

Studies on structural, morphology and electrical conductivity of Nickel oxide doped polyaniline (NiO/PANI) nanocomposite

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ABSTRACT

The combination of two components with uniform distribution in nano scale is expected to facilitate wider applications of the material. In this study, polyaniline (PANI) and polyaniline/Nickel oxide (NiO) nanocomposite were prepared by in-situ chemical oxidative polymerization method using persulfate of ammonium as oxidant. The PANI / NiO composites have been synthesized with various compositions viz., 10, 20, 30, 40 & 50 Wt. % of NiO in PANI. The structural analysis of pure polyaniline and its composites are studied using X-ray diffraction (XRD) technique. Surface morphology of Polyaniline and its composites are studied using Scanning electron microscope technique. The ac conductivity of the samples are studied as function frequency and dc conductivity was carried out as function temperature.

Keywords:

1. Introduction:

Since by the discovery of electrically conducting polymer in 1976 by Alan MacDiarmid, Alan J. Heeger, and Hideki Shirakawa, intensive investigations have been carried out on the new generation of "synthetic metals" due to their unique combination of electronic and optical properties and processing advantages [1,2]. Among the conducting polymers, the cheap and easily availability of the raw materials which is popularly known as PANI, easy synthesis route, good environmental stability, PANI is a phenylene based polymer having - NH - group of either side of phenylene. The electrical conductivity is achieved in the conjugated polymers by means of delocalized of the π - electrons that allow charge mobility along the backbone of the polymer chain. The synthesis of conducting polymers has been accomplished by oxidizing or reducing process either through chemical doping [3] or electrochemical doping [4]. Various applications of conducting polymers have been proposed as transducers of biosensor [5], electrodes of rechargeable batteries [6], artificial nerves and muscles [7], gas sensors [8], solid electrolytic capacitor, diodes and transistors [9], anti-static electromagnetic shielding [10], and biomedical applications [11]. Polyaniline (PANI) continues to attract considerable attention because its electrical and optical properties can be changed by oxidation and protonation of the amine nitrogen atoms. PANI is known for its excellent thermal and environmental stability but poor processibility due to insolubility and brittleness that limits its commercial applications. PANI could be more process able in the composites form with another water soluble polymers such as PVA, poly (vinyl pyrrolidone), poly (acrylic acid) and poly (styrene sulphuric acid) (PSSA) which are used as stabilizers. A functionalized photonic acid can be added into the composites to chemically polymerize PANI. The PANI dispersion can then be casted to form composite film containing PANI nanoparticles [12]. To improve the conductivity further, conducting polymers have been irradiated with x-rays [13,14], gamma radiation [15], and gamma electron beams. Nickel oxide is the chemical compound with the formula NiO. It can be either a green or black crystalline powder. NiO adapts the NaCl structure with octahedral Ni and O₂. The simple structure is commonly known as the rock salt structure like many other binary metal oxide, NiO is often non stoichiometric, the meaning that the NiO ratio deviates from 1:10. NiO can be prepared by multiple methods. Upon heating above 400°C nickel powder reacts with oxygen to give NiO.

2. Materials and Methods:

The most important characteristic feature of monomer molecules for the formation of conducting polymer is the requirement of the conversion of closed shell system to a corresponding cation or anion radical and the stability of the product to form during the process. Polyaniline synthesized either by chemical or electrochemical oxidation of aniline in an aqueous medium is preferred. The synthesis of polymer either by chemical or electrochemical methods depends upon the intended application of the polymer. The most

preferred method for synthesis is to use either hydrochloric or sulphuric acid with ammonium persulphate as an oxidant [16-20]. It has been noticed that better polymer formation occurs if the monomer solution is acidic and oxidants are cooled separately before initiating polymerization.

