Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Applied Science Research, 2010, 2 (1) 247-253
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Characterizations of zinc oxide nanoparticles reinforced conducting polyaniline composites

S. B. Kondawar[a], S. D. Bompilwar[b], V. S. Khati[b], S. R. Thakre[c], V. A. Tabhane[b], D. K. Burghate[c]

[a]*Department of Physics, R.T.M. Nagpur University, Nagpur (India)*
[b]*Department of Physics, Institute of Science, Nagpur (India)*
[c]*Shri Shivaji Science College, Congress Nagar, Nagpur (India)*

Abstract

A simple approach for the formation of Zinc oxide (ZnO) nanoparticles is described. The particles of the synthesized zinc oxide are in spherical nano-sized form as confirmed from its TEM characterization. Composites of different molar concentration of aniline and ZnO nanoparticles have been prepared. During the polymerization of the monomer (aniline) by using oxidizing agent (ammonium persulphate) and dopant (H_2SO_4) under constant stirring at 0 - 4^{o}C, synthesized nanostructure zinc oxide powder was added. The presence of the vibration band of the dopant ion and other characteristic bands confirm that the polymer nanocomposites are in conducting emeraldine salt phase as characterized by their FTIR. Nanocomposites reveal polycrystalline nature and show homogeneous distribution of zinc oxide in PANI. The electrical property of nanocomposites is a function of the filler as well as the matrix. In the case of PANI/ZnO nanocomposites, ZnO is semi-conducting; the electrical conductivity is predominantly due to the PANI. Composites exhibit resistivity in between pure PANI and the ZnO nanoparticles. The change in the resistivity of the composites indicates a change in the doping state of the polymer. The composite PANI-ZnO (1:2) shows higher conductivity as compared to other ratios.

Keywords*:* Nanocomposites; conducting polymers; ZnO nanoparticles; electrical conductivity;

Introduction

Nanocomposite materials significantly encompass a large variety of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials, made of distinctly dissimilar components and mixed at the nanometer scale. The properties of nanocomposite materials depend not only on the properties of their individual parents, but also on their morphology and interfacial characteristics. Polymer materials in the form of nanocomposites are useful due to certain advantages such as high surface area to volume ratio. There has been a growing interest in new ways of producing conducting polymer nanocomposites. The conductivity of conducting polymers can be tuned by chemical manipulation of the polymer backbone, by the nature of the dopant or by the degree of doping or by blending with others. Conducting polymers have potential applications at all levels of microelectronics [1]. Among different conducting polymers, conducting polyaniline (PANI), as one of the heteroatomic conducting polymers, has attracted considerable attention because of its interesting electrical conductivity, novel electronic structure [2,3] and mechanism of electrical conductivity [4,5] as well as the possibility for application as a new electronic material. Recent investigations [6,7] showed that PANI can be an excellent matrix for forming semiconductor composite films. However, when they are taken in composite form their electrical properties are altered from those of basic materials.

Conducting polymer nanocomposites of PANI and ZnO nanoparticles can exhibit some novel properties. ZnO is an interesting material from several points of view. It is one of the few oxides that show quantum confinement effects in an experimentally accessible size range [8]. Secondly, a sol–gel preparation method by Spanhel and Anderson [9] offers a simple route to quantum sized ZnO particles. ZnO is a wide band-gap semiconductor (Eg = 3.4 eV and $\sigma = 5 \times 10^{-5}$ Scm^{-1} at RT) with a high exciton binding energy (60meV). Zinc oxide (ZnO) particles with a variety of particle shape - from spheres and ellipsoids to hexagons and star-like particles - have a narrow particle size distribution typically from 20 nm to 1000m and specific surface area (SSA) in the range of 5 – 60 m2/g. Moreover, the wide range of morphological diversity in the nano-regime has made this material a promising candidate in the field of nanotechnology and opened up new possibilities for the fabrication of high performance devices based on these nanostructures [10–12]. A number of groups have reported studies on the electrical conductivity of composites of a variety of conducting polymers. It has been shown that the conductivity of these heterogeneous systems depends on a number of factors such as the concentration of conducting fillers, their shape, size, orientation and interaction between filler molecules (impurity) and host matrix [13, 14]. In this paper, we report a simple and novel method for the preparation of ZnO nanoparticles and PANI–ZnO nanocomposite systems and characterization by FTIR, XRD, TEM and electrical conductivity.

Materials and Methods

Experimental

Zinc acetate (0.1 M) was added in starch solution prepared by adding starch (2.5g) in distilled water (250 ml). After complete dissolution of zinc acetate under constant stirring to the solution, ammonia (0.2 M) was then added drop wise. The reaction was allowed to proceed for 2 hours. Then the solution was allowed to settle for over night and supernatant solution was then discarded carefully. The obtained nanoparticles were washed many times using distilled water and then dried at 80°C for overnight. During drying complete conversion of $Zn(OH)_2$ into ZnO takes place.

The polymerization of the monomer (aniline) was initiated by the drop-wise addition of the oxidizing agent (ammonium persulphate) in acidified solution prepared using doubly distilled water under constant stirring at 0 - 4°C. During this stirring for one hour zinc oxide nanoparticles in different proportion with aniline was added for synthesizing the composites. The monomer to oxidizing agent ratio was kept at 1:1. After complete addition of the oxidizing agent the reaction mixture was kept under constant stirring for 4 hours. Precipitated polymer was filtered and washed with distilled water until the filtrate was colorless. Finally, the polymer was dried in an oven at 80 °C for 12 hours [15].

A Hitachi H-7000 Transmission electron microscope operated at 100 kV and ~30 μA was used to observe TEM images of synthesized zinc oxide. The FTIR spectra of the composites were taken on a Shimatzu FTIR-8101A spectrophotometer between 400 and 4600 $cm.^{-1}$. X-ray diffractograms were recorded on a Philips PW1710 automatic X-ray diffractometer. Dry powder samples were made into pellets using a steel die in a hydraulic press under a pressure of 7 tons. Temperature dependent electrical conductivity of the composites was studied by four probe resistivity method.

Results and Discussion

The TEM sample was prepared by dispersing the powder sample in the solvent (ethanol) with ultrasonic bath and then transferred 2-3 drops on the carbon coated Cu grid.

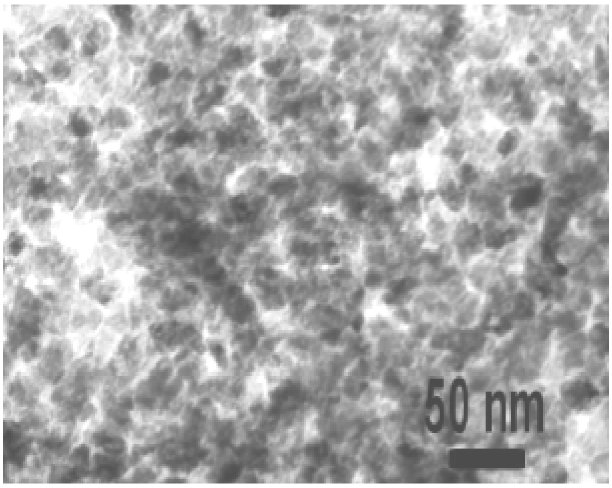

Figure 1: TEM image of synthesized zinc oxide

The particle size of the synthesized zinc oxide is in nanometer range as confirmed from figure 1 and morphologically the particles are spherical in shape.

Figure 2 shows XRD pattern of synthesized pure ZnO, PANI-ZnO (1:2), and pure PANI. It is observed from these figures that the zinc oxide is uniformly dispersed in the polyaniline matrix. The XRD study suggests that PANI undergoes interfacial interactions with ZnO crystallites and looses its own morphology by its mixing with ZnO crystallites due to which the composites show less conductivity than that of pure PANI as confirmed from dc conductivity measurement of the synthesized materials.

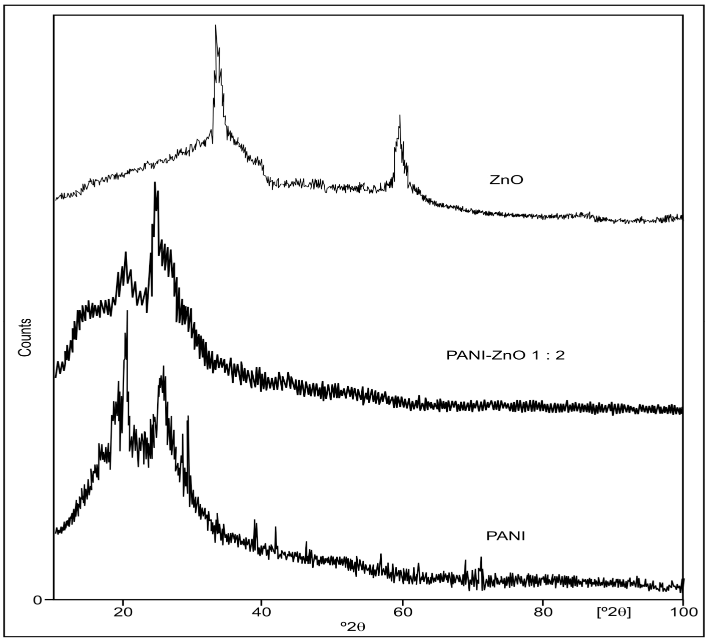

Figure 2: XRD pattern of pure ZnO, PANI-ZnO (1:2), and pure PANI

Figure 3 represents the FTIR spectra of composites of PANI and ZnO in the molar ratio 1:1, 1:2 and 1:3. From the figure the intensities of the peaks in the region 1600 – 500 cm^{-1} are affected by the presence of ZnO during PANI synthesis. These differences in IR spectra can be explained on the basis of constrained growth and restricted modes of vibration in PANI grown in the presence of ZnO. In such a case the aniline monomer gets absorbed on oxide particles, which were dispersed in the reaction mixture and the polymerization proceeds initially on the surface of the oxide particles when ammonium persulphate is added to the solution. This leads to the adhesion of the polymer to the ZnO particles. As a result the characteristics stretching frequencies are shifted towards lower frequency side, as compared with pure PANI. Table 1 gives the characteristic bands and their positions. Similar characteristic bands of the conducting emeraldine salt phase of polymer were observed in all the polymer composites.

Table 1: Characteristic frequencies of composites of PANI and ZnO nanoparticles

Wavenumber (cm^{-1})				**Band characteristics**
PANI–ZnO (1:1)	PANI–ZnO (1:2)	PANI–ZnO (1:3)	PANI pure	
573	576	578	570	▪ C–H out of plane bending vibration
806	809	811	772.3	▪ Paradisubstituted aromatic rings indicating polymer formation
1110	1113	1115	1108.3	▪ C–H in plane bending vibration
1290	1292	1295	1300.9	▪ Vibration band of the dopant anion
1490	1495	1507	1488.8	▪ C–N stretching of benzenoid rings
1560	1585	1600	1566.0	▪ C–N stretching of quinoid rings
2365	2380	2392	2340	▪ *v*(N–H)+ unsaturated amine
2924	2926	2930	2918	▪ C–H stretching due to composite
3410	3421	3428	3437.2	▪ N–H stretching vibration

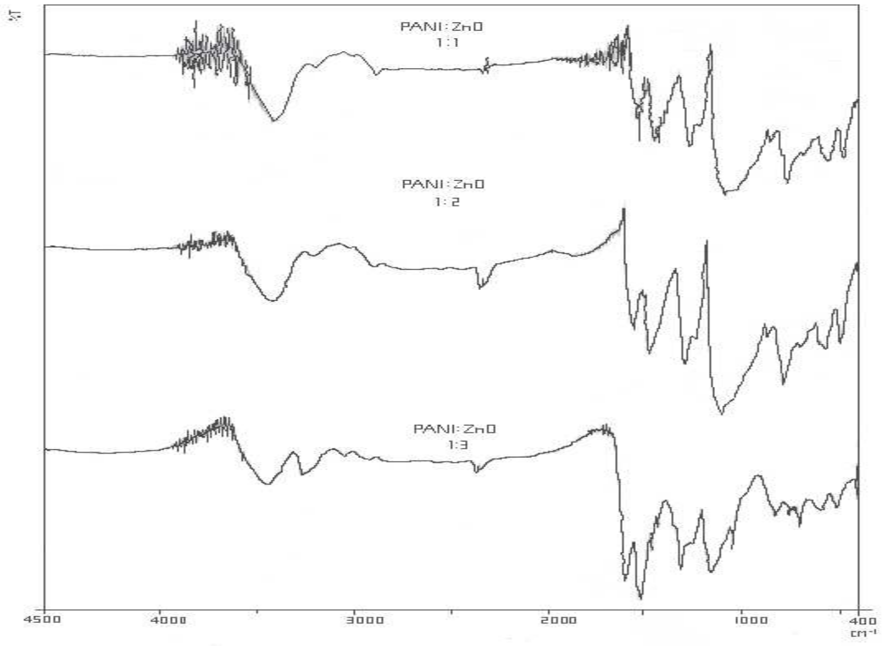

Figure 3: FTIR spectra of PANI-ZnO composites

The plot of dc conductivity ($\sigma_{d.c}$) of PANI/ZnO composites verses temperature shown in figure 4. It has been observed that σ_{dc} of the composites is found to increase with the increase in temperature, representing the semiconducting nature of the nanocomposites. From this figure, we observe the increase in $\sigma_{d.c.}$ with temperature in composites, thereby indicating the behaviour of disordered conductor. Further, composite of 1:2 shows the higher $\sigma_{d.c.}$ values than other composites over the entire temperature range. The increase in conductivity in 1:2 composite may be due to more contribution of polarons and bipolarons bands formed in the widen band gap of this composites [16]. The changes in the resistivity of the composites indicate a change in the doping state of the polymer.

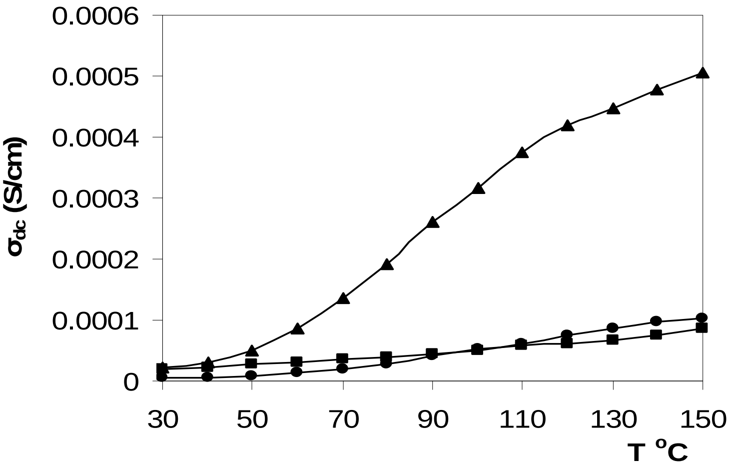

Figure 4: D.C. conductivity of composites **●PANI-ZnO (1:1), ▲PANI-ZnO (1:2), ■PANI-ZnO (1:3)**

Table 2: Transport parameters for PANI-ZnO composites

Materials	σ_{dc} (S/cm)	T_o (K)	α^{-1} (nm)	R (nm)	W (eV)
1:1	0.12×10^{-4}	4007	2.19	1.86	0.142
1:2	0.21×10^{-4}	3821	2.53	2.08	0.131
1:3	0.23×10^{-4}	3660	2.47	2.06	0.137

The temperature dependence conductivity was fitted to an Arrhenius type equation.

$$\sigma_{dc} = \sigma_o \exp(-Ea/2kT)$$

It has been observed that σ_{dc} of the composites found to increase with the increase in temperature. In the present studies the temperature dependence conductivity is fitted to Zeller equation [17].

$$\sigma_{dc} = \sigma_o \exp[-(T_o/T)^{1/2}]$$

In Zeller equation, T_o (characteristic temperature) is related to charge localization length (α^{-1}), most probable hopping distance (R) and hopping energy (w) by the following relations

$$\alpha^{-1} = \frac{8}{T_o} N(E_F) Zk$$

$$R = \left(\frac{T_o}{T}\right)^{1/2} \frac{\alpha^{-1}}{4}$$

$$w = \frac{ZkT_o}{16}.$$

In these relations, Z is the number of nearest neighboring chains (~4), k is Boltzmann constant and $N(E_F)$ the density of states per electron volt (2 – ring unit suggested for polyaniline [18]). The value of T_o is determined graphically from log (σ_{dc}) vs $T^{-1/2}$ and other parameters are computed from the data as shown in table 2. Composites show lesser σ_{dc} than that of pure PANI but higher than that of pure ZnO. The changes in the values of T_o (characteristic temperature), charge localization length (α^{-1}), most probable hopping distance (R) and hopping energy (w) in the composites may be due to different mole ratio of nanostructure zinc oxide.

Conclusion

The electrical property of nanocomposites is a function of the filler as well as the matrix. In the case of PANI/ZnO composites, the electrical conductivity is predominantly due to the PANI. The change in the conductivity of the composites indicate a change in the doping state of the polymer due to incorporation of ZnO in the polymer chain.

Acknowledgments

Authors (SBK & SRT) are grateful to UGC, New Delhi for financial assistance provided to carry out research work under major research project UGC No. F.No.33-7/2007 (SR).

References

[1] T. Skotheim, Ed., Marcel Dekker, *Handbook of Conducting Polymers*, Vols. **1** and **2**, Inc., New York, (**1986**).
[2] S. Stafstrom, J. L. Bredas and A. J. Epstein, *Phys. Rev. Lett*. 59 (**1987**) 1464.
[3] R. P.McCall, J. M. Ginder and J. M. Leng, *Phys. Rev*. B, 41 (**1990**) 5202.
[4] F. Zuo, M. Angelopoulos and A. G. MacDiarmid, *Phys. Rev*. B 36 (**1987**) 3475.
[5] A. G. MacDiarmid and A. J. Epstein, *Faraday Discuss. Chem. Soc*. 88 (**1989**) 317.
[6] S. Pethkar, R. C. Patil and J. A. Kher, *Thin Solid Films*. 349 (**1999**) 105.
[7] J. Luo, H. G. Huang and H. P. Zhang, *J. New Mater. Electrochem. Syst*. 3 (**2000**) 249.
[8] U. Koch, A. Fojtik and H. Weller, *Chem. Phys. Lett*. 122 (**1985**) 507.
[9] L. Spanhel and M. A. Anderson, *J. Am. Chem. Soc*. 113 (**1991**) 2826.
[10] C. Klingshrin, Chem. Phys Chem. 8 (**2007**) 782.
[11] Z. L. Wang, *Mater. Today* 7 (**2004**) 26.
[12] Y. Cui, Q. Q. Wei, H. K. Park and C. M. Libera, *Science* 293 (**2001**) 1289.
[13] M Kryszewaski, *Synth. Met.* 45 (**1991**) 289.
[14] M Blaszkiewicz, D S McLachian and R Newnham, *J. Polym,. Eng. Sci.* 32 (**1992**) 421.
[15] S B Kondawar, M J Hedau, V A Tabhane, S P Dongre, U B Mahatme and R A Mondal, *Mod. Phys. Let. B, World Sci. Publ.* Vol. 20(23), (**2006**) 1461.
[16] S D Patil, S C Raghvendra, P Narsimha and M V M Ambika Prasad *Bull. Mater. Sci.,* Vol. 30(2), (**2007**) 88.
[17] V. K. S. Shante, C. M. Verma and A. N. Bloch; *Phys. Rev.* 138 (**1973**) 4885.
[18] D. C. Sindhimeshram and M. C. Gupta, *Ind. J. Chem*., Vol. 34 A (**1995**) 260.