

Fabrication of a Novel Flexible Room Temperature Hydrogen Sulfide (H₂S) Gas Sensor based on Polypyrrole Films

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Abstract: Polypyrrole (PPy) was synthesized by chemical oxidative polymerization technique using Ferric Chloride (FeCl₃) as an oxidant and Pyrrole as a monomer. The ratio of oxidant to monomer was 2.5:1. The polymerization was carried out at ~ 5 °C. The materials were characterized by using SEM, FTIR and XRD. The electrical conductivity was measured by two probe method and was found to be 1.389×10^{-2} S/cm at room temperature. H₂S gas sensor was fabricated by casting thin films of Polypyrrole on the integrated electrodes, at room temperature. Sensing experiments were performed on these films with the injection of 10 ppm to 100 ppm level H₂S at room temperature. The response and recovery time were obtained. It was found that, response time decreased from 64 sec to 13 sec as the concentration of H₂S increased from 10 ppm to 100 ppm, while the recovery time increased from 192 sec to 644 sec. The possible response mechanism is discussed.

Keywords: Polypyrrole, Chemical polymerization, SEM, FTIR, XRD, Electrical conductivity, Room temperature H₂S sensor.

1. Introduction

A variety of toxic gases, that can be harmful to humans, have been found in nature, for example, Hydrogen sulfide (H₂S), Nitrogen dioxide (NO₂), Carbon monoxide (CO), Ammonia (NH₃). Hydrogen Sulfide (H₂S) is a toxic and irritating gas. Exposure to low concentrations may cause headache, dizziness and affect human nervous system. High concentrations (higher than 250 ppm) may lead to death [1]. It is released from mines, petroleum fields and natural gas production. Also, it can be produced by the breakdown of organic matter and human or animal waste. H₂S gas detection is of great importance in many fields such as commercial gas and oil exploration, auto ventilation units, and the medical field of dentistry [2]. Its threshold limit value (TLV) is 15 ppm and hence, detection at low or sub-ppm concentrations, has become the focus of research [3].

Gas sensor is a device that detects the presence of toxic or harmful gases in an area. Most of the gas sensors available in the market are inorganic metal oxide semiconductor-based sensors. Sensors based on metal oxides such as ZnO, Fe₂O₃, SnO₂, WO₃ have been studied due to long term stability and simple preparation [4]. There are few disadvantages of metal oxide sensors such as lack of selectivity and they can be operated only at high temperature from 200 to 500°C, to ensure their sensitivity [5],[6]. Therefore, a room-temperature gas sensor is needed.

Conducting polymers such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh) polyacetylene (PAC) and their derivatives have been used as active layers for gas sensors. [7],[8]. The most important advantage of these conducting polymer sensors is their room temperature operation, low cost, flexibility and high sensitivity [8]. PPy, one of the most stable conducting polymers, has been extensively studied in

gas sensing area [9], [10]. PPy is unique among the family of conducting polymers because it has a high level of electrical conductivity with environmental stability and is an extremely useful material for gas-sensing applications [11]. PPy has been reported for sensing of hydrogen sulfide (H₂S), ammonia (NH₃) and nitrogen dioxide (NO₂) successfully. [12],[13].

In this communication, we present the chemical synthesis of PPy using Ferric Chloride (FeCl₃) as an oxidant. The structure and surface morphology of the PPy powder have been analyzed by SEM, FTIR and XRD respectively. We have also measured dc conductivity behaviour as a function of temperature using two probe method. Polypyrrole films fabricated on interdigitated electrode (IDE) has shown good responses to low H₂S concentrations (10–100 ppm) with operating at room temperature. We have determined the response time, the recovery time and repeatability of the response. The obtained experimental results provide a possible method for H₂S gas room temperature operative sensor.

2. Experimental Technique

2.1 Materials

Pyrrole was obtained from Spectrochem Pvt. Ltd, Mumbai and was double distilled before use. Ferric chloride anhydrous and m-cresol were procured from S. D. Fine Chem. Ltd., Mumbai. These chemicals were of AR grade and were used as received. H₂S gas canister was purchased from Chemtron Science Lab. Pvt. Ltd. Mumbai

2.2 Synthesis of Polypyrrole

Polypyrrole (PPy) was synthesized by chemical oxidative

polymerization technique. 1M Pyrrole solution was prepared by using distilled water. This mixture was then cooled at $\sim 5^{\circ}\text{C}$ in an ice bath and stirred on a magnetic stirrer for 30 minutes. 1M solution of FeCl_3 (oxidizing agent), was prepared using distilled water, precooled and then added drop wise to the pyrrole solution. The oxidant to monomer ratio 2.5:1 was maintained. Then the polymerization was conducted for 5 hours under constant stirring. This mixture was allowed to settle for 24 hours to ensure complete polymerization. The polypyrrole powder was filtered under reduced pressure and washed with distilled water several times to remove the unreacted monomer, oxidant and ferric or ferrous contamination and was dried under vacuum at room temperature.

