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Preparation and Characterization of CoFe₂O₄/Poly Vinyl Acetate Nanocomposite

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CoFe₂O₄ (CFO) nano-particles have been synthesized successfully by a redox chemical reaction in aqueous solution of cobalt chloride and ferric chloride. The synthesized CFO nanoparticles have been used for preparation of CFO/Poly vinyl acetate (CFO/PVAc) nanocomposite by in situ emulsion polymerization method. The nanocomposite exhibited superparamagnetic behavior at room temperature under an applied magnetic field. The synthesized CFO/PVAc nanocomposite has been analyzed using FT-IR spectra, X-ray diffraction (XRD), scanning electron microscopy (SEM) and a vibrating sample magnetometer (VSM). The obtained results showed that CFO nanoparticles with the particle sizes of about 150 nm were well dispersed in PVAc matrix.

Keywords CoFe₂O₄; Magnetic material; Polymer-nanocomposite; PVAc; X-ray diffraction

INTRODUCTION

Due to the enhanced physicochemical properties of the nanoparticles, they have attracted great interest in fundamental sciences and technological applications^[1,2]. Magnetic behavior of nanoparticles has been studied for applications in electronic devices and biological systems. In the stable magnetic fluids such as ferrofluids, ultrafine magnetic particles are dispersed as colloidal suspensions in an organic or aqueous carrier medium consisting^[3–5]. Cobalt ferrite, CFO, is a magnetic spinel material with very high cubic magnetocrystalline anisotropy and moderate saturation magnetization^[6].

The paramagnetic nanoparticles not only have been developed as imaging agents in magnetic resonance imaging (MRI), but they have also been used in various bioseparation applications^[7,8]. The spinel materials such as CFO, with general formula “AB₂O₄” (A refers to cations in tetrahedral sites, and B refers to cations in the octahedral positions), has a cubic structure. In the spinel crystalline structures, two cation configurations are possible. The normal structure presents the A(B₂)O₄ and B(AB)O₄ distributions. In both

cases, the parentheses indicate the octahedral sites. The unit cell of spinel structure is illustrated in Figure 1. In this figure, Co²⁺ and Fe³⁺ ions reside in the tetrahedral and octahedral sites (A and B) respectively^[9,10].

The physicochemical properties of spinel ferrites are greatly affected by the synthesis route. Therefore, various synthesis methods have been reported in literatures for nanoscale spinel particles including coprecipitation^[11,12], oxidation of the ferrous hydroxide gels^[13], oil-in-water emulsion route^[14], hydro/solvothermal processes^[15], thermal decomposition of the different types of precursors such as FeCl₃ and Fe(CO)₅^[16,17] and metal complex precursors method^[18,19]. Considering the high magnetostriction coefficient of CFO, it is a potential candidate for the electromagnetic composites fabrication.

The magnetic properties of well-dispersed, CFO nanoparticles within a polymer matrix have attracted much attention in recent years. Nanocomposites based on ferrites have different applications in electromagnetic interference (EMI) shielding^[18,20], drug delivery^[21], and drug targeting^[22]. Magnetic polymer matrix nanocomposites have superior physical and chemical properties compared to the constituent polymer matrices.

In this work, by considering the simplicity, good stoichiometric control, low cost and the use of an aqueous-based processing system, a convenient coprecipitation method is used for synthesis of CFO nanoparticles. The synthetic CFO is used for preparing of a stable CFO/PVAc nanocomposite with high CFO loading content. The synthesized CFO/PVAc nanocomposite has been characterized using FT-IR spectra, X-ray diffraction (XRD), scanning electron microscopy (SEM) and a vibrating sample magnetometer (VSM). The obtained results indicated that magnetic CFO/PVAc nanocomposites exhibit the advantages of both CFO and PVAc.

EXPERIMENTAL

Materials

Commercial grade of VAc and PVA (degree of hydrolysis 88% degrees of polymerization 580) were supplied from

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FIG. 1. Schematic of the spinel structure, showing octahedral and tetrahedral sites occupied by A (Co²⁺) and B (Fe³⁺) cations. (Color figure available online.)

