POLYANILINE –POLY VINYL ALCOHOL COMPOSITES FILMS MODIFIED BY IRON CHLORIDE, AS AN DOPANT FOR AMMINE GAS SENSORS

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Abstract-

Synthesized Polyaniline -Polyvinyl alcohol Composites thin films modified by dopant like Iron chloride in situ chemical oxidative polymerization, for ammine hazardous chemical gas sensor. These polymer materials were characterized by Chemical analyses, spectral studies UV-visible and FTIR and conductivity measurement. The surface morphology as seen in the SEM image was observed to be granular, uniformly covering the entire substrate surface. The I–V characterizations show that these thin films have ohmic behaviors. The Polyaniline -Polyvinyl alcohol Composites thin films were used for different concentration (ppm) of ammine hazardous chemical gas investigation at room temperature (304k) for lower ppm concentration.

***Keywords*- Conducting polymer, Gas sensor, Composites and Polyaniline.**

1.INTRODUCTION

Most of the carrying out polymers, polyaniline (PANI) belongs to the most potentially useful undertaking polymer as a result of its low cost, ease of coaching, wonderful environmental stability, and controllable physical and electrochemical houses by oxidation and protonation developed a template-unfastened approach through self-assembly approach to put together PANI nanostructures(1-2). The universality and controllability of the approach to prepare micro/ nanostructured conducting polymers have been confirmed by means of converting the polymer chain, dopant structure, and polymerization conditions. Therefore, the oxidant has an essential role in controlling the shape and bodily properties of PANI. Usually, ammonium persulfate[$(NH_4)_2S_2O_8$, APS] is used as an oxidant within the polymerization of PANI based on our preceding proposed micelle formation mechanism for the self-assembled nanostructures prepared by way of a template-free technique (3-4). Its miles anticipated that the structure of the oxidant, specially the oxidation/ reduction potential, will have an effect on the morphology and size of the micelle seemed as the soft-templates, which leads to converting the morphology and size of the nanostructures.

Such reasoning leads us to examine using another oxidant in preference to APS to put together micro/nanostructured PANI with the aid of a template-free technique. Herein, the self-assembled PANI nanofibers with 17– 30 nm in average diameter were efficaciously organized by the usage of ferric chloride ($FeCl_36H_2O$) as an oxidant as the dopant. As compared with the Nano fibers oxidized by way of APS as an oxidant, the resulted Nano fibers now not simplest are thinner in diameter, however also have higher crystallinity and conductivity. We determined that the dimensions of received nanostructures impacts the conductivity, specifically, decrease in the Nano fiber diameter became associated with multiplied conductivity regardless of the used oxidant.

Our interests lies in room temperature sensing of ammonia vapors the usage of ferric chloride - Doped Polyaniline / Poly(Vinyl alcohol) thin films–based sensors. The gas sensing traits of a given sensing element relies upon the material used, the technique of preparation, and the ensuing nano-to micro-shape. Inside the present observe, natural and ferric chloride - Doped Polyaniline/ Poly (Vinyl alcohol) thin movies, had been organized chemical oxidative polymerization, using microwave oven approach on glass substrate. The electric and gas sensing properties of those movies had been investigated. The reality we are capable of measure ammonia and trimethyl ammonia concentrations using ferric chloride -Doped Polyaniline / Poly(Vinyl alcohol) thin movies at room temperature makes possible a variety of latest sensing application.

2. EXPERIMENTAL

2.1. Chemical Used for Synthesis

Analytical grade aniline (Rankem ,Ranbaxy New Delhi) was purified by distillation under reduced pressure in presence of zinc dust prior to use ,Poly(vinyl alcohol) (mw.14,000 quiligen fine–chem., India). Hydrochloric acids (qualigen fine –chem. India). Ammonium peroxydisulphate (Spectro Chem, India). All processes were carried out in double distilled conductivity water.

2.2. Synthesis of ferric chloride -Doped PANI-PVA Blend Thin Films

We have synthesized ferric chloride -Doped PA-PVA blend thin films at room temperature on glass substrate by using chemical oxidative polymerization method. Initially we have optimized the molar concentration of monomer (aniline 0.4M), primary dopant (HCL1M), polymer additive matrix (PVA-50mg), then ferric chloride with different molar concentration ratio like (0.05 to.0.5 molar) are mixed in stoichiometric proportion were kept in microwave oven for 10 sec, then oxidize with ammonium peroxydisulphate as oxidant, then after kept in water bath at 10^0c for 24 hour to obtain the thin uniform and good morphology films. These synthesis films washed with distilled water to remove monomer another substrate remain without polymerization. The synthesis films dried with dryer at room temperature.

2.3. Characterization

The structural and morphological characterization of ferric chloride Doped PANI-PVA blend thin films was performed UV and FTIR. The UV-visible and FTIR spectra of all polymer samples were recorded at room temperature in Dimethyl sulphoxide (DMSO) solvent. The surface morphology was characterized by using scanning electron microscopy (SEM) at different magnification range by (JEOL -JSM-6360 ^{A}).

Synthesized PANI-PVA doped ferric chloride films were subjected to the Ammonia and TMA gas at room temperature by using indigenously developed computer controlled gas sensor system and electrical conductivity (I-V characteristics) of the films was recorded using four probe- methods computer control system.

3. RESULTS AND DISCUSSION

3.1 FTIR Study

The infrared absorption spectrum of Synthesized PANI-PVA doped ferric chloride composite film is shown in Figure.1. The broad strong bands between 3470 –3350 cm^{-1} corresponds to the stretching vibrations of the intra-molecular hydrogen bond (N-H) of PVA and this frequency also shows the absorption of N-H stretching of polyaniline. The frequency at 2920 cmto the stretching vibration of C–H bond. The absorption at

1652 cm^{-1} was assigned to the C=C ring stretching of polyaniline. The band at 1380 cm^{-1} vibrations C-H vibrations (5). The peak at 1136 cm^{-1} is due to C-H, The peak at 1080 cm^{-1} corresponds to the O-H group and C-O symmetric stretching of PVA. The band at 1020 cm^{-1} is due to in-plane deformation of C and N–H bond of polyaniline ring, Here due films it slightly change and percentage of transmittance is less in DMSO solvent.

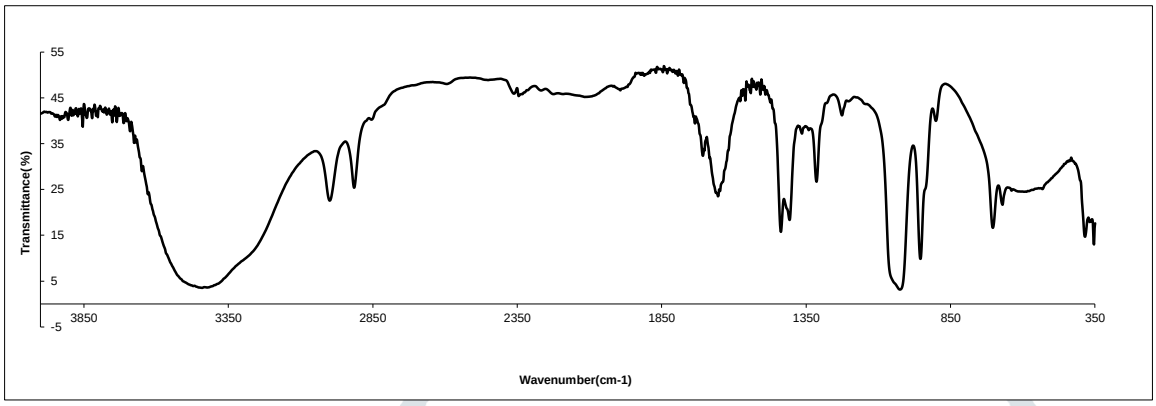

Fig-1 FTIR Study of PANI-PVA and ferric chloride doped PANI-PVA

3.2 UV-Visible Spectra

The UV-Visible absorption spectra of ferric chloride doped PANI- PVA films were recorded in air backgrounds on glass deposited thin films using UV - Visible 1601 Shimadzu spectrophotometer in the range of 250 doped PANI-PVA blend thin films show three peaks at 308nm,446 nm and 809 nm respectively. The first peak was due to nat 308 nm. The second peak for corresponds to benzenoid, rings while the sharp groove. Third peak represents Together with the extended tail at 809 nm representing the conducting emerald salt localized polarons which are characteristic of protonated ferric chloride doped PANI-PVA film. with the extended tail at 810 nm Fig-2.

