



Sn-PANI Synthesis and its Application as Ammonia Gas Sensor

Research Article

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Abstract. Gas sensing is required in various fields like industries, environmental studies and space. Gas sensors based on change in resistance are widely in demand because of its low cost and high stability. Polyaniline (PANI) and Tin oxide (SnO_2) have been reported as good gas sensors. This has motivated us in studying the behavior and characteristics of composites of Sn-PANI. In this study we have synthesized Sn-PANI composite and characterized using FTIR, XRD and SEM as displayed. Sn-PANI composite is one such proposed gas sensor which has appreciable response to ammonia. The blending of SnO_2 with PANI has greatly increased the sensitivity towards ammonia as compared to SnO_2 sensors alone.

Keywords. Polyaniline; Gas sensor; Environmental studies; Blending; Composite

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1. Introduction

For the last several years gas sensors are extensively used in various fields to detect the existence of many pollutant gases to avoid harmful effects on mankind. Gas sensors possess wide range of application in various aspects of modern day technologies. Amidst chemical industries requirement of effluent gas sensing, control and treatment has always been necessary in order to prevent accidents. Gas sensing technology is widely used in automotive industries (e.g.,

detection of pollutant gases from vehicles, medical applications (electronic noses, simulating the human olfactory system), indoor air quality supervision (detection of carbon monoxide) and environmental studies (greenhouse gas monitoring) [1]. A selection of material for a good gas sensor is based on

- (1) *Sensitivity*: the minimum volume of gas concentration that could be detected,
- (2) *Selectivity*: the ability of gas sensors to identify a specific gas among mixture,
- (3) *Response time*: the time taken by a sensor to respond to an existence of a particular gas,
- (4) *Recovery time*: the time taken by sensor to get ready for next sensing cycle,
- (5) *Fabrication cost*, and
- (6) *Shelf life* [1, 16].

Ammonia gas is extensively used in many industries like chemical industry in nitric acid manufacturing, petrochemical industries, industrial hygiene monitors and in calibration gas mixtures in environmental emission monitors as well as it is used as refrigerating fluid in household refrigerators [2–4]. A high concentration of ammonia is dangerous to 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) can cause pulmonary edema (accumulation of fluid in the lungs). In all cases, the sensing of higher concentration of ammonia in environment is a major concern for preventing hazardous results [5].

Several attempts were made to synthesize an economical sensor with the help of metal oxides and conducting polymers [6–8]. Among the various types of gas sensors, conducting polymers and metal oxides have been studied extensively for sensing different gases because the interaction with various analytes may influence the redox and doping states of both, leading to a change of resistance. Tin oxide (SnO_2) has been recognized as an attractive material with excellent optical properties, chemical durability and transparent conductivity. Due to these properties SnO_2 is widely used for monitoring toxic gases. SnO_2 shows excellent sensitivity towards gas pollutants. However, there are some limitations of SnO_2 , such as lack of selectivity and sensitivity at ambient humidity and higher operating temperatures (170-900 °C) [9]. Conducting Polymers may be the good alternatives for metal oxides sensors. Electrical conductivity of these conducting polymers is affected through exposure to diverse organic and inorganic gases. This feature has led to the investigation of these materials as gas sensing materials. Conducting polymers that can be used as gas sensing materials include polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh) and their derivatives [10]. Among these Polyaniline attracted more researchers due to its high sensitivity, short response time, low cost of fabrication, simple and portable structure and low energy consumption. However, PANI shows some drawbacks also, such as long-time instability, irreversibility and poor selectivity [10].

To overcome drawbacks of SnO_2 and PANI for gas sensing application, we blended SnO_2 with PANI to form composite Sn-PANI. Both were prepared by sol-gel method and characterized using X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) techniques. The gas sensitive characteristics were investigated

by recording their electrical responses when exposed to aqueous ammonia vapour at room temperature with the help of simple laboratory made gas sensing set up.

2. Materials and Methods

Polyaniline Synthesis

Polyaniline (PANI) was synthesized by using chemical oxidation method. An appropriate amount of double distilled Aniline and water were mixed together. 1M H₂SO₄ as a dopant was added to the above solution. Ammonium persulphate (APS) as an oxidizing agent was also added drop by drop to this solution till polymerization took place. The whole procedure was carried out under constant magnetic stirring for 6 hours at low temperature as this reaction was highly exothermic. The precipitate was filtered, washed several times and then dried at 60 °C for 12 hours to obtain a dark green powder.

