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PPY-PVA Blend Thin Films as a Ammines Gas Sensor

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Abstract: Synthesis of polypyrrole–polyvinyl alcohol blend thin by in situ chemical oxidative polymerization, on glass substrate for development of Ammonia and Trimethyl ammine hazardous gas sensor. The all experimental process carried out at room temperature (304 k). These polymer materials were characterized by Chemical analyses, spectral studies (UV-visible and IR) and conductivity measurement by four –probe technique. The surface morphology as seen in the SEM image was observed to be granular, tubular, uniformly covering the entire substrate surface having porous in nature. The current–voltage characterization show that these thin films have conducting in nature having ohmic behaviors. The sensor was used for different concentration (ppm) of TMA and Ammonia gas investigation at room temperature (304 k). This study found to possess improved electrical, mechanical and environmental stability PPY-PVA films. *Copyright © 2009 IFSA.*

Keywords: Polymer blend, Thin film, Conducting polymer, Ammonia, TMA-Gas sensor, Polypyrrole, Polyvinyl alcohol

1. Introduction

In the last few years investigations have centered mainly on the improvements have of the physical properties of polypyrrole, such as process ability, stability or mechanical integrity. Such as blend or composite formation , are being optimized in order to prepare processable material which can be used and processed like common polymers .Those possibilities as well as the improvements in atmospheric stability of polypyrrole make these materials serious candidates for use in the specific technological applications [1].

Environmental pollution is a burring global issue, pollution has raised its ugly head high in the global environment, and various polluting and toxic gases result in crucial chemical pollutants like Nitrogen oxides (NO and NOx), H_2S, CO, CO_2, Ammonia, TMA causing air pollution. It can be cause serious health hazards .The gases containing TMA, Ammonia can result in undesirable disastrous deformations such as infection to respiratory track and lung cancer [2]. Infection to respiratory track causes difficult breathing or breathing under pressure [3].The advantages of conducting polymer gas sensor are low cast, suitable for fabrication on various substrates [4-5].

In the present investigation of gas sensor at room temperature, operation which is in expensive and can be used for detection of TMA (trimethyl ammine)gases at lower concentration 50 ppm-800 ppm or above level with best response and recovery time having uniform ,porous surface morphology ,good mechanical strength and environmental stability.

2. Experimental

2.1. Chemical Used for Synthesis

All chemical used were analytical reagent (AR) grade for synthesis of PPY-PVA thin films. Pyrrole was distilled twice before use (99 %) Rankem and polyvinyl alcohol with an average degree of polymerization (mw.14,000 quiligen fine–chem., India). All processes were carried out in double distilled conductivity water. Anhydrous ferric chloride (spectrochem), hydrochloric acids (qualigen fine –chem. India).

2.2. Synthesis of PPY-PVA Blend Thin Films

We have synthesized PPY-PVA blend thin films at room temperature on glass substrate by using chemical oxidative polymerization method. The pyrrole (monomer) was double distilled prior to use. The glass substrates were cleaned using chromic acids solution, followed by rinsing with double distilled conductivity water. Initially we have optimized the molar concentration of monomer (pyrrole), primary dopant (HCL), polymer additive matrix (PVA), and oxidant ($FeCl_3$) as follows. The polyvinyl alcohol dissolved in conductivity water with constant stirring then optimize molar concentration of pyrrole (monomer 0.5 M), primary dopant (HCL – 1M), PVA additive (25 mg), Oxidant ($FeCl_3$-0.5M).

A suitable combination which shows good response to Ammonia and TMA gas has been selected further synthesis and characterization. The glass substrate was submerged the (20 ml) of suspension homogeneous solution reaction mixture. This reaction mixture along with glass substrate kept (24 hour) duration in closed vessel at room temperature to get uniform PPY-PVA blend thin films.

2.3. Characterization

The structural and morphological characterization of PPY-PVA blend thin films was performed UV-visible and FTIR by UV-visible. The UV-visible and FTIR spectra of all polymer samples were recorded at room temperature in Dimethyl sulphoxide (DMSO) solvent. The surface morphology was characterized by using scanning electron microscopy (SEM) at different magnification range by (JEOL-JSM-6360 A). Synthesized PANI-PVA doped organic acids films were subjected to the Ammonia and TMA gas at room temperature by using indigenously developed computer controlled gas sensor system and electrical conductivity (I-V characteristics) of the films was recorded using four probe- methods computer control system.

