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PVP-Assisted Synthesis of Cobalt Ferrite ($CoFe_2O_4$) Nanorods

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Cobalt ferrite ($CoFe_2O_4$) nanorods were synthesized by iron chloride ($FeCl_3.6H_2O$) and cobalt sulfate hexahydrate ($CoSO_4.7H_2O$) as precursor in the presence of ethylene glycol agent and poly vinyl pyrrolidone (PVP) surfactant. The samples were characterized to identify the physical properties. XRD pattern of cobalt ferrite samples showed the structure of body center cubic (bcc) structure. The diameter of as-prepared samples was determined about 20 nm and annealed one was about 30 and 50 nm in diameter at 500 °C and 1100 °C, respectively. The TEM studies showed that the particles change from rod shaped to sphere-liked shaped particles by increasing annealing temperature. Peaks in the FTIR spectrum determined the element of Fe-Co nanoparticles. EDS shows peaks of iron and cobalt with fewer impurities in prepared samples and Fe/Co ratio was also decreased with increasing annealing temperature. The result of magnetic measurements showed saturation magnetization around 59.5 emu g^{-1} for annealed samples.

Keywords: $CoFe_2O_3$ nanorods, Ethylene glycol, PVP, Chemical synthesis

INTRODUCTION

Unique properties of magnetic nanoparticles compared with bulk material have been investigated by many researchers [1]. Magnetic nanocomposite are of continuing interest because of their use as memory devices, spintronic and magnetic recording media. When the size of particles decreases the total surface or the interfacial energy of the system increases and the particles often agglomerate. To prevent the sintering of the particles in the higher temperatures, one must use the stabilizers and capping agent such as poly vinyl pyrrolidone (PVP), polyvinyl alcohol (PVA) and poly oxyethylene lauryl ether (POLE) [2-4]. Fabrication of the Iron cobalt (FeCo) nanocomposite has been also the technological interest in the magnetic recording media, because it has the highest saturation magnetization [5]. Many methods concerning the fabrication of these nanoparticles have been studied [6,7].

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The methods for synthesis of the FeCo nanoparticles include polyol [8], hydrothermal [9], thermal decomposition [10], wet chemical [11] and coprecipitation [12]. In this paper, cobalt ferrite magnetic nanoparticles are synthesized using iron chloride precursor and cobalt sulfate in the presence of PVP surfactant and ethylene glycol agent. The novelty of this work is the new form of Cobalt Ferrite ($CoFe_2O_4$) nano-rods by using PVP-mediated and ethylene glycol. Structural and surface morphological properties are discussed by XRD, HRTEM, FESEM, EDS, VSM and FTIR analyses.

EXPERIMENTAL

All materials were purchased from Merck Company. Iron cobalt nanorods were synthesized as follows. To synthesze the FeCo nanoparticles, 2 g $FeCl_3.6H_2O$ was added to 50 ml distilled water while stirring at room temperature. After that 4 g PVP surfactant was added to the solution. After 10 min 50 ml ethyleneglycol was slowly added to the solution. Then 2 g of $CoSO_4.7H_2O$ was added

to the solution and the mixed solution was stirred with a magnetic stirrer at 85 °C. The color of solution changed to dark red by adding cobalt sulfate. The pH = 3 was maintained during the synthesis. The product was evaporated for 3.5 h, cooled to room temperature and finally calcined at 500 °C and 1100 °C for 3 h. All analyses were carried out for samples without any washing and purification. The specification of the size and structure properties of the as-synthesis and annealed nanoparticles were carried out. Crystalline phase and structure of the samples were identified by x-ray diffractometer (XRD) with 2θ in the range of 4-85°. FeCo morphology was carried out by field emission scanning electron microscopy (FESEM). To determine the exact size of particles, transmission electron microscopy (TEM) with type Zeiss EM-900, 80 kV was used. Fourier transform infrared spectroscopy (FTIR) was performed to detect the functional groups and Fe-Co stretching vibration was measured with WQF 510. Magnetic properties were carried out using vibration sampling magnetometer (VSM). Elemental analysis of the Fe and Co was done by energy dispersive spectroscopy (EDS) type VEGA, 15 kV. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Figure 1a shows the XRD pattern of iron cobalt sample before annealing. Figures 1b and 1c show the XRD patterns of iron cobalt after annealing at 500 °C and 1100 °C, respectively. The exhibited peaks show the body center cubic (BCC) structure of the samples. The size of the $CoFe_2O_3$ nanocomposites was determined by Debye-Sherrer formula as follows:

$$D = \frac{0.89\lambda}{B\cos\theta} \quad (1)$$

The shape factor has a typical value of about 0.89, but varies with the actual shape of the crystallite. λ is the X-ray wavelength depending on the X-ray sources. B is the line broadening at half the maximum intensity (FWHM), in radians, and θ is the Bragg angle. The mean size of as-

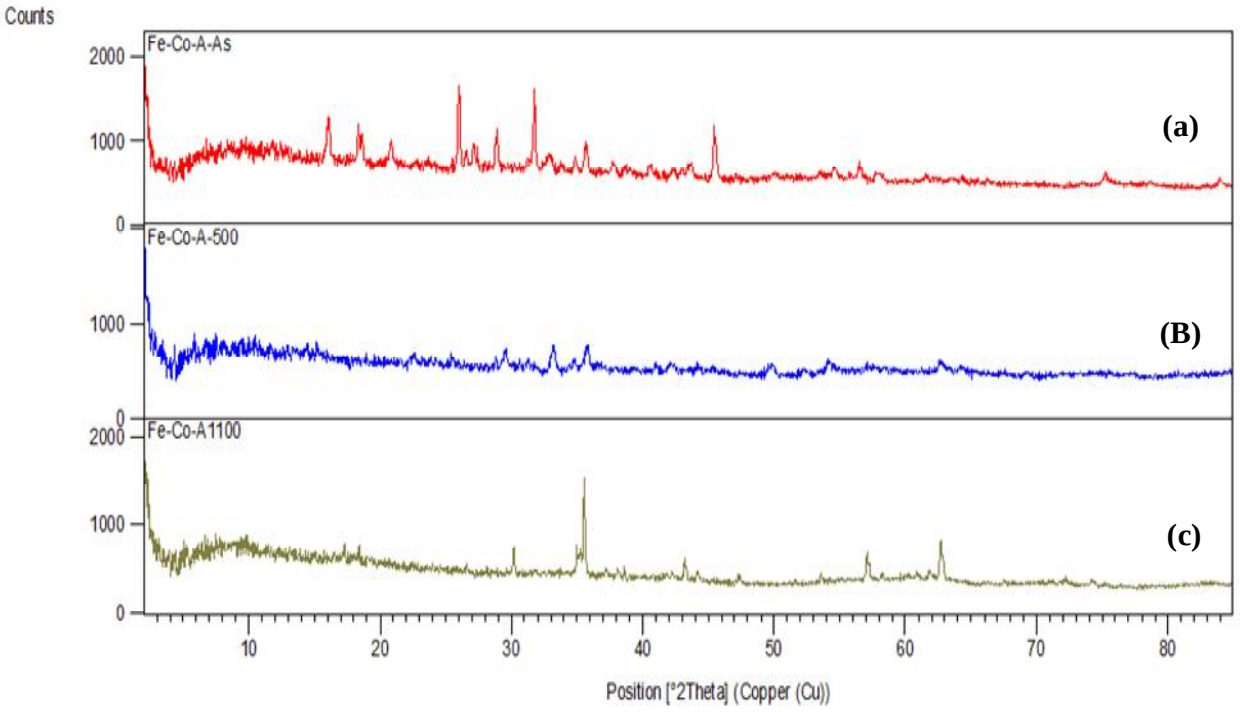

Fig. 1. XRD patterns of $CoFe_2O_3$ samples (a) as-prepared (b) annealed at 500 °C and (c) at 1100 °C.

