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# Humidity-tolerant and highly sensitive gas sensor for hydrogen sulfide based on WO<sub>3</sub> nanocubes modified with CeO<sub>2</sub>

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The influence of ambient humidity on the gas-sensing characteristics of metal oxide semiconductors has been one of the greatest obstacles for gas-sensing applications. In this paper, the pure WO<sub>3</sub> and CeO<sub>2</sub>-modified WO<sub>3</sub> nanocubes were prepared by a simple hydrothermal method, and their gas-sensing characteristics in dry and humid atmospheres were investigated. The results show that CeO<sub>2</sub>/WO<sub>3</sub> demonstrated excellent gas-sensing properties toward H<sub>2</sub>S with high sensitivity and high selectivity at 115 °C. Noteworthy, the humidity independence of the CeO<sub>2</sub>/WO<sub>3</sub> increased compared to the WO<sub>3</sub>. The response retentions over the whole humidity range of the CeO<sub>2</sub>/WO<sub>3</sub>-6 and CeO<sub>2</sub>/WO<sub>3</sub>-15 sensors were 70.3, and 76%, respectively, which were much higher than the WO<sub>3</sub> sensor (17.9%). The gas-sensing mechanism of CeO<sub>2</sub>-modified WO<sub>3</sub> is discussed based on the gas sensitivity properties. The obtained results provide a promising route to enhance the anti-humidity properties of metal oxide semiconductor gas sensors.

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## 1. Introduction

Hydrogen sulfide (H<sub>2</sub>S) is a flammable and highly toxic gas, that is widespread in nature and industrial processes. Inhalation of this gas by human beings can easily lead to paralysis of the central nervous system and respiratory system or even death. Consequently, highly sensitive, reliable, and stable H<sub>2</sub>S sensors are in great demand. Metal oxide semiconductors (MOS) gas sensors have become one of the most practical gas sensors due to their high sensitivity, low power consumption, real-time monitoring, and portability.<sup>1–3</sup> However, atmosphere water vapor (H<sub>2</sub>O) will affect the sensitivity and accuracy of the practical detection to H<sub>2</sub>S. Consequently, eliminating the humidity cross-sensitivity is a challenge that needs to be solved.<sup>4–6</sup>

Recently, various strategies have been explored to suppress the humidity dependence of gas-sensing properties.<sup>7–10</sup> Endowing the sensing material with hydrophobic properties could efficiently prevent the H<sub>2</sub>O molecules from contacting with the sensing surface, and enhance the anti-humidity property of the gas sensor.<sup>11–13</sup> Gao *et al.* synthesized the hydrophobic sensing material by coating the

polydimethylsiloxane layer onto the Pd/TiO<sub>2</sub> surface. The sensors exhibited excellent humidity resistance when humidity was varied across a wide range (0–90% RH).<sup>14</sup> Jia *et al.* coated the surface of ZnSnO<sub>3</sub> hollow microspheres with 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFDS) layer. The PFDS/ZnSnO<sub>3</sub> sensors maintained a stable response as the condition changed from dry to 80% RH.<sup>15</sup> Although the anti-humidity property was highly improved by surface modifications, their gas-sensing properties were inevitably suppressed because the active sites of the sensing surface were covered by the hydrophobic layers. Loading or doping of the materials with high affinity to H<sub>2</sub>O molecules has been verified effective in promising humidity resistance of gas sensors.<sup>16,17</sup> Choi *et al.* overcame the humidity dependence problems of gas sensors by loading the CuO to SnO<sub>2</sub> hollow spheres. The CuO acts as a hydroxyl absorber to preferentially capture water vapor and form a Cu–OH bond. The sensing materials exhibited nearly consistent responses toward H<sub>2</sub>S in humidity variation.<sup>18</sup> Jeong *et al.* suppressed the humidity dependence by introducing the calcium silicate nanosheet as a water-trapping layer in SnO<sub>2</sub> nanowires. The sensors achieved high humidity resistance in NO<sub>2</sub> gas sensing.<sup>19</sup> However, the water-trapping effect may easily get saturated, when the sensors are exposed to highly humid atmospheres. Additionally, their selectivity and gas sensitivity will be partially reduced due to their complex modulation methods. To date, the design of the gas sensor that simultaneously possesses excellent gas-sensing properties and humidity resistance is still in the initial stages, and requires an

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efficient new route to further breakthroughs in high and continuously changing humidity.

Herein, we achieved the enhancement in both the gas sensing and humidity-resistant properties of the MOS-based gas sensors by employing the CeO<sub>2</sub>-modified WO<sub>3</sub> as the sensing material. The gas-sensing properties of WO<sub>3</sub> with different CeO<sub>2</sub> loading concentrations were investigated to understand the anti-humidity mechanism. The main focus of this work is to design CeO<sub>2</sub>/WO<sub>3</sub> heterojunction and confirm the optical CeO<sub>2</sub> loading concentration to increase the humidity independence of the gas-sensing properties and accomplish high sensitivity and selectivity towards H<sub>2</sub>S in highly humid environments.

## 2. Experimental section

### 2.1. Chemicals and materials

All of the chemical reagents are of analytical grade and used without purification, including sodium tungstate dehydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, A. R. Aladdin), cerium acetate hydrate ((CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>Ce·xH<sub>2</sub>O, A. R. Aladdin). All chemicals were used as received without any purification.

### 2.2. Preparation of CeO<sub>2</sub>-modified WO<sub>3</sub> nanocubes

The WO<sub>3</sub> nanocubes were fabricated *via* the hydrothermal process reported before.<sup>20</sup> The CeO<sub>2</sub>-modified WO<sub>3</sub> was obtained by a secondary hydrothermal process using cerium acetate ((CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>Ce·xH<sub>2</sub>O) as the Ce source, the synthesis route is shown in Fig. 1a. 0.232 g WO<sub>3</sub> powder was dispersed in ethanol solution and stirred continuously for 20 min, followed by adding 10 mL cerium acetate solution to the mixture. The mixing solution was transferred to the 100 mL Teflon-lined stainless autoclave and subjected to hydrothermal reaction at 180 °C for 12 h. The synthesized powder was collected and alternately washed

with deionized water and ethanol, then dried for subsequent use. The CeO<sub>2</sub>/WO<sub>3</sub> composites with different Ce concentrations (0.5 at%, 2 at%, 6 at%, 15 at%) were obtained by adjusting the concentration of the cerium acetate solution. These samples are labeled as CeO<sub>2</sub>/WO<sub>3</sub>-0.5, CeO<sub>2</sub>/WO<sub>3</sub>-2, CeO<sub>2</sub>/WO<sub>3</sub>-6, and CeO<sub>2</sub>/WO<sub>3</sub>-15 with Ce concentrations 0.5 at%, 2 at%, 6 at%, 15 at%, and the pure WO<sub>3</sub> nanocubes is labeled as WO<sub>3</sub>.

