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Nanocrystalline nickel ferrite reinforced conducting polyaniline nanocomposites

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ABSTRACT

Nanocrystalline nickel ferrite ($NiFe_2O_4$) powder of crystallite size ~20 nm was synthesized by refluxing method. Electrically conductive polyaniline-nickel ferrite (PANI/$NiFe_2O_4$) nanocomposites have been synthesized by an in-situ polymerization of aniline monomer in the presence of as-prepared $NiFe_2O_4$ in different weight percentage (5%, 10%, and 15%). These nanocomposites were subsequently characterized for morphological, crystalline, structural, electrical and magnetic properties by Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), Four Probe Resistivity (FPR) and Vibrating Sample Magnetometer (VSM). Existence of $NiFe_2O_4$ in the nanocomposites was confirmed by XRD, FTIR and TEM analysis. The change in morphology with crystallite size ~ 50 nm was observed for the nanocomposites clearly indicate the coating of PANI on $NiFe_2O_4$. Nanocomposites showed increase in saturation magnetization as compared to that of PANI and increase in electrical conductivity as compared to that of $NiFe_2O_4$ indicating the synergistic effect of individual components. The saturation magnetization drastically increased as nickel ferrite content changed from 5 to 15% in nanocomposites. The conductivity of nanocomposites increased with temperature, exhibiting typical semiconductor behavior. The nanocomposites show semiconducting and ferromagnetic behavior. The electrical conductivity of nanocomposites decreased from 1.089 to 0.268 S/cm, but saturation magnetization increased from 0.97 to 2.803 emu/g, when ferrite content changed from 5 to 15 wt%, indicates such nanocomposites are good for electromagnetic devices. Copyright © 2014 VBRI press.

Keywords: Conducting polymer, polyaniline, nickel ferrite, nanocomposites, VSM.

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Introduction

Intrinsically conducting polymers have been studied extensively due to their intriguing electronic and redox properties and numerous potential applications in many fields since their discovery in 1970s **[1].** Conducting polymers are attractive class of materials similar to metals while retaining flexibility and processibility of conventional polymers **[2-4].** Most commonly studied conducting polymers are Polythiophene, Polypyrrole, Polyacetylene and Polyaniline. Among the various conducting polymers synthesized, polyaniline (PANI) occupies a prime position, because of its unique characteristics like inexpensiveness of the monomer, ease of processing and excellent stability. PANI in its pure and doped forms find extensive applications in making devices like polymer light emitting diodes, photovoltaics, sensors, batteries and super capacitors **[5]**. The relative content of the benzoid and quinoid forms in PANI depends on the acid concentration and the degree of oxidation of the polymer **[6].** It can be protonated by aqueous acid with increase in conductivity of almost 10 orders of magnitude, forming a polysemiquinone radical which contains a delocalized half-filled broad polaron energy band**.**

Conducting polymer-based magnetic nanocomposites represent a new concept in the development of systems exhibiting functional properties resulting from the synergistic interaction between polyaniline and magnetic nanoparticle. The properties of conducting polymers like non-corrosiveness, light weight, mechanical strength, and the possibility to tune electrical conductivity can be utilized along with magnetic properties of ferrite nanoparticles to make multifunctional structure **[7].** Nowadays, the PANI has been successfully utilized in preparation of different nanocomposites **[8-11].** These nanocomposites have been widely used because of their lower density as well as their good environmental stability. Such material possesses advantages of both low dimensional system and organic conductors with magnetic properties. Our aim in making PANI – ferrite nanocomposites because of its great technological applications in several areas like colour imaging, ferrofluids, magnetic refrigeration, electromagnetic shielding, rechargeable batteries, light emitting diodes, nonlinear optical devices, sensor for medicine and pharmaceutics apparatus, membranes for separation of gas mixture, protection against corrosion, conducting paints and glues and others. In order to study on nanocomposites, Aphesteguy et al synthesized ferrite-polyaniline composite by the method of in-situ polymerization **[7].** Kazantseva et al. reported the method of oxidation of aniline in the presence of ferrite to focus on the ferrite-PANI interface and also the properties of PANI **[12].** Reddy et al synthesized iron oxide poly (3,4 ethylenedioxythiophene) (PEDOT) composite by the method of in-situ chemical oxidative polymerization of EDOT with Fe_3O_4 nanoparticles **[13].** Although ferrite-polyaniline composites have been prepared, the magnetic and conductive properties are relative poor due to the synthetic method. Surender et al synthesized microwave assisted nanocrystalline Mn-Zn ferrites **[14].** Chemical method was used by Shrivastava et al for the synthesis of Ni-Zn ferrites **[15].** Singh et al prepared Zn doped nickel ferrite using chemical combustion route and improved ferromagnetic properties of ferrite nanoparticles **[16].** Nanopowder of nickel ferrite was synthesized by Dixit et al using the nitrates of nickel and iron along with citric acid as the host [**17**]. Thus, for further development of synthetic methods, we have used reflux method for the preparation of nanocrystalline nickel ferrite and used them to prepare conducting polyaniline nanocomposites by using in-situ polymerization method. In this paper, we have reported the effect of nanocrystalline nickel ferrite ($NiFe_2O_4$) on electrical and magnetic properties of polyaniline nanocomposites in order to find the application of such multifunctional composites in electromagnetic devices.

