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Synthesis and Characterization of Nanocrystalline Polypyrrole by *in situ* polymerization technique for NH_3 Gas Sensor

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Abstract: *Polypyrrole (PPy) nano composites were synthesized by in situ polymerization technique and characterized by Fourier transform infrared spectra (FTIR), Field Emission Gun Scanning Electron Microscopy (FEG-SEM). The synthesized materials were further used for sensing of NH_3 gas. The change in resistance of the material with time was recorded after the response of NH_3 gas. The increase in electrical resistance is due to transfer of charge from the sensing material to the analyzed gas and absorption of gas into the polymer matrix. The sensitivity was found maximum for NH_3. The PPy nano composite showed maximum sensitivity (48 %) for 400 ppm of NH_3 gas.*

Keywords: *Conductive polymer, NH_3 gas sensor, Time response.*

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I. Introduction

With the discovery in 1960 of intrinsically conducting polymers (ICPs), an attractive subject of research was initiated because of the interesting properties and numerous application possibilities of ICPs. It was expected that ICPs would find their potential applications in multidisciplinary areas such as electrical, electronics, thermoelectric, electrochemical, electromagnetic, electromechanical, electro-luminescence, electro-rheological, chemical, membrane, and sensors [1–4]. However, many of the potential uses for ICPs have yet to be explored because of a number of obstacles that need to be overcome. Among the available ICPs, polypyrrole is found to be the most promising because of its ease of synthesis, low cost monomer, tunable properties, and better stability compared to other ICPs. Hence, we have carried out extensive studies on the synthesis, characterization and application of PPy and its composites [5–20]. However, the main problem associated with the effective utilization of all ICPs including PPy is inherent in their lower level of conductivity compared to metal, and their infusibility and poor solubility in all available solvents [21, 22]. However, the solubility of some ICPs can be improved through doping with a suitable dopant or modifying the starting monomer [6, 11]. Therefore, there is ample scope for modifying the conductivity and processability of PPy through the selection of a suitable dopant and suitable level of doping and also by controlling its structure during synthesis [5, 6]. Another avenue for the successful utilization of PPy is through blending it with a commercially available polymer that has good processability and mechanical properties. Polymer composites containing PPy, where it is used as conducting filler in other polymers (matrixes), have received much attention because of the combination of improved processability and fairly good mechanical properties coupled with good conductivity. Consequently, there is a wider scope for the practical applications of such composites [15–23].

In the present context, the synthesized PPy nano composites were characterized with FTIR, FESEM and electrical conductivity studies. In addition to these, the sensing parameters were studied for various gases like LPG, NH_3, CO_2 and H_2S gas.

II. Experimental Details

Fig. 1 is a schematic representation of synthesis of polymer nanocomposites, in this work, synthesis of polymer nanocomposites was done by *in situ* polymerization. The monomer was dissolved in 1 M HCl [used as a protonic acid] and stirred for 10 minutes to get monomer hydrochloride. To this solution, 0.1 M of Ammonium persulphate (which acts as oxidant was added drop wise with continuous starring for 1 hr at 0-5^{0}C to polymerize. This reaction mixture was stirred for 3 hr at 0-5 ^{0}C with magnetic stirrer. The suspension was left for 20 Hr for polymerization. Finally, the suspension was filtered and washed with distilled water repeatedly and dried under vacuum at 60^{0}C for 8 hr. The obtained nanocomposites were crushed into fine powder in an agate mortar.

The pellets of 13 mm diameter were formed with thickness varying 1.5 to 2 mm by applying a pressure 8 tons using pellet maker. For sensor studies, the copper electrodes were placed on each of the surface of pellets to obtain a better ohmic contact.

