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Research Article

STRUCTURAL AND GAS SENSING PROPERTIES OF ZnO: NiO NANOCOMPOSITE TOWARDS HYDROGEN GAS

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ABSTRACT

In the present study we describe the design, fabrication and gas sensing performance of p-NiO/n-ZnO nanocomposite synthesized by sol-gel followed by impregnation method. The formation of ZnO: NiO nanocomposite was confirmed by Energy Dispersive X-Ray (EDX) and X-Ray Diffraction (XRD) analysis. The microstructure of the sample was visualized by Transmission Electron Microscope (TEM) which revealed the formation of hexagonal structure of size ~10nm. Furthermore, we investigated the gas sensing performance of ZnO: NiO nanocomposite which showed excellent sensitivity and selectivity towards hydrogen in comparison to other interfering gases. The significantly improved performance was thoroughly explained in terms of adsorption – oxidation - desorption pathway. The achieved features make the sample a prospective candidate for the fabrication of H_2 gas detection sensor.

INTRODUCTION

Nanotechnology is a new area of science which involves working with materials and devices at the nanoscale region. Nanostructured materials have triggered tremendous motivation to explore the possibilities in various shapes and size for sensing applications. ZnO an n-type II–VI semiconductor material with wide and direct band gap energy of 3.37 eV and high exciton binding energy of 60 m eV. Semiconductor oxides have attracted a lot of attention throughout the world, due to their wide applications in luminescence, photosensitization, magnetism, lithium batteries and gas sensors especially in the field of gas sensors (1-3). Nanostructure-based sensors have become the focus of intensive research because of the advantages of higher sensitivity and rapid response associated with individual nanostructures due to the high surface-to-volume ratio compared to thin film gas sensors (4, 5). Metal oxide nanomaterials are the most important class of materials due to their excellent properties and wide applications in various areas of science and technology (6-9).

Nanocomposites based on the combination of p-type and n-type semiconducting (SC) oxides have come under intense scrutiny for the possibility of joining the intrinsic properties of individual components with the multifunctional behavior exhibited by low-dimensional materials (10-13). In this regard, p-n oxide-based nanocomposites have been investigated for various technological applications, such as magnetism, optoelectronics, photocatalysis, and gas sensing (14-16). As regards gas sensing applications, the combination of p- and n-type nanomaterials can provide higher sensitivities and faster responses due to the formation of a more extended depletion layer (17, 18). The synergistic combination of these two SCs paves the way to the development of gas sensors characterized by improved sensitivity/selectivity and mild working temperatures (19).

H_2 is a clean, efficient, and renewable energy source that will be extensively used in the future for power generation in automotive and energy-storage industries (20-22). However, safety issues involving H_2 gas such as a wide explosive concentration range (4−75%), low ignition energy (0.02 mJ),

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and high flame propagation velocity are major challenges in the development of H_2-based applications (23-25). However, there is a serious safety concern. Excellent monitoring and leak detector systems are required because hydrogen is invisible, odorless, and highly flammable. Considerable research has been focused on the development of hydrogen (H_2) based energy storage to overcome environmental problems associated with fossil energy sources, such as air pollution, global warming, and exhaustion of the Earth's resources (26), leak detection sensors etc. (27).

Among various gas sensor materials, metal oxide semiconductor (MOS) gas sensors also known as chemiresistor, are promising sensing materials and extensively used for monitoring hazardous and toxic gases due to their advantages such as high sensitivity, fast response and recovery, low detection limits simple sensing mechanism, lower maintenance costs, better stability, and simplicity in fabrication (28, 29). The higher sensitivity with regard to the chemical sensors is attributed to the behavior of grain boundaries formed at the interfaces of the nano grains, which exhibits a large change in resistance during adsorption and desorption of gas molecules showing significant influence on gas sensing performance (30-33). Effective H_2 sensor for early detection of leaks, quantification at low concentration is necessary and LEL (lower explosive limit) of 4% by volume coupled with its colourless and odorless nature poses a challenge for safety requirements and precautions (34).

