Development of Conducting Polymer Metal Oxide Nanocomposite for Ammonia Gas Sensor

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Polymer metal oxide nanocomposite (PMON) material is synthesized by the chemical oxidative polymerization. The synthesized nanocomposite is characterized by the Field Emission Scanning Electron Microscope (FESEM), X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The FESEM images of the PANI (polyaniline) shows the formation of nanofibers of length 200 nm and diameter 50 nm. The FESEM micrograph composite shows that polyaniline is encapsulating the TiO2-Al3+ nanomaterials. The average size of the encapsulation is found to be 300 nm in diameter. The well defined peaks in the XRD spectra confirm the crystalline structure of TiO2-Al3+. Our sensor is able to detect up to 5 ppm concentration of ammonia gas. The sensor is stable up to 100 days and works at room temperature. The slight shift of base line is seen. The sensor is recovered automatically without flushing nitrogen gas. The sensor has the sensitivity of 1.0913 ppm-1.

Keywords: ammonia, metal oxide, nanoparticle, nanocomposite, sensor.

1. Introduction

In the present scenario monitoring different gasses present in an environment is important. Poisonous gasses such as ammonia, methyl isocyanides, dimethyl methylphosphonte (DMMP) etc are harmful for public health. Development of an electronics nose (sensors) for detection of trace amount of poisonous gas became necessary to prevent from fatal accident. The working principle of gas sensor is based on change in resistance (chemi-resistance). The metal oxide, metal halide and conducting polymer gives better detection of ammonia gas at room temperature [1-9]. Conducting polymers are synthesized by various techniques such as chemical polymerization [10-11], electro-chemical polymerization [12], interfacial polymerization [13] and plasma polymerization [14]. An ideal gas sensor should have following characteristics: (i) operation at room temperature; (ii) working in ambient environment and no requirement of oxygen or air supply; (iii) no external stimulus such as

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Joule heating or UV illumination for response/recovery; (iv) low detection limit; (v) high sensitivity and reproducibility; (vi) fast response and recovery; (vii) low cost and eco-friendly, etc [15].

Among the various sensor materials, conducting polymer have various advantages, such as less expensive, lighter and can be operated at room temperature. The graphene/PANI (polyaniline) polymer nanocomposite film is deposited on the surface of QCM (quartz crystal microbalance). The sensor shows the good respond toward the ammonia [16]. Flexible PANI/α-Fe2O3 sensors is fabricated and used for detecting the ammonia gas at room temperature. The sensor can detect the ammonia from 5 ppm to 100 ppm [17]. Sadek et.al [18] have developed a polyaniline/In2O3 nanofiber sensor for H2, CO and NO2. Polyaniline is used for various gas detection such as methanol [19], hydrogen [20], ammonia [21], carbon dioxide [22] etc. Polyaniline titanium dioxide nanocomposite sensor is able to sense 23 ppm of ammonia gas [23]. Pawar et.al [24] have also synthesized PANI/TiO2 by chemical oxidative polymerization of aniline with TiO2. This sensor can detect ammonia gas up to 20 ppm. Other conducting polymer nanocomposites such as polypyrrole base sensor are also used for detecting the ammonia gas [10, 25, 26], NO2 [27, 28] and DMMP gas [29].

In the present work we are reporting synthesize of PANI/TiO2-Al3+ nanocomposite for ammonia gas sensing. We are selecting the PANI because it is environmentally stable, easy to synthesize by simple methods and cost effective. The sensor is capable of detecting lowest concentration of 5 ppm of ammonia gas. The prepared sample is characterized by the FESEM, XRD and FTIR.

2. Experimental Method

2.1 Materials

Aniline, sulphuric acid (H2SO4), titanium dioxide(TiO2), hydrochloric acid (HCl) , sodium hydroxide (NaOH), ammonium per sulphate (APS) and aluminium chloride (AlCl3) all are purchased from the Himedia.

