



Superior ethanol-sensing properties based on Ni-doped SnO₂ p–n heterojunction hollow spheres

Yuejiao Chen, Ling Yu, Dandan Feng, Ming Zhuo, Ming Zhang, Endi Zhang, Zhi Xu, Qihong Li*, Taihong Wang*

Key Laboratory for Micro-Nano Optoelectronic Devices of Ministry of Education, and State Key Laboratory for Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, China

ARTICLE INFO

Article history:

Received 16 September 2011
Received in revised form 5 December 2011
Accepted 8 December 2011
Available online 17 December 2011

Keywords:

Ni-doped SnO₂
p–n heterojunction
Ethanol sensor
Enhanced response

ABSTRACT

This paper reported a novel sensing material of porous Ni-doped SnO₂ hollow spheres with nanoheterostructures, which were synthesized by a low-cost and environment-friendly hydrothermal strategy. In the process of synthesis, long-chain polymers nickel nitrilotriacetic acid (NiNTA) were formed previously and then successfully heteroconnected with SnO₂ through a series of hydrothermal reactions for the reason that nitrilotriacetic acid (NTA) could be dissolved in the aqueous solution of NaSnO₃, leading to the complete change of previous morphology. The response of the sensor based on porous Ni-doped SnO₂ hollow spheres is up to 59 at 100 ppm ethanol and the detection limit can be dropped to 1 ppm-level, which exhibits enhanced response compared with many ethanol sensors based on pure SnO₂ hollow spheres. Such good performance is probably attributed to the formation of p–n junctions between NiO and SnO₂, which increase the resistance of sensor and the depletion layers.

© 2012 Published by Elsevier B.V.

1. Introduction

Metal-oxide semiconductor gas sensors have attracted much attention for their diverse applications in air-quality control, toxic gas detection, environment monitoring, medicine diagnosis, optimization of combustion efficiency and so on [1–4]. Until now, a number of gas sensors based on SnO₂ [5], TiO₂ [6], ZnO [7], and Fe₂O₃ [8] have been successfully obtained. As one of most representative sensor materials, SnO₂ has been prepared as kinds of nanostructures to utilize its excellent chemical and electrical properties. Gas sensor is generally characterized by its response, response-recovery time and selectivity [9], among which the response weighs a lot because a higher response usually means a significant ability for gas detection at lower concentration level. Therefore, many efforts have been concentrated on the improvement of response towards different gases.

It is well-known that the gas sensing characteristics are greatly dependent on its morphology and structure, such as porosity, grain size, surface-to-volume ratio and shape. Based on above traits, many previous papers have reported various types of SnO₂ nano-materials, such as nanorods [10], nanotubes [11], and nanobelts

[12]. These unique structures play an important role in improving gas sensing performance. However, it should be noticed that besides the structure characterization, doping has already been proved to be another effective route to improve the sensitivity of SnO₂ to reducing gas. Recently, many materials, such as noble metals (Pt, Pd, and Ag) [13–15], rare earth metals [16], and other metals (Cu, Zn, and Co) [17–19] have been introduced to SnO₂, which can result in the formation of p–n junctions or generate catalytic activity for the enhancement of the sensitivity. The high cost limits their potential for practical application although noble metals additives have been proved to be a very effective dopant. Therefore, it is necessary to investigate an economic substitute to enhance the sensing performance as well as decrease the cost of sensor materials.

In this paper, we have successfully prepared the Ni-doped SnO₂ porous hollow spheres and systematically examined their gas sensing performances. NiO can be implanted into SnO₂ via dissolution of the pre-synthesized NiNTA in aqueous solution of NaSnO₃ under hydrothermal condition. A possible sensing mechanism is also proposed for the Ni-doped SnO₂ based sensor, on the basis of the fact that NiO is a p-type semiconductor and can easily form heterojunctions with SnO₂. The doped NiO increases the sensor resistance and the depletion layers height, thus can enhance the response of pure SnO₂ based sensor on ethanol. Gas-sensing tests demonstrate that the Ni-doped SnO₂ porous hollow spheres have potential application in detecting ethanol.

* Corresponding authors. Tel.: +86 0731 88823407; fax: +86 0731 88823407.
E-mail addresses: liqihong2004@hotmail.com (Q. Li), thwang@hnu.edu.cn (T. Wang).

2. Experimental

2.1. Synthesis

2.1.1. Synthesis of $(-Ni-NTA)_n$ nanorods

The $(-Ni-NTA)_n$ precursors of nanorods [20] were presynthesized by a hydrothermal method. In a typical synthesis, 6 mmol $NiCl_2 \cdot 6H_2O$ was firstly dissolved in the mixed solution of 20 mL distilled water and 20 mL ethanol to form a green solution. Then 2 mmol nitrilotriacetic acid (NTA) was added to the above solution under magnetic stirring for 30 min. After that, the mixture was transferred into a 50 mL Teflon lined steel autoclave and maintained at 160 °C for 24 h. Finally, the resultant green precipitate was collected by centrifugation, and washed with deionized water and absolute ethanol several times, and dried at 60 °C for 12 h to gain $(-Ni-NTA)_n$ nanorods.

2.1.2. Preparation of Ni-doped SnO_2 porous hollow spheres

In a typical procedure, 1 mmol of $Na_2SnO_3 \cdot 3H_2O$ was firstly dissolved in 40 mL mixed solution of ethanol and water with equal volumes under magnetic stirring for 10 min. Next, 0.075 g of the $(-Ni-NTA)_n$ precursors was added to the above solution with stirring for 20 min. Then, the above mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave and maintained at 200 °C for 24 h. Finally, the precipitate was centrifuged and thoroughly washed with deionized water and ethanol before drying in air at 70 °C. The Ni-doped SnO_2 mesoporous hollow spheres were obtained after the above products were annealed at 400 °C for 4 h. For comparison, pristine SnO_2 hollow spheres were synthesized following the same procedure without the addition of the $(-Ni-NTA)_n$ precursors.

