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In Situ-Ex-Situ Polymerization and Characterization of $CoCr_2Fe_2O_4$ /PANI Nanocomposite

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ARTICLE DETAILS

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ABSTRACT

The $CoCr_2Fe_2O_4$/PANI nanoparticles were synthesized by solution combustion method and synthesized powder were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Thermogravimetric analysis(TGA), Scanning electron microscope (SEM)and Vibrating sample magnetometer (VSM) technique. The XRD results confirm the cubic spinel structure of the ferrites and crystallite size (D) found in the range of 40-50 nm. The SEM micrographs reveal that the composites showed different aggregations for the different $CoCr_2Fe_2O_4$contents. The results of thermogravimetric analysis indicated that the addition of $CoCr_2Fe_2O_4$ nanoparticles to PANI improved the nanocomposites thermal stability.The FTIR measurements between 400 and 4000 cm-1 confirmed the absorption bands in the spectrum. Magnetic analysis is carried out using VSM technique. Shielding effectiveness (SE) of the as-prepared sample is found to have a maximum value of 50 dB, this SE value clearly indicate that the as-prepared PANI/$Co_{0.5}Ni_{0.5}Fe_2O_4$ nanocomposite can be used for electromagnetic interference shielding.

1. Introduction

Magnetic materials are materials studied and used mainly for their magnetic properties. The magnetic response of materials is largely determined by the magnetic dipole moment associated with the intrinsic angular momentum, or spin, of its electrons. A material's response to an applied magnetic field can be characterized as diamagnetic, paramagnetic, ferromagnetic or antiferromagnetic. Magnetic field is a force which is generated due to energy change in a volume of space. A magnetic field is produced by an electrical charge in motion e.g. current flowing in a conductor, orbital movement and spin of electrons. The magnetic field can be described by imaginary lines as shown in the figure below for a magnet and a current loop.

If a magnetic field, H, is generated by a cylindrical coil (solenoid) of n turns and length l, H = nI/l (A/m). Magnetic flux density, B It is the magnitude of the field strength within a substance subjected to a field H, B = μH (Tesla or Weber/m^2) μ, called the permeability, is the measure of the degree to which a material can be magnetized. In vaccum, B =μoH.μo is the permeability of vacuum and is a universal constant, μo= $4\pi x10^{-7}$(H/m). μr= μ/μo is the relative permeability. A ferrite is a type of ceramic compound composed of iron (III) oxide (Fe_2O_3) combined chemically with one or more additional metallicelements. They are

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both electrically nonconductive and ferrimagnetic, meaning they can be magnetized or attracted to a magnet. Ferrites can be divided into two families based on their magnetic coercivity, their resistance to being demagnetized. *Hard ferrites* have high coercivity, hence they are difficult to demagnetize. They are used to make magnets, for devices such as refrigerator magnets, loudspeakers and small electric motors. *Soft ferrites* have low coercivity. They are used in the electronics industry to make ferrite cores for inductors and transformers, and in various microwave components. Ferrite compounds have extremely low cost, being made of iron oxide (i.e. rusted iron), and also have excellent corrosion resistance. They are very stable and difficult to demagnetize, and can be made with both high and low coercive forces.

2. Experimental

a. Preparation method:

The $CoCr_2Fe_2O_4$ nanoparticles were synthesized using solution combustion method. Homogeneous aqueous solution was prepared by dissolving stoichiometric amounts of oxidizers (Copper nitrate, Chromium nitrate and Ferric nitrate) and fuel (Urea) in distilled water. This homogeneous aqueous solution containing redox mixture was heated in a muffle furnace maintained at 500°C till complete combustion. The combustion finally yields porous and voluminous powder containing $CoCr_2Fe_2O_4$ nanoparticles. $CoCr_2Fe_2O_4$/PANI nanocomposites were synthesized by in situ polymerization method. 50wt% $CoCr_2Fe_2O_4$ nanoparticles with respect to aniline monomer was suspended in a 1 M HCl solution and stirred for half an hour to get well dispersed. To the above suspension 2mL aniline monomer is added and stirred for 30 min. 1M HCl solution containing 4.98 g ammonium per sulfate was then added drop wise to the suspension mixture with a constant stirring. The suspension mixture was stirred for 12 hours at room temperature. A CoCr2Fe2O4/PANI nanocomposite in powder form was then obtained by filtering and washing the suspension with 1 M HCl and distilled water. Filtrate is then dried at 60 ◦C for 24 hours [10].

