

RESEARCH PAPER

ZnO Nanoparticles as Sensing Materials with High Gas Response for Detection of n-butanol Gas

Zhezhe Wang¹, Hongchao Shang², Rongjun Zhao¹, Xinxin Xing¹, Yude Wang^{1,3*}

¹ Department of Physics, Yunnan University, 650091 Kunming, People's Republic of China.

² School of Materials Science and Engineering, Yunnan University, 650091 Kunming, People's Republic of China.

³ International Joint Centre for National Optoelectronic Energy Materials, Yunnan University, Kunming 650091, Peoples' Republic China.

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ABSTRACT

The high crystallinity ZnO nanoparticles with an average particle diameter 30 nm have been successfully synthesized with a surfactant-mediated method. The cationic surfactant (cetyltrimethylammonium bromide, CTAB) and the hydrous metal chlorides ($\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$) appear to be the good candidates for obtaining a high yield of nanoparticles. The structural and morphological characterizations were carried out by X-ray powder diffraction, scanning electron microscope and transmission electron microscopy, respectively. The resulting powders are highly crystalline and largely monodisperse ZnO nanoparticles. When used as a sensing material in gas sensor, it exhibits the high-performance gas sensing performances including high gas response, good selectivity, fast response/recovery time, good repeatability as well as stability towards low-ppm-level (10 to 100 ppm) n-butanol gas. At the optimal operating temperature (260 °C), its gas response toward 100 ppm butanol is 174.8. The response and recovery time are 18 and 11 seconds, respectively. These findings not only provide a novel approach to fabricate ZnO nanoparticles via a surfactant-mediated method, but also explore a promising gas sensor towards n-butanol.

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INTRODUCTION

As an important solvent of organic synthesis raw material and extracting agent, n-butanol is widely used in laboratory and factory. Such an agent is a stimulating and narcotic liquid. Exposing to n-butanol vapor could cause several symptoms such as headache, dizzy, drowsiness, dermatitis and discomfort of eyes, nose as well as throat [1]. Many countries' specified threshold limit value of n-butanol in the work place is only 152-304 mg/m³, such as 200 mg/m³ for China, 304 mg/m³ for Occupational Safety and Health Administration (OSHA), 152 mg/m³ for the American Conference of Governmental Industrial Hygienists (ACGIH), and so on. Moreover, n-butanol is also inflammable. Air mixture which contains of 1.45 % to 11.25 %

* Corresponding Author Email: ydawang@ynu.edu.cn

n-butanol by volume may cause explode or flash fire at a temperature higher than its flash point (35 °C). Its product of combustion contains CO and CO₂ which are suffocating gases. Thus high performance sensors to monitor n-butanol for laboratories and factories are needed. Compared with traditional method such as chromatograph [9], semiconductor metal oxide based gas sensor is thought to be the most promising miniaturized gas-sensing device owing to its high sensitivity, fast response, low cost and small size. The focus is on the development of the sensing materials with new structures or morphologies to improve sensitivity, selectivity and stability of sensors and also on the development of new and better fabrication techniques to ensure reliability, safety,

reproducibility, and cost reduction in the last decade.

ZnO is an excellent substance used for detection of volatile organic compounds (VOCs, such as ethanol, ammonia, acetone, dimethylbenzene, methanol, formaldehyde, ethanol, isopropanol n-butanol, and so on) due to its low cost, high sensitivity and quick gas recovery [2,3]. The gas sensing process of metal oxide sensors generally involves a catalytic reaction between the gas to be monitored and the adsorbed oxygen on the surface of the sensor. In view of the sensing mechanism, the particle size, defects, surface and interface properties, and stoichiometry directly affect the state and the amount of oxygen species on the surface of the sensors, and consequently the performance of metal oxide-based sensors. Recent contributions have shown that the gas sensor performance indexes could be improved by a smaller grain size which will result in higher specific surface area [4,5]. It is believed that sensor response can be improved both by doping and the increase of sensitive surface areas of the materials. It was demonstrated that the decrease of the crystallite size in the sensing layer leads to a considerable increase in gas response [6]. Therefore, the well crystallized ZnO nanocrystalline powder with small grain size ought to have good gas sensing properties. Up to now, lot of different morphological ZnO and ZnO based composites have been prepared and used for detecting n-butanol such as ZnO nanoflakes [7], ZnO nanowires [8], ZnO microflowers [4], Au-functionalized porous ZnO microsheets [9], and so on. Though they get a better gas response toward n-butanol than other metal oxide semiconductor, the performances including gas response, selectivity, response and recovery time for n-butanol detecting is still unideal. The high sensing material for the detection of n-butanol gas is still to be developed.

