

Synthesis and Characterization of Sn-PANI Composite for Humidity Sensing Application

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Abstract—The measurement of humidity and moisture control are some of the prime factors in the case of industrial processes and environmental studies. Thus, the fabrication of highly sensitive humidity sensor is of keen interest for many researchers. Humidity sensors are widely used in semiconductor, pharmaceutical, health care, automobile, textile, paper and agriculture industries. Traditional humidity sensors are fabricated by using alumina, ceramics, metal oxides and polymers. Of all available sensors, resistive type humidity sensors are widely in demand due to their low cost and easy sensing mechanism. Sensors fabricated by using polymers have been reported good stability whereas sensors based on metal oxides have been reported good sensitivity. This has motivated us in studying the behavior and characteristics of sensors based on Polyaniline (polymer) and Tin oxide (metal oxide). In present study, we synthesized Sn-PANI composite and characterized it using FTIR, XRD and SEM techniques as displayed. Sn-PANI composite is one such proposed sensor that has appreciable response to humidity. The blending of SnO₂ with PANI has greatly increased the sensitivity towards humidity as compared to SnO₂ and PANI sensors alone.

1. INTRODUCTION

For the last several years sensors are extensively used in various fields to detect the existence of many pollutant gases and humidity to avoid toxic effects on mankind. Sensors possess wide range of application in various aspects of modern day technologies. As reported, humidity plays a major role in every part of the earth and its adjoining ambience. To have a desirable surrounding atmosphere for manhood, it is essential to monitor, detect and control the ambient humidity under different conditions [1]. The measurement of humidity and moisture control are some of the leading factors in the case of manufacturing practices also. Humidity sensors are comprehensively used in different industries such as semiconductor, pharmacological, health care, automobile, textile, paper and agronomy industries [2].

A selection of material for a good sensor is based on 1. Sensitivity: the minimum volume of concentration that can be detected, 2. Response time: the time taken by a sensor to respond to an existence of moisture, 3. Recovery time: the

time taken by sensor to get ready for next sensing cycle, 4. Fabrication cost and 5. Shelf life [3].

Several attempts were made to synthesize sensor satisfying above parameters with the help of metal oxides, polymers, ceramics and alumina [4]. These materials show fluctuations in their physical and electrical properties when exposed to the different atmospheric humidity circumstances of the adjacent environment. These changes are mainly due to the adsorption or desorption of water molecule on the surface of the sensor material [5]. Humidity sensors based on polymers and metal oxides are resistive type sensors. Resistive type sensors are the sensors, which shows change in surface resistance when exposed to humidity. These sensors are of easy mechanism and cost effective. In case of metal oxide sensors, the surface metal oxides are getting covered with hydroxyl groups when exposed to humid atmosphere thus hydrogen-bonding forms to further adsorb water molecules [6]. In the first stage of the interaction a few water vapour molecules are chemically adsorbed (chemisorption) on surface. As a second stage, after chemical completion of the first layer, subsequent water vapour layers are physically adsorbed (physisorption) on the first formed hydroxyl layer. This leads to the hydroxyl multilayer formation on the surface of the metal oxide. With this hydroxyl groups on surface of the sensor results in the increase in conductivity. In case of polymer based humidity sensors, sensing principle is same as metal oxide humidity sensors [7].

Tin oxide (SnO₂) has been recognized as an attractive material with excellent optical properties, chemical durability and transparent conductivity. Due to these properties SnO₂ is widely used for monitoring humidity. However, there are some limitations of SnO₂ [8]. Polyaniline attracted more researchers due to its high sensitivity, short response time, low cost of fabrication, simple structure and low energy consumption. However, PANI shows some drawbacks also, such as long-time instability and irreversibility [9]. To overcome drawbacks of SnO₂ and PANI for humidity sensing application, we blended SnO₂ with PANI to form composite

Sn-PANI. These were prepared by sol-gel method and chemical oxidative method respectively. Sample was characterized using X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) techniques. The humidity sensitive characteristics were investigated by recording their electrical responses when exposed to humidity with the help of simple laboratory made set up.

