# Preparation and $CO_2$ Gas sensing behavior of Polypyrrole Thick Film Sensor

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***Abstract:*** In the present work, Polypyrrole (PPy) was synthesized by chemical oxidative polymerization route, using monomer pyrrole (Py) and ammonium persulfate (APS) as an oxidant. The screen printing technique was adopted for preparation of the polypyrrole thick film gas sensor. The structural properties of polypyrrole (PPy) were investigated by X-ray diffraction (XRD). Fourier transform infrared spectroscopy (FTIR) confirm the formation of PPy The polymer chain separation value of as-synthesized PPy sample was found to be 5.07 Å. The sensing response of as-prepared thick film was determined by two probe method. Sensor showed linear variation of the response value with $CO_2$ concentration but a saturation effect was observed at higher concentrations. The optimum value $CO_2$ sensing for PPy was found to be 0.055.

***Keywords:*** *Carbon dioxide, Polypyrrole, Oxidative polymerization.*

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## 1. INTRODUCTION

From last decade polypyrrole (PPy) is mostly used for commercial purpose or used in industry, due to their high conductivity, good environmental stability, high flexibility in preparation and good mechanical properties. PPy is mostly used as a light-weight batteries [1], gas sensors [2-4], solid electrolytic capacitors [5], electronic and electro chromic devices [6-8]. In recent years, PPy have attracted a great deal of attentions due to its efficient gas sensing ability, high yield in redox process and optimum performance at room temperature.

Dallolio et al and its co-workers synthesized PPy thin film with the help of dilute sulfuric acid by electrochemical polymerization method [9]. The PPy composite has been prepared by vapor state polymerization method. Ojjo et al in 1996, suggested gas state polymerization method for preparation of highly transparent and electrically conducted PPy/PVA composite thin film [10].

In the present work, the conducting PPy thick film is synthesized by chemical oxidation of pyrrole monomer with ammonium persulfate (APS) in aqueous media, by mixing a solution of pyrrole with an oxidizing solution of ammonium persulfate using molecular weight ratio. The as-synthesized PPy powder is deposited on glass substrate by screen printing method. The change in electrical resistance has been determined by two probe method. Sensing response is studied at room temperature (303K) for different concentration of $CO_2$ gas. The properties of polypyrrole thick film are investigated by X-ray diffraction (XRD) and FTIR spectroscopy.

## 2. EXPERIMENTAL

The chemical oxidative polymerization route was adopted for the synthesis of polypyrrole (PPy). The analytical grade monomer pyrrole (Py) from SD fine ($C_4H_5N$, M.W. 67.09) and oxidizing agent ammonium per-sulfate APS ($(NH_4)_2S_2O_8$ M=228.19g/mol) E-merc, Germany both were used without further purification. First 10 ml aqueous solution of 2.28 gm ammonium per-sulfate (APS) was prepared in round bottom flask. It is observed that in polymerization reaction, as the monomer pyrrole (Py) 0.6 ml was added to aqueous solution of ammonium per-sulfate (APS), the colour changed instantly and the solution became dark greenish black. During polymerization, temperature of solution increased rapidly, this indicated that the reaction was exothermic type. Maximum yield was obtained after termination of polymerization process. This reaction was carried out at room temperature (303 K) and the precipitate polymer was filtered by vacuum filtration using cellulose nitrate filter papers. The polymer was washed successively three times with distilled water. Subsequent to this step, the obtained powder dried first at room temperature for 12 h at 45°C. PPy thick film was deposited on pre cleaned glass substrate, using screen printing method. The highly conducting silver electrodes were deposited on the adjacent side of film with the help of conducting silver paint, for measurement of surface resistance. Two probe method was used to investigate change in surface resistance in the presence of $CO_2$ gas. In this study sensing response of $CO_2$ gas was examined at room temperature (303K) for varying concentration of $CO_2$ gas. The chemical structure of as-synthesized polypyrrole (PPy) was investigated by FTIR spectroscopy. The as-synthesized powder of PPy was characterized by X-ray diffraction technique (XRD).

## 3 .RESULTS AND DISCUSSION

### 3.1. FTIR Analysis

The FT-IR spectra of the PPy powder samples were recorded in the range 4000-450 $cm^{-1}$ to confirm polymerization. Figure 1 shows the FTIR spectrum of as-synthesized sample. As prepared PPy powder was analyzed by FTIR. FTIR spectra showed the main characteristic peaks at 1558 $cm^{-1}$, corresponding to the fundamental vibrations of polypyrrole ring. The band at 1294 $cm^{-1}$ corresponds C-H deformation. The peaks at 1685 $m^{-1}$ and 801 $cm^{-1}$ represents C=N and C-N bonds, the bond of C-H in plane deformation vibration is situated at 985 $cm^{-1}$ and of the C-C out of plane ring deformation vibrations or C-H rocking is at 681 $cm^{-1}$ which occurs at 695 $cm^{-1}$ in our spectrum [11]. Above listed data agrees well with the available the literature, which confirming the formation of PPy [12, 13]. The conductive form of polymer was confirmed by strong bands in the 1600–900 cm−1 region that are characteristic of PPy.

