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Flower-like ZnO hollow microspheres loaded with CdO nanoparticles as high performance sensing material for gas sensors

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ABSTRACT

CdO decorated flower-like ZnO hollow microspheres were successfully prepared via a two-step hydrothermal strategy. CdO nanoparticles (~12 nm) equably loaded on the surfaces of ZnO nanosheets, which could be clearly observed from SEM and TEM images. The results of X-ray photoelectron spectroscopy and H_2 temperature-programmed reduction (H_2-TPR) indicated that the amount of chemisorbed oxygen was increased after the introduction of CdO nanoparticles. Compared with the flower-like ZnO hollow microspheres, the 2.6 mol% CdO:ZnO heterostructure composites exhibited highest response (65.5) to 100 ppm ethanol at 250 °C, which was about 16 folder higher than that of pure ZnO at the same operating temperature of 250 °C. Significantly, the detection limit of the 2.6 mol% CdO:ZnO heterostructure could reach ppb level (500 ppb). The mechanism of the enhanced ethanol sensing was also discussed systematically.

1. Introduction

Up to now, the research of gas sensors has attracted continually increasing interest because of their extensive applications [1–3]. Among the various types of gas sensors, the semiconductor oxides sensors hold a central position due to their low cost, high sensitivity, simplify in fabrication and compatibility with modern electronic devises [4,5]. It is known to all that the fundamental operating mechanism is the remarkable resistance change caused by the surface reaction upon exposure to different gas ambients. Consequently, for the purpose of improving the gas sensing properties, various effective approaches have been centered on the design of the semiconductor oxides with excellent sensing performance and numerous results have demonstrated that the sensing performance of metal semiconductors oxide is not only highly dependent on their microstructures [6,7], but also related to their further functionalization with metal elements [8–11], heterogeneous oxide [12,13], and so on. To date, among these strategies, expanding the sensing materials from single component metal semiconductor oxide to multicomponent heterostruture has become more and more fascinating, such as ZnO/SnO_2 [14], α-Fe_2O_3/ZnO [15], NiO/ZnO [16], α-Fe_2O_3/SnO_2 [17], CdO/In_2O_3 [18], and CuO/ZnO [19] have been successfully prepared and have indeed improved the sensing properties, because they are supposed to integrate the physical and chemical properties of their individual component. The constant need for gas sensors with high sensitivity, low operating temperature, and good stability continues to stimulate the progress of gas sensing. Therefore, it is very important to make efforts in the rational design and synthesis of new-type composites.

As an important n-type semiconductor with wide band-gap of ~3.4 eV, ZnO has been regarded as the most potential sensing material because it has response to the target gases and easily for synthesizing [20]. It is found that hierarchical structure, as a higher dimension of micro- and nanostructures assembled from low dimensional blocks, has been used to improve sensitivity of ZnO [21,22]. However, the pure ZnO as sensing material still has the following problems: low response, worse selectivity and high operating temperature. Consequently, in order to further improve the gas sensing properties of pure ZnO nanostructure, heterostructure formation between ZnO and other oxide semiconductors has been developed [16,19]. Cadmium oxide (CdO), as a n-type semi-

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conductor oxide with a narrow band gap of ~2.4 eV [23] has the following advantages: high carrier mobility and high conductivity (103 Ω^{-1} cm^{-1}), due to its native defects of oxygen vacancies in the lattice [23–26]. Recently, some studies have demonstrated that combining ZnO with CdO could improve gas sensing properties compared with single component of oxide. For example, Kim et al. [27] have synthesized ZnO/CdO core/shell nanorod arrays via three kinds of method, which demonstrated a high sensitivity towards ethanol at high operating temperature. Ban et al. [28] have manifested CdO nanoflake arrays on ZnO nanorods arrays was a promising gas sensing material for detection of diethyl ether. Although some studies have reported on CdO/ZnO composites gas sensors, there is no report on 3D ZnO hierarchical structure decorated by 0D CdO nanoparticles. The distinct feature of this kind of heterostructur is highly advantageous for gas sensors due to the synergistic integration of the merits of individual components and the formation of heterostructure. In addition, this kind of heterostructur can maintain a well-dispersed configuration after decorating nanoparticles, which is a favorable structure for facile gas permeation and results in both of them are highly accessible for gas detection [29,30].

Inspired by these, we present a strategy for the preparation of CdO-decorated flower-like ZnO hollow microspheres composites. First, the flower-like ZnO hollow microspheres were prepared via a hydrothermal route. After that, CdO nanoparticles with a diameter of ~12 nm were decorated on the surfaces of ZnO nanosheets by hydrothermal process. Furthermore, nanoparticles are well-distributed on the ZnO hollow spheres. A systematically comparative gas sensing investigation between the pure ZnO and CdO/ZnO hollow microspheres composites was performed. These results indicated that the CdO/ZnO hollow microspheres composites with a Cd:Zn molar ratio of 2.6:100 showed the highest response to ethanol, which was nearly ~16 fold higher than that of pure ZnO at 250 °C. The dramatic improvement in gas sensing properties may be attributed to the change of the n-n heterojunction barrier height at the different gas atmospheres and the synergetic effect between CdO and ZnO.

2. Experimental

2.1. Materials synthesis

2.1.1. Preparation of the flower-like ZnO hollow microspheres

All the reagents were analytical grade and were used as received without further purification. The flower-like ZnO hollow microspheres were synthesized by facile one-step hydrothermal route. First, 0.439 g of $Zn(CH_3COO)_2{\cdot}2H_2O$, 0.4 g of glycine and 0.4 g of $Na_2SO_4{\cdot}10H_2O$ were completely dissolved into a mixture of 15 mL of deionized water and 10 mL of ethanol at the same time, under vigorous stirring for 5 min. Then 0.4 g of NaOH was added into the prepared solution with magnetic stirring for about 1 h. Afterward the mixed solution was transferred into a 45 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. After the autoclave cooled naturally down to room temperature, the precipitates were collected by centrifugation, washed several times with distilled water and absolute ethanol respectively, and dried in air at 80 °C for 12 h, and calcined at 400 °C for 2 h.

2.1.2. Synthesis of the CdO/ZnO heterostructure composites

A series of 0, 0.4, 0.9, 2.6, 4.4 mol% CdO:ZnO heterostructure composites (the molar percentage was defined as the ratio of the moles of CdO to that of ZnO) were also synthesized via a simple hydrothermal method, which can be described briefly as follows: First, 30 mg of the obtained ZnO powders mentioned above were dispersed in 30 mL of DMF under continuous magnetic stirring to form a homogeneous solution. Then a certain amounts of $Cd(NO_3)_2{\cdot}4H_2O$ and CH_4N_2S were added into the prepared homogeneous solution with stirring for 10 min. Afterwards, 300 μL of isopropanol was added into the solution, which was stirred for 10 min and ultrasonicated for 30 min. After that the solution was transferred into a 45 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 10 h, followed by cooling to room temperature naturally. The pre-synthesized precipitates were centrifuged and rinsed several times with deionized water and ethanol alternately, and dried in air at 60 °C for 10 h. Finally, the as-prepared precursors were annealed under an air atmosphere at a temperature of 500 °C for 3 h in an electronic oven with a temperature ramp of 1 °C min^{-1} to convert CdS to CdO.

2.2. Materials characterization

Crystallinity and composition of the final samples were identified by X-ray powder diffraction (XRD) (Rigaku D/Max–2550 V X-ray diffractometer) using high-intensity Cu Kα radiation (λ = 1.5403 Å) in the range of 20°–70° (2θ) with a scanning speed of 2° min^{-1}. The morphology and microstructure of the products were directly observed by field-emission scanning electron microscopy (FESEM JEOL JSM-7500F, operated at an accelerating voltage of 15 kV). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were recorded on a JEOL JSM-2100F operating at an accelerating voltage of 200 kV. X-ray spectrometry (EDS) pattern were also observed through the attachment of TEM. The X-ray photoelectron spectroscopy (XPS) measurements were performed with Al Kα X ray source. The XPS Peak 4.1 software was used to fit peaks in the XPS spectra. The H_2 temperature-programmed reduction (H_2-TPR) was investigated by employing 100 mg sample in each measurement. The samples were firstly pretreated by Ar at 300 °C for 30 min, then cooled down to room temperature, and followed by turning the flow of 10% H_2/Ar into the system with a flow rate of 30 mL/min. The samples were heated from room temperature to 750 °C at a rate of 10 °C/min.

2.3. Fabrication and measurement of the gas sensor

The schematic of the fabricated gas sensor was shown in Fig. S1 and the fabrication process of the sensor device could be described as follows: First, an appropriate amount of the pure ZnO and CdO/ZnO hollow microspheres composites samples were thoroughly mixed with deionized water in a motor to form the homogeneous paste. Then, the paste was coated onto an alumina tube (external diameter: 1.2 mm, internal diameter: 0.8 mm, and length: 4 mm; a couple of Au electrodes were previously printed on the end of the tube, and each electrode was connected with a pair of Pt wires) to form a thick sensing film. After that, the device was calcined at 400 °C for 2 h. A Ni—Cr alloy coil was inserted through the alumina tube as a heater, and we could control the operating temperature by tuning the heating current flowed through the heater. Finally, the gas sensor was obtained by aging at 100 mA relative current for 5 days.

The sensing performances of sensors were measured by a static testing system [31]. The humidity was maintained at 30% RH. The response (S) of the sensor was defined as the ratio of Ra/Rg, where Ra and Rg were the sensor resistance in the air and target gases. The response time (τ_{res}) and recovery time (τ_{rec}) were defined as the time taken by the sensor to achieve 90% of the total resistance change in the case of adsorption and desorption, respectively.