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Ultrasensitive ethanol sensor based on 3D aloe-like SnO_2

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ABSTRACT

3D aloe-like SnO_2 nanostructures were synthesized by a simple hydrothermal method. The scanning electron microscopy result indicated that this unique structure was assembled by leaf-like sheets, which consisted of large amount of small protrusive nanosheets with width of 5–10 nm. The sensor fabricated by aloe-like SnO_2 nanostructures exhibited an excellent response and selectivity to ethanol. The developed sensor can detect ethanol as low as 50 ppb at 285 °C. The ultrasensitive ethanol detection was probably related to the less agglomerative and thinner structure of aloe-like SnO_2. The modulation of the conductance of aloe-like SnO_2 by the small nanosheets could also be considered to explain the ultrasensitive behavior to the low concentration of ethanol.

1. Introduction

Semiconductor oxide based gas sensors play an important role in environmental monitoring, chemical process control and personal safety. Current research on gas sensor technology has focused on the development of sensors which can show high sensitivity, good selectivity, and also can extend the detection range including lower and higher concentration limit to target gas [1–3]. Semiconductor oxide, such as ZnO, SnO_2 and In_2O_3, has been widely chosen as gas sensing materials and exhibited excellent sensing properties [4–7]. Among the semiconductor oxide, SnO_2 is a prominent *n*-type semiconductor with a wide band-gap of 3.62 eV at 298 K and has been demonstrated as a good candidate for gas sensors. Recently, various methods have been developed for preparing diverse morphologies of SnO_2, such as nanotube [8], nanorod [9,10], mesoporous and microporous structure [11,12], nanotriangle [13] and hollow nanosphere [14]. Studies have proven that the sensing properties of nanomaterials can be dramatically affected by structure features [15,16]. Semiconductor oxide with a large surface-to-volume ratio is expected to behave high performances because of more active sites available on the surface of the material for physical or chemical interaction [17]. Meanwhile, recent research has been reported that for semiconductor oxide, the sensing performance is related to the surface depletion [18,19]. When the grain sizes of sensing materials are close to Debye length (L_d), the sensing properties can be greatly affected. However, serious agglomeration can reduce the surface-to-volume ratio of nanomaterials and result in decreasing sensitivity of gas sensors. In addition, according to the reported, the low detection limit of gas sensors usually higher than 1 ppm which may limit potential applications [20–23]. Developing a novel sensor with detection limit lower than 1 ppm has great significance.

In this letter, we reported an ultrasensitive ethanol sensor based on aloe-like SnO_2 nanostructures. The average diameter of aloe-like SnO_2 was about 2 μm where large amount of protrusive SnO_2 nanosheets stand on them with a width of about 5–10 nm. The aloe-like SnO_2 nanostructures sensor exhibits a low detection limit and high sensitivity to ethanol at 285 °C. Both the small diameter and less agglomeration contribute pronouncedly to gas sensing. Our study demonstrated that three-dimensional (3D) aloe-like SnO_2 nanostructures with the plenty of small protrusive nanosheets has potential applications in high performance gas sensors.

2. Experimental details

Aloe-like SnO_2 nanostructures can be easily prepared by a hydrothermal route. In a typical experiment, 5 mL of 0.3 M $SnCl_2{\cdot}2H_2O$ aqueous solution was added into 10 mL of 1.0 M NaOH solution and stirred for 20 min to obtain a clear solution. Then 2 mM sodium dodecyl sulphate and 20 mL ethanol solution was added to the above clear solution and stirred for 10 min. After that, it was transferred into a 60 mL Teflon-lined autoclave and maintained at 160 °C for 24 h. After the mixture cooled naturally to room temperature, the white product was collected by centrifugation, repeatedly

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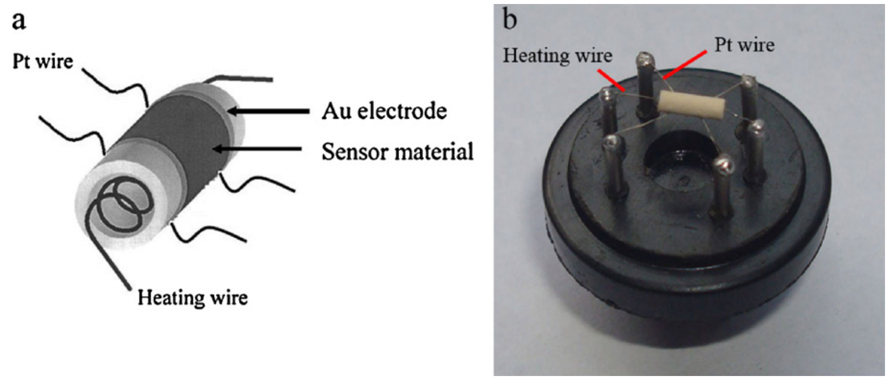

Fig. 1. (a) Schematic illustration of the sensor structure; (b) photograph of the sensor.

washed distilled water and ethanol to remove impurities. Finally, the products were annealed at 550 °C for 2 h in a muffle furnace.

