Zinc tungstate doped polyaniline as room temperature humidity sensing composite

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Abstract: Zinc Tungstate (ZnWO₄) a bi-metal oxide is doped in low concentration to polyaniline (PANI) by 'In-situ' chemical polymerization method to form a composite. The FTIR characterization technique is used to confirm the formation of polyaniline salt phase and its composites. X-RD & SEM characterization techniques are used to verify the existence of ZnWO₄ in PANI matrix. The temperature dependent conductivity shows an exponential behaviour which is thermally activated; the conductivity of the composites has been enhanced by 10 Ohms when compared with pristine PANI. It is reported that electrical resistance decrease, when the composite matrix are exposed to the wide range of humidity from 20 to 90% RH. The decrease of resistance has been recognized as; the chemically adsorbed water vapour donates the electron to the sensing surface in this composite and also due to capillary condensation.

1. Introduction
Humidity sensors using novel composite materials are in increasing demand for controlled humidity environments, wide range of industries required these sensors namely food processing, agricultural storage, pharmaceuticals, electronic, agriculture plantation etc., [1]. The sensors of metal oxide, suffers with low range of sensing, reduced mechanical flexibility, slow degree of gabbing and cross sensitivity effects [2]. Among all conducting polymers, polyaniline (PANI) has emerged as an electric, dielectric, gas and humidity sensors studies of its composites with the various metal oxides and bi-metal oxides, because of its controlled synthesis, good stability, more yield and good response [3]. Humidity sensing with capillary condensation of PANI with MgCrO₄ [4], Fair humidity sensing response with good recovery time of PANI with Ho₂O₃ [5] Polypyrrol with metal disulphate - TaS₂ [6]. Humidity sensing at room temperature of PANI with WS₂ [7], Humidity sensing is due to increase in disorderliness of PANI with Sr₃(AsO₄)₂ [8], has been studied for sensing the humidity, but because of their high sensitivity, sensing range, response times and recovery time, shaped the chance to discover better PANI composites to enhance humidity sensing properties. 2D-materials are the emerging novel materials in this field with many applications, still the metal-oxide and bi-metal-oxides are given the attention and curiosity in expedition for various research and technological studies [9 - 11]. Semiconducting inorganic metal-oxides like SnO₂, ZnO₃, WO₃, CuO, and In₂O₃ shows good sensor response to recognize and distinguish, various gaseous ingredient of a combustion gas is demonstrated in recent years, [12]. Metal oxides have revealed that, all the sensor data collected could be related fairly well with the surface morphology of metal oxides. It was found that enhancement of sensitivity
of the gas sensor with ZnO particles coated on alumina substrate, enhancement of sensitivity of metal oxide CdO₂, LPG sensing property of Bi metal oxide [13 -17].

In current report, we aim to study PANI / ZnWO₄ composites for sensing application at room-temperature and try to understand the sensing mechanism in conducting polymer composite.

2. Experimental

All the chemicals used are analytical grade (AR). The synthesis of Polyaniline – Zinc Tungstate (ZnWO₄) composites has been completed by one step chemical polymerization technique. 0.1 M aniline was added to 1 M HCl to form aniline-hydrochloride. Fine grinded crystals of Zinc Tungstate (ZnWO₄) in weight percent (wt%) was added against the yield to the above solution and stirred vigorously by a magnetic stirring to keep the Zinc Tungstate crystals hanging in the solution during the polymerization to achieve uniform distribution. To polymerize the aniline an oxidant such as, ammonium persulphate [(NH₄)₂S₂O₈] with 0.1 M is added slowly in the form of drops with continuous stirring for 4 – 6 hours at 0 – 5⁰C freezing mixture. The thick green powder precipitate was formed; this green powder was first filtered and then washed with deionised water constantly until HCl is separate completely. Finally the precipitate is extracted by filtration is dried for 24 hours in a vacuum controlled oven to achieve a consistent weight, the same procedure is repeated for different wt of ZnWO₄ (0.1, 0.2, 0.3, 0.4 & 0.5 wt of yield PANI) in PANI [4 - 6]. The composite powder is sintered on an insulating substrate to form film like structure to expose large surface area of the composite to humidity. The two ends of the film is silvered with electrodes for the measurement of resistance.

