Materials Letters 223 (2018) 142–145

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Bicone-like ZnO structure as high-performance butanone sensor

Cecilia A. Zito, Tarcísio M. Perfecto, Taís N.T. Oliveira, Diogo P. Volanti *

Laboratory of Materials for Sustainability (LabMatSus), Ibilce, São Paulo State University (Unesp), R. Cristóvão Colombo, 2265, S. J. Rio Preto, SP 15054-000, Brazil

ARTICLE INFO

Article history:
Received 19 February 2018
Received in revised form 28 March 2018
Accepted 5 April 2018
Available online 6 April 2018

Keywords:
Sensors
Semiconductors
Template-free
Volatile organic compounds
Zinc oxide

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

* Corresponding author.
E-mail address: volanti@ibilce.unesp.br (D.P. Volanti).

https://doi.org/10.1016/j.matlet.2018.04.026
0167-577X/

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

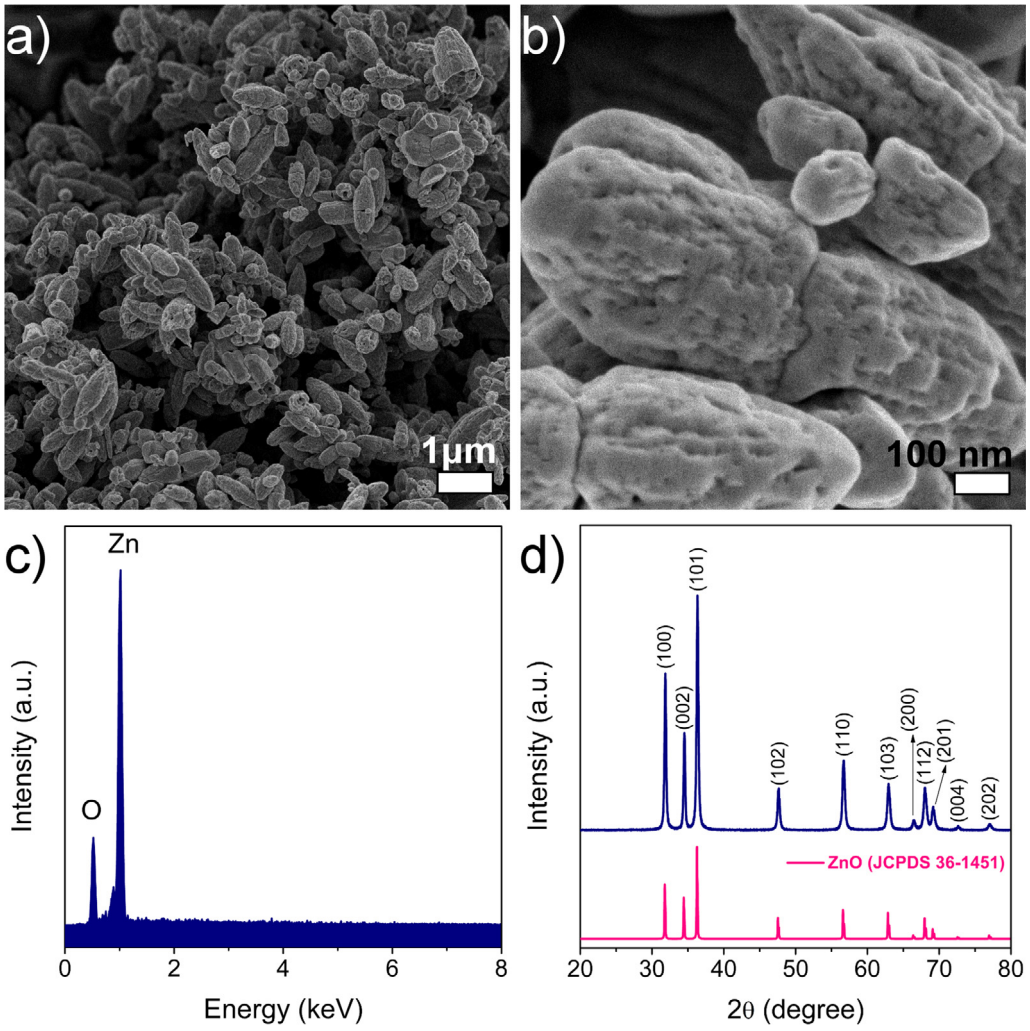

Fig. 1. (a,b) FESEM images in different magnifications, (c) EDS spectra, (d) XRD pattern of bicone-like ZnO structure.

