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Conductive polyaniline-tin oxide nanocomposites for ammonia sensor

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ABSTRACT

Tin oxide (SnO_2) nanoparticles have been synthesized by simple route of sol-gel method. Polyaniline-tin oxide (PANI/SnO_2) nanocomposite (sample A) was prepared by an in-situ polymerization of aniline in the presence of as-synthesized SnO_2 nanoparticles. Similarly, tin oxide-intercalated polyaniline nanocomposite (sample B) was prepared using tin chloride ($SnCl_4.5H_2O$) as precursor during polymerization of aniline. Morphology and structure of both the nanocomposites have been studied using XRD pattern, FTIR spectra and SEM images which reveals that SnO_2 was uniformly mixed within the PANI matrix. In this paper we report the comparison of polyaniline-tin oxide (PANI/SnO_2) nanocomposites sample A and B for the response to ammonia. A laboratory set up for sensing ammonia has been built up using four probe resistivity unit and the response of the prepared PANI/SnO_2 nanocomposites to ammonia vapour for different concentration (5, 10, and 15%) was tested. PANI/SnO_2 nanocomposites were found to be good materials for NH_3 detection even at room temperature as compared to that of pure SnO_2. By comparing the response of sample A and B to the ammonia vapour, the sample A was found to be more sensitive than sample B due to highly porosity and surface activity of sample A. The results were reproducible and checked by repeating observations. Synthesis route for the preparation of PANI/SnO_2 nanocomposites is an important factor while selecting the materials for ammonia sensing.

Keywords: Conducting polymers; polyaniline; tin oxide; nanocomposites; ammonia sensor.

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Introduction

Gas sensors have a broad range of ever-increasing applications in everyday life, such as industrial production, food processing, environmental monitoring, health care, etc. Among the various types of gas sensors, semiconducting metal oxides have been studied extensively for sensing different gases. The high temperature operation of these sensors makes the lifetime of the sensor shorter and thus requires more power for operation. Other problem associated with metal oxide thin film sensor is their poor performance regarding the sensitivity, stability and selectivity at certain low concentration of the gases in ambient conditions, therefore the sensitivity of pure metal oxide is not satisfactory for detecting a trace amount of gas. Gas sensors based on metal oxides such as SnO_2, ZnO, In_2O_3 etc must be operated at temperature above 200^oC for the catalytic process to take place. Several strategies have been explored to fabricate the sensors with a high efficiency, sensitivity and selectivity at lower operating temperatures [**1-3**]. The organic materials, particularly conducting polymers receive a growing attention in the field of gas sensors. Conducting polymers are good candidates for chemical and biological sensors because the interaction with various analytes may influence the redox and doping states of conducting polymers, leading to a change of resistance, current or electrochemical potential [**4**]. Due to high sensitivity in change of electrical and optical properties when exposed of conducting polymers to different types of gases, is great use of such polymeric materials as sensing elements in sensor applications [**5**].

Recently, Shukla et al. has established crystalline polyaniline film for humidity sensing applications [**6**]. Khushwah et al. reported the performance of nanopolyaniline–fungal enzyme based biosensor for water pollution [**7**]. Tiwari et al. reported the nanofibrous polyaniline thin film prepared by plasma-induced polymerization technique for the detection of NO_2 gas [**8**]. An electrically active redox biomaterial using gum arabic-graft-polyaniline for sensor applications is reported by Tiwari [**9**]**.** The shelf life and electrical conductivity of the copolymer were monitored to evaluate their potential application in the fabrication of semiconductor sensor devices. *I-V* characteristics and acid–base sensitivity of the novel electrically active, water soluble gum acacia-polyaniline (GA–PANI) hybrid material were extensively investigated by Tiwari [**10**]. Looking to sensing applications, conducting polymers are in use as an alternative to metal oxide materials for gas sensing applications. The conducting polymers have improved many aspects of the gas sensors especially in lowering the operating temperature to around room temperature. In addition to this, the ability to incorporate specific binding sites into conducting polymers promises them to improve both selectivity and sensitivity.

