STUDY ON SENSITIVITY AND DYNAMIC RESPONSE OF PPY-ZNO NANOCOMPOSITES SENSOR TO SENSE NH_3 GAS

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ABSTRACT

Nanocomposites of PPy (polypyrrole)-ZnO were prepared by chemical oxidative polymerization technique using an anhydrous ferric chloride ($FeCl_3$) as an oxidizing agent. The characterization of prepared sensor was done using XRD and SEM (Scanning electron microscope) to determine the crystal size and porosity, respectively. Thick films of the sample were prepared on clean glass plate with the help of screen printing technique. Then sensors were studied by measuring resistance in air and ammonia environments at room temperature.

Sensitivity of the sensors was determined at different concentrations of ammonia gas. It was found that PZ4 sensor (80% PPy + 20 % ZnO) was best among the others as it showed maximum sensitivity at 72 ppm of NH_3 gas. Also from dynamic response, response time and recovery times were found to be 2 min and 12 min. respectively.

Keywords: *PPy- ZnO nanocomposites, sensitivity, dynamic response.*

1. Introduction

In today's environment, we face with toxic, volatile and combustible gases in the environment. Detecting these harmful gases is vital in order to control air pollution, prevent human life, and protect nature from being damaged. Ammonia is widely used in industrial process and medical diagnoses. Hence its detection is very impotent [1-6].

NH_3 sensors based on conducting polymers have shown better sensing responses among various sensors based on different materials. Polypyrrole (PPy) is one of the most stable conducting polymers under ambient conditions. It has attracted more attention as an NH_3 sensor because of its unique conducto-metric response to NH_3 [7-8].

Zinc Oxide (ZnO) has been extensively studied for various applications in sensing, acoustic wave resonator, acoustic optic modulator. The origin of various applications the lies in its crystal structure, in which the oxygen atoms and zinc atoms are tetrahedral, bonded. In such a non-Centro symmetric structure, the center of positive charge and negative charge can be displaced due to external pressure induced lattice distortion. In fact, among the tetrahedrally bonded semiconductors, ZnO has the highest wide band gap semiconductor with a band gap ~3.3 eV at room temperature which provides a large electro-mechanical coupling. This property of ZnO nanostructures was also investigated for their potential applications in nano systems [9-11].

The present study deals with the synthesis, characterization of PPy-ZnO nano-composites, sensitivity and dynamic response.

2. Experimental

A. Synthesis of ZnO Nanoparticles:

GR grade, sd-Fine, India (purity 99.99%) chemicals were used for the preparation of ZnO nanoparticles. Zinc acetate dehydrate $Zn(O_2CCH_3)_2(H_2O)_2$, sodium hydroxide, Methanol and de-ionized water was used. In the preparation of Zinc Oxide (ZnO), 0.2M Zinc Acetate dehydrates dissolved in 100 ml de-ionized water, was ground for 15 min and then mixed with 0.02 M solution of NaOH with the help of glass rod. After the mixing the solution was kept under constant magnetic stirring for 15 min. and then again it was grinded for 30 min. The white precipitate product was formed at the

bottom. Then abundant liquid was discarded and the product was washed many times with the deionized water and methanol to remove byproducts. The final product was then filtered by using Watt-man filter paper to obtain precipitate in the form of white paste. Now this paste was kept in a vacuum oven at 80°C for 4 hrs. so that the moisture will be removed from the final product and we will get dry product. Then this dry product was crushed into a fine powder by using grinding machine and finally this fine nano-powder of ZnO was calcinated at temperature 800°C for 6 hrs. in the auto controlled muffle furnace (Gayatri Scientific, Mumbai, India.) so that the impurities from product will be completely removed and got a final product of ZnO nanoparticles.

