Interfacial energy barrier tuning of hierarchical Bi$_2$O$_3$/WO$_3$ heterojunctions for advanced triethylamine sensor

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Abstract: Traditional triethylamine (TEA) sensors suffer from the drawback of serious cross-sensitivity due to the low charge-transfer ability of gas-sensing materials. Herein, an advanced anti-interference TEA sensor is designed by utilizing interfacial energy barriers of hierarchical Bi$_2$O$_3$/WO$_3$ composite. Benefiting from abundant slit-like pores, desirable defect features, and amplification effect of heterojunctions, the sensor based on Bi$_2$O$_3$/WO$_3$ composite with 40% Bi$_2$O$_3$ (0.4-Bi$_2$O$_3$/WO$_3$) demonstrates remarkable performance in terms of faster response/recovery time (1.7-fold/1.2-fold), higher response (2.1-fold), and lower power consumption (30 °C-decrement) as compared with the pristine WO$_3$ sensor. Furthermore, the composite sensor exhibits long-term stability, reproducibility, and negligible response towards interfering molecules, indicating the promising potential of Bi$_2$O$_3$/WO$_3$ heterojunctions in anti-interference detection of low-concentration TEA in real applications. This work not only offers a rational solution to design advanced gas sensors by tuning the interfacial energy barriers of heterojunctions, but also provides a fundamental understanding of hierarchical Bi$_2$O$_3$ structures in the gas-sensing field.

Keywords: Bi$_2$O$_3$/WO$_3$; heterojunctions; hierarchical structures; triethylamine (TEA); gas sensors

1 Introduction

Triethylamine (TEA), known as one of the most common volatile organic compounds (VOCs), not only easily causes open fire and explosions, but also brings great damage to human dermal, ocular, and respiratory system due to its corrosivity and toxicity [1–3]. According to the permissible exposure degrees stipulated by the Occupational Safety and Health Administration (OSHA), the threshold value of toxic TEA concentration that humans can tolerate is 10 ppm [4–6]. The TEA is also a sort of quite important industrial raw materials that served as organic solvents, synthetic dyes, and catalysts in organic synthesis, especially as a noteworthy biomarker of the decomposition from fish and other seafood [7,8]. Ref. [9] has shown that the TEA released from 200 g of putrid crucian for 7 d is less than 4 ppm, reflecting significant potential in freshness detection of seafood. Traditional TEA detection methods such as chromatography and colorimetry are limited due to their

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high cost and cumbersome detection procedures [10–12]. Therefore, reliable TEA sensors with high response, low cost, and convenient operation are required for promising applications in industrial production, food safety, and human health. In addition, the traditional TEA sensors still suffer from the drawback of serious cross-sensitivity, mainly due to low charge-transfer ability of gas-sensing materials.

Metal oxide semiconductors (MOSs) have been widely used in the gas sensors due to their attractive physical and chemical properties [13–15]. Generally, a semiconductor gas sensor is composed of a receptor function and a transducer function, which recognizes the adsorption and reaction of target gases on a sensing layer. The change in the electrical resistance of the sensing materials is recorded as a sensor signal. Among various MOSs, tungsten oxide (WO3) demonstrates high sensitivity, fast response, and long-term stability towards various gas species, owing to its non-toichiometry and chemical diversity [16]. However, the high activation energy for the chemisorption results in relatively high operating temperatures of WO3-based sensors. The formation of the heterojunctions and the heterogeneous structures has definitely proved that they can improve the sensing behavior of the MOSs [17–19]. As reported in Refs. [20,21], the valence bands of WO3 and bismuth oxide (Bi2O3) are 3.44 and 3.13 eV, respectively. Thus, the holes on the valence bands of both WO3 and Bi2O3 have a strong oxidative capability that is similar to TiO2, making them attractive for photocatalytic applications. Recently, the heterojunction between Bi2O3 and WO3 has attracted special attention for photodegradation and water splitting. Wei et al. [22] designed the porous WO3 microspheres embedded with Bi2O3 nanosheets, facilitating the separation and migration of charge carriers for dye photodegradation. Khan et al. [23] synthesized Bi2O3/h-WO3 nanocomposite as photoactive materials for water splitting, which exhibited a decreased bandgap and minimized recombination of the charge carriers due to the strain effect of Bi2O3. As is well known, the adsorption and reaction behavior of the target gases on the gas-sensing materials has relations with the catalytic process. From the viewpoint of the accessible materials, Bi2O3 possesses advantages of tunable electrical conductivity and high electron affinity [24]. Although pure Bi2O3 is rarely used for the gas-sensing purpose due to its slow electronic mobility at low temperatures [25], it was reported that the Bi2O3/SnO2 materials are sensitive to CO due to the participation of the Bi2Sn2O7 phase [26]. The Bi2O3/WO3 heterogeneous materials thus show great potential to achieve reliable gas sensors, and more related research is needed to explore.

