Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 42 (2016) 90–96

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Solid-state synthesis of Y-doped ZnO nanoparticles with selective-detection gas-sensing performance

Jing Xie, Yali Cao*, Dianzeng Jia*, Yizhao Li, Yang Wang

Key Laboratory of Material and Technology for Clean Energy, Ministry of Education, Key Laboratory of Advanced Functional Materials, Autonomous Region, Institute of Applied Chemistry, Xinjiang University, Urumqi, Xinjiang 830046, China

Received 23 February 2015; received in revised form 21 July 2015; accepted 21 July 2015
Available online 12 August 2015

Abstract

Y-doped ZnO nanoparticles have been fabricated by simple solid-state chemical reactions and subsequent calcinations. X-ray diffraction (XRD) and energy disperse X-ray spectrum (EDS) indicated that Y element have been successfully doped into the pure bulk ZnO. From the observation of field emission scanning electronic microscopy (FESEM) and transmission electron microscopy (TEM), the Y-doped ZnO nanoparticles have diameters around 20–50 nm. The gas-sensing test indicated that the Y-doped ZnO nanoparticles have higher sensitivity and fast response than the pure ZnO sensor, and the gas sensors based on the Y-doped ZnO nanoparticles exhibit excellent selectivity toward gasoline at 200 °C, while to ethanol at 400 °C. The results showed that the Y-doped ZnO nanoparticles can be used as the sensing materials for the temperature-regulated detectors.

Keywords: D. ZnO; E. Sensors; Nanomaterials; Solid-state synthesis

1. Introduction

Gas sensor is very important for environmental problems and human safety owning to the effective detection and monitoring of toxic and harmful gases [1–4]. The progress of gas sensor largely depends on the improvement of the sensitive characteristics of the materials. Recently, nano-sized semiconductor oxides have attracted widespread attentions due to their high sensitivity and fast response for the target gases [5–8]. As one of the most important n-type oxide semiconductor, ZnO has been employed for the detection of oxidizing and reducing gases due to its good chemical and thermal stability, low cost and simple device [9]. Although ZnO nanomaterials have high sensitivity to some gases, but the selectivity is not good enough, which make it difficult to practical application for the high requirements. Therefore, various attempts have been carried out to improve the selectivity of ZnO nanomaterials, including control of the size and morphology [10,11], the recombination with other semiconductors, and the doping by noble metals [3,12–14] or rare earth oxides (REO) [15–18]. Especially, it was observed that the addition of REO into ZnO nanomaterials can significantly increase the sensitivity and improve the selectivity.

Rare earth elements such as La, Ce, Sm and Eu are the most commonly used doping ions to improve the sensing properties of ZnO nanomaterials due to their fast oxygen ion mobility and catalytic properties. A variety of methods have been successfully employed for the doping of REO into bulk ZnO nanomaterials, such as the impregnation method, hydrothermal method, sol–gel dip coating method and electrospinning method [19–21]. However, these methods usually require harsh conditions, complicated process and long periods. Therefore, it is desired to explore a simple, cheap, mild and fast method for the fabrication of REO-doped ZnO nanomaterials.

It is well known that solid-state chemical reaction is an effective way to fabricate inorganic nanomaterials, which shows the features of simple process, high yield, gentle condition and low cost [22–25]. Here, we report a facile strategy for the synthesis of Y-doped ZnO nanoparticles through an improved two-step solid-state chemical reaction, including the synthesis of

*Corresponding authors. Tel.: +86 991 8581183; fax: +86 991 8588883.
E-mail addresses: caoyali@xju.edu.cn (Y. Cao), jdz@xju.edu.cn (D. Jia).

http://dx.doi.org/10.1016/j.ceramint.2015.07.135
0272-8842/

precursor by the room-temperature solid-state chemical reaction and the thermal decomposition of precursor. The as-prepared Y-doped ZnO nanomaterials exhibits excellent sensing properties to gasoline and ethanol.

2. Experimental

2.1. Synthesis

All the reagents were analytically pure from commercial sources and used without further purification. Metal salts including 10 mmol solid $Zn(CH_3COO)_2 \cdot 2H_2O$ and 0.1 mmol solid $Y(NO_3)_3 \cdot 6H_2O$ were weighted and ground for about 5 min in agate mortar to ensure the evenness of starting materials, then 10 mmol solid sodium dodecyl sulfate (SDS) were added. After the mixture was ground for 5 min, 40 mmol of solid NaOH were added into the mixture and grounded for 40 min. At this point, the solid state chemical reaction between metal salts and NaOH was accomplished and the solid precursor that is insoluble in water was obtained. Finally, the mixture including the insoluble precursor, the soluble by-products and SDS were washed with distilled water and alcohol in ultrasonic bath for some times to obtain the pure precursor. After drying at room temperature in air, the as-synthesized precursor was annealed at 300 °C for 40 min, then the final Y-doped ZnO nanoparticles were fabricated. Pure ZnO nanoparticles were synthesized by a similar process as described above, except for the addition of $Y(NO_3)_3 \cdot 6H_2O$ into the agate mortar as the starting materials.