B. Synthesis of Polypyrole (PPy):

The Py monomer, anhydrous iron (III) chloride ($FeCl_3$) and methanol were used as received for synthesis of PPy. The solution of 7 ml methanol and 1.892 g $FeCl_3$ was first prepared in round bottom flask. Then 8.4 ml Py monomer was added to ($FeCl_3$ + methanol) solution with constant stirring in absence of light. The amount of Py monomer added to the solution (1/2.33 times of $FeCl_3$) was in such a way to get maximum yield. The resulting black precipitates are filtered and washed with copious amount of distilled water until the washings are clear. PPy so obtained is dried by keeping in oven at 600°C for 3 h. The synthesized material was characterized by using XRD and SEM.

C. Preparation thick films:

Synthesized nanomateirals of ZnO, and PPy were mixed with different weight percentage. The binder was prepared by using 8 wt% butyl carbitol and 92 wt% ethyl cellulose. On chemically cleaned glass plate, paste of Al_2O_3 was screen printed and it was kept for 24 hr to dry it at room temperature and then heated at 100°C for 2 hrs to remove the binder. Paste or ink of PPy+ZnO was then screen printed on Al_2O_3 layer. Again plate was dried at room temperature for 24 h and binder was removed by heating it at 130°C for 3 hrs. Finally integrated electrons (fig. 1) were made using silver paint for electrical connections (fig. 2). Sample codes are given in table 1.

Fig. (1)

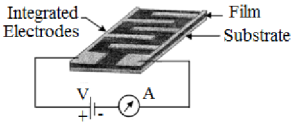

Fig. (2)

Table 1: Sample Codes

Sr. No.	Composites	Codes
1	95 % PPy + 5 % ZnO	PZ1
2	90 % PPy + 10 % ZnO	PZ2
3	85 % PPy + 15 % ZnO	PZ3
4	80 % PPy + 20 % ZnO	PZ4
5	75 % PPy + 25 % ZnO	PZ5
6	70 % PPy + 30 % ZnO	PZ6

3. Result and Discussion

A. XRD (X-Ray Diffraction):

XRD patterns of all the composites of PPy and ZnO are as shown in Fig. 3.