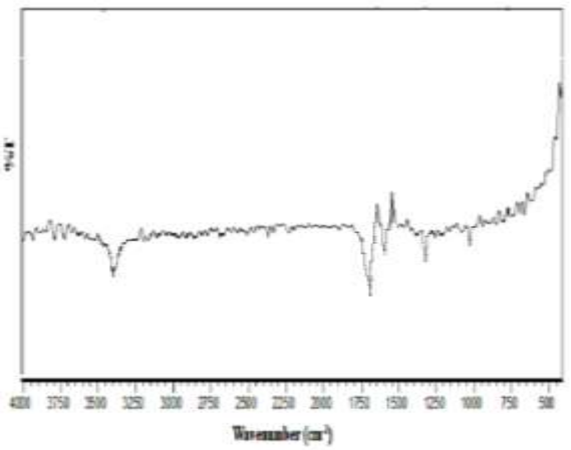

Figure 1 FTIR spectra of chemically synthesized polypyrrole

3.2. XRD Diffraction Analysis

The typical XRD pattern for chemically synthesized PPy sample prepared using oxidant ammonium per-sulfate (APS) as shown in figure 2.The noisy variation of pattern clearly revealed the amorphous nature of PPy. The broad hump appeared at 2θ=15-30 with three shoulder peaks are characteristic of amorphous PPy which indicated short range arrangement chain [14] and were due to the scattering from PPy chains at the interplanar spacing [15]. The average chain separation can be calculated from these maxima using the relation (1) [16-20].

$$R = \frac{5\lambda}{8\sin\theta} \quad \text{------ (1)}$$

Where, R is the polymer chain separation, λ is the X-ray wavelength and θ is the diffraction angle at the maximum intensity of the amorphous halo. The average chain separation (R) was found to be 5.07 °A.

As the gas sensing material deposited on glass substrate, it has thickness range between 450 to 500 µm. It indicated that our sensing layer is in thick layer form.

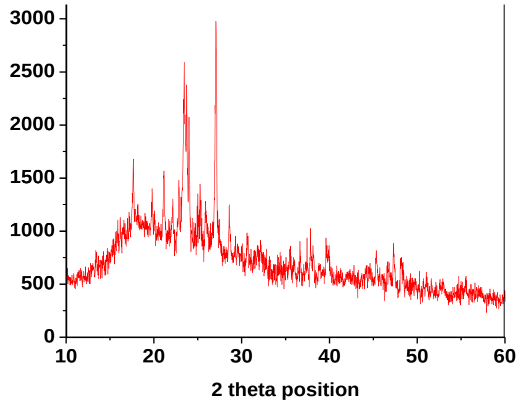


Figure 2 XRD spectra for PPy Powder sample prepared by oxidative polymerization.

3.3. $CO_2$ Gas Sensing Response

The $CO_2$ gas sensing response of as-synthesized PPy powder is shown in figure 3. Sensor showed linear variation of the response value with an increase in $CO_2$ concentration but no saturation effect was observed up to 50 ppm.

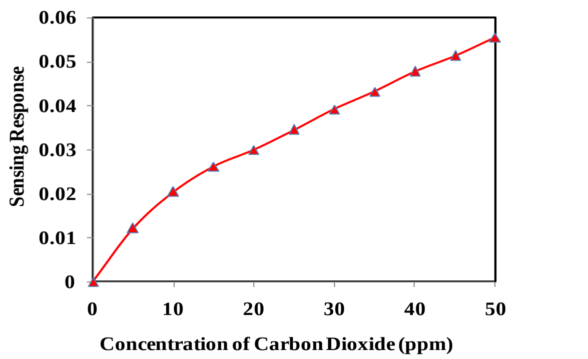


Figure 3 Carbon dixode sensing response of PPy film.

In $CO_2$ gas sensing mechanism of PPy, $CO_2$ gas permeability depends on the kinetic diameter of $CO_2$ molecules and the pore size in the PPy structure. The $CO_2$ molecules form weak bonds with π-electrons of the PPy surface. This causes an increase in resistance of the material in the presence of $CO_2$ gas.

Besids that in the context of bridging oxygen mechanisum, we suggest that the oxygen is adsorbed on the sensing surface may be involved in the sensing process of $CO_2$. The interface involving atmospheric oxygen and sensor surface are shown below [21].

$O_2$ (gas) $\rightarrow$ $O_2$ (ads)

$O_2$ (ads) + $e^-$ $\rightarrow$ $O_2^-$ (ads)

$O_2^-$ (ads) + $e^-$ $\rightarrow$ $2O^-$ (ads)

Therefore, $CO_2$ may initially adsorb on pre-adsorbed oxygen and form surface carbonate.

## 4. CONCLUSIONS

In the summery of present work, we successfully synthesized the PPy powder by chemical oxidative polymerization route using ammonium persulfate as an oxidant. PPy thick film was easily deposited on pre cleaned glass substrate, using screen printing method. The chemical composition of as-synthesized sample by FTIR spectroscopy clearly pointed out the formation of PPy. The XRD analysis revealed amorphous nature of PPy. Similarly, the average polymer chain separation of as-synthesized PPy was estimated using XRD data, which was found to be 5.07 Å. The oxygen adsorbed on the sensing surface was explained on the basis of bridging oxygen mechanisum. The linear sensing response curve showed good dependence on the concentration of $CO_2$ gas. No saturation effect was observed up to 50 ppm.

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