Inorganic Acids Doped PANI-PVA Composites Films as a Gas Sensor.

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ABSTRACT

In present work we have developed PANI-PVA blend thin films polymeric material doped with inorganic acids like (CrO_3, HIO_3, H_2SO_4, and $HClO_4$). These films were synthesized by chemical oxidative polymerization in aqueous medium. This polymeric material characterized by UV-visible, Fourier Transform Infrared (FTIR) spectroscopy, X-ray diffraction spectroscopy, and surface morphology by Scanning Electron Microscope (SEM). Their electrical conductivity was measured by the four probe technique. The linear Ohmic behavior was observed by I-V characteristics. Gas sensing properties of the sensor was checked against hazardous gases like trimethyl amine (TMA) and ammonia. The sensor shows almost stable and repeatable response up to 5-800ppm. The increase in sensitivity is discussed in terms of increased resistivity, due to surface modification of inorganic acid dopants to improve electrical and environmental stability of sensor.

(Keywords: polymer blend, polyvinyl alcohol, polyaniline, conducting polymer, inorganic acids, gas sensor)

INTRODUCTION

Recently significant interest in the scientific community has been devoted to the progress achieved in the synthesis, structural characterization, and physical property investigation of nanostructures, due to their peculiar characteristics and size effects [1]. Presently, the use of '***organic–inorganic composites'*** polymeric materials has generated widespread interest in developing new materials, especially for monitoring techniques in a broad range of areas (e.g., medical, pharmaceuticals, environmental, defense, bio-processing, or food technology) has lead to the development of gas sensors [2-3]. The United States Environmental Protection Agency (EPA) has found gases like CO_2, TMA, H_2S, and ammonia, cause health hazards when people are exposed to low ppm levels or minimum concentrations [4], for relatively short periods of time. These effects include nausea, salivation, sensory disturbances, liver injury, kidney damage, and inhibiting respiration [5]. There is an essential need to control simple, rapid, and continuous monitoring techniques for these gases.

Inorganic acids like (CrO_3, HIO_3, H_2SO_4, and $HClO_4$) have complex chemistry, low thermal conductivity, thermal expansion coefficient, high stability, and the ability to accommodate defect [6]. In view of these important properties, the inorganic acids was used to increase the electrical conductivity and modification of surface morphology for gas monitoring. The cross-linked polyvinyl alcohol (PVA) additive matrix added may have a protective role against thermal and environmental degradation of the conducting polymer blend [7].

In short, these composites represent conducting polymer based films suitable for application in different sophisticated devices. Among these the organic conducting polymers, polyaniline (PANI) is the only conducting polymer whose properties not only depend on the oxidation state but also on its protonation state/doping level and also the nature of dopants [8]. Elamin et al. (1997) reported that PANI doped with H_3PO_4 or tartaric acid shows the semiconductor behavior and follows the VRH mechanism. In principle, a wide variety of anions can be include by doping into the conducting polymer matrix.

The present investigation deals with a comparative study of the influence of inorganic acid dopants like (CrO_3, HIO_3, H_2SO_4, and $HClO_4$) on the synthesis of PANI-PVA blend thin films. These synthesized films were characterized by UV-visible, FTIR, surface morphology by SEM, electrical conductivity, and I-V characteristics. The gas sensing behavior for monitoring of TMA and ammonia gas vapors were at room temperature from 5-800ppm concentration.

EXPERIMENTAL

Chemicals Used for Synthesis: All chemicals used were of analytical reagent (AR) grade for synthesis of PANI-PVA doped inorganic acids (CrO_3, HIO_3, H_2SO_4, and $HClO_4$) thin films. Aniline was distilled twice before use (99%) (Ranchem). Polyvinyl alcohol with an average degree of polymerization (mw.14000 Quiligen Fine–Chemicals, India.); CrO_3, HIO_3, H_2SO_4 (Quiligen Fine–Chemicals); and $HClO_4$ (Merck India.) were used. Each process was done with double distilled conductivity water. Ammonium peroxy-disulphate, hydrochloric acids (Qualigen Fine–Chemicals, India) were used.

