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W-doped Nanoporous TiO_2 for High Performances Sensing Material Toward Acetone Gas

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ABSTRACT

W-doped TiO_2 with nanoporous structure was synthesized by a one-step low temperature hydrothermal method using $TiOSO_4$ and $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ as titanium and tungsten sources. Structure, morphology, specific surface area and chemical state of samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). W-doped nanoporous TiO2 samples were used as sensing materials of indirect-heating sensors and their gas-sensing performances were studied to detect acetone. The experimental results show that 7.5% W-doped nanoporous TiO_2 can adsorb more oxygen molecules on the surface and provide large amount of active reaction sites on interface to profit reaction between material and gas molecules. The gas sensor based on 7.5% W-doped nanoporous TiO_2 exhibits good gas-sensing performances, including high gas response value, shortened response/recovery time and good reproducibility, which make it a promising candidate in acetone detection. Apart from these, the mechanism related to the advanced properties was also investigated and presented.

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INTRODUCTION

Acetone has been extensively used in many industrial processes. As a harmful gas, it is one of the primary sources of indoor environmental pollutants, which can cause dizziness, a feeling of drunkenness, drowsiness, nausea and vomiting when the concentration reaches 2000 ppm [1-3]. It can cause coma, collapse and death under the higher concentration of acetone [4,5]. In the last decade, with the improvement of living standard, it is in desperate need of manufacturing sensor which is accurate and dedicated in monitoring and controlling environmental pollution in order to create a better environment quality [6,7]. Therefore, effective ways to detect acetone are needed for atmospheric environmental assessment and control. It is a desirable way to fabricate gas sensor for response towards acetone. And the acetone gas sensor plays an important role in protecting human health and safety.

TiO_2 is a typical wide-band semiconductor with band gap of 3.2 eV (anatase phase) [8-10].

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TiO_2 has the properties of low cost, non-toxicity and good chemical stability comparing with other metal oxides [11], so it has been widely used in heterogeneous lithium-ion batteries [12], photocatalysis [13], and solar cell [14]. However, the high resistance of TiO_2 results in its not very satisfying gas-sensing performances [15]. Doped chemical elements or introducing other metal-oxide forming multiple compositions is the effective way to reduce the resistivity of TiO_2 and benefit the gas-sensing performances [16]. On the other hand, the gas-sensing performances of semiconductor metal oxides (SMO) based gas sensors are generally associated with catalytic reaction between adsorbed oxygen and objective gases happened on the interface of SMO materials [17]. Therefore, it is believed that the increase of specific surface area is favorable to provide larger amount of active sites, and further benefits gas-sensing properties [12,16]. Hence, a more convenient, economical, effective and surfactant/template-free method is in desperate need to synthesizing TiO_2 with both porous structure and large specific surface area.

In this paper, we successfully synthesized W-doped nanoporous TiO_2 with large specific surface area by a one-step hydrothermal method without using of surfactant. TiO_2 samples with various W-doped ratios were utilized to prepare resistance-type gas sensor. Gas-sensing properties, including selectivity, gas response/recovery time and reproducibility, of W-doped TiO_2 based gas sensor were evaluated by recording its gas response towards acetone, formaldehyde, isopropanol, ethanol, ammonia and methanol, respectively. What's more, possible mechanism is explained via studying the relationship between morphology, specific surface area and surface chemical state of W-doped TiO_2 samples.

MATERIALS AND METHODS

Synthesis of W-doped nanoporous TiO_2

W-doped TiO_2 samples were synthesized through a one-step low temperature hydrothermal method. Titanyl sulfate ($TiOSO_4$) and $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ were both utilized as titanium and tungsten resources, respectively. The synthesis process is similar as our previous literatures [1,2]. Firstly, 4.899 g $TiOSO_4$ and appropriate amount of $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ (atomic ratio of W/Ti were controlled as 0.0%, 1.0%, 2.5%, 5.0%, 7.5% and 10.0%, respectively) were successively dissolved in 50 mL deionized water under vigorous stirring to form a homogenous precursor. After 2 h, the solution was transferred into a Teflon-lined autoclave. Secondly, the autoclave was placed into a preheated lab oven of 180 °C with the holding time of 4 h. Then, the autoclave was naturally cooled down to room temperature in standard atmosphere. Thirdly, the white precipitates were thoroughly centrifuged and washed with deionized water. After dried at 60 °C overnight, undecorated W-doped TiO_2 samples were obtained.

