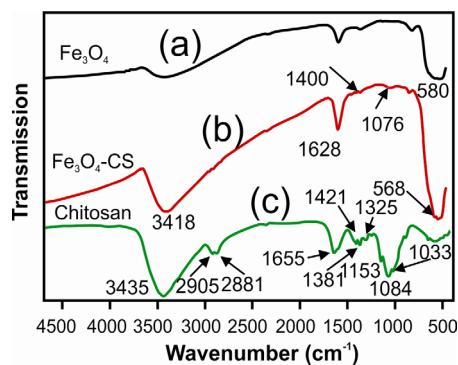


Figure 4: IR spectra of Fe₃O₄ (a), Fe₃O₄-chitosan nanocomposites (b), and chitosan (c)

The influence of chitosan/ Fe_3O_4 mass ratio value on morphologies of product was also investigated. The results of TEM observations are presented in

Fig. 5. The results implied that capping ability of NH_2 group of chitosan effects on the morphologies of products [16].

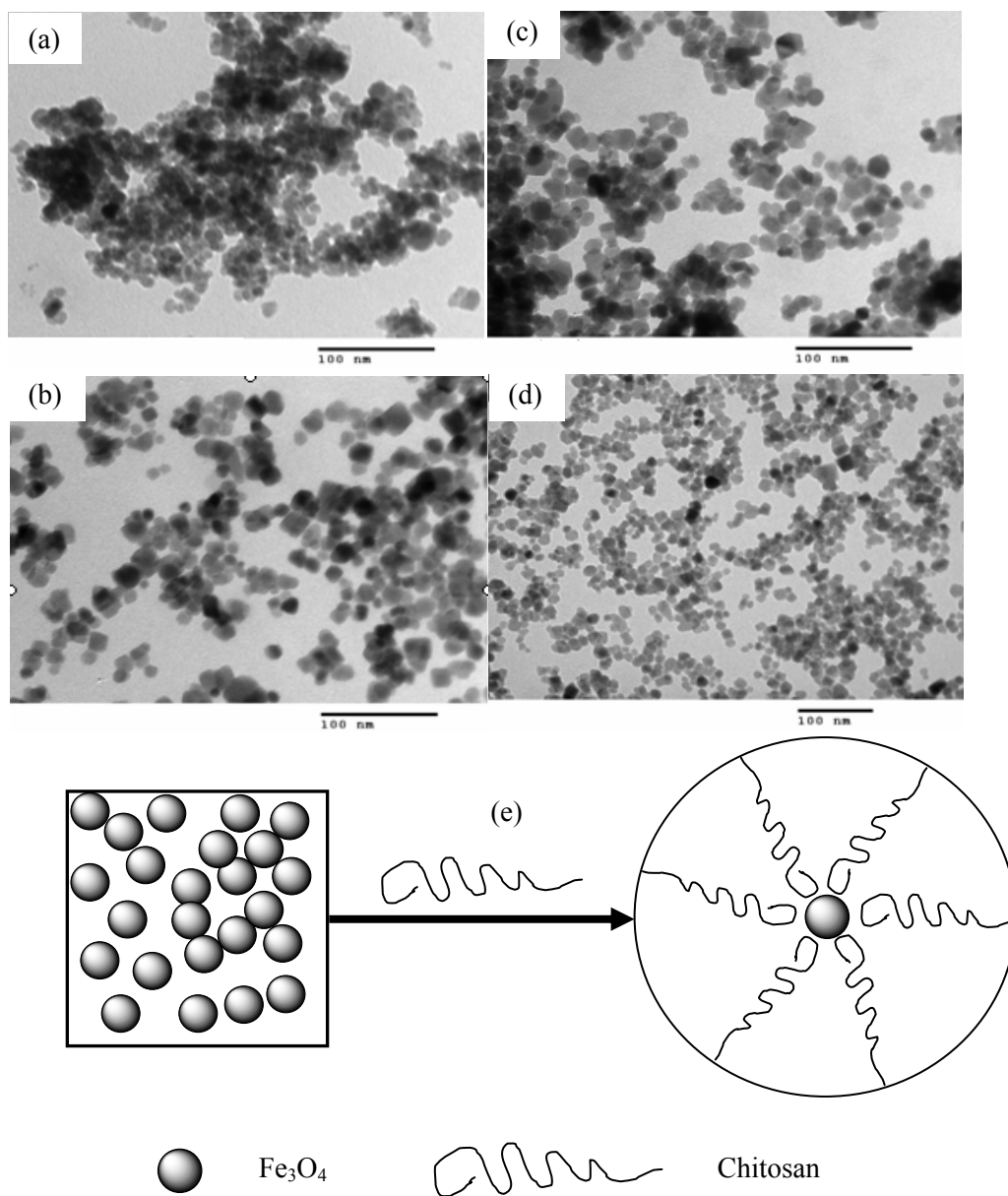


Figure 5: TEM images of uncoated Fe_3O_4 (a), Fe_3O_4 /chitosan various ratios: 4:1 (b), 2:1 (c), 1:1 (d) and schematic illustration for the formation of the Fe_3O_4 -chitosan (e)

4. CONCLUSIONS

The Fe_3O_4 -chitosan NPs with core-shell structure core were successfully prepared by two step method. The as-prepared composite NPs possess good crystal structure with a cubic inverse spinel structure. The particle size of the composite NPs was 10 nm and its size distribution was narrow.

Based on TEM, IR results of the evidences of the successful coating of Fe_3O_4 NPs by chitosan, a

schematic illustration for the formation of the Fe_3O_4 -chitosan NPs is shown in Fig. 5e.

The Fe_3O_4 -chitosan NPs exhibited high saturation magnetization (60 emu/g) and superparamagnetic. The interaction of Fe_3O_4 NPs and chitosan were confirmed using IR. The obtained Fe_3O_4 -chitosan with high saturation magnetization, uniform particles and superparamagnetism meets the requirements of biomedical applications.

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