



Effects of morphologies on acetone-sensing properties of tungsten trioxide nanocrystals

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ABSTRACT

In this work, triclinic WO₃ nanoplates and WO₃ nanoparticles were comparatively investigated as sensing materials to detect acetone vapors. Single-crystalline WO₃ nanoplates with large side-to-thickness ratios were synthesized via a topochemical conversion from tungstate-based inorganic–organic hybrid nanobelts, and the WO₃ nanoparticles were obtained by calcining commercial H₂WO₄ powders at 550 °C. The acetone-sensing properties were evaluated by measuring the change in electrical resistance of the WO₃ sensors before and after exposure to acetone vapors with various concentrations. The WO₃ nanoplate sensors showed a high and stable sensitive response to acetone vapors with a concentration range of 2–1000 ppm, and the sensitivity was up to 42 for 1000 ppm of acetone vapor operating at 300 °C. The response and recovery times were as short as 3–10 s and 12–13 s, respectively, for the WO₃ nanoplate sensors when operating at 300 °C. The acetone-sensing performance of the WO₃ nanoplate sensors was more excellent than that of the WO₃ nanoparticle sensors under a similar operating condition. The enhancement of the WO₃ nanoplate sensors in the acetone-sensing property was attributed to the porous textures, single-crystalline microstructures and high surface areas of the aggregates consisting of WO₃ nanoplates, which were more favorable in rapid and efficient diffusion of acetone vapors than the WO₃ nanoparticles.

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1. Introduction

Chemical sensors on the basis of semiconductor metal oxide nanomaterials have extensively been developed to detect volatile organic reagents and toxic gases [1–16]. The general mechanism of the oxide semiconductor sensors is based on the changes in electrical properties before and after exposure to the target gases or vapors [1]. Acetone, a common reagent widely used in industries and labs, is harmful to health, and it is also a biomarker for diagnosis of diabetes [2]. Recently, there is increasing attention attracted on the investigation of acetone-sensing materials and devices [3–16]. ZnO-based nanocrystals [3–6], perovskite ABO₃-type oxides [7–9], SnO₂-based nanocrystals [10–15] and La₂O₃ nanocrystals [16] have

been investigated as the sensitive materials for the detection of acetone vapor at various concentration levels.

Tungsten oxides, *n*-type semiconductor materials with a band gap of 2.5–3.0 eV, have widely been investigated as photocatalysts [17], electrochromic materials [18] and electrodes for solar cells [19]. Recently, tungsten oxide nanocrystals have also been found to be promising candidate materials for gas-sensing applications [20]. WO₃ nanowires [21–23], WO₃ nanofibers [24], WO₃ hollow microspheres [25], WO₃ nanocrystals [26,27], WO₃ thin films [28] and h-WO₃/MWCNTs composites [1] have been used as the sensing materials for the detection of nitrogen oxides (N₂O, NO, NO₂). The sensors based on W₁₈O₄₉ nanowires [29], h-WO₃ nanocrystals [30], (Cr, V, Cu)-added WO₃ powders [31] and Cr-doped WO₃ nanocrystals [32] have been reported for NH₃ sensing applications. WO₃-based nanocrystals and films have also been investigated for gas-sensing applications in H₂ [28,33], ethanol [34,35], CO [36], H₂S [37], ozone [38] and humidity [39]. As far as we know, there are few reports on the acetone-sensing property of WO₃ nanocrystals [20].

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Recently, we developed a facile and efficient route to synthesize ultrathin WO₃ nanoplates with large side-to-thickness ratios, using tungstate-based inorganic–organic hybrid nanobelts as the precursors [40,41]. Our further research indicated the sensors using the above WO₃ nanoplates as the sensing material showed a highly sensitive property to alcohols [42].

In this work, we investigate the acetone sensing properties of the two-dimensional WO₃ nanoplates derived from a topochemical conversion route. For purposes of investigating the morphological effects, we also synthesize WO₃ nanoparticles by calcining commercial H₂WO₄ powders, and their acetone-sensing properties are also investigated. The related mechanisms for gas sensing are discussed.

2. Materials and methods

WO₃ nanoplates were synthesized according to our previously reported methods with some modification [40]. Firstly, H₂W₂O₇·xH₂O powders were prepared by leaching [Bi₂O₂] layers from layered Bi₂W₂O₉ using an HCl aqueous solution [43]. Secondly, the as-obtained H₂W₂O₇·xH₂O powders reacted with *n*-octylamine in a nonpolar solvent of heptane to form tungstate-based inorganic–organic hybrid nanobelts with a lamellar microstructure, alternately consisting of inorganic [WO₆] layers and organic ammonium layers [41]. Thirdly, removal of the organic ammonium layers from the tungstate-based inorganic–organic hybrid nanobelts led to the formation of ultrathin plate-like H₂WO₄ nanosized particles. Finally, the as-obtained H₂WO₄ nanoplates were then calcined at 250 °C for 5 h in air to synthesize WO₃ nanoplates. For purposes of comparison, commercial H₂WO₄ powders (AR, Sinopharm Chemical Reagent Co., Ltd.) were calcined at 550 °C for 2 h to prepare WO₃ nanoparticles.

The phase compositions of the products were determined by X-ray diffraction (XRD, Rigaku D/Max-3B diffractometer with Cu K α radiation). The morphologies of the as-obtained products were observed on a scanning electron microscope (SEM, JEOL JSM-5600, 10 kV, coating Au) and a transmission electron microscope (TEM, JEOL JEM-2100F, 200 kV). The cell parameters of the products were calculated on the basis of their XRD patterns using a UnitCell program (by TJB Holland and SAT Redfern, 1995) by minimizing the sum of squares of residuals in 2θ .

The as-obtained WO₃ nanoplates (or nanoparticles) were used to make sensors for investigation of their acetone-sensing performance using a similar method reported in Ref. [42]. WO₃ nanoplates (or nanoparticles) were firstly mixed with a small amount of de-ionized H₂O to form WO₃ pastes in a glass dish. The WO₃ pastes were then coated onto the surfaces of an Al₂O₃ microtube with four Pt electrodes. After the WO₃ coating was air-dried, the coating process was repeated until a complete coating was formed. The WO₃-coated Al₂O₃ microtube was then fixed to a special pedestal with 6 poles by welding the four Pt electrodes to 4 poles of the pedestal, respectively. A heating coil was then inserted through the Al₂O₃ microtube and its two ends were welded to the other two poles of the pedestal.

The acetone sensing response of the WO₃ nanoplate or nanoparticle sensors was measured using a commercial computer-controlled HW-30A system under a static testing condition. The sensors, integrated in a large circuit board with 32 inlet-sites, were encased in a transparent glass chamber with a volume of 13.8 L. The testing system was placed in a ventilating cabinet with a large draught capacity. Acetone vapors with various concentrations were used as the target gases to characterize the sensing performance of the WO₃ sensors. Acetone was sampled using a syringe-like sampler. Liquid acetone was injected to a hot stage located in the chamber, and then the liquid acetone evaporated quickly to form

an acetone vapor. The acetone vapor concentrations (2–1000 ppm) were calculated according to the acetone density and the volume of the chamber. The amounts (V_{acetone} , μL) of liquid acetone were determined according to Eq. (1).

$$V_{\text{acetone}} = \frac{10^{-9}V_0 \cdot M \cdot C_{\text{acetone}}}{22.4\rho \cdot p} \quad (1)$$

Here, V_0 is the volume of the chamber ($V_0 = 13.8 \text{ L}$), ρ is the density of acetone (g cm^{-3}), M is the mole mass (g mol^{-1}) of acetone, p is the rate of purity of acetone, and C_{acetone} is the acetone concentration (ppm). The operating temperature was 100–300 °C, controlled by an electric heating system. The relative humidity (RH) was 30–40%.