In this work, we design an advanced TEA sensor by utilizing the interfacial energy barriers of the hierarchical Bi2O3/WO3 composite. The composite was prepared through the hydrothermal–ultrasonic combination procedure followed by thermal treatment. On the basis of the hierarchical Bi2O3/WO3 composite, the designed sensor possesses a high response of the TEA of 9.2–50 ppm at a low temperature of 140 °C. The response and recovery time are 1.7-fold and 1.2-fold, respectively, as compared with those of the pristine WO3 sensor. Furthermore, the composite sensor exhibits long-term stability, reproducibility, and negligible response towards the interfering molecules, indicating its potential application for anti-interference detection of the low-concentration TEA. Herein, the superior TEA-sensing performance is attributed to abundant slit-like pores, desirable defect features, and amplification effect of the heterojunctions between WO3 and Bi2O3. The presented work offers an easy solution for the rational design of other binary MOS sensors by utilizing the interfacial energy barriers of hierarchical metal oxides.

2 Experimental

2.1 Preparation of hierarchical Bi2O3

In a typical process, Bi(NO3)3 of 0.97 g was dissolved in a mixture of ethanol of 34 mL and ethylene glycol of 17 mL under magnetic stirring at room temperature to form a uniform transparent solution. After stirring for 30 min, the resulting solution was transferred into a Teflon-lined stainless-steel autoclave of 50 mL and heated at 160 °C for 5 h. The white precipitates were collected by centrifugation, washed with ethanol for several cycles, and then dried in an oven at 60 °C for 8 h.

2.2 Preparation of hierarchical WO3 and Bi2O3/WO3 composites

Hierarchical WO3·H2O was prepared via rapid sonochemical method [27]. Typically, Na2WO4·2H2O of 3.912 g and oxalic acid of 1.500 g were dissolved in deionized water of 48 mL with stirring at room temperature for 20 min. Then, certain amounts of 3 M HCl solution were added dropwise to the clear solution.
After sonicating for 1 h, the resulting WO$_3$·H$_2$O precipitates were washed with deionized water several times followed by drying overnight. The as-synthesized WO$_3$·H$_2$O was dehydrated and transformed into anhydrous WO$_3$ during the subsequent thermal treatment. A sequence of the hierarchical Bi$_2$O$_3$/WO$_3$ composite was then prepared by mixing hierarchical Bi$_2$O$_3$ and WO$_3$ with different Bi$_2$O$_3$ molar ratios. When the Bi$_2$O$_3$ contents are 20%, 40%, 60%, and 80%, the composites are labelled as 0.2-Bi$_2$O$_3$/WO$_3$, 0.4-Bi$_2$O$_3$/WO$_3$, 0.6-Bi$_2$O$_3$/WO$_3$, and 0.8-Bi$_2$O$_3$/WO$_3$, respectively.

