# Polypyrrole Nanonetwork Embedded in Polyvinyl Alcohol as Ammonia Gas Sensor

**Baruah Kabita, Das Mausumi and Sarkar Deepali\***
Department of Physics, Gauhati University, Guwahati-781014, Assam, INDIA

## Abstract

*Polypyrrole (PPy) is known for its wide variation of electrical property through doping (oxidation) and dedoping (reduction). This has been efficiently utilized for fabrication of gas sensors. PPy in its nano form is known to enhance this property even further. In this article we have presented ammonia sensing by PPy nano networks developed in polyvinyl alcohol (PVA) film. Prior to the gas sensing study, the composite films are characterized by FESEM, XRD, FTIR and current-voltage (I-V) characteristics. These confirm formation of network, evidence of presence of PPy and PPy-PVA cross linking and moderately high in-plane electrical conductivity with ohmic nature of I-V. Ammonia sensing using this template as chemiresistor shows appreciable change in sensitivity in moderately low response time with fair reversibility.*

**Keywords**: Polypyrrole, nanonetworks, PVA template, ammonium gas sensor, polymer composite.

## Introduction

Since polyacetylene was reported by Shirakawa et al. in 1977[1] conducting polymers containing conjugated structures have been studied because of their intrinsic electrical conductivity at room temperature and potential use for electronic devices. Conducting polymers, which can exhibit significant level of electrical conductivity on doping, include polyacetylene, polyaniline, polypyrrole, polythiophene and polyphenylene etc. have got versatile promising application in the field of energy storage, sensors, electronics and optical devices and so on. Among all the conducting polymers, Polypyrrole (PPy) is a particularly promising material; it has relatively high conductivity, good environmental stability, and it is easy to polymerize[2]. The heteroatomic and extended π-conjugated backbone structure of PPy provides it with chemical stability and electrically stability respectively[3]. Recently, conducting nano/micro materials based on PPy or polyaniline have attracted interests of many researchers[4,5]. Such nanomaterials are applicable in various electronic devices, such as conducting films obtained by solvent casting; polymer electrodes obtained by blending and conducting fillers of electromagnetic shielding materials[6-11].

Although, polypyrrole exhibit high electrical conductivity, environmental stability and good redox properties still it has major disadvantages of poor processibility and mechanical strength. There are various ways to enhance the processing of PPy via rapid mixing polymerization[12,13], interfacial polymerization[14], electrochemical polymerization[15], template and surfactant guided polymerization[16,17] etc along with blending as blending of polymers may result in reducing their basic cost, improving their processing and maximizing their important properties[18]. Template based methods of polymerization produces flexible films with ease which was first reported by Yang and Sun[19]. Templates may be soft (DNA, protein, micelle etc.) or hard (of porous alumina, porous silicon or sheet of dry synthetic high polymer). In some of our recent publications, we have reported PPy composite fabrication by interfacial polymerization[14], by soft template and their application in making FET[20]. Different nanostructures of polypyrrole were obtained in the above two methods with one dimensional nanostructures in the first while spherical nanoparticles in the later. However, nanonetworks formation of PPy facilitates high surface-volume ratio which is advantageous of sensing application. Furthermore, conducting polymers have good mechanical properties, which allow a facile fabrication of sensors. As a result, more and more attentions have been paid to the sensors fabricated from conducting polymers. Conducting polymers like polypyrrole and polyaniline have shown capability in sensing technology and are used as sensors for air borne volatile organic compounds referred to as electrical nose, especially for detection of alcohols, $NO_2$[21]. Though polypyrrole is highly sensitive to gases, yet it shows saturation effect at high concentration of gases[22,23]. Different criteria are used for measuring sensitivity to gases, like changes in mechanical, optical and electrical properties[24, 25]. Electrical detection is the most commonly used and is based on the change in resistance or capacitance of the sensor on exposure to gases. In the present paper, we report polymerization of pyrrole from its vapour in the channels of preformed PVA to grow nanonetworks of PPy in the PVA channels and its application as ammonia ($NH_3$) gas sensor. Its sensing capability is studied by exposing it to different concentration of ammonia gas. The morphological, structural and electrical properties of the polypyrrole composite are also reported in this paper which are studied through SEM, FTIR, XRD and current-voltage (I-V) characteristics.