3. Results and Discussions

The synthesized PPY-PVA blend thin films characterized by following analysis.

3.1. UV-Visible Spectra

The UV-Visible absorption spectra of the polymer films were recorded by dissolving the polymer film in Dimethyl Sulfoxide (DMSO) solvent and the absorption spectra of, PPY and PPY- PVA Fig. 3.1. The band observed at 270-280 nm and for PPY samples corresponds to π -π * transition of in PPY and PPY-PVA films. The bands appear at the 380-395 nm is due to n-π * in PPY and PPY-PVA film due to lone pair on nitrogen in pyrrole ring ,which is inter charge transfer band associated of benzenoid to quinoid ring .The transitions of quinone-imine groups, together with the extending tail at 990 - 1100 nm. The conducting emeraldine salt (E S) phase in the polymer is identified by broad peak at 992 nm. Thus from the UV-visible spectroscopic measurements it was observed that the polymer is composed of mixed phase i.e. conducting and insulating of the polymer. All these UV –visible spectral data clear that in these synthesized films PPY and PPY-PVA formation take place.

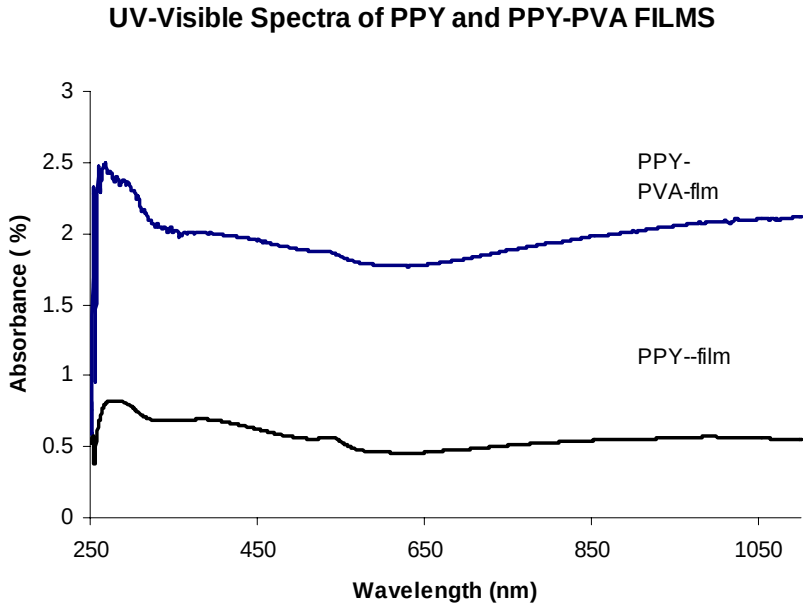

Fig. 3.1. UV- Visible Spectra of PPY and PPY-PVA Blend films.

3.2. FTIR Analysis of Synthesized PPY –PVA Blend Thin Film

The Infrared spectra of all PPY- PVA Blend films are similar appear when dissolved in DMSO solvent. The molecular structure of synthesized PPY -PVA films was characterized by FTIR spectroscopy. The FTIR spectrum of synthesized PPY and PPY-PVA Blend thin film is shown in Fig. 3.2. The bands related to N–H stretching of an aromatic amine (> NH stretching) normally appear in the region between 3100 and 3600 cm-^{1}[6]. A broad band near at 3459 cm^{-1} for PPY and 3471 cm^{-1} for PPY-PVA film, the same time NH region also shows dependence of the doping anion. Anion which typically forms hydrogen bond with amine group shows variations in the intensity and shape of the NH band, which indicates that the doping is higher in the sample .The band appear at 2900 and 3000 cm $^{-1}$ due to CH_3 and CH_2 (C-H stretching). The two bands observed in the 1410 – 1440 cm^{-1}

regions are related to the stretching of the C–N bonds of the benzonic and quinonic rings, respectively and are present due to the conducting state of the polymer [7].The intensity of these bands illustrates an idea of the oxidation state of PPY. When they appear unequal intensities, PPY is in the emeraldine base form. The bands corresponding to quinoid (N=Q=N) and benzenoid (N–B–N) ring stretching modes were observed at 1666 $cm^{-1}$for (C=N) Stretching and 1439 cm^{-1} for (C-N), respectively. We attributed the shoulder bands at 1033 cm^{-1} as the asymmetric and symmetric C-O stretching vibrations of polyvinyl group, and peaks at 707 cm^{-1}assigned to C-H bending. All these characteristic bands confirm the presence of conducting emeraldine salt phase of the polymer of PPY and PPY-PVA Blend material functional group.