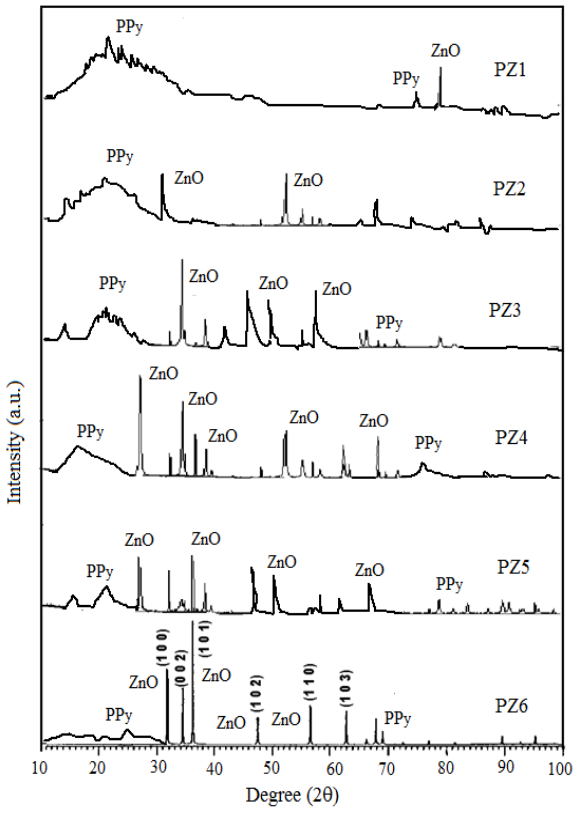

Fig. 3: XRD of PPy and ZnO composites

XRD pattern of PPy manifested amorphous nature of PPy. At 27° broad peak occurred which is the characteristics of amorphous nature of polypyrrole. Occurrence of this broad peak is due to the scattering of X-Rays from polymer chains at the interplaner spacing. The maximum intensity position of amorphous also depends on monomer to oxidant ratio [12]. The average grain size, determined from XRD pattern using Scherrer formula is about 87 nm [13]. The main diffraction peaks for the ZnO, which are located at 2θ = 31.4°; 34.2°; 36.7°; 47.6; 56.1°; 63.4° and correspond to Bragg reflections (100), (002), (101), (102), (110), (103), respectively, allowed us to identify a hexagonal wurzita type structure (a = 3. 25 Å and c = 5.21 Å) for ZnO. These peaks are in agreement with the data obtained for ZnO [14]. From XRD pattern of composites, it is observed that average crystallite size of PZ4 sensor (80%PPy + 20%ZnO composition) is least (82 nm) as compared to other compositions and hence PZ4 sensor has large active area which tends to increase the sensitivity of PZ4 sample.

B. SEM Analysis:

The surface morphology of composites of PPy and ZnO materials were studied by SEM and its pictures are shown in the following figures.

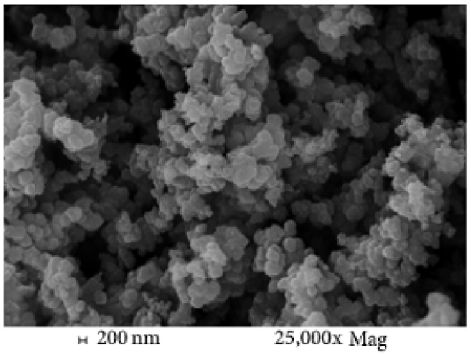

Fig. 4: SEM of PZ1 (95 % PPy + 5 % ZnO)

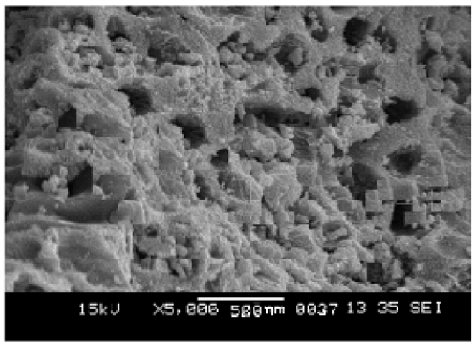

Fig. 5: SEM of PZ2 (90 % PPy + 10 % ZnO)

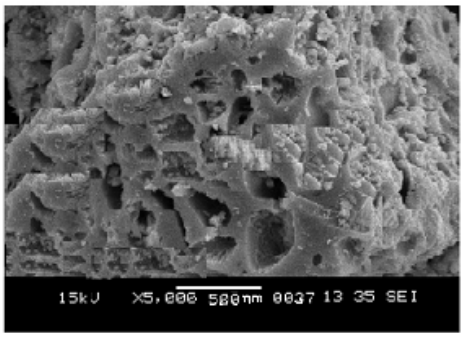

Fig. 6: SEM of PZ3 (85 % PPy + 15 % ZnO)

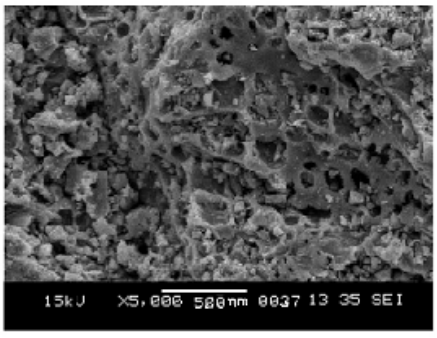

Fig. 7: SEM of PZ4 (80 % PPy + 20 % ZnO)

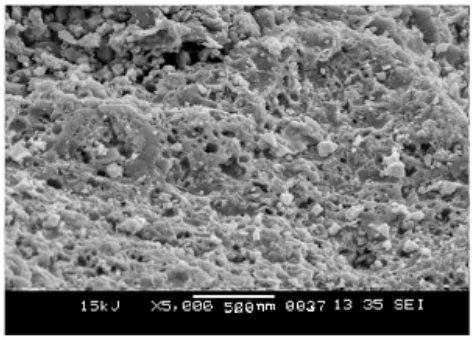

Fig. 8: SEM of PZ5 (75 % PPy + 25 % ZnO)

