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Original Research

Synthesis and Characterization of Cobalt Ferrite Nanoparticles

Raghavender AT

Department of Physics, College of Natural and Computational Sciences, Wollega University,
Post Box No: 395, Nekemte, Ethiopia

Abstract

Cobalt ferrite can be synthesized using several techniques. However, to have wide applications in electronic, medical fields etc., the synthesis technique should be simple and inexpensive. The synthesis technique used to prepare nanoparticles should not consume lot of time and energy. Also it should yield narrow particle size distribution and homogeneity in the prepared material. It was observed that surface modification such as with silica coating on the cobalt ferrite will have significant effect on the structural and magnetic properties. It is also observed that, silica coated nanoparticles could be used in biomedical applications (Hong et al., 2013). In this work we have chosen sol-gel method to synthesize pure cobalt ferrite ($CoFe_2O_4$) and silica coated ($CoFe_2O_4$ / SiO_2) nanoparticles. To observe the effect of silicate coating on the structural and magnetic properties of $CoFe_2O_4$ we have carried out the present study. $CoFe_2O_4$ nanoparticles were synthesized with SiO_2 coating and in pure form by sol-gel method. The obtained particle sizes were 24 and 26 nm in both the cases. The X-ray diffraction patterns showed the formation of $CoFe_2O_4$ spinel structure without any traces of SiO_2 in the prepared samples. The Infrared spectra showed the bands corresponding to tetrahedral and octahedral sites as feature of typical spinel ferrites and also band due to SiO_2. The particle size and morphology of $CoFe_2O_4$ / SiO_2 was found to be uniform but in the case of pure $CoFe_2O_4$ somewhat agglomerated which is accounted for magnetization of ferrites. The magnetization value for $CoFe_2O_4$ / SiO_2 showed a drastic decrease when compared to pure $CoFe_2O_4$ due to presence of non-magnetic coating layer.

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***Corresponding Author:**

Raghavender AT

E-mail:
raghavi9@gmail.com

INTRODUCTION

Research in coating of $CoFe_2O_4$ magnetic nanoparticles for biomedical applications has increased in recent years due to their potential in a variety of applications such as targeted drug delivery for gene therapy, genetic screening and toxicity cleansing (Calero-DdelC *et al.,* 2007; Sahoo *et al.,* 2003; Gould, 2004), magnetic cell sorting schemes (Ramchand *et al*., 2001), and binding of magnetic nanoparticles to antibodies to label molecules and other biological targets from blood or other fluid and tissue samples (Sahoo *et al.,* 2003). The applications of $CoFe_2O_4$ are strongly influenced by its magnetic properties. For biomedical applications, $CoFe_2O_4$ nanoparticles are required to have a narrow size distribution, high magnetization values. A great variety of techniques has been used to obtain magnetic nanoparticles such as reverse micelle preparation (Calero-DdelC *et al.,* 2007), hydrothermal (Li *et al.,* 2010; Baruwati *et al.,* 2008), coprecipitation (Zi *et al.,* 2009), microemulsion (Lee *et al.,* 2005), reduction–oxidation route (Gu *et al.,* 2008), continuous-flow microreactors (Hassan e*t al.,* 2012) etc., but the main difficulty of many synthesis methods is that the prepared nanoparticles are mostly agglomerated with poor size and shape control, which greatly restrict their applications (Bhattacharyya *et al.,* 2005). The SiO_2 coated $CoFe_2O_4$ nanoparticles were found to have significant magnetization values of 43.3 emu/g which is expected to have potential application in biomedicine. Because of its high coercivity and anisotropy constant, cobalt ferrite nanoparticles have been widely studied. High coercivity gives cobalt ferrite potential in high-capacity magnetic storage, whereas high magnetic anisotropy forces the particles to relax through the Brownian mechanism, giving them potential applications as sensors (Calero-DdelC *et al.,* 2007). In our previous work (Hong *et al.,* 2013), we presented the results and applications of only silica coated $CoFe_2O_4$ in the biomedical applications. In this work, firstly we want to investigate the effect of silica coating on the structural and magnetic properties of CoFe2O4 nanoparticles. And secondly, the observed results would be used to see the effect of pure $CoFe_2O_4$ and $CoFe_2O_4$ / SiO_2 nanoparticles on the biomedical applications which will be investigated and reported at later stage.

