ISSN (Print) : 0974-6846
Indian Journal of Science and Technology, *Vol 10(20), DOI: 10.17485/ijst/2017/v10i20/112920, May 2017* ISSN (Online) : 0974-5645

Synthesis and Characterization of Polyaniline Doped with HCl, H_2SO_4 and PVA as Secondary Dopant for Toxic Gas (Ammonia) Sensor

K. P. Kakde*

Departmment of Electronic Science, Rayat Shikshan Sanstha's SSGM College Kopargaon, Ahmednagar – 423601, Maharashtra, India; kpkakde@yahoo.in

Abstract

In the present work, by simple chemical polymerization technique, H_2SO_4 (Sulphuric acid), HCl (Hydorochloric acid), poly (vinyl sulphonic acid) and PVA on PMMA substrate have been successfully synthesized PANI films for ammonia gas sensing. The polyaniline (PANI) thin films were synthesized by simple chemical polymerization technique, H_2SO_4 (Sulphuric acid), HCl (Hydorochloric acid), poly (vinyl sulphonic acid) and PVA on PMMA substrate as dopant. The ratio of monomer, dopant, and oxidant and reaction temperature has been optimized for better surface morphology of the synthesized PANI film. Scanning electron microscopy (SEM), ultraviolet-visible (UV-Vis), and Fourier transforms infrared spectroscopy (FTIR) is used for characterization of synthesized thin films of PANI. Also the response of the films towards ammonia gas (in the range from 20 to 250 ppm) is carried out. It was observed that these process parameters i.e. ratio of monomer, oxidants, doping acids, and deposition time and reaction temperature has major effect on the surface morphology of PANI film. The synthesized thin film structures of polyaniline doped with HCl, H_2SO_4 and PVA on polymethylmethacrylate (PMMA) shows the response to ammonia gas sensing in the range 20ppm-250ppm and can be used for ammonia sensing application.

Keywords: Ammonia Gas Sensing, Chemical Polymerization, HCl, H_2SO_4 and PVA Dopant, Polyaniline, Polymer Composite, PMMA Substrate

1. Introduction

The first conducting polymer has been synthesized by the Nobel award winner[1,2]. Conducting polymers are valuable sensing materials for various organic vapors[3] hazardous gases[4] and humidity[5]. Conducting polymers shows changes in conductivity when they are exposed to different gases and humidity[6-8]. Due to high conductivity, easy synthesis by chemical polymerization and good thermal stability polyaniline is preferred as a sensing material. It has also some disadvantages such as low sensitivity, slow response time and incomplete reversibility of the sensor, so the research was extended to polyaniline (PANI)[9]. It is the conducting polymer whose electronic structure and electrical properties can be reversibly controlled by both oxidation and protonation[10]. The properties of the conductive PANI are affected by the type of dopant employed. The concentration of dopants, ion size of dopant has considerable effect on properties of conducting polymers. In the present work, by simple chemical polymerization technique, H_2SO_4 (Sulphuric acid), HCl(Hydorochloric acid), poly (vinyl sulphonic acid) and PVA on PMMA substrate have been successfully synthesized PANI film .For better surface morphology of the synthesized of PANI film, the influence of process parameters has been studied. It was observed that these process parameters ratio of monomer, oxidants, doping acids, and deposition time and reaction temperature have major effect on the surface morphology of PANI film.

2. Experimental

Chemicals Used for Synthesis: All chemicals used were of AR grade for synthesis of PANI-PVA doped acids (HCl,H_2SO_4,) thin films. Aniline was distilled twice before use (99%) (Ranchem). Polyvinyl alcohol with an

* *Author for correspondence*

average degree of polymerization (mw.14000 Quiligen Fine–Chemicals, India.); H_2SO_4, HCl, Ammonium peroxydisulfate was purchased from SpectroChem (India)

3. Polymerization Blend Thin Films

Aniline (monomer) was double distilled prior to use. PVA was dissolved in conductivity water. Then with the optimized ratio of aniline, primary dopant (HCl), $H_2SO_4$and PVA additive (50 mg), as a secondary dopant as shown in Table1. Polyaniline (PANI) has been synthesized on PMMA substrate using chemical polymerization. The polymerization of aniline with ammonium peroxydisulfate as an oxidant was performed in an aqueous medium containing primary dopant (HCl), H_2SO_4 and PVA additive (50 mg), as a secondary dopant. Aniline and APS were separately dissolved in distilled water. The PMMA substrate was submerged in the reaction mixture of aniline and ammonium peroxydisulfate. The polymerization was carried out at 10°C ±0.5 in a temperature controlled water bath for 20 hour. The samples were rinsed with distilled water to remove the PANI precipitate, and dried in air

