



Investigating the Sensing Response of Polyaniline for Ammonia Prepared at Lower Room Temperature

Abhay G. Shrivastava,¹ N. S. Patil and ²L. S. Patil

¹Department of Physics Bhusaval Arts Sci and P.O.Nahata Commerce College Bhusaval-425201

²Department of Electronics, Dr. Anna Saheb G.D. Bendale Mahila Mahavidyalaya, Jalgaon -425001

Abstract : The useful ammonia (NH₃) gas sensor based on polyaniline (PANI) film as an active sensing layer. The PANI films prepared on a Glass substrate by a simple in-situ polymerization technique. In FTIR spectroscopy N-H and C-H stretching observed at the 3400 /cm which confirms the functional group of PANI. In UV-Visible absorption spectrum of the synthesized PANI film extended tail at 800nm representing the conducting ES state of Polyaniline. Ammonia (NH₃) gas-sensing properties of the films prepared at 0°C conditions were examined at room temperature in the range of 10 to 100ppm. The room temperature functioning of the sensor is critical, which facilitates low-power operation and also enhances the life time of a sensor. The observed variation in resistance of PANI film corresponding to 10 ppm and 100 ppm of NH₃ exposure. Furthermore, good reproducibility and long-term stability were also observed over a concentration range from 10 to 100 ppm. These results indicate that the PANI films on glass substrate promising for portable on-site detection.

I. Introduction

The most commonly studied classes of conducting polymer is polyacetylene, polythiophene, polypyrrole, polyaniline and derivatives, being investigated as conducting matrices for electronics applications such as Functional electrodes, Electrochromic devices, Optical switching devices, Batteries, TFTS, OLED, Sensors and so on. [1-3] Among all these conducting polymer, polyaniline is one of the most studied material because of its high conductivity upon doping with acids, its well-behaved electrochemistry, and easy preparation under reproducible conditions by electrochemical polymerization and chemically oxidation of aniline, chemical and electrical stability and good environmental stability. [4-15].

In recent times, we have witnessed for development of ammonia gas sensor for detection of toxic gases with a fast response time. Anhydrous ammonia (NH₃) is one such toxic gas, which is colourless and water-soluble with an execrable odour. Hence, due to the deleterious effects of NH₃ to human health and the environment monitoring of the NH₃ level has become extremely important. [16] [17] The polymerization temperature is an important characteristic in the synthesis and it plays the important role in sensing of gases.

To the best of our knowledge, the sensor explained by Waghule et al. shows response above 100ppm [18]. and the synthesis of PANI at 5°C are not been yet studied for detection of NH₃ gas. Following this idea, in the present work, PANI sensor was developed and operated at room

temperature where it shows good response and excellent recovery time 100 ppm of NH₃ gas. In addition, the sensors demonstrated a linear response in the range of 20-100 ppm as well as satisfying the conditions of stability and reproducibility too. we also show the Fourier transform infrared spectroscopy (FTIR), and U-Visible spectroscopy for confirmation of PANI.

II Experimental Setup, Materials and Equipment:

All the chemicals and solvents used were dried and purified by standard methods. Analytical grade Aniline Hydrochloride, Ammonium Peroxi- disulphate (APS) and Hydrochloric acid (HCL), Acetone, DMF and for filtration of precipitate, What man's filter paper were used. The Polyaniline films produced were characterized by FTIR spectroscopy (Nicolet-380), UV-spectrophotometer (SHIMADZU-1601), and Conductivity measurement is done by the two-probe technique.

A. Synthesis of conducting polymer:

In present paper the conducting polymer is synthesized by chemical method by oxidizing the corresponding monomer. The thin film of PANI has been prepared successfully by chemical oxidative polymerization and CBD technique. The physical properties of the film are characterized by the FTIR spectroscopy; the FTIR spectroscopy gives details of stretching bond in the prepared polymer film. The UV-vis spectrum is useful for gauging and providing information about the extent of conjugation, the electronic spectrum is indicative of polymer morphology, the presence of a free carrier tail. The change in conductivity due to temperature variations were observed with two probe method at room temperature.