Experimental

Materials

Aniline with molecular weight 93.13gm/mole (S. D. Fine-Chem. Ltd., 99.5%) was vacuum distilled prior to use. Ferric nitrate having molecular weight 404gm/mole [$Fe(NO_3)_3$-$9H_2O$] with purity 99%, nickel nitrate having molecular weight 290.81gm/mole [$Ni(NO_3)_2$-$6H_2O$] with the purity 99.5% were purchased from Hi-media and used as received. All other chemicals like ammonium peroxydisulfate with molecular weight 228.2gm/mole (APS, 98%), ethanol (99.9%), sulphuric acid with molecular weight 98.08gm/mole (98%) were bought from S. D. Fine-Chem. Ltd. and used as received without further purification. All chemicals were of analytical grade. Solutions were prepared in de-ionized water.

Methods

PANI/$NiFe_2O_4$ nanocomposites have been characterized by XRD (Philips PW 1730 automatic X-ray diffractometer with Cu-Ka radiation of λ=1.5428˚A), TEM (Hitachi H-7000 operated at 100 kV and 30 μA), Magnetic measurement using EG & G PAR model 4500 vibrating sample magnetometer and electrical resistivity measurement using four point probe technique was done to study the effect of nanocrystalline nickel ferrite on the electrical and magnetic properties of polyaniline.

Synthesis of nanocrystalline $NiFe_2O_4$

$NiFe_2O_4$ nanoparticles were prepared by the simple approach of reflux method **[18].** In a typical procedure, specific molar concentration of nickel nitrate and ferric nitrate as precursors were mixed in a starch solution and

stirred for half an hour. Under reflux condition, NaOH was added drop by drop for 4 h to provide a net negative surface charge to the nuclei limiting their further growth and aggregation. After refluxing, the solution was kept overnight and then filtered and dried in hot air oven at 80°C for 12 h. Dried sample was treated at different temperatures 800°C, 900°C, 1000°C, 1100°C in order to maintain the stability of compound.

Synthesis of PANI/$NiFe_2O_4$ nanocomposites

The PANI/$NiFe_2O_4$ nanocomposite was prepared by an in-situ chemical oxidation polymerization of aniline using APS as an oxidant in presence of as-synthesized $NiFe_2O_4$ nanoparticles at room temperature in air. Aniline (0.1M) and APS (0.1M) were dissolved separately in1 M H_2SO_4 solution and stirred for 1 hour. As-synthesized $NiFe_2O_4$ nanoparticles were suspended separately in 1 M H_2SO_4 solution and sonicated for 1 hour to reduce aggregation of $NiFe_2O_4$ nanoparticles. 100 ml aniline solution and 10 ml $NiFe_2O_4$ nanoparticles suspension were mixed and further sonicated for 30 min. 100 ml APS solution was then slowly added drop wise to well dispersed suspension mixture with a continuous stirring. After 3 hours, a good degree of polymerization was achieved. The precipitate produced in the reaction was removed by filtration, washed repeatedly with 1 M H_2SO_4 and dried under vacuum for 24 hours. The composite powder thus obtained was conductive emeraldine salt (ES) form of PANI/$NiFe_2O_4$ nanocomposite. The different contents PANI/$NiFe_2O_4$ nanocomposites were synthesized using 5, 10, 15 weight % of $NiFe_2O_4$ with respect to aniline monomer. The nanocomposites were abbreviated as PNF-5, PNF-10, PNF-15 respectively for PANI/ $NiFe_2O_4$ (5%), PANI/ $NiFe_2O_4$ (10%), PANI/ $NiFe_2O_4$ (15%).