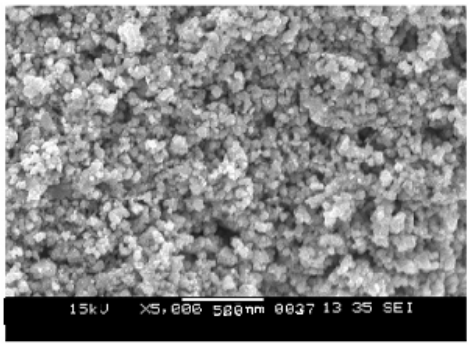

Fig. 9: SEM of PZ6 (70 % PPy + 30 % ZnO)

From the SEM photos, it is observed that in every inch of the region, number of pores was different and an average numbers of pores were taken for comparative study. From every photo, porosity was calculated for one inch square area. From figures, it is found that porosity of PZ4 sample is more among the samples. Due to high porosity, surface area increases and hence it tends to more response of the gas.

C. Sensitivity Measurement:

The sensitivity is expressed by the formula:

$$S = \frac{\text{Change in resistance}}{\text{Original resistance}} = \frac{R_{gas} - R_{air}}{R_{air}}$$

Where,

R_{gas} = Resistance of the sensor in presence of NH_3 gas environment and
R_{air} = Resistance of the sensor in presence of air.

When PPy is exposed to electron donating gases like NH_3, a redox reaction occurs and its effective number of charge carrier decreases, thus reducing its conductance i.e. resistance increases during NH_3 exposure, indicating a p-type-like gas sensing behavior [15]. PPy-ZnO sensors exhibit good dependence on NH_3 gas concentration up to 80 ppm, where it reaches a saturation level at room temperature (300K). By keeping surface area fixed, a lower gas concentration implies a lower coverage of gas molecules on the surface. An increase in the gas concentration raises the surface coverage eventually leading to saturation level and thus determining the upper limit of detection. Amongst the prepared sensors, PZ4 sensor showed more sensitivity as 20 % of ZnO mixed with 80 % of PPy produces more porosity (Fig. 7) and hence enhanced surface area thereby increasing gas sensitivity. The variation of sensitivity with NH_3 gas concentration is shown in the figure 10.