Synthesis of PANI-PVA Doped Organic Acids Blend Thin Films: We have synthesized PANI-PVA doped inorganic acids composites thin films at room temperature on glass substrates by using the chemical oxidative polymerization method. The aniline (monomer) was double distilled prior to use. Initially we have optimized the molar concentration of monomer (aniline), primary dopant (HCl), polymer additive matrix (PVA), secondary organic dopants (CrO_3, HIO_3, H_2SO_4, and $HClO_4$) and oxidant (APS) as follows: The polyvinyl alcohol was dissolved in conductivity water with constant stirring, then optimized the molar concentration of aniline (monomer 0.4 M), primary dopant (HCl 1M), PVA additive (50 mg), oxidant (APS 0.5M), and each inorganic acid (CrO_3, HIO_3, H_2SO_4, and $HClO_4$ 0.02M) as a secondary dopant.

A suitable combination, which shows good response to ammonia and TMA gas, has been selected for the synthesis and characterization.

Characterization: The structural and morphological characterizations of PANI-PVA composite thin films were performed on UV-visible and FTIR by UV-visible Shimadzu. The UV-visible and FTIR spectra of all polymer samples were recorded at room temperature in dimethyl sulfoxide (DMSO) solvent.

Surface morphology was characterized by using a SEM at different magnification ranges by JEOL-JSM-6360. The electrical conductivity (I-V characteristics) of the films were recorded using the four probe method.

Synthesized PANI-PVA doped inorganic acid films were subjected to the ammonia and TMA gas at room temperature by using an indigenously developed computer controlled gas sensor system.

RESULTS AND DISCUSSION

UV-Visible Spectra: UV-visible spectroscopy is a very sensitive tool for the study of PANI-PVA composite thin film protonation, and more precisely, for the elucidation of the dopant inorganic acids into the thin films. UV-visible study selected those films which have uniform and good sensor response time.

These sample films were dissolved in (DMSO) solvent, and then the UV-visible spectra recorded in the range 250-1000 nm. The sample yields sharp peaks within the 320-350nm range and a broad band at the 601-680nm wavelength range. In DMSO the sample, however exhibits a broad peak around 632 nm indicating formation of emerladine base.

Table 1: UV-Visible Spectra Peaks.

Sr No.	Sample	Peak position (nm)	
1	PANI-PVA- CrO_3	302	622
2	PANI-PVA- HIO_3	337	638
3	PANI-PVA- H_2SO_4	338	648
4	PANI-PVA- $HClO_4$	351	636

The comparative study of these three inorganic acids at same molar concentrations (0.02M) is presented below.

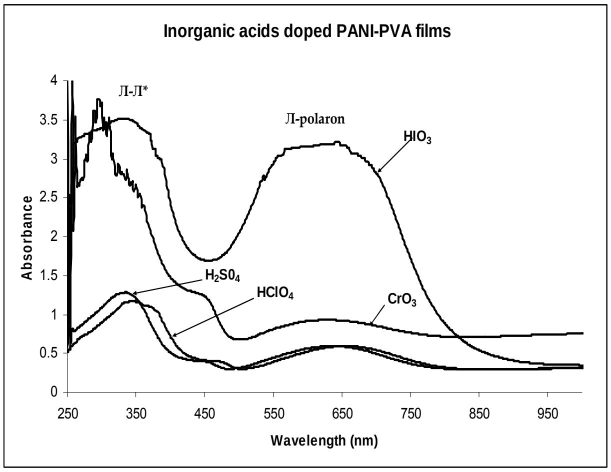


Figure 1: UV-Visible Spectra of PANI-PVA Doped Inorganic Acids (CrO_3, HIO_3, H_2SO_4 and $HClO_4$).

FTIR-Spectra: The FTIR-spectra of doped inorganic acids (CrO_3, HIO_3, H_2SO_4, and $HClO_4$) in PANI-PVA composite thin films were recorded in the range of 4000-400 cm^{-1} using DMSO as solvent and are shown in Figure 2. The principal characteristics band occurrence indicates the type of functional group present in the polymer. The medium strong band observed at 2900 cm^{-1} suggests the presence of C-H stretch. The spectra shows the peak at 1660 cm^{-1}, which is due the presence of C=C group of aromatic benzonids ring.