Results and discussion

The reinforcement of conducting polymer PANI is done by fillers like ferrite nanoparticles which play a major role in strengthening properties of polymer nanocomposites. When nanosized ferrite particles are magnetic in polymer matrix, then such nanocomposites show enhanced magnetic and transport properties over their individual constituents. **Fig. 1** shows the XRD pattern of the nickel ferrite nanoparticles, polyaniline and PANI/$NiFe_2O_4$ nanocomposites (PNF- 5, 10, 15). XRD pattern of nickel ferrite (NF) shows all the peaks corresponds to spinnel ferrite phase matches well with JCPDS data 10-325. The average crystallite size of the $NiFe_2O_4$ was found to be 14nm. $NiFe_2O_4$ belongs to the class of ferrites with inverse spinel structure having structural formula $Fe^{3+}[Ni^{2+}\ Fe^{3+}]O_4$ **[18].** XRD pattern of PANI shows sharp peak at $2\theta = 20^o$ and 26^o which is clear indication of the semi crystalline nature of the sample matches with those of literature **[19].** XRD pattern of PANI/$NiFe_2O_4$ nanocomposites (PNF- 5, 10, 15) shows diffraction peaks as superposition of those of polyaniline and nickel ferrite nanoparticles, indicating the formation of PANI/$NiFe_2O_4$ nanocomposites. We conclude from the XRD results that nanocomposites have a more ordered arrangement and better crystallinity than that of pure polyaniline.

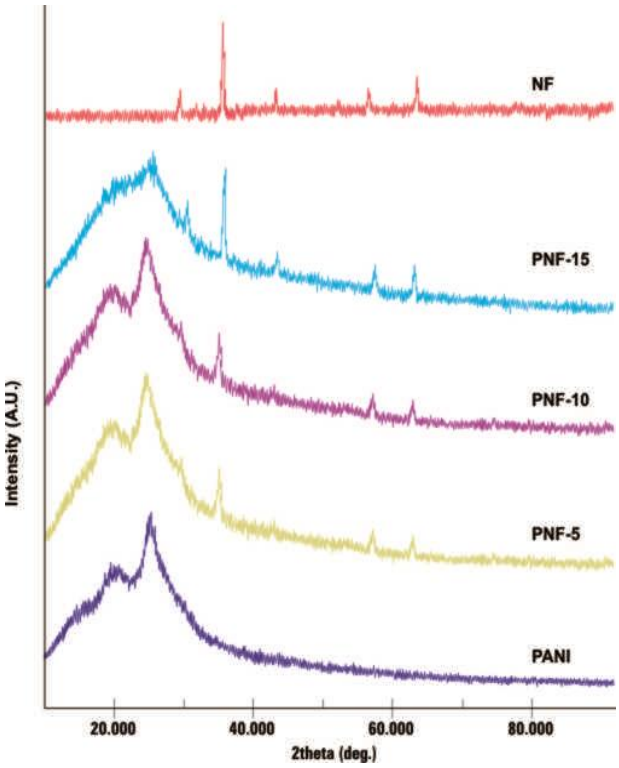

Fig. 1. XRD pattern of PANI, $NiFe_2O_4$ and PANI/$NiFe_2O_4$ nanocomposites.

Fig. 2 shows the FTIR spectra of the nickel ferrite nanoparticles, polyaniline and PANI/$NiFe_2O_4$ nanocomposites (PNF- 5, 10, 15). The absorption bands υ_1 and υ_2 around 611.12 cm^{-1} and 465.90 cm^{-1} in $NiFe_2O_4$ are attributed to the stretching vibration of tetrahedral and octahedral group complexes of ferrites, respectively **[20].** The bands at 1578.39 and 1487.89cm^{-1} in pure PANI are the characteristics bands of nitrogen quinoid and benzoid forms due to the conducting state of the polymer. In PANI/$NiFe_2O_4$ nanocomposites, there are characteristic bands of $NiFe_2O_4$ located around 600 cm^{-1} and 400 cm^{-1}, indicating the well wrapping of $NiFe_2O_4$ nanoparticles with PANI in the PANI/$NiFe_2O_4$ nanocomposites. The interaction of nickel ferrite with polyaniline is confirmed from IR spectra of the nanocomposites.

