Development of ammonia sensor using poly(aniline) film doped with acrylic acid

K. P. KAKDE, H. J. KHARAT, P. A. SAVALE, K. DATTA, P. GHOSH, R.D. MHASKE and M. D. SHIRSAT*

Optoelectronics and Sensor Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad - 431 004 (India)

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ABSTRACT

In the present investigation we have developed ammonia sensor using polyaniline film doped with acrylic acid. We have synthesized polyaniline by oxidative polymerization of aniline using ammonium peroxodisulfate on poly (methyl methacrylate) substrate in the presence of acrylic acid as a primary dopant without using other acids. The synthesized films were characterized by using UV-Vis Spectroscopy, FTIR spectroscopy, Scanning Electron Microscopy (SEM) and the electrical conductivity. The sensing behavior of the synthesized films for ammonia was studied by using indigenously developed computer controlled gas chamber. The synthesized polyaniline films show excellent sensing behavior for 50, 100 and 250 ppm of ammonia gas.

Keywords: Conducting polymer, polyaniline, chemical polymerization, acrylic acid, primary dopant, PMMA substrate, gas sensing

INTRODUCTION

Conducting polymers are the materials which have been used for the application in diverse fields including electronics, energy storage, chemical sensing etc.\(^1\-\^7\). Polyaniline (PANI) is unique among conducting polymers in its wide range of electrical, electrochemical and optical properties. PANI can be typically synthesized by oxidizing aniline either electrochemically\(^8\) or chemically\(^9\-\^10\). Similarly conductivity of the polymers can be varied by doping different protonic acids or by using functionalized protonic acids, which make the polymers conducting as well as soluble in organic solvents. Many functional dopants have been introduced in the polymeric matrix by in situ doping method, secondary doping method and blending the polymer with doping species such as dodecylbenzenesulfonic acid, camphor sulfuric acid, poly(styrene sulfonic acid), poly(acrylic acid) etc\(^11\-\^13\). It is believed that the dopant species are so small that they may evaporate or sublime out of the polymer\(^14\). To overcome this drawback, several polymeric acids have been used as dopants, such as polyacrylic acid and polystyrene sulphonic acid\(^15\). In modern chemical industry the acrylic acid (AA) has been widely used because it has two functional group with chemical activity i.e. C = C and – COOH. Yongsheng et al have investigated the scientific mechanism of the combination of AA and PANI\(^16\). The PANI films have been synthesized by doping with HCl in conjunction with AA and these PANI films are sensitive to ammonia vapor as well\(^17\-\^19\). However, to the best of our knowledge no systematic study has been reported for the synthesis of PANI only in the presence of AA as a primary dopant without using other acids for the development of ammonia sensor. Therefore, in this study we have synthesized the PANI in the presence of AA as a primary dopant without using other acids, on the poly(methyl methacrylate) (PMMA) substrate for ammonia sensing at room temperature (H=30°C).
The synthesized PANI films were characterized by using UV-visible, FTIR spectroscopy, SEM and electrical conductivity. The sensing behavior of the PANI films for ammonia gas was studied.

**EXPERIMENTAL**

Aniline monomer and AA were purified by distillation prior to use. All other reagents were analytical grade and were used as received. PANI-AA was synthesized using in-situ polymerization of aniline monomer by using ammonium peroxysulfate (APS) as an oxidant in the presence of AA as a dopant. The polymerization was carried out at 10°C ± 0.5 in a temperature controlled water bath for 20 hour. In this process, 0.50 M of AA aqueous solution and 0.25 M of aniline were added into 10 ml of distilled water, and (then) the solution was stirred by an electromagnetic stirrer for about half hour. Then the solution was cooled down to 10°C, 10 ml of APS aqueous solution (0.25 M) was added drop wise to the solution containing AA and aniline monomer with continuously stirring. The PMMA substrate was submerged in the reaction mixture of aniline and APS and as a result PANI film was deposited on PMMA substrate. Then the resulting film was removed from the solution, washed with distilled water and dried.

**RESULTS AND DISCUSSION**

**Synthesis of PANI films**

PANI films in presence of AA were synthesized as per the procedure illustrated in the experimental section. The synthesized films were subjected with various characterization techniques. UV-Visible characterization of synthesized PANI films

The UV-Visible absorption spectrum of the synthesized PANI films doped with AA is shown in Fig.1. 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 film

**FTIR Analysis of synthesized PANI films**

The molecular structure of synthesized PANI films was studied using FTIR spectroscopy. The FTIR spectrum of synthesized PANI film is shown in Fig. 2. It can be seen that quinoid and benzenoid ring stretching bands are present at 1653 and 1423 cm⁻¹. The C-H in plane and C-H out of plane bending vibrations appears at 1024 and 952 cm⁻¹. The peak at 1315 cm⁻¹ is assigned to C–N stretching of secondary aromatic amine. In addition, a relative weak peak at 1700 cm⁻¹ appears in the spectrum is due to the stretching vibration of carbonyl group and it shows presence of AA in the film. Band at 3440 cm⁻¹ is assigned to the N-H stretching band. All these characteristic bands confirm the presence of conducting ES phase of the polymer. This shows very good agreement with earlier reported work.

![Fig. 1: UV-Visible spectrum of synthesized PANI film](image1)

![Fig. 2: FTIR spectrum of synthesized PANI](image2)
Surface Morphology of synthesized PANI film

The surface morphology of the synthesized PANI films was studied by using scanning electron microscope (SEM). The scanning electron micrograph of the synthesized PANI film is shown in Fig. 3. We observed granular and porous surface morphology with very good uniformity which is suitable for sensor applications.

I-V characteristics of synthesized PANI films

The current-voltage (I-V) characteristics of the synthesized PANI films were studied to ensure ohmic behavior of the films. A linear relationship of the I-V characteristics shown in Fig. 4 reveals that the polyaniline film has an ohmic behavior.

Sensing behaviour of synthesized PANI films

Sensing behaviour of the synthesized PANI films was studied using indigenously developed computer controlled gas sensing chamber. The synthesized PANI films were exposed to ammonia gas for 7 minutes. The recovery time was measured by exposing the film to the air for 7 minutes. The change in resistivity of the film was

![Image of the scanning electron micrograph of synthesized PANI film](image1)

![Image of the I-V characteristic of synthesized PANI film](image2)

![Image of the response of the synthesized PANI film to ammonia gas](image3)

Fig. 3: The scanning electron micrograph of synthesized PANI film

Fig. 4: I-V characteristic of synthesized PANI film

Fig. 5: Response of the synthesized PANI film to Ammonia gas
(a) 50 ppm (b) 100 ppm (c) 250 ppm
recorded at an interval of 15 second. It is reported that anything above 120 ppm of ammonia in the environment is hazardous and dangerous to health of the human being. Therefore, we have tested synthesized PANI-AA films for 50, 100 and 250 ppm of ammonia. The relationship between change in resistivity of the synthesized PANI film with time when exposed to 50 ppm, 100 ppm and 250 ppm concentration of ammonia gas is shown in Fig. 5. It was observed that the resistivity of the polyaniline film increases when it is exposed to ammonia; it reaches to the maximum value and becomes constant. The resistivity decreases steadily to a minimum value, when the ammonia gas was removed, however, a drift from its original value was observed. The response time for the film was found to be 180 s and the recovery time is found to be 300 s.

CONCLUSIONS

The present study reveals that acrylic acid is promising dopant for the chemical synthesis of PANI film. The synthesized PANI film in presence of acrylic acid shows uniform, granular and porous surface morphology which is suitable sensor applications. It shows excellent sensing behaviour for 50, 100 and 250 ppm concentration of ammonia.

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