

SYNTHESIS OF CoFe₂O₄-POLYANILINE NANOCOMPOSITE AND EVALUATION OF ITS MAGNETIC PROPERTIES

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Abstract Particles of Cobalt ferrite, CoFe₂O₄, were coated with polyaniline (PANI) sulphate and phosphate during in-situ polymerization of aniline in an aqueous solution of sulfuric and phosphoric acid. The PANI-ferrite composites were characterized by Fourier transform infrared (FTIR) spectroscopy. Structures and morphology of products were studied by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The crystallite size calculated by XRD was 16.65 nm. Magnetic measurement shows that CoFe₂O₄ and nanocomposite exhibit ferromagnetic behavior. The saturation magnetization, M_s, remanent magnetization M_r and coersivity H_c for PANI sulphate/CoFe₂O₄ nanocomposite were 40 emu/g, 20 emu/g and 301 Oe respectively. The same variables for PANI phosphate/CoFe₂O₄ nanocomposite were 12 emu/g, 28 emu/g and 333 Oe respectively.

Keywords Nanocomposite, Polyaniline, Ferrite, Magnetic Properties

چکیده در این مقاله، ذرات فریت کبالت، CoFe₂O₄ با سولفات و فسفات پلی آنیلین در حین پلیمریزاسیون در جای آنیلین در محلول آبی اسید سولفوریک و اسید فسفریک پوشش داده شدند. کامپوزیت‌های پلی آنیلین-فریت توسط تکنیک FTIR مشخصه یابی شدند. ساختار و مورفولوژی محصولات به دست آمده به ترتیب توسط تکنیک پراش اشعه ایکس و میکروسکوپ الکترونی روبشی مورد بررسی قرار گرفتند. بر اساس نتایج تفرق اشعه ایکس، اندازه کریستالیت‌های بدست آمده ۱۶/۶۵ نانومتر بودند. اندازه گیری‌های مغناطیسی نشان می‌دهند که فریت کبالت و نانوکامپوزیت حاصله رفتار فرومغناطیسی دارند. M_s، M_r و H_c برای نانوکامپوزیت‌های سولفات پلی آنیلین/فریت کبالت به ترتیب مقادیر ۴۰ emu/g، ۲۰ emu/g و ۳۰۱ اورستد و برای نانوکامپوزیت‌های فسفات پلی آنیلین/فریت کبالت به ترتیب مقادیر ۱۲ emu/g، ۲۸ emu/g و ۳۳۳ اورستد به دست آمدند.

1. INTRODUCTION

Magnetic polymer nano-composites represent a class of functional materials, where magnetic nanoparticles are embedded in polymer matrices. These nano-composites hold immense potential for applications in cell separations, enzyme immunoassay, drug targeting, electromagnetic device application, and electromagnetic interference suppression [1-3]. Multi component conducting polymer systems with nanoparticles of metal oxides can be tailored to obtain desired mechanical properties in addition to novel electrical, magnetic, and optical properties. Conducting polymers, such as PANI may improve the corrosion resistance of metals. Coating iron oxides with conducting polymers is a logical extension in the design of

new anti-corrosion pigments.

Ferrites have the general formula MO.Fe₂O₃ where M is an element in bivalent state, e.g., M⁺² can be Fe⁺², Co⁺², Ni⁺², Mn⁺², Zn⁺², Mg⁺², etc., or a combination of them. Nickel-cobalt ferrites have been coated electrochemically with polypyrrole and used as composites electrodes for hydrogen peroxide formation [4]. Micrometer-sized manganese-zinc ferrites particles have recently been coated with PANI by chemical oxidation of aniline [5]. A number of articles have been published on the magnetic properties, and it has been observed that the magnetic properties of ferrites are influenced by coatings of a conducting polymer [6-10].

In this paper, CoFe₂O₄ ferrite particles have been coated with polyaniline by in-situ polymerization of aniline.

2. EXPERIMENTAL

2.1. Preparation of Ferrites $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaOH, SDS (Sodium dodecyl sulfate), PVP (Polyvinylpyrrolidone) and CTAB (Cetyl trimethylammonium bromide) (Merck reagents), were used as starting materials. Aqueous solutions of 0.2 M $\text{Fe}(\text{NO}_3)_3$ and 0.1M $\text{Co}(\text{NO}_3)_2$ were slowly added to the 100 ml of 0.8 M NaOH aqueous solution under vigorous stirring for about 30 minutes.