Characterization of as-prepared samples

Identification of crystal structure and phase of as-synthesized materials were characterized on Rigaku D/MAX-3B powder diffractometer installed with Cu K_{a1} radiation (λ = 1.54056 Å). Before XRD measurement, the samples were prepared by flattening powders into the groove of a small round aluminum tray with diameter of 20 mm and thickness of 2 mm. The samples were scanned in 2ϑ range of 10° - 80° in steps of 0.02°. Crystallite sizes (D) were calculated on the basis of Scherrer's equation: $D = 0.9l/(DW\cos q)$, here l is wavelength of X-ray (l = 1.54056 Å), q is Bragg's diffraction angle, and DW is full width at half maximum (FWHM) of XRD peak. TEM analysis was performed on a JEM-2100 to get morphological information of as-synthesized samples. XPS measurements were recorded using ESCALAB 250 system with Al-K_α X-ray beam as excitation source at room temperature. During XPS analysis, vacuum pressure of instrument chamber was controlled at $1\acute{}10^{-7}$ Pa. Specific surface area and pore size distribution of the as-synthesized samples were analyzed by Brunauer-Emmett-Teller (BET) nitrogen adsorption isotherm on a Micromeritics ASAP 2010 automated sorption analyzer at 77.3 K. All the gas-sensing properties of W-doped TiO_2 based gas sensor were measured on a WS-30A test system (Weisheng Instruments Co. Zhengzhou, China).

Fabrication and measurement of gas sensors

The gas sensor was fabricated based on the literature [17]. First of all, the obtained W-doped nanoporous TiO_2 was mixed with a few drops of deionized water to form uniform slurry. Then, the slurry was carefully daubed onto the outside of alumina tube (4 mm in length, 0.8 mm in internal diameter, and 1.2 mm in external diameter) equipped with a pair of Au electrodes at both

ends connecting with Pt conducting wires. The thickness of gas-sensing sample was about 0.6-0.8 mm, which uniformly covered the whole surface of alumina tube and Au electrodes. Then, the alumina tube was dried in an electrically heated drying oven at 120 ºC for 2 h and calcined in a tube furnace at 400 ºC for 1 h. Subsequently, a Ni-Cr alloy heating wire was inserted through alumina tube to provide operating temperature by adjusting heating voltage. After soldered it on the plastic pedestals through Pt wires, the sensor was aged at 340 ºC for 150 h in air to benefit its repeatability and stability. In gas-sensing measurement, relative humidity during the test is controlled at 25 ~ 30%. The gas response value of gas sensor was defined as R_a/R_g, here R_a and R_g are the resistance of gas sensor in air and in objective gas, respectively. The test system, test principle and schematic structure of gas sensor have been shown in our previous researches [18,19].