2. METHODS AND MATERIALS

Polyaniline Synthesis (PANI)

Polyaniline (PANI) was synthesized by using chemical oxidation method. An appropriate amount of double distilled Aniline and water were mixed together. 1M H₂SO₄ as a dopant was added to the above solution. Ammonium persulphate (APS) as an oxidizing agent was also added drop by drop to this solution till polymerization took place. The whole procedure was carried out under constant magnetic stirring for 6 hours at low temperature, as this reaction was highly exothermic. The precipitate was filtered, washed several times and then dried at 60° C for 12 hours to obtain a dark green powder.

Tin Oxide Synthesis (SnO₂)

Tin Oxide (SnO₂) was synthesized by sol-gel reaction. An appropriate amount of Tin chloride (SnCl₂.2H₂O) was added to distilled water and kept for constant stirring at 450 rpm. 1M NaOH was added to above solution drop by drop to adjust pH in the range 8-9 on pH scale. Once pH got adjusted solution again stirred for 2 hours at 60° C. It was observed that colour of solution changed from white to grey in this process. The precipitate was then filtered, washed several times and then air-dried. The sample was sintered in a furnace at 400°C for 6 hours.

Sn-PANI Composite

To form composite Sn-PANI, SnO₂ powder was blended with PANI with different concentrations by simple grinding process. For better results of characterization the sample was shaped in pellet form. The pellets were formed by applying a pressure of 6 tones for 5 minutes. The nature of bonding, structural and surface morphology of the PANI, SnO₂ and composite were analyzed by FTIR, XRD and SEM respectively. The sensing characteristic was examined by monitoring the changes in resistance using Keithley source meter.

3. RESULTS AND DISCUSSIONS

In order to study the structure and grain size of synthesized material, we characterized the material by XRD technique. The XRD patterns for PANI, SnO₂ and Sn-PANI nanocomposite are shown in Fig. 1, 2 and 3 respectively. For PANI, The characteristic peak appeared at 26° corresponding to (200) crystal plane. On comparing the observed XRD peaks

for SnO₂ and Sn-PANI composite, it can be seen that the nanocrystalline SnO₂ peaks are observed and matched with those peaks along (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (3 1 0) and (2 0 2) having primitive tetragonal structure (JCPDS DATA CARD 41-1445).

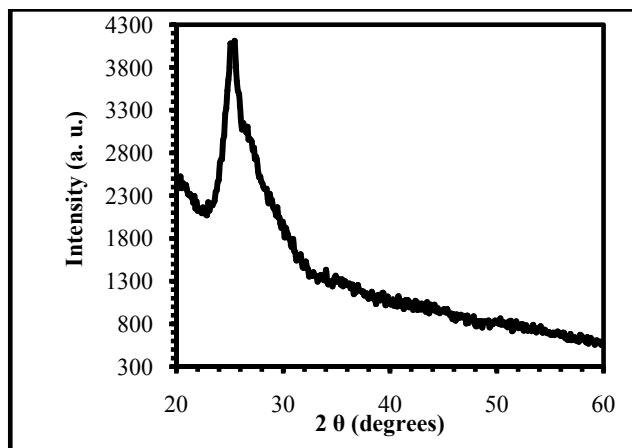


Fig. 1: XRD of PANI

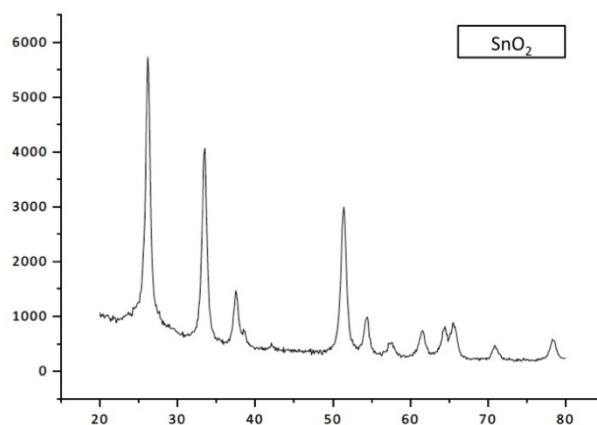


Fig. 2: XRD of SnO₂

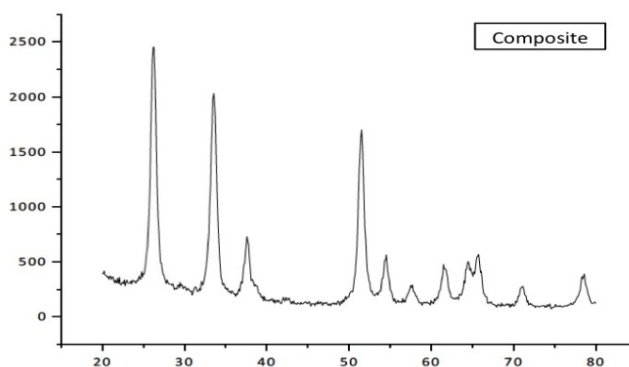


Fig. 3: XRD of Sn-PANI

However, these peaks are slightly shifted from their respective standard positions, which may be due to PANI matrix. In addition, we observed reduced intensity of the peaks compared with XRD of pure SnO₂. This suggests that tin oxide is present in the PANI matrix, and presence of PANI has influenced the preferred orientation of tin oxide grains in composite to some extent. The average particle size of the nanoparticles is estimated from the line broadening of the XRD peaks, it can be calculated by using Scherrer's formula, The average grain size of the SnO₂ is estimated to be 23.75 nm.

The surface morphology of PANI, SnO₂ and Sn-PANI composite were studied by SEM technique. The surface morphology of the PANI, which confirms the interconnected polyaniline nanofibers having rod like structure. The fibers are relatively smooth with random distribution and the size around 80 nm (Fig. 4). The SEM image of SnO₂ shows tetragonal nature having average size 70-90 nm (Fig. 5). It can be seen from Fig. 6 that the composite particles are highly dispersed with agglomeration. The formation of polymer shell around the nano crystalline particles can be seen in SEM image. The observed difference in the measurement of the grain size by XRD and SEM would be due to the fact that two or more crystallites may be fused together to form a particle.

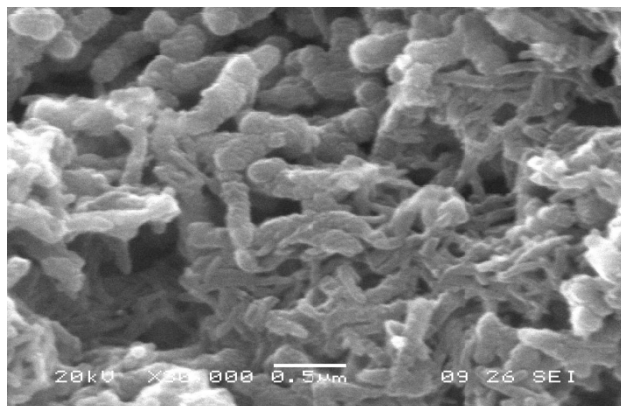


Fig. 4: SEM of PANI

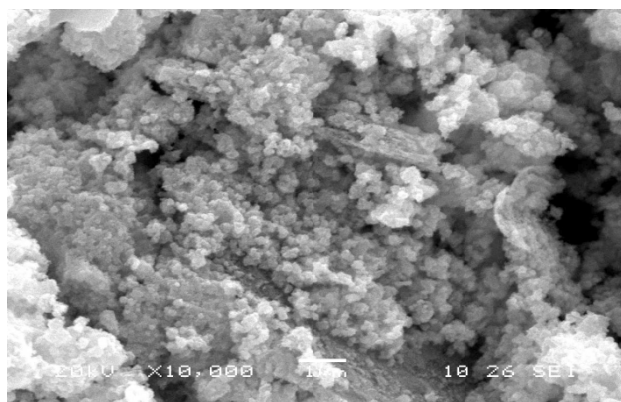


Fig. 5: SEM of SnO₂

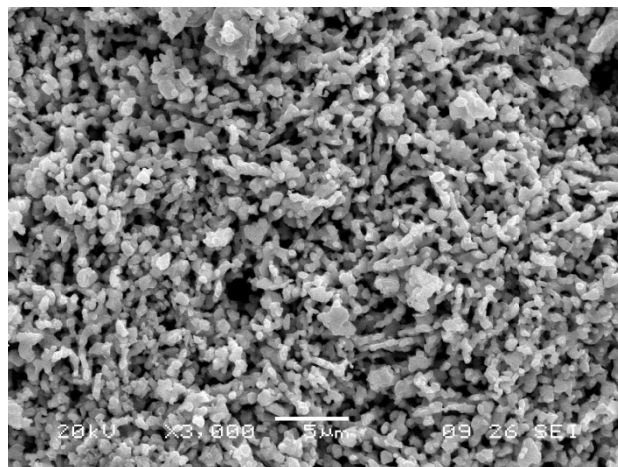


Fig. 6: SEM of Sn-PANI

In order to find the nature of bonding we studied FTIR spectrum of Sn-PANI composite. Fig. 7 shows the FTIR spectrum for Sn-PANI composite, having peaks at wave numbers 2983, 1557, 1493, 1259, 1039, and 758 cm⁻¹. The peak 2983 is attributed C-H stretch. The peaks at wave numbers 1557 and 1493 cm⁻¹ are corresponds to C≡N and C=C stretching mode for the quinoid and benzenoid rings. The strong peak at 1397 is of C-H rock. The peaks at wave number 1259 and 1039 cm⁻¹ are due to C-N stretching. The peak at the wave number 758cm⁻¹ is due to C-H out of plane bending vibrations. However, these peaks are slightly shifted from their original positions as compared with pure PANI. This shifting might be due to the presence of tin oxide in the PANI matrix. Furthermore, a peak observed 617 cm⁻¹ is due to the antisymmetric Sn-O-Sn mode in SnO₂ as in literature [10]. Thus it confirms the presence of tin oxide in the PANI matrix.

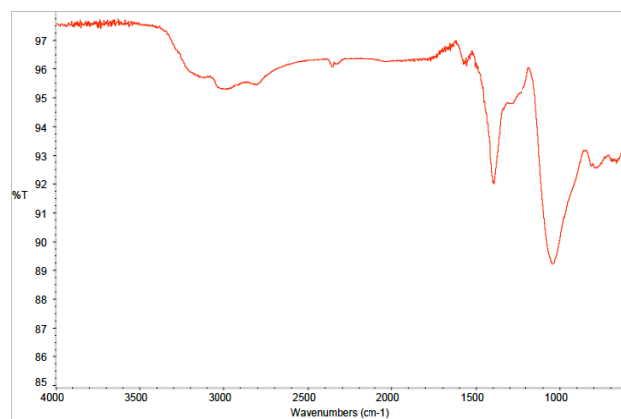


Fig. 7: FTIR of Sn-PANI

Humidity Sensing

The electrical response of the Sn-PANI composite was studied as a function of percent of exposed humidity. The composite in the form of pellet having diameter 12mm was placed in

glass chamber then water vapour was passed through the chamber.

The significant change in the electric resistance of the composite Sn-PANI pellet was observed when exposed to water vapour as shown in Fig. 8.

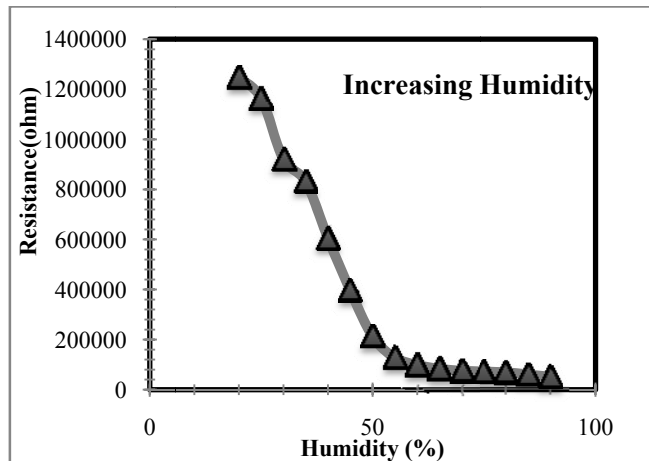


Fig. 8: Electrical Response of Sn-PANI for increasing Humidity

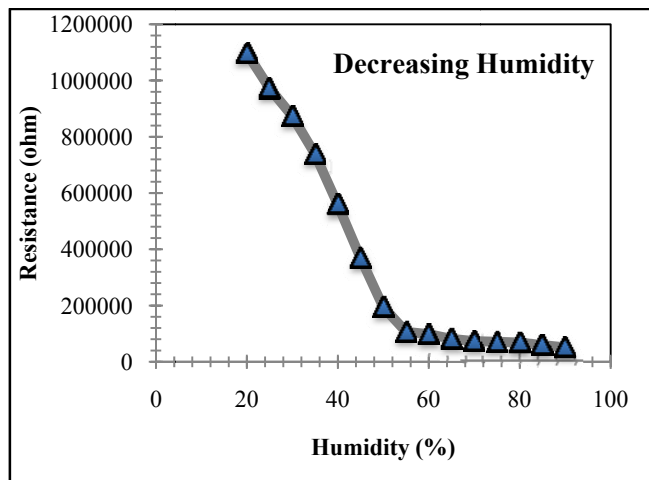


Fig. 9: Electrical Response of Sn-PANI for decreasing Humidity

The sensing mechanism is governed by the adsorption and desorption phenomenon of water vapour. It showed that the resistance of composite decreased when exposed to water vapour and subsequent increase in resistance was observed with removal of water vapour from chamber.

This is mainly due to the a few water vapour molecules are chemically adsorbed (chemisorption) on the surface of pellet, which is accompanied with a dissociative mechanism of vapour molecules to form hydroxyl groups (two hydroxyl ions per water molecule). As an interaction between the surface ions of composite and the adsorbed water, the hydroxyl group of each water molecule is adsorbed on metal cations that are present on the surfaces and possess high charge carrier density

and strong electrostatic fields, thus providing mobile protons. The protons migrate from site to site on the surface and react with the neighbour surface O_2^- groups (oxygen) to form a second hydroxyl (OH^-) group [11, 12]. After accomplishment of the first layer, consequent water vapour layers are physically adsorbed (physisorption) on the first formed hydroxyl layer. Thus, the multilayer formation carried out on the surface of the composite. Hence, singly bonded water vapour molecules become mobile and able to form continuous dipoles and electrolyte layers between the electrodes, resulting in an increased conductivity and thus decreasing resistance [13]. Exact reverse effect observed when water vapours were removed from chamber.

The initial resistance of composite was 1246843 ohm and when humidity reached its maximum value (90%) the resistance was recorded 51453 ohm. In case of decreased humidity when humidity was 20% the resistance was recorded 1097928 ohm. This decreased resistance for 20% humidity is might be due to the trapping of water molecules on the surface of composite material.

4. CONCLUSIONS

Nano sized Tin oxide, Polyaniline and Sn-PANI composite were successfully synthesized. They have been well characterized by FTIR, XRD and SEM. The characterization of Sn-PANI composite reveals that tin oxide was uniformly blended with Polyaniline. The composite Sn-PANI showed good response to humidity. Thus, Sn-PANI could be good material for humidity measurements.

5. ACKNOWLEDGEMENT

Author N. Deshpande would like to acknowledge support from University Grant Commission (UGC)- India for study leave and Dept. of Environmental Science, S.P. Pune University for making available research facilities.

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