SENSING PROPERTIES OF MNO_2-DOPED POLYANILINE/POLY (VINYL ALCOHOL) BLEND

D. B. Dupare[1], M. D. Shirsat[2], A. S. Aswar[3]

[1]Department of Chemistry, Shri Dr.R.G.Rathod Arts and Science College Murtizapur Di-Akola444107 (M.S.) India
[2]Optoelectronics and Sensors Research laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, 431004 (M.S.) India
[3]Department of Chemistry S.G.B. Amravati University Amravati 444602 (M.S.) India
dharamdupare@yahoo.co.in

Abstract

MnO_2-Doped Polyaniline/Poly (Vinyl alcohol) thin films were prepared chemical oxidative polymerization, using microwave oven technique on glass substrate. These thin films prepared by using Analytical Reagent grade solutions of Polyaniline, Poly (Vinyl alcohol), MnO_2, primary dopant hydrochloric acid are mixed in stoichiometric proportion. The solutions were kept in microwave for 10 sec then oxides with ammonium peroxydisulphate oxidant, then after kept in water bath to obtain the uniform thin films. Films were dries it in air medium for an hour. The electrical and gas sensing properties of these films were investigated. MnO_2, Doped Polyaniline/Poly(Vinyl alcohol) thin films showed better ammonia and trimethyl ammine vapour response as compared to undoped Polyaniline / Poly (Vinyl alcohol) thin films. The gas response was observed to be increased with their stoichiometric composition of films.

***Keywords:** - Trimethyl ammine, ammonia, Polyaniline, Poly (Vinyl alcohol) and dopant.*

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1. INTRODUCTION

Ammonia is extensively used in many chemical industries, food processing, medical diagnosis, fertilizer factories, refrigeration systems, environmental protection etc. A small leakage of ammonia in the system can result the health hazards. Ammonia is harmful and toxic in nature. Its exposure may cause chronic lung disease, irritating and even burning the respiratory track. Therefore all industries working on and for ammonia should have an alarm system detecting and warning for dangerous ammonia concentrations [1-2)]. Detection and measurement of ammonia concentrations is of considerable commercial and medical interest. Ammonia sensors based upon Polyaniline and polypyrrole-poly (vinyl alcohol) thin film coatings have been reported [3]. It is therefore necessary to monitor ammonia and trimethyl ammonia gas. The efforts are made to develop the MnO_2-Doped Polyaniline/ Poly(Vinyl alcohol) thin films based NH_3 and trimethyl ammonia gas sensors.

Our interest lies in room temperature sensing of ammonia and trimethyl ammonia vapors using MnO_2- Doped Polyaniline / Poly(Vinyl alcohol) thin films–based sensors. The gas sensing characteristics of a given sensing element depends upon the material used, the method of preparation, and the resulting nano-to micro-structure. In the present study, Pure and MnO_2-Doped Polyaniline/ Poly (Vinyl alcohol) thin films, were prepared chemical oxidative polymerization, using microwave oven technique on glass substrate. The electrical and gas sensing properties of these films were investigated. The fact we are able to measure ammonia and trimethyl ammonia concentrations using MnO_2-Doped Polyaniline / Poly(Vinyl alcohol) thin films at room temperature makes possible a variety of new sensing applications, such as those associated with clinical use and monitoring food safety[4].

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 MnO_2-Doped PA-PVA Blend Thin Films

We have synthesized MnO_2-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

MnO_2 with different molar concentration ratio like (0.1m to.0.5m) **are** mixed in stoichiometric proportion. The solutions were kept in microwave oven for 10 sec, then oxidize with ammonium peroxydisulphate as oxidant, then after kept in water bath at 10 ^{0}c 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 MnO_2-Doped PA-PVA blend thin films was performed UV-visible 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 MnO_2 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 MnO_2 composite film is shown in Figure.1. The broad strong bands between 3450 –3350 cm^{-1} corresponds to the stretching vibrations of the intra-molecular hydrogen bond (υ_{O-H}) of PVA and this frequency also shows the absorption of N–H stretching of polyaniline. The frequency at 2920 cm^{-1} refers to 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} is due to C–H vibrations[7]. The peak at 1136 cm^{-1} is due to C-C stretching. The peak at 1080 cm^{-1} corresponds to the in-plane deformation of O-H group and C-O symmetric stretching of PVA. The band at 1020 cm^{-1} is due to in-plane deformation of C–H bond and N–H bond of polyaniline ring, Here due do MnO_2 dopant films it slightly change and percentage of transmittance is less in DMSO solvent.

