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TOXIC GAS (AMMONIA) SENSOR USING POLYANILINE DOPED WITH $HCLO_4$ (PERCHLORIC ACID) AND PVA ON PMMA SUBSTRATE

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ABSTRACT

In this work, the simple and inexpensive technique for the development of toxic gas(ammonia) sensor using conducting polymer films is described. The Polyaniline films were synthesized by of oxidative polymerization of aniline using ammonium peroxydisulfate on poly (methyl methacrylate) substrate. In the present investigation, $HClO_4$ (Perchloric acid) and PVA on PMMA substrate has been successfully synthesized PANI film by simple chemical polymerization technique. The synthesized Polyaniline films were characterized by using UV-visible, FTIR, SEM and the electrical conductivity. The ammonia sensing behaviour of the synthesized structure was studied by indigenously developed computer controlled gas chamber. The synthesized PANI structure shows excellent sensing behavior for 20-250 ppm of ammonia.

KEYWORDS: Polymer Composite, Polyaniline, Chemical Polymerization, $HClO_4$, PVA, Ammonia Gas Sensing.

Ammonia is a natural gas that is present throughout the atmosphere in concentrations of low-ppb to sub-ppb levels as a result of emission from anthropogenic and natural sources. It is produced in large quantities by chemical industries for the production of fertilizers and other nitrogen-containing compounds and for the use in refrigeration systems as cooling agent, natural source include production by bacteria. In the environment, high concentrations of ammonia lead to eutrophication and acidification of both ground and water, whereas in indoor environments it is a health hazard to human being. Therefore ammonia is an important target gas in applications like leakage control in refrigeration systems and air conditioners on one hand and in the emission control and quality monitoring of waste and drinking water on the other hand. Other application areas for ammonia sensors include high temperature sensing in the exhaust of cars and, as it is a product of biochemical processes, ammonia is also a useful reporter molecule in a variety of applications. This needs have supported the development of devices capable of detection and quantification of gaseous ammonia. Many aspects of ammonia sensing and related information can be found in recent reviews (Timmer et al., 2005). Electrically conducting polymers have been widely investigated as effective materials for chemical sensors (Koul et al., 1997) (Gallazzi et al., 2003). The interest of these materials has been recognized by the awarding of the Nobel Prize in Chemistry in 2000 to Heeger (Heeger, 2001) and MacDiarmid (MacDiarmid, 2001) and H. Shirakawa, who synthesized the first conducting polymers and proved their potentialities in a large number of applications. Conducting polymers have recently gained popularity as valuable sensing materials for various organic vapors (Bartlett and Ling-Chung, 1989) hazardous gases (Agbor et al.,1995) and humidity (Barker, et al.,1994) and as a fabricating material for sensor devices because of their applicability at room temperature. Many conducting polymers have shown changes in resistivity on exposure to different gases and humidity. Besides, some commercial electronic noses are based on electronic conducting polymers organized in an array (Guadarrama et al.,2000) .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, so the research was extended to polyaniline (PANI) (Schöllhorn et al.,1998). 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 (Dominuque et al., 2003) (Li and Wan, 1998). 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,

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oxidant, synthesis temperature, and time of synthesis. It is advantageous for mass production and hence widely used in industries (Genies et al., 1990). 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.

Protonic acids can be used to synthesize PANI films to increase the sensitivity and to improve 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. The properties of conducting polymers depend strongly on the doping level, ion size of dopant, protonation level, and water content.

In the present investigation, $HClO_4$ (Perchloric acid) and PVA on PMMA substrate has been successfully synthesized PANI film by simple chemical polymerization technique. The synthesis of polyaniline (PANI) films was carried out by oxidative polymerization of aniline using ammoniumperoxydisulfate (APS) on polymethylmethacrylate (PMMA) substrate in the presence of $HClO_4$ (Perchloric acid) and PVA as dopant.

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. concentrations of monomer, oxidants, doping acids, and deposition time and reaction temperature have considerable effect on the surface morphology of PANI film.

EXPERIMENTAL

Chemicals used during synthesis of PANI films

Chemicals Used for Synthesis: All chemicals used were of analytical reagent (AR) grade for synthesis of PANI-PVA thin films doped with $HClO_4$ acid ((Perchloric acid)). Aniline was distilled twice before use (99%) (Ranchem).

Polyvinyl alcohol with an average degree of polymerization (mw.14000 Quiligen Fine–Chemicals, India.); $HClO_4$ (Perchloric acid), Ammonium peroxydisulfate was purchased from SpectroChem (India).

Polymerization Blend Thin Films:

The polyaniline films were synthesized doped with $HClO_4$ acid and PVA composites on PMMA substrates by using the chemical oxidative polymerization method. The aniline (monomer) was double distilled prior to use. Initially the optimization of the molar concentration of monomer (aniline), primary dopant, secondary dopant and oxidant is carried out.