2.3 Characterization

The crystal phases and morphologies of the samples were studied by an X-ray diffractometer (DX2700, Dandong Haoyuan Instrument Co., Ltd.) and a scanning electron microscope (SEM; 250 FEG Quanta) attached with energy dispersive spectroscopy (EDS). The specific surface area of the 0.4-Bi$_2$O$_3$/WO$_3$ sample was characterized with a Brunauer–Emmett–Teller (BET) analyzer (Autosorb-iQ2, Quantachrome). Thermogravimetric (TG) analysis was carried out in a dynamic air atmosphere by a TG analyzer (STA 449 F5 Jupiter, Netzsch). Raman spectra were acquired by a Raman spectrometer (HR800, Horiba), which was performed with an excitation wavelength of 785 nm. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a spectrophotometer (U-3900H, Hitachi) with an integrating sphere. Photoluminescence (PL) spectra were determined by a spectrofluorometer (Fluoro-max-4, Horiba).

2.4 Fabrication and gas-sensing test of sensors

The fabrication of the gas sensor was divided into several steps. Firstly, the as-prepared samples of 1 mg and terpineol (binding agent) of several microliters were ground in an agate mortar for 5 min to form a uniform slurry. The obtained slurry was slowly and evenly coated on a commercial Ag/Cr interdigital electrode by spinning at 2000 r/min for 15 s. As shown in Fig. S1(a) in the Electronic Supplementary Material (ESM), a successive gas-sensing layer on the surface of the interdigital electrode was formed after annealing at 400 °C for 2 h. Finally, the sensor element was aged at 200 °C for 10 h to improve the stability and repeatability. The sensor resistance in air ($R_0$) or target gas ($R_g$) was tested under a direct current (DC) bias voltage of 3 V in a homemade chamber connected with a computer-controlled sourcemeter (2612B, Keithley), as shown in Fig. S1(b) in the ESM. The response value of the gas sensor is calculated by the expression of $R_0/R_g$ for the reducing gas. Moreover, the response and recovery time are defined as the time required for the sensor to reach 90% of the total variation values.