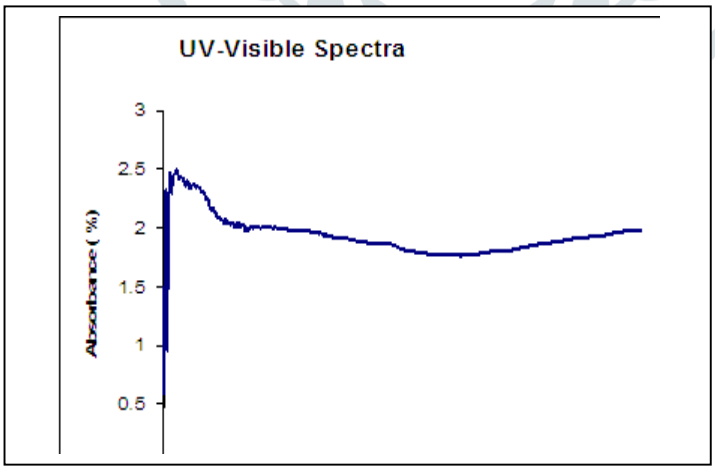

Fig-2 UV-Visible absorption spectra of ferric chloride PANI- PVA films

3.3 SEM Study:

The microstructure of the blends, characterized by scanning electron microscopy (SEM) is presented in Fig. 3. In this Figure it is shown the ferric chloride PANI- PVA films embedded in the PVA matrix. As shown in Fig. 3a SEM micrographs of ferric chloride PANI- PVA composite thin film taken at different magnifications

showed the polycrystalline nature of the film with an average grain size of <0.250um.The evolved microstructure of doped PANI-PVA films consisting of grains is schematically shown interaction between ferric chloride PANI- PVA understand the fig.3b. is only PANI having uniform surface morphology.

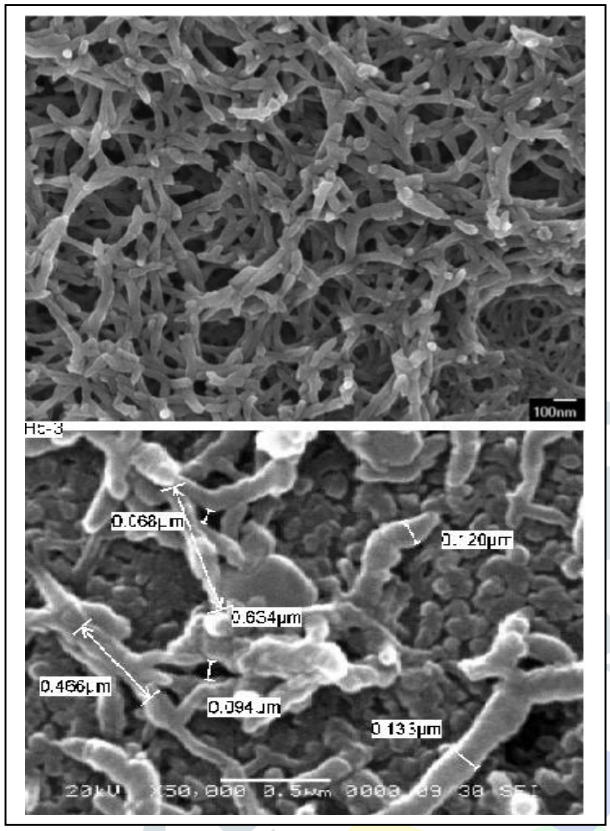

Fig 3(a) -SEM micrographs of the ferric chloride PANI- PVA.

3.5 Electrical Characterization

The synthesized ferric chloride doped PANI-PVA films are subjected to I – V characterization to room temperature on the Ohmic behavior of the film. The electrical characterization of film is done by the four - probe method at room temperature. Fig. 5 shows the I-V characteristics ferric chloride doped PANI-PVA film which gives the linear relationship. As we increase the applied voltage the current is increase in proportion with the applied voltage. This reveals that the Polyaniline film has an Ohmic behavior.The graph indicates that the conductivity of the films increased with increasing of PANI- loading. This could be due to the addition of PANI-emeraldine salt form which contains highly p conjugated backbone. Electrons were delocalised along the conjugated backbones of PANI- which subsequently developed free movement of electrons from atom to atom and generating electrical charge. Meanwhile, ferric chloride doped PANI-PVA conductive films demonstrated improved electrical conductivity compared with PANI-PVA films conductive films. The result is supported by Li et al. in which they reported that the conductivity of the synthesided ferric chloride doped PANI-PVA was higher than the single PANI-PVA conductive In addition, there were several reports proposing that $FeCl_3$ can perform as dopant and oxidant at the same time as $FeCl_3$, being an acidic salt, offers protons in aqueous solution by hydrolysis. No acidic solvent (dopant) was used in this research to dope the PANI-PVA. The ability of the oxidant ($FeCl_3$) to perform as dopant has been utilised and it resulted in higher electrical conductivity compared to the films without $FeCl_3$.

