



Coprecipitation Synthesis of CoFe_2O_4 Nanoparticles for Hyperthermia

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ABSTRACT

Cobalt ferrite (CoFe_2O_4) nanoparticles have attracted significantly attentions for spintronics, recording media and bioapplications due to their unique magnetic and chemical properties. In this work, single phase CoFe_2O_4 nanoparticles were synthesized at various coprecipitation temperatures (60, 80 and 90 °C) without post calcination. The effects of oleic acid as surfactant on the microstructure, magnetic properties and heating rate were characterized by X-ray diffraction, infrared spectroscopy, scanning electron microscopy and vibrating sample magnetometry techniques. The small particle size and narrow size distribution were achieved using oleic acid. IR spectra showed the oleic acid molecules adsorbed on particle surface, leading to the lower growth rate and then the smaller nanoparticles. The CoFe_2O_4 nanoparticles showed ferromagnetic behavior. The highest saturation magnetization of 45 emu/g and coercivity of 950 Oe were achieved at the coprecipitation temperature of 80 °C without using oleic acid. However, the saturation magnetization increased from 8 to 37 emu/g with the coprecipitation temperature due to the increase of crystallinity and particle size. The coprecipitated CoFe_2O_4 nanoparticles at 80 °C exhibited the AC heating temperature of 7.5°C and specific loss power of 18.3 W/g under magnetic field of 100 Oe and frequency of 200 kHz. The heat generation mechanism was attributed to the hysteresis loss.

Keywords: CoFe_2O_4 ; Coprecipitation, Magnetic properties, Hyperthermia.

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1. Introduction

Magnetic nanoparticles have become interesting subject of research because of their unique physical and chemical properties in comparison with bulk [1, 2]. Spinel magnetic ferrites (MFe_2O_4 ; $\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Fe}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+}$) have attracted a great attention on account of several remarkable physical properties along with chemical stability and low cost [3]. Among spinel ferrites, cobalt ferrite (CoFe_2O_4) is a well-known semihard magnetic material with the moderate saturation magnetization (80 emu/g) and strong magnetocrystalline anisotropy ($K_1 \approx 2 \times 10^6$ erg/cm³), making it suitable for magnetic recording media, spintronics, magnetic resonance imaging,

drug delivery, hyperthermia, cell separation, etc. [4-6]. Spinel cubic ferrites were constructed of 32 closely packed oxygen atoms with 64 tetrahedral sites and 32 octahedral sites. Only 8 tetrahedral (A) and 16 octahedral [B] sites are occupied for electrical neutrality. The distribution of cation between A- and B-sites determines the type of spinel ferrite. In the normal spinel structure, the A- and B-sites are entirely occupied by the M^{2+} and Fe^{3+} cations, respectively. In the inverse spinel structure, the B-sites are occupied by the M^{2+} cations and half of the Fe^{3+} cations and the other half of the Fe^{3+} cations are in A-sites. In the mixed spinel structure, both M^{2+} and Fe^{3+} randomly occupy

both tetrahedral (A) and octahedral [B] sites [7]. The most physicochemical properties of spinel ferrites depend significantly on the distribution of cations between the A- and B-sites as well as the stoichiometry and synthesis method [8, 9].

Several various synthesis methods such as hydrothermal routes [10], solvothermal [11], thermal decomposition of organic-metal complexes [12] and coprecipitation [13] are employed for preparation of cobalt ferrite nanoparticles. Among these methods, the coprecipitation is a simple, reproducible and accessible route for mass production of magnetic spinel ferrite nanoparticles [14]. The coprecipitation is based on the simultaneous precipitation of hydroxides and oxalates of cations by NaOH or NH₄OH. The coprecipitation is the result of a process of inorganic polycondensation involving the hydrolysis of metal ions in solution and the condensation of hydroxylated complexes, leading to nucleation of metal oxides. Then, the growth of nuclei occurs through the addition of matter [15]. However, the coprecipitated CoFe₂O₄ nanoparticles exhibit the lower crystallinity and wide particle size distribution, due to the uncontrolled aggregation of particles. Therefore, many parameters like the coprecipitation temperature, counter ions, ionic strength, pH and post-calcination temperature have been modified for preparation of the monodisperse cobalt ferrite nanoparticles [16]. Akbari et al. [17] studied the effects of polyvinyl alcohol (PVA) addition on the particle size distribution and heating rate of coprecipitated magnesium ferrite nanoparticles. The saturation magnetization increased and size distribution became narrower using PVA during coprecipitation, due to the redistribution of cations in tetrahedral (A) and octahedral [B] sites.