3 Results and discussion

As shown in Fig. 1(a), the hierarchical WO$_3$ and Bi$_2$O$_3$ architectures were prepared through the hydrothermal and ultrasonic procedures, respectively, and the hierarchical Bi$_2$O$_3$/WO$_3$ composite was obtained after the mixing and thermal treatment. The formation process of the hierarchical WO$_3$ architectures can be explained by the ultrasonic cavitation and Ostwald ripening [28]. At the initial stage of the reaction, oxalic acid is considered as the chelating agent to control the nucleation rate and slow down the sol–gel process in an aqueous solution. After that, the colorless WO$_4^{2-}$ ions are transformed into a yellow H$_2$WO$_4$ precursor. In the ultrasonic process, the nucleophilic addition reaction between the water molecule and the H$_2$WO$_4$ molecule results in the formation of hexagonal WO(OH)$_4$(H$_2$O) octahedra. Due to the mono-oxo coordination nature of W$^{6+}$, each W atom is connected by four bridging oxygens (OH) in the $XY$ plane, one terminal oxygen W=O in the $Z$ axis, and one water molecule by hydrogen bonds at the symmetric position of W=O bonds. This octahedral structure easily forms a lamellar structure in the $XY$ plane through a co-angular polycondensation reaction, and water molecules are located between these lamellas. Finally, the WO(OH)$_4$(H$_2$O) lamellas were reasssembled by edge-tacking along the $Z$ axis under dipole interaction, and the hierarchical WO$_3$·H$_2$O was formed, which was further dehydrated and transformed into anhydrous WO$_3$ after the heat treatment. For the formation of the hierarchical Bi$_2$O$_3$ architectures, numerous Bi$_2$O$_3$ nanocrystals nucleate from the solution and aggregate into nanosheets. Under the tendency of thermodynamic stability, the formed Bi$_2$O$_3$ nanosheets rearrange themselves and stack with each other to form the hierarchical architectures. The hierarchical WO$_3$·H$_2$O and Bi$_2$O$_3$ architectures were mixed with the assistance of terpineol to form pastes, and then coated onto the commercial Ag/Cr interdigital electrode by spinning at
2000 r/min for 15 s. After drying, it was calcined at 400 °C for 2 h to get good stability and remove the terpineol on the interdigital electrode. Herein, the calcination temperature was determined from the TG analysis of the composite (Fig. S2 in the ESM), where a major mass loss is observed at the temperature ranging from 100 to 350 °C due to the loss of chemically bonded water from WO$_3$·H$_2$O and the decomposition of residual carboxylate in the composite. Figures 1(b)–1(d) and Fig. S3 in the ESM show the SEM images of the pure WO$_3$, pure Bi$_2$O$_3$, and the Bi$_2$O$_3$/WO$_3$ composite with different Bi$_2$O$_3$ ratios after calcination at 400 °C. Differently from the hierarchical Bi$_2$O$_3$ (Fig. 1(c)), the sintering growth of the hierarchical WO$_3$ under the calcination is observed (Fig. 1(b)). In the 0.4-Bi$_2$O$_3$/WO$_3$ composite (Fig. 1(d)), the nanosheet-assembled WO$_3$ microspheres (2–3 mm) are separated by nanosheet-assembled Bi$_2$O$_3$ microspheres (4–6 mm). Besides, the addition of Bi$_2$O$_3$ significantly suppressed the Ostwald ripening of the WO$_3$ microspheres during the calcination, resulting in smaller sizes of the WO$_3$ microspheres in the Bi$_2$O$_3$/WO$_3$ composite. The EDS analysis confirms the homogeneity of W, Bi, and O elements in the whole 0.4-Bi$_2$O$_3$/WO$_3$ composite (Fig. 1(e)). The porous structure of the 0.4-Bi$_2$O$_3$/WO$_3$ composite was confirmed by the nitrogen adsorption–desorption isotherms. As shown in Fig. S4 in the ESM, the isotherms exhibit a type-H3 hysteresis loop, suggesting the existence of slit-like pores in the hierarchical composite. The specific surface area of the 0.4-Bi$_2$O$_3$/WO$_3$ sample was calculated to be 50.98 m$^2$/g by the BET method.

To investigate the phase structure, crystallinity, and composition, X-ray diffraction (XRD) patterns were collected for the Bi$_2$O$_3$, WO$_3$, and Bi$_2$O$_3$/WO$_3$ samples, as shown in Fig. 2(a) and Fig. S5 in the ESM. For the hierarchical Bi$_2$O$_3$, the smooth and sharp diffraction peaks can be indexed to the monoclinal α-Bi$_2$O$_3$ (JCPDS No. 71-2274) [29]. For the hierarchical WO$_3$, the three overwhelming diffraction peaks with 2θ = 23.12°, 23.59°, and 24.38° corresponded to the (002), (020), and (002) planes of WO$_3$ (JCPDS No. 43-1035) [30], respectively. For the hierarchical Bi$_2$O$_3$/WO$_3$ composite, the corresponding gas sensors. SEM images of (b) hierarchical WO$_3$, (c) Bi$_2$O$_3$, and (d) 0.4-Bi$_2$O$_3$/WO$_3$. (e) Elemental mappings of hierarchical 0.4-Bi$_2$O$_3$/WO$_3$ composite, showing W, Bi, and O distributions.
composite, all the diffraction peaks belonging to Bi$_2$O$_3$ and WO$_3$ can be observed, suggesting the mixed phases of Bi$_2$O$_3$ and WO$_3$ in the composite. The Raman peaks at 184, 260, 312, 703, 801, and 954 cm$^{-1}$ are consistent with monoclinic WO$_3$ [31]. For the pure Bi$_2$O$_3$, the characteristic Raman peaks from 100 to 500 m$^{-1}$ are in good agreement with monoclinic α-Bi$_2$O$_3$ [32]. All the characteristic peaks of WO$_3$ and Bi$_2$O$_3$ are obviously present in the Raman spectrum of Bi$_2$O$_3$/WO$_3$ composite curves (Fig. 2(b)), suggesting the formation of the Bi$_2$O$_3$/WO$_3$ composite with no impurities. Along with the increase of Bi$_2$O$_3$ content in the composite, the relative intensity of the characteristic peaks from WO$_3$ decreases, and the relative intensity of the characteristic peaks from Bi$_2$O$_3$ increases (Fig. S6 in the ESM). Herein, the slight variations in the position, width, and relative intensity of these characteristic peaks are observed, which may be attributed to the slight structural variations and sample shape of the Bi$_2$O$_3$/WO$_3$ composite, as compared with those of the pristine Bi$_2$O$_3$ and WO$_3$. Figure 2(c) compares the UV–Vis absorption spectra of the as-prepared materials, in which the WO$_3$ and Bi$_2$O$_3$ have similar absorption edges at 450–500 nm, whereas the Bi$_2$O$_3$/WO$_3$ composite shows an absorption edge at around 567 nm. In general, the optical band gaps ($E_g$) of the semiconductors can be calculated from the absorbance data according to Eq. (1):