2.2. Characterization

The crystal structure of samples was characterized by X-ray diffraction (XRD, Siemens D-5000) with $Cu K\alpha$ ($\lambda = 1.5418 \text{ \AA}$). The morphology of the synthesized samples was examined using a field-emission scanning electron microscope (SEM) [Hitachi S-4800]. Measurement of specific surface area and analysis of porosity for the Ni-doped hollow SnO_2 spheres were performed through measuring Nitrogen adsorption-desorption isotherms with a Micromeritics ASAP2020 apparatus (Autosorb-1C/TCD, USA).

2.3. Sensor performance measurement

The preparation and testing principle of the gas sensor are similar to that depicted in our previous report [21]. Firstly, The Ni-doped SnO_2 sample was dispersed into an adhesive terpeneol to form a paste and then coated onto the outside surface of an alumina tube. A Ni-Cr alloy coil crossed tube was employed as a heater by tuning the heating voltage which is equivalent to the operating temperature. To improve their stability and repeatability, the gas sensors were sintered at 300 °C for 10 days in air. The working principle is shown in Fig. 1. A load resistor was connected in series with a gas sensor. The circuit voltage (V_c) was set at 5 V and the sensor signal voltage (V_{out}) was collected by a computer. The working temperature was adjusted through varying the heating voltage (V_h). The resistance of a sensor in air or test gas was measured by monitoring V_{out} . The ethanol vapour was injected into the test chamber. The sensor response (S) is defined as $S = R_a/R_g$, where R_a is the sensor resistance in air and R_g the resistance in the test gas. The response and recovery time was the time needed for the sensor-resistance to change by 90% of the difference from the maximum after injecting and removing the detected gas.

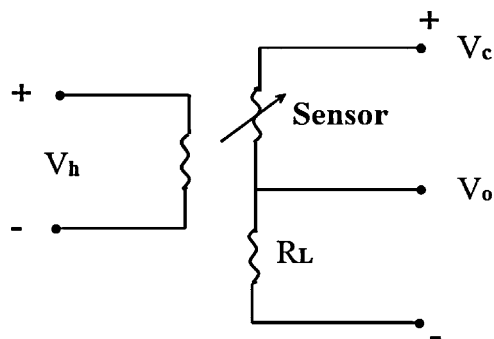


Fig. 1. Working principle of the gas sensing test (V_h : heating voltage, V_c : circuit voltage, V_o : signal voltage and R_L : load resistance).

3. Results and discussion

3.1. Morphology and structure

Fig. 2 presents the typical scanning electron microscopy images of the products at various reaction stages. A low magnification image of the $(-Ni-NTA)_n$ precursor nanorods is shown in Fig. 2a, clearly demonstrating that the precursors are entirely consisted of nanorods with a smooth surface. After heat-treating, the NiNTA precursor nanorods exhibit highly loose and porous microstructure which can be attributed to the formation of long-chain polymers during hydrothermal reaction and a removal of NTA after annealing, as shown in the inset of Fig. 2b. After the NiNTA precursors were dissolved in aqueous solution of $NaSnO_3$ under the hydrothermal conditions, the nanorods microstructure disappeared and formed a spherical structure as shown in Fig. 2c. It displays the SEM images of as-synthesized materials after the calcination at low magnification. The spheres are porous and hollow as shown by the magnified figure of a broken sphere (inset in Fig. 2b). Fig. 2d clearly displays large quantities of Ni-doped SnO_2 porous spheres which are agglomerated loosely by small nanoparticles whose diameters are estimated to be between 20 nm and 30 nm. Fig. 2d is the EDS spectrum of the sample, in which the peak of Ni can be clearly observed. According to the results of the EDS analysis (inset in Fig. 2d), the atomic ratio of Ni/Sn in the spheres is estimated to be 7.6 mol%.

Fig. 3 shows the XRD pattern of the as-prepared Ni-doped SnO_2 porous hollow spheres. All diffraction peaks are indexed to the tetragonal rutile structure of SnO_2 , which agree well with the reported values from JCPDS card (41-1445). However, there are no characteristic peaks pertaining to NiO, which is probably due to the low content of Ni-dopant (7.6 mol% by EDS spectrum). These results are similar to those reported in some other publications [22–24]. Moreover, it is known that NiO additives segregate on the surface of SnO_2 rather than become incorporated into the SnO_2 lattice when the addition is up to 30 mol% [25]. The above indicates that Ni should get incorporated in SnO_2 hollow spheres lattice.

The product calcined at 400 °C was further characterized by nitrogen sorption and desorption isotherms and corresponding pore size distribution (inset) is shown in Fig. 4. It is found that the Ni-doped SnO_2 hollow nanostructures have a BET surface area of $83.15 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.226 \text{ cm}^3 \text{ g}^{-1}$. The pore size distribution of the sample shows that a narrow peak appears in pore size region of 3–7 nm and its top value is located at 5.0 nm. It clearly indicates that the Ni-doped SnO_2 hollow sample exhibits a high specific surface areas and a large textural porosity which might be advantageous for gas sensing applications.

3.2. Possible mechanism of formation

Fig. 5 displays a possible synthesis mechanism to explain the formation of porous Ni-doped SnO_2 hollow spheres. Initially, Ni^{2+} ions

Download English Version:

<https://daneshyari.com/en/article/742550>

Download Persian Version:

<https://daneshyari.com/article/742550>

[Daneshyari.com](https://daneshyari.com)