In the case of oxide gas-sensing materials, it is generally a surface controlled process that is responsible for the sensitivity. The detection and monitoring of toxic and noxious gas emissions is extremely important for human safety and environmental protection (35-37). In order to make the sensors more efficient, there is a need to develop materials to suite the generic technologies (38). In nanomaterials, because the surface-to-bulk ratio is much greater than for coarse materials, surface properties become paramount, which makes these materials particularly appealing in applications in which such properties, are exploited as in gas sensors (39).

Recently, an observation on graphene/PANI nanocomposite based sensor where the sensitivity of S=16.5% towards 10,000ppm H_2 gas is reported by Laith Al-Mashat *et al* (40). Reinaldo David Martinez-Orozco *et al* reported a sensitivity of S=17% towards 30,000ppm H_2 gas using Palladium – graphene (PdGO) nanostructures (41).

The present work aims to describe the behavior of ZnO: NiO nanocomposite towards H_2 gas as a safety concern. The results show that the NiO is crucial for enhancing the interaction between H_2 molecules and the sensing surface thereby increasing the sensor response to S= 0.90 which is the key for improving H_2 gas sensing performance and selectivity. Hence ZnO: NiO is found to be a suitable candidate for development of sensitive and selective H_2 gas sensor.

MATERIALS AND METHODS

Synthesis of Nanocomposite

Zinc oxide (ZnO) nanoparticles were synthesized via sol-gel protocol. In a typical synthesis procedure $0.5x10^{-3}$M (3.2g) of Poly ethylene glycol (PEG) was dissolved in distilled water under stirring to which 0.015M (3.4g) of Zinc acetate was added and the solution was adjusted to pH 7 by addition of ammonia solution. The mixture was further stirred for 4hrs and filtered, washed with D.I. water, rinsed with acetone and finally dried in hot air oven at 60^{o}C/ 8h. The dried compound was calcined at 400^{o}C for 4hrs to get ZnO nanoparticles. In order to investigate the affect of NiO on gas sensing properties of ZnO, 1wt% of (optimized) percentage of NiO was added to ZnO by impregnation method to form ZnO: NiO nanocomposite. The formed material was pulverized manually and calcined at 400^{o}C to obtain pure ZnO: NiO nanocomposite.

For chemical-sensor application, ZnO: NiO nanocomposite thick films were fabricated by mixing the powder with DI water and the resulting paste was applied on alumina tube substrate having silver electrodes on either sides. The sensors thus fabricated were fired at 400 ^{o}C for 2hrs. The changes in electrical resistance during adsorption desorption of gas molecules on the material surface is estimated by measuring the electrical resistance of the sensor in air (Ra) to that in presence of test gas (Rg), The sensitivity S, defined as the ratio (Ra $-R$g/Ra). All the gas sensing measurements were carried out towards 1000 ppm H_2 gas in the temperature range of 50 - 400 ^{o}C.

Equipment used for characterization of ZnO: NiO Nanocomposite

X-ray powder diffraction data was recorded on Siemens (D5000) diffractometer using Cu Kα radiation (λ = 1.5406 A°) in the range of 2θ = 2–65 ^{o}. Particle size was recorded by particle size analyzer Horiba SZ100. The morphological Evaluations were carried out by transmission electron microscopy (TEM). A drop of the reaction mixture was placed over carbon-coated copper grids and the solvent was allowed to dry. Images were acquired on a Philips Technai-FE 12 TEM (120 KV). The energy dispersive X-ray spectroscopy (EDX) analysis was performed by scanning electron microscopy (SEM) with Model S520 (Hitachi, Japan) equipped with an EDX detector (Model: Oxford LINK-ISIS 300). The EDX spectrum was measured at 10 kV accelerating voltage.

