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Facile synthesis and gas sensing properties of the flower-like NiO-decorated ZnO microstructures

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ABSTRACT

In this paper, the pure and NiO-decorated ZnO flower-like structures with uniform sizes were synthesized by a simple two-step process. As the gas sensing materials of oxide semiconductors gas sensors, their sensing properties were investigated systematically. The results manifested that the sensor based on 8.0 at% NiO-decorated ZnO microflowers showed improved gas sensing properties compared with those of pure ZnO microflowers. The introduction of NiO is believed to not only change the quantity of chemisorbed oxygen, but also form the *p-n* junction with ZnO. Thus, the functionalization of ZnO with NiO may be a promising method for designing and fabricating the high performance gas sensor.

1. Introduction

In recent years, the environmental pollution and human security are attracting increasing attention worldwide. Oxide semiconductors gas sensors are regarded as one of the effective tools for detecting inflammable, explosive, and toxic gases because of the remarkable characteristics of low cost, high sensitivity, easy manufacture and facile integration [1,2]. Over the past few decades, numerous metal oxide semiconductors such as (*n*-type) SnO_2 [3,4], ZnO [5,6], α-Fe_2O_3 [7,8], In_2O_3 [9,10], WO_3 [11] and (*p*-type) NiO [12], Co_3O_4 [13] have been developed for gas sensing. It has been widely acknowledged that the mainly sensing mechanism of sensors using semiconductor oxides is that the adsorption and reaction of oxygen and target gases result in a remarkable change in the electrical conductivity [14]. In order to enhance the sensing properties, considerable efforts have been made including transition metal doping, novel metal loading, as well as the construction of heterojunction formed between different semiconductor oxides [15]. Recently, much research has demonstrated that the performance of gas sensors could be significantly improved by applying heterostructure semiconductor composites because they are supposed to integrate the physical and chemical properties of their individual component. Up to now, composites consisting of two or more metal oxides, such as α-Fe_2O_3/SnO_2 [16,17], ZnO/α-Fe_2O_3 [18,19], In_2O_3/WO_3 [20], ZnO/SnO_2 [42], NiO/SnO_2 [21], have been successfully prepared and have indeed improved the sensing properties such as high sensitivity, fast response/recovery speed, low operating temperature and good stability. Though many satisfying results regarding sensing properties of semiconductor oxides have been obtained, it is an urgent need for satisfying the increasing demands for making sensors work in more complicated systems and under more harsh conditions. Thus, the design of new-type composites to achieve dramatic improvement in gas sensing properties deserves more efforts.

ZnO and NiO, as two kinds of important semiconductors, with energy gaps of ~3.3 eV and ~3.7 eV, respectively [22], have received extensive attention for their potential applications involving gas sensors [23,24], photocatalysis [25,26], supercapacitor [27] and lithium-ion batteries [28]. Recently, the NiO/ZnO composites have showed enhanced gas sensing properties compared with single component of oxide (NiO or ZnO). Li et al. [29] have fabricated NiO/ZnO-based sensors, demonstrating a high sensitivity towards TMA. Ju et al. [30] have synthesized ZnO nanosheets with NiO nanoparticles by combining hydrothermal and pulsed laser deposition method, and the work have manifested the composites to be a promising gas sensing material for TEA. However, many of the approaches involve high temperature, complex operation steps or especial additives, which may result in increasing cost and limiting the potential application. For this reason, it is very meaningful to develop a facile synthetic strategy for designing NiO/ZnO het-

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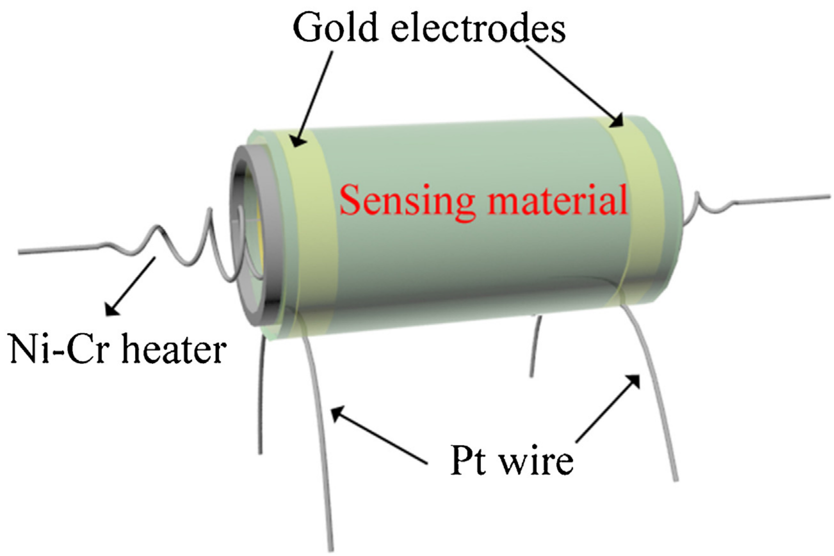

Fig. 1. Schematic structure of the gas sensor.

erostructures with novel morphology, as well as improved gas sensing properties, which could meet the increasing requirements.

