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Synthesis and Characterization of Polyaniline-SnO2 Composite for Volatile Organic Compounds (VOCs) Detection

Varade PS, Gangal SA, Shaligram AD

Department of Electronic Science, Savitribai Phule Pune University, Pune (Maharashtra), India.

ABSTRACT

Polyaniline- SnO2 nanocomposite was synthesized using an in-situ polymerization of aniline in presence of synthesized SnO2 nanoparticles. Structural and elemental characterization was done using FT-IR, XRD and FE-SEM techniques. The gas sensitivity of Polyaniline- SnO2 nanocomposite material to volatile organic compounds (VOCs - ethanol, methanol, acetone and toluene) was studied. Thin films of polyaniline - SnO2 nanocomposite material were deposited by drop cast method on interdigited structure (IDT). DC resistance of the films was measured using electrometer. The resistance of the films in normal air is in the range of 0.2 to 0,8 GΩ. It is observed that polyaniline-SnO2 composite material is sensitive to VOCs at room temperature. The sensitivity of the material for VOCs is studied in ppm range of 200 -1000. The polyaniline-SnO2 composite material shows the linear increase in sensitivity with the increase of ethanol concentration. It is observed that polyaniline - SnO2 thin film is more sensitive to ethanol (50.68%) as compared to methanol (9.74%), acetone(7.22%) and toluene (4.99%). The response mechanism of polyaniline-SnO2 material to VOCs is also discussed.

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Keywords Polyaniline- SnO2 composite, Volatile organic compounds, sensitivity.

INTRODUCTION

Volatile organic compounds (VOCs) are organic chemicals which have a high vapor pressure at room temperature. Their high vapor pressure results in low boiling point, which causes large numbers of molecules to evaporate or sublimate from the liquid or solid form of the compound and enter the surrounding air, These kinds of chemicals can enter the human body through many ways such as breathing, touching or swallowing. These VOCs causes an adverse effect on human health, so detection of VOCs has become important. Different types of sensors are available for detection of the VOCs. Sensors TGS 812(Figaro) for propane, butane detection and STEINEL SGAS 2000 for ethanol detection [1] are commercially available. These sensors basically operate above room temperatures. Many studies showed that the inorganic semiconductors such as TiO_2, ZnO, SnO_2,and Fe_2O_3 are used for making sensors, but they need to be operated at temperature above 3000C which increases the power consumption and reduce operating life of the sensor. In commercial devices organic semiconductors are used because they operates at low temperatures .But the main limitation is their slow response time [1-2].

To manifest the characteristics of pure inorganic and organic materials and explore the sensing materials with low operating temperature and good selectivity, organic-inorganic sensing composites have been developed. GENG Li-na [3] reported that polyaniline-SnO_2 composite material has good sensitivity to VOCs at 900C and can respond at a wide concentration range with fast response (10-32, 54-148 ,79-49 seconds) and recovery times(47-109 , 79-118,65-160 seconds) for ethanol, methanol and acetone respectively. H. Gong et. al.[4] reported that thin films of tin oxide show maximum sensitivity to VOCs at 4500C, Min-Hyun Seo et.al.[5]reported that the TiO_2 nanotubes can detect toluene upto 50 ppm at an elevated temperature of 5000C in dry air. Anjali A. Athawale et. al. [6] synthesized pd-polyaniline nanocomposite by oxidative polymerization and tested the response for methanol, ethanol and isopropanol for the concentrations of 1,5,10,100 and 2000 ppm. It is reported that Pd-polyaniline nanocomposite is highly sensitive (8.9 x 105 Ω ppm-1) and selective in presence