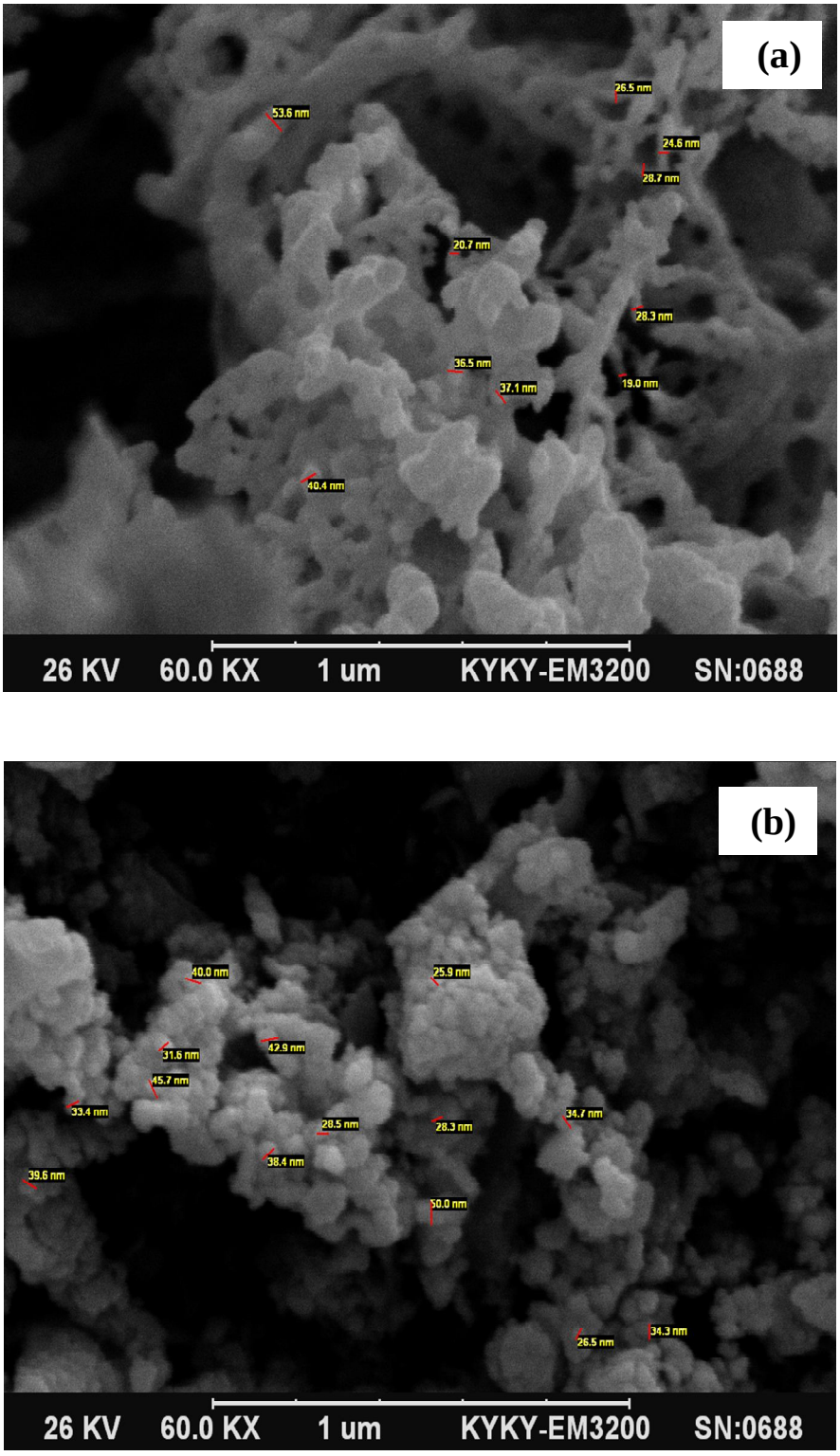

Fig. 2. SEM images of the $CoFe_2O_3$ nanoparticles (a) as-prepared, (b) annealed at 500 °C and (c) annealed at 1100 °C.