Subsequently, the mixture was poured into a 40 ml Teflon-lined autoclave, sealed into a stainless steel tank and heated at 180°C for 24 h. After the autoclave was cooled naturally to room temperature, precipitates were collected by filtration, washed three times with distilled water and absolute ethanol to remove residual ions and excessive surfactant. Finally, the precipitates were dried at 60°C overnight.

2.2. Coating of Ferrite with Polyaniline In order to prepare polyaniline-ferrite nanocomposite, 0.1 M aniline, 0.125 M ammonium persulfate, sulfuric and phosphoric acid as two different acid sources were used to produce PANI sulphate and PANI phosphate. Then, 2 gr ferrite powder was immediately added to both solutions under gentle stirring conditions. The mixed solutions were then filtered and washed after 30 minutes with distilled water and dried at 50°C for 15 hours. The nano-composites of ferrite with PANI sulphate and PANI phosphate were designated as FP-S and FP-Ph, respectively.

2.3. Characterization X-ray diffraction patterns of samples were recorded by X-ray diffractometer model Philips PW 3710 using copper $K\alpha$ radiation ($\lambda = 1.5418\text{\AA}$) in the interval $20^\circ \leq 2\theta \leq 80^\circ$ at a scan speed of $2^\circ/\text{minute}$ giving a step size 0.02° . FT-IR spectra of the nano-composites were taken by Bruker spectrometer model Vector 33. For IR analysis, first 1 mg of the powder sample was carefully mixed with 300 mg of KBr (infrared grade) and pelletized under vacuum. Then the pellet was analyzed in the range of 400 to 4000 cm^{-1} at a scan speed of $23\text{ scan}/\text{minute}$ with 4 cm^{-1} resolution. Surface morphologies of nano-composite coatings were examined by scanning electron microscope (SEM) using a Philips model MV2300 operated at 25 kV. Magnetic properties of ferrite-

polyaniline nano-composites were measured by vibrating sample magnetometer, VSM.

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction Analysis X-ray diffraction pattern of ferrite (Figure 1) shows the characteristic peaks of CoFe_2O_4 . Average crystallite size of the particles was determined utilizing Sherrer formula:

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

Where d is the mean crystallite size of the powder, λ is the wavelength of Cu $K\alpha$ ($\lambda = 0.154051\text{ nm}$). B is the full width at half maximum (FWHM) intensity of the peak in radians, θ is Bragg's diffraction angle and k is a constant usually equal to ~ 0.9 [12]. The crystallite size was calculated to be about 16.65 nm.

The characteristic peaks of CoFe_2O_4 are revealed in XRD patterns of FP-Ph and FP-S nano-composites, but their intensity decreases. This is because of the amorphous nature of PANI that the crystalline behavior of ferrite is suppressed as a result of encapsulation by PANI.

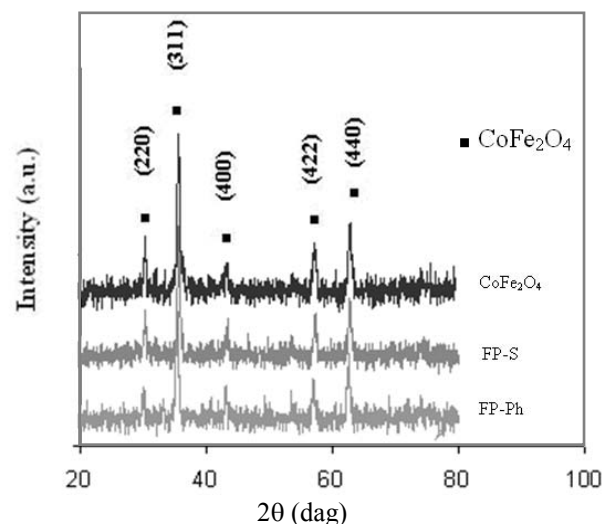


Figure 1. X-ray diffractogram of CoFe_2O_4 and FP-Ph and FP-S nano-composites.