Gas sensor process

Fabrication of the sensor element

The substance used for the fabrication of the sensor element was alumina tube of 10 mm length, having two silver electrodes on either side separated by 6 mm, 5 mm external diameter and 3 mm internal diameter. For chemical sensor application, the sensor materials were mixed and ground with deionized water in an agate mortar to form a paste, then the resulting paste was coated on an alumina tube substrate having a pair of silver electrodes on either side followed by drying and calcination at 400^{o}C for 2 h. Finally, a Ni–Cr heating wire was inserted into the tube to heat the sensor. The resulting sensor element was subjected to measurements of the electrical resistance in the presence and absence of H_2 gas in air. The operating temperature and concentrations of H_2 gas were varied in order to establish maximum sensor response. For the resistance measurements the sensor element was placed on a temperature-controlled tungsten coil heater inside the enclosure. A load resistor RL was connected in series with the

sensor element Rs. A chromel–alumel thermocouple (TC) was placed on the device to indicate the operating temperature. The schematic of the measurement set-up is shown in our previous publication (Ranjith kumar, *et.al*. (12)).

The sensitivity (S), defined as the ratio ($S=R_a-R_g/R_a$), where R_a and R_g are the sensor resistance in air and in test gas, respectively. The response time is defined as the time required for the variation in conductance to reach 90% of the equilibrium value after which a test gas is injected. The recovery time is the time necessary for the sensor to return to its original conductance state in air.

RESULTS AND DISCUSSIONS

Energy Dispersive X-Ray Spectra

Figure 1 represents the compositional analysis of ZnO: NiO nanocomposite under the energy dispersive X-ray analysis (EDX). The EDX spectrum confirms the presence of Zn, O & Ni signal in the sample without any other impurities, strongly indicates the high purity of the final product obtained.

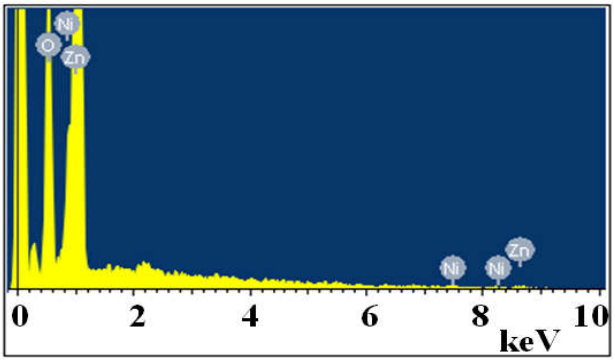

Figure 1 EDX spectrum of ZnO: NiO nanocomposite

X-Ray Diffraction

Chemical composition, crystal structure and phases of ZnO: NiO nanocomposite was examined by powder X-ray diffraction (XRD) as shown in the figure 2.

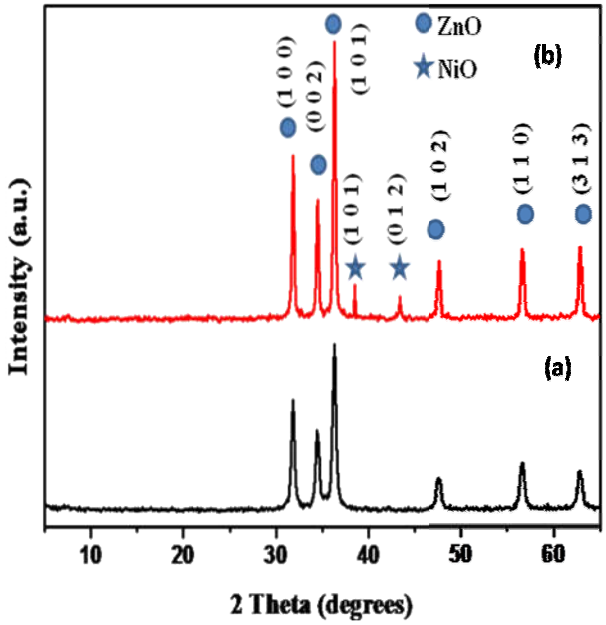

Figure 2 X-Ray Diffraction Patterns of (a) ZnO (b) ZnO: NiO Nanocomposite

The sharp diffraction peaks indicate the high crystalline hexagonal ZnO (JCPDS card no. 89-7102) with lattice constants of a=b=3.24A^o c=5.20A^o, α=β=90^o γ=120^o. The peaks appearing at 37.21^o and 43.22^o corresponding to [101] and [012] crystal planes are attributed to NiO (JCPDS card no. 89-7390) with lattice constants of a=b=2.95A^o c=7.22A^o, α = β = γ =90^o and the other planes in the shown pattern are attributed to ZnO respectively. The crystallite size was calculated by Scherrer's formula,

$$D = K.\lambda/\beta Cos\theta \quad (1)$$

where K is Scherrer's constant (~0.9), λ is the X-Ray wavelength (~1.54 A^o), β is full width at half maximum and θ is Bragg's diffraction angle. The crystallite size is calculated to be 17.76nm.