Iranian petrochemical Co. and Kuraray Chemical Co., Japan respectively. Sodium lauryl sulfate (SLS 99%) was supplied by Fluka. Ammonium persulfate (APS), sodium bicarbonate (NaHCO₃), CoCl₂·6H₂O, FeCl₃, NaOH and HCl were supplied by Merck Co. Inc., Germany. All chemicals were used without further purification. Water was distilled after being ion-exchanged.

Preparation of CFO Nanoparticle

CFO nanoparticles were prepared via a convenient coprecipitation method^[11]. In a typical procedure, an equimolar mixture solution of CoCl₂·6H₂O and FeCl₃ added to a 500 ml three-neck round-bottom flask equipped with a mechanical stirrer. The solution was stirred at 35°C for 40 min and then gradually mixed with 3 M NaOH until the pH reached 10. The solution in the elevated temperature (80°C) maintained for 3 h with continuous stirring. Then the black precipitated product washed using deionizer water several times until neutrality.

Synthesis of CFO/PVAc Nanocomposite

The CFO/PVAc nanocomposite was prepared by in situ emulsion polymerization of VAc monomer in the presence of CFO magnetic nanoparticles. CFO nanoparticles were stirred vigorously overnight and then were dispersed by ultrasonication to prevent aggregation of nanoparticles. Then this solution was added to a three-neck flask with a water jacket to maintain a constant temperature (±0.1°C). The glass reactor was fitted with a reflux condenser, funnel and mechanical stirrer. The speed of agitation with stirring was stable at 200–300 rpm.

Monomer poured into the dropping funnel, a quantity of distilled water was poured into the glass reactors and

the initiator (APS) and the buffer solution of NaHCO₃ were added and maintained under constant agitation (200–300 rpm). The aqueous emulsified solution containing PVA and SLS were added to the reaction system. The mixture was stirred at 300 rpm and heated up to 75°C. Afterwards, the monomer was fed into the reactor in a separate stream with constant flow rates to maintain the reaction system at 75°C. The time of feeding was almost 70 min and after addition of the monomers, the polymerization was carried out for 4 h. Afterwards, the temperature was maintained at 90°C for 1 h with constant stirring. Finally, the filtered CFO/PVAc nanocomposite was washed with deionized water and then ethanol. Subsequently, the nanocomposite was dried at 60°C for 24 h.

Characterization

Fourier transform infrared (FT-IR) spectroscopy were recorded by (Magna 550; Nicolet) in the range of 4000–400 cm⁻¹ using KBr pellets. XRD patterns of the samples were collected on a Philips X'Pert MPD X-ray diffractometer with Cu-Kα radiation (λ = 1.54 Å) at a generator voltage of 40 kV and a generator current of 40 mA. The saturation magnetization, coercivity of samples have been determined from the magnetic moment versus magnetization curve recorded for various samples with the help of a vibrating sample magnetometer (VSM), maximum magnetic field of 10 kOe.

RESULTS AND DISCUSSION

FT-IR Spectra

The FT-IR spectra of the CFO magnetic nanoparticles and CFO/PVAc nanocomposite are shown in Figure 2. In Figure 2a, two main broad metal-oxygen bands are seen in the range 440 and 590 cm⁻¹. Based on the geometrical

FIG. 2. FT-IR Spectra of (a) CoFe₂O₄ and (b) CFO/PVAc nanocomposite.

configuration of the oxygen nearest neighbors, the metal ions are usually situated in two different sublattices in ferrites, designated as the tetrahedral and octahedral sites^[23]. In the spectrum of the CFO/PVAc nanocomposite (Figure 2b), the peak observed at 3436 cm^{-1} can be attributed to the hydroxyl stretching vibration, the peak obtained at 2927 cm^{-1} can likely be assigned to the C–H stretching vibration, and the peak found at 1740 cm^{-1} originates with the C=O stretching vibration. The peak at 1437 cm^{-1} comes from the C–H bending vibration, the peaks observed at 1240 and 1120 cm^{-1} are associated with the C–O–C symmetrical stretching vibration^[24]. The absorption peaks at 604 cm^{-1} observed in Figure 2b may be attributed to the intrinsic vibration of the tetrahedral and octahedral sites in the CFO particles^[7].

X-ray Diffraction

Figure 3 shows the XRD patterns of the synthesized CFO nanoparticles. As shown in Figure 3a, the diffraction peaks at $2\theta = 30.51^\circ, 36.04^\circ, 43.65^\circ, 54.20^\circ, 57.68^\circ, 63.44^\circ$ and 75.06° are perfectly indexed to the spinel structure reported in the standard card (JCPDS No. 22–1086)^[7]. The XRD pattern of the CFO/PVAc nanocomposite shown in Figure 3b contains the characteristic peaks of both PVAc and CFO nanoparticles, which confirms the formation of the CFO/PVAc nanocomposite. Furthermore, the diffraction peaks for the CFO/PVAc nanocomposite compared to that for the CFO nanoparticles are broader due to the polymer matrix's restriction on the nanoparticles^[25].

Morphology

Figure 4a shows the SEM photomicrographs of the synthesized CFO nanoparticles. According to this figure,

FIG. 3. XRD patterns of (a) CoFe_2O_4 and (b) CFO/PVAc nanocomposite. (Color figure available online.)

(a)

(b)

FIG. 4. Representative SEM images at low magnifications of the (a) CoFe_2O_4 and (b) CFO/PVAc nanocomposite.

the CFO nanoparticles are almost spherical in shape, uniform in size and have very narrow diameter distributions. The average particle size is estimated about 150 nm. SEM images of CFO/PVAc sample in Figure 4b showed that the average of the particles size is about 300 nm.

Magnetic Properties

The magnetic property of the synthesized of CFO nanoparticles and CFO/PVAc nanocomposites were investigated with a vibrating sample magnetometer at room temperature. Figure 5 shows the magnetization hysteresis loop of the samples. According to this figure, the magnetization of the CFO/PVAc nanocomposite exhibits a clear

FIG. 5. Hysteresis loops for (a) the CoFe₂O₄ and (b) CFO/PVAc nanocomposite.

superparamagnetic behavior, indicating that the size of the CFO particles in the PVAc matrix is smaller than the superparamagnetic critical size^[21]. The obtained magnetic parameters of the samples, such as saturation magnetization (M_s) and coercivity (H_c) are given in Table 1. The value of M_s for the CFO/PVAc nanocomposite was significantly decreased compared to that of the CFO nanoparticles.

The decrease of M_s suggests the decrease of interacted magnetic state towards a paramagnetic state^[25,26]. The magnetic order of CFO is due to super exchange interaction mechanism occurring between the metal ions in the tetrahedral A-sites and octahedral B-sites^[27]. The M_s of the CFO/PVAc nanocomposite depends mainly on the volume fraction of magnetic CFO nanoparticles. However, due to the non-magnetic PVAc coating contribution and its important role in isolating the magnetic CFO nanoparticles, the M_s of the synthesized CFO/PVAc nanocomposite is much lower than that for the CFO nanoparticles. In addition, the demagnetization effect of PVAc may cause to reduce the M_s of the CFO/PVAc nanocomposite^[28]. Therefore, the magnetization of the CFO/PVAc nanocomposites was lower than that of the pure CFO nanoparticles.

TABLE 1

The values of M_s and H_c for CFO nanoparticles and CFO/PVAc nanocomposite

Samples	M_s (emu/g)	H_c (Oe)
CFO	37.21	64.53
PVAc/CFO	3.84	0

CONCLUSIONS

CFO nanoparticles have been synthesized via a redox chemical reaction in aqueous solution. The synthesized CFO nanoparticles have been used for preparation of homogenous CFO/PVAc nanocomposite by in situ emulsion polymerization method. The synthesized CFO/PVAc nanocomposite has been analyzed using FT-IR, XRD, SEM, and VSM. According to the results obtained the CFO magnetic nanoparticles are well dispersed in the PVAc polymer matrix. Due to the non-magnetic PVAc coating contribution, the M_s of the synthesized CFO/PVAc nanocomposite was much lower than that for the CFO magnetic nanoparticles. The morphology of the synthesized CFO/PVAc nanocomposite was observed with SEM. The obtained results indicated that in situ polymerization approach used here is able to disperse the CFO magnetic nanoparticles in PVAc polymer matrix and to stabilize the dispersion after polymerization.

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