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Large-scale synthesis of flowerlike ZnO nanostructure by a simple chemical solution route and its gas-sensing property

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ABSTRACT

A large-scale flowerlike ZnO nanostructure is prepared using a very simple solution method at near room temperature. The flowerlike ZnO nanostructure is self-assembled by thin and uniform nanosheets with a thickness of approximately 18 nm. X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to characterize the structure and morphology. The possible growth mechanism is carefully discussed based on the reaction process. The as-prepared ZnO nanoflowers exhibit a good response and reversibility to some organic gases, such as ethanol and n-butanol. The responses to 100 ppm ethanol and n-butanol are 25.4 and 24.1, respectively, at a working temperature of 320 °C. In addition, the sensors exhibit a good response to acetone, 2-propanol, and methanol. The relationship between the gas-sensing properties and the microstructure of the as-prepared ZnO nanoflowers is also investigated.

1. Introduction

Recently, three-dimensional (3D) nanoscale materials have received considerable attention due to their remarkable properties as applied in optoelectronic and electronic nanodevices [1–4]. In particular, semiconductor nanomaterials are very interesting from the point of view of application in gas sensors [5,6]. Of interests, ZnO is recognized as one of the most promising oxide semiconductor materials because of its good optical, electrical and piezoelectrical properties. It can be used in many areas, such as field emission displays, solar cells and gas sensors [7–9]. However, many studies have currently been focused on the gas-sensing properties of ZnO nano-dots, nanorods, nanowires and nanoplates [10–15]. Very few detailed reports are seen on the gas-sensing properties of ZnO nanoflowers assemblied with nanosheets. The gas-sensing efficiency of a material depends on its microstructural properties which are related to its method of preparation, the latter plays a very important role with regard to the chemistry, structure and properties of ZnO nanomaterials.

Catalysts or templates are commonly used to prepare 3D ZnO superstructures [16,17]. Recently, wet chemical process without any catalyst or template has been employed to synthesize ZnO nanoflowers with nanorods [18–26] and ZnO nanoflowers with nanosheets [27–31]. For example, a large-scale flowerlike ZnO nanostructure assembled by many hexagonal-structured ZnO nanosheets was achieved in a relatively pure ethanol circumstance through a very simple solvothermal method [27]. Hou et al. [28] prepared flowerlike ZnO constructed from nanosheets via a microemulsion method at room temperature. Zuo et al. [29] synthesized flowerlike ZnO architectures with nanosheets through a very simple solvothermal method. Zhao et al. [30] prepared flowerlike ZnO nanostructure with nanosheets on a large scale through a very simple solution method in the present of tri-potassium citrate. Until now, most of flowerlike ZnO structures were fabricated through the surfactants or structure-directing reagents assistant assembly mechanism. But the self-assembly of nanoparticles into the flowerlike morphologies and hierarchical architectures in the absence of any surfactants still remains a tremendous challenge. Importantly, different experimental methods, which always affect the crystalline quality and fine structure of samples, will directly influence the sensing properties of the fabricated nanostructures. In this paper, ZnO nanoflowers are prepared by a simple chemical solution route in the absence of high temperature, surfactant, template and structure-directing solvent. The gas-sensing properties of the ZnO nanoflowers are also discussed. We found that the process is convenient, environmentally friendly, inexpensive and efficient.

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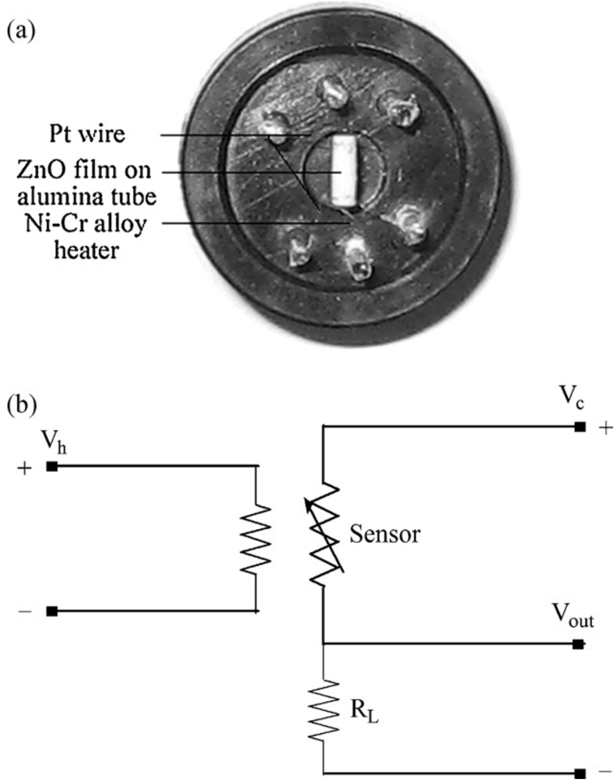