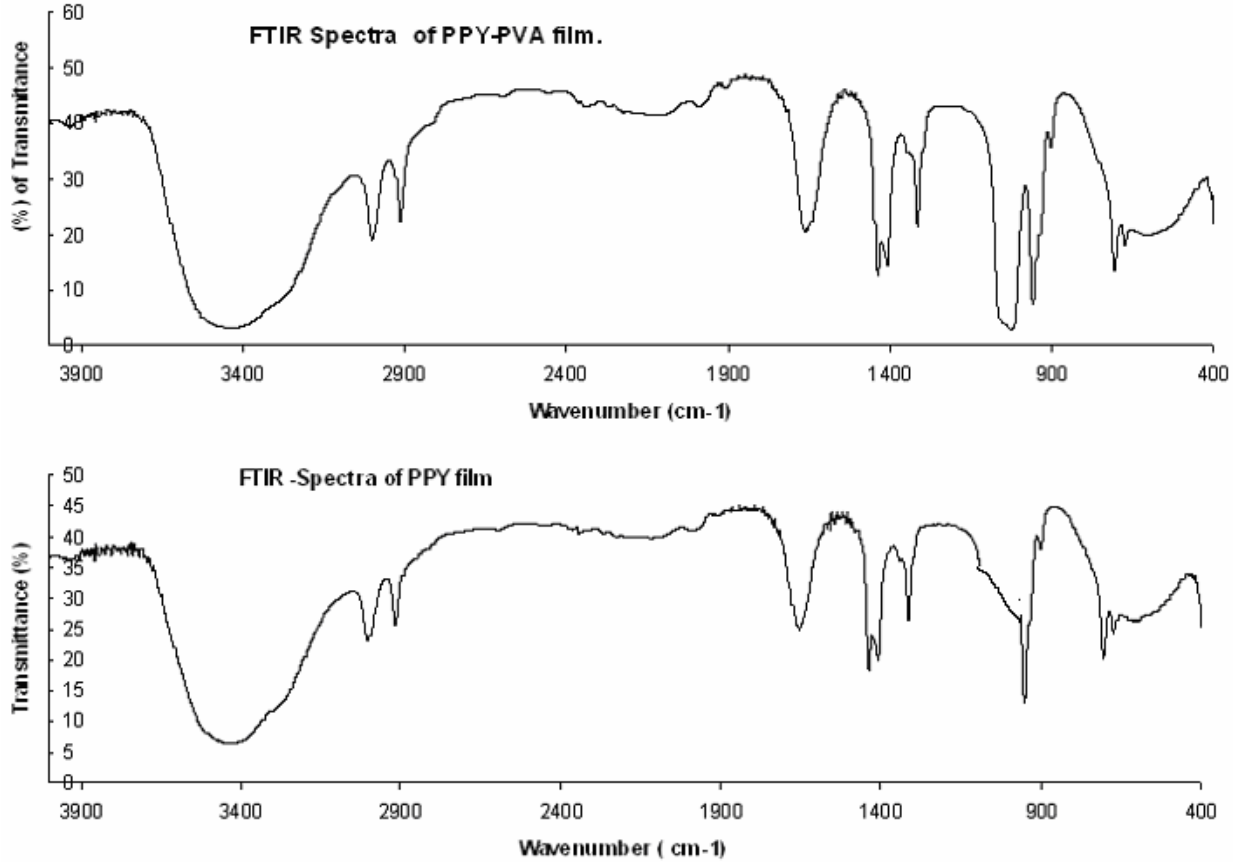

Fig. 3.2. FTIR Spectra of (a) PPY, (b) PPY- PVA Blend.