$$\alpha h\nu = A(h\nu - E_g)^n$$

(1)

where $\alpha$, $h$, $\nu$, and $A$ are the absorption coefficient, the Planck constant, the light frequency, and a constant, respectively, and $n = 0.5$ for the allowed direct transition. From the intersection of the tangent line of the curve, extrapolated to the $h\nu$-axis intercept, the band gaps of Bi$_2$O$_3$, WO$_3$, and Bi$_2$O$_3$/WO$_3$ composites were estimated to be 2.83, 2.78, and 2.42 eV, respectively (the inset in Fig. 2(c)). As compared with those of single components, the decreased band gap of the Bi$_2$O$_3$/WO$_3$ composite may be attributed to the formation of defects and impurity energy levels within the forbidden band gap [33].

In order to further investigate the surface chemical compositions and chemical states, the XPS studies were carried out for the obtained samples. As shown in Fig. 2(d), two oxidation states of W$^{6+}$ and W$^{5+}$ exist in the WO$_3$ and Bi$_2$O$_3$/WO$_3$ samples. The dominant chemical state of W is W$^{6+}$ in the samples, which displays the highest binding energy peak [34]. The existence of W$^{5+}$ atom proves that there are considerable amounts of defects in the crystal structure of WO$_3$. Figure 2(e) exhibits that both Bi$_2$O$_3$ and Bi$_2$O$_3$/WO$_3$ composites have the same peaks at 158.8 and 164.2 eV, which can correspond to the Bi 4f$_{5/2}$ and 4f$_{7/2}$ spectra of Bi$^{3+}$.

![Fig. 2](image-url) (a) XRD patterns, (b) Raman spectra, and (c) UV–Vis absorbance spectra of Bi$_2$O$_3$, WO$_3$, and 0.4-Bi$_2$O$_3$/WO$_3$. The inset in (c) shows the calculated band gap values. High-resolution XPS spectra showing (d) W 4f and (e) Bi 4f of WO$_3$ and 0.4-Bi$_2$O$_3$/WO$_3$, and (f) O 1s of Bi$_2$O$_3$, WO$_3$, and 0.4-Bi$_2$O$_3$/WO$_3$.

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respectively [35]. In the O 1s spectra (Fig. 2(f)), the binding energies of 530.68, 530.28, and 532.38 eV are attributed to the W–O bond, Bi–O bond, and lattice oxygen, respectively. As compared with those of Bi$_2$O$_3$ and WO$_3$, obvious shifts of the XPS spectra are observed for the Bi$_2$O$_3$/WO$_3$ composite, reflecting a change in the local environment and electronic properties of surface atoms caused by the heterojunction. This result further demonstrates the co-existence of WO$_3$ and Bi$_2$O$_3$ in the composite, which is in agreement with the SEM (Fig. 1), XRD (Fig. 2(a)), and Raman (Fig. 2(b)) results.

