Structural, morphological and transport property study of Nickel oxide doped polyaniline composite (PANI/NiO)

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Abstract:

Among all the polymers, the polyaniline (PANI) is considered as a promising material due to its easy synthesis, environmental stability and high electrical conductivity on doping. The present study reports the chemical oxidative polymerization preparation of polyaniline and nickel oxide doped polyaniline composite in order to describe the variations in the polyaniline structure, morphology and conductivity upon doping and synthesis condition. The prepared samples were further characterized using -ray diffraction (XRD) and scanning electron microscope to reveal the surface morphology information and formation of crystalline domain embedded in an amorphous matrix within the polyaniline. The temperature dependent DC and frequency dependent AC conductivity of the prepared composites was carried using two probe techniques.

Key Words: PANI, NiO, PANI/NiO, XRD, SEM, AC, DC
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1. Introduction:

Polymers are the one perhaps imagines common plastic, like polythene may be come across in daily life. One can convert a polymer to conducting polymers by filling it with conductors like metals or metal oxides or carbon particles. These conducting polymers are termed conjugated conducting polymers or conductive polymers or organic polymeric conductors. Around 150 years ago, the polyaniline was discovered and it is considered as promising materials due to its high electrical conductivity when it is doped. The polyaniline was first synthesized in 1834 and later has been the subject of mild research ever since. In polyaniline, the electrical conductivity can be tuned by the process of doping. Due to this property of the PANI, it has replaced the material in many areas of applications [1].

PANI has wide range of application due to its flexible properties in different areas such as solar cells, LED, sensors, radiation absorbers and electromagnetic shields. It is possible to alter the properties of the PANI by the process of doping metal oxide or various types of particles with Polyaniline. The conductivity results in the Polyaniline composite are due to the redox behavior. There are many oxidation forms of the Polyaniline, among these the most important form of Polyaniline is green protonated emeraldine which can prepared by using chemical oxidative polymerization method. When the metal oxide or various types of particles are doped with Polyaniline, the charge-transfer reaction takes place between

Polyaniline and doping agent. The bond length and angles change when charges are removed from the Polyaniline upon chemical doping. In the Polyaniline, main part is to minimize the residual presence in the Polyaniline and along with to obtain yield. Hence ammonium persulfate (APS), ammonium Dichromate (ADC) was used as an oxidant [2].

Transition metal oxides exist with various structure and properties and it is extremely interesting of materials. The bonds of the oxygen in metals are usually a covalent bond either highly ionic or metallic bond. The transition metals have very important unique properties and application in all the field due to the presence of outer d-electrons. Due to this d-electrons, the electrical conductivity of the transition metals oxides spans the wide range 10^{-10} to $10^{2}0$ S cm $^{-1}$ [3].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 O_2.The simple structure is commonly known as the rock salt structure like many other binary metal oxide, NiO is often non stochiometric, the meaning that the NiO ratio deviates from 1:10.NiO can be prepared by multiple methods. Upon heating above 400^{0}C nickel powder reacts with oxygen to give NiO.

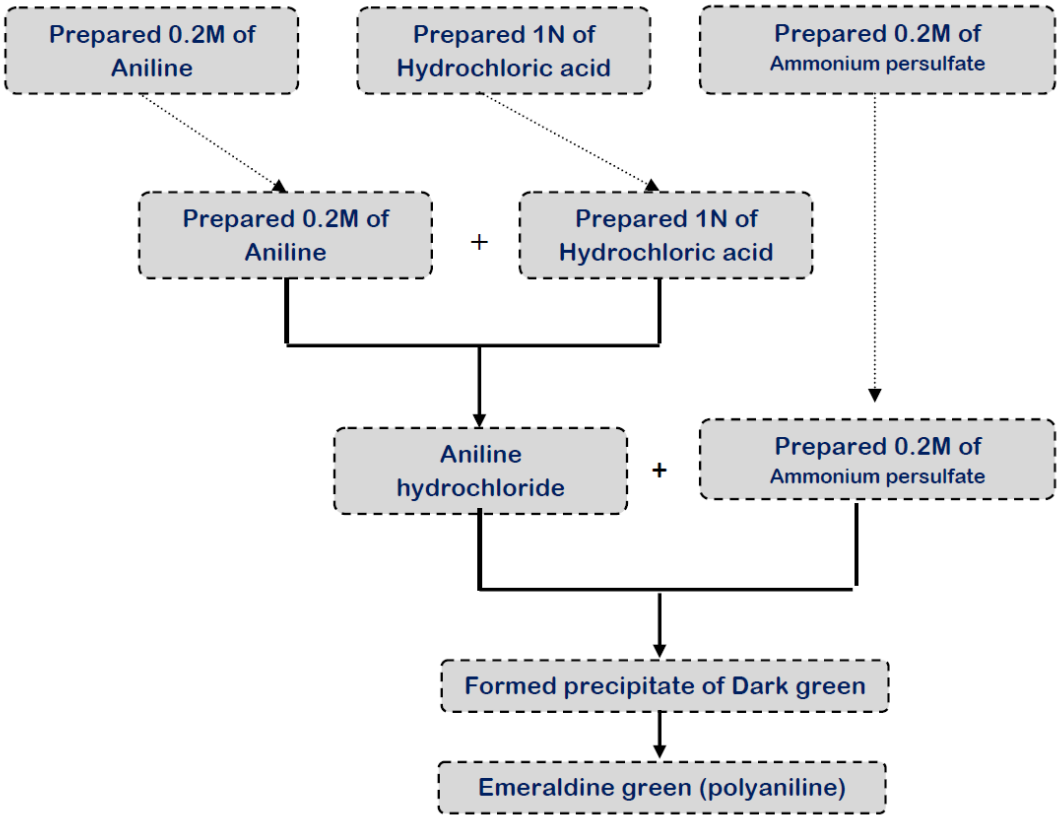
2. Materials and Methods:

2.1. Preparation of polyaniline (PANI)

Ammonium persulphate of 0.25M was prepared andthe same is added drop wise to a stirred solution to prevent warming of the aniline 0.25M solution prepared earlier. Further dissolved in 1 mol of an aqueous solution of hydrochloric acid (1N) 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 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. 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. 0.25M of prepared aniline was dissolved in 1M of HCl and stirred for 2 hours to form aniline hydrochloride. Nickel oxide was added in the mass fraction (25%) to the above solution with vigorous stirring in order to keep the NiO homogeneously suspended in the solution. To this mixture, 0.25 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 [4].



Scheme-Preparation of pure PANI

3. Result and Discussion:

3.1. X-Ray diffraction (XRD):

Crystallinity degree of the polymers can be described by the X-ray diffraction technique [5]. Crystalline orientation of the polymers specially conducting polymers is found to be important and promising due to more highly ordered system [6]. Figure-1(a&b) describe the XRD spectra of the undoped PANI and PANI/NiO composite. 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. The broad peak 2θ = 25.7 corresponds to [110] plane of PANI due to the parallel and perpendicular periodicity of the polymer (PANI) chain [7].

XRD pattern of PANI/NiO composite shows six absorption peak at 20.8, 26.44, 32.9, 38.48, 51.48, 58.02 representing Bragg's reflections from (110), (200), (210), (211), (311), (321) planes of nickel oxide. This is shown in Figure 1(b). 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 Braggs' angle (deg.).

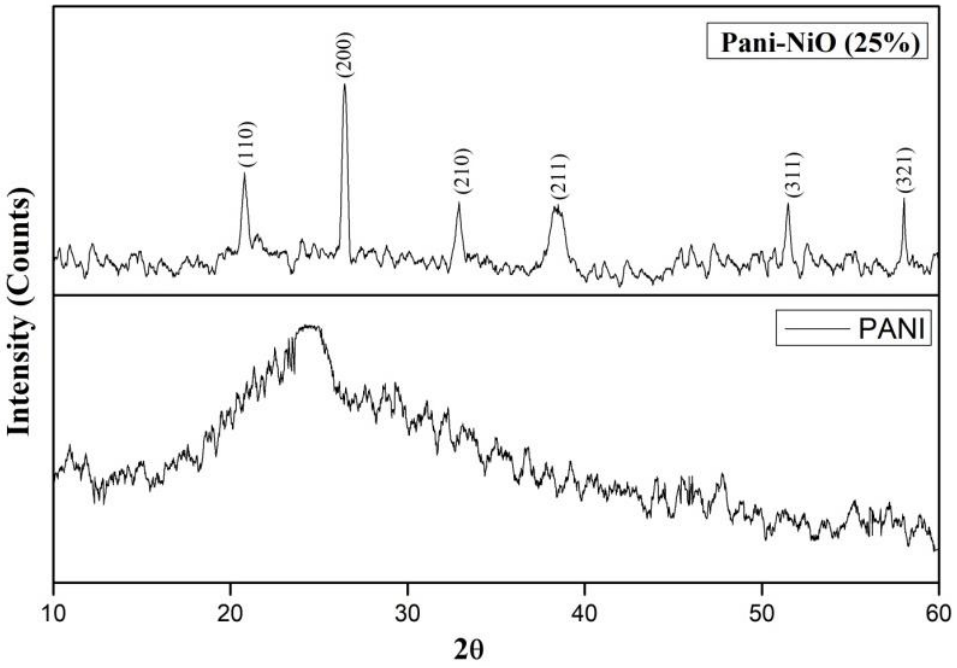


Figure 1: The XRD pattern of PANI and PANI/NiO composite

3.2. Scanning Electron Microscope (SEM):

Morphology of the polyaniline mainly depends on the conditions of the synthesis process [8]. The most common morphology of the polyaniline prepared by polymerization technique is granular morphology with strong oxidants and high aniline concentration [9]. The PANI prepared in such technique is highly aggregated and rapid sedimentation from solution is generally observed.

Figure-2 shows the SEM image of pure PANI and NiO doped PANI composites at different magnifications. The SEM micrographs reveals that, PANI and composite showing crystalline, spherical shape with agglomeration nature with uniform particle size. The micrograph clearly indicates the uniform morphology due to insertion the crystalline oxide material in the PANI.The improved status is observed in the higher oxide composites of PANI. Increased particle size and enhanced agglomeration may be observed.

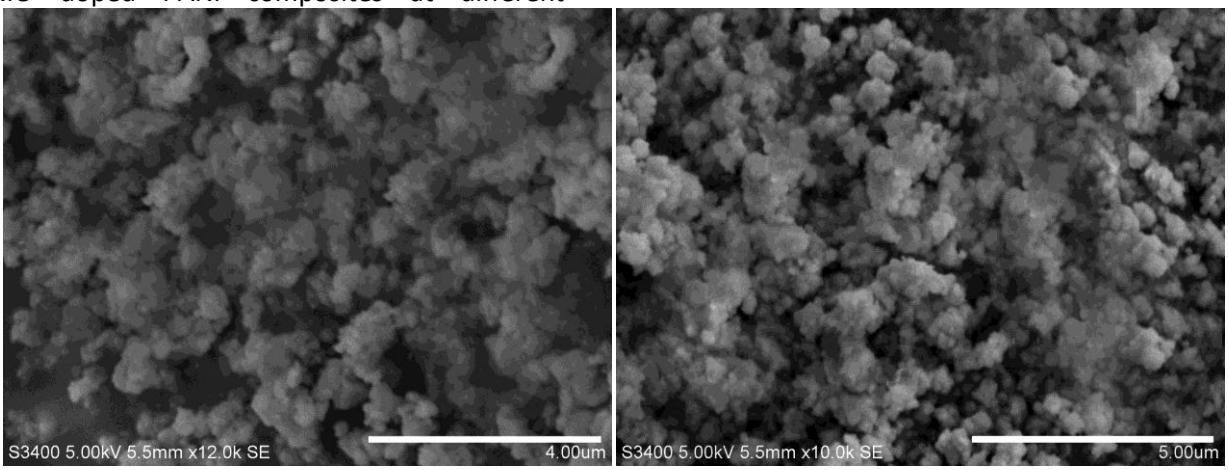


Figure 2: SEM micrograph of PANI and PANI/NiO composite

3.3. AC conductivity:

The room temperature frequency dependent ac conductivity of the undoped PANI and PANI/NiO composite was shown in figure-3. Based on the conductivity graph, the conductivity of PANI and composite increasing with increase in frequency. There is a sudden increase in ac conductivity of both samples at higher frequency range, which is the characteristic property of disordered materials. Compared to undoped PANI, the ac conductivity of the composite sample is less due to the extendedchain length of polyaniline which facilitate the polarization ofcharge carriers. Further, the decrease in AC conductivity may be due to the lowpolarization of charge carriers. The maximum value of conductivity is 0.0737 s/cm observed for PANI and 0.0515 foe composite samples. This behaviour is attributed to addition of NiO in polymer matrix.

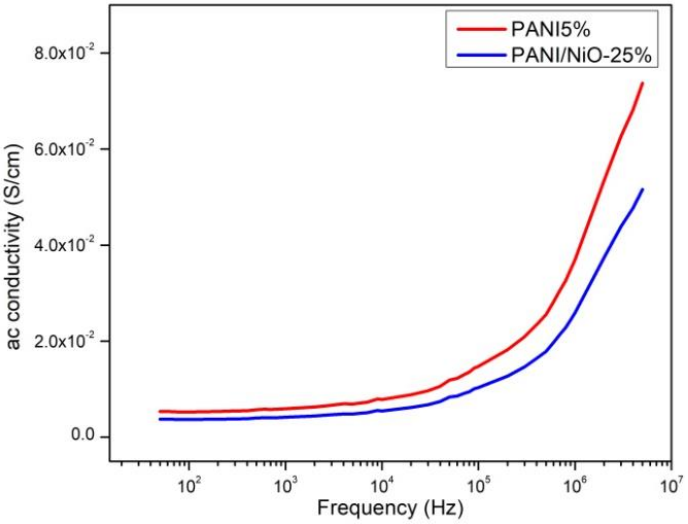


Figure 3: AC conductivity PANI and PANI/NiO composite

3.4. DC Conductivity:

The change in dc conductivity of the undoped PANI and PANI/NiO composite as function of temperature was shown in figure-4. It is observed that the value of dc conductivity of these composites increases exponentially with temperature. It remains nearly constant up to 100^0C and there after it increases exponentially. The decrease in the values of conductivity of the composite sample may 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. The maximum value of conductivity is 0.0164 s/cm observed for PANI and 0.010 for composite sample.There is a sudden increase in dc conductivity of both samples at higher temperature range [10-12].

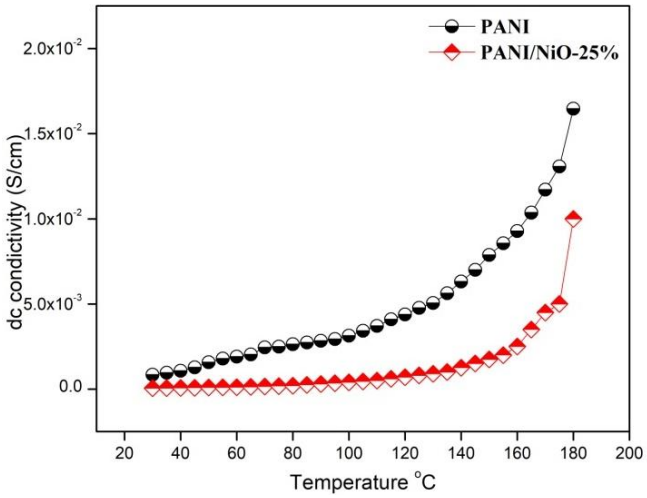


Figure 4: DC conductivity of PANI and PANI/NiO composite

4. Conclusion:

The composite of PANI/NiO were successfully prepared chemically by polymerization method. It is found that the doping of nickel oxide affects the structural, morphological, electrical of polyaniline. Structural analysis of polymer samples were carried out by X-ray diffraction, amorphous peak of polyaniline was found in the range 25-28 degree .The SEM micrographs reveals that, PANI and composite showing crystalline, spherical shape with agglomeration nature with uniform particle size. The present synthesis method, which leads to formation of nickel oxide and polyaniline composite are able to decrease the ac and dc electrical conductivity of PANI. It is found that the ac and dc conductivity of composite is less compared to the undoped PANI. Moreover, substantial future research is vital important for most effective use and preparation of functionalized advanced conducting PANI/NiO composites with excellent chemical properties. The future scope is to carry change in resistance of such composites with respect to LPG.

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