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Ag-PANI Matrix on Nanostructured ZnO: A Sensor Perspective

[1]Sivanantham Nallusamy, [2]Balamurugan Deenadhayalan,
[3]Rajan KalpoondiSekar and [2]John Bosco Balaguru Rayappan
[1]Department of Physics, Nehru Memorial College, Puthanampatti, Trichy-621 007, India
[2]School of Electrical and Electronics Engineering,
[3]School of Chemical and Biotechnology, Center for Nanotechnology and
Advanced Biomaterials (CeNTAB), SASTRA University, Thanjavur-613 401, India

Abstract: The Ag-PANI nanocomposite material was coated on nanostructured ZnO thin film using the spray pyrolysis technique. Structural and optical characterization of the prepared ZnO/Ag-PANI nanocomposite thin film was carried out using FE-SEM, UV-Vis spectrophotometer , respectively. The chemical composition of the material was confirmed using the FTIR spectrometer. The sensing behaviour of ZnO/Ag-PANI nanocomposite film was studied towards the various concentrations of ethanol and Trimethylamine (TMA). Response and recovery of pure ZnO and ZnO/Ag-PANI nanocomposite thin film towards ethanol and TMA was compared.

Key words: Gas sensors, silver-PANI matrix, ethanol, ZnO, nanostructures, nanocomposites, thin films

INTRODUCTION

Metal Oxide Semiconductors (MOS) based gas sensors are in extensive use today to detect wide ranges of gases including toxic, exclusive, organic, inorganic humidity and odors. Gas chromatography, nondispersive infrared spectroscopy, mass spectroscopy, etc., techniques have been used for detecting the presence of these gases in the ambient. But these techniques can be used for limited applications and also they are not cost effective. With reference to the size of the metal oxide gas sensors the size of these instruments are also very large in size. Moreover MOS based gas sensors can be used for various gas sensing applications (Varghese and Grimes, 2004) due to its size, simple principle of operation and mainly these sensors can be effectively interfaced with electronic systems to design a product.

MOS based gas sensors have a significant sensitivity towards the gases but the selectivity is a major concern and hence researchers find it hard to tune them for a particular gas. Another concern with reference to sensitivity is the performance at room temperature. In order to achieve a very good sensitivity in addition with selectivity, researchers have started working on the inorganic and organic mixtures.

In the metal organic mixture metal atoms are linked with organic atoms and they form porous material. They have potential applications in molecular adsorption and separation processes, gas storage, gas sensing, gas separation, catalysis and gas purification etc. Due to the crystalline supramolecule assembly along with highly porous nature these materials offer better selectivity towards gases (Schroder and Fischer, 2010).

Polyaniline is one of the conducting polymers and possesses better environmental stability. Silver is having better thermal stability and adhesive property to other materials. Comparing to other nanocomposite materials the Ag/PANI composites is having the enhanced electrical properties (Choudhury, 2009). The research fellows have reported the synthesis of Ag/PANI nanocomposites via an in situ photo-redox mechanism and one pot synthesis, respectively (Jing *et al*., 2006).

Among the various methods, wet chemical synthesis method is an easy and better technique for reducing the size of the particles. Similarly for fabricating the thin film, spray pyrolysis technique is a simple and cost effective. Using this technique large area of film can be coated with desired thickness.

In the present study, Ag-PANI matrix was prepared using wet chemical synthesis. For enhancing the selectivity of ZnO gas sensing performance and to enhance the sensitivity at room temperature, the metal-organic mixture was coated on the ZnO thin film using spray pyrolysis technique. The sensing behaviour of the prepared nanocomposite materials was studied towards the various concentrations of ethanol and trimethylamine. Since, these two volatile organic compounds are very good biomarkers of milk quality analysis.

Corresponding Author: John Bosco Balaguru Rayappan, School of Electrical and Electronics Engineering, Center for Nanotechnology and Advanced Biomaterials (CeNTAB), SASTRA University, Thanjavur-613 401, India

MATERIALS AND METHODS

Materials required: For the preparation of Ag-PANI nanocomposite over nanostructured ZnO thin film silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), Brij 35, ammonium peroxodisulphate ($(NH_4)_2S_2O_8$), aniline monomer, zinc acetate were taken as materials.