RESULTS AND DISCUSSION

Structure and phase of as-synthesized 7.5% W-doped nanoporous TiO_2 were studied by XRD and are displayed in Fig. 1(a). Diffraction curves can be fully indexed to anatase TiO_2 (JCPDS No. 21-1272) without any trace of byproducts such as WO_3. It indicates that the doped W probably replaces the position of Ti atom in crystal lattice. All of the XRD peaks can be readily indexed to anatase TiO_2, space group: I41/amd (141). Structural features of W-doped nanoporous TiO_2 were further investigated by TEM characterization. Fig. 1(b) shows the high-resolution TEM (HRTEM) image of as-synthesized 7.5% W-doped nanoporous TiO_2. Clear and well-developed lattice fringes demonstrate the good crystallinity of 7.5% W-doped TiO_2. Specific surface area and pore size distribution were characterized through Nitrogen adsorption-desorption isotherms analysis. As shown in Fig. 1(c), the specific surface area of 7.5% W-doped nanoporous TiO_2 is calculated to be 98.77 m^2/g, which provides sufficient active reaction sites on the surface of sample [20]. Pore size distribution calculated by the Barrett-Joyner-Halenda (BJH) method is shown in the inset of Fig. 1(c), and the main pore size of 7.5% W-doped nanoporous TiO_2 is about 3.58 nm. The porous structure can benefit diffusion of acetone gas in as-synthesized W-doped TiO_2 and the high surface area can provide large contact interface between acetone and sample, which play important roles in improve gas-sensing properties of W-doped TiO_2 [21]. XPS spectrum was used to get more information of compositions and surface chemical state of 7.5% W-doped nanoporous TiO_2. As shown in Fig. 1(d), high-resolution spectra of O 1s can be fitted into two oxygen species: peaks locating at 530.26 eV and 532.21 eV are assigned to oxygen ions in crystal lattice ($O_{lattice}$) and adsorbed oxygen species (O_x^-, including O^-, O^{2-} and O_2^- ions), respectively [16]. $O_{lattice}$ is regarded be very stable and contributes little to gas-sensing performance, for it refers to oxygen ions in crystal lattice. While O_x^- has large influence in improving gas-sensing performance for its oxidative ability [22]. To demonstrate the existence of W, composition analysis was examined using energy-dispersive Xray spectrometry (EDX) as for 7.5% W-doped nanoporous TiO_2, as indicated in Fig. 1(e). The peaks of O, Ti and W (Cu peaks are attributed to the copper grids) can be clearly seen, suggesting the high purity of the products.

Potential application of as-synthesized 7.5% W-doped nanoporous TiO_2 was investigated by analyzing its fundamental gas-sensing performances in detecting acetone. The operating temperature plays an important role in determining practicability of sensors, because it is closely related to the oxidation-reduction reactions on the surface of materials [2]. One can see that the gas response of as-synthesized 7.5% W-doped nanoporous TiO_2 based gas sensor researches its maximum value at 240 °C from Fig. 2(a). The gas response value decreases when operating temperature exceeds 240 °C. Therefore, 240 °C is selected as optimum working temperature of the as-synthesized 7.5% W-doped nanoporous TiO_2 to carry out following gas-sensing detection. As shown in Fig. 2(b), one can observe that 7.5% W-doped nanoporous TiO_2 based gas sensor shows higher gas response value and better selectivity to acetone. Its gas response value reaches as high as 173.67 towards 500 ppm acetone, and the response values to methanol, isopropanol, formaldehyde, ethanol and ammonia are 9.69, 40.14, 17.39, 17.39 and 6.72 tested at the same conditions. The response value to acetone is calculated to be 4.33 and 33.59 times higher than that to isopropanol and formaldehyde, which confirms the favorable selectivity to acetone of 7.5% W-doped nanoporous TiO_2 based sensor.

The reproducibility is another important factor in evaluating practical application of gas sensors. Fig. 3(a) shows the response-recovery curve of