The observed medium intensity band in the region 1410-1433 cm^{-1} suggests the presence of C-N stretch (Athawale et al., 1999). The PANI-PVA material (doublet) splits into triplets and shifts towards lower frequency at 1313 cm^{-1}. Boyer et al 1998, have made a similar observations and attributed it to the polymer chain length increase. In fact they have treated these bands as the diagnostics of chain length, (conformational change) leading to exposure of the hidden $C\text{-}N^+$ group as (NH, $^+NH_2$, ^+NH=, $C=N^+$) in PANI-PVA depends on the nature and percentage of doping which may effect the population of charge defect center (polaron and bipolaron) and ultimately the electrical conductivity.

The C-O stretching vibrations in plane and out of plane, the bending vibration were observed at 1051cm^{-1} and 702 cm^{-1}.

The entire characteristics of the band confirms the presence of inorganic acids doped conducting PANI-PVA thin films in Figure 2.

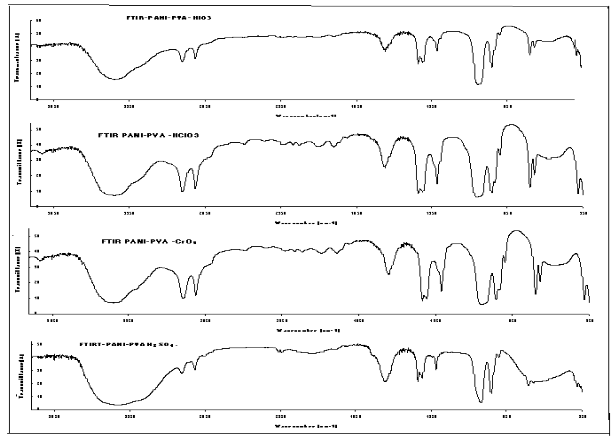


Figure 2: The FTIR Spectra of PANI-PVA Doped Inorganic Acids (CrO_3, HIO_3, H_2SO_4 and $HClO_4$).

SEM Study: A typical SEM image of 0.02M film is shown in Figure 3. SEM images give first hand information about a molecular level combination of the components and possibility for application as gas sensors. All thin films surface morphology study indicates that the films have porous surfaces and are uniform in nature, which is one of the essential conditions for gas sensors.

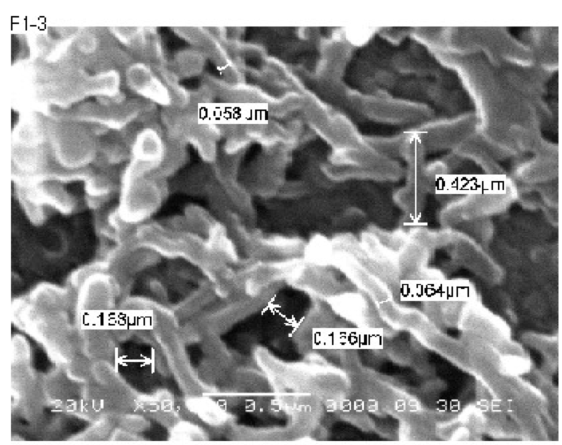


Figure 3A: H_2SO_4-Doped PANI-PVA Films.

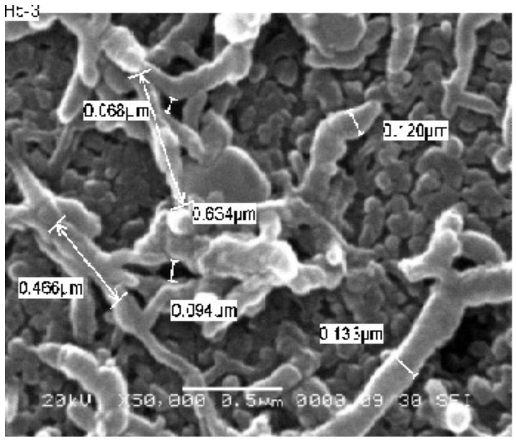


Figure 3B: CrO_3-Doped PANI-PVA Films.

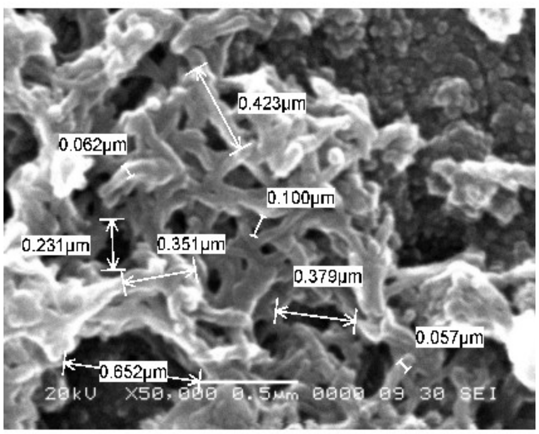


Figure 3C: HIO_3 -Doped PANI-PVA Films.

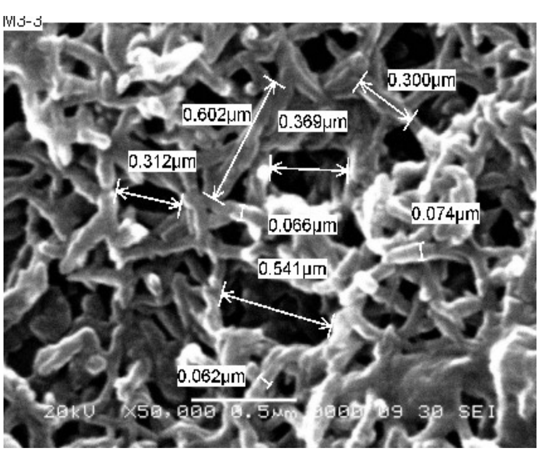


Figure 3D: $HClO_4$ -Doped PANI-PVA Films.

X-Ray Diffraction Studies: The conducting polymer synthesized by chemical route generally is semi-crystalline in nature, whereas the conducting polymer prepared by electrochemical route is amorphous in nature. The structure of the various modified polymers was investigated by WAXD; using a powder X-ray diffract meter (Phillips PW 1830 model). All of the scans are recorded in the 2 region of 20-60 at a scan rate of 4/min. From the 2 θ value for the reflections, d values were calculated using Bragg's equation.

$$2d \sin \theta = n\lambda$$

$$d = n\lambda / 2\sin\theta$$

From the data obtained from the XRD, d value (i.e., the inter-chain separation of different modified polymer) is calculated. Wide-angle X-RAY Diffraction (WXRD) studies were done in order to analyzed the structures of synthesized doped inorganic acid doped PANI-PVA composite thin films. The conducting polymer doped with inorganic acids doped films shows semi crystalline structure.

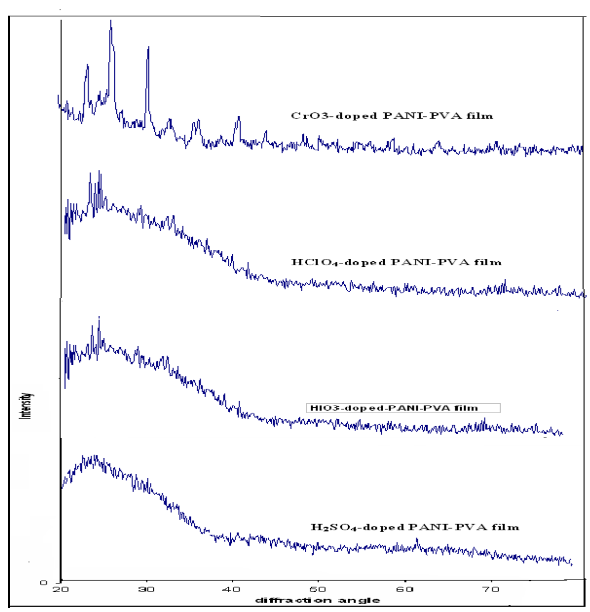
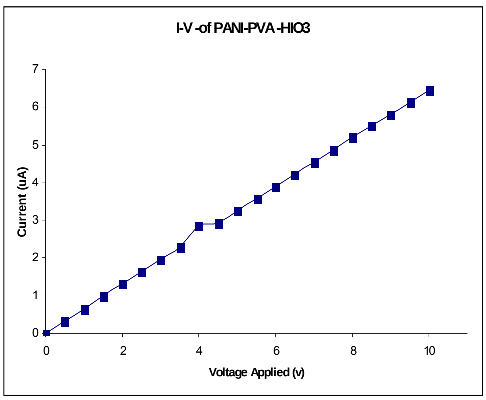


Figure 4: XRD-Spectra of Inorganic Acids PANI-PVA Composites Thin Films.

