

# Synthesis of Nano-Sized ZnO and Polyaniline-Zinc Oxide Composite: Characterization, Stability in Terms of DC Electrical Conductivity Retention and Application in Ammonia Vapor Detection

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**ABSTRACT:** Nano-sized particles of Zinc oxide (ZnO) were synthesized using a new chemical route. The chemical oxidative polymerization of aniline in the presence of nano ZnO was employed to synthesize a polyaniline-zinc oxide (PANI-ZnO) nanocomposite. The material was characterized by using transmission electron microscopy, XRD, scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR), and Thermogravimetric analysis (TGA). The conductivity measurements showed the resulting composites possessed higher conductivity as compared to pure polyaniline (PANI). The nanocomposite exhibited fairly sensitive towards solution of aqueous ammonia (NH<sub>3</sub>), when it

was exposed to various concentrations of NH<sub>3</sub> in an ambient room temperature. The results show that the sensor has good sensitivity and good repeatability upon repeated exposure to NH<sub>3</sub>. PANI-ZnO nanocomposite was also used to study electrical conductivity under isothermal conditions in the temperature range 50–130°C. The composite was found stable under ambient conditions below 90°C in terms of DC electrical conductivity retention. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1601–1607, 2010

**Key words:** conducting polymer; nanocomposite; electrical conductivity; sensor

## INTRODUCTION

Nanocomposites of metal–polymer or metal oxide–polymer are expected to be an important class of materials in the area of nanotechnology. Recently, conductive polymer-inorganic nanocomposites with different combinations of the two components had received more and more attention, because they have interesting physical properties and many potential applications in various areas.<sup>1</sup> ZnO is a typical n-type semiconductor as well as an important electronic and photonic material with many potential applications such as field effect transistors, ultra-sensitive nano-sized gas sensors, nanoresonators, nanocantilevers, UV detector, piezoelectronic materials, catalysts, hydrogen storage materials, chemical sensors, and biosensors.<sup>2–12</sup> Polyaniline is one of the typical conductive polymers which are usually considered as p-type material used in making lightweight battery electrode, electromagnetic shielding device, anticorrosion

coatings, and sensors.<sup>13,14</sup> In the recent past the conducting polymer-based nanocomposite have drawn attention in their application as gas sensing application.<sup>15–22</sup> Therefore, PANI-ZnO nanocomposites have been most intensively studied among various composites, because it could combine the merits of PANI and nanocrystalline ZnO within a single material, and are expected to find applications in electrochromic devices, sensor, nonlinear optical system, and photoelectrochemical devices. Ammonia is one of the important industrial exhaust gases with high toxicity. With the increasing of the human awareness of environmental problems in industrial gases, the requirement of detecting these gases has greatly increased. Nanocomposite based sensors have been demonstrated for the detection of NH<sub>3</sub> under ambient conditions.<sup>23</sup>

In present work, attempts have been made to synthesize approximately uniform hexagonal ZnO nano particles and PANI-ZnO nanocomposite for ammonia vapor sensing application. The characterization had been carried out by transmission electron microscopy (TEM), x-ray diffraction, fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric analysis and the conductivity measurement by four probe. The isothermal stability of the composite material in terms of DC electrical conductivity retention at 50, 70, 90, 110, and 130°C in an air oven at an interval of 10 min in the accelerated ageing experiments, has also been reported in the present research work.

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## EXPERIMENTAL

### Reagents

Aniline (Qualigen) was distilled twice just before use. Ammonium persulphate (C.D.H.) was used as received. Ethanol (Riedel-deHaen), Methanol (Qualigence), Zinc acetate dihydrate (99.5%)  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , Ethylene glycol  $\text{CH}_2\text{OHCH}_2\text{OH}$ , 2-Propyle alcohol  $(\text{CH}_3)_2\text{CHOH}$ , glycerol  $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$  and all other chemicals were used of A.R. grade. Doubly distilled water obtained from distillation plant (Borosilicate).

### Synthesis of zinc oxide nano particles

Slightly modified form of sol-gel method reported earlier<sup>24</sup> was used to synthesis of zinc oxide. 100 g zinc acetate dihydrate was mixed with 20 mL of ethylene glycol in a round bottom flask fitted with a condenser and kept at 150°C for 15 min over a hot plate to obtain a uniform transparent solution. The solution was solidified to a transparent brittle solid on cooling at room temperature. This solid was dissolved in 200 mL of 2-propyle alcohol. On addition few drops of water, the solution was converted in to gel. Triethylamine  $(\text{C}_2\text{H}_5)_3\text{N}$  was added to hydrolyse of zinc acetate. The resulting solution was placed in an oven at a temperature of 200°C for 7 h. The solution was turned in to light brown powder. Now this powder was heated in a programmable furnace at 700°C for 8 h to remove all organic impurities. Finally white pure zinc oxide powder was obtained.

### Fabrication of polyaniline-zinc oxide composite

PANI-ZnO nanocomposite was synthesized by following steps: the different weight percent of ZnO powder was added in aniline solution (1 mL aniline + 3 mL toluene + 50 mL water). 50 mL solution of 0.1 M ammonium persulphate mixed with above solution with vigorous magnetic agitation at 5°C for 2 h. A greenish black precipitate was obtained after keeping the resulting mixture at low temperature (5–10°C) over night. The precipitate was filtered and washed several times with distilled water to remove unreacted chemicals. The precipitate was dried in an oven at 50°C and then kept in desiccators for further studies. The fine powder of composite was obtained by grinding the material with the help of pastel mortal. The fine powder of the composite was pressed in pellets form using a hydraulic press.

### Characterization

The FTIR spectra of zinc oxide and polyaniline-zinc oxide composites were recorded by a Perkin Elmer 1725 instrument. TEM was carried out using a Philips EM-400 Microscope, a drop of sample prepared in ethanol was placed on an ultra thin carbon coated

copper grid. XRD data were recorded by Bruker D8 diffractometer with Cu  $K\alpha$  radiation at 1.540 Å in the range of  $20^\circ \leq 2\theta \leq 80^\circ$  at 40 keV). A LEO 435-VF scanning electron microscopy was used to obtain the micrograph of the samples. The thermogravimetric analysis were performed on the selected samples of composites and polyaniline by using a Perkin-Elmer (Pyris Dimond) instrument heating from  $\sim 25^\circ\text{C}$  to  $600^\circ\text{C}$  at the rate of  $10^\circ\text{C min}^{-1}$  in nitrogen atmosphere with the flow rate of  $30 \text{ mL min}^{-1}$ .

### Sensor testing apparatus and measurements

The sensing material (PANI-ZnO) were dried in air for 30 min and then placed in an oven at 80°C for 24 h to remove any excess solvent. The gas sensitive characteristics of the composites were investigated by recording their electrical responses when exposed alternately to different concentration of aqueous ammonia vapor and air at room temperature using four-probe in a glass chamber. The sensing material was placed into the glass chamber and gently pressed by four-probe to record the current-voltage characteristics using digital microvoltmeter (DMV 001) and low current sources (LCS 02), the assembly is shown in Figure 1. The vapor sensitivities were recorded by their electrical responses. The distance between sensing material and solvent was kept 3–4 cm at the time of exposure of different concentration of aqueous ammonia on the sensing material at room temperature. DC electrical conductivity ( $\sigma$ ) was calculated using eqs. (1)–(4) and the temperature dependence electrical conductivity measurements were done using a temperature controller (PID-200).

$$\rho = \frac{\rho_0}{G_7(W/S)} \quad (1)$$

$$G_7(W/S) = \left(\frac{2S}{W}\right) \ln 2 \quad (2)$$

$$\rho_0 = \left(\frac{V}{I}\right) 2\pi S \quad (3)$$

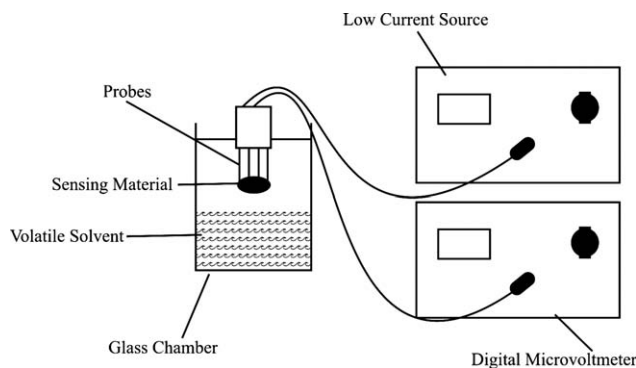
$$\sigma = 1/\rho \quad (4)$$

The initial resistivity of sensing material was allowed to stabilize before the addition of the solvent. The required solvent was poured into the chamber through the funnel. The sensing material was exposed to the solvent for appropriate time and then washed with double distilled water to remove the solvent and return the sensor in air.

## RESULTS AND DISCUSSION

### Characterization

In Figure 2 all the peaks were well indexed to hexagonal phase ZnO reported in JCPDS card No. 36-1451.<sup>25,26</sup> The particle size of ZnO was about 22.70

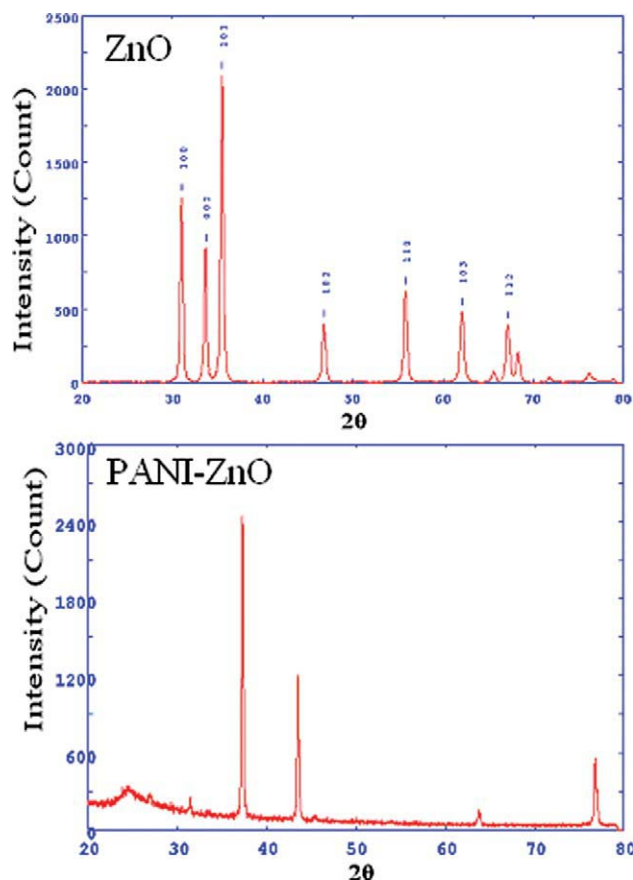


**Figure 1** Set-up of sensitivity testing apparatus.

nm calculated according to Scherer's equation estimated from the line width of the (101) XRD peak.

The intensity of the main peaks characterizing the inorganic ZnO system shifted to high intensity. This indicates the formation of PANI-ZnO composite. Other weakened peaks of ZnO system are not appearing in PANI-ZnO system. This can be attributed to dominate the amorphous nature of polyaniline which may the influence of the crystallinity of inorganic ZnO particles as shown in Figure 2.

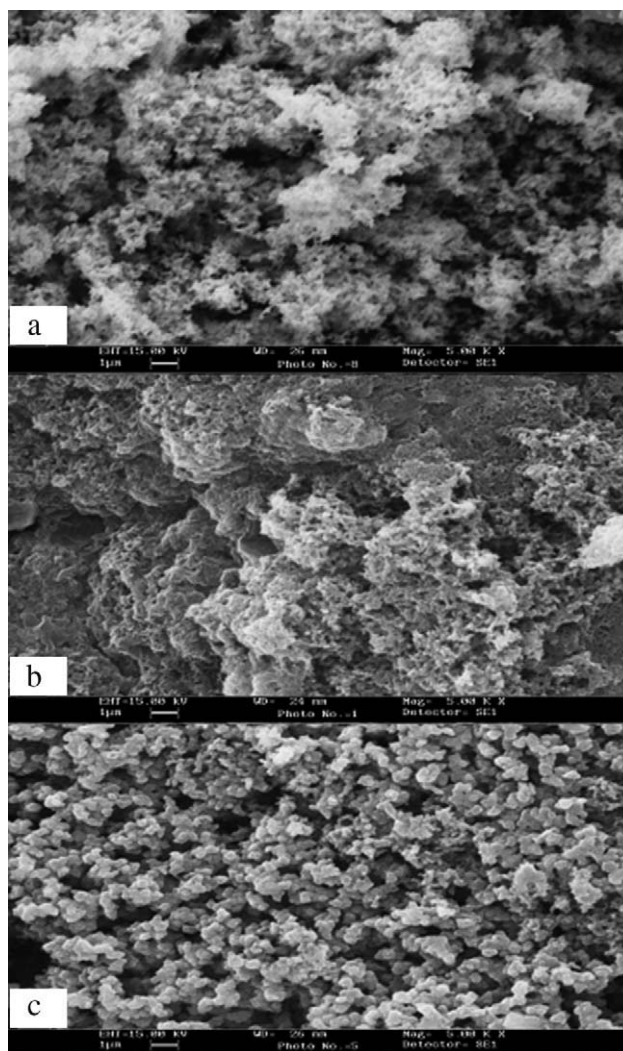
XRD pattern of PANI-ZnO has shown semicrystalline structure and the size of the composite was found to be 34.17 nm according to the highest inten-



**Figure 2** XRD pattern of ZnO and PANI-ZnO.

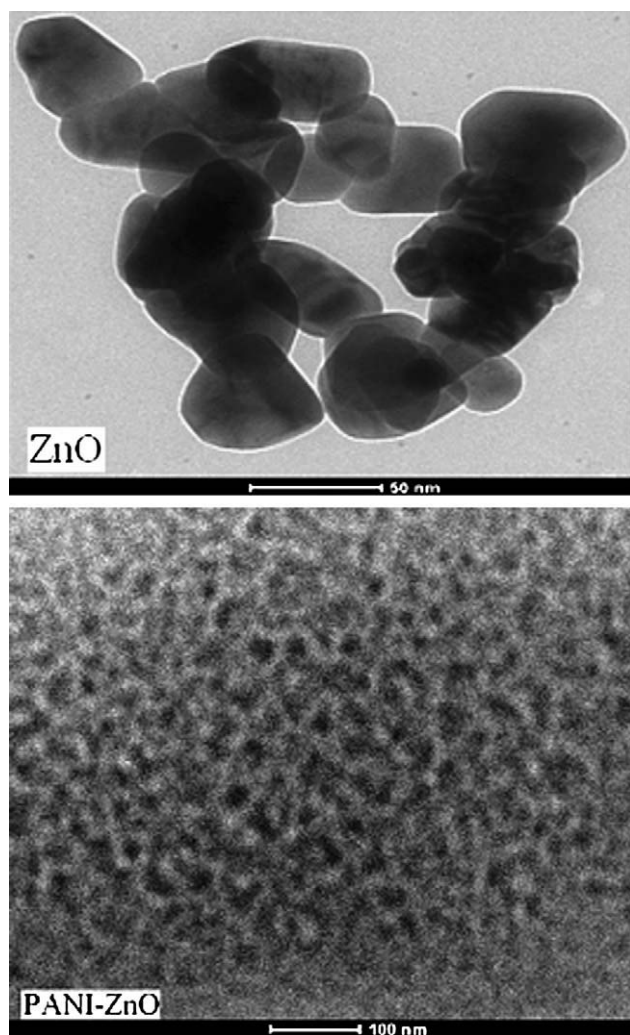
sity peak in the figure. XRD pattern of semicrystalline PANI-ZnO composite can be supported by SEM images of ZnO, polyaniline and PANI-ZnO composite (Fig. 3), where nearly hexagonal particles of ZnO [Fig. 3(c)] hampered on addition of amorphous polyaniline [Fig. 3(a)] after the formation of PANI-ZnO composite [Fig. 3(b)]. The nano particles of ZnO were attached with polyaniline during the curing of the polymer, thus a new phase of PANI-ZnO appeared. Hexagonal type structure of the average particle size 20–30 nm can be seen in the TEM (Fig. 4) of ZnO. However in the TEM image of PANI-ZnO, the ZnO particles encapsulated with polyaniline and suggest a new phase of composite material with the particle size of 30–50 nm. Thus the structure morphology of the materials can be explained with the help of XRD pattern, SEM and TEM images.

In FTIR spectra (Fig. 5) a peak observed at  $512\text{ cm}^{-1}$  is assigned to Zn–O of ZnO<sup>27</sup> which



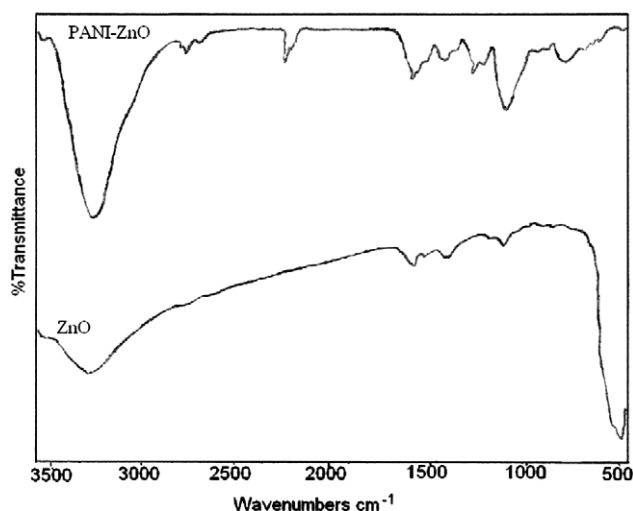
**Figure 3** SEM images of PANI (a), PANI-ZnO (b) and ZnO (c).





**Figure 4** TEM images of ZnO nanoparticles and PANI-ZnO nanocomposite.

confirms the formation of ZnO. The hydrogen bonding between the imine group of PANI and ZnO nanoparticle has been confirmed from the presence of the



**Figure 5** FTIR spectra ZnO and PANI-ZnO.

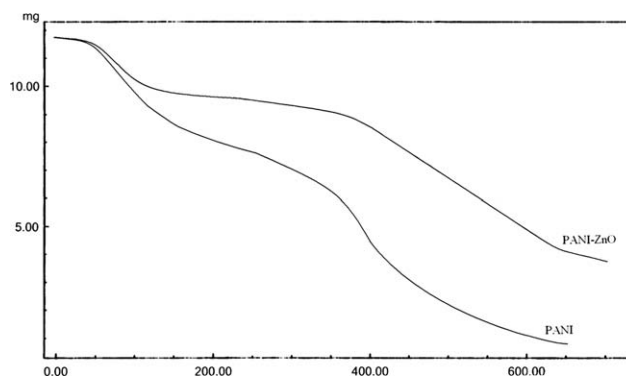
band at  $1148\text{ cm}^{-1}$  in the FTIR spectra of PANI-ZnO composite. The characteristic peaks of emeraldine salt form of PANI at  $1562\text{ cm}^{-1}$  (C=C stretching mode of the quinoid rings),  $1479\text{ cm}^{-1}$  (C=C stretching mode of benzenoid rings),  $1263\text{ cm}^{-1}$  (C-N stretching mode) and  $1124\text{ cm}^{-1}$  (N=Q=N, where Q represents the quinoid ring) appear in the FTIR spectrum of PANI-ZnO composite, showing the formation of polyaniline in the composite.

Figure 6 shows the TGA curve of polyaniline and PANI-ZnO composite. It can be seen PANI has been decomposed completely before  $600^\circ\text{C}$ . The TGA curve of the PANI-ZnO composite shows the weight loss in the  $400\text{--}650^\circ\text{C}$  range attributed to the degradation of the skeletal PANI chain structures. Comparing both curves, it can be seen that the thermal stability of the PANI-ZnO composite is stronger than that of pure PANI.

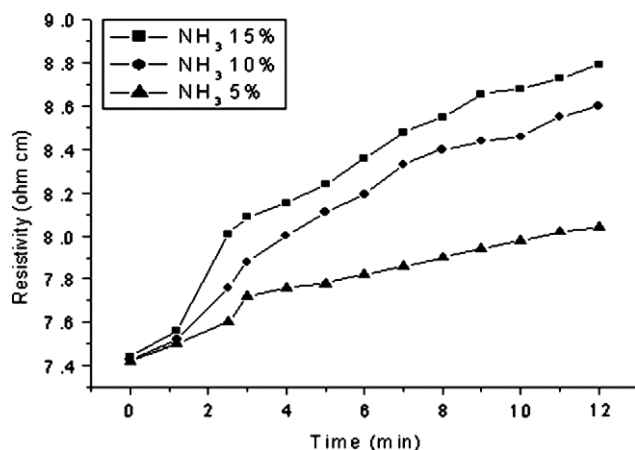
#### Electrical conductivity

The conductivities of PANI-ZnO composite with different amounts of ZnO were measured by four probe method. The results show that in the studied content range of ZnO (1–40%), the conductivity of composite increased obviously as compared with that of PANI. The conductivity of PANI-ZnO composite first increases with the increasing ZnO content, and reaches an optimum value  $1.93\text{ S/cm}$  when ZnO content is about 20%, with the further increase in ZnO content, the conductivity of PANI-ZnO composite was almost stable. This could be explained by the fact that on the one hand, ZnO nanoparticles hinder the carrier transport between different conjugated chains of PANI, and on the other hand the existence of interaction between PANI and ZnO nanoparticles will lead to the reduction of the conjugated lengths in the PANI chains.<sup>28,29</sup>

On the basis of higher electrical conductivity, the 20% ZnO weight content composite was selected for all studies.



**Figure 6** TGA curve of PANI and PANI-ZnO.



**Figure 7** Resistivity response of PANI-ZnO at 5, 10, and 15%.

### Sensitivity

There are some possible interactions, such as chemical bonding, hydrogen bonding and van der-Waals force, between the polyaniline and adsorbed vapor molecule. Generally, conductivity sensors made of polyaniline are based on the reversible reaction of acid/base. For this mechanism, the conductivity response of polyaniline is increased when it is exposed to acid atmosphere, and decreased when it is exposed to base atmosphere.

The surface resistivity of sensing material shows a remarkable change when exposed to different percent of aqueous ammonia as function of time depicted in Figure 7.

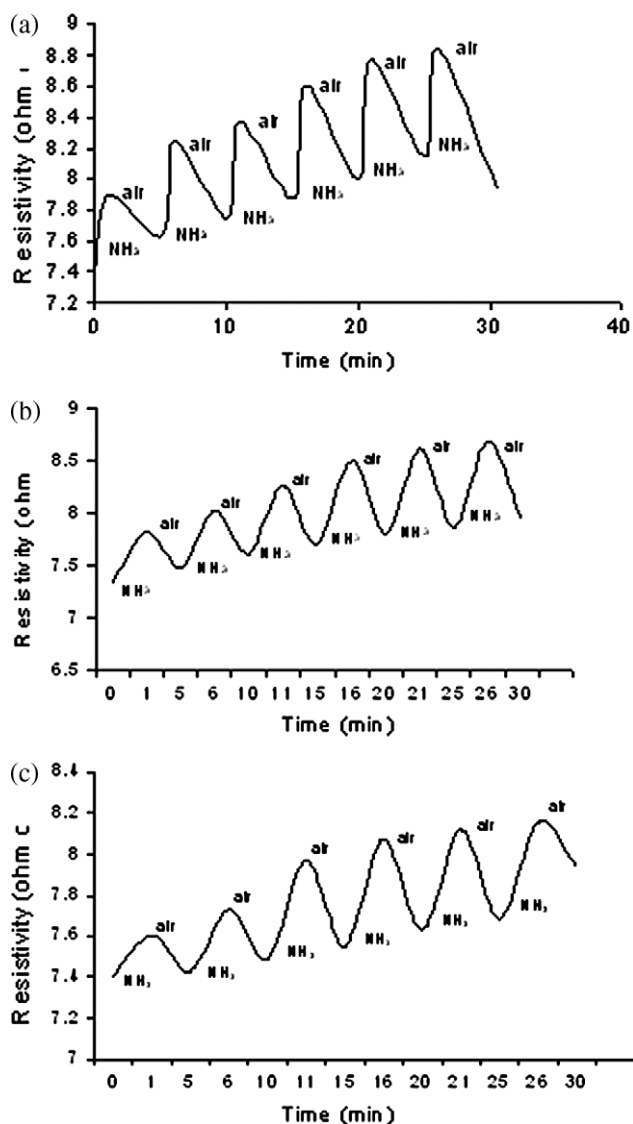
Depending on ammonia concentration, the response time of the sensor to ammonia exposure ranged from 1 to 10 min, while the recover time was about 20 min upon return to dry air. The sensing mechanism is governed by the protonation/deprotonation phenomena. It shows that resistivity of the material increases when it is exposed to increasing percentage 5, 10, and 15% of aqueous ammonia. On high concentration of aqueous ammonia (15%) the sensing material has shown the fast response. The resistivity of composite increases because of the undoping or the reduction of charge carriers by adsorption of ammonia on the surface of composite material. Ammonia gas molecules withdraw protons from N<sup>+</sup>-H sites to form energetically more favorable NH<sub>4</sub><sup>+</sup>. This deprotonation process reduces PANI from the emeraldine salt state to the emeraldine base state, leading to the reduced hole density in the PANI and thus an increased resistivity.<sup>30,31</sup>

When the sensor is purged with dry air, the process is reversed, NH<sub>4</sub><sup>+</sup> decomposes to form NH<sub>3</sub> and a proton, and the initial doping level and resistance recover. The result shows that the adsorption-desorption process on the polyaniline film was highly reversible for ammonia molecules.

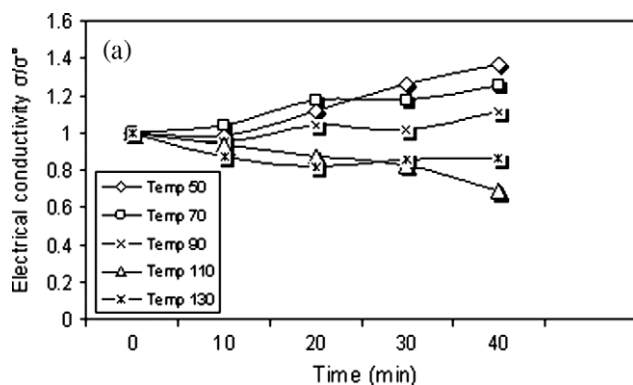
### Repeatability

In these studies, the material was exposed to ammonia vapor (with different concentration) for 1 min and to air for 5 min, a cyclic response of electrical resistivity was observed. The material showed a well defined response which can be discussed as follows:

On exposing the sensing material for 1 min, in presence of 15% aqueous ammonia, the change in the resistivity was observed from 7.41 (initial resistivity) to 7.82 Ω cm (due to the deprotonation of polyaniline by adsorption of NH<sub>3</sub>) and keeping it for 5 min in air, the resistivity fall back to 7.73 Ω cm. After the sensor is purged with air, the resistivity is observed to recover slowly due to desorption of ammonia gas molecules from the surface of sensing material. Now the material again exposed to 15% ammonia vapor for one min, the resistivity was



**Figure 8** Cyclic response of PANI-ZnO nano composite (a) 15% NH<sub>3</sub> (b) 10% NH<sub>3</sub> (c) 5% NH<sub>3</sub>.



**Figure 9** Isothermal stability of PANI-ZnO nano-composite.

observed  $8.17 \Omega \text{ cm}$  and again it was exposed for 5 min in air the resistivity back  $7.83 \Omega \text{ cm}$ . On repeating the experiment, the initial resistivity could not come back. The cyclic tests present similar responses more than five times. Similar comparative studies of cyclic response behavior of the sensing material were performed for 10% and 5% ammonia vapor and air with respect to time Figure 8 shows the cyclic response of electrical resistivity with respect to time at room temperature. It was found that the change in resistivity was somewhat less for 10% and 5% as compared to 15% aqueous ammonia concentration.

#### Stability in terms of DC electrical conductivity retention

As reported earlier the conductivity of the composite material depends on time and temperature.<sup>32–34</sup> The isothermal stability of the composite material in term of DC electrical conductivity retention was carried out at 50, 70, 90, 110, and 130°C in an air oven. The electrical conductivity measurements were done five times every after an interval of 10 min at a particular temperature. The electrical conductivity measured with respect to time is presented in Figure 9. It was observed that all the composite materials followed Arrhenius equation for the temperature dependence of the electrical conductivity from 50 to 90°C and after that a deviation in electrical conductivity was observed, it may be due to the loss of dopant and degradation of materials. The stability of PAN-ZnO composite in terms of DC electrical conductivity retention was found to be fairly good as studied by isothermal technique. The polyaniline-zinc oxide composite can be used in electrical and electronic applications below 90°C under ambient conditions.

## CONCLUSION

In conclusion, ZnO nano particles were prepared using simple chemical approach. A good yield of ZnO nearly hexagonal crystal structure at relatively high purity and low cost was obtained by this method. PANI-ZnO nanocomposite has been synthesized by *in situ* chemical oxidative polymerization method. The materials were well characterized by XRD, TEM, FTIR and SEM. The PANI-ZnO nanocomposite could be a good material for  $\text{NH}_3$  detection at room temperature. Electrical conductivity, Sensitivity and reversibility are very important parameters for evaluating sensor properties. We can notice that the present sensor exhibits very attractive performances. The incorporated ZnO nano particles played a significant role by enhancement in the porosity and the surface activities of the composite material. Thermal stability in term of DC electrical conductivity retention is fairly good as studied by several experimental techniques. Most of the formulations of the composites so prepared are suitable for use in electrical and electronic applications below 90°C under ambient conditions.

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