The conformation of polymerization of aniline into polyaniline and polyaniline – zinc tungstate composite are carried out by the Infra-red spectra (FTIR), is recorded on the Perkin Elmer spectrophotometer (Model1600) in the medium Potassium Bromide (KBr). Retention of crystallinity of zinc tungstate is confirmed by X – ray diffraction of composites by Phillips - PW3710, X – ray diffractometer with source of radiation Cu Kα. Surface morphology essential for sensing properties is visualized by Phillips XL 30 ESEM Scanning Electron Micrographs polyaniline and polyaniline composites of zinc tungstate. These three characterizations are sufficient for the present work of testing the polyaniline composites for sensing mechanism.

The measurement of resistance is one of important study of the present work, which is carried out using temperature controlled oven and Keithely – 2000 multimeter (USA). The film resistance is recorded by closed glass chamber in controlled humidity from 20% to 90% of relative humidity. The sensor chamber consist of glass vessel of known volume, inside the chamber the sample holder with hygrometer probe to measure Relative humidity, a vaporizer to introduce water vapours by controlled power with dimmer-state, the planar resistance is recorded by voltage source and electrometer. Initially the humidity inside the chamber is lowered by calcium chloride in presence of sample, then slowly the water vapours were introduced into the chamber, corresponding resistance of the composite is measured from 20 to 90 % of RH. Figure (1) gives the block diagram of sensor chamber used to measure humidity sensing property of the composites.

![Figure 1: Humidity sensing chamber setup and accessories (block diagram)](image-url)
3. Results and discussions

3.1 Fourier Transform Infra-Red Spectra (FTIR):
An infra-red spectrum (FTIR) of PANI / ZnWO₄ composite is as shown in figure (2). All the samples are in powdered form are made into pellets using KBr medium with different weight percent of ZnWO₄ in PANI and recorded between 400–4000 cm⁻¹. Prominent peaks and their assignment are 3434 cm⁻¹ is NH bond-stretching, 1627 & 1569 cm⁻¹ are Benzenoid and Quinoid ring bond stretching, 1488 cm⁻¹ is N=H bond-stretching + C-C bond-stretching. Formation of polyaniline and polyaniline – zinc tungstate composites are confirmed from the stretching frequencies and stretching frequency assignment is well in agreement with the reported data [18, 19]. FTIR spectra shows strong bonds in the region 750 – 1700 cm⁻¹ which are the characteristic stretching frequencies of pure PANI and PANI / ZnWO₄ composites. Comparison of stretching frequencies of PANI and composites confirms that, frequencies of bond-stretching of the composites are increased little in the format ion composite, which suggests week bond interaction between ZnWO₄ and polyaniline chine. This kind of week bond interaction is attributed to Vander wall’s kind of interaction, which confirm the formation the composites in consistence with the earlier reports [20]. The peaks 696 cm⁻¹ & 612 cm⁻¹ are stretching frequencies of metal and oxygen bond in pure ZnWO₄ in composite strongly confirm the formation of PANI / ZnWO₄. The intensity of metal oxygen stretching peaks of FTIR spectra grows with increase in weight percent of ZnWO₄ in PANI [21].

![Figure 2: FTIR Spectra of PANI / ZnWO₄ composite](image)

3.2 X–RD (X-Ray Diffraction):
X-RD diffraction pattern outline of PANI / ZnWO₄ matrix is as shown in Figure (3). These results obtained from the experimental technique are discussed as below. All the reflection peaks from the crystal planes are indexed completely which shows highly crystalline nature, the crystal structure of monoclinic crystal is in agreement with the reported values (JCPDS file no.: 88-0251, space group: P2₁/c) for ZnWO₄ [17]. It is seen from figure that the monoclinic structural peak of ZnWO₄ indicates the crystalline nature is retained in the composite. The X-RD pattern of composite is compared with ZnWO₄, the important peaks corresponds to the angle 2θ = 18.91⁰, 21.55⁰, 32.57⁰, 35.74⁰ and 48.49⁰ are due to miller indices (100), (110), (020), (021) and (022) planes of ZnWO₄. By relating the X-RD outline graph of the composite and ZnWO₄, it is confirms that bi-metal oxide ZnWO₄ is retained its crystalline monoclinic-structure in the PANI matrix during chemical polymerization reaction.

3.3 SEM (Scanning Electron Micrograph):
Figure (4) shows SEM image of PANI / ZnWO₄ composite that confirms presence of ZnWO₄ and uniformly distributed throughout with variable grain size within the composite sample. A small variation in the dimensions of ZnWO₄ crystals was observed, thus dispersed in PANI has been
confirmed. The composites have crystalline granule along with spongy structure like pours, in addition the image shows capillary minute opening interlinked with each other because of inconstant grain size of ZnWO$_4$. This kind surface structure in any composites is likely to absorb vapours and make possible changes in the physical properties, also due to the increased surface area interacting with vapours and capillarity [22].

![Figure 3: X-RD (diffraction) peaks of PANI / ZnWO$_4$ composite](image)

![Figure 4: Image Scanning Electron Micrograph of PANI / ZnWO$_4$ composite](image)

**3.4 DC Conductivity:**

The dc-conductivity measurements of PANI / ZnWO$_4$ composites is as shown in figure (5a) and the difference in conductivity with temperature in comparison with pure PANI. We observe the thermally activated behavior in conducting polymer and its composites, the conductivity will increases along with increase in temperature. There will be increase in charge transfer effectiveness of between polymer interlinked chains and ZnWO$_4$ crystals with temperature [23, 24]. On heating there may be molecular re-arrangement, which may also facilitate the electron delocalization from polymer molecules to increase the conductivity [25]. It is also recommended that, due to the thermal uncurling affect, rearrangement of polymer chain takes place with increase in conjugation length and this is responsible for conductivity increase. Mott’s suggested VRH model (Variable Range Hopping) which is used to clarify temperature dependent conductivity of disordered materials [26]. The electronic charge transfer in disordered and also non-metallic materials and the behavior of conductivity with temperature is restricted by the thermally supported hopping of the electrons in between contained electronic states distributed randomly near the electron traps. The expression for variation of conductivity with temperature may be given by

$$\sigma (T) = \sigma_0 \exp \left[ - \frac{(T_0/T)^{1/4}}{T} \right]$$

Where: $\sigma (T)$ - Conductivity, $T$ - Temperature, $\sigma_0$ - Conductivity at attributed temperature $T_0$. The varying values of powers in conductivity expression (e.g. $T^{1/2}$, $T^{1/3}$, $T^{1/4}$) have been reported and to interpret this data, different models have been used [27].

The variation of dc-conductivity with wt% of ZnWO$_4$ in PANI, at three fixed temperatures viz, 50, 100 & 150 °C is as shown in figure (5b). Maximum conductivity was observed for 20 & 40 wt% of ZnWO$_4$ in composite at 150°C. The decreases in conductivity for 10, 30 & 50 wt% of ZnWO$_4$ in composites. The change in conductivity at two different temperature is as shown in table - 1. The conductivity increase with temperature may be recognized due to distribution of small grain size of ZnWO$_4$ may facilitate the hopping of charge carriers. This mechanism is due to decrease in the barrier potential with decrease in grain size between the localized wells, the increase in hopping of charge carrier between the restricted electron sites, therefore the conductivity increases.
Table 1. Change in conductivity at two different temperatures.

| Composite                  | Temperature dependent conductivity (In S cm⁻¹) | Range of conductivity change (In S cm⁻¹) |
|----------------------------|-----------------------------------------------|----------------------------------------|
|                            | 40 °C                                         | 200 °C                                 |
| PANI                       | 0.0033                                       | 0.234                                  | 0.2307                                  |
| PANI / 10 wt% ZnWO₄        | **0.0135**                                    | **2.619**                              | **2.6055**                              |
| PANI / 20 wt% ZnWO₄        | 0.0126                                       | 1.684                                  | 1.6714                                  |
| PANI / 30 wt% ZnWO₄        | **0.0122**                                    | **6.045**                              | **6.0328**                              |
| PANI / 40 wt% ZnWO₄        | **0.0111**                                    | **3.109**                              | **3.0979**                              |
| PANI / 50 wt% ZnWO₄        | 0.0107                                       | 1.871                                  | 1.8603                                  |

3.5 Humidity sensor:
Figure 6 (a) shows the variations of resistance verses of humidity for PANI / ZnWO₄ composites in the form of films for the five different wt of ZnWO₄ (0.1, 0.2, 0.3, 0.4 & 0.5 wt) in PANI. The decrease in resistance and hence increase in conductivity is observed with increase in relative humidity inside closed chamber, can be recognized as mobility of ZnWO₄ ion which are loosely bound to the conducting polymer main chain by a weak Vander walls forces of attraction which was confirmed in FTIR spectra. This mobility of ions facilitates the charge hopping between the localized sites hence decrease in resistance and increase in conductivity. The increase in conductivity is again depending on capillarity of the pours, the water condensation in pours causing ionic movement in the porous structure of the sensing materials. As porosity of the material increases, then the capillary condensation also increase which leads to the decrease in resistance [28].

Figure 5: (a) D.C conductivity of PANI / ZnWO₄ composites with increase in temperature. (b) D.C conductivity variation verses variation in wt% of ZnWO₄ in PANI

Figure 6: (a) Resistance variation with relative humidity (RH) of PANI / ZnWO₄ composites. (b) Variation of resistance with wt% of ZnWO₄ in PANI at three constant RH (20, 50 and 90 % RH)
The performance characteristics of humidity sensor, are correlate to its microstructure. The correlation was found between the resistance change and amount of water vapors filled up in pores of composite materials, which will depend on specific surface area available for sensing activity. For low humidity RH conditions the specific surface area is responsible, while under high RH conditions mesopore volume dominates [29].

The movement of the ZnWO₄ ion are controlled at low humidity, under these dry surroundings, polymer long chains will twist up into compressed coil form. At high humidity, there is a wet condition in which the polymer chains will absorbs water molecules, then the compact coil is untwisting into straight chains (opposite to twist) and are linked with respect to each other. The geometrical change in the polymer is encouraging and improved movement of the ZnWO₄ ion or the transfer of charges along the polymer main chains and hence the decrease in resistance [4]. Figure (6b) the variation of resistance with weight percent of ZnWO₄ in PANI at three constant relative humidity (20 % RH, 50 % RH and 90 % RH), wherein it is observed that, resistance increases as weight of ZnWO₄ in PANI increases. The decreases in conductivity can be attributed to decrease in porosity with increase in ZnWO₄ within the composite, the range of resistance change with relative humidity is as shown in Table - 2 [30].

### Table 2. Change in resistance at two different relative humidity.

| Composite          | Resistance at relative humidity (In Ohms) | Rang of resistance change (In Ohms) |
|--------------------|------------------------------------------|------------------------------------|
|                    | 20% RH | 90% RH |                                    |
| PANI               | 158.90 | 54.30  | 104.6                             |
| PANI / 10 wt% ZnWO₄| 21.68  | 18.74  | 2.94                              |
| PANI / 20 wt% ZnWO₄| 23.19  | 19.06  | 4.13                              |
| PANI / 30 wt% ZnWO₄| 23.99  | 19.71  | 4.28                              |
| PANI / 40 wt% ZnWO₄| 24.74  | 20.66  | 4.08                              |
| PANI / 50 wt% ZnWO₄| 25.35  | 21.21  | 4.14                              |

### 4. Conclusions

The composite of Polyaniline / Zinc Tungstate (PANI / ZnWO₄) composite matrix is produce by novel chemical polymerization method known as ‘in situ’ polymerization. Formation of assorted phase of the polymer matrix composite along with conducting polyaniline emeraldine salt was established from the different characterization techniques. The variation of conductivity with temperature measurement shows an exponential behaviour with thermal activation. Enhancement of 10 S cm⁻¹ in the conductivity of PANI/ZnWO₄ composites was reported in comparison with conductivity of pure PANI. The composites 10, 30, 40 wt% of ZnWO₄ in PANI has shown wide range of change in conductivity. The resistance decreases with increase in relative humidity, which will be recognized as the movement of ZnWO₄ ions that are attached by weak bond to the polymer main chain and these loosely bound ions is due to weak Vander-walls bond of attraction. This may also due to capillary condensation of water vapours in the pores of the sensing material. The composite of 30 wt% of ZnWO₄ in PANI has shown wide range of change in resistance, will the promising composite for sensor device.
References

[1] Farahani H, Wagiran R, Hamidon M N. Sensors. 2014; 14: 7881.
[2] Qin Y, Howlader M M R, Deen M J, Haddara Y M, Selvaganapathy P R. Sensors & Actuators B: Chemical. 2014; 202: 758.
[3] Ciric Marjanovic G. Syntheti. Metals. 2013; 177: 1.
[4] Machappa T, Ambika Prasad M V N. Bulliton of Materials Science. 2012; 35: 75.
[5] S. Msunjunstha, Machappa T, Y T Ravikiran, B. Chethan, M. Revanasiddappa, Applied Physics A. 2019; 125:361.
[6] Sunil kumar A, S. Msunjunstha, Y T Ravikiran, B. Chethan, Machappa T, Sensors and Actuators A: Physical. 2019; 298: 111593.
[7] S. Msunjunstha, Machappa T, Y T Ravikiran, B. Chethan, Sunil kumar A, Appli. Physica B: Chemical. 2019; 561:170.
[8] Prabakaran Shankar, John Bosco Balaguru Rayappan, Science letters journal. 2015; 4: 126.
[9] Machappa T, Badrunnisa. S, Journal of Physics: Conferrence Series. 2020; 1706: 012015.
[10] Machappa T, Ambika Prasad M V N, Ferroelectrics, 2009; 392: 71.
[11] Machappa T, Ambika Prasad M V N. Physica B: Condensed matter. 2009; 404: 4168.
[12] Weon-Pil Tai, Jun-Gyu Kim, Jae-Hee Oh, Young-Sung Kim, Sensors & Actuators B: chemical. 2005; 105: 199.
[13] Koenig J L, 1999 (2nd ed) Spectroscopy of polymers (Amsterdam: Elsevier).
[14] Pavia D L, Lampman G M and Kriz G S, 2001 (3rd edition) Introduction to spectroscopy (Fort Worth: Harcourt College Publishers).
[15] Machappa T, Ambika Prasad M V N, Electronic process in non-crystalline materials.1979; (edu) (Clarendon press, Oxford).
[16] Salunkhe. R. R, Shinde. V. R, Lokhande. C. D. Sensors and Actuators B. 2008; 133: 296.
[17] Yamazoe N, Shimizu Y. Sensors & Actuators B, 1986; 10: 379.
[18] Kan-Sen Chou, Tzy-Kuang Lee, Feng-jiun Liu. Sensors & Actuators B. 1999; 56: 106.
[19] Seema Agarwal, G. L. Sharma, Sensor and Actuators B: Chemical, 2002; 85: 205.