Fig. 1. (a) Photograph of the sensor and (b) test principle of the gas-sensing measurement system (V_h: heating voltage; V_c: circuit voltage; V_{out}: signal voltage and R_L: load resistor).

Furthermore, the obtained ZnO nanoflowers exhibited an excellent gas-sensing sensor signal with test gases.

2. Experimental details

2.1. Preparation of flowerlike ZnO nanostructures

Briefly, $Zn(NO_3)_2{\cdot}6H_2O$ was dissolved in distilled water to form a 0.13 M solution. Excess NaOH was dissolved in the above solution at room temperature ([NaOH] = 1.3 M). The above solution was heated in an oil bath at 50 °C for 90 min. Then the heating was terminated and the solution was allowed to cool down to room temperature. The product was separated using centrifugation, washed with absolute ethanol three times, and dried at 40 °C in a vacuum. Finally, the flowerlike ZnO nanostructures were obtained. The obtained ZnO nanoflowers were used as the sensitive materials in the experiments.

2.2. Characterization

The products were characterized by X-ray diffraction (XRD, Shimadzu XRD-6000, with high-intensity Cu Kα radiation, wavelength 1.54178 Å), scanning electron microscopy (FE-SEM, Hitachi S-4800, operated at 5 kV), and transmission electron microscopy (TEM, Hitachi H-800 with an accelerating voltage of 200 kV). The energy dispersive spectroscopy (EDS) was achieved on a scanning electron microscope (FE-SEM, Hitachi S-4800, operated at 15 kV).

2.3. Gas sensor fabrication and response test

The as-prepared flowerlike ZnO nanostructures were directly coated on the outer surface of an alumina tube-like substrate on which a pair of Au electrodes had been printed previously, followed by drying at 60 °C for about 2 h and subsequent annealing at 400 °C for about 3 h. Finally, a small Ni–Cr alloy coil was inserted into the tube as a heater, which provided the working temperature of the gas sensor. The gas sensor fabricated with a flowerlike ZnO nanostructure film on a ceramic tube is shown in Fig. 1a.

In order to improve the long-term stability, the sensors were kept at the working temperature for 2 days. A stationary state gas distribution method was used for testing gas response in dry air. In the measurement of electric circuit for gas sensors (Fig. 1b), a load resistor was connected in series with a gas sensor. The circuit voltage was set at 5 V, and the output voltage (V_{out}) was the terminal voltage of the load resistor. The working temperature of a sensor was adjusted through varying the heating voltage. The resistance of a sensor in air or test gas was measured by monitoring V_{out}. The test was operated in a measuring system of ART-2000A (Art Beijing Science and Technology Development Co., Ltd., PR China). A headspace sample (HP-7694) was used to inject the test gases into a 1000 ml sensor test chamber, where a ZnO gas sensor was set. Detecting gases, such as C_2H_5OH, were injected into a test chamber and mixed with air. Fig. 2 shows the experimental setup. The gas response of the sensor in this paper was defined as $S = R_a/R_g$ (reducing gases), where R_a and R_g were the resistance in air and test gas, respectively. In this measurement system, the gas response of the sensor also can be calculated by the following equation: $S = (V_{gas} \cdot (5000 - V_{air}))/(V_{air} \cdot (5000 - V_{gas}))$, where V_{air} and V_{gas} were the output voltages in air and test gas, respectively. The response or recovery time was expressed as the time taken for the sensor output to reach 90% of its saturation after applying or switching off the gas in a step function.