3.2. FTIR Analysis Figure 2 shows the FTIR spectrum of pure PANI synthesized from sulfuric acid containing solution. The spectrum reveals the N-H stretching vibrations peak corresponding to PANI at 3449.229 cm^{-1} while the peaks corresponding to benzenoid (NH-B-NH) and quinonoid (NH-Q-NH) rings are observed at 1635 , 1456 and 1383 cm^{-1} , respectively. The CN vibration peak is observed at around 1091 cm^{-1} . The FTIR spectrum proves that PANI has been produced.

In Figure 3, the FT-IR spectra of all samples exhibit a small peak at 3000 cm^{-1} , which can be associated with the O-H stretching vibrations in physically adsorbed hydrogen-bonded water molecule. The prominent peak at 587 cm^{-1} in the CoFe_2O_4 , is attributed to Fe-O and Co-O stretching vibration modes. The characteristic peak of ferrite at around 580 cm^{-1} in the PF-S and PF-ph nano-composites confirms the presence of ferrite particles and the composite nature of the $\text{CoFe}_2\text{O}_4/\text{PANI}$ nano composites.

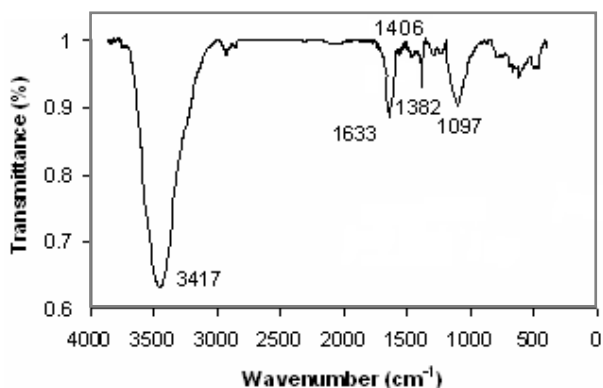


Figure 2. FTIR spectrum of PANI-sulphate.

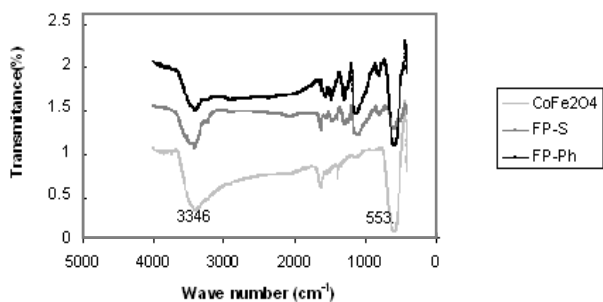


Figure 3. FTIR spectra of CoFe_2O_4 and nano-composites.

3.3. Morphological Characterization Figure 4 shows the microstructure of ferrite confirming that the particles are in nano scale.

PANI is a porous network-like structure and appears to be well interconnected (Figure 5). The SEM micrographs of two nano-composites are shown in Figure 6. Both micrographs of ferrite-PANI nano-composites exhibit a two phase system where the bright phase corresponds to the ferrite, while dark phase constitutes PANI. The microstructure of nano-composite with PANI phosphate is more homogenous than that with PANI sulfate. The SEM of nano-composite with PANI phosphate shows homogeneous nano-porous microstructure.

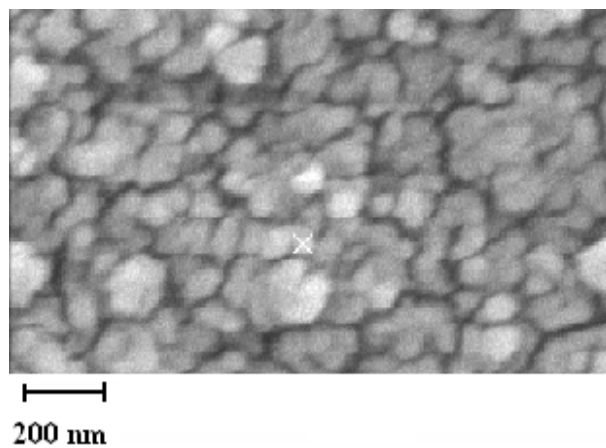


Figure 4. SEM micrograph of CoFe_2O_4 .