### 2.3. Material characterization

The morphology of materials was characterized by scanning electron microscopy (SEM, FEI Sirion 200, FEI, The Netherlands) and transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-YWIN). The crystal structure of materials was investigated by powder X-ray diffraction (XRD, D/max-2600PC, Rigaku Corporation, Tokyo, Japan). The surface composition and chemical state were measured by an X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi, Thermo Scientific, Waltham, MA, USA).

### 2.4. Fabrication and evaluation of gas sensors

The fabrication of the gas sensor is described as follows. First, a proper amount of sample was dispersed into distilled water to form the paste. Then, the paste was coated onto a ceramic tube to develop the sensing layer, followed by annealing at 500 °C for 2 h in air. The corresponding gas sensor device structure is displayed in Fig. 1b. The gas-sensing properties of the as-fabricated sensor were measured by a WS-30A system (Winsen Electronics Technology Co., Ltd, Zhengzhou, China). The response was defined as the ratio of the sensor resistance ( $R_a$ ) in the air to the sensor resistance ( $R_g$ ) in the target gas. The response and recovery time were defined as the times of the gas sensor reaching 90% of its resistance changes upon exposure to the target gas and to the air.

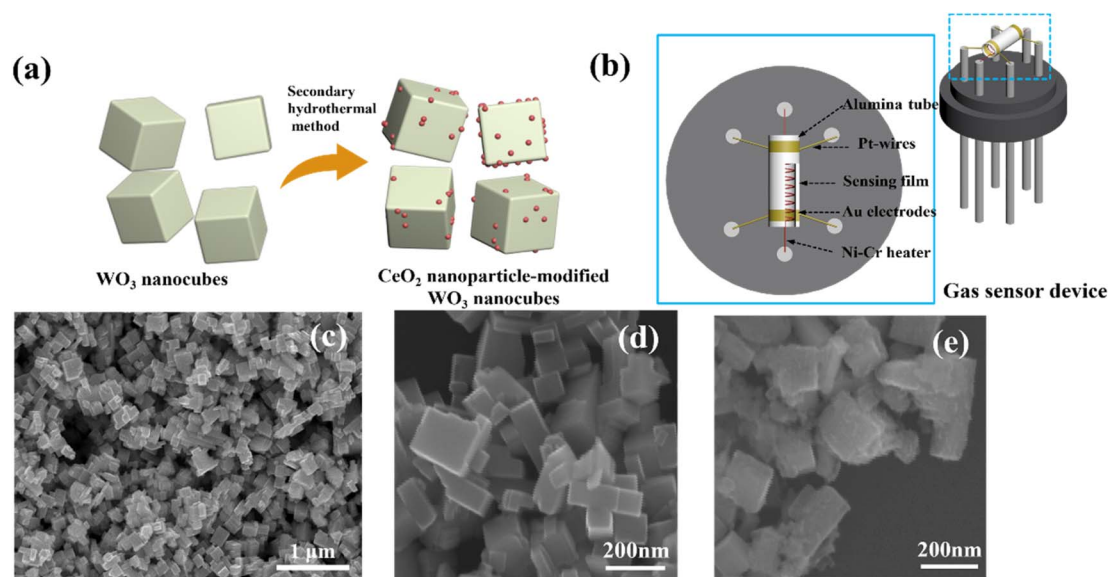


Fig. 1 (a) Synthetic route of the CeO<sub>2</sub>-modified WO<sub>3</sub> nanocubes; (b) the structure diagram of the sensor device; typical SEM images of (c and d) WO<sub>3</sub> nanocubes and (e) CeO<sub>2</sub>-modified WO<sub>3</sub> nanocubes.



### 3. Result and discussion

#### 3.1. Characterizations of materials

The morphology and microstructure of the materials were characterized by SEM and TEM images. As shown in Fig. 1c and d, the microstructure of the pure  $\text{WO}_3$  is composed of typical nanocubes, and the length size is 80–150 nm. After the  $\text{CeO}_2$  modification, the surface of  $\text{WO}_3$  nanocubes appears more rough and uneven according to Fig. 1e.

To investigate the more detailed morphology and characteristics of  $\text{CeO}_2$ -modified  $\text{WO}_3$ , we selected typical samples for TEM characterization. As recorded in Fig. 2a–f, the  $\text{CeO}_2$  particles attach randomly on the  $\text{WO}_3$  surface. The intensity of  $\text{CeO}_2$  nanoparticles on the  $\text{WO}_3$  nanocube surfaces increases as the  $\text{CeO}_2$  loading concentration increases. However, as the  $\text{CeO}_2$  concentration further increases to the maximum, these  $\text{CeO}_2$  nanoparticles are very compactly distributed on the surface of  $\text{WO}_3$  and form a stacking layer. The sensing surface of the  $\text{WO}_3$  nanocube is wrapped by the  $\text{CeO}_2$  nanoparticle layer, which may significantly affect the surface defects and absorption sites for the sensing layer. More detailed crystalline features of the  $\text{CeO}_2$ -

modified  $\text{WO}_3$  nanocubes have been characterized by HRTEM images of the typical samples, as shown in Fig. 2g and h. The nanoparticles with an average diameter of 5–10 nm on the nanotube can be clearly visible. The crystal plane spacing of 0.313 nm and 0.314 nm correspond to the (111) plane of cubic  $\text{CeO}_2$ .<sup>21</sup> Additionally, the lattice fringes of 0.364 nm and 0.363 nm correspond to the (200) plane of monoclinic  $\text{WO}_3$ .<sup>22</sup>