In this work, the effects of coprecipitation temperature and oleic acid on the structure, particle size and size distribution, magnetic properties and heating rate of cobalt ferrite nanoparticles were reported. It was found that the saturation magnetization decreased using oleic acid due to the reduction of particle size.

2. Experimental procedure

Cobalt chloride (CoCl₂·6H₂O), iron chloride (FeCl₃·6H₂O), sodium hydroxide (NaOH) and oleic acid (C₁₈H₃₄O₂) were purchased from Merck Co.

In the coprecipitation procedure, a mixed aqueous solution was prepared by dissolving required amounts of iron and cobalt chlorides with the molar ratio of Fe³⁺ to Co²⁺ as 2:1, and then was transferred to a burette containing 2 ml of hydrochloric acid. Drops of metal chlorides were added into a reaction vessel containing 1.5 M NaOH solution as a precipitating agent, heated to

the desired temperature (60, 80 and 90 °C). The pH of the reaction solution was fixed at 12 during the process by adding chloric acid or sodium hydroxide solution. Furthermore, the oleic acid (0.5 v/v%) was added into the reaction vessel for investigation of surfactant effect. The resultant precipitations were collected by a strong magnet and then washed with distilled water for several times until the pH reached to neutral and finally the precipitates were dried in an oven at 100 °C for 2 hours.

Phase evolution was analyzed by PANalytical X'pert X-ray diffractometer (XRD) using monochromatic CuKα radiation with a voltage of accelerator 40 kV and a current of 30 mA. The average size of the crystallite in the samples was calculated by measuring the width of the diffracted peak (311) using the Scherrer's equation.

Infrared spectra in the range of 400–4000 cm⁻¹ were measured by Fourier transform infrared (FTIR) spectrometer (8500S SHIMADZU). Microstructure of the as-coprecipitated CoFe₂O₄ powders were observed by scanning electron microscopy (SEM). A vibrating sample magnetometer (VSM) (Meghnatis Daghig Kavir Co., Iran) was also employed to measure the magnetic properties at room temperature.

Induction heating of 20 mg laurate-coated CoFe₂O₄ nanoparticles in 2 mL distilled water solution was performed in a plastic tube using a homemade instrument with 5 cm diameter coil (5 turns). Samples were placed at the center of the coil without any insulation and the applied frequency was 200 kHz at the field amplitude of 100 Oe. Temperature rise (ΔT) was measured using an alcohol thermometer with an accuracy of ±1 °C for three times. The external temperature was 26 °C. Heat dissipation by magnetic nanoparticles under an AC magnetic field was measured in terms of specific loss power (SLP) (W/g) [18]:

$$SLP = C \left(\frac{dT}{dt} \right) \left(\frac{m_s}{m_m} \right) \quad (\text{eq. 1})$$

Where C is specific heat capacity of suspension (4.186 J/(g °C)), (dT/dt) is the initial slope of temperature versus time graph, m_s is the mass of suspension and m_m is the mass of the magnetic material in suspension.

3. Results and discussion

XRD patterns of the as-coprecipitated CoFe₂O₄ nanoparticles are shown in Fig. 1. Single phase CoFe₂O₄ ferrite was formed without any impurity phases at all coprecipitation temperatures. The indexed (111), (220), (311), (400), (422), (511), (440) and (533) peaks are related to the cubic spinel structure (JCPDS card no. 36-0398). Diffraction peaks become narrower and sharper with the increase of coprecipitation temperature, indicating

the increase of crystallinity and crystallite size. The crystallite size increases from 9 to 14 nm with the increase of coprecipitation temperature. However, the as-coprecipitated CoFe_2O_4 powders using oleic acid showed the smaller crystallite size, due to the prevention of the particle agglomeration [19].

