

Fabrication of electro-chemical humidity sensor based on zinc oxide/polyaniline nanocomposites

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ABSTRACT

The present work reports the synthesis of nano size zinc oxide encapsulated polyaniline by wet-chemical method at ambient condition. The prepared composite was characterized by XRD, SEM, TGA and UV-Vis spectroscopy. The results revealed the formation of the crystalline homogenous ZnO centered composite with electrical conductance in the range of 10^{-2} scm^{-1} and thermal stability up to 280 °C. Further, electrical resistance of a ZnO/PANi film of ~200 nm thickness was monitored against humidity to use as humidity sensitive element. The observed sensing parameters were response time, 32 sec; and recovery time, 45 sec; sensor has exhibited better sensing characteristics than pure PANi and other reported humidity sensors. Copyright © 2012 VBRI Press.

Keywords: ZnO/PANi nanocomposite; electrical properties; conduction mechanism; humidity sensing.



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Introduction

Polyaniline (PANi) has been extensively studied as a conducting polymer for different applications including chemical and biosensors. PANi shows a wide range of electrical properties from insulator-semiconductor – conductor due to different ratios of benzenoid to quinoid (oxidized to reduced) structure due to employed synthetic routes [1-2]. In general, conducting polymers have poorer electrochemical and thermal stability that limits their use in various applications. Several attempts have been made to solve these problems by compositing it with bio-polymer

Table 1. Organic and inorganic materials used for humidity sensing.

Materials	Methods	Sensitivity range (%)	Reference
ZnO–In ₂ O ₃	Electrical types	11-95	17
ZnSnO	Electrical type	11-97	18
Chitosan	Optical types	20-95	19
Polyaniline nanofiber	Impedance	20-90	20
ZnO	Electrical resistance	45- 88	21
Polypyrrole	Impedance	11- 95	22

and metal-oxide nanostructures but still it needs intensive study [3-4]. Recently such nanocomposites have been become as a focus area of research due to their important role in electronic and optical device because of better properties and faster switching speeds than their corresponding constituent materials [5-7].

Metal oxide/polyaniline composite has been used for preparation of flexible nano generator. Metal oxides–conjugate polymer also forms electron donor- acceptor pairs between n type metal oxide and a p-type conjugated polymer and explore the possibility for the formation of p-n junction [8]. Yoneyama et al. prepared TiO₂/PANi composite film by electrochemical deposition [9]. Somani and coworkers also prepared TiO₂/PANi composite with piezo-resistive properties [10]. Further, ZnO is a wide band gap (3.6 eV) semiconductor and PANi narrow band gap (1.5 eV) p-type semiconductor.

The interfacial region of these materials promises a unique possibility for different applications such as photovoltaic devices and other electronic devices. ZnO/PANI composite has been prepared by some scientists [11-13], but not used for humidity sensing purpose as per our observation. However humidity sensor is an important sensor, widely used in life comforts instruments, packaging industry and environmental monitoring [14-16]. Many organic and inorganic materials used for humidity sensing purposes but they bear some limitations and all sensing parameters were not addressed (Table 1).

The above development encouraged us to prepare organic-inorganic material for humidity sensing applications. In this communication, we report the synthesis and characterization of ZnO/PANI composite by simple chemical route. The electrical resistance of a ZnO/PANI composite film with ~200 nm thickness was monitored measured against relative humidity of a closed chamber maintained by saturated salt solution method for humidity sensing purpose.

Experimental

Materials and method

Aniline (99.5%), zinc acetate (99.98%) and penta hydrated cupric sulphate (99.5%) were procured from E. Merck, Germany and used without any further purification. All other chemicals were of analytical grade and solutions were used with double distilled water.

The prepared ZnO/PANI composite film has been characterized using XRD, SEM and TGA and UV-vis

techniques. The crystalline structure and morphology of the ZnO/PANI composite film was studied by Rigaku Rotaflex (RAD/Max-200B) XRD spectrometer, Rigaku Corporation Japan at 1° min⁻¹ scanning speed and S-3700N Hitachi scanning electron microscope, operated at 15 kV. The films were sputter-coated with a thin layer of gold (~20 nm) prior to the morphological examination. The thermal analysis was carried out with a Rigaku Thermoflex PTC-10A thermal analyzer at 10 °C min⁻¹ heating rate. UV-vis study was carried out on a UV2501PC, Shimadzu spectrophotometer using dimethyl formamide as solvent. However the electrical resistance was measured by RISH-MAX digital laboratory multimeter for humidity sensing purposes using the experimental set shown in Fig. 1 [23].

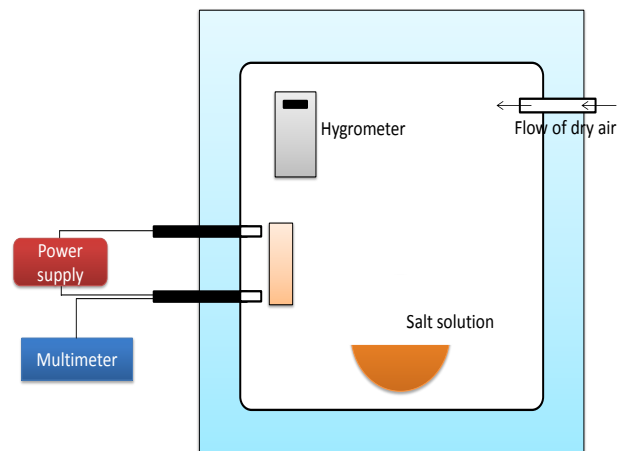


Fig. 1. Schematic set up used for humidity sensing.

Preparation of ZnO/PANI nanocomposite

Firstly, ZnO was prepared from our earlier reported method [15]. Typically, 100 mg prepared ZnO was mixed in aniline (2 ml)/ methanol (5 ml) solution mixture. The resulting mixture was stirred for 1 h at room temperature on a magnetic stirrer and finally a transparent solution was obtained. In this solution, 5 ml of 0.5M aqueous CuSO₄ solution was added drop by drop with constant stirring at 25 °C for 3 h. A dark blackish green color precipitate was collected at the end of reaction. The precipitate was allowed to settle, filtered and dried under vacuum at 25 °C for 6 h.

Humidity sensing

The ZnO/ PANI thin film was prepared by spin-coating method. ZnO/PANi nanocomposite (100 mg) was dissolved in 5 mL DMF. The solution was used as a precursor solution to cast the film at 500 rpm on a glass slide. For the humidity sensing, the ZnO/ PANi coated film with (1 × 1) cm was fixed inside the wall of an air-tight evacuated glass chamber (5 × 6 × 8) cm via holder at a fixed %RH. The relative resistance change of composite film before and after exposure at various %RH points has been monitored using laboratory digital multimeter. The saturated solution of KOH was used to control %RH of the glass chamber and also monitored by a reference hygrometer. The relative humidity inside the sensing chamber was variably controlled up to 80%. A thermometer with least count of 0.1 °C was also fixed inside the chamber for monitoring the temperature chamber. All experiments were conducted at 25 °C, with the same sensor used for each set of measurements. Prior to each measurement the film was heated under vacuum at 60-75 °C for 5 h to completely remove the adsorbed moisture over the ZnO/PANi film surface.

Results and discussion*Synthesis and characterization of ZnO/PANi nanocomposite*

The chemical treatment ZnO with aniline makes a layer of aniline like micelles due to transfer of lone pair of electron from aniline to ZnO. Since ZnO is a weak lewis acid and aniline is weak lewis base and the aniline coated ZnO structure serves as a nucleating cum polymerizing centre due to partial oxidation of aniline. Further the addition of polymerizing agent oxidizes the aniline and polymerization process starts. A schematic diagram for synthetic route of composite is shown **Fig. 2**.

XRD spectra of prepared nano-composite are shown in **Fig. 3a**. The presence of peaks reflects the formation of crystalline composite. The peaks at 33.5° and 25° are due to the presence of ZnO and PANi respectively. SEM photograph of composite is shown in **Fig. 3b**. The micrographs confirm the formation of binary type hybrid materials. TGA curve of composite is shown in **Fig. 3c**. It indicates the decomposition between 300-400 °C with a single step weight loss. Generally polyaniline decomposes at 200 °C but in the present case we feel that the presence of ZnO provides better thermal stability to the PANi.

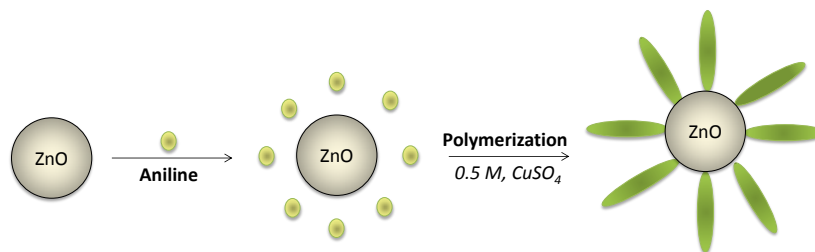


Fig. 2. Schematic representation of ZnO/PANi nanocomposite formation.

Conduction mechanism

The electrical conductivity of ZnO/PANi composite is $1.5 \times 10^{-2} \text{ Scm}^{-1}$. This value is lies between PANi and ZnO. It encouraged us to understand the electrical conductance behavior of composite material by using UV-vis spectra. The peaks of PANi and ZnO/PANi composite are listed in **Table 2**.

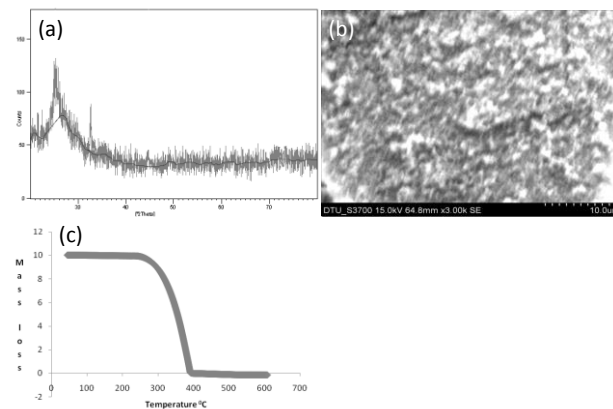


Fig. 3. (a) XRD pattern (b) SEM micrograph and (c) TGA of ZnO/PANi nanocomposite.

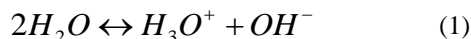
Table 2. Major peaks of PANi and ZnO/PANi composite in UV-vis spectrum.

Materials	Peak positions (nm)	
	I st	II nd
PANi	320	430
ZnO/PANi	290	370

The shift in peaks in composite shifted than pure PANi is because of composite formation while the peaks at 680 is due to interaction between metal and aniline and supports the proposed structure in **Fig. 4a**. Thus it confirms the interaction between ZnO and PANi matrix, since ZnO is nonmetallic (lewis acid) in nature and aniline is weak base. Thus aniline donates a lone pair of electron towards ZnO and forms complex type structure due nonmetallic (lewis acid) nature of ZnO and basic nature of aniline. It forms ionized polymeric chain and produces efficient switching effect in materials.

Humidity sensing

The earlier reports deal with fabrication of humidity sensing by single semiconducting materials with high resistance. The resistance or impedance changes of humidity sensing materials change with dissociative adsorption of H₂O molecule (eq. 1) but due to lack of directional flow the efficiency was always compromised.



The present hybrid matrix of ZnO/PANi serves as sensing platform like p-n junction. The adsorption of H₂O generates ions and subsequent causes efficient directional charge conduction. The probable mechanism is presented in Fig. 4b. Further, to evaluate the suitability of composite towards sensing behavior, the extent of H₂O adsorption was measured by monitoring mass change (isothermal TG) after exposing PANi, ZnO and ZnO-PANi in 80% RH for 30 min.

The adsorption capacity in ZnO/PANi possess 3 times better adsorption capacity (hydrophilicity) than PANi. ZnO increases the hydrophilicity may be due to increases in the porosity in composite as realized by SEM photographs. Further, the trend in change of resistance of composite with percentage relative humidity is shown in Fig. 5a.

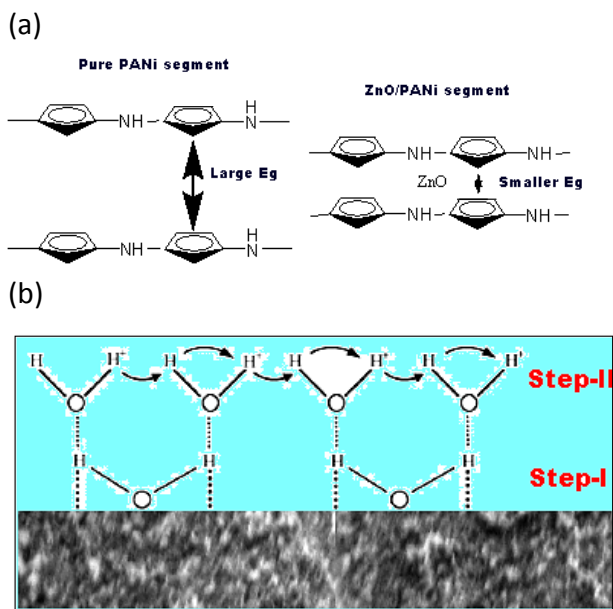


Fig. 4. Schematic illustrations of (a) p-n junction type heterogeneity and (b) electrochemical humidity sensing mechanism in ZnO/PANi nanocomposite.

It indicates the linear decrease in resistance with increasing humidity in 5-80% RH and thus proves the suitability of composite for humidity sensing purposes. The sensitivity was calculated with slope of curve and is found ~40. Further change in resistance at 80% RH with time is measure and curve is shown in Fig. 5b. It reveals the response time (80% change) of material is 32 sec and recovery time after blowing dry air is in 45 sec.

Conclusion

Crystalline and binary structure type ZnO/PANi homogeneous nanocomposite was prepared. The composite was electrically responsive to humidity under a closed chamber in the range of 5-80% RH. The synthesized organic/inorganic composite of (ZnO/PANi) can be used to prepare electrochemical humidity sensors. The sensors based on composite shows better sensitivity, linearity, and quicker response time.

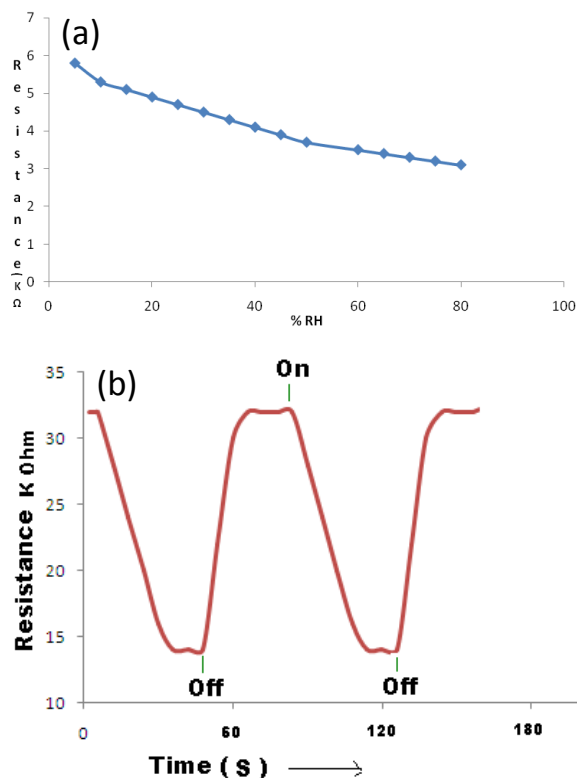


Fig. 5. Change in resistance of ZnO/PANi nanocomposite with (a) humidity and time at 80% relative humidity.

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