International Journal on Emerging Technologies(Special Issue on NCRIET-2015) **6**(2): 105-109(2015)

ISSN No. (Print) : 0975-8364
ISSN No. (Online) : 2249-3255

Synthesis, Characterization and DC Conductivity of Pani/$NiFe_2O_4$ Nanocomposites

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(Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: The polyaniline-nickel ferrite (PANI/$NiFe_2O_4$) composites have been prepared by an interfacial polymerization using ammonium persulphate as an oxidizing agent. The composites have been synthesized with different weight percentage (10, 30 and 50 wt %) of $NiFe_2O_4$ in PANI. The composites are characterized by various methods such as Fourier transform infrared spectra (FTIR) and the dominant peaks confirmed the formation of PANI/$NiFe_2O_4$ nanocomposites, Scanning electron microscopy (SEM) images shows morphology of PANI and Transmission electron microscopy (TEM) images of pure $NiFe_2O_4$ nanoparticles and PANI/ $NiFe_2O_4$ nanocomposites which confirms the interaction of $NiFe_2O_4$ with PANI. The temperature dependent DC conductivity of PANI/ $NiFe_2O_4$ composites has been studied in the temperature range 30-160^oC and conductivity of PANI and all PANI/ $NiFe_2O_4$ nanocomposites increases with increase in temperature, exhibiting typical semiconductor behavior. The results of PANI/ $NiFe_2O_4$ indicate interaction of PANI with $NiFe_2O_4$ in the composites.

Key Words: Polyaniline, Temperature, Conductivity, Nickel ferrite, Composites.

I. INTRODUCTION

Research in the field of nanocomposites is the systematic and revolutionary enterprise that builds and organizes the modern scientific world. Organic-inorganic nanocomposites have received greater attention and lots of importance over the last one and half decade because of the most interesting possibilities for their modified structures and promising potential applications in chemistry, biology, medicine and material science.

Conducting polymer composites is some suitable composition of a conducting polymer with one or more inorganic nanoparticles so that, their desirable properties are combined successfully to get various benefits. Inorganic-organic composite materials are important due to their extraordinary properties which arise from the synergism between the properties of the components. The combination of a wide range of organic-inorganic materials results in the formation of nanocomposites with unique electrical, magnetic, catalytic and optical properties (Ansari.M.O. et.al. 2011, Raman.N. et.al. 2011, Baykal.A. et.al. 2013)

Study in the field of conducting polymer nanocomposites are the result of the combination of polymer and organic/inorganic fillers at the nanometric scale.

Polyaniline is the only conducting polymer whose electrical properties can be controlled suitably by charge-transfer doping and/or protonation (Mahesh Bedre D. et.al. 2012),easy synthesis, low cost, excellent environmental stability and high electrical conductivity(Gospodinova.N. et.al. 1998) are the qualities of polyaniline which has helped in the extensive and intensive study from the root level. There are several routes to these materials, but probably the most prominent one is the incorporation of inorganic building blocks in organic polymers. These materials have gained much interest due to the remarkable change in properties such as mechanical (Mallikarjun N.N. *et.al.* 2005), thermal (Gilman.J.W.1999, Gilman. J.W. et.al 2005, Porter D. et.al.2000, Zanetti. M. et.al.2000), electrical (Mahesh Bedre D. et.al.) and magnetic (Godovski. D.Y. 1995) compared to pure organic polymers. Among various nanomaterials, mainly spinel ferrite (MFe_2O_4 , M=Ni, Co, Mn, Zn etc.,) nanoparticles have become popular magnetic materials for a wide variety of applications such as electronic ignition systems, generators, vending machines, magnetic sensors, inductor cores, recording equipment, magnetic fluids, microwave absorbers, telecommunication, medical implants and other high frequency applications (Prithviraj P.M. *et.al.* 2011, Snelling E.C.,1989, Jiles. D.C.,1991,Willard. M.A *et.al.* 2004, Mathew. O.S *et.al.* 2007).

Further, their part reveals the authors report on the preparation of PANI, $NiFe_2O_4$ nanoparticles and PANI/$NiFe_2O_4$ nanocomposites with different weight percentage of $NiFe_2O_4$ in PANI and their characterization through Fourier transform infra-red (FTIR) spectra, Scanning electron microscope (SEM) and Transmission electron microscope (TEM), DC conductivity of these composites were investigated in the range of 30^{o}C-160^{o}C temperature .Thus, the present paper quenches the needs of present modern and luxurious life.

