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Research paper

Hierarchical porous ZnO microflowers with ultra-high ethanol gas-sensing at low concentration

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ABSTRACT

Hierarchical porous and non-porous ZnO microflowers have been successfully fabricated by hydrothermal method. Their crystal structure, morphology and gas-sensing properties were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and chemical gas sensing intelligent analysis system (CGS). Compared with hierarchical non-porous ZnO microflowers, hierarchical porous ZnO microflowers exhibited ultra-high sensitivity with 50 ppm ethanol at 260 °C and the response is 110, which is 1.8 times higher than that of non-porous ZnO microflowers. Moreover, the lowest concentration limit of hierarchical porous ZnO microflowers (non-porous ZnO microflowers) to ethanol is 0.1 (1) ppm, the response value is 1.6 (1).

1.Introduction

Ethanol, as a kind of renewable energy sources, has been extensively applied in the fields of national defence industry, health care, organic synthesis, food processing, energy industry. However, ethanol will become a toxic gas when its concentration goes beyond the limit value. It will make an adverse impact on human health and air quality of our environment. So, it is necessary to make a kind of ethanol gas sensor to monitor low concentrations of ethanol.

In recent years, a variety of investigations of ethanol gas sensors has been finished in order to avoid danger happened, such as In_2O_3 gas sensor [1,2], Fe_2O_3 gas sensor [3,4], SnO_2 gas sensor [5,6] and ZnO gas sensor [7,8]. Among them, ZnO gas sensor, as a sort of vitally important n-type metal oxide semiconductor, has attracted much attention due to its easy fabrication and low cost. However, the low-dimensional non-porous ZnO micro- and nanostructures have lots of drawbacks, such as weak selectivity, low sensitivity and high working temperature. Consequently, many methods of synthesising hierarchical porous ZnO micro- and nanostructures were executed to improve gas sensing properties. For example, biotemplate method [9], hydrothermal method [10], wet-chemical method [11] and flame method [12]. Hierarchical ZnO structure has been widely applied in lithium – ion batteries [13], solar cell [14], supercapacitor [15] and gas sensor [16], especially in gas sensor. Meanwhile, lots of modifications of hierarchical ZnO structure has been researched, such as noble metal decoration [17–19] , fabrication of metal oxide heterostructures [20–22] and synthesis of 2D materials [23–25]. However, there are little reports about large pore density and rather high gas sensitivity of flower-like ZnO obtained by a simple hydrothermal method. Therefore, we obtained hierarchical porous ZnO microflowers with many pores on the surface of material. And the as-prepared sample shows very high gas sensitivity to ethanol at low concentration.

In this work, we systemically synthesized the hierarchical porous ZnO microflowers by simple hydrothermal method and compared its gas-sensing properties with hierarchical non-porous ZnO microflowers. The experiment results indicate the hierarchical porous ZnO microflowers have ultrahigh sensitivity, wonderful selectivity and rapid response and better recovery time to ethanol than hierarchical non-porous ZnO microflowers. This novel hierarchical porous structure provides much effective reactive sites and is good for contacting between the target gas and materials, which can immensely enhance the gas-sensing properties of the materials.

2.Experimental

2.1. Product synthesis

All chemical reagents in the experiment were of analysis grade and were used without further purification. Zn $(NO_3)_2{\cdot}6H_2O$ and

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$C_6H_5Na_3O_7{\cdot}2H_2O$ were obtained from Sinopharm Chemical Reagent Co. Ltd, CO $(NH_2)_2$ was purchased from Sigma-Aldrich. Briefly, 1.0 g Zn $(NO_3)_2{\cdot}6H_2O$, 0.3301 g CO $(NH_2)_2$ and 0.189 g $C_6H_5Na_3O_7{\cdot}2H_2O$ were dissolved into 90 ml distilled water to form a uniform solution under stirring for 1 h. Then the as-prepared solution was transferred into a Teflon-lined stainless steel autoclave (100 ml) where it was heated to 130 °C and maintained for 4 h. Then the precipitates were synthesized after cooling down to environment temperature. And the as-obtained samples were thoroughly washed with distilled water and ethanol several times to eliminate impurity, and dried in a vacuum at 70 °C. Finally, the target products were calcinated in a muffle furnace at 350 °C and 400 °C for 5 h. As a result, the hierarchical porous ZnO microflowers and non-porous ZnO microflowers were synthesized. The process for synthesis of hierarchical porous ZnO microflowers is presented in Fig. 1.

2.2. Characterization

X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.15418 Å) was used to analyze the structures of hierarchical porous ZnO microflowers. The Scanning electron microscopy (SEM) images were recorded using SSX-550 (Japan) instrument to investigate morphology of the obtained products. Transmission electron microscope (TEM) pictures were performed on a JEM – 2200Fs (Japan). Thermogravimetric analysis (TGA) was obtained on Perkin Elmer Pyris 1 TGA analyzer. Gas-sensing performance was measured with a CGS8 (chemical gas - sensing) intelligent analysis system (Beijing Elite Tech. Co. Ltd, China).

2.3. Fabrication of sensor

The fabrication process and the structure mode of gas sensor are described as follows: the as-prepared hierarchical porous ZnO microflowers powder was mixed with a certain volume of deionized water to form a paste. Later on, the paste was coated on a ceramic tube with a couple of Pt wires positioned with a pair of gold electrodes. Then a Ni-Cr alloy was inserted into a ceramic tube as a heater to reach the operating temperature. The sensor response for n-type semiconductor was defined as S = Ra/Rg, where Ra and Rg are resistance in dried air and in target gas, respectively [26,27] (see Fig. 2).

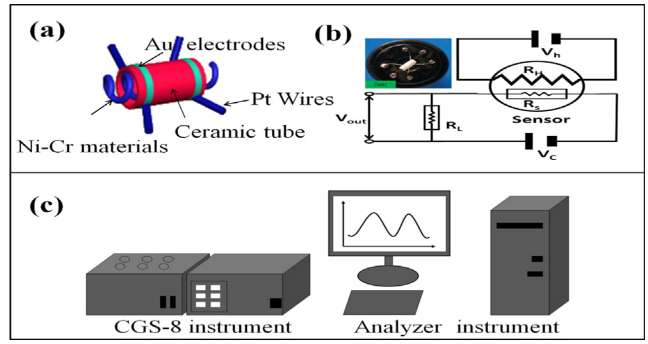

Fig. 2. (a) The design of device sensor structure; (b) circuit diagram; (c) gas sensing test instrument.

3. Results and discussion

3.1. Structure and morphology

Fig. 3 shows the XRD patterns of hierarchical ZnO microflowers at different calcination temperatures in air for 5 h. The crystal planes are (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), and (1 0 3). From this picture, it can be easily observed that all crystal planes are completely consistent with the standard ZnO simple (JCPDS card and no. 36-1451). In addition, no other impurities peaks were detected in this picture, which indicated that the hierarchical porous ZnO microflowers were of high purity [28]. And a series of strong and sharp peaks demonstrates that the as-obtained product possesses good crystallinity [29]. Meanwhile, the XRD patterns of hierarchical ZnO microflowers calcined at different temperatures (350–600 °C) are rigorously analyzed. It is indicated that the intensities of peaks increasing during the annealing temperature is increased. This phenomenon is mainly due to the growth of crystalline grain and the increase of crystallization. The above observation illustrates that the crystallite size will be increase with the calcination temperature increases.

The morphology of hierarchical non-porous and porous ZnO microflowers was characterized by SEM. Fig. 4a–b displays a SEM image of hierarchical porous ZnO microflowers. From Fig. 4a, it is obviously seen that as-prepared product has good uniformity. As shown in Fig. 4D, the ZnO microflowers are composed of ultrathin nanosheets; we can seen that the surface of nanosheet exhibited

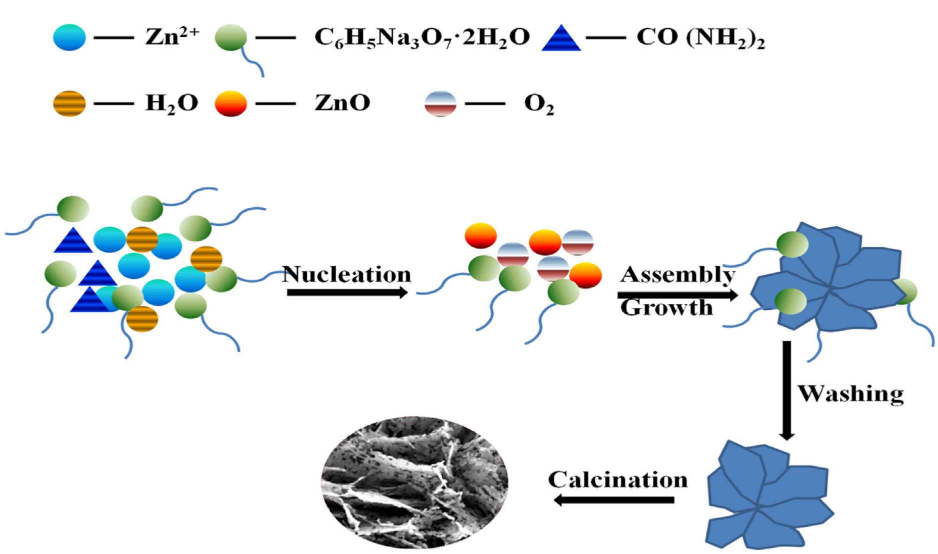

Fig. 1. A scheme illustrating the process and growth mechanism for synthesis of hierarchical porous ZnO microflowers.