IR spectra of the coprecipitated CoFe_2O_4 powders at 80 °C in the presence and absence of oleic acid was shown in Fig. 2. The two absorption bands at 586 and 426 cm^{-1} are related to the stretching vibrations of the M-O bonds in the tetrahedral and octahedral sites of spinel ferrites, respectively [20, 21]. The O-H stretching vibration of physically adsorbed water onto the nanoparticle surface leads

to the broad band between 3600 and 3000 cm^{-1} centered at 3400 cm^{-1} [22]. The absorption bands at about 2924 and 2850 cm^{-1} are assigned to the C-H stretching vibration of absorbed oleic acid coatings on the particle surface. The absorption of the O-H bonds on the surface is reduced during coprecipitation in the presence of oleic acid, may be due to the replacement of oleic acid molecules in the surface of particles [23].

SEM images of the as-coprecipitated cobalt ferrite nanoparticles at 80 °C in the presence and absence of oleic acid are compared in Fig. 3. The average size of as-coprecipitated spherical-like particles without using oleic acid is ~75 nm which

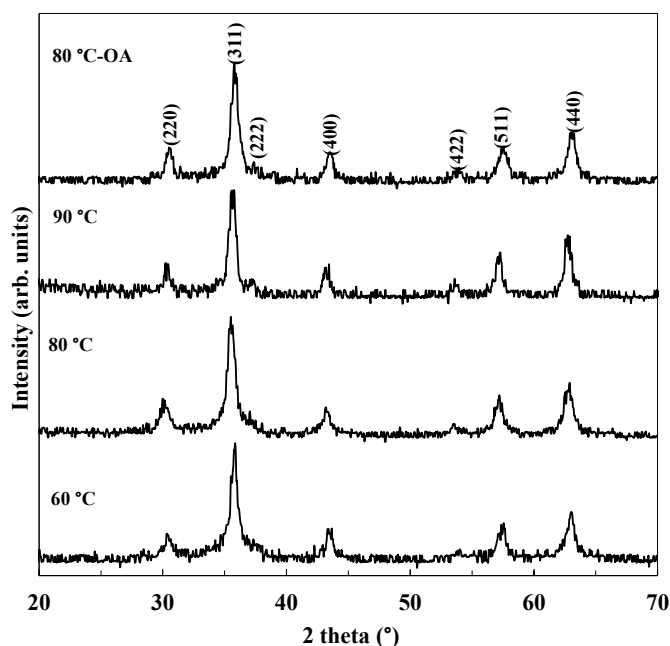


Fig. 1- XRD patterns of the as-coprecipitated CoFe_2O_4 nanoparticles.

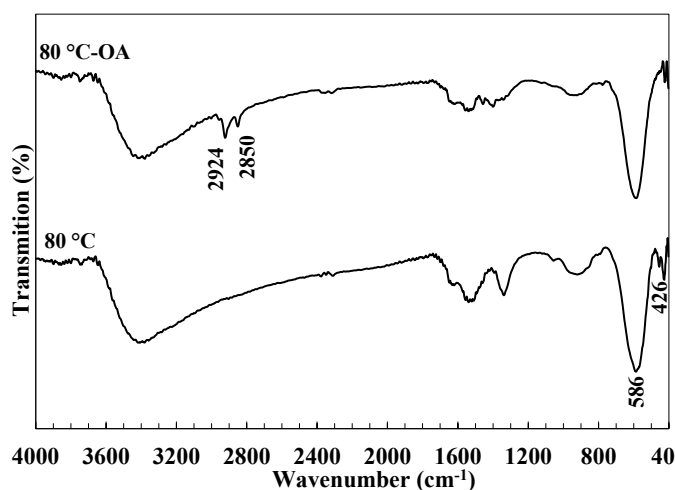


Fig. 2- IR spectra of the CoFe_2O_4 nanoparticles coprecipitated at 80 °C at the presence and absence of oleic acid.

decreased to ~ 40 nm for the oleic acid assisted coprecipitation. Furthermore, the particle size distribution becomes narrower using oleic acid. It can be attributed to the surface adsorption of oleic acid molecules, lowering the growth rates of the particles and leading to the formation of smaller nanoparticles [24].