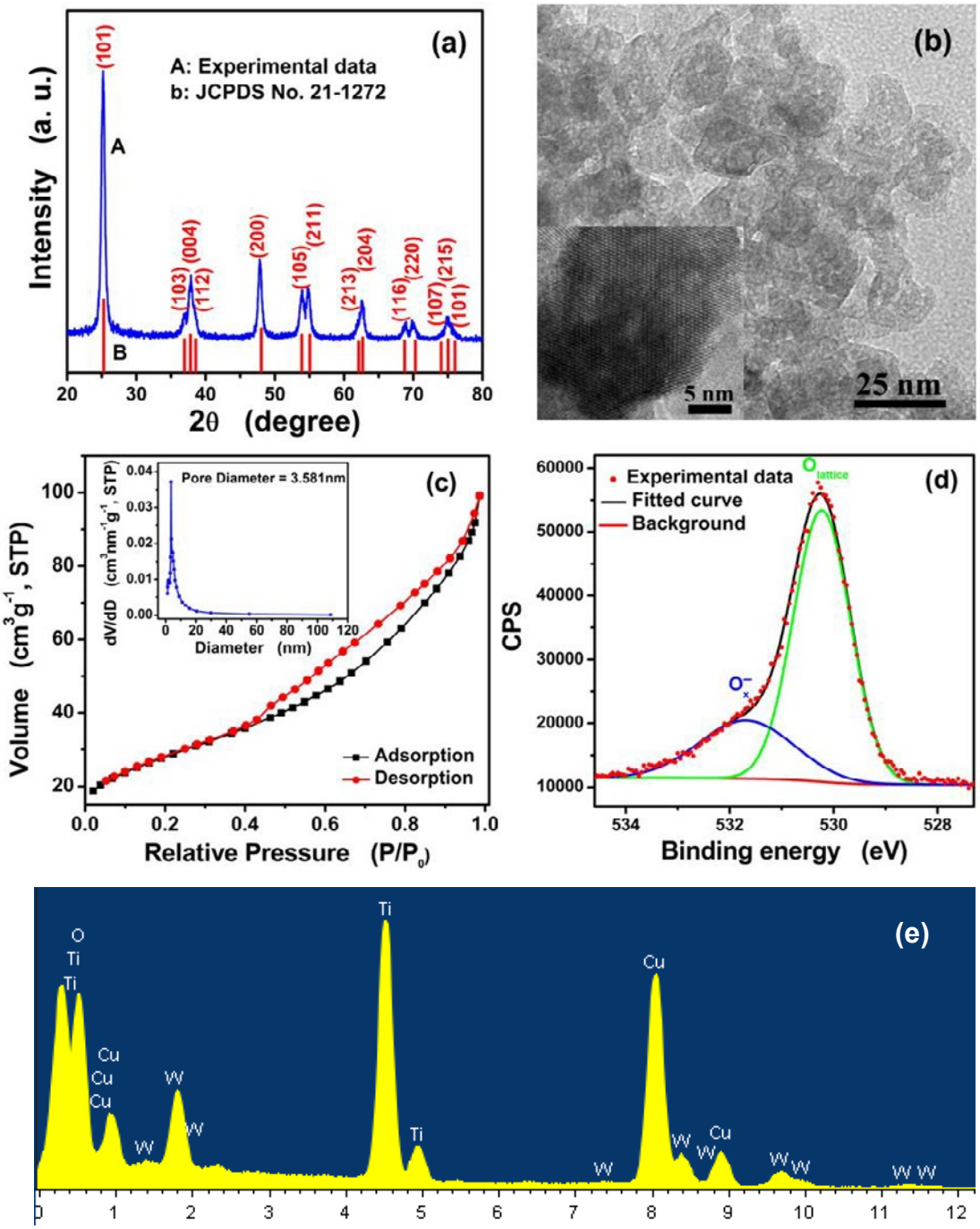

Fig. 1. (a) X-ray diffraction analysis, (b) TEM and HRTEM (inset) images, (c) Nitrogen adsorption-desorption isotherms and the corresponding pore size distributions (inset), (d) High-resolution XPS survey spectra of O 1s and (e) EDX spectrum of as-synthesized 7.5% W-doped nanoporous TiO_2.

7.5% W-doped nanoporous TiO_2 based gas sensor to acetone under the gas concentration from 5 ppm to 1000 ppm. The reproducibility can be deduced from the response-recovery curve: the adsorption platforms display a stepwise increment with the increase of gas concentration recover to base value once releasing acetone. Correspondingly, response and recovery time of 7.5% W-doped TiO_2

