Polyaniline-SnO_2 Nanocomposite Based Room Temperature Ammonia Sensor

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Abstract: A Polyaniline-SnO_2 nanocomposite is used as sensing material for ammonia detection. Polyaniline-SnO_2 nanocomposite was synthesized by an in-situ polymerization of aniline in presence of synthesized SnO_2 nanoparticles using ammonium persulphate (APS) as an oxidant in acidic medium. The characterization of the sensing material is carried out using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). Ammonia detection is carried out by depositing sensing film on chemiresistor and surface acoustic wave (SAW) device for different concentrations of Ammonia. SAW delay line device is developed using photolithography technique. 128^0 YX – cut $LiNbO_3$ is used as the substrate for SAW device. Chemiresistor is developed using glass epoxy PCB. The results of ammonia detection using both the techniques are compared here. Change in resistance is measured as the sensor response for chemiresistor, while change in frequency and insertion loss is measured as the sensor response for SAW sensor. The changes in frequency and insertion loss are measured using network analyzer. SAW sensor showed better sensitivity and linear response to ammonia as compared to chemiresistor.

Index Terms **- Polyaniline, SAW, chemiresistor, sensitivity.**

1. INTRODUCTION

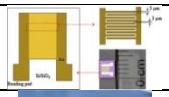
Ammonia (NH_3) is natural gas and its contents in the atmosphere are increasing because of human activities. European Commission for the environment and quality of life estimated the value of NH_3 emission throughout the world to be 20-30 Tg. Higher concentrations (1000 ppm or more) of NH_3 may cause pulmonary edema, accumulation of fluid in the lungs and even death. Due to its acute toxicity; development of highly selective, stable, reliable and cost-effective sensor is strongly required. So far, several methods have been employed to obtain a highly sensitive NH_3 sensor. For example, chemical stability and excellent conductivity of SnO_2 based sensors make them promising candidates for NH_3 sensing [1]. These sensors have a high response and recovery time. However, the requirement of high temperature for optimal function as well as issues with sensitivity and selectivity are certain drawbacks associated with SnO_2 based devices. To overcome these problems, new sensors based on doping of SnO_2 materials (with metals and inorganic materials) have been designed which improved sensing characteristics of these sensors.
It is necessary to design new hybrid materials with better performance, resulting in less consumption of energy and less damage to the environment. A portable gas sensor system based on the surface acoustic wave (SAW) using conducting polymer nanocomposites as sensing material is considered to be more effective for ammonia detection. It was found that most of the organic conducting polymers such as polypyrrole, polythiophene, and polyaniline (PANI) possess excellent gas sensing properties. Among these materials, polyaniline is one of the most versatile polymers. It is very eco-friendly and easy to synthesis, have good sensing properties. Since it has good physical and chemical properties, it is widely used for the detection of NO_2,H_2 ,CO_2, H_2S, and ammonia [2-4]. In order to improve the sensing properties, hybrid sensors, has been smartly utilized for various gas sensing applications.
In the present study, nanocomposites of PANI/SnO_2 is prepared using in-situ polymerization of aniline in presence of synthesized SnO_2 nanoparticles using ammonium persulphate (APS) as an oxidant in acidic medium and is used as ammonia sensing material at room temperature. The thin films of PANI/SnO_2 nanocomposite were deposited on the delay line portion of the SAW device. The developed sensor shows excellent ammonia gas sensing activity at low concentrations (25-100 ppm) of ammonia. The gas sensor operated on mass loading effect due to the adsorption of ammonia gas molecules on the delay line portion of SAW. This sensor shows good reproducibility in gas sensing and also environmental stability. Moreover, it shows best sensitivity, fast response and recovery times for 25 ppm of ammonia concentration.

2. DESIGN CONSIDERATIONS FOR AMMONIA SENSOR

Wide research across the world has resulted in availability of many types of commercial sensors. Accuracy is among the important measurement characteristics of the sensors. The accuracy of a sensor is typically given as a percentage of full-scale. For example, if the sensor is for the range of 0-100 ppm with a 5% of full-scale, a reading of 30 ppm will be ±5 ppm. Typical sensor accuracy is between ±3ppm. Response time is another important parameter. Different sensors have different response times. Most manufacturers give response time as time interval between10% and 90% of full-scale. A typical value for electrochemical and solid-state is < 30 seconds to 90%. For high concentration infrared sensors it is 90 seconds. The charged carrier injection sensors response is less than 10 seconds. The polymer thin-film capacitive sensor response time is effected by the length of the absorption/desorption cycle and currently is of the order of 90 seconds [3, 5, 6].
While designing the ammonia sensor following main parameters are taken in account: Concentration ranges, Environmental conditions, Background gases, Detector life and Measurement characteristics- Accuracy, time response, sensitivity, selectivity.

