Chemical vapour sensing properties of electrospun nanofibers of polyaniline/ ZnO nanocomposites

Subhash B. Kondawar[*], **Pallavi T. Patil, Shikha P. Agrawal**

Department of Physics, Polymer Nanotech Laboratory, RTM Nagpur University, Nagpur 440033, India

[*]Corresponding author. Tel: (+91) 712-2042086; E-mail: sbkondawar@yahoo.co.in

ABSTRACT

Zinc oxide (ZnO) nanoparticles were synthesized by simple route of sol-gel method and nanofibers of polyaniline (PANI) and PANI/ZnO nanocomposites prepared using the electrospinning technique. Electrospun nanofibers of PANI and PANI/ZnO nanocomposites were collected on aluminum substrate for characterization and on Cu-interdigited electrodes to prepare chemiresistor sensor. Electrospun nanofibers of PANI and PANI/ZnO nanocomposites have been characterized by UV-Visible (UV-Vis), Fourier transform infrared (FTIR), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). UV-Visible spectra of nanofibers of PANI/ZnO nanocomposites show hypsochromic shift as that of PANI and some interaction due to ZnO in PANI matrix. The observed changes in the FTIR spectra of the fibers of PANI/ZnO nanocomposites are asssociated with the formation of H-bonding between ZnO and the N-H group present in the PANI chains. X-ray diffraction patterns exhibits hexagonal wurtzite structure of ZnO and broad amorphous peaks of PANI. Heterogeneous structures with fibrous characteristics of diameter less than 300nm of PANI/ZnO nanocomposites are identified in the SEM images. The electrical properties were characterized by I-V characteristic measurements. The changes in resistance of the chemiresistor sensor were utilized for detection of HCl and NH_3 chemical vapour at room temperature. The resistance of the sensors was found to be decreased when they were exposed to HCl vapours whereas the resistance of the sensors was found to be increased when they were exposed to NH_3 vapours. It was observed that PANI/ZnO nanocomposite sensor shows a high response and sensitivity with good repeatability as compared to that of pure PANI. Sensitivity result shows that PANI/ZnO nanocomposite is highly sensitive to chemical vapours even at room temperature and at very low concentration. Copyright © 2014 VBRI press.

Keywords: Polyaniline/ZnO nanocomposites; electrospun nanofibers; chemiresister; chemical sensor.

Subhash B. Kondawar is currently working as Professor in Department of Physics, Rashtrasant Tukadoji Maharaj, Nagpur University, Nagpur, India. He did Ph.D. from Department of Physics, Institute of Science, Nagpur, India. His main research activities include the synthesis of advanced materials at nanoscale and conducting polymer nanocomposites. His current research is focused on fabrication of electrospun nanofibers of conducting polymers and nanocomposites for gas sensors, biosensors and supercapacitors. He has published more than 35 research articles in journals of international repute. He has completed three major research projects funded by UGC, New Delhi, India.

Pallavi T. Patil is a Research Scholar registered for Ph.D. under the guidance of Dr. Subhash B. Kondawar, Department of Physics, Polymer Nanotech Laboratory, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, India. She has obtained her Master's degree in Physics from R. T. M. Nagpur University, Nagpur,

India. Her research interest includes the development of chemiresistors based on electrospun nanofibers of conducting polymer nanocomposites for gas sensing applications.

Shikha P. Agrawal is working as Project Fellow under Major Research Project funded by UGC, New Delhi, in Polymer Nanotech Laboratory, Department of Physics, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, India. She has obtained her Master's degree in Physics from R.T.M. Nagpur University, Nagpur, India. She has registered for Ph.D. under the guidance of Dr. S. B. Kondawar in Department of Physics, R.T.M. Nagpur University, Nagpur. Her main research interest is fabrication and characterizations of electrospun nanofibers of conducting polymer nanocomposites.