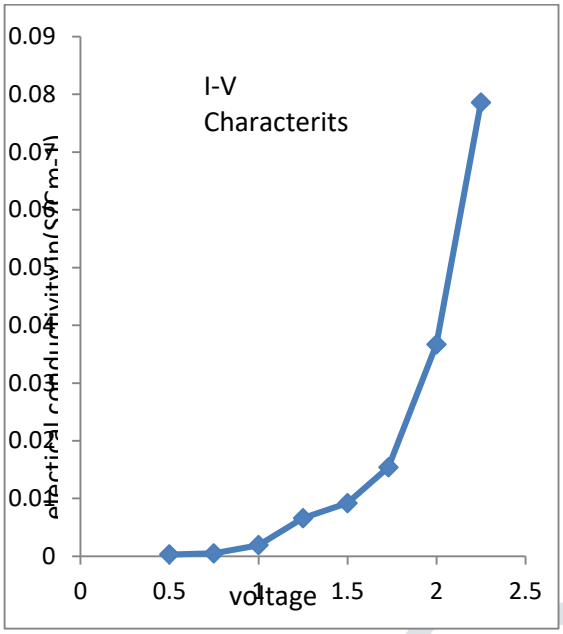

Fig-3.5a) I – V characterization

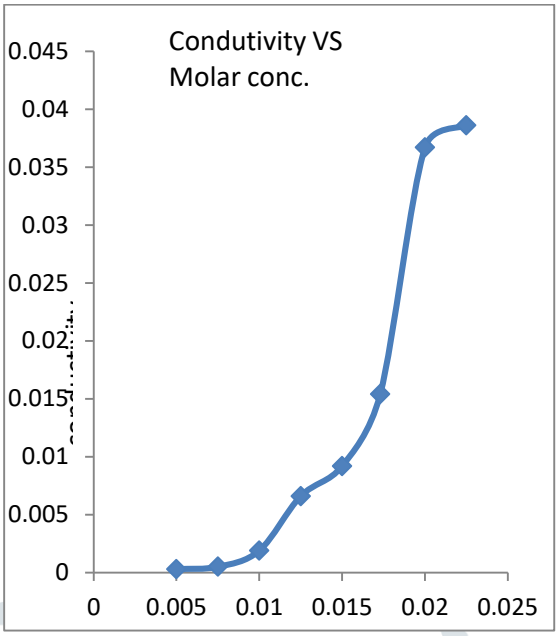

Fig-3.5b) conductivity mole concentration

3.6 TMA and Ammonia Gas Sensing

To observe the TMA and ammonia gas-sensing characteristics of the synthesized ferric chloride doped PANI–PVA Blend thin films at room temperature, we have used the Four-probe technique of resistivity measurement; this film was enclosed in indigenously designed and fabricated a gas chamber. The synthesized ferric chloride doped PANI–PVA films were exposed to TMA and ammonia gas for 5 minutes. The recovery time was measured by exposing the film to the air for 5 minutes. The change in resistivity of the film was measured at an interval of 10s. All the sample films show response to the ammonia and TMA gases vapor. We have explored the ammonia and TMA gas-sensing curves of ferric chloride doped PANI–PVA films at different concentrations of ammonia gas 2 ppm to 800 ppm. It was observed that the resistivity of the ferric chloride doped PANI–PVA films increases in the presence of ammonia and TMA gases and after a few minutes becomes saturated and the resistivity decreases steadily to a minimum value, when the ammonia and TMA gas was removed however, a drift from its original value was observed. The conductivities of these films were decreased by exposure to NH_3 vapors. The sensing mechanism is explained by the compensation effect (5-6). it can be seen from the figures, the conductivities of polymers show marked changes when exposed to NH3 gas. The change in conductivity of polymers can be attributed to the different nature of both dopant anions and NH_3 gas. Dopant anions have different sizes and to NH_3 vapors can differently diffuse in Polymer matrix. The gas sensing behaviour showed quite good response to the ammonia and TMA gas concentration in the range 25-800 ppm, for ferric chloride doped PANI–PVA films for both gases. The surface morphology observed for ferric chloride doped PANI–PVA was porous, granular and globular responsible for good response for both TMA and Ammonia gas vapour.

