Research Article

Study of temperature effect on sensitivity of ammonia sensor based on Polythiophene

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ABSTRACT

Polythiophene has been chemically synthesized by using 2,5-dibromothiophene as a chemical precursor. The synthesized polymer was characterized by UV-Visible spectroscopy, FTIR and X-ray diffraction for its structural and morphological studies. Two probe method was used to calculate conductivity (σ) of polythiophene. D. C. electrical conductivity value of polythiophene, was 2.067×10^{-9} S/cm. Log σ versus 1/T graph show semiconducting behavior of the sample. Ammonia (500 ppm and 1000 ppm) gas sensing was carried out using polythiophene at various temperatures ranging from room temperature (28^0C) to 150^0C and also at various voltages from 1 V to 15 V. After exposure to ammonia the change in resistance of sensor was recorded as a function of time. At 500 ppm and 1000 ppm of ammonia gas polythiophene shows maximum sensitivity (S) at 100^0C. Graph of % S versus voltage show maximum sensitivity at 100^0C. The sensor shows maximum sensitivity (16%) at 100^0C for 1000 ppm concentration of ammonia gas.

KEYWORDS

1. INTRODUCTION

Permanent monitoring of environmental pollution is necessary now a day's as environment is getting polluted day by day and pollution level is increasing particularly in urban area. Gas sensor play vital role in detecting, monitoring and controlling the presence of hazardous and poisonous gases in the atmosphere at very low concentrations. Conducting polymers (CP) such as polyaniline (PANI), polypyrrol (PPy), polythiophene (PTh) and their derivatives, have been used as the active layers of gas sensors since early 1980s. [1-5]

Ammonia is one of the toxic gas, which is colourless and water soluble with sharp, distinct, penetrating, extremely bad odour detectable at every low concentrations. Inhalation of this gas may cause various acute respiratory conditions including bronchiolitis and pulmonary oedema. It is used either directly or indirectly in many industrial processes and exposure may occur in wide range of industrial settings. In case of explosives, ammonia nitrate is used which gradually decomposes and releases trace amounts of ammonia, which if detected would be helpful in detection of explosive [6]. The reaction of the polymer with ammonia causes a change in the conductivity of material, making it a suitable material for ammonia detection [7]. In the present work, we report the results of pure polythiophene as a new material for sensing ammonia. It is found to exhibit high sensitivity at 1 V for 500 ppm.

2. MATERIALS AND METHODS

2.1. Sample Preparation

The polythiophene has been chemically synthesized as reported by T. Yamamoto et al [8]. Polythiophene in powder form has been obtained through chemical synthesis by treating 5 gm (21 m mole) of 2, 5 dibromothiophene with 0.51 gm (21 m mole) of magnesium (Mg) in 20 ml of dry tetrahydrofuran (THF) in the presence of 20 mg (0.07 m mole) of nickel chloride, acting as a catalyst, added at last. The reaction mixture was continuously magnetically stirred for 2 hours. The Mg reacts with either bromide to form either 2-bromo-5-magnesiobromothiophene or 2-magnesiobromo-5-bromothiophene which is self coupled with the nickel catalyst to form a thiophene dimmer carrying an MgBr at one end and a Br at the other. This condensation is propagated and eventually polythiophene is formed. As shown in Fig. 1.

The synthesized polymer was de-doped by adding 1 gm of it to a mixture of 20 ml of liquid ammonia (99 % pure) and 80 ml of distilled water. The reaction mixture is magnetically stirred for 2.5 hours. It was then filtered, washed with distilled water and methanol alternately till the filtrate is colourless and then dried.

2.2. Characterization

Fourier transforms infrared (FTIR) spectra in the spectral range 400 cm^{-1} to 4000 cm^{-1} was recorded using Shimadzu-FTIR-8400S spectrophotometer (Japan). The UV –Visible was carried out using UV- 1700 Pharma Spectrophotometer model of Shimadzu make. The spectra were recorded in the wavelength range from 230nm to 800 nm. The absorption in UV region reveals the electronic structure of the samples where as the absorption in the visible region gives information of band gap energy of the material. The wide angle X-ray diffraction (WAXD) pattern of sample was recorded using Bruker axs D8 Advance deffractometer unit. Nickel – filtered copper K$_\alpha$ radiation was incident on the sample, which was scanned at 1^0/ minute in

reflection over a range of $2\theta = 5^0$ to 45^0. Electrical conductivity measurements were carried out, using a two probe method and by applying voltages from 0 V to 100 V in steps of 10 V. The current was measured using a Keithley electrometer (model no. 6514) USA. These measurements were repeated at various temperatures in steps of 10 K from 313 K to 373 K. Figure 2 shows the electrical circuitry used for measurements. All the measurements were carried out on pressed pellets with electrical probes of 1 cm^2 size.

2.3. Gas Sensing

Sensing of ammonia gas using polythiophene, was carried out using gas sensing device. The synthesized sample in pellet form was used for gas sensing purpose.

The schematic diagram of the gas sensing unit is,

The gas sensing unit consisting of heater, electrode, temperature sensor, gas chamber assembly, power supply, display unit. It is basically a two probe method with temperature variation facility. In this assembly, the sample is held by two electrodes & voltage (1V to 18V) was applied to two electrodes. The pellet is suspended on heater and temperature of heater can be varied from room temperature to 400 K using dimmer stat.

The current flowing through the sample is measured by an ammeter, which is connected in series with the electrodes. The assembly has inlet and outlet valves for gas. Whole assembly is enclosed in the glass chamber so as to provide isolation from the surrounding.

3. RESULTS AND DISCUSSION

The IR spectra of sample as shown in figure, two bands of medium intensity at 692.47 cm^{-1} and 671.25 cm^{-1} associated to Cγ-H appears. A sharp band appears at 788.91 cm^{-1} which is characteristic for the α, α'-coupling of poly-2, 5-thiophene [9] associated with =C–H out of plane vibration in undoped polythiophene, indicating that the synthesized sample is polythiophene. Also band at 965cm^{-1} attributed to C–Br bands [10] does not appear in FTIR spectrum of synthesized polythiophene confirming that the synthesized sample is polythiophene and the monomer is absent in the synthesized sample. A band appearing at 1020.38 cm^{-1} is associated with C–H in plane bends. Thiophene ring alternately changes into two different structures. The characteristic frequency of each structure is 1230 cm^{-1} and 1400 cm^{-1} called υ cycles. After polymerisation also these characteristics frequencies appear in IR band and in the present case appear at 1220.98 cm^{-1} and 1425.44 cm^{-1}, near to above reported values. A sharp band at 1633.76 cm^{-1} associated to C=C stretch also appears in the IR spectra of undoped polythiophene. These bands of synthesized sample match very well with the values reported by G. Tourillon [9]. This also confirms that the sample synthesized is polythiophene.

The UV–Visible spectra of polythiophene samples are shown in figure 3. UV-visible spectrum of polythiophene shows peak wavelength at 360 nm. At this wavelength polythiophene absorb maximum energy. And this value of wavelength gives the band gap energy of 3.44 eV. The band gap energy of Polythiophene belongs to the semiconductor range.

Table 2 summarizes the result of X-ray diffractions. From the XRD analysis, as shown in figure 5 it is observed that three peaks appear in polythiophene at 2θ values of 18.4,22, and 26^0.

In the present work Manjunath et al [11] analysis is used to calculate the crystallinity of the sample with 5 to 8% error. The crystallinity index is given the formula,

Crystallinity index = 1–R.