For semiconductor materials, when the electrons or defects of the transitions migrate to a higher energy level, and then return to the ground state after illumination excitation, they will emit certain characteristic spectra. Therefore, the PL is an effective means to study the defects of semiconductors [36]. Figure 3(a) shows that all the obtained samples present luminescence in both the ultraviolet and the visible regions, which may be caused by the photoexcited electron–hole pairs or intrinsic defects. Figures 3(b)–3(d) show the defect-related luminescence of the PL spectra obtained by Gaussian fitting for the WO$_3$, Bi$_2$O$_3$, and Bi$_2$O$_3$/WO$_3$ samples. As is well known, near-band-edge (NBE) emission in the ultraviolet region is caused by the inter-band transitions and exciton recombination, while deep level (DL) emission in the visible region is caused by a shift in the subcenter of the laser in the deep energy level. The DL is associated with the defects such as oxygen vacancies and interstitial particles, whose intensity is proportional to defect density. Therefore, the higher ratio ($I_{DL}/I_{NBE}$) of DL emission to NBE emission means a higher relative content of defects in the sample. For WO$_3$ and Bi$_2$O$_3$, the relative PL ratios of $I_{DL}/I_{NBE}$ were calculated to be about 18.6 and 13.1, respectively. For the Bi$_2$O$_3$/WO$_3$ samples, there is no NBE emission lower than 400 nm, showing that more defects are present in the Bi$_2$O$_3$/WO$_3$ structure, and more electrons can participate in the redox reaction with the adsorbed oxygen.

The resistance and response of the semiconductor gas sensors are strongly dependent on the operating temperature, which provides heat energy to overcome the activation barriers of chemical adsorption and the reaction between the target gases and the sensor surface. Figure 4(a) shows the temperature-dependent responses of the gas sensors to 50 ppm TEA with the operating temperature ranging from 95 to 200 °C. For the 0.4-Bi$_2$O$_3$/WO$_3$ sensor, the response rapidly increases from 2.1 to 9.2 upon increasing the operating temperature from 95 to 140 °C. However, its values gradually decrease with the further increase in the operating temperature. Hereinafter, 140 °C is selected as the

![Figure 3](https://example.com/fig3.png)

**Fig. 3** (a) PL spectra of Bi$_2$O$_3$, WO$_3$, and Bi$_2$O$_3$/WO$_3$. The inset shows the ratio of $I_{DL}/I_{NBE}$. Gaussian fittings of (b) Bi$_2$O$_3$, (c) O$_2$, and (d) Bi$_2$O$_3$/WO$_3$. The insets show the areal ratios of sub-peaks.
optimum operating temperature for the gas-sensing tests. As compared with the pure WO$_3$ sensor, whose peak response is 4.3 at 170 °C, the sensor based on the 0.4-Bi$_2$O$_3$/WO$_3$ composite exhibits a much higher response (2.1-fold) to the TEA at a lower operating temperature (30 °C-decrement), revealing the advantage of the Bi$_2$O$_3$/WO$_3$ composite in TEA detection. Herein, the performances of recent TEA sensors based on various metal oxides are compared [37–46], as summarized in Table 1. There is no doubt that the Bi$_2$O$_3$/WO$_3$ sensor possesses the ideal gas-sensing characteristics, including high response and low power consumption. Furthermore, the resistance variations of the 0.4-Bi$_2$O$_3$/WO$_3$ sensor towards 50 ppm TEA were measured under different operating temperatures, as shown in Fig. 4(b). The sensor resistance gradually decreases with the increase in the temperature, mainly because the quantity and mobility of the carriers are influenced by the temperature.

