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# Hierarchical heterostructure of porous NiO nanosheets on flower-like ZnO assembled by hexagonal nanorods for high-performance gas sensor

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ABSTRACT

A novel hierarchical heterostructure consisting of porous NiO nanosheets and flower-like ZnO assembled by hexagonal nanorods was successfully fabricated by a simple two-step hydrothermal approach. Flower-like ZnO was obtained by the first step hydrothermal method. Through the second step hydrothermal method, porous NiO nanosheets grew on the surface of flower-like ZnO to realize integration of ZnO and NiO, so the p-n heterostructure between ZnO and NiO formed. The samples were investigated by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and energy dispersive X-ray (EDX). Gas sensing test results showed that the sensor based on NiO/ZnO composite exhibited superior sensing properties to acetone. The sensor response to 100 ppm acetone was about 205.14 at the optimum working temperature of 240 °C, and the response and recovery times were about 7 and 20 s, respectively. The enhanced response might be attributed to heterojunction and larger specific surface area provided by attached porous NiO nanosheets. The rapid response and recovery characteristics and improved selectivity attributed to the porous structure and good catalytic actions of NiO nanosheets.

## 1. Introduction

Since researchers began to find metal oxide semiconductor (MOS) material with gas-sensing properties, a new field in the research of gas sensor was created. Some metal oxides with characteristics of n/p type semiconductor, as the main gas-sensing materials, have been successively developed and applied, such as $SnO_2$, ZnO, $TiO_2$, $Fe_2O_3$, $In_2O_3$, $WO_3$ (*n*-type MOS), NiO, $Co_3O_4$, CuO (*p*-type MOS), etc. As "gas-electric" information conversion device, metal oxide gas sensor has the advantages of low cost, high sensitivity, controllable preparation. But these oxide semiconductors with pure phase are a broad-spectrum sensitive material, they still exist some drawbacks. The development of modern science and technology put forward higher requirements to the gas-sensing materials, in addition to possessing higher sensitivity, better gas selectivity and stability are also needed.

Recently, many studies have demonstrated that metal oxide composites with the certain structure have more excellent gas-sensing characteristics than single compounds. The sensing properties of these composites are closely related to different chemical components, their architectures and surface morphologies, so development of new gas-sensing materials by research the preparation and performances of the metal oxide composites has attracted more and more attention. Up to now, various heterojunction composites, such as NiO/CuO, $Bi_2O_3$/$In_2O_3$, CuO/ZnO, $TiO_2$/$SnO_2$, $SnO_2$/α-$Fe_2O_3$, and $La_2O_3$/$WO_3$ etc. have been successfully prepared, and a lot of studies have shown that many excellent properties have a direct relation with heterojunction. Therefore, to obtained high sensitivity, good selectivity, fast response/recovery rate, low operating temperature, and good stability of gas sensor, design and synthesis of novel gas sensing materials still need to be made a great effort. As a significant n-type gas sensing material, zinc oxide (ZnO) is widely used in detection many gases, but the mediocre selectivity characteristic and high operating temperature will hinder their further application in the gas sensor [1–6]. Nickel oxide (NiO), as a catalysts, can play a promote role of selective oxidation to varies volatile organic compounds [7–9]. As gas-sensing material, the gas sensor based on NiO has lower operating temperature [10–12]. Furthermore ZnO (*n*-type) and NiO (*p*-type) are the different conductive types. Considering all above factors, to make best use of their advantages and bypass their disadvantages, a new promising gas-sensing material can be synthesized by combining ZnO and NiO. Hitherto, some ZnO/NiO composites with various morphologies prepared through different methods have been reported. For example,

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Yanli Liu et al. firstly prepared ZnO flower-like structures by a simple chemical bath deposition (CBD) method and followed with the dispersion of NiO by controlled precipitation of metal cations with urea for detecting acetone [13]. NiO/ZnO heterojunction nanofibers were fabricated by Chao Li et al. via an electrospinning method and calcination technique for forming a TMA sensor [14]. Dianxing Ju et al. firstly synthesized ZnO nanosheet by a simple hydrothermal method on ordinary $Al_2O_3$ ceramic tubes with predesigned electrodes, and NiO nanoparticles were implanted onto the surface of ZnO nanosheets by pulsed laser deposition (PLD) for enhanced TEA-sensing performances [15].

Herein, the three-dimensional nanoflower assembled by hexagonal ZnO nanorods were firstly prepared through a hydrothermal route. Then the two-dimensional NiO nanosheets were orderly attached on the surfaces of ZnO nanorods by the second hydrothermal process. For comparison, pure NiO nanosheets were also prepared by hydrothermal method. The sensor based on as-obtained NiO/ZnO composite showed much more excellent sensing performances in respect of sensitivity, operating temperature, selectivity, and response/recover rate compared with pure flower-like ZnO and NiO nanosheets.

## 2. Experimental

All of the chemicals and organic solvents involved in this experiment were of analytical grade and directly used without any further purification. This experiment used a facile two-step hydrothermal method.