2.1. Preparation of polyaniline

Ammonium persulphate (0.2 M) was added drop wise to a stirred solution to prevent warming of the aniline (0.2 M) solution dissolved in 1 mol of an aqueous solution of hydrochloric acid (1 N) at a temperature of 0–5° C. Following this addition, stirring was resumed for 2 hours using a magnetic stirrer to ensure completion of the reaction. The time of the initial coloration of mixing the reactants depends upon the temperature and concentration of the portico acid. During the polymerization reaction, HCl was used as a protic acid and the temperature was maintained at room temperature by using a freezing mixture. The end product was a green-colored precipitate. This precipitate was filtered, washed with deionised water, with acetone in order to remove the oligomers and excess ammonium persulphate, and with 1 N HCl solution to remove the Cl⁻ ions and un reacted aniline. Finally, the precipitate was dried in an air oven for 24 hours at a temperature of room temperature to achieve a constant mass.

2.2. Preparation of PANI-NiO composites

Synthesis of the PANI–nickel oxide composites was carried out by polymerization in situ. Aniline (0.2 mole) was dissolved in 1 M of HCl and stirred for 2 hours to form aniline hydrochloride. Nickel oxide was added in the mass fraction to the above solution with vigorous stirring in order to keep the NiO homogeneously suspended in the solution. To this mixture, 0.2 M of ammonium persulphate, which acts as an oxidant was slowly added drop-wise with continuous stirring at room temperature for 8 h to completely polymerize the monomer aniline. The precipitate was filtered, washed with demonized water, and finally dried in an oven for 24 h to achieve a constant mass. In this way, PANI–NiO composites containing various mass fractions of NiO (10%, 20%, 30% 40% & 50%) in PANI were synthesized.

3. Result and Discussion:

3.1. X-Ray diffraction (XRD):

Figure-1 exhibits the typical room temperature XRD spectra of the oxidative polymerization synthesized pure polyaniline (PANI) and NiO doped polyaniline composite (NiO-PANI). The oxide dispersed PANI shows characteristic peaks of PANI and some broad peak may be due to masking of crystalline oxide into the polymer matrix. In addition to the sharpness of the peak in the pattern may be the dispersed of the NiO particles into the PANI matrix. Additional NiO peaks may be observed in the pattern. This confirms the formation of the composite. It is also observed that, the intensity of the peaks are increased form approximately 80 to 250 as doping increased from pure to 50%. This suggests the NiO is dispersed in the polyaniline matrix.

The average crystalline size of the PANI are estimated to be approximately 10-20nm are calculated by using Debye -Scherrer formula,

$$(D=K\lambda/(\beta \cos\theta))$$

Where D is average crystalline size, λ is wavelength of the X-ray, K is crystallite shape factor a good approximation is 0.9, β is the full width at half the maximum (FWHM) of the X-ray diffraction peak and 2θ is the Bragg's angle (deg.) and lattice strain was estimated to be 0.0088.

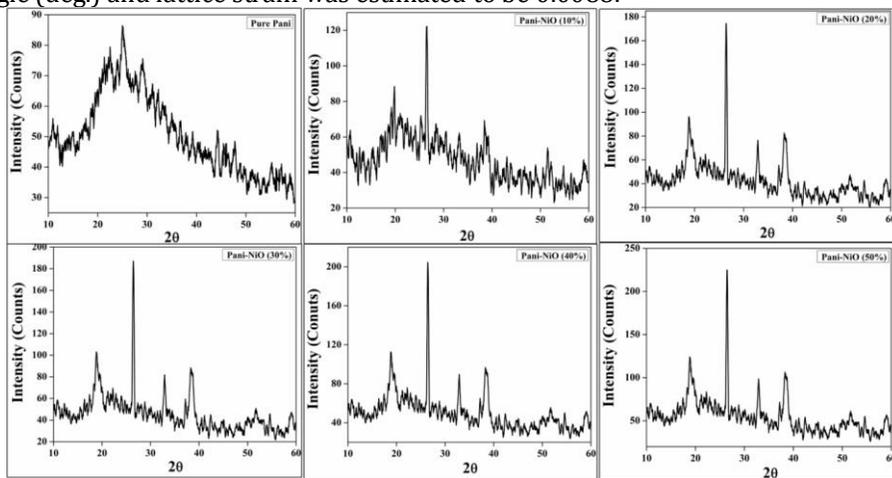


Figure-1: X-ray diffraction patterns of (a) Pure PANI, (b) NiO (10%)/PANI, (c) NiO (20%)/PANI, (d) NiO (30%)/PANI, (e) NiO (40%)/PANI, (f) NiO (50%)/PANI.

