

Water Vapour Sensing Mechanism of PANI Doped With ZnO Nanocomposites

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Abstract:

In this PANI is prepared by situ polymerization method and Zinc Oxide (ZnO) nanoparticle prepared by wet chemical method at room temperature. ZnO nanoparticles were combined with PANI via polymerization in acidic aqueous solution to obtain a new type of inorganic – organic composites nanostructured. The samples are prepared in the form of thick film. It is observed that PANI doped ZnO nanocomposites sensor shows a high response and sensitivity with good repeatability as compared to that of pure PANI and ZnO nanoparticle. The effect of hysteresis of the sensors, the effect of pure and composite oxide on sensitivity of the sensors were studied. The crystallinity and the crystallite size were examined by X-Ray Diffraction technique.

Keywords: Polyaniline, ZnO Nanocomposites, Humidity Sensors.

Introduction

The possibility of reliable, reasonably accurate, relatively inexpensive and commercially viable humidity sensors is under investigation using organic-inorganic composites. Humidity sensors are useful for the detection of relative humidity in various environments [1-3]. Humidity, the concentration of water molecules in air, affects various materials used in daily life and industrial processing of drugs, beverages, food, electronic goods etc. High and low humidity affects human beings adversely. Excessive high humidity causes corrosion in metallic components and failure of electronic as well as optical devices [4, 5]. Therefore, humidity is an important parameter to be controlled. Recently, there have been increased demands for humidity sensing elements for use in automatic humidity control systems. Polymer, polymer composites and modified polymers with hydrophilic properties [6] show excellent humidity sensing properties. Conductivity of polyaniline can be varied over a broad range and hence, it can find wide use in making sensors [7-12]. Capacitive humidity sensors utilize conductive plates formed on a dielectric film. This forms a capacitor that is sensitive to the amount of water vapours in the air. The active portion of the sensor changes its dielectric constant as it absorbs atmospheric humidity, which varies the sensor's capacitance in proportion to variation in relative humidity. Another mode of humidity sensors is resistive sensors which uses a moisture-sensitive material between two metal plates or on an inter digitated electrode substrate [13, 14]. The device's resistance varies with variations in relative humidity. The main advantage of resistive technology

for humidity sensors is that it suits to varying, difficult and condensing environments. It can be synthesized easily and has long stability. In the present work ion conducting metal doped polyaniline pellets have been used as sensing material which is based on variation of the electrical conductivity with variation in humidity.

Experimental : Synthesis of material :

A) Synthesis of Polyaniline (PANI):

In this Polyaniline (PANI) is synthesized by chemical polymerization method in which 0.2 M aniline hydrochloride is used as monomer unit. The synthesis is done by oxidative polymerization with 0.25 M ammonia peroxy sulphate in aqueous medium, both solution kept 1 hour at room temperature then mixed in beaker, briefly stirred. And left at rest to polymerize, next day, the green colour Pani precipitate was collected on a filter and washed with 0.2 M HCL solution and similarly with acetone. The Polyaniline hydrochloride powder was dried in air and then in vacuum at 60°C. Polyaniline prepared under these reaction and processing condition are further referred to as standard sample [15].

B) Synthesis of Zinc oxide:

For the preparation of ZnO nanoparticle, the aqueous solution of 2M of zinc nitrate hexa hydrate in 100 ml of distilled water. To this aqueous zinc nitrate solution 0.2 M sodium hydroxide is added and the reaction mixture was heated at 80°C along with stirring and the process is carried out for four 1 hour after which the white precipitate was obtained. Then the precipitate is centrifuged and washed 2 to 3 times with de-ionised water. The obtained material were calcinated at 600°C and finally the pure ZnO nanoparticles were obtained.

Characterization :

XRD Pattern of ZnO

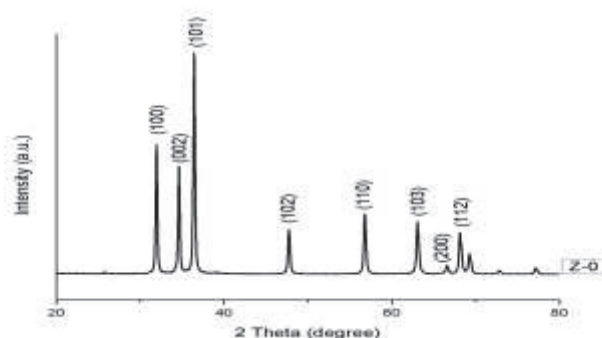


Figure 1: XRD of Pure ZnO

The Figure 1 shows the X-Ray Diffraction pattern of pristine zinc oxide (ZnO) nanostructure synthesized by liquid phase method which is calcinated at 600°C. The crystalline nature with 2 θ peak lying at (100), (002), (101), (102), (110) and (103) planes. All the peaks match well the standard hexagonal wurtzite structure of zinc oxide (ZnO) with lattice constants, $a = b = 0.3249$ nm and $c = 0.5206$ nm [JCPDS card no. 36-1451]. All the peaks are perfectly match with pure ZnO structure, which indicates the high purity of the obtained ZnO nanoparticle. The average crystalline size was found to be 37.32 nm calculated by Debye-Scherrer formula [16].

Result and Discussions:

Hysteresis Plot:

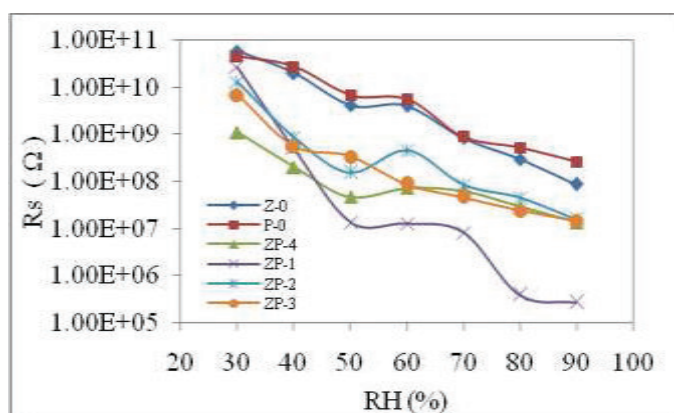


Figure 2: Variation of Resistance with Relative Humidity

Hysteresis plot shows the variation between resistances of sample with respect to the relative humidity in increasing and decreasing order from 30 to 90 % RH as shown in the fig. 2. A very small hysteresis present during forward and reverse cycle of relative humidity, where as a very significant average change observed in the value of resistance of sample, in the sample ZP-1 (10ZnO – 90PANI) the change in value of resistance is from $10^{11} \Omega$ to $10^5 \Omega$, these is a remarkable change in the value of resistance.

Sensitivity

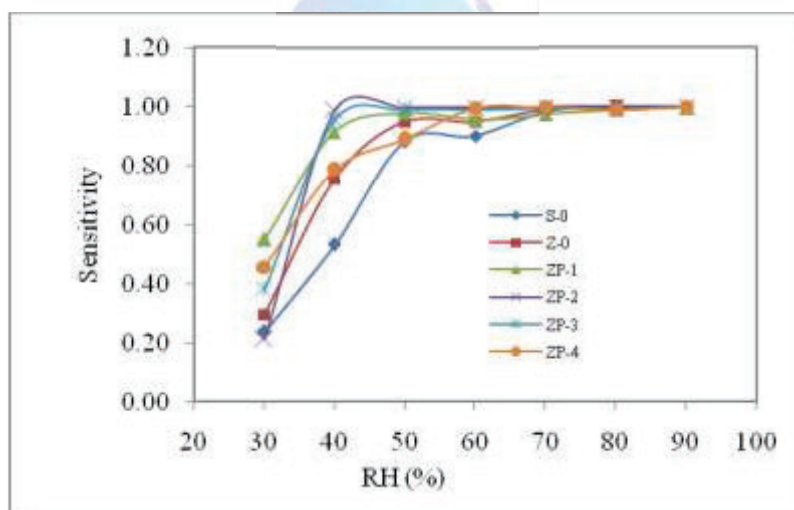


Figure 3: Variation of Sensitivity with Relative humidity

In the above samples the sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant as shown in fig. 3. For higher RH the sensitivity is found to be higher in case of all samples of thick films. The sensitivity of ZP-1 (10ZnO-90PANI) is more than ZP-2, ZP-3, and ZP-4 samples and also from the pristine samples P-0 and Z-0. The (ZnO-PANI) composite sensors exhibits significantly higher sensitivity than sensor constructed specially from ZnO nanoparticles and PANI itself due to the formation of heterogeneous interface between them and more adsorption site was created to absorbed more water vapours.

Conclusion

Nanostructured ZnO was successfully prepared via chemical precipitation method and PANI with IUPAC polymerization technique. Minimum crystallite size was found to be for ZnO is 37.32 nm. The Hysteresis plot shows very significant average change in the value of the resistance from $10^{11} \Omega$ to $10^5 \Omega$ during forward and reversed cycles of sample ZP-1(10ZnO-90PANI). The sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant. Amongst all the prepared samples ZP-1 is more sensitivity than other prepared composite samples.

Reference:

1. Y. Zhang, K. Yu, D. Jiang, Z. Zhu, H. Geng and L. Luo, Zinc oxide nanorod and nanowire for humidity sensor, *Applied Surface Science*, Vol. 242, No. 1-2, 2005, pp. 212-217.
2. N. Yamazoe and Y. Shimizu, *Humidity Sensors: Principles and Applications*, *Sensors and Actuators*, Vol. 10, No. 3-4, 1986, pp. 379-398.
3. Y. Sakai, Y. Sadaoka and M. Matsuguchi, *Humidity Sensors Based on Polymer Thin Films*, *Sensors and Actuators B*, Vol. 35, No. 1-3, 1996, pp. 85-90.
4. R. Lindström, Lars-Gunnar Johansson, G. E. Thompson, P. Skeldon and Jan-Erik Svensson,
5. *Corrosion of Magnesium in Humid Air*, *Corrosion Science*, 46, 5, 2004, p. 1141-1158.
6. H. Ishida and R. Johnson, *The inhibition of copper corrosion by azole compounds in humid environments*, *Corrosion Science*, 26, 9, 1986, pp. 657-667.
7. S. Virji, R. B. Kaner, and B. H. Weiller, *Hydrogen sensors based on conductivity changes in polyaniline nanofibers*, *J. Phys. Chem. B*, 110, 44, 2006, pp. 22266-22270.
8. C. P. L. Rubinger, C. R. Martins, M.-A. De Paoli and R. M. Rubinger, *Sulfonated polystyrene polymer humidity sensor: Synthesis and characterization*, *Sensors and Actuators B: Chemical*, 123, 1, 2007, pp. 42-49.
9. L. S. Hwang, J. M. Ko, H. W. Rhee and C. Y. Kim, *A polymer humidity sensor*, *Synthetic Metals*, 57, 1, 1993, pp. 3671-3676.
10. S. Hatamie, V. Dhas, B. B. Kale, I. S. Mulla and S. N. Kale, *Polymer-embedded stannic oxide nanoparticles as humidity sensors*, *Materials Science and Engineering: C*, 29, 3, 2009, pp. 847-850.
11. Y. Sakai, *Humidity sensors using chemically modified polymeric materials*, *Sensors and Actuators B: Chemical*, 13, 1-3, 1993, pp. 82-85.
12. G. Delapierre, H. Grange, B. Chambazand, and L. Destannes, *Polymer-based capacitive humidity sensor: characteristics and experimental results*, *Sensors and Actuators*, 4, 1983, pp. 97-104.
13. S. C. Raghavendra, S. Khasim, M. Revanasiddappa, M. V. N. A. Prasad and A. B. Kulkarni, *Synthesis, characterization and low frequency ac conduction of polyaniline/fly ash composites*, *Bull. Mater. Sci.* 26, 7, 2003, pp. 733-739.
14. N. Parvatikar, S. Jain, S. Khasim, M. Revanasiddappa, S. V. Bhoraskar, M. V. N. A. Prasad, *Electrical and humidity sensing properties of polyaniline/WO₃ composites*, *Sensors and Actuators B*, 114, 2006, pp. 599-603.
15. R. P. Tandon, M. R. Tripathi, A. K. Arora, S. Hotchandani, *Gas and humidity response of iron oxide - Polypyrrole nanocomposites*, *Sensors and Actuators B*, 114, 2006, pp. 768-773.
16. A. Mostafaei, *A Zolriasatein, Synthesis and characterization of conducting polyaniline nanocomposites containing ZnO nanorods*, *Progress in Natural Science: Materials International*, Volume 22, Issue 4, August 2012, Pages 273-280.
17. Cullity B D, *Elements of X-ray diffraction* (Addison-Wesley). 102, (1970).