The conducting polyaniline (PANI) is one of the promising conducting polymers due to its high conductivity, ease preparation, good environmental stability and large variety of applications [**11**]. However, PANI is not as sensitive as metal oxides towards gas species, and its poor solubility in organic solvents limits its applications, but it is suitable as a matrix for preparation of conducting polymer nanocomposites [**12, 13**]**.** Therefore, there has been increasing interest of the researchers for the preparation of nanocomposites based on PANI. The literature review on conducting polymer nanocomposites show that PANI has been successfully utilized for the preparation of nanocomposites [**14, 15**]. These materials have special properties obtained from both the parent organic and inorganic class of materials. In literature, there are some reports concerning PANI / inorganic nanocomposite sensors [**16-19**]. However, very few researchers have studied the composite SnO_2/PANI for sensor application. Tin oxide (SnO_2) was chosen due to its unique physical and chemical properties such as large energy gap, dielectric constant, and environmental-friendliness and easy to synthesis. There are various methods for the preparation of nanoparticles of SnO_2 out of which sol-gel is the simplest and easiest way [**20-25**]. In particular, SnO_2 films have been investigated as sensors for different gases [**26-28**]. The gas reacts with the negatively charged oxygen adsorbed on the surface of SnO_2 nanoparticles and supplies electrons to the conduction band, leading to a decrease in electric resistance. Therefore the combination of conducting polymer (PANI) and SnO_2 due to their unique properties presents a fascinating structure, which has shown promising application in the field of gas sensor. It has been reported that doping of SnO_2 further improves the gas sensing performance of PANI for various gases [**29, 30**]. With the synergistic effect of PANI and SnO_2, we prepared PANI/SnO_2 nanocomposites by two different approaches and compared the samples for characterizations using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The response of the prepared PANI/SnO_2 nanocomposites was tested for ammonia vapour in different concentration (5, 10, and 15%) using a simple laboratory built up sensing apparatus.

Experimental

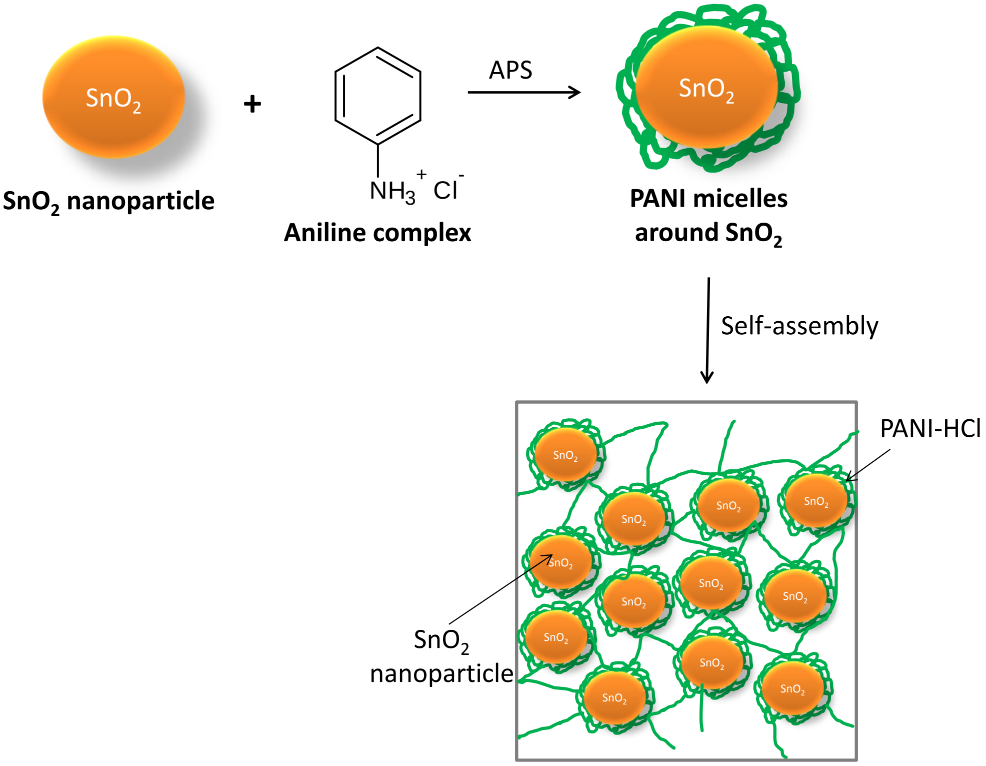
Materials and methods

Aniline monomer was distilled under reduced pressure prior to use. Aniline (99.5%), Tin chloride ($SnCl_4 \cdot 5H_2O$) (99%), hydrogen peroxide (H_2O_2) (99.5%) were procured from E. Merck. Ammonium persulphate (98%), starch (98.5%) and ammonia (99%) were purchased from Hi-media and used as received. All chemicals were of analytical grade and solutions were prepared with double distilled water.

Shimadzu-8101A spectrophotometer was used for FTIR spectra. Philips- PW1710 automatic X-ray diffractometer was used for XRD pattern. SEM- MODEL-LE0440A was used for scanning electron microscopy images. The gas sensitive characteristics of the nanocomposites were investigated by recording their electrical responses when exposed to different concentration of aqueous ammonia vapour at room temperature using laboratory built up four probe resistivity units in a glass chamber. The sensing material was placed into the glass chamber and gently pressed by four-probe to record the current-voltage using constant current source and digital microvoltmeter.

Synthesis of SnO_2 nanoparticles

Sol-gel method was used for the synthesis of SnO_2 nanoparticles [**20**]. In a typical method, 0.1M $SnCl_4.5H_2O$ was added in 1M starch solution and the mixture was stirred for half an hour. Then 0.2M ammonia was added drop wise in the solution under constant stirring. The stirring was continued for further 2 hours and then the solution was allowed to settle for overnight. Supernatant liquid was then discarded carefully and the remaining solution was centrifuged for 10 minute and then filtered. The precipitate of SnO_2 was washed completely using distilled water to remove by-product and the excessive starch those were bound with the nanoparticles. The product was dried in hot air oven at 80°C for overnight.



Scheme 1. Schematic illustration of PANI/SnO_2 nanocomposite formation.

Then powder was sintered at 600°C for 10 hours and nanocrystalline SnO_2 was obtained.

Synthesis of PANI/SnO_2 nanocomposites

PANI/SnO_2 nanocomposite (Sample A) was synthesized by an in-situ polymerization [**31**] of aniline in presence of as-synthesized SnO_2 nanoparticles using ammonium persulphate (APS) as an oxidant in acidic medium. Aniline (0.1M) and APS (0.1M) were dissolved separately in 1M HCl solution and stirred for 1 hour. As-synthesized SnO_2 nanoparticles were suspended separately in 1 M HCl solution and sonicated for 1 hour to reduce aggregation of SnO_2 nanoparticles. 100 ml aniline solution and 10 ml SnO_2 nanoparticles suspension were mixed and further sonicated for 30 min. 100 ml APS solution was then slowly added drop wise to well dispersed suspension mixture with a continuous stirring. After 3 hours, a good degree of polymerization was achieved. The precipitate produced in the reaction was removed by filtration, washed repeatedly with 1 M HCl and dried under vacuum for 24 hours. The composite powder was conductive emeraldine salt (ES) form of PANI/SnO_2 nanocomposite (Sample A). The solution route technique [**13**] was used to synthesize SnO_2/PANI nanocomposite (Sample B). In this technique, formation of nanocomposite proceeds through an inorganic/organic interface reaction. 2g of $SnCl_4.5H_2O$ in 50 ml of double distilled water was stirred for half an hour and its pH was maintained ≤ 4 using 0.1M HCl. 10 ml hydrogen peroxide (H_2O_2) was added in the above solution, which oxidized tin ions to tin oxide. The solution turned into a white colour suspension of SnO_2 and this reaction mixture was mixed with 0.1M aniline and kept below 4°C. 0.1M ammonium persulphate solution was added in the above mixture at room temperature, the colour of the solutions was turned to blue and then to green after few minutes. The precipitate produced in the reaction was removed by filtration, washed repeatedly with 1 M HCl and dried under vacuum for 24 hours. The composite powder was conductive emeraldine salt (ES) form of PANI/SnO_2 nanocomposite (Sample B).

Results and discussion

Schematic diagram for the formation of PANI/SnO_2 nanocomposite is shown in **Scheme 1**, which provides reaction mechanism for formation of such kind of structures. The grain growth of nanoparticles in such composites may be understood through collision between two clusters.