## Material and Methods

Materials used for the study are pyrrole, FeCl$_3$ and PVA. The first two reagents are obtained for Aldrich, whereas the last one from Emerck. Pyrrole is purified by repeated vacuum distillation whereas other chemicals are used as supplied. PVA templates containing FeCl$_3$ in weight ratio of 10:3 and 10:1 are prepared by spin-coating. Polymerization has been carried out in a vaporization chamber under vacuum by exposing the PVA template to distilled vapours till the template turned black in colour, indicating the formation of polypyrrole. Steps of preparation are illustrated in the flow chart in figure-1. Henceforth, we call these two films as 1 and 2. The resulting PPy-PVA template is washed, and dried and preserved under static vacuum for needed investigation. FESEM measurements have been carried out by Sigma VP G8 Advanced modeled scanning electron microscope, XRD by X'Pert Pro modeled X-Ray diffractometer from Philips (Now Panalytical) and I-V characteristic of the film by Keithley 595 Quasistatic CV meter. The characterized PPy-PVA film is then used to study gas sensing properties. The film is placed in the sample holder having two pressure contacts made with silver paste. This is placed in an airtight metallic chamber with two valves for the passing the gas inside the chamber. The chamber is connected with a built-up set up for gas sensing in which ammonia is kept in a flask taking nitrogen as carrier. Electrical resistance is measured in chemiresistor configuration of the PPy film using two silver contacts on film surface as electrical rods which is shown by figure-2.
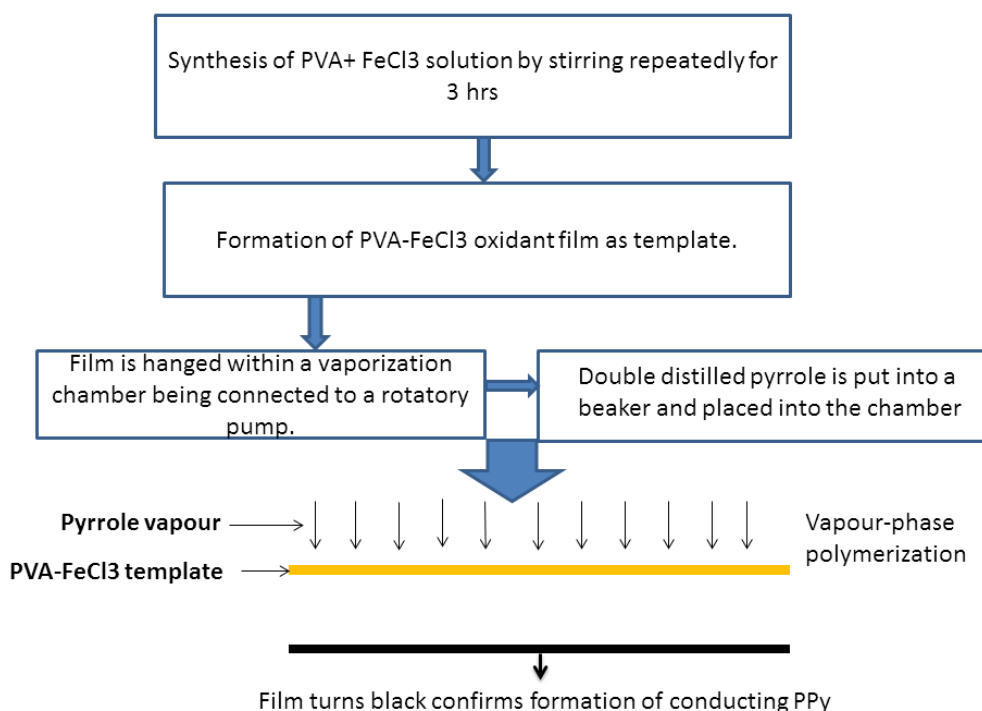