Tin Oxide Synthesis

Tin Oxide (SnO₂) was synthesized by simple chemical route reaction. An appropriate amount of Tin chloride (SnCl₂.2H₂O) was added to distilled water and kept for constant stirring at 450 rpm. 1 M NaOH was added to above solution drop by drop to adjust pH in the range 8-9 on pH scale. Once pH got adjusted solution again stirred for 2 hours at 60 °C. It was observed that colour of solution changed from white to grey in this process. The precipitate was then filtered, washed several times and then air dried. The sample was sintered in a furnace at 400 °C for 6 hours.

Sn-PANI Composite

SnO₂ powder was blended with PANI with different concentrations. The pellets were formed by applying a pressure of 6 tones for 5 minutes. The nature of bonding, structural and surface morphology of the PANI, SnO₂ and composite were analyzed by FTIR, XRD and SEM respectively. CuK_α X-rays with wavelength of 1.54 Å were used for XRD.

3. Results and Discussions

3.1 Structural Morphology

From the diffracted peaks obtained in the XRD spectrum (Figures 1 and 2), the average grain size of the synthesized SnO₂ and PANI particles were determined with the help of the Debye-Scherrer formula. The values of interplaner spacing (*d* spacing) were calculated by using Bragg's relation and were compared with the JCPDS data. For SnO₂, the peaks are observed and matched with those peaks along (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (0 0 2), (3 1 0) and (1 1 2). The peaks were sharp indicating high crystallinity of SnO₂. The lattice constants $a = b = 0.4743$ nm and $c = 0.3186$ nm, which matches well with the standard XRD data file of SnO₂ (JCPDS-041-1445). For PANI, The characteristic peak appeared at 26° corresponding to (200) crystal plane.

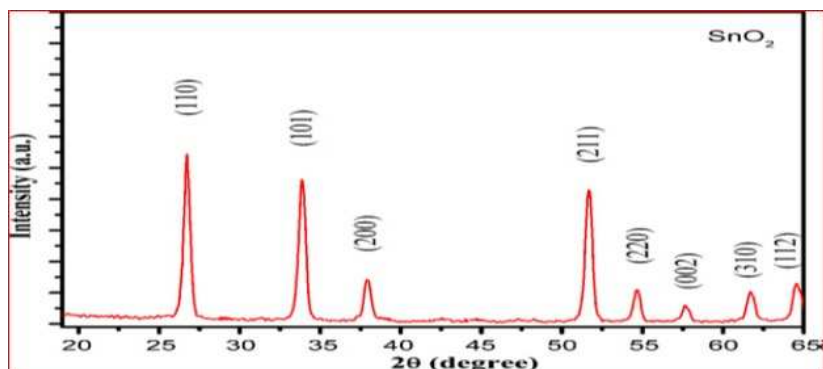


Figure 1. XRD of SnO₂

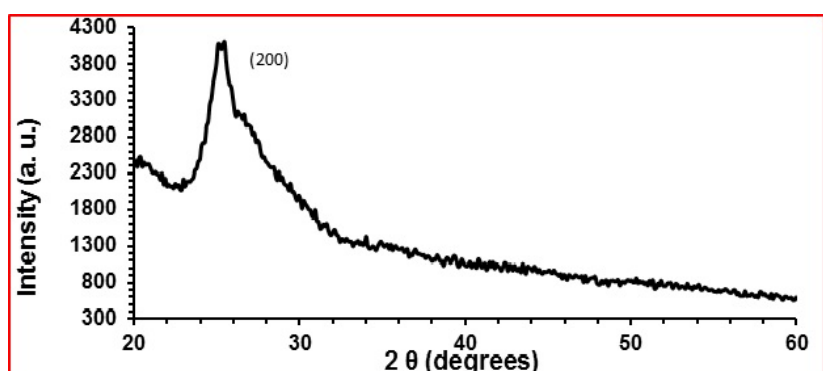


Figure 2. XRD of Polyaniline

3.2 Surface Morphology

The surface morphology of SnO₂, PANI and Sn-PANI composite were studied by SEM images (Figures 3, 4 and 5). The SEM image of SnO₂ shows spherical nature having average size 90 nm and the SEM image of PANI shows uniform size distribution in tubular form having average size 80 nm. It can be seen from Figure 5 that the composite particles are highly dispersed with agglomeration. The formation of polymer shell around the nano crystalline particles can be seen in SEM image.