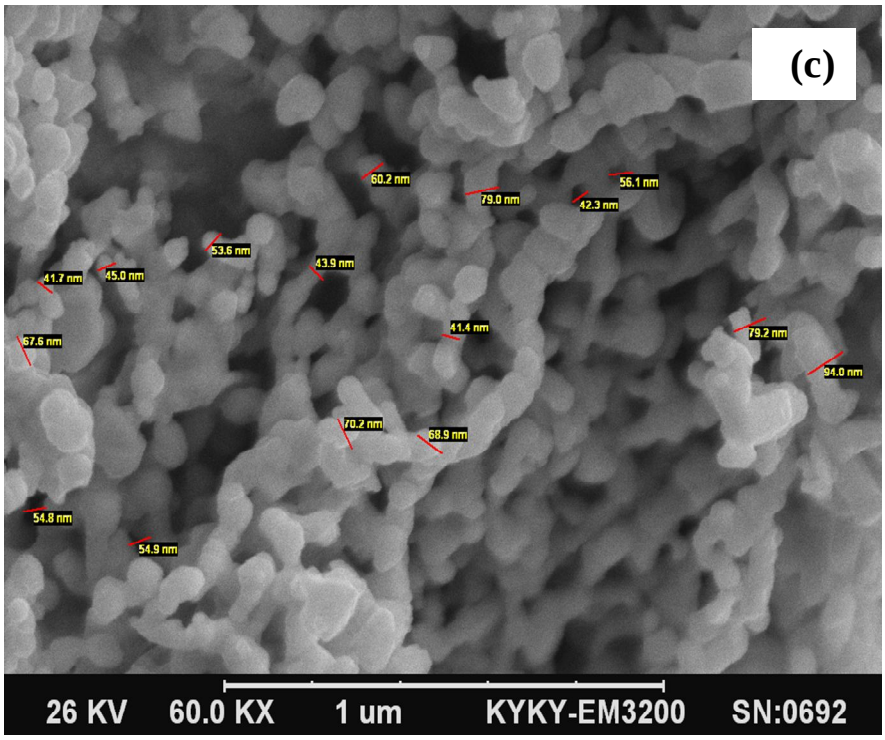

Fig. 2. Continued.

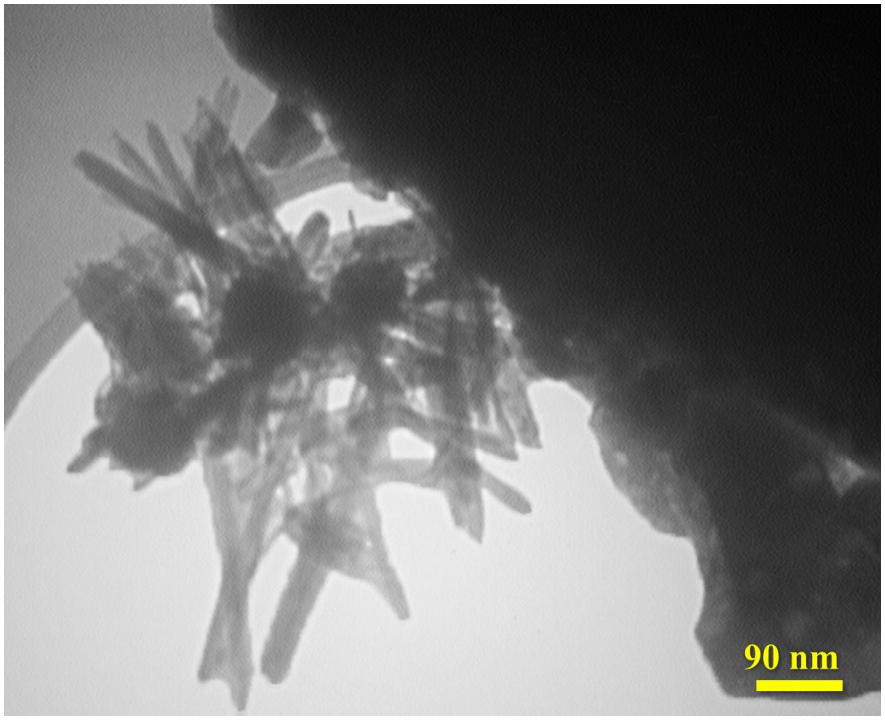

Fig. 3. TEM image of the as-prepared cobalt ferrite nanorods.

prepared samples was around 20 nm from this Debye-Sherrer equation.