Introduction

The detection of ammonia (NH_3) in air is of great significance for environmental monitoring and process control because of the high toxicity of this gas. The measurement of the NH_3 concentration is also important from safety and health point of view in working places. High concentrations of ammonia could be a threat to the human health. Immediate and severe irritation of the nose and throat occurs at ammonia concentrations as low as 500 ppm. Exposure to high ammonia concentrations (1000 ppm or more) can cause pulmonary edema (i.e., accumulation of fluid in the lungs). In all cases, the measurement of the ammonia concentration is vital for further actions [1]. One-dimensional (1D) nanostructured materials such as nanowires, nanorods, nanowhiskers, nanotubes and nanofibers have been intensively studied worldwide owing to their potential technological applications in many areas including mechanics, nano-electronics, photonics, and sensing. Conducting polymers such as polyaniline, polypyrrole, and polythiophene have been widely investigated as effective materials for chemical sensors. Conducting polymers are new class of sensing materials, which can be prepared by a simple chemical oxidative polymerization method. They exhibit reversible pH-induced spectroscopic and gas-induced conductivity changes. They also provide a suitable structure for immobilization of ligands, enzymes and antibodies [2]. Among the conducting polymers, polyaniline (PANI) is frequently used because of its ease of synthesis, environmental stability and intrinsic redox reaction. There is a tremendous approach for the enhancement of the mechanical strength and characteristics of sensors by combining the organic materials with inorganic counterparts to form composites.

To obtain the materials with synergistic or complementary behaviour, various composites of polyaniline with inorganic nanoparticles have been synthesized in recent years for the development of novel chemical and biological sensors [3-8]. Semiconducting nanomaterials (i.e. ZnO, SnO_2, TiO_2, WO_3, In_2O_3 etc.) have shown excellent properties from fundamental research to future devices. Especially, ZnO provide a direct band gap (3.37 eV) and a large excitation binding energy (60 meV), which make ZnO suitable for a wide range of device applications, such as FETs, optoelectronic devices, and sensor devices (chemical, gas, and biosensors) [9]. However, chemical sensors incorporated with ZnO require an elevated temperature for operation. Most recently, ZnO-based nanofibers fabricated by electrospinning have been of great interest due to wide potential applications of nanofibers. ZnO nanofibers based vapour sensors have been demonstrated excellent sensitivity, fast response and recovery; however the often-used higher operation temperature restricts their practical use for detecting gaseous pollutants in the environment [10]. Therefore, it is highly desirable to develop a new sensor platform that can be operated at room temperature. While most studies have focused on the use of polyaniline in the form of thin films, recent advances in the fabrication of nanofibers have opened new methods to construct low power consumption devices and sensors based on these nanofibers. Apart from large surface to volume ratio, high aspect ratio of nanofibers makes them ideal candidates for use as ultrasensitive chemical sensors with the additional advantage of having a faster response time. However PANI is not as sensitive as metal oxides towards gas species and its poor solubility in organic solvents limits its applications. Addition of ZnO improves its sensitivity towards the gas species due to the synergistic effect. Several methods have been used in the past to obtain polyaniline nanofibers that include the use of a template or without a template, interfacial polymerization and electrospinning. Of the aforementioned techniques, electrospinning is the easiest method of obtaining isolated and relatively long polymer nanofibers. Electrospinning has attracted a lot of interest as a technique that is very simple and inexpensive in the production of micro to nanofibers. It provides a potential way to fabricate infinite, continuous fibers. This led to the idea of fabricating PANI/ZnO nanofibers which can work at room temperature as chemiresistive sensors. To date, there has not been any report on electrospun nanofibers of PANI/ZnO nanocomposites.

Therefore, in this paper we report first time the fabrication of electrospun nanofibers of PANI/ZnO nanocomposites and their sensing properties for chemical vapours. PANI/ZnO nanocomposites were initially synthesized through solution route technique followed by fabrication of nanofibers via electrospinning. The synthesized conductive electrospun nanofibers of PANI/ZnO nanocomposites were characterized by FTIR, SEM, XRD, and UV-VIS. The response of the prepared nanofibers of PANI/ZnO nanocomposites was tested for NH_3 and HCl vapours using a simple laboratory built up sensing apparatus at room temperature and systematically compared to other conducting polymer nanocomposites.

Experimental

Materials

Aniline (99.5%) and zinc acetate (99%) were procured from E. Merck. Acetone (95%) and chloroform (90%) were procured from Fisher Scientific. N-Methyl 2-pyrrolidone (98.5%) from LOBA Chemie and Ammonium persulphate (98%), starch (98.5%), liquor ammonia (99%) and D-Camphor-10-Sulphonic acid ($C_{10}H_{16}O_4S$) were purchased from Hi-media and used as received. Aniline monomer was distilled under reduced pressure prior to use. All chemicals were of analytical grade and solutions were prepared with de-ionised water.

