

Iron (III) Phthalocyanine (FePcTSA) Doped Polypyrrole for Fast Detection of Carbon Dioxide

Santhosh Paul and S. Radhakrishnan

Abstract---The present studies deal with the doping of polypyrrole (PPy) with Iron(III)phthalocyanine-4,4',4'',4'''-tetra sulfonic acid monosodium salt, compound with oxygen hydrate (FePcTSA) for improving the response speed for gas sensing capability and selectivity for carbon monoxide (CO). The chemical synthesis of PPy doped with FePcTSA was carried out in aqueous medium with anhydrous FeCl₃ as an oxidant using various compositions. The incorporation of FePcTSA was confirmed by different characterization techniques such as real-time in-situ UV-Vis spectroscopy, FTIR, EDAX etc. The sensors fabricated in surface cell configuration using these polymers gave almost instantaneous rise of resistance when exposed to 300 ppm CO gas. The response time thus obtained is extremely short: less than 1 second. Repeated measurements show the reproducibility and recovery of the material by purging the calibration bottle with air after each cycle of measurements. The highest response factor and response characteristics for a particular composition of FePcTSA-PPy are more than 50 percentage and 700 Ohm per second.

Keywords--- Chemical Sensor, Fe(III)phthalocyanine, Polypyrrole, Carbon monoxide

I. INTRODUCTION

Using phthalocyanines in the form of thin films has some advantages but for large scale applications especially in the form of micro electro machined devices (MEMs) or electronic nose as well as low cost disposable sensors, it is essential to fabricate the sensors by simpler method such as solution spinning, dipping, micro-drop coating etc. It is essential to improve the performance of PPy as regards sensitivity, selectivity and speed of response for applications in practical sensors. It was therefore thought to be appropriate to modify PPy with FePcTSA for the detection of carbon monoxide. The present study deals with the in situ. incorporation of iron(III) phthalocyanine tetrasulfonic acid monosodium salt (FePcTSA) into polypyrrole as a dopant and investigating the carbon monoxide gas sensing properties of the same.

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II. EXPERIMENTAL

A. Chemical synthesis

PPy doped with FePcTSA was synthesized by following method. Typically, to a well stirred solution of 10 mg (1% by wt. of Py) FePcTSA with 1.62 g (0.1 M) anhydrous ferric chloride in 100 ml distilled water, 1 ml Py (silica column purified) was added with continued stirring for 4 h. It was filtered through a Whatman filter paper and the first filtrate was collected and UV-Vis. spectra of the same were recorded. Also, the progress of the reaction was monitored by recording continuously, the UV-Vis spectra of small sample of the reactant mixture. The residual black colored PPy doped with FePcTSA was washed well with distilled water and dried at 50°C; yield is 362 mg. The reaction with varying concentration of FePcTSA (1 to 15%) with respect to pyrrole was carried out by the same route under the conditions described above.

The increase of yield from 289 mg/1ml pyrrole of virgin PPy to 609 mg/ml pyrrole for FePcTSA doped sample indicates that the incorporation of FePcTSA in the polymer as well as the catalytic activity of FePcTSA. The polymerization process was monitored continuously using spectro-electrochemical unit with fiber optics while the reaction being carried out in the 10 mm path length disposable cell (model USB 2000, Ocean Optics, USA) connected to a computer. The spectra were scanned from 300 nm to 1000 nm and recorded every minute (the spectrometer can record the scans in few milliseconds).

B. Characterization of the modified PPy

The PPy polymer modified with FePcTSA was characterized by various techniques such as FT-IR spectroscopy, UV-Vis spectroscopy, Energy dispersive X-ray analysis (EDAX), atomic absorption spectroscopy (GFAAS) etc. using standard instruments from Perkin Elmer, Phoenix, Avanta Sigma respectively.

C. Sensor element and CO measurements with PPy-FePcTSA

Sensing elements with PPy-FePcTSA active polymer films were prepared on 100 micron polyester film as substrates having vacuum (better than 10⁻⁶ torr) deposited gold films to form inter-digitated electrodes as indicated in Fig. 1. The inter-electrode distance was 0.5 mm and effective length was 10mm. Polyethylene oxide was dissolved in methanol with an addition of 10% CuCl₂ and stirred continuously to form homogenous solution. The PPy-FePcTSA active polymer powder samples (100 mg each) prepared in the above manner were then dispersed in the solution and stirred for 10 h to form uniform slurry. Two drops of this slurry were placed on the

gold coated substrates and the solvent evaporated thoroughly so as to form the test sensor in surface cell configuration.