II. MATERIALS & METHODS

All the chemicals and reagents used were of analytical grade. Double distilled water was used throughout the work. Ammonium persulphate was purchased from Qualigens. Aniline was double distilled before use and HCl was purchased from Aldrich chemicals.

Synthesis of Pani. The synthesis of polyaniline was based on mixing aqueous solutions of aniline, hydrochloride and ammonium persulphate at room temperature followed by the separation of polyaniline hydrochloride precipitates by filtration and drying. Aniline hydrochloride (equimolar volumes of aniline and hydrochloric acid) was dissolved in double distilled water in a volumetric flask to 100 ml of solution. Ammonium persulphate (0.25M) was dissolved in water also to 100 ml solution were kept for 1 hour at room temperature (25^{o}C), then mixed in a beaker, stirred mechanically and left rest to polymerize. After 24 hours the polyaniline precipitate was collected on a filter, washed with portions of 0.2M HCl and similarly with acetone. Polyaniline hydrochloride powder was dried in air and then vacuum at 60^{o}C to achieve a constant mass.

Synthesis of Pani/ $NiFe_2O_4$ Nanocomposites Via Interfacial Polymerization. PANI/$NiFe_2O_4$ nanocomposites were prepared with different weight percentage of nickel ferrite (10, 30 and 50 wt %). One gram of aniline was dissolved in 40 ml of $CHCl_3$. 0.1M ammonium persulphate is dissolved in 1M HCl and the $NiFe_2O_4$ nanoparticles (synthesized by microwave route) are slowly added to the above mixture of aqueous and organic phase. After 5 minutes dark green precipitate formed slowly at the interface and then gradually diffused into the aqueous phase. After 24 hours, the entire aqueous phase was filled homogeneously with dark green colour film, organic layer observed shows orange colour due to the formation of aniline oligomers. The aqueous phase was then collected washed with ethanol and water to remove the unreacted aniline. The residue of polymer thus obtained is purified and dried in vacuum oven at 40^{o}C for 36 hours. The dried PANI/$NiFe_2O_4$ nanocomposites sample is used for structural characterization.

Preparation of Pellets. The powders of PANI and PANI/ $NiFe_2O_4$ nanocomposites so obtained are crushed finely in the presence of acetone medium in agate mortar. The pellets of 10 mm diameter were prepared with thickness varying from 1 to 2 mm by applying a pressure of 90 M Pa in a hydraulic press. In temperature dependent conductivity studies, both surfaces of the pellets were coated with silver paste to obtain better contacts.

Characterization. The FTIR spectra of all the samples were recorded on a ThermoNicolet, Avatar 370 spectrometer in KBr medium at room temperature. The surface morphology of the samples was investigated by scanning electron microscope Joel Model JSM-6390LV and transmission electron microscope PHILIPS-CM 200.The temperature dependence DC conductivity for the samples in a temperature range between 30-160^{o}C were performed using a Keithley-6514 system electrometer.

III. RESULTS AND DISCUSSION

A. FTIR Analysis

The FTIR spectra of $NiFe_2O_4$ nanoparticles, PANI and PANI/$NiFe_2O_4$ (10 & 50 wt %) nanocomposites are shown in figures 1(a), 1(b) and 1(c)-1(d) respectively.

In ferrites, the metal ions are situated in two different sub lattices, designated tetrahedral and octahedral according to the geometrical configuration of the oxygen nearest neighbours (Yavuz. O. *et.al.* 2005, Selvan R.K. et.al. 2003). Intrinsic stretching vibrations of the metal at the tetrahedral site are observed in the range of 620-550 cm^{-1}. Octahedral-metal stretching vibrations are observed in the range of 450-385 $cm^{-1.}$ The FTIR spectrum of $NiFe_2O_4$ is shown in fig 1(a). First metal oxygen band (Fe-O) observed at 553.07 cm^{-1} and another (Ni-O) observed at 461.63 cm^{-1}.