MATERIALS AND METHODS

Nanocrystalline $CoFe_2O_4$ with SiO_2 coating and uncoated was prepared by sol-gel method. The A.R grade citric acid ($C_6H_8O_7.H_2O$), Cobaltous nitrate hexahydrate $Co(NO_3)_2.6H_2O$, Ferric nitrate nonahydrate $Fe(NO_3)_3$. $9H_2O$, TEOS (Tetraethoxysilane) and ethanol from Sigma Aldrich (≥99%) were used as starting materials. Nanocrystalline pure $CoFe_2O_4$ were prepared using sol-gel technique (Raghavender *et al.,* 2007). The molar ratio of metal nitrates to citric acid was taken as 1:3. The metal nitrates were dissolved together in a minimum amount of de-ionized water to get a clear solution. An aqueous solution of citric acid was mixed with metal nitrates solution, then ammonia solution was slowly added to adjust the pH at 7. The mixed solution was moved on to a hot plate with continuous stirring at 90 °C. During evaporation, the solution became viscous and finally formed a very viscous brown gel. When finally all remaining water was released from the mixture, the sticky mass began to bubble. After several minutes, the gel automatically ignited and burnt with glowing flints. The decomposition reaction would not stop before the whole citrate complex was consumed. The auto-ignition was completed within a minute, yielding the brown-colored ashes termed as a precursor. Nanocrystalline $CoFe_2O_4$ / SiO_2 were prepared by modified sol-gel method. In this process all the metal nitrates were dissolved in minimum amount of deionized water. Ammonia solution was slowly added to adjust the pH at 7. The mixed solution was moved on to a hot plate with continuous stirring at 90 ^{0}C. When water level was reduced then 10 ml of ethanol containing 10 μL of TEOS (Tetraethoxysilane) was added. A green gel was formed after couple of hours. When all the water molecules evaporated completely, the gel automatically ignited with glowing flints. The entire synthesis process finished within few minutes yielding black / brown colored ashes. The obtained powders of $CoFe_2O_4$ and SiO_2 coated $CoFe_2O_4$ were heat treated separately at 500 ^{0}C for five hours.

Structural characterization of the obtained ferrite powders were carried out using Inel XRD (France) system with Ni filter using CoKα radiation (wavelength, λ = 1.78894 Å).The crystallite size was calculated by using the Scherrer formula after subtracting instrumental broadening. Transmission IR Spectra were obtained by Perklin Elmer FTIR (USA) spectrometer using KBr pellet. The particle size and morphology was verified using FEI Quanta (USA) FEG 200 High Resolution Scanning Electron Microscope (HR-SEM). Hysteresis loops were obtained from a Lakeshore vibrating sample magnetometer (USA) VSM 7410.

RESULTS AND DISCUSSIONS

Figure 1 shows X-ray diffraction patterns of nano-crystalline pure $CoFe_2O_4$ and $CoFe_2O_4$ / SiO_2. The XRD pattern clearly indicates that, the prepared samples were exclusively of cubic spinel structure. A close examination of XRD patterns reveals that, the diffraction peaks are broad which an indication of nanocrystallinity. No secondary phases due to SiO_2 were observed in the XRD spectra. The particle size in the case of pure $CoFe_2O_4$ was found to be 26 nm and that of $CoFe_2O_4$ / SiO_2 is 24 nm (Table 1). From the XRD (Figure 1b) it is observed that, the intensity of SiO_2 coated $CoFe_2O_4$ was found to be very less than pure $CoFe_2O_4$. This may be due to the presence of non-magnetic layer. The lattice parameters did not show any considerable change, but the obtained values were smaller compared to bulk $CoFe_2O_4$.