This paper describes a simple surfactant-mediated method to prepare ZnO nanoparticle powder with high crystallinity for sensor purposes. The obtained ZnO nanoparticle powder was used to fabricate gas sensor which shows high gas response, good selectivity, fast response and recovery toward n-butanol gas.

MATERIALS AND METHODS

Synthesis of ZnO nanoparticles

All the chemical reagents used in the experiments were obtained from commercial sources as

guaranteed-grade reagents and used without further purification. The purity of CTAB is 98% and of the inorganic precursors are not less than 98% respectively.

The synthesized method was based on the use of the cationic surfactant (CTAB) and the simple chemical materials (hydrous metal chlorides and NH_4OH) as inorganic precursors. Reaction was performed at room temperature. To prepare ZnO nano-oxide particles, the CTAB were mixed with distilled deionized water with stirring until a homogenous solution (0.08 M) was obtained. The solution of diluted NH_4OH (25 wt.% solution, 10 ml) was then added into the CTAB solution with stirring. When the mixing solution became homogenous, a solution of ZnCl_2 (0.40 M) was added respectively, under vigorous stirring. After stirring 4h, the products were aged at ambient temperature for 96 h. The resulting products were filtered, washed with distilled water to remove surfactant, and then dried at ambient temperature. Complete evolution of the surfactant from the as-prepared products to yield the ZnO nanoparticles was achieved through thermal treatment: 2 h at 500 °C under flowing air atmosphere.

Characterization of ZnO nanoparticles

Powder X-ray diffraction (XRD) data were carried out with a Rigaku D/MAX-3B powder diffractometer using Cu K_α radiation ($\lambda = 1.54056 \text{ \AA}$). The samples were scanned from 25° to 80° (2 θ) in steps of 0.01°. Scanning electron microscopy (SEM) images of the morphology of porous materials were obtained from FEI QUANTA200 with microscope operating at 30 kV. The samples for SEM were prepared by dispersing the final powders in the conductive glue; this dispersing was then sprayed with gold. Detailed studies of the microstructure were also carried out by transmission electron microscope (TEM) images and high-resolution transmission electron microscope (HRTEM) images examined on a JEOL JEM-2100 with an acceleration voltage of 200 kV. The samples for TEM were prepared by dispersing the ZnO QDs sol in ethanol, this dispersing was then dropped on carbon-copper grids covered by an amorphous carbon film.

Preparation of gas sensor

As-prepared ZnO nanoparticles were measured by a WS-30A gas sensor measurement system (Weisheng Instruments Co. Zhengzhou, China) for the humidity of 35% at 25 °C in dry air. The gas sensor was fabricated according to the literature

[6]. First, a slurry was prepared by mixing and grinding the obtained ZnO nanoparticles with a very small amount of deionized water in agate mortar. Then the slurry was carefully coated onto the outside of an alumina ceramic tube (4 mm in length, 0.8 mm in internal diameter, and 1.2 mm in external diameter) by a paint pen to form a uniformly thin film about 0.6-0.8 mm between two Au electrodes, which had been previously printed on the tube and were connected with Pt conducting wires. The alumina tube was dried at 120 °C for about 2 h and calcined in air at 400 °C for 2 h to improve the mechanical strength. Subsequently, a small Ni-Cr alloy crossed alumina tube was used as a resistor. This resistor ensured both substrate heating and temperature control with different heating voltages. After soldered them on the pedestals, the gas sensor was aged at 350 °C for 120 h in air to improve long-term stability and repeatability. During the testing process, the operating temperature was obtained via adjusting the heating voltages according to the system-provided temperature-power comparison. The air in our laboratory is considered to be the clean air. The desired amount of target solution was injected into the chamber (18 L in volume) by a microsyringe at room temperature after the resistance of the sensor was stable. Then the analyte solution was evaporated by a quick evaporator and mixed with air immediately by two

installed fans, which constitutes the measurement atmosphere. Afterwards, the chamber was opened and the air became clean with free expansion. The response of gas sensor was defined as the ratio of R_a to R_g . Where R_a is the electrical resistance in air and R_g is that in a test gas, respectively. The basic testing principle, schematic structure of the gas sensor, and the completed gas sensor are the same as in our previous work [10].