X-ray powder diffraction was employed to analyze the phases and crystal structure of the materials. As can be seen in Fig. 3, the diffraction peaks at  $23.2^\circ$ ,  $23.6^\circ$ ,  $24.4^\circ$ ,  $33.3^\circ$ ,  $34.2^\circ$ ,  $49.9^\circ$ , and  $55.9^\circ$  correspond to the (002), (020), (200), (022), (202), (400) and (420) crystallographic facets of the monoclinic  $\text{WO}_3$  (JCPDS 83-0950), respectively.<sup>23</sup> It indicates that the  $\text{WO}_3$  nanocubes are well crystallized, which is consistent with the TEM results. Apart from the peaks that belong to the  $\text{WO}_3$ , the diffraction peaks of  $\text{CeO}_2/\text{WO}_3$  located at  $28.5^\circ$ ,  $33.1^\circ$ , and  $47.5^\circ$  correspond to the (111), (200), (220) planes of fluorite cubic  $\text{CeO}_2$  (JCPDS 34-0394).<sup>24</sup>

XPS analysis was employed to further investigate the surface elemental composition and the chemical state of the materials. The W 4f narrow-scanning spectrum of the  $\text{CeO}_2/\text{WO}_3$ -2 is

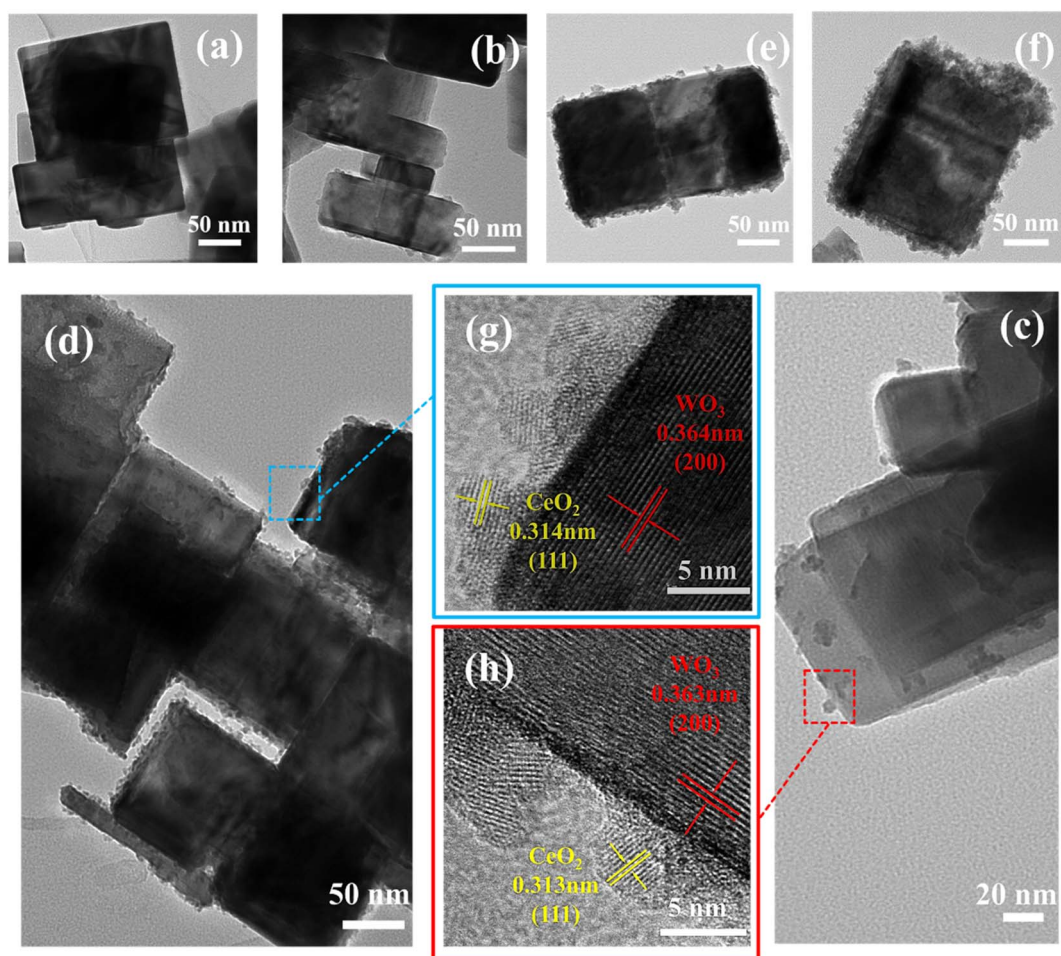


Fig. 2 Low-magnification TEM image of (a)  $\text{WO}_3$  nanocubes, (b)  $\text{CeO}_2/\text{WO}_3$ -0.5, (c)  $\text{CeO}_2/\text{WO}_3$ -2, (d and e)  $\text{CeO}_2/\text{WO}_3$ -6, (f)  $\text{CeO}_2/\text{WO}_3$ -15; corresponding HRTEM images of the marked positions (g and h).



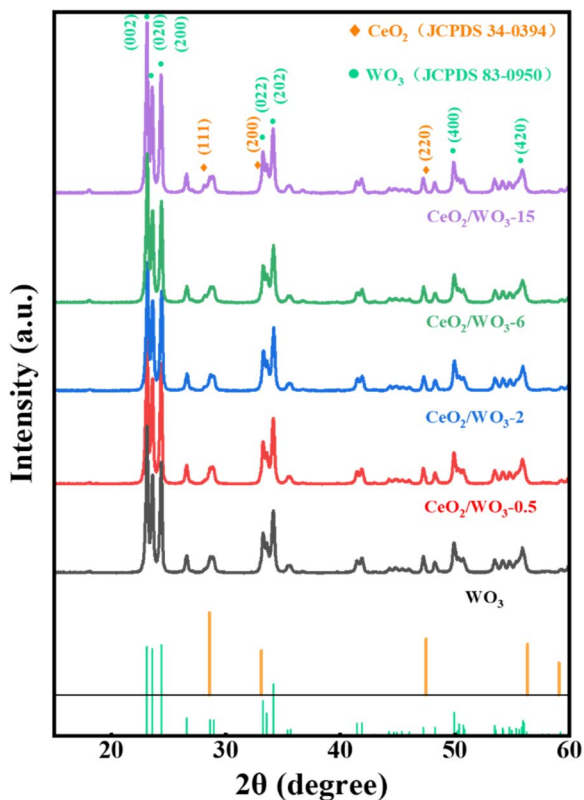


Fig. 3 XRD patterns of the  $\text{WO}_3$  and  $\text{CeO}_2/\text{WO}_3$ .