**Figure-1**
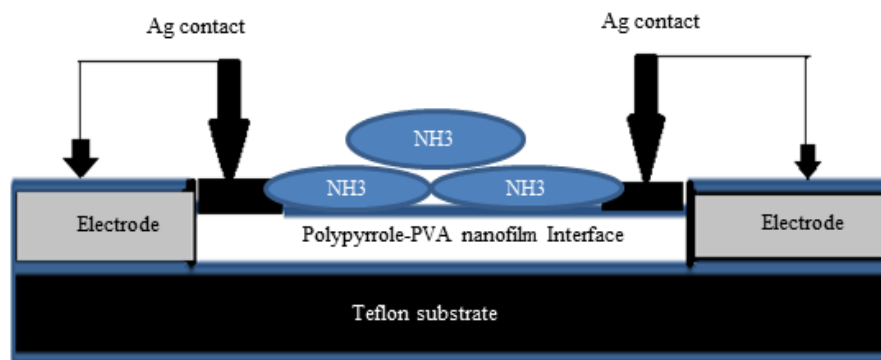**Flowchart showing steps of preparation of PPy-PVA template**



**Figure-2**
**Chemiresistor configuration of PPy-PVA film for ammonia gas sensing**

**Table-1**
**Table shows a comparison between different peaks obtained in FTIR spectra**

| PVA | 10:3 | 10:1 |
|---|---|---|
| 00 | 3753.48 | 00 |
| 3460 | 3622.32 | 2931.80 |
| | 2364.73 | 2360.87 |
| 1638.7 | 1654.92 | 1647.21 |
| 1562.6 | 1570.06 | 1585.49 |
| 1337 | 1338.60 | 1330.88 |
| 1027.9 | 1099.43 | 1091.71 |
| 00 | 987.55 | 975.98 |
| 00 | 00 | 918.12 |
| 00 | 00 | 848.68 |
| 454 | 428.20 | 470.63 |

## Results and Discussion

The field emission scanning electron microscopy image of the PPy-PVA films is shown as in figure-3 for the two films 1 and 2. There shows an organized three dimensional growth with completely different and very regular network type structure. The diameter of the network ranges from 500nm to 600nm for film 1 while it is less distinct for film2, but there is some sort of alignment here. This different nature of structure is very likely resulting from steric effects of the long alkyl chain ending with a chloride ion[26] coming from $FeCl_3$. Also the coagulation arises from Coulomb repulsion between particles. The molecular template of PVA binds the pyrrole monomer to form molecular complexes which are dispersed in water to form colloidal particles. Upon polymerization, the pyrrole monomer forms polypyrrole and remain attached to the template to form the template-polypyrrole complex. By judicious choice of the template molecule and the polymerization conditions, stable sub-micron size colloidal particles of PPy-template aggregate can be formed during polymerization[27].

The FT-IR spectroscopy was used to identify the molecular structures of polypyrrole prepared by template polymerization. It is generally known that the vibrational spectra provide information on the chemical structure of polymer, and can help investigate the state of conjugation of polymer. For the two films, these results are shown along with that of the bare PVA film in figure-4. It shows peaks at $2360.87 cm^{-1}$ characteristic of C-H vibration in the $–CH_3$ group[28]; $1647.21 cm^{-1}$ characteristic of (C=O) vibration due to presence of $FeCl_3$[29]; $1338 cm^{-1}$ characteristic of C-N stretching vibration in the ring; $1091 cm^{-1}$ characteristic of N-H in plane stretching[30]; $918.12 cm^{-1}$ characteristic of in plane C-H bending and $848.68 cm^{-1}$ characteristic of out of plane C-H bending. Characteristic bands at $1090 cm^{-1}$, $1547 cm^{-1}$ indicate the formation of polypyrrole ring. Few new peaks were seen in the range $(420-470) cm^{-1}$. However, in plane and out of plane C-H bending is seen only in film 2 and also the characteristic band for pure PVA is obtained at $3460 cm^{-1}$. These results suggest strong cross-linking between PPY and PVA.