Characterizations

Bruker Alpha spectrophotometer was used for FTIR spectra. X'Pert Powder PANalytical X-ray diffractometer was used for XRD pattern. JEOL Model JFM- 6390LV was used for scanning electron microscopy images. Fibers were drawn by ESPIN-NANO machine purchased from PECO Chennai-India. The gas sensitive characteristics of the composites were investigated by recording their electrical responses when exposed to different concentration of aqueous ammonia and HCl vapours at room temperature using laboratory built up resistivity unit in a glass chamber. The Cu-interdigited electrode coated by sensing material PANI/ZnO nanofibers, soldered at two points was placed into the glass chamber and another two terminals of copper wire were attached to the digital multimeter to record the resistance of the material at different concentration of ammonia and HCl vapours. The temperature dependence electrical conductivity was studied by using four probe method to record the current-voltage using constant current source and digital micro-voltmeter.

Synthesis of ZnO nanoparticles

Zinc acetate (0.1 M) was added in starch solution prepared by adding starch (2.5g) in de-ionized 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 overnight and supernatant solution was then discarded carefully. The obtained nanoparticles were washed many times using de-ionized water and then dried at 80°C for overnight. During drying complete conversion of $Zn(OH)_2$ into ZnO takes place [11]. Now this powder was heated in a programmable furnace at 600°C for 4 h to remove all organic impurities. Finally white pure zinc oxide powder was obtained [12].

Synthesis of PANI/ZnO nanocomposites

In a typical polymerization reaction, PANI/ZnO nanocomposite was synthesized by an in-situ polymerization. To oxidize 0.2M aniline with 0.25M ammonium persulphate in acidic aqueous medium, aniline and as-synthesized ZnO nanoparticles (w/w 10%) were dissolved in 50ml solution of 1.0M HCl and the solution was sonicated for half an hour. The aqueous solution of ammonium persulphate in 1.0M HCl was added drop wise in above solution and the reaction was constantly stirred for 2 hours. During the polymerization process, the colour changed from colourless to light blue and then to dark green. The solution was left at rest for over night. Next day, the precipitate was collected by filtration. PANI/ZnO in emeraldine salt form powder was dried in vacuum oven at 80°C [13]. A similar procedure

followed for the synthesis of pure PANI without the use of ZnO nanoparticles. Normally PANI and its composite in emeraldine salt (ES) form are not soluble directly in any organic solvent and it is difficult to process it in conducting form. Therefore, firstly PANI (ES) and its composites were converted into emeraldine base (EB) form and then protonated with D-Camphor-10-Sulphonic acid (CSA) to make it conducting processable solution for drawing nanofibers [14]. In the typical process, as-synthesized PANI and PANI/ZnO nanocomposite were separately used to prepare PANI (EB) and PANI/ZnO (EB) form. For that doped PANI and PANI/ZnO i.e. emeraldine salt (ES) precipitate was dissolved separately in 35 ml of liquor ammonia solution, with stirring for 24h at room temperature and filtered. The wet powder was washed thoroughly with de-ionized water and dried in vacuum oven at 50°C to obtain emeraldine base, denoted as dedoped PANI and dedoped PANI/ZnO hereafter [15]. Then 1.6 g of PANI (EB) and the PANI/ZnO (EB) composite powders were separately mixed with D-Camphor-10-Sulphonic acid (CSA) and chloroform by grinding in a smooth agate mortar for 1h. Then soluble and conducting PANI and PANI/ZnO nanocomposites were obtained for electrospinning. 7% PMMA in N-Methyl 2-pyrrolidone stirred for 30 min at 60°C then 10% of conducting PANI and PANI/ZnO mixtures separately added in PMMA/NMP solution and stirred for 24 hours [16]. The true solutions of PANI and PANI/ZnO were separately filled in syringe for electrospinning process to obtain their nanofibers.
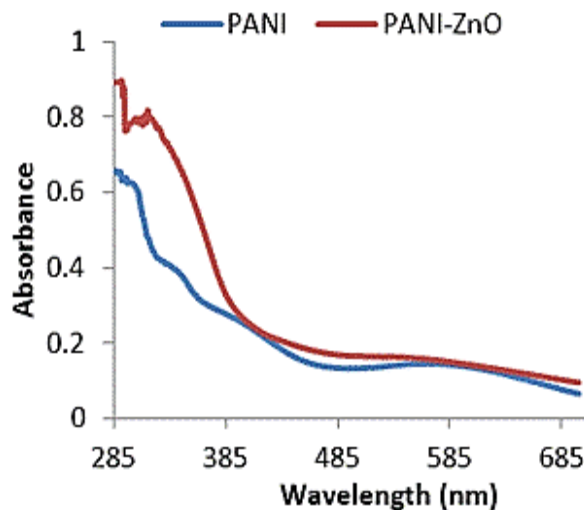

Fig. 1. UV-Vis Spectra of PANI and PANI-ZnO nanofibers.