shown in Fig. 4a. The two peaks are attributed to the  $\text{W } 4f_{7/2}$  and  $\text{W } 4f_{5/2}$  state of  $\text{WO}_3$ , respectively.<sup>25</sup> As recorded in Fig. 4b, it indicates that there is a certain amount of  $\text{Ce}^{3+}$  existence in  $\text{CeO}_2/\text{WO}_3$ -2. This may be attributable to the unique chemical

properties of  $\text{CeO}_2$ . Due to the high mobility of lattice oxygen of  $\text{CeO}_2$ , the unstable lattice oxygen may be transported and adsorbed on the surface of the  $\text{WO}_3$  nanocubes.  $\text{Ce}^{4+}$  will form  $\text{Ce}^{3+}$  by capturing the electrons left behind by the lattice oxygen, potentially resulting in the formation of oxygen vacancies.<sup>26,27</sup>

It is well known that the gas-sensing properties are closely related to the oxygen adsorption on the sensing surface.<sup>28</sup> To verify the oxygen adsorption state of the materials. The O 1s XPS pattern of  $\text{CeO}_2/\text{WO}_3$ -2 is displayed in Fig. 4d. The pattern can be deconvoluted into three peaks located at 530.45 eV, 531.40 eV, and 532.75 eV, which correspond to lattice oxygen species ( $\text{O}_L$ ), oxygen vacancies ( $\text{O}_V$ ), and adsorbed oxygen species ( $\text{O}_C$ ), respectively.<sup>29</sup> The O 1s XPS spectrum of  $\text{WO}_3$  is shown in Fig. 4c. It is obvious that both the intensity and area of the  $\text{O}_C$  peak are smaller than the results of  $\text{CeO}_2$ -modified  $\text{WO}_3$ . This suggests that  $\text{CeO}_2$  modification has resulted in a higher adsorption capacity of the  $\text{WO}_3$  nanocubes for chemisorbed oxygen species. Therefore, the ability of chemisorbing oxygen highly contributes to the gas-sensing toward  $\text{H}_2\text{S}$  gas.

### 3.2. Gas sensing performance

To investigate the effect of  $\text{CeO}_2$  modification on the gas-sensing properties, the  $\text{WO}_3$  and  $\text{CeO}_2/\text{WO}_3$  were employed as sensing materials to prepare gas sensor devices. It is well known that the operating temperature significantly affects the gas-sensing properties of the gas sensors. The response of the sensors to 5 ppm  $\text{H}_2\text{S}$  gas at different operating temperatures of 80 °C, 115 °C, 160 °C, and 205 °C are shown in Fig. 5a. The response gradually increases with a temperature rise from 80 °C to 115 °C, which may be caused by two factors. One aspect is that the temperature increase enables the gas molecules to overcome the activation energy barrier of the surface reaction. The other is that

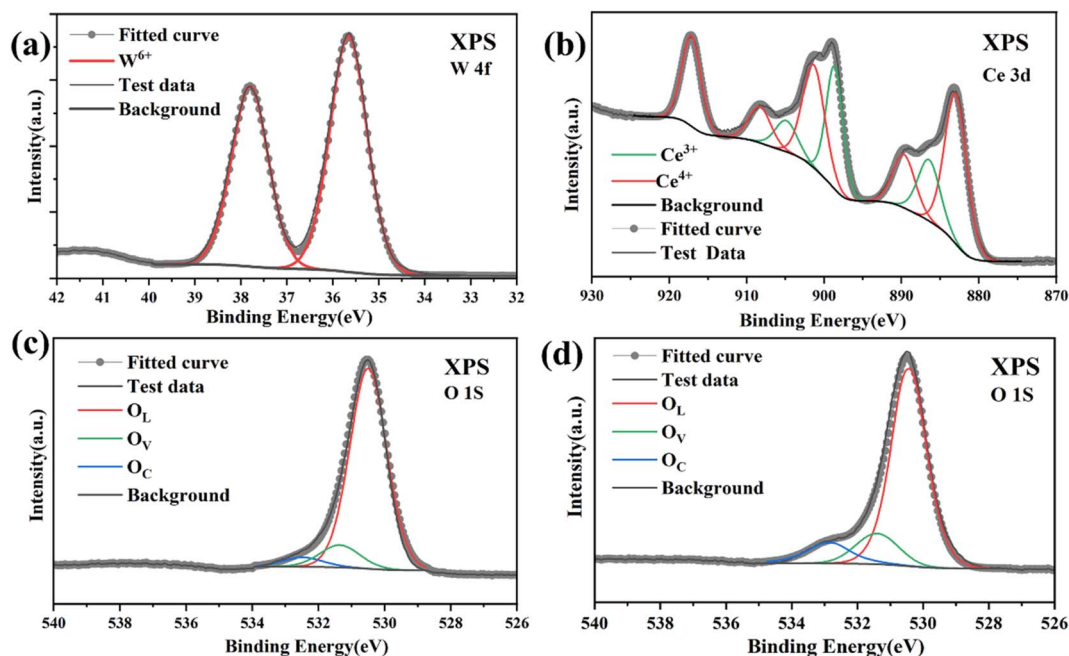


Fig. 4 XPS analysis of (a) W 4f; (b) Ce 3d of  $\text{CeO}_2/\text{WO}_3$ -2; (c) O 1s spectra of pure  $\text{WO}_3$ . (d) O 1s spectra of  $\text{CeO}_2/\text{WO}_3$ -2.



