Physica E 54 (2013) 313–318

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

Synthesis of multifarious hierarchical flower-like SnO_2 and their gas-sensing properties

Wen Zeng [a,b,*], Qiongyao He [a], Kangguan Pan [a], Yang Wang [a]

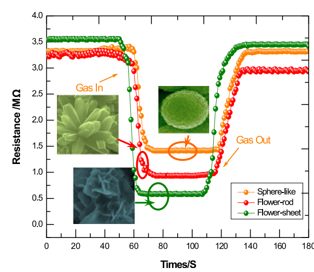
[a] College of Materials Science and Engineering, Chongqing University, Chongqing 400030, China
[b] State Key Laboratory of Power Transmission Equipment and System Security and New Technology, Chongqing University, Chongqing 400030, China

HIGHLIGHTS

- The flower-sheet SnO_2 sensor displayed particular response to the target gas.
- Property improvement is independent of operating temperature and gas concentration.
- Enhanced key gas sensing property meets basic needs for practical applications.
- Sensing properties of nanocrystals can be improved by tailoring their shape and structure.

GRAPHICAL ABSTRACT

The flower-sheet SnO_2 sensor displayed particular response to the target gas, rendering SnO_2 as a potential gas-sensing material for a broad range of future sensor applications.



ARTICLE INFO

Article history:
Received 5 February 2013
Received in revised form
17 July 2013
Accepted 23 July 2013
Available online 2 August 2013

Keywords:
Hydrothermal process
SnO_2
Nanostructure
Gas-sensing

ABSTRACT

We successfully synthesized variant hierarchical assembled flower-like SnO_2 via a simple hydrothermal technique and subsequent calcination. The structures and morphologies of the 3D nanostructures were investigated by means of powder X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM). The formation mechanism of these materials were proposed in detail. The gas-sensing performances of the as-prepared SnO_2 were investigated towards ethanol. It is noted that the flower-sheet SnO_2 sensor displayed particular response to the target gas, rendering SnO_2 as a potential gas-sensing material for a broad range of future sensor applications.

1. Introduction

Tin oxides (SnO_2), an important functional material with a wide direct band gap (E_g=3.6 eV) has attracted vast interests due to its physical and chemical properties [1], and its tremendous potential applications in the field of catalysts [2], solar cell [3,4], optoelectronic devices [1,5], electrode materials [6] and gas sensors [7–9]. Moreover, SnO_2 is one of the promising candidates for gas sensing properties because of its high sensitivity and selectivity to different gases, for instance, H_2S [10], H_2, [11], C_2H_5OH [12–14], CO [15], and volatile organic compounds (VOC) [16]. In general, most of the applications, including many of its excellent intrinsic properties, depend critically on its specific structure and morphology [17]. Thus, it is of great interest to design and fabricate SnO_2 nanostructures with novel morphologies [18].

Recently, in order to enhance the multi-functionality and tailor esthetic morphologies, great interests have been focused on the synthesis of SnO_2 complex nanoarchitectures. Particularly, 3D hierarchical architectures that are assembled using 1D and 2D

* Corresponding author at: College of Materials Science and Engineering, Chongqing University, Chongqing 400030, China. Tel.: +86 23 65 102 465.
E-mail addresses: wenzeng@cqu.edu.cn, zeng_wen1982@yahoo.com.cn (W. Zeng).

1386-9477/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physe.2013.07.014

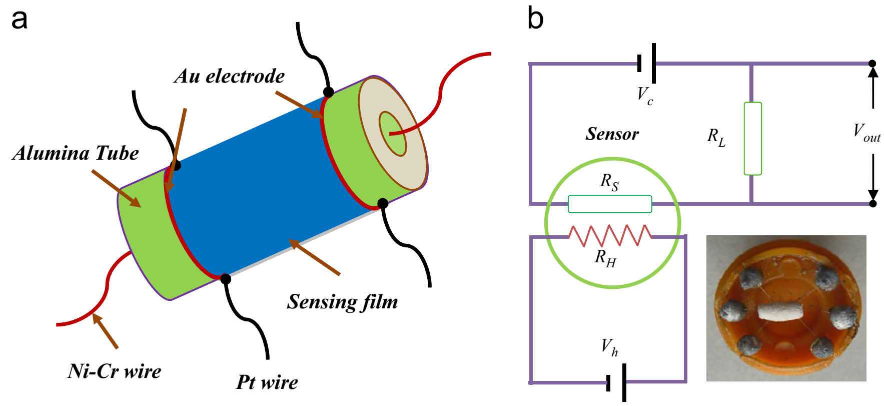


Fig. 1. (a) Schematic of the gas sensor configuration. (b) The electric circuit which was used to test the gas-sensing properties.

