

Studies of Dedoping Effect of Zinc Oxide Nanoparticles on Polyaniline Nanoparticles

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Abstract: Studies on advanced nanocomposites of conducting polymers, especially polyaniline and inorganic metal oxide nanoparticles, have been reported for many promising applications. We have studied the dedoping effect of zinc oxide nanoparticles on doped polyaniline nanoparticles in a straightforward route. Results obtained from the electrical conductivity study, FTIR, UV-visible spectroscopy, and XRD analysis support the dedoping of polyaniline salt, and a decrease in electrical conductivity and increased stability of electrical conductivity of samples treated with comparatively large amounts of zinc oxide nanoparticles were also observed. The report also suggests that the approach may be used to design and tailor the electrical properties of polyaniline salt and its nanocomposites.

Index Terms: Conducting Polymers, Electrical Conductivity, Polyaniline, zinc oxide, nanoparticles.

1. INTRODUCTION

When the size of materials shrinks to the nanometer scale, many of their physical and chemical properties change compared to their bulk counterparts. As a result, these properties deviate from their usual bulk properties of materials. The electron confinement in the nanorange leads to unusual behavior [1,2]. Nanostructured semiconducting materials are extensively used for their potential application and novel properties. The creation of nanoscale hybrid materials of inorganic oxide semiconductors and conducting polymers has drawn a lot of interest lately because of the numerous potential uses in field effect transistors and optoelectronic devices [3,4]. Because of their high surface-to-volume ratio, inorganic fillers

at the nanoscale are predicted to significantly alter the electrical, optical, and dielectric characteristics of polymers. There are numerous straightforward methods for integrating inorganic and organic components, such as direct/melt mixing [5,6].

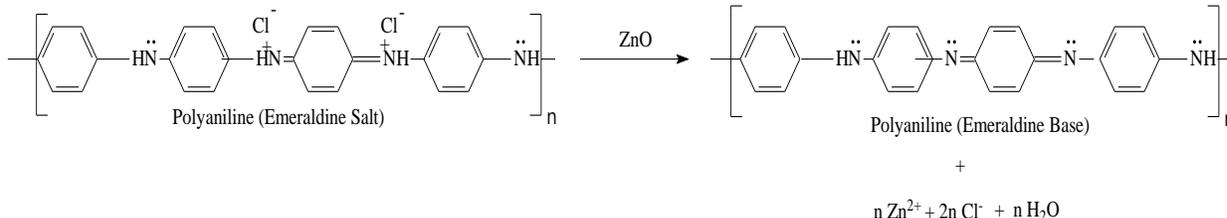
There are many reported studies on the synthesis, electrical, optical, and morphological studies of zinc oxide and polyaniline nanocomposites. Semiconducting zinc oxide (ZnO) is attracting much attention owing to its unique properties, such as its direct wide band gap of ~3.37 eV and large exciton binding energy of ~60 meV at room temperature [7-10]. Due to these properties, ZnO has been studied extensively for making electronic and optical devices. Polyaniline (PANI), on the other hand, is the most studied members of conducting polymers due to its relatively easy preparation, good environmental stability, tailorable electrical conductivity, redox behavior, etc. [11,12]. In this paper, we have tried a different approach to study the interaction of zinc oxide nanoparticles with polyaniline nanoparticles in terms of dedoping behavior. This approach would be constructive and promising in controlling the electrical conductivity of polyaniline and other conducting polymers.

2. MATERIALS AND METHODS

The materials used during this study include ammonia (Qualigen, India), aniline (Merck, India), hydrochloric acid (Rankem, India), potassium persulphate (CDH, India), and ZnO nanoparticles (avg. size 50 nm) (mknano, Canada). Double distilled

water, doubly distilled aniline was used and all other chemicals were used as-received.

Polyaniline (emeraldine base) nanoparticles were prepared as discussed by Mohammad and Ansari [13]. The emeraldine base was doped with 1M HCl



(1)

After the due treatment, all samples were thoroughly washed with excess of double distilled water to eliminate water soluble portion of the product which contained zinc chloride and the samples were dried in air oven at 60°C for 2 days. Table-1 gives the detailed conditions of treatment.

Table 1 Details of treatment of polyaniline (ES-II) with zinc oxide nanoparticles under ultrasonic condition at 60°C.

Sample ID	Amount of ES-II (mg)	Amount of ZnO nanoparticles (mg)	Volume of water (ml)
S-Z0	1000	0	25
S-Z1	1000	10	25
S-Z2	1000	30	25
S-Z3	1000	50	25
S-Z4	1000	70	25
S-Z5	1000	90	25

3. CHARACTERIZATIONS

All the samples were studied for their DC electrical conductivity and the stability of electrical conductivity in terms of its retention by a four-in-line technique using a DC electrical conductivity measuring instrument (Scientific Equipments, Roorkee, India). FTIR, TEM UV-Visible spectroscopy, and XRD analysis of selected samples were performed on Perkin Elmer-Spectrum RX-IFTIR, Philips CM-10, Shimadzu (UV-1700 Pharma Spec), and Panalytical's X'Pert Pro.

4. RESULTS AND DISCUSSION

4.1 Fourier Transform Infrared (FTIR) Studies

for 6 hrs to get polyaniline salt (ES-II). Polyaniline (ES-II form) was ultrasonically treated with different amounts of zinc oxide nanoparticles for 1 hr at 60°C. The idea may be represented in Equation 1 as given below:

FTIR spectra of selected samples of PANI are presented in Figure 1. FTIR peak obtained around 795 cm⁻¹ may be assigned to out-of-plane bending vibration of C-H bond of *p*-disubstituted benzene rings of PANI [14], peak at 1114 cm⁻¹ may be assigned to vibration mode of N=Q=N ring, peaks at 1239 cm⁻¹, 1294 cm⁻¹ can be assigned to the stretching mode of C-N bond, 1492 cm⁻¹ peak for C=C stretching of benzenoid and peak at 1571 cm⁻¹ is due to C=C stretching of quinoid [15,16]. The characteristic peaks lying between 3400 cm⁻¹ & 2900 cm⁻¹ can be assigned to the free (non-hydrogen bonded) N-H stretching vibration and asymmetric stretching of CH of PANI respectively [17].

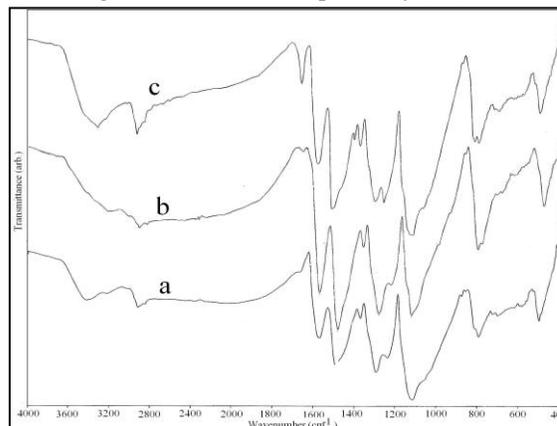


Figure 1. FTIR spectra of sample a) S-Z0, b) S-Z3 and c) S-Z5.

4.2 UV-Visible Spectroscopy

Optical properties play a crucial role in the elucidation of the basic electronic structure and solution properties of the conducting polymers, e.g. PANI. The absorbance of selected samples of PANI was plotted using a UV-visible spectrometer. The

wavelength range was 340-700nm. The characteristic peaks of pure PANI lie in the range of 280-335 nm and 638 nm. The emeraldine base gives absorption peak at 320 nm and 620 nm in NMP solution, which is assigned to π - π^* transition [18]. NMP, being a polar solvent, interacts with the emeraldine salt and converts a portion of it to emeraldine base form, which may be seen in the UV-visible spectra of selected samples [19]. However, as per our hypothesis that zinc oxide acts as a dedoping agent of emeraldine salt, the absorption Vs concentration graph was plotted for all samples at 320 nm wavelength. This plot confirms that there is an increase in absorption for samples with an increase in the amount of zinc oxide [20].

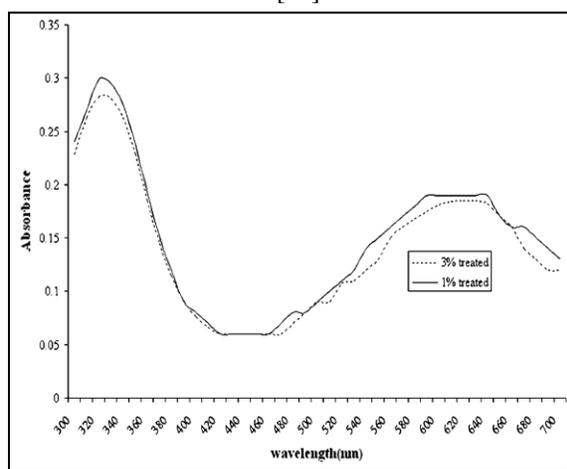


Figure 2. UV-Visible spectra of sample S-Z1 and S-Z3

4.3 Transmission Electron Microscopy

Transmission Micrographs were also obtained for the constituents used, i.e., zinc oxide and emeraldine base nanoparticles. The TEM micrographs show that these particles are in the nano range. The average sizes of both particles are below 50 nm.

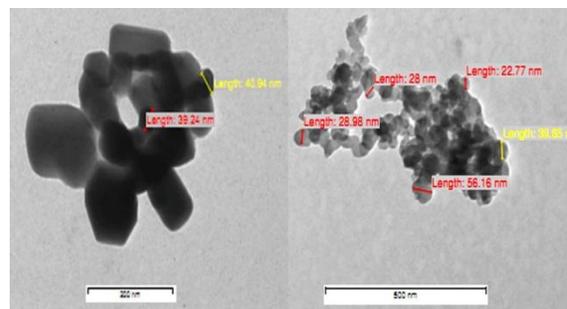
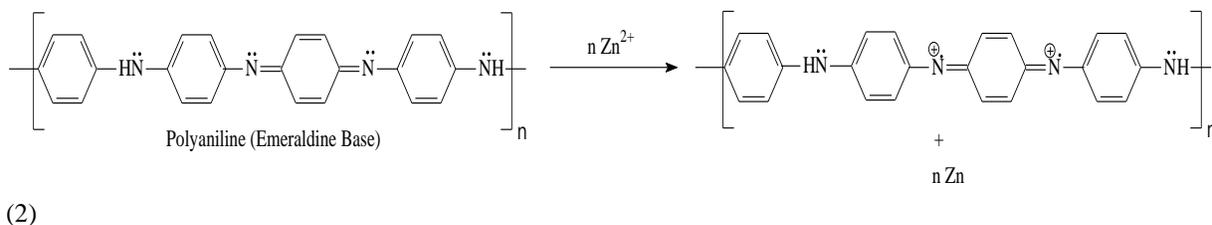


Figure 3. TEM micrographs of a) zinc oxide [9] and b) emeraldine base nanoparticles.

4.4 Electrical Conductivity Studies

4.4.1 Electrical Conductivity: Temperature Dependence-Arrhenius plot

Electrical conductivity is a critical property of conducting polymers. Polyaniline, in its emeraldine salt form, efficiently conducts electricity. The electrical conductivity of doped polyaniline ranges from 10^{-4} - 10^2 Scm^{-1} . Many factors affect and alter the electrical conductivity of polyaniline salt. Polyaniline, on treatment with zinc oxide nanoparticles in ultrasonic conditions, showed a lowering in electrical conductivity (Equation 2) and stability in terms of electrical conductivity retention. The DC electrical conductivity obtained for polyaniline in the absence of zinc oxide under ultrasonic conditions is in the semi-conducting region, and the Arrhenius plot of electrical conductivity also supports the semi-conducting nature of polyaniline salt. Those samples that were treated with zinc oxide nanoparticles showed a lowering in electrical conductivity (Figure 4), except S-Z3 which show a higher electrical conductivity compared to S-Z4 and S-Z5 due to the fact that ZnCl_2 act as dopant to certain extent but not as good dopant [20]. The electrical conductivities of polyaniline samples were measured from 40°C to 150°C with dry pellets by the standard four-point probe method [21,22].



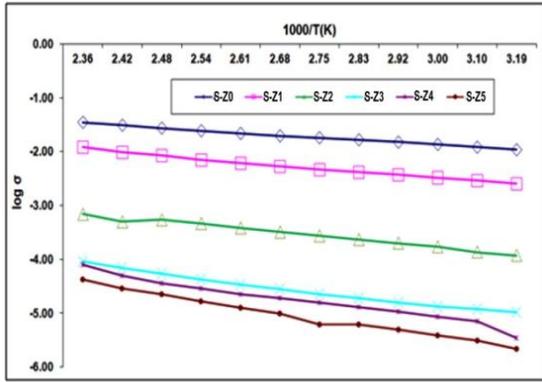


Figure 4. Arrhenius plot of electrical conductivity of samples.

4.4.2 Electrical Conductivity: Stability Study (Cyclic Ageing Condition)

The thermal stability of the selected PANI samples in terms of DC electrical conductivity retention was studied by measuring DC electrical conductivity using a four-in-line probe technique for DC electrical conductivity measurement with an increasing temperature from 40°C to 150°C repeatedly. Each sample was studied for 5 cycles by repeatedly heating and cooling the sample at an interval of 45 min. The data obtained from this study were plotted as $\log \sigma$ versus $1000/T$, which is simply known as the Arrhenius plot for each cycle. It was observed that after the first cycle, there is little increase in electrical conductivity, which may be due to the removal of moisture and strong networking of the polymer chain. [21, 22].

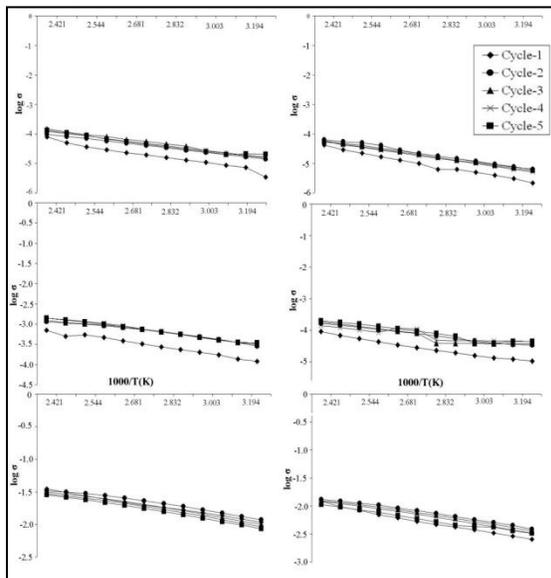


Figure 5. Cyclic Ageing Stability study of electrical conductivity

4.4.3 Electrical Conductivity: Stability Study (Isothermal Ageing Condition)

The thermal stability of the electrical conductivity of the PANI samples in terms of DC electrical conductivity retention was also studied under isothermal conditions by using a four-in-line DC electrical conductivity measuring instrument. During isothermal ageing condition, the electrical conductivity study of all the samples was carried out at 50°C, 70°C, 90°C, 110°C and 130°C under the accelerated aging conditions. The electrical conductivity measurements were done at an interval of 10 min. for 50 min at each temperature (50°C, 70°C, 90°C, 110°C and 130°C) separately. The obtained data were plotted for DC electrical conductivity versus time. This graph gives us an idea of the isothermal stability in terms of DC electrical conductivity retention of the samples [21, 22].

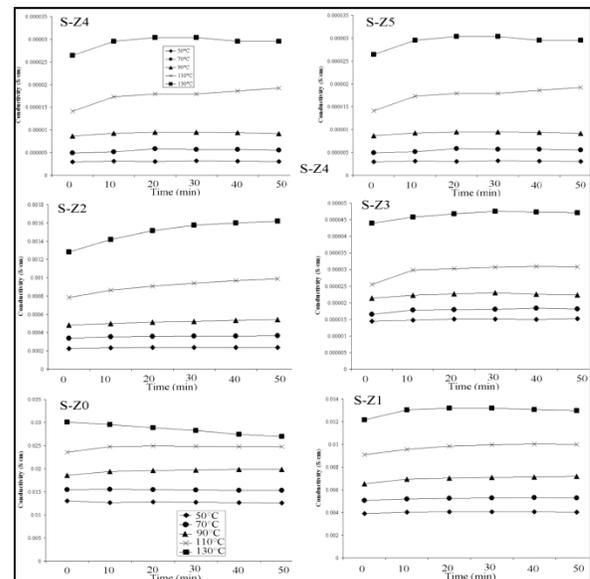


Figure 6. DC electrical conductivity stability in isothermal ageing condition.

4.5 XRD Studies

X-ray diffractions of the PANI samples were carried out using the instrument “X’pert Pro XRD X-ray diffractometer” and “filtered $\text{CuK}\alpha$ radiations”. The diffraction patterns of the selected samples S-Z0, S-Z3, and S-Z5 were obtained by scanning the samples at a rate of $2^\circ/\text{min}$ and in the range $2\theta = 0-60^\circ$. It may clearly be seen in Figure 7, that the peaks obtained

from $2\theta = 5-30^\circ$ that are assigned for polyaniline salts diminish with an increase in the amount of zinc oxide treatment and subsequently support the decrease in crystallinity, which in turn may be assigned to increased content of emeraldine base in the sample of the study. In other words, it may also be said that the amount of emeraldine base form increases with an increase in the amount of zinc oxide nanoparticles, as has been confirmed from UV-visible spectra of different samples. It is also to be noted that at lower concentrations, no zinc oxide peaks were observed in the XRD pattern; however, as the concentration of zinc oxide increased to a certain level, its specific peaks started to appear in the XRD spectrum [7,9].

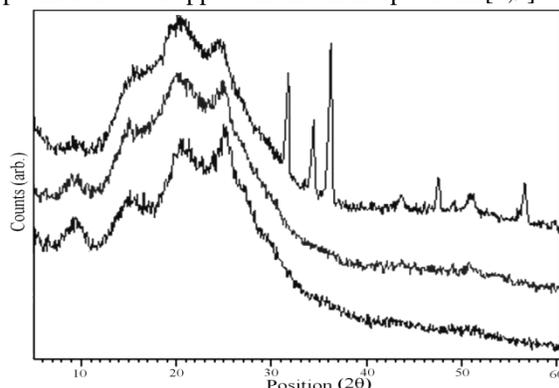


Figure 7. XRD spectra of sample a) S-Z0, b) S-Z1 and c) S-Z5

5. RESULTS AND DISCUSSION

It has been confirmed from the above studies that treatment of polyaniline salt with zinc oxide nanoparticles caused dedoping of the polyaniline salt, and therefore, a decrease in electrical conductivity was observed. Zinc oxide reaction with the polyaniline salt caused neutralization of charge on polyaniline salt to a reasonable extent by removing the chloride ion as zinc chloride and leaving a higher concentration of undoped fraction in studied samples.

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