In this work, the polyaniline (PANI) films were 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 $HClO_4$ ((Perchloric acid)), 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 molar concentrations of the PANI, $HClO_4$ ((Perchloric acid)) and PVA with the different combinations is shown in the Table 1. The samples were rinsed with distilled water to remove the PANI precipitate, and dried in air.

Table 1:

Sample Film	Concentration (M)		
	Monomer	Acid	Oxidant
PANI-(Perchloric acid) -PVA-1	0.25	0.25	0.25
PANI-(Perchloric acid) -PVA-2	0.25	0.50	0.25
PANI-(Perchloric acid) -PVA-3	0.25	0.75	0.25
PANI-(Perchloric acid) -PVA-4	0.25	1.00	0.25

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 .

RESULTS AND DISCUSSION

The polymerization of aniline with ammonium peroxydisulfate as an oxidant was performed in an aqueous medium containing one of the acid viz. $HClO_4$ (Perchloric acid) and PVA additive (50 mg), as a secondary dopant. Various concentration ratio of the monomer-oxidant-dopant i.e. aniline-APS-acids were considered. The PANI films were further exposed to ammonia gas with different concentrations (in the range from 20 to 250 ppm).

UV-Visible characterization of synthesized PANI film

The UV-Visible absorption spectra of the polymer doped with $HClO_4$ and PVA were recorded by dissolving the polymer film in Dimethyl Sulfoxide (DMSO) and the absorption spectra of , $HClO_4$ depicted in Fig.1. The band observed at 324 nm for PANI 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 conducting emeraldine salt ES phase in the polymer is identified by broad peak at 820 nm.

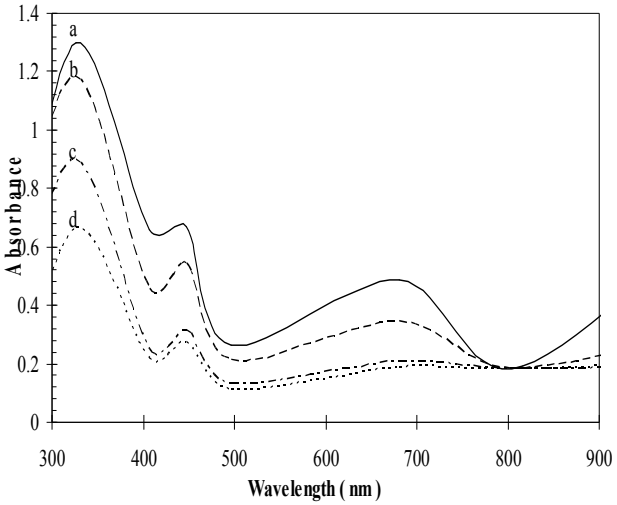

Figure 1: UV-Visible spectra of synthesized Polyaniline films (a). PANI- (Perchloric acid) -PVA -1(b) PANI- (Perchloric acid) -PVA -2 (c) PANI- (Perchloric acid) -PVA -3 (d) PANI- (Perchloric acid) -PVA -4

FTIR Analysis of synthesized PANI film

The infrared spectra of all Films doped with $HClO_4$ (Perchloric acid) and PVA are similar. The IR spectrum of the molecular structure of synthesized PANI films was characterized by 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 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. 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 indicates that the doping is higher in the sample. All these characteristic bands confirm the presence of conducting ES phase of the polymer.

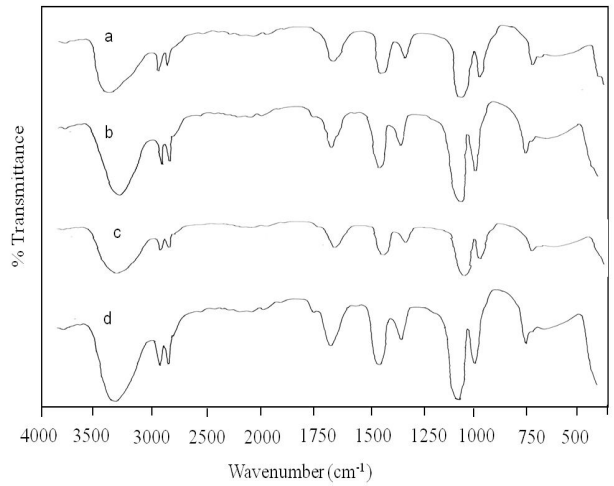

Figure 2: FTIR spectra of synthesized PANI films (a). PANI- (Perchloric acid) -PVA -1(b) PANI- (Perchloric acid) -PVA -2 (c) PANI- (Perchloric acid) -PVA -3 (d) PANI- (Perchloric acid) -PVA -4

Morphology of the PANI film

The surface morphology of the synthesized PANI films was studied by using scanning electron microscope (SEM). The SEM images of the synthesized PANI films are shown in Fig.3. (a) - (b). It has been observed better porous, granular and globular surface morphology with very good uniformity and adhesiveness for synthesized film sample (a). PANI- (Perchloric acid) -PVA -1.