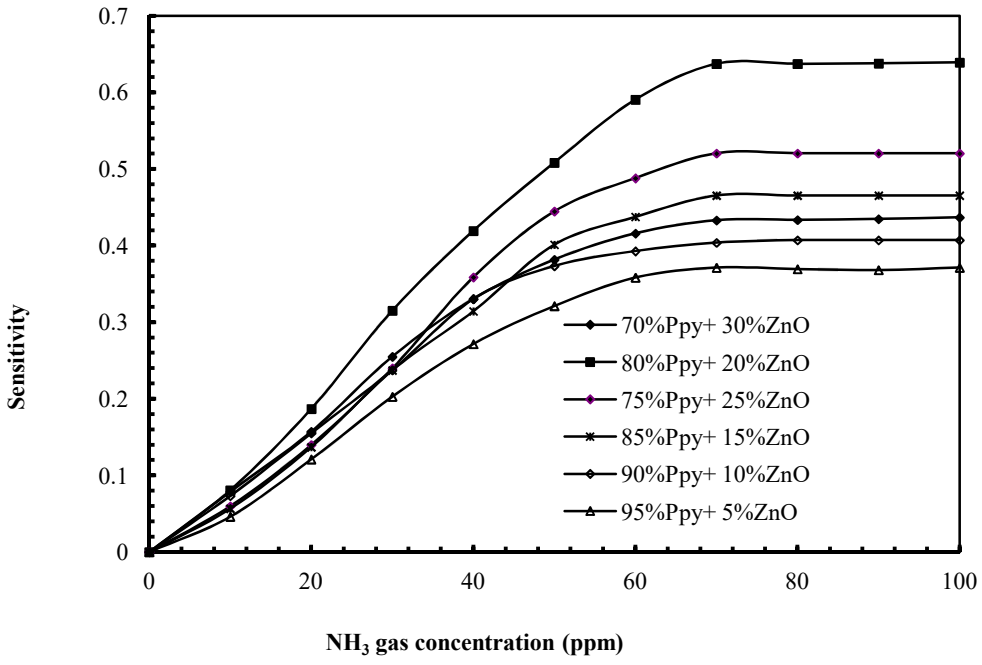

Fig. 10: Variation of sensitivity with concentration of NH_3 gas for different sensors

D. Dynamic Response:

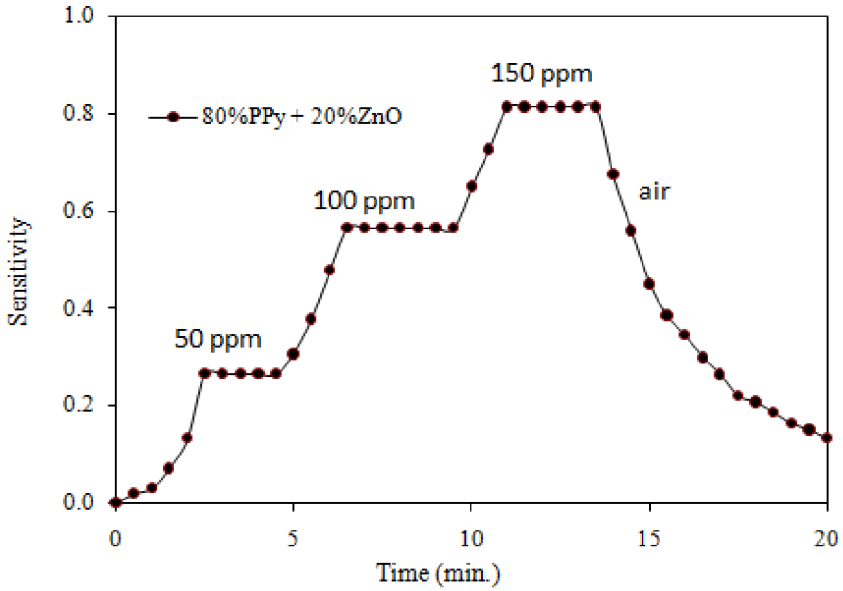

Fig. 11: Dynamic response of PZ4 sensor for 50, 100, 150 ppm of NH_3 gas

Figure 11 shows the dynamic response of PZ4 (80%PPy + 20%ZnO) sensor for 50, 100, 150 ppm of NH_3 gas at room temperature (300 K). Time required to attain 90 % of maximum resistance change due to exposure of gas. The recovery time is defined as the time taken to reach 90% of the recovery when gas is turned off. Response time was found to be about 2 min and recovery time was found to be nearly 12 min. This shows that PZ4 sensor is fast i.e. it shows quick response but slow in recovery.

The gas sensing mechanism for the prepared sensors may be explained on the basis of interactions between the sensing film and adsorbed gas. It has been proposed that NH_3 can adsorb and donate a lone pair of its electrons to PPy. Electrons will recombine with existing holes in the p-type PPy, leading to a resistance increase in agreement with the observed NH_3 response. By adding unloaded ZnO nanoparticles (ZnO NPs), the response is enhanced. This could reasonably be explained by interaction of gas with increased specific area of ZnO nanoparticles. From the SEM image, ZnO NPs addition results in considerable increase of film porosity and hence the surface area.

4. Conclusion

Porosity of PZ4 sample was found to be more and its average crystalline size was found to be 82 nm, from XRD pattern. PZ4 sensor showed more sensitivity (about 0.68) at 72 ppm concentration of NH_3 gas among the remaining sensor. From dynamic response, response time and recovery times were found to be 2 min and 12 min. respectively. It manifested that PZ4 sensor is fast in action.

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