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Chemical Synthesis and Characterization of Poly (aniline) Film doped with p-toluene sulphonic acid for Ammonia gas Sensing

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Abstract

The Polyaniline films were synthesized by oxidative polymerization of aniline using ammonium peroxydisulfate on poly (methyl methacrylate) substrate in the presence of p-toluene sulphonic acid for the development of ammonia sensor. The synthesized polyaniline films were characterized by using UV-visible, FTIR, SEM and the electrical conductivity. The ammonia sensing behavior of the synthesized film was studied by indigenously developed computer controlled gas chamber. The synthesized PANI film shows excellent sensing behavior for 20, 100 and 250 ppm of ammonia.

Keywords: Polymer composite, polyaniline, chemical polymerization, p-toluene sulphonic acid, PMMA substrate, gas sensing.

1. INTRODUCTION

In recent years conducting polymers have attracted the interest of scientific and technological researchers. These materials have widespread applications, such as electronics, energy storage, chemical sensing etc. [1-6]. The interest of these materials has been recognized by the awarding of the Nobel Prize in Chemistry in 2000 to

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Heeger [7] and MacDiarmid [8] and H. Shirakawa, who synthesized the first conducting polymers and proved their potentialities in a large number of applications. Besides, some commercial electronic noses are based on electronic conducting polymers organized in an array [9] however; no commercial systems are yet developed because of the remained poor selectivity and reversibility of these materials [10]. The advantages of conducting polymers compared to inorganic materials used until now are their diversity, their easy synthesis and particularly, their sensitivity at room temperature. Polypyrrole has been one of the first polymers used in gas sensors. However, it shows a lower sensitivity, a slow response time, controlled high temperature (100°C) requirement and an incomplete desorption of gas molecules, i.e. an incomplete reversibility of the sensor response [11]. So the research was extended to polyaniline (PANI) [12]. Polyaniline (PANI) is a particularly attractive material because it has moderately high conductivity upon doping with acids; it is easily synthesized by chemical or electrochemical oxidation of aniline, and has good thermal and oxidative stability Also it is the only conducting polymer whose electronic structure and electrical properties can be reversibly controlled by both oxidation and protonation. [13-16].Electrochemical method can control the oxidation reaction; however, it is expensive and not suitable for mass production, whereas chemical synthesis is very simple, inexpensive in which oxidation can be controlled by proper choice of process parameters viz. concentration of monomer, dopant, oxidant, synthesis temperature, and time of synthesis. It is advantageous for mass production and hence widely used in industries. [17-18]

The polyaniline film can be synthesized from aniline monomer by oxidation using chemical polymerization technique. The oxidative chemical polymerization is direct and easy deposition of film. The PANI film synthesized by this technique will have excellent porosity, uniformity, environmental stability, conductivity, and will give significant reversible change in the conductivity when exposed to different gases such as ammonia, hydrogen sulfide.[19] Several of oxidizing agents can be used for the synthesis of PANI such as Ammonium persulfate ($(NH_4)_2S_2O_8$),potassium dichromate ($K_2Cr_2O_7$),Cerium sulfate ($Ce(SO_4)_2$), Sodium vanadate ($NaVO_3$),potassium ferricyanide $K_3Fe(CN)_6$,potassium iodate (KIO_3),hydrogen peroxide (H_2O_2). Ammonium persulfate has been found most suitable oxidant for chemical polymerization of aniline.[20-21].The PANI films synthesized by various methods have been used for the detection of various gases but it exhibits relatively low sensitivity and long response time.[12,22-23]. Recently PANI has been used for various sensing applications. However, PANI has not been explored much for ammonia gas sensing application. Therefore, in the present investigation, considerable efforts have been devoted to develop ammonia sensor using PANI film synthesized by simple chemical polymerization technique. I have used an effective dopant, oxidant,

and their optimized concentrations to detect low level ammonia for different biomedical, environmental, and industrial applications. Protonic acids can be used to synthesize PANI films to increase the sensitivity and to reduce the response and recovery time of sensor. The electrical properties, surface morphology of the PANI film are important factors for interaction of ammonia with PANI, which will govern the device performance. The properties of the conductive PANI are affected by the type of dopant employed. For instance, the use of acids such as camphor sulphonic acid, dodecylbenzene sulphonic acid with large anions as a dopant increases the solubility of PANI [24-27]. Incorporation of a large size dopant anions viz.nafion, polyvinyl alcohol, polymethylmethacrylate, polystyrene sulfonate, polyvinyl sulfonate, dodecylbenzene sulfonate, and p-toluene sulfonate etc in PANI film can make it more conducting and porous [26, 28-31]. Therefore, in the present investigation, I have used p-toluene sulphonic acid (p-TSA) as a dopant. The present investigation deals with the synthesis of PANI– p-TSA films on polymethylmethacrylate substrate by chemical polymerization. The concentration of monomer, dopant, oxidant and reaction temperature has been optimized. The synthesized films were characterized by scanning electron microscopy (SEM), ultraviolet-visible (UV-Vis), and Fourier transforms infrared spectroscopy (FTIR). The PANI films were further exposed to ammonia gas with different concentrations (in the range from 20 to 250 ppm). Sensitivity of the films has been measured in terms of change in electrical resistivity with ammonia concentration by using indigenously developed computer controlled gas sensing characterization system.

2. EXPERIMENTAL

Materials: All chemicals used were of Analytical reagent (AR) grade. Aniline was purchased from Rankem Ranbaxy New Delhi (India). Ammonium peroxydisulfate was purchased from SpectroChem (India) and p-toluene sulfonic acid was purchased from Loba Chemie (India). Aniline was doubly distilled before use.

Polymerization

We have synthesized polyaniline (PANI) on PMMA substrate using chemical polymerization. The oxidation of aniline with ammonium peroxydisulfate was performed in an aqueous medium containing p-toluene sulfonic acid (p-TSA) as a dopant using different concentration ratio of oxidant-monomer-dopant as shown in Table 1.

Table 1: The effect of the variation of monomer: oxidant: dopant ratio on conductivity and uniformity of chemically synthesized PANI film.

Sample	monomer: oxidant: dopant ratio	conductivity of Synthesized film ($S\ Cm^{-1}$)	Surface Uniformity
P1	1: 1: 1	0.123	Uniform
P2	2: 1: 1	0.061	Uniform
P3	3: 1: 1	-----	Non- Uniform
P4	4: 1: 1	-----	Non- Uniform
P5	1: 1: 2	0.012	Uniform
P6	1: 1: 3	0.085	Non- Uniform
P7	1: 1: 4	0.021	Uniform
P8	1: 2: 1	0.042	Non-Uniform
P9	1: 3: 1	0.027	Non-Uniform
P10	1: 4: 1	0.092	Non-Uniform

Aniline and APS were separately dissolved in distilled water. The p-toluene sulfonic acid was used as dopant. The PMMA substrate of 2 mm in diameter and 25 mm thick was used for the deposition of the PANI. The PMMA substrate was submerged in the reaction mixture of aniline and ammonium peroxydisulfate. The polymerization was carried out at 10°C for 1 hour. Substrate was covered on one side with an adhesive tape to allow the coating on one side only. The samples were rinsed with distilled water to remove the PANI precipitate, and dried in air.

The UV-visible spectra of the synthesized PANI film dissolved in DMSO were recorded by using a Chemito-UV-2100 a spectrophotometer in the range 300-900 nm. The FTIR spectra of the synthesized PANI film were taken on Shimadzu-8400 spectrophotometer between 400-4000 cm^{-1}. The morphology of the PANI film has been studied by Scanning Electron Microscope at various magnifications, using JEOL, JSM-6360A SEM machine and the electrical conductivity of the PANI film was recorded by a four- probe method at room temperature. The ammonia gas-sensing characteristics of the synthesized polyaniline film was studied by measuring the change in electrical conductivity on exposure to ammonia gas at different concentrations using indigenously designed and fabricated gas sensing chamber.

3. RESULTS AND DISCUSSION

Since number of electrons taken by the oxidant in the oxidation reaction is different in general, the optimization of. concentration of monomer, oxidant and dopant is very important. Therefore we have synthesized PANI film with different concentration of monomer, oxidant and dopant ratio. The synthesized PANI films were examined for surface uniformity and adhesiveness. The polymerization of aniline with ammonium peroxydisulfate as an oxidant was performed in an aqueous medium containing p-toluene sulphonic acid as a dopant. Various concentration ratio of the monomer-oxidant-dopant i.e. aniline- APS- p-TSA were considered and each combination has been named as sample P1, P2, P3 etc. as shown in table 1.The synthesized PANI films were having uniform morphology for the samples P1,P2,P5 and P7.

3.1. UV-Visible Characterization of synthesized PANI film

UV-Visible spectroscopy is a very sensitive tool for the studies of polyaniline protonation and more precisely for the elucidation of the interactions between the doping anion and the polymer chain. The UV-Visible absorption spectra of the polymer doped with p-TSA films (samples P1, P2, P5 and P7) were recorded by dissolving the polymer film in Dimethyl Sulfoxide (DMSO) and are depicted in Fig.1.

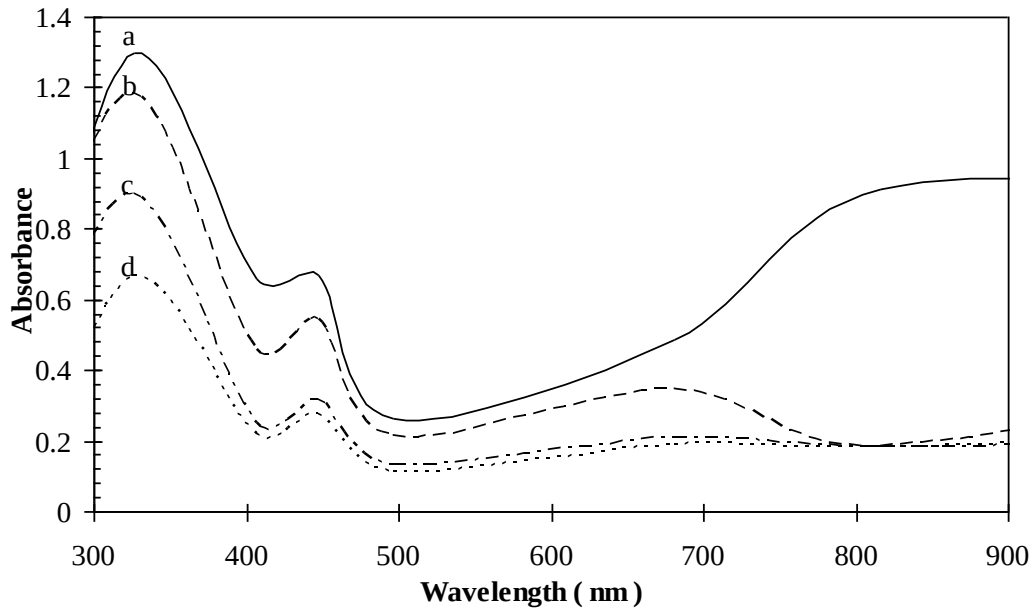

Fig.1. UV-Visible spectra of Polyaniline film for samples a) P1 b) P2 c) P7 and d) P5.

Among these spectra, the absorbance and sharpness of the peak at 420 nm found to be higher for a sample P1 as well as the free carrier tail at 800 nm is predominant for this sample. The sample P2, P5 and P7 shows a small carrier tail at 800 nm. The peak at 320 nm corresponds to the π-π transition of the benzenoid rings, while the sharp peak

at 440 nm can be assigned to the localized polarons which are characteristic of the protonated polyaniline, together with the extended tail at 800 nm representing the conducting ES form of the polymer for all the samples.

3.2. FTIR Analysis of synthesized PANI film

The molecular structure of synthesized PANI films was also characterized by FTIR spectroscopy. The FTIR spectra of synthesized PANI films (samples P1, P2, P5 and P7) are shown in Fig. 2.