The SEM micrographs of SnO_2/PANI nanocomposites, Sample A and B are shown in **Fig. 1.** A and B, respectively. It can be seen from these figures that the composite particles are highly dispersed with agglomeration. In both the cases, formation of polymer shell around the nanocrystalline particles can be seen in SEM images, assisting the growth and further aggregates formation indicating a diffusion limited cluster aggregation type mechanism as every collision between two clusters results in the formation of a new cluster, the aggregate of the two colliding clusters.

Fig. 2 shows the FTIR spectra of SnO_2/PANI nanocomposites, sample A and B. The peaks in both the samples at wave numbers 1576, 1487, 1447, 1284, 1364, 1158, and 736 cm^{-1} corresponds to most of the characteristic peaks for PANI.

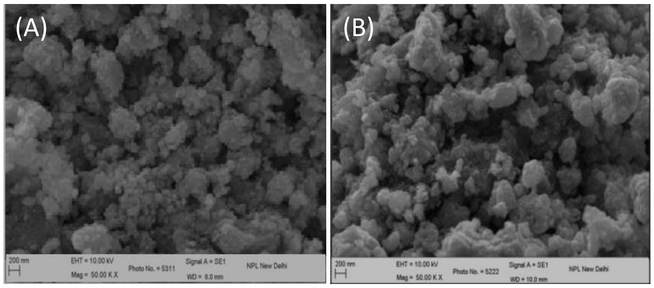


Fig. 1. (A**)** PANI/SnO$_2$ nanocomposite (Sample A) and (B) PANI/SnO$_2$ nanocomposite (Sample B).

The peaks at wave numbers 1576 and 1487 cm^{-1} are attributed to C-N and C-C stretching mode for the quinoid and benzenoid rings; while the peak at wave number 1447 cm^{-1} is attributed to C–C aromatic ring stretching of the benzenoid diamine unit. The peaks at wave numbers 1284 and 1364 cm^{-1} are attributed to C–N stretching; and peak at wave number 1158 cm^{-1} is considered to be due to N Q N stretching. The peak at the wave number 736 cm^{-1} is attributed to C–H out of plane bending vibrations. These peaks are slightly shifted with respect to their normal positions for pure PANI [**7**] due to the presence of tin oxide in the PANI matrix. A strong peak at wave number 613 cm^{-1} in both the samples is due to the antisymmetric Sn-O-Sn mode in tin oxide which confirms the presence of tin oxide in the PANI matrix. Dutta et al [**32**] observed similar results for tin oxide/PANI nanocomposites**.**

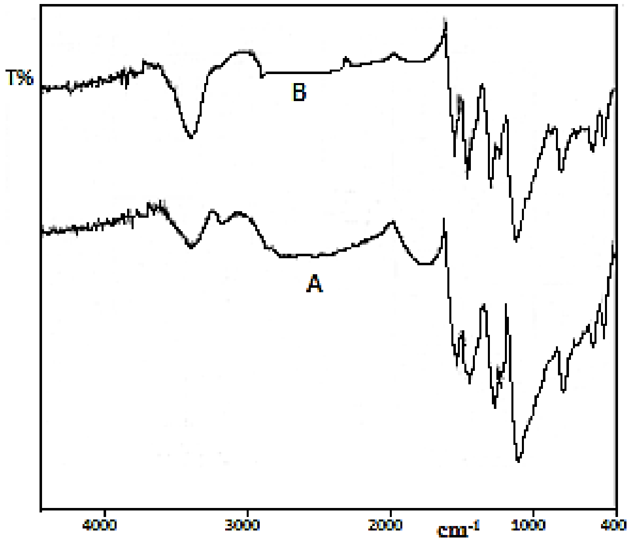


Fig. 2. FTIR spectra of PANI/SnO$_2$ nanocomposites A and B.

The XRD pattern for PANI/SnO$_2$ nanocomposites A and B samples are shown in **Fig. 3**. On comparing the observed XRD peaks for both the samples, it can be seen that the nanocrystalline SnO$_2$ peaks are observed and matched with those peaks along (1 1 0), (1 0 1), (2 0 0), (2 11), (3 1 0) and (3 0 1) having primitive tetragonal structure (*JCPDS DATA CARD 41-1445*). However, these peaks show slightly shifted from their respective standard positions which may be due to PANI matrix. In addition, we observed reduced intensity of the peaks, and relatively larger peak broadening, compared with XRD of pure SnO$_2$. This indicates still smaller average size of tin oxide nanocrystallites in composites, compared to that of pure SnO$_2$. This suggests that tin oxide is present in the PANI matrix, and presence of PANI has influenced the preferred orientation of tin oxide grains in both the composites to some extent. The lattice constant was found to be $a = b =$ 4.741 Å, $c =$ 3.31 Å for sample A, and $a = b =$ 4.732 Å, $c =$ 3.28 Å for sample B. The average crystallite size was found to be nearly 20-25 nm for both the samples.

The electrical resistivity of the nanocomposites was determined as a function of exposing time of the ammonia. The assembly of a simple laboratory built up four probe resistivity unit in a glass chamber is shown in **Fig. 4**. The sensing material was placed into the glass chamber and gently pressed by four-probe to record the current-voltage.

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. The resistivity (ρ) and then conductivity (σ) were calculated using equations (1)–(4).

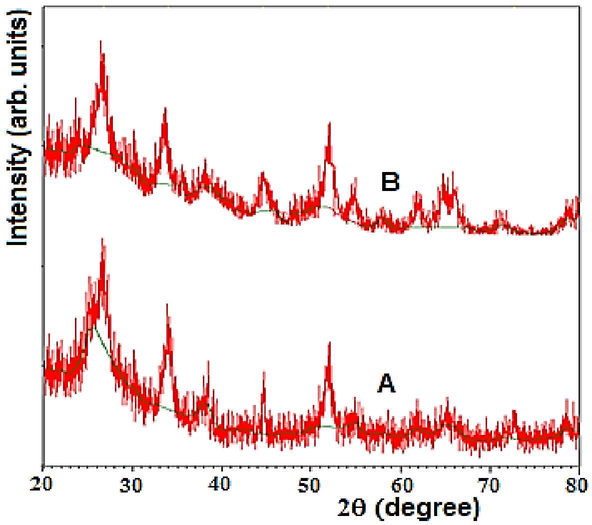


Fig. 3. XRD pattern of PANI/SnO$_2$ nanocomposites A and B.

$$\rho = \frac{\rho o}{G7(W/S)} \tag{1}$$

$$G7\,(w/s) = \frac{2S}{W}\, ln2 \tag{2}$$

$$\rho o = \left(\frac{V}{I}\right) 2\pi s \tag{3}$$

$$\sigma = \left(\frac{1}{\rho}\right) \tag{4}$$

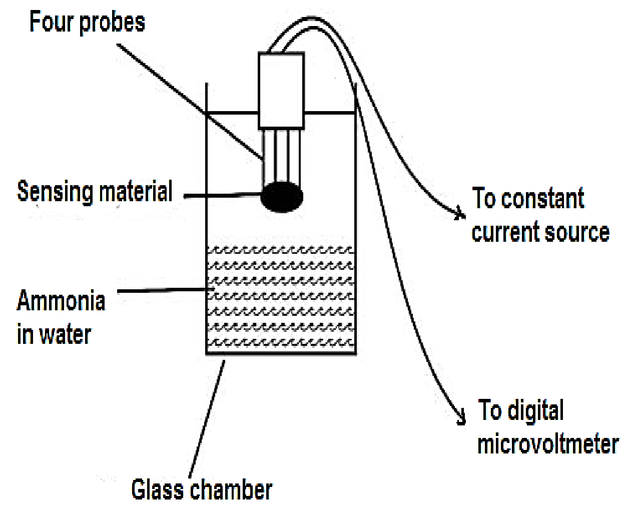


Fig. 4. Four probe laboratory set up for ammonia sensing.

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. 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 [**33**]. The electrical resistivity of PANI/SnO$_2$ nanocomposites A and B shows a remarkable change when exposed to different percent (5, 10, 15%) of aqueous ammonia as shown in **Fig. 5**. 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. Both the samples A and B shows similar response to the ammonia vapour. On high concentration of aqueous ammonia (15%) the sensing material has shown the fast response. The resistivity of both the composites increases because of the undoping or the reduction of charge carriers by adsorption of ammonia on the surface of material [**34**]. Ammonia gas molecules withdraw protons from N$^+$–H sites to form energetically more favourable NH$_4^+$ due to which PANI changes from the emeraldine salt state to the emeraldine base state, leading to the reduced hole density in the PANI and thus an increased resistivity [**35**]. When the sensor is purged with dry air, the process is reversed; NH$_4^+$ decomposes to form NH$_3$ and resistance recovered.