Results and discussion

UV–visible spectra of nanofibers of pure PANI and PANI/ZnO nanocomposites are shown in **Fig. 1**.

Polyaniline strongly absorbs visible light and shows two distinctive peaks appear at about 312nm and 609nm, which are attributed to the π-π* of benzenoid ring and π-polaron transition shows the polaronic band which is due to the inter-ring charge transfer associated with excitation from benzenoid to quinoid moieties, respectively. Moreover, the peak at 609 nm is shifted from 609 nm to 613nm indicates that the insertion of ZnO nanoparticles, which has the effect on the doping of conducting polyaniline. Additionally, the peak of PANI around 312 nm is based on π-π* transition of the benzenoid ring where the peak of PANI-ZnO nanocomposite was arround 323nm, which is red shifted compared with the absorption peaks of pure PANI. This may be because of interactions between PANI chains and ZnO nanoparticles which cause easy charge transfer from PANI to ZnO via hydrogen bonding [17].
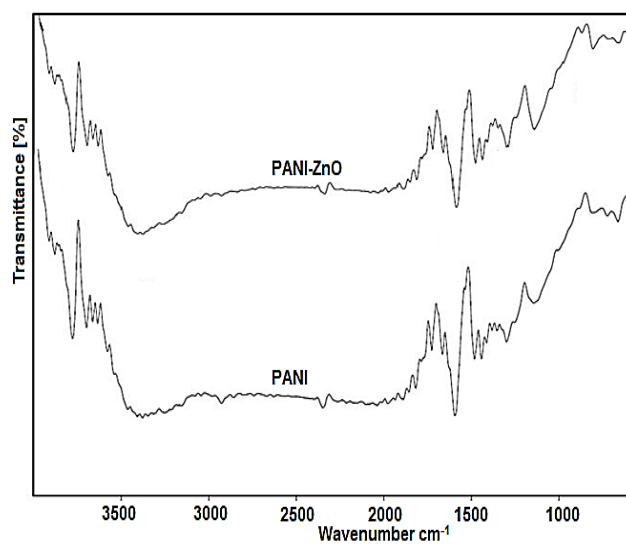
Fig. 2. FTIR spectra of PANI and PANI-ZnO nanofibers.
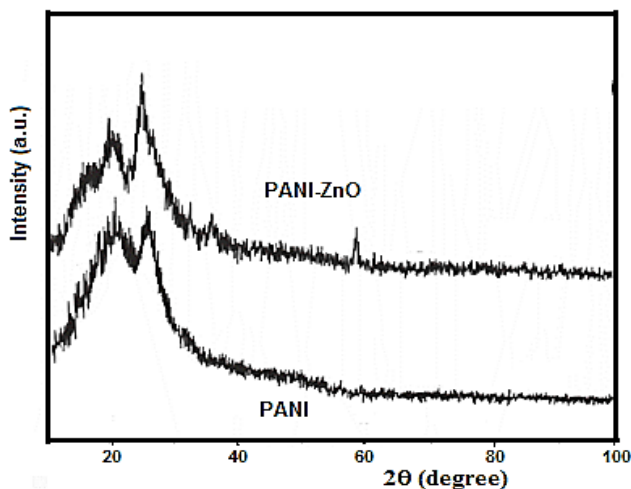
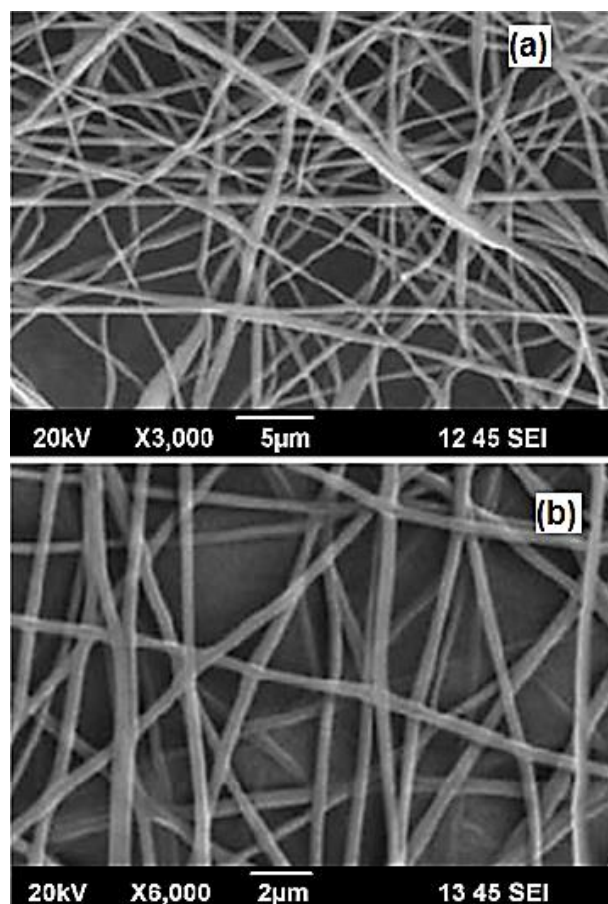**Fig. 3.** XRD pattern of PANI and PANI-ZnO nanofibers.

Fig. 4. SEM images of (a) PANI and (b) PANI/ZnO nanofibers.

FTIR spectra of PANI and PANI–ZnO nanofibers are shown in **Fig. 2.** The characteristic peaks of emeraldine salt form of PANI at 1592 cm^{-1} (C=C stretching mode of the quinoid rings), 1481cm^{-1} - 1440.56 cm^{-1} (C–C stretch in benzenoid ring and C–H mixed vibrations), 1411.74 cm^{-1} (C–C stretch in quinoide, C–H bending in benzenoid ring), 1297.38 cm^{-1} (C– N stretching, C–H bending) and 1141.53 cm^{-1} (S=O bonding for camphor sulfonic acid), 808.78cm^{-1} (C–H out of plane bonding in benzenoid ring) and 661.10 cm^{-1} - 720.92 cm^{-1} (C–C, C–H bonding mode of aromatic ring) appear in the FTIR spectrum of PANI-ZnO composite, indicating the formation of PANI in the composites. The peaks in the range 3377.92 cm^{-1} corresponds to N-H band stretching vibration. Comparing to the corresponding peaks of pure PANI, the peaks of PANI/ZnO shifted towards lower wave number. This shifting of peaks may be due to the action of hydrogen bonding between the hydroxyl groups on the surface of ZnO nanoparticles and the amine groups in the PANI molecular chains. Such interaction between PANI and ZnO nanoparticles is also observed by Ahmed et al **[3]**, Mostafaei et al. **[18]** and Patil et al **[19].**

Fig. 3 shows the XRD patterns of PANI/ZnO nanocomposites and pure PANI. The XRD pattern of PANI has a weak broad peak at $2\theta = 25°$, because of its amorphous structure with low crystallinity. The XRD patterns of PANI/ZnO nanocomposite include the characteristic peaks of both PANI and ZnO with the crystalline structure of hexagonal wurtzite, which confirms the formation of nanocomposite with lower crystallinity [20, 7].

The SEM images of PANI and PANI/ZnO nanofibers are shown in **Fig. 4**. From SEM micrographs it is clear that the nanofibers of PANI and PANI-ZnO were successfully synthesized via electrospinning technique. The SEM images show smooth fibers with several millimeters length and an average diameter, in the range of about 200 nm to 300 nm. While comparing images of PANI and PANI/ZnO, fibers of composite are well aligned with more porosity indicates the composite is good for chemical sensing as compared to that of pure PANI.
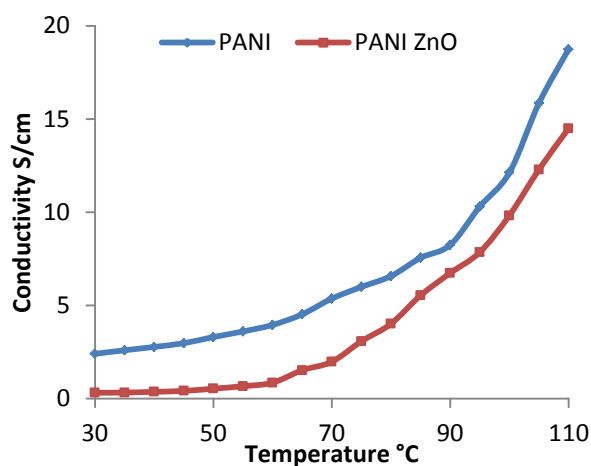

Fig. 5. Electrical conductivity of PANI and PANI-ZnO nanocomposites.

