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# Highly stabilized and rapid sensing acetone sensor based on Au nanoparticle-decorated flower-like ZnO microstructures

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ABSTRACT

Hierarchical flower-like ZnO microstructures were synthesized by a two-step hydrothermal method. Flower-like ZnO microstructures were made up of ZnO nanorods (NBs) with the diameters of about 100 nm. Then Au nanoparticles (NPs) with the diameter of 10–20 nm were decorated on the surface of flower-like ZnO microstructures by the wet decorating process. The properties of the sensing material were analyzed with X-Ray diffraction (XRD), Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). Gas sensing device was prepared by thick film technology and tested primarily for acetone gas at different testing temperatures as well as concentrations. At the optimum operating temperature of 280 °C the sensor showed a good response and rapid response-recovery time. Furthermore, because of the stable microstructure the sensor had an excellent stability for six months.
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## 1. Introduction

Various oxide semiconductor based gas sensors have been used to detect harmful and toxic gases. The most representative sensor materials such as $SnO_2$ [1–3], ZnO [4–6], $In_2O_3$ [7–9], $Fe_2O_3$ [10], $Co_3O_4$ [11], $TiO_2$ [12], $WO_3$ [13] and so on, show excellent gas-sensing properties to reducing or oxidizing gases. ZnO, as a type of wide-band gap semiconductor, has been investigating and applying in many fields such as solar cell, ultraviolet detection, luminescence and sensor etc [14–16]. In gas-sensing field, ZnO nanomaterial has been proven to be a kind of excellent gas-sensing material with high sensitivity to ppm (parts per million) level and sometimes even better.

Over the past decades, one-dimensional (1D) ZnO nanostructures (nanowires, nanotubes, nanosheets and nanobelts) have attracted a great deal of research interests [17]. Various physical and chemical methods have been developed for the synthesis of 1-D nanostructured metal-oxides such as hydrothermal, ultrasonic irradiation, electrospinning, anodization, sol–gel, molten-salt and carbothermal reduction, etc. ZnO materials with different sizes and morphologies have been successfully synthesized, including nanowires [18], nanorods [19], nanofibers [20], nanobelts [21], nanotubes [22], etc. At present, the assembly and integration of these 1D ZnO nanomaterials into three-dimensional arrays or hierarchical structures are desirable for further improving their sensing property [23,24]. Because their special structures can usually provide a large surface-to-volume ratio that can facilitate gas diffusion and mass transport in sensor material and improve the sensitivity and response time of the gas sensor [25,26]. In addition, a stable microstructure which had less agglomeration and better morphology maintenance was an important factor for the stability of the sensor.

On the other hand, noble metals, well known as active catalysts, have been confirmed to possess the promoting effects on many semiconductor gas sensors [27,28]. Au nanoparticles have attracted considerable attention. For example, Liu et al. etc. fabricated 3D hierarchically porous ZnO architectures with Au nanoparticles loading on the surface, which demonstrated excellent sensor properties in terms of higher and faster response [29].

In this paper, hierarchical flower-like ZnO microstructures were successfully synthesized by a two-step hydrothermal method.

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Firstly, ZnO nanorods with the diameter of about 1–3 μm were prepared. Subsequently, flower-like ZnO microstructures were assembled by the second hydrothermal. In the end, the Au nanoparticles were decorated on the flower-like ZnO microstructures by the wet decorating process. Their acetone sensing properties were examined and the possible mechanism was discussed.

## 2. Experimental section

### 2.1. Chemical reagent

Zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), tetrachloroauric (III) acid trihydrate ($HAuCl_4 \cdot 3H_2O$) were purchased from National Chemical Reagent Co. Ltd. Hexamethylenetetramine ($C_6H_{12}N_4$) was purchased from East China Reagent Factory in Tianjin. All the reagents were of analytical grade and used as received without further purification.

#### 2.1.1. Preparation of flower-like ZnO microstructures

Flower-like ZnO microstructures were synthesized by two steps. In the first step, ZnO NBs were grown by a simple hydrothermal reaction of $Zn(CH_3COO)_2 \cdot 2H_2O$ (Reagent Grade, 98% Sigma–Aldrich) in the presence of $C_6H_{12}N_4$ as the promoter. In a typical procedure $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.1 M, 1.1 g) was dissolved in 50 mL of deionized water and added $C_6H_{12}N_4$ (0.25 M, 1.75 g) by vigorous stirring for 20 min. Then the above mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and maintained at 90 °C for 6 h. A white precipitate was produced which was collected by centrifugation and washed thoroughly with deionized water.

In second step, the precipitate and $C_6H_{12}N_4$ (0.25 M, 1.75 g) were dissolved in 50 mL deionized water under stirring for 20 min, and then transferred in a 100 mL capacity autoclave with Teflon liner followed by uniform heating at 90 °C for 6 h. After completion of the reaction, it was cooled to room temperature and powdered samples were collected by centrifugation. Powdered sample was thoroughly washed with deionized water and ethanol and dried at 60 °C for later use.

