Nanowires-assembled WO₃ nanomesh for fast detection of ppb-level NO₂ at low temperature

Di LIU, Xiaowei REN, Yesheng LI, Zilong TANG*, Zhongtai ZHANG

State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Received: May 7, 2019; Revised: July 14, 2019; Accepted: July 15, 2019
© The Author(s) 2019.

Abstract: Hierarchical WO₃ nanomesh, assembled from single-crystalline WO₃ nanowires, is prepared via a hydrothermal method using thiourea (Tu) as the morphology-controlling agent. Formation of the hierarchical architecture comprising of WO₃ nanowires takes place via Ostwald ripening mechanism with the growth orientation. The sensor based on WO₃ nanomesh has good electrical conductivity and is therefore suitable as NO₂ sensing material. The WO₃ nanomesh sensor exhibited high response, short response and recovery time, and excellent selectivity towards ppb-level NO₂ at low temperature of 160 °C. The superior gas performance of the sensor was attributed to the high-purity hexagonal WO₃ with high specific surface area, which gives rise to enhanced surface adsorption sites for gas adsorption. The electron depletion theory was used for explaining the NO₂-sensing mechanism by the gas adsorption/desorption and charge transfer happened on the surface of WO₃ nanomesh.

Keywords: WO₃ nanomesh; controlling agent; NO₂ sensing; charge transfer

1 Introduction

NO₂, as one of the most toxic and harmful gases in the atmosphere, is the precursor of acid rain and photochemical smog. It is generated by the fuel burning and has caused a seriously harmful effect to the living environment [1,2]. Thus, the development of NO₂ gas sensors with high sensitivity and low detect limitation is urgently necessary. At present, metal oxide semiconductors with various nanostructures, such as SnO₂ [3–5], ZnO [6,7], WO₃ [8,9], and TiO₂ [10], have been well investigated to detect NO₂ owing to their low cost, simple operation, and nontoxic nature. Among them, tungsten oxide, a n-type semiconductor with wide bandgap (2.6–3.2 eV), has been considered as a promising sensing material for the detection of NO₂ because of its low cost, high sensitivity, and good repeatability [11–13]. However, the operating temperature of WO₃ gas sensors is usually above 200 °C due to the poor electrical conductivity of some WO₃ nanostructures [14–16]. For example, WO₃ nanoparticles synthesized by spark ablation were required to detect NO₂ gas at a high operating temperature of 200 °C due to their high electrical resistance [15]. Triple-shelled WO₃ spheres synthesized by ultrasonic spray pyrolysis showed a large resistance (>1 GΩ) when exposed to NO₂ gas at low operating temperature [16]. A general strategy to solve this problem is surface functionalization with noble metals (Au, Ag, and Pt) [8,17–20]. Gao’s group reported Ag-loaded mesoporous WO₃ showed excellent response to NO₂ at 75 °C [17]. Recently, Zhao et al. [8] reported Au@WO₃...
core–shell nanospheres showed an improvement in NO₂ sensing performance in terms of sensitivity, response/recovery rate, and detection limit at 100 °C. However, the method is not always effective, because the noble metal particles tend to catalytic poisoning and noble metal modification increases the fabricating cost [21]. Another way to achieve this is to increase their surface-to-volume ratio by preparing hierarchical nanostructures. Hierarchical WO₃ nanostructures can increase the active adsorption sites for NO₂ molecules and these thin structural units can provide efficient electron transport pathways [22]. Many techniques have been used to synthesize WO₃ in various forms and investigate the effect of morphology on their gas-sensing performance. Various morphologies of WO₃, such as nanofibers, nanoflowers, and nanoplates, have been prepared by a variety of methods including electrospinning, thermal evaporation, and hydrothermal and plasma spraying [23–27]. Compared to other synthetic techniques, hydrothermal method is more advantageous due to low-temperature synthesis and ease of mass production [28–32].

In this work, hierarchical tungsten trioxide nanomesh assembled by single-crystalline nanowires was fabricated via a facile hydrothermal method using thiourea (Tu) as the morphology-directing agent. Hexagonal WO₃ nanomesh has good electrical conductivity owing to the assembled nanowires promoting electron transport. The as-prepared WO₃ nanomesh exhibited high sensibility, short response and recovery time, and good sensing selectivity to NO₂ at a relatively low working temperature of 160 °C. Such excellent performance can be attributed to the highly exposed surface area, which propels the interaction between NO₂ gas and sensing element. The sensing mechanism is explained in terms of the gas adsorption/desorption and electron transport between gas molecules and WO₃ nanomesh.

2 Experimental

2.1 Materials

Hydrogen peroxide solution (H₂O₂, analytical reagent, 30 wt% in H₂O) was obtained from Sigma-Aldrich Corporation (Shanghai, China). Tungstic acid (H₂WO₄, guarantee reagent), Tu (CH₄N₂S, analytical reagent), and ethanol absolute (C₂H₅O, analytical reagent) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Deionized water was used for all experiments.

2.2 Synthesis of WO₃ nanomesh

In a typical procedure, 1.25 g tungstic acid was dissolved in 25 mL hydrogen peroxide solution heated in water bath at 90 °C with magnetic stirring. After stirring for 1 h and 20 min, the above solution was diluted to 60 mL with deionized water, then taking 42 mL of diluted solution and adding 168 mL deionized water and 14 mL HCl (3 mol/L) into above diluted solution. Next, Tu with different weight was added to above solution to achieve different concentration (0, 0.05, 0.1, and 0.2 M), followed by magnetic stirring for 20 min forming a suspension solution. Next, 30 mL of above solution was taken to 50 mL teflon-lined stainless steel autoclave. After heating in an electric oven at 180 °C for 12 h, the autoclave was naturally cooled down. The product was obtained by filtration, washed with enough deionized water and absolute ethanol, and dried under vacuum at 60 °C overnight. The as-prepared product was subsequently annealed in air at 300 °C for 2 h to improve the crystallinity.

2.3 Characterizations

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-V2500 diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained with scanning electron microscope (SEM, Zeiss, Germany) and transmission electron microscope (TEM, JEM-2100F, Japan), respectively. X-ray photoelectron spectroscopy (XPS) was recorded with an ESCALAB 250Xi instrument (Thermo Fisher Scientific, USA). Raman spectra were carried out on a LabRAM HR800 Raman spectrometer with 632.8 nm laser radiation. The Brunauer–Emmett–Teller (BET) surface area and Barrett–Joyner–Halenda (BJH) pore size and pore distribution were analyzed by nitrogen adsorption using an American Contador QuadraSorb SI-MP instrument. The current–voltage (I–V) characteristics of the sensors were measured using an electrochemical workstation (CHI-660E, China).

2.4 Fabrication and measurement of gas sensors

The annealed powder sample was placed in an agate mortar and thoroughly ground after adding an appropriate amount of ethanol. The obtained sensing slurry was deposited on the cleaned Au interdigital electrodes by a thin brush. Then, the electrodes with sensing film were dried at 70 °C in air for 12 h. The gas-sensing properties
of the electrodes were measured in a computer-controlled gas-sensing testing system consisting of mass flow controllers (MFC, Beijing Qixing Co., Ltd., China), a test chamber with a heating plate, and a data-acquisition system. The electrical resistances of the sensors were recorded by a digital multimeter (Agilent 34465A), and the upper limit of the digital multimeter is 1.2 GΩ. The test NO2 gas was mixed by 10 ppm NO2 (Beijing AP BAIF Gases Industry Co., Ltd., China) and background gas. The flow rates of 10 ppm NO2 and background gas were controlled using mass flow controllers. The total gas flow rate was fixed at 200 mL/min. The desired gas concentration is determined by the multiple of the NO2 gas diluted by background gas. The sensor response was defined as \( \frac{R_g}{R_a} \) for oxidizing gas or \( \frac{R_a}{R_g} \) for reducing gas, where \( R_g \) and \( R_a \) are the resistances of the sensor in targeted gas and in air, respectively. The response and recovery time were defined as the time taken by the sensor to achieve 90% of the total resistance change.

3 Results and discussion

3.1 Material characteristics

The crystal structure of the samples synthesized in precursor with different concentration Tu after heating treatment at 300 ℃ for 2 h was confirmed by XRD as illustrated in Fig. 1. The main diffraction peaks of the sample synthesized without adding Tu can be well indexed to the orthorhombic phase \( \text{WO}_3\cdot0.33\text{H}_2\text{O} \) (JCPDS No. 54-1012). With the increase of precursor Tu concentration, the diffraction intensity of the (111) peak for the orthorhombic \( \text{WO}_3\cdot0.33\text{H}_2\text{O} \) gradually decreases. When the sample is prepared in precursor with a Tu concentration of 0.2 M, the (111) peak for the orthorhombic \( \text{WO}_3\cdot0.33\text{H}_2\text{O} \) disappears and the main diffraction peaks can well correspond to the hexagonal phase \( \text{WO}_3 \) (JCPDS No. 85-2460). It is worth noting that the crystalline phase of the sample can be adjusted by the concentration of Tu in the precursor from the XRD results.

The morphology and microstructure of the samples after heating treatment at 300 ℃ for 2 h were examined by SEM measurement. As shown in Fig. 2(a), the sample

![Fig. 1 XRD patterns of samples prepared in precursor with Tu concentration of 0, 0.05, 0.1, and 0.2 M.](image1)

![Fig. 2 SEM images of samples prepared in precursor with Tu concentration of 0, 0.05, 0.1, and 0.2 M.](image2)
synthesized in precursor without Tu consists of micron-level flowers assembled with rectangular blocks. As shown in Fig. 2(b), the sample synthesized in precursor with 0.05 M Tu consists of micron-level flowers assembled with rectangular sheets. As shown in Fig. 2(c), the sample synthesized in precursor with 0.1 M Tu consists of urchin-shaped spheres assembled with needlelike units. As shown in Fig. 2(d), the sample synthesized in precursor with 0.2 M Tu consists of nanomesh assembled with nanowires. It is worth noting that the morphologies and microstructure of the samples can be adjusted by the concentrations of Tu in the precursor from the SEM results. Therefore, Tu, an anionic surfactant, acted as a structure-directing agent in the process of aggregation as well as a morphology-directing agent by confining crystal growth in certain directions.

The $I-V$ curves of the sensing devices based on annealed samples that were synthesized in precursor with 0.05, 0.1, and 0.2 M Tu were recorded by an electrochemical workstation. Figure 3 shows the $I-V$ curves of the sensors measured from $-5$ to $+5$ V to investigate the electrical contact between the sensing material and the Au interdigital electrodes in air at room temperature ($25\pm5$ ℃). When the voltage increases, the current also increases linearly suggesting good electrical contact between the sensing material and electrodes. As shown in Fig. 3, the resistances of sensors based on annealed samples that were synthesized in precursor with 0.05, 0.1, and 0.2 M Tu could be calculated to be 424, 28, and 3 MΩ, respectively. The resistances of the sensing devices based on annealed samples decrease sharply with the increase of the concentration of Tu in precursor. The sensing device based on the annealed sample synthesized in precursor with 0.2 M Tu exhibits linear ohmic behavior and the best electrical conductivity. As a result, the annealed sample synthesized in precursor with 0.2 M Tu was selected as sensing material in the following characterization and gas sensing tests.

The high-magnification SEM and TEM images of the annealed sample synthesized in precursor with 0.2 M Tu are shown in Fig. 4. As shown in Figs. 4(a) and 4(b),

![Fig. 4 SEM and TEM images of the annealed sample synthesized in precursor with 0.2 M Tu.](image)

---

**Fig. 3** $I-V$ characteristics of the sensors based on samples prepared in precursor with Tu concentration of 0.05, 0.1, and 0.2 M.
the high-magnification SEM images show the sample consists of nanowires forming a nanomesh morphology. Figure 4(c) shows the TEM image of interlaced nanowires, whose diameters are tens of nanometers and lengths are over several micrometres. The corresponding selected area electron diffraction (SAED) pattern (the inset in Fig. 4(c)) exhibits the diffraction rings, corresponding to the (100), (002), and (111) planes of hexagonal WO$_3$. Figure 4(d) shows that the fringe interval of 0.383 nm agrees well with the $d$-spacing of (002) lattice planes perpendicular to the long axis of the nanowire.

The surface chemical state of the WO$_3$ nanomesh was determined by XPS spectra. The C 1s peak of 284.8 eV was used to calibrate all binding energies. Figure 5(a) shows the high-resolution XPS spectrum of the O 1s. The intense peak at 530.4 eV can be assigned to lattice oxygen in WO$_3$. Figure 5(b) shows the high-resolution XPS spectrum of the W 4f. The small peak at 41.5 eV can be attributed to the W 5p$^{3/2}$ of WO$_3$ [17,33]. The two evident peaks at 35.5 and 37.7 eV, belonging to W 4f$^{7/2}$ and W 4f$^{5/2}$ of WO$_3$, respectively, suggest that the tungsten oxide nanostructure exists as W$^{6+}$ [34–36]. The structural and electronic properties of the WO$_3$ nanomesh were further characterized by Raman spectroscopy. As shown in Fig. 5(c), Raman peaks centered at about 262, 326, 708, and 802 cm$^{-1}$ can be observed clearly, which can be assigned to the fundamental modes of hexagonal WO$_3$ [37]. The sharp peaks located at about 262 and 326 cm$^{-1}$ are assigned to the W–O–W bending mode; the evident peaks at about 708 and 802 cm$^{-1}$ are attributed to the O–W–O stretching mode [38,39]. No peaks associated to impurities were observed indicating the high purity of the annealed WO$_3$ nanomesh.

The specific surface area and pore-size distribution of the WO$_3$ nanomesh were measured by the nitrogen adsorption/desorption isotherms, as shown in Fig. 5(d). The BJH pore size distribution (the inset in Fig. 5(d)) is widely distributed in the range of 1–135 nm. The pores are mainly centered at 12.5 nm, which arise from the space between nanowires. The BET surface area of the WO$_3$ nanomesh is 104.3 m$^2$/g. In view of its large pore size and high exposed surface area, the WO$_3$ nanomesh has great potential to show high gas-sensing performance.

3.2 Gas sensing properties

First, the response curves of the WO$_3$ nanomesh sensor at different temperatures were measured. For the temperatures less than 160 °C, the resistances of the sensor

---

**Fig. 5** (a) O 1s and (b) W 4f region XPS spectra of the WO$_3$ nanomesh; (c) Raman spectra of the WO$_3$ nanomesh; (d) nitrogen adsorption/desorption isotherm and the corresponding BJH pore size distribution plots (inset) of the WO$_3$ nanomesh.
in NO$_2$ gas was too large to measure by the multimeter. Therefore, the operating temperature of 160 °C or higher temperature was used in the gas-sensing tests.

The response of the WO$_3$ nanomesh-based sensor to 500 ppb NO$_2$ was measured at various operating temperatures. As shown in Fig. 6(a), the sensor response decreases as the temperature increases. Therefore, the optimal operating temperature of the WO$_3$ nanomesh sensor is 160 °C. Figure 6(b) shows the response and recovery time of the WO$_3$ nanomesh sensor to 500 ppb NO$_2$ as a function of operating temperature. As the operating temperature increases, the response and recovery time of the sensor becomes shorter. These results indicate that the increase in temperature increases the adsorption and desorption rate of NO$_2$ gas on the surface of WO$_3$ nanomesh. Figure 6(c) shows a typical dynamic response curve for WO$_3$ nanomesh-based sensor to NO$_2$ at a concentration ranging from 50 to 500 ppb at an optimum operating temperature of 160 °C. When the sensor is exposed to the oxidizing gas of NO$_2$, its resistance increases; when the air is introduced, the resistance of the sensor returns to its original value. Figure 6(d) shows the relationship between the response of the WO$_3$ nanomesh sensor and the NO$_2$ concentration at 160 °C. As the NO$_2$ concentration increases from 50 to 500 ppb, the response of the sensor increases. Moreover, there is a relatively good linear relationship between response and NO$_2$ concentration. This indicates that the WO$_3$ nanomesh sensor has the advantage of detecting low concentrations of NO$_2$. It is worth mentioning that the detection limit (LOD) of the WO$_3$ nanomesh sensor is as low as 50 ppb.

Table 1 summarizes the comparison of NO$_2$ sensing performance between WO$_3$ nanomesh-based sensors fabricated in this work and other reported WO$_3$ nanostructures. It is clear from Table 1 that the WO$_3$ nanomesh material in this work exhibits the lowest detection limit at low operating temperature compared to other materials from Refs. [40–44]. In the absence of noble metal modification and ion doping, the intrinsic WO$_3$ nanomesh material exhibits high response and very low detection limit at low operating temperature. There is no doubt that the WO$_3$ nanomesh material prepared in this work is a competitive sensing material with good application prospects.

In order to evaluate the selectivity of the WO$_3$ nanomesh-based sensor towards NO$_2$ gas, sensing tests were also performed in other gases at the operating

![Fig. 6](image-url)
Table 1  Gas sensing properties to NO\textsubscript{2} in the present study and those reported in the literature

| Materials                  | Target gas | Low limit of detection | Temperature (\degree C) | Response | Ref. |
|----------------------------|------------|------------------------|-------------------------|----------|-----|
| WO\textsubscript{3} nanowires | NO\textsubscript{2} | 10 ppm                | 150                     | 1.46     | [40]|
| WO\textsubscript{3} film     | NO\textsubscript{2} | 5 ppm                 | 200                     | 1.16     | [41]|
| WO\textsubscript{3} nanorods | NO\textsubscript{2} | 2 ppm                 | 200                     | 1.5      | [42]|
| WO\textsubscript{3} nanotubes| NO\textsubscript{2} | 1 ppm                 | 300                     | 1.44     | [43]|
| Annealed WO\textsubscript{3} nanorods | NO\textsubscript{2} | 100 ppb               | 250                     | 2        | [44]|
| WO\textsubscript{3} nanomesh | NO\textsubscript{2} | 50 ppb                | 160                     | 1.25     | Present study |

Annealed WO\textsubscript{3} nanorods at a temperature of 160 \degree C. Figure 7 shows the response of WO\textsubscript{3} nanomesh-based sensor to NO\textsubscript{2} (500 ppb), C\textsubscript{2}H\textsubscript{6}O (10 ppm), NH\textsubscript{3} (10 ppm), CO (50 ppm), and H\textsubscript{2}S (5 ppm). It indicates that the WO\textsubscript{3} nanomesh sensor has a significant response to NO\textsubscript{2} compared to other gases, although the concentrations of other gases are higher. Therefore, it can be concluded that the prepared WO\textsubscript{3} nanomesh sensor exhibits excellent selectivity to NO\textsubscript{2}. Repeatability and long-term stability are also important indicators for evaluating gas sensor performance. As shown in Fig. 8(a), the WO\textsubscript{3} nanomesh-based sensor after 30 days of storage was used to test its cyclic response curve to 500 ppb NO\textsubscript{2} at 160 \degree C. It can be observed that the response curve of the sensor was excellent in repeatability, indicating good long-term stability of the sensor based on the WO\textsubscript{3} nanomesh. The effect of humidity on the sensor response was investigated by comparing the NO\textsubscript{2} sensing performance in dry air and humid air (produced by bubbling water). The response curve of the WO\textsubscript{3} nanomesh-based sensor to 500 ppb NO\textsubscript{2} under dry and humid conditions at 160 \degree C is shown in Fig. 8(b). Considering the margin of error, the response of the WO\textsubscript{3} nanomesh sensor to NO\textsubscript{2} is slightly reduced in a humid atmosphere. Therefore, it can be concluded that humidity has a small effect on the NO\textsubscript{2} sensing characteristics of the WO\textsubscript{3} nanomesh sensor.

3.3 Gas sensing mechanism

The electron depletion theory is well known to explain gas-sensing mechanisms by charge transfer between gas molecules and sensing materials [36,45]. Figure 9 shows the schematic diagram of NO\textsubscript{2}-sensing mechanism for WO\textsubscript{3} nanomesh sensor. In air, oxygen molecules are adsorbed on the surface of WO\textsubscript{3} nanomesh forming the adsorbed oxygen at low temperature (< 200 \degree C) as described in the following reaction:

\[
\text{O}_2(\text{gas}) + e^- \rightarrow \text{O}_2(\text{ads}) \qquad (1)
\]

Thus, an electron depletion layer is formed by reducing the free charge carrier consequently increasing

![Fig. 7](image_url) Responses of WO\textsubscript{3} nanomesh sensor to NO\textsubscript{2} (500 ppb) and other several gas species such as C\textsubscript{2}H\textsubscript{6}O (10 ppm), NH\textsubscript{3} (10 ppm), CO (50 ppm), and H\textsubscript{2}S (5 ppm) at 160 \degree C.

![Fig. 8](image_url) (a) Cyclic response curve of WO\textsubscript{3} nanomesh sensor after 30 days of storage to NO\textsubscript{2} (500 ppb) at 160 \degree C; (b) response curves of WO\textsubscript{3} sensor to NO\textsubscript{2} (500 ppb) at 160 \degree C in dry and humid condition.
Fig. 9  Schematic diagram of gas-sensing mechanism for WO3 nanomesh sensor: (a) in air and (b) in air with NO2.

the resistance of the sensor. When WO3 nanomesh is exposed to oxidizing gas of NO2, NO2 molecule can easily capture electron from the surface of sensing material forming NO2− as described in the following reaction:

$$\text{NO}_2\text{(gas)} + e^- \rightarrow \text{NO}_2\text{(ads)}$$

Thus, a wider electron depletion layer is formed when NO2 is introduced and the resistance of the WO3 nanomesh increases. The WO3 nanomesh composed of WO3 nanowires can provide a higher specific surface area than conventional bulk materials, thereby providing more surface active sites for gas adsorption and improving NO2 sensing performance. Moreover, the high-purity single crystal nanowire assemblies promote rapid electron transfer and thus improve the gas sensing performance of WO3.

In order to verify the NO2-sensing mechanism proposed above, the responses of the WO3 nanomesh sensor to NO2 (500 ppb) in different backgrounds at 160 °C were measured. It can be shown in Fig. 10 that the response of the gas sensor decreases as the oxygen concentration in the background atmosphere increases. According to the above NO2-sensing mechanism, oxygen is not required when the WO3 nanomesh sensor detects NO2 gas. The WO3 nanomesh sensor has the same resistance when exposed to NO2 in different backgrounds. This means oxygen may not compete with NO2 for active sites on the WO3 nanomesh surface and therefore cannot affect the concentration of adsorbed NO2. This is why the sensor response (Rg/Ra) decreases as the oxygen in the background gas increases.

4 Conclusions

Hierarchical WO3 nanomesh assembled from single-crystalline WO3 nanowires was prepared via a hydrothermal method using Tu as a structure-directing agent and a morphology-controlling agent in the nucleation crystallization and assembly process. The interdigitated single crystal nanowires increase electron transfer so that the WO3 nanomesh has good conductivity and is suitable as a NO2-sensing material. The sensor based on WO3 nanomesh exhibits high response, fast response and recovery behavior, and excellent selectivity towards ppb-level NO2 at low temperature of 160 °C. The excellent NO2-sensing performance may be primarily attributed to the large specific surface area of WO3 nanomesh and high purity nanowire assemblies improving gas absorption/desorption and electron transfer process. The prepared WO3 nanomesh material is a high-performance NO2 gas sensing material capable of working at low temperature, and therefore has a good application prospect. Our synthetic strategy towards hierarchical WO3 nanomesh with high gas sensitivity provides a way for developing high-performance gas sensor based on other wide-bandgap metal oxides.

Acknowledgements

The National Key Basic Research Program of China (973 Program) (No. 2013CB934301) supported this work.

References

[1] Afzal A, Cioffi N, Sabbatini L, et al. NOx sensors based on semiconducting metal oxide nanostructures: Progress and perspectives. Sensor Actuat B: Chem 2012, 171: 25–42.
[2] Fine GF, Cavanagh LM, Afonja A, et al. Metal oxide semi-
conductor gas sensors in environmental monitoring. Sensors 2010, 10: 5469–5502.

[3] Sukunta J, Wisitsooar A, Tuantranont A, et al. WO3 nanotubes–SnO2 nanoparticles heterointerfaces for ultrasensitive and selective NO2 detections. Appl Surf Sci 2018, 458: 319–332.

[4] Wang ZY, Zhao C, Han TY, et al. High-performance reduced graphene oxide-based room-temperature NO2 sensors: A combined surface modification of SnO2 nanoparticles and nitrogen doping approach. Sensor Actuat B: Chem 2017, 242: 269–279.

[5] Minh Nguyen QT, van Duy N, Phuong NT, et al. Superior enhancement of NO2 gas response using n-p-n transition of carbon nanotubes/SnO2 nanowires heterojunctions. Sensor Actuat B: Chem 2017, 238: 1120–1127.

[6] Geng X, Lu PF, Zhang C, et al. Room-temperature NO2 gas sensors based on rGO@ZnO1-x composites: Experiments and molecular dynamics simulation. Sensor Actuat B: Chem 2019, 280: 690–702.

[7] Chen XX, Shen YB, Zhou PF, et al. NO2 sensing properties of one-pot-synthesized ZnO nanowires with Pd functionalization. Sensor Actuat B: Chem 2018, 273: 151–161.

[8] Zhao SK, Shen YB, Zhou PF, et al. Design of Au@WO3 core–shell structured nanospheres for ppb-level NO2 sensing. Sensor Actuat B: Chem 2019, 282: 917–926.

[9] Zhang ZY, Haq M, Wen Z, et al. Ultrasensitive ppb-level NO2 gas sensor based on WO3 hollow nanospheres doped with Fe. Appl Surf Sci 2018, 434: 891–897.

[10] Wang LL, Gao J, Wu BF, et al. Designed synthesis of In2O3 Beads@TiO2–In2O3 composite nanofibers for high performance NO2 sensor at room temperature. ACS Appl Mater Interfaces 2015, 7: 27152–27159.

[11] González-Borrero PP, Sato F, Medina AN, et al. Optical band-gap determination of nanostructured WO3 film. Appl Phys Lett 2010, 96: 061909.

[12] Zheng HD, Ou JZ, Strano MS, et al. Nanostructured tungsten oxide-properties, synthesis, and applications. Adv Funct Mater 2011, 21: 2175–2196.

[13] Korotcenkov G, Cho BK. Metal oxide composites in conductometric gas sensors: Achievements and challenges. Sensor Actuat B: Chem 2017, 244: 182–210.

[14] Kim DH, Jung JW, Choi SJ, et al. Pt nanoparticles functionalized tungsten oxinitride hybrid chemiresistor: Low-temperature NO2 sensing. Sensor Actuat B: Chem 2018, 273: 1269–1277.

[15] Isaac NA, Valenti M, Schmidt-Ott A, et al. Characterization of tungsten oxide thin films produced by spark ablation for NO2 gas sensing. ACS Appl Mater Interfaces 2016, 8: 3933–3939.

[16] Kim JS, Yoon JW, Hong YJ, et al. Highly sensitive and selective detection of ppb-level NO2 using multi-shelled WO3 yolk-shell spheres. Sensor Actuat B: Chem 2016, 229: 561–569.

[17] Wang YL, Cui XB, Yang QY, et al. Preparation of Ag-loaded mesoporous WO3 and its enhanced NO2 sensing performance. Sensor Actuat B: Chem 2016, 225: 544–552.

[18] Choi SJ, Lee I, Jang BH, et al. Selective diagnosis of diabetes using Pt-functionalized WO3 Hemitube networks as a sensing layer of acetone in exhaled breath. Anal Chem 2013, 85: 1792–1796.

[19] Xiong Y, Tang ZL, Wang Y, et al. Gas sensing capabilities of TiO2 porous nanoceramics prepared through premature sintering. J Adv Ceram 2015, 4: 152–157.

[20] Zhang HW, Wang YY, Zhu XG, et al. Bilayer Au nanoparticle-decorated WO3 porous thin films: On-chip fabrication and enhanced NO2 gas sensing performances with high selectivity. Sensor Actuat B: Chem 2019, 280: 192–200.

[21] Miller DR, Akbar SA, Morris PA. Nanoscale metal oxide-based heterojunctions for gas sensing: A review. Sensor Actuat B: Chem 2014, 204: 250–272.

[22] Jia QQ, Ji HM, Wang DH, et al. Exposed facets induced enhanced acetone selective sensing property of nanostructured tungsten oxide. J Mater Chem A 2014, 2: 13602.

[23] Shendage SS, Patil VL, Vanalakar SA, et al. Sensitive and selective NO2 gas sensor based on WO3 nanowires. Sensor Actuat B: Chem 2017, 240: 426–433.

[24] Xiao BX, Zhao Q, Xiao CH, et al. Low-temperature solvothermal synthesis of hierarchical flower-like WO3 nanostructures and their sensing properties for H2S. CrystEngComm 2015, 17: 5710–5716.

[25] Jaroenapibal P, Boonma P, Saksilaporn N, et al. Improved NO2 sensing performance of electrospun WO3 nanofibers with silver doping. Sensor Actuat B: Chem 2018, 255: 1831–1840.

[26] Wu QF, Huang J, Li H. Deposition of porous nano-WO3 coatings with tunable grain shapes by liquid plasma spraying for gas-sensing applications. Mater Lett 2015, 141: 100–103.

[27] Lee K, Baek DH, Na H, et al. Simple fabrication method of silicon/tungsten oxide nanowires heterojunction for NO2 gas sensors. Sensor Actuat B: Chem 2018, 265: 522–528.

[28] Zhang YJ, Zeng W, Li YQ. New insight into gas sensing performance of nanorods assembled and nanosheets assembled hierarchical WO3·H2O structures. Mater Lett 2019, 235: 49–52.

[29] Zhai CB, Zhu MM, Jiang LN, et al. Fast triethylamine gas sensing response properties of nanosheets assembled WO3 hollow microspheres. Appl Surf Sci 2019, 463: 1078–1084.

[30] Lu J, Xu C, Cheng L, et al. Acetone sensor based on WO3 nanocrystallines with oxygen defects for low concentration detection. Mater Sci Semicond Process 2019, 101: 214–222.

[31] Zhang YX, Zeng W, Li YQ. NO2 and H2 sensing properties for urchin-like hexagonal WO3 based on experimental and first-principle investigations. Ceram Int 2019, 45: 6043–6050.

[32] Xue DP, Wang Y, Cao JL, et al. Improving methane gas sensing performance of flower-like SnO2 decorated by WO3 nanoplates. Talanta 2019, 199: 603–611.
[33] Yin L, Chen DL, Hu MX, et al. Microwave-assisted growth of In$_2$O$_3$ nanoparticles on WO$_3$ nanoplates to improve H$_2$S-sensing performance. J Mater Chem A 2014, 2: 18867–18874.

[34] Nayak AK, Ghosh R, Santra S, et al. Hierarchical nanostructured WO$_3$–SnO$_2$ for selective sensing of volatile organic compounds. Nanoscale 2015, 7: 12460–12473.

[35] Lee JS, Kwon OS, Shin DH, et al. WO$_3$ nanonodule-decorated hybrid carbon nanofibers for NO$_2$ gas sensor application. J Mater Chem A 2013, 1: 9099.

[36] Shen YB, Wang W, Chen XX, et al. Nitrogen dioxide sensing using tungsten oxide microspheres with hierarchical nanorod-assembled architectures by a complex surfactant-mediated hydrothermal route. J Mater Chem A 2016, 4: 1345–1352.

[37] Daniel MF, Desbat B, Lassegues JC, et al. Infrared and Raman study of WO$_3$ tungsten trioxides and WO$_3$–xH$_2$O tungsten trioxide hydrates. J Solid State Chem 1987, 67: 235–247.

[38] Zheng Y, Chen G, Yu YG, et al. Urea-assisted synthesis of ultra-thin hexagonal tungsten trioxide photocatalyst sheets. J Mater Sci 2015, 50: 8111–8119.

[39] Shi JJ, Cheng ZX, Gao LP, et al. Facile synthesis of reduced graphene oxide/hexagonal WO$_3$ nanosheets composites with enhanced H$_2$S sensing properties. Sensor Actuat B: Chem 2016, 230: 736–745.

[40] Pan CT, Su CY, Luo YC. Study on comparing WO$_3$ and W$_{18}$O$_{49}$ gas sensing abilities under NO$_2$ environment. Microsyst Technol 2017, 23: 2113–2123.

[41] Mane AT, Kulkarni SB, Navale ST, et al. NO$_2$ sensing properties of nanostructured tungsten oxide thin films. Ceram Int 2014, 40: 16495–16502.

[42] Behera B, Chandra S. Synthesis of WO$_3$ nanorods by thermal oxidation technique for NO$_2$ gas sensing application. Mater Sci Semicond Process 2018, 86: 79–84.

[43] An S, Park S, Ko H, et al. Fabrication of WO$_3$ nanotube sensors and their gas sensing properties. Ceram Int 2014, 40: 1423–1429.

[44] Horprathum M, Limwichean K, Wisitsoraat A, et al. NO$_2$ sensing properties of WO$_3$ nanorods prepared by glancing angle DC magnetron sputtering. Sensor Actuat B: Chem 2013, 176: 685–691.

[45] Hu J, Liang YF, Sun YJ, et al. Highly sensitive NO$_2$ detection on ppb level by devices based on Pd-loaded In$_2$O$_3$ hierarchical microstructures. Sensor Actuat B: Chem 2017, 252: 116–126.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.