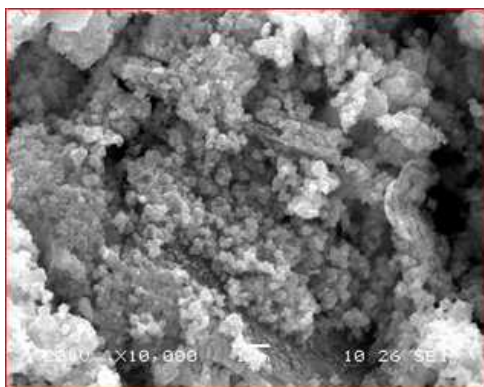


Figure 3. SEM of SnO₂

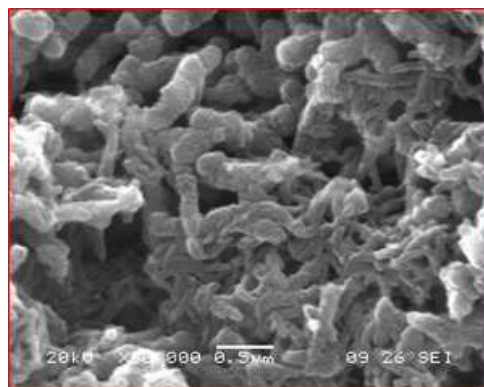


Figure 4. SEM of Polyaniline

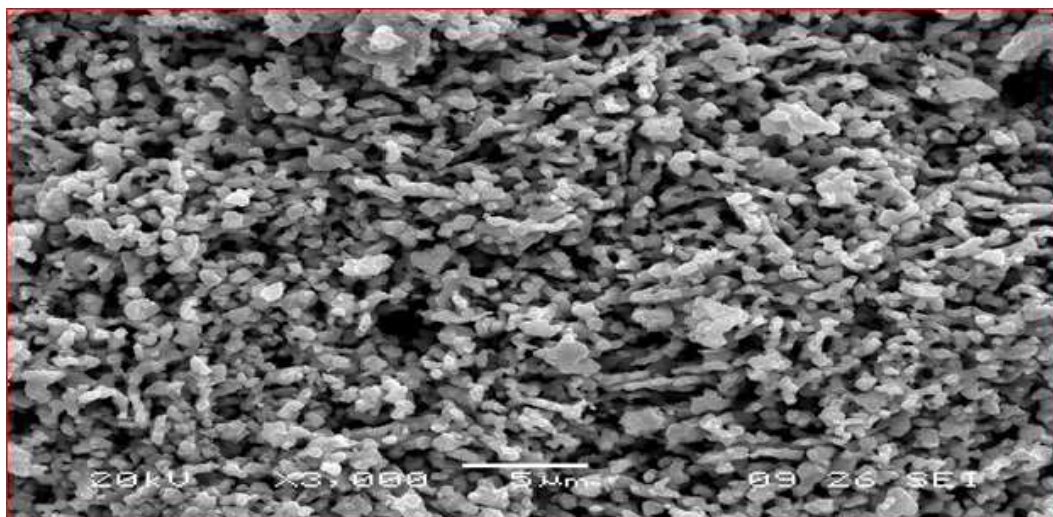


Figure 5. SEM of Sn-PANI Composite

3.3 FTIR

In order to find the nature of bonding we studied FTIR spectrum of Sn-PANI composite. Figure 6 shows the FTIR spectrum for Sn-PANI composite, having peaks at wave numbers 1581, 1493, 1449, 1288, 1365, 1159, and 738 cm^{-1} . The peaks at wave numbers 1581 and 1493 cm^{-1} are corresponds to $\text{C}\equiv\text{N}$ and $\text{C}=\text{C}$ stretching mode for the quinoid and benzenoid rings and the peak at wave number 1449 cm^{-1} is attributed to $\text{C}-\text{C}$ aromatic ring stretching of the benzenoid diamine unit. The peaks at wave numbers 1288 and 1365 cm^{-1} are attributed to $\text{C}-\text{N}$ stretching and peak at wave number 1159 cm^{-1} is due to $\text{N}=\text{Q}=\text{N}$ stretching. The peak at the wave number 738 cm^{-1} is due to $\text{C}-\text{H}$ out of plane bending vibrations. However, these peaks are slightly shifted from their original positions as compared with pure PANI. This shifting might be due to the presence of tin oxide in the PANI matrix. Furthermore, a peak observed 615 cm^{-1} is due to the antisymmetric $\text{Sn}-\text{O}-\text{Sn}$ mode in S_nO_2 as in literature. Thus it confirms the presence of tin oxide in the PANI matrix [11, 12].

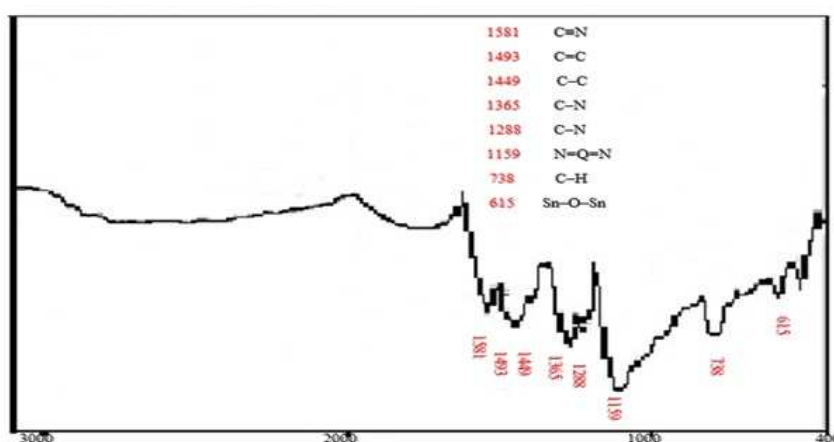