The morphologies and microstructures of as-synthesized SnO_2 nanostructures were characterized by scanning electron microscopy (SEM; Hitachi S-4800) and the crystalline structure of the sample was determined by X-ray diffraction (XRD) with Cu Kα (λ = 0.15406 nm).

The detailed fabrication procedures of the sensor were similar to our previous reports [24,25], and had been described as follows: aloe-like SnO_2 nanostructures were mixed with terpineol to form a paste and then coated uniformly onto the outside surface of an alumina tube. The diameter of the tube was 1 mm and its length 5 mm. A small Ni–Cr alloy coil was placed through the tube to supply the operating temperature. Electrical contacts were made with two Pt wires attached to each gold electrode. The sensor was connected to the outside electronics to monitor its resistance change independently. The schematic diagrams of the sensor are displayed in Fig. 1. To improve their stability and repeatability, the sensor was sintered at 300 °C for 10 days in air. The sensing properties were measured by using a high precision sensor testing system NS-4003 series was made by China Zhong-Ke Micro-nano IOT (Internet of Things) Ltd. The sensing properties were investigated at working temperatures from 240 °C to 330 °C and ambient relative humidity of 57%. The sensor response (S) was defined as $S = R_a/R_g$, where R_a was the sensor resistance in air and R_g the resistance in the reducing target gas. The response time and recovery time of the sensor was the time required for a change in the sensor conductance to reach 90% of the equilibrium value after injecting and removing the detected gas.

3. Results and discussion

The XRD pattern of aloe-like SnO_2 nanostructures is shown in Fig. 2. It reveals that all the diffraction peaks are indexed to the tetragonal rutile structure of SnO_2, which agree well with the reported values from JCPDS card (41-1445). No diffraction peaks from impurities are found.

Fig. 3 shows the SEM images of aloe-like SnO_2 nanostructures calcined at the temperature of 550 °C. The low-magnification SEM image Fig. 3(a) clearly reveals that our SnO_2 sample is composed of dispersive aloe-like nanostructures with diameter about 2 μm. And the high-magnification SEM images are given in Fig. 3(b and c). Fig. 3b is shown that the leaf-like nanosheets are arranged in a radial form. Fig. 3c is demonstrated that the surface of leaf-like sheets has massive protrusive nanosheets with a width of 5–10 nm. The large amount of protrusive nanosheets can provide stable support between the 3D SnO_2 nanostructures to avoid agglomeration. Generally, the less-agglomerated SnO_2 nanostructures are promising candidate for gas sensors because they have the larger active area and superior surface-to-volume ratio.

For the semiconductor oxide sensors, working temperature is an important factor. Fig. 4 shows the sensor response at different working temperatures to 50 ppm ethanol. The sensor response increases and reaches its maximum at about 270 °C and then decreases rapidly with the increase of temperature. However, recovery time of the sensor is very long at the working temperature lower than 285 °C. And Fig. 5 shows the typical dynamic response curve of aloe-like SnO_2 sensor to 50 ppm ethanol at 285 °C. It can be seen that the resistance of the sensor decreases rapidly upon exposure to 50 ppm ethanol, and then recovers to its initial value after ethanol is released. The response of the sensor is up to 23, and the response time and recovery time of the sensor was about 1.2 s and 76 s, respectively. Therefore, 285 °C was designated to be the optimum working temperature. Furthermore, the selectivity of the sensor was also investigated. Fig. 4 shows the response to 50 ppm methanol, acetone, isopropanol and ammonia at different working temperatures. The results demonstrate that the sensor have a high response and good selectivity to ethanol.

