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RESEARCH ARTICLE

Simple Synthesis and Characterization Studies of $CoFe_2O_4$ Nanocrystalline by Co-precipitation process

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ABSTRACT

Cobalt ferrite is a well-known hard magnetic material with high coercivity and moderate magnetization. Its nanoparticles at ambient temperature were effectively synthesized via the reproducible solvothermal process. The crystal structure morphology of the sample was determined by X-ray diffraction (XRD) and Scanning Electron Microscopy(SEM). The X-ray diffraction spectrum shows that the synthesized particle has been spinel structure. The average crystalline size was 32 nm. The SEM observation showed that the $CoFe_2O_4$ particle were aggregated in a spherical form and the average particle size was around 35 nm, which is in consistent with the result from XRD according to the Scherrer's formula. The chemical composition and optical properties of the synthesized cobalt ferrite particles were characterized by FTIR spectrum and UV – Visible absorption.

INTRODUCTION

Microwave absorption materials have been paying attention in the last few decades for their electronic, magnetic properties and their potential application in various fields, especially in electromagnetic interference shielding and radar systems. Ferrites might be a hopeful applicant as the microwave absorbing materials for the reason those of their high specific resistance, fascinating magnetic and electromagnetic properties. These properties, along with their great physical and chemical stability, make $CoFe_2O_4$ nanoparticles suitable for magnetic recording applications such as audio and videotape and high-density digital recording disks *etc*. [14, 17]. The motivation in choosing ferrites lied in their predicted high spin - polarization [18]. Spinel ferrites are materials of great concern because of their number of technological applications. Recently, as an important member of ferrites family, $CoFe_2O_4$ has good stability, high magnetic properties, suitability. Furthermore, nanosized magnetic powders of $CoFe_2O_4$ are occupying an important place in the realm of synthetic and biological chemistry for their unusual properties such as multiferroic materials [21], doping or strain enhanced coercivity [3], photo-induced magnetic effects [6] and magnetic labeling of biological systems [15, 1]. The properties of $CoFe_2O_4$ in above applications are highly affected by the particle size. It has been indicated that nanocrystalline $CoFe_2O_4$ was especially good for the property promotion. Much effort have therefore been undertaken to synthesize cobalt ferrite with well-defined properties which include important examples such as mechanochemical method [20], ball milling, electro-deposition, thermal plasma synthesis, sonochemical reactions [16], co-precipitation [8,9,13], micro-emulsion procedure [10] and others [5,11,12,19]. Among them, solvothermal co-precipitation method was well known to obtain higher quality with less impurities and uniform thickness. In the present work, we report the solvothermal co-precipitation method for preparing $CoFe_2O_4$ nanoparticle and characterized by XRD, SEM, UV-Visible and FTIR spectroscopy.

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EXPERIMENT

Synthesis of CoF_2O_4 nanoparticles

All chemicals and solvents were obtained from AR grade. Cobalt ferrite ($CoFe_2O_4$) nanopowders were synthesized by co-precipitation methods from nitrate precursors. In a typical synthesis, 20 ml of 0.01M $Co(NO_3)_2 \cdot 6H_2O$ with aqueous ethanol solution was added drop wise to 20 ml of 0.01M $Fe(NO_3)_2$. $9H_2O$ aqueous ethanol solutions and mixed with aqueous NH_4OH solution and stirred for 6 hours under a high stirring rate condition using magnetic stirrer at room temperature.

$$Co(No_3)_2.6H_2O + Fe(No_3)_2.9H_2O \rightarrow CoFe_2O_4$$

The precipitating agent of 5M NaOH solution with 100 % molar excess oleic acid was added to the suspension at 30 wt. % respects to the formation of cobalt ferrite. A dense reddish brown colored solid precipitate was obtained. The synthesized $CoFe_2O_4$ was filtered off, washed with distilled water, then absolute ethanol and final with acetone to remove free water from the particle surface and dried in an oven at 90 – 95° C. Finally reddish brown $CoFe_2O_4$ nano-powder was produced.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded with a Bruker AXS D8 Advance powder X-ray diffractometer (X-ray source: Cu, Wavelength 1.5406 Å). The morphology was determined by scanning electron microscopy using Hitachi SEM S2460N model with an energy dispersive Xray Spectrometer(EDXS). FTIR spectra are recorded using KBr pellets on a Shimadzu 8400S FTIR spectrophotometer, in the range of 4000 - 400 cm^{-1}. The synthesized $CoFe_2O_4$ nanoparticles, optical absorption spectra are recorded in

aqueous ethanol solution with a Perkin Elmer Lamda–20 UV/Visible 2995S spectrophotometer in the range of 200 - 1200 nm.