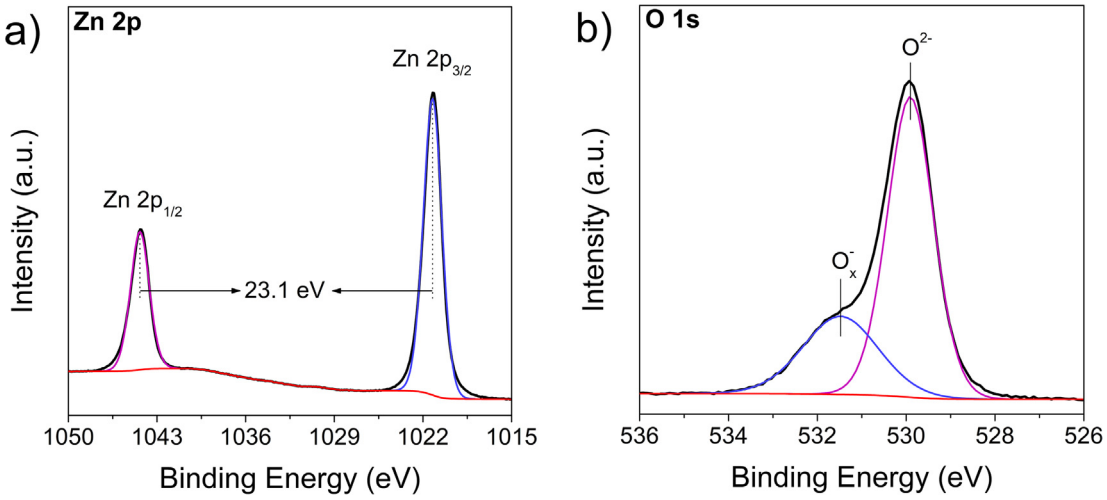

Fig. 2. High-resolution XPS spectrum of (a) Zn 2p and (c) O 1s.