The WO₃ sensor (R) is connected in series with a load resistor (R_0) with a known resistance (22–1700 K Ω), and a source voltage (U_0) of 5 V is loaded on the circuit [42]. The system measured the voltages (U) loaded on the resistor R_0 , and the resistances (R) of the WO₃ sensors can therefore be calculated according to Eq. (2). For the reducing gas of acetone and *n*-type semiconducting WO₃ sensors, the sensitivity (S_r) is defined as Eq. (3), where R_a and R_g are the resistances of the WO₃ sensor in air ambient and in acetone ambient, respectively. The response time (T_{res}) is defined as the time required for the sensor to reach 90% of the stabilized value of its resistance in the presence of the test gas. Similarly, the recovery time (T_{rec}) is defined as the time required for the sensor to reach 10% of the initial steady state value of its resistance after the gas was removed.

$$R = \frac{U_0 - U}{U} \times R_0 \quad (2)$$

$$S_r = \frac{R_a}{R_g} \quad (3)$$

3. Results and discussion

Fig. 1a shows the XRD pattern of the WO₃ nanoplates derived from tungstate-based inorganic–organic hybrid nanobelts. As Fig. 1a shows, there are intense peaks at $2\theta = 23.19^\circ$, 23.72° and 24.44° , and these diffraction peaks can readily be indexed to 002, 020 and 200 reflections of a triclinic WO₃ phase (S.G.: P1 [1]), respectively, according to the literature data (JCPDS card No. 32-1395). According to its XRD result, the cell parameters of the WO₃ nanoplates are calculated to be $a = 0.728(2) \text{ nm}$, $b = 0.751(2) \text{ nm}$,

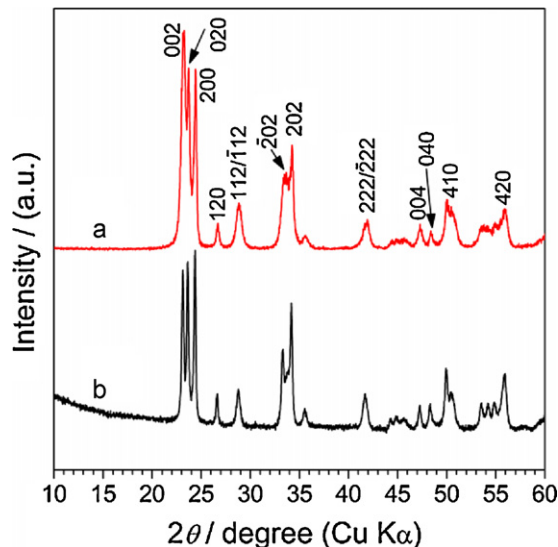


Fig. 1. Typical XRD patterns of (a) the WO₃ nanoplates derived from tungstate-based inorganic–organic hybrid nanobelts and (b) the WO₃ nanoparticles from commercial H₂WO₄ powders.

$c=0.769(2)$ nm, $\alpha=88.6(2)^\circ$, $\beta=91.1(3)^\circ$ and $\gamma=91.0(3)^\circ$, which are close to the literature values ($a=0.7309$ nm, $b=0.7522$ nm, $c=0.7678$ nm, $\alpha=88.81^\circ$, $\beta=90.92^\circ$, $\gamma=90.93^\circ$). In the previous report, we indexed the WO_3 nanoplates to a monoclinic phase [40], but our further refined results indicate that the calculated cell parameters of the WO_3 nanoplates are closer to a triclinic phase than a monoclinic one. Fig. 1b shows the XRD pattern of the WO_3 nanoparticles derived from commercial H_2WO_4 powders. There are intense reflections at $2\theta=23.13^\circ$, 23.60° and 24.37° , which can also be indexed to a triclinic WO_3 phase. The calculated cell parameters are $a=0.731(1)$ nm, $b=0.754(1)$ nm, $c=0.770(1)$ nm, $\alpha=88.2(1)^\circ$, $\beta=91.4(1)^\circ$, $\gamma=90.5(1)^\circ$, which are close to those of WO_3 nanoplates. The (002) reflection in Fig. 1b is the third largest peak in relative intensity, similar to the literature data. When comparing Fig. 1a and b, one can easily find that the (002) reflection in Fig. 1a is the first largest peak. The enhanced intensity indicates that the WO_3 nanoplates present a preferred orientation along the [002] direction. Also, one can find that the peaks in Fig. 1b are sharper than the corresponding ones in Fig. 1a, indicating that the

WO_3 nanoplates have a smaller crystal size than that of the WO_3 nanoparticles. In fact, the WO_3 nanoplates have a specific surface area of $180\text{ m}^2/\text{g}$, according to the BET result [40].

Fig. 2a–d shows the typical TEM observations of WO_3 nanoplates derived from the tungstate-based inorganic–organic hybrid nanobelts. The low-magnification TEM image (Fig. 2a) indicates that the product obtained is of a predominant plate-like morphology according to the shallow contrast. Fig. 2b shows a single nanoplate with a dimension of ca. $200\text{ nm} \times 400\text{ nm}$. A typical HRTEM image of a WO_3 nanoplate is shown in Fig. 2c. The clear two-dimensional ordered lattice structure indicates that the obtained WO_3 nanoplate is single-crystalline. The interplanar distance values of ca. 0.364 and 0.376 nm can be readily assigned to the reflections from (200) and (020) planes of triclinic WO_3 , respectively. Its corresponding SAED pattern is shown in Fig. 2d. The uniform, wide and ordered diffraction spots can be assigned to a single-crystalline triclinic WO_3 phase along the [002] zone axis. The TEM observation of the WO_3 nanoplates is very close to our previous report [40]. Since the WO_3 nanoplate is lying along the