To oxidize 0.2M Aniline hydrochloride with 0.25M Ammonium peroxidisulphate aqueous medium Aniline Hydrochloride was dissolved in deionised water in volumetric flask to 50 ml. of solution. Ammonium peroxidisulphate was dissolved in deionised water in volumetric flask to 50 ml. of solution. Both solutions are kept below room temperature for 1 hour, then mixed in beaker, and left to polymerize. The polymerization was carried out in a temperature-controlled water bath for 24 hours at 5°C. After 24 hrs. Polyaniline precipitate was formed and collected on What man's filter paper, washed with thrice 100 ml portion of 0.2M HCL and thereafter with

Acetone. Polyaniline (Emerdine) powder was formed. This powder was immersed in 0.1 M NH₄OH and washed and dried in air and vacuo at 60^o C. Oxidation of aniline hydrochloride with ammonium Peroxodisulphate yields Polyaniline as shown in Figure.1[19]

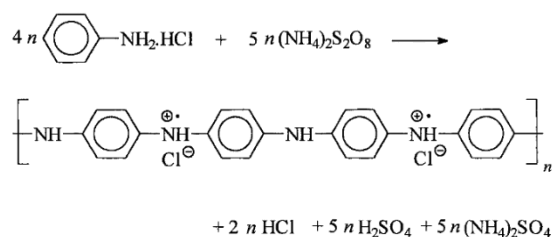


Figure. 1

Oxidation of aniline hydrochloride with ammonium Peroxodisulphate yields PANI (Emeraldine) hydrochloride

B. Preparation of the polymer thin film:

For measurement of conductivity Polyaniline film was form by spin coating technique. In this process, the purified polymer dissolved in NMP to form the Gel. The Polyaniline Emerdine salt is dissolved in NMP with 0.5 g: 10 ml with 3 hrs stirring. The Polyaniline solution spread on rotating substrate, repeating this process for two / three times the uniform film was obtained. After evaporation of solvent, a thin-film is formed. During the deposition of the film the temperature of the spinning machine assembly and surrounding temperature are maintained below the room temperature throughout the deposition process. Initially the speed of machine is at the 500 rpm for 20 seconds and thereafter 1200 rpm for 50 seconds.

C. Testing/characterization of sensing element:

The Ammonia sensing study is out using a static gas chamber to sense the ammonia in inner environment of chamber. The thin-film polyaniline, used as the sensing element, which was kept on two-probe assembly in the gas chamber. During the sensing study the film is allowed to get exposed by different concentration of NH₃ and the corresponding changes in electrical resistance of film were recorded

II RESULT AND DISCUSSION:

The synthesized PANI films with optimized concentration of monomer, dopant and oxidant prepared at a specific temperature 5^oC are subjected to study the optical and structural properties of (PANI). The optical property of PANI films were characterized by analysing UV-Visible spectroscopy. The physical and structural properties of synthesized film are studied by FTIR spectroscopy.

3.1. FTIR Analysis of Synthesized PANI:

The IR spectrum of PANI deposited on Si-substrate is exhibited in Figure 2. This study is useful to determine the chain orientation, structure of polymer and also used to elucidate mechanism of polymerization. The FTIR analysis was done by Nicolet 380 spectrophotometer in our laboratory. The IR spectrum shows N-H stretching vibration band at 3557 cm⁻¹. The characteristic band appeared at 1583 cm⁻¹ indicates nitrogen bond between benzoid and quinoid rings respectively. The band at 1668 cm⁻¹ corresponds to C=C stretching. The peak at 1305 cm⁻¹ is assigned to C-N stretching of tertiary aromatic amine. The peak at 815 cm⁻¹ is due to an aromatic =C-H plane bending. [20-21].

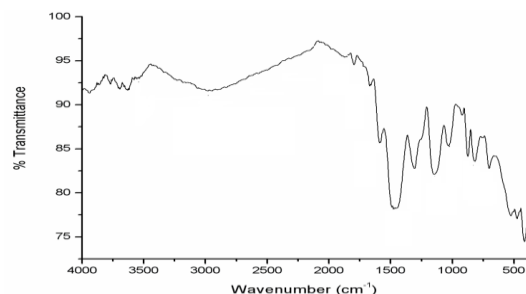
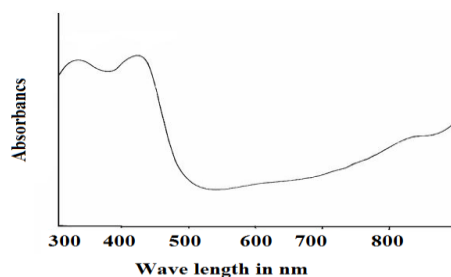


Figure. 2 FTIR spectra of PANI film

3.2 UV-Visible Analysis of Synthesized PANI Films

The Figure-3 shows the UV-Visible absorption spectrum of the synthesized PANI film. The peak at 320nm corresponds to the π-π transition of the Benzenoid ring, while the sharp trough at 440nm can be assigned to the localized polaron which are characteristics of the protonated Polyaniline, together with extended tail at 800nm representing the conducting ES state of Polyaniline.