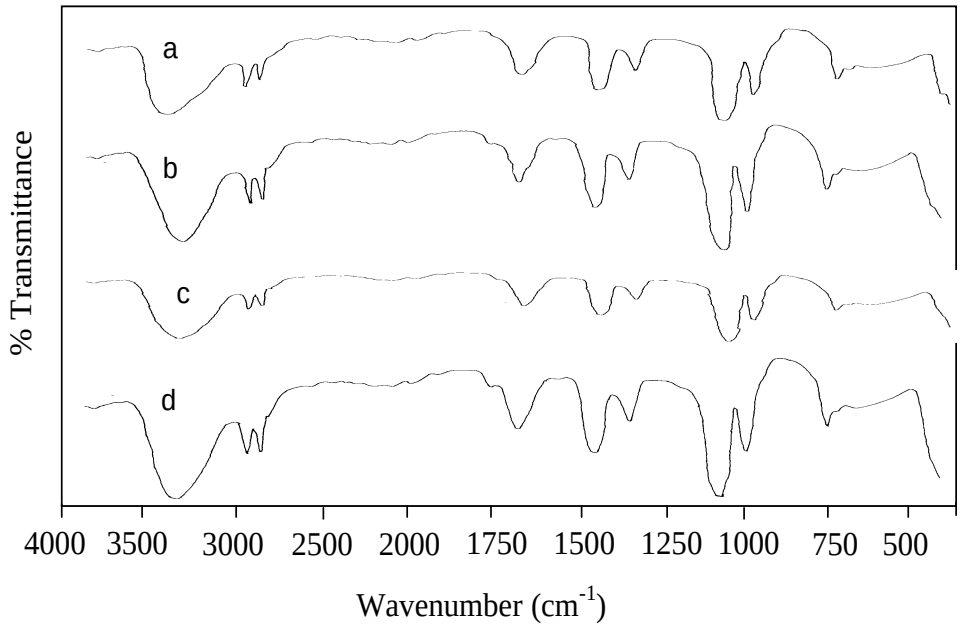

Fig.2. FTIR spectrum of Polyaniline film of samples a) P1 b) P2 c) P5 and d) P7.

It can be seen that quinoid and benzenoid ring stretching bands are present at 1656 and 1429cm^{-1}. The C-H in plane and C-H out of plane bending vibrations appears at 1033 and 952 cm^{-1}. The peak at 1313cm^{-1} is assigned to C–N stretching of secondary aromatic amine. Band at 3440 cm $^{-1}$ is assigned to the N-H stretching band. It can be seen form these spectra of the sample P1, P2, P5 and P7, there is slightly change in intensity of the peaks. The intensity peak 1033 is high in the sample P7, which is due to the enhanced concentration of dopant. At 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 is sharp and high in sample P7, which indicates that the doping is higher in the sample. All these characteristic bands confirm the presence of conducting ES phase of the polymer. This shows very good agreement with earlier reported work [32].

3.3. Morphology of the PANI film

The surface morphology of the synthesized PANI film has been studied by using scanning electron microscope (SEM).The scanning electron micrograph of the synthesized PANI films (samples P1, P2, P5 and P7) are shown in Fig. 3.