3. Results and discussion

3.1. Structure and morphology

Fig. 3 shows the XRD pattern and EDS of the as-prepared nanoflowers. From Fig. 3a, all of the peaks of the nanoflowers can be indexed to wurtzite (hexagonal) structured ZnO (JCPDS card no. 79-2205). No characteristic peak is observed for other impurities such as $Zn(OH)_2$, etc. The strong and sharp reflection peaks suggest that the products are highly crystalline. The EDS result (Fig. 3b) demonstrates only elements Zn and O contained in the sample (the silicon comes from the silicon substrate). Hence the as-prepared product is hexagonal wurtzite ZnO.

The SEM images of the sample are shown in Fig. 4. Fig. 4a and b is the image of the ZnO nanoflowers in low magnification and medium magnification, respectively. From the SEM observations, the ZnO product contains numerous flowerlike aggregates with multi-leaves, and almost all of them show same morphology. The ZnO nanoflowers had diameters of about 1–3 μm. The insert (Fig. 4b) is the image of a ZnO nanoflower in high magnification. Clearly, each flower is made up of many thin nanosheets, which are spoke wise, i.e. projected from a common central zone. Careful examination reveals that these ZnO nanosheets are 200–600 nm in width and about 18 nm in thickness. Furthermore, each nanosheet has almost the same thickness perpendicular to its 2D face, indicating the sheet growth is strictly extended in the 2D plane throughout the whole growing process.

To give a further understanding of these ZnO nanoflowers, the sample was intensively sonicated for 2 h in ethanol. Many ZnO nanoflowers and little individual nanosheets (most of the nanosheets connected together and could not be moved off by the sonication) can be observed in the sonicated sample. Fig. 5 shows the TEM image of some ZnO nanoflowers after sonication. Fig. 5a indicates that the flower is mainly composed of vertical nanosheets, which is in good agreement with the SEM observation. From Fig. 5b,

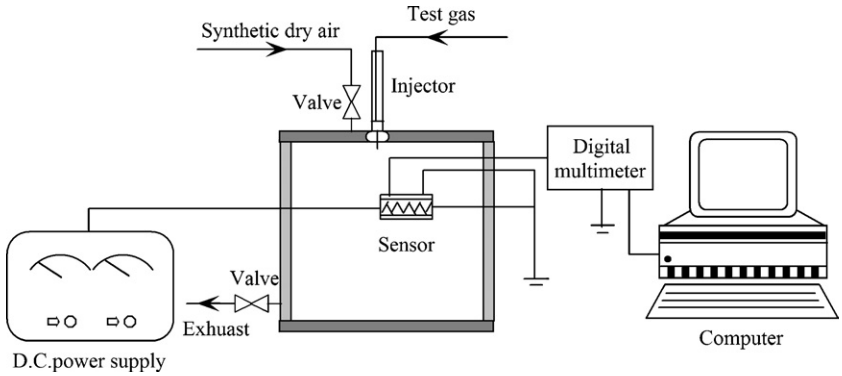

Fig. 2. The experimental set-up.

it is clear that the nanostructures build from not only the vertical nanosheets but also some horizontal nanosheets, which exhibit a single crystalline diffraction pattern (inset).

3.2. *Studies on the growth process*

Synthesis of ZnO nano- or microstructures from aqueous solution containing $Zn(OH)_4{}^{2-}$ ions has been reported just from the near recent years. The growth process of ZnO crystallites is generally accepted via the following mechanism:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow \quad (1)$$

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4{}^{2-} \quad (2)$$

$$Zn(OH)_4{}^{2-} \rightarrow ZnO + 2H_2O + 2OH^- \quad (3)$$

The reaction (1) could be easily observed when adding NaOH to the Zn^{2+} solution. As more of the NaOH solution was added, the $Zn(OH)_2$ precipitate dissolved to yield a homogenous aqueous solution containing $Zn(OH)_4{}^{2-}$ ions. Upon increasing the time further, ZnO nuclei formed from the dehydration of $Zn(OH)_4{}^{2-}$ ions and followed by crystal growth. During the process, $Zn(OH)_4{}^{2-}$ is proposed to be the growth unit that is directly incorporated into ZnO crystallites under given conditions.