of Pd nanoparticles to methanol vapors with stable response for a sufficiently long time at room temperature. Recently K. Inyawilert et.al.[7]reported that sparked-In2O3 sensing films with different thicknesses can be used for ethanol and acetone sensing applications. The sensor with optimal thickness of ~3μm (100 sparking cycles) exhibited the highest ethanol/acetone response of ~19. Shortest response times within seconds and lowest detection limit 100 ppm at 350 ◦C. Very few researchers [1, 6] worked on VOCs detection using polyaniline-SnO_2 nanocomposite at room temperature . So we focused on the study of polyaniline -SnO_2 nanocomposite material synthesis to improve its sensitivity, In present work , polyaniline -SnO_2 nanocomposite is prepared by in situ polymerization of aniline in presence of synthesized SnO_2 nanoparticles using ammonium persulphate (APS) as an oxidant in acidic medium. The composite is characterized by FTIR, XRD and FE-SEM with EDS. The prepared material is tested for four different volatile organic compounds (ethanol, methanol, acetone and toluene) with their exposure range of 200-1000 ppm. The results related to sensitivity of the sensing material to VOCs have been discussed.

METHODOLOGY

Aniline (99.5%) monomer was distilled using condenser method to remove the additives and to get pure aniline monomers before its use. Tin chloride ($SnCl_4$: $5H_2O$) (99%), hydrogen peroxide (H_2O_2) (99.5%) Ammonium per sulphate (98%), starch (98.5%) and ammonia (99%) were purchased from High Purity Laboratory Chemicals PVT. LTD. All chemicals were of analytical grade and used as they are. The solutions were prepared with distilled water.

Synthesis of SnO2 nanoparticles

Sol-gel method was used for the synthesis of SnO_2 nanoparticles In a typical method, 0.1M $SnCl_4$:H_2O was added in 1M starch solution and the mixture was stirred for half an hour. Then 0.2M ammonia was added drop wise in the solution under constant stirring. The stirring was continued for further 3 hours and then the solution was allowed to settle overnight. Supernatant liquid was then discarded carefully and

the remaining solution was centrifuged for 15 minutes and then filtered. The precipitate of SnO2 was washed completely using distilled water to remove by-product and the excessive starch those were bound with the nanoparticles. The product was dried in hot air oven at 80°C for overnight. Then powder was sintered at 600°C using oven for 6 hours and nanocrystalline SnO2 was obtained [8].

Synthesis of polyaniline-SnO2 nanocomposite

Polyaniline - SnO2 nanocomposite was synthesized by an in-situ polymerization of aniline in presence of synthesized SnO2 nanoparticles using ammonium persulphate (APS) as an oxidant in acidic medium. Aniline (0.1M) and APS (0.1M) were dissolved separately in 1M HCl solution and stirred for 80 minutes. As-synthesized SnO2 nanoparticles were suspended separately in 1 M HCl (100 ml) solution and sonicated for 90 minutes to reduce aggregation of SnO2 nanoparticles. 100 ml aniline solution and 10 ml SnO2 nanoparticles suspension were mixed and further sonicated for 90 minutes. 100 ml APS solution was then slowly added drop wise to well disperse suspension mixture with continuous stirring. After 2 hours, a good degree of polymerization was achieved. The green color precipitate was obtained. The precipitate produced in the reaction was removed by filtration, washed repeatedly with 1 M HCl and dried at room temperature in dust free environment. The composite powder was in conductive emeraldine salt (ES) form of polyaniline -SnO2 nanocomposite [8].

Structural and morphological Characterization of polyaniline-SnO2 nanocomposite

The FTIR spectra of synthesized product were recorded by using Bruker spectrophotometer in the wavenumber range of 400-4000 cm-1. Phase identification of the composite was done by X-ray diffraction using Bruker AXSD8 diffractometer with Cu-Kα radiation source. The morphological study of the composite was carried out by field emission scanning electron microscope (FESEM- Nova NanoSEM NPEP303), and SEM JEOL, OXFORD instruments).