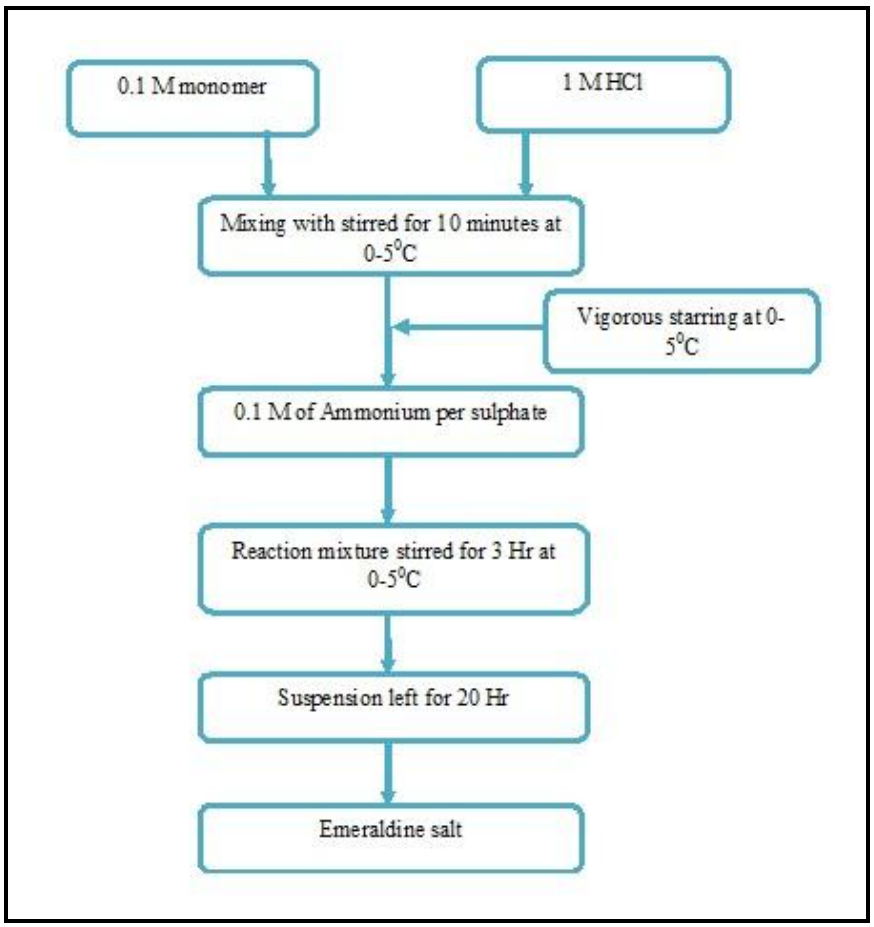

Fig. 1: Flow chart for the synthesis of polymer by *in situ* polymerization method.

2.1 Characterization

Nova Nano FEG-SEM 450 with EDAX (Mapping System) facility was used to study sample size, shape, surface features at nano scale level along with elemental analysis. For measurement of voltage, current and resistance of pellets, a programmable 4½ Digital multimeter SM5015 along with homemade gas sensing unit were used. The suspension was dried in vacuum at 60^{0}C in homemade oven.

2.2 FTIR analysis

Fig 2 shows the FTIR spectra of PPy powder. The peaks at 790 cm^{-1}, 921 cm^{-1} are attributed to C–H wagging. The characteristic peaks at 1549.95 cm^{-1} and 1469.55 cm^{-1} correspond to the C = C stretching, whereas peaks at 1631.60 cm^{-1} and 1302.46 cm^{-1} represent to respectively, C = N and C – N bonds. The occurrence of small peaks at 3432.66 cm^{-1} is assigned to presence of N – H stretching vibrations. All these peaks are the main characteristic of PPy [24-26].