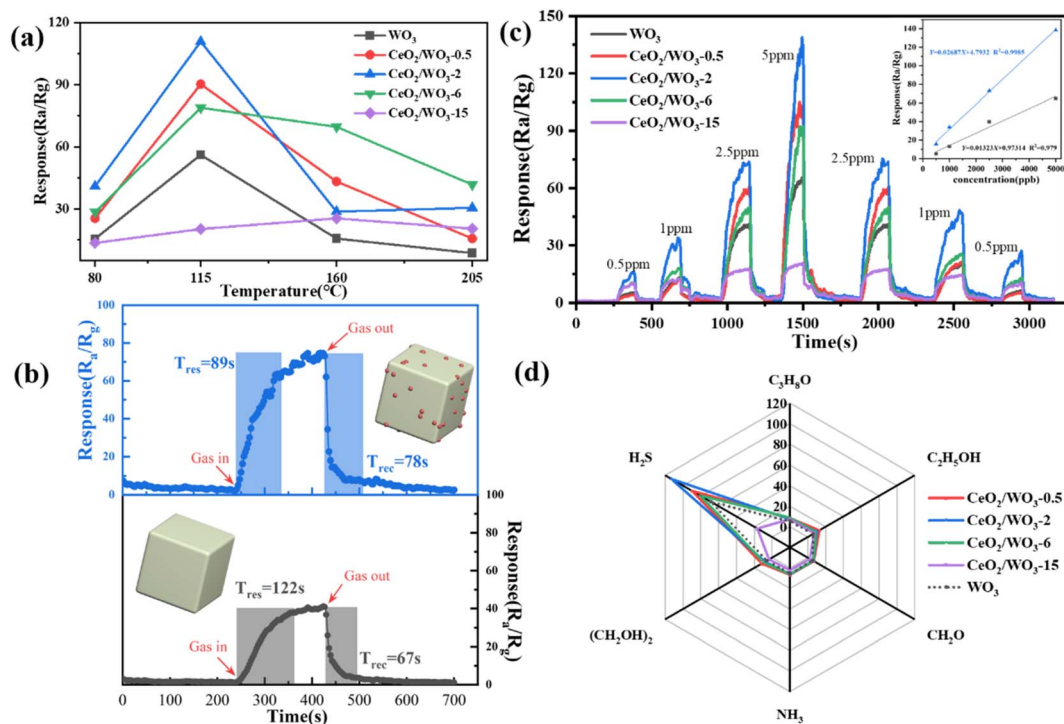


Fig. 5 (a) Gas response of the gas sensors toward 5 ppm  $\text{H}_2\text{S}$  under different operating temperatures; (b) response–recover time curve of the  $\text{WO}_3$  and  $\text{CeO}_2/\text{WO}_3$ -2 sensor to 2.5 ppm  $\text{H}_2\text{S}$  gas at 115 °C; (c) dynamic response curves of the  $\text{WO}_3$  and  $\text{CeO}_2/\text{WO}_3$  sensors to 0.5–5 ppm  $\text{H}_2\text{S}$  gas at 115 °C; (d) the selectivity to 5 ppm  $\text{H}_2\text{S}$  and other volatile gases for  $\text{WO}_3$  sensor and  $\text{CeO}_2/\text{WO}_3$  sensors at 115 °C.

the carrier concentration of sensing layer rises with increasing the operating temperature, which promotes the adsorption of chemisorbed oxygen on the surface. However, the response decreases with further increasing the operating temperature to 205 °C. The decrease in response can be attributed to the significant desorption of gas molecules at higher temperatures, thereby impeding the gas-sensing reaction. Therefore, it could be confirmed that the optimal working temperature of the gas sensor is 115 °C. The sensors in this work show the best response at a much lower temperature relative to the results reported previously, which means lower power consumption for sensors in practical applications.<sup>30</sup> All subsequent gas-sensing properties were investigated at an operating temperature of 115 °C.

As can be seen in Fig. 5a, the response values of sensors have been significantly improved for  $\text{CeO}_2/\text{WO}_3$ -0.5 and  $\text{CeO}_2/\text{WO}_3$ -2. However, the response values deteriorate notably for further increasing the concentration of  $\text{CeO}_2$ . The  $\text{CeO}_2/\text{WO}_3$ -2 sensor exhibits the maximum response ( $R_a/R_g = 113$ ) to 5 ppm  $\text{H}_2\text{S}$  gas, which is significantly higher than the  $\text{WO}_3$  sensor under identical conditions. The enhanced response performance is attributed to the modification of  $\text{CeO}_2$  nanoparticles. Based on the TEM image, the  $\text{CeO}_2$  nanoparticles are randomly distributed on the surface of  $\text{WO}_3$  nanocubes. For the  $\text{CeO}_2$ -modified  $\text{WO}_3$ , such ultrafine  $\text{CeO}_2$  nanoparticles might have endowed  $\text{CeO}_2$  with a highly active surface and formed the  $\text{CeO}_2/\text{WO}_3$  heterojunction to promote the gas-sensing properties. When the  $\text{CeO}_2$  nanoparticle loading concentration increases to a certain amount, the excess  $\text{CeO}_2$  nanoparticles on the  $\text{WO}_3$

nanocube surfaces hinder electron transport and reduce the efficiency of the gas-sensing reaction.<sup>31</sup> This reveals that a suitable amount of  $\text{CeO}_2$  modification can effectively enhance the response properties of  $\text{WO}_3$  nanocubes to  $\text{H}_2\text{S}$  gas.

The response and recovery properties of gas sensors are also additional parameters in practical applications. Fig. 5b shows the response and recovery time curves of the  $\text{WO}_3$  sensor and  $\text{CeO}_2/\text{WO}_3$ -2 sensor to 2.5 ppm  $\text{H}_2\text{S}$ . It is observed that the response time of the  $\text{CeO}_2/\text{WO}_3$ -2 sensor is shorter than the  $\text{WO}_3$  sensor. To further investigate the response characteristics of the gas sensors, Fig. 5c presents the dynamic response curves of the sensors to 0.5–5 ppm  $\text{H}_2\text{S}$ . As shown, the response of  $\text{CeO}_2/\text{WO}_3$ -2 is significantly higher than the  $\text{WO}_3$  sensor at different  $\text{H}_2\text{S}$  gas concentrations. It is observed that the response values of sensors rise with increasing  $\text{H}_2\text{S}$  gas concentration. Additionally, the inset in Fig. 5c demonstrates the linear fitting function curves based on the response and concentration. The fitting coefficient ( $R^2$ ) of the  $\text{CeO}_2/\text{WO}_3$ -2 sensor is also significantly higher than the  $\text{WO}_3$  sensor, which indicates the  $\text{CeO}_2/\text{WO}_3$ -2 sensor possesses better linearity.