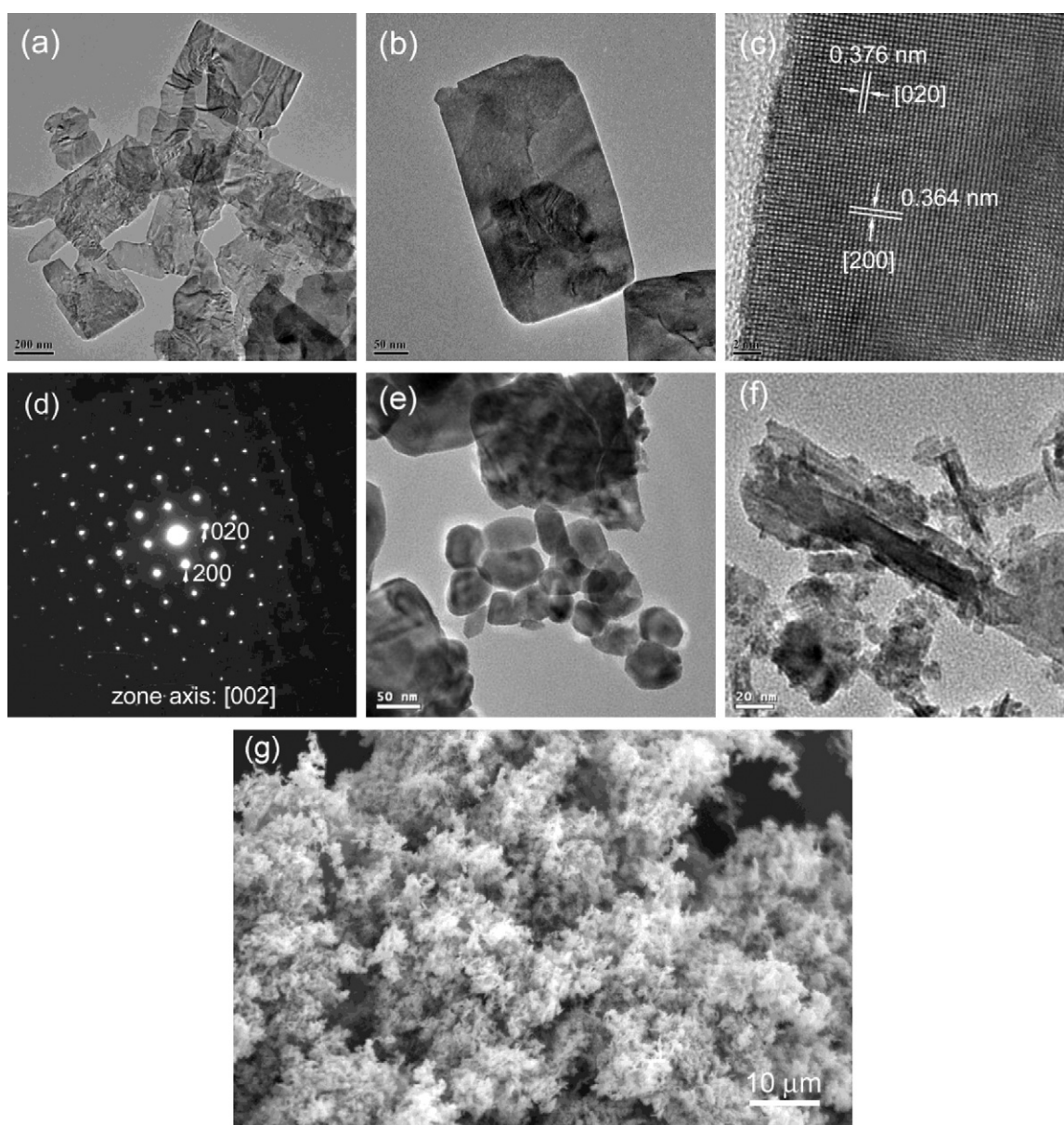


Fig. 2. (a and b) TEM images, (c) HRTEM image and (d) SAED pattern of WO_3 nanoplates; TEM images of (e) WO_3 nanoparticles and (f) the corresponding commercial H_2WO_4 powders; (g) SEM image of the as-obtained WO_3 nanoplates.

Cu grid, the thickness of the WO_3 nanoplate can be considered to be the [002] direction (*i.e.*, *c*-axis). The point is also corroborated by the XRD result that the WO_3 nanoplates show a higher intensity from the (002) plane than that of the WO_3 nanoparticles, as shown in Fig. 1.

Fig. 2e shows a typical TEM image of the WO_3 nanoparticles obtained from commercial H_2WO_4 powders. There are several morphologies, including spherical nanoparticles with sizes of 30–60 nm and plate-like aggregates with sizes 200–300 nm. The morphology of their precursor of H_2WO_4 is shown in Fig. 2f. It consists of particles with various sizes and shapes, including small nanoparticles with sizes of several nanometers, one-dimensional nanostructures with apparent diameters of 10–40 nm and lengths of 100–150 nm, and large particle aggregates with sizes of about 100 nm. Due to the wide size-distribution and multi-shapes of the H_2WO_4 powders, the resultant WO_3 nanoparticles accordingly take on diversiform morphologies with various sizes.

Fig. 3 shows the acetone-sensing response profiles of the sensors made using the as-obtained WO_3 nanoplates as the sensitive material. Fig. 3a shows a typical response profile of the WO_3 nanoplate sensors operating at 300 °C to acetone vapors with various con-

centrations from 2 ppm to 1000 ppm. One can find that there are sharp rises and drops in U values when the acetone vapors are injected and discharged, respectively, which indicates that the WO_3 nanoplate sensors are of fast response and recovery speeds to acetone vapors. Fig. 3b shows a similar rapid acetone-sensitive response of the WO_3 nanoplate sensors at an operating temperature of 250 °C. When we compare the U values of Fig. 3a and b, the change amounts in U of the WO_3 nanoplate sensors operating at 250 °C are less than those of the WO_3 nanoplate sensors operating at 300 °C. Fig. 3c shows typical response results of the WO_3 nanoplate sensors operating at 200 °C, and Fig. 3d shows the response curve operating at 100 °C. One can find that when the operating temperature decreases to 100 °C, the change amounts in U obviously decrease, the response speed and the detectable limits decrease, and the response profiles become unstable, as shown in Fig. 3a–d.

Fig. 4a presents the sensitivities (R_a/R_g) of the WO_3 nanoplate sensors operating at various temperatures and acetone concentrations. As Fig. 4a shows, the sensitivities of the WO_3 nanoplate sensors decrease as the operating temperature decreases in the range of 100–300 °C under the same acetone concentrations in the range of 2–1000 ppm. Also, we can find that the sensitivity