nanoscale building blocks. Up to now, numerous types of 3D hierarchical nanostructures have been designed and synthesized in current reports such as highly oriented straight SnO_2 nanowire arrays [19], SnO_2 hierarchical nanostructures, and flowerlike SnO_2 nanorod bundles [20]. Various routes, such as the thermal evaporation technique [21], the sol–gel method [22,23], chemical vapor deposition (CVD) [24] and so forth have been employed successfully to assemble building blocks into 3D ordered superstructures. Among them, the hydrothermal method provides a mild condition with low cost and effective way for the preparation of SnO_2 nanocrystals which have a narrow size distribution, little or no micro-agglomeration, well crystallization and phase homogeneity [25]. Besides, hydrothermal treatments present a positive effect in enhancing thermal stability and gas response [26].

Flower-like morphology, as a special three-dimensional structure, has been paid much attention in the recent years because of its good performance in gas sensing properties [27]. Herein, flower-rod, flower-sheet and sphere-like morphologies of SnO_2 nanostructures were successfully synthesized via a simple hydrothermal technique. Furthermore, the crystal structure, morphologies, growth mechanism are elaborated, and their ethanol sensing properties are also investigated. We found that the unique 3D flower-sheet SnO_2 nanostructures showed the best sensing properties to ethanol owing to the largest specific surface area.

2. Experimental

2.1. Synthesis of SnO_2 flower-sheets and nanospheres

All chemicals are analytical-grade reagents from Chongqing Chuandong Chemical Reagent Co., Ltd. and are used without any further purification. The SnO_2 with desirable nanostructures was fabricated via the hydrothermal process. Typically, $SnCl_2 \cdot 2H_2O$ (4 mM), $Na_3C_6H_5O_7 \cdot 2H_2O$ (14 mM) were dissolved into a basic ethanol–water solution completely. Then 0.1 g NaOH was added and continuously stirred for 10 min. After that, the mixtures were transferred into a Teflon-lined stainless steel autoclave, and then heated in an oven at 180 °C for 12 h. After cooling to room temperature naturally, the product was collected by centrifugation and washed several times with distilled water and absolute ethanol, subsequently. A yellow precipitate was harvested by centrifugation and dried at 60 °C overnight. Finally, the sample was sintered at 400 °C for 2 h.

2.2. Synthesis of SnO_2 flower-rod and nanosphere

In a typical hydrothermal process, $SnCl_4 \cdot 5H_2O$(0.45 g), NaOH (0.4 g) were dissolved into 40 ml basic mixture of ethanol and water (1/1, V/V) completely. Next, 0.08 g citric acid was dissolved into the mixture solution. Afterwards, the solution was transferred into a Teflon-lined stainless steel autoclave and maintained at 190 °C for 24 h. Finally, the product was collected by centrifugation, washed with distilled water and ethanol for several times, and finally dried at 60 °C overnight. SnO_2 nanospheres were obtained in the same process except that citric acid was added.

2.3. Structure characterization

The phase structure and phase purity of the as prepared samples were characterized by X-ray diffraction (XRD) using a Rigaku D/Max-1200X diffractometer with CuKα radiation (30 kV, 100 mA). The morphology of the obtained products was investigated using a Nova 400 Nano field emission scanning electronic microscopy (FE-SEM).

2.4. Gas-sensing property characterization

The gas sensors were fabricated by first dispersing the mixed powders with ethanol to form pastes. The pastes were subsequently coated onto an alumina ceramic tube to form a thin layer of sensing film (thickness about 10–20 μm), positioned with a pair of Au electrodes at each end point. After drying at 400 °C for 2 h in air, a Ni–Cr heating wire was inserted into the alumina tube to control the operating temperature by tuning the heating voltage. The structure and photograph of the sensor are shown in Fig. 1.The gas sensors were finally aged at 240 °C for 72 h to improve stability and repeatability.

The gas sensing properties of the samples were conducted using a HW-30A gas sensitivity instrument (Hanwei Electronics Co. Ltd., PR China). The gas was introduced by injecting a given amount of target gas into the glass chamber. The operating temperature of the sensor could be adjusted via varying the heating voltage (V_h). The resistance (R) of the gas sensor was estimated from $R=R_L(V_c-V_{out})/V_{out}$, where V_c and V_{out} were the circuit and output voltage, respectively. In this paper, we described the sensitivity as gas response (S), which was defined as $S=R_g/R_a$, where R_a and R_g were resistances of the sensors in air and ethanol vapor, respectively. And the response and recovery time are counted as the time taken by the sensor to reach 90% of the total resistance change in the case of adsorption and desorption, respectively.

3. Results and discussion

3.1. Structural and morphological characterization

The phase and purity of the products were identified by X-ray powder diffraction (XRD) measurement. Fig. 2 illustrates the