SEM analysis shows the high crystallinity emerged on the surface of samples by increasing annealing temperature. For these particles, with increasing temperature the morphology of the particles changes from rod-shaped to sphere-like shaped. Figure 2a shows the SEM image of the 20 nm as-prepared $CoFe_2O_3$ samples were prepared by this method. Figure 2b exhibits the SEM image of the annealed $CoFe_2O_3$ at 500 °C for 3 h with average particle size of 30 nm. Figure 2c indicates the SEM image of the annealed $CoFe_2O_3$ nanoparticles at 1100 °C for 3 h with average particle size of 50 nm. The sphere-like shaped particles with clumped distributions are visible through the SEM analysis. The particle stabilization and growth control are two important effects for stabilization of the particles [13]. The carbonyl groups from the pyrrolidone ring of the PVP coordinate to the surface of Fe and Co atoms of FeCo nanoparticles [14,15].

In Fig. 4, the infrared spectrum (FTIR) of the annealed $CoFe_2O_3$ nanoparticles was in the range of 400-4000 cm^{-1} wavenumber identifying the chemical bonds as well as functional groups in the compound. Figure 4a shows the FTIR spectra of the as-prepared samples and Fig. 4b shows the FTIR spectra of the annealed cobalt ferrite sample at 500 °C. The large broad band at 3398 cm^{-1} is ascribed to the O-H stretching vibration in OH groups. The absorption peaks around 1639 cm^{-1} and 1489 cm^{-1} are due to the asymmetric and symmetric bending vibration of C=O. The bands corresponding to Fe-Co stretching mode are seen at 661 cm^{-1}, 609 cm^{-1} and 583 cm^{-1}. The broad peak at 3493 cm^{-1} is characteristic of O-H bonds, present on the surface of cobalt ferrite samples. As indicated in Fig. 4b, the transmittance at 525 cm^{-1} decrease because of decreasing in the size of particles in order to change the particles from rod shaped to sphere like shape by increasing annealing temperature. In fact the number of monomer increases by decreasing the size of particles and the transmittance percentage decreases after heat treatment.

Energy dispersive spectroscopy (EDS) of $CoFe_2O_3$ samples prepared by wet synthesis is shown in Fig. 5 which confirms the existence of Fe and Co with weight percentage. EDS shows peaks of iron and cobalt with fewer Bromide and sodium element for as-prepared samples (Fig. 5a). The weight percentages of C and N elements were decreased by increasing temperature from room temperature