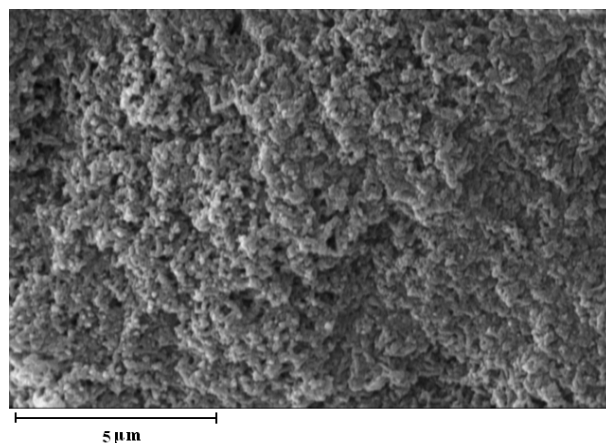
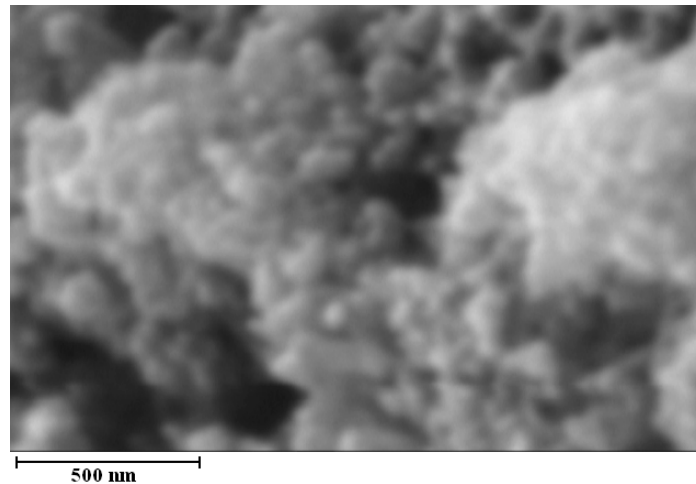
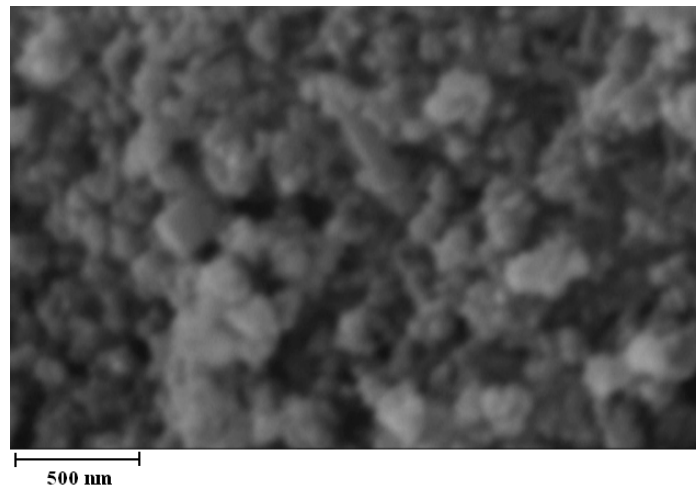


Figure 5. SEM micrograph of PANI.



(a)



(b)

Figure 6. SEM micrographs of nano-composites, (a) PANI sulphate and (b) PANI phosphate.

3.4. Magnetic Properties Figure 7 shows plots of magnetization, M vs. Applied magnetic field, H (-8000 to +8000) for pure PANI, ferrite, FP-S and FP-Ph. Figure 7a shows the diamagnetic nature of PANI. The hysteresis loop of ferrite in Figure 7b exhibits the presence of an ordered magnetic structure in spinel system. The saturation magnetization is 85 emu/g at 10 kOe which is in agreement with other studies [12]. Remanent magnetization (M_r) and coercivity (H_c) are determined to be 40 emu/g and 666.6 Oe respectively. Encapsulation of ferrite nano-particles by PANI leads to a significant

decrease in the magnetic nature of the overall nano-composite owing to the diamagnetic nature of PANI (Figure 7c,d). M_s values were found to be 40 and 28 emu for FP-S FP-Ph respectively. Therefore, it can be concluded that encapsulating of nano-ferrites with PANI sulfate is less than PANI phosphate. The difference in measured values of M_s is due to different interactions developed at the interface of $\text{CoFe}_2\text{O}_4/\text{PANI}$ nano-composite. The SEM images confirm that encapsulating of nano-ferrites with PANI phosphate is more than PANI sulphate (see Figure 6).