In FTIR spectra of pure PANI the bands at 1478.15 cm^{-1} and 1301.22 cm^{-1} are the characteristic bands of nitrogen quinoid and benzoid forms due to the conducting state of the polymer. The FTIR spectra of PANI/$NiFe_2O_4$ (10 & 50 wt %) nanocomposites shows the characteristic peaks at 3202-3208 cm^{-1}, 1580-1583 cm^{-1}, 1493-1496 cm^{-1}, 1302-1304 cm^{-1}, 1134-1136 cm^{-1} and 814-833 cm^{-1}. The peak at 1580-1583 cm^{-1} is due to C=C double bond quinoid rings, 1493-1496 cm^{-1} is due to vibrations of C=C double bond associated with the benzenoid ring, 1302-1304 cm^{-1} is due to combination of C-N in quinoid and benzenoid sequences. The peaks at 814-833 cm^{-1} are be the characteristic peaks of polyaniline backbone, which indicates the coating of PANI on $NiFe_2O_4$ nanoparticles (Nandapure.A.I. *et.al.* 2014).

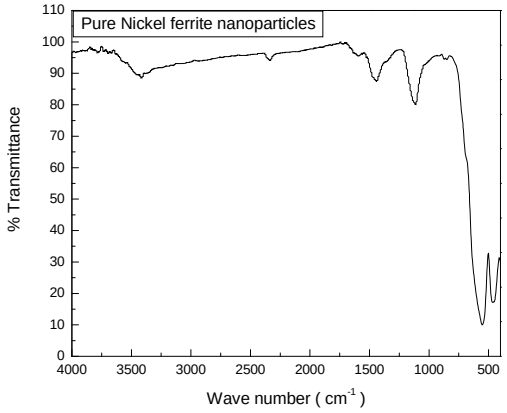

Fig. 1. a FTIR Spectra of pure $NiFe_2O_4$ nanoparticles

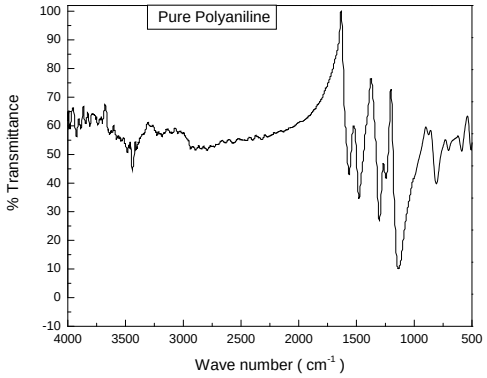

Fig. 1. b FTIR Spectra of pure PANI.

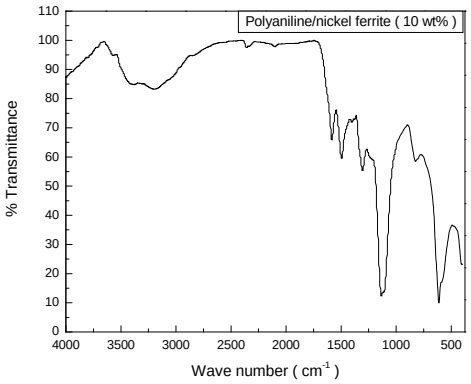

Fig. 1. c FTIR Spectra of $PANI/NiFe_2O_4$ (10 wt %) nanocomposites.

B. SEM Analysis

Figure 2 shows the scanning electron micrograph of pure PANI which is of a highly agglomerated granular structure and has a substantial intragranular distance between the grains. The average grain size was found to be 2-5 µm (Ajai kumar S.M *et.al.* 2015).

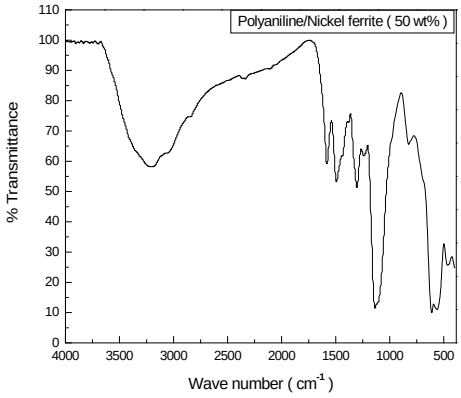

Fig. 1. D. FTIR Spectra of $PANI/NiFe_2O_4$ (50 wt %) nanocomposites.