Table 1. Ratio of aniline, dopant acid (PANI-HCl, PANI- H_2SO_4 and PVA) and Ammonium peroxydisulfate

Sample Film	Concentration (M)		
	Monomer	Dopants	APS
PANI- H_2SO_4-PVA-1	0.25	0.25	0.25
PANI- H_2SO_4-PVA-2	0.25	0. 50	0.25
PANI- H_2SO_4–PVA-3	0.25	0.75	0.25
PANI- H_2SO_4–PVA-4	0.25	1.00	0.25
PANI-HCl-PVA-1	0.25	0.25	0.25
PANI-HCl-PVA-2	0.25	0.50	0.25
PANI-HCl-PVA-3	0.25	0.75	0.25
PANI-HCl-PVA-4	0.25	1.00	0.25

4. Instrumentation

The characterization of films was carried out by using UV Visible 1601 spectrophotometer, Shimadzu, The FTIR spectra of the synthesized PANI film were taken on Shimadzu-8400 FTIR, Surface morphology by using SEM JEOL JSM-6360 and the ammonia gas-sensing characteristics by measuring the using indigenously designed and fabricated gas sensing chamber.

5. Results and Discussions

The optimization of ratio of monomer, oxidant and dopant is very important. Therefore optimization of ratio of monomer, dopant, and oxidant has been carried out. The uniformity and adhesiveness of synthesized PANI thin films were checked. The chemical polymerization of aniline with APS (ammonium peroxydisulfate) as an oxidant was performed in an aqueous medium containing one of the acid viz. HCl, $H_2SO_4$and PVA additive (50 mg), as a secondary dopant. Various ratio of the monomer-oxidant-dopant i.e. aniline-APS-acids were considered. Also the response of the films towards ammonia gas (in the range from 20 to 250 ppm) is carried out.

6. UV-Visible characterization of synthesized PANI film

The UV-Visible absorption spectra of the synthesized thin films of polyaniline were recorded by dissolving the polymer films in Dimethyl Sulfoxide (DMSO) . Figure 1 shows the absorption spectra of films, The band at 324 nm for samples corresponds to π-π * transition of aniline. The broad bands at the 600 nm is due to π-π * transitions of quinone-imin groups, together with the extending tail at 800nm.The broad peak at 820 nm shows the conducting emeraldine salt ES phase in the polymer.

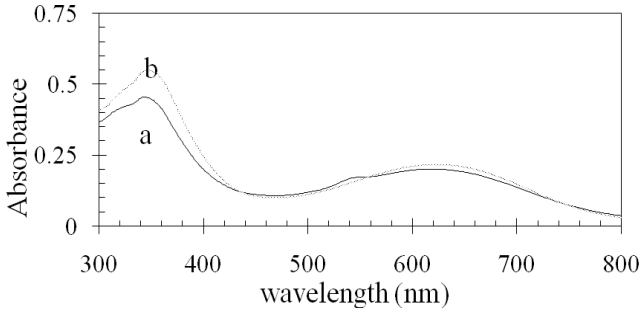

Figure 1. UV-Visible spectra of synthesized Polyaniline films (a). PANI-HCl-PVA (b) PANI- H_2SO_4PVA.

7. FTIR Analysis of Synthesized PANI Film

The FTIR of synthesized PANI film is shown in Figure 2. The 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. The change in the intensity peak 1033 is due to the enhanced concentration of dopant. 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 indicates that the doping is higher in the sample. All these characteristic bands confirms the polymer is of conducting ES phase.

