Material Science Research India Vol. **5**(1), 195-200 (2008)

Development of ammonia sensor using poly (aniline) film doped with poly (vinyl sulphonic 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)

(Received: February 12, 2008; Accepted: April 04, 2008)

ABSTRACT

In the present investigation we have developed ammonia sensor using polyaniline film doped with poly (vinyl sulphonic acid). We have synthesized polyaniline by oxidative polymerization of aniline using ammonium peroxydisulfate on poly(methyl methacrylate) substrate in the presence of poly (vinyl 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 behaviour of the synthesized film was studied by indigenously developed computer controlled gas chamber. The synthesized PANI film shows excellent sensing behavior for 50, 100 and 250 ppm of ammonia.

Key words: conducting polymer, polyaniline, chemical polymerization, polyvinyl sulphonic acid, PMMA substrate, gas sensing.

INTRODUCTION

Conducting polymers have attracted the interest of scientific and technological researchers in recent years. These materials have widespread applications, such as electronics, energy storage, chemical sensing etc.[1-9], along with probable uses in the future. Among all of the electrically conductive polymers, 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[9-12]. Also it is only conducting polymer whose electronic structure and electrical properties can be reversibly controlled by both oxidation and protonation .The conductivity of the polymers can be varied by doping them with different protonic acids or by using functionalized protonic acids which make the polymers conducting as well as soluble in organic solvents. One problem associated with short-chain protonic acid dopants is ease of dedoping by aging or by contact with water and consequently the loss of its electrical conductivity. It is believed that the dopant species are so small that they may evaporate or sublime out of the polymer[13]. To overcome this drawback, several polymeric acids have been used as dopants, such as polyacrylic acid and polystyrene sulphonic acid[14]. However, little attention has been given to the substituted derivatives of polyaniline synthesized using polymeric acid dopants. Therefore in this studies we have synthesized the PANI in the presence of poly (vinyl sulphonic acid) PVSA as a primary dopant, on the polymethylmethacrylate (PMMA) substrate for ammonia gas sensing at room temperature (H≈30°C). It was expected that the study would be helpful in leading a new conducting polymer useful in various sensor applications. The polymethylmethacrylate (PMMA) substrate was submerged in the reaction mixture of aniline and ammonium peroxydisulfate as a result PANI was

deposited on PMMA. The synthesized PANI films were characterized by using UV-visible, FTIR spectroscopy, SEM and electrical conductivity and sensing for ammonia gas was studied

EXPERIMENTAL

Prior to use, aniline monomer was purified by distillation and stored under at 10°C. All other reagents were analytical grade and were used as received. PANI was synthesized via in situ doping polymerization of aniline monomer by using ammonium persulfate (APS) as an oxidant in the presence poly (vinyl sulphonic acid) PVSA as a dopant. In a typical process, 0.250 M of poly (vinyl sulphonic acid) PVSA aqueous solution and 0.25 M of aniline was added into 10 ml of distilled water, and then the solution was stirred by an electro-magnetic stirrer for about half an hour. After 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 poly (vinyl sulphonic acid) PVSA and aniline monomer with continuously stirring. The polymethylmethacrylate (PMMA) substrate was submerged in the reaction mixture of aniline and ammonium peroxydisulfate which resulted in a deposition of PANI on PMMA. The mixture was subsequently kept at 10°C in a temperature controlled bath for 24 hour. Then the resulting film was separated from the solution and washed with distilled water several times. Finally, the films were dried in air.

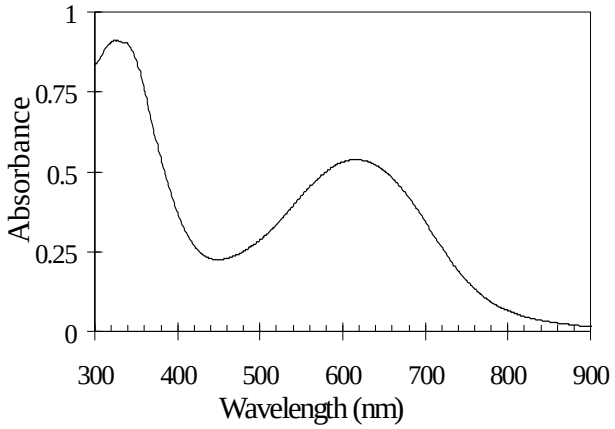

Fig.1. UV-Visible spectra of synthesized Polyaniline film

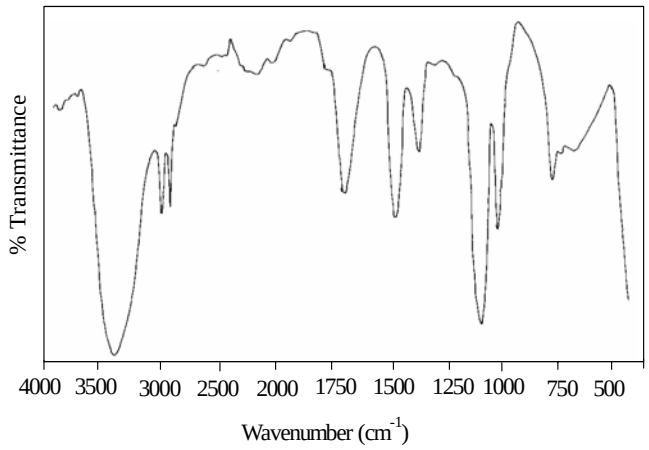

Fig. 2. FTIR spectrum of synthesized Polyaniline film

RESULTS AND DISCUSSION

UV-Visible characterization of synthesized PANI film

The UV-Visible absorption spectrum of the polymer doped with poly (vinyl sulphonic acid) PVSA acid was recorded by dissolving the polymer film in Dimethyl Sulfoxide (DMSO) and is depicted 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 for sample[15].