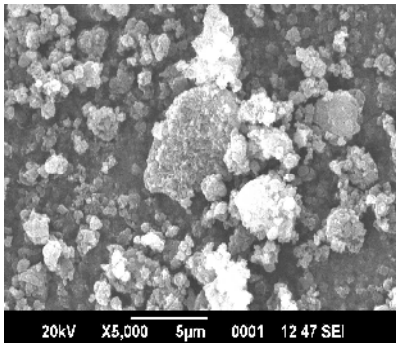

Fig. 2.SEM image of pure polyaniline

C. TEM Analysis

Figure 3(a) and 3(b) shows the TEM images of pure $NiFe_2O_4$ nanoparticles and PANI/ $NiFe_2O_4$ (50 wt %) nanocomposites respectively. Figure 3(b) shows TEM image of $NiFe_2O_4$ nanoparticles (50 wt %) with polygonic morphologies are observed. Average size of nanoparticles was obtained as 32.62 nm. Figure 3(b) shows TEM image of PANI/ $NiFe_2O_4$ (50 wt %) nanocomposites, the average size of the composite was increased and found to about 42 nm, which confirms the interaction of $NiFe_2O_4$ with PANI.

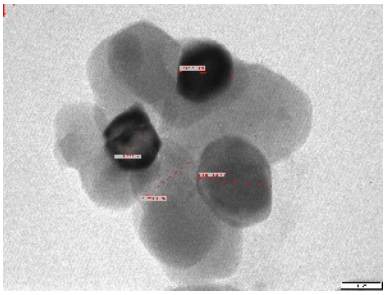

Fig. 3.a TEM image of pure nickel ferrite nanoparticles.

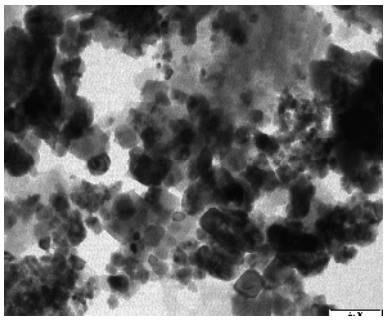

Fig. 3.b TEM image of PANI/ $NiFe_2O_4$ (50 wt %) nanocomposites**.**

The selected area electron diffraction (SAED) pattern of the PANI/ $NiFe_2O_4$ (50 wt %) nanocomposites is shown in figure 4. The SAED pattern consists of concentric rings with spots over the rings. This feature indicates the nanocomposites are crystalline in nature (Pawaskar. N.R *et.al* 2002, Wang.Q *et.al.* 1998).

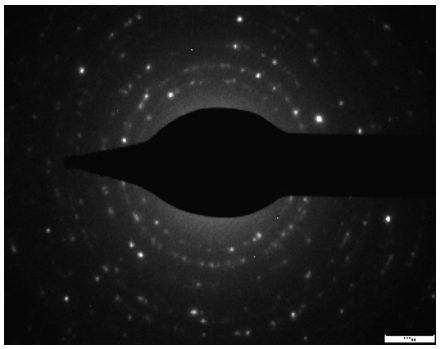

Fig. 4. SAED pattern of PANI/ $NiFe_2O_4$ (50 wt %) nanocomposites

D. DC Conductivity (σ_{dc})

Figure 5(a) and 5(d) shows the variation of DC conductivity (σdc) as a function of temperature for PANI and PANI/$NiFe_2O_4$ nanocomposites respectively in the temperature range from 30oC to 160oC. From the figures it is observed that conductivity of PANI and all PANI/ $NiFe_2O_4$ nanocomposites increases with increase in temperature, exhibiting typical semiconductor behavior.

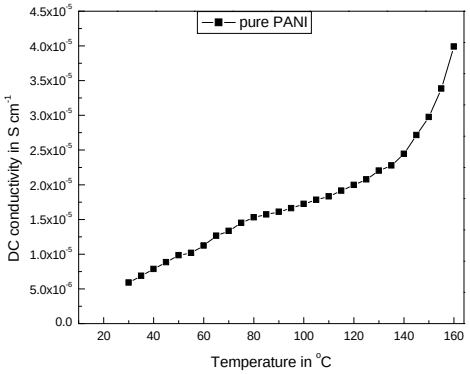

Fig. 5.a DC conductivity of pure PANI.