VOC Sensing characteristics of Polyaniline - SnO2 nanocomposite

The film of synthesized Polyaniline-SnO2 nanocomposite was formed by drop casting method on the interdigitated structure (IDT) made in copper film on glass

epoxy. IDT structure has five finger pairs having finger width and gap of 2mm each. 20 micro-liter solution was dropped from micropipette on the IDT structure. The film is dried at room temperature before use for VOC detection. The experimental set-up used for VOCs detection is shown in figure1. The gas sensing characteristics were studied in a custom-made testing chamber. The testing chamber is made of glass having air tight plastic cap on which the gas inlet rubber and electrical contacts for sensor are fitted. The volume of the chamber is 500cc.The vapors of VOCs in liquid form are added in the chamber by using the plastic syringe. The sensor was tested for 200- 1000 ppm (VOCs concentration). The sensitivity of the sensor was determined by measuring the resistance of the sensor at room temperature with and without presence of the VOCs using Keithley's Electrometer (Model -2000).

Figure 1: Experimental set-up for VOC study

RESULTS AND DISCUSSION

Figure 2 shows the XRD pattern of the obtained Polyaniline- SnO2 composite. It can be seen that the nanocrystalline SnO2 peaks are observed at 2θ values of 26.580 ,34.900,38.140,52.130,66.120 and matched with those peaks along planes (1 1 0), (1 0 1), (2 0 0), (2 1 1), and (3 0 1) having primitive tetragonal structure (*JCPDS DATA CARD 41-1445*). The XRD spectrum peaks are close to the standard XRD of SnO2]. However, these peaks show a small shift (0.20 to 0.50) from their respective standard positions which may be due to polyaniline matrix. In addition, we observed relatively larger peak broadening, compared with XRD of pure SnO2 [9] This suggests that tin oxide is present in the polyaniline matrix, and presence of
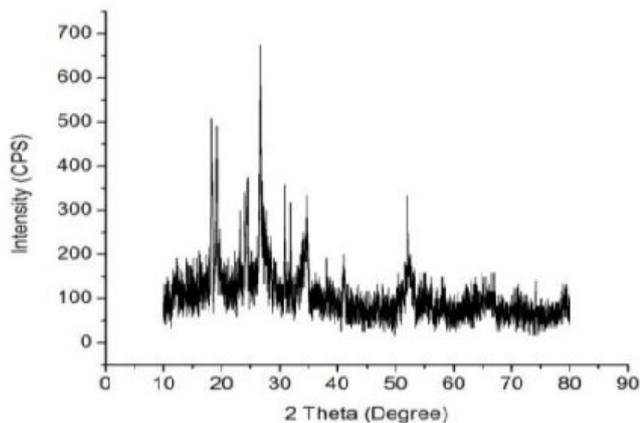
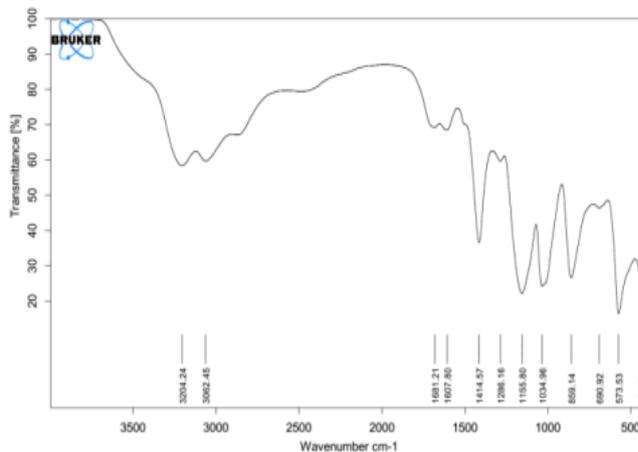**Figure 2:** XRD of polyaniline -SnO2 Composite
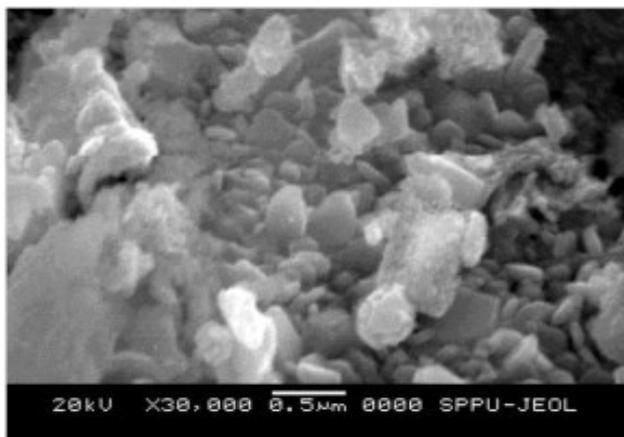

Figure 3: FTIR spectra of polyaniline-SnO$_2$ Composite
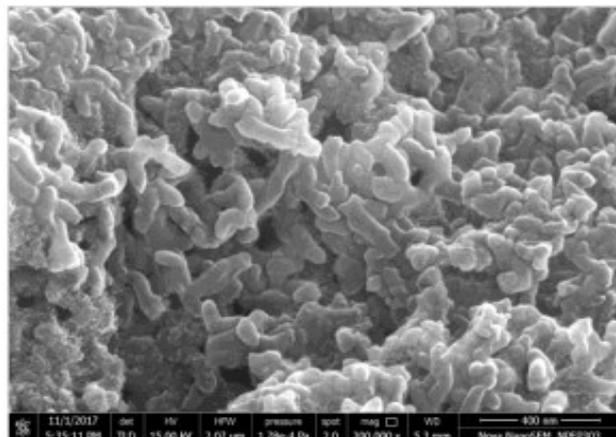

Figure 4: SEM of SnO$_2$ nano particles

Figure 5: FE- SEM of polyaniline-SnO$_2$ nanocomposite

composite was characterized by Fourier Transform Infrared (FTIR) spectroscopy.

In the FTIR spectrum of a composite (figure 3), the characteristic peaks at 3062.45 & 3204.24 cm-1 & 1681.21cm-1 correspond to C-H stretching vibrations, and C=C stretching vibrations respectively. Peaks at 1607.80 and 1414.57 cm-1 correspond to quinoid and benzene rings of polyaniline, while the peak at 690.92 cm-1 corresponds to the anti-symmetric Sn-O-Sn mode [8,10]. Thus it shows the characteristics of polyaniline as well as the tin oxide. Figure 4 shows the SEM image synthesized SnO2 nanoparticles. Which shows that the particle size is not uniform. Figure 5 shows the field emission scanning electron microscopic image of polyaniline-SnO2 image.We took the images at different points on the material. At few places it is observed the particle structure like nano rods with their length varying from ~450-700nm.
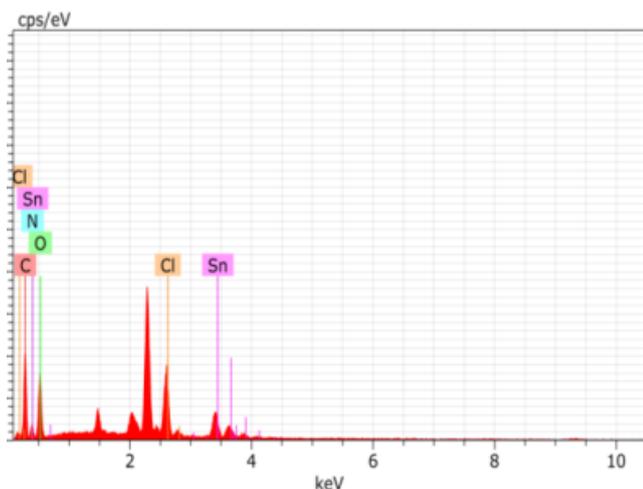

**Figure 6:** EDS of PANI-SnO2 Composite

polyaniline has influenced the preferred orientation of tin oxide grains in the composite to some extent. The lattice constant was found to be $a = b = 4.741$ Å, $c = 3.31$. Peaks in Figure 2 are similar to those observed by other researchers [8,10].The chemical structure of the

Table 1. Concentrations of chemical elements composing the sample

Elements	C	O	N	Sn	Cl
EDX at %	48.86	30.33	16.39	1.42	3.00
EDX Weight %	37.22	30.78	14.56	10.72	6.74
Chemical Analysis, Weight %	25.26	20.89	9.88	7.27	4.57
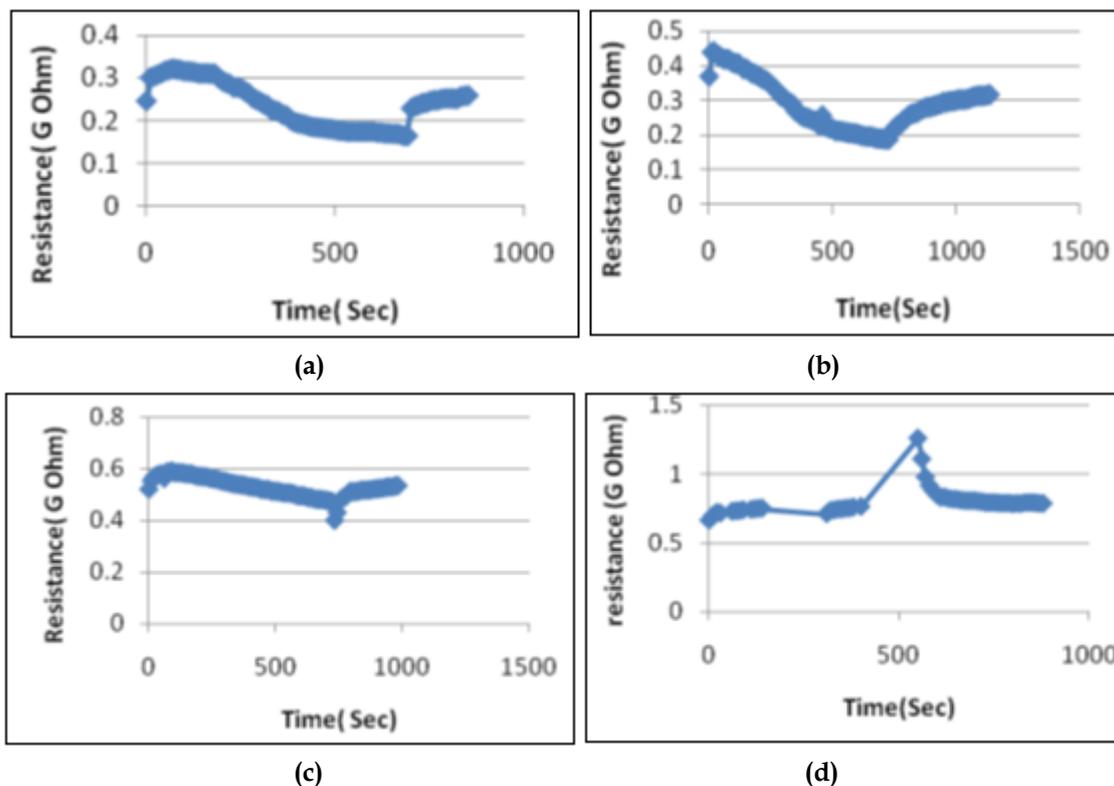
Figure 7: VOCs (a) ethanol, b) methanol, c) acetone d) , toluene) response to PANI- SnO2 nanocomposite

Study of the composition of samples by the technique of EDX microanalysis has shown (Figure 6.) that in the spectrum of characteristic X-ray radiation appearing at interaction of the electron probe with the sample surface, there are peaks of chemical elements entering the experimental set-up for VOC study composition of polyaniline (only C and N, because this technique does not detect H) and tin dioxide (Sn and O), as well as the peaks of sulfur and chorine. Measurements were performed in different regions of the sample surface [10].

Table 1 lists average values of concentrations of chemical elements in the sample. sensitivity of the sensor is defined as the ratio of the change in resistance of the sensor on exposure to the target gas to the original resistance in air. The relation for sensitivity S is as:

$$S = (Rg-Ra)/Ra,$$

where Ra and Rg are the resistance of sensing materials in air and in a target gas medium respectively.

Figure 7 shows the responses of polyaniline-SnO2 film to the ethanol methanol, acetone and toluene respectively at room temperature. These responses are recorded for 200-1000 ppm of these VOCs. The response shown in figure 7 is for 200 ppm exposure of each VOC to the sensor. For exposure of these VOCs it is observed that the resistance initially increases for short time and then it decreases. Initially the adsorption of oxygen from VOCs on the surface of sensing material increases the resistance of the sensor material due to transport of electrons from conduction band to adsorbed oxygen [1, 2], this indicate that our material is p type. After short time the resistance of polyaniline-SnO2 materials decreases because of water content in VOCs is get adsorbed on the

material, which increases the surface conductivity of the material. The decrease in resistance is below the base line resistance of the composite material. This is due to higher conductivity of adsorbed water molecules, which takes more time to desorbed. The gas sensitivity of polyaniline- SnO2 materials to VOCs may be explained by the creation of positively charged depletion layer on the surface of the SnO2, which could be formed owing to inter-particle electron migration from SnO2 to polyaniline at the p-n heterojunctions. This would cause a lowering of the activation energy and enthalpy of physisorption for vapors with good electron-donating characteristics [1, 2]. For all the four VOCs the response time observed is less than recovery time.

Figure 8 shows the sensitivities versus the amount of VOCs exposure. It shows that the sensitivity of the sensing material is more for ethanol than the other three VOCs.
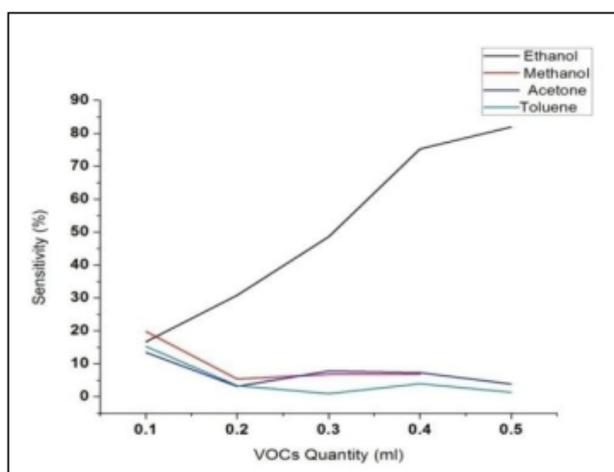
Figure 8: Sensitivities of ethanol, methanol, acetone and toluene to polyaniline- SnO2 nanocomposite film

Because ethanol consumes six O-ads, methanol consumes three O-ads for complete oxidation. Acetone consumes four O-ads. But surface reactivity of acetone and toluene is less as compared to ethanol and methanol. The surface reactivity depends on functional groups involved in the reaction. The average sensitivity to the VOCs is in the order-ethanol (50.68%)> methanol (9.74%)>acetone (7.22%)> toluene (4.99%).

CONCLUSION

The sensitivity values of polyaniline- SnO2 composite to the four organic vapors (VOCs) increases in the order of ethanol > methanol > acetone > toluene. Among these, the sensitivity increases with increasing number of methyl groups involved, suggesting that the sensitivity corresponds to the amount of oxygen adsorbed or the amount of surface lattice oxygen atoms consumed for the complete oxidation per alcohol molecule for total reducibility. The low sensitivity to toluene may be due to absence of oxygen atom in toluene. Acetone has no particular H atoms or groups which are easily dissociated, therefore less dissociative adsorption of oxygen on SnO2 surface and therefore relatively less sensitivity as compared to ethanol and methanol is seen.

Conflicts of interest: The authors stated that no conflicts of interest.

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