Selectivity is another important parameter in terms of gas sensors. The selectivity of the sensors was studied by measuring the response to  $\text{C}_3\text{H}_8\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{CH}_2\text{O}$ ,  $\text{NH}_3$ ,  $(\text{CH}_2\text{OH})_2$ , and  $\text{H}_2\text{S}$  gas. The responses of the sensors to different volatile gases are shown in Fig. 5d. It can be seen that the response of the sensors to  $\text{H}_2\text{S}$  is significantly higher than those for other volatile gases. The results indicate that all the sensors showed a high selectivity to  $\text{H}_2\text{S}$  against other gases.



### 3.3. Anti-humidity performance

The response–recovery curves of the  $\text{WO}_3$  sensor and  $\text{CeO}_2/\text{WO}_3$  sensors to 5 ppm  $\text{H}_2\text{S}$  under relative humidity (RH) in the range of 20–80% are presented in Fig. 6a–e. The plot of response retention as a function of relative humidity for different sensors is shown in Fig. 6f. As presented in Fig. 6a, the response value of the  $\text{WO}_3$  sensor decreases significantly with the humidity increasing from 20% RH to 80% RH. As shown in Fig. 6f, the response of the  $\text{WO}_3$  sensor measured under 60% RH and 80% RH was only 37.2%, and 17.9% compared with that measured under 20% RH. It indicates that the  $\text{WO}_3$  sensor exhibited a typical humidity dependence on the  $\text{H}_2\text{S}$  gas-sensing process.

The response curves of  $\text{CeO}_2/\text{WO}_3$  sensors across various humidity conditions are shown in Fig. 6b–e. Notably, the humidity dependence is slightly mitigated, when the Ce concentration is 0.5–2 at%. As the  $\text{CeO}_2$  loading concentration further increases, the response  $\text{CeO}_2/\text{WO}_3$ -6 and  $\text{CeO}_2/\text{WO}_3$ -15 exhibited much lower degradation over the whole humidity range, compared to the other sensors. When the relative humidity changed from 20% RH to 80% RH, the response retentions of  $\text{CeO}_2/\text{WO}_3$ -6 and  $\text{CeO}_2/\text{WO}_3$ -15 were 70.3, and 76%, which is much higher than the pure  $\text{WO}_3$ . Fig. 6g

demonstrates the contact angles of  $\text{WO}_3$  and  $\text{CeO}_2/\text{WO}_3$ -15, the contact angle of  $\text{CeO}_2/\text{WO}_3$ -15 is much larger than that of  $\text{WO}_3$ . The excellent moisture resistance of  $\text{CeO}_2/\text{WO}_3$ -15 could be attributed to the hydrophobic nature of  $\text{CeO}_2$ .<sup>32</sup> Additionally, compare the sensitivity of  $\text{WO}_3$  and  $\text{CeO}_2/\text{WO}_3$ -6 sensors measured in highly humid atmospheres (60% RH, 80% RH). It can be seen that the response value of the  $\text{CeO}_2/\text{WO}_3$ -6 sensor was much higher than the  $\text{WO}_3$  sensor. In conclusion, the humidity dependence of the response steadily decreased with increasing  $\text{CeO}_2$  loading concentration. A certain amount of  $\text{CeO}_2$  modification can efficiently enhance the stability of  $\text{WO}_3$  against changes in humidity, and simultaneously increase the sensitivity in various humidity, particularly within high-humidity conditions.

### 3.4. Gas sensing mechanism

It is well known that the gas-sensing properties of MOS-based gas sensors are associated with the capacity of adsorbing oxygen onto the surface. Particularly, when the sensing materials are exposed to air, oxygen will adsorb on their surfaces, and form chemisorbed oxygen species by capturing electrons from the conduction band of  $\text{WO}_3$  and  $\text{CeO}_2$ . This process will result in the formation of an

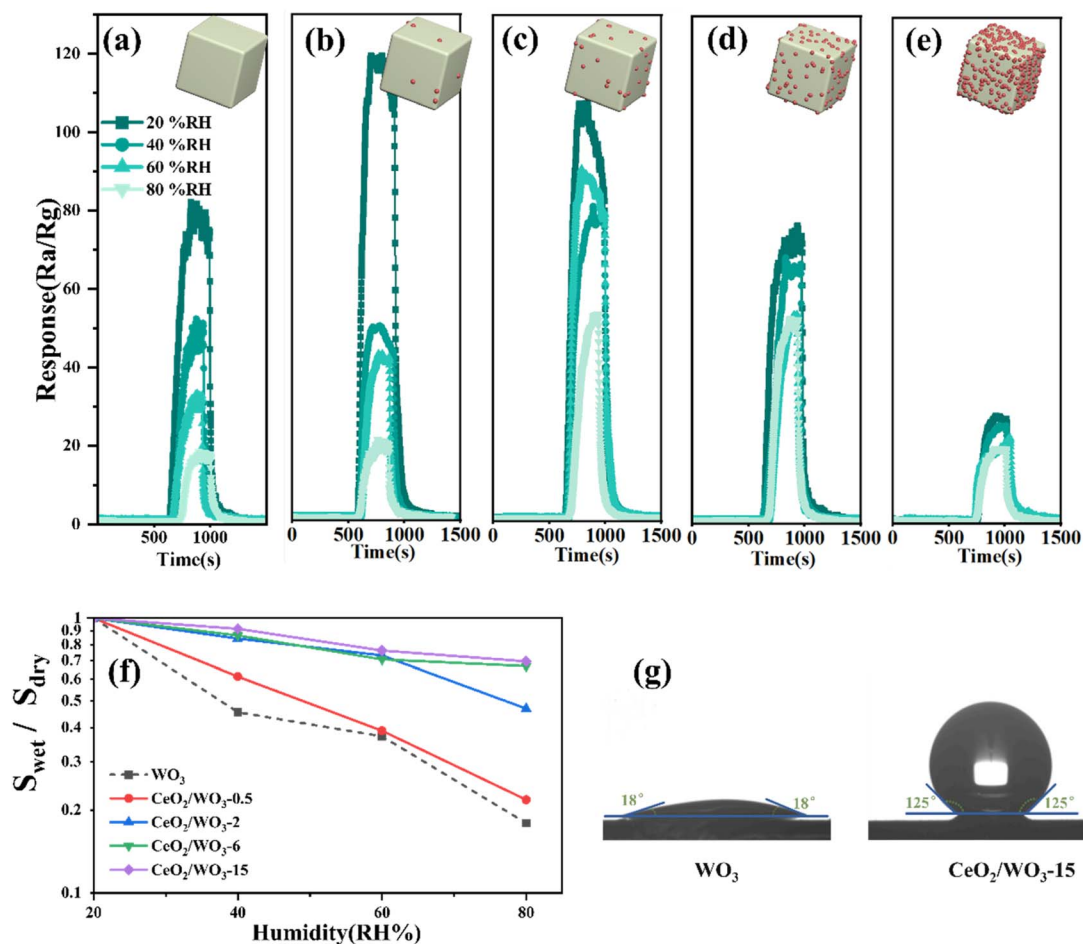
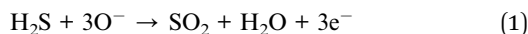