In liquid medium, although the growth habit of ZnO crystal is mainly determined by its intrinsic structure, it is also affected by the external conditions such as pH value of the solution, concentration of $Zn(OH)_4{}^{2-}$ ions, and so on. The growth process was also monitored by time-dependent observations. Fig. 6a–d shows the SEM images of the products that were obtained after aging for 10, 20, 40, and 1.5 h. It could be concluded that the formation of such flowerlike ZnO nanostructures was achieved via a two-

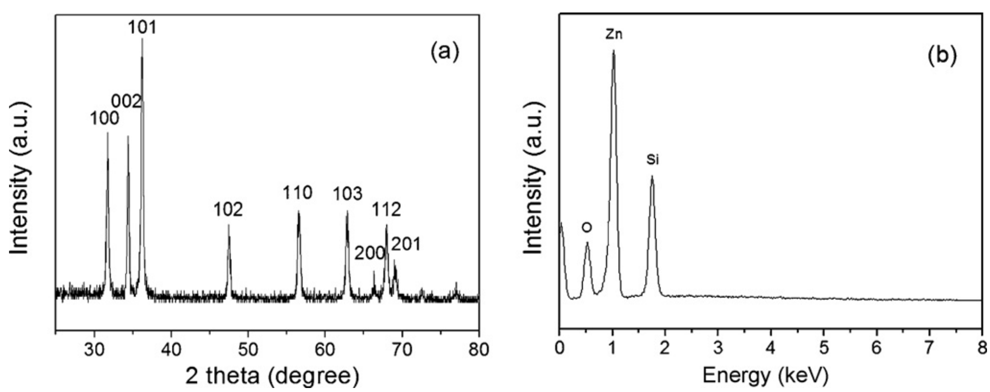

Fig. 3. XRD pattern (a) and EDS (b) of the as-prepared ZnO nanoflowers.

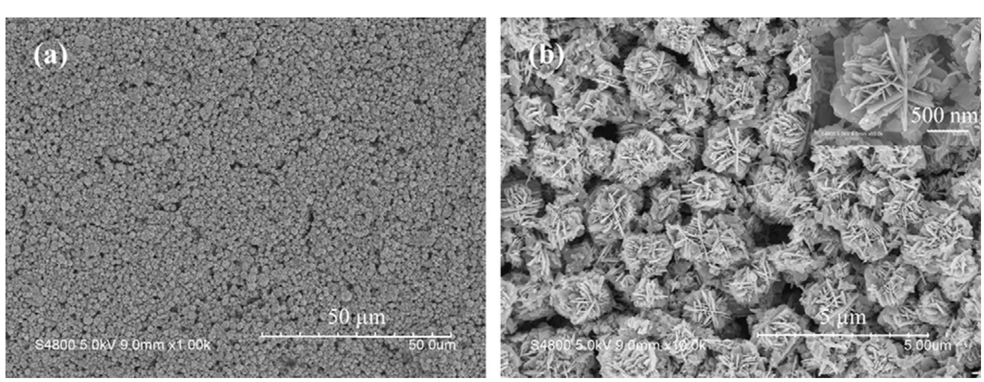

Fig. 4. Representative SEM images of the ZnO nanoflowers in different scales: (a) is the low magnification image and (b) is the medium magnification image with high magnification image (inset).

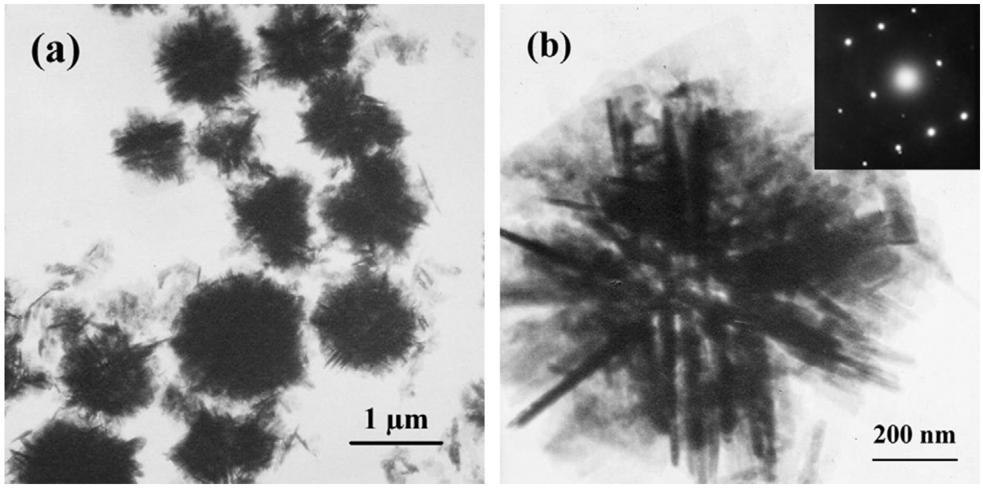

Fig. 5. TEM images of (a) the as-synthesized ZnO nanoflowers with (b) their high magnification observation, with inset SAED pattern.

step nucleation and growth mechanism. Initially, ZnO nanosheets were formed through conventional nucleation and a subsequent crystal growth process. Then, ZnO nanosheets with some nanoparticles were formed via another conventional nucleation on the ZnO nanosheet and a subsequent crystal growth process. In the crystal growth process, each nanocluster in the aggregates or on the nanosheets has its own orientation and works as a nucleus for further growth. These grown progresses are related to both the anisotropic crystal structure of ZnO and the involved solution conditions (Fig. 6a). As afore-mentioned, the growth habit of ZnO crystal could control the ZnO crystal to grow into plates. At the same time, conventional nucleation on the nanosheet occurred for the high concentration of $Zn(OH)_4{}^{2-}$ transforming to ZnO. From the thermodynamics point of view, the surface energy of an individual nanosheet was quite high with two main exposed planes, and thus they tended to aggregate to decrease the surface energy by reducing exposed areas (Fig. 6b and c). The surface energy was substantially reduced when the neighboring nanosheets were grown (Fig. 6d). As a result, flowerlike ZnO nanostructures were constructed by this two-step nucleation and growth process. Fig. 7 shows the schematic growth diagram of the ZnO nanoflowers fabricated by the solution process.

3.3. Gas-sensing properties of the ZnO nanoflowers

Panels *a* and *b* of Fig. 8 show the real-time response curve and the sensing responses of a fabricated sensor upon exposure to different concentrations of ethanol at a working temperature of 320 °C, respectively. The as-prepared flowerlike ZnO nanostructures have a good response to ethanol. At a low concentration of 1 ppm of

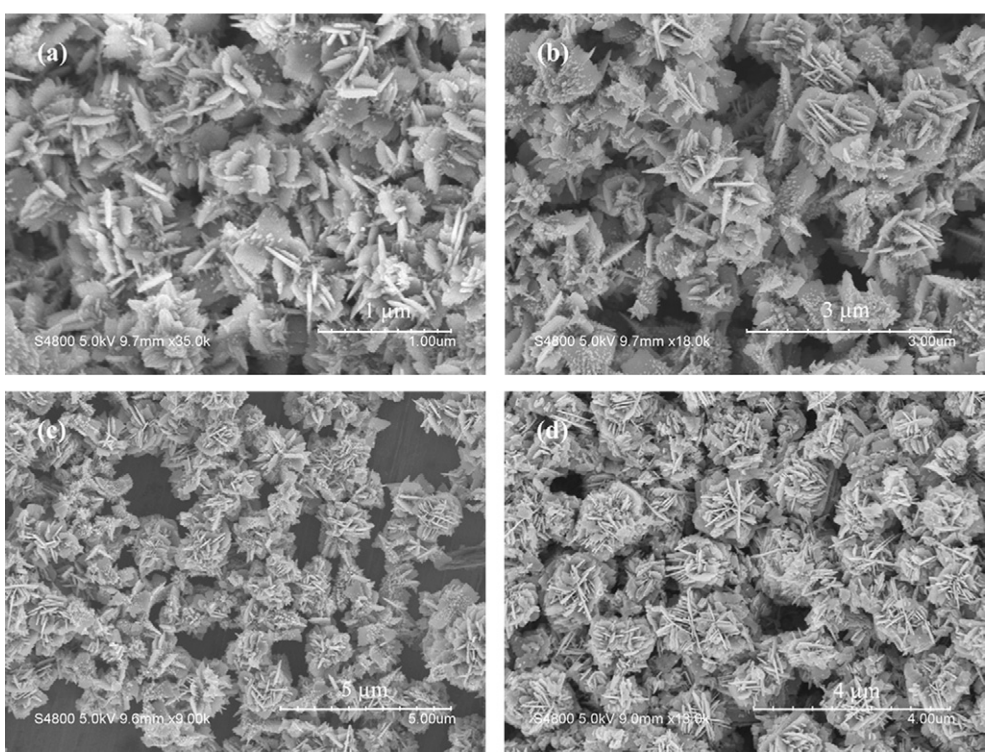

Fig. 6. SEM images of ZnO obtained after different aging times. (a) Amorphous nanoplates with some nanoparticles obtained in 10 min; (b) flowerlike and plates products obtained in 20 min; (c) amorphous flowerlike ZnO after aging for 40 min; (d) nanoflowers made up of nanoplates after aging for 1.5 h.

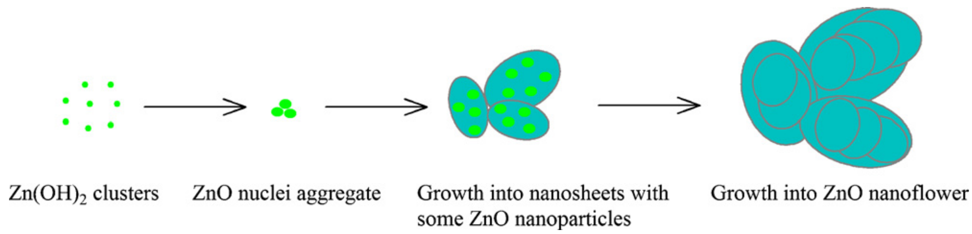

Fig. 7. The schematic growth diagram of the ZnO nanoflowers fabricated by the solution process.

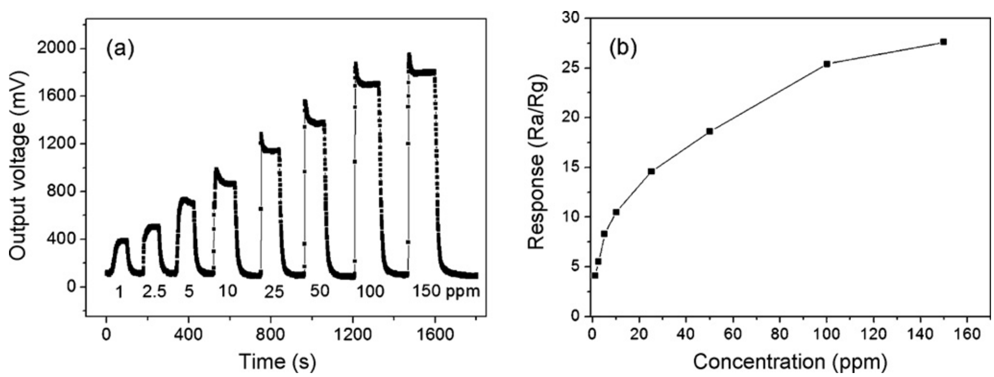

Fig. 8. Real-time response curve (a) and sensor responses (b) of the sensor device upon exposure to different concentrations of ethanol at a working temperature of 320 °C.

ethanol, the sensitivity is about 4.1. When increasing the concentration, the response of the sensor also sharply increased, as shown in Fig. 8b. The response to 100 ppm ethanol is up to 25.4, and the response time and recovery time were about 2 s and 15 s, respectively. Furthermore, according to Fig. 8a, we could observe that the sensor also had a good reversibility. The comparison of sensing responses of various pure ZnO gas sensors for ethanol sensing is summarized in Table 1. Accordingly, the response of the flowerlike ZnO nanostructures is much higher than those of ZnO nanowires [33], nanorods [11], nanoplates [14], and flowerlike ZnO structures composed of rods [34].