3.3. Morphology of the PPY –PVA Blend Film

Scanning Electron Microscopy is concerned with the surface structure (morphology) of polymer. The object of electron microscopy is to observe the relationship between adjacent particles and small group of particles. The surface morphology of the synthesized PPY and PPY-PVA Blend thin films was studied by using scanning electron microscope (SEM). The SEM images of the synthesized PPY films are shown in Fig. 3.3. We have observed better porous, granular and globular surface morphology with very good uniformity and adhesiveness for synthesized film samples suitable for sensor application. The average sizes of porous present in PPY-PVA films is (0.117 um) and molecular sizes is 0.184 um - 0.134 um) in diameter, from this SEM study it clear that films is porous having uniform.

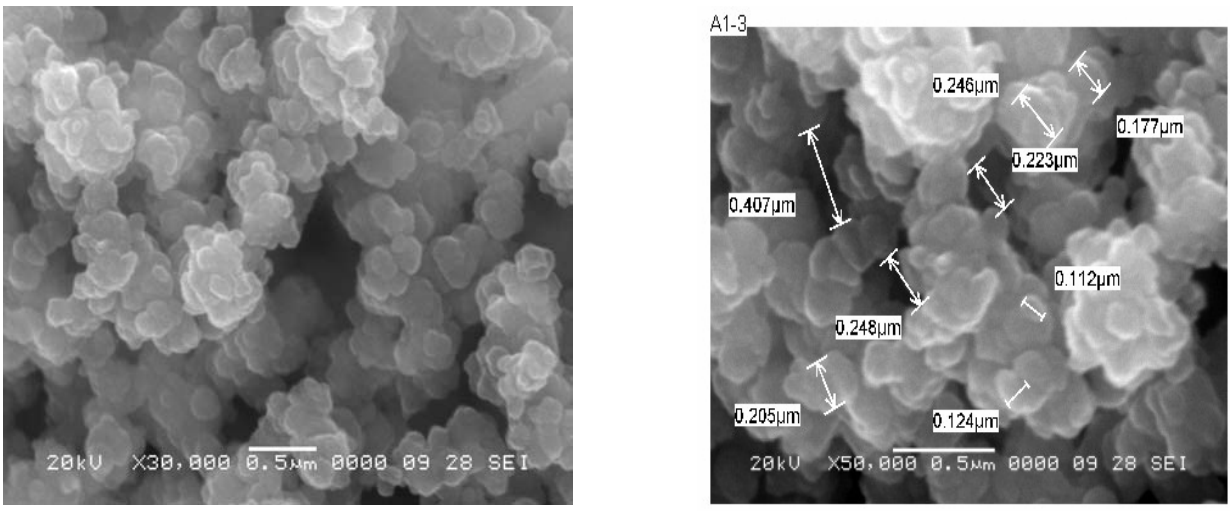

Fig. 3.3. a) PPY-film Micrograph.

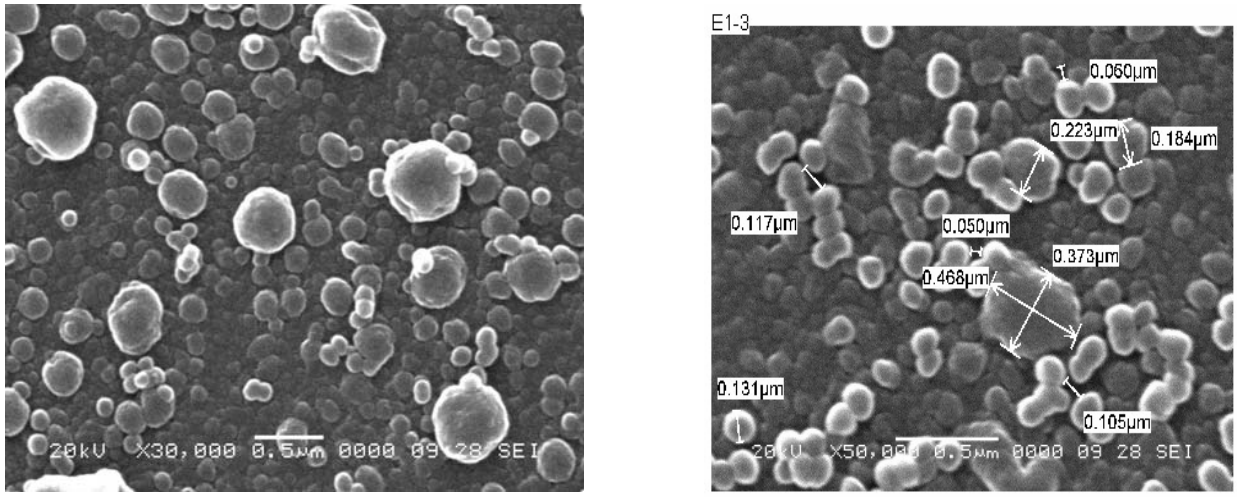

Fig. 3.3. b) PPY-PVA film Micrograph.

3.4. Conductivity Measurement

The electrical conductivity of the PPY and PPY-PNA Blend thin film was measured by an indigenously developed computer controlled conductivity measurement system using four- probe method at room temperature. It permits measurements of resistivity in samples having wide variety of shapes, including the resistivity of small volume within bigger pieces of semiconductor. It is assumed that the resistivity of the material is uniform in the measurement area. The surface on which the probes rest must be flat with no surface leakage. Instead of this, the four probes for resistivity measurements must contact the surface at points that lie in a straight line. Furthermore, the diameter of the contact between the metallic probes and the material should be small compared to the distance between probes. The percolation behavior of the resulting films is affected by the design of the blends. Further increase of the particles (above the percolation threshold) in the blends results in improvement of the conducting network and hence enhance the conductivity of the blend increases than PPY film. It is interesting to notice that, despite the insertion of an insulating PVA, the DC conductivity of the PPY-PVA blends at 50 mg wt. (with appropriate weight ratio of pyrrole) is found to be significantly higher

than the bare polymer PPY at room temperature (Fig. 3.4). The electrical conductivity was computed from measured resistance and sample dimensions by the equation.

$$R = \rho . l / a \quad (a)$$

where R is the resistance of film;
a is the cross section area of film;
l is the thickness of film;
ρ is the resistivity.

Table 3.4. Conductivity measurement of PPY and PPY-PVA Blend films.

SAMPLE	Amount of PVA (mg)	DC Conductivity (S/cm)
PPY	0.05M	0.6921×10^{-5}
PPY-PVA-(I)	25	0.9816×10^{-5}
PPY-PVA-(II)	50	0.7873×10^{-5}
PPY-PVA-(III)	75	0.5842×10^{-5}
PPY-PVA(IV)	100	0.4658×10^{-5}

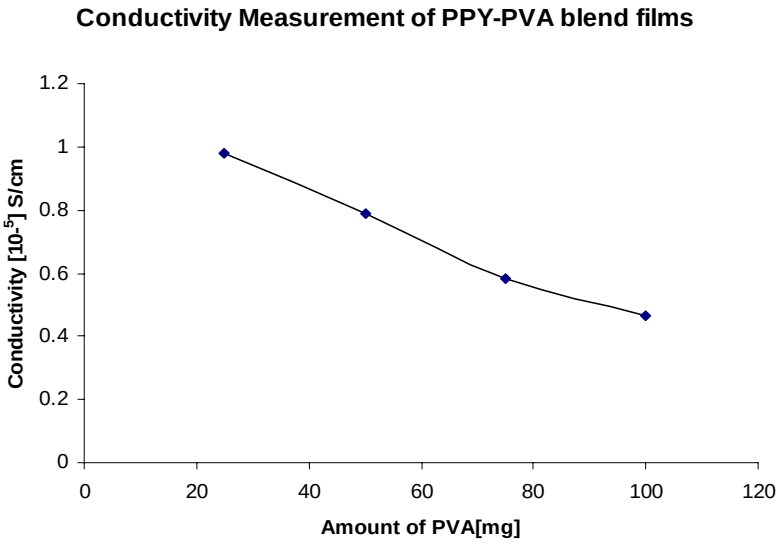

Fig. 3.4. Conductivity measurement of PPY-PVA Blend films.

3.5. I-V Measurement

The I-V characterization measurement of the PPY-PVA film was recorded by an indigenously developed computer controlled I-V measurement system using four- probe method at room temperature. The current–voltage (I-V) characteristics of the synthesized PPY –PVA Blend thin films were studied to ensure an ohmic behavior of the films. A linear relationship of the I-V characteristics shown in Fig. 3.5 reveals that the A) PPY-PVA Blend thin film and B) PPY- film has an ohmic behavior.