RESULTS AND DISCUSSION

XRD *Studies*

Typical synthesis of $CoFe_2O_4$ nanopowder was carried out in a solvothermal system by a co-precipitation reaction between $Co(NO_3)_2$ and $Fe(NO_3)_3$. The well-defined crystalline homogeneous nature of the complex was observed from XRD analysis. Powder X–ray diffraction studies are useful to determine the structure, the particle size of synthesized nanoparticles and also are used to obtain further evidence about the structure of the nanoparticles. The powder X–ray diffractogram of the $CoFe_2O_4$ nanoparticle was given in Figure 2. The observed *d*–space values of the $CoFe_2O_4$ nanoparticles are compared with the standard *d*–space values of the free Cobalt (II) and $CoFe_2O_4$ nanoparticles from JCPDS data file. The experimental *d*–space values of the $CoFe_2O_4$ nanoparticles match with the JCPDS data *d*–space values.

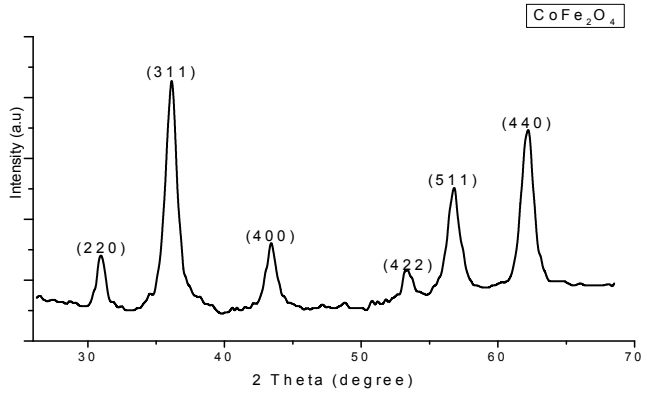

Figure 1. Powder X-ray diffraction pattern of $CoFe_2O_4$ nanoparticle

From this Table, the *d*–space value (JCPDS data) of the free Cobalt(II) and their $CoFe_2O_4$ nanoparticles are well agreed with the experimental *d*–space values of $CoFe_2O_4$ nanoparticles, which confirm the presence of metal atom [Co(II)] and their $CoFe_2O_4$ nanoparticles.

The main diffraction peaks appeared at ~ 29.9°, 35.3°, 42.8°, 53.1°, 56.6° and 62.2°, which corresponds to (111), (220), (400), (422), (511) and (440) crystal planes of cubic $CoFe_2O_4$ with spinel structure. No secondary phase was detected in phase purity of the final product. As shown in Figure 1, the reflection peaks can be easily indexed as spinel system $CoFe_2O_4$ with unit cell parameter of a = 8.4309Å which is in consistent with the reported value (JCPDS 22-1012, *a* = 8.403 Å). The grain size of the sample was determined from the full width at half maximum (β) of the (440), (220) and (311) peaks by using Debye – Scherer's equation [4,7] as

$$D = 0.9\,\lambda / \beta\cos\theta \longrightarrow (1)$$

where λ is the wavelength of the X–ray radiation (λ = 0.154 nm), β is the full width half maximum of the characteristic peak (in radians) corrected for instrumental broadening, θ is Bragg diffraction angle for the *hkl* plane and D is the grain size (nm). The calculated size was found between 32 nm.

SEM *Studies*

SEM allows imaging of individual crystallites and the development of a statistical description of the size and shape of the particles is given in a sample. The overall morphology of the particle shows uniform thickness with smooth interface having perfect regular shape was given in Figure 2. A broad size distribution was observed, which consists of nearly octahedral crystals with an average size of about 35 nm.

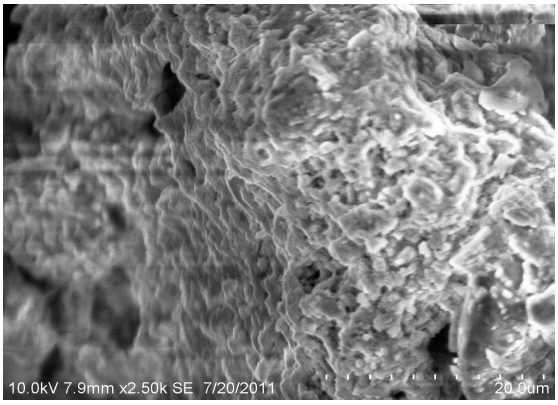

Figure 2. SEM image of $CoFe_2O_4$ nanoparticle

Table 1. Powder X-ray diffraction pattern of $CoFe_2O_4$ nanoparticle

Experimental *d*-space value [Å]	Standard *d*-space value [Å] (JCPDS file)	
$CoFe_2O_4$	Co (89-7373)	$CoFe_2O_4$ (22-1086)
4.819	2.170	4.847
2.951	2.036	2.968
2.524	1.915	2.531
2.411	1.485	2.408
2.168	1.254	2.100
2.039	1.151	1.926
1.964		1.713
1.708		1.615
1.619		1.483
1.475		1.419
1.411		1.327
1.281		1.279
1.262		1.265
1.090		1.093
0.962		0.989
0.874		0.969
		0.938
		0.879
		0.823
		0.807