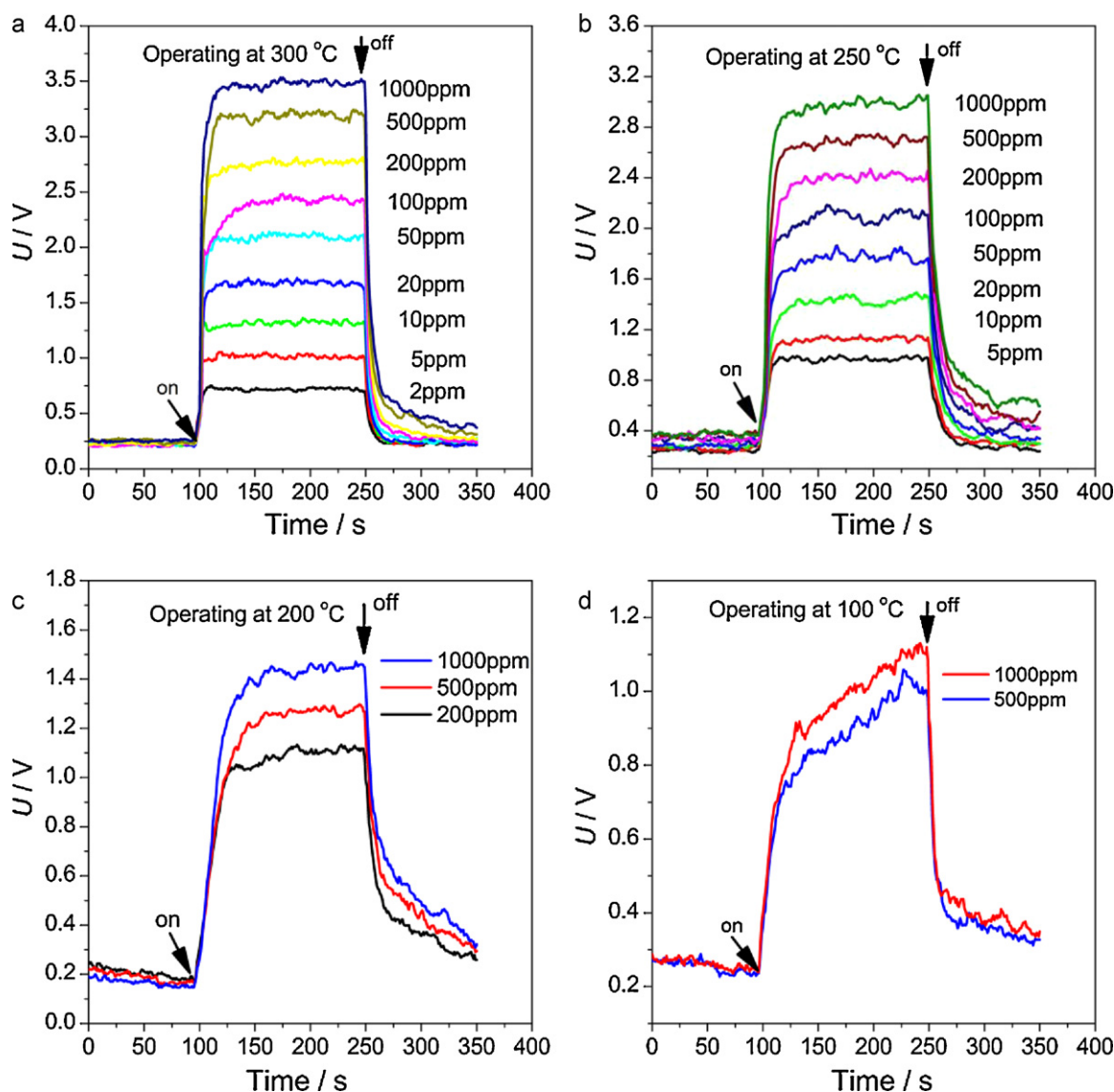


Fig. 3. Acetone-sensing response profiles of the WO_3 nanoplate sensors operating at various temperatures and various acetone vapor concentrations. The R_0 values are 22 k Ω , 100 k Ω , 100 k Ω and 470 k Ω , respectively, for the measurements operating at (a) 300 °C, (b) 250 °C, (c) 200 °C and (d) 100 °C.

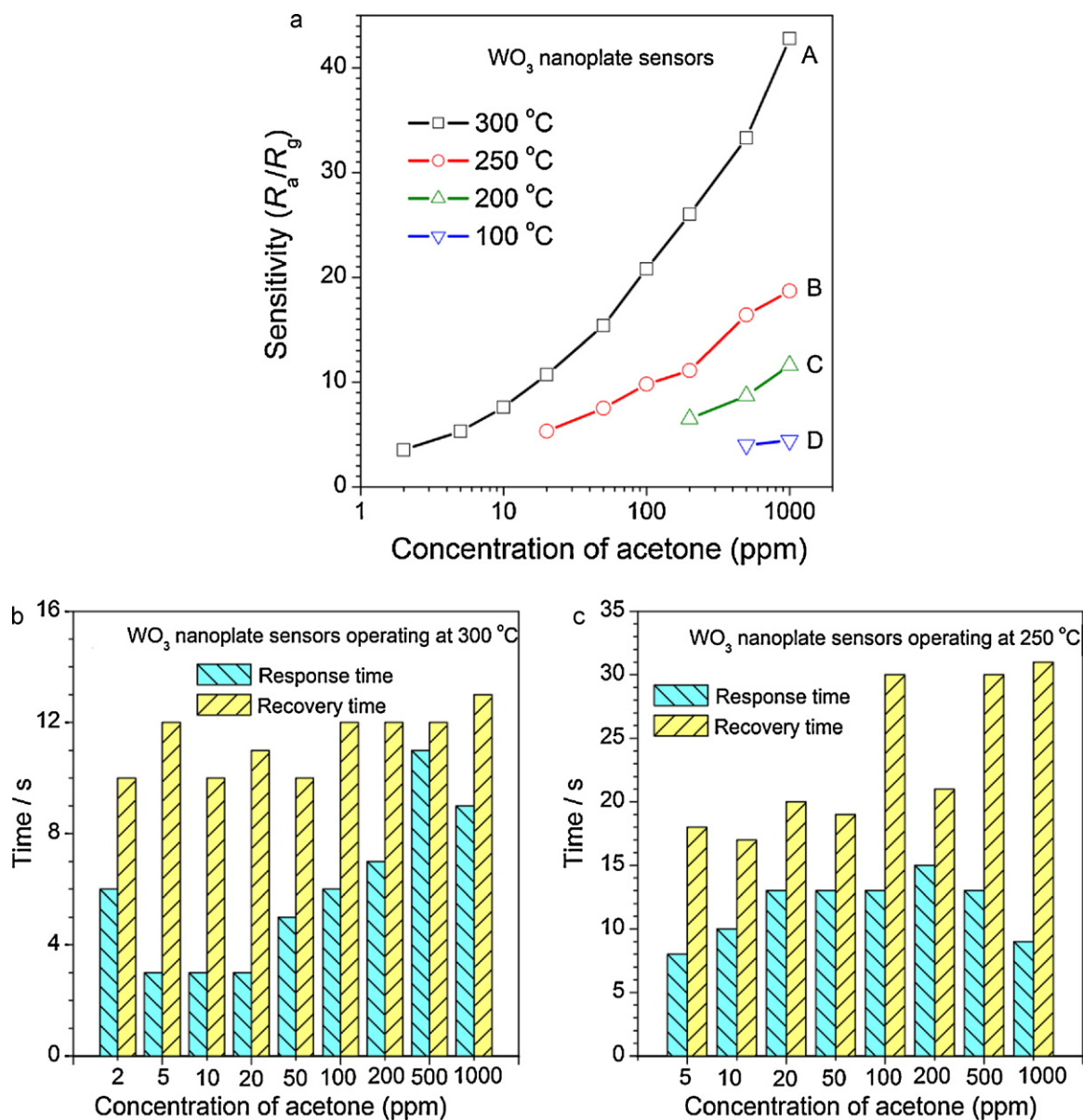


Fig. 4. (a) Sensitivities of the WO_3 nanoplate sensors as a function of the concentration of acetone vapor at various operating temperatures, and (b and c) response and recovery times of the WO_3 nanoplate sensors to acetone vapor with various concentrations operating at (b) 300 °C and (c) 250 °C.

increases with an increase in the acetone concentration at the same operating temperature, which is similar to the results of the $\text{La}_{0.68}\text{Pb}_{0.32}\text{FeO}_3$ sensors [7]. At an operating temperature of 300 °C, the WO_3 nanoplate sensor has a sensitivity as high as 42 for a 1000 ppm acetone vapor, and it has a detectable limit as low as 2 ppm of acetone vapor with a sensitivity of about 4, as shown as curve A. At a low operating temperature of 100 °C, the sensitivities of the WO_3 nanoplate sensors are about 3 for 100–500 ppm acetone vapors (curve D in Fig. 4a).