2.2. Characterization

The phase structure and purity were characterized by X-ray diffraction (XRD), with filtered Cu Kα radiation (Bruker D8). The photoluminescence (PL) measurements were carried out using the excitation of Xe Lamp (Hitachi F4500, wavelength 325 nm). Energy disperse X-ray spectrum (EDS) was examined on an energy disperse X-ray spectroscope (Oxford 2000). The morphology of the obtained samples was investigated using field emission scanning electronic microscopy (FESEM Hitachi S-4800, at 5 kV) and transmission electron microscopy (TEM Hitachi H-600, at 75 kV). The gas-sensing properties of pure and Y-doped ZnO sensors were measured using a WS-30A gas sensing measurement system (Wei Sheng Electronics Science and Technology Co., Ltd., Henan Province, China).

2.3. Gas sensor fabrication and measurements

The fabrication of ZnO gas-sensitive materials were similar to previous reports [26,27]. First, the as-obtained ZnO powders were mixed and grounded with ethanol in an agate mortar to form a gas-sensing paste. Then the paste used as a sensitive body was coated on an alumina tube with Au electrodes and platinum wires. Finally, a Ni–Cr heating wire was inserted into the alumina ceramic tube to supply the operating temperature. To improve the stability and repeatability, the sensors were aged at 300 °C for 5 days in air. The gas-sensing properties were examined in a chamber (18,000 cm^3). The resistance of the sensor was measured using a conventional circuit, in which the element was connected with an external resistor in series at a circuit voltage of 5 V. The relative humidity during the test process is 10–25%. The response of the gas sensor in this work was defined as Response=R_a/R_g, where R_a and R_g are the resistance of the sensor in air and the testing gas atmosphere, respectively. The response or recovery time was expressed as the time taken for the sensor output of reach 90% of its saturation after applying or switching off the gas in a step function.

3. Results and discussion

3.1. The structural characterization of products

Fig. 1(a) shows the XRD patterns of the as-prepared pure and 1 at% Y-doped ZnO products. It indicates that all the diffraction peaks could be indexed from the hexagonal wurtzite structure ZnO according to the standard JCPDF (No. 36-1345). It is noticed that the intensity of characteristic diffraction peaks

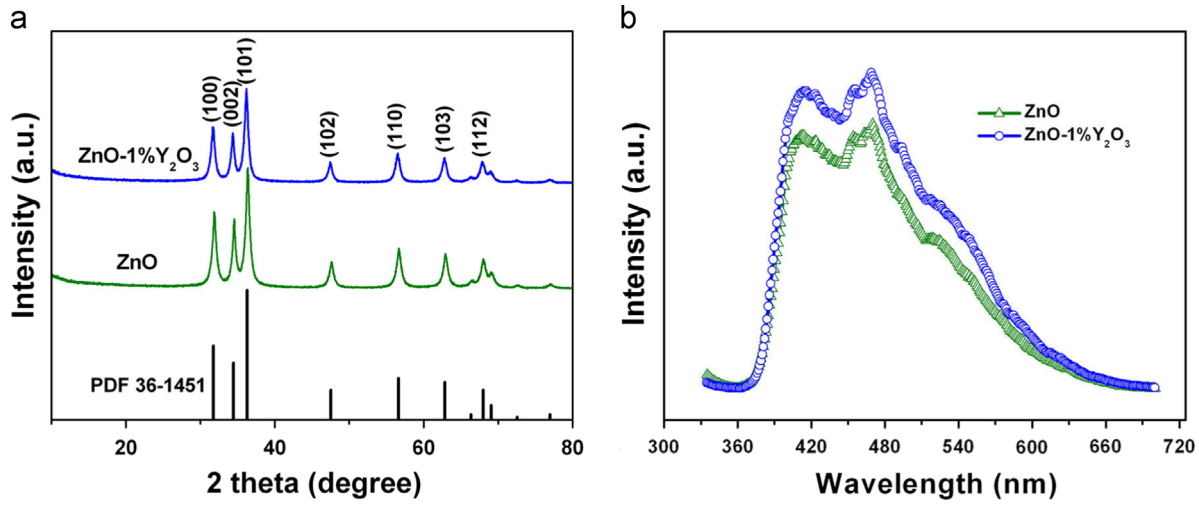

Fig. 1. XRD patterns (a) and PL spectrum (b) of pure ZnO and 1 at% Y-doped ZnO nanoparticles.