2.3 Fabrication of H_2S sensor

The sensor consisting of an Inter Digitated Electrode (IDE) with a layer of PPy coated on top was fabricated. The IDE consisted of five pairs of Cu tracks screen-printed onto an epoxy glass substrate. The width of a Cu track and the gap between two successive tracks were 1 mm each. The size of the entire device was $30\text{ mm} \times 20\text{ mm}$ [14]. Polypyrrole powder was dissolved in m-cresol and stirred for 24 hours to get the casting solution. The paste was then brush-coated on the IDE epoxy glass substrates to form films. Films were dried at 35°C for 24 hours and used to evaluate the H_2S sensing characteristics. The schematic diagram of a fabricated H_2S sensor is shown in Fig. 1.

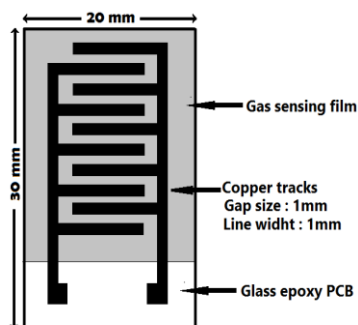


Figure 1: Structure of fabricated H_2S sensor

2.4 Instruments and Analysis

The morphological examination of polypyrrole was carried out using scanning electron microscope (SEM) (JEOL, JSM-5400) at accelerating voltage 20kV. Chemical structure was examined by FTIR spectroscopy (Perkin-Elmer Ltd. system 2000), in the $600\text{--}4000\text{ cm}^{-1}$ range. The polypyrrole was characterized by XRD using Panalytical X'Pert (Philips). The XRD patterns were recorded between $2\theta = 10^{\circ}$ to 80° . The fine powder of polypyrrole was pressed into pellet (diameter 10 mm and thickness 0.8 mm) at 7 ton/cm^2 pressure. The pellets were then coated with silver paint and dried at 35°C before taking any electrical measurement. The electrical conductivity was measured by two probe method, in the temperature range of 303K to 343K.

2.5 Gas sensing measurements

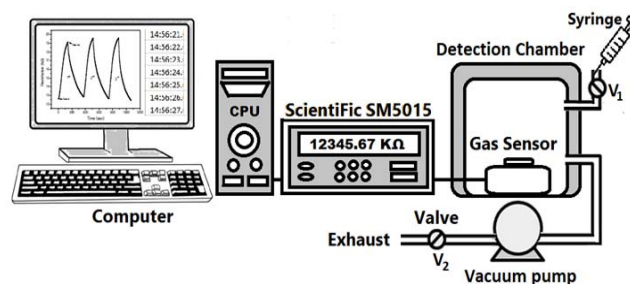


Figure 2: Measurement System for testing H_2S gas sensor

For measuring the gas response, specially prepared gas chamber (1000 cm^3) was used. An IDE sensor was fixed inside the gas chamber. The schematic diagram of a typical gas sensing unit is shown in Fig. 2. Measured quantity of H_2S gas (from a canister of 1000 ppm concentration) was injected through syringe so as to yield desired gas concentration in the chamber. The resistance was measured by using Scientific Programmable $4\frac{1}{2}$ digit Digital Multimeter (SM5015). Once steady state was achieved, recovery of sensor was recorded by exposing the sensor to air. This was done by opening both the valves V_1 and V_2 of the chamber simultaneously. At the same time, the vacuum pump was switched on. Valve V_1 allowed fresh air to enter into the chamber while valve V_2 allowed the gas to exit the chamber. The vacuum pump accelerated the process of degassing. All the gas sensitivity measurements were carried out at room temperature.