Fig. 4b and c shows the response and recovery times of the WO_3 nanoplate sensors under various concentrations of acetone vapors at operating temperatures of 250–300 °C. As Fig. 4b shows, the response times of the WO_3 nanoplate sensors operating at 300 °C are 3–10 s in the vapor concentration range of 2–1000 ppm, and their corresponding recovery times are 6–13 s. For the case of the response of the WO_3 nanoplate sensors operating at 250 °C, as shown in Fig. 4c, the response times lie in a range of 8–15 s, and their recovery times are 15–31 s. Both the response times and

recovery times increase with the increase in operating temperature.

For purposes of comparison, Fig. 5 shows the acetone-sensing response profiles of the WO_3 nanoparticle sensors using the calcined products of commercial H_2WO_4 powders as the sensing material. Fig. 5a–c presents the typical results operating at 300 °C, 250 °C and 200 °C, respectively. At relative high operating temperatures of 250–300 °C (Fig. 5a and b), the WO_3 nanoparticle sensors show a rapid and detectable response to acetone vapors with concentrations of 2–1000 ppm, whereas the response profiles become not typical at an operating temperature of 200 °C, as shown in Fig. 5c.

The sensitivities of the WO_3 nanoparticle sensors are shown in Fig. 6a. The sensitivity of the WO_3 nanoparticle sensor increases with the increase of acetone concentration from 2 for 2 ppm of acetone vapor to 19 for 1000 ppm of acetone vapor, operating at 300 °C, as shown as curve A in Fig. 6a. For the cases of operating at 250 °C and 200 °C, as shown as curves B and C in Fig. 6a, their sensitivi-

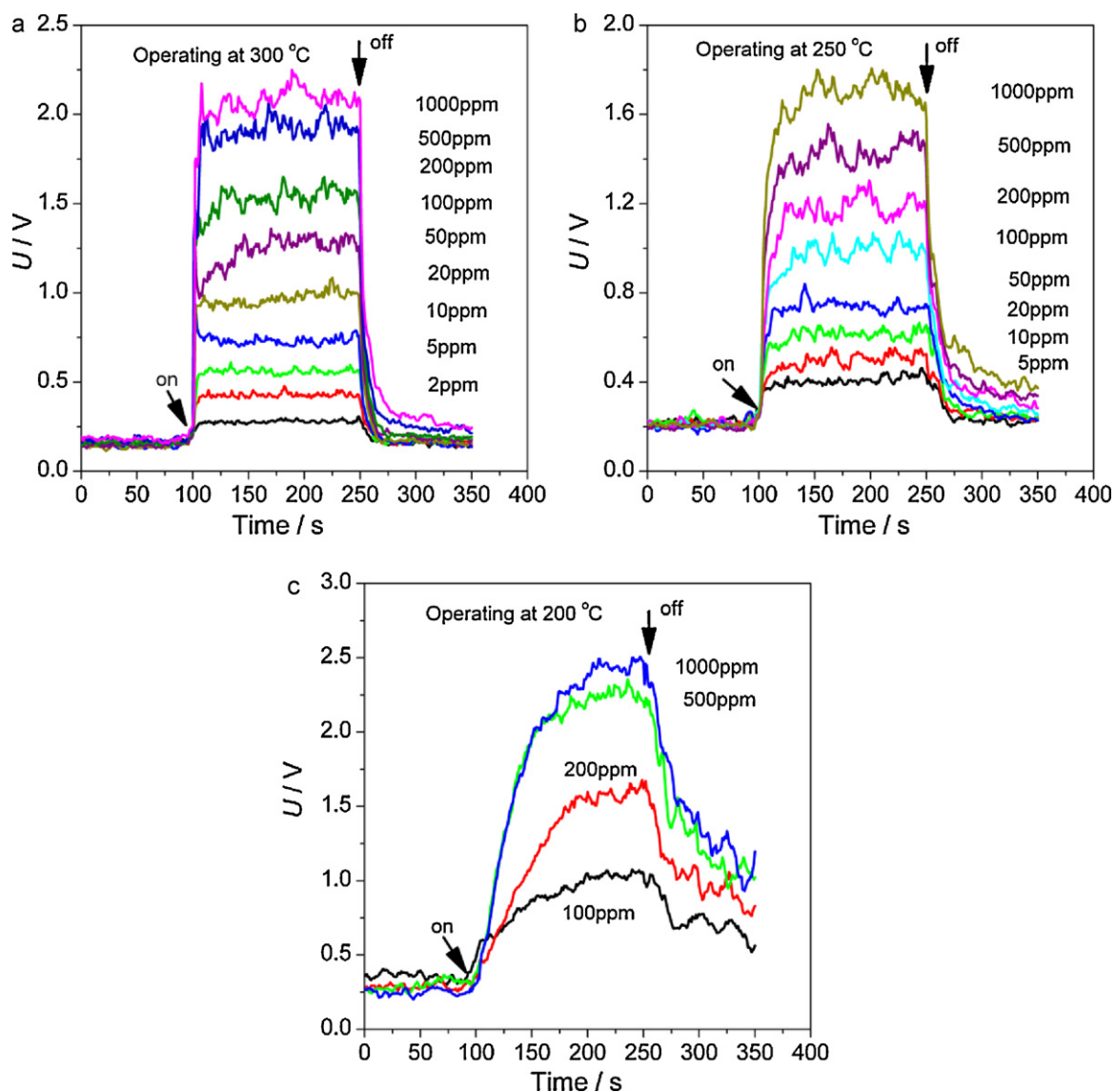


Fig. 5. Acetone-sensing response profiles of the WO_3 nanoparticle sensors operating at various temperatures and various acetone vapor concentrations. The R_0 values are 47 k Ω , 470 k Ω and 1700 k Ω , respectively, for the measurements operating at (a) 300 °C, (b) 250 °C and (c) 200 °C.

ties increase with the increase in concentrations of acetone vapors, but the values are less than 15. The change trends in sensitivity of the WO_3 nanoparticle sensors are similar to those of the WO_3 nanoplate sensors (Fig. 4a).

Fig. 6b shows the response times of the WO_3 nanoparticle sensors operating at 300 °C under acetone vapors with various concentrations of 2–1000 ppm. The response times are less than 10 s in the testing concentration range, and the corresponding recovery times are 10–17 s. When the operating temperature decreases to 250 °C, the response times are 4–20 s, and their recovery times are 17–35 s, as shown in Fig. 6c.

When comparing the acetone-response properties (Figs. 3 and 4) of the WO_3 nanoplate sensors and those (Figs. 5 and 6) of the WO_3 nanoparticle sensors, we can reach the following points: (1) the WO_3 nanoplate sensors have much higher sensitivities than the WO_3 nanoparticle sensors in an acetone concentration range of 2–1000 ppm at operating temperatures of 250–300 °C; (2) the WO_3 nanoplate sensors have faster response speeds than the WO_3 nanoparticle sensors; (3) the WO_3 nanoplate sensors show more stable response performance than the WO_3 nanoparticle sensors.

