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Research paper

Highly selective gas sensors from photo-activated ZnO/PANI thin films synthesized by mSILAR

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ABSTRACT

Zinc oxide (ZnO) nano-polycrystalline thin films has been prepared by cost-effective microwave assisted successive ionic layer adsorption and reaction (mSILAR) technique. ZnO/PANI prepared by in situ polymerization technique and thin films were fabricated using spin coating. X-ray Diffraction analysis confirms the presence of hexagonal wurtzite ZnO structure in the ZnO/PANI composite. The field emission scanning electron microscope revealed the porous nature of ZnO/PANI films with nanosized grains. We observed PANI intensively affected the structural and electrical properties of ZnO films. The examination of sensors was carried out in the liquefied petroleum gas (LPG) concentration range of 30 to 450 ppm. It was noticed that ZnO/PANI nanocomposite film possesses excellent LPG sensing properties at a room temperature compared with other volatile organic compounds, at an applied voltage of 1.5 V. The composite films also exhibited significant sensing response of $\sim 6.11 \times 10^2$ towards temperature and light with recovery and response time of ~3.5 min and 2.16 min, respectively. Finally, the fabricated sensor showed good repeatability and sensitivity upon cyclic exposure to gas, light, and temperature. The ZnO/PANI nanocomposite film demonstrated overall sensing behavior in terms of sensor recovery time and response as well as repeatability.

1. Introduction

Polymer nanocomposites (PNCs) play a significant role in industrial research due to their wide range applications in biomedical, optoelectronic, electrical, and electronic fields [1–5]. These materials have the potential to be lower in production cost and ease of manufacturing when compared to non-polymeric materials. Zinc oxide (ZnO) is an inorganic material with many applications in photocatalytic devices, photovoltaics, and sensors that are used to fabricate PNCs with targeted properties [6,7]. It has a wide band gap of 3.37 eV and exciton binding energy of 60 mV [8]. This large band gap helps to accumulate high-energy photons and make ZnO a promising candidate for the optoelectronic industry [6,9,10].

Among different polymers, polyaniline (PANI) is one of the desirable conductive (conjugated) polymers because of its eco-friendly nature, ease of synthesis in an aqueous medium, and thermal stability [8,11]. The different techniques employed for the fabrication of PANI composites are solution casting technique, sol-gel spin coating, and electrochemical polymerization [11–13]. The PANI has various applications, such as in rechargeable batteries, light emitting diodes, electrochromic devices, and non-linear optical devices [12–14]. However many disadvantages include long-time instability, irreversibility, among others. Considering the limitations of the polymer (PANI) can overcome those by incorporating inorganic nanofillers and thereby achieving improved optical and electronic properties for the composites. Thus, the final composite will show a synergistic effect in property enhancement from the polymer and the inorganic material. There are many reports on various properties of ZnO/PANI composites [8,11,15–20]. Mixing ZnO with conducting polymer like PANI provides a high active surface area for the sensing reaction and enhances the

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stability of the final nanocomposite.

Both small and large-scale industries take serious environmental measures to monitor the eluting pollutants into suitable manufacturing products. The problems due to liquefied petroleum gas (LPG), CO, CO_2, and H_2S are considered to be serious in industrial as well as domestic fields. Several respiratory and allergic diseases arise due to the leakage of these toxic gases [21]. As LPG is employed as a fuel for vehicles and cooking purposes of faultless and comfortable use of LPG is necessary. In the beginning reports on the detection of these toxic gases are very few but later on the increase tremendously. Hence quick detection of low concentration of gases has found to be high in demand to examine the leakage areas accurately [22–25]. It has been noted that, designing an efficient gas sensor to examine LPG at trace levels in severe environmental conditions is inevitable [26]. A lot of metal oxide based sensors have been noticed, where transition metal oxides found to be the best candidate for LPG detection [27–30]. The working principles of these sensors are based on the relative resistance variation in the presence of LPG. Many groups have been fabricated highly sensitive, selective, stable and low-cost gas sensors for sudden detection of toxic gases employing a lower concentration of material. However, various factors influence the sensor parameters mainly the synthesis of nanomaterials and fabrication of gas sensors.

The present study focuses on the synthesis of ZnO/PANI thin films and its structural, electrical and sensing properties. Scanning electron microscopy (SEM) and X-ray diffraction characterization techniques were used to investigate the surface morphology and structural information. The comparative investigations on sensing properties of the hybrid nanocomposite thin films of ZnO and ZnO/PANI towards temperature, photo and gas sensing were studied. The studies illustrated the possibility to tune the sensing responses to the desired level by PANI coating and electron beam irradiation during fabrication, in addition to its promising applications in solar panels and space technology.

2. Experimental details

2.1. Materials

The chemicals used in the experiments were anhydrous aluminum chloride [$AlCl_3$], Zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$), and sodium hydroxide (NaOH) pellets (Merck, Inc, USA). Analytical Reagents grade quality chemicals were employed in this experiment and were used without further purification. Ultrapure water (< 18.2MΩ cm; Milli-Q-Plus system, Millipore, Inc, City, State, Country) aqueous solutions was used in the experiments.

2.2. Method of synthesis

The microwave assisted successive ionic layer adsorption reaction (mSILAR) technique was used to synthesize ZnO thin films on a substrate. The method of preparation is reported elsewhere [7]. The PANI/ZnO was synthesized by coating 40% PANI on the ZnO thin film following in-situ polymerization method [31]. To synthesize ZnO/PANI thin film, the resultant film was annealed on a hot plate.

2.3. Characterization

Structural analysis (X-Ray) of the samples was done by Bruker AXS-8 using CuKα radiation, and SEM analysis was performed using JEOL −JSM6490 (model, company, city, state, country). A digital multimeter (Keithley 2100, company, city, state, country) was employed for the current, voltage, and electrical resistance measurements of the samples. The photoconductivity of the gold electrode coated samples were done using Keithley 6485 picometer at 365 nm photon wavelength and 1.4 mW/cm^2 power density. During the electron beam irradiation for the samples, an electron beam of 8 MeV energy was used from the Microtron. For the experiments, the samples of ~0.9 μm thickness were kept at 30 cm distance from the target electron beam. The aluminum electrodes were coated on both sides of the sample using thermal evaporation technique prior to the measurement. The Photolithographic patterned electrode was used with a gap between the electrode of 500 nm, width of 10 mm and an active-area of 4500 nm^2. The sensing studies on the sample were carried out, and the relative resistance (A_R) was calculated using Eq. (1). [32–34]

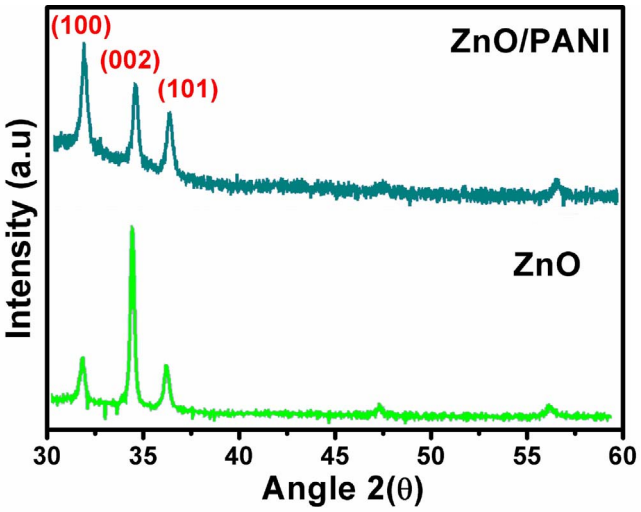

Fig. 1. XRD patterns of (a) ZnO thin film and (b) ZnO/PANI nanocomposites.

$$A_R = \frac{R_0 - R}{R_0} \times 100 \quad (1)$$

R_0 and R are the respective electrical resistance of the material in air and presence of analyte gas or temperature.

3. Results and discussion

3.1. Structural characterization

The XRD patterns of ZnO thin film and ZnO/PANI nanocomposites are depicted in Fig. 1(a) and (b). It can be observed that the diffraction peak (002) has a maximum intensity at 2θ = 34.410° in ZnO thin film. The other peaks appeared at 31.761° and 36.208° corresponded to (100) and (101) reflections (JCPDS no.36-1451).

Table 1 shows the observed values of 2θ and relative intensities of the ZnO sample and ZnO/PANI nanocomposites. From Fig. 1, it is noted that the intensity of the (002) peak is suppressed with the coating of PANI to ZnO thin film. It can be observed that the intensity of the (002) peak is suppressed and the conductivity is enhanced for the pure ZnO by coating with PANI.

3.2. Morphological analysis by SEM

The morphological analysis of ZnO/PANI nanocomposite thin film was done using SEM (Fig. 2). Granular morphology can be clearly observed in the nanostructures. For the pure ZnO, most of the particles have smooth surfaces and are crystalline with size 20–40 nm (Fig. 2a and 2c). The ZnO/PANI nanocomposite is partially homogeneous, and

Table 1
Observed values of 2θ and relative intensity of ZnO sample.

ZnO		ZnO/PANI	
2θ (°)	Relative intensity (cps °)	2θ (°)	Relative intensity (cps °)
31.761	445	31.732	414
34.410	1562	34.446	252
36.208	515	36.226	228