2.2 Synthesis of TiO2-Al3+ Nanoparticle (np)

TiO2 and AlCl3 are suspended in 10 M of NaOH and heated for 3 hr at 100oC under reflux with constant stirring. The ph of the suspension is maintained at 5 by adding 1 M of HCl with continuous stirring for 5 hr, so that ion exchange can take place completely forming, NaCl. The solution is allowed to stay for 8 hr and suspended nanoparticles TiO2-Al3+ are settled down. After filtering and washing with deionize (DI) water the nanoparticles are dried at 900C for 6 hr. The synthesized nanoparticles are heated at 4000C for 9 hr.

2.3 Synthesis of PANI/TiO2-Al3+

5 g of TiO2-Al3+ (np) is dispersed in 100 ml of DI water and sonicated for 2 hr. The sonication is followed by stirring. 0.1 M of aniline and 0.1 M of H2SO4 are added and stirred for 1hr. 0.1 M of APS solution is added drop wise to the above solution and kept the solution for 8 hr for polymerization to complete. PANI/TiO2-Al3+ polymer nanocomposite

is filtered and washed with deionize water several times. 0.1 M solution of methanol is used to wash so as to dissolve the unreactived molecules and finally washed with DI water. The nanocomposite is dried at 600C for 2 hr. The sensing material is deposited over the flexible mica sheet. The fabricated sensor is placed inside the gas chamber. The fabricated sensor has the dimension of 2.9 cm X 1 cm and its optical image is shown in Fig. 1. The change in resistance of sensor when exposed to the ammonia gas is recorded by the LCR meter (Hioki-35-32 50).

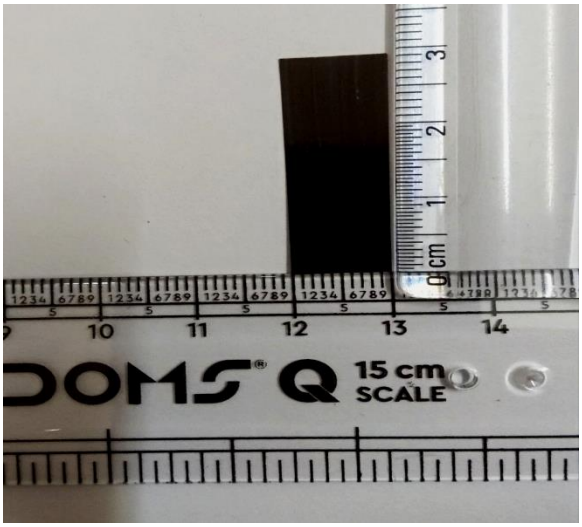

Fig.1 Optical Image of Fabricated Sensor

3. Characterization

The synthesized polymer metal nanocomposite is characterized by the Field Emission Scanning Electron Microscope (FESEM), X-ray Diffraction (XRD) and Fourier Transformation Infrared Spectroscopy (FTIR).

4. Result and Discussion:

4.1 FESEM, XRD and FTIR Studies

The Fig. 2 (a) shows the FESEM image of the PANI. Nanofibers of length of 200 nm and diameter of 50 nm are observed in PANI. Fig. 2 (b) shows the FESEM image of PANI/TiO2-Al3+. In the image the polyaniline is encapsulating the TiO2-Al3+ nanomaterials. The average size of the encapsulation is found to be around 300 nm.

Fig. 2 (c) shows the XRD of PANI and PANI/TiO2-Al3+. The PANI shows single broad peak at 22.750 which infer the amorphous nature of the polymer. In the XRD of polymer nanocomposite the profound peak of PANI is sink and shift to lower angle. This shift in the peak of PANI suggested the formation of the polymer nanocomposite as well as increase is crystallinity of TiO2(np)-Al3+ in polymer nanocomposite is formed [17]. The peaks

correspond to various planes such as (1,0,1), (0,0,4), (2,0,0), (1,0,5), (2,1,1) and (2,0,4) are correspond to the TiO2 nanoparticles. The peaks (1,1,1), (2,2,0) and (3,1,1) correspond to Aluminium. The XRD data matches with the JCPDS Card No. 21-1272 for TiO2 and JCPDS 04-0787 for Al respectively.

