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An investigation on synthesis and magnetic properties of nanoparticles of Cobalt Ferrite coated with SiO$_2$

ABSTRACT

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SiO$_2$-coated Cobalt Ferrite (CoFe$_2$O$_4$) nanoparticles were obtained by the hydrolysis of tetraethylorthosilicate in the presence of CoFe$_2$O$_4$ nanoparticles in co-precipitation. The effects of SiO$_2$coating on the magnetic properties of CoFe$_2$O$_4$ nanoparticles were investigated. The structural, morphological and magnetic properties of as-prepared sample were characterization by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectra, transmission electron microscopy (TEM), Field emission scanning electron microscopy/energy dispersive x-ray analysis (FESEM-EDAX) and magnetic measurements were investigated using vibrating sample magnetometer (VSM). The morphology analysis confirmed that the obtained composite nanoparticles consisted of CoFe$_2$O$_4$ coated by SiO$_2$. It was shown that the saturation magnetization and coercivity of CoFe$_2$O$_4$ decreased after SiO$_2$ coating, which can be interpreted by the interparticle dipole-dipole interactions related to the magnetic particle volume fraction in the composite nanoparticles.

Keywords: *Synthesis; Magnetic properties; SiO$_2$-coated cobalt ferrite; Nanoparticles; X-ray diffraction (XRD); Energy dispersive*.

INTRODUCTION

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Magnetic NPs have attracted much interest because of its extensive applications in the past decades. It was widely used in magnetic resonance imaging (MRI), drug targeted therapy, bioactive molecule separation such as enzyme and protein [1-4]. Among these magnetic NPs, spinel ferrite nanoparticles have attracted much attention because of their electronic, magnetic, and catalytic properties, all of which are different from those of their bulk counterparts. Among spinel ferrites, re in which, cobalt ferrite (CoFe$_2$O$_4$) has an inverse spinel structure in which, in the ideal state, all Co^{2+} ions are in octahedral sites, and Fe^{3+} ions are equally distributed between tetrahedral and octahedral sites.

Cobalt ferrite has been widely studied due to its high electromagnetic performance, excellent chemical stability, mechanical hardness, high coercivity, and moderate saturation magnetization, which make it a good candidate for the electronic components used in computers, recording devices and magnetic cards [5-6]. These applications depend on its unique magnetic properties, such as superparamagnetism. Besides, the crystallinity, size, monodispersity and size distribution of magnetic NPs have critical influence on the magnetic properties of as-prepared NPs. In the present decade, core/shell structured nanoparticles have received much attention, due to their enhanced combination of optical, electronic, and magnetic properties compared to those of single-component nanomaterials [7]. Thus, coating magnetic nanoparticles with silica is becoming a promising. Silica and its derivatives coated onto the surfaces of magnetic nanoparticles may help to change their surface properties. With the appropriate coating, the magnetic dipolar attraction between magnetic nanoparticles may be screened thus minimizing or even preventing aggregation. The coating film could also provide a chemically inert layer for the nanoparticles, which is particularly useful in biological systems [8]. Also, silica-coated magnetic nanoparticles can be easily allowed to conjugate its surface with various functional groups [9].In this article, we developed an effective method for the preparation of $CoFe_2O_4/SiO_2$ nanoparticles through the hydrolysis of tetraethylorthosilicate in co-precipitation, where $CoFe_2O_4$ was synthesized by a soft chemistry method [10]. The effects of the SiO_2 coating on the magnetic properties of $CoFe_2O_4$ nanoparticles were investigated on the basis of the structure characterization and morphology analysis.

EXPERIMENTAL

Materials

All the reagents were of analytical grade and used as received without further purification, including $CoCl_2.6H_2O$, $FeCl_3.6H_2O$, ethanol, NaOH, ammonia solution (25%), cetyltrimethylammonium bromide (CTAB) and tetraethyl orthosilicate (TEOS). Deionized water was used as a solvent.

Preparation of samples

• **Preparation of $CoFe_2O_4$ nanoparticles**

The $CoFe_2O_4$ nanoparticles were synthesized by coprecipitation method. 1 g of CTAB was dissolved in 20 ml of distilled water. Then 5 ml of sodium hydroxide solution (3 M) was added into the CTAB solution. Subsequently, the mixture of 2.5 ml of $CoCl_2.6H_2O$ (0.5 M) and 5 ml of $FeCl_3.6H_2O$ solution (0.5 M) was dripped into the CTAB solution with dripping rate fixed under the magnetic stirring and nitrogen protection. During the dripping process, the solution was gradually changed to black. The resulting black solution was maintained at 70^0C for 1 h and then the solution was cooled to room temperature. Finally, the stable colloidal solution was obtained and nanoparticles were separated by centrifugation, washed with distilled water and ethanol, finally dried at room temperature. It is reasonable to assume that growth and nucleation reaction between $FeCl_3$ and $CoCl_2$ would take place following the reaction mechanism below:

$$2FeCl_3 \cdot 6H_2O + CoCl_2 \cdot 6H_2O + 8NaOH \rightarrow CoFe_2O_4 + H_2O$$
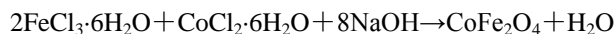
• **Preparation of $CoFe_2O_4/SiO_2$ nanoparticles**

Silica-coated magnetic nanoparticles were prepared using the modified Stöber method. The particles were dispersed in 200 mL of ethanol, then 2 mL of 25% ammonia, 20 mL of deionized water and 2 mL of TEOS were added in that order. The mixture was degassed and then stirred vigorously at 50^oC for 3 h under nitrogen gas to obtain the core/shell $CoFe_2O_4/SiO_2$ nanoparticles were separated using external magnet, and washed with ethanol and water several times. The samples have been dried at 40°C for 24 h.

Characterization

The powder XRD was performed at room temperature with a PW 1800 (PHILIPS) X-ray diffractometer equipped with a Cu Ka radiation source (k = 0.154056 nm). The lattice constant and the average crystallite size were determined by the positions and full width at half maximum (FWHM) of the (311) peaks by using Scherrer formula. The element analysis was carried out by an energy dispersive X-ray analysis (EDAX) on a Field emission scanning electron microscopy (FESEM, Hitachi F4160 oxford instrument). The morphology

of the particles was observed by a transmission electron microscope (TEM) (JEM2010). For characterizing the likely impure phase of the residual organic materials that cannot be detected by XRD, the Fourier transform infrared spectra (FT-IR) (NICOLET 5700) were also measured. The magnetic measurements were performed by using a vibrating sample magnetometer (VSM) on a physical property measure system (VSM Lecshore).

RESULTS AND DISCUSSION

XRD Characterization

The structures of the $CoFe_2O_4/SiO_2$ nanoparticles were investigated by X-ray diffraction and FT-IR spectroscopy. Figure 1 shows the X-ray diffraction patterns of the as-prepared $CoFe_2O_4$ and $CoFe_2O_4/$ SiO_2 nanoparticles. In Figure 1(a), the diffraction peaks at 2θ= 18.28, 30.08, 35.46, 43.27, 53.55, 57.08 and 62.84 assigned to scattering from the (111), (220), (311), (400), (422), (511) and (440) planes of the spinel $CoFe_2O_4$ are in agreement with the reported data (JCPDS card NO. 86-2267). As shown in Figure 1(b), in addition to the characteristic diffraction peaks of the spinel phase $CoFe_2O_4$, the peaks at 2θ=25 corresponding to phase SiO_2 also can be observed.
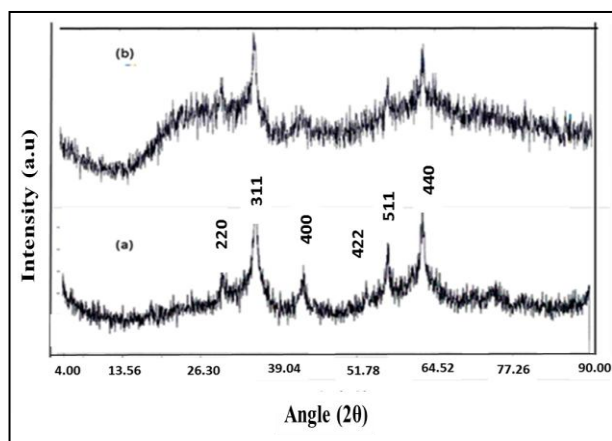

Fig. 1. XRD patterns of $CoFe_2O_4$ (a)and $CoFe_2O_4/SiO_2$ (b) nanoparticles. Peak broadening observed in SiO_2 coated nanoparticles can be related to the decrease in crystallinity.

FT-IR spectra

Figure 2 shows the FT-IR spectra of $CoFe_2O_4$ (a) and $CoFe_2O_4/SiO_2$ (b) nanoparticles.

In the spectra, the strong peaks near 592 cm^{-1} and 516 cm^{-1} are associated with the stretching vibrations of the Fe-O and Co-O bonds, which represents the presence of magnetic NPs. The peaks around 3000-3500 cm^{-1} and 1624 cm^{-1} are related to the stretching and bending vibrations of the H–O–H bond, respectively, showing the physical absorption of H_2O molecules on the surfaces. As shown in Figure 2(b), the characteristic peaks of spinel $CoFe_2O_4$ appear in the infrared spectrum of $CoFe_2O_4/SiO_2$ nanoparticles. The band at 1085cm^{-1} can be attributed to the Si–O–Si asymmetric stretching vibrations; these vibrations are expected to have strong IR absorption consistent with how they appear in the spectrum. The weak band at 964 cm^{-1} is due to Si–OH deformation from the incomplete condensation of TEOS sol.
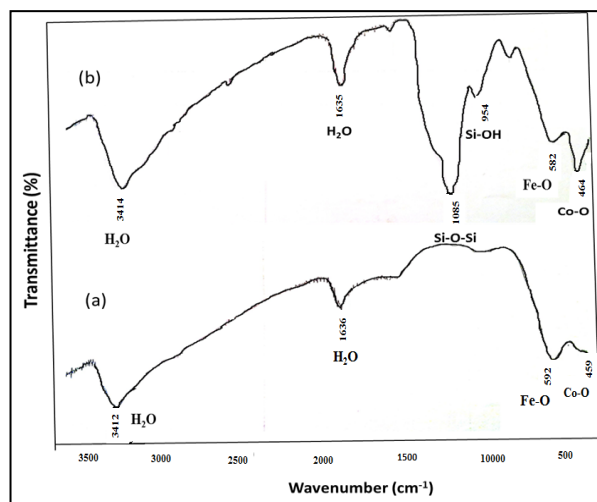

Fig. 2. FT-IR spectrum of $CoFe_2O_4$(a) and $CoFe_2O_4/SiO_2$ (b) nanoparticles

TEM

Figure 3(a) shows the TEM image of $CoFe_2O_4$ nanoparticles. The morphologies showed spherical shape with homogeneous dispersed distribution. The average sizes of the nanoparticles are close to the crystalline grain values calculated by using Scherrer's equation The slight difference may be due to the presence of multi-grain particles.It is observed that the crystallite size of $CoFe_2O_4$ nanoparticles is estimated to be in the range of 10-13 nm.
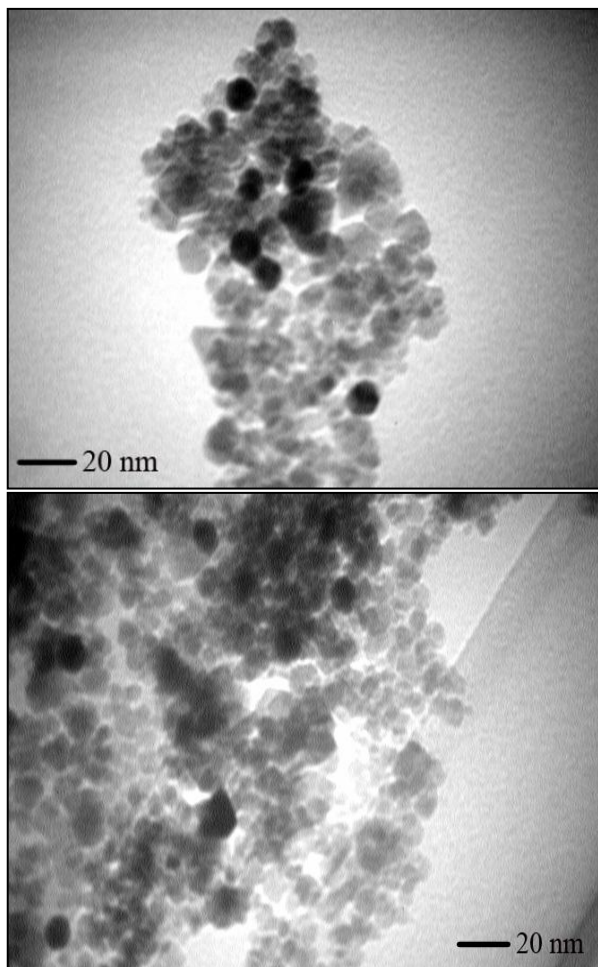
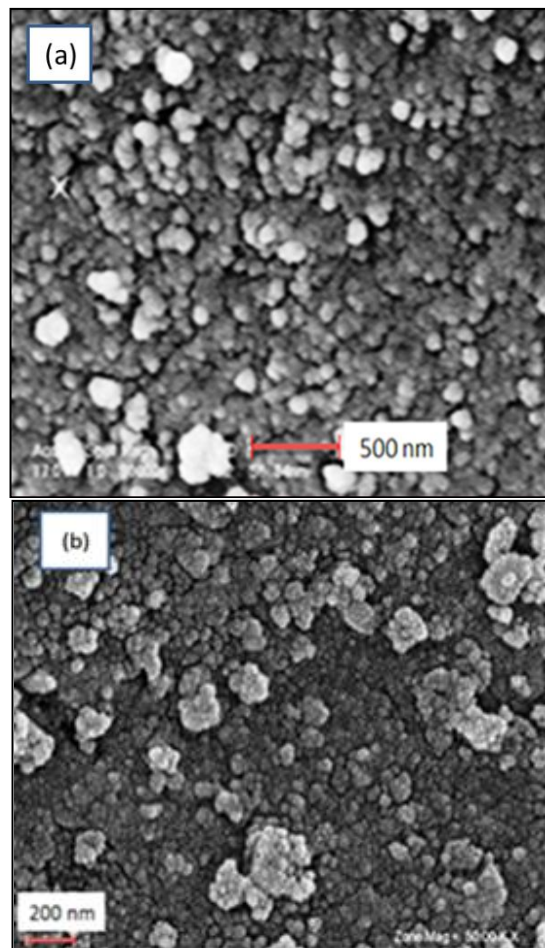**Fig. 3.** TEM images of the as-prepared CoFe₂O₄ nanoparticles

Fig. 4. FESEM images of the CoFe₂O₄ (a) and CoFe₂O₄/SiO₂ core–shell nanoparticles (b)

FESEM and EDAX

The surface morphology of the magnetic nanoparticles has been studied by Field emission scanning electron microscopy (FESEM) method. Figure 4 (a, b) represents FESEM images of CoFe₂O₄ and CoFe₂O₄ /SiO₂ core-shell nanoparticles. The X-ray energy dispersive data (EDAX) of these two materials are given in Figure 5 (a, b) and Table 1.The elemental analysis shows the presence of Co, Fe, O (see Figure 5a) indicates the formation of cobalt ferrite. Also elemental analysis shows the presence of Fe, O, Co, Si (see Figure 5b) indicates the formation of CoFe₂O₄/SiO₂ nanoparticles.

Table1. EDAX quantification (standard less) element normalized for CoFe₂O₄ and CoFe₂O₄/SiO₂ nanoparticles

Sample	Element	%wt	%At
CoFe₂O₄	Fe₂O₃	64.89	46.45
	CoO	35.11	53.55
CoFe₂O₄/SiO₂	Fe₂O₃	46.58	30.68
	CoO	28.61	17.86
	SiO₂	5.62	7.36
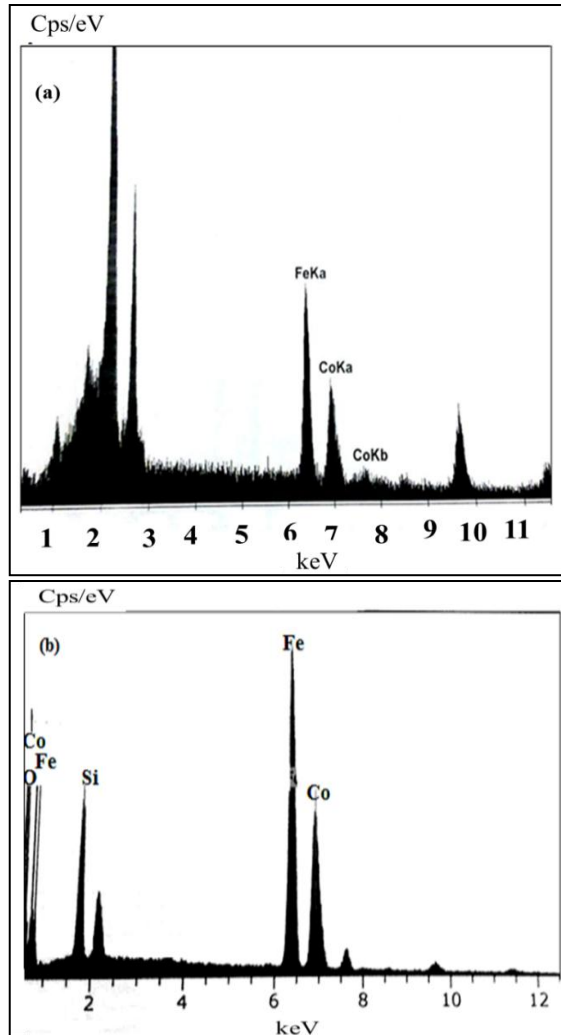
Fig. 5. Dispersive analysis of X-ray (EDAX) of CoFe₂O₄ (a) and CoFe₂O₄/SiO₂ core-shell nanoparticles (b)

Fig. 6. Hysteresis loops of the as-prepared CoFe₂O₄ (a) and CoFe₂O₄/SiO₂ (b) nanoparticles with a magnetic field of 15kOe

Table 2. Magnetic parameters of $CoFe_2O_4$ and $CoFe_2O_4/SiO_2$ nanoparticles

Samples	Ms (emu/g)	Hc (Oe)
CoFe₂O₄	32.1 emu/g	112
CoFe₂O₄/SiO₂ nanoparticles	8.5 emu/g	23

Magnetic properties

Figure 6 shows the magnetic hysteresis loops of the as-prepared $CoFe_2O_4$ and $CoFe_2O_4/SiO_2$ nanoparticles at room temperature. The magnetization for the as-prepared sample exhibits a clear hysteretic behavior under applied magnetic field. The magnetic parameters such as saturation magnetization (Ms) and coercivity (Hc) of $CoFe_2O_4$ determined by hysteresis loops (Table 2) clearly decrease upon coating. There have been several reports on the decrease of Ms and Hc for the magnetic nanoparticles coated with nonmagnetic matrix when interparticle interactions have decreased, due to the increase of particle-particle separation [11-13].
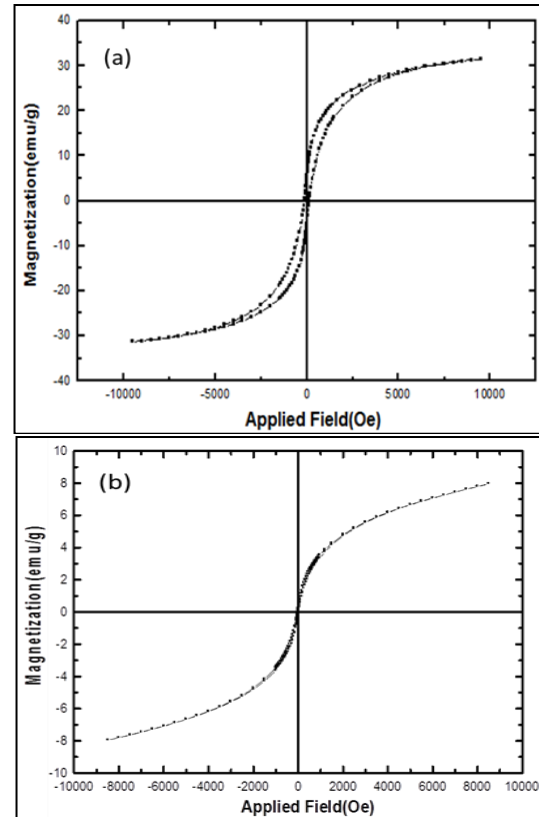
Figure 6(b) shows the saturation magnetization and coercivity of $CoFe_2O_4$ decreased after SiO_2 coating. Core/shell ferrite nanoparticles show lower magnetization saturation than the uncoated ferrite nanoparticles, this is due to the effect of silica shell coating where each particle was separated from its neighbors by the shell layer leading to decrease the magneto static coupling between the particles.

CONCLUSIONS

Soft and hard magnet ($CoFe_2O_4$) nanoparticles were successfully synthesized by chemical solution methods. Particle diameter was tuned from 13.26 nm to 34 nm by varying reaction conditions.

It has been found that the magnetic properties of the as-synthesized $CoFe_2O_4$nanoparticles are dependent on particle size and measurement temperature.

All of the as-synthesized $CoFe_2O_4$nanoparticle with size greater than 12 nm were ferromagnetic.

Due to the nonmagnetic SiO_2 coating layer contribution to the total magnetization, the saturation magnetization decreased upon SiO_2 coating. A decrease in magnetic surface anisotropy after SiO_2 coating led to the reduction of coercivity.

In this study, the reported soft and hard magnetic nanoparticles have potential for many technological applications such as ultrahigh density recording media, biotechnology ferrofluids, and fabrication of exchange-coupled nanocomposite permanent magnets. The synthesis processes explored in this study are simple and easy to achieve the desired particle size distribution and can be scaled up for mass production.

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