FTIR Analysis of synthesized PANI film

The molecular structure of synthesized PANI films was characterized by FTIR spectroscopy. The FTIR spectra of synthesized PANI are shown in Fig. 2. It can be seen that quinoid and benzenoid ring stretching bands are present at 1654 and

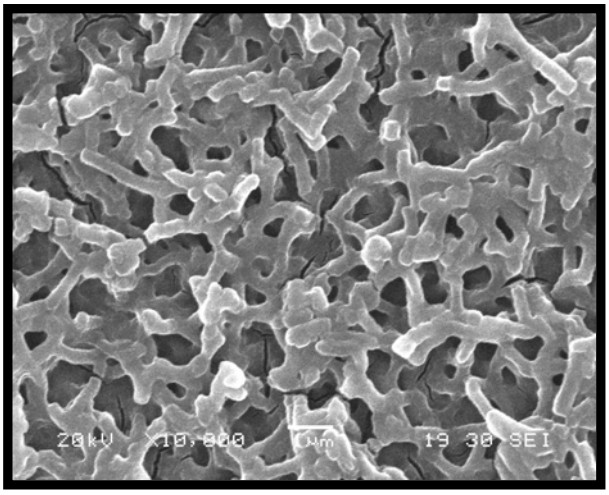

FIG.3. The scanning electron micrographs of PANIfilm

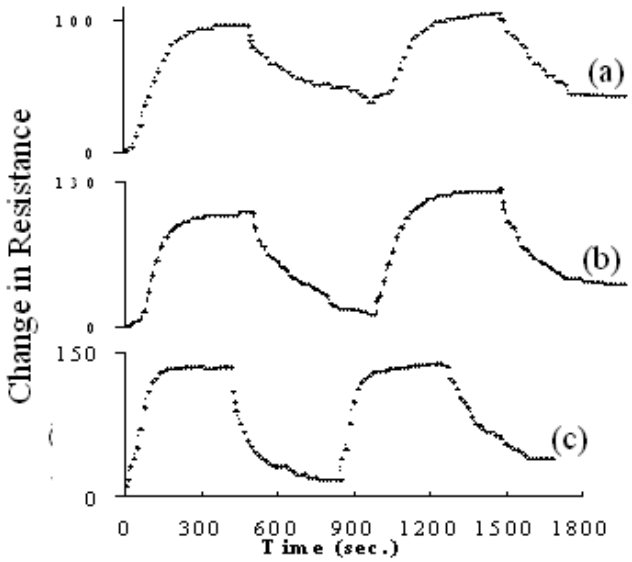

Fig.5. Response of the synthesized PANI film to ammonia gas (a) 50 ppm (b) 100 ppm (c) 250 ppm

1427cm^{-1}. The C-H in plane and C-H out of plane bending vibrations appears at 1028 and 952 cm^{-1}. The peak at 1313cm^{-1} is assigned to C–N stretching of secondary aromatic amine. Band at 3436 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[15-17].

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 film is shown in Fig. 3. We observed fibrillar and porous surface morphology with very good uniformity and adhesiveness .

I-V characteristics of polyaniline films

The I-V characteristic of the synthesized PANI film was studied by measuring the voltage with varying current at room temperature. The voltage was measured with varying current at room temperature (H≈30° C) 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 film has an ohmic behavior.

Ammonia gas sensing characteristics

The sensing behaviour of PANI film doped with (polyvinyl sulphonic acid) PVSA was studied using indigenously developed computer controlled gas chamber. The synthesized PANI film was 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 measured at an interval of 15 s. Here we have explored the ammonia gas-sensing curves of PANI at three different concentrations of ammonia gas, 50 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

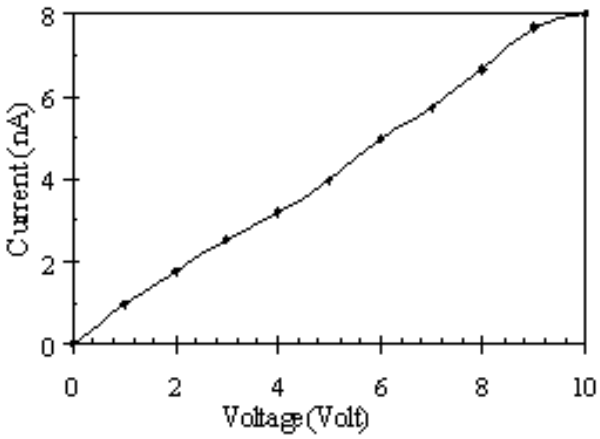

Fig.4. I-V characteristic of the synthesized synthesized Polyaniline film

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, when exposed to different concentration of ammonia gas is shown in Fig. 5. It is found that the resistance of the synthesized PANI film increases when it is exposed to ammonia gas. It shows excellent sensing behaviour for 50,100 and 250 ppm of ammonia. The observed response and recovery time is 105 sec. and 300 sec. respectively.

CONCLUSIONS

The conductive polyaniline films have been successfully synthesized by chemical polymerization of aniline doped with the poly (vinyl

sulphonic acid) PVSA as dopant on the polymethylmethacrylate substrate. The electrical, optical, and morphological properties and sensitivity to ammonia gas of synthesized film has been successfully studied. The synthesized PANI film shows excellent sensing behaviour for 50,100, and 250 ppm of ammonia.

ACKNOWLEDGEMENT

Authors are thankful to the University Grants Commission, New Delhi, India for the financial assistance and author K.P. Kakde express his gratitude for the award of Teacher fellowship under FIP scheme of UGC, New Delhi, India

REFERENCES

1. Boopathi M., Won M. and Shim Y. A sensor for acetaminophen in a blood medium using a Cu (II)-conducting polymer complex modified electrode,*Anal Chim.Acta.* **512**:1 91-197 (2004).
2. Toczy³owska, R., Pokrop, R., Dybko, A., Wróblewski, WPlanar potentiometric sensors based on Au and Ag microelectrodes and conducting polymers for flow-cell analysis. *Anal.chim.Acta* .**540**: 167-172 (2005).
3. Nicolas-Debarnot,Poncin-epaillard,F. Polyaniline as a new sensitive layer for gas sensors *Anal. Chim. Acta,* **475**: 1-15 (2003).
4. Pickup, P. G., Murray R. W. Redox conduction : its use in electronic devices. *J. Electrochem. Soc.* **131**: 833-839 (1984).
5. Zhang, C., Hoger, S., Pakbaz,K., Wudl, F., and Hegger, A. J., Improved efficiency in green polymer light-emitting diodes with air-stable electrodes. *J. Electron. Mater.* **23**: 453-458 (1994).
6. Li, F. B., Albery, W. J., Electrochemical polymerization of poly (thiophene-3-ethyl acetate)-a new candidate for a rechargeable battery cathode. *J. Electroanal. Chem.* **302**: 279-284 (1991).
7. Atta, N. F., Galal, A, Karagozler, A. E., Russ, G. C., Zimmer, H., Mark, H. B., Electrochemistry and detection of some organic and biological molecules at conducting poly (3-methylthiophene) electrodes. *Biosensors. Bioelectron.* **6**: 333-341 (1991).
8. Shirale, D.J., Gade, V.K., Gaikwad, P.D., Kharat, H.J., Kakde, K.P., Savale, P.A., Hussaini,S.S., Dhumane,N.R., Shirsat, M.D.,The influence of electrochemical process parameters on the conductivity of poly(n-methylpyrrole) films by galvanostatic method . Mater. Lett. **60**: 1407-1411 (2006).
9. Gade, V.K., Shirale, D.J., Gaikwad, P.D., Kharat, H.J., Kakde, K.P., Savale, P.A., Shirsat, M.D., Immobilization of god on electrochemically synthesized ppy-pvs composite film by cross-linking via glutaraldehyde for determination of glucose. React.and Fun.Polym.(In Press).
10. Li, W., Wan, M. Porous polyaniline films with high conductivity. Synth. Met. **92**: 121-126 (1998).
11. Jing, X.B., Wang, X.H., Geng, Y.H., Wang, L.X., Wang, F.S. Thermal behaviors of doped polyaniline. *Synth. Met.* **69**: 265-266 (1995).
12. Genies, E.M., Boyle, A., Lapkowski, M., Tsintavis, C. Polyaniline: a historical survey. *Synth. Met.* **36**: 139-182 (1990).
13. Chen, S. A., Lee, H. T., Structure and properties of poly (acry1ic acid)-doped polyaniline,Macromolecules **28**: 2858-2866 (1995).
14. Hu, H., Cadenas, J. L., Saniger, J. M., Nair, P. K., Elecrically conducting polyaniline-

poly(acrylic acid) blends. Polymer International **45**: 262 -270 (1998).

15. Kang, E. T., Neoh, K. G., Tan, K. L., Polyaniline: A Polymer with Many Interesting Intrinsic Redox States. *Prog. Polym. Sci.* **23**: 277-324 (1998).
16. MacDiarmid, A.G., Polyaniline and polypyrrole: where are we headed? Synth Met. **84**: 27-34 (1997).
17. Kulkarni, M.V.,Vishwanath, A.K., Khanna, P.K., Investigayion of spectroscopic and thermal properties of poly (o-toluidine) doped with polymeric acids,*J.Macro.Sci.* A**43**: 197-203 (2006).