Fig. 6 shows the real-time response curve of the sensor upon exposure to different concentrations of ethanol at 285 °C. The sensor is sensitive to ethanol even as the concentration is as low as 50 ppb. The resistance of the sensor decreases rapidly from 2.25 MΩ in air to 1.47 MΩ in 50 ppb ethanol and the response is calculated to be about 1.53. Then the resistance of the sensor recovers to its initial state after ethanol is released. With increasing the ethanol concentration, the response increases gradually. The resistances of

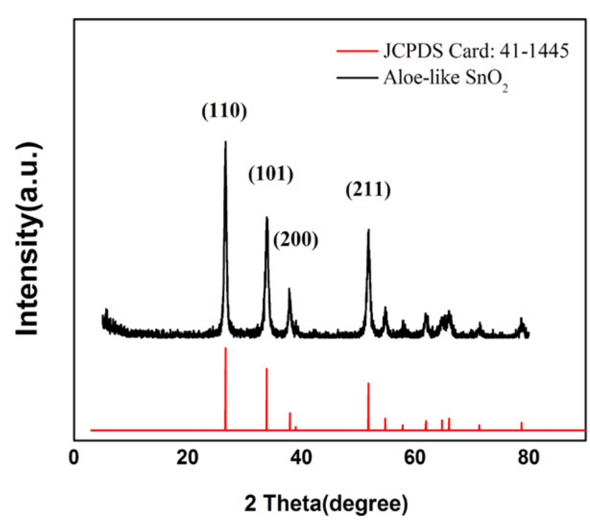

Fig. 2. XRD patterns of aloe-like SnO_2 nanostructures obtained at 550 °C.

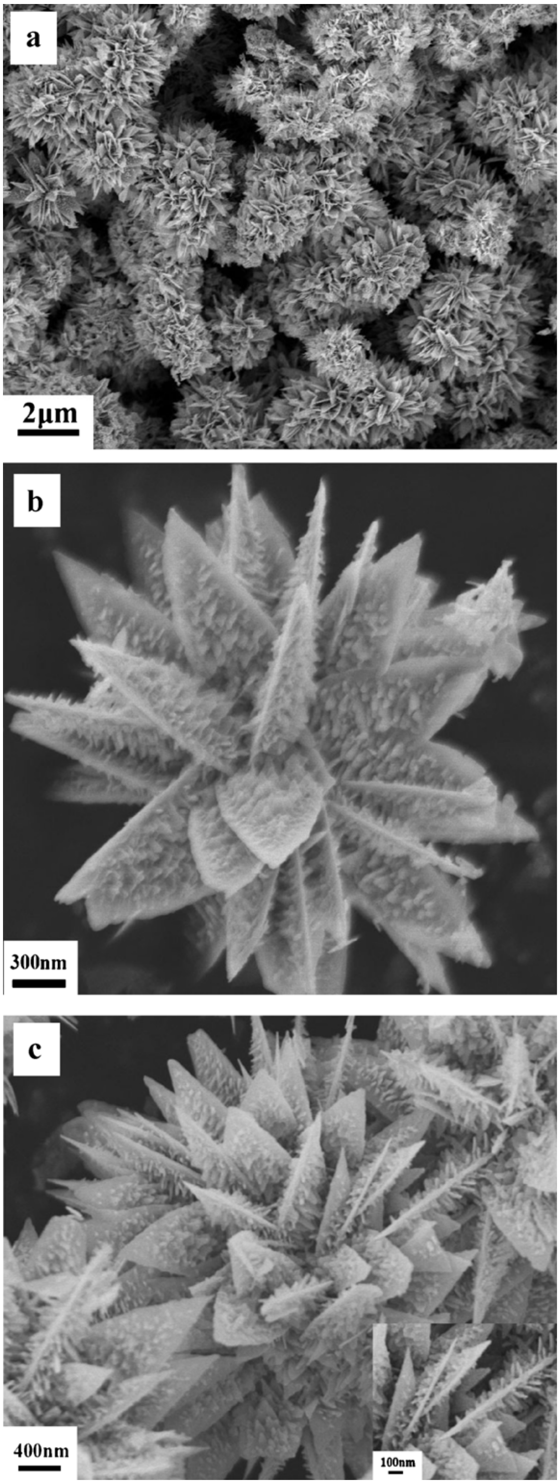

Fig. 3. Low and high-magnification SEM images of aloe-like SnO_2 nanostructures obtained at 550 °C.

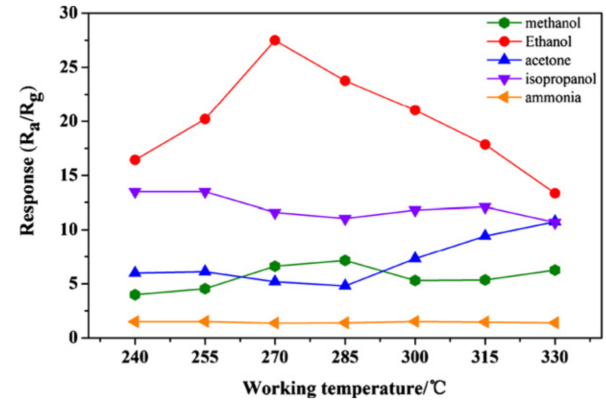

Fig. 4. The response of aloe-like SnO_2 nanostructures based sensor to 50 ppm ethanol, methanol, acetone, isopropanol and ammonia at different working temperatures.

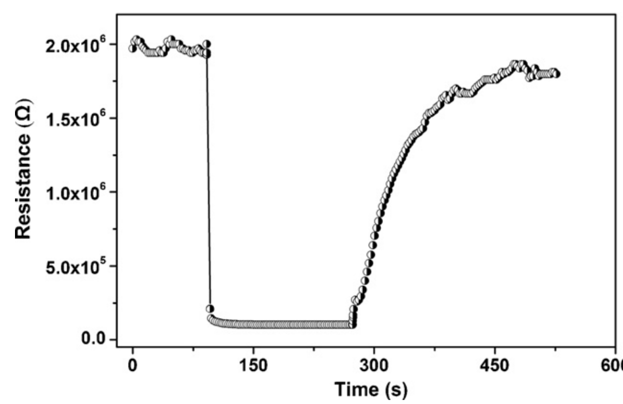

Fig. 5. Real time response of aloe-like SnO_2 nanostructures to 50 ppm ethanol at a working temperature of 285 °C.

the sensor are 1.12, 0.9, 0.75 and 0.7 MΩ, and the responses are 1.9, 2.4, 2.7 and 3.2 to 100, 200, 500 and 1000 ppb ethanol, respectively. Furthermore, after many cycles between the ethanol and fresh air, the resistance of the sensor could recover its initial state, which indicates that the sensor have good repeatability. The sensor can also detect ethanol in a high concentration. When greatly increasing the concentration of ethanol, the response of the sensor also sharply increases, as shown in Fig. 7. The responses to 10, 50 and 100 ppm ethanol are about 6.2, 23 and 29, respectively. When ethanol concentration is in the range of 0.05–10 ppm, the logarithm of the sensor response showed good linearity with the logarithm of the ethanol concentration, as shown in Fig. 8, which is in agreement with the theory of power laws for semiconductor sensors [26].

Currently, there have been few studies to report detection down to ppb level ethanol concentration. The aloe-like SnO_2 sensor shows obvious response to low concentration of ethanol and exhibits better sensing performance as compared to other oxide based ethanol sensors available in literatures as shown in Table 1. The ability to detect ethanol down to ppb level without any metal catalyst modification is probably related to the structure of aloe-like

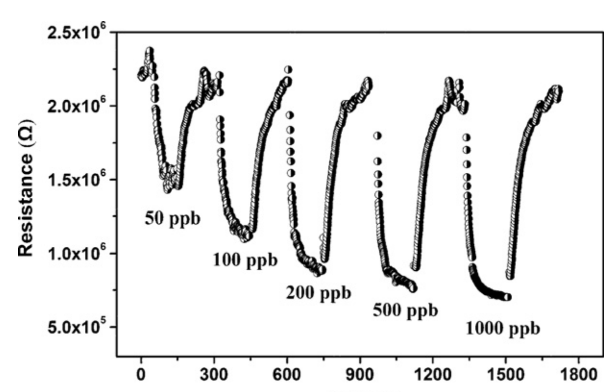

Fig. 6. Real time response of aloe-like SnO_2 nanostructures to ethanol with concentrations in the range of 50–1000 ppb at 285 °C.

Table 1
Ethanol sensing properties of different metal oxide nanostructures.

Metal oxide	Response (S)	Detection limit	Working temperature (°C)	Reference
Branched SnO_2	2.3	0.5 ppm	300	[1]
$ZnSnO_3$	2.7	1 ppm	300	[2]
Porous SnO_2 Nanotubes	11	5 ppm	200	[21]
SnO_2 nanorods	4.2	10 ppm	300	[22]
SnO_2 nanoparticles	4	1.7 ppm	220	[27]
SnO_2 hollow spheres	2.3	1 ppm	300	[28]
In-doped ZnO	3	1 ppm	300	[29]
Aloe-like SnO_2	1.53	50 ppb	285	This work

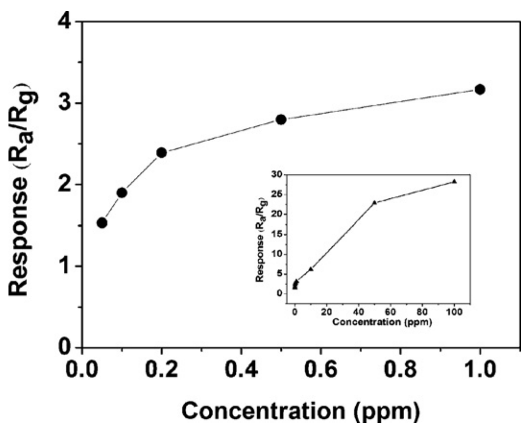

Fig. 7. Response of aloe-like SnO_2 nanostructures to various concentrations of ethanol at 285 °C.