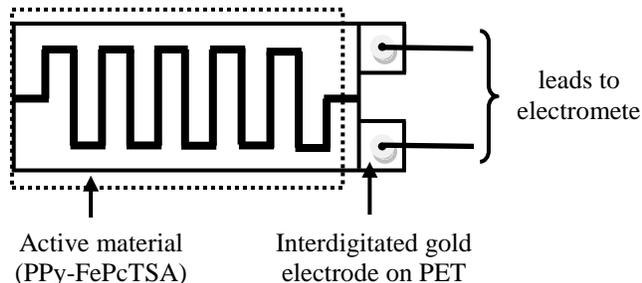


Figure 1: Schematic of the Sensor in Surface Cell Configuration

The test cells prepared with PPy-FePcTSA containing different concentration of FePcTSA were soldered on to a glass epoxy board fixture which could be inserted in the port of a calibration bottle (supplied by Drager, Germany) used for carbon monoxide sensors. This bottle contains standard ampoules with calibrated concentrations (300 ppm, 100 ppm etc) of the CO gas, which are broken internally after placing the sensors. The sensor terminals were connected to digital Keithley electrometer interfaced to computer with Test Point software so as to monitor the sample conductivity continuously with fast sampling speed of ten points per second.

III. RESULTS

A. UV-Vis. Spectroscopy

The real time UV-Vis spectroscopy of pyrrole reaction with 1 wt% FePcTSA is shown in Fig. 2 for monitoring the polymerization reactions carried out with respect to time. It is seen that as the reaction proceeds, the major changes are seen to occur in the region of 450–460 nm, 640–650 nm and 850–880 nm respectively. The major peak at 375–380 nm appears to change little since it is the basic $\pi-\pi^*$ transition belonging to the pyrrole ring. An absorption peak at 465 nm is seen to evolve within 15 seconds of the reaction and it appears throughout the reaction period. This peak is reported as oligomeric formation of pyrrole [1], which subsequently polymerizes to give PPy. On the other hand, the peak at 640 nm wavelength which corresponds to the characteristic absorption of FePcTSA reduces in intensity with the progress of the reaction. This is because of the decrease in the concentration of dissolved component since it gets incorporated inside the polymer. The broad band at 850–880 nm is associated with the bipolaronic band in PPy [2] which is seen to evolve considerably with the progress of the reaction. The real time spectra clearly indicate the completion of the reaction after a particular period of time (90 min for 1% FePcTSA pyrrole reaction) after which very little change is seen the spectra .

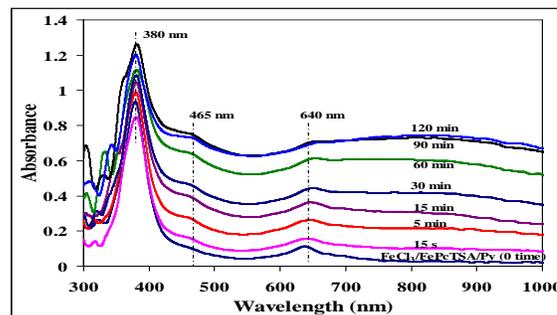


Figure 2: Online UV-Vis. Spectroscopy of 1 wt% FePcTSA Reaction with PYRROLE the Spectra Recorded for the Reaction Mixture at the Specified Time within Few Seconds.

When the filtrate samples obtained after the completion of reaction were analyzed by UV-Vis spectroscopy, these exhibited mainly a peak at 450 nm region (see Fig. 3). Further, the intensity of this peak decreased with the increase of FePcTSA content in the initial reaction mixture, which clearly suggests that higher conversion takes place (i.e. less amount of soluble oligomers remain in filtrate) in these cases than PPy synthesized without FePcTSA. Also, it can be noted that the 640 peak of FePcTSA is totally absent in the spectra of filtrates suggesting that this is fully incorporated inside the PPy and does not get leached out.