Fig. 6 The response curves of (a)  $\text{WO}_3$ , (b)  $\text{CeO}_2/\text{WO}_3$ -0.5, (c)  $\text{CeO}_2/\text{WO}_3$ -2, (d)  $\text{CeO}_2/\text{WO}_3$ -6, (e)  $\text{CeO}_2/\text{WO}_3$ -15 to 5 ppm  $\text{H}_2\text{S}$  gas under different humidity conditions; (f) plot of response retention as a function of relative humidity for different sensors, (g) contact angle tests on the  $\text{WO}_3$  and  $\text{CeO}_2/\text{WO}_3$ -15 materials.



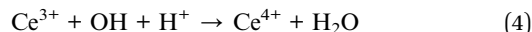
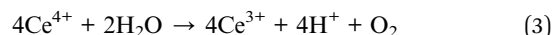
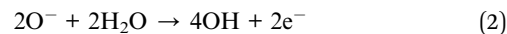
electron depletion region on the surface, which results in an overall high resistance of the gas sensors.

Once the gas sensor is exposed to the H<sub>2</sub>S gas, the chemisorbed oxygen reacts with H<sub>2</sub>S molecules, which release electrons back into the conduction band of the sensing material. This process causes a decrease in the electrical resistance of the gas sensors, as shown in eqn (1).



Compared to the WO<sub>3</sub> sensor, the CeO<sub>2</sub>/WO<sub>3</sub> sensors exhibit higher response properties towards H<sub>2</sub>S gas. The enhanced performance is attributed to the construction of the CeO<sub>2</sub>/WO<sub>3</sub> heterojunction, and the higher adsorption capacity of CeO<sub>2</sub>/WO<sub>3</sub> for chemisorbed oxygen, as confirmed by previous XPS analysis. The formation of heterojunction is considered to be the main factor. The heterojunction is formed as the CeO<sub>2</sub> nanoparticles are modified on the WO<sub>3</sub> surface. The energy band diagram of the CeO<sub>2</sub>/WO<sub>3</sub> heterojunction is shown in Fig. 7a and b. Since the work function of WO<sub>3</sub> (5.2 eV) is larger than CeO<sub>2</sub> (4.9 eV), electrons will flow from the conduction

band of CeO<sub>2</sub> to WO<sub>3</sub>.<sup>21</sup> The electron migration process leads to the formation of a hole accumulation layer on the surface of CeO<sub>2</sub> and an electron accumulation layer on the surface of WO<sub>3</sub>. The hole accumulation layer of CeO<sub>2</sub> at the heterojunction interface would further increase the number of electrons that were released from chemisorbed oxygen when the CeO<sub>2</sub>/WO<sub>3</sub> sensors were exposed to H<sub>2</sub>S gas.<sup>33,34</sup> As a result, the CeO<sub>2</sub>/WO<sub>3</sub> sensors exhibit higher resistance variations, namely, greater responses, than the WO<sub>3</sub> sensor.



When the sensor is in humid atmospheres, the H<sub>2</sub>O molecules consume the chemisorbed oxygen on the surface, and

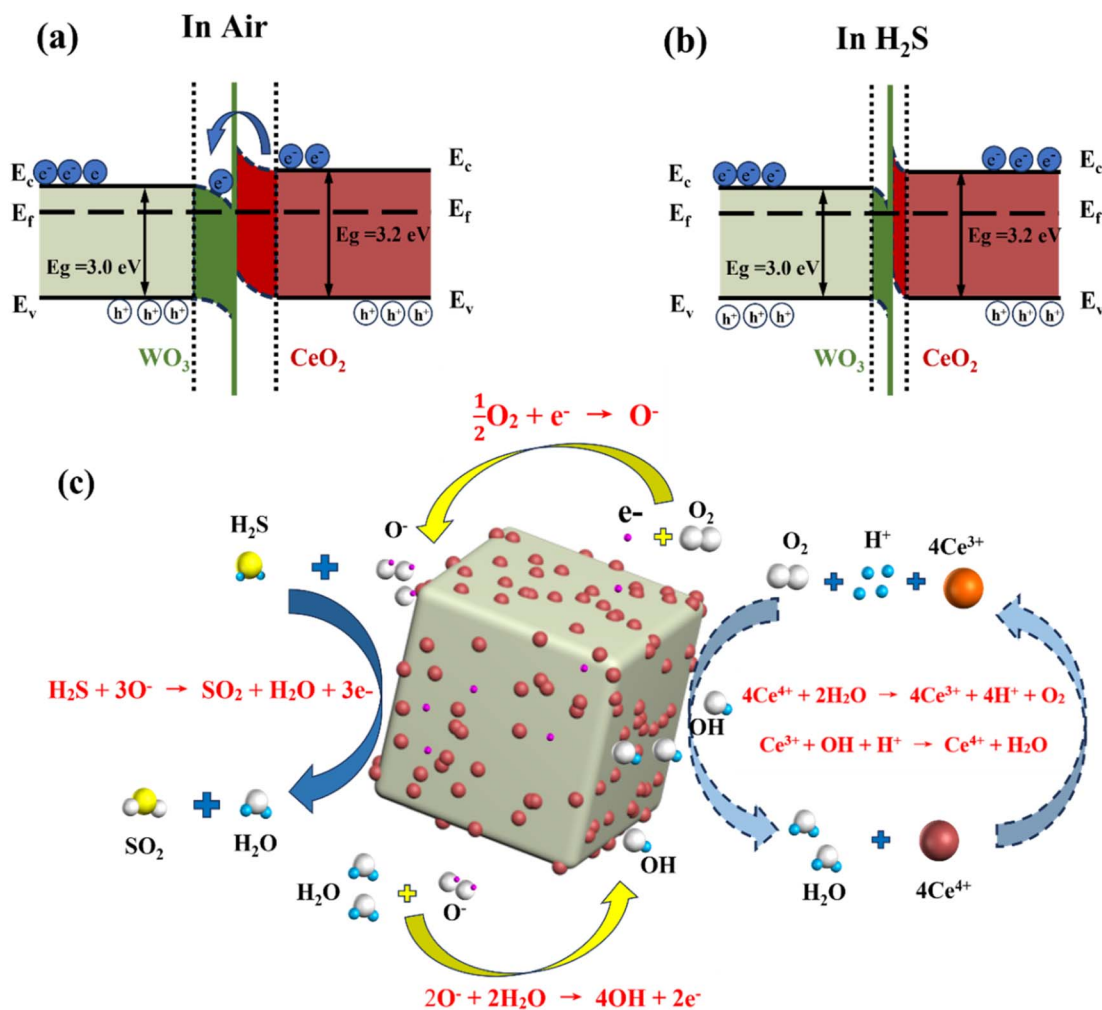


Fig. 7 Schematic of the energy bands of CeO<sub>2</sub>-modified WO<sub>3</sub> in the air (a) and H<sub>2</sub>S atmospheres (b), respectively, and (c) schematic of the anti-humidity detection to H<sub>2</sub>S gas.



generate hydroxyl radicals to occupy the active sites of the sensing layer, which significantly deteriorates the response properties of gas sensors. This humidity-sensitivity process is described by eqn (2).

In contrast to the  $\text{WO}_3$  sensor, the  $\text{CeO}_2/\text{WO}_3$  sensors exhibited a more stable response in humid conditions, which is attributed to the modification of  $\text{CeO}_2$  to  $\text{WO}_3$ .

Firstly, the  $\text{CeO}_2$  exhibits excellent hydrophobicity because the Ce atoms tend not to exchange electrons and form hydrogen bonds with interfacial  $\text{H}_2\text{O}$  molecules.<sup>35,36</sup> Secondly, the humidity dependence of gas sensors can be efficiently suppressed due to the highly reversible redox interaction between the multivalent states of the Ce elements.<sup>37,38</sup> when  $\text{CeO}_2$  is decorated on the surface of  $\text{WO}_3$ ,  $\text{CeO}_2$  preferentially captures  $\text{H}_2\text{O}$  molecules and reacts with them as follows. Firstly,  $\text{Ce}^{4+}$  ions are reduced to  $\text{Ce}^{3+}$  ions, and  $\text{H}_2\text{O}$  molecules are decomposed into  $\text{O}_2$  and  $\text{H}^+$  (eqn (3)). Then, the hydroxyl radicals produced by humidity-sensitivity are scavenged by  $\text{Ce}^{3+}$  (eqn (4)). Additionally, the oxygen ( $\text{O}_2$ ) stored on the surface of  $\text{CeO}_2$  is reionized into active adsorbed oxygen ( $\text{O}^-$ ) by electrons captured on the surface (eqn (5)), which promoting the gas-sensing reaction of the  $\text{H}_2\text{S}$  gas. The anti-humidity mechanism is explained in Fig. 7c. The above process effectively protects  $\text{WO}_3$  from interference by  $\text{H}_2\text{O}$  molecules while partially enhancing the gas-sensing properties of sensors to  $\text{H}_2\text{S}$ .

## 4. Conclusion

In summary, the pure  $\text{WO}_3$  and  $\text{CeO}_2$ -modified  $\text{WO}_3$  were synthesized by hydrothermal method. Compared to the pure  $\text{WO}_3$  nanocubes, the  $\text{CeO}_2$ -modified  $\text{WO}_3$  demonstrated excellent gas sensing performance toward  $\text{H}_2\text{S}$  gas at 115 °C with high sensitivity and high selectivity. The response of  $\text{CeO}_2/\text{WO}_3$ -2 sensor reached 113 for 5 ppm  $\text{H}_2\text{S}$  at 115 °C, which is two times of the  $\text{WO}_3$  sensor. The results of humidity stability show that  $\text{CeO}_2$ -modified  $\text{WO}_3$  can increase the anti-humidity property. When the relative humidity changed from 20% RH to 80% RH, the response retention of  $\text{CeO}_2/\text{WO}_3$ -15 sensor was 76%, which is four times of the  $\text{WO}_3$  sensor. The enhanced response sensitivity and humidity stability are attributed to the formation of  $\text{CeO}_2/\text{WO}_3$  heterojunctions, and the distinctive physico-chemical property of catalytic  $\text{CeO}_2$  plays a key role in mitigating humidity dependence. Therefore, this work provides a constructive strategy for preparing low-temperature, high-sensitivity, and anti-humidity gas sensors.

## Author contributions

Zhixiang Deng data curation: lead; investigation: lead; writing – original draft: equal; writing – review & editing: equal. Zhixuan Wu data curation: supporting; investigation: supporting. Zhengai Chen data curation: supporting. Xinkuan Liu data curation: equal; writing – review & editing: supporting. Yan Sun data curation: equal; funding acquisition: lead; supervision: equal; writing – review & editing: lead. Meiying Ge data curation: equal; visualization: supporting; writing – review & editing:

equal. Ning Dai funding acquisition: supporting; writing – review & editing: supporting.

## Conflicts of interest

There are no conflicts to declare.

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