Figure-3
UV-Visible spectra of PANI film

3.3.1. Gas sensing Measurement:

In order to compute the response for Ammonia (NH₃) gas, the changes in resistance of PANI sensors (films) were measured in the presence of air atmosphere and the test gas. To measure resistance of the sensor, two silver contact electrodes separated by one centimetre apart were made onto a sensor using silver paste. The whole/complete gas sensing study was carried out at room temperature by indigenously developed airtight gas chamber made up of glass container containing sample holder. A known concentration of NH₃ was injected by using syringe inside the chamber. The recovery phase of the sensor was initiated by opening the lid of gas chamber. The corresponding change in resistance of sensor was recorded as function of time. The PANI sensor prepared at 5^oC was subjected to successive injections of NH₃ gas are 100, 60, 80, 40ppm and the lowermost 20ppm concentration and results obtained were noted. For every new cycle/dose of the test gas, the gas inside the chamber was replaced by fresh air, in order to evacuate the chamber.

We observed increase in the resistance of polyaniline film when it was exposed to ammonia gas as shown in Figure 4. When polyaniline interacts with ammonia, the following reversible reaction occurs.



Where, PA and PAH⁺ are the initial undoped repeated block and proton-doped repeated block of polyaniline chains respectively. In the presence of ammonia, this reaction goes predominantly towards the right, as NH₃ molecule take up protons from the polyaniline, and forming energetically more favourable ammonium NH₄⁺. It is the PANI de-doping (de-protonation) reaction. But in the air (with no ammonia) the above reaction (1) begins towards left. Ammonium de-composes into ammonia and protons which being added to PANI molecules, restore the initial level of doping. In this way reversibility of the ammonia on

PANI occurs. Thus when ammonia interacts with polyaniline, two competing processes of proton gain (by ammonia and by PANI) occurs. The probabilities of the two processes are more or less the same because the heat of ammonia adsorption onto polyaniline is low. The results revealed that ammonia gets adsorbed onto polyaniline film. It shows maximum responses at higher concentrations of ammonia because the number of molecules striking over the polymer increases as the concentration increases from 20ppm to 100 ppm

The following Figure: 4 show the change in resistance of the PANI film as a function of time for 100ppm concentration of NH₃ gas. The sudden increase in resistance was noted upon interaction of gas molecules; along with very fast response and recovery time intervals.

The response of PANI film/ sensor was calculated by using following relation.

$$\text{Response of sensor (\%)} = \frac{R_a - R_b}{R_a} * 100$$

Where 'Ra', is initial resistance and 'Rb', is the final resistance of the film when exposed to the test gas. From Figure: 4, it was observed that PANI film showed considerable response during a dose of 100ppm of NH₃ gas. The exposure to ammonia gas was further repeated for concentration 20 ppm, 40 ppm, 60 ppm, 80 ppm and 100ppm and the related responses were studied. The increase of concentration of NH₃ gas enhances the rate of diffusion of ammonia molecules into the PANI film. Maximum responses were observed at higher concentrations of NH₃ because the number of molecules striking over the film increases as the concentration increases from 20ppm to 100 ppm. [22,23] The response and recovery time is an important parameter for a gas sensor. The response and recovery times were calculated by using the dynamic response curve using a process reported elsewhere [24].

As the concentration of NH₃ was increased 20ppm to 100ppm both the response and recovery times were found varied inversely i.e. response time was decreased while recovery time was increased from 100 ppm to 20 ppm thereby evidencing good response and recovery capabilities of the exposed PANI sensor.

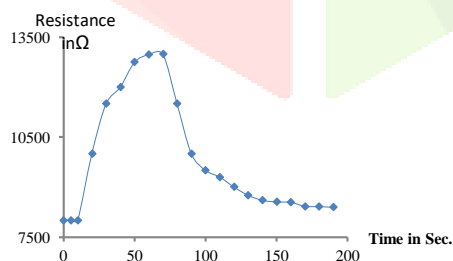


Figure 4:

Response of PANI NH₃ gas at 100 ppm

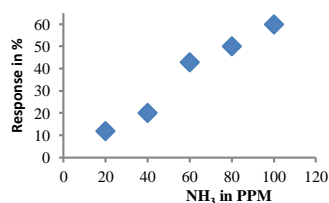


Figure 5:

Responses of PANI film for different concentrations of ammonia.