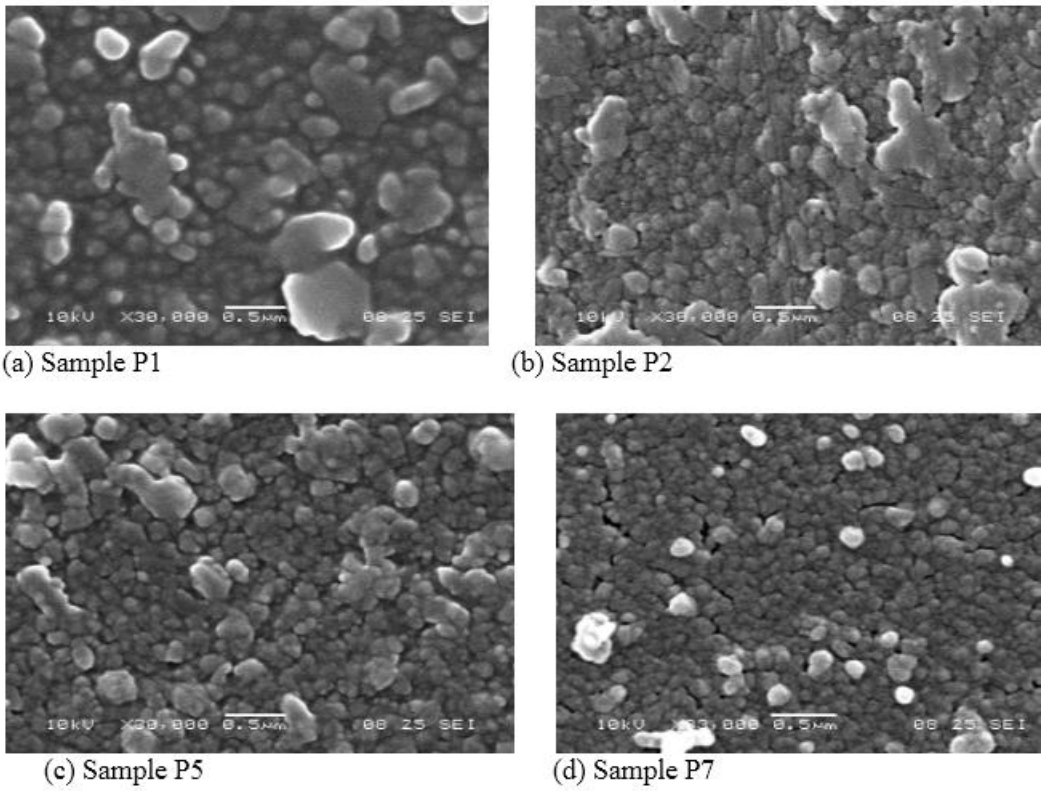

Fig.3. The scanning electron micrograph of PANI films of the samples a) P1 b) P2 c) P5 and d) P7

I observed globular surface morphology with very good uniformity and adhesiveness for all the samples. However, surface morphology of the synthesized PANI films of sample P7 and P5 was more porous as compared to sample P1 and P2.

3.4. I-V characteristics of polyaniline films.

The I-V characteristic of the synthesized PANI films (samples P1, P2, P5 and P7) was studied by measuring the voltage with varying current at room temperature. The voltage was measured with varying current at room temperature in order to see whether the polyaniline film possesses the ohmic or rectifying contacts. A linear relationship of the I-V characteristic is shown in Fig. 4. reveals that the polyaniline films have an ohmic behavior.

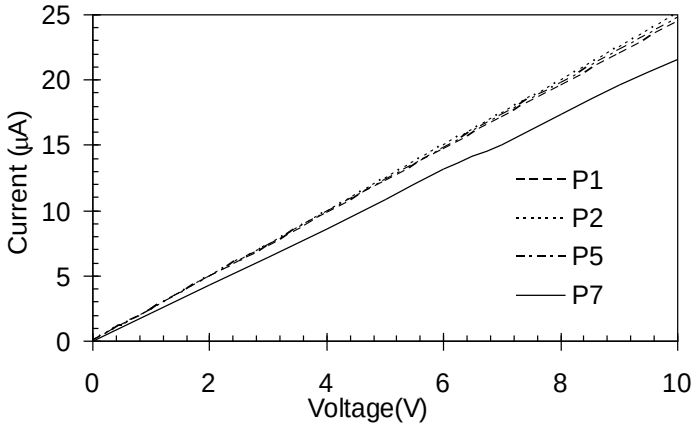

Fig.4. I-V characteristic of the sample P1, P2, P5 and P7 Polyaniline film

3.5. Ammonia Gas Sensing Characteristics

In order to evaluate the ammonia gas-sensing characteristics of the synthesized PANI film we have used the Four-probe technique of resistivity measurement, where four electrical contacts were made on the polyaniline film. The polyaniline film was enclosed in indigenously designed and fabricated a gas chamber. The change in resistivity of the film was measured when the synthesized PANI film was exposed to ammonia gas. The recovery time was measured by exposing the film to the air. Here we have explored the ammonia gas-sensing curves of PANI at three different concentrations of ammonia gas, 20 ppm, 100 ppm, and 250 ppm. It was observed that the resistivity of the polyaniline increases in the presence of ammonia and after a few minutes becomes saturated and the resistivity decreases steadily to a minimum value, when the ammonia gas was removed. However, a drift from its original value was observed. The relationship between change in resistivity and time of the synthesized PANI films of samples P1, P2, P5 and P7 when exposed to different concentration of ammonia gas are shown in Fig. 5 -8.

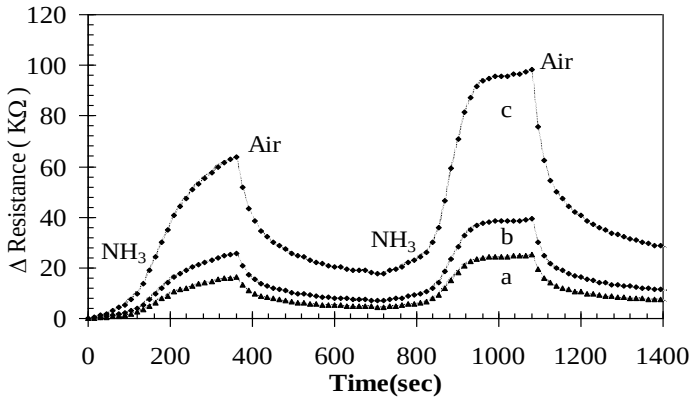

Fig.5 Resistance change for PANI film sample P7 in NH_3 gas. NH_3 concentration (a) 20 ppm (b) 100 ppm (c) 250 ppm

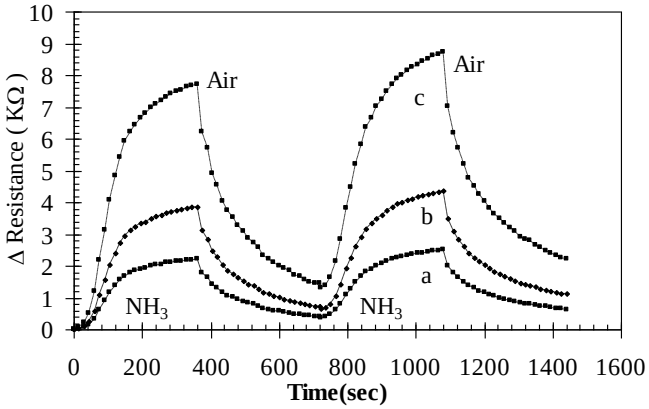

Fig.6 Resistance change for PANI film sample P5 in NH_3 gas. NH_3 concentration (a) 20 ppm (b) 100 ppm (c) 250 ppm

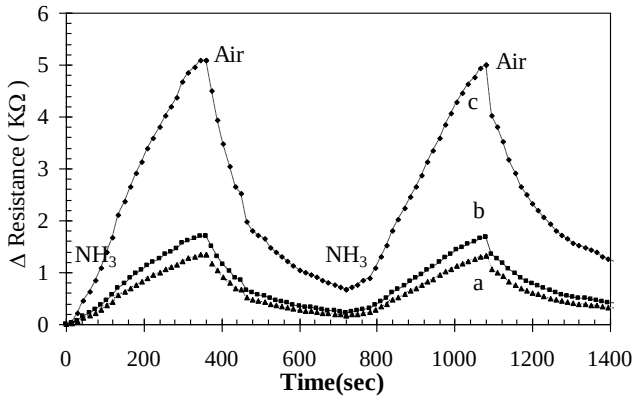

Fig.7 Resistance change for PANI film sample P2 in NH_3 gas. NH_3 concentration (a) 20 ppm (b) 100 ppm (c) 250 ppm

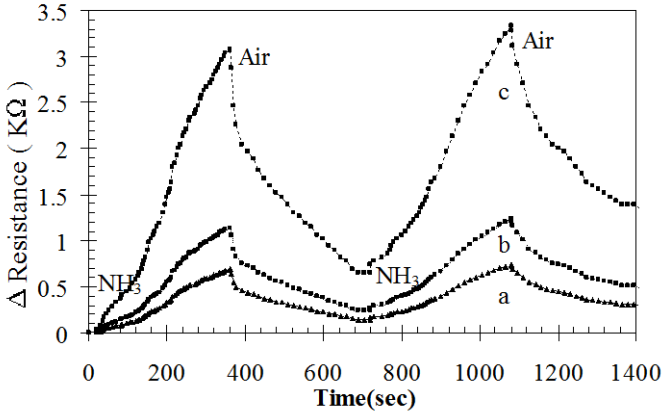

Fig.8 Resistance change for PANI film sample P1 in NH_3 gas.NH_3 concentration (a) 20 ppm (b) 100 ppm (c) 250 ppm

It was found that the resistance of the synthesized PANI film increases when it is exposed to ammonia gas. The increase of concentration enhances the rate of diffusion of ammonia molecules towards and into the polymer thin film. Increasing concentrations lead to increased chemisorbed ammonia, which in turn enhances the desorption rates and sensing site renewal. The PANI is known to be a p-type semiconductor, NH_3 molecules acts as a donor after being adsorbed and form an electric barrier near the surface of the sample. The barrier height increases with adsorbed gas concentration [33]. The change in resistance (ΔR) is found to be linearly proportional to the ammonia concentration as shown in table 2.

Table 2: The change in resistance and sensitivity of the synthesized PANI films (samples P1, P2, P5 and P7) when exposed to the different concentration of ammonia gas.

Sample	Conc. Of NH_3 (Ppm)	Change in Resistance (KΩ) (ΔR)	Sensitivity (ΔR/R)
P1	20	0.615	0.062
P2	20	0.739	0.074
P5	20	2.189	0.154
P7	20	21.199	0.269
P1	100	1.060	0.126
P2	100	1.073	0.100
P5	100	3.838	0.241
P7	100	26.379	0.294
P1	250	3.081	0.351
P2	250	5.096	0.352
P5	250	7.720	0.442
P7	250	63.786	0.662

The sensitivity of the sensor has been calculated in terms of ($\Delta R/R$), where the ΔR is the change in resistance of the PANI film when exposed to ammonia gas and R is the original resistance of the PANI film. The relationship between the sensitivity and ammonia gas concentration of the synthesized PANI films (samples P1, P2, P5 and P7) is shown in Fig. 9.It can be seen from the Fig.9. that the sample P7 exhibit highest sensitivity as compared to other samples, because the synthesized PANI film of sample P7 was having more porous surface morphology as compared to other samples

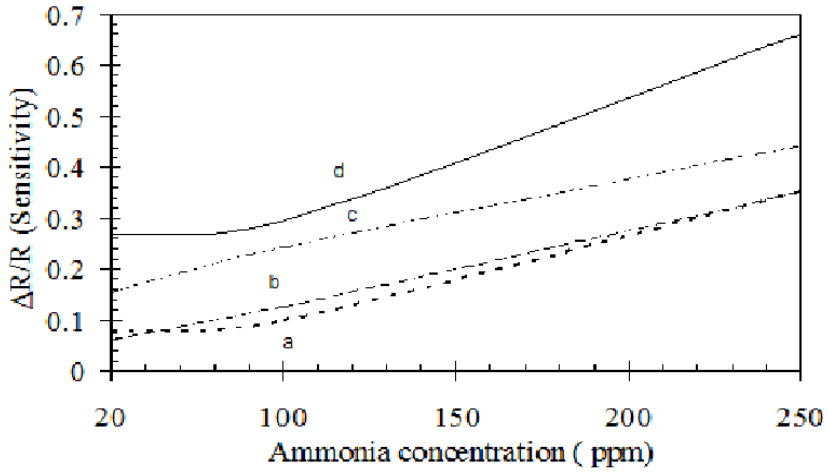

Fig. 9. The relationship between sensivity and concentration of ammonia gas of the PANI films sample a) P1 b) P2 c) P5 d) P7.

4. CONCLUSIONS

Successfully synthesized PANI films doped with p-toluene Sulphonic acid by chemical polymerization on PMMA substrate.Also optimized concentration ratio of monomer: oxidant: dopant of the synthesized PANI film and it is 1:1:4.The synthesized PANI film with optimized concentration ratio of monomer: oxidant: dopant (1:1:4) shows globular and porous surface morphology which is suitable for sensor applications (Ammonia Gas Sensing).The synthesized PANI film with concentration ratio of monomer: oxidant: dopant (1:1:4) shows excellent sensing behavior for ammonia gas.

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