#### 2.1.2. Synthesis Au nanoparticle-decorated flower-like ZnO microstructures

To decorate nanorods with Au nanoparticles, flower-like ZnO microstructures were first dispersed in the reaction solution containing 60 mL deionized water and 30 mL ethanol, followed by the addition of 0.6 mL NaOH solution (0.1 M). After heated to 90 °C, 10 mL of $HAuCl_4$ solution (5 mM) was added. Note that ethanol was used as the reducing agent to facilitate the growth of Au [30]. The mixed solution was kept at 90 °C for 6 h, resulting in the deposition of Au NPs on the surfaces of flower-like ZnO microstructures. The products were centrifuged, washed with deionized water and ethanol, and then dried at 60 °C in the air for later use.

### 2.2. Characterization

X-Ray diffraction (XRD) analysis was conducted on a Scintag XDS-2000 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) images were performed on an SHIMADZU SSX-550 (Japan) instrument. Energy-dispersive X-ray spectroscopy (EDX) was obtained on a JEM-ARM200F microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a TECNAI G2 electron microscope.

### 2.3. Fabrication and measurement of gas sensor

Sensor device was fabricated by similar method in our previous work [31,32]. The as-prepared samples were mixed with deionized water in weight ratio of 100:25 and ground in a mortar to form a paste. Then the paste was coated on a ceramic tube as a sensing film with a thickness of about 300 μm. A pair of Au electrodes was previously printed on the sensing film and contacted with Pt lead wires. After the ceramic tube was calcined at 300 °C for 2 h, a Ni–Cr heating wire was inserted in the tube as a heater for controlling the operating temperature. Schematic mechanism for the formation of Au nanoparticle-decorated flower-like ZnO microstructure was shown in Fig. 1.

Gas sensing properties were measured by a chemical gas sensor-8 (CGS-8) intelligent gas sensing analysis system (Beijing Elite Tech Co. Ltd., China) under room condition (25 °C, 40 RH%). The gas sensing properties were tested by the CGS-8 analysis system (shown in figure below) which can record the sensors' resistance values at a specified time interval (1 s in the experiment). The operating temperature was controlled by the current throughout the heating wire of the sensor. All the sensors were pre-heated at different operating temperatures for about 30 min. When the resistances of the sensors were stable, the target gas was injected into the test chamber (1 L in volume) by a microinjector through a rubber plug. After the sensor resistances reached new constant value, the sensor was moved out of the target gas and put it in the air until the sensor restored the stable value. The response of the sensor to reducing gas was defined as $R_a/R_g$ and to oxidizing gas was defined as $R_g/R_a$, where $R_a$ and $R_g$ were the resistance in air and in test gas, individually. The time taken by the sensor resistance to change from $R_a$ to $R_a - 90\% \times (R_a - R_g)$ was defined as response time when the target gas was introduced to the sensor, and the time taken from $R_g$ to $R_g + 90\% \times (R_a - R_g)$ was defined as recovery time when the ambience was replaced by air.

## 3. Results and discussion

### 3.1. Structural and morphological characteristics

Fig. 2 shows the XRD pattern of the Au NPs decorated flower-like ZnO microstructures. It can be observed that the crystal phase of the final product was the mixture of Au and ZnO. Compared with the data in JCPDS No. 36–1451, most of the peaks in the pattern can be indexed to wurtzite ZnO. The other diffraction peaks can be indexed to Au, which was well agreed with the reported values from the Joint Committee on Powder Diffraction Standards Card (JCPDS, 04–0784) [33,34]. But the strength of the peaks was weak because of the low content [35–37]. And no other diffraction peaks corresponding to impurities were observed, which implied the absence of other impurities.

Fig. 3(a) shows the morphology of ZnO microstructures by the first hydrothermal method. The well-aligned homogeneous ZnO NBs are easily seen from Fig. 3(a). And Fig. 3(b) shows the morphology of flower-like ZnO microstructures with the size of 1–3 μm by the second hydrothermal method. It shows that the diameter of the NBs is not uniform throughout the length and it is tapered at the top. Furthermore, it demonstrates that the morphology of the sample is not the single rod especially in Fig. 3(a), but is more like a bunch of flowers which is composed of uniform NBs. For the decoration of Au NPs, we choose flower-like ZnO microstructures as the support for Au deposition, and the morphology after they were reacted with $HAuCl_4$ in the chemical reduction process was shown in Fig. 3(c) and (d). The TEM images of individual ZnO nanorod of flower-like assembly and the flower-like ZnO microstructure were exhibited in Fig. 4(a) and (b). Evidently, a large quantity of NPs with a size of 10–20 nm was present on the surfaces of ZnO microstructures. As it can be observed, the wet decorating process does not seem to affect the morphology of the preformed ZnO microstructures. The corresponding EDX spectrum

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