Where R is lateral order of crystallinity given by–

$$R = \frac{m_1 + 2m_2 + 2m_3 + - - - - - m_{n-1}}{h_1 + h_2 + h_3 + - - - - - h_n}$$

Where m_1, m_2, m_3, - - - - - m_{n-1} are heights of minima between two peaks from base line and h_1, h_2, h_3, - - - - - h_n are heights of peaks from base line. It is observed that crystallinity of polythiophene sample is 41.92% indicating amorphous nature.

3.1. Electrical-Conductivity Measurement

The electrical conductivity measurements of polythiophene were carried out using a two probe method. For room temperature, electrical conductivity of polythiophene was found to be 2.066 x 10^{-9} S/cm. Measurements of conductivity at various temperatures were carried out to reveal the conduction mechanism in the sample. Figure 6 shows log σ versus 1/T graph at 50 v/cm field. In this case initially (from 312 K to about 323 K) the conductivity decreases and from 323 K to 368 K the conductivity increased. The initial decrease in conductivity with rise in temperature indicates the metallic behaviour in the temperature range from 312 K to 323 K. The increase in conductivity with increase in temperature above 323 K indicates semiconducting behaviour of the polythiophene sample.

3.2. Gas sensing

The sample was exposed to ammonia gas of 500 ppm and then to 1000 ppm concentration. The voltage applied to sample was varied as 1V, 5V, 10V and 15 V. The corresponding current was noted before and after exposing the sample to ammonia gas. The above procedure was repeated for 28^0 C, 50^0 C, 100^0 C and 150^0 C. When the sample was exposed to gas the current was found to reduce as compare to current before exposing the gas i.e. resistance of the polythiophene increases when it is exposed to ammonia gas and this was observed at all the mentioned temperatures and at both concentrations. Ammonia being a electron donating gas. Its presence in polythiophene affects the alternating double bond and single bond structure of polythiophene chain. Alternate single and double bond structure is essential for conducting electron through the polymer chain and since it is getting affected; hence there is reduction in the current of polythiophene when exposed to ammonia gas. Even the rise in temperature could not regulate the flow of electrons in the polythiophene chain once it is exposed to ammonia gas. The percentage sensitivity of polythiophene to ammonia gas was calculated using the relation [12]

$$\% S = \left(1 - \frac{I_{air}}{I_{gas}} \right) \times 100$$

The graph of % sensitivity versus temperature at various voltages was plotted and is as shown in figure 7(a) and 7 (b). From this graph it is observed that maximum sensitivity occurs at 100^0 C at all the applied voltages and sensitivity decreases with increase in applied voltage from 1 V to 15 V. This is because as the voltage increases current increases according to ohm's law. As the applied voltage increases more and more charge carriers i.e. electrons are released from the

polythiophene chain. Also ammonia is electron donar gas. These electrons along with those released due to applied voltage increases in such a number that they themselves creat hurdle in transporting from one point to other. Hence current reduces as the applied voltage increases. Hence sensitivity decreases with increase in applied voltage from 1 V to 15 V. There by showing maximum sensitivity at 1V of applied voltage.

As temperature increases more and more number of double bonds in polythiophene breaks and releases more number of free electrons and hence as temperature is raised from 28^0 C to 100^0 C current and hence sensitivity increases. Above 100^0 C due to large number of free electrons which in turn creates hurdle to motion of free electrons the current and hence sensitivity decreases. At 1000 ppm also polythiophene shows maximum sensitivity at 100^0C

4. CONCLUSION

Polythiophene can be synthesized chemically. FTIR results confirm that synthesized sample is polythiophene. From UV-VIS analysis bandgap of polythiophene is 3.44 eV andit falls in semiconducting range. The D.C. electrical conductivity (σ) of polythiophene at room temperature is 2.066 X 10^{-9} S/cm and this value resembles to semiconducting range. Log σ versus 1/T shows that as temperature increases electrical conductivity of the material increases indicating semiconducting nature of the material. XRD results show amorphus nature of the sample. Current through the sample in presence of ammonia gas is lower than the current in absence of ammonia gas. Polythiophene shows maximum sensitivity at 100^0 C for all the applied voltages. Also it shows maximum sensitivity at 1 V for all the temperature values.