The enhancement in acetone-response properties of the WO_3 nanoplate sensors should be attributed to the ultrathin two-dimensional plate-like morphology of the single-crystalline WO_3 nanoplates, derived from tungstate-based inorganic–organic hybrid nanobelts via a topochemical conversation route. The ultrathin WO_3 nanoplates with large side-to-thickness ratios show a favorable tendency to form loose and poriferous aggregates in a natural manner. In fact, this poriferous microstructure can be clearly corroborated by the SEM observation, as shown in Fig. 2g. The loose and poriferous structured aggregates provide numerous channels for the efficient and rapid diffusion of acetone vapors [42]. Also, the plate-like morphology of the WO_3 nanoplates is helpful to form an interconnected film for the gas-sensing applications. Furthermore, the single-crystalline structure of the WO_3 nanoplates provides a favorable precondition both for the rapid sorption–desorption of acetone vapors and for the high efficient circulation of electrons produced in the response process, because of the large surface areas and the low rates of crystalline defects for the WO_3 nanoplates. Whereas for the WO_3 nanoparticles from commercial H_2WO_4 powders, their morphologies are not uniform and their sizes are large,

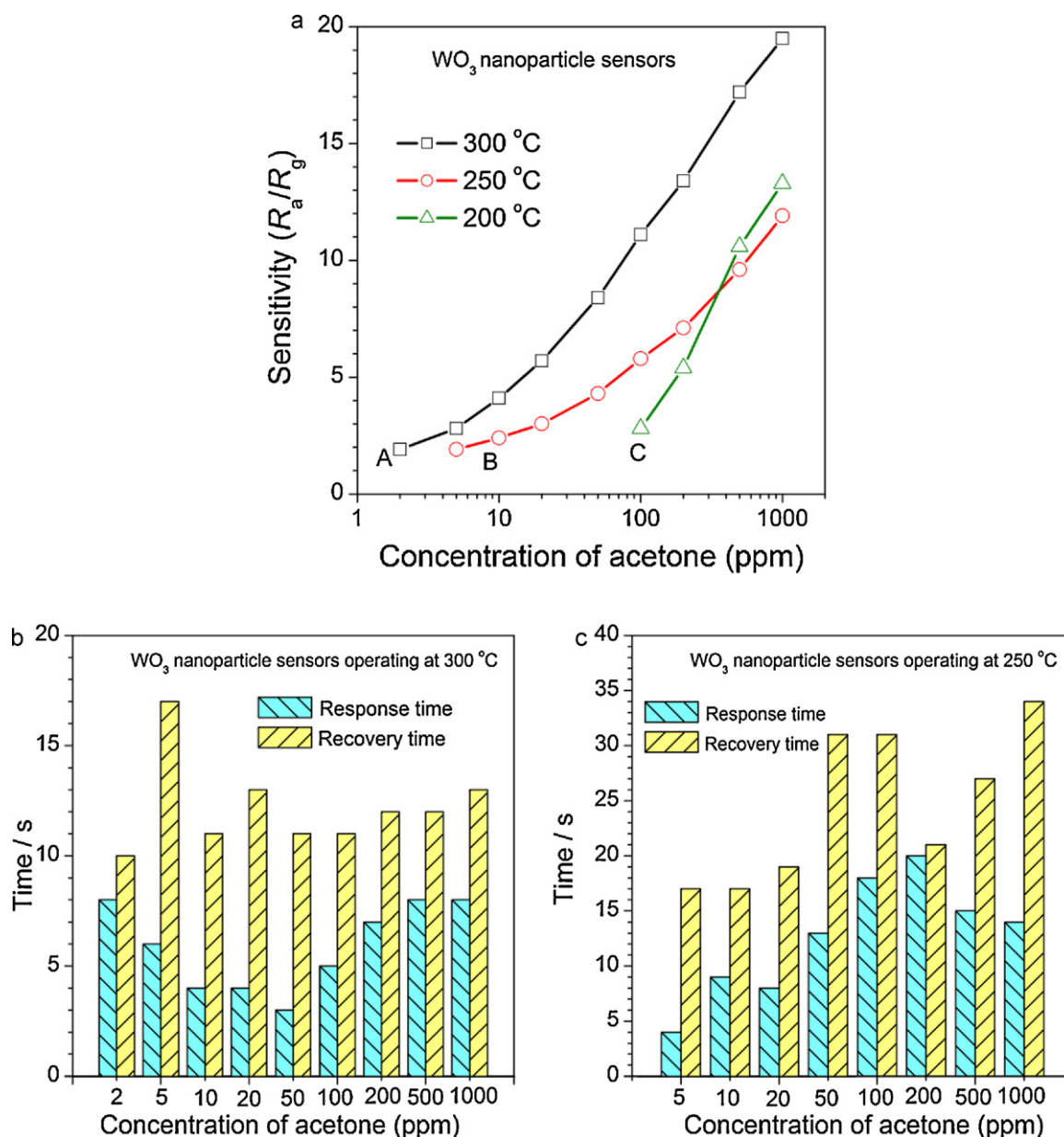


Fig. 6. (a) Sensitivities of the WO₃ nanoparticle sensors as a function of the concentration of acetone vapor at various operating temperatures, and (b and c) response and recovery times of the WO₃ nanoparticle sensors to acetone vapor with various concentrations operating at (b) 300 °C and (c) 250 °C.

which led to hard aggregates (Fig. 2e). Therefore, the morphological difference between the WO₃ nanoplates from hybrid precursors and the WO₃ nanoparticles from commercial H₂WO₄ powders and the difference in textures of the resultant aggregates account for the different performance of the WO₃ sensors toward acetone vapors with various concentrations operating at 100–300 °C.

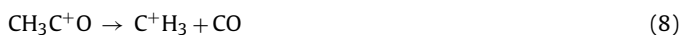
The gas-sensing mechanisms for the same type semiconductors are usually of some similarity, and WO₃ is an *n*-type semiconductor, similar to ZnO and SnO₂ [42]. Therefore, the acetone-sensing mechanisms of WO₃ nanocrystals are also similar to those of ZnO and SnO₂ nanocrystals [5,13], and can be explained using a depletion-layer model [44]. For acetone vapor sensing of WO₃ nanocrystals, oxygen sorption plays a critical role in the electrical resistance. In an air environment, the oxygen ionosorption depletes conduction electrons and then enhances the resistance of the WO₃ sensors, whereas their resistance can sharply decrease upon exposure to the reducing substance of acetone vapor.

When the WO₃ sensors are exposed to air, the O₂ molecules in air react with WO₃ and produce oxygen species of O₂⁻, O₂²⁻ and O⁻, which are adsorbed on the surfaces of WO₃ nanocrystals at an elevated temperature. The amounts of the oxygen species adsorbed are strongly dependent on the operating temperature, and the higher the operating temperature, the larger the amounts of O₂⁻ and O⁻ are in the testing temperature range [5]. The related reaction kinetics can be described as Eqs. (4)–(6).