Cyclic response of electrical resistivity for both the samples at 15% concentration of ammonia vapour was observed. In the study of cyclic response, the material was exposed to ammonia vapour for 1 min and to air for 5 min, both the materials showed a well-defined response alternately to ammonia and air.

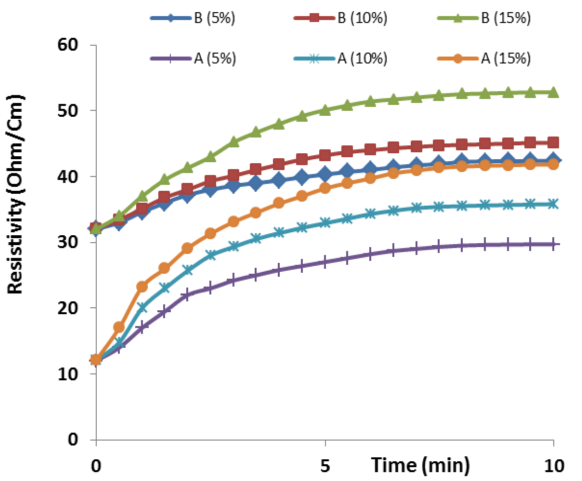


Fig. 5. Resistivity response of PANI/SnO$_2$ nanocomposites A and B at 5, 10 and 15% concentration of ammonia.

Table 1. Sensitivity of nanocomposites for ammonia sensor.

Nanocomposites	Sensitivity (%)
PANI/SnO$_2$ (A)	91.7
PANI/SnO$_2$ (B)	15.6
PANI/SnO$_2$ [**13**]	16.0
PPY/MWNT [**4**]	28.0
PANI/ZnO [**38**]	18.9

On exposing the sensing material for 1 min, in presence of 15% aqueous ammonia, the change in the resistivity was observed from 12.1 ohm cm (initial resistivity) to 23.2 ohm cm for sample A and from 32 ohm cm (initial resistivity) to 37 ohm cm for sample B due to the deprotonation of polyaniline by adsorption of NH$_3$ **[36]** and keeping them for 5 min in air, the resistivity fall back to 19.8 ohm cm in case of sample A and 35.3 ohm cm in case of sample B. After the sensors were 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 materials again exposed to 15% ammonia vapour for 1 min, the resistivity was observed 14.5 ohm cm for A and 33.4 ohm cm for B sample and again exposed for 5 min in air the resistivity back 21 ohm cm for A and 34.6 ohm cm for B sample. On repeating the experiment, the initial resistivity could not come back. This difference between two samples took place due to incorporated SnO$_2$ nanoparticles in PANI matrix played a significant role by enhancement in the porosity and the surface activities of sample A as compared to that of sample B due to which conductivity of sample A was found to be more than that of sample B. The sensor sensitivity (S) as the ratio $S = [(\rho_a - \rho_v)/\rho_a] \times 100$, where ρ_a represents the resistivity in air and ρ_v the resistivity in vapour [**37**], for both the samples was also determined at 15% ammonia vapour. The S was found to be 91.7% for sample A and 15.6% for sample B. This result shows that sample A is highly sensitive to ammonia vapour as compared to sample

B. **Table 1** shows the comparison of sensitivity of these two samples along with other nanocomposites reported for ammonia sensor.

Conclusion

Tin oxide (SnO_2) nanoparticles, PANI/SnO_2 nanocomposite (sample A) and PANI/SnO_2 nanocomposite (sample B) were successfully synthesized. Nanocomposites have been well characterized by XRD, FTIR and SEM which reveals that SnO_2 was uniformly mixed within the PANI matrix. The PANI/SnO_2 nanocomposites could be good materials for NH_3 detection at room temperature. By comparing the response of sample A and B to the ammonia vapour, the sample A is more sensitive than sample B due to highly porosity and surface activity of sample A.

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