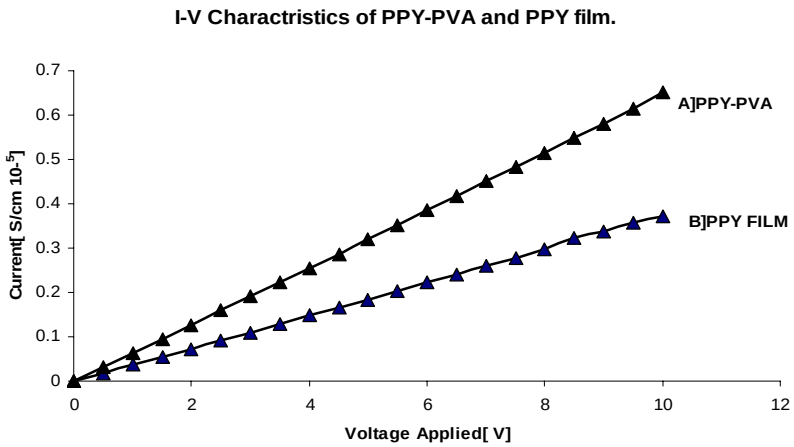

Fig. 3.5. I-V Characteristics of A) PPY-PVA Blend thin film and B) PPY-film.

3.6. TMA and Ammonia Gas Sensing Characteristics

In order to observe the TMA and ammonia gas-sensing characteristics of the synthesized PPY–PVA Blend thin films at room temperature, we have used the Four-probe technique of resistivity measurement, where four electrical contacts were made on the PPY and PPY-PVA film. This film was enclosed in indigenously designed and fabricated a gas chamber. The synthesized PPY-PVA films were exposed to TMA and ammonia gas for 5 minutes. The recovery time was measured by exposing the film to the air for 5 minutes. The change in resistivity of the film was measured at an interval of 10s. All the sample films show response to the ammonia and TMA gases vapor. We have explored the ammonia and TMA gas-sensing curves of PPY–PVA at different concentrations of ammonia gas 5 ppm to 800 ppm. It was observed that the resistivity of the PPY-PVA Blend thin film increases in the presence of ammonia and TMA gases and after a few minutes becomes saturated and the resistivity decreases steadily to a minimum value, when the ammonia and TMA gas was removed however, a drift from its original value was observed. The relationship between change in resistivity and time of the synthesized PPY-PVA Blend film when exposed to different concentration of TMA and ammonia gas are shown in (Fig. 3.6.1.–3.6.2). The conductivities of PPY-PVA Blend film were decreased by exposure to NH_3 vapors. The sensing mechanism is explained by the compensation effect [24]. When the conductive emeraldine salt is exposed to NH_3 gas, the dopant is partially reduced, which leads to a decrease of electrical conductivity [25]. Extensive studies of the gas-sensing properties of conducting polymers show that when these polymers are exposed to electron-donating gases such as ammonia and TMA, if the gases are absorbed, the polymers exhibit an increase in resistance [26], it can be seen from the figures, the conductivities of polymers show marked changes when exposed to NH_3 gas. The change in conductivity of polymers can be attributed to the different nature of both dopant anions and NH_3 gas. Dopant anions have different sizes and to NH_3 vapors can differently diffuse in Polymer matrix.

The gas sensing behaviour Showed quite good response to the ammonia and TMA gas concentration in the range 50-800 ppm, for PPY–film for both gases. The repeatability behaviour of PPY-film shows that at lower level 50 ppm gas sensing for both ammonia and TMA gases and at higher level 800 ppm or beonds for both TMA and ammonia gases from Figs. 3.6.1-3.6.3. But from Fig. 3.6.6 PPY-PVA Blend film showed that response and recovery time at 20 ppm for TMA gas and response time and recover time 50 ppm for Ammonia gas quite good response. The repeatability behaviour of PPY-PVA-film shows that at lower level 20 ppm gas sensing for both TMA gas and at higher level 800 ppm or beonds for both TMA .The ammonia gas at lower level did not show a good response at -20 ppm but show at 50 ppm lower level and 800 ppm or beonds at higher level from Figs. 3.6.4-3.6.6. Although

the surface morphology observed for PPY-PVA was porous, granular and globular responsible for good response for both TMA and Ammonia gas vapours.

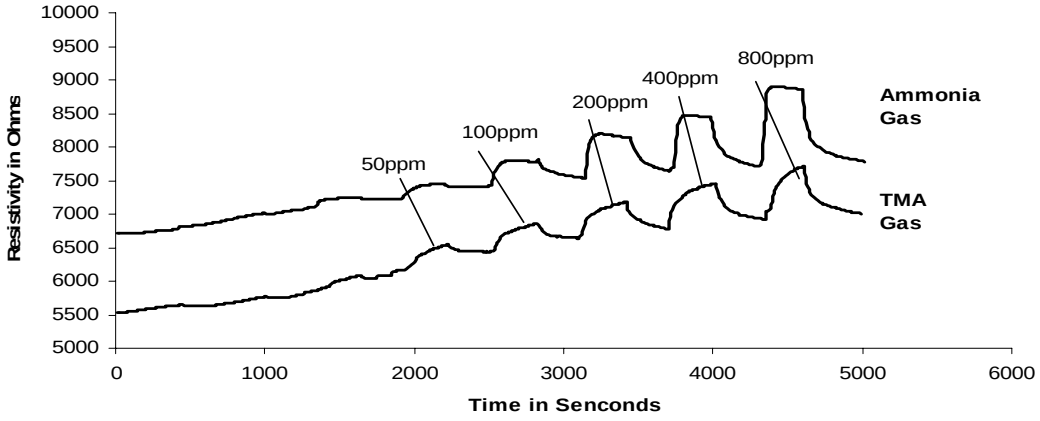

Fig. 3.6.1. PPY-Film A) Ammonia gas B) TMA gas sensing Response from 50-800 ppm.

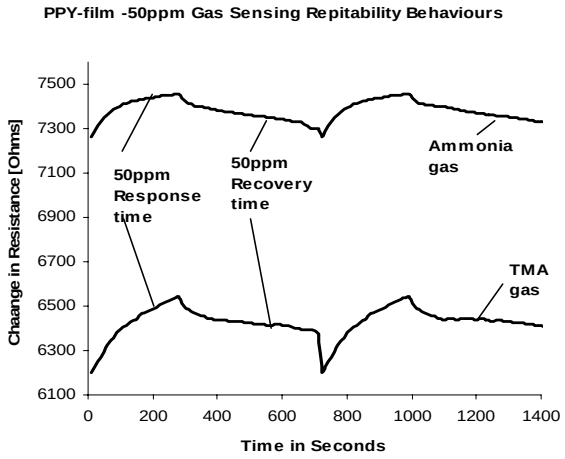

Fig. 3.6.2. PPY-Film A) Ammonia gas B) TMA-50 ppm gas sensing Repeatability Behaviors.

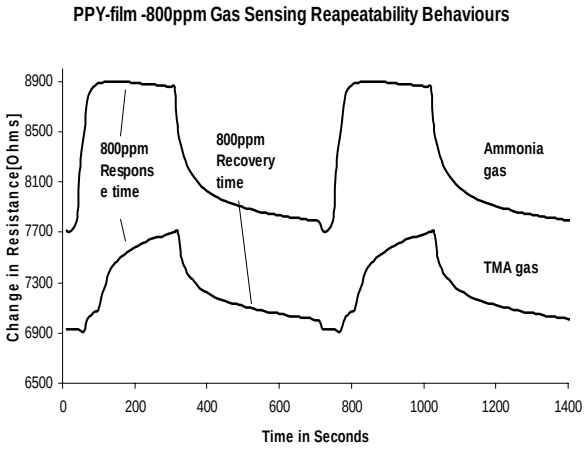

Fig. 3.6.3. PPY-Film A) Ammonia gas B) TMA-800 ppm gas sensing Repeatability Behaviors.

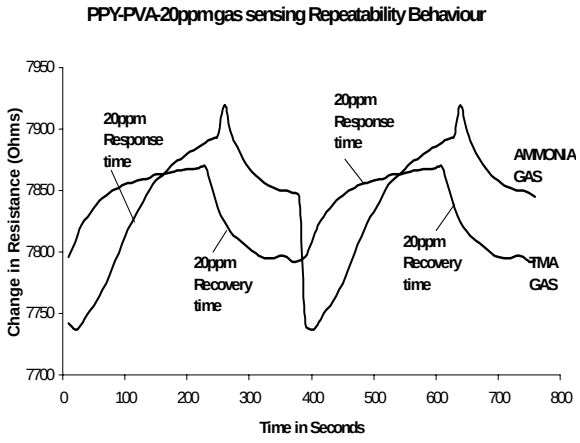

Fig. 3.6.4. PPY-PVA-Film A) Ammonia gas B) TMA-20 ppm gas sensing Repeatability Behaviors.