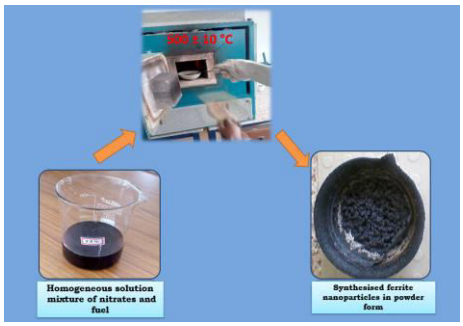

Fig. 1 Synthesis of Polyaniline/$Co_xCr_{0.5-x}Fe_2O_4$Nanocomposites

b. Characterization method:

The X-ray diffraction patterns of the synthesized samples were recorded using Panalytical X-Pert Pro MPD instrument. The samples were analyzed in the 2θ range of 10-80o. The morphological analysis of the synthesizedsamples were performed using the FESEM CARL ZEISS instrument. a c conductivity studies on the synthesized samples have been undertaken using impedance analyzer model HIOKI 3532-50 LCR HI TESTER Version 2.3 (frequency range 50 Hz–5 MHz). Magnetic studies on prepared samples were conducted using Lakeshore vibrating sample magnetometer 7410. The thermal properties of prepared Ag nanocomposite samples were studied using a TA-STD Q600 instrument under dry nitrogen atmosphere at the flow rate of 100mL/min. The samples were heated from room temperature to 700°C at predetermined rate of 20°C/ min.

3. Results and discussion

3.1 X-Ray Diffraction Studies on as prepared $CoCr_2Fe_2O_4$/PANI Nanocomposite

XRD patterns of PANI, and PANI/Co0.5Mn0.5Fe PANI/$CoCr_2Fe_2O_4$ nanocomposite are shown in Fig. 1. The XRD pattern of as prepared PANI/$CoCr_2Fe_2O_4$ nanocomposite matches with JCPDS file no 22-1086 and the particles show cubic crystal structure. This indicates that the product consists of crystalline single-phase PANI/$CoCr_2Fe_2O_4$. The XRD pattern of PANI (Fig. 2a) shows that PANI has partly crystalline structure and the two broad peaks are observed at $2\boldsymbol{\theta}$ =35.23° and 36.02°due to the densely packed phenyl rings and thus an extensive inter chain pi–pi orbital overlap [1–5]. Crystallinity of polyaniline is due to the presence of Benzinoid and Quinoid rings of Polyaniline chain. The major diffraction peaks for PANI/$CoCr_2Fe_2O_4$ nanoparticles (Fig.3.1a & 1b) are identified at (220), (311), (222), (400), (422), (511), and (440). Among these diffraction peaks (311) is found to have maximum intensity.

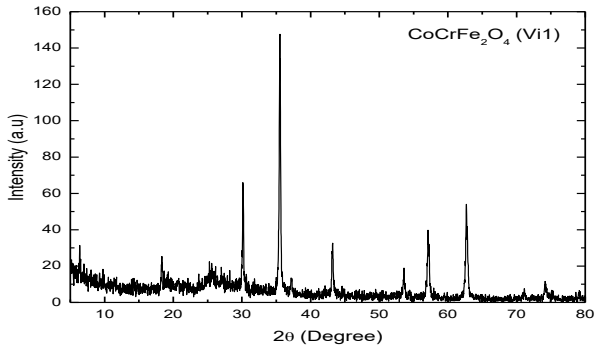

Fig 3.1(a). XRD Spectra of prepared PANI/*$CoCr_2Fe_2O_4$ In-Situ* nanoparticles

The average crystallite size of the samples was estimated by Debye-Scherrer method $D = \frac{k\lambda}{\beta cos\theta}$ where D is the average crystallite size, λ is the wavelength of the X-ray and β is the full width at half maxima (FWHM) of (311) reflection peak. The average crystallite size of the PANI/*$CoCr_2Fe_2O_4$*nanoparticles is estimated to be around 47 nm. The presence of combined peaks of both polyaniline and *$CoCr_2Fe_2O_4$* nanoparticles can be clearly identified from Fig.3.1a and Fig.3.1b. The average crystallite size was obtained as 20 ± 9 nm[6].

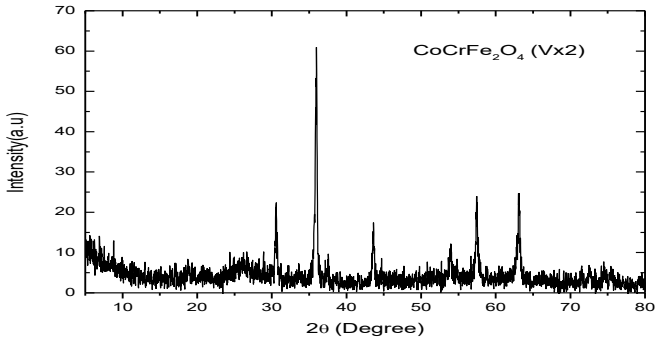

Fig 3.1(b). XRD Spectra of prepared PANI/*$CoCr_2Fe_2O_4$ Ex-Situ* nanoparticles

3.2. FTIR Analysis

The FT-IR spectra of PANI/*$CoCr_2Fe_2O_4$* nanocomposite are shown in Fig. 3a and b respectively. In Fig. 3a the peaks at 3419, 1560/1475, 1290, 1128 cm^{-1} are attributed to the N–H stretching vibration, C=C stretching vibration of the quinone (Q) ring and benzene (B) ring, N–H bending stretching of the benzenoid ring, C–H in-plane bending vibration, respectively [7-10]. In Fig. 2b the absorption peaks at 3445, 1575/1485, 1297, and 1128 cm-1 can also be attributed to the PANI. The FT-IR absorption of these functional groups are different in PANI and the NP.

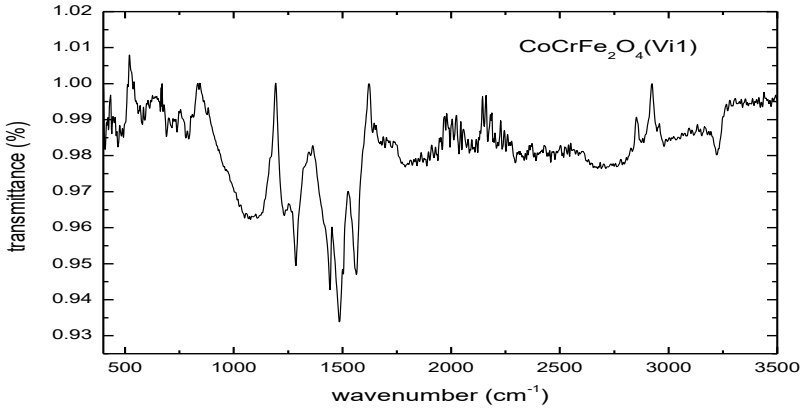

Fig 3.2(a). FTIR spectra of PANI/*$CoCr_2Fe_2O_4$ In-Situ* nanoparticles

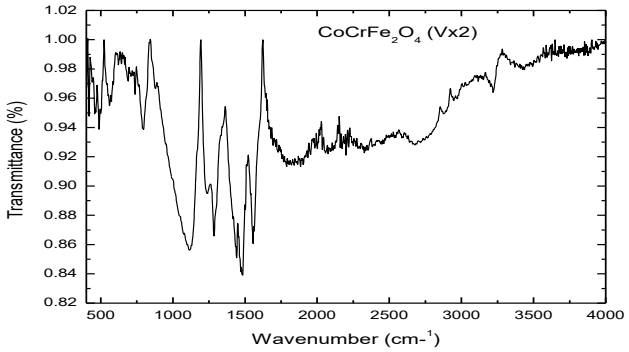

Fig 3.2(a). FTIR spectra of PANI/$CoCr_2Fe_2O_4$ *Ex-Situ* nanoparticles

These peaks have displayed red-shift, due to the interactions between magnetic nanoparticles and PANI, the interaction between the N–H, C–N and the N–Q–N bonds weaken. In addition, the absorption at 460 cm^{-1} is octahedral stretching vibration, (m2), of M–O and the peaks at 572 cm-1 is due to the tetrahedral M–O stretching, vibration (m1), of the spinel structure of Co0.5Mn0.5Fe2O4. All these results also showed that the synthesized nanocomposite consisted of PANI/$CoCr_2Fe_2O_4$NPs and there are intermolecular interactions between them [11].

3.3. FESEM Analysis

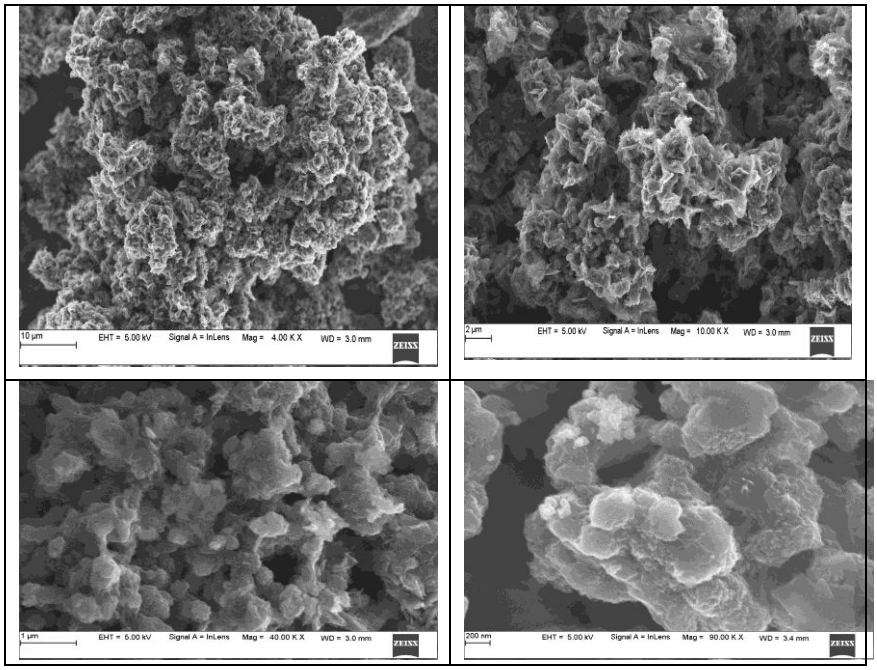

Fig 3: FESEM micrograph of PANI/$CoCr_2Fe_2O_4$.

The morphology of the as-prepared PANI/$CoCr_2Fe_2O_4$nanocomposite was determined by SEM and few micrographs were presented in Fig. 3a and b respectively. SEM micrographs images shows somehow Globular agglomerations with much finer internal structure. Samples exhibit large grains in the range of 100-200 nm. These particles exhibit a network with voids and pores typical of combustion – synthesized powders. PANI layers may have wrapped on the surface of PANI/$CoCr_2Fe_2O_4$nanocomposite, forming these agglomerated globules. A closer examination of these primary structures indicate nearly spherical particles with average particle size of 25 nm. When compared with the crystallite size estimated from X-ray [12]

3.4. VSM Measurements:

M-H curve for PANI/$CoCr_2Fe_2O_4$nanocomposite at room temperature are as shown in Figure 5. It is clear from the curves that the magnetization in the prepared samples increases as the applied field increases and attains saturation. The saturation magnetization (Ms) and coercivity (Hc) values of PANI/$CoCr_2Fe_2O_4$ nanocomposites.

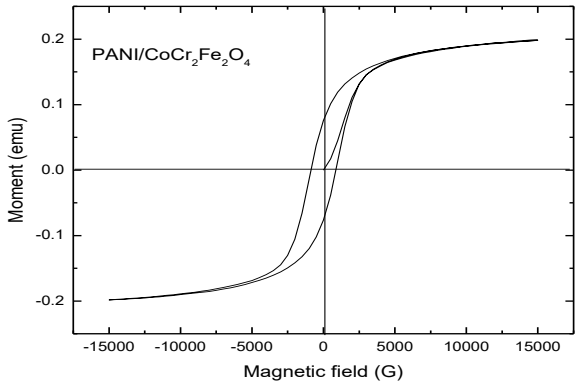

Fig 4: Hysteresis loop of PANI/$CoCr_2Fe_2O_4$nanocomposites.

The Polyaniline coating causes the value of saturation magnetization of $CoCr_2Fe_2O_4$ from 0.72992 to 0.19874 emu. In saturation magnetization (Ms) of PANI/$CoCr_2Fe_2O_4$ nanoparticles by the coating of polyaniline is due to interaction between the particles because of increase in particle–particle separation [13].

4. Conclusion

PANI/$CoCr_2Fe_2O_4$ nanocomposites were successfully prepared by in situ polymerization with excellent structural, magnetic and dielectric properties. The combined results of XRD, VSM, FTIR and VSM spectra showed that nickel ferrite nanoparticles enhanced the electrical and magnetic properties of the composites, referring to the presence of some interaction between nanoferrite particles and PANI. FTIR and XRD results of composites confirmed that the addition of the coalt ferrite nanoparticles did not damage the backbone structure of PANI and the presence of nickel ferrite as a spinel in the amorphous structure of PANI. The conductivity of composites increased with increasing PANI/$CoCr_2Fe_2O_4$ in the sample. It is attributed to the polaron/bipolaron formation. The conduction mechanism has been explained according to the three-dimensional hopping model proposed by Greaves. The results obtained refer to that specific properties can be tailored in the nanocomposites by mixing different proportions of PANI and $CoCr_2Fe_2O_4$ nanoparticles. PANI/$CoCr_2Fe_2O_4$samples exhibit Superparamagnetic behavior at room temperature as discussed in VSM.

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