3.2. Scanning Electron Microscope (SEM):

Figure-2 shows the SEM image of pure PANI and NiO doped PANI composites at different magnifications. Pure PANI SEM image shows the fine crystalline nature having varied particle size. Most of the particles are in spherical shape with agglomeration. Figure-2(b) shows the SEM image of the NiO (10%) dispersed PANI. This image clearly indicates the non- uniform morphology due to insertion the crystalline oxide material in the PANI. Irregular homogeneity and enhanced particle size with some compactness is observed. The improved status is observed in the higher oxide composites of PANI. Increased particle size and enhanced agglomeration may be observed.

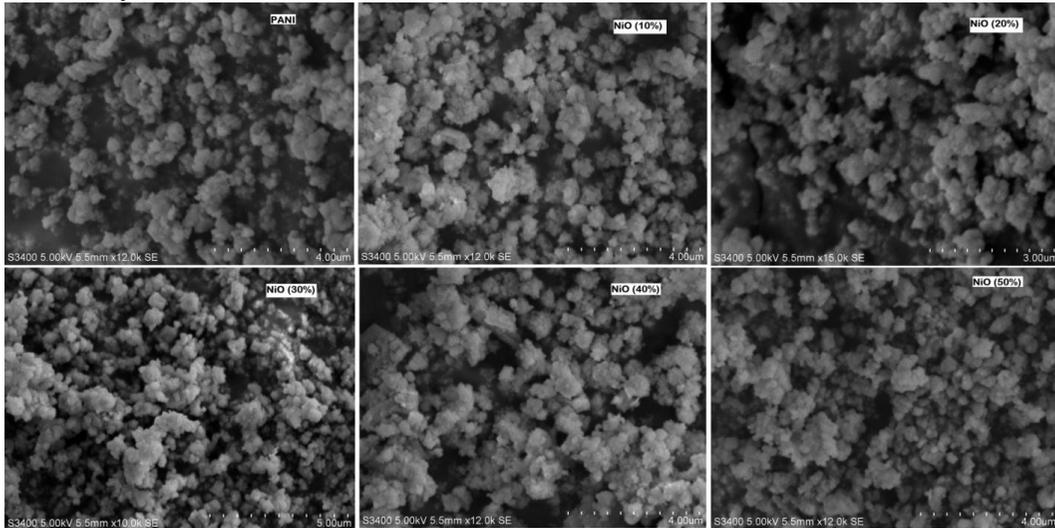


Figure-2: SEM image of (a) Pure PANI, (b) NiO (10%)/PANI, (c) NiO (20%)/PANI, (d) NiO (30%)/PANI, (e) NiO (40%)/PANI, (f) NiO (50%)/PANI.

3.3. AC conductivity:

Figure-3 shows the frequency dependence of ac conductivity of PANI and NiO/PANI with different content of NiO in the PANI matrix at room temperature. The value of ac conductivity of the PANI and all the composite increased as frequency increased. It is observed that the conductivity increases for 10, 20, 30 and 40 wt% of NiO polyaniline and decreases for 50 wt%. This may be due to the extended chain length of polyaniline which facilitate the polarization of charge carriers and variation in distribution of NiO particles which may support for more number of charge carriers to polarize between favourable localized sites causing increase in conductivity. Further, the decrease in AC conductivity may be due to the low polarization of charge carriers.