Figure 6. FTIR of Sn-PANI Composite

3.4 Gas Sensing Studies

The electrical resistance of the Sn-PANI composite was determined as a function of exposing time of ammonia gas. The composite in the form of pellet of diameter 12 mm was placed into the glass chamber; 100 ppm ammonia gas was passed into the chamber. The gas sensitive characteristics were investigated by recording resistance when pellet was exposed to ammonia at room temperature. The several gas sensing cycles were recorded in order to investigate the response of Sn-PANI composite to ammonia.

The significant change in electrical resistance of Sn-PANI composite was observed when it was exposed to ammonia gas as shown in Figure 7. The sensing mechanism is governed by the protonation/deprotonation phenomena. It showed that resistance of the material increases when it was exposed to ammonia. For every sensing cycle material showed same response. The resistance of Sn-PANI composite increased because of the undoping or the reduction of charge carriers by adsorption of ammonia on the surface of pellet [13]. Ammonia gas molecules withdraw protons from $N^+ - H$ sites to form energetically more favorable NH_4^+ due to which PANI was changed from the emeraldine salt state to the emeraldine base state, leading to the reduced hole density in the PANI and thus an increased resistance [14, 15]. When the pellet was exposed to air; the reversible nature was recorded. NH_4^+ decomposes to form NH_3 and resistance recovered.