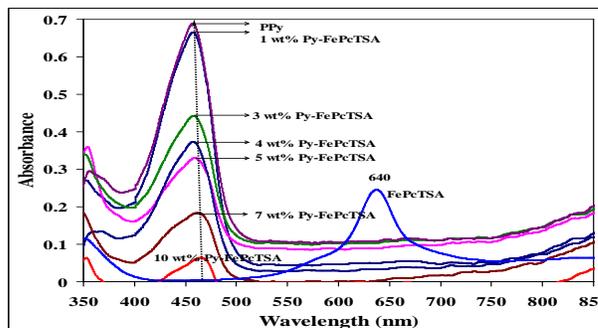


Figure 3: UV-Vis. Spectra of the Filtrates Obtained after Reaction is Completed and Polymer Filtered out for FePcTSA-PPY with Different Compositions.

B. FT-IR Spectroscopy

FT-IR spectra give a very good supportive evidence for the incorporated FePcTSA in the PPy chain. The spectra were recorded in Perkin Elmer–Spectrum GX instrument using KBr pellets. FT-IR spectra of FePcTSA, Polypyrrole and FePcTSA doped sample were shown in Fig. 4. The characteristic sulfonated phthalocyanine as well as aromatic phenyl peaks were present in FePcTSA doped PPy sample. Usually sulfonic acid groups give four major characteristic peaks in the region 1230–1030 cm^{-1} and 3450–3000 cm^{-1} [4], which are assigned to three $-\text{SO}$ and one sharp and strong S-phenyl vibrations. A characteristic broad hump at 3436 cm^{-1} is a clear indication of the presence of $-\text{SO}_3\text{H}$ in the doped polymer and a similar broad band is seen in FePcTSA at 3436 cm^{-1} . The characteristic sulfonic acid peaks are available in the FePcTSA doped PPy sample in the frequency regions 1147 cm^{-1} and 1110 cm^{-1} . The presence of bands at 1455 cm^{-1} , 746 and 700 cm^{-1} in the FePcTSA doped sample are assigned to

aromatic ring stretching frequency and –CH deformation of benzene ring respectively. This also confirms the presence of FePcTSA in the polymer. A prominent peak at 1556 cm⁻¹ in both polypyrrole and FePcTSA doped PPY sample is due to the secondary amine –NH bending frequency.

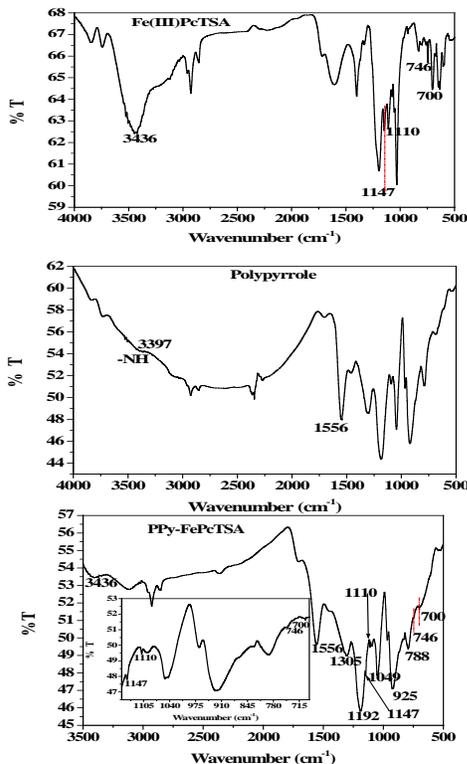


Figure 4: FTIR Spectra of Polypyrrole, FePcTSA Alone and FePcTSA Doped Polypyrrole Powders Recorded as KBr Disks

C. Elemental analysis by EDAX and AAS

The samples were analyzed by EDAX and GFAAS to determine the presence of FePcTSA. Fig. 5 shows the typical EDAX pattern obtained in PPy-FePcTSA (10%) sample. It is seen that there are peaks corresponding to C, N, Cl, S, O and Fe clearly indicating the incorporation of the FePcTSA in the matrix. Further, the expected percent content of Fe is about 0.6% which more or less matches with the observed results. GFAAS also confirmed the above findings and the Fe content increased with the increase of functional dopant in the reaction mixture. It was also observed that the Cl is present in all cases which indicate that the PPy is mainly doped with Cl⁻ as expected when polymerization is carried out with FeCl₃. It may be mentioned here that in original PPy without FePcTSA, there was no Fe or S found by both the techniques. The increase of the peak intensity was also observed when FePcTSA content in the reaction mixture was increased.