5. ACKNOWLEDGEMENTS

6. REFERENCES

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Table 1. Values of IR absorption peaks of chemically synthesized polythiophene.

For undoped PT in present work cm^{-1}	Association
1543.1 and 1633.76	C=C stretch
1425.44	υ cycle
1220.98	υ cycle
1220.38	C-H in plane bend
788.91	C-H out of plane bend
692.47 and 671.25	Cγ-H

Table 2. Sample and its peak position (2 θ) and crystallinity.

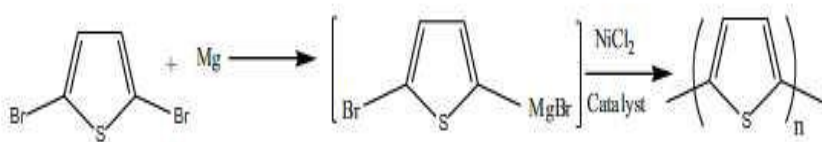| Sample	Peak position at 2θ	Crystallinity
Polythiophene	a) 18.4	41.92 %
	b) 22	
	c) 26	

Fig. 1. Polythiophene chemical synthesis steps.
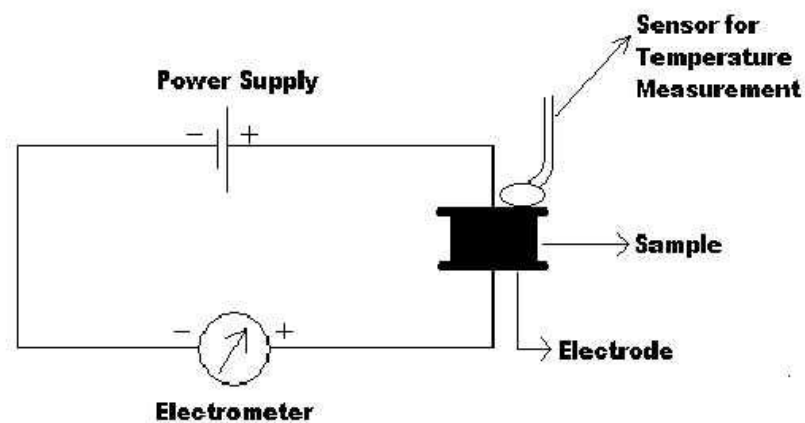
Fig. 2. I-V Measurement Experimental Set up.
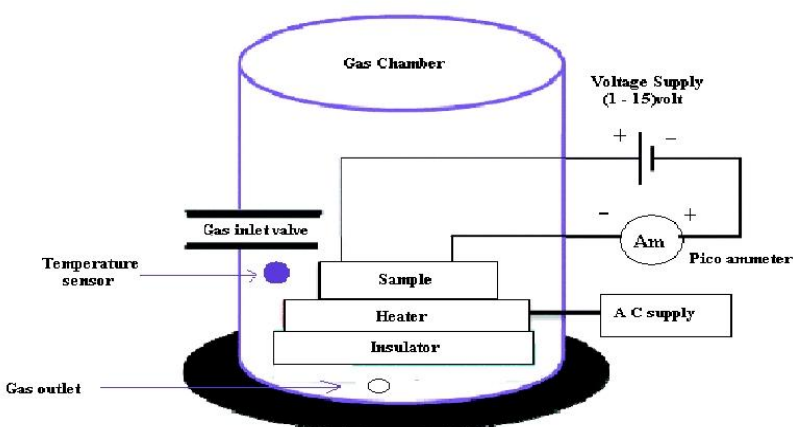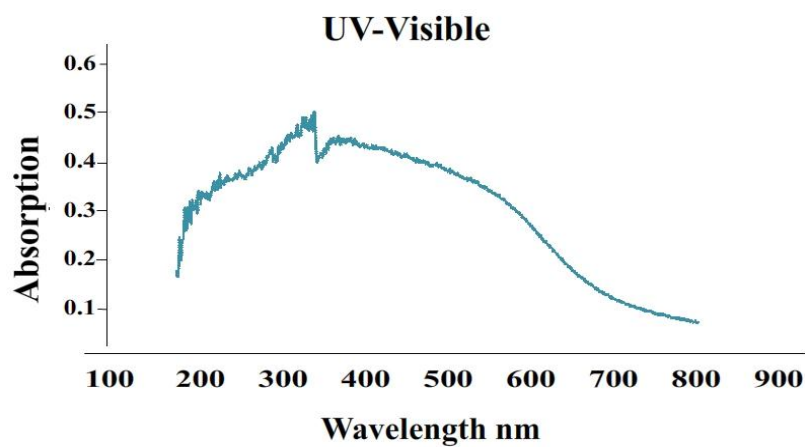