Some of the types of commercial sensors as summarized in the following table 1 [5-7].

Table 1: Different types of ammonia sensors

Sensor Type	Sensor Configuration	Characteristics
Electrochemical		Concentration Ranges:0-50 ppm,0-200 ppm,0-1,000 ppm . Response time: <30 seconds, Accuracy: +/-5% of full scale.
Solid-State		Concentration Ranges:0-500 ppm,0-1,000 ppm,0-10,000 ppm (0-1%), Response time: <30 seconds, Accuracy: +/-3% of full scale.
Infrared		Concentration Ranges: 0-20,000 ppm (0-2%), Response time: <90 seconds. Accuracy: +/-5% of full scale.
Charged Carrier Injection		Concentration Ranges: 20-200 ppm, 30-1,000 ppm, 30-10,000 ppm (0-1%), 30-30,000 ppm (0-3%) Response time: <10 second, Accuracy: +/-10% of reading.
Polymer Thin film Capacitive		Concentration Ranges: 0-100 ppm,0-1,000 ppm, Response time: <90 seconds, Accuracy: +/-10 ppm + 20% of reading
Catalytic Bead (Pellistor)		Concentration Ranges: 0-50% LFL, Response time :< 45 seconds, Accuracy: +/-5% of full-scale.

Toxic gas monitoring applications necessitate ammonia sensors that are capable of accurately measuring low concentrations of ammonia in air (i.e. 0-200 ppm or lower).If the sensor is expected to react to higher concentrations, it is doubtful that concentrations of ammonia at toxic gas levels will be safely controlled. A detector range should be selected such that any alarm or critical control settings ranges are triggered at concentrations near the maximum reading for the detector.

3. METHODOLOGY

Aniline (99.5%) monomer was distilled using condenser method to remove the additives and to get pure aniline monomers before its use. Tin chloride ($SnCl_4$:$5H_2O$) (99%), hydrogen peroxide (H_2O_2) (99.5%), Ammonium per sulphate (98%), starch (98.5%) and ammonia (99%) were purchased from High Purity Laboratory Chemicals PVT. LTD. All chemicals were of analytical grade and used as they are. The solutions were prepared with distilled water. The resulting nanocomposite films were used in constriction of thin film chemo-resistive and SAW sensors. Five sample of each type of sensors were fabricated and results are reported in subsequent sections.

3.1 Synthesis of SnO_2 nanoparticles

Sol-gel method was used for the synthesis of SnO_2 nanoparticles. In a typical method, 0.1M $SnCl_4$:H_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 3 hours and then the solution was allowed to settle overnight. Supernatant liquid was then discarded carefully and the remaining solution was centrifuged for 15 minutes 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 70°C for overnight. Then powder was sintered at 600°C using oven for 6 hours and nanocrystalline SnO_2 was obtained[2,5] .

3.2 Synthesis of Polyaniline-SnO_2 nanocomposite

Polyaniline - SnO_2 nanocomposite was synthesized by an in-situ polymerization of aniline in presence of 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 70 minutes. As-synthesized SnO_2 nanoparticles were suspended separately in 1 M HCl (100 ml) solution and sonicated for 90 minutes to reduce aggregation of SnO_2 nanoparticles. 100 ml aniline solution and 10 ml SnO_2 nanoparticles suspension were mixed and further sonicated for 90 minutes. 100 ml APS solution was then slowly added drop wise to well disperse suspension mixture with continuous stirring. After 2 hours, a good degree of polymerization was achieved. The green color precipitate was obtained. The precipitate produced in the reaction was removed by filtration, washed repeatedly with 1 M HCl and dried at room temperature in dust free environment. The composite powder was in conductive emeraldine salt (ES) form of polyaniline -SnO_2 nanocomposite [2, 5].

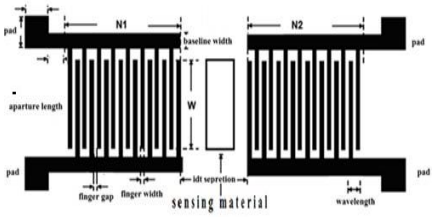
3.3 Structural and morphological Characterization of polyaniline-SnO_2 nanocomposite

The FTIR spectra of synthesized product were recorded by using Bruker spectrophotometer in the wave-number range of 400-4000 cm^{-1}. Phase identification of the composite was done by X-ray diffraction using Bruker AXSD8 diffractometer with Cu-Kα radiation source. The morphological study of the composite was carried out by field emission scanning electron micro-scope (FESEM- Nova NanoSEM NPEP303), and SEM JEOL, OXFORD instruments.