When the WO₃ sensors are exposed to acetone vapors, the ionic oxygen species adsorbed on the surface of WO₃ nanocrystals react with reducing acetone molecules, as shown as Eqs. (7)–(9) [5]. The released electrons in the reactions compensate to the conduction

band, and thus enhance the conductance of the WO₃ sensors [13].



According to the above acetone-sensing mechanism, one can easily conclude that large surface areas, high crystallinity, and expedite diffusion channels of WO₃ nanocrystals are favorable in enhancing the acetone-sensing performance of the resultant sensors. The WO₃ nanoplates with high specific surface areas (~180 m²/g⁻¹) and high crystallinity are of more excellent acetone-sensing properties than the WO₃ nanoparticles in this work.

Cao and co-workers [20] reported an acetone-sensing result of WO₃ nanotubes and found that the WO₃ nanotube sensors had a peak sensitivity of 32.7 at 340 °C for a 5 × 10⁻⁵ mol/L acetone vapor, but the sensitivities were less than 20 when the operating temperatures were lower and higher than 340 °C. More and co-workers [11] reported the acetone-sensing property of Co-doped SnO₂ thin films, but their response and recovery times were longer than 100 s even at an operating temperature higher than 300 °C. Xu and co-workers [13] investigated the acetone-sensing performance of SnO₂ nanowire sensors, but their peak sensitivity was less than 10. Therefore, the WO₃ nanoplate sensors reported here are of good overall properties to acetone sensing applications comparing these literature results.

4. Conclusions

We have comparatively investigated the acetone-sensing properties of the WO₃ nanoplates from tungstate-based inorganic–organic hybrid nanobelts and the WO₃ nanoparticles from commercial H₂WO₄ powders in an acetone-concentration range of 2–1000 ppm operating at 100–300 °C. The WO₃ nanoplate sensors showed a high and stable sensitive response to acetone vapors, and the sensitivity was up to 42 for 1000 ppm of acetone vapor operating at 300 °C. The response and recovery times were as short as 3–10 s and 12–13 s, respectively, for the WO₃ nanoplate sensors when operating at 300 °C. The acetone-sensing performance of the WO₃ nanoplate sensors was more excellent than that of the WO₃ nanoparticle sensors under a similar operating condition. The enhancement of the WO₃ nanoplate sensors in the acetone-sensing property could be attributed to the porous textures, single-crystalline microstructures and high surface areas of the aggregates consisting of WO₃ nanoplates, which were favorable in rapid and efficient diffusion of acetone vapors.

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References

- [1] C. Balási, K. Sedláková, E. Llobet, R. Ionescu, Novel hexagonal WO₃ nanopowder with metal decorated carbon nanotubes as NO₂ gas sensor, *Sens. Actuators B: Chem.* 133 (2008) 151–155.
- [2] L. Wang, X. Yun, M. Stanacevic, P.I. Gouma, An acetone nanosensor for non-invasive diabetes detection, *Olfaction Electron. Nose* 1137 (2009) 206–208.
- [3] Y. Anno, T. Maekawa, J. Tamaki, Y. Asano, K. Hayashi, N. Miura, N. Yamazoe, Zinc-oxide-based semiconductor sensors for detecting acetone and capronaldehyde in the vapour of consommé soup, *Sens. Actuators B: Chem.* 25 (1995) 623–627.
- [4] P.P. Sahay, Zinc oxide thin film gas sensor for detection of acetone, *J. Mater. Sci.* 40 (2005) 4383–4385.
- [5] S.J. Chang, T.J. Hsueh, I.C. Chen, S.F. Hsieh, S.P. Chang, C.L. Hsu, Y.R. Lin, B.R. Huang, Highly sensitive ZnO nanowire acetone vapor sensor with Au adsorption, *IEEE T. Nanotechnol.* 7 (2008) 754–759.
- [6] Y. Zeng, T. Zhang, M.X. Yuan, M.H. Kang, G.Y. Lu, R. Wang, H.T. Fan, Y. He, H.B. Yang, Growth and selective acetone detection based on ZnO nanorod arrays, *Sens. Actuators B: Chem.* 143 (2009) 93–98.
- [7] L. Zhang, H. Qin, P. Song, J. Hu, M. Jiang, Electric properties and acetone-sensing characteristics of La_{1-x}Pb_xFeO₃ perovskite system, *Mater. Chem. Phys.* 98 (2006) 358–362.
- [8] X. Liu, J. Hu, B. Cheng, H. Qin, M. Jiang, Acetone gas sensing properties of SmFe_{1-x}Mg_xO₃ perovskite oxides, *Sens. Actuators B: Chem.* 134 (2008) 483–487.
- [9] M. Yang, L.H. Huo, H. Zhao, S. Gao, Z.M. Rong, Electrical properties and acetone-sensing characteristics of LaNi_{1-x}Ti_xO₃ perovskite system prepared by amorphous citrate decomposition, *Sens. Actuators B: Chem.* 143 (2009) 111–118.
- [10] J. Zhao, L.H. Huo, S. Gao, H. Zhao, J.G. Zhao, Alcohols and acetone sensing properties of SnO₂ thin films deposited by dip-coating, *Sens. Actuators B: Chem.* 115 (2006) 460–464.
- [11] S.B. Patil, P.P. Patil, M.A. More, Acetone vapour sensing characteristics of cobalt-doped SnO₂ thin films, *Sens. Actuators B: Chem.* 125 (2007) 126–130.
- [12] M.M. Zhang, G.S. Jiang, Gas sensing properties of Co₃O₄-loaded SnO₂ to ethanol and acetone, *Chin. J. Chem. Phys.* 20 (2007) 315–318.
- [13] L. Qin, J. Xu, X. Dong, Q. Pan, Z. Cheng, Q. Xiang, F. Li, Template-free synthesis of square-shaped SnO₂ nanowires: the temperature effect and acetone gas sensors, *Nanotechnology* 19 (2008) 185705.
- [14] C.H. Fang, S.Z. Wang, Q. Wang, J. Liu, B.Y. Geng, Coraloid SnO₂ with hierarchical structure and their application as recoverable gas sensors for the detection of benzaldehyde/acetone, *Mater. Chem. Phys.* 122 (2010) 30–34.
- [15] A.A. Zvyagin, A.V. Shaposhnik, S.V. Ryabtsev, D.A. Shaposhnik, A.A. Vasil'ev, I.N. Nazarenko, Determination of acetone and ethanol vapors using semiconductor sensors, *J. Anal. Chem.* 65 (2010) 94–98.
- [16] L. Tang, Y. Li, K. Xu, X. Hou, Y. Lv, Sensitive and selective acetone sensor based on its cataluminescence from nano-La₂O₃ surface, *Sens. Actuators B: Chem.* 132 (2008) 243–249.
- [17] M. Sadakane, K. Sasaki, H. Kunioku, B. Ohtani, R. Abe, W. Ueda, Preparation of 3-D ordered macroporous tungsten oxides and nano-crystalline particulate tungsten oxides using a colloidal crystal template method, and their structural characterization and application as photocatalysts under visible light irradiation, *J. Mater. Chem.* 20 (2010) 1811–1818.
- [18] N.A. Galiote, R.L.T. Parreira, J.M. Rosolen, F. Huguenin, Self-assembled films from WO₃: electrochromism and lithium ion diffusion, *Electrochem. Commun.* 12 (2010) 733–736.
- [19] L. Meda, G. Tozzola, A. Tacca, G. Marra, S. Caramori, V. Cristino, C.A. Bignozzi, Photo-electrochemical properties of nanostructured WO₃ prepared with different organic dispersing agents, *Solar Energy Mater. Solar Cells* 94 (2010) 788–796.
- [20] M. Kang, C. Cao, X. Xu, B. Lian, Molten-salt synthesis of tungsten oxide nanotubes: morphological and gas sensitivity, *Chin. Sci. Bull.* 53 (2008) 335–338.
- [21] C.S. Rout, K. Ganesh, A. Govindaraj, C.N.R. Rao, Sensors for the nitrogen oxides, NO₂, NO and N₂O, based on In₂O₃ and WO₃ nanowires, *Appl. Phys. A: Mater. Sci. Process.* 85 (2006) 241–246.
- [22] J. Polleux, A. Gurlo, N. Barsan, U. Weimar, M. Antonietti, M. Niederberger, Template-free synthesis and assembly of single-crystalline tungsten oxide nanowires and their gas-sensing properties, *Angew. Chem. Int. Ed.* 45 (2006) 261–265.
- [23] B. Deb, S. Desai, G.U. Sumanasekera, M.K. Sunkara, Gas sensing behaviour of mat-like networked tungsten oxide nanowire thin films, *Nanotechnology* 18 (2007) 285501.
- [24] S. Piperno, M. Passacantando, S. Santucci, L. Lozzi, S.L. Rosa, WO₃ nanofibers for gas sensing applications, *J. Appl. Phys.* 101 (2007) 124504.
- [25] C.-Y. Lee, S.-J. Kim, I.-S. Hwang, J.-H. Lee, Glucose-mediated hydrothermal synthesis and gas sensing characteristics of WO₃ hollow microspheres, *Sens. Actuators B: Chem.* 142 (2009) 236–242.
- [26] I. Jiménez, J. Arbiol, A. Cornet, J.R. Morante, Structural and gas-sensing properties of WO₃ nanocrystalline powders obtained by a sol-gel method from tungstic acid, *IEEE Sens. J.* 2 (2002) 329–334.
- [27] S.-H. Wang, T.-C. Chou, C.-C. Liu, Nano-crystalline tungsten oxide NO₂ sensor, *Sens. Actuators B: Chem.* 94 (2003) 343–351.
- [28] Y. Shen, T. Yamazaki, Z. Liu, D. Meng, T. Kikuta, N. Nakatani, Influence of effective surface area on gas sensing properties of WO₃ sputtered thin films, *Thin Solid Films* 517 (2009) 2069–2072.
- [29] Y.M. Zhao, Y.Q. Zhu, Room temperature ammonia sensing properties of W₁₈O₄₉ nanowires, *Sens. Actuators B: Chem.* 137 (2009) 27–31.
- [30] C. Balási, L. Wang, E.O. Zayim, I.M. Sziláyi, K. Sedláková, J. Pfeifer, A.L. Tóh, P.I. Gouma, Nanosize hexagonal tungsten oxide for gas sensing applications, *J. Eur. Ceram. Soc.* 28 (2008) 913–917.
- [31] F. Morazzoni, R. Scotti, L. Origoni, M. D'Arizeno, I. Jiménez, A. Cornet, J.R. Morante, Mechanism of NH₃ interaction with transition metal-added nanosized WO₃ for gas sensing: in situ electron paramagnetic resonance study, *Catal. Today* 126 (2007) 169–176.