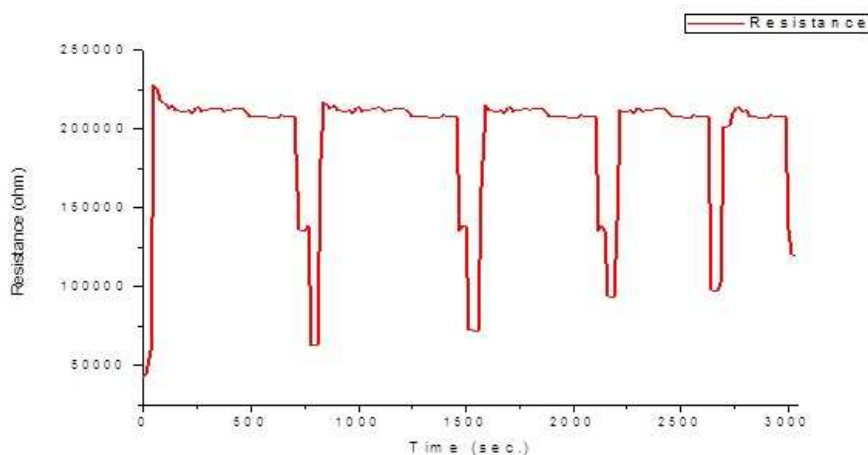


Figure 7. Resistance response of Sn-PANI composite to 100 ppm ammonia gas

For first cycle the initial resistance of Sn-PANI composite was 42764 ohm. When 100 ppm ammonia gas was exposed to pellet, the resistance of pellet was recorded as 227604 ohm and when pellet was exposed to air, the resistance got decreased to 63004 ohm. On repeating sensing cycles with constant ammonia concentration, it was observed that the initial resistance went on increasing and response resistance goes on decreasing. The initial resistance could not come back to 42764 ohm. This could be due to the trapping of ammonia molecules on surface of composite. The sensitivity of Sn-PANI was observed 81.21%. The response time was about 1.5 minutes and the recovery time was about 15 minutes.

4. Conclusions

Nano sized Tin oxide, Polyaniline and Sn-PANI composite were successfully synthesized. They have been well characterized by FTIR, XRD and SEM. The characterization of Sn-PANI composite reveals that tin oxide was uniformly blended with Polyaniline. The blending of SnO₂ with PANI (Sn-PANI) has greatly increased the sensitivity towards ammonia. compared to SnO₂ and PANI sensors. Thus, Sn-PANI could be a good material for detection of ammonia gas at room temperature. The sensitivity and the response time can be improved with improved signal processing and data acquisition.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

References

- [1] X. Liu, S. Cheng, H. Liu, S. Hu, D. Zhang and H. Ning, *Sensors* (2012), 9635-9665.
- [2] A.J. Buonicore and W.T. Davis, *Air Pollution Engineering Manual*, Air and Waste Management Association, USA (1992).
- [3] H.M. Gomaa and D.T. Cindricr, *35th Annual Ammonia Symposium*, United States Environment Protection Agency, NC, USA (1991).
- [4] J.H. Currey, *Iron Steel Engineering*, Association of Iron and Steel Engineers, 43-45 (1991).
- [5] A. Navarchian, Z. Hasanzadeh and M. Joulazadeh, *Adv. Polym. Technol.* **32** (2) (2013).
- [6] S.G. Pawar, S.L. Patil, M.A. Chougule, B.T. Raut, S.A. Pawar, R.N. Mulik and V.B. Patil, *J. Mater. Sci.: Mater. Electron.* **23** (1) (2012), 273-279.
- [7] A.K. Sharma, Y. Sharma, R. Malhotra and J.K. Sharma, *Adv. Mat. Lett.* **3** (2) (2012), 82.
- [8] A. Menzel, K. Subannajui, R. Bakhda, Y. Wang, R. Thomann and M. Zacharias, *J. Phys. Chem. Lett.* **3** (2012), 2815-2821.
- [9] Fortunato, D. Ginely, H. Hosono and D.C. Paine, *MRS Bulls.* **32** (2007), 242-247.
- [10] H. Bai and G. Shi, *Sensors* **7** (2007), 267-307.
- [11] N.G. Deshpande, Y.G. Gudagea, R. Sharma, J.C. Vyas, J.B. Kim and Y.P. Lee, *Sensors and Actuators B* **138** (2007), 76-84.
- [12] S.K. Dutta, *Mater. Lett.* **61** (2007), 4967-4971.
- [13] Z. Jin, Y.X. Su and Y.X. Duan, *Sens. Actuators B* **72** (1) (2001), 75.

- [14] M.E. Nicho, M. Trejo, A. Garcia-Valenzuela, J.M. Saniger, J. Palacios and H. Hu, *Sens. Actuators B* **76** (1-3) (2001), 18.
- [15] S.B. Kondawar, S.P. Agrawal, S.H. Nimkar, H.J. Sharma and P.T. Patil, *Adv. Mat. Lett.* **3** (5) (2012), 393-398.
- [16] S. Chakane, S. Jain, S.V. Bhoraskar, A.B. Samui and V.N. Krishnamurthy, *Sensors and Actuators B* (2012), 81.