The conductivity of PANI-ZnO composite was measured by four probe method. It has been observed from the **Fig. 5** that conductivity of the composite was found to be increased with the increase in temperature as that of pure PANI, representing the semiconducting nature of the nanocomposites. The increase in the conductivity is due to the increase of efficiency of charge transfer by contribution of polaron and bipolaron bands formed in the widen band gap of the composite between ZnO and polymer chains with increase in temperature. The changes in the conductivity of the composites indicate a change in the doping state of the polymer.

The resistance of the composite nanofibers was determined as a function of exposing time of the ammonia and HCl vapors. The assembly of a simple

laboratory built up resistivity unit in a glass chamber. The Cu-interdigited electrode coated by sensing material soldered at two points was placed inside the glass chamber and attached to high sensitive digital multimeter to record the resistance of the material at different concentration of ammonia and HCl vapours at room temperature.
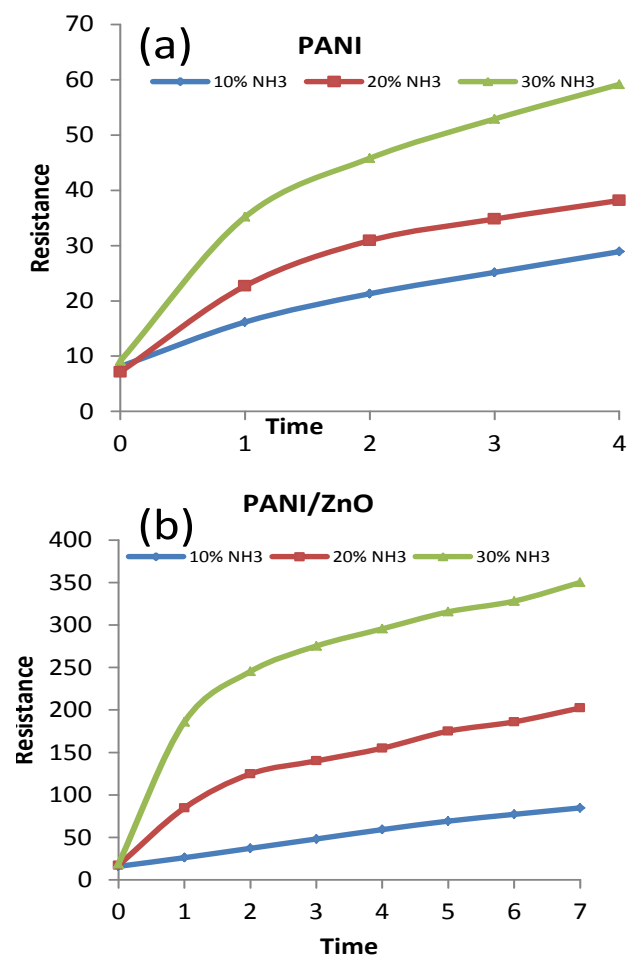
Fig. 6. Response of (a) PANI (b) PANI-ZnO for ammonia.

Ammonia vapour sensing

The initial resistance 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. There are some possible interactions, such as chemical bonding, hydrogen bonding and van der-Waals force, between the polyaniline and adsorbed vapour 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 [21].

The resistance of sensing material shows a remarkable change when exposed to different percent of aqueous ammonia as function of time as shown in **Fig. 6.** Depending on ammonia concentration, the response time of the sensor to ammonia exposure ranged from 1 to 7 min, while the recovery time was about 14 min upon return to dry air. And resistance of the material increased when it is exposed to increasing percentage 10%, 20% and 30% of aqueous ammonia. On high concentration of aqueous ammonia (30%) the sensing material has shown the fast response. The resistance of PANI/ZnO composite increased because of the dedoping or the reduction of charge carriers by adsorption of ammonia on the surface of composite material. Ammonia gas molecules withdraw protons to form energetically more favorable. 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 resistance [22].
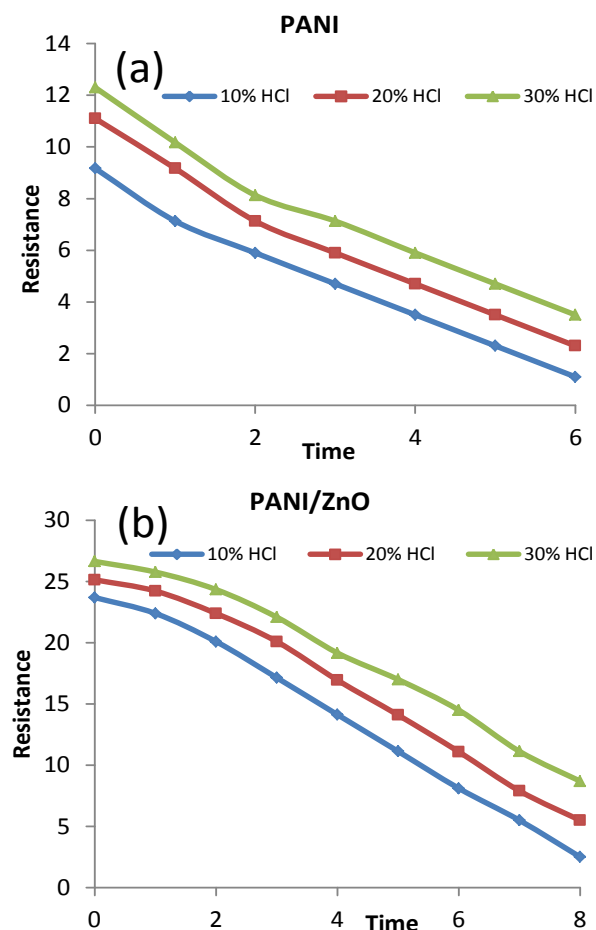

Fig. 7. Response of (a) PANI and (b) PANI-ZnO for HCl vapour.

HCl vapour sensing

After deprotonation process reduced PANI (emeraldine base) having reduced hole density in the PANI and PANI-ZnO with increased resistance when exposed to different percent (10%, 20%, 30%) of aqueous HCl vapours as function of time, shows decrease in resistance [23]. From **Fig. 7**, it is clear that, resistance of the material decreased when it exposed to increasing percentage 10%, 20% and 30% of aqueous HCl vapours.

On high concentration of aqueous HCl vapours (30%) the sensing material has shown the fast response. Cyclic response of resistance for both the samples at 30% concentration of ammonia vapour was observed. In the study of cyclic response, the material was exposed to ammonia and HCl vapour for 1 min and to air for 5 min, both the materials showed a well-defined response alternately to ammonia and air as well as HCl and air. On exposing the sensing material for 1 min, in presence of 30% aqueous ammonia, the change in the resistance was observed from 9.15 ohm (initial resistance) to 59.15 ohm for PANI and from 18.9 ohm (initial resistance) to 350 ohm for PANI/ZnO due to the deprotonation of polyaniline by adsorption of NH_3 and keeping them for 5 min in air, the resistance fall back to 21.10 ohm in case of PANI and 18.9 ohm in case of PANI/ZnO. After the sensors were purged with air, the resistance was observed to recover slowly due to desorption of ammonia gas molecules from the surface of sensing material.

In case of HCl sensing, on exposing the sensing material for 1 min, in presence of 30% aqueous HCl, the change in the resistance was observed from 12.3 ohm (initial resistance) to 3.5 ohm for PANI and from 26.65 ohm (initial resistance) to 8.7 ohm for PANI/ZnO due to the protonation of polyaniline by adsorption of HCl. The sensor sensitivity S = [(Ro - Rv)/Ro] x 100, where Ro represents the resistance in air and Rv the resistance in vapour [24], for both the samples was also determined at 30% ammonia and 30% HCl vapour. Sensitivity result shows that PANI/ZnO is highly sensitive to ammonia vapour as well as to HCl vapour at low response time as compared to PANI. This difference may be due to incorporated ZnO nanoparticles in PANI matrix played a significant role by enhancement in the porosity and the surface activities of PANI/ZnO as compared to that of PANI.

Conclusion

Nanofibers of PANI-ZnO nanocomposites were synthesized successfully via electrospinning technique. SEM micrograph reveals the formation of nanofibers of nanocomposites of diameters around 200nm, with a general uniform thickness along the nanofibers. The XRD, UV-VIS and FTIR study suggests that PANI undergoes interfacial interactions with ZnO crystallites. PANI/ZnO nanofibers showed high response and high

sensitivity with good repeatability for ammonia and HCl vapours as compared to that of pure PANI.

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