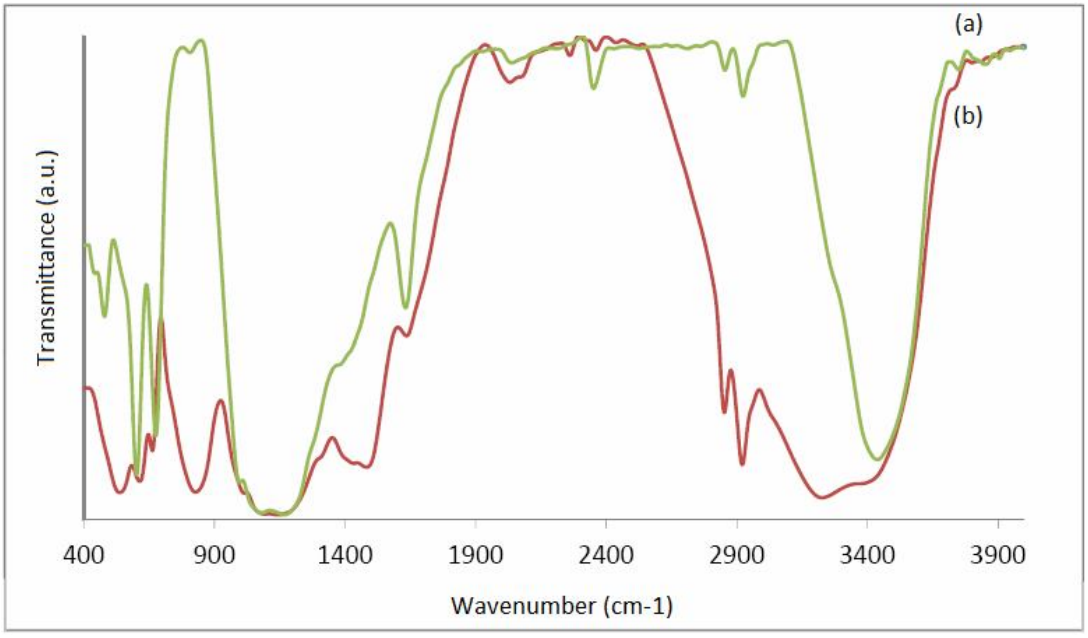

Fig. 4. FTIR spectrum of (a) as-prepared and (b) annealed $CoFe_2O_3$ sample at 500 °C.