RESULTS AND DISCUSSION

The structure of as-prepared ZnO nanoparticle powder was characterized by the XRD. The assignment is further confirmed by the refinement of the diffraction pattern with the Rietveld method using the program FULLPROF. The experimental pattern, together with the calculated pattern obtained from Rietveld refinement and difference profile are shown in Fig. 1. It reveals well-developed reflections of zinc oxide (ICSS PDF No. 89-1397), space group F_4^2/m (186). No crystalline by-products such as CTAB, $ZnCl_2$ or other zinc oxides are found in the pattern, indicating that the as-prepared sample is phase pure ZnO with wurtzite-type ZnO structure. The volume-weight average crystallite size calculated from the Rietveld profile refinement is 26.7 nm. The other structural parameters obtained from the Rietveld profile refinement are presented in Table 1.

The morphology of the ZnO nanoparticles was

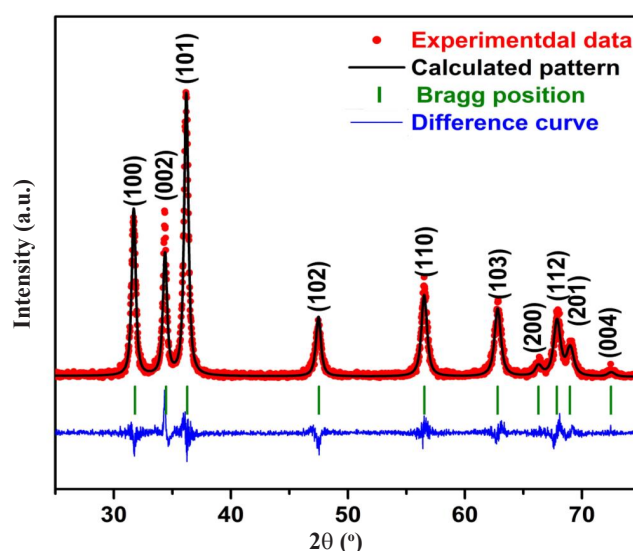


Fig. 1. X-ray diffraction analysis of ZnO nanoparticles. The experimental data is shown in red, the calculated patterns in black, and the difference curves in blue. The short vertical bars in green represent the positions of the Bragg reflections.

Table 1. Structural data and refinement parameters for the ZnO nanoparticles calculated by Rietveld refinement of the experimental XRD powder pattern.

Space group	<i>P63mc</i>
Lattice parameters	
<i>a</i> (Å)	3.2556
<i>c</i> (Å)	5.2159
Zn	
<i>x</i>	0.3333
<i>y</i>	0.6667
<i>z</i>	-0.0026
O	
<i>x</i>	0.3333
<i>y</i>	0.6667
<i>z</i>	0.3849
Crystallite size (nm)	26.7 nm

characterized by SEM. The SEM image for the sample under investigation is shown in Fig. 2. As shown in Fig. 2, the ZnO nanoparticles show a compact arrangement of uniform particles and are almost irregular in shape. SEM image reveals that there are various sizes of particles in the as-prepared sample. The large particles are composed of small crystallites and show particle aggregates of irregular shapes and large sizes (0.5–1 μm).

