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Ceramics International 38 (2012) 2295–2304

CERAMICS INTERNATIONAL

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Synthesis, characterization and alcohol sensing property of Zn-doped SnO_2 nanoparticles

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Received 14 October 2011; received in revised form 27 October 2011; accepted 28 October 2011
Available online 4 November 2011

Abstract

The Zn-doped SnO_2 nanoparticles synthesized by the chemical co-precipitation route and having dopant concentration varying from 0 to 4 at%, were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) for structural and morphological studies. XRD analyses reveal that all the samples are polycrystalline SnO_2 having tetragonal rutile structure with nanocrystallites in the range 10–25 nm. The TEM images show agglomeration of grains (cluster of primary crystallites). A corresponding selected area electron diffraction pattern reveals the different Debye rings of SnO_2, as analyzed in XRD. Alcohol sensing properties of all the Zn-doped samples were investigated for various concentrations of methanol, ethanol and propan-2-ol in air at different operating temperatures. Among all the samples examined, the 4 at% Zn-doped sample exhibits the best response to different alcohol vapors at the operating temperature of 250 °C. For a concentration of 50 ppm, the 4 at% Zn-doped sample shows the maximum response 85.6% to methanol, 87.5% to ethanol and 94.5% to propan-2-ol respectively at the operating temperature of 250 °C. A possible reaction mechanism of alcohol sensing has been proposed.

Keywords: SnO_2 nanoparticles; Structural properties; Alcohol sensing; Sensor response

1. Introduction

Tin oxide (SnO_2), an important n-type wide direct band gap semiconductor (E_g = 3.67 eV at 300 K), has been the subject of great interest for researchers because of its numerous and wide-ranging applications, such as in flat panel displays, catalysis, heat mirrors, transparent electrodes preparation, gas sensing, etc. [1–7]. More recently, this material has received a growing attention as a nanostructured material due to its interesting electrical and optical properties arising out of large surface-to-volume ratio, quantum confinement effect, etc. [8–12]. Morphology, size and size distribution of SnO_2 nanoparticles play an important role in deciding their properties. One important method to modify the characteristics of the nanoparticles is the introduction of dopants in the parent system, which, in turn, influences the performance of the gas sensors based on these nanoparticles. Various dopants like Al, In, Cu, etc. have been used to improve sensitivity and selectivity performance of the gas sensors based on the SnO_2 nanoparticles [13–15]. Ménini et al. [13] have investigated the CO response of a nanostructured SnO_2 gas sensor doped with palladium and platinum. Microstructure In/Pd-doped SnO_2 sensor for low-level CO detection has been studied by Zhang et al. [14]. Thomas et al. [15] have examined the influence of Cs doping in spray deposited SnO_2 thin films for LPG sensors.

Though a large number of studies on the gas sensors based on SnO_2 nanoparticles (in various forms) have been carried out, but to the best of our knowledge, a very little attention has been paid to the investigation of the Zn-doped SnO_2 nanoparticles for gas sensing applications [16]. In recent times, environmental regulations for VOCs have been tightened all over the world. At high concentrations in air, VOCs with their speedy evaporation and toxic or carcinogenic nature are extremely dangerous to human beings [17]. Alcohols (methanol, ethanol and propan-2-ol) are widely used in many applications. Among them, methanol is highly toxic and often fatal to human beings, whereas excessive exposure of propan-2-ol results in headache, dizziness, nausea, vomiting, etc. Thus, seeing the importance of health risks, the alcohol sensing properties of the Zn-doped SnO_2 nanoparticles have been investigated and reported in this

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doi:10.1016/j.ceramint.2011.10.081

paper. For a material to be used as a chemical gas sensor, it should exhibit high response at low operating temperatures and the low concentrations of tested gases. Keeping this in view, the low concentrations (10–50 ppm) of alcohols were tested.

To prepare active nanocrystalline powders, several chemical techniques have been investigated and reported in the literature. Among the various methods of preparing nanostructured SnO_2, co-precipitation [18], sol–gel [19], spray pyrolysis [20], hydrothermal routes [21], etc. are popular. In the present investigation, we have used co-precipitation method for the preparation of Zn-doped SnO_2 nanoparticles as this method requires little manipulation and no sophisticated equipment.

2. Experimental

The Zn-doped SnO_2 nanoparticles were synthesized by the chemical co-precipitation route. All the chemicals used were of analytical grade. Firstly, stannic tetrachloride hydrated ($SnCl_4 \cdot 5H_2O$) was dissolved in distilled water to prepare 0.1 M solution. Zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] was then added to the solution as the source of Zn-dopant. The dopant concentration (at% Zn to Sn) was varied from 0 to 4 at%. Ammonia solution was then added into the solution under constant agitation to form white slurry. The slurry was filtered and washed thoroughly with distilled water several times to remove the chloride ions completely from the precipitate. The resulting precipitate was dried at 90 °C and then calcined at 600 °C for 10 h in air. The dried mass was then crushed into fine powder. The structural analysis of the SnO_2 powder was carried out using PANalytical X'Pert Pro X-ray Diffractometer with Cu Kα radiation (λ = 1.5418 Å) as X-ray source at 40 kV and 30 mA in the scanning angle (2θ) from 20° to 65°. The morphologies and dimensions of the powders were determined by transmission electron microscopy (TEM) which was done on a Philips model Tecnai-20 using an accelerating voltage of 200 kV.

The fine powders, both undoped and Zn-doped, separately were pressed into pellets of 12 mm diameter and 2.5 mm thickness at a pressure of ~15 MPa using a hydraulic press. These pellets were sintered at around 600 °C for 5 h in air. High temperature silver paste was used for making ohmic contacts on the two flat surfaces of the sintered pellets. The alcohol sensing properties of the pellets were carried out in an experimental set up shown in Fig. 1. The experimental set-up was so designed that there was a complete dry air (free from humidity) in the surrounding areas of the experimental films to be examined. Therefore, the effect of humidity on the sensor response has not been taken into account in the present investigation. The pellet was mounted on a home-made two-probe assembly which was inserted coaxially inside a resistance-heated furnace. The temperature of the pellet was monitored using a chromel–alumel thermocouple with the help of a Motwane digital multimeter (Model: 454). The electrical resistance of the pellet was measured before and after exposure to alcohol vapour by a 6½ Digit USB Digital Multimeter (Keithley Model: 2100). The measurement of alcohol concentration was carried out by taking required amount of liquid alcohol in a Hamilton micro syringe and then injecting it into the enclosure. The response of the pellet towards alcohol vapour was studied at different operating temperatures in the range 150–250 °C for various concentrations ranging from 10 ppm to 50 ppm in air.

3. Results and discussion

3.1. Structural and morphological studies

XRD patterns of the 0 at%, 1 at%, 2 at%, 3 at% and 4 at% Zn-doped SnO_2 nanoparticles are shown in Fig. 2. All the diffraction peaks in the pattern can be indexed as the tetragonal rutile structure of the polycrystalline SnO_2 in the standard data (JCPDS File No. 72-1147) for samples. No phase corresponding to zinc or other zinc compound is found in the pattern. It is

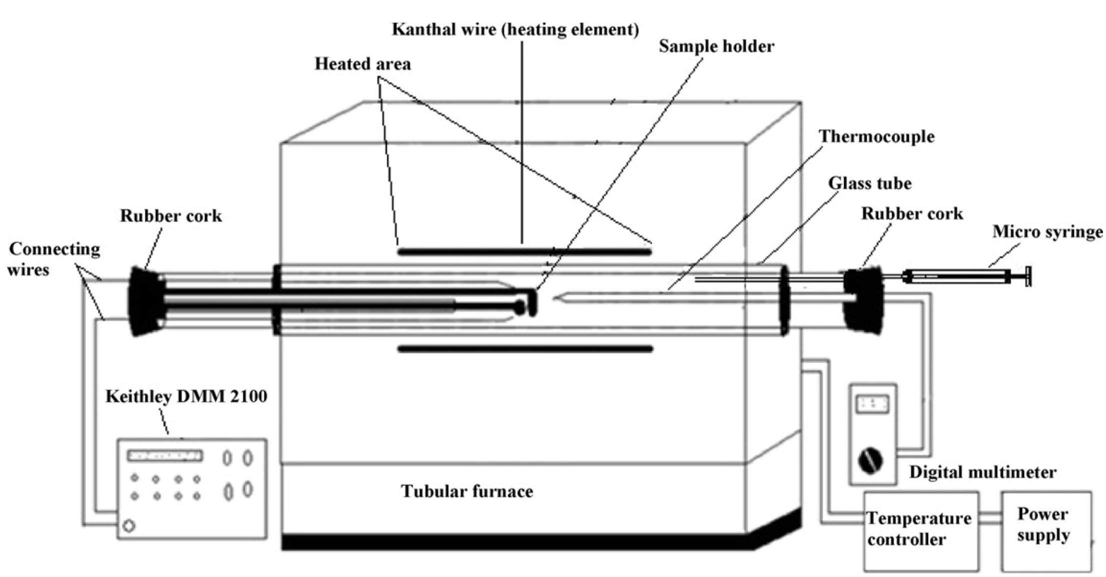

Fig. 1. Experimental set-up for alcohol sensing studies.