3. Results and Discussion

3.1 SEM Analysis

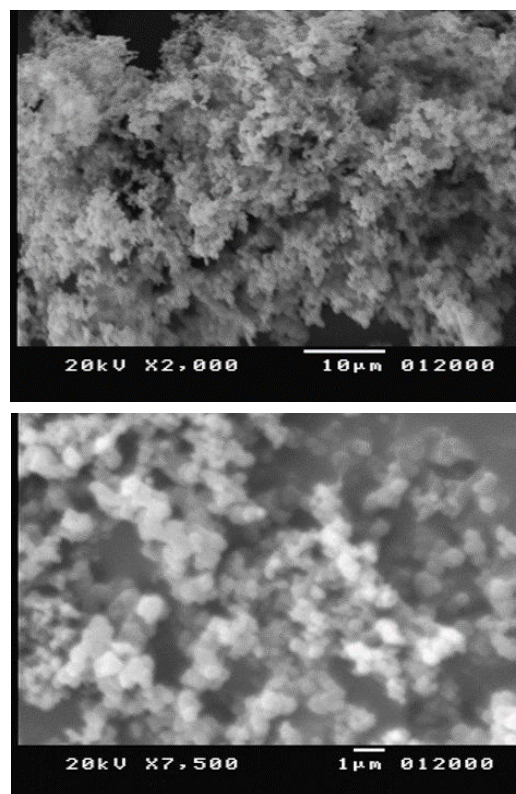


Figure 3: SEM images of PPy

The microstructure of polypyrrole is shown in Fig 3. It has uniform globular structure and the average size of the globules is found to be ~ 0.6 μm [15],[16]. The uniform globular morphology is suitable for gas sensing applications and it promotes absorption of gas molecules [17],[18].

3.2 FTIR Analysis

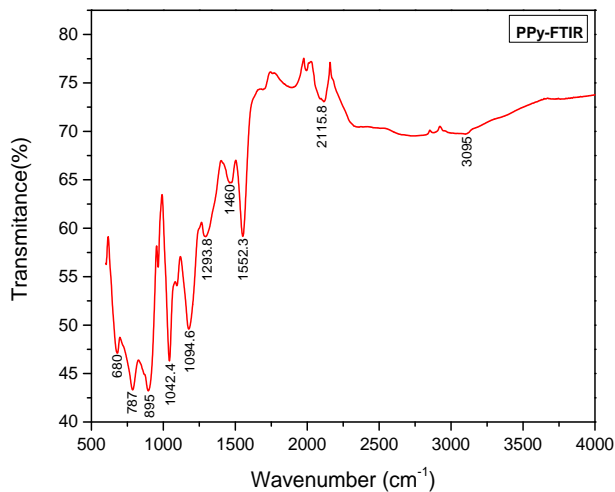


Figure 4: FTIR Spectrum of PPY

The FTIR spectra of the synthesized polypyrrole powder was recorded in the range 600–4000 cm⁻¹ which is shown in Fig. 4. FTIR spectra showed the main characteristic peak at 680 cm⁻¹ corresponding to C–H wagging [19]. Peaks around 725–1110 cm⁻¹ represent the C–H in plane and C–H out plane deformation in polypyrrole units [17]. The characteristic peak for polypyrrole is observed at 1460cm⁻¹ and 1552.3 cm⁻¹ attributed to vibration of pyrrole ring. Peak at 1293.8 cm⁻¹ corresponds to C-H deformation [16]. The broad peak in range of 3400–3500 cm⁻¹, especially the small peak at 3095 cm⁻¹ was ascribed to stretching of N–H and C–H bonds [19], [20]. The peaks observed in the present work were in agreement with the reported literature, confirming the formation of polypyrrole.

3.3 XRD analysis

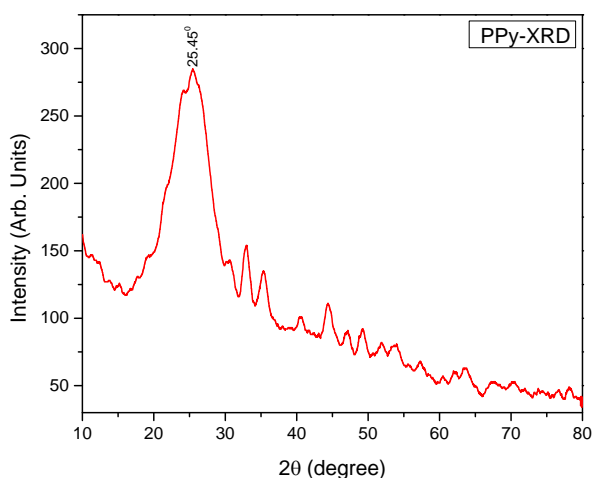


Figure 5: XRD pattern of PPY

The XRD patterns of the polypyrrole powder are shown in Fig.5. The broad peak was observed at $2\theta = 25.45^\circ$. This peak was characteristic of amorphous nature [21] and indicated short range arrangement chains of polypyrrole [22]. The average crystallite size for polypyrrole from a sharp peak at 25.45° was estimated by using the Scherrer's formula,

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

where D is the average size of the crystallite, λ is the wavelength of the X-ray radiation, β is the peak full line width at half of maximum (FWHM) in radian and θ is the diffraction peak position [18].