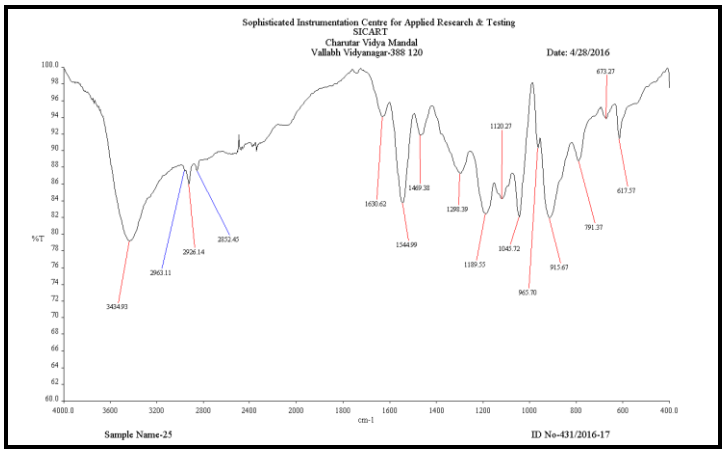

Fig 2: FTIR spectra pure PPy

The microstructure of a PPy thin film is shown in Figure 3. The film has a uniform granular morphology and the average grain size is ~ 0.5 µm. One can clearly observe that the fiber is chemically coated by the spherical nanostructures [27]. A higher porosity usually led to a better response owing to a higher rate of gas absorption.

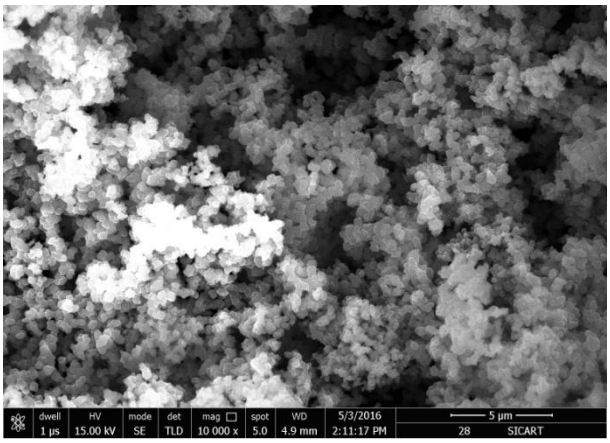

Fig. 3: SEM of pure PPy

2.3 Electrical Conductivity Measurement

An electrical resistance of the pellets was measured at room temperature using the four-point probe technique. The conductivity σ of the pellet is given by,

$$\sigma = \frac{1}{\left[\left(\pi/\ln 2\right) x\ R\ x\ d\right]} \quad \ldots\ldots\ldots\ldots (1)$$

Where, R is the sheet resistance and d is the thickness of the pellet.

Fig. 4 shows the variation of current with different voltages which was measured by using the four point probe technique; Model Keithley. The conductivity σ of the pellet was calculated by using the above equation. In oxidative method, the conductivity of the prepared CdO - PPy nano composites pellets is 0.471459 S/cm.

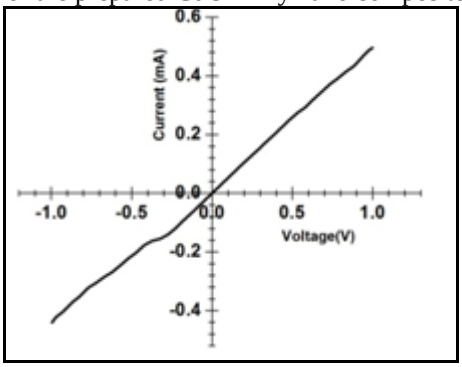

Figure 4: I - V characteristic of PPy

2.4 Sensor Response towards Ammonia

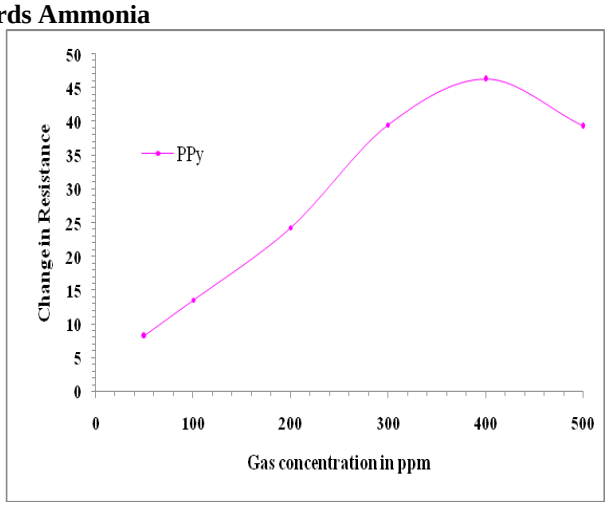

Figure 5: Sensitivity for various test gases at 400 ppm of NH_3 gas

Fig. 5 shows the change in electrical resistance with concentration of NH_3 in parts per million at constant volume of pure PPy at room temperature (27^0C).

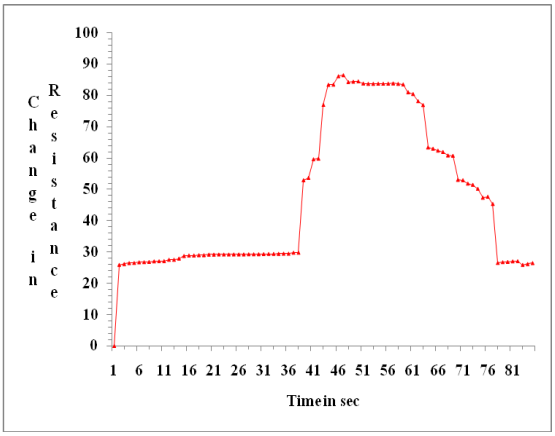

Figure 6: Recovery and response time of PPy

Fig. 6 shows the sensitivity against time for PPy nano composites. It is observed that, the sensitivity lies at 48%. The response time is 39 sec and recovery time 43 sec for PPy. The change in the resistance may be due to the adsorption of gas on the surface of the sensing materials which increases the size of the sensing layer. The increase in volume causes an increase in resistance which disturbs the conductive pathway through the material. When the gas is desorbed the polymer returns to its original size, restoring the conductive pathways. Thus electrical resistance increases with increase in the concentration of gas.

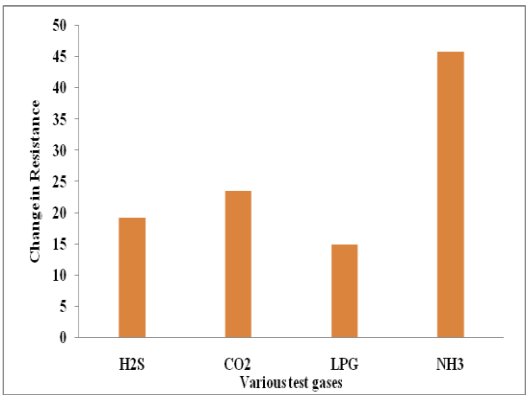

Figure 7: **Variation of sensitivity for various gases test gases**

Fig. 7 shows the variation of sensitivity of the PPy nano composites for various gases such as H_2S, CO_2, LPG and NH_3. It is observed that the 50% CdO / PPy nano composites showed 24% response for CO_2 gas, 18% for LPG, 48% for NH_3 whereas 21% for H_2S gas. The maximum response for NH_3 gas may be due to interaction in PPy nanoparticles with NH_3 and also due to their oxidizing nature. Hence it is one of the promising NH_3 sensing materials for device fabrication.

III. Conclusion

In this present paper, we have fabricated a PPy nano composites gas sensor. The nano composites were synthesized by *in situ* polymerization. In case of PPy nano composites, it is due to both the PPy sensing mechanism of swelling and sensing mechanism of surface charge that are responsible for variation of resistance with increase in concentration of gas within the sensing material. The minimum concentration of NH_3 that can be determined is 50 ppm. The high sensitivity of about 48 is obtained for 400ppm of NH_3 at room temperature.

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