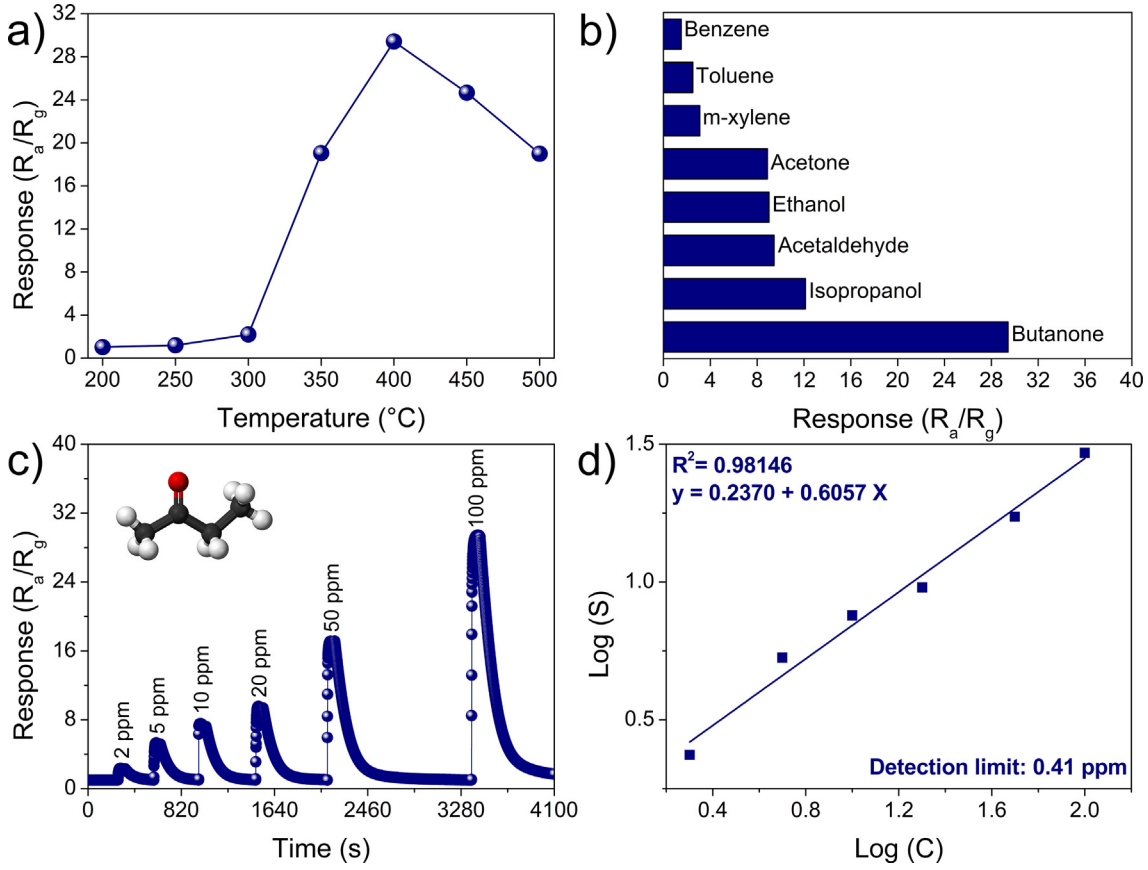

Fig. 3. (a) Response to 100 ppm of butanone at different operating temperatures (200–500 °C), (b) response to different VOCs at 400 °C, (c) dynamic response to butanone in the concentration range of 2–100 ppm at 400 °C, (d) logarithm of the butanone response (S) *versus* logarithm of butanone concentration (C).

response reached a value of ~2.4 when the concentration of butanone was 2 ppm, indicating an excellent sensitivity. Fig. 3d shows the di-logarithm graphic of the butanone response (S) and butanone concentration (C). The extension of the fit line revealed that the detection limit for butanone is ~0.41 ppm, further confirming the high sensitivity of the sensor.

When ZnO is exposed to air, oxygen molecules can adsorb on its surface and ionize in the form of O_2^-, O^- or O^{2-} [15]. This process occurs due to the electron transfer from the conduction band (CB) of ZnO, which creates a depletion layer near the surface. After bicone-like ZnO sensor is exposed to butanone (a reducing vapor), butanone molecules react with the ionosorbed oxygen species, releasing the electrons back to the CB of ZnO. Consequently, the depletion layer and the electrical resistance decrease. In this study, ZnO presented a high butanone response, which can be attributed to the unique bicone-like structure, because each bicone-like structure is composed of assembled nanoparticles, creating more actives sites for gas reaction.

4. Conclusion

In summary, bicone-like ZnO structure, which are constructed of nanoparticles, have been successfully prepared by a simple template-free MAH method. When applied as a VOC sensor, bicone-like ZnO structure presented an excellent butanone-sensing performance in terms of selectivity, sensitivity, and detection limit, which may be related to its unique morphology. Therefore, bicone-like ZnO structure is a promising material for high-performance butanone sensors.

Acknowledgments

The authors thank São Paulo Research Foundation – FAPESP (2017/01267-1, 2016/22219-2, 2016/25267-8, 2016/04371-1, 2013/23886-4) and National Council for Scientific and Technological Development – CNPq (444926/2014-3). FESEM and XPS facilities were provided by LMA/IQ/Unesp and LNNano/CNPEM (proposal 21594), respectively.