The magnetization curves of the as-coprecipitated CoFe_2O_4 nanoparticles are shown in Fig. 4. Magnetic properties are also listed in Table 1. The as-coprecipitated CoFe_2O_4 nanoparticles show ferrimagnetic behavior. With the increase of coprecipitation temperature from 60 to 80 °C, the saturation magnetization (M_s) of CoFe_2O_4 nanoparticles increases from 37 to 45 emu/g. However, in spite of higher crystallinity for coprecipitation at 90 °C, the saturation magnetization decreases to 40 emu/g, may be due to the cation redistribution. The as-coprecipitated CoFe_2O_4 nanoparticles using oleic acid exhibit the lower saturation magnetization for all

reaction temperatures. However, their saturation magnetizations continuously increases from 8 to 37 emu/g and are lower than those of unassisted coprecipitation. The coercivity (H_c) increases from 653 to 972 Oe and then decreases to 302 Oe without using oleic acid. The H_c decreases from 750 to 205 Oe for oleic acid assisted coprecipitation, due to the particles growth with reaction temperature. In other words, the coercivity increases with the decrease of particle size, due to the increase of domain walls as pinning factors for movement of magnetic domains [25].

Fig. 5 shows the temperature versus time curve for the as-coprecipitated CoFe_2O_4 nanoparticles at 80 °C using oleic acid under the applied magnetic field of 100 Oe and the frequency of 200 kHz. The AC heating temperature (ΔT) and SLP are 7.5 °C and 18.3 W/g, respectively. It is well-known the magnetic nanoparticles generate heat in alternating magnetic field via eddy current, hysteresis loss and relaxation (Brownian and Neel)

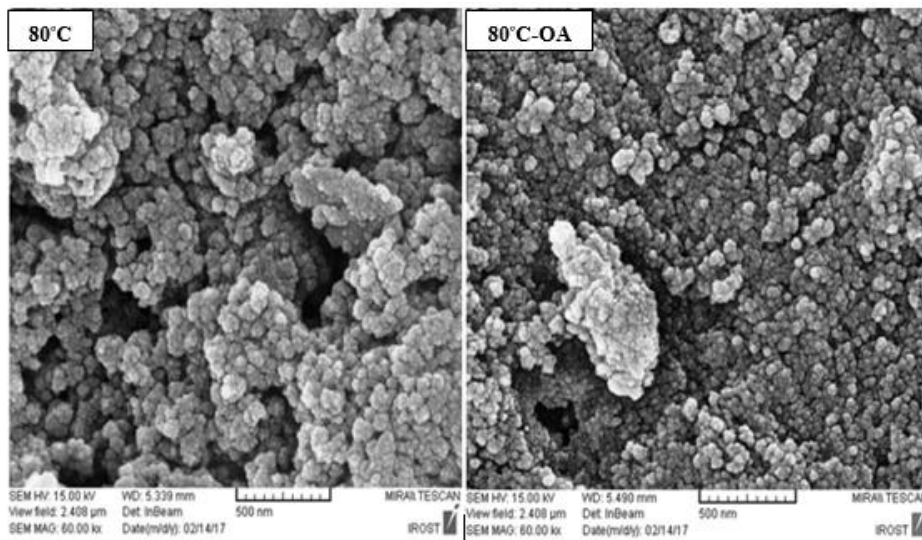


Fig. 3- SEM micrographs of the CoFe_2O_4 powders coprecipitated at 80 °C at the presence and absence of oleic acid.