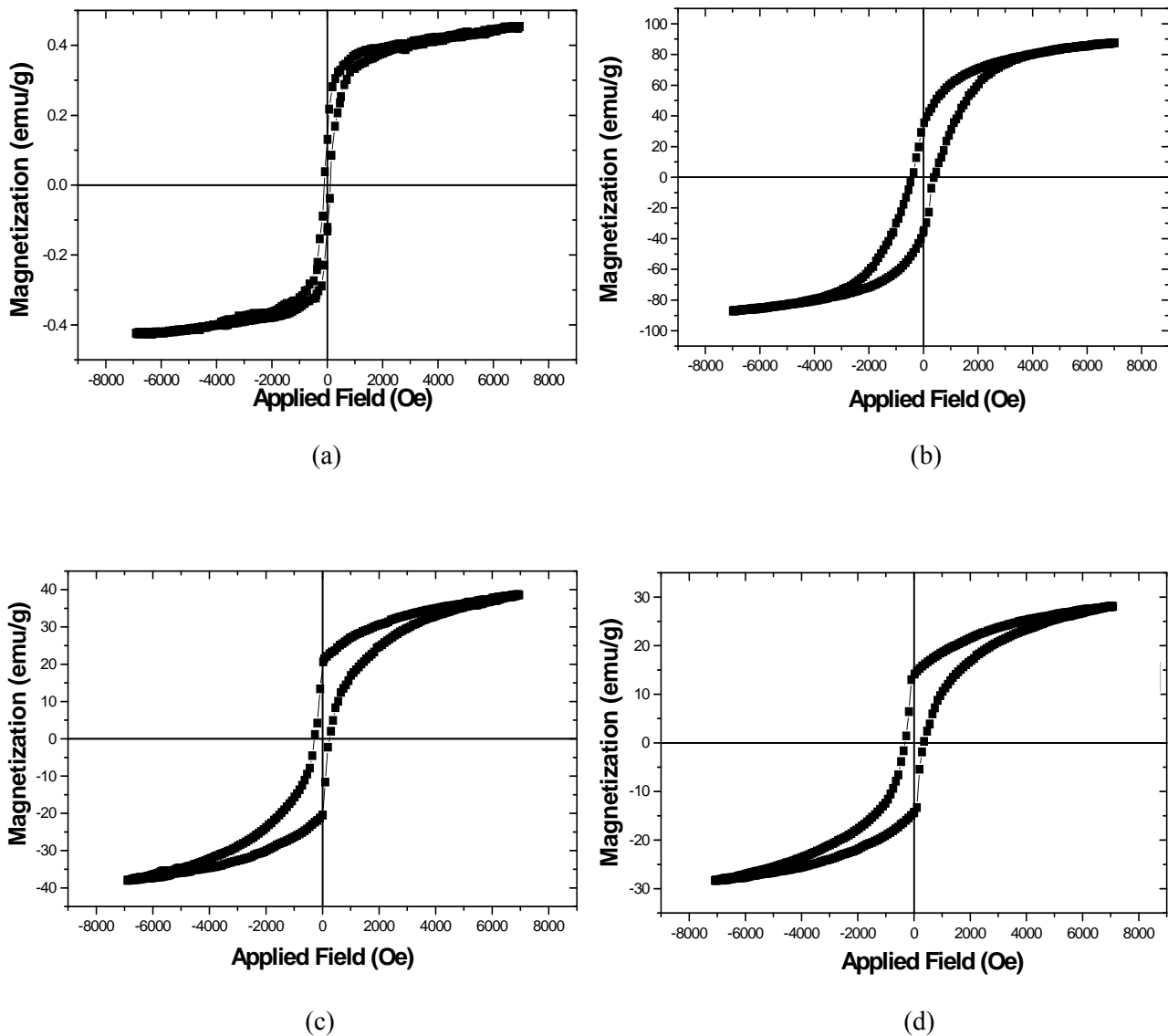


Figure 7. Magnetization curve of (a) PANI, (b) CoFe_2O_4 , (c) PF-S and (d) PF-Ph.

4. CONCLUSION

A simple chemical method was adapted for the synthesis of CoFe_2O_4 nano-composite where the nano-particles interrupt the growing of PANI chains. The improvements made in physical properties of the present nano-composite are expected to enhance the application potential of the polymer without damaging its magnetic properties. The inherent magnetic behavior of the ferrites is responsible for increasing their magnetic properties.

5. REFERENCES

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