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Rapid and selective detection of acetone using hierarchical ZnO gas sensor for hazardous odor markers application

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HIGHLIGHTS

- ZnO spheres fabricated via solvothermal method are with (0 0 2) polar facet exposed.
- Response time of ZnO sensor for detecting 100 ppm acetone is as short as 3 s.
- R_a/R_g toward 100 ppm acetone is 33 when operated at 230 °C.
- ZnO sensor exhibits good selectivity against other toxic gases and water vapor.
- Porous structure and exposure of polar facet contribute to good sensing properties.

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ABSTRACT

Hierarchical nanostructured ZnO dandelion-like spheres were synthesized via solvothermal reaction at 200 °C for 4 h. The products were pure hexagonal ZnO with large exposure of (0 0 2) polar facet. Side-heating gas sensor based on hierarchical ZnO spheres was prepared to evaluate the acetone gas sensing properties. The detection limit to acetone for the ZnO sensor is 0.25 ppm. The response (R_a/R_g) toward 100 ppm acetone was 33 operated at 230 °C and the response time was as short as 3 s. The sensor exhibited remarkable acetone selectivity with negligible response toward other hazardous gases and water vapor. The high proportion of electron depletion region and oxygen vacancies contributed to high gas response sensitivity. The hollow and porous structure of dandelion-like ZnO spheres facilitated the diffusion of gas molecules, leading to a rapid response speed. The largely exposed (0 0 2) polar facets could adsorb acetone gas molecules easily and efficiently, resulting in a rapid response speed and good selectivity of hierarchical ZnO spheres gas sensor at low operating temperature.

1. Introduction

With the rapid development of industry, the volatilization of hazardous gases such as acetone, ammonia, and toluene has become a serious problem which is harmful to human health and safety [1]. Particularly, acetone, which is widely used as good solvent and raw material for organic synthesis, can volatilize easily and cause damages to eyes, noses, and central nervous system when the concentration is higher than 450 mg/m^3 (173 ppm). Besides, acetone in human breath is a biomarker for type-1 diabetes [2]. The acetone concentration from the breath of healthy body is lower than 0.8 ppm, while that from a diabetic patient is higher than 1.8 ppm [3,4]. Therefore, the development of gas sensors for rapid and selective detection of acetone attracts the interest of researchers in recent years.

Among several gas sensing materials studied so far, zinc oxide (ZnO) is a wide-band-gap semiconducting material (E_g = 3.37 eV) with good sensing properties toward various oxidizing and reducing gases. It has the advantages of low cost, simplicity in fabrication, and miniaturized [5–7]. Compared with bulk materials, nanostructured ZnO exhibit more excellent gas sensing properties [8–10]. Specially, hierarchical nanostructures using lower dimension nanocrystals as the building blocks attract more interest due to their less gas diffusion length, higher mobility, and relatively larger specific surface area than the agglomerated nanoparticles [11]. Up to now, hierarchical ZnO architectures with different shapes were synthetized by chemical vapor deposition [12], thermal oxidation method [13], microwave hydrothermal [14], and solvothermal method [15], and they were used as gas sensing

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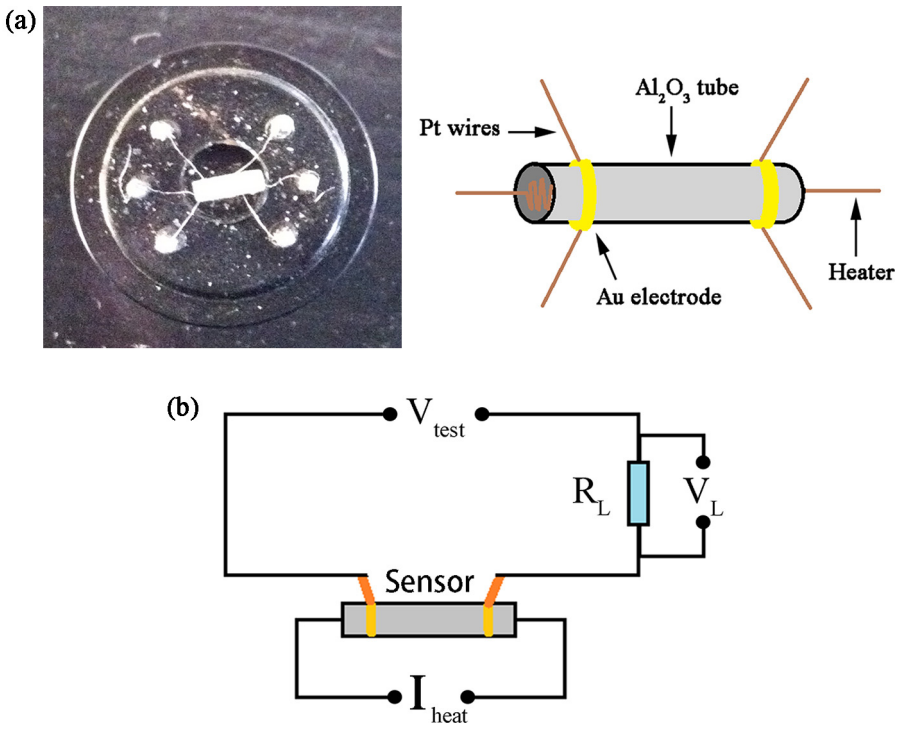

Fig. 1. (a) Digital photo and schematic diagram of a typical gas sensor and (b) measuring electric circuit of gas sensing properties.

materials. Urchin-like ZnO spheres exhibited excellent selectivity and fast response to acetone; however, the response to 100 ppm acetone was not very high ($R_a/R_g = 10$) [16]. The response of porous ZnO nanostructures and nest-like 3D ZnO hierarchically structures to 100 ppm acetone were 20.27 and 17.4, respectively, but the operating temperature was too high (400 and 420 °C) [17,18]. The response of ZnO hollow nanofibers to 100 ppm acetone was 67.7 operated at 220 °C, which was one of the highest response reported so far [19]. Nevertheless, the response time (17 s) was slightly longer [20,21] due to the limited rate of the adsorption–desorption on the fiber surface at 220 °C [22]. Since there are a lot of problems exist in the acetone detection research, acetone gas sensors with high sensitivity, short response time, low working temperature, and good selectivity are urgently needed.

In our previous work, the preparation conditions of dandelion-like ZnO were fully discussed and the ZnO materials exhibited gas response to ethanol [23]. In this work, we present a further study of the prepared hierarchical ZnO spheres concerning the hazardous odors (acetone particularly) sensing properties for application as the acetone gas sensor. The gas sensing mechanisms are discussed in detail.

2. Experimental

2.1. Synthesis of hierarchical ZnO spheres

The hierarchical ZnO spheres were fabricated via a simple solvothermal method. In a typical synthesis, 0.702 g $Zn(CH_3COO)_2{\cdot}2H_2O$ was dissolved in 40 mL of ethanolamine with magnetic stirring to form a homogeneous solution. The solution was transferred into a Teflon-lined stainless autoclave (50 mL capacity). The sealed autoclave was maintained at 200 °C for 4 h and 6 h, separately, and then cooled to room temperature. White precipitates were centrifuged and washed alternately with distilled water and ethanol for several times. Finally, the obtained products were dried in air at 80 °C for 4 h.

2.2. Characterization

The morphology of the synthesized ZnO was investigated by scanning electron microscope (SEM: Hitachi, S4800), transmission electron microscopy and high-resolution transmission electron microscopy (TEM, HR-TEM, FEI Tecnai G2 F20). The crystalline structures were examined by X-ray diffraction (XRD) via a Rigaku D/max 2500 diffractometer at 40 kV and 200 mA with Cu Kα radiation (λ = 0.15406 nm), ranging from 20° to 80°. The photoluminescence (PL) spectroscopy was performed at room temperature using a spectrometer (Jobin Yvon Fluorolog 3-21, Jobin Yvon Inc.) with an excitation wavelength of 325 nm. The average crystal size was calculated by Scherrer equation:

$$D = \frac{k\lambda}{B\cos\theta} \quad (1)$$

where D is the crystal size perpendicular to the facet direction, k is the Scherrer constant, λ is the wavelength of X ray (0.15406 nm), B is the peak width at half weight, and θ is the diffraction angle.

2.3. Preparation of gas sensor and measurement of gas sensing properties

Fig. 1 displays (a) the digital photo and schematic diagram of the sensor, (b) the measuring electric circuit of gas sensing properties. The preparation and measurement of the side-heating sensor were similar to those depicted in our previous report [24]. A proper amount of ZnO powder was mixed with several drops of distilled water to form a paste, which was then coated onto the alumina tube posited with a pair of Au electrodes and four Pt wires. A Ni–Cr alloy filament which was inserted into the tube was used as heater, and the temperature of coated tube was controlled by regulating the heating current. A heating current (I_{heat}) range from 0 to 300 mA was applied, and a test voltage (V_{test}) was supplied to the sensor. A load resistor R_L was connected to the sensor, whose resistance was measured and used for calculating and outputting the sensor resistance. The gas sensing properties were measured by CGS-8