I-V Characteristics: The electrical conductivity of the synthesized inorganic acid (CrO_3, HIO_3, H_2SO_4, and $HClO_4$) doped PANI-PVA-composite films studied at room temperature by a four probe indigenous developed computer controlled (I-V) system. It is observed that with increasing concentration levels, the electrical conductivity of the thin films gradually increases.

The current-voltage (I-V) characteristics of synthesized films were studied to ensure an Ohmic behavior of all thin films samples. A linear relationship of the I-V curve is shown in Figure 5.

A



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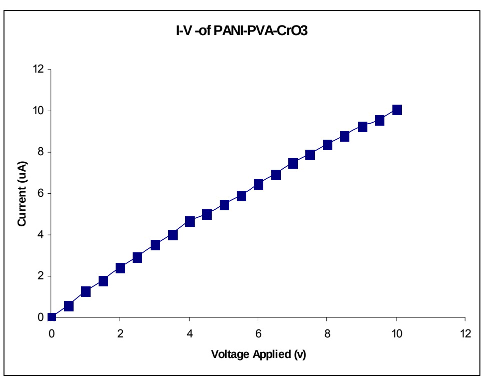

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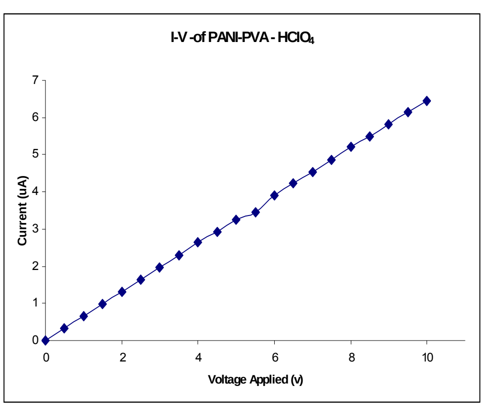

D

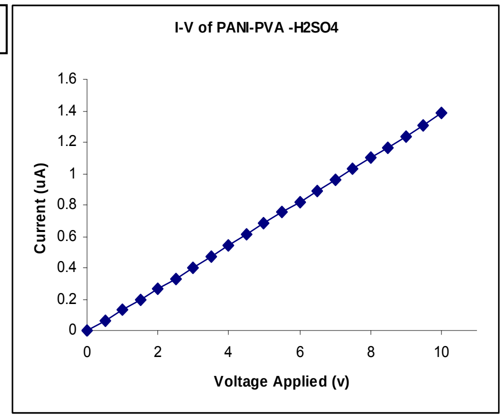

Figure 5: I-V Characteristics of Inorganic Acid Doped PANI-PVA Composite Thin Films.

TMA and Ammonia Gas Sensing Behaviors: All synthesized inorganic acid doped PANI-PVA composite thin films were studied for ammonia and TMA gas at room temperature (303k) by using an indigenous developed computer controlled gas sensing system. Initially, the films were allowed to saturate for one half hour before exposing to them ammonia and TMA gas. The film was first exposed for five minutes to predefined concentrations of ammonia and TMA gas, and then were exposed to air to recover their initial resistance for five to seven minutes.

The same process was repeated for 5-800 ppm concentrations of both gases. Interactions of TMA and ammonia gas with the doped inorganic acid PANI-PVA films were found to increase the films' resistance and when exposed to dry air, their resistances decrease. The change in resistance of the gas exposed and its recovery were measured. The barrier height increases when absorption of TMA and ammonia gas concentration increase in the ppm range. This change in resistance is found to increase linearly for all thin films (Figure 6).

CONCLUSION

1) The inorganic acid doped (CrO_3, HIO_3, H_2SO_4 and $HClO_4$) PANI-PVA composites have been successfully synthesized by oxidative chemical polymerization techniques at room temperature.

2) It shows that 0.02M inorganic acid doping is the best molar ratio for TMA and ammonia gases for their recovery and response time.

3) All films are stable to environmental with stability up to 3-5 months at room temperature.

4) The synthesized PANI-PVA-CrO_3 films show lower concentration up to 5-10ppm for TMA and ammonia gases and it indicates excellent sensing behaviors up to 800ppm higher level.

5) The (I-V) characteristics show that all inorganic acid (CrO_3, HIO_3, H_2SO_4 and $HClO_4$) doped PANI-PVA composite thin films have ohmic behavior.

6) All characteristics studied show inorganic acid dopant effects on sensing behavior as well as conductivity .

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