Fig. 2 (d) shows the FTIR spectra of PANI/TiO2-Al3+ nanocomposite material. The characteristics peaks at 1112.12 cm-1 & 1088 cm-1 are due to C-H plane bending, 1306.15 cm-1 is related to C=N stretching mode, 1486.20 cm-1 & 1483.31 cm-1 correspond to C=C stretching in benzenoid ring, 1576 cm-1 is due to C=C stretching quiniod ring and 794.12 cm-1 correspond to C-H bending vibrations. The peaks found between 600 cm-1 to 450 cm-1 are due to PANI/TiO2-Al3+, which confirms the interaction between PANI and TiO2-Al3+ [30-32, 33].

4.2 Ammonia Gas Sensing:

The ammonia gas sensing set up is shown in the Fig. 3 (a). The sensor performance is studied for different concentration of ammonia. The sensing response (S. R.) of the sensor is calculated by the given formula [10]:

$$\text{S. R. \%} = \frac{R_{gas} - R_{air}}{R_{air}} \text{ x } 100 = \frac{\Delta R}{R}\% \qquad (1)$$

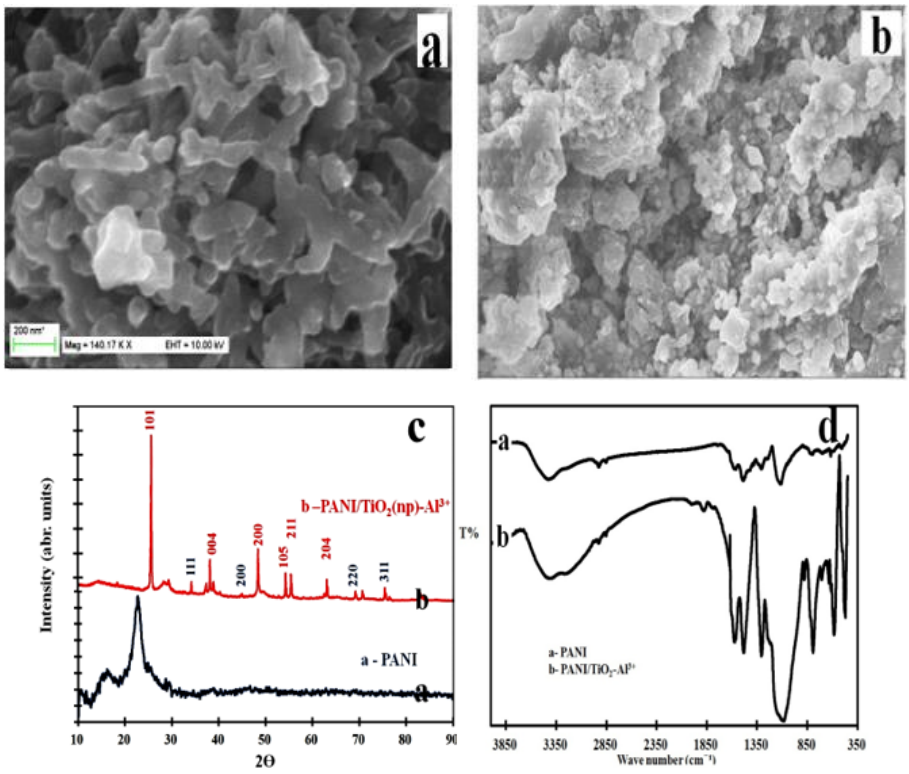

Fig. 2 (a) FESEM microgram of PANI, (b) FESEM micrograph of PANI/TiO2-Al3+, (c) XRD plot of PANI and PANI/TiO2-Al3+, (d) FTIR plot of PANI and PANI/TiO2-Al3+

Fig. 3 (b) shows the sensor response to ammonia. The sensor is exposed to 5 ppm concentration of ammonia gas and studied the sensing action. The stability of the sensor is checked for various duration of operation up to 100 days. The sensing response of the sensor is fairly constant and the sensor is recovered to the base line without heating. The sensitivity of the sensor remains unchanged from the day one to last day (100 days), the sensing response is found to be 4.25%. But we observed a slight change in the base line of the sensor.