In this work, we reported the synthesis of the pure and NiO-decorated ZnO microflowers by a facile two-step process at a low temperature. A systematically comparative gas sensing investigation between the pure and NiO-decorated ZnO microflowers was performed. These results indicated that the sensor based on NiO functionalized ZnO, in which the molar ratio of Ni:Zn was 8:100, showed the highest response towards acetone, which was nearly 3.8 fold higher than that of primary ZnO. The dramatic improvement in gas sensing properties might be ascribed to the increase of adsorption sites due to the introduction of NiO as an effective oxidative catalyst and the *p-n* junction formed between ZnO and NiO.

2. Experimental

All the reagents in the experiment were analytical-grade purity (Beijing Chemicals Co. Ltd.) and used as received without any further purification.

2.1. Preparation of flower-like ZnO microstructures

In our experiment, 100 mL of aqueous solution containing 1.0 g zinc acetate dihydrate ($Zn(CH_3COO)_2{\bullet}2H_2O$) was first prepared in a beaker (250 mL) at room temperature. Then, 3.4 mL of ammonia (30 wt% NH_3 in water) was added into the above solution drop by drop. After thorough mixing, the beaker containing the resulting transparent solution was placed in a water bath pot to be heated and maintained at 80 °C for 40 min. After that, a white precipitate was obtained. When cooled to room temperature, the precipitate was collected via centrifugation, washed with ethanol and deionized water several times before drying at 60 °C.

2.2. Preparation of flower-like NiO-decorated ZnO microstructures

35 mg of as-synthesized ZnO microflowers were dispersed into 6 mL of ethanol, followed by the addition of appropriate amounts of nickelous nitrate hexahydrate ($Ni(NO_3)_2{\bullet}6H_2O$) (the molar ratios of Ni/Zn were 4.0 at%, 8.0 at%, and 12.0 at%, respectively). Then the mixture was stirred at room temperature to go dry. Finally, the NiO-decorated ZnO microflowers were obtained by annealing the dry powder at 500 °C for 2 h in a muffle furnace.

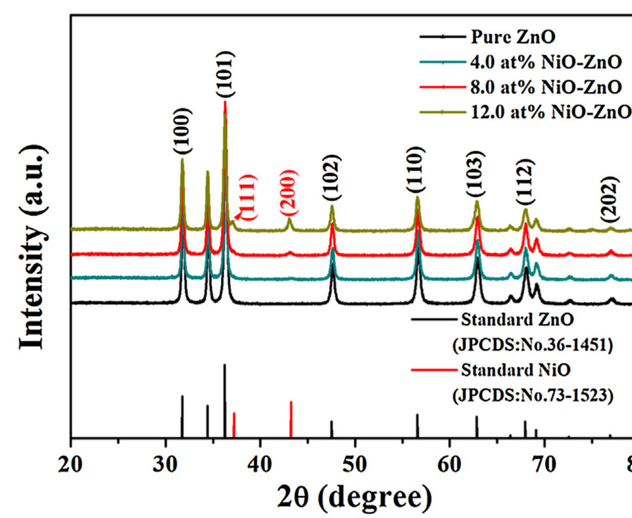

Fig. 2. XRD patterns of the pure, 4.0 at%, 8.0 at%, and 12.0 at% NiO-decorated ZnO samples.

2.3. Characterization

The phase structures of the as-obtained samples were analyzed by X-ray diffraction (XRD), using a Rigaku TTRIII X-ray diffractometer at a scan rate of 4/min ranging from 20 to 80 with high-intensity Cu Kα radiation(=1.5406 Å). The morphology of the samples was investigated using a field-emission scanning electron microscope (FESEM, JEOL JSM-7500F, operated at an accelerating voltage of 15 kV). Transmission electron microscopy (TEM) and high-resolution TEM images were obtained on a JEM-2200FS (JEOL) transmission electron microscope with an operating voltage of 200 kV. The energy-dispersive X-ray spectrometry (EDS) was also applied to study the chemical component of the products.

2.4. Fabrication and measurement of gas sensor

The as-prepared sensing materials (ZnO and NiO-decorated ZnO) were mixed with deionized water in a weight ratio of 4: