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Featured Letter

Bicone-like ZnO structure as high-performance butanone sensor

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ABSTRACT

Sensors based on metal oxide semiconductors have been widely applied for the detection of several volatile organic compounds (VOCs). However, the development of sensing materials with high selectivity, improved sensitivity, low detection limit is still a challenge. In this work, bicone-like ZnO structure was synthesized by a rapid template-free microwave-assisted hydrothermal method and then applied as VOC sensor. The VOC-sensing tests revealed that ZnO structure presented a higher response toward butanone than to other VOCs, such as benzene, toluene, *m*-xylene, acetone, ethanol, acetaldehyde, and isopropanol. Moreover, the ZnO-based sensor showed an enhanced butanone-sensing performance at 400 °C, including a response of 29.4–100 ppm of butanone, high sensitivity to detect low butanone concentration (2 ppm), and a low detection limit of 0.41 ppm. Therefore, the unique bicone-like ZnO structure might be a promising candidate for butanone sensors.

1. Introduction

The development of volatile organic compounds (VOCs) sensor has attracted considerable attention for air-quality monitoring and disease diagnosis [1,2]. Some VOCs in exhaled breath are known to be biomarkers for different diseases [3], for example, butanone and toluene might be related to gastric and lung cancer [4,5] respectively, while acetone is associated to diabetes [6]. Thus, VOC sensors with sensitivity enough to detect low ppm (parts per million) are required.

Metal oxide semiconductors (MOS) have been widely used as chemiresistive sensors for VOCs detection, due to its easy production, low cost, and simplicity of use [7,8]. However, the production of sensors with high selectivity, sensitivity, and low detection limit is still a challenge. Among the MOS, zinc oxide (ZnO), an n-type MOS, has demonstrated a great potential for the detection of several VOCs, including acetone [9], ethanol [10], acetaldehyde [11], formaldehyde [12], triethylamine [13], and so on. Nevertheless, to the best of our knowledge, there has been still no reports of ZnO as a chemiresistive sensor for butanone vapor.

In this paper, bicone-like ZnO structure was prepared by a template-free microwave-assisted (MAH) method and the VOC-sensing performance was presented. Due to its unique structure, the ZnO-based sensor exhibited high butanone sensing performance regarding sensitivity, selectivity, and low detection limit.

2. Material and methods

The bicone-like ZnO structure was prepared by a template-free MAH method. First, 2 mmol of $Zn(CH_3COO)_2{\cdot}2H_2O$ (Sigma–Aldrich, ≥98%) was dissolved in 70 mL of deionized water. Then, 280 μL of NH_4OH (Sigma–Aldrich, 28.0–30.0% NH_3 basis) was added with stirring until complete homogeneity. The final solution was transferred to polytetrafluoroethylene autoclave, sealed, and heated at 140 °C for 1 h in a microwave system (2.45 GHz/800 W). After the heating, the autoclave was naturally cooled down, and the product was centrifuged and washed with deionized water and ethanol, then dried at 80 °C.

The sample was characterized by X-ray diffraction (XRD, Rigaku MiniFlex 300), field-emission scanning electron microscopy (FESEM, JEOL JSM-7500F), and X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer). The XPS spectra were calibrated using the C 1s peak (284.8 eV). Specific surface area was measured by the Brunauer–Emmet–Teller (BET) method through nitrogen physisorption (Gemini VII – Surface Area and Porosity analyzer).

The dispersion prepared by mixing 4.8 mg of the sample with 1 mL of isopropanol was dropped into alumina substrates with interdigitated gold arrays as electrodes. The as-prepared sensor was dried at 250 °C for 1 h. The sensor was placed inside the test chamber and heated at the desired operating temperature. The electrical resistance variations were measured after VOCs exposure using a high-voltage source-measure unit (Keithley SourceMeter 2400), applying a voltage of 5 V. The VOCs were injected into the test chamber with a syringe, and then the chamber was cleaned using

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an air flow of 250 mL min^{-1}. The sensor response was defined as the ratio R_a/R_g, where R_a and R_g is the resistance in air and after VOCs exposure, respectively.

3. Results and discussion

The morphology of the sample was determined by FESEM. The FESEM image (Fig. 1a) revealed the formation of a bicone-like ZnO structure, which means that each structure is composed of two cones. The bicone structure presents an average length of 1 µm and a diameter of ~400 nm. The high-magnification FESEM image (Fig. 1b) shows in detail the boundary interface between the two cones. It can be noticed that smaller particles are assembled, acting as building blocks to form the bicones. As shown in Fig. 1c, the energy dispersive X-ray (EDS) spectrum revealed the presence of only Zn and O elements, confirming the absence of impurities. According to the XRD pattern of bicone-like ZnO structure (Fig. 1d), the diffraction peaks could be indexed to the hexagonal ZnO wurtzite structure (JCPDS 36-1451; space group $P6_3mc$ (1 8 6), a = 3.249 Å, c = 5.206 Å). No secondary phase was observed, indicating the high purity of the prepared sample. The bicone-like ZnO structure presented a specific surface area of 21 $m^2\,g^{-1}$.

