

Electrical conductivity study of poly(*p*-anisidine) doped and undoped ZnO nanocomposite

Kaniappan Rathidevi^{1,2}, Nanjan Velmani³ and Damodaran Tamilselvi^{1,4}

¹ Research & Development Centre, Bharathiar University, Coimbatore – 641 046, Taminadu, India

² Assistant Professor, Department of Science and Humanities, Kumaraguru College of Technology, Coimbatore – 641 049, Taminadu, India

³ Assistant Professor, Department of Chemistry, Government Arts College, Coimbatore - 641 018, Taminadu, India

⁴ Assistant Professor, Department of Science and Humanities, Rathinam Technical Campus, Coimbatore – 641 021, Taminadu, India

Abstract: Polymeric blends of Poly (*p*-anisidine) with ZnO nanoparticles was prepared by chemical oxidative polymerization. Zinc oxide doped PPA polymer nanocomposite (ZPPA) and Magnesium doped Zinc oxide PPA polymer nanocomposites (MZPPA) are synthesized with the addition of semiconductor metal oxide to the polymeric solution. The X-ray diffraction studies of ZnO nanoparticles shows hexagonal wurzite structure. The surface morphological study also confirms the formation of hexagonal structured nanoparticles. The peak for Magnesium and Zinc in EDS spectra confirms the formation of Magnesium doped polymer nanocomposite. The addition of ZnO/MgZnO onto PPA conducting polymer shows agglomeration of semiconductor material results in spherical shaped polymer nanocomposite and irregular overlapping over the PPA polymeric surface. The electrochemical conductivity studies suggested that the doped PPA conducting polymeric blends showed enhanced conductivity nature.

Keywords: Poly (*p*-anisidine); Zinc oxide; Polymeric composite blends; Conductivity studies.

1. Introduction

Conducting polymers play a significant role in the field of material science and technology. The presence of polyconjugated structure in the conducting polymers play an important role in determining the electrical property which are unique from other conventional polymers. There are several studies to obtain conducting polymer based composites and semiconductor doped polymers with improved properties¹. Due to their excellent electrical, chemical and electrochemical properties, conducting polymers with desired properties can be synthesized for specific technological applications^{2,3}. Some of the important advantages of conducting polymers were ease of preparation, better conductivity and desired surface area which have enormous applications in electrochemical field⁴. In this present technological era, emerging materials like polymers having desirable properties find a wide range of applications in growing technology. The chemical and physical property of polymer can be improved by doping with nanoparticles and fillers to provide better performance than pure polymers⁵. Materials with unique properties like environmental stability, suitable mechanical property, low cost, and

lightweight will meet the demand of upcoming advancements in technology. In recent years, researchers have been focussed on synthesizing nanomaterials by reducing the size of the ordinary materials which exhibits novel optical and electrical properties. Among various nanostructured metal oxides, ZnO received more attention by the researchers due to its versatile applications⁶. Various transition metals can also be doped with ZnO to make some desirable property changes in the zinc metal oxide matrices⁷⁻¹⁰. Innumerable attempts were made to dope these nanostructured inorganic metal oxides into organic conducting polymers to change the conductivity of polymeric backbone. This type of doping material into the polymer matrix improves the property of conducting polymers¹¹. The property of new hybrid material is influenced by both organic polymer and inorganic nanostructured metal oxide¹².

Generally, the presence of conjugated π -electrons in the polymeric backbone produces conductivity in these polymers. Among conducting polymers, Polyaniline (PANI), Polypyrrole (PPy) and Polythiophene (PTh) were found to be widely used since there were thermally stable till 250°C, ease synthesis and use of less toxic

solvents during the synthesis. Polyaniline (PANI) is the cheapest, eco-friendly, good conductor of electricity widely used in chemical sensors, biomedical science, batteries, electromagnetic interference, corrosion devices, solar cells and many more¹³⁻¹⁶. Addition of substituent into polymers causes a finite change in its chemical, physical properties, thermal properties and its ability to reverse from insulating material to conducting material.

Apart from the addition of substituent, doping of metal oxide also causes a measurable change in the structural property of the material, thereby causing a change in its optical and electrical properties etc. Such finite changes affect the thermal conductivity of the material. One of the important applications of the conducting polymers is its ability to act as an anticorrosive agent against metals¹⁷. The catalytic property of polyaniline forms a protective passive layer over the metal surface and enhances its anticorrosive property. The disadvantage of using polyaniline (PANI) is its poor solubility and lower conductivity. Polyaniline (PANI) along with substituents ($-\text{CH}_3$, $-\text{OCH}_3$ and $-\text{OC}_2\text{O}_5$) results in better solubility, processability and conductivity nature¹⁸. The electrochemical performances of the substituted polyaniline were estimated by cyclic voltammetry (CV), galvanostatic charging-discharging and electrochemical impedance spectroscopy (EIS) techniques. In particular addition of methoxy group ($-\text{OCH}_3$) in the polyaniline increases the specific capacitance of the material. This unusual superior conductivity property was due to the higher surface area, stable electrochemical properties and excellent redox properties^{19,20}. The effect of substituents on the conductivity of polyaniline in the fabrication of supercapacitors was studied by Basnayaka et al. and it is found that the methoxy substituted polyaniline can be used in supercapacitors²¹. Azza Mazrouaa et al. studied the influence of metal dopant on the electrical conductivity of poly o-anisidine and reported the addition of metal oxides increases the conducting nature of poly o-anisidine²². F. Chouli et al. observed doping of poly p-anisidine with TiO_2 nanoparticle produces an electroactive polymer with good electrochemical response²³. Asif Ali Khan et al. studied the electrical conductivity of poly o-anisidine nanocomposite and found to behave as an electrically conducting material that could be used in electrical applications²⁴.

In the present investigation, the electrochemical conductivity studies of Zinc oxide/ Poly (p-anisidine) (ZPPA) nanocomposite, Magnesium doped ZnO/Poly (p-anisidine) (MZPPA) and Pure Zinc Oxide were performed. The synthesized polymers and composite blends were characterized using spectral studies. The surface morphological nature, crystallographic properties and functional group present in the polymer and the composites were analyzed using SEM, EDS, XRD and FTIR techniques. The optical studies and

electrochemical conductivity studies also conducted in an attempt to verify the use of the nanocomposites for various applications. Only very few attempts have been made by the researchers on the synthesis and conducting study of poly p anisidine.

2. Characterization methods

The functional groups present in the polymer and composite blends are analyzed using X-ray Diffraction studies (XRD) and Fourier Transform Infrared Spectroscopy (FTIR), surface morphological nature of the synthesized materials are analyzed using Scanning Electron Microscopy (SEM). The absorption spectra of the nanoparticle and nanocomposites are recorded by using Ultraviolet Visible spectroscopy (UV-Vis). The elemental composition of polymer nanocomposite is analyzed by EDS spectrum. The electrochemical conductivity studies are analyzed using four probe DC electrical conductivity instrument. The thermal stability of the polymer and polymeric composite blends are analyzed using TGA studies through SDT Q600 V20.9.

3. Results and Discussion

3.1. FTIR Characterization

The FTIR characterization spectra of the PPA conducting polymer, ZnO nanoparticles, ZPPA and MZPPA polymeric blends are shown in Figure 1. The characteristic peaks at 3236 cm^{-1} attributed to the N-H stretching frequency of the secondary amine. The aromatic and aliphatic C-H stretching frequency corresponds to the vibration peaks at 2924 cm^{-1} and 2850 cm^{-1} , respectively. The two peaks observed at 1490 and 1545 cm^{-1} corresponds to the benzenoid and quinoid groups²⁵. Other peaks observed at 1210 , 1132 and 910 cm^{-1} were due to the 1, 2, 4-trisubstituted benzene rings. All these observations correspond to the Poly (p-Anisidine) conducting polymer.

The FTIR spectrum (Figure 1) of ZnO nanoparticle shows a broader peak at 3445 cm^{-1} and 1630 cm^{-1} due to the free hydroxyl groups, O-H stretching and bending frequencies. The sharp narrow peak at 600 cm^{-1} corresponds to the Zn-O stretching mode of metal oxide bond. The peaks at 2600 cm^{-1} correspond to the intermolecular bonding of zinc and oxygen atoms which results in the formation of zinc oxide. All the peaks observed in the ZnO FTIR spectrum except hydroxyl peak were sharp and intense, which suggests that the formed ZnO were crystalline nature. The peak at $1400\text{ cm}^{-1} - 1450\text{ cm}^{-1}$ in MZPPA corresponds to Mg-O stretching vibrations²⁶. With the addition of nanoparticles of Zinc oxide and Magnesium doped Zinc oxide onto PPA polymer shows a significant change in the vibrational and stretching peaks of the polymer. There exists a finite change in the peak shift with respect to the addition of zinc oxide and magnesium doped zinc oxide.

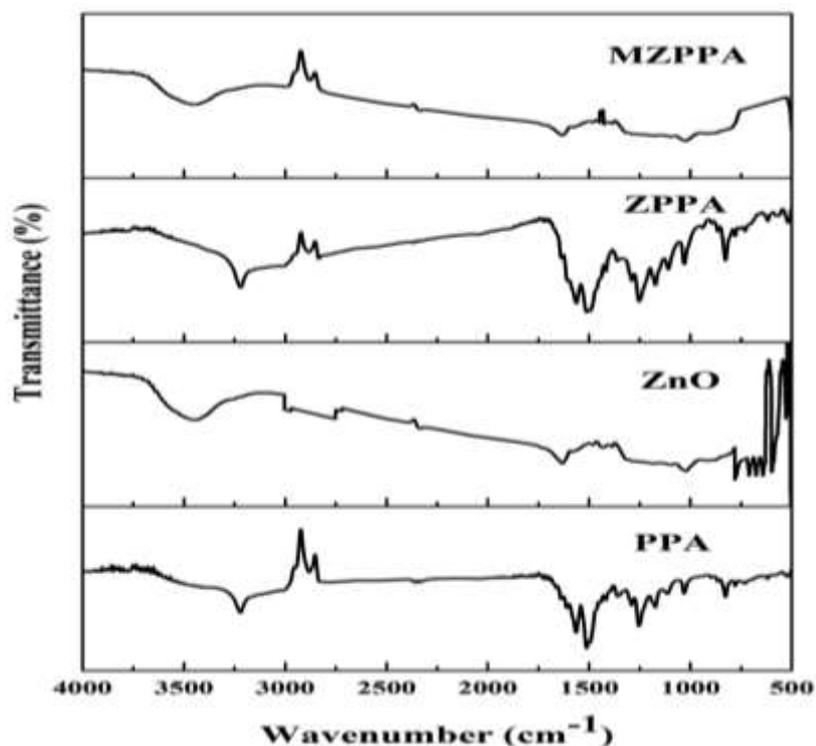


Figure 1. FTIR spectrum of PPA polymer; ZnO nanoparticles; ZPPA and MZPPA Polymeric composite blends

3.2. XRD Characterization

The XRD image of the polymer PPA, ZnO nanoparticle, ZPPA and MZPPA polymer nanocomposites are represented in Figure. 2. The XRD image of the semiconductor material ZnO shows hexagonal wurtzite structure. The 2θ peaks in Figure. 2 at 31.81° (100), 34.44° (002), 36.31° (101), 47.602° (102), 56.62° (110), 63.01° (103), 66.48° (200), 67.97° (112) and 69.19° (201) planes in agreement with JCPDS no. 36-1451. The depiction of sharp narrow peaks indicates that the

ZnO formed is of highly crystalline in nature. The broad peak of PPA conducting polymer is due to the amorphous nature. Since the conducting polymeric material is in the mesoporous form, formation of infinite non-uniform pores on the surface of the polymer attributed the amorphous nature of the material. It is observed that the doping of ZnO nanoparticles onto the conducting polymeric network resulted in crystalline nature polymer nanocomposites.

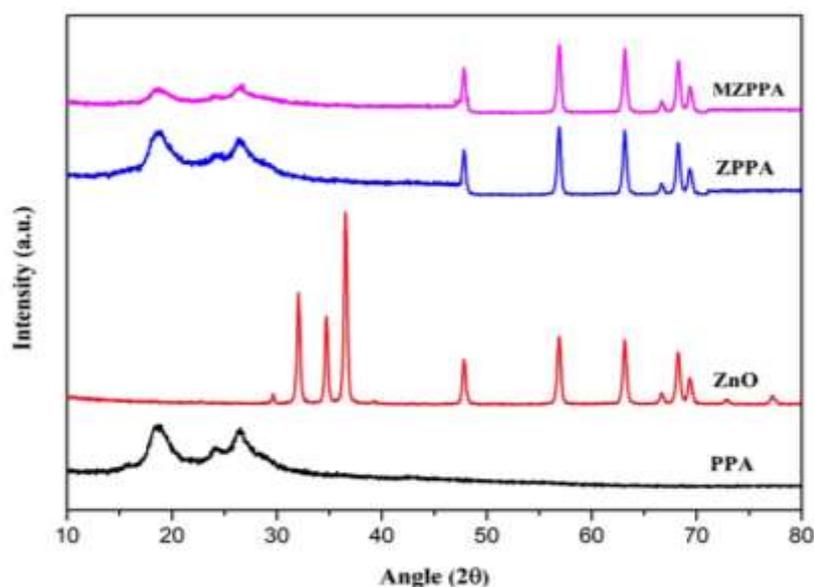


Figure 2. XRD image of PPA conducting polymer, ZnO nanoparticles, ZPPA and MZPPA polymeric nanocomposite.

3.3. UV-Vis Characterization

Figure 3 shows the UV-vis absorption spectra of the nanoparticle ZnO, polymer PPA and polymer nanocomposites ZPPA and MZPPA. The results of UV-Vis spectra show a small peak at ~260nm which is attributed to p-anisidine and broad absorption peak above 520 nm corresponds to the substituted aniline. The broad absorption peak at ~310-320 nm in PPA, ZPPA and MZPPA could be ascribed due to π - π^* transition of benzenoid ring present in the polymer ²⁷. The existence of an absorption broad band above 400 nm corresponds polaron - π^* transition in the case of PPA, ZPPA and MZPPA. The weak broader band above

500 nm in PPA, ZPPA & MZPPA is believed to be due to n- π^* transitions in the quinoid structure of the polymer ²⁸. Appearance of absorption bands above 300 nm and broader region above 500 nm justifying characteristic basic skeleton of the polymeric chain in emeraldine form. It is also observed that the doping of Mg with PPA shifted the broad absorption spectrum to lower wavelength ²⁹. Apart from those UV spectra of polymer and composites, ZnO exhibited a band at 350 nm and an excitonic peak appeared at 260 nm which evident the presence of ZnO as nanoparticles which is present below the band gap of 3.46 eV. The nanoparticles are present in monodispersive nature.

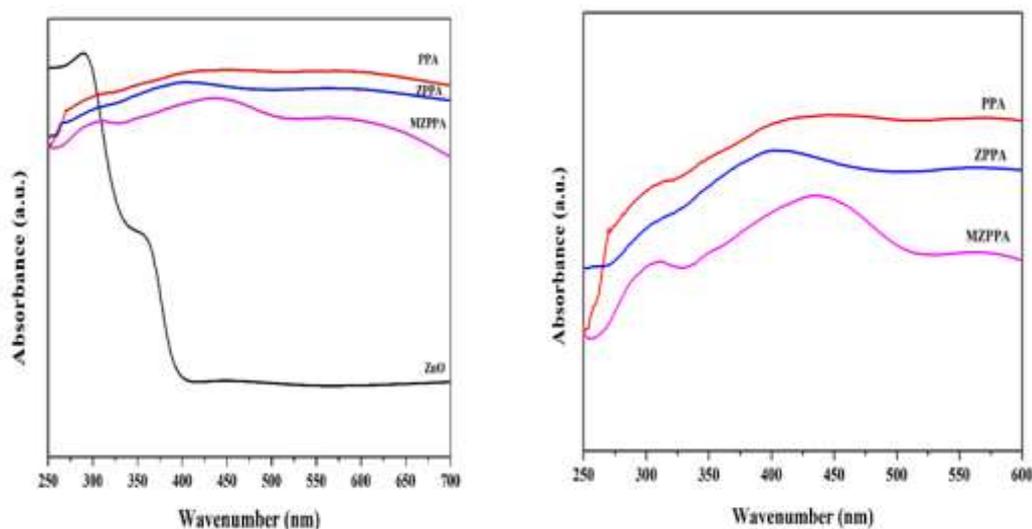
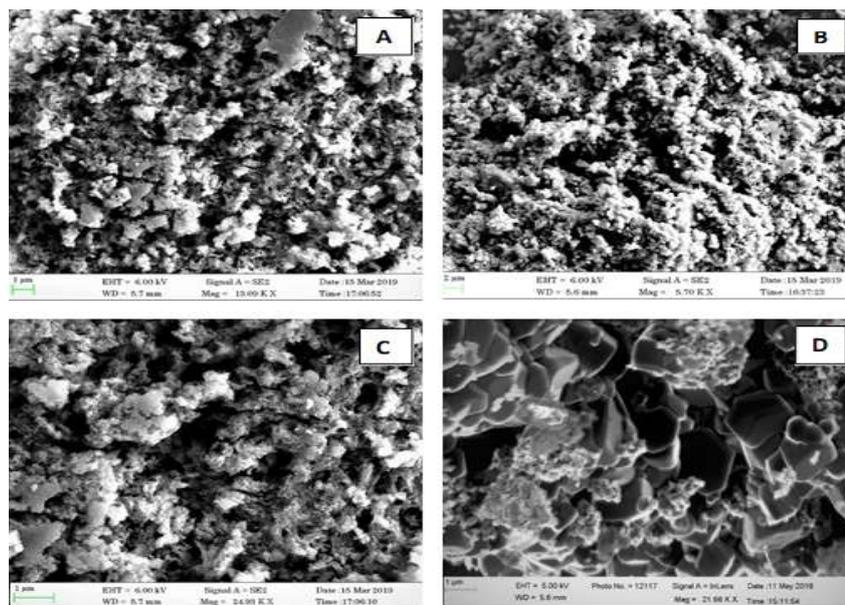


Figure 3. UV-Vis spectra of PPA conducting polymer, ZnO nanoparticles, ZPPA and MZPPA polymeric nanocomposite.

3.4. SEM Analysis

Figure 4A corresponds to the SEM image of PPA polymer which shows agglomeration of particles with

non-uniform morphology. Irregular pores are observed onto the surface of the conducting PPA polymer.



Figures 4. SEM images of PPA polymer; 4B: SEM image of ZPPA polymeric composite and 4C: SEM image of MZPPA polymeric composite blend and 4D: SEM image of ZnO nanoparticle

Addition of nanoparticle onto the polymeric matrix shows spherical shape of polymer nanocomposite and the nanoparticles are impregnated in the polymeric chains which is shown in Figure 4B & 4C. In Figure 4C, the dispersed particles are almost uniform and the two distinct phases exists, the bright phase may contribute the ZnO existence and the dark phase may be that of polymer interconnected with chain pattern. Non-uniform deposition of nanoparticles into the pores present on the polymer resulted in the enhanced conductivity nature of the polymeric composite blends.

The SEM image of ZnO nanoparticles shows hexagonal shaped particles with porous nature is shown in Figure 4D. The pores present on the surface of the nanoparticles are not of same size. The average size of the nanoparticles is found to be 110 nm respectively.

3.5. EDS Characterization

The elemental analysis of EDS spectra clearly depicts the presence of Mg and Zn which confirms the formation of magnesium doped polymer composite MZPPA

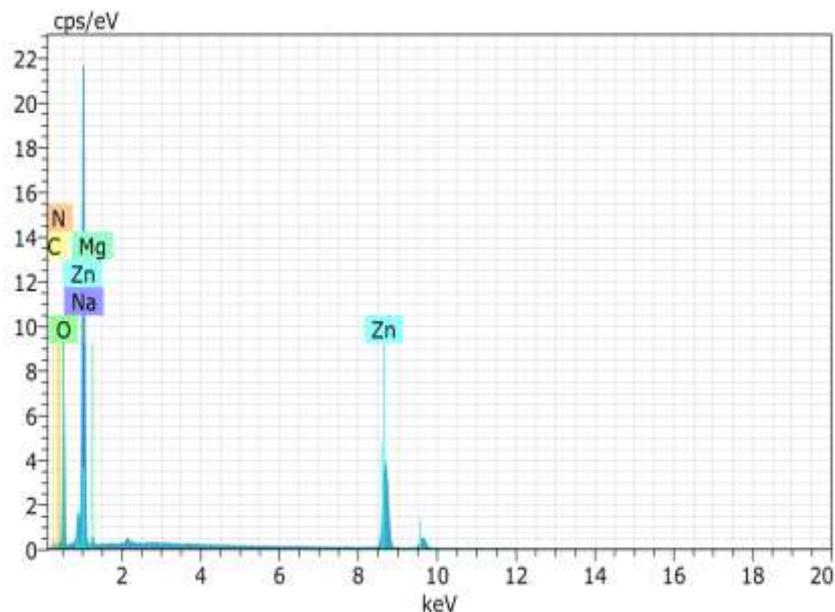


Figure 5. EDS spectra of MZPPA polymer nanocomposite

3.6. Thermogravimetric analysis

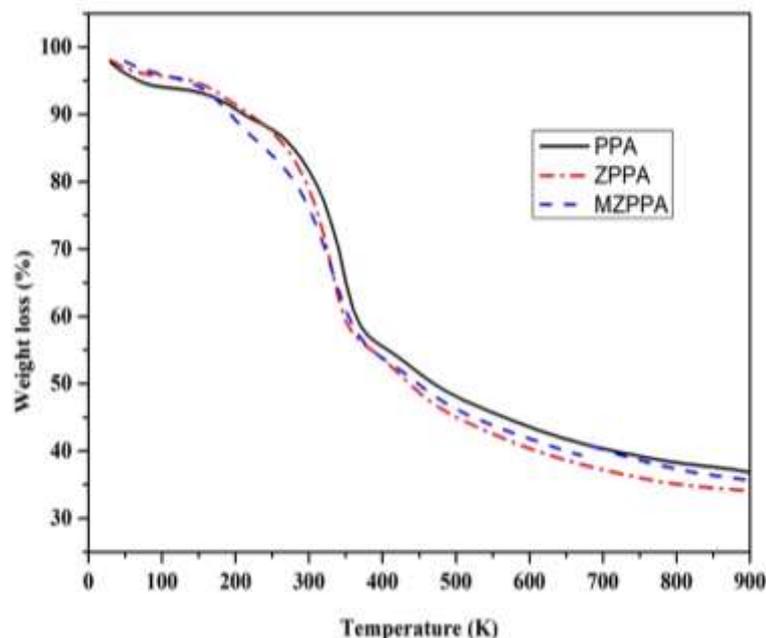


Figure 6. TGA thermograph of PPA polymer, ZPPA and MZPPA polymeric composite blends.

Figure 6 shows the TGA thermogram of the polymer PPA and polymer nanocomposites ZPPA and MZPPA. The thermal degradation takes place at two stages. The first stage of degradation occurs at 30 to 100°C due to the expulsion and removal of water molecules present in the polymeric matrix and the second stage of decomposition takes place at 300 to 900°C due to the degradation and decomposition of dopant along with the conducting polymeric chain³⁰. The weight loss of all three synthesized polymeric materials showed finite-difference in the thermogram, suggesting that the thermal degradation of the pure, as well as doped polymer, takes place with a similar pattern. The doped polymeric material shows some slight decrease in the weight loss when compared with the pure polymer depicting that the nanocomposite polymeric material shows higher stability when compared with that of pure polymer.

3.7. Conductivity studies

The conductivity studies of ZnO, Poly (*p*-anisidine) (PPA) conducting polymer, zinc doped PPA polymeric blend (ZPPA) and Magnesium doped zinc oxide PPA

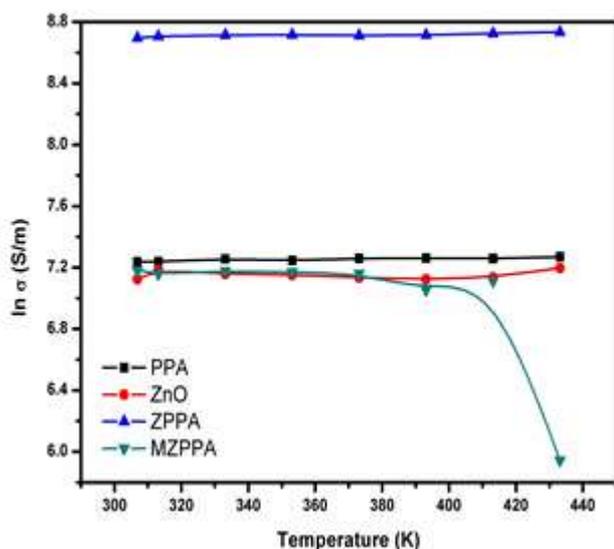


Figure 7. Variation in electrical conductivity with synthesized conducting materials against temperature difference.

The Arrhenius plot of dc conductivity with respect to variation in temperature is shown in Figure 8. With the addition of dopant Zinc oxide and magnesium doped zinc oxide onto the PPA polymer which results due to change in atomic defect and electrical activity at the grain boundary. The shallow nature with deep donor atoms present in the semiconductor material doped conducting polymer shows decrease in the bandgap edge of the semiconductor material. This result in the increased electrical conductance of the material as the temperature is increased.

polymeric blend (MZPPA) with respect to temperature is shown in Figure. 7. There is a slow and steady increase in the electrical conductivity with increase in temperature. The difference in the electrical conductivity of the PPA, ZPPA and MZPPA conducting polymer mainly depends on the thermal energy. With increase in temperature, the conductivity slowly increases for all four conducting polymeric materials. The polymer nanocomposite ZPPA is observed to show enhanced conductivity than PPA, ZnO & MZPPA. The presence of lone pair of electrons in PPA contributes to the conducting nature of the polymer, further the doping of ZnO into the PPA polymeric network improved its conductivity and this is due to the increasing efficiency of charge transfer between the polymer PPA and ZnO dopant with the raise of temperature³¹. The conductivity of MZPPA decreases when the temperature reaches above 430K may be due to increasing temperature increases the agglomeration of composites which results in decreasing the conductivity of lone pair of electrons in the polymeric network.

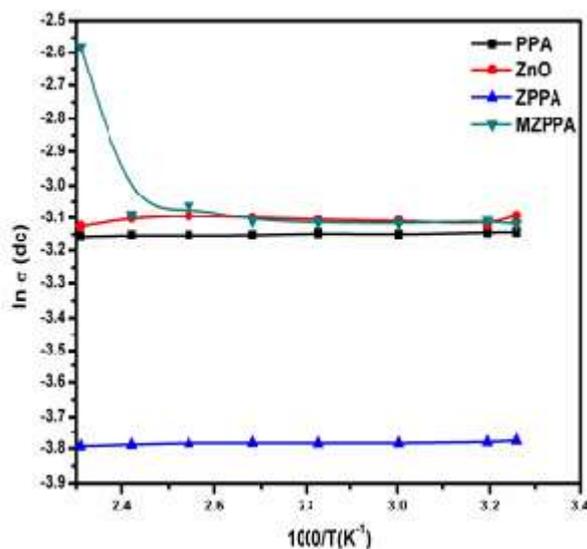


Figure 8. Arrhenius plot of dc conductivity against difference in temperature

4. Conclusion

ZnO, Poly(P-Anisidine) (PPA) conducting polymer, ZPPA and MZPPA polymeric composite blends are prepared using oxidative polymerization using ammonium persulphate (APS). The surface morphological and structural assessment justified the formation of polymeric composite blends. The XRD images confirm the formation of Zinc oxide with sharp peaks and addition of PPA polymer resulted in the broad peaks. The UV studies show an absorption band above 520 nm corresponding to the substituted polyaniline. Increase in electrical conductance with increase in temperature is observed. Temperature plays a pivotal role in increasing the thermal conductance of

the polymeric composite material. Upon comparison, ZPPA polymeric composite blend shows enhanced electrical conductance due to the presence of lone pair of electrons present both in the amine functional group of the polymer.

5. Experimental

5.1. Materials required

p-anisidine ($\text{CH}_3\text{OC}_6\text{H}_4\text{NH}_2$, Sigma-Aldrich, Germany); Ammonium persulphate (APS) ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, Merck, India); Hydrochloric acid (HCl, 37%, Loba chemicals, India), Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Sodium hydroxide (NaOH), Millipore water are purchased and used as such for experiments.

5.2. Preparation of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ nanoparticles

To prepare pure ZnO, the following steps were involved. 1M of ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was added in 100 ml distilled water in a beaker which forms Solution-A. 2M of 100 ml NaOH solution was added drop-wise to solution-A under vigorous stirring until the pH is 12. The stirring action was continued for almost 12 hours.

During the preparation of nanoparticles, pH of the solution is maintained at 12 because this pH seems to be the optimum value for the formation of ZnO particles. The formed precipitate was then filtered and washed with distilled water, ethanol, dried in an oven at 100°C for 2hrs. The dried precipitates were collected and ground in an agate mortar. The collected nanopowder was annealed at 500°C for two hours, followed by stepwise cooling. A similar procedure was followed to prepare $\text{Zn}_{0.94}\text{Mg}_{0.06}\text{O}$ (Mg-doped ZnO) using stoichiometric ratios of starting precursors.

5.3. Synthesis of Poly (*p*-Anisidine) (PPA)

Synthesis of PPA conducting polymer was synthesized by the chemical oxidative polymerization technique. About 0.2 M of *p*-anisidine was slowly added into 300 ml of 1 M HCl aqueous solution until completely dissolves. The solution is cooled to 0°C . To the solution slowly added 0.2 M ammonium persulphate in 200 ml of 1 M HCl and kept under stirring for 24 hours. Formation of dark green precipitated polymer confirms the end of the polymerization.

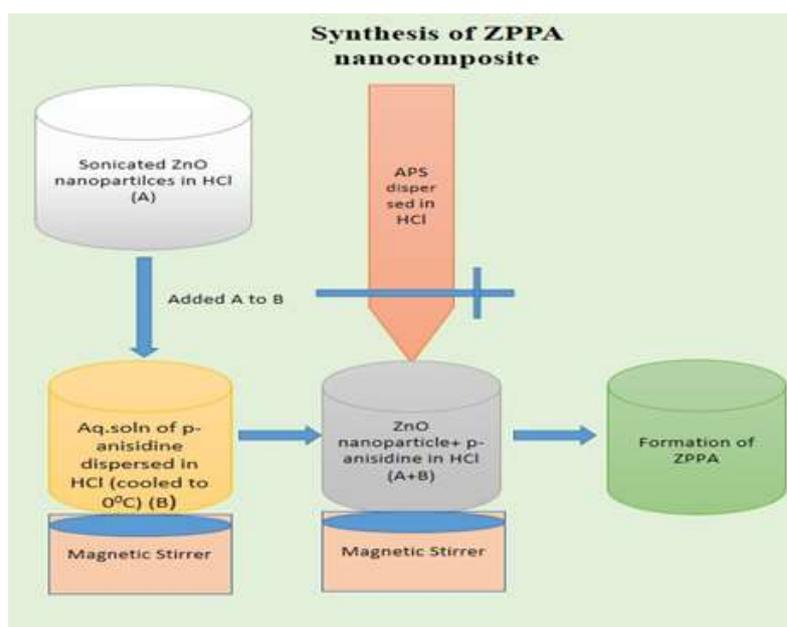


Figure 9. Schematic diagram for the formation of polymer nanocomposite.

The obtained polymer was filtered and stirred with 1 M NH_4OH for 2 hours and the product was washed with deionized water and finally washed with ethanol to remove the unreacted monomer and dried at 100°C for 6 h. For the synthesis of zinc doped polymer nanocomposite (ZPPA) and magnesium doped zinc oxide polymer nanocomposite (MZPPA) the similar procedure is followed by adding 10 mg of the zinc oxide and magnesium doped zinc oxide separately before the addition of ammonium persulphate solution into the *p*-anisidine monomer which is represented in Figure 9.

References

- 1- A.K. Mishra, Conducting Polymers: Concepts and Applications, J. at. mol. condens. nano phys, **2018**, 5(2), 159-193.
- 2- J.C. Lacroix, Polyaniline: A Very Fast Electrochromic Material, J. Electrochem. Soc, **1989**, 136(5), 1308-1313.
- 3- G. Gustafsson, Y. Cao, G.M. Treacy, F. Klavetter, N. Colaneri, A.J. Heeger, Flexible light-emitting diodes made from soluble conducting polymers, Nature, **1992**, 357(6378), 477-479.
- 4- G. Yu, A.J. Heeger, High efficiency photonic

- devices made with semiconducting polymers, *Synth. Met*, **1997**, 85(1-3), 1183–1186.
- 5- C. Harito, D.V. Bavykin, B. Yuliarto, H.K. Dipojono, & F.C. Walsh, *Polymer Nanocomposites Having a High Filler Content: Synthesis, Structures, Properties, and Applications*, *Nanoscale*, **2019**, 11(11), 4653–4682.
 - 6- Y. He, A novel emulsion route to sub-micrometer polyaniline/nano-ZnO composite fibers, *Appl Surf Sci*, **2005**, 249(1-4), 1–6.
 - 7- M. Cavas, Investigation morphological, electrical, and optical properties of Mn-doped ZnO thin film by sol-gel spin-coating method, *J Theoretical and Applied Physics*, **2017**, 11(4), 325–331.
 - 8- K.K. Nagaraja, S. Pramodini, A. Santhosh Kumar, H.S. Nagaraja, P. Poornesh, D. Kekuda, Third-order nonlinear optical properties of Mn doped ZnO thin films under cw laser illumination, *Optical Materials*, **2013**, 35(3), 431–439.
 - 9- S. Sharma, R.S. Kundu, A. Singh, S. Murugavel, R. Punia, N. Kishore, Structural, optical, electrical, and magnetic properties of $Zn_{0.7}Mn_xNi_{0.3x}O$ nanoparticles synthesized by sol-gel technique, *Cogent Physics*, **2015**, 2(1), 1-11.
 - 10- R.K. Sharma, S. Patel, K.C. Pargaien, Synthesis, characterization and properties of Mn-doped ZnO nanocrystals, *Adv. Nat. Sci: Nanosci. Nanotechnol*, **2012**, 3(3), 1-5.
 - 11- A. Matei, I. Cernica, O. Cadar, C. Roman, V. Schiopu, Synthesis and characterization of ZnO – polymer nanocomposites, *Int. J. Mater. Form*, **2008**, 1(S1), 767–770.
 - 12- X. Lei and Z. Su, Conducting polyaniline-coated nano silica by in situ chemical oxidative grafting polymerization, *Polym. Adv. Technol*, **2007**, 18(6), 472-476.
 - 13- W.S. Huang, B.D. Humphrey, A.G. MacDiarmid, Polyaniline, a novel conducting polymer. Morphology and chemistry of its oxidation and reduction in aqueous electrolytes, *J. Chem. Soc. Faraday Trans.1*, **1986**, 82(8), 2385-2400.
 - 14- W. Li, M. Wan, Porous polyaniline films with high conductivity, *Synth. Met*, **1998**, 92(2), 121–126.
 - 15- E.M. Geniès, A. Boyle, M.L. Apkowski, C. Tsintavis, Polyaniline: A historical survey, *Synth. Met*, **1990**, 36(2), 139–182.
 - 16- A.G. MacDiarmid, A.J. Epstein, Polyanilines: a novel class of conducting polymers, *Faraday Discuss. Chem. Soc*, **1989**, 88, 317-332.
 - 17- A. Olad, A. Rashidzadeh, Preparation and anticorrosive properties of PANI/Na-MMT and PANI/O-MMT nanocomposites, *Prog Org Coat*, **2008**, 62(3), 293–298.
 - 18- M. Mastragostino, Conducting polymers as electrode materials in supercapacitors, *Solid State Ion*, **2002**, 148(3-4), 493–498.
 - 19- K. Liu, Y. Zhang, W. Zhang, H. Zheng, G. Su, Charge-discharge process of MnO_2 supercapacitor, *T Nonferr Met Soc*, **2007**, 17(3), 649–653.
 - 20- S. Chen, J. Zhu, X. Wu, Q. Han, X. Wang, Graphene Oxide– MnO_2 Nanocomposites for Supercapacitors, *ACS Nano*, **2010**, 4(5), 2822–2830.
 - 21- A. Punya Basnayaka, Farah Alvi, K. Manoj Ram, Robert Tufts, Ashok Kumar, A Comparative Study on Substituted Polyanilines for Supercapacitors, *Mater Res Soc Symp Proc*, **2012**, 1388.
 - 22- A. M. Mazrouaa, M. Yahia Abed, N.A. Mansour, M.G. Mohamed, Synthesis and Characterization of Poly O-Anisidine Nanoparticles and their Nanocomposite, *J Material Sci Eng*, **2012**, 1(01), 1-5.
 - 23- F. Chouli, I. Radja, E. Morallon, A. Benyoucef, A novel conducting nanocomposite obtained by p-anisidine and aniline with titanium (IV) oxide nanoparticles: Synthesis, Characterization, and Electrochemical properties, *Polym. Compos*, **2017**, 38(S1), E254–E260.
 - 24- A. Ali Khan, S. Shaheen, Thermal stability and electrical properties of conducting polymer based ‘polymeric-inorganic’ composites: Poly-o-anisidine and poly-o-toluidine Sn (IV) tungstate, *Mater. Res. Bull*, **2012**, 47(12), 4414 – 4419.
 - 25- I. Radja, H. Djelad, E. Morallon, A. Benyoucef, Characterization and electrochemical properties of conducting nanocomposites synthesized from p-anisidine and aniline with titanium carbide by chemical oxidative method, *Synth Met*, **2015**, 202, 25–32.
 - 26- J. Singh, M.S.L. Hudson, S.K. Pandey, R.S. Tiwari, O.N. Srivastava, Structural and hydrogenation studies of ZnO and Mg doped ZnO nanowires, *Int J Hydrogen Energ*, **2012**, 37(4), 3748–3754.
 - 27- T. Abdiryim, R. Jamal, I. Nurulla, Doping effect of organic sulphonic acids on the solid-state synthesized polyaniline, *J. Appl. Polym*, **2007**, 105(2), 576–584.
 - 28- J. Longun, B. Buschle, N. Nguyen, M. Lo, J. O. Iroh, Comparison of Poly(o-anisidine) and Poly(o-anisidine-co-aniline) Copolymer Synthesized by Chemical Oxidative Method, *J. Appl. Polym.*, **2010**, 118(6), 3123–3130.
 - 29- J. Iqbal, T. Jan, M. Ismail, N. Ahmad, A. Arif, M. Khan, A. Arshad, Influence of Mg doping level on morphology, optical, electrical properties and antibacterial activity of ZnO nanostructures, *Ceram. Int.*, **2014**, 40(5), 7487–7493.
 - 30- K. Luo, N. Shi, C. Sun, Thermal transition of electrochemically synthesized polyaniline, *Polym. Degrad. Stabil.*, **2006**, 91(11), 2660–2664.
 - 31- M. Neetika, J. Rajni, K. Pramod Singh, B. Bhattacharya, Vijay Singh, S.K. Tomar, Synthesis and properties of polyaniline, poly (o-anisidine), and poly [aniline-co (o-anisidine)] using potassium iodate oxidizing agent, *High Perform. Polym.*, **2017**, 29(3), 266–271.