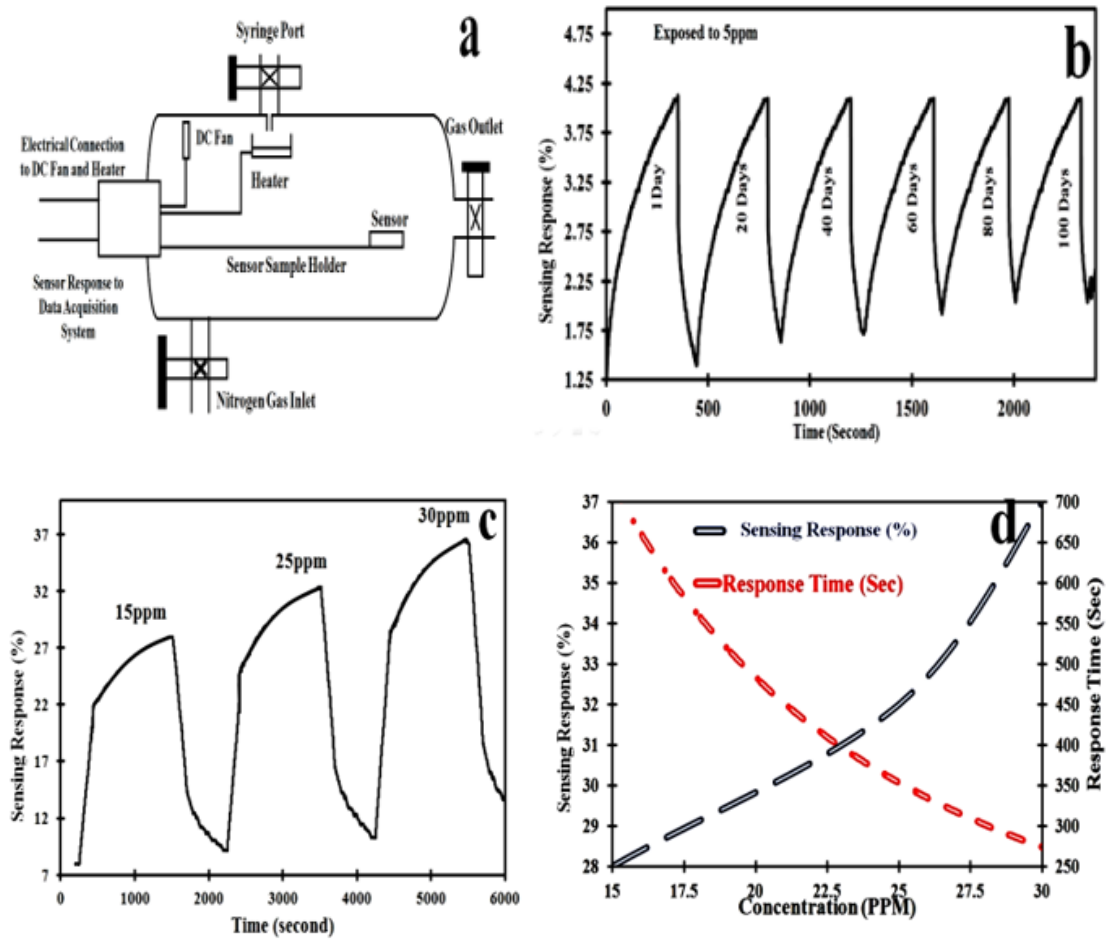

Fig. 3 (a) Gas chamber, (b), (c) sensitivity with time and (d) sensitivity, concentration and response time

Table I comparison with the reported data

Composition	Gas	Lowest Concentration (ppm)	Sensitivity (ppm^{-1})	Authors
PANI/ TiO_2-Al^{3+}	**NH_3**	**5**	**1.0913**	**Present work**
PANI-DBSA	NH_3	30	-	Yadav et al [34]