References

[1] C. Wang, X. Cui, J. Liu, X. Zhou, X. Cheng, P. Sun, X. Hu, X. Li, J. Zheng, G. Lu, Design of superior ethanol gas sensor based on Al-doped NiO nanorod-flowers, ACS Sens. 1 (2015) 131–136.
[2] D. Jiang, W. Wei, F. Li, Y. Li, C. Liu, D. Sun, C. Feng, S. Ruan, Xylene gas sensor based on α-MoO_3/α-Fe_2O_3 heterostructure with high response and low operating temperature, RSC Adv. 5 (2015) 39442–39448.
[3] S.-J. Choi, B.-H. Jang, S.-J. Lee, B.K. Min, A. Rothschild, I.-D. Kim, Selective detection of acetone and hydrogen sulfide for the diagnosis of diabetes and halitosis using SnO_2 nanofibers functionalized with reduced graphene oxide nanosheets, ACS Appl. Mater. Interfaces. 6 (2014) 2588–2597.
[4] T. Ligor, J. Szeliga, M. Jackowski, B. Buszewski, Preliminary study of volatile organic compounds from breath and stomach tissue by means of solid phase microextraction and gas chromatography–mass spectrometry, J. Breath Res. 1 (2007) 16001.
[5] J. Shin, S.-J.J. Choi, I. Lee, D.-Y.Y. Youn, C.O. Park, J.-H.H. Lee, H.L. Tuller, I.-D.D. Kim, Thin-wall assembled SnO_2 fibers functionalized by catalytic Pt nanoparticles and their superior exhaled-breath-sensing properties for the diagnosis of diabetes, Adv. Funct. Mater. 23 (2013) 2357–2367.
[6] S.-J.J. Choi, I. Lee, B.-H.H. Jang, D.-Y.Y. Youn, W.-H.H. Ryu, C.O. Park, I.-D.D. Kim, Selective diagnosis of diabetes using Pt-functionalized WO_3 hemitube networks as a sensing layer of acetone in exhaled breath, Anal. Chem. 85 (2013) 1792–1796.
[7] C. Dong, X. Liu, X. Xiao, G. Chen, Y. Wang, I. Djerdj, Combustion synthesis of porous Pt-functionalized SnO_2 sheets for isopropanol gas detection with a significant enhancement in response, J. Mater. Chem. A. 2 (2014) 20089–20095.
[8] J. Zhang, Z. Qin, D. Zeng, C. Xie, Metal-oxide-semiconductor based gas sensors: screening, preparation, and integration, Phys. Chem. Chem. Phys. 19 (2017) 6313–6329.
[9] B.A. Vessalli, C.A. Zito, T.M. Perfecto, D.P. Volanti, T. Mazon, ZnO nanorods/graphene oxide sheets prepared by chemical bath deposition for volatile organic compounds detection, J. Alloys Compd. 696 (2017) 996–1003.
[10] L. Zhu, W. Zeng, A novel coral rock-like ZnO and its gas sensing, Mater. Lett. 209 (2017) 244–246.
[11] G.K. Mani, J.B.B. Rayappan, ZnO nanoarchitectures: Ultrahigh sensitive room temperature acetaldehyde sensor, Sens. Actuators, B. 223 (2016) 343–351.
[12] X. Xing, X. Xiao, L. Wang, Y. Wang, Highly sensitive formaldehyde gas sensor based on hierarchically porous Ag-loaded ZnO heterojunction nanocomposites, Sens. Actuators, B. 247 (2017) 797–806.
[13] W. Li, H. Xu, T. Zhai, H. Yu, Q. Xu, X. Song, J. Wang, B. Cao, High-sensitivity, high-selectivity, and fast-recovery-speed triethylamine sensor based on ZnO micropyramids prepared by molten salt growth method, J. Alloys Compd. 695 (2017) 2930–2936.
[14] Z. Wang, J. Xue, D. Han, F. Gu, Controllable defect redistribution of ZnO nanopyramids with exposed {10$\bar{1}$1} facets for enhanced gas sensing performance, ACS Appl. Mater. Interfaces 7 (2015) 308–317.
[15] A. Gurlo, Interplay between O_2 and SnO_2: oxygen ionosorption and spectroscopic evidence for adsorbed oxygen, ChemPhysChem 7 (2006) 2041–2052.