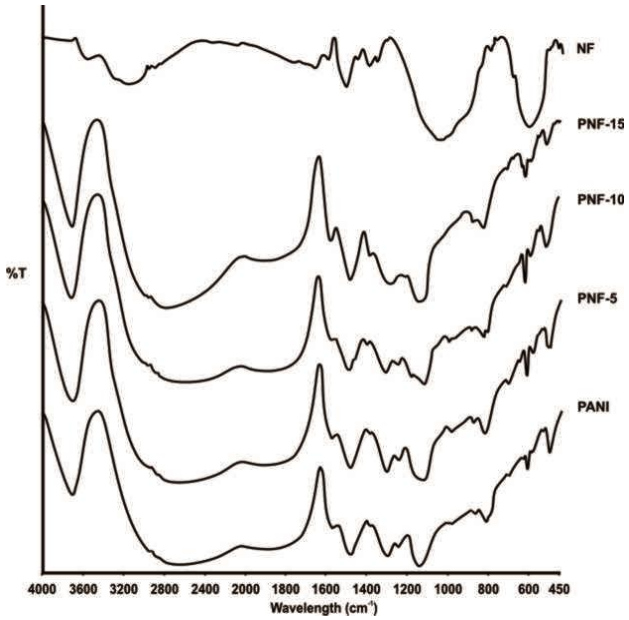

Fig. 2. FTIR spectra of PANI, $NiFe_2O_4$ and PANI/$NiFe_2O_4$ nanocomposites.

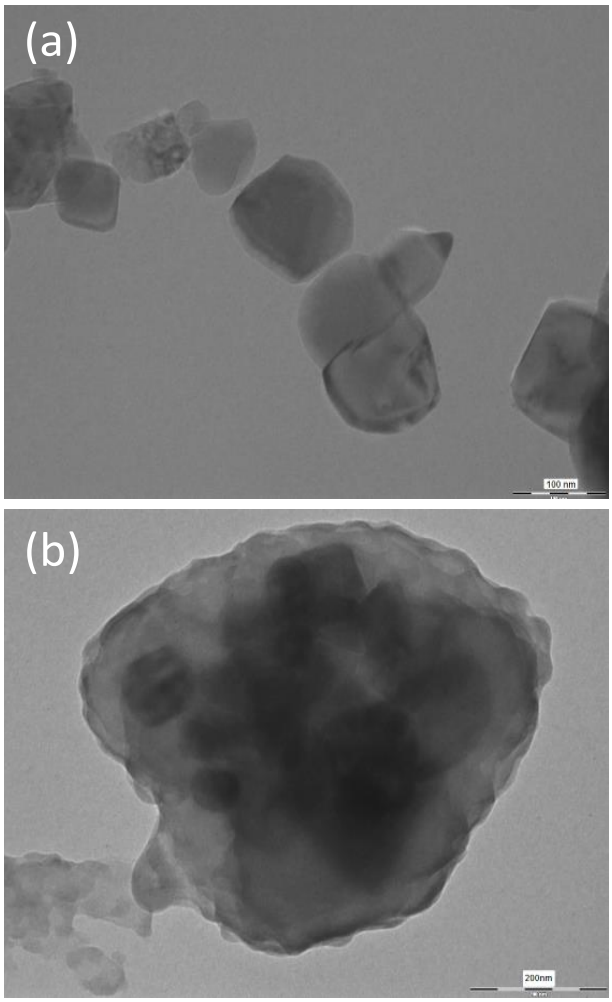

Fig. 3. TEM image of (a) $NiFe_2O_4$ and (b) TEM image of PANI/ $NiFe_2O_4$ 15% nanocomposites.

TEM images of $NiFe_2O_4$ and PANI/$NiFe_2O_4$ nanocomposites (PNF-15) are shown in **Fig. 3(a)** and **3(b)** respectively. The particles of the synthesized ferrite are mostly in the form of square and paralelloids as well as their truncated forms. Large number of small scattered grains with the strongest spotty patterns as observed in TEM, indicating highly crystalline spinel structure with the particle size about 20 nm. The bright and dark field images of PANI/$NiFe_2O_4$ nanocomposite (15%) shows coatings of PANI on nanostructure ferrite due to which the particle size of the nanocomposites was increased and found to about 50 nm further confirmed the interaction of nickel ferrite with polyaniline.

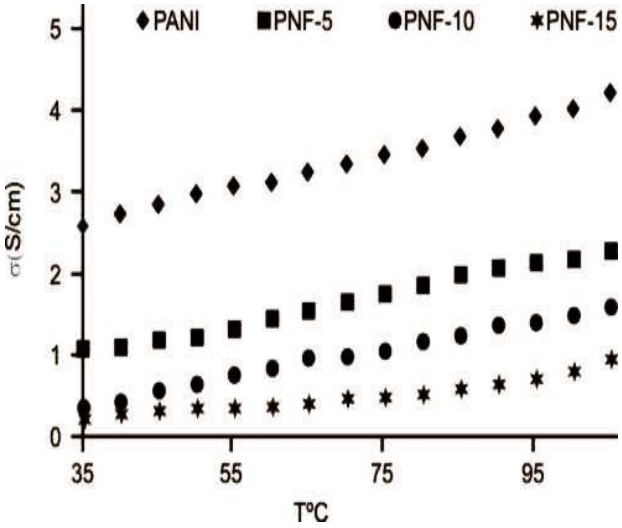

Fig. 4. DC conductivity of PANI and PANI/$NiFe_2O_4$ nanocomposites.

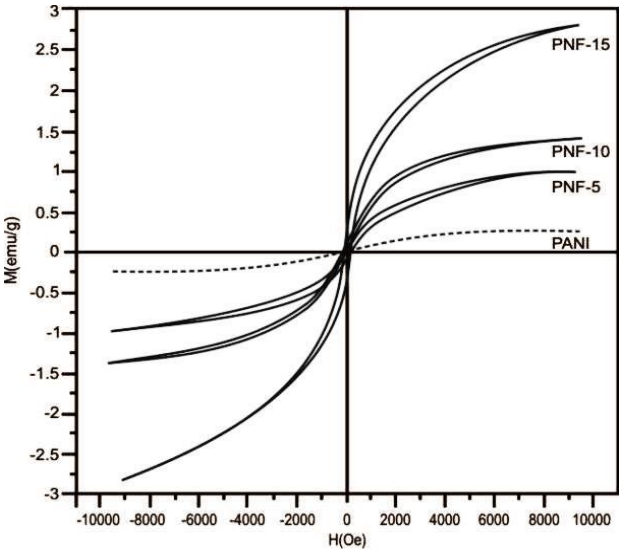

Fig. 5. M-H curves for PANI and PANI/$NiFe_2O_4$ nanocomposites.

Fig. 4 shows the DC conductivity behavior of PANI and PANI/$NiFe_2O_4$ nanocomposites. The conductivity of pure PANI and all nanocomposites was found to be decreased with decrease in temperature, exhibiting typical semiconductor behavior. The incorporation of $NiFe_2O_4$ nanoparticles significantly affects the conductivity of resulting nanocomposites. Room temperature conductivity of nanocomposites (PNF- 5, 10,15) was reduced from 1.089 S/cm of pure PANI to 0.268 S/cm which is much higher than the values 0.094S/cm for nanocomposites obtained by other method **[21]**. This tendency of decreasing conductivity after ferrite nanoparticles embedded into PANI matrix was quite typical **[22, 23]** and may be due to the partial blockage of the conductivity path by the ferrite nanoparticles dispersed in the PANI matrix.

The specific magnetization curve for PANI and PANI/$NiFe_2O_4$ nanocomposites obtained from room temperature VSM measurement are shown in **Fig. 5**. The saturation magnetization of PANI was found to be 0.2514 emu/g with zero coercive field that shows its paramagnetic nature. Nanocomposites show ferromagnetic as that of pure nickel ferrite. The values of saturation magnetization of nanocomposites (PNF- 5, 10,15) increased drastically from 0.97 emu/g to 2.803 emu/g as the content of ferrite nanoparticles changed from 5% to 15% indicating the application of such nanocomposites as good electro-ferromagnetic materials in electromagnetic devices. The corecivity value for nanocomposites greatly increased from 101.944 Oe to 115.134 Oe, showing increased in magnetization results from very well interaction between nanocrystalline $NiFe_2O_4$ and PANI.

Conclusion

Nanocrystalline nickel ferrite and PANI/$NiFe_2O_4$ nanocomposites have been successfully synthesized by reflux and in-situ chemical oxidation polymerization respectively. FTIR, XRD and TEM analyses showed good interaction between PANI and $NiFe_2O_4$ nanoparticles. The nanocomposites show semiconducting and ferromagnetic behavior. The electrical conductivity of nanocomposites decreased from 1.089S/cm to 0.268S/cm, but saturation magnetization increased from 0.97emu/g to 2.803emu/g when ferrite content changed from 5 to 15 wt%, indicates such nanocomposites are good for electromagnetic devices.

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