The chemical composition of the sample's surface was determined by XPS. The high-resolution XPS spectrum (Fig. 2a) of Zn 2p displays two symmetric peaks at ~1021.2 eV and 1044.3 eV related to Zn $2p_{3/2}$ and $2p_{1/2}$, respectively, with the splitting energy of the two peaks was of 23.1 eV, indicating the single oxidation state of Zn^{2+}. The high-resolution O 1s spectrum (Fig. 2b) presents an asymmetric peak which is resolved into two components at ~529.9 eV and 531.5 eV. The peak at 531.5 eV is related to the oxygen species (O_x^-) adsorbed on ZnO surface, whereas the peak at 529.9 eV can be assigned to the lattice oxygen (O^{2-}) in ZnO.

The response to 100 ppm of butanone as a function of the sensor operating temperature was evaluated, as displayed in Fig. 3a. The sensor presented the highest response of 29.4 at 400 °C. When the temperature is higher than 400 °C, the butanone molecules begin to desorb of the ZnO surface before the reaction with the adsorbed oxygen species, which causes a reduction of the butanone response [14]. Thus, the optimum operating temperature of 400 °C was used to further evaluate the VOC-sensing properties. To study the sensor selectivity, the responses to 100 ppm of several VOCs at 400 °C were evaluated (Fig. 3b). Clearly, the bicone-like ZnO structure presents the highest response to butanone, which was about 2.4–19.4 times higher than that of other VOCs. This result suggests the excellent selectivity of bicone-like ZnO structure to butanone.

The dynamic response curve to different butanone concentrations is shown in Fig. 3c. The sensing response increased with increasing the butanone concentration from 2 to 100 ppm. The

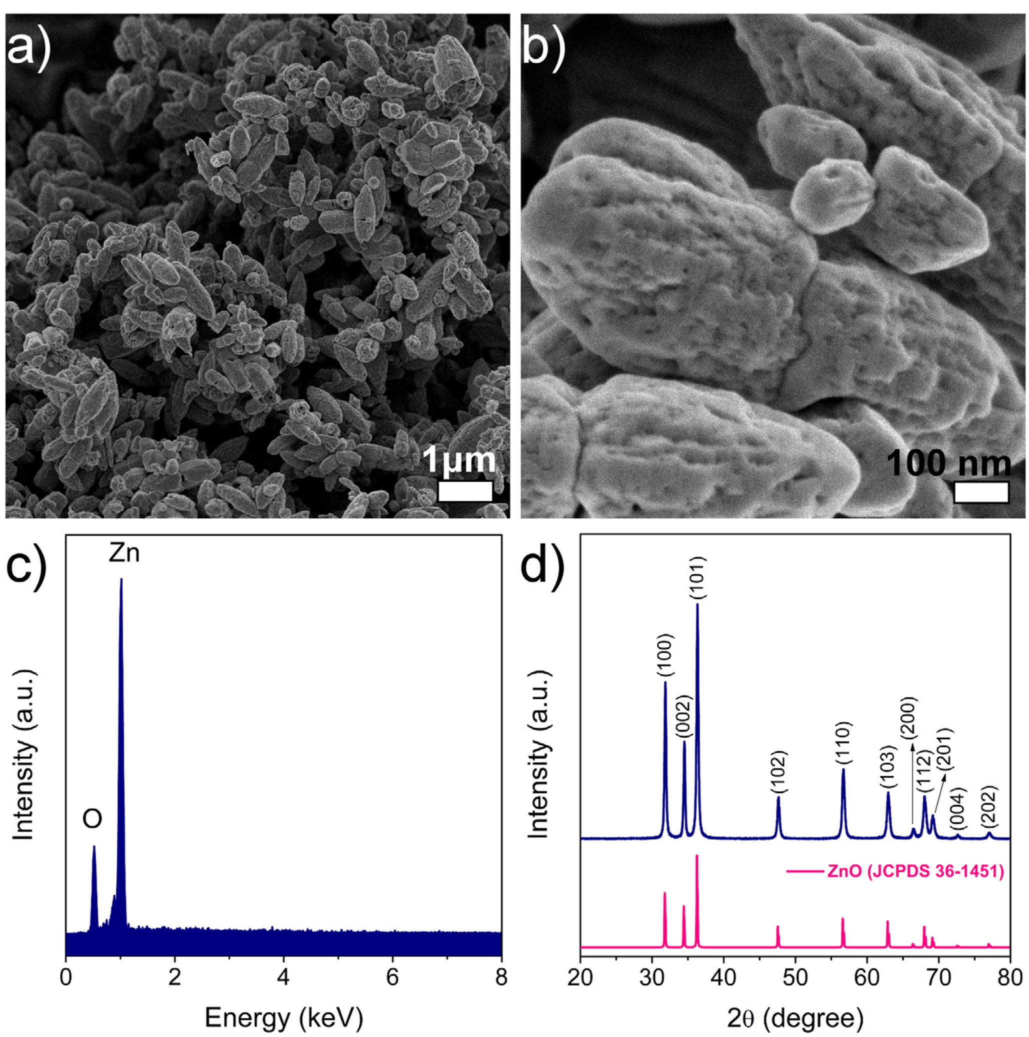

Fig. 1. (a,b) FESEM images in different magnifications, (c) EDS spectra, (d) XRD pattern of bicone-like ZnO structure.