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ORIGINAL ARTICLE

Synthesis and characterization of cobalt-zinc ferrite nanoparticles coated with DMSA

Sohrab Manouchehri[1], Zeinab Ghasemian[2], Daryoush Shahbazi-Gahrouei[2]*, Mohammad Abdolahi[3]
[1]Department of Physics, Malek-Ashtar University of Technology, Shahinshahr, Isfahan, (IRAN)
[2]Department of Medical Physics and Medical Engineering, School of Medicine, Isfahan University of Medical Sciences, Isfahan, (IRAN)
[3]Department of Medical Physics and Radiation Technology, School of Paramedical Sciences, Bushehr University of Medical Sciences, Bushehr, (IRAN)
E-mail: shahbazi24@yahoo.com; shahbazi@med.mui.ac.ir
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Abstract : Cobalt-zinc ferrite magnetic nanoparticles (CZF-MNPs) were prepared in air environment by conventional co-precipitation method using ferric, zinc and cobalt salts with sodium hydroxide, at 80 °C of solution temperature, and coated with biocompatible Dimercaptosuccinic acid (DMSA). The morphology of desired nanoparticles was investigated by Transmission Electron Microscopy (TEM) and the average size of bare and coated nanoparticles were about 16 and 40 nm. The structural and crystal phase of CZF-MNPs was determined by X-ray diffraction (XRD) and the results confirmed the single phase spinel ferrite formation. The average of crystallite sizes was calculated about 13 nm using Scherrer's formula from the broadening of the most intense peak (311). Magnetization measurements of samples were performed up to maximum field of 9000 Oe at room temperature with a device Alternating Gradient Field Magnetometry (AGFM). The saturation magnetization of coated nanoparticles was less than the bare nanoparticles. Also, the results showed that, the saturation magnetization decreased by increasing molarity of DMSA coated. The FTIR spectra results of the samples were analyzed in the frequency range of 400-4000 cm^{-1}, which also confirmed the results of XRD and formation of Co-Zn ferrite phase. These spectra showed the presence of DMSA cover on the surface of nanoparticles.

Keywords : Magnetic nanoparticles; DMSA coated; Co-precipitation method; Biocompatible.

INTRODUCTION

Synthesis of magnetic nanoparticles have been desperately interested because of their unique features and potential applications, such as magnetic resonance imaging, treatment of cancer and biomedical drug delivery[1-6]. Spinel ferrite nanoparticles and their coated, specially Co-Zn ferrite have been extensively investigated during the recent years, due to their favorable magnetic properties in all areas of biomedicine and bioengineering, such as contrast-enhanced magnetic resonance imaging, cell separation, hyperthermia, detoxification of biological fluids, drug delivery and tissue regeneration[1,2,7-10]. These MNPs should have high magnetization values and size smaller than 100 nanometers, so that the particles have the identical chemical and physical properties. It is also necessary that the surfaces of particles coated with non-toxic materials and also be biocompatible[7,8].

In addition, metallic nanoparticles are made of iron, nickel or cobalt, mostly due to their chemical instability for biological applications are ignored and are easily oxidized in the presence of water and oxygen[11]. Therefore, metallic MNPs are normally protected by coatings, such as gold or silica, because their core-shell structure will cause sustainability metal nanoparticles[11]. Different types of monomers such as DMSA were assessed as anchors for easy attachment of polymer coatings on magnetic nanoparticles[12].

Le Thi Mai H et al. have shown that Fe_3O_4 magnetic nanoparticles were prepared by co-precipitation method and then they coated with two layers of sodium oleate and PEG-6000, respectively. They showed that the agglomeration is very vigorous between pure nanoparticles. Whereas, after coating, there is a little aggregation[13]. Cobalt zinc ferrite nanoparticles have been synthesized by different methods, such as co-precipitation, hydrothermal, sol-gel and other chemical methods[14-16]. Girgis et al. in 2011 synthesized core-shell cobalt ferrite, zinc ferrite and cobalt zinc ferrite nanoparticles by a modified citrate gel method and coated them with silica shell[10]. In another study, in 2013 $Co_{0.3}Zn_{0.7}Fe_2O_4$ and $Co_{0.3}Zn_{0.7}Fe_2O_4$ @ polyvinyl acetate nanocomposites were synthesized[1]. Although cobalt zinc ferrite nanoparticles have been synthesized using different methods, but according to our knowledge, they have not been prepared with DMSA coating.

In this paper, magnetic nanoparticles of $Co_{0.5}Zn_{0.5}Fe_2O_4$ and $Co_{0.5}Zn_{0.5}Fe_2O_4$ were synthesized and coated with different concentration of DMSA by co-precipitation method. Their characterization was investigated by transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and alternating gradient field magnetometry (AGFM).

EXPERIMENTAL

Materials

$FeCl_3.6H_2O$, $ZnCl_2$, $CoCl_2.6H_2O$ and NaOH were purchased from E. Merck Co., Germany with purity of more than 99%. DMSA was purchased from Aldrich Co., with purity of more than 98%.

(a) Synthesis bare and coated magnetic nanoparticles

Cobalt-zinc ferrite nanoparticles were prepared using co-precipitation method. For preparing of nanoparticles, solutions of $FeCl_3.6H_2O$, $ZnCl_2$, $CoCl_2.6H_2O$ and NaOH were prepared by double-distilled water with molar ratio of 2: 0.5: 0.5: 8, respectively. First, the solution of NaOH was poured into a beaker and was placed on a magnetic stirrer, until the temperature of the solution reached to 80 °C. Also, $FeCl_3.6H_2O$, $ZnCl_2$ and of $CoCl_2.6H_2O$ were poured into another beaker and placed on another magnetic stirrer, until the temperature of the solution reached to 80 °C. Then, the contents of the first beaker were quickly poured into the second beaker and placed on a magnetic stirrer for 1 h at a constant temperature of 80 °C, till a blackish brown precipitate was formed. The precipitant was centrifuged and dried for bare sample. The sample was named CZF_0. The chemical composition is shown as follows.

$$2\ FeCl_3 + 0.5\ ZnCl_2 + 0.5\ CoCl_2 + 8\ NaOH \longrightarrow Co_{0.5}Zn_{0.5}Fe_2O_4 + 4\ H_2O + 8\ NaCl$$

For coated sample, the precipitant was centrifuged and washed with distilled water. Then, distilled water was added into the sample and the process continued at 60 °C in the nitrogen atmosphere (1 bar). The solutions of 0.001 and 0.01 M DMSA were prepared in the same volume separately and were added drop by drop into the beaker of the bare sample. The samples were named CZF_1 and CZF_2, respectively. After that, the samples were centrifuged and washed with distilled water frequently.

Characterization

(a) Particles size and morphology

Nanoparticles size and morphology were examined by Transmission Electron Microscopy (EM 900 model, Co. Zeiss).

(b) X-ray powder diffraction

The average crystallite size (L) was measured by Scherer's equation:

$$L\ (nm) = K\,\lambda\ (nm) / \beta \cos\theta \qquad (1)$$

β is the peak full width at half maximum height that its quantity was obtained using XRD software, θ is the angle of diffraction peak and K (=0.9) is a constant value.

(c) FT-IR characterization

The FTIR of particles were recorded by employing FT Infrared Spectroscope (JASCO, FT/IR-6300, Japan) in the range of 400–4000 cm^{-1}. FTIR spectra of bare and coated MNPs were obtained in KBr pellets with a Nicolet-Impact-400 D.

(d) Magnetization measurements

Magnetization measurements were carried out by Alternating Gradient Field Magnetometry (AGFM) at room temperature up to 9000 Oe.

(e) Chemical analysis

The content of Fe^{2+} in the pure and coated MNPs was done by atomic absorption spectrophotometer (Shimadzu, AA-680).

RESULTS AND DISCUSSION

Particles size and morphology

Transmission Electron Miscroscopy micrographs of CZF_0 and CZF_1 are demonstrated in Figures 1-a and 1-b, respectively. As can be seen from these figures, particles have nearly spherical structures in both images and can be clearly identified that particles distribution are mainly uniform. The average nanoparticles sizes of CZF_0 and CZF_1 are 16 and 40 nm, respectively. The average particle size of coated nanoparticles is greater than the average bare nanoparticles and this is logical.

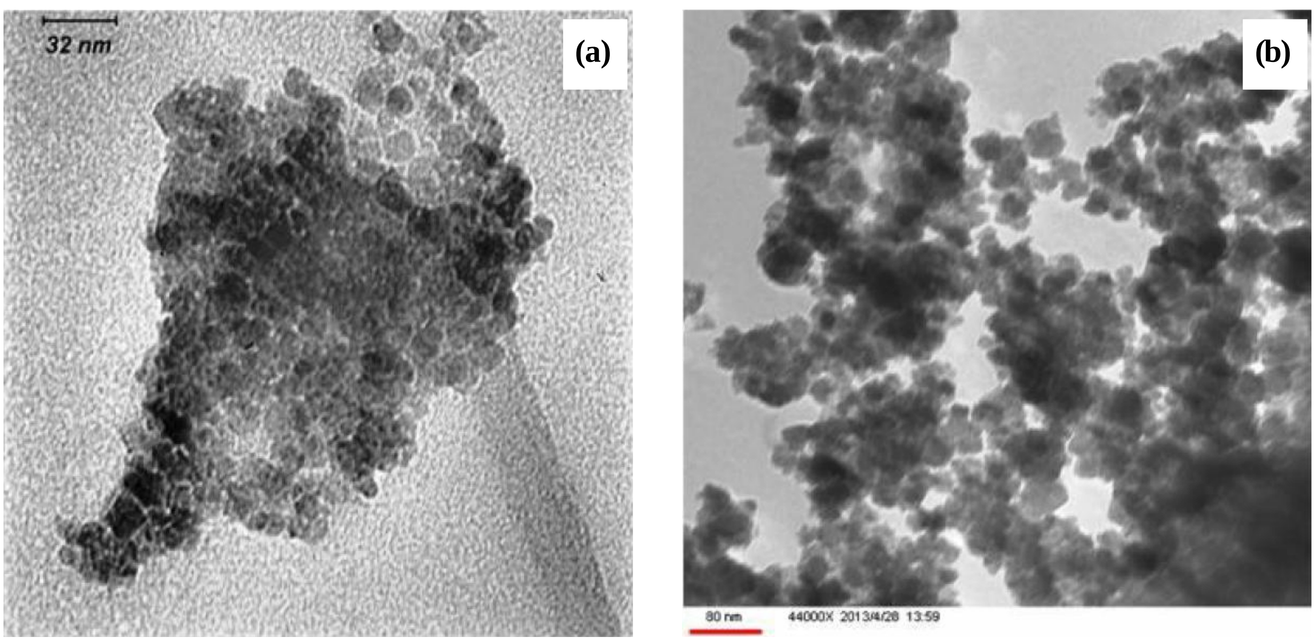

Figure 1 : TEM micrographs of (a) CZF_0 and (b) CZF_1.

X-ray powder diffraction

X-ray diffraction pattern of CZF_0 is shown in Figure 2. Wide spread peaks demonstrated that the average size of crystalline grains is in the nanometer scale. The sample has spinel structure (according to the reference files 22-1086, $CoFe_2O_4$ and 22-1012, $ZnFe_2O_4$). Using of equation (1), the average crystallite size was obtained about 13 nm that is a little smaller than that of result of TEM for bare sample.

FT-IR characterization

To prove the presence of the surface coating, the magnetic nanoparticles pre- and post- DMSA coated were evaluated using the FTIR method (Figure 3). Peaks at 3425 and 1643 cm^{-1} are related to OH bands which indicated the presence of water in the structure of matter. Peaks at 580 and 427 cm^{-1} indicated that the spinel structure was formed and confirmed the result of XRD pattern. Peaks at 928, 1160, 1360 and 1701 cm^{-1} which showed in Figure (3b) indicated that DMSA coated on the CZF-MNPs surface. The FTIR diagrams analysis confirmed the formation of Co-Zn ferrite phase and showed the presence of cover on the surface of nanoparticles and also the presence of water content in the samples.

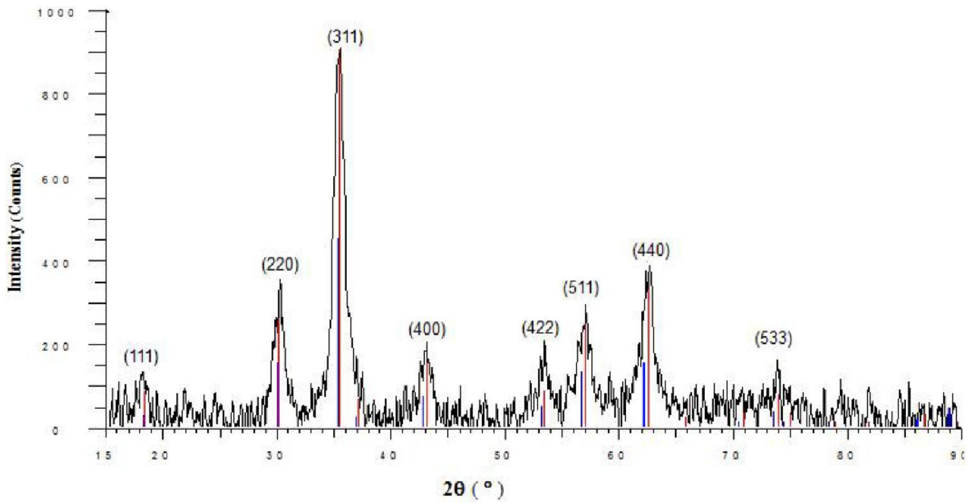

Figure 2 : X-ray diffraction pattern of CZF_0.

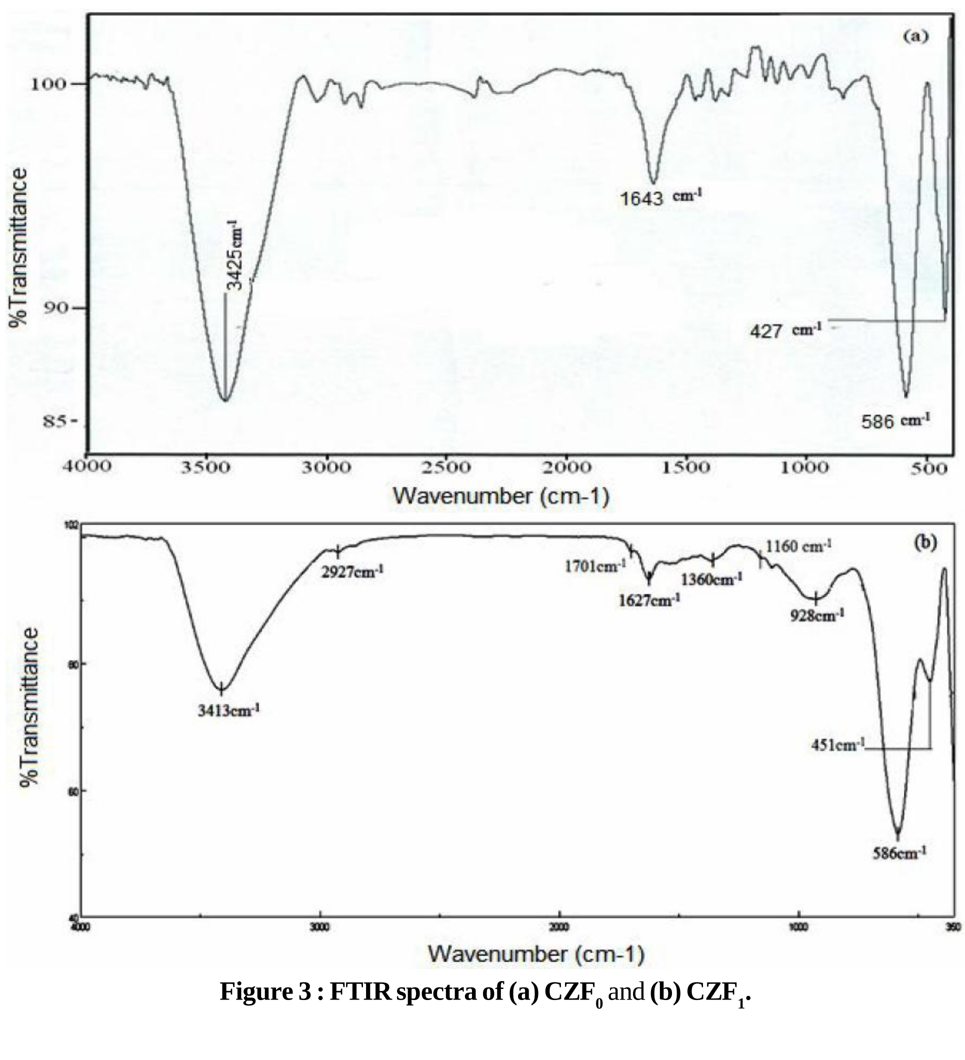

Figure 3 : FTIR spectra of (a) CZF_0 and (b) CZF_1.

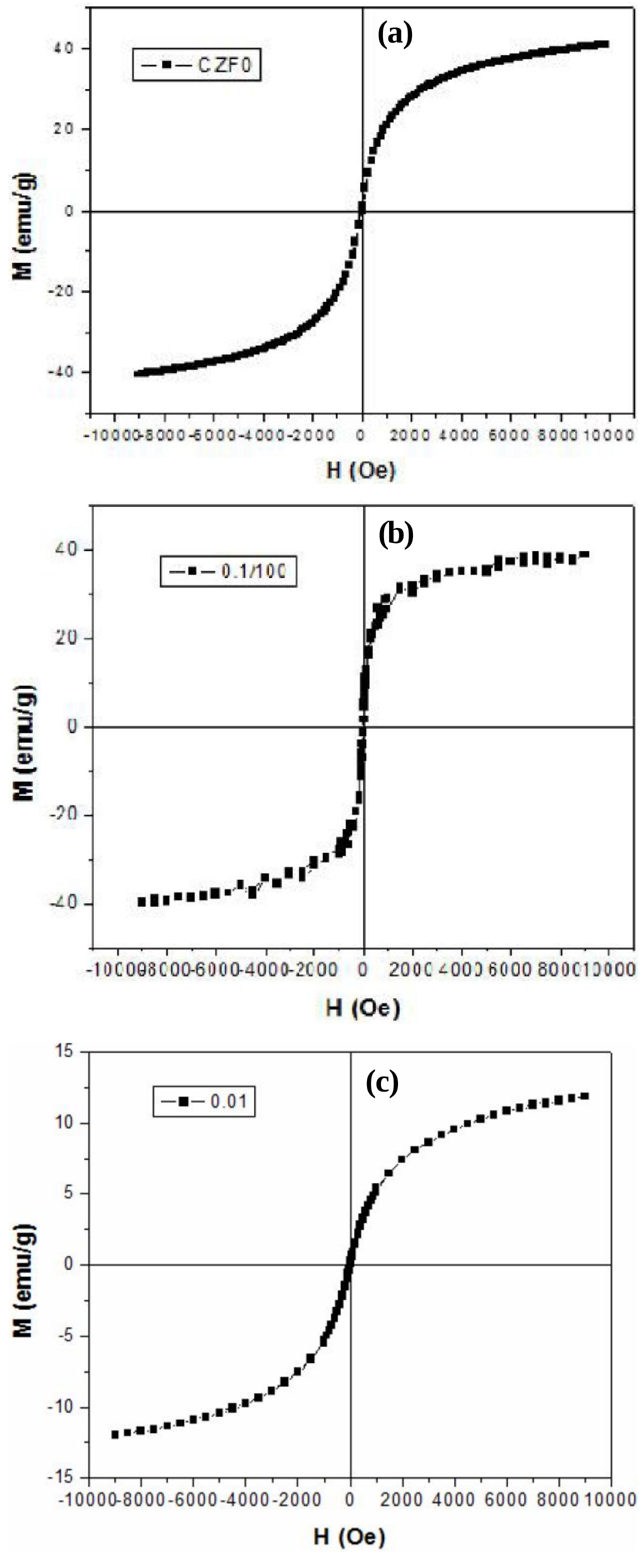

Figure 4 : Magnetization curves of (a) CZF_0, (b) CZF_1 and (c) CZF_2 at room temperature.

Magnetization measurements

The magnetic properties of CZF_0, CZF_1 and CZF_2 powder were measured by AGFM. The plots of magnetization versus magnetic field at room temperature for the samples are shown in Figure 4. The magnetization values at 9 kOe were obtained 40.4, 39.3 and 12.0 emu/g for CZF_0 (Figure 4a), CZF1 (Figure 4b) and CZF_2 (Figure 4c), respectively. All samples did not saturate. But, the magnetization of CZF_1 is close to the bare sample and the magnetization decreased by increasing the concentration of DMSA, that can be due to the formation a thicker coated on the particles. The values of saturation magnetization of the samples were calculated from extrapolation of the curves M versus 1/H. The saturation magnetization of CZF_0, CZF_1 and CZF_2 are 43.1, 42.4 and 13.9, respectively.

Chemical analysis

The concentration of Fe in CZF_0 and CZF_1 are 325 and 225 ppm. This small concentration indicated the presence of DMSA coated on the surface of the bare MNPs.

CONCLUSIONS

Findings showed that Cobalt-zinc ferrite nanoparticles and CZF-MNPs coated with DMSA with a nanoparticle size of approximately 16 nm and 40 nm can be synthesized using co-precipitation method. Nanoparticles which synthesized using this method have some water content. The decrease of magnetization and molar mass loss after coated and chemical analysis of FTIR spectra confirmed the formation of the CZF-MNPs @ DMSA. In other words, DMSA cover is located on the surface of pure CZF-MNPs. The saturation magnetization of coated nanoparticles decreased by increasing the molarity amount of DMSA coated up to 0.01 M. These nanoparticles can be suggested for biomedicine applications due to their small size of less than 100 nm and also high magnetization value. Of course, the cytotoxicity of these synthesized nanoparticles should be studied and verified using of different cell lines.

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ORIGINAL ARTICLE

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