FTIR-Spectrum

The typical FTIR spectrum of ZnO: NiO Nanocomposite is shown in figure 3. Mixed phases of ZnO: NiO is observed in the synthesized nanocomposite, the peak around 400-500cm^{-1} corresponds to Zn-O stretching vibration and peak at 900-1000cm^{-1} corresponds to Ni-O stretching vibration. Broad band at around 3000- 3500cm^{-1} corresponds to O-H stretching vibrations, possibly from H_2O, another broad peak at 1604cm^{-1} correspond to hydroxyl group of chemisorbed and/or physisorbed H_2O molecules on the particle surface.

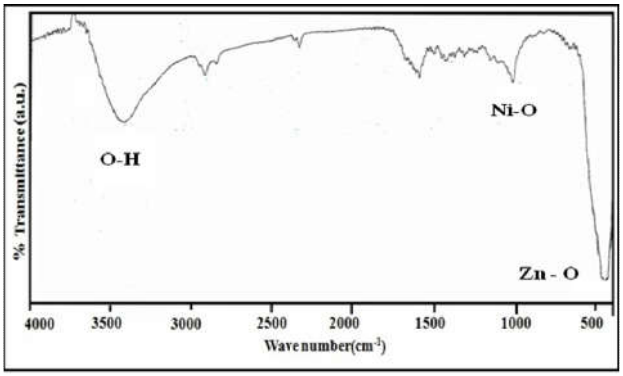

Figure 3 FTIR Spectrum of ZnO: NiO Nanocomposite

Transmission Electron Microscopy

Particle size and nano structure of ZnO: NiO nanocomposite has been examined through Transmission electron microscope (TEM) as shown in Figure 4(a, b). It indicates that ZnO: NiO nanocomposite is uniform in crystalline size having hexagonal structure. It reveals that the crystalline size of the sample are in the range of 10-20nm, which is consistent with the results of XRD analysis.

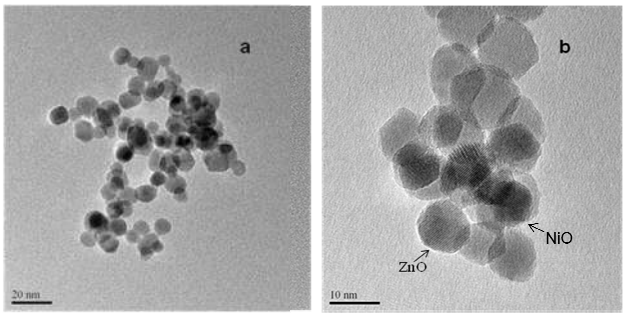

Figure 4 a,b TEM images of ZnO: NiO nanocomposite

Particle size analysis spectrum

Particle size distribution of ZnO: NiO Nanocomposite is shown in Figure 5 which picturises the particle size analysis spectrum of NiO impregnated in ZnO. The spectrum clearly shows that most of the particles are approximately 15 nm respectively.

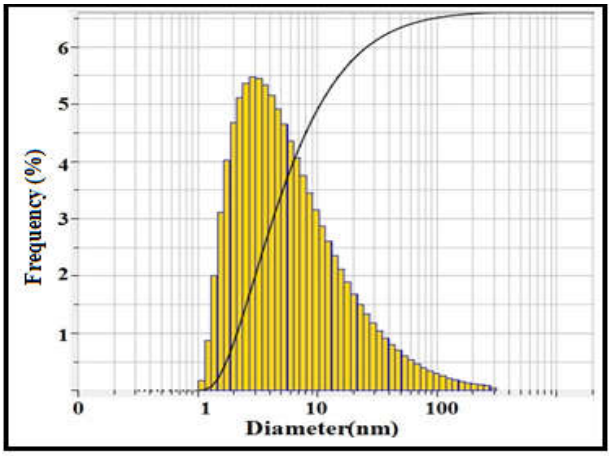

Figure 5 Particle size analysis spectrum of ZnO: NiO nanocomposite

Gas sensing characteristics

To investigate the effect of NiO loading into nano ZnO, different wt% (i.e., from 0.6wt% to 5wt% - coded as ZN0.6, ZN0.8, ZN1, ZN3, ZN5) of NiO was incorporated into nano ZnO and the sensor response of all the samples were studied. As shown in Figure 6. It is seen that 1wt% NiO impregnated ZnO (ZN1) shows higher sensitivity of S=0.9 comparatively, thus the sample ZN1 was optimized and used for further studies.

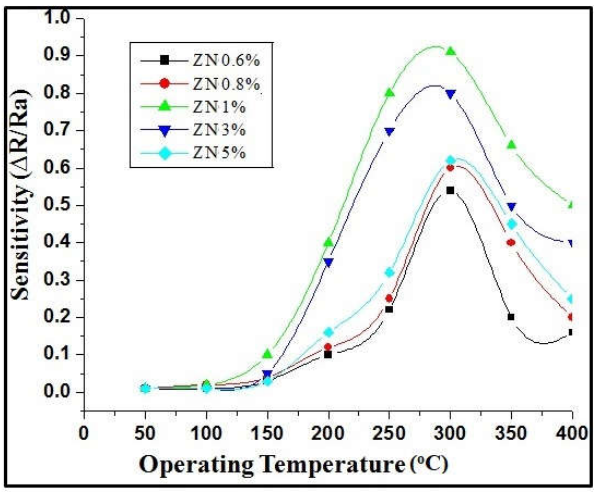

Figure 6 Sensitivity vs. Operating temperature for different wt% of NiO incorporated ZnO

Figure 7a shows the gas sensing of ZnO: NiO nanocomposite as a function of operating temperature towards 1000ppm of H_2 gas. The response increases with increase in operating temperature and reaches maximum limit at 300°C followed by a decrease with increase in operating temperature. Optimization of the operating temperature is crucial for establishing high sensitivity of the sensor to the target gas. Further, a significant enhancement in the performance could be achieved with the incorporation of NiO. The sensing response increases as a function of concentration and reaches saturation, and also shows reasonably good response to low concentration of 100ppm as shown in figure 7b.

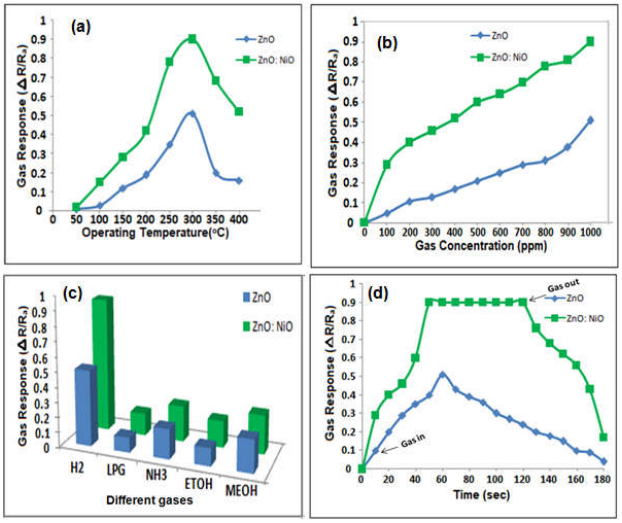

Figure 7 Gas sensor response of ZnO and ZnO: NiO nanocomposite towards 1000ppm of H_2 gas at 300°C (a) Operating temperature (b) different gas concentrations of H_2 (c) different interfering gases (d) as a function of response time

Figure 7c shows the sensing responses to different interfering gases like ammonia, LPG, Ethanol, Methanol and hydrogen to 1000ppm gas at 300°C. The selectivity is measured for evaluating the specificity of ZnO: NiO sensor by comparing the response to different gases, the sensor showed higher response to H_2 compared to other test gases. Response and recovery times are the important parameters of gas sensors, which can be defined as the time taken for the sensor to reach 90% of its total change in sensitivity after exposure to H_2 gas and the time taken for the sensor to reach its initial sensitivity value once the H_2 atmosphere ceases to exist. The ZnO: NiO sensor exhibited a response and recovery time of ~50s & ~60s respectively at 300°C towards 1000ppm H_2 as shown in figure 7d.

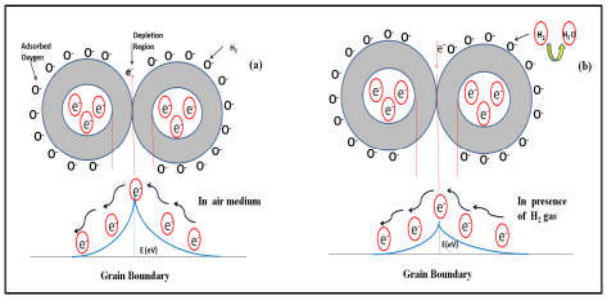

Figure 8 Gas Sensing Mechanism of ZnO: NiO sensor in (a) air medium and (b) In presence of H_2 gas

Gas Sensing Mechanism

A plausible gas sensing mechanism based on adsorption – oxidation - desorption pathway, which plays an important role in gas sensing mechanism is proposed. At equilibrium, the sensor surface is exposed to oxygen (O_2) in air Oxygen molecules are adsorbed on the ZnO:NiO (ZN) nanocomposite surface gets ionized ,creating adsorbed oxygen species (O_2 ,O^-, O^{2-}) on the sensor surface.

$$O_{2\,gas} \longleftrightarrow O_{2\,ads} + e^- \longleftrightarrow O_{2\,ads}^- + e^- \overrightarrow{KT}\ O_{ads}^- + e^- \overrightarrow{KT}\ O^{2-} \qquad (2)$$

The ionization of oxygen molecules occurs due to the capture of electrons from the conduction band of ZN sample acting as electron acceptors, resulting in electron depletion region with reduced electron mobility near the oxide surface. This phenomenon enhances the surface potential and the work function. Further, when the sensor is exposed to air, O_2 adsorbed on the ZN sample, traps electrons from the conduction band due to strong electro negativity of the oxygen atom, and produces adsorbed oxygen O_2^{n-} (ads) as shown in Eqn. (2). Thus an increase in electrical resistance is observed.

$$\boldsymbol{H_2 \rightarrow 2H^+ + 2e^-} \quad (3)$$

$$\boldsymbol{2H^+ + O^{2-} \rightarrow H_2O} \quad (4)$$

$$\boldsymbol{H_2 + O^{2-} \rightarrow H_2O + 2e^-} \quad (5)$$

When the sensor is exposed to reducing gas in the present study hydrogen, the hydrogen molecules react with the adsorbed oxygen species and a chemical redox reaction occurs between H_2 and O_2^{n-} (ads), the gas gets oxidized releasing electrons on the sensor surface. Electrons produced from this redox reaction as shown in Eqn. (3) reduces the depletion region there by resulting in drop in its resistance thus increasing the sensitivity of the sensor as illustrated in Fig. 8. As the redox reaction is exothermic it results in fast desorption of produced H_2O molecules from the surface as shown in Eqn. (4). When the hydrogen ambient is removed in presence of air, the accumulated layer of electrons would be eliminated as shown in Eqn. (5) leading to the recovery of initial resistance.

CONCLUSIONS

In summary the compositional and elemental analysis of the sample examined by EDX spectrum confirmed the presence of Zn, O and Ni signal. The sensor based on ZnO: NiO material showed excellent sensitivity and selectivity towards H_2 gas. The high response was obtained at 300^{o}C towards1000ppm of H_2 gas with response and recovery times of ~50s and ~60s respectively. The present material is a novel and cost effective and is a suitable candidate for development of sensitive and selective H_2 gas sensor.

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