- [32] I. Jiménez, M.A. Centeno, R. Scotti, F. Morazzoni, J. Arbiol, A. Cornet, J.R. Morante, NH₃ interaction with chromium-doped WO₃ nanocrystalline powders for gas sensing applications, *J. Mater. Chem.* 14 (2004) 2412–2420.
- [33] R. Calavia, A. Mozalev, R. Vazquez, I. Gracia, C. Can, R. Ionescu, E. Llobet, Fabrication of WO₃ nanodot-based microsensors highly sensitive to hydrogen, *Sens. Actuators B: Chem.* 149 (2010) 352–361.
- [34] J. Ederth, J.M. Smulko, L.B. Kish, P. Heszler, C.G. Granqvist, Comparison of classical and fluctuation-enhanced gas sensing with Pd_xWO₃ nanoparticle films, *Sens. Actuators B: Chem.* 113 (2006) 310–315.
- [35] Y.S. Kim, Thermal treatment effects on the material and gas-sensing properties of room-temperature tungsten oxide nanorod sensors, *Sens. Actuators B: Chem.* 137 (2009) 297–304.
- [36] R.-J. Wu, W.-C. Chang, K.-M. Tsai, J.-G. Wu, The Novel CO sensing material CoOOH–WO₃ with Au and SWCNT performance enhancement, *Sens. Actuators B: Chem.* 138 (2009) 35–41.
- [37] R. Ionescu, A. Hoel, C.G. Granqvist, E. Llobet, P. Heszler, Low-level detection of ethanol and H₂S with temperature-modulated WO₃ nanoparticle gas sensors, *Sens. Actuators B: Chem.* 104 (2005) 132–139.
- [38] W. Belkacem, A. Labidi, J. Guérin, N. Mliki, K. Aguir, Cobalt nanograins effect on the ozone detection by WO₃ sensors, *Sens. Actuators B: Chem.* 132 (2008) 196–201.
- [39] C.L. Dai, M.C. Liu, F.S. Chen, C.C. Wu, M.W. Chang, A nanowire WO₃ humidity sensor integrated with micro-heater and inverting amplifier circuit on chip manufactured using CMOS-MEMS technique, *Sens. Actuators B: Chem.* 123 (2007) 896–901.
- [40] D. Chen, L. Gao, A. Yasumori, K. Kuroda, Y. Sugahara, Size- and shape-controlled conversion of tungstate-based inorganic–organic hybrid belts to WO₃ nanoplates with high specific surface areas, *Small* 4 (2008) 1813–1822.
- [41] D. Chen, Y. Sugahara, Tungstate-based inorganic–organic hybrid nanobelts/nanotubes with lamellar mesostructures: synthesis, characterization, and formation mechanism, *Chem. Mater.* 19 (2007) 1808–1815.
- [42] D. Chen, X. Hou, H. Wen, Y. Wang, H. Wang, X. Li, R. Zhang, H. Lu, H. Xu, S. Guan, J. Sun, L. Gao, The enhanced alcohol-sensing response of ultrathin WO₃ nanoplates, *Nanotechnology* 21 (2010) 035501.
- [43] M. Kudo, H. Ohkawa, W. Sugimoto, N. Kumada, Z. Liu, O. Terasaki, Y. Sugahara, A layered tungstic acid H₂W₂O₇·nH₂O with a double-octahedral sheet structure: conversion process from an aurivillius phase Bi₂W₂O₉ and structural characterization, *Inorg. Chem.* 42 (2003) 4479–4484.
- [44] L. Liao, H.B. Lu, J.C. Li, H. He, D.F. Wang, D.J. Fu, C. Liu, W.F. Zhang, Size dependence of gas sensitivity of ZnO nanorods, *J. Phys. Chem. C* 111 (2007) 1900–1903.

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