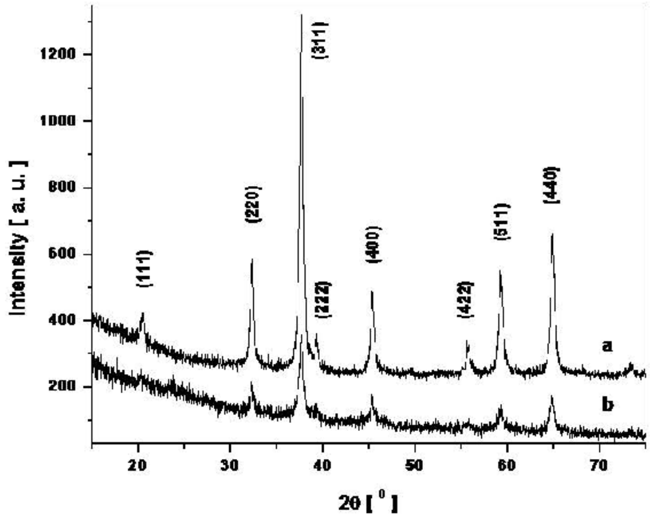


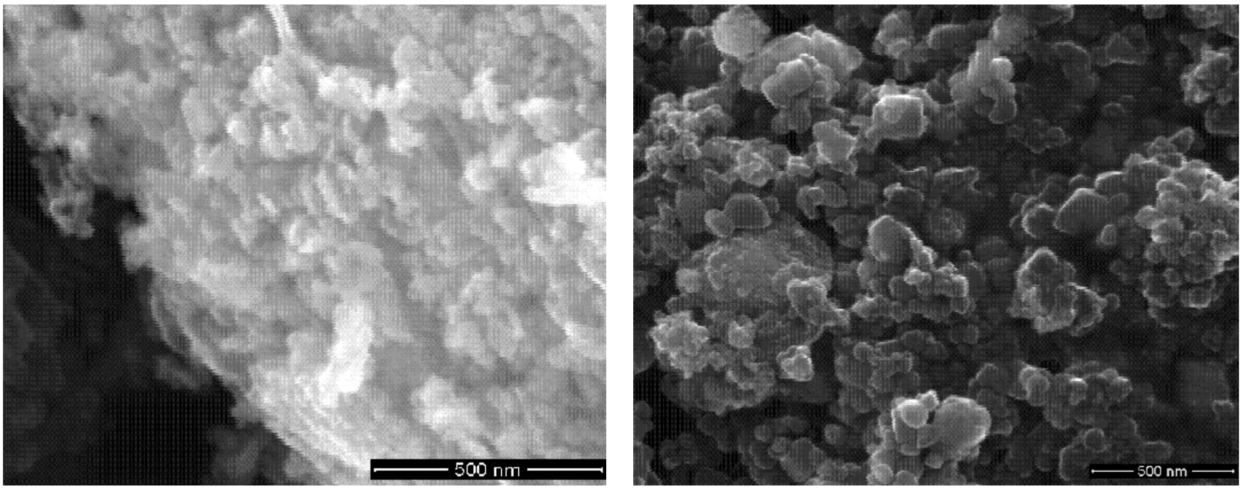
Figure 1: X-ray diffraction patterns of (a) pure $CoFe_2O_4$ nanoparticles (b) $CoFe_2O_4$ / SiO_2 nanoparticles annealed at 500 ^{0}C.

Table 1: Particle size (*D*), Magnetization (M), Coercive field (H_C) and remnant magnetization (M_r), squareness ratio (M_r/M).

Sample	D (nm)	M (emu/g)	H_C (Oe)	M_r (emu/g)	M_r/M
$CoFe_2O_4$	26	72.5	1372	30.2	0.43
$CoFe_2O_4$ /SiO_2	24	43.3	1821	21.3	0.49

HR-SEM images for pure $CoFe_2O_4$ and $CoFe_2O_4$/ SiO_2 are presented in Figure 2. The micrograph (Figure 2(a)) of pure $CoFe_2O_4$ suggests that there is agglomeration among the particles, which are associates to the magnetization of ferrites. The micrograph of $CoFe_2O_4$/ SiO_2 as shown in Figure 2(b) distinctly exhibit narrow grain size distribution and present mainly sphericity. It can be clearly seen that a SiO_2 is enwrapped on the $CoFe_2O_4$ surface forming a core-shell structure of nanocomposites.

The IR spectra of pure $CoFe_2O_4$ and $CoFe_2O_4$ / SiO_2 nanoparticles are shown in Figure 3. In Figure 3 (a) for the $CoFe_2O_4$ spectra exhibits the characteristic bands corresponding to typical spinel ferrites (Waldron, 1955). The band ν_1 at 573 cm^{-1} arises due to tetrahedral complexes (the stretching vibrations of the tetrahedral metal-oxygen bond) and ν_2 at 369 cm^{-1} is due to octahedral complexes (metal-oxygen vibrations in octahedral sites). As seen in Figure 3(b) for $CoFe_2O_4$ / SiO_2 also exhibits bands corresponding to tetrahedral and octahedral sites at ν_1 = 541 cm^{-1} and ν_2 = 318 cm^{-1} and also stretching vibration band of Si – O - Si at 464 cm^{-1} which indicates the formation of silica shells (Fu *et al.,* 2007; Monte *et al.,* 1997). These results indicate that the product has a core-shell structure, which is combined through the chemical bonding. From Figure 3(b) we draw a conclusion that $CoFe_2O_4$ nanoparticles are well coated with SiO_2. The band positions ν_1 and ν_2 were sensitive to preparation conditions and the type of chemical environments due to change in its positions.



(a) (b)

Figure 2: SEM micrograph of (a) pure $CoFe_2O_4$ nanoparticles (b) $CoFe_2O_4$ / SiO_2 nanoparticles.