3.4 Ammonia sensing characteristics of Polyaniline-SnO_2 nanocomposite

The film of synthesized Polyaniline-SnO_2 nanocomposite was formed by drop casting method on the delay line portion of the SAW device. The film is dried at room temperature before use for ammonia detection. The gas sensing characteristics were studied in a custom-made testing chamber. The testing chamber is made of glass having airtight plastic cap on which the gas inlet rubber and electrical contacts for the sensor are fitted. The volume of the chamber is 500cc.The vapors of ammonia were added in the chamber by using the plastic syringe. The sensor was tested for 25-100 ppm concentration of ammonia. The sensitivity of the sensor was determined by measuring the change in frequency of the sensor at room temperature with and without the presence of

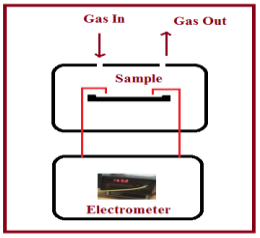
the ammonia using a network analyzer. The sensitivity of chemiresistor sensor was determined by measuring change in resistance for different concentrations of ammonia. Figure1 (a) shows the SAW delay device structure and figure1 (b) shows the measurement setup for SAW based ammonia sensor respectively.Figure1(c) and 1(d) shows the chemiresistor and its measurement setup respectively.



(a)

(b)

(c)



(d)

Fig.1 (a) SAW delay line Device (b) Measurement Setup for SAW-based ammonia sensor (c) Chemiresistor for Ammonia sensing (d) Measurement Setup for chemiresistor ammonia sensor.