Furthermore, the sensor fabricated with the flowerlike ZnO nanostructures at a working temperature of 320 °C also shows a significant response to n-butanol, acetone, 2-propanol, and methanol, as shown in Fig. 9. The sensing responses to 100 ppm of the above four gases were 24.1, 14.6, 14.2, and 13.8, respectively. However, the responses to toluene and ammonia are relatively low, as shown in Fig. 10. On the basis of the slope of the response curves and the signal of the sensor responses shown in Figs. 8 and 9, it could be easily found that the sensor device presents the best response for n-butanol and alcohol. At the same time, an additional two sensors were fabricated with the flowerlike ZnO nanostructures under the same process. Similar gas-sensing properties were obtained, which suggests the good repeatability of the sensors.

It is obvious that the gas sensor exhibits rapid gas-sensing behaviors when the target gases are injected or released. This can be explained from the aspect of gas diffusion. Assuming Knudsen flow, the diffusion coefficient of the target gases can be defined by Eq. (4) [32]:

$$D_K = \frac{\varepsilon d}{3\tau}\left(\frac{8RT}{\pi M}\right)^{1/2} \tag{4}$$

where D_K is the Knudsen diffusion coefficient in a porous medium; ε, τ, d, R, T, and M are dimensionless porosity, dimensionless tortuosity, pore diameter, gas constant, temperature, and molar mass, respectively. From the equation presented above, the gas diffusion is directly proportional to the porosity and pore diameter, while it is inversely proportional to the pore tortuosity. The thickness of ZnO nanosheets is only about 18 nm. Besides, the tortuous pore network has been investigated by observations of the morphology of flowerlike ZnO with nanosheets. Therefore, the 3D flowerlike ZnO nanostructure film is suggested to allow fast diffusion of gas molecules, resulting in the high rates of gas adsorption and desorption. This could be considered as a contributor to

Table 1
Comparison of sensing performances towards ethanol of ZnO gas sensors fabricated by different approaches.

	Fabrication approach	Ethanol concentrated (ppm)	Temp (°C)/rel humidity (%)	Sensor response (S) R_{air}/R_{gas}	Response time/recove ry time (s)	Ref
ZnO nanowires	Electrospun	160	220/in air	10	16/25	[33]
ZnO nanorods	Hydrothermal route	100	332/in air	13.5	–/–	[11]
Porous ZnO nanoplates	Thermal evaporation and condensation	100	380/inair	8.9	32/17	[14]
Flowerlike ZnO with nanorods	Hydrothermal route	100	300/20% RH	14.6	–/–	[34]
Flowerlike ZnO with nanosheets	Solution route	100	320/in air	25.4	2/15	This work

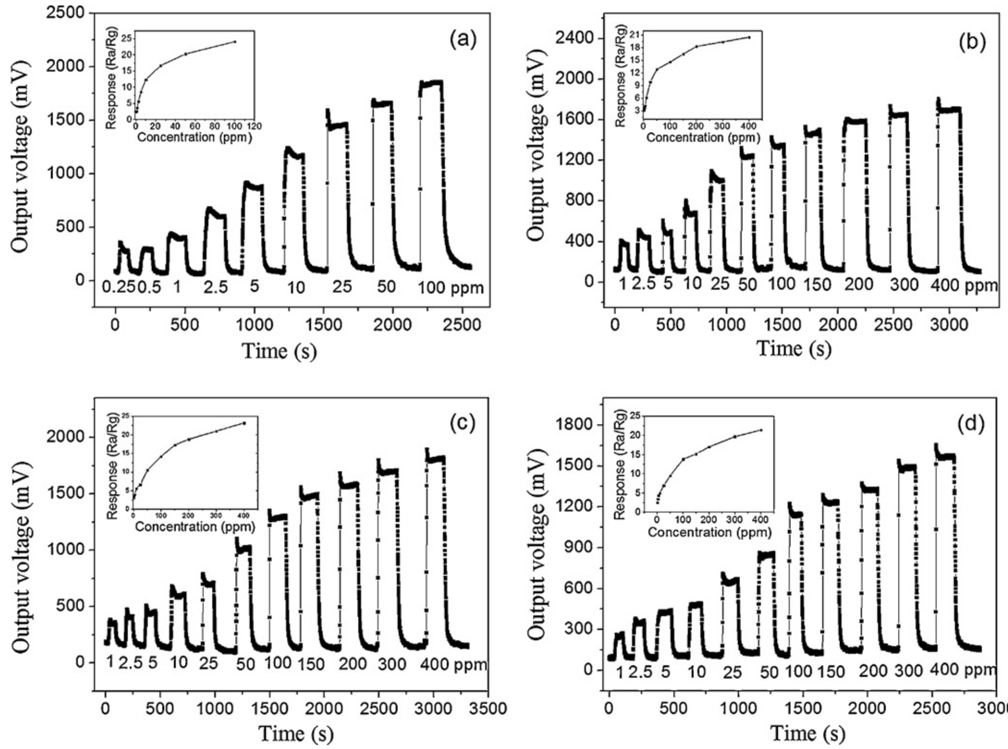

Fig. 9. Real-time response curves of the sensor device upon exposure to different concentrations of methanol (a), n-butanol (b), 2-propanol (c), and acetone (d) at a working temperature of 320 °C. The insets show the corresponding sensor response curves.

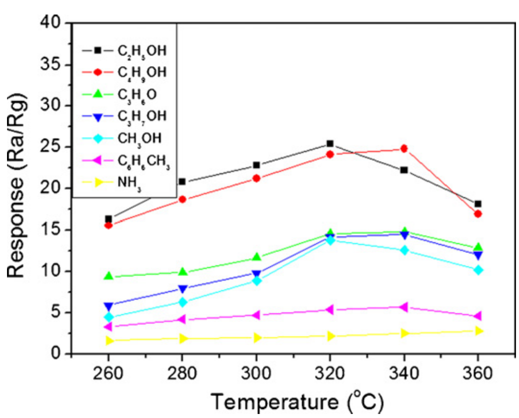

Fig. 10. Sensor responses of the sensor device upon exposure to ethanol (100 ppm) at different working temperatures.

the highly sensitive performance of the as-fabricated gas sensor. As a result, small thickness of ZnO nanosheets and 3D flowerlike nanostructures contribute to a higher sensing response. For the semiconductor oxide sensors, working temperature is an important factor. Fig. 10 presents the relationship between the sensor responses and the working temperature. In the range of 260–360 °C, the sensing response to ethanol was sharply increased with increasing working temperature, and up to 25.4 at 320 °C. Then, the sensor response is decreased at higher working temperature. So, the optimum working temperature of the sensor device was 320 °C.

The gas-sensing stability of the sensor device is very important for its further application. So we measured the sensor responses exposed to 100 ppm of ethanol one month after the previous measurement. We found that the fluctuation of the sensitivity is less than 4.2%. This indicates that the as-obtained gas sensor possesses a significant stability for potential applications.

4. Conclusions

Flowerlike ZnO nanostructures made up of nanosheets have successfully been synthesized by a facile chemical solution route without any surfactants. The nanosheets are single crystals in nature and about 18 nm in thickness. The simple synthesis approach casts new light on the controllable fabrication of novel 3D ZnO architectures. Furthermore, the gas-sensing measurements show that the flowerlike ZnO nanostructures exhibit high sensitivity, fast response/recovery and good reversibility toward some reducing gases. The sensing responses to 100 ppm of n-butanol and ethanol were 25.4 and 24.1, respectively, at a working temperature of 320 °C. The good gas-sensing properties were attributed to small thickness of ZnO nanosheets and 3D structures of the flowerlike ZnO nanostructures.

Acknowledgements

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Biographies

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