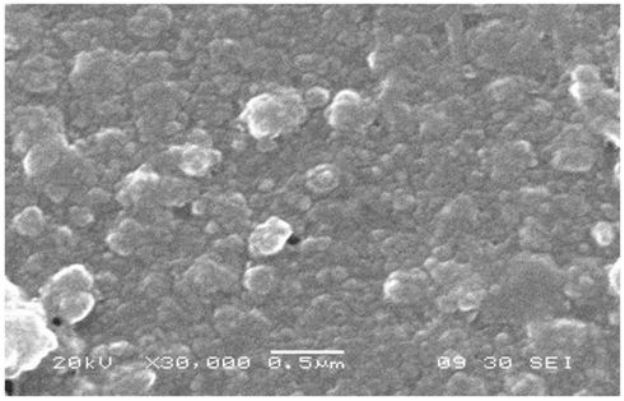

Figure 3(a): The Scanning Electron Micrograph of the PANI film sample PANI-(Perchloric acid) -PVA-1

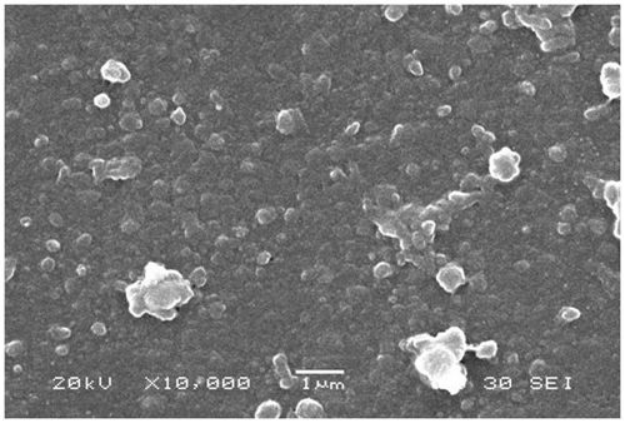

Figure 3(b): The Scanning Electron Micrograph of the PANI film sample PANI-(Perchloric acid) –PVA-1

Ammonia Gas Sensing Characteristics

The synthesized PANI films 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.

I have explored the ammonia gas-sensing curves of PANI at three different concentrations of ammonia gas, 20 ppm, 50 ppm, and 250 ppm. 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 Fig. 4. 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 (Kang et al., 1998). The sensing mechanism is explained by the compensation effect (Kukla et al., 1996). When the conductive emeraldine salt is exposed to NH_3 gas, the dopant is partially reduced, which leads to a decrease of electrical conductivity (Wang et al., 1989). Extensive studies of the gas-sensing properties of conducting polymers show that when these polymers are exposed to electron-donating gases such as ammonia, if the gases are absorbed, the polymers exhibit an increase in resistance (Matsuguchi et al.,2002), while an increase in conductivity is observed with gases such as HCl (Koul and Chandra, 2005).

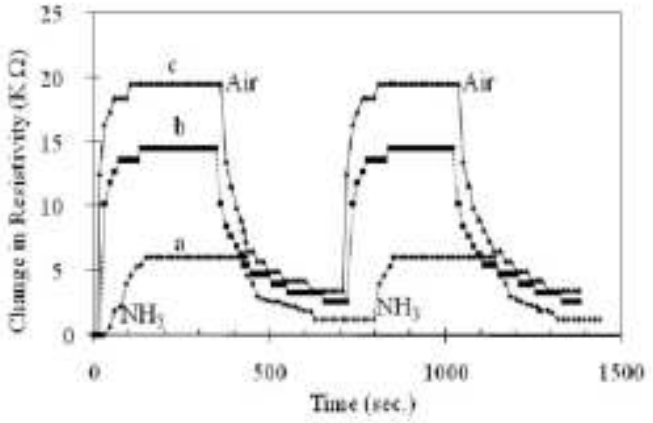

Figure 4: Response of the synthesized PANI film (PANI- $HClO_4$ -PVA) to ammonia gas (a) 20 ppm (b) 50ppm (c) 250 ppm.

PANI-PVA-$HClO_4$ (Perchloric acid)-1 showed good response to the ammonia gas concentration in the range 20-250 ppm, while other samples showed the less response to the ammonia gas in the range 20-250 ppm as compared to the above films. The response time 60 s was observed for sample film PANI-PVA-$HClO_4$ (Perchloric acid)-1 and the recovery time observed for the film was 105 s for the 20 ppm of ammonia gas.

CONCLUSION

It was found that these process parameters viz. concentrations of monomer, oxidants, doping acids, and deposition time and reaction temperature have considerable effect on the surface morphology of PANI film. The response to ammonia was greatly dependent on the nature of dopant anion in the polymer. The PANI-$HClO_4$-PVA-1 (with monomer: Oxidant: acid dopant ratio 1:1:1) can be used as the ammonia gas sensing.

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