4. RESULTS AND DISCUSSION

4.1. Results of Material Characterization

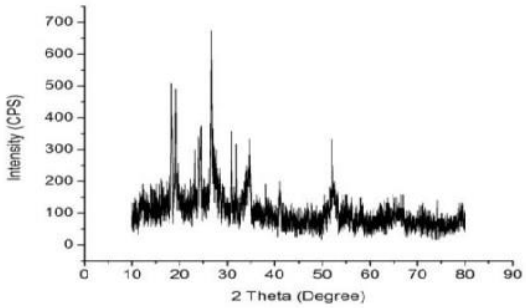


Fig 2. XRD of polyaniline – SnO_2 nanocomposite

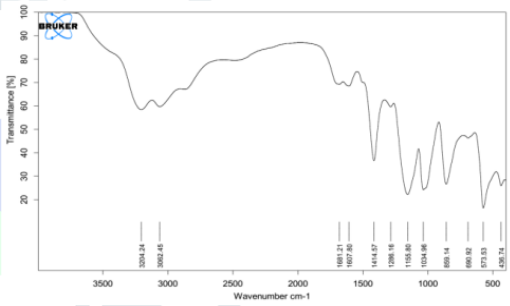


Fig 3. FTIR of polyaniline – SnO_2 nanocomposite

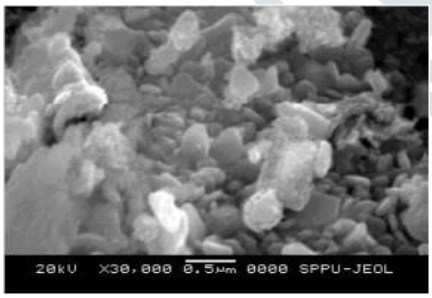


Fig 4. SEM of SnO_2 nanoparticles

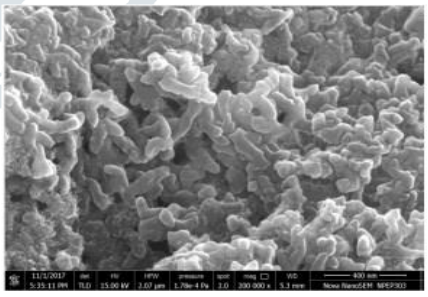


Fig 5. FE-SEM of polyaniline-SnO_2 nanocomposite

Figure 2 shows the XRD pattern of the obtained Polyaniline-SnO_2 composite. It can be seen that the nanocrystalline SnO_2 peaks are observed at 2θ values of 26.58^0 ,34.90^0,38.14^0,52.13^0,66.12^0 and matched with those peaks along planes (1 1 0), (1 0 1), (2 0 0), (2 1 1), and (3 0 1) having primitive tetragonal structure (*JCPDS DATA CARD 41-1445*). The XRD spectrum peaks are close to the standard XRD of SnO_2. However, these peaks show a small shift (0.20 to 0.50) from their respective standard positions which may be due to polyaniline matrix. In addition, we observed relatively larger peak broadening, compared with XRD of pure SnO_2. This suggests that tin oxide is present in the polyaniline matrix, and presence of polyaniline has influenced the preferred composite. In the FTIR spectrum of a composite (figure 3), the characteristic peaks at 3062.45 cm^{-1},3204.24 cm^{-1} & 1681.21cm^{-1} correspond to C-H stretching vibrations, and C=C stretching vibrations respectively. Peaks at 1607.80 cm^{-1} and 1414.57 cm^{-1} correspond to quinoid and benzene rings of polyaniline, while the peak at 690.92 cm^{-1} corresponds to the anti-symmetric Sn-O-Sn mode. Thus it shows the characteristics of polyaniline as well as the tin oxide. Figure 4 shows the SEM image synthesized SnO_2 nanoparticles. This shows that the particle size is not uniform. Figure 5 shows the FESEM image of polyaniline-SnO_2 composite. We took the images at different points on the material. At few places it is observed the particle structure like nano rods with their length varying from ~450- 700nm. Table 2 lists average values of concentrations of chemical elements in the sample observed in the EDAX study.

Table 2: Concentrations of chemical elements composing the sample

Elements	C	O	N	Sn	Cl
Atomic Weights %	48.86	30.33	16.39	1.42	3.00

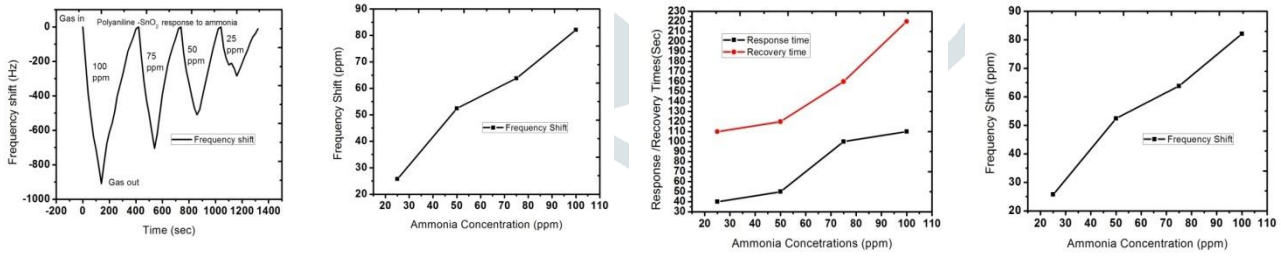
4.2 Ammonia sensing using PANI- SnO_2Nanocomposites film coated Chemiresistor and SAW Sensor

Ammonia sensing tests were carried out in a labmade air-tight glass chambers at room temperature. The sensing performance of polyaniline nanocomposite was measured using thin film deposited chemiresistors and SAW delay line device by exposing to ammonia, for different concentrations from 25 to 100ppm. The resistance of chemiresistors was measured using Keithly's Electrometer for different concentrations of ammonia. For SAW sensor the change in frequency and insertion loss was measured using network analyzer for different concentrations of ammonia. The change in frequency is linear with the change in ammonia concentrations for the 25-100 ppm concentrations. The sensitivity of both chemiresistors and SAW sensor are expressed as, $S_1 = \frac{\Delta R}{R}$ and $S_2 = \frac{\Delta f}{f}$. Where ΔR and Δf are the change in resistance and change in frequency respectively.

(a) (b)

Fig 6. (a) Chronometric response of polyaniline–SnO_2 nanocomposite based chemiresistor to ammonia (b) Response-recovery times for different concentrations of ammonia.

Figure 6(a) shows the Chronometric response of polyaniline–SnO_2 nanocomposite based chemiresistor to different concentrations of ammonia. The change in resistance increases for higher concentrations. It shows that resistance of the material decreases when it is exposed to increasing concentrations (25-100 ppm) of ammonia. This is mainly due to SnO_2 nanoparticles, which may act as a percolated high mobility path for electrons. PANI incorporation into oxide matrix creates an imbalance and a charge separation occurs at a polymer - nanoparticles interface. Thus, PANI-SnO_2 nanocomposite forms a large number of p-n hetero-junctions throughout the surface, giving rise to very high resistance at room temperature. When PANI-SnO_2 comes in contact with ammonia (NH_3), this charge separation is released by NH_3 rupturing the hetero-junctions and the resistance decreases. The depletion region that was created at the interface because of the difference in motilities of semiconductor and polymer is broken and inter-particle electron migration occurs through SnO_2. The response/recovery times increases with gas concentrations as shown in figure 6(b). The recovery times are larger than response times; this could be attributed to the large dissociation rate of ammonia molecules.