Fig. 3. Gas sensing unit.

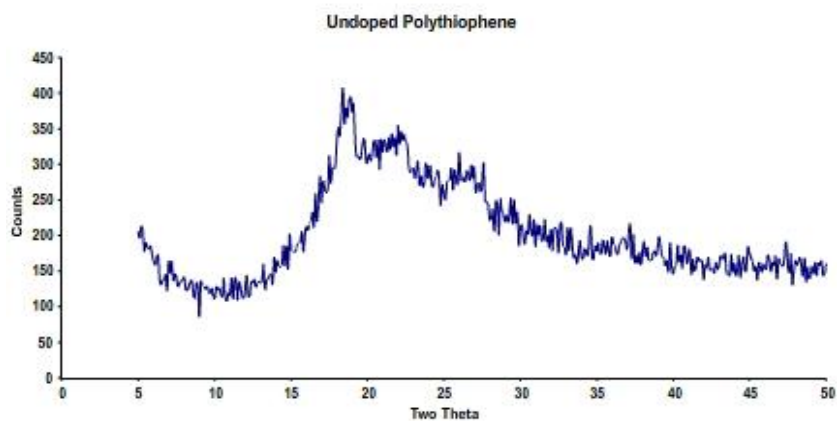**Fig. 4.** UV-Visible spectra of polythiophene.
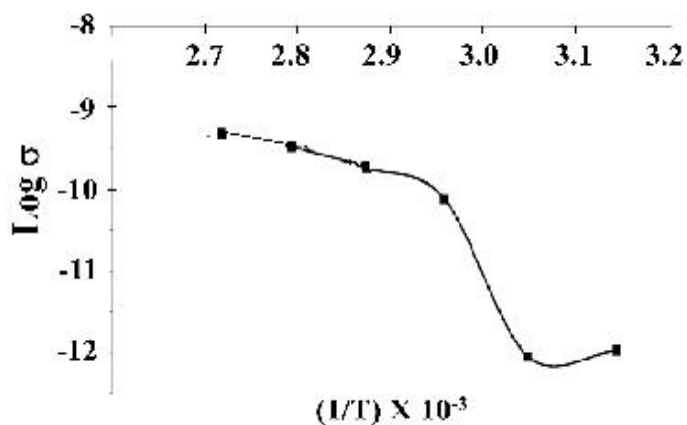
Fig. 5. XRD Scan of Polythiophene.