The morphology and structure of the product were further examined with TEM and HRTEM. From Fig. 3(a), one can observe that the particles with small agglomerates have rather uniform

near-sphere shape as well as size. It is obvious that ZnO nanoparticles are crystalline with a particle size of about 20-30 nm in the TEM image. This is a good agreement with the XRD result. To get further insight into the atomic order of the ZnO nanoparticles, high-resolution image was recorded. The HRTEM micrographs (Fig. 3(b) and (c)) show well-developed lattice fringes, which are randomly oriented with respect to each other. The clear lattice fringes displayed in Fig. 3(c) demonstrate high crystallinity and randomly oriented of the ZnO nanoparticle powder, which explain the strong diffraction peaks and non-oriented XRD pattern. The selected area electron diffraction (SAED) pattern (Fig. 3(d)) taken from them reveals ZnO nanoparticles with wurtzite structure, which is in consistent with the above XRD result.

Particle formation is a very complex process. It involves nucleation, growth, coagulation and flocculation, all of which may be influenced significantly by the surfactant assemblies. The addition of surfactant CTAB can effect the nucleation during the oxides crystallization process. After nucleation, surfactant can influence particle growth, coagulation and flocculation. Therefore, surfactant plays an important role in the preparation of these metal oxides nanoparticles [11]. This work only involves an aspect that can be applied to the synthesis of nanocrystalline materials prepared by the surfactant-mediated method. More detailed studies about the factors of control particle size, as well as the effects of nucleation growth process, are currently in progress.

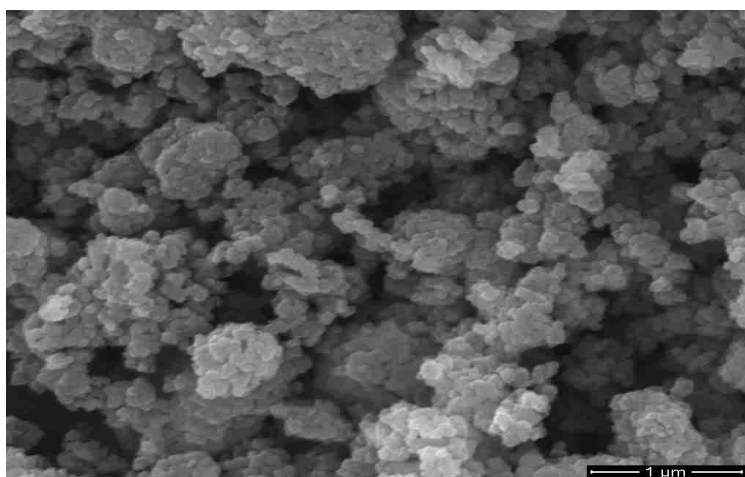


Fig. 2. SEM image of the as-prepared ZnO nanoparticles.

To evaluate the potential applicability in gas sensor for n-butanol gas, we investigated fundamental gas sensing properties of the as-prepared ZnO nanoparticles. The sensing performances of a sensor not only depend on the gas atmosphere but also on the operating temperature. Our experiments show the relation between the response and operating temperature for sensor. We find that 260 °C is the optimal operating temperature for gas sensor based on as-prepared ZnO nanoparticles. The gas response to n-butanol at operating temperature of 260 °C shows a good linear dependence on the gas concentration from 10 to 100 ppm in dry air. As shown in Fig. 4, the line for n-butanol is the calibration curve and the experimental data were fitted as:

$$\beta = 1.87C - 4.88 \quad (1)$$

where β is the gas response and C is the concentration of n-butanol. Fig. 4 shows that the

ZnO nanoparticles exhibited a high gas response of 174.8 for 100 ppm n-butanol. Therefore, such a good linearity between the gas response and gas concentration provides potential application in quantitative measurement of n-butanol concentration.

The response and recovery time is also an important factor to evaluate the gas sensing properties of the sensor. Not only a good gas response, but also quick response/recovery time is observed with this sensor at the optimal operating temperature of 260 °C. The response change of the gas sensor to n-butanol gas concentrations of 20 ppm is shown in Fig. 5. The results indicate that the sensor immediately responded when methanol gas was introduced and then rapidly recovered to its initial value after the n-butanol was released. Response time and recovery time (defined as the time required reaching 90% of the final equilibrium value) was 18 s and 11 s, respectively. It also indicates that the interaction between the sensing elements and the gas to be

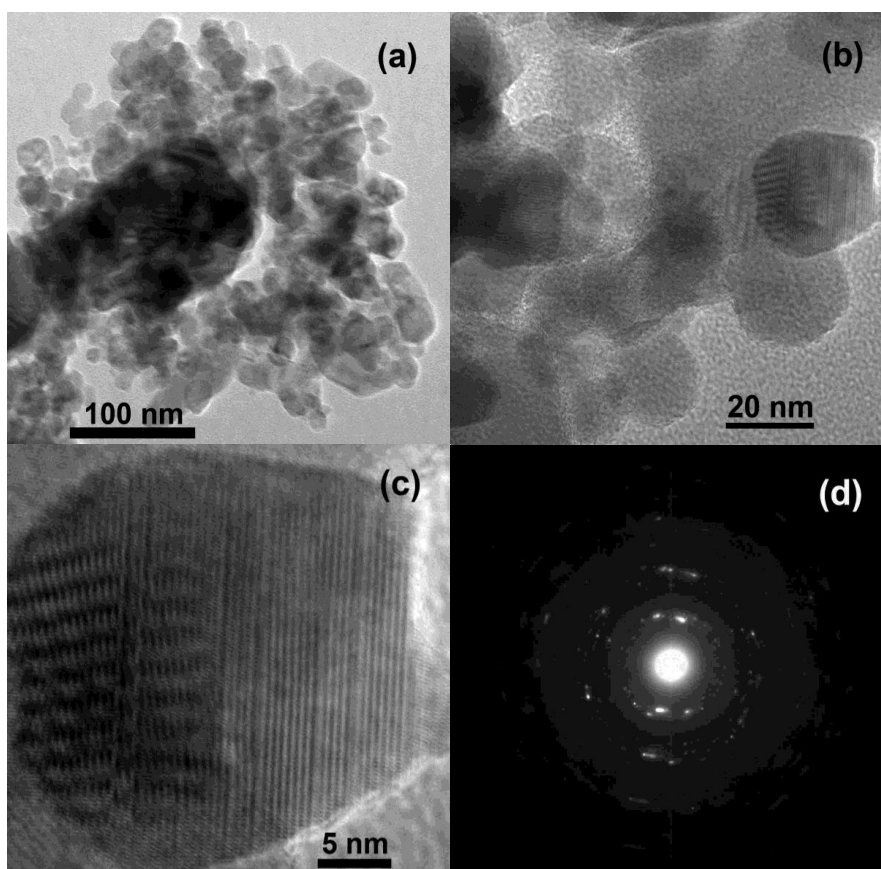


Fig. 3. TEM image of ZnO nanoparticles (a), HRTEM image of ZnO nanoparticles (b), HRTEM image of an isolated ZnO nanoparticle (c), and selected area electron diffraction (d).

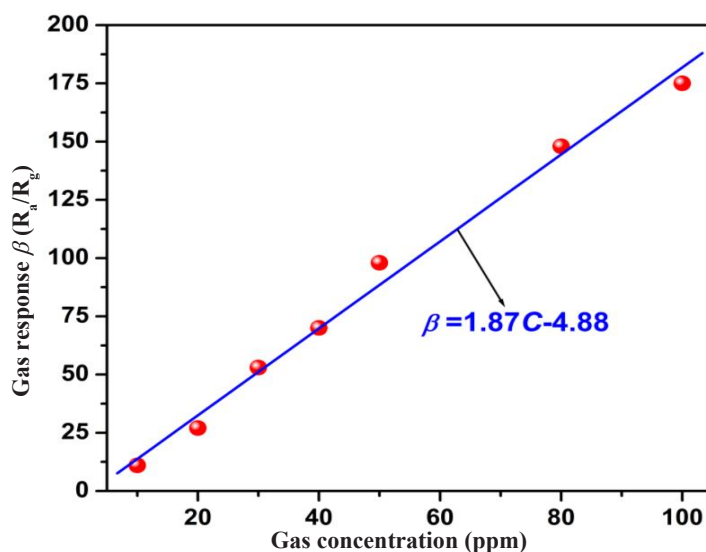


Fig. 4. Gas response of ZnO nanoparticles based gas sensors to different concentrations of n-butanol at the optimal operating temperature of 260 °C.

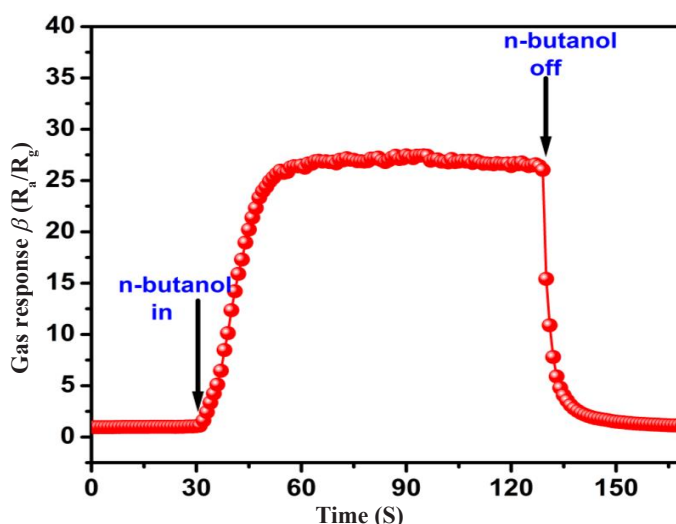


Fig. 5. Response and recovery characteristics of the sensor based on as-prepared ZnO nanoparticles at 260 °C to 20 ppm n-butanol.

detected is reversible, with a fast equilibration time.

As an efficient gas sensor, selectivity is a remarkable parameter. Good selectivity to measure a target gas in the presence of various gases molecules, especially with similar chemical and physical properties, is very significant for an excellent sensing element in practical applications [12]. The gas responses of ZnO nanoparticles towards various VOCs such as n-butanol ($\text{CH}_3(\text{CH}_2)_3\text{OH}$), ethanol ($\text{C}_2\text{H}_6\text{O}$), isopropanol ($(\text{CH}_3)_2\text{CHOH}$), methanol (CH_4O), formaldehyde (HCHO), acetone (CH_3COCH_3), dimethyl-benzene

(C_8H_{10}), ammonia ($\text{NH}_3\text{-OH}$) and methylbenzene (C_7H_8) were tested at the optimum temperature of 260 °C and the gas concentration were controlled as 100 ppm. It is obvious that the gas sensor using ZnO nanoparticles exhibits the best performance towards all of these VOCs as is shown in Fig. 6. It is obvious that the response toward n-butanol is the highest than other gases. The response toward n-butanol is probably 6.4, 4.4, 17.8, 29.2, 3.3, 13.4, 15.8 and 38.7 times higher than that toward ethanol, isopropanol, methanol, formaldehyde, acetone, dimethyl-benzene, ammonia and

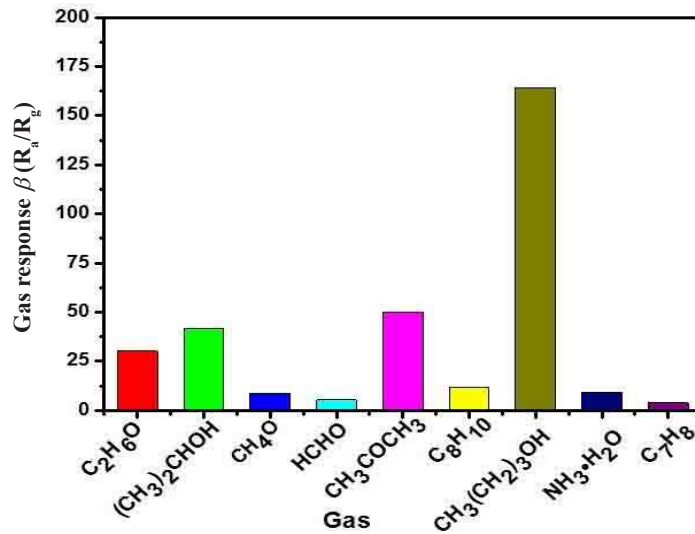


Fig. 6. Gas response of ZnO nanoparticles based gas sensors to various gases of 100 ppm at the optimal operating temperature (260 °C).

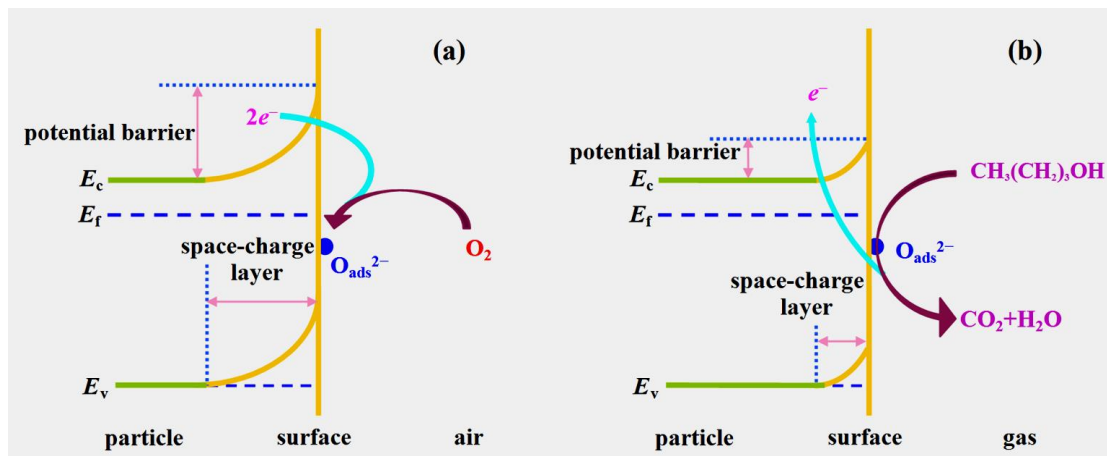
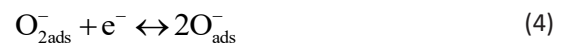


Fig. 7. A schematic diagram of the proposed reaction mechanism of ZnO nanoparticles based sensor to n-butanol. (a) in air, (b) in n-butanol.

methylbenzene, respectively. The results indicate that the as-prepared ZnO nanoparticles display superior selectivity to n-butanol against other interference gases. It is very suitable for detecting n-butanol at the operating temperature of 260 °C.

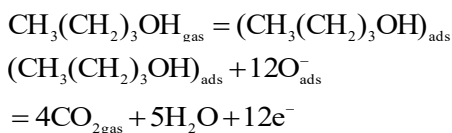
The principle of n-butanol detection of the as-fabricated sensor is based on its conductance variation, which can be interpreted by Wolkentein's model [13,14] in the following way (see Fig.7). Oxygen species in the air are adsorbed on the ZnO particle surface and ionized to adsorbed oxygen ions (O_{ads}^- and O_{ads}^{2-}) by capturing free electrons from the particles, which leads to the formation of a thick space-charge layer and a consequent

high resistance of the sensor. This process can be described using follow equations:



When the sensor was exposed to n-butanol gas, n-butanol would react with O_{ads}^- or O_{ads}^{2-} to form CO_2 and H_2O . And the electrons captured by O_{ads}^-

or O_{ads}^{2-} would be released again, which results in thinning of space-charge layer and decreasing of potential barrier. This process leads to decrease of resistance and can be expressed as follows [7,15-17]:



The maximum observed the gas response data in Fig. 4 may be explained by assuming that a maximum in the dynamic adsorption/desorption equilibrium of oxygen is reached at this temperature. The sensors have good stability to n-butanol gas for more than 60 days under the operating temperature 260 °C (data not shown). The stability mechanism is more complicated and further work is to be done to get a definite understanding.

CONCLUSIONS

ZnO nanoparticles with good gas-sensing properties have been successfully prepared by a simple surfactant-mediated method. The sample was structurally characterized by means of XRD, SEM and TEM in order to correlate physical properties with gas sensing behaviors. Gas sensor based on ZnO nanoparticles was fabricated and tested towards n-butanol gas. The as-fabricated sensor presents a high gas response, fast response and recovery, good selectivity toward n-butanol gas at an operating temperature of 260 °C. The present results imply the potentialities of using ZnO nanoparticles for detecting n-butanol gas.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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