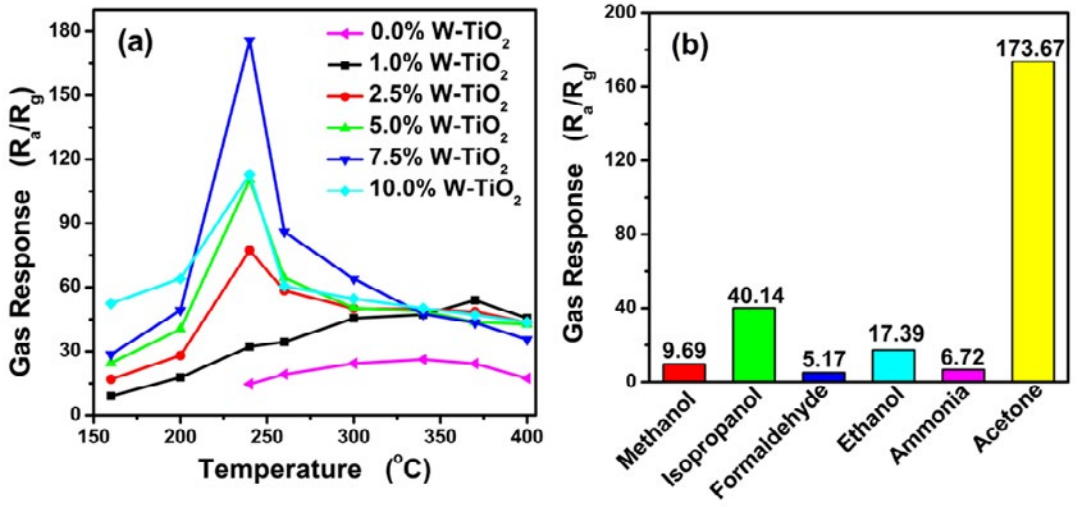

Fig. 2. (a) Gas responses of the sensors based on pure and different molar ratios of W-doped nanoporous TiO_2 at different operating temperature toward 500 ppm acetone. (b) Selectivity of acetone in relation to various gases for a gas sensor based on 7.5% W-doped nanoporous TiO_2 at a fixed concentration of 500 ppm at operating temperature of 240 °C.

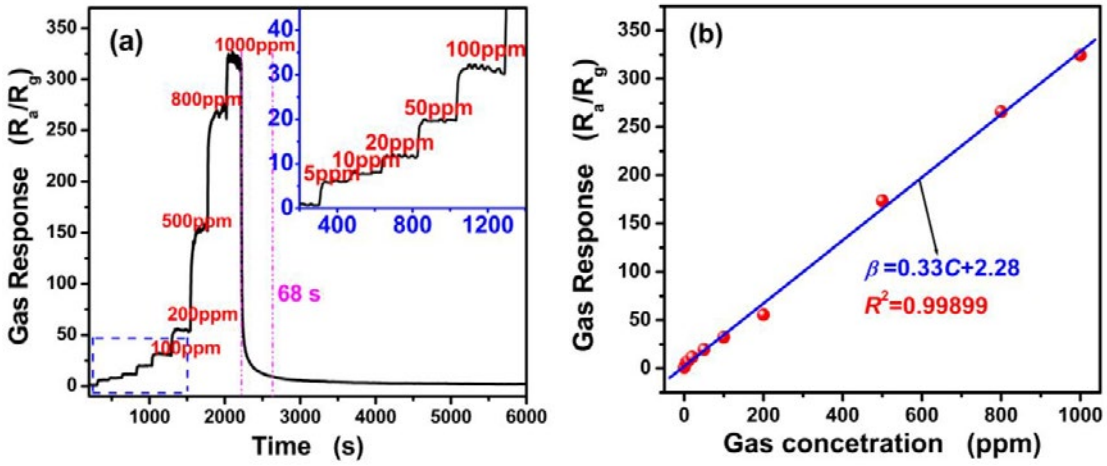

Fig. 3. (a) Dynamic response/recovery curve of the sensor based on 7.5% W-doped nanoporous TiO_2 to different acetone concentration from 50 to 1000 ppm at the operating temperature of 240 °C. (b) Linear dependence relation between response sensitivity and gas concentration in a range of 5-1000 ppm.

based gas sensor towards 500 ppm acetone are 14 s and 9 s, respectively. The relationship between gas response and concentration of acetone has been investigated at the concentration range of 5 to 1000 ppm and shown in Fig. 3(b). The relationship can be fitted into straight line:

$$\beta = 0.33C + 2.28$$

Here β is gas response and C is gas concentration, respectively. Correlative coefficients value (R^2) is higher than 0.99, indicating that the linear relationship between gas response value and gas concentration of acetone has guiding significance in judging corresponding gas concentration by gas response value.

A brief comparison of gas response of various TiO_2 nanostructures based gas sensor towards acetone is listed in Table 1. It is obvious that 7.5% W-doped nanoporous TiO_2 based gas sensor reported in this work displays higher gas response value when comparing with the response of pure TiO_2 and its composites in detecting acetone [23-32].

Table 1. Comparison of varied titanium oxide nanostructures and their composites in acetone sensing performances

Materials	Operating temperature (°C)	β	Reference
7.5%W-doping nanoporous TiO_2	240	12.22@20 ppm 19.69@50 ppm 31.49@100 ppm 55.87@200 ppm 173.67@500 ppm 322.08@1000 ppm	This work
Surface-coarsened TiO_2 nanobelts	350	4.6@300 ppm	[21]
TiO_2 nanobelts		2.9@300 ppm	
TiO_2 nanorods	500	20@500 ppm	[22]
TiO_2	400	0.75@100 ppm	[23]
TiO_2-V_2O_5	300	9.5@100 ppm	
Pure TiO_2	400	5.6@400 ppm	[24]
1 at% Nb/ TiO_2		8.1@400 ppm	
3 at% Nb/ TiO_2		13.0@400 ppm	
5 at% Nb/ TiO_2		8.0@400 ppm	
TiO_2	350	0.5@100 ppm	[25]
TiO_2-WO_3(L)		12.0@100 ppm	
TiO_2 thin film	300	0.35@25 ppm	[26]
TiO_2/NiO 99/1		0.45@25 ppm	
TiO_2/NiO 95/5		0.70@25 ppm	
TiO_2/NiO 90/10		15.00@25 ppm	
TiO_2 thin film	150	1.15@50 ppm	[27]
TiO_2 nanotubes	150	2.08@10^3 ppm	[28]
Ni-TiO_2 nanotubes	100	5.56@10^3 ppm	
Pd-TiO_2 nanotubes	100	33.30@10^3 ppm	
TiO_2 nanorod	400	5.82@200 ppm	[29]
NiO-TiO_2 nanorod		9.33@200 ppm	

As a typical n-type semiconductor material, the gas-sensing mechanism of W-doped TiO_2 depends on the resistance change of corresponding gas sensor [33]. Based on Wolkenstein's model for semiconductors [32], tungsten dopant in TiO_2 leads to remarkable improvement of several gas-sensing performances in detecting acetone. In general, enhanced gas-sensing abilities are closed related to special porous morphology, large specific surface area, proper amount of dopant and the amount of adsorbed oxygen ions [17]. In our previous research, it can be concluded that the amount of adsorbed oxygen ions changes along with temperature [34]. High temperature can easily excite free electrons from valence band and impurity energy level to conduction band, then electrons are captured by oxygens adsorbed on the surface of gas-sensing material forming increased amount of adsorbed oxygen ions (like O^-, O^{2-} and O_2^- ions). These processes can be illustrated as follows [35,36]:

$$O_{2gas} \leftrightarrow O_{2ads} \quad (1)$$

$$O_{2ads} + e^- \leftrightarrow O^-_{2ads} \quad (2)$$

$$O^-_{2ads} + e^- \leftrightarrow 2O^-_{ads} \quad (3)$$

$$O^-_{ads} + e^- \leftrightarrow O^{2-}_{ads} \quad (4)$$

W-doped nanoporous TiO_2 leads to remarkable improvement in gas response value towards acetone. The reason is attributed to that W acts as the role of enhancing chemical activity of acetone, thus improves the amount of adsorbed oxygen ions on the surface of gas-sensing material. As a typical n-type semiconductor, gas-sensing performances of TiO_2 are mostly associated with the change of surface occupation. According to Wolkenstein's model for semiconductors [32], the analogous model for W-doped nanoporous TiO_2 in this work is similar to the previous reported work [35]. In air, oxygen molecules adsorbed on the surface of W-doped nanoporous TiO_2 can capture electrons on conduction band forming adsorbed oxygen ions (O^-_x), increasing the thickness of space-charge layer and further increase the resistance of gas sensor [37].

Gas-sensing mechanisms of W-doped nanoporous TiO_2 based gas sensor in detecting acetone is shown in Fig. 4. It is obvious that increased amount of adsorbed oxygen ions on the surface of W-doped nanoporous TiO_2 material results in a series of enhanced gas-sensing performance, like high gas response value, fast response/recovery time and good selectivity and reproducibility [38,39]. Even so, it is still needed to further investigate the validity of this assumption.

Once the sensor is exposed to acetone, acetone molecules will react with adsorbed oxygen ions on the surface of material. Then electrons are released from adsorbed oxygen ions to conduction band of material, leading to a decrease of thickness of space-charge layer and resistance of gas sensor [22]. The process can be depicted as follows [40]:

$$CH_3COCH_3(gas) \leftrightarrow CH_3COCH_3(ads) \quad (5)$$

$$CH_3COCH_3(gas) + 8O^- \rightarrow 3CO_2(gas) + 3H_2O(gas) + 8e^- \quad (6)$$

$$CH_3COCH_3(ads) + 4O_{2ads}{}^- \rightarrow 3CO_2(gas) + 3H_2O(gas) + 4e^- \quad (7)$$

Based on the above analysis of possible gas-sensing mechanism, abundant adsorbed oxygen ions on the surface of as-synthesized 7.5% W-doped nanoporous TiO_2 (as the result in XPS) have great effects on the gas-sensing properties. Besides, morphology and structure of TiO_2, and proper amount of tungsten dopant are also important factors in promoting gas-sensing performance of W-doped nanoporous TiO_2 based gas sensor.

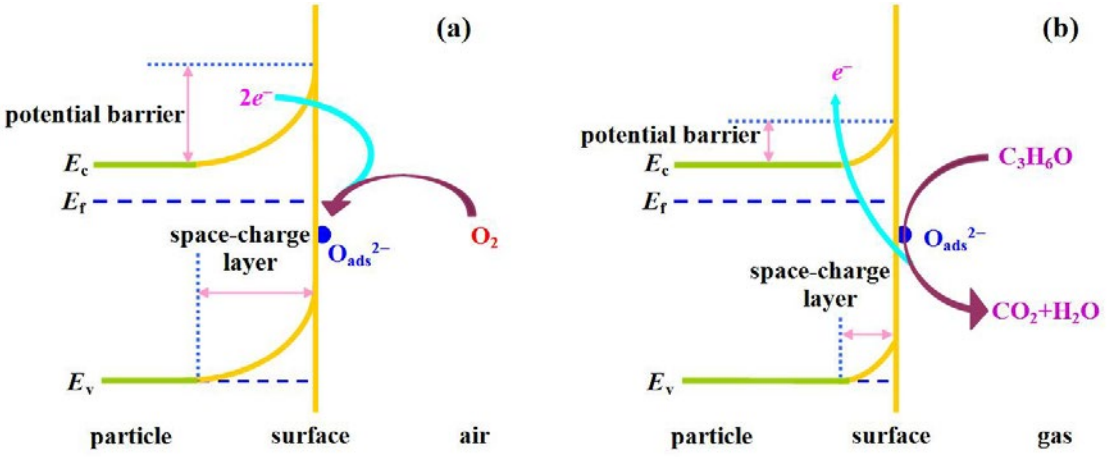

Fig. 4. Schematic diagram of proposed reaction mechanism of the TiO_2-based sensor in air (a) and in acetone (b).

CONCLUSION

In conclusion, W-doped nanoporous TiO_2 was successfully prepared via a one-step hydrothermal method. The sensors using W-doped nanoporous TiO_2 as gas-sensing material were utilized to test the gas-sensing ability of W-doped TiO_2 material by detecting acetone. Results of gas-sensing measurements indicate that 7.5% W-doped nanoporous TiO_2 based gas sensor demonstrates excellent response value, fast response/recovery time, good selectivity and reproducibility to acetone, illustrating the potential use of 7.5% W-doped nanoporous TiO_2 based gas sensor in detecting acetone.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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