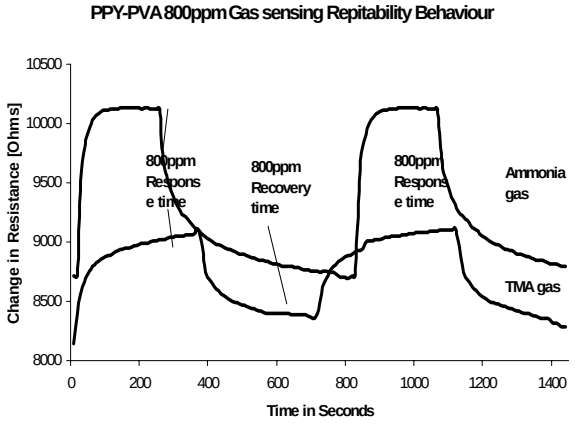

Fig. 3.6.5. 5PPY-PVA-Film A) Ammonia gas B) TMA-800 ppm gas sensing Repeatability Behaviors.

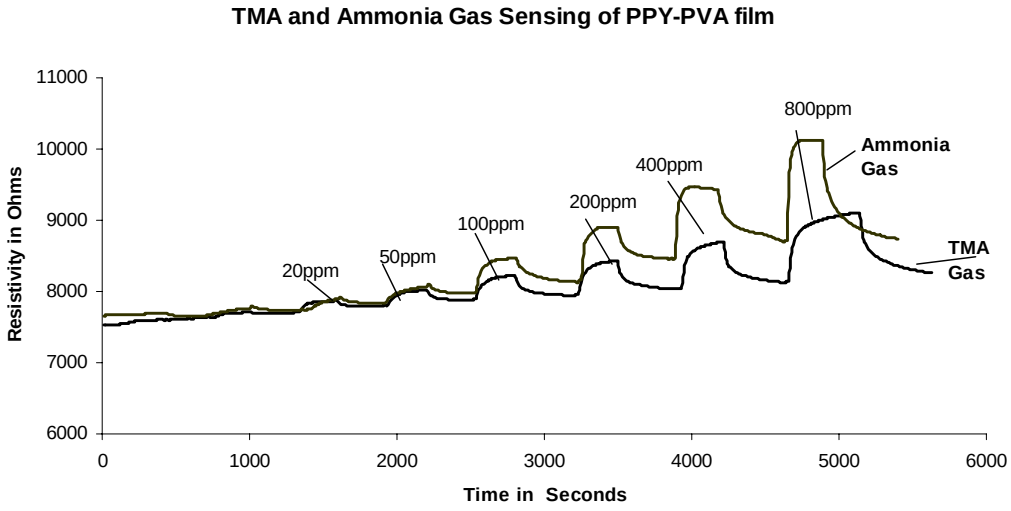

Fig. 3.6.6. PPY-PVA Blend Film A) Ammonia gas B) TMA gas sensing Response from 20-800 ppm.

4. Conclusions

1. In this present investigation, we have presented ammonia and TMA gases sensors based on PPY and PPY-PVA Blend thin film on glass substrate and their comparative study.

2. The synthesis of PPY and PPY-PVA films was carried out by oxidative polymerization of pyrrole using anhydrous ferric chloride ($FeCl_3$) on glass substrate in the presence of acids such as HCL, as a primary dopant. The influence of process parameters for better surface morphology of the synthesized of PPY-PVA has been studied.

3. The PPY-PVA Blend thin films having more environmental and thermal stability due to polymer PVA additive matrix has more sensitivity films than PPY films for TMA and ammonia gases.

4. The PPY-PVA Blend thin show 20 ppm lower level TMA gas responses and recovery but not shown good responses and recovery for ammonia gas vapours.

5. Hence from present investigation we are concluded that synthesized PPY-PVA blend thin film, more environmental ,thermal stability and good response to lower level ppm of gases at room temperature than synthesized PPY-thin film and this work are applicable for environmental pollution monitoring.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

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