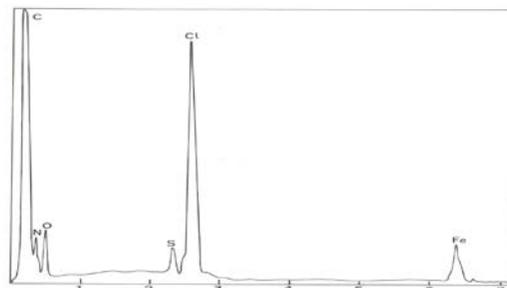
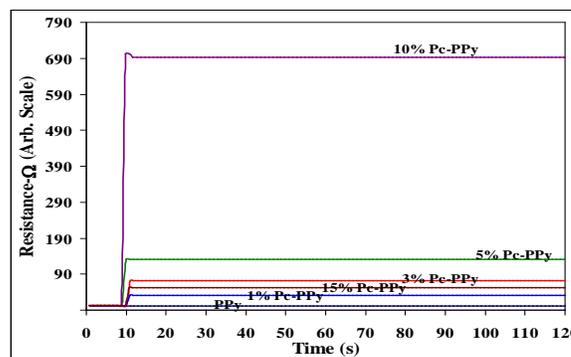


Figure 5: Typical EDAX spectrum obtained for the FePcTSA doped PPY

D. Studies on sensors response to carbon monoxide

The sensor samples were tested for sensitivity to 300 ppm carbon monoxide gas which is below the allowable limits for exposure [5] by monitoring the resistance continuously for the interdigitated surface cells. The resistance was in the range of 0.5 to 5 KΩ depending on the composition and concentration of the dopant. There is very rapid increase of resistance observed within 0.5–1.5 seconds after exposure to 300 ppm CO gas mixture with air. Fig. 6 shows a typical response curve obtained for PPy-FePcTSA samples. A typical response curve obtained for 20 ppm CO which shows that these materials are not only highly sensitive to CO gas but also recover without permanent change after the gas is removed (see inset of Fig. 6). The sensitivity factor ($\Delta R/R_0$), where (ΔR) is change in resistance while R_0 is the original resistance value, was estimated for all samples after exposure to CO repeatedly. The sensitivity factor increased from 0.6% to 52% at certain composition as indicated in Figure 7 and above the critical concentration of FePcTSA, the sensitivity factor again drops to lower value. The speed of response determined from the t_{50} value, i.e. the time required to attain 50% of maximum change, was quite low (0.51 s) in certain composition (10 wt% of PPy-FePcTSA) and depended very much on the composition.



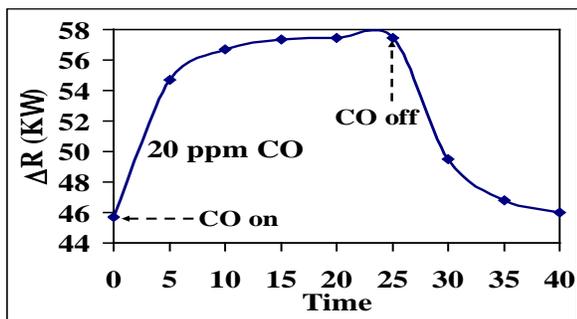


Figure 6: The Response of Various FePcTSA Doped PPy Samples Exposed to 300 ppm CO Gas at Room Temperature in the Presence of Air. Inset shows the typical response curve for 20 ppm CO gas Giving both Rise and Decay of Resistance.

These various sensor characteristic parameters for different compositions are given in Table 1. Fig. 8 indicates the variation of speed of response with composition for these films shows high sensitivity as well as fast response at room temperature has been observed for certain concentration of the functional additive, which demonstrates its applicability to these to fast response sensors.