PANI/ZnO	NH_3	20	~1.2	Das et al [35]
TiO_2-SiO_2/PANI	NH_3	10	~0.12	Pang et al [36]
Cellulose/TiO2/PANI	NH_3	10	-	Pang et. al [37]
PANI/TiO_2	NH_3	23	~0.039	Tai et al [38]
PANI/TiO_2	NH_3	20	-	Pawar et al [24]
PANI/ZnO	NH_3	25	-	Talwar et al [39]

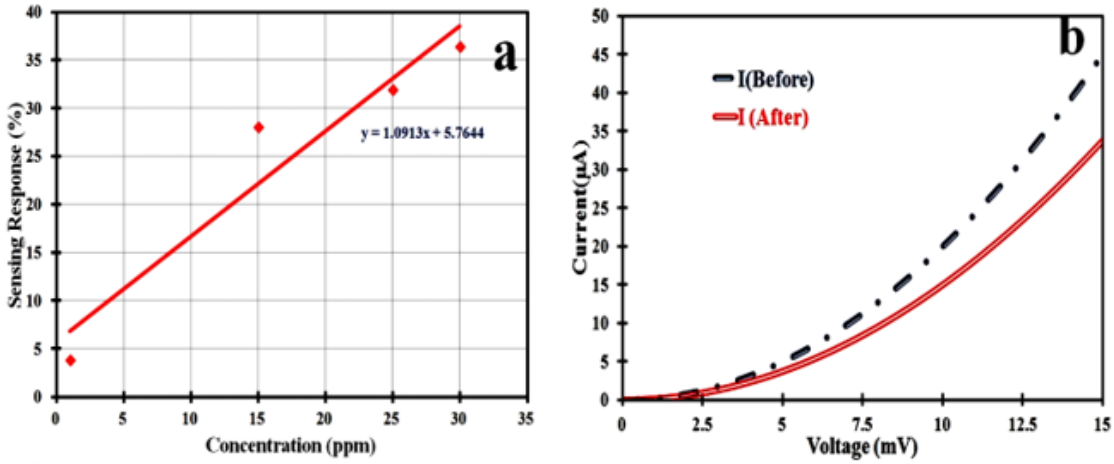

Fig. 4 I-V characteristic of the sensor before and after exposing to the gas

This changed in the base line may be due to the increase in the resistance of the sample caused by the proton donation from the ammonia molecule to the sensor (polymer nanocomposite). The sensor is exposed to different concentrations of gas from 15 ppm to 30 ppm as shown in Fig. 3 (c). After every measurement chamber is flashed with the nitrogen gas. As the concentration of the gas increases, the sensing response of sensor increases from 4.25% to 37% respectively. But the response time of the sensor decreases as the concentration of the ammonia gas increases. Fig. 3 (d) shows the graph between the sensing response and response time with the concentration.

Fig. 4 (a) shows the graph between the sensing responses with concentration, which give the sensitivity of the fabricated gas sensor. The sensitivity of a given sensor is the slope of the graph that plot between the sensing response and concentration ($\Delta R/\Delta C$). Thus the sensitivity of the fabricated sensor is found to be 1.0913 ppm-1. Fig. 4 (b) shows the change in resistance of the sensor before and after exposing to ammonia. As PANI in p-type semiconducting material when ammonia molecule came in contact with PANI, the doublet of nitrogen in ammonia looses an electron to the nitrogen of polymer. This electron transfer from ammonia to PANI/TiO2-Al3+ decreases the positive holes density as a result of which the conductance of the sensor decreases and resistance of the sensor increases. Table I shows the comparison between the previous reported work with the present work.

5. Conclusion:

The polymer nanocomposite is synthesized by the chemical polymerization of aniline with TiO2-Al3+ nanomaterials. The FESEM image shows the formation of nanoparticle is encapsulated by polymer. The XRD peaks show the formation of the crystalline structure of the nanomaterials. The sensor can detected the ammonia gas up to 5 ppm concentration. The sensing response of the sensor remained unchanged even after the operation for 100 days. The sensitivity of the sensor is 1.0913 ppm-1.

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