Table 1. Magnetic properties of the as-coprecipitated CoFe_2O_4 nanoparticles

Coprecipitation Temperature (°C)	Surfactant	M_s (emu/g)	H_c (Oe)
60	-	37	653
80	-	45	972
90	-	40	302
60	OA	8	750
80	OA	37	296
90	OA	37	205

mechanisms. The significant resistive heating is produced by eddy currents induced by rapidly changing magnetic flux [26]. The eddy currents are only produced in centimeter sized particles. The hysteresis loss is due to the irreversible magnetization processes in an AC magnetic field. The hysteresis loss is only for larger particle size than that of superparamagnetic limit. However, the superparamagnetic nanoparticles produce heat by Brownian relaxation (when the particle spins to align itself with the magnetic field) and Neel relaxation (when the magnetic moment spins within the crystal structure of particle). The heating mechanism of coprecipitated CoFe_2O_4 nanoparticles at 80 °C can be attributed to the hysteresis loss, due to their larger particle size (~40 nm) than that superparamagnetic limit (~10 nm) [27].

4. Conclusions

In this study, single phase cobalt ferrite nanoparticles with a particle size of ~70 nm were synthesized by co-precipitation method at 80 °C. The particle size decreased to ~40 nm and size distribution became narrower using oleic acid. The highest saturation magnetization of 45 emu/g and coercivity of 950 Oe were achieved at 80 °C without using oleic acid, due to the higher crystallinity. The coprecipitated CoFe_2O_4 nanoparticles at 80 °C exhibited the AC heating temperature of 7.5 °C and specific loss power of 18.3 W/g under magnetic field of 100 Oe and frequency of 200 kHz.

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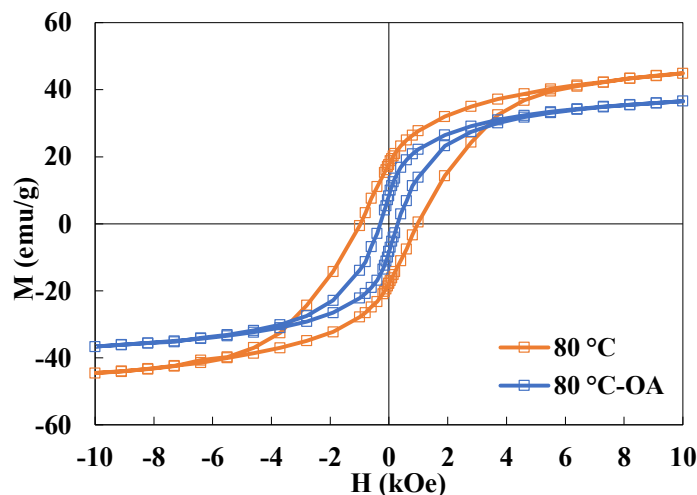


Fig. 4- SEM micrographs of the as-coprecipitated CoFe_2O_4 nanoparticles at the presence and absence of oleic acid.

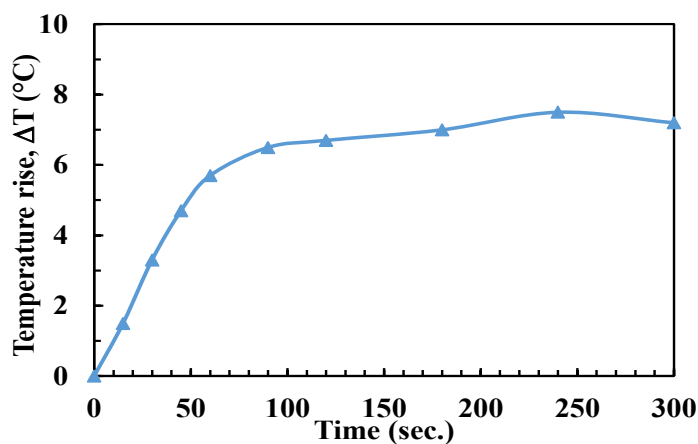


Fig. 5- Temperature versus time curves for the CoFe_2O_4 nanoparticles coprecipitated at 80 °C without using oleic acid.

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