For a clear comparison, the dynamic response curves of all the sensors at 140 °C towards 50 ppm TEA are shown in Fig. S7 in the ESM, and the response characteristics of all the sensors are summarized in

![Fig. 4](image)

(a) Response of sensors to 50 ppm TEA under different operating temperatures. (b) Variations in resistance value of 0.4-Bi$_2$O$_3$/WO$_3$ sensor as a function of time towards 50 ppm TEA at 140 °C. (c) Response value, response time, and recovery time and (d) corresponding transient plots as a function of Bi$_2$O$_3$ contents.

**Table 1  Comparison of TEA sensors based on various metal oxides**

| Sensing material                  | Operating temperature (°C) | Concentration (ppm) | $R_0/R_g$ | Response/recovery time (s) | Ref. |
|-----------------------------------|----------------------------|---------------------|-----------|-----------------------------|------|
| Porous CuO                        | 230                        | 100                 | 7.7       | 21/150                      | [37] |
| Hierarchical NiCo$_2$O$_4$        | 300                        | 50                  | 1.35      | 49/54                       | [38] |
| (Cu,Zn)Fe$_2$O$_4$                | 160                        | 50                  | 6.77      | 58/136                      | [39] |
| Co$_3$O$_4$@MnO$_2$               | 250                        | 50                  | 5         | 93/92                       | [40] |
| CuCrO$_2$ nanoparticles           | 140                        | 100                 | 5.2       | 90/120                      | [41] |
| Al$_2$O$_3$/α-Fe$_2$O$_3$         | 250                        | 50                  | 10.6      | 1/17                        | [42] |
| Hollow CuO                        | 260                        | 100                 | 4         | 21/25                       | [43] |
| Hierarchical Co$_3$O$_4$/WO$_3$   | 300                        | 1                   | 2.6       | 13/152                      | [44] |
| Hierarchical NiO/g-C$_3$N$_4$     | 280                        | 500                 | 20.36     | 157/350                     | [45] |
| UV-activated ZnO–SnO$_2$          | 220                        | 100                 | 9.9       | 1.9/58                      | [46] |
| Hierarchical WO$_3$               | 170                        | 50                  | 4.3       | 151/194                     | This work |
| Hierarchical Bi$_2$O$_3$/WO$_3$   | 140                        | 50                  | 9.2       | 89/162                      | This work |
Figs. 4(c) and 4(d). The 0.2-Bi2O3/WO3 and 0.4-Bi2O3/WO3 sensors exhibit baseline resistance of 2.02 and 3.05 MΩ, respectively, which are lower than that of pristine WO3 (4.51 MΩ). Herein, the reduced resistance may be attributed to the band bending caused by the formation of the heterojunction between Bi2O3 and WO3. The electrons from the conduction band of WO3 are captured by the oxygen molecules adsorbed on the surface of WO3 to form the chemically adsorbed oxygen and an electron depletion layer. The electron depletion layer will decrease the carrier concentration, increasing the baseline resistance of WO3. Moreover, the electron transfer between the heterojunctions is accelerated, facilitating the reaction between the gas species and the gas-sensing materials, thus delivering a fast response and recovery of the sensor. During desorption, the baseline resistance returns to the initial values, indicating that the chemical reaction between the Bi2O3/WO3 composite and the TEA is highly reversible. The above phenomenon was also demonstrated by the extended long-term stability and reproducibility tests, as well as the transient plots to different concentrations of the TEA. The resistance value of the composite is gradually decreased as the molar ratio of Bi2O3 increases, mainly because Bi2O3 provides a larger band gap, reducing the number of the electrons in the conduction band of the Bi2O3/WO3 composite. The Bi2O3/WO3 sensor exhibits no response at higher temperatures, which may be attributed to a combined effect of the instability of the TEA molecules to adsorb on the sensing materials and repulsion of these molecules with previously adsorbed oxygen molecules.