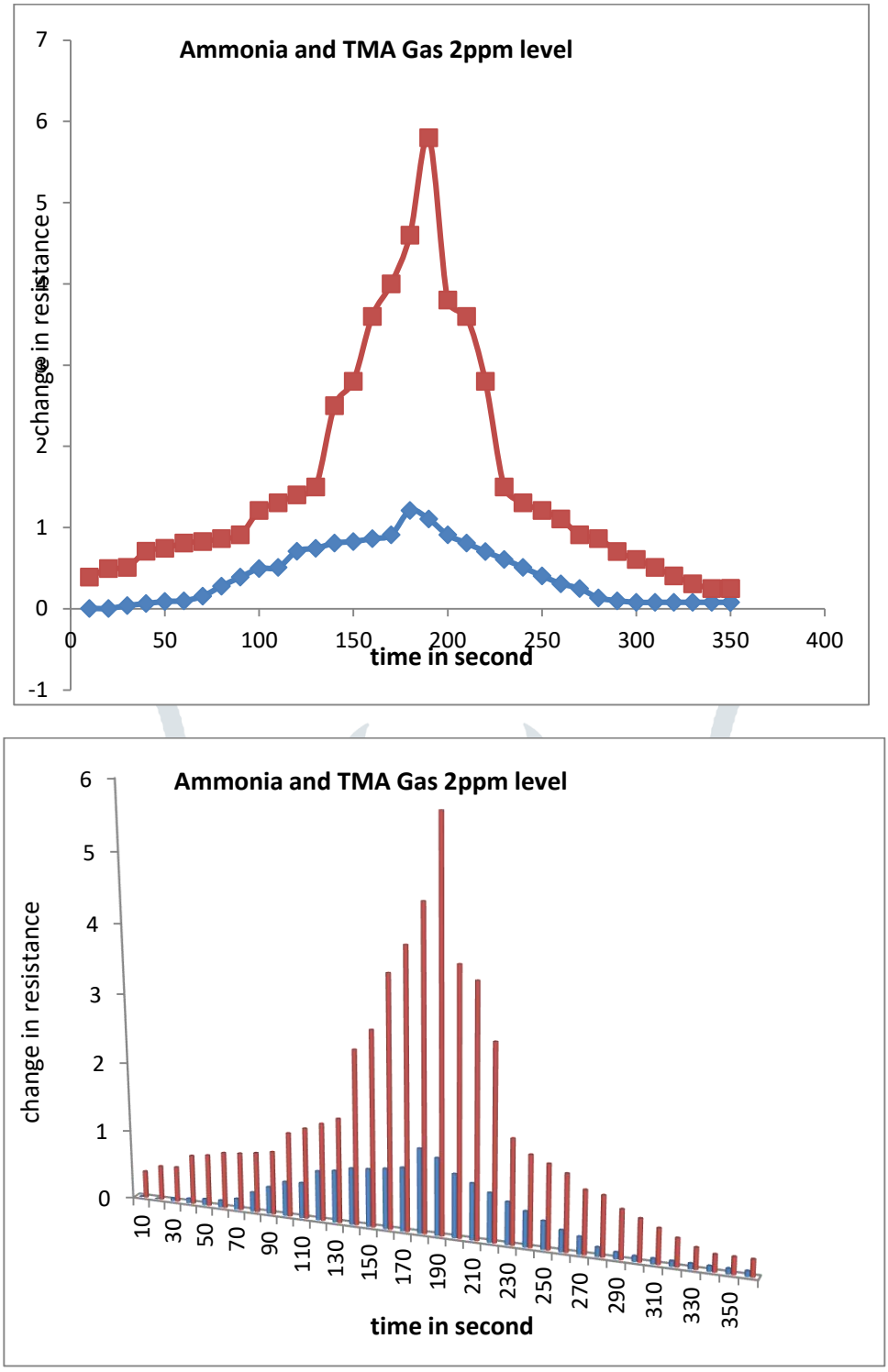

Fig.6-TMA and ammonia gas-sensing characteristics of ferric chloride doped PANI–PVA films.

CONCLUSIONS

- Ferric chloride doped PANI–PVA doped nanocrystalline gas sensing material was successfully prepared by microwave oven technique.
- We have developed ferric chloride doped PANI–PVA thin film gas sensor by using microwave oven technique.

- The high sensitivity and good selectivity for ammonia and TMA detection have been achieved from the graphical study fig- 6, of times against change in resistance of ferric chloride doped PANI–PVA thin films.
- The ferric chloride doped PANI–PVA film presents better sensitivity compared to pure PANI-PVA due to the distribution of particles ferric chloride in grain boundaries of nanocrystalline PANI-PVA films fig-3 from study of surface morphology.
- The TMA measurement results indicate that the developed TMA sensor's working at room temperature is about 27-37 ◦C, it is much less than commercial available.
- The sensor has good sensitivity to low ammonia concentration such as 2 ppm.
- The selectivity of the sensors was studied by exposing the sensor to various inference gases like TMA and the sensor is less sensitive to common interference gases.

FUTURE WORK

- In future we are study of other metal oxides doped films for ammonia gas sensing material
- In future we are study high temperature based gas sensing films material
- In future we are study various different types of gases sensing ability

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