Synthesis, characterization and low temperature electrical conductivity of Polyaniline/NiFe$_2$O$_4$ nanocomposites

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Abstract. Conducting polymer/ferrite nanocomposites with an organized structure provide a new functional hybrid between organic and inorganic materials. The most popular among the conductive polymers is the polyaniline (PANI) due to its wide application in different fields. In the present work nickel ferrite (NiFe$_2$O$_4$) nanoparticles were prepared by sol-gel citrate-nitrate method with an average size of 21.6nm. PANI/NiFe$_2$O$_4$ nanoparticles were synthesized by a simple general and inexpensive in-situ polymerization in the presence of NiFe$_2$O$_4$ nanoparticles. The effects of NiFe$_2$O$_4$ nanoparticles on the dc-electrical properties of polyaniline were investigated. The structural components in the nanocomposites were identified from Fourier Transform Infrared (FTIR) spectroscopy. The crystalline phase of nanocomposites was characterized by X-Ray Diffraction (XRD). The Scanning Electron Micrograph (SEM) reveals that there was some interaction between the NiFe$_2$O$_4$ particles and polyaniline and the nanocomposites are composed of polycrystalline ferrite nanoparticles and PANI. The dc conductivity of polyaniline/NiFe$_2$O$_4$ nanocomposites have been measured as a function of temperature in the range of 80K to 300K. It is observed that the room temperature conductivity $\sigma_{RT}$ decreases with increase in the relative content of NiFe$_2$O$_4$. The experimental data reveals that the resistivity increases for all composites with decrease of temperature exhibiting semiconductor behaviour.

1. Introduction

Among the conducting polymers, polyaniline (PANI) has been extensively studied due to its easy synthesis, low cost, excellent environmental stability, and high electrical conductivity [1]. PANI has attracted much attention because of its potential application in molecular electronics, electromagnetic interference (EMI) shielding, chemical sensors, antistatic coatings, rechargeable batteries, corrosion inhibitors, absorbing materials [2], etc. It is well known that conducting polymers can effectively shield electromagnetic waves generated by an electric source. However, electromagnetic waves from a magnetic source can be effectively shielded only by magnetic materials [3]. Thus, a combination of magnetic constituents and conducting polymeric materials opens new possibilities to provide shielding from various electromagnetic sources.

Many kinds of materials can be used as magnetic part of the composite materials, such as Ni Fe, Co, Fe$_2$O$_3$, ZnFe$_2$O$_4$, CoFe$_2$O$_4$, NiFe$_2$O$_4$, Co$_3$O$_4$ and BaFe$_{12}$O$_{19}$ [4,5]. Among magnetic materials, the
spinel ferrites exhibit remarkable magnetic properties particularly in radio-frequency region, physical flexibility, high electrical resistivity, mechanical hardness and chemical stability [6]. Their properties are particularly enhanced when the size of the particles reaches the nanometer range [7]. NiFe₂O₄ is an important magnetic ferrite which has been found its extensive applications in diverse areas such as permanent magnets, recording media, Ferro fluids and gas sensors.

In this paper, NiFe₂O₄ nanoparticles were prepared by citrate-nitrate method, and NiFe₂O₄/PANI nanocomposites were then synthesized via an in situ polymerization of aniline monomer in an aqueous. It is pointed out that the NiFe₂O₄ and PANI/NiFe₂O₄ nanoparticles obtained in our experiment have cubic spinel phase. The electrical, thermal stability and the structural characterization have been investigated through XRD, FTIR and SEM methods. The temperature dependence of dc conductivity on PANI/NiFe₂O₄ nanocomposites was investigated in the temperature range 80-300 K.

2. Preparation
Nickel ferrite nanoparticles have been prepared by citrate-nitrate method [5, 8] using nickel nitrate and ferric nitrate in the molar ratio 1:2. A certain amount of citric acid was dissolved in a molar ratio 1:1 of nitrate to citric acid. The combustion reaction during the process can be described as:

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\text{Ni(NO}_3\text{)}_2.6\text{H}_2\text{O} + 2\text{Fe(NO}_3\text{)}_3.9\text{H}_2\text{O} + \text{C}_6\text{H}_8\text{O}_7.9\text{H}_2\text{O} + \text{H}_2\text{O} \xrightarrow{\text{stir at 120°C, pH=7}} \text{Sol Gel} \xrightarrow{\text{Ignition 250°C}} \text{NiFe}_2\text{O}_4 + \text{CO}_2 + \text{NO} + \text{H}_2\text{O}
\]

Polyaniline/NiFe₂O₄ nanocomposites were prepared by a simple in-situ polymerization method [5, 8, 9] in the presence of NiFe₂O₄ nanoparticles. Different PANI/NiFe₂O₄ nanocomposites were synthesized using 0wt%, 20wt% (N1), 40wt% (N2), 60wt% (N3), and 80wt% (N4) of NiFe₂O₄ nanoparticles with respect to aniline monomer.

3. Characterization
X-ray diffraction (XRD) pattern of the samples were collected on a Philips X’pert Pro MPD X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å) at a scanning rate of 0.05° per step with 15s/step in the range of 10–80°. FT-IR spectroscopy was recorded on a PERKIN-ELMER (model-1000) spectrometer in the range of 400–4000 cm⁻¹ using KBr pellets. Scanning Electron Micrograph (SEM) was carried out in a Hitachi model S-3200N microscope.

The DC electrical conductivity was carried by four probe method using Keithley source meter (model 220) and a multimeter (Model 2000) in the temperature range 80-300 K by using Lakeshore auto tuning temperature controller (Model-330). The measurements were recorded during cooling cycle.