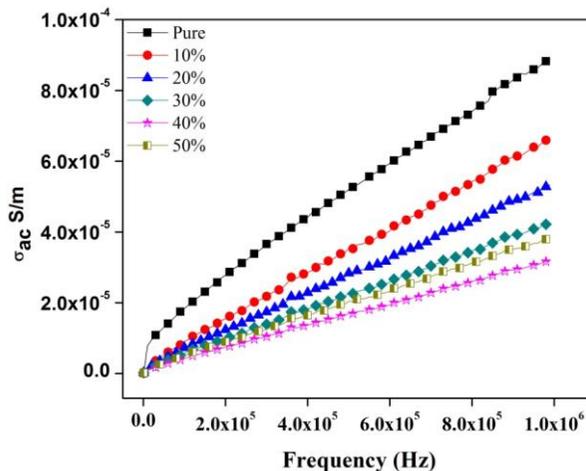


Figure-3: AC conductivity of PANI & Composite

3.4. DC Conductivity:

Figure-4 shows the variation of dc conductivity as a function of temperature for NiO in polyaniline. It is observed that the value of dc conductivity of these composites increases exponentially with temperature. It

remains nearly constant up to 100°C and there after it increases exponentially. The conductivity behaviour is the characteristic of amorphous materials. The initial increase in the values of conductivity is due to the extended chain length of polyaniline due to which the charge carriers can hop between the favourable localized sites. The decrease in the values of conductivity of all the wt% of the composite is due to partial blocking of charge carriers. Further, gradual increase in conductivity is noticed due to the variation in distribution of NiO particles in PANI.

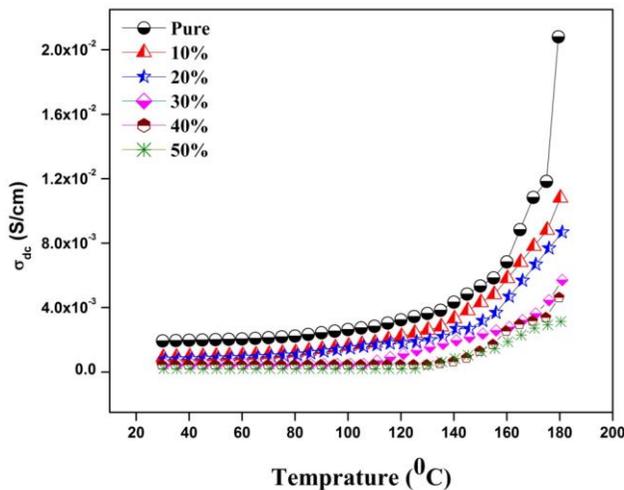


Figure-4: Shows the DC conductivity of polyaniline – NiO composites

4. Conclusion:

The present work was an attempt to synthesize pure polyaniline and NiO doped polyaniline with different concentrations (10%, 20%, 30%, 40% & 50%) and are characterized by various techniques such as structural (XRD) & microstructural (SEM).

We have reviewed more number of literatures of pure polyaniline and doped polyaniline apart from them NiO is finalized for the substitution in polyaniline. Stoichiometric amount of aniline, hydrochloric acid, ammonium persulphate, NiO are weighed and mixed in a proper proportion like 0.2M aniline, 0.2M ammonium persulphate, 1N hydrochloric acid, 10%, 20%, 30%, 40% & 50% of NiO.

Structural analysis of polymer samples were carried out by X-ray diffraction, amorphous peak of polyaniline was found in the range 25-28 degree. As we increase the composition NiO from 10% to 50% it shows that crystallinity of the PANI. These micro structural images clearly demonstrate the formation of agglomeration and irregular shaped NiO doped PANI. A non-uniform morphology and chemical homogeneity observed. Chemical composition is confirmed the percentage of magnesium and PAN. No other impurity peaks are observed by SEM shows agglomeration and irregular shapes of PANI and NiO doped PANI. It is confirmed that the NiO particles were equally distributed in the polymer matrix. The value of ac conductivity of the PANI and all the composite increased as frequency increased. It is observed that the conductivity increases for 10, 20, 30 and 40 wt% of NiO polyaniline and decreases for 50 wt%. This may be due to the extended chain length of polyaniline which facilitates the polarization of charge carriers and variation in distribution of NiO particles which may support for more number of charge carriers to polarize between favorable localized sites causing increase in conductivity. The value of dc conductivity of the composites increases exponentially with temperature. The decrease in the values of dc conductivity of all the wt% of the composite is due to partial blocking of charge carriers.

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