XRD spectra are studied to know about the crystalline nature of the polypyrrole nanonetwork. The XRD patterns are shown in figure-5 for these two films. This shows a peak centered at $2\theta = 19.03°$ for both film 1 and 2 which is the characteristic peak of PVA. However the difference in intensity of the peak in the two films agrees with the lower concentration of PVA in film 1. There is a hump at $2\theta= 40°$ for film 1 which appears as a broad peak for film 2. Appearance of hump means the incoherent scattering from an amorphous solid suggests that most regions of synthesized PPy are amorphous[31]. The broadness of the peak in film 2 agrees its higher concentration of PVA compared to film 1(10:3) which reduces the process of agglomeration with PVA coating around smaller granules as has been modeled by S. Percec *etal* recently[32] for the polymerization of pyrrole within PVA.
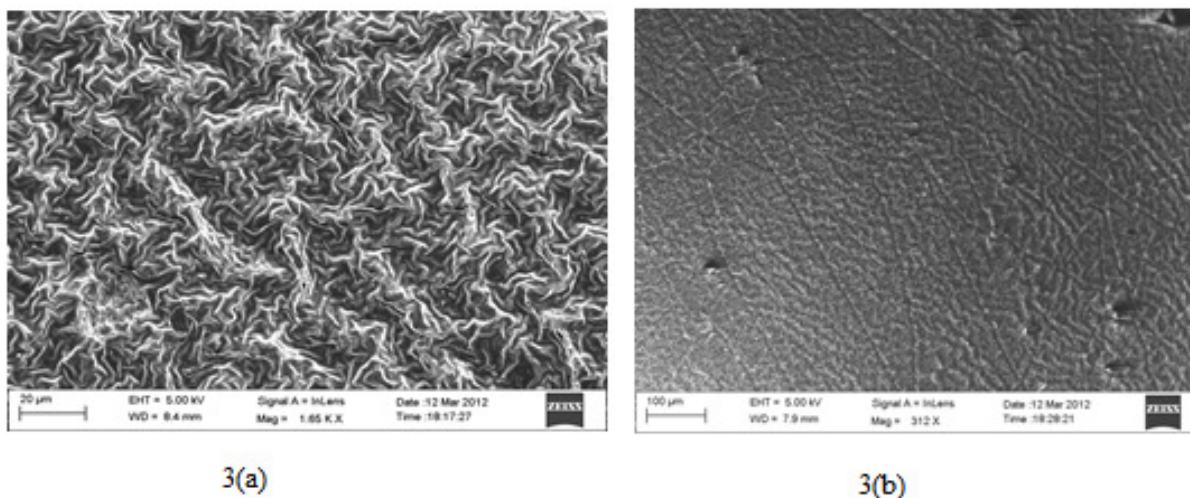


3(a)



3(b)

**Figure-3**
**FESEM image of PPy formed on PVA: $FeCl_3$ template for ratio (a) 10:3 (b) 10:1**

The in-plane I-V characteristics of the two composite films are shown in figure-6. These show ohmic nature up to voltage range of -6 to +6 volt. The measured four-probe conductivity is in the range $10^{-1}$ S/cm. It is in agreement with the high value of polypyrrole conductivity as reported[33]. It is seen that the conductivity decreases with decreasing oxidant concentration.

This is due to the fact that the oxidant ($FeCl_3$) carries chlorine ($Cl^-$) ion which work as free radical for conduction. As $FeCl_3$ decreases, chlorine ($Cl^-$) ion decreases. Also, increase in the concentration of PVA with decreasing oxidant concentration results less conductivity as PVA is an insulator which dominates some properties of PPy in its processiblity.
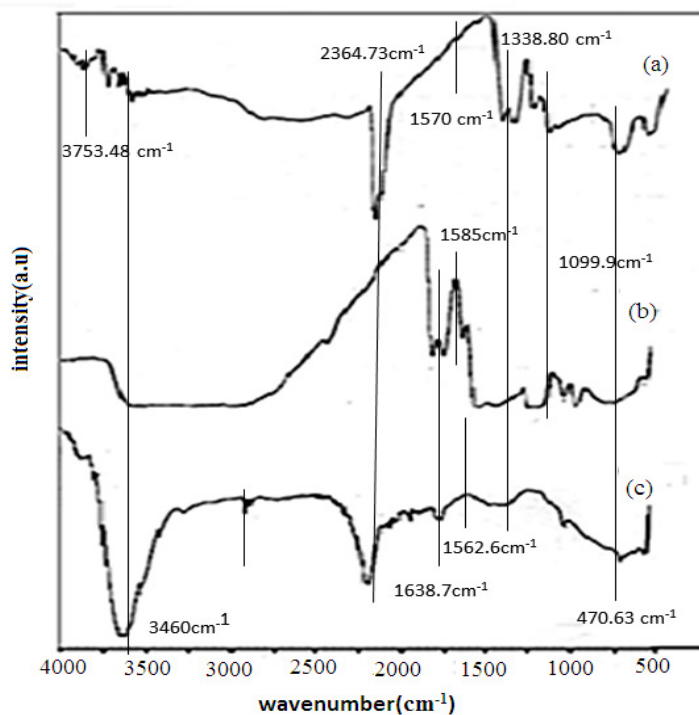


**Figure-4**
**FT-IR spectroscopy of PPy formed on (a) PVA: FeCl$_3$ (10:3), (b) PVA-FeCl$_3$(10:1)template c) PVA**
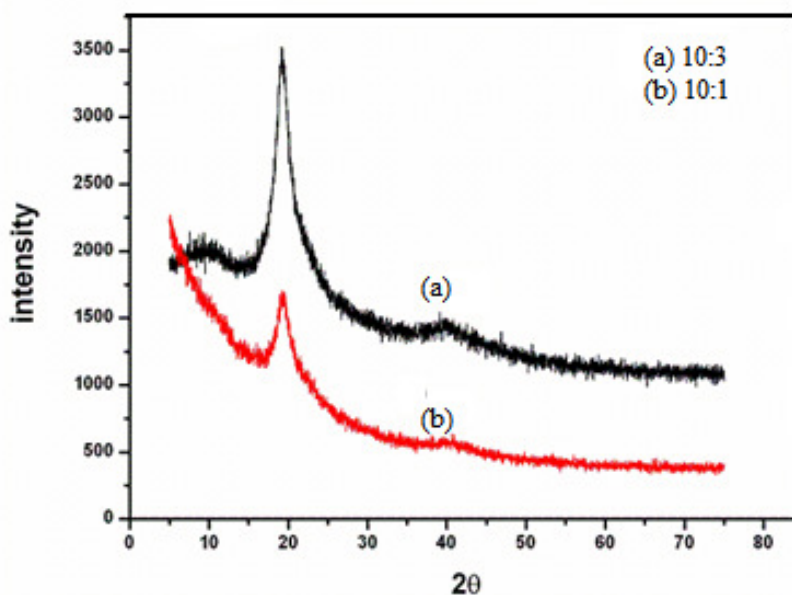


**Figure-5**
**X-ray scattering patterns of PPy nanonetwork on PVA: FeCl$_3$ template for ratios (a) 10:3 (b) 10:1**

**Gas sensors: sensor response to NH₃ gas:** Figure-7a shows the graph of sensitivity versus time for polypyrrole nano networks for film 1(10:3) for five different concentration of ammonia (NH₃). Figure-7b shows the graph for maximum response for five different concentration of ammonia. The sensitivity of the PPy film is calculated using the formula 1 given as:

$$S \, (\%) = (R_g - R_a)/R_a \times 100 \qquad (1)$$

Where, $R_g$ is the resistance in gas and $R_a$ is the resistance in air.

It is observed from the curves that the PPy films on the PVA template show gradual increase or decrease of sensitivity with the exposure and the removal of ammonia gas. The increase of sensitivity parameter (S) (which is related to electrical resistance of the PPy film) with ammonia intake is due to dedoping/ reduction of PPy possibly involving the following reactions[34, 35] given by equation 2 and 3 respectively.
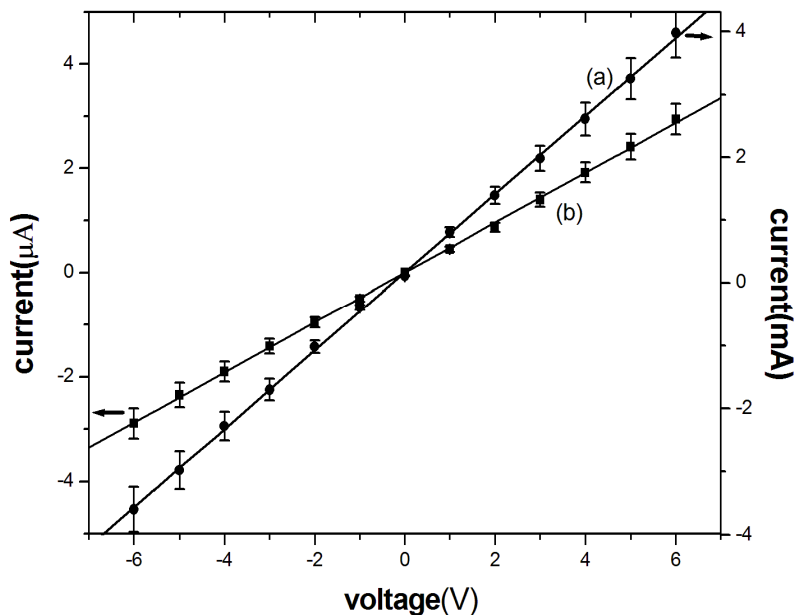
$$PPy^+ + NH_3 \rightarrow PPy^0 + NH_3^+ \quad \text{Adsorption} \qquad (2)$$
$$PPy^0 + NH_3^+ \rightarrow PPy^+ + NH_3 \quad \text{Desorption} \qquad (3)$$



**Figure-6**
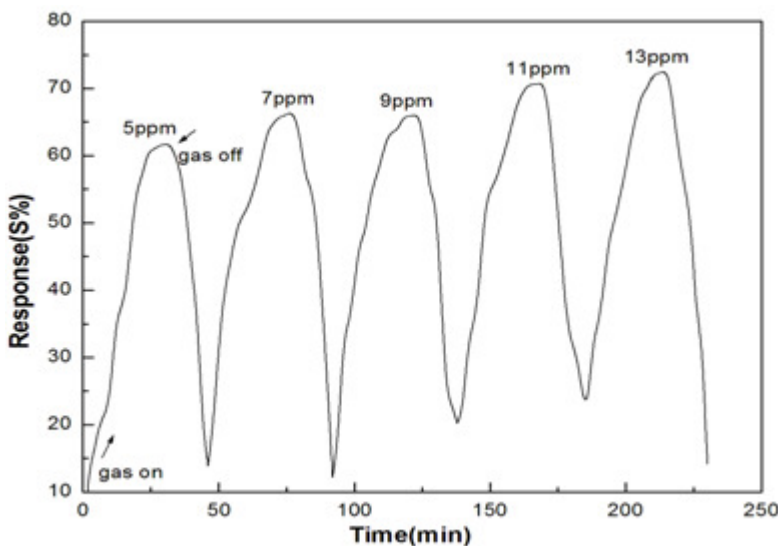**I-V characteristic of PPy nanonetwork formed on PVA-FeCl₃ template for the ratio (a) 10:3 (b) 10:1**



**Figure-7a**
**Graph for sensitivity versus time for polypyrrole nano networks for film 1(10:3) for five different concentration of ammonia (NH₃)**
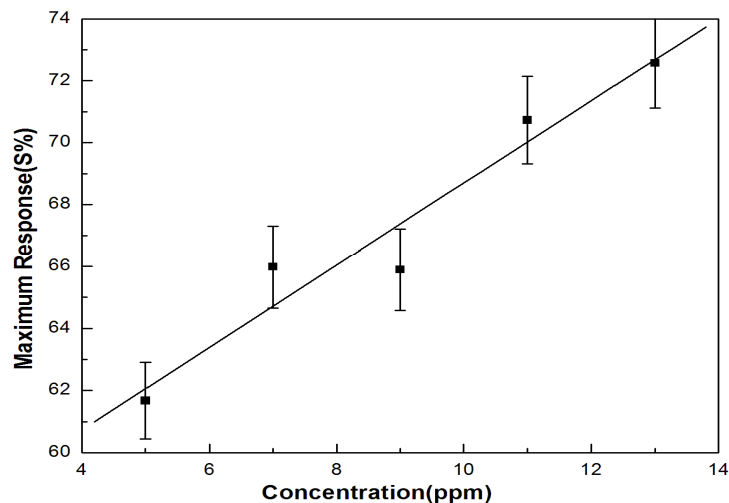
**Figure-7b**
**Graph for maximum response for five different concentration of ammonia**

Upon exposure to ammonia, it shows that the response and recovery time of the sensor does not depend on heating temperature. At room temperature the sensor shows lower resistance than the original value when ammonia gas was almost completely desorbed from the surface, while this phenomenon disappeared after certain time. This may be due to the losing of polarity of PPy after gaining an electron from the lone pair of electrons of $NH_3$ during the process of adsorption. These results in increase of sensor resistance and decrease of conductivity. While during the process of desorption, the neutral PPy donate an electron to the positively charged ammonia thus again polarizing PPy and neutralizing $NH_3$. Polarity of PPy which serves as a free radical results in increase of conductivity thus decreasing the sensor resistance. Thus polymer chain could continuously change through swelling/shrinking due to the adsorption/desorption of ammonia gas. Also the interaction between conducting polymer and gas analyte is rather strong at room temperature. The sensor shows a stability for a period of 15minutes. The dynamic range of this sensor is found to be 5ppm-13ppm and its lower detection limit is 5ppm. The sensor can distinguished the lowest concentration difference of 2ppm. The response time for this sensor is found to be 25 minutes which is the time to reach 90% of the total resistance change. The sensor works continuously for 50 minutes, thus it is the life cycle of this sensor. To visualize the effect of $NH_3$ context, we have plotted maximum sensitivity ($S_{max}$) $NH_3$ concentration. This plot is shown in figure-7b. This shows increase in $S_{max}$ with increasing $NH_3$. The sensitivity of the sensor is shown by the slope of the linear graph which is found to be 1.36% per ppm of $NH_3$ in the concentration range of 5-13 ppm. The sensor shows selectivity towards ammonia ($NH_3$) with no detectable response to other gases even at high concentration. However, the detection of other gases by polypyrrole can be obtained by incorporation of metal oxide into its 1D nanostructure.

## Conclusion

Films of PPY have been grown on PVA template by template polymerization method. The films are investigated by a combination of FESEM, FTIR, XRD and current-voltage (I-V) characteristics. The morphology shows fully grown organized three dimensional PPy nanonetworks. FTIR indicates presence of molecular structure of PPy and also that it is chemically crosslinked to PVA. XRD peaks show amorphous nature of PPy and the broadness of amorphous humps at higher ratio of PVA. Ohmic nature of I-V characteristics is shown by both films. The in-plane conductivity is in the range of $10^{-1}$ S/cm. Ammonia sensing shows a very gradual increase and decrease of sensitivity with exposure and removal of the gas. Study of sensitivity with different concentration of ammonia gas shows a sharp increase and decrease of sensitivity with higher concentration of ammonia gas showing a good response at higher concentration.

## Acknowledgement

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