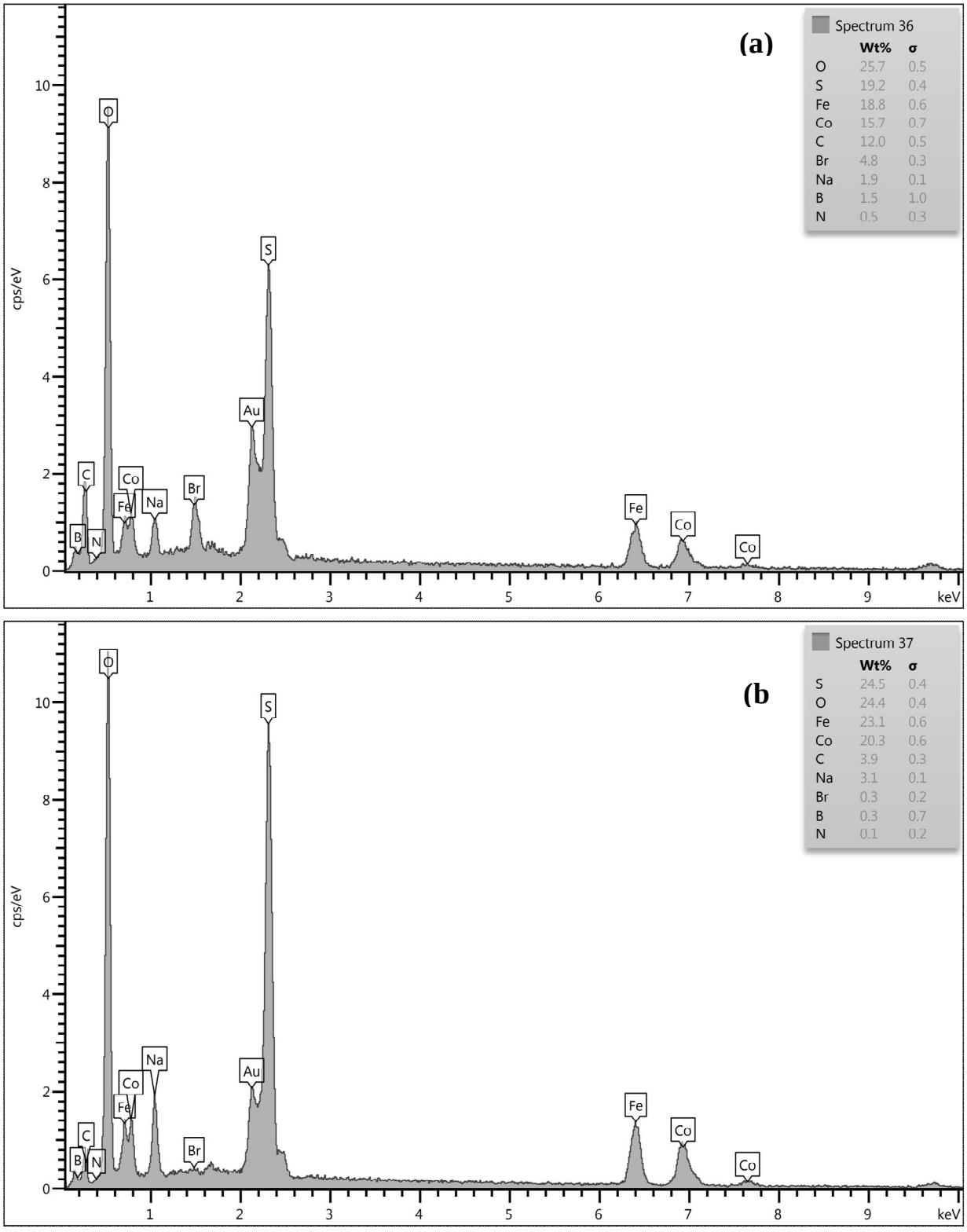

Fig. 5. EDS spectra of the (a) as-synthesized and (b) annealed $CoFe_2O_3$ particles.

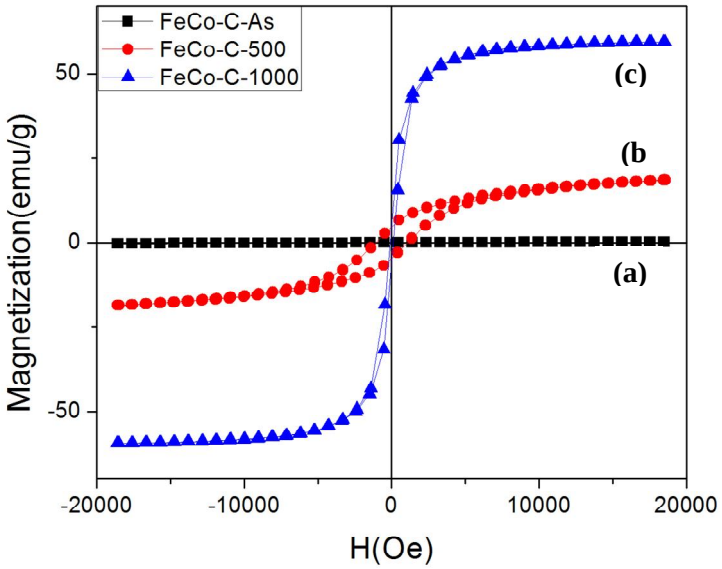

Fig. 6. Magnetic hysteresis loops at 300 K for representative as-synthesized and annealed $CoFe_2O_3$ samples.

to 500 °C (Fig. 5b). The samples were not washed and purified to prevent oxidation. It can be seen that the Fe/Co ratio is 1.20 and 1.13 for as-prepared and annealed one, respectively. It is realized that Fe diffused into the Co matrix is decreased by increasing annealing temperature because of atomic interaction.

Figure 6a shows the coercive field and saturation magnetization around 155 G and 0.25 emu g^{-1} for as-prepared sample and Fig. 6b shows the coercive field and saturation magnetization around 1084 G and 19 emu g^{-1} for annealed one at 500 °C. Figure 6c shows the coercive field and saturation magnetization around 124 G and 59.5 emu g^{-1} at 1100 °C for 3 h.

CONCLUSIONS

The $CoFe_2O_3$ nanorods were successfully synthesized using iron chloride and cobalt sulfate in the presence of ethylene glycol agent and PVP surfactant. XRD spectrum showed body centered cubic structure of the samples. SEM images indicated that with increasing temperature the morphology of the particles is changed from rod shaped to sphere like shape with less agglomeration. TEM image exhibited the as-synthesized cobalt ferrite nanoparticles with an average diameter about 20 nm and annealed one around 50 nm at 1100 °C. FTIR data showed the presence of Fe-Co stretching mode. The EDS spectrum showed peaks of iron and cobalt with fewer impurities and Fe/Co ratio was also decreased with increasing annealing temperature. Magnetic measurement determined the increasing saturation magnetization from 19 emu g^{-1} to 59.5 emu g^{-1} by increasing temperature from 500 °C to 1100 °C, respectively.

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