Sample preparation

Synthesis of Ag nanoparticle: For synthesis of silver Nanoparticle, silver nitrate ($AgNO_3$) in various concentrations (0.05, 0.10, 0.15 M) is used as precursor. For this precursor, sodium borohydride ($NaBH_4$) is chosen as the reducing agent in the ratio of 1:2. For controlling and stabilizing the size of the particle, surfactant Brij 35 is added. The Precursor solution and surfactant mixture is kept in constant stirring for 20 min. Then surfactant is added drop by drop to reduce silver nitrate. As the solution gets reduced the color of the solution changes to yellow (Fig. 1). This confirms the silver nanoparticle colloidal in the solution.

The Nanocomposite Metal Organic Framework (NMOF) is synthesized by taking silver nanoparticle and aniline hydrochloride solution. To polymerize the mixture, ammonium peroxodisulphate solution is used as oxidizing agent to obtain Ag/PANI matrix. The ammonium peroxodisulphate is added drop by drop for 30 min. After adding the oxidizer, the solution is kept in constant stirring for 12 h at a temperature of 2-8°C. The color of the colloidal solution changes from yellow to pink and then blue, the final Ag/PANI matrix is seen as dark green color. This color confirms the formation of Ag/PANI matrix colloidal.

Film deposition

ZnO thin film: For preparing ZnO thin film, Zinc acetate solution of 0.05 M is taken as the precursor solution. The cleaned glass substrate is kept at constant temperature of 230°C and the precursor solution is sprayed over the preheated substrate. In the spray time the precursor solution droplets are hit the heated glass substrate. The Zinc acetate solution decomposes to form (ZnO) thin film on the substrate. After coating the deposited film is annealed at 300°C for one h to form homogeneous ZnO film.

ZnO-Ag/PANI nanocomposite thin film: The Ag/PANI nanocomposite was prepared by adding PVA (poly vinyl alcohol) as binder. The mixture is ultrasonificated for 30 minutes. The sonicated solution is sprayed on to the ZnO film using spray pyrolysis technique which is kept at a constant temperature of 40°C.

RESULTS AND DISCUSSION

Structural characterization: The XRD pattern of Ag-PANI nanocomposite films prepared from 0.1 M of Ag and polyaniline concentration is shown in Fig. 2. The obtained XRD pattern is found to agree with the standard JCPDS cards (JCPDS card number: 03-0869 for polyaniline, JCPDS card no: 4-0783 for silver), indicating the nature of silver and polyaniline matrix. The peaks are indexed to (100) (002) (111) (102) and (103) planes, respectively.

The peak at 2θ values of 31° corresponds to polyaniline peak. Also the peak at 31° reveals the sequential growth of polyaniline chain on the silver nanoparticles. The peak corresponding to 2θ value of 36° reveals the crystalline nature of silver oriented in (111) plane.

Optical characterization: The optical characterization of Ag-PANI nanocomposite film on ZnO substrate was

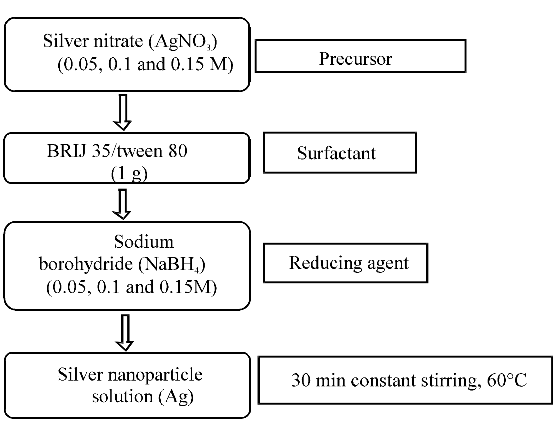

Fig. 1: Synthesis of silver nanoparticle colloidal

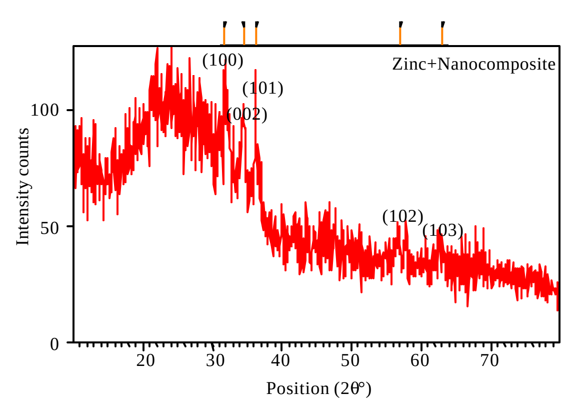

Fig. 2: XRD pattern of Ag-PANI nanocomposite on ZnO films

carried out using UV-Visible spectrophotometer. The absorption and transmittance of the film is shown in Fig. 3.

From the absorbance spectrum, one can confirm the presence of silver in the silver PANI nanocomposite matrix at the wavelength range of 382 and 453 nm. The spectrum shows a shift in peaks towards blue which confirms the size of the composites in nanorange.

FTIR studies: FTIR spectrophotometric studies were carried out for the Ag-PANI nanocomposite film deposited on ZnO substrate. The resultant spectrum is shown in Fig. 4. From FTIR analysis C-N, N-H, C-H, amine functional group, conjugated bonds appeared in the nanocomposite samples. From the result it confirms the nanocomposite material of polyaniline.

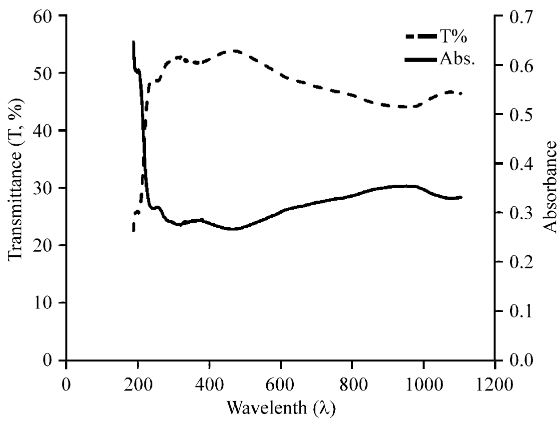

Fig. 3: Absorbance and transmittance spectra

Polyaniline structure

Polyaniline has: Amine groups, C-N stretching with aromatic ring and Conjugated bond from property.

Sensing characteristics: The sensing characteristics of the ZnO/Ag-PANI nanocomposite film was observed at room temperature towards various concentrations of ethanol and Trimethylamine (TMA). The change in electrical resistance of the sensing element, before and after injection of ethanol and TMA inside the gas testing chamber was observed and is shown in Fig. 5 and 6. A decrease in the resistance was noted after the injection of ethanol into the chamber. This may be due to the increase in the charge carrier concentration of the sensing material in the presence of ethanol. The reaction equation is given below:

$$O_2+e^-_{ZnO}\rightarrow O_2^- \quad (1)$$

$$2C_2H_5OH+O_2^-\rightarrow 2CH_3CHO+2H_2O+e^- \quad (2)$$

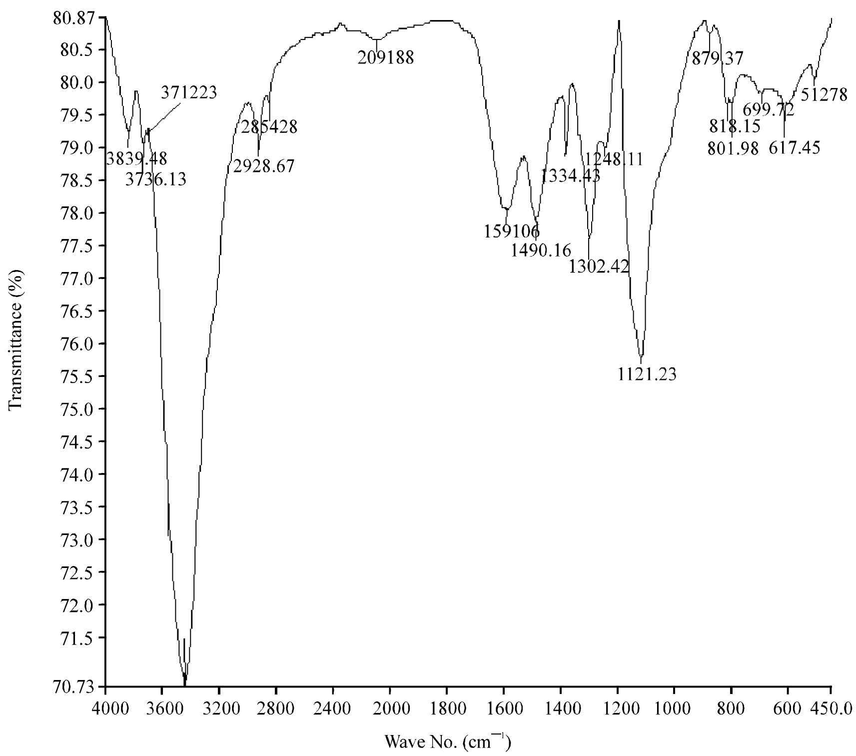

Fig. 4: FTIR spectrum of Ag-PANI nanocomposite

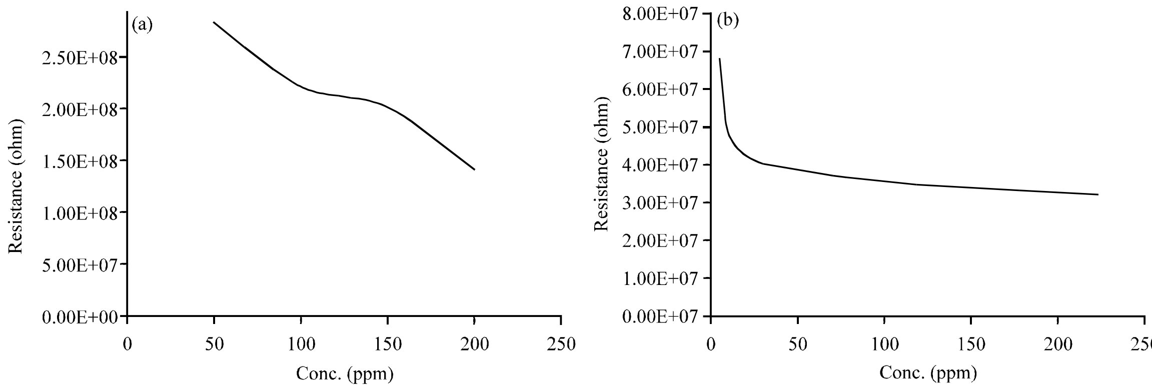

Fig. 5(a-b): Change in resistance with respect to ethanol concentration; (a) ZnO and (b) Ag-PANI/ZnO nanocomposite

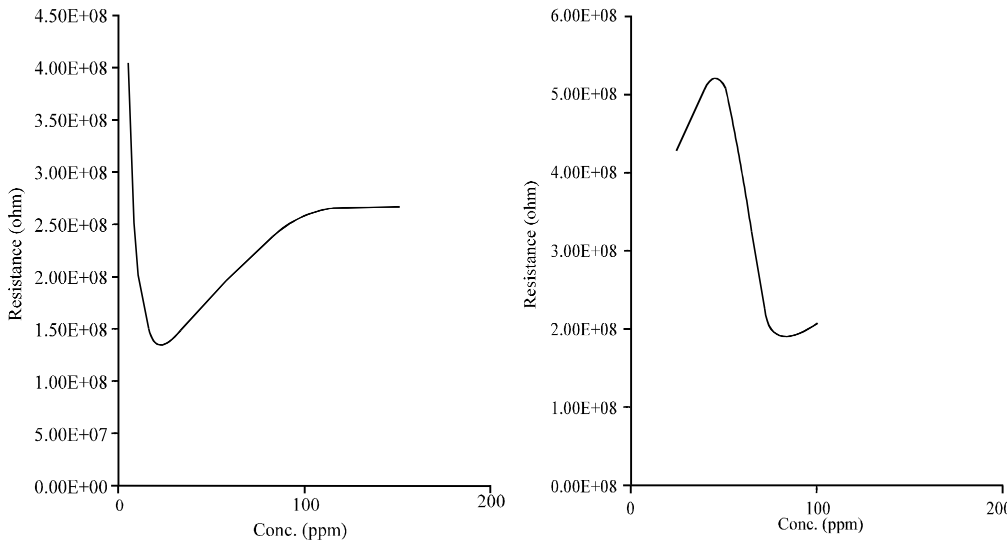

Fig. 6(a-b): Change in resistance with respect to TMA concentration; (a) ZnO and (b) Ag-PANI/ZnO nanocomposite

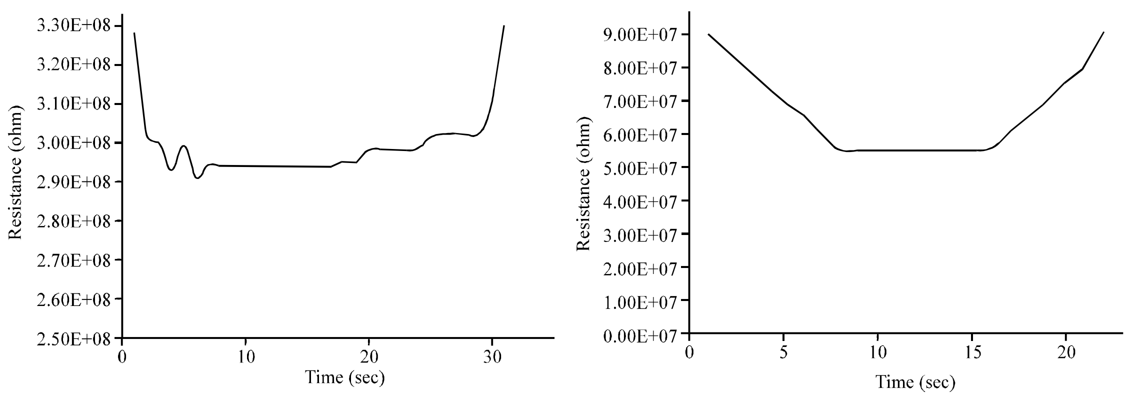

Fig. 7(a-b): Response and recovery plot for ethanol; (a) ZnO and (b) Ag-PANI/ZnO nanocomposite

Equation 1 indicates the oxidation reaction between ZnO surface and atmospheric air. Under this condition, the film was exposed to ethanol which leads to the decrease in resistance due to the reaction as given in Eq. 2.

Similarly for TMA gradual increase in the resistance was noted after the injection of TMA into the chamber. This is may be due to the reducing gas and because of the lack of the charge carrier concentration of the sensing material in the presence of TMA.

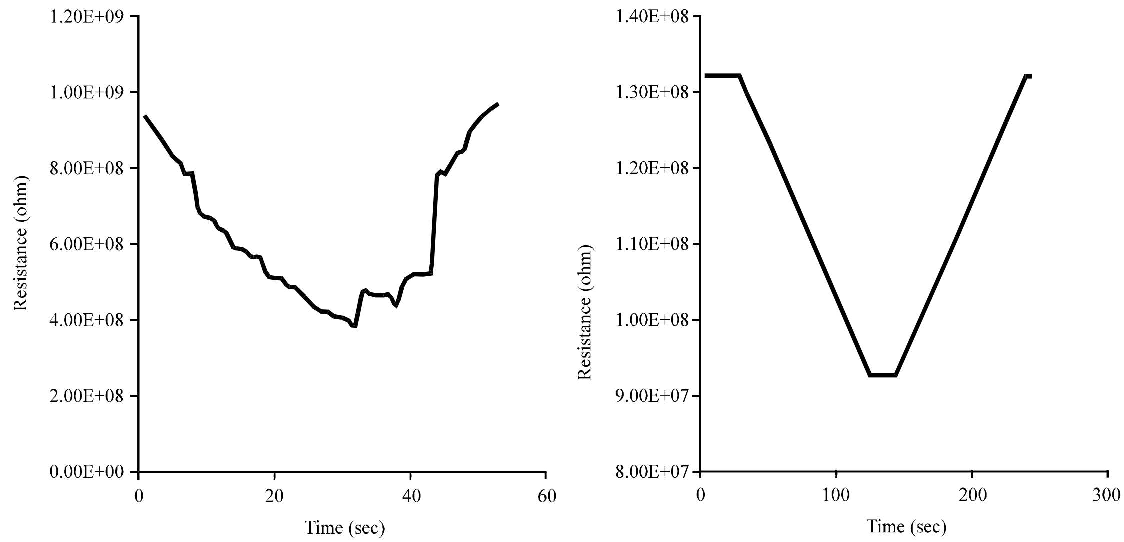

Fig. 8(a-b): Response and recovery plot for TMA; (a) ZnO and (b) ZnO/Ag-PANI

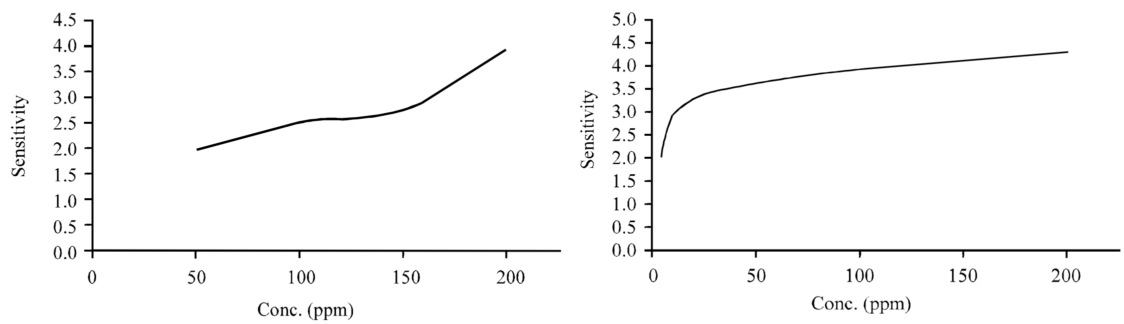

Fig. 9(a-b): Ethanol sensitivity vs. concentration plot for; (a) ZnO and (b) Ag-PANI/ZnO nanocomposite

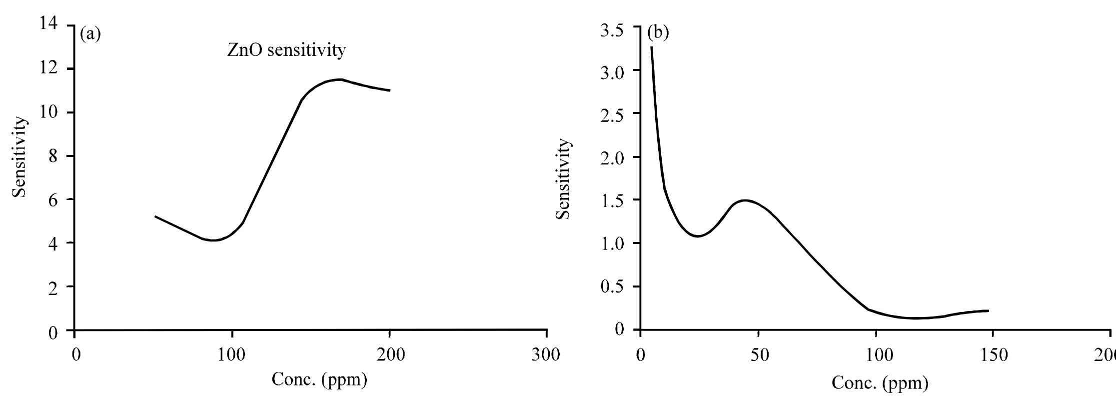

Fig. 10(a-b): TMA sensitivity vs. concentration plot for; (a) ZnO and (b) Ag-PANI/ZnO nanocomposite

The response and recovery time of the ZnO thin film and ZnO/Ag-PANI thin film towards 50 ppm of ethanol and TMA was observed and the same is plotted as shown in Fig. 7 and 8. From the response curve it is noted that the response and recovery time of the Ag-PANI coated on ZnO thin film towards ethanol is appreciable compared to pure ZnO with the value of 10 and 25 sec, respectively. But in the presence of TMA the response and recovery of the material is high because of the reducing gas of TMA.

From the observed change in response and recovery of ZnO and ZnO/Ag-PANI nanocomposite towards various concentrations of ethanol, the sensitivity (S) of the film towards reducing gas was calculated using the following equation:

$$S = \frac{R_0 - R_g}{R_g} = \frac{R_0}{R_g}$$

The calculated sensitivity of the films towards various concentrations of ETHANOL and TMA is plotted and is shown in Fig. 9 and 10. From the plot sensitivity of ZnO/Ag-PANI nanocomposite is found to be appreciable. But compare to pure ZnO the ZnO/Ag-PANI nanocomposite in the presence of TMA is poor.

CONCLUSION

In summary, the Ag/PANI nanocomposites were successfully synthesized using the wet chemical method and the same material is deposited on the ZnO substrate as a thin film through spray pyrolysis technique. The thin films were characterized by XRD, SEM and UV-Vis spectroscopy. The XRD analysis confirms the presence of silver nanoparticles. The peak at 26° in XRD profile confirms the sequential growth of polyaniline chain with silver nanoparticles, also the peak at 38° confirm the aggregation of silver nanoparticle. The sensing behavior of ZnO-Ag/PANI nanocomposite is found to be appreciable response and recovery time of 20 and 25 sec, respectively towards 50 ppm of ethanol at room temperature. The sensing behavior of ZnO-Ag/PANI nanocomposite thin film is studied towards the ethanol and trimethyl amine VOCs. The response- recovery and sensitivity towards the ethanol and Tri methyl amine is compared between the pure ZnO and ZnO-Ag/PANI nanocomposite thin films. From the response recovery and sensitivity plots found that compared to pure ZnO, the ZnO-Ag/PANI coated thin film having good recovery and its sensitivity also high towards the ethanol. But in the same comparison towards the Tri methyl amine shows the poor response recovery and low sensitivity in ZnO-Ag/PANI nanocomposite thin films. Hence it is concluded that ZnO-Ag/PANI nanocomposite can be used to sense lower concentration of ethanol at room temperature effectively with appreciable sensitivity.

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