SnO_2 nanostructures and the modulation of the conduction by the small–size protrusive nanosheets.

It is well known that semiconductor oxide sensor performance is greatly dependent on the width of surface depletion layer resulting from oxygen adsorption [18]. When the SnO_2 sensor is exposed to air, the oxygen molecules are adsorbed on the surface of aloe-like SnO_2, and capture electrons from the conduction band of SnO_2 to form O^- or O_2^-, seeing Eqs. (1)–(3).

$$O_2(\mathrm{gas}) \leftrightarrow O_2(\mathrm{ads}) \tag{1}$$

$$O_2(\mathrm{ads}) + e^- \leftrightarrow O_2^-(\mathrm{ads}) \tag{2}$$

$$O_2(\mathrm{ads}) + 2e^- \leftrightarrow 2O^-(\mathrm{ads}) \tag{3}$$

Electron depletion layer forms on the surface of aloe-like SnO_2 nanosheets, resulting in a decrease of carrier concentration and conductance of the sensor. L_d is crucial to the response of sensors

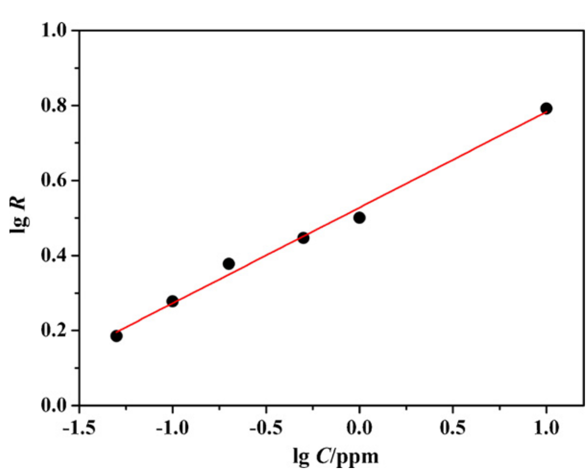

Fig. 8. The relationship between the sensor response and the ethanol concentration.

[30]. It can be expressed by [31]: $L_d = (\varepsilon kT/2e^2 n_c)^{1/2}$, where ε is the static dielectric constant, kT is the thermal energy, e is the electrical charge of the carrier and n_c *is* the carrier concentration. For SnO_2 in air, the calculated L_d is about 3 nm according to above equation. The width of the nanosheets on aloe-like SnO_2 nanostructures is close to $2L_d$. The electrons in nanosheets of SnO_2 are almost completely depleted due to oxygen adsorption in air. When the sensor is exposed to ethanol, the reductive ethanol react with the absorbed O^- or O_2^-, as described in Eq. (4), and the depleted electrons are released to the conduction band, leading to a decreasing depletion width and an increasing carrier concentration of the SnO_2 sensor. As a result, the resistance of the sensor greatly decreases. It is a conductance switch whose entire conductivity is fully determined by the surface of the sensors [32].

$$C_2H_5OH(\mathrm{gas}) + 6O^- \rightarrow 2CO_2 + 3H_2O + 6e^- \tag{4}$$

Aloe-like SnO_2 has a less-aggregative nanostructure and a large surface-to-volume ratio, which enhance the probability to absorb oxygen molecules. On the other hand, plenty of small protrusive nanosheets probably modulate the conductance of SnO_2 nanostructures, which could be also considered to explain the ultrasensitivity at the low ethanol concentration. The result indicates that aloe-like SnO_2 nanostructures is a good gas sensing material for detecting low concentration of ethanol, which can be applied for monitoring alcohol in the environment.

4. Conclusion

We have introduced an ultrasensitive gas sensor based on aloe-like SnO_2 nanostructures, which consist of a large amount of nanosheets. The sensor based on aloe-like SnO_2 can detect ethanol as low as 50 ppb. The sensor exhibit a low detection limit, fast response, high sensitivity and excellent stability due to its thinner structure and less agglomerated. It is believed that aloe-like SnO_2 nanostructures sensor is a promising candidate for the efficient detection of ethanol at ppb level.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.snb.2011.06.054.

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