Optical absorption spectral studies

Optical properties of the synthesized $CoFe_2O_4$ nanoparticle were determined from optical absorption measurement in the range 200 - 450 nm using UV-Visible Spectrometer. UV-Visible absorption spectra of $CoFe_2O_4$ were shown in Figure 3. The optical absorption spectra of the $CoFe_2O_4$ show the absorption peak around 363 nm. The absorption beginning wavelength of bulk $CoFe_2O_4$ is at 325 nm. This confirms the blue shift in the band gap of the synthesized sample in comparison to that of bulk $CoFe_2O_4$ due to the quantum confinement effect. From the optical absorption coefficients (α) and incident photon energy (hv) can be correlated to the following equation as

$$\alpha = A(h\nu - E_g)^n / h\nu \longrightarrow \quad (2)$$

Direct band gap (E_g) of the sample was evaluated by plotting $(\alpha h\nu)^2$ against $h\nu$ and then extrapolating the straight portion of the curve on $h\nu$ axis. The calculated band gap value was 1.81 eV for $CoFe_2O_4$ nanoparticle and this value was higher than the bulk value (1.94 eV) of $CoFe_2O_4$. Particle size has been calculated by putting the band gap value in Brus equation [2] and it was found to be 25.6 nm.

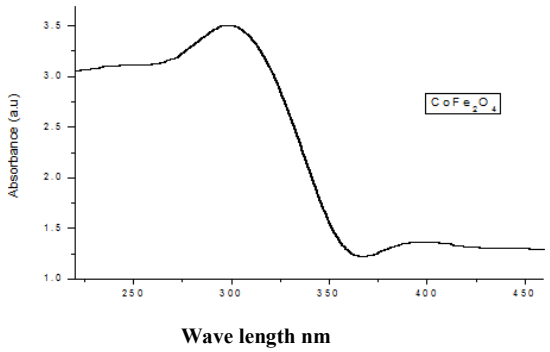

Figure 3. UV-Visible absorption spectrum of $CoFe_2O_4$ nanoparticle

FTIR Spectral Studies

The FTIR spectra provide valuable information regarding the nature of the functional group attached to the metal ion. The FTIR absorption spectrum of the $CoFe_2O_4$ nanoparticles is recorded in the wave number range of 4000 – 400 cm^{-1}). FTIR spectra of $CoFe_2O_4$ nanoparticle was shown in Figure4. In Figure 4, the Fe–O (ν_1) stretching vibration of ferrite was observed at 580 cm^{-1} and ν_2 stretching vibration was observed around 435cm^{-1} for the spinel structure.

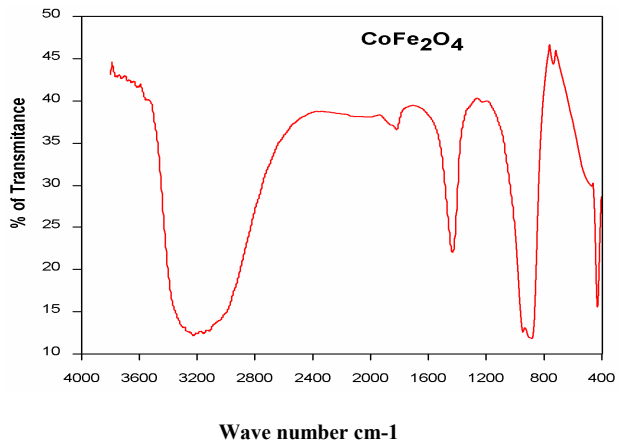

Figure 4. *FTIR spectra of $CoFe_2O_4$ nanoparticle*

Conclusion

$CoFe_2O_4$ nanoparticle was prepared by chemical co-precipitation method. XRD analysis revealed the high purity of $CoFe_2O_4$. Nanocrystals exhibited octahedral morphology as observed from SEM. Average crystallite size calculated from Debye Scherer equation as 32 nm agrees well with the SEM estimated average particle size of ~35 nm. This is a good indication of each particle being a single crystal. The bandage energy of the synthesized nanoparticles was evaluated from the UV-Visible measurement. From the FTIR spectrum exhibited ν_1 and ν_2 fundamental bands, corresponding to octahedral and tetrahedral sites in the ferrite structure. The results suggest that the $CoFe_2O_4$ nanoparticles could be a potential candidate for biomedical applications.

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