(a) (b) (c) (d)

Fig 7 (a) Chronometric response of polyaniline - SnO_2 nanocomposite based SAW sensor (b) SAW sensor frequency shift with for different ammonia concentration(c) SAW sensor response –recovery times (d) SAW sensor sensitivity.

Figure 7(a) shows the chronometric response of polyaniline–SnO_2 nanocomposite based SAW sensor to different concentrations (25-100ppm) of ammonia. It shows that the change in frequency is quite linear as compared to the chemiresistor sensor response (figure 6). Figure 7(b) shows the actual frequency shift for different concentrations of ammonia, which shows that the frequency decreases as the concentration of ammonia increases. This is attributed to the mass loading effect executed by SAW sensor, but there could be some contributions of film conductivity change and film stiffness change. These are not taken into account because there is no positive shift in frequency observed [8, 9].

Figure 7(c) shows the response-recovery times for different concentrations of ammonia. The response and recovery times are less as compared to response–recovery times of chemiresistor sensor. Thus SAW sensor gives faster responses as compared to chemiresistor. The response time (t_{res}) and recovery time ($t_{rec.}$) were measured and found to be 110s and, 220s respectively for 100 ppm ammonia concentration. This is surely a good response time of the device as compared to the reported values in the literature [10] for this range of SAW resonance frequency. Figure 7(d) shows the SAW sensor sensitivity. This sensor has good sensitivity as compared to chemiresistor sensor.

CONCLUSION

Tin oxide (SnO_2) nanoparticles, polyaniline-SnO_2 nanocomposite films were successfully synthesized. Nanocomposites have been well characterized by XRD, FTIR and FE-SEM which reveals that SnO_2 was uniformly mixed within the PANI matrix. The polyaniline-SnO_2 nanocomposites could be good materials for ammonia detection at room temperature. The SAW sensor response to ammonia is quite linear as compared to chemiresistor response. The sensitivity values of polyaniline- SnO_2 nanocomposite to ammonia using SAW device are greater than using chemiresistor sensor. This is due to the high mass sensitivity of SAW device as compared to chemiresistor.

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REFERNCES

[1] Muzamil Ahmad Khan, Farah Qazi, Zakir Hussain, Muhammad UmairIdrees, Shahid Soomro, Saeeda Soomro 2017. Recent Trends in Electrochemical Detection of NH_3, H_2S and NOx Gases. International Journal of Electrochemistry Science, 12:1711 – 1733.
[2] Varade P.S., Gangal S.A., and Shaligram A.D. 2017. Synthesis and Characterization of Polyaniline-SnO_2 Composite for Volatile Organic Compounds (VOCs) Detection. International Res. Journal of Science Engineering, Special Issue A1: 117-122.
[3] Aditee C. Joshi and S. A. Gangal 2016. Implication of potassium trimolybdate nanowires as highly sensitiveand selective ammonia sensor at room temperature. Material Res. Express 3, 095008.
[4] Manisha Atul Bora, Pravin Bhikaji Adhav, V. V. Chabukswar 2019. Room temperature operating sensitive and reproducible ammonia sensor based on PANI/hematite nanocomposite. Polymer-Plastics Technology and Materials, ISSN: 2574-0881.
[5] Todd B. Jekel, Douglas T. Reindl. Ammonia Sensor Overview, Industrial Refrigeration Consortium, University of Wisconsin-Madison, 949 East Washington Ave, Suite 2, Madison,Wi 53703.
[6] J.F.M. Oudenhovena, W. Knoben, R. van Schaijk 2015. Electrochemical detection of ammonia using a thin ionic liquid film as the electrolyte, Procedia Engineering 120: 983 – 986.
[7] Bj¨ornTimmer, Wouter Olthuis, Albert van den Berg 2005. Ammonia sensors and their applications- a review. Sensors and Actuators B, 107:666–677.
[8] Wei Li, Yuanjun Guo. Youngling Tang, Xiaotao Zu, Jinyi Ma, Lu Wang , Yong Qing Fu 2017.Room-temperature ammonia sensor based in ZnO nanorods deposited on ST-cut Quartz surface acoustic wave device. Sensors, 17:1142.
[9] Yi- Tian Li, Hsu- Chao Hao, Mei-Ching Chen, Tai-Hsuan Lin, Pei- Hsin Ku, Chia- Min Yang 2011. Polymer -Coated Surface Acoustic Wave Sensor Array for Low concentration Detection. Kaohsung Taiwan.
[10] Chi-Yen Shen, Shih-Yuan Liou 2008. Surface acoustic wave gas monitor for ppm ammonia detection. Sensors and Actuators B 131:673–679.