### 2.1. Preparation of flower-like ZnO assembled by hexagonal nanorods

The flower-like ZnO assembled by hexagonal nanorods were synthesized by a hydrothermal reaction. 1.594*g* of $Zn(CH_3COO)_2 \cdot 2H_2O$ were dissolved into a mixture solution containing 10 ml of ethanol and 20 ml of de-ionized water under vigorous stirring. Then, under continuous magnetic stirring, ammonia ($NH_3 \cdot H_2O$, 25%) was added into the above mixed solution drop by drop until the pH value was to be 10 at room temperature. After thorough mixing, the resulting precursor solution was transferred to a 50 ml Teflon-lined autoclave and maintained at 140 °C for 10 h. After reaction, white products were collected and washed with de-ionized water and absolute ethanol by centrifugation, dried at 60 °C for 4 h, and then annealed in a furnace at 500 °C for 2 h.

### 2.2. Preparation of NiO/ZnO hierarchical flower-like heterostructure

For the generation of NiO/ZnO heterostructure, the 40 mg of as-synthesized ZnO with flower-like morphology and 25 mg of $NiCl_2 \cdot 6H_2O$ were dispersed into 10 ml of ethanol and 20 ml of de-ionized water under vigorous stirring. The mixture was transferred into a 50 ml Teflon-lined autoclave and kept at 120 °C for 10 h. The final product was collected and washed with de-ionized water and absolute ethanol several times by centrifugation, dried at 60 °C for 4 h, and annealed at 500 °C in air for 2 h.

For comparison, pure NiO nanosheets were also synthesized using the same method that we synthesized flower-like ZnO before, just replacing $Zn(CH_3COO)_2 \cdot 2H_2O$ by $NiCl_2 \cdot 6H_2O$.

### 2.3. Materials characterization

The structure and purity of the materials were examined through X-ray diffraction (XRD) on a Scintag XDS-2000 X-ray diffractometer with Cu Ka radiation (λ=0.15406 nm) at a rate of 1.2° (2θ)/min and scanning range of 30–100° (2θ). The surface morphologies were investigated by using JSM-6701F field emission scanning electron microscope (FESEM) at a voltage of 20 kV. Transmission electron microscopic (TEM), high-resolution transmission electron microscopic (HRTEM), and selected area electron diffraction (SAED) images, as well as the energy dispersive X-ray (EDX) analysis results were obtained by USA FEI Tecnai $G^2$ TF20 transmission electron microscope (TEM) under an accelerating voltage of 200 kV. The specific surface area and pore size distribution were determined by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively, using the JW-004 instrument to measure Nitrogen adsorption–desorption isotherms.

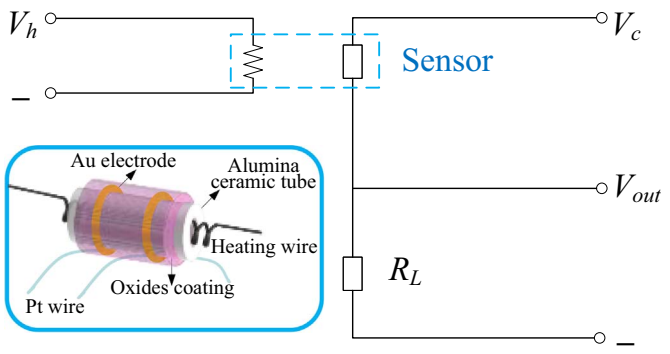


**Fig. 1.** The measuring electric circuit and the structure sketch of the gas sensor.

### 2.4. Fabrication and measurement of the gas sensors

The structure and the measuring electric circuit of the gas sensor are shown in Fig. 1. A pair of Au electrodes was previously printed on the each end of the ceramic tube. And each Au electrode was connected with two Pt conducting wires. A little bit of grinding NiO, ZnO or NiO/ZnO powders were mixed with de-ionized water to form paste, respectively. The obtained each paste to form about 0.5 mm sensing film was coated on a ceramic tube. While a Ni–Cr heating wire was inside of the ceramic tube. The working temperature of sensor was controlled by adjusting the heating voltage. Then, the ceramic tube was dried at 80 °C for 2 h and welded onto the pedestal.

Gas-sensing properties were tested with WS-60A gas sensing measurement system (Wei Sheng Electronics Science and Technology Co. Ltd., Henan Province, China). The sensor was put into the chamber filled with pure air, and then a given amount of the target gas was injected into the closed chamber for the gas sensitive performance testing, the resistance of sensor could change correspondingly. The resistance of sensor in air ($R_a$) or the target gas ($R_g$) could be measured by monitoring $V_{out}$. The desired concentration of the test gas could be calculated by means of the static liquid gas distribution method as follow [16]:

$C = \frac{22.4 \times \phi \times \rho \times V_1}{M \times V_2} \times 1000$Where C is the test gas concentration (ppm), φ is the required gas volume fraction, ρ is the density of the liquid (g/ml), $V_1$ is the injection volume (μl), $V_2$ is the test chamber volume (l), and M is the molecular weight of liquid (g/mol). For n-type ZnO and p-NiO/*n*-ZnO, the sensor response ($S_r$) for reducing gases is defined as $R_a/R_g$. For p-type NiO, the sensor response ($S_r$) for reducing gases is defined as $R_g/R_a$. The response time can be defined as the time needed to reach 90% of its saturated pulse height, while the recovery time is the time needed for the pulse to reach 10% from its base line [17].

## 3. Results and discussion

### 3.1. Crystalline structure

The crystalline structures and purity of the as-obtained products were characterized by powder X-ray diffraction (XRD). The XRD patterns of the ZnO nanoflower, NiO nanosheets and NiO/ZnO composite are shown in Fig. 2(a). Obviously, all the diffraction peaks of ZnO and NiO samples are well indexed to the wurtzite structure ZnO