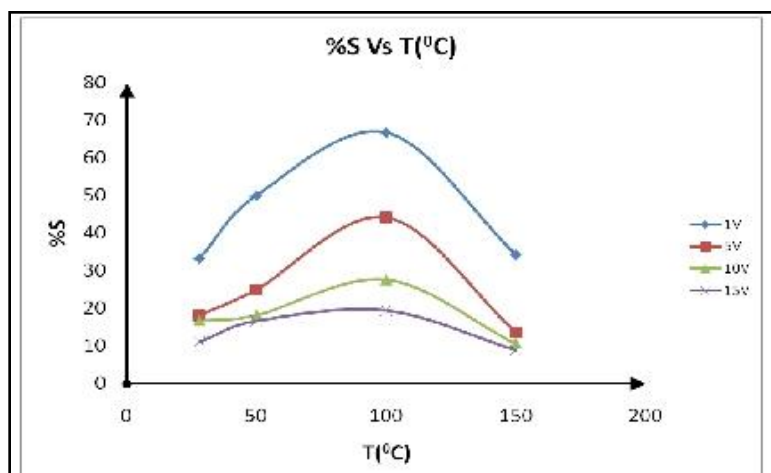**Fig. 6.** log σ Vs 1/T for polythiophene at 50 V/cm.

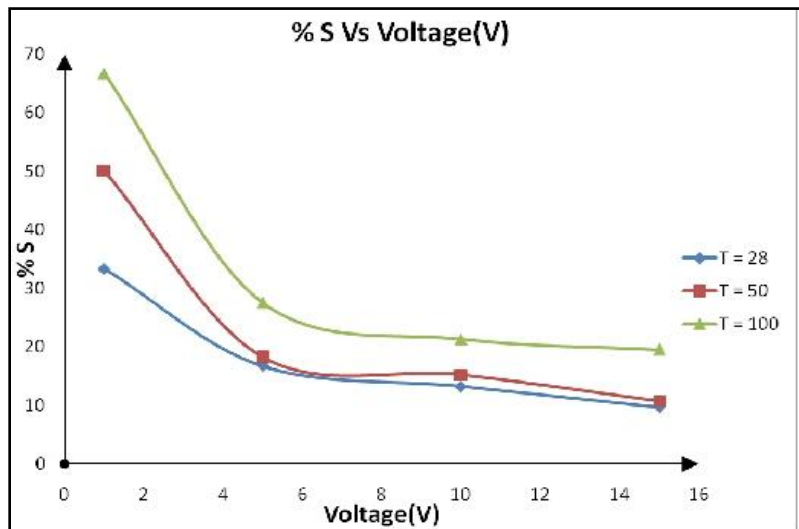**Fig. 7 (a).** % S Vs T(^{0}C) for polythiophene for 500 PPM concentration.

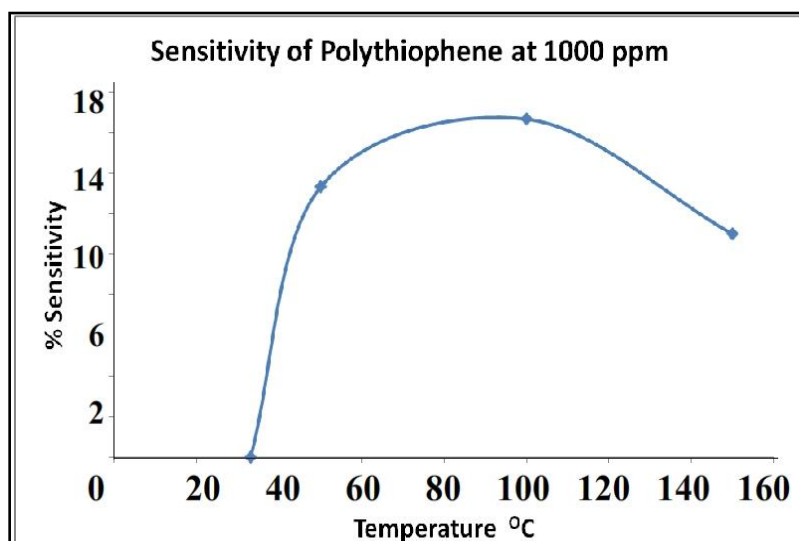**Fig. 7 (b).** % S Vs V(V) for polythiophene for 500 PPM concentration.

Fig. 8. %S Vs T (^{0}C) Concentration (1000 ppm)