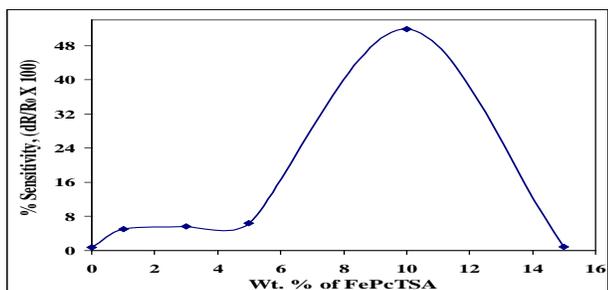


Figure 7: Sensitivity Graph of 300 ppm CO against Varying Concentrations of FePcTSA in Polypyrrole

In order to understand the underlying processes in the sensing mechanism, one has to look into the various types of possible interactions between the conducting polypyrrole, FePcTSA and CO molecule. It should be noted that the resistance of virgin PPy slightly decreases after long time with the exposure of CO gas where as all the samples containing FePcTSA exhibited a very rapid increase of resistance. The former suggests that the direct interaction of CO with the PPy main chain can lead to slight effects of increase in the free carrier (hole) density. On the other hand, the interaction of CO with Fe complexes is known to be quite fast and much more pronounced [6]. It is known that CO binds 300 times faster than oxygen with haemoglobin [7]. It should be remembered here that there is no permanent change in the material and it recovers quickly after the chamber is purged with air (see inset of Fig. 6). Hence, only the charge disturbance of transport mechanism would be true. In this case, after exposure to CO, the samples containing FePcTSA change the oxidation state of Fe(III) to Fe(II), which decreases the charge transport between the polypyrrole chains and cause a sudden increase of resistance. This is depicted in Fig. 9. It may be interesting to note here that, in our earlier studies on PPy doped with ferrocene [8], it was also observed that the electrical resistance increased and not decreased during exposure to CO gas.

However, the process was not very fast. In the present case, the speed of response is very fast, which may be attributed to larger interchain separation of PPy due to the large dopant/functional group incorporated in it. This can give rise to higher free volume and easy diffusion of CO molecules in and out of the films [9]. It also suggests that though many Fe complexes may be interacting with CO molecules in similar way but after incorporation in the polymer, the response is dependent also on the morphology/internal molecular arrangements in the bulk of the matrix.

Table 1: Response Characteristics of PPy Doped with Different Amount of FePcTSA Samples Towards 300ppm CO gas

Composition	Wt% of FePcTSA	% Sensitivity	Response time (t_{50})
PPy	0	0.768	390
1% Pc-PPy	1	5.05	1.47
3% Pc-PPy	3	5.72	1.5
5% Pc-PPy	5	6.4	1.5
10% Pc-PPy	10	51.8	0.51
15% Pc-PPy	15	0.9	1.5

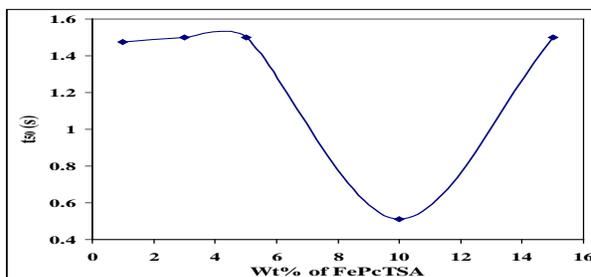
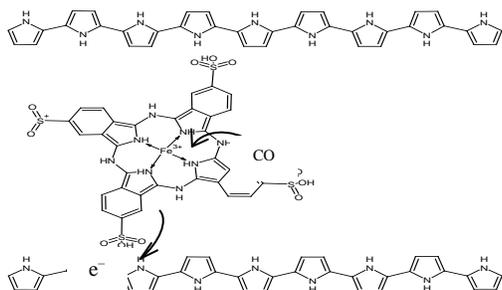


Figure 8: Compositional Dependence of Response time (t_{50}) for PPy with FePcTSA Exposed to 300 ppm Carbon Monoxide

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IV. CONCLUSION

Fe(III)PcTSA is a wonderful dopant with polypyrrole to act as a rapid CO sensing material in ppm level at room temperature. It acts as a very good catalyst for the efficient conversion of pyrrole molecules into polypyrrole. The response characteristics of the modified PPy are taking place within seconds and saturates quickly. It shows very fast recovery with repeated experimental cycles. It has been noted that the sensitivity of virgin polypyrrole is essentially nothing and a tremendous change observed with a very less concentration of doped FePcTSA. The method of synthesis (doping) is simple as well as the fabrication of the material on interdigitated electrodes. Change of resistance over a period of time is huge

(700 Ω/s) and also t_{50} for a particular composition is short (0.51 s) when the material is exposed to CO gas. Optimization for superior performance of the material against hazardous gases like CO for industrial and polluted places requires more attention and will be finally fabricated as a sensor device for micro electronics at the cheapest cost.

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