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$_2$O$_4$) and silica coated (CoFe$_2$O$_4$ / SiO$_2$) nanoparticles. To observe the effect of silicate coating on the structural and magnetic properties of CoFe$_2$O$_4$ we have carried out the present study. CoFe$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ / SiO$_2$ was found to be uniform but in the case of pure CoFe$_2$O$_4$ somewhat agglomerated which is accounted for magnetization of ferrites. The magnetization value for CoFe$_2$O$_4$ / SiO$_2$ showed a drastic decrease when compared to pure CoFe$_2$O$_4$ due to presence of non-magnetic coating layer.

INTRODUCTION

Research in coating of CoFe$_2$O$_4$ 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, magnetic 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$_2$O$_4$ are strongly influenced by its magnetic properties. For biomedical applications, CoFe$_2$O$_4$ 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 et 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$_2$O$_4$ 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$_2$O$_4$ in the biomedical applications. In this work, firstly we want to investigate the effect of silica coating on the structural and magnetic properties of CoFe$_2$O$_4$ nanoparticles. And secondly, the observed results would be used to see the effect of pure CoFe$_2$O$_4$ and CoFe$_2$O$_4$ / SiO$_2$ nanoparticles on the biomedical applications which will be investigated and reported at later stage.
MATERIALS AND METHODS

Nanocrystalline CoFe$_2$O$_4$ with SiO$_2$ coating and uncoated was prepared by sol-gel method. The AR grade citric acid (C$_6$H$_{12}$O$_7$·H$_2$O), Cobaltous nitrate hexahydrate Co(NO$_3$)$_2$·6H$_2$O, Ferric nitrate nonahydrate Fe(NO$_3$)$_3$·9H$_2$O, TEOS (Tetraethoxysilane) and ethanol from Sigma Aldrich (≥99%) were used as starting materials. Nanocrystalline pure CoFe$_2$O$_4$ 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$_2$O$_4$ / 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 °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$_2$O$_4$ and SiO$_2$ coated CoFe$_2$O$_4$ were heat treated separately at 500 °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 Perkin 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 nanocrystalline pure CoFe$_2$O$_4$ and CoFe$_2$O$_4$ / 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$_2$O$_4$ was found to be 26 nm and that of CoFe$_2$O$_4$ / SiO$_2$ is 24 nm (Table 1). From the XRD (Figure 1b) it is observed that, the intensity of SiO$_2$ coated CoFe$_2$O$_4$ was found to be very less than pure CoFe$_2$O$_4$. 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$_2$O$_4$.

HR-SEM images for pure CoFe$_2$O$_4$ and CoFe$_2$O$_4$ / SiO$_2$ are presented in Figure 2. The micrograph (Figure 2(a)) of pure CoFe$_2$O$_4$ suggests that there is agglomeration among the particles, which are associated to the magnetization of ferrites. The micrograph of CoFe$_2$O$_4$ / 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$_2$O$_4$ surface forming a core-shell structure of nanocomposites.

The IR spectra of pure CoFe$_2$O$_4$ and CoFe$_2$O$_4$ / SiO$_2$ nanoparticles are shown in Figure 3. In Figure 3 (a) for the CoFe$_2$O$_4$ spectra exhibits the characteristic bands corresponding to typical spinel ferrites (Waldron, 1955). The band $v_1$ at 573 cm$^{-1}$ arises due to tetrahedral complexes (the stretching vibrations of the tetrahedral metal-oxygen bond) and $v_2$ at 369 cm$^{-1}$ is due to octahedral complexes (metal-oxygen vibrations in octahedral sites). As seen in Figure 3(b) for CoFe$_2$O$_4$ / SiO$_2$ also exhibits bands corresponding to tetrahedral and octahedral sites at $v_1$ = 541 cm$^{-1}$ and $v_2$ = 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$_2$O$_4$ nanoparticles are well coated with SiO$_2$. The band positions $v_1$ and $v_2$ were sensitive to preparation conditions and the type of chemical environments due to change in its positions.

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$_2$O$_4$ | 26     | 72.5      | 1372       | 30.2          | 0.43    |
| CoFe$_2$O$_4$ /SiO$_2$ | 24     | 43.3      | 1821       | 21.3          | 0.49    |
The hysteresis loops of pure CoFe$_2$O$_4$ and CoFe$_2$O$_4$/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$_2$O$_4$ nanoparticles when compared to Figure 4(a) for pure CoFe$_2$O$_4$. The decrease in the magnetization in the case of CoFe$_2$O$_4$/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$_2$O$_4$ nanoparticles is found to be 1372 Oe when compared to CoFe$_2$O$_4$/SiO$_2$ nanoparticles of 1821 Oe (Table 1). This discrepancy may be due to coating of SiO$_2$ on CoFe$_2$O$_4$, 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$_2$O$_4$/SiO$_2$ nanoparticles was small compared to pure CoFe$_2$O$_4$ nanoparticles. The squareness ratio for CoFe$_2$O$_4$/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$_2$O$_4$ nanoparticles, which weakens the magnetic moment due to the occurrence of thicker CoFe$_2$O$_4$/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$_2$O$_4$ 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$_2$O$_4$/SiO$_2$ was found to be uniform but in the case of pure CoFe$_2$O$_4$ somewhat agglomerated which was accounted for
magnetization of ferrites. The magnetization value for CoFe$_2$O$_4$/SiO$_2$ showed very less value than pure CoFe$_2$O$_4$ 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$_2$O$_4$ and CoFe$_2$O$_4$ / SiO$_2$ nanoparticles on the biomedical applications will be further investigated.

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