The incorporation of $NiFe_2O_4$ nanoparticles significantly affects the conductivity of PANI/$NiFe_2O_4$ nanocomposites. Room temperature conductivity of PANI is $5.89x10^{-6}$ S cm^{-1} and that for PANI/ $NiFe_2O_4$ (10, 30 & 50 wt %) nanocomposites are $6.28x10^{-9}$ S/cm, $1.13x10^{-6}$ S/cm and $2.51x10^{-9}$ S cm^{-1} respectively, may be due to the $NiFe_2O_4$ nanoparticles blocking the conduction path in the PANI matrix (Stejskel.J *et.al.*1998, Stejskel.J *et.al* 2006).

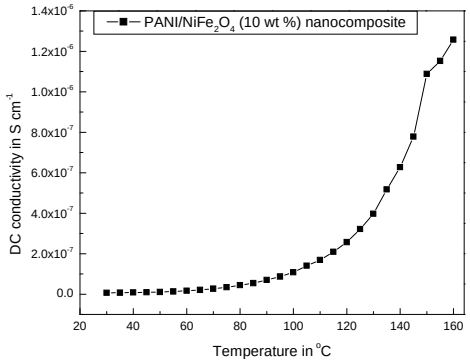

Fig. 5. b DC conductivity of PANI/$NiFe_2O_4$ (10 wt %) nanocomposites.

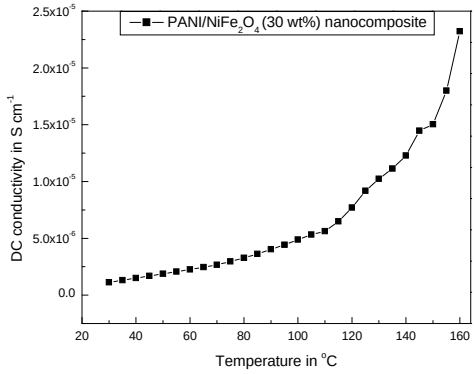

Fig. 5.c DC conductivity of PANI/$NiFe_2O_4$ (30 wt %) nanocomposites.

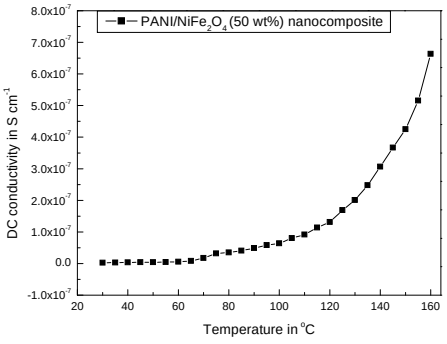

Fig.5. d DC conductivity of PANI/$NiFe_2O_4$ (50 wt %) nanocomposites.

V. CONCLUSION

The PANI/$NiFe_2O_4$ nanocomposites with different weight percentages of $NiFe_2O_4$ in PANI were synthesized by interfacial polymerization. Detailed characterizations of the nanocomposites were carried out using the techniques such as FTIR, SEM & TEM. The results of SEM & TEM reveals that the crystalline nature of the PANI/$NiFe_2O_4$ nanocomposites. FTIR spectra of the nanocomposites show the characteristic absorption bands of $NiFe_2O_4$ at 612 cm^{-1}, 618 cm^{-1}, 506 cm^{-1} and 611 cm^{-1}, which confirms the formation of PANI/$NiFe_2O_4$ nanocomposites. The DC conductivity as a function of temperature for PANI and PANI/$NiFe_2O_4$ nanocomposites was studied in the temperature range from 30°C-160°C. At higher temperatures, DC conductivity increases because of hopping of polarons from one localized state to other localized states. The DC conductivity of the nanocomposites increases with an increase in temperature, which is characteristic behavior of semiconducting materials.

ACKNOWLEDGEMENTS

The author would like to acknowledge Sophisticated Analytical Instrument Facility (SAIF) of CUSAT, Cochin, India, for FTIR and SEM analysis of the samples, Sophisticated Analytical Instrument Facility (SAIF) of IIT, Bombay, India, for TEM analysis and wish to express sincere thanks to Dr. M V N Ambika Prasad , Chairman Dept. of Material Science, Gulbarga University, KALABURGI, Karnataka, India.

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