NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2016, 7 (4), P. 707–710

$ZnO/SnO_2/Zn_2SnO_4$ nanocomposite: preparation and characterization for gas sensing applications

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PACS 81.07.-b **DOI 10.17586/2220-8054-2016-7-4-707-710**

Zinc oxide (ZnO) / Tin oxide (SnO_2) / Zinc stannate (Zn_2SnO_4) nanocomposite is prepared via hydrothermal route followed by calcination. The nanocomposite is characterized by X–ray powder diffraction, Fourier Transform Infrared spectroscopy and UV spectroscopy techniques. The nanocomposite's morphology and the elemental composition is recorded using field emission scanning electron microscopy and energy dispersive X–ray spectroscopy analysis. The nanorods dispersed in the matrix of nanoparticles increases the surface active sites for gas adsorption and this material would be explored as a potential candidate for gas sensing applications at room temperature with quick response and recovery in the near future.

Keywords: zinc oxide, tin oxide, zinc stannate, hydrothermal.

Received: 5 February 2016

Revised: 26 April 2016

1. Introduction

A hybrid nanomaterial comprised of zinc oxide (ZnO) and tin oxide (SnO_2) act as multi-component system in which two or more of its combinations result in the enhancement of functional properties. Both ZnO and SnO_2 are well-known wide direct band gap ($E_g = 3.37$ eV and 3.6 eV at 300 K respectively) semiconductors and both serve as potential candidates in the field of gas sensors, solar cells, optoelectronic devices, LED, lithium ion batteries and so on. Recent investigations also state that the addition of a secondary component oxide in the form of the composite inhibits the grain growth of the host material [1] and these coupled oxides with different band gap widths are the effective approaches to enhance the storage capacity, photocatalytic activity, sensing of gases etc., [2] Voluminous reports are available for synthesizing such composites with unique hierarchical morphologies [3]. In this present work, $ZnO/SnO_2/Zn_2SnO_4$ composite is prepared via a hydrothermal route and it is characterized with various state-of-the art techniques and is reported herein.

2. Experimental details

0.1 M aqueous zinc chloride and stannous chloride solution together with glyoxylic acid monohydrate ($C_2H_2O_3 \cdot H_2O$) was prepared. Ammonium hydroxide was added dropwise under constant stirring at room temperature to adjust the pH to 9. The gel was then transferred into a Teflon – lined stainless – steel autoclave and maintained at 160 °C for 3 h. Aerogel was collected, washed with absolute ethanol and deionized water several times and dried in air. The product obtained was calcined at 600 °C for 3 h.

The X-ray powder diffraction (XRD) pattern of the sample was carried out using PANalyticalX'Pert PRO diffractometer with Cu-Kα radiation (λ= 1.54 Å) in 2θ ranging from 20 °–80 °. The crystalline nature of the samples and the identification of different phases were accomplished by comparing the XRD pattern with standard data provided by the International Center for Diffraction data (ICDD). The lattice parameters were calculated by least squares method and the average crystallite size (D) was calculated using the Scherrer formula:

$$D(nm) = \frac{K\lambda}{\beta \cos\theta}, \quad (1)$$

where K is a constant (app 0.9 assuming the particles are spherical), λ is the wavelength of CuKα radiation (1.54056×10^{-10} m), β is full width at half maximum (FWHM) (in radian) and θ is the angle of diffraction (in °). The surface morphology of the sample was examined using ZEISS ultrafield emission scanning electron microscope (FE-SEM). The elemental composition analysis was carried out using an energy dispersive X-ray (EDAX) spectrometer (Oxford EDS INCA PENTA FETX3) attached with FE-SEM. Fourier Transform Infrared (FT-IR) spectra of the samples were recorded in the 4000 – 400 cm^{-1} region using a Perkin Elmer RX1 FT-IR spectrometer by KBr pellet technique. UV-visible spectrum was obtained using JASCO – UV VIS spectrophotometer.

3. Results and discussion

Figure 1 shows the XRD pattern of the as prepared sample. The peaks obtained in the XRD pattern matches both the hexagonal wurtzite structured ZnO(ICDD No:36-1451) and tetragonal structured SnO_2 (ICDD No: 41-1445).

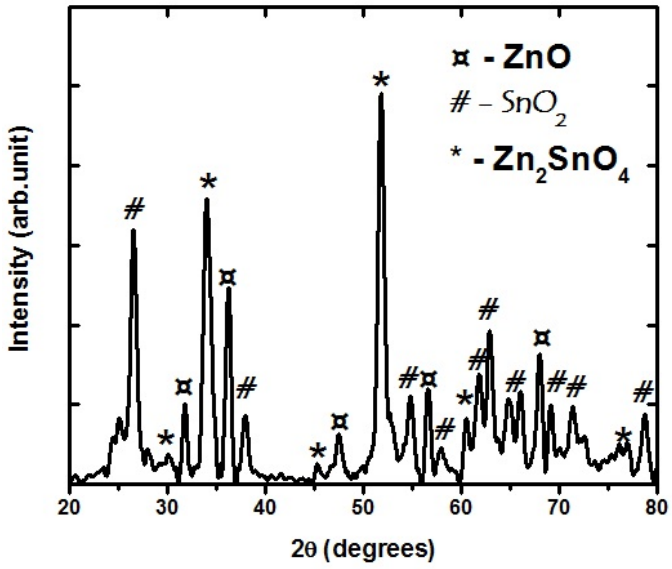

FIG. 1. XRD pattern of ZnO/SnO_2/Zn_2SnO_4 nanocomposite material

In this context, only negligible variation in the lattice parameters occurs for both the phases, which suggests that Zn^{2+} ions might not have been substituted into the SnO_2 lattice due to its larger ionic radius ($Zn^{2+} = 0.79$ Å and $Sn^{4+} = 0.68$ Å). In addition to these two individual oxides, two sharp peaks at (311) and (422) of the secondary phase corresponding to the spinel Zn_2SnO_4 (ICDD No: 24-1470) were observed. This reveals the polycrystalline nature of the composite material and is also supported by the formation of SnO_2 nanoparticles amidst the ZnO nanorods in the FeSEM image. The diffractogram displays a preferential orientation to the ZnO reflection at $2\theta \sim$ 36.195°, SnO_2 reflection at $2\theta \sim$26.476° and Zn_2SnO_4 reflections at $2\theta \sim$ 34.290° and 51.796°. The existence of these three phases for an equimolar (1:1) mixture of Zn/Sn nanocomposite at a higher calcination temperature is supported by the reports of Wang et al [1], Ruvini Dharmadasa et. al. [2]. The crystallite size of the composite material comprising the peaks of ZnO, SnO_2 and Zn_2SnO_4 were calculated using the Scherrer formula is around 30 nm, 29 nm and 21 nm respectively. The observed smaller crystallite size of 27 nm would enhance the sensitivity of the composite material towards gases.

Fe–SEM image of the composite material in Fig. 2(a) depicts both the smaller spherical and larger hexagonal structured nanoparticles clouded amidst the nanorods. The hexagonally-faceted nanorods of length 105 nm and diameter 30 nm correspond to ZnO. The spherical-shaped nanoparticles of grain size around 25 nm correspond to the SnO_2 nanoparticles. The formation of hexagonal shaped nanoparticles of about 20 nm is due to the existence of the secondary phase Zn_2SnO_4 which inhibits the growth of ZnO nanorods. The presence of Zn (26.79%), Sn (28.81%) and O (44.40%) observed from the EDAX analysis (Fig. 2(b)) also supports the equimolar mixture of the precursors. The nanorods in the matrix of the nanoparticles would increase the surface area of the composite material which might provide more surface active sites for the adsorption of gas molecules.

The FT-IR spectrum of the composite material is shown in Fig. 3. The strong absorbance band around 3524 cm^{-1} corresponds to the stretching vibration (H-O-H) and a peak around 1515 cm^{-1} corresponds to the

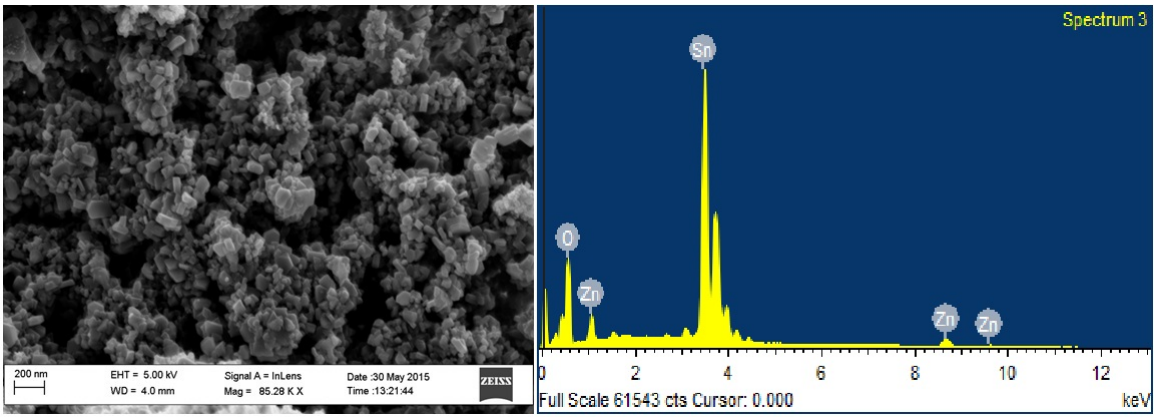

FIG. 2. (a) Fe–SEM image of ZnO/SnO_2/Zn_2SnO_4 nanocomposite material; (b) EDAX spectrum of ZnO/SnO_2/Zn_2SnO_4 nanocomposite material

bending vibrations (O-H) between oxygen and hydrogen atoms of the bound water. The absorption bands at 664.89, 866.81 and 1696.90 cm^{-1} are due to the vibration of M–O or M–O–M groups in ZnO, SnO_2 and Zn_2SnO_4 [4]. The results obtained by FT-IR analysis further confirm the formation of the composite and thus agree with the results obtained in XRD analysis.

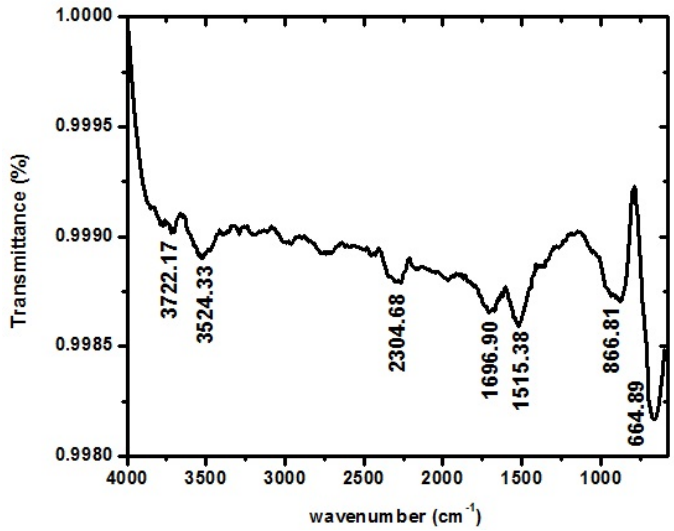

FIG. 3. FT–IR spectrum of ZnO/SnO_2/Zn_2SnO_4 nanocomposite material

Figure 4 shows the UV–Vis absorption spectrum of the composite material measured in the wavelength range of 200–800 nm. The absorption band edges were observed around 223 nm, 226 nm and 376 nm which correspond to the characteristic bands of SnO_2, Zn_2SnO_4 and ZnO respectively. Investigations done on such equimolar mixture of Zn/Sn composites obtain similar kind of absorption edge for the nanoparticles ranging from 40–70 nm. The reported band gap values of ZnO, SnO_2 and Zn_2SnO_4 are 3.37 eV, 3.65 eV and 3.6 eV respectively. The band gap value of the composite material calculated using the Tauc plot (shown in Fig. 5) is 3.7 eV. The smaller band gap value obtained by the composite material is attributed to the synergistic effect of the material.

4. Conclusion

ZnO/SnO_2/Zn_2SnO_4 nanocomposite has been successfully synthesized via a hydrothermal route followed by calcination. The formation of the composite was confirmed by XRD and FT–IR. Fe–SEM image revealed the presence of SnO_2 nanoparticles among the ZnO nanorods. The secondary phase Zn_2SnO_4 in the material inhibited the growth of nanorods, resulting in a larger surface area.

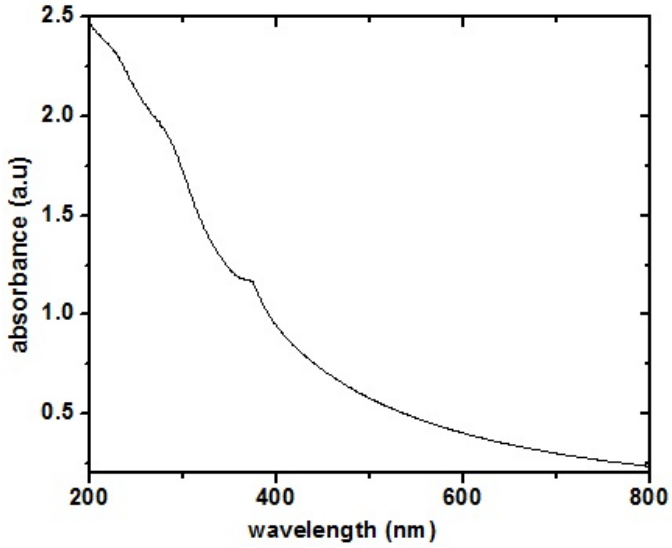

FIG. 4. UV–Vis spectrum of $ZnO/SnO_2/Zn_2SnO_4$ nanocomposite material

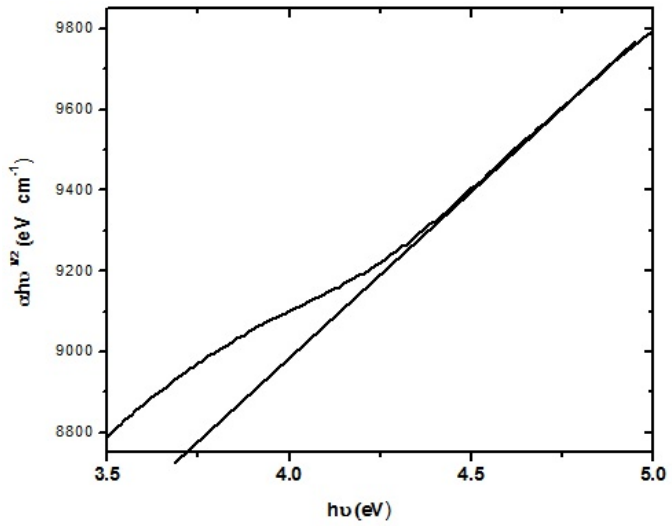

FIG. 5. Tauc plot of $ZnO/SnO_2/Zn_2SnO_4$ nanocomposite material

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