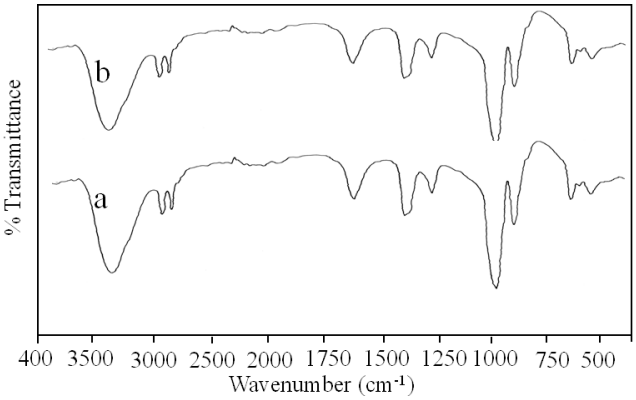

Figure 2. FTIR spectra of synthesized PANI film (a) PANI-HCl-PVA (b) PANI- H_2SO_4 –PVA.

8. Morphology of the PANI film

Scanning electron microscope (SEM) is used to study the surface morphology of the synthesized PANI films. The SEM images of the synthesized PANI films are shown in Figure 3 (a) - (b). It shows better porous, granular and globular surface morphology with very good uniformity and adhesiveness for synthesized film samples PANI-HCl-PVA-4 , PANI- H2SO4 –PVA-1 .

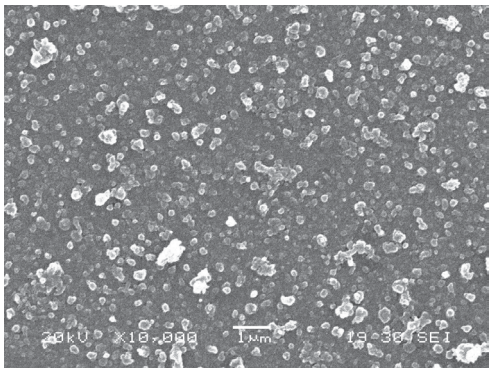

Figure 3(a). The Scanning Electron Micrograph of the PANI film sample PANI-HCl-PVA-4.

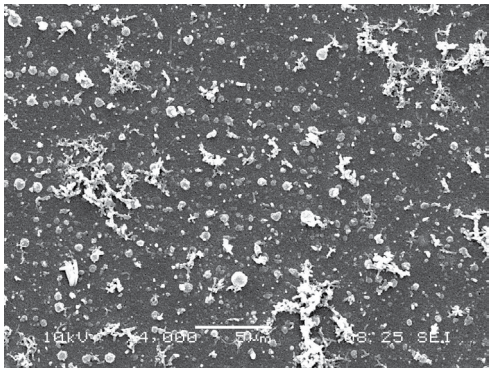

Figure 3(b). The Scanning Electron Micrograph of the PANI film sample PANI-H_2SO_4 –PVA-1.

9. Ammonia Gas Sensing Characteristics

The synthesized PANI films (PANI-HCl-PVA-4, PANI-H_2SO_4 –PVA-1) were exposed to ammonia gas for 6 minutes. The recovery time was measured by exposing the film to the air for 6 minutes. The change in resistivity of the film was measured at an interval of 15 s. It was observed that the resistivity of the polyaniline film 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 film when exposed to different concentration of ammonia gas are shown in Figure 4 – Figure 5. The conductivities of PANI were decreased by exposure to NH_3 vapors. The changes in conductivity of polymers are attributed to the consumption of charges from the polymeric backbone. The sensing mechanism is explained by the compensation effect. When the conductive emeraldine salt is exposed to NH_3 gas, the dopant is partially reduced, which leads to a decrease of electrical conductivity[11].

As can be seen from the figures, the resistivity of polymers show marked changes when exposed to NH_3 gas. The change in resistivity of polymers can be attributed to the different nature of both dopant anions and NH_3 gas. PANI synthesized using these different acids were studied as sensors for ammonia gas. It has been found that all polymers respond to ammonia vapors. Differences related to the response time, recovery time and reproducibility of these polymers towards ammonia vapors were observed.

PANI-HCl-PVA-4. The response time 60 s was observed for sample film PANI-HCl-PVA-4 and the recovery time observed for the film was 105 s for the 20 ppm of ammonia gas.

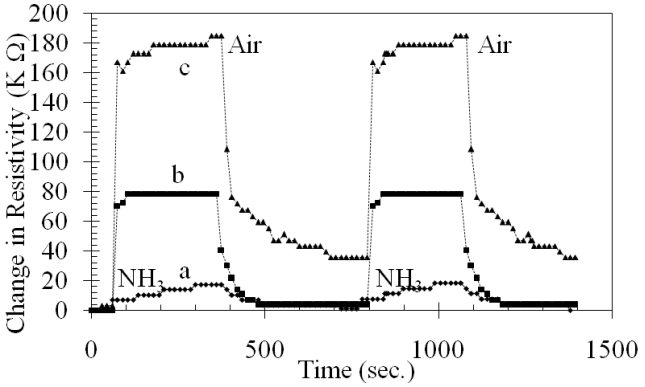

Figure 4. Response of the synthesized PANI film (PANI-HCl-PVA-4) to ammonia gas (a) 20 ppm (b) 50ppm (c) 250 ppm.

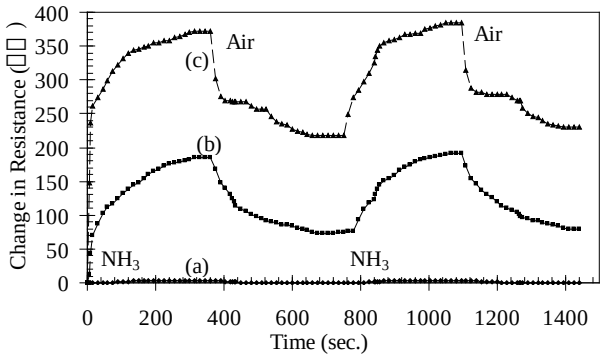

Figure 5. Response of the synthesized PANI film (PANI-H_2SO_4 –PVA-1) to ammonia gas (a) 20 ppm (b) 50ppm (c) 250 ppm.

10. Conclusions

In the present investigation, the influence of process parameters for better surface morphology of the synthesized of PANI has been studied. It was found that these process parameters viz. ratio of monomer, oxidants, doping acids, and deposition time and reaction temperature have considerable effect on the surface morphology of PANI film. The PANI-HCl-PVA-4(with monomer: Oxidant: acid dopant ratio 1:1:4)showed best response to ammonia among all the films.

11. Acknowledgment

Author is thankful to the UGC New Delhi, India, Savitribai Phule Pune University, and University of Mumbai for the financial assistance.

12. References

1. Heeger AJ. Semiconducting and metallic polymers: the fourth generation of polymeric materials. Synthetic Metals. 2001 Nov; 125(1):23–42. Crossref
2. Alan G. MacDiarmid, Synthetic metals: a novel role for organic polymers, Synthetic Metals. 2001 Nov; 125(1):11–22. Crossref
3. Bartlett PN, Ling-Chung SK. Conducting polymer gas sensors: Part III. Results for four different polymers and five different vapours. Sens Actuators. 1989 Dec; 20(3):287–92. Crossref
4. Agbor NE, Petty MC, Monkman AP. Polyaniline thin films for gas sensing. Sens Actuators. 1995 Oct; 28(3):173–9. Crossref
5. Barker PS, Chen JR, Agbor NI, Monkman AP, Mars P, Petty MC. Vapour recognition using organic films and artificial neural networks. Sens. Actuators.1994 Jan; 17(2):143–7. Crossref
6. Prasad GK, Radhakrishnan TP, Kumar DS, Krishna MG. Ammonia sensing characteristics of thin film based on polyelectrolyte template polyaniline. Sens Actuators. 2005 May; 106(2):626–31. Crossref
7. Guadarrama A, Rodriguez-Mendez ML, de Saja JA, Rios JL, Olias JM. Array of sensors based on conducting polymers for the quality control of the aroma of the virgin olive oil. Sens and Actuators. 2000 Oct; 69(3):276–82. Crossref
8. Schollhorn B, Germain JP, Pauly A, Maleysson C, Blanc JP. Influence of peripheral electron-withdrawing substituents on the conductivity of zinc phthalocyanine in the presence of gases. Part 1: reducing gases. Thin Solid Films. 1998 Aug; 326(1-2):245–50. Crossref
9. Nicolas-Debarnot D, Poncin-Epaillard F. Polyaniline as new sensitive layer for gas sensor. Analytica Chimicaacta. 2003 Jan; 475(1-2):1–15. Crossref
10. Li W, Wan M. Porous polyaniline films with high conductivity. Synth Met. 1998 Jan; 92(2):121–6. Crossref
11. Matsuguchi M, Io J, Sugiyama G, Sakai Y. Effect of NH3 gas on the electrical conductivity of polyaniline blend films. Synth Met. 2002 Apr; 128(1):15–9. Crossref