The value of d-spacing for polypyrrole powder was found 3.4970 \AA , and it corresponded to (0 2 1) plane value [23], [24], [25].

3.4 Conductivity Measurement

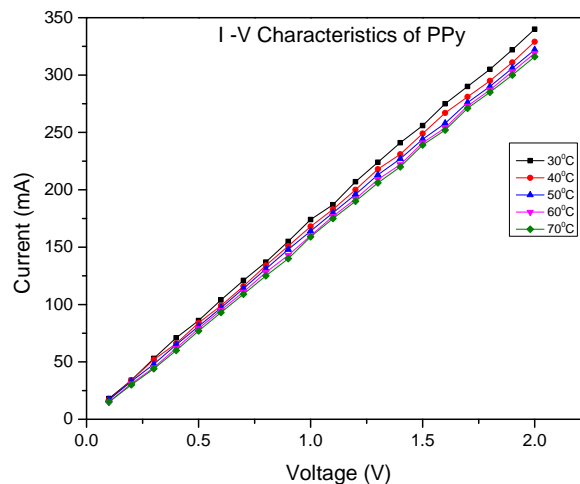


Figure 6: I-V Characteristics of PPY at different temperatures

In order to determine the current conduction mechanism in polypyrrole, temperature dependence of electrical conductivity was studied in the temperature range of 303K to 343K. Plots of I vs. V for polypyrrole are as shown in Fig. 6. Linear relationship of the I-V curve was found. The electrical conductivity of polypyrrole was found to be $1.389 \times 10^{-2} \text{ S/cm}$ at room temperature (303K). The mechanism of conduction was supported by polarons and bipolarons formation due to the dopant molecules [16]. The electrical conductivity behavior can be explained using Arrhenius Model and Mott's Variable Range Hopping (VRH) Model [25],[26].

3.5 Gas Sensing Performance

The response of the sensor (S) is given by

$$S \% = \frac{R_{air} - R_{gas}}{R_{air}} \times 100\% = \frac{\Delta R}{R_{air}} \times 100\%$$

where R_{gas} and R_{air} are the electrical resistances of the sensor in H₂S gas and air respectively.

Response time is the time taken for the sensor to attain 90% of maximum change in resistance on exposure to gas. Recovery time is the time taken by the sensor to get back 90% of the original resistance. The gas sensing studies were carried out for H₂S gas at room temperature.

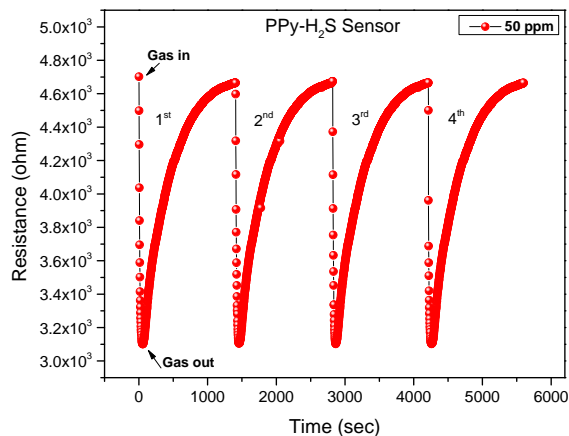


Figure 7: Repetitive response of PPy sensor to 50 ppm of NO₂ gas

When the sensor was exposed to 50 ppm H₂S gas, it was found that there was sudden drop in the resistance. The graphical response in respect to time is as shown in Fig.7. It was seen that the drop in resistance was about 1.6 kΩ and this change took place in less than 30 sec. When the gas was desorbed, the resistance started increasing again and reached its steady value of approx. 4.7 kΩ in about 670 sec. Fig 7 also shows the cyclic behaviour of the sensor, when the gas is in (absorbed) and when the gas is out (desorbed).

