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High performance H_2 sensor based on $ZnSnO_3$ cubic crystallites synthesized by a hydrothermal method

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ABSTRACT

Zinc stannate ($ZnSnO_3$) cubic crystallites have been successfully synthesized by hydrothermal reaction at 140 °C. X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) have been employed to characterize the crystal structure and morphology of the as-synthesized $ZnSnO_3$. The $ZnSnO_3$ cubic crystallites exhibited selective sensing performance towards H_2 in terms of higher gas response, rapid response-recovery, repeatability and relatively lower operating temperature. This experimental result demonstrates that the synthesized $ZnSnO_3$ cubic crystallites have noteworthy H_2 sensing characteristics which make them a promising material for the fabrication of high performance H_2 sensor.

1. Introduction

In recent years, metal oxide nanostructures including nanoparticles, nanorods, nanotubes, nanowires and nanoribbons have been investigated for gas sensing applications due to some advantageous features such as low cost, simplicity in fabrication, non-toxicity, high gas response, fast response and recovery, selectivity and suitability to different doping [1–3]. The significantly increased surface-to-volume ratio, great level of crystallinity and modified physical/chemical properties of these nanostructures are believed to provide numerous active sites for the interaction with the target gas, which results in excellent gas sensing behavior even at room temperature [2–4]. At the same time, the synthesis method has an effect on the sensor performance largely since it affects the morphology and structure of the sensing material. Various transition metal oxide nanostructures such as Co_3O_4 nanorods [5], CdO nanoparticles [6], α-Fe_2O_3 nanorods [7], SnO_2 nanotubes [8], In_2O_3 nanowires [9], CuO nanoribbons [10] and ZnO nanorods [11] have been studied as gas sensing materials during the past few years.

$ZnSnO_3$ with various morphologies have been investigated recently as a new type of good gas sensing material [12–16]. However, these gas sensing investigations are limited to ethanol, formaldehyde, butane and H_2S. For example, Xu et al. [12] have reported the synthesis of hexagonal shaped $ZnSnO_3$ microparticles via a hydrothermal reaction without any surfactant and investigated their H_2S sensing properties. Xue et al. [13] have synthesized $ZnSnO_3$ nanowires by thermal evaporation method and studied their ethanol sensing properties. Zeng et al. [14] have reported the synthesis of hierarchical $ZnSnO_3$ nanocages via a hexamethylenetetramine (HMT)-assisted hydrothermal reaction and investigated the ethanol sensing properties. Wang et al. [15] have prepared $ZnSnO_3$ cubic crystallites via a solution process at a reaction temperature of 0 °C without any surfactant, which exhibited high sensitivity, fast response and short recovery times towards HCHO gas. The synthesis of $ZnSnO_3$ hollow microspheres by the cetyltrimethyl ammonium bromide (CTAB)-assisted hydrothermal reaction was reported by Fan et al. [16] and they have studied the butane sensing properties.

Hydrogen (H_2) is a potential fuel for cars, buses, and other vehicles [17]. It is also already used in medicine and space exploration as well as in the production of industrial chemicals and food products. As it is tasteless, colorless and odorless, it cannot be detected by human beings. It is potentially hazardous due to the high possibility of explosion accidents caused by leakage or by human error. Therefore, hydrogen detection is of great importance during its production, storage and use.

Within the present investigation, experiments have been carried out for the fabrication of a fast responding and selective H_2 sensor based on $ZnSnO_3$ cubic crystallites. There is hardly any report on H_2 sensor based on $ZnSnO_3$ cubic crystallites. In this study, the $ZnSnO_3$ cubic crystallites were synthesized via a HMT-assisted hydrothermal reaction at 140 °C. Sensing characteristics of the $ZnSnO_3$ cubic crystallites to H_2 were systematically investigated. A sensing mechanism was also discussed based on experimental findings.

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2. Experimental

2.1. Synthesis of $ZnSnO_3$ cubic crystallites

The synthesis of $ZnSnO_3$ cubic crystallites was carried out using analytical grade zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), stannic chloride hydrated ($SnCl_4 \cdot 5H_2O$), HMT ($(CH_2)_6N_4$) and sodium hydroxide (NaOH) without further purification. In a typical experiment, 0.2 mmol $Zn(CH_3COO)_2 \cdot 2H_2O$, 0.2 mmol $SnCl_4 \cdot 5H_2O$ and 0.015 mmol $(CH_2)_6N_4$ were dissolved in double distilled water and stirred continuously for 1 h at room temperature (25 °C). An appropriate amount of NaOH was added drop-wise to the reaction mixture with continuous stirring until the final solution pH value of about 10 was achieved. The solution was transferred to a Teflon-lined stainless steel autoclave, maintained at 140 °C for 8 h and then cooled to room temperature naturally. The white colored precipitate was collected by centrifugation, washed several times using double distilled water and ethanol, and then dried in an oven at 100 °C overnight to obtain the end-product for further characterization.

2.2. General characterization

The structural analysis of the as-synthesized $ZnSnO_3$ cubic crystallites was carried out using X-ray diffractometer (XRD, D8 Advance, Bruker AXS) with CuK_α radiation ($\lambda = 1.5418$ Å), whereas the surface morphological studies were performed using a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan) and a transmission electron microscope (TEM, 1200 EX, JEOL, Japan).

2.3. Gas sensing measurements

The $ZnSnO_3$ cubic crystallites powder was pressed into pellets under a pressure of 15 MPa and the ohmic contacts were made with the help of silver paste to form the sensing element. The schematic diagram of the sensing element is shown in Fig. 1. The gas sensing studies were carried out on these sensing elements in a static gas chamber to sense H_2 in air ambient. The sensing element was kept directly on a heater in the gas chamber and the temperature was varied from 200 to 400 °C. The temperature of the sensing element was monitored by chromel–alumel thermocouple placed in contact with it. The known volume of the H_2 was introduced into the gas chamber pre-filled with air with a micro-syringe so as to yield a desired concentration and it was maintained at atmospheric pressure. The electrical resistance of the sensing element was measured before and after exposure to H_2 under a voltage of 5 V using an electrometer (6517B Electrometer, Keithley) controlled by the test software supplied by Biotronic systems, Mumbai, India. The performance of the sensing element is presented in terms of gas response (S), which is defined as

$$S = \frac{R_{air}}{R_{gas}} \quad (1)$$

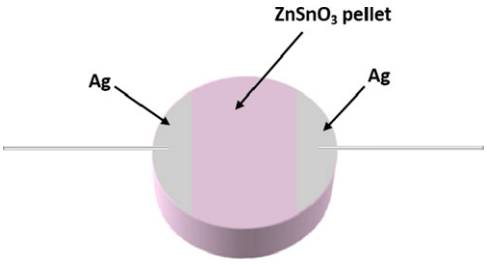

Fig. 1. Schematic diagram of the sensor device.

where R_{air} and R_{gas} are the electrical resistance values of the sensor element in air and in the presence of H_2 gas, respectively.

3. Results and discussion

3.1. XRD analysis

The XRD pattern of as-synthesized product is depicted in Fig. 2(a). All of the diffraction peaks can be indexed to the standard $ZnSnO_3$ with the perovskite structure (JCPDS no.: 11-0274), confirming that the as-synthesized product has a typical face centered cubic (FCC) crystal structure. No diffraction peaks due to impurities or other crystalline byproducts such as ZnO or SnO_2 were detected, indicating that pure $ZnSnO_3$ crystallites could be obtained under present synthesis conditions.

3.2. Morphological studies

Fig. 2(b) shows the FESEM image of the as-synthesized product, which reveals the formation of microcubes with an average edge lengths of about 250–400 nm. Besides, the random aggregation of amorphous nanoparticles is seen on the surface of cubes. The TEM image of the the as-synthesized product is shown in Fig. 2(c). The formation of $ZnSnO_3$ microcubes observed by FESEM previously was confirmed by the TEM. The corresponding selected area electron diffraction (SAED) pattern (as shown in Fig. 2(d)) further confirms that the microcubes have good crystallinity and there is no secondary phase.

3.3. Gas sensing performance

In order to determine the optimum operating temperature, the gas response of the $ZnSnO_3$ cubic crystallites based sensor towards 50 ppm H_2 was investigated as a function of operating temperature and the corresponding result is shown in Fig. 3. It can be seen that the operating temperature significantly affects the gas response. In general, the change in the operating temperature alters the kinetics of the adsorption and reaction occuring on the sensor surface, which leads to the variation in the gas response. As can be seen from Fig. 3, the gas response continuously increases when the operating temperature varies from 200 to 375 °C and then gradually decreases with a further increase in the operating temperature.

As the progressive adsorption and subsequent surface reactions occur with an increase in the temperature, the gas response of the sensor continuously increases as the temperature increases from 225 to 375 °C. At temperature 375 °C, the optimum balances between the adsorption and desorption, the surface reactions and diffusion length may be established and consequently, the H_2 reacts most effectively with chemisorbed oxygen at such particular temperature, which results in the significant decrease in the resistance of the sensor. Therefore, the maximum gas response of the $ZnSnO_3$ cubic crystallites based sensor towards H_2 is expected at such particular temperature. At higher temperatures (> 375 °C), desorption process is dominant and also the diffusion length becomes lower. Therefore, in presence of the H_2, the probability of the reduction reaction of the gas with chemisorbed oxygen is less, which results into a very small change in resistance of the sensor at higher temperatures. Therefore, the $ZnSnO_3$ cubic crystallites operate as a sensing element to the H_2 only within a specific temperature window. The maximum gas response for 50 ppm H_2 is about 652.36 at 375 °C. Therefore, the temperature of 375 °C was chosen for further evaluating the H_2 sensing characteristics of the $ZnSnO_3$ cubic crystallites.