In practical applications, both the response value and response/recovery time are crucial parameters. In light of this, transient plots of the gas sensors based on the pure WO3 and 0.4-Bi2O3/WO3 composites were further studied at the optimal working temperature. As shown in Fig. 5(a), the response time of the 0.4-Bi2O3/WO3 composite is shortened from 151 to 89 s, and the recovery time is shortened from 194 to 162 s. When the 0.4-Bi2O3/WO3 composite is exposed to the TEA, the rise in the response implies that the materials exhibit the characteristics of an n-type semiconductor. When exposed to dry air, the response gradually decreases and eventually recovers to the initial value, indicating that the sensor response is stable. Furthermore, we evaluated the selectivity of the sensors based on the WO3, Bi2O3, and Bi2O3/WO3 composites towards 50 ppm of the interfering molecules including methanol (CH3OH), ethanol (C2H5OH), acetone (C3H6O), isopropanol (C3H7OH), toluene (C7H8), ammonia (NH3), and TEA (C6H15N). As shown in Fig. 5(b), all the 0.2-Bi2O3/WO3, 0.4-Bi2O3/WO3, and 0.6-Bi2O3/WO3 sensors exhibit good selectivity. Especially, the response of the 0.4-Bi2O3/WO3 sensor reaches about 9.2 towards the TEA while only 1–3.5 towards other gases. Herein, the high response and good selectivity of the composite sensor to the TEA is mainly attributed to the following two aspects: (1) the intrinsic acidic feature of WO3, which is beneficial for the adsorption of the TEA molecule with N atom served as the Lewis basic site; (2) the formation of the heterojunction between Bi2O3 and WO3, which promotes the charge transfer. As reported, the bond energy of O–H (methanol, ethanol), C=O (acetone), C=C (toluene), N–H (ammonia), and C–N (TEA) is 459, 799, 345, 610, 392, and 307 kJ/mol [47], respectively. The lower C–N bond energy facilitates the reaction activity of the TEA molecules among the above gases. As compared with other VOCs, the TEA molecule more easily loses the electron, and its N atom serves as the Lewis basic site, which is easily absorbed on the surface of acidic WO3 [9].

In order to intuitively highlight the advantages of each sensor in different aspects and obtain the balance between the superior and the optimal working conditions, the performance parameters of S, Q, 1/T, 1/τre, and 1/τrc are multidimensionally compared in a wind rose diagram, as shown in Fig. 5(c). It is visible that the area of 0.4-Bi2O3/WO3 is larger than the area of others, confirming that the optimal 0.4-Bi2O3/WO3 sensor possesses a more balanced sensing performance for the TEA detection. Figure 5(d) illustrates the transient responses of the WO3 and Bi2O3/WO3 sensors upon exposure to various concentrations of the TEA at 140 °C. With the increase in the TEA concentration, the response of the 0.4-Bi2O3/WO3 sensor increases quickly from 2.8 at 0.5 ppm to 10.3 at 100 ppm. Meanwhile, the response can rapidly restore to its original baseline after the TEA is released. This result manifests that the 0.4-Bi2O3/WO3 sensor is reproducible and has widely detection range from 0.5 to 100 ppm. The linear relationship between the sensor response and the gas concentration implies the advantage of the sensor in detecting low concentrations of the TEA (Fig. 5(e)). The detection limit (Dl) of the sensor can be extrapolated from the linear regime of the response values, which should be distinguishably differentiated.
Fig. 5 (a) Dynamic response–recovery curves for WO₃ and Bi₂O₃/WO₃ sensor to 50 ppm TEA. (b) Sensor responses towards 50 ppm of various target gases at 140 °C. (c) Wind rose of response (S), selectivity (Q), and reciprocals of optimum operating temperature (1/T), response rate (1/τₑ), and recovery rate (1/τᵣₑ) for evaluating parameters of Bi₂O₃, WO₃, and Bