SYNTHESIS OF POLYANILINE–ZINC OXIDE NANOCOMPOSITE: ELECTRICAL AND AMMONIA VAPOR SENSING PROPERTIES

3.1. 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 thus find many potential applications in various areas [1]. ZnO is a typical n–type semiconductor as well as an important electronic and photonic material with many potential applications such as in field effect transistors, ultra–sensitive nano–sized gas sensors, nanoresonators, nanocantilevers, UV detector, piezoelectronic materials, catalysts, hydrogen storage materials, chemical sensors, biosensors [2–12], etc. Polyaniline is one of the typical conducting polymers which is usually considered as p–type material used in lightweight battery electrode, electromagnetic shielding device, anticorrosion coatings, and sensors [13,14]. In the recent past the conducting polymer–based nanocomposite have drawn attention in their application as gas sensing material [15–22]. Therefore, PANI–ZnO nanocomposites have been most intensively studied among various composites, as 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 increase in human awareness of environmental problems in industrial gas, the requirement of detecting these gases has greatly increased. Nanocomposite based sensors have been demonstrated for the detection of NH₃ under ambient conditions [23].

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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, X-ray diffraction, fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric analysis and the conductivity measurement was done by four probe. The isothermal stability of the composite material in terms of DC electrical conductivity retention at 50 °C, 70 °C, 90 °C, 110 °C and 130 °C was carried out in an air oven at an interval of 10 min in the accelerated ageing experiments.

3.2. EXPERIMENTAL

3.2.1. Chemicals and Reagents
Aniline (Qualigens) was distilled twice just before use. Ammonium persulphate (C.D.H.) was used as received. Ethanol (Riedel-deHaen), Methanol (Qualigens), Zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O) (99.5%), Toluene (Qualigens), Ethylene glycol CH$_2$OHCH$_2$OH, 2-Propyl alcohol (CH$_3$)$_2$CHOH, Glycerol CH$_2$OCHOHCH$_2$OH and all other chemicals used were of A.R. grade.

3.2.2. Synthesis of Zinc Oxide Nano Particles
Slightly modified form of sol–gel method reported earlier [24] was used to synthesized zinc oxide. 100g 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-Propyl alcohol. On adding few drops of water, the solution converted into a gel of zinc acetate. Triethylamine (C$_3$H$_7$)$_3$N was added to hydrolyze zinc acetate and the resulting solution was placed in an oven at a temperature of 200 °C for 7 hours which turned into a light brown powder. This
powder was heated in a programmable furnace at 700 °C for 8 hours to remove all organic impurities. Finally white pure zinc oxide powder was obtained.

3.2.3. Synthesis of Polyaniline–zinc oxide Composite

PANI–ZnO nanocomposite was synthesized by following steps: 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 molar ammonium persulphate was mixed with above solution with vigorous magnetic agitation at 5 °C for 2 hours. 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 in order 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 pestle mortar. The fine powder of the composite was pressed in pellets form using a hydraulic pressure machine.

![Diagram of the formation of PANI–ZnO nanocomposite](image)

Fig 3.1. Schematic diagram of the formation of PANI–ZnO nanocomposite.
3.2.4. Characterization

The FT-IR spectra of zinc oxide and polyaniline–zinc oxide composites were recorded by a Perkin Elmer 1725 instrument. Transmission electron microscopy was carried out using a Philips EM-400 Microscope, a drop of sample was prepared in ethanol and placed on an ultra thin carbon coated copper grid. XRD data were recorded by Bruker D8 diffractometer with Cu Kα radiation at 1.540 Å in the range of 20° ≤ 2θ ≤ 80° at 40 keV). A LEO 435–VF scanning electron microscopy was used to obtain the micrograph of the samples. The thermo–gravimetric analysis were performed on the selected samples of composites using a Perkin Elmer (Pyris Dimond) instrument, heating the materials from ~25 °C to 600 °C at the rate of 10 °C min⁻¹ in nitrogen atmosphere with the flow rate of 30 mL min⁻¹.

3.2.5. Sensor Testing Apparatus and Measurements

The sensing material (PANI–ZnO) were dried in air for 30 minutes and then placed in an oven at 80 °C for 24 hours 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 Fig. 3.2. The vapor sensitivities were recorded by their electrical responses. The distance between the sensing material and solvent was kept 3–4 cm at the time of exposure to different concentration of aqueous ammonia on the sensing material at room temperature. The electrical sensitivities were measured by using a four–in–line probe technique.

The initial resistivity of sensing material was allowed to stabilize prior to 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.
Fig 3.2. Laboratory made set-up of sensitivity testing apparatus
3.3. RESULTS AND DISCUSSION

3.3.1. Characterization

In Fig. 3.3 all the peaks were well indexed to hexagonal phase ZnO as reported in JCPDS card No. 36-1451 [25,26]. The particle size of ZnO was calculated according to Scherer's equation estimated from the line width of the (101) XRD peak.

\[ D = \frac{0.89 \lambda}{\beta \cos \theta} \]  

(1)

where \( \lambda \) is the X-ray wavelength, \( \beta \) is the half-height width of the XRD peak, and \( \theta \) is the Bragg's angle. According to the \( \beta \) values of the ZnO (101) peak as calculated by eq. (1), the ZnO particle size was about 22.70 nm. XRD pattern of PANI-ZnO in Fig 3.4 has shown semicrystalline structure and the size of the composite was found to be 34.17 nm according to the highest intensity 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. 3.5), where nearly hexagonal particles of ZnO (Fig. 3.5c) are wrapped with amorphous polyaniline (Fig. 3.5a) resulting in the formation of PANI-ZnO composite (Fig. 3.5b). 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. 3.5a) of ZnO. However in the TEM image of PANI-ZnO (Fig. 3.5b), the ZnO particles is seemed to be 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.
Fig 3.3. XRD pattern on ZnO nano particle

Fig 3.4. XRD pattern of PANI–ZnO nano composite
Fig 3.5. SEM images of polyaniline (a), PANI–ZnO (b) and ZnO (c)
Fig 3.6. TEM images of (a) ZnO nano particles and (b) PANI-ZnO
In FTIR spectra (Fig 3.7a) a peak observed at 512 cm$^{-1}$ is assigned to Zn–O of ZnO [27] which confirms the formation of ZnO. The hydrogen bonding between the imine group of PANI and ZnO nano particle has been confirmed from the presence of band at 1148 cm$^{-1}$ in the FTIR spectra of the nanocomposite (Fig 3.7b). The characteristic peaks of emeraldine salt form of PANI at 1562 cm$^{-1}$ (C=C stretching mode of the quinoid rings), 1479 cm$^{-1}$ (C=C stretching mode of benzenoid rings), 1263 cm$^{-1}$ (C–N stretching mode) and 1124 cm$^{-1}$ (N=Q=N, where Q represents the quionoid ring) appear in the FTIR spectrum of PANI–ZnO composite (Fig. 3.7b), showing the presence of polyaniline in the composite.

Fig 3.8 shows the TGA curve of polyaniline and PANI–ZnO composite. It can be seen that PANI has decomposed completely before 600 °C. The TGA curve of the PANI–ZnO composite (Fig 3.8 a&b) shows the weight loss in the 400–650 °C range attributed to the degradation of the skeletal PANI chain structures. Comparing Fig 3.8a and b, it can be seen that the thermal stability of the PANI–ZnO composite is more than that of pure PANI. This may be due to the formation of hydrogen bond between ZnO nanoparticles and polyaniline chain as suggested by FTIR structure.
Fig 3.7. FTIR spectra of (a) Zno and (b) PANI-ZnO.
Fig 3.8. TGA curve of pure PANI (a) and PANI–ZnO composite (b)
3.3.2. Mechanism of Formation of PANI–ZnO Composite

ZnO nanoparticles, aniline, toluene, ammonium persulphate and water were mixed and exposed to magnetic agitation resulting in the formation of emulsion similar to that of water in oil. The toluene solution of aniline was in the droplets, while the water solution of ammonium persulphate became the continuous phase. The ZnO nanoparticles spontaneously assembled at the surfaces of toluene droplets, forming toluene/ZnO core–shell structures [28]. Aniline in the droplets diffused to the toluene/water interface and was adsorbed on the surface of the ZnO nanoparticles, later this adsorbed aniline was polymerized by ammonium persulphate to yield PANI. This resulted in PANI enwrapping the ZnO nanoparticles, forming PANI–ZnO composites.

3.3.3. 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 was 10–40% as shown in Table 3.1, 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 to an optimum value of 1.93 S/cm when ZnO content was about 20%, with the further increase in ZnO content, the conductivity of PANI–ZnO composite remained almost stable. This could be explained by the fact that on one hand, ZnO nano particles hindered the carrier transport between different conjugated chains of PANI while on the other hand the existence of interaction between PANI and ZnO nano particles lead to the reduction of the conjugated lengths in the PANI chains [29,30]. On the basis of higher electrical conductivity PANI–ZnO (20%) nanocomposite was selected for further studies.
Table 3.1. Preparation details of polyaniline–zinc oxide composite.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Amount of ZnO (%)</th>
<th>Amount of aniline (mL)</th>
<th>Electrical conductivity σ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI–ZnO</td>
<td>10%</td>
<td>1</td>
<td>1.08</td>
</tr>
<tr>
<td>PANI–ZnO</td>
<td>15%</td>
<td>1</td>
<td>1.31</td>
</tr>
<tr>
<td>PANI–ZnO</td>
<td>20%</td>
<td>1</td>
<td>1.93</td>
</tr>
<tr>
<td>PANI–ZnO</td>
<td>25%</td>
<td>1</td>
<td>1.94</td>
</tr>
<tr>
<td>PANI–ZnO</td>
<td>30%</td>
<td>1</td>
<td>1.94</td>
</tr>
<tr>
<td>PANI–ZnO</td>
<td>40%</td>
<td>1</td>
<td>1.95</td>
</tr>
</tbody>
</table>
3.3.4. Sensitivity

It is well known that zinc oxide is an n-type semiconductor, while PANI is normally a p-type semiconductor. This is due to the fact that during the polymerization process of aniline, acids (such as HCl) are used, which acts as dopant for PANI molecules are usually bonded with the central N atom of aniline (monomer) molecule, like H⁺ –N–Cl⁻ (other bonds on sides of N atom are left here for the sake of clarity). In equilibrium at room temperature, the positive charge of bonded hydrogen shifts on N atom, making the structure look like H–N⁺–Cl⁻ and the negative charge on Cl⁻ is retained with it and remains localized. The positive charge on nitrogen becomes mobile charge in PANI matrix, via its other bonds, making the PANI as a p-type semiconductor [31].

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 up of polyaniline are based on the reversible reaction of acid and base. It is clear that 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 the sensing material shows a remarkable change when exposed to different percent of aqueous ammonia as a function of time as depicted in Fig. 3.9. Depending on ammonia concentration, the response time of the sensor to ammonia exposure ranged from 1 to 10 min, while the recovery time was about 20 min when returned to air. It shows that resistivity of the material increases when it is exposed to increasing percentage i.e. 5%, 10% and 15% of aqueous ammonia. On exposure to lower concentration of aqueous ammonia (5% and 10%), the material attains a lower change in resistivity values than 15%.

When protonic acid (HCl) doped PANI–ZnO nanocomposite is exposed to aqueous ammonia solution, it is the dopant which interacts with NH⁺ ions through the formation of weak charge complex structure [Cl⁻ NH₄⁺]. Under this condition the mobility of the dopant ion is restricted causing an increase in the resistivity [32,33]. Hence the charge complex is neutral in nature and attains a time dependent stability...
with different concentration of aqueous ammonia. This is the reason when composite is kept in air, the resistivity value regained was higher than the original value. This weak charge complex structure, dissociates after certain specific period of time when kept at room temperature in air. The proposed structure of PANI-ZnO composite can be shown according to scheme 1 which is given below.

![Scheme 1](image)

The result shows that the change in resistivity values after and before exposing to aqueous ammonia. Moreover, the sensing ability of the PANI-ZnO composite sensor is significantly improved in the presence of ZnO, which could be attributed to the higher vapors permeability of the composite, due to the larger surface area provided by ZnO present in the composite near the imine nitrogens. However, for blank PANI the response value increases linearly up to 15% and saturates thereafter or slightly decreases for larger ammonia concentrations. In case of PANI-ZnO nanocomposite, a smooth increase of response was seen up to 15% and then it remains constant thereafter. It can be seen that at 15% concentration of aqueous ammonia vapor, both for pure PANI and PANI-ZnO composite had highest response as depicted in Fig 3.10.
Fig 3.9. Resistivity response of PANI-ZnO at 15%, 10% and 5%
Fig 3.10. Sensitivity versus concentration plot for PANI and PANI–ZnO composite.
3.3.5. Repeatability
We also studied the response and recovery time of the composite with respect to ammonia vapor exposure. The response time, and the recovery time are defined as the time required for sensor resistivity to reach its saturation value from the starting value on gas exposure and on removal of the gas, respectively. In case of pure PANI, the response time was relatively fast but as usual the recovery times were relatively larger than that of PANI–ZnO nanocomposite. It indicates that the larger recovery times are due to the slower out diffusion rate (concentration dependent) of the gas. It may be seen that the PANI–ZnO nanocomposites showed faster recovery time as compared to the pure PANI. The typical repeating response of the PANI–ZnO nanocomposite with respect to time, for repeated exposure and removal of ammonia vapor is discussed as follows:

On exposing the sensing material for 1 min, in the presence of 15% aqueous ammonia, the change in the resistivity was observed from 7.41 (initial resistivity) to 7.82 Ωcm (due to the deprotonation of polyaniline by adsorption of NH₃) and later when it was kept in air for 5 min, the resistivity falls back to 7.73 Ωcm. When the sensor was purged with air, the resistivity was observed to recover slowly due to desorption of ammonia gas molecules from the surface of sensing material. When the material was again exposed to 15% ammonia vapor for 1 min, the resistivity observed was 8.17 Ωcm and on returning to air for 5 min the resistivity came back to 7.83 Ωcm. On repeating the experiment, the initial resistivity could not come back. The cyclic tests showed similar responses more than five times. Similar comparative studies of cyclic response behavior of the sensing material were performed for 5% and 10% ammonia vapor and air with respect to time; Fig 3.11 shows the repeating response of electrical resistivity with respect to time at room temperature. It was found that the change in resistivity response was somewhat less for 5% and 10% as compared to 15% aqueous ammonia concentration.
(a) 

Resistivity (ohm cm) 

Time (min) 

(b) 

Resistivity (ohm cm) 

Time (min) 

Continued...
Fig 3.11. Repeating response of PANI-ZnO nano composite (a) 15% NH₃ (b) 10%NH₃ and (c) 5% NH₃
3.3.6. Stability in Terms of DC Electrical Conductivity Retention

As reported earlier the conductivity of the composite material depends on time and temperature [33–35]. The isothermal stability of the composite material in terms of DC electrical conductivity retention was carried out at 50 °C, 70 °C, 90 °C, 110 °C and 130 °C in an air oven. The electrical conductivity measurements were done five times every after an interval of 10 minutes at a particular temperature. The electrical conductivity was measured with respect to time and is presented in Fig 3.12. 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, which may be due to the loss of dopant and degradation of materials. The stability of PANI–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.
Fig 3.12. Isothermal stability of PANI–ZnO nanocomposite
3.4. 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 NH₃ detection at room temperature. We can notice that the present sensor exhibits very attractive performances such as good electrical conductivity, sensisitivity and reversibility which are very important parameters for evaluating sensor properties. The incorporated ZnO nano particles played a significant role by enhancing the porosity and the surface activities of the composite material. Thermal stability in terms of DC electrical conductivity retention is fairly good as studied by several experimental techniques. Most of the formulations of the composites prepared so far are suitable for use in electrical and electronic applications below 90 °C under ambient conditions.
3.5. REFERENCES