Fig-1 FTIR Study of PANI-PVA and MnO_2 doped PANI-PVA

3.2 UV-Visible Spectra

The UV-Visible absorption spectra of MnO_2 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- 900 nm. The PANI-PVA blend thin films show three peaks at 308nm,446 nm and 809 nm respectively. The first peak was due to n-π* transition at 308 nm. The second peak for π-π* transition at 446 nm corresponds to benzenoid, rings while the sharp groove. Third peak represents Together with the extended tail at 809 nm representing the conducting emerald salt can be assigned to the localized polarons which are characteristic of protonated MnO_2 doped PANI-PVA film. with the extended tail at 810 nm[8] Fig-2.

Fig-2 UV-Visible absorption spectra of MnO_2 doped 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 MnO_2 doped PANI-PVA grains embedded in the PVA matrix[9].

As shown in Fig. 3a SEM micrographs of MnO_2 doped 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 MnO_2 doped PANI-PVA films consisting of MnO_2 a network of grains is schematically shown in Fig. 3a. The absence of interaction between MnO_2 in composite films helps us to understand the fig.3b. is only PANI-PVA composite thin film having uniform surface morphology.

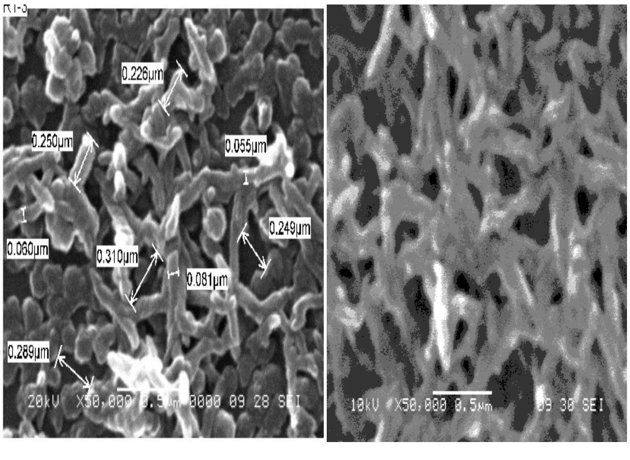

Fig 3(a) -SEM micrographs of MnO_2 doped PANI-PVA composite thin film (b) -PANI-PVA composite thin film

3.4 X-RD Study

From the X-RD analysis of the composite film, it can be seen that the MnO_2 dopant PANI-PVA film exhibited broad scattering peaks at 2θ value around 25° C and 40° C respectively, which suggest that theMnO_2 dopant PANI-PVA film highly disordered little bite crystalline in nature.

Polyaniline-polyvinylacohol composite films are virtually amorphous. Previous X-ray scattering studies of polypyrrole films have been reported to be highly disordered and non-crystalline [6]Fig -4 shows the X-RD diffractogram of MnO_2 doped PANI-PVA film conducting polymer composite film.

Fig. -4 XRD-diffractogram of MnO_2 doped PANI-PVA film

3.5 Electrical Characterization

The synthesized MnO_2 doped PANI-PVA films are subjected to I – V characterization to room temperature on the ohmic behaviour 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 MnO_2 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 behaviour [8].

Fig-5 I – V characterization

3.6 TMA and Ammonia Gas Sensing

To observe the TMA and ammonia gas-sensing characteristics of the synthesized MnO_2 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 MnO_2 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 MnO_2 doped PANI–PVA films at different concentrations of ammonia gas 5 ppm to 800 ppm. It was observed that the resistivity of the MnO_2 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 [9-11]. it can be seen from the figures, the conductivities of polymers show marked changes when exposed to NH_3 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 20-800 ppm, for MnO_2 doped PANI–PVA films for both gases. The surface morphology observed for MnO_2 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 MnO_2 doped PANI–PVA films.

CONCLUSIONS

- MnO_2 doped PANI–PVA doped nanocrystalline gas sensing material was successfully prepared by microwave oven technique.
- We have developed MnO_2 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 MnO_2 doped PANI–PVA thin films.
- The MnO_2 doped PANI–PVA film presents better sensitivity compared to pure PANI-PVA due to the distribution of particles MnO_2 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 5 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 [14].
- In future we are study biosensor application of these types of films.
- In future we are study various different types of gases sensing ability [15].

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