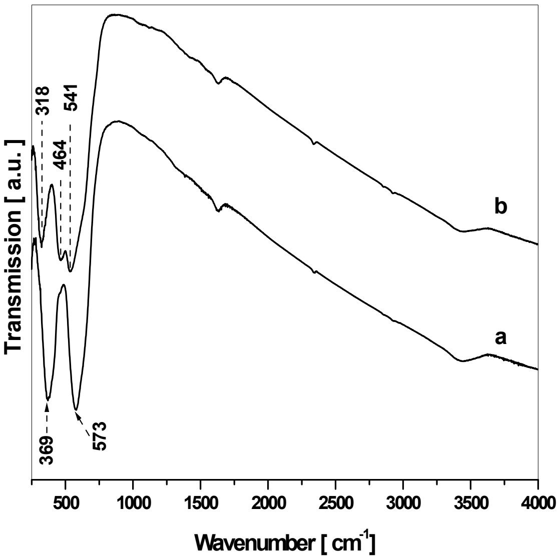


Figure 3: IR spectra of (a) pure $CoFe_2O_4$ nanoparticles (b) $CoFe_2O_4$ / SiO_2 nanoparticles.

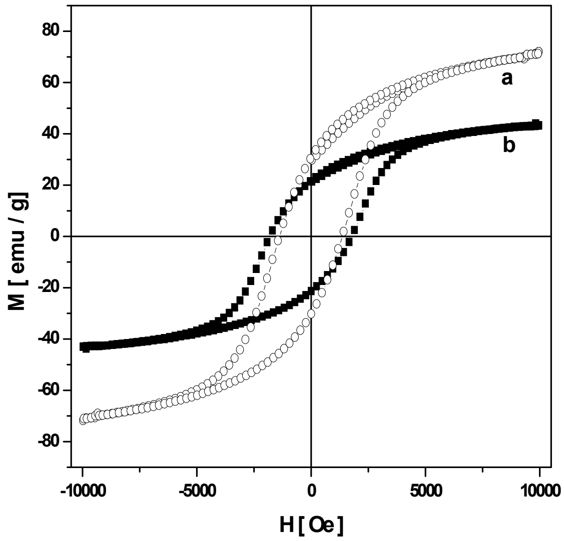


Figure 4: Hysteresis loop at room temperature of (a) pure $CoFe_2O_4$ nanoparticles (b) $CoFe_2O_4/SiO_2$ nanoparticles

The hysteresis loops of pure $CoFe_2O_4$ and $CoFe_2O_4$ / SiO_2 nanoparticles are shown in Figure 4. From the hysteresis loops the measured parameters such as magnetization (*M*), coercive field (H_C) and remnant magnetization (M_r) are as presented in Table 1. It is clearly seen from Figure 4(b) that the value of magnetization decreased drastically with SiO_2 coating on $CoFe_2O_4$ nanoparticles when compared to Figure 4(a) for pure $CoFe_2O_4$. The decrease in the magnetization in the case of $CoFe_2O_4/SiO_2$ nanoparticles may be due to non-magnetic coating layer on the sample volume. In addition, the non-magnetic coating layer can be considered as a magnetically dead layer at the surface, thus affecting the uniformity or magnitude of magnetization due to quenching of surface moments (Ma *et al.,* 2005; Kaiser *et al.,* 1970). The coercivity for pure $CoFe_2O_4$ nanoparticles is found to be1372 Oe when compared to $CoFe_2O_4$ / SiO_2 nanoparticles of 1821 Oe (Table 1). This discrepancy may be due to coating of SiO_2 on $CoFe_2O_4$, which causes the effect on the surface layer (Lien *et al.,* 2008). The remnant magnetization showed the similar trend as magnetization. The remnant magnetization for $CoFe_2O_4$ / SiO_2 nanoparticles was small compared to pure $CoFe_2O_4$ nanoparticles. The squareness ratio for $CoFe_2O_4$/ SiO_2 nanoparticles showed highest coercivity of 0.49. The results of lower magnetization is attributed to the diamagnetic contribution of SiO_2 shells covering $CoFe_2O_4$ nanoparticles, which weakens the magnetic moment due to the occurrence of thicker $CoFe_2O_4$ / SiO_2 shells.

CONCLUSIONS

Cobalt ferrite nanoparticles with and without SiO_2 coating were synthesized by sol-gel method with particle sizes 24 nm and 26 nm. The X- ray diffraction patterns confirmed the formation of single phase $CoFe_2O_4$ ferrites. The infrared spectra showed the bands corresponding to tetrahedral and octahedral sites and also band due to SiO_2. The particle size and morphology of $CoFe_2O_4$ / SiO_2 was found to be uniform but in the case of pure $CoFe_2O_4$ somewhat agglomerated which was accounted for magnetization of ferrites. The magnetization value for $CoFe_2O_4/SiO_2$ showed very less value than pure $CoFe_2O_4$ due to presence of non-magnetic coating layer. The prepared nanoparticles will be used for biomedical applications in continuation to our previous work (Hong *et al.,* 2013). Also the effect of pure $CoFe_2O_4$ and $CoFe_2O_4$ / SiO_2 nanoparticles on the biomedical applications will be further investigated.

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