4. Result and discussion
4.1. Structural and morphological characterization
Diffraction pattern for NiFe₂O₄ nanoparticles (figure 1) shows a cubic spinel phase with fcc crystal structure [10] with no extra reflections and are well-indexed to the crystallographic planes of spinel ferrite (220), (311), (222), (400), (422), (511), and (440) with 100% intensity at 2θ = 31.04° that corresponds to the reflection plane (311). The diffraction result well agrees with the standard XRD data (JCPDS card No. 74-1913). The average particle size was determined by Debye-Scherrer’s formula and for pure NiFe₂O₄ it is found to be 21.6 nm; and increases with decreasing content of NiFe₂O₄ in PANI. It is also evident from the figure that, the pure polyaniline has broad peak in the region of 20-30° with a maximum at around 25° indicating its semicrystalline nature and with increasing content of NiFe₂O₄ nanoparticles in the composite the relative intensity of the characteristic peaks of PANI/NiFe₂O₄ nanocomposites increase regularly, clearly indicating an increase in the NiFe₂O₄ content in nanocomposites.
Figure 1. XRD patterns of pure PANI, NiFe$_2$O$_4$ and PANI/NiFe$_2$O$_4$ nanocomposites.

Figure 2. FTIR spectra of PANI/NiFe$_2$O$_4$ nanocomposites.

Figure 2 shows the FTIR spectra of pure polyaniline and PANI/NiFe$_2$O$_4$ nanocomposites. The characteristic peaks of PANI occur at 1563, 1483, 1298, 1242, 1143 and 800 cm$^{-1}$ [11]. The peaks at 1563 and 1483 cm$^{-1}$ are attributed to the characteristic C=C stretching of the quinoid and benzenoid rings, the peaks at 1298 and 1242 cm$^{-1}$ are assigned to C-N stretching of the benzenoid ring, the broad peak at 1143 cm$^{-1}$ which is described by MacDiarmid et al. [12] as the “electronic-like band” is associated with vibration mode of N=Q=N, indicating that HCl doped PANI is formed in our samples, and the peak at 800 cm$^{-1}$ for PANI is attributed to the out-of-plane deformation of C-H in the 1,4-disubstituted benzene ring [11]. We can notice that the FTIR spectra for PANI and PANI/NiFe$_2$O$_4$ nanocomposites are similar and the characteristic peak value of PANI at 1143 and 1483 cm$^{-1}$. The peaks of the PANI/NiFe$_2$O$_4$ nanoparticles shift to lower wave numbers. This indicates that the PANI/NiFe$_2$O$_4$ powders are composed of NiFe$_2$O$_4$ nanocomposites, which infer there is some interaction between NiFe$_2$O$_4$ particles and PANI backbone.

Figure 3. SEM images of pure NiFe$_2$O$_4$, PANI and PANI/NiFe$_2$O$_4$ nanocomposites (40 wt% of NiFe$_2$O$_4$).

The SEM images of NiFe$_2$O$_4$ nanoparticles, PANI and PANI/NiFe$_2$O$_4$ nanocomposites are shown in the figure 3. It can be observed that the NiFe$_2$O$_4$ nanoparticles appear uniform sphere-like shape. The SEM micrograph of the PANI indicates the big globular agglomerates with smooth surface. It is noticeable that the SEM micrograph of PANI/NiFe$_2$O$_4$ (40 wt%) nanocomposites presents different morphology as compared with the bare NiFe$_2$O$_4$ nanoparticles. The PANI layers are wrapped on the surface of NiFe$_2$O$_4$ nanoparticles appearing as small aggregated globules [5, 11].

4.2. DC electrical properties

The temperature dependent of resistivity of PANI was measured in the temperature range of 80 to 300K. The resistivity of PANI increases with decreasing temperature exhibiting semiconducting behavior as shown in figure 4. The room temperature conductivity for pure PANI is 5.15 S cm$^{-1}$ and it increases with temperature.
Figure 4. Temperature dependent of resistivity and conductivity of pure Polyaniline.

Figure 5. Temperature dependent resistivity of PANI/NiFe$_2$O$_4$ nanocomposites.

Figure 5 shows, the resistivity of all PANI/NiFe$_2$O$_4$ nanocomposites which increases with decreasing temperature exhibiting semiconducting behavior [4]. Since the NiFe$_2$O$_4$ nanoparticles are embedded in the PANI matrix, interactions between the polymer matrix and NiFe$_2$O$_4$ nanoparticles will increase the charge carrier scattering and thus increase the sample's resistivity resulting in decrease in the conductivity of PANI/NiFe$_2$O$_4$ composites with increase in NiFe$_2$O$_4$ content [13, 14]. Other effects like increased charge carrier trapping, either by the nanoparticles themselves or by morphological changes and defects induced by them, could also play a role.

5. Conclusion

In summary, NiFe$_2$O$_4$ nanoparticles were prepared by sol-gel citrate-nitrate method with an average size of 21.6nm. PANI/NiFe$_2$O$_4$ nanoparticles were synthesized by a simple general and inexpensive in-situ polymerization in the presence of NiFe$_2$O$_4$ nanoparticles. The result of XRD, FTIR spectroscopy and SEM shows the formation of the composite and indicate an interaction between PANI and NiFe$_2$O$_4$ nanoparticles. The effect of NiFe$_2$O$_4$ nanoparticles on the dc-electrical properties of polyaniline was investigated and the conductivity of the nanocomposite decreases with increase in the doping concentration of NiFe$_2$O$_4$.

6. References

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