Stability and repeatability of PANI sensor:

In order to examine the reproducibility, the response PANI sensor was measured by exposing NH₃ gas repeatedly and the equivalent outcome was displayed. These observations revealed that, the response of sensor was unchanged during three cycles of measurements; this represents good repeatability of PANI sensor. It is observed that, even after repeated cycles of exposure and recovery, the resistance response levels of the sensor are maintained

Further, we also studied the other sensing properties viz reproducibility and stability with respect to NH₃ gas concentration for the fabricated PANI sensor. In order to examine the reproducibility, the response of PANI sensor was measured by exposing repeatedly to NH₃ gas in three cycles continuously and it was observed that the response of sensor was unchanged during the measurements, thereby representing good repeatability of the sensor.

Stability is an important parameter of a sensor. The stability of PANI sensor was tested towards NH₃ gas for total 32 days by the interval of 4 days. The observed study was highlighted in Figure: 7. the response value of PANI Sensor was decreased with the number of days. Initially, the sensor showed the response of 50%; which was decreased with time and stable response of 5% was attained after 28 days. Such a reduced response might be due to the humidity, temperature or aging induced effect.

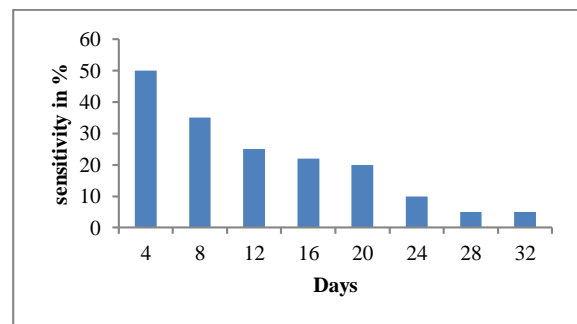


Figure.6

Stability of PANI sensor for 100ppm concentration of Ammonia

IV Conclusions

In present work Polyaniline has been successfully synthesized by chemical oxidation technique. Its physical and optical property of PANI films is investigated successfully. It can see that the deposited film can be used to prepare efficient active layer for sensors because of its ease in synthesis and environmental stability. The sensing observations carried out for different concentration of Ammonia gas. It is observed that as concentration increases the resistance of PANI increases and response slowdown for at higher concentrations, it is also observing that the sensitivity of sensor decreases as no of days' increases. The sensitivity confirmed that the sensor fabricated in our lab demonstrated better response to ammonia gas. The sensitivity of the PANI sensor was calculated by the surface resistance as a function of the concentration of ammonia gas. It was observed that the resistance of electro active polymer PANI film increases with increase in concentration of ammonia.

Reference:

- [1] ABHAY G. SHRIVAS, A. M. MAHAJAN, Effect of variation in preparation temperature on the conductivity of PANI optoelectronics and advanced materials rapid communications Vol. 2, No. 12, December 2008, p. 859 – 862
- [2] Karl Crowley, Aoife Morrin, et.al Fabrication of Polyaniline-Based Gas Sensors Using Piezoelectric Inkjet and Screen Printing for the Detection of Hydrogen Sulfide IEEE SENSORS JOURNAL, VOL. 10, NO. 9, SEPTEMBER 2010
- [3] Joshi Rajesh ,A Preparation and Characterization of PolyanilineThin Films for Sensor Applications *Int. Res. J. of Science & Engineering*, 2016; Vol. 4 (2): 51-55
- [4] G. Wu, N.H. Mack, W. Gao, S. Ma, R. Zhong, J. Han, J.K. Baldwin, P. Zelenay, Nitrogen-doped graphene-rich catalysts derived from heteroatom polymersfor oxygen reduction in non-aqueous lithium-O₂battery cathodes, *ACS Nano*6 (2012) 9764–9776.
- [5] S. Sönmezöğlü, R. Tas, S. Akın, M. Can, Polyaniline micro-rods based heterojunction solar cell: structural and photovoltaic properties, *Appl. Phys.Lett.* 101 (2012) 253301,
- [6] E.W. Paul, A.J. Ricco, M.S. Wrighton, Resistance of polyaniline films as function of electrochemical potential and the fabrication of polyaniline-basedmicroelectronic devices, *J. Phys. Chem.* 89 (1985) 1441–1447.
- [7] Y. Yang, J. Ouyang, L. Ma, R.J.-H. Tseng, C.-W. Chu, Electrical switching and bistability in organic/polymeric thin films and memory devices, *Adv. Funct. Mater.* 16 (2006) 1001–1014.
- [8] H. Chang, Y. Yuan, N. Shi, Y. Guan, Electrochemical DNA biosensor based on conducting polyaniline nanotube array, *Anal. Chem.* 79 (2007) 5111–5115.
- [9] S. Virji, J. Huang, R.B. Kaner, B.H. Weiller, Polyaniline nanofiber gas sensors: examination of response mechanisms, *Nano Lett.* 4 (3) (2004) 491–496.
- [19] N. G. Deshpande, Y. G. Gudage, R. S. Devan, Y. R. Ma, Y. P. Lee, Rampal Sharma , Room temperature gas sensing studies of polyaniline thin films deposited on different substrates, *J. Smart Materials and Structures* 2010, 18:095010
- [20] S. T. Navale, A.T. Mane, M. A. Chougule, V. B. Patil, Simple and low-temperature polyaniline-based flexible ammonia sensor: a step towards laboratory synthesis to economical device design *Synth. Met.*, 2014, 189, 111.
- [21] Rajendra S. Jadhav, Dilip G. Hundiware, Pramod P. Mahulikar, Synthesis of nano polyaniline and poly-o- anisidine and applications in alkyd paint formulation to enhance the corrosion resistivity of mild steel, *J. Coat, Technol. Res.* 2010, 7(4):449-454
- [22] H. J. Kharat, K. P. Kakade, P. A. Salve, K. Datta, P. Ghosh and M. D. Shirsat, Development of PPy-PVS optical fiber ammonia sensor, *J. Optoelectronics And Advanced Materials –Rapid communication* 2008, 2-9:553-560
- [23] Alok Srivastava, Virendra Singh, Chetna Dhand, Manindar Kaur, Tejvir Singh, Karin Witte, Ulrich W. Scherer, Study of Swift Heavy Ion Modified Conducting Polymer Composites for Application as Gas Sensor, *J. Sensors* 2006, 6:262-269
- [10] S. Bhadra, D. Khastgir, N.K. Singha, J.H. Lee, Progress in preparation, processing and applications of polyaniline, *Prog. Polym. Sci.* 34 (2009) 783–810.
- [11] G.C. Marjanovic¹, Recent advances in Polyaniline research: polymerization, mechanism structural aspects, properties and applications, *Synth. Met.* 177(2013) 1–47.
- [12] P. Kunzoa, P. Lobotka, M. Micusik, E. Kovacova, Palladium-free hydrogen sensor based on oxygen-plasma-treated polyaniline thin film, *Sens. ActuatorsB: Chem.* 171–172 (2012) 838–845.
- [13] N. Menegazzo, B. Herberta, S. Banerji, K.S. Booksh, Discourse on the utilization of polyaniline coatings for surface plasmon resonance sensing of ammoniavapor, *Talanta* 85 (2011) 1369–1375.
- [14] N. Menegazzo, D. Boyne, H. Bui, T.P. Beebe Jr., K.S. Booksh, DC magnetron sputtered polyaniline-HCl thin films for chemical sensing applications, *Anal.Chem.* 84 (2012) 5770–5777.
- [15] G. Rizzo, A. Arena, N. Donato, M. Latino, G. Saitta, A. Bonavita, G. Neri, Flexible,all-organic ammonia sensor based on dodecylbenzene sulfonic acid-doped polyaniline films, *Thin Solid Films* 518 (2010) 7133–7137
- [16] M.J. Fedoruk, R. Bronstein, B.D. Kerger, Ammonia exposure and hazardassessment for selected household cleaning product uses, *J. Exposure Anal. Environ. Epidemiol.* 15(2005) 534–544.
- [17].Mehto A, Mehto VR, Chauhan J, Singh IB, Pandey RK (2017) Preparation and charecterization of Polyaniline/ZnO Composite Sensor. *J Nanomed Res* 5(1): 00104. DOI: 10.15406/jnmr.2017.05.00104
- [18] S. A. Waghuley, S. M. Yenorkar, S. S. Yawale, S. P. Yawale, “Application of chemically synthesized conducting polymer-polypyrrole as a carbon dioxide gas sensor”, *Sensors and Actuators B*, 128 (2008) 366.