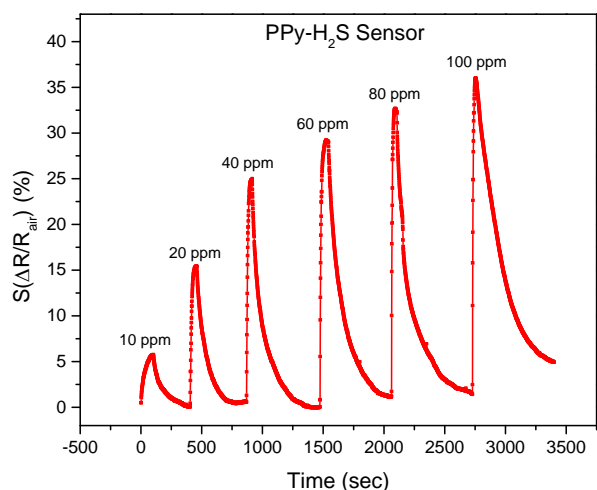


Figure 8: Response of PPy sensor for various concentrations of H₂S

To determine the sensitivity of the sensor, in the test chamber, H₂S gas concentration was varied from 10 ppm to 100 ppm. The response obtained in terms of sensitivity is shown in Fig.8. Change in resistance (conductivity) was detected on interaction of PPy with hydrogen sulfide gas. Recovery of the original state back on exposure to air was also observed. The whole process of reversible reactions may be represented by the following possible mechanism [27].

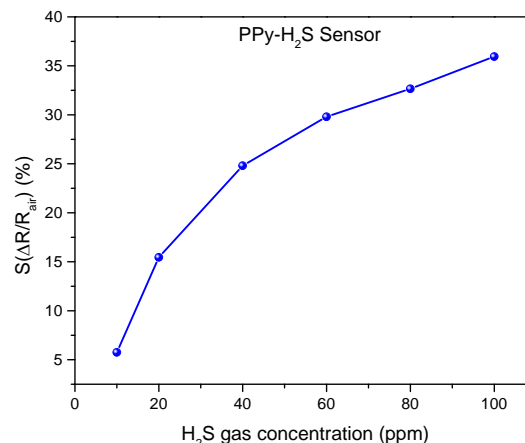
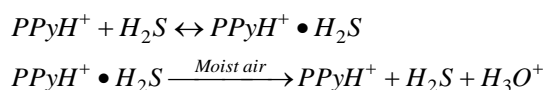


Figure 9: Sensor response as a function of H₂S concentration

The response of the sensor to 10 - 100 ppm H₂S gas was investigated. The results are shown in Fig. 9. It was observed that the response values increased continuously with increase in gas concentration, upto 100 ppm and then tended to saturation. The result signified that the sensor can be used in the range 10 –100 ppm.

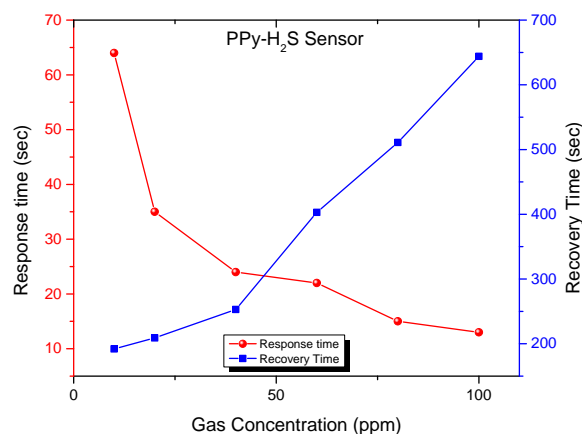


Figure 10: Response and recovery times of PPy sensor for various concentrations of H₂S gas

The response and recovery time are important parameters for a sensor. Fig. 10 shows the response and recovery time of PPy sensor. It was found that, the response time decreased from 64 sec to 13 sec as the concentration of H₂S increased from 10 ppm to 100 ppm, while the recovery time increased from 192 sec to 644 sec. This may be due to products of PPy reaction with H₂S left behind after the gas interaction, resulting in decrease in desorption rate and therefore increase in the recovery time with increasing concentration of H₂S [19].

4. Conclusion

The bulk samples of PPy conducting polymer were successfully prepared by chemical polymerization technique. The globular structure of PPy was confirmed by SEM and the average size of globules was found ~ 0.6μm. The structure of PPy was confirmed by using FTIR and XRD investigation. The electrical conductivity was measured by two probe

method and was found to 1.389×10^{-2} S/cm at room temperature. H₂S gas sensor based on PPy thin film was successfully fabricated on an IDE-epoxy glass substrate. The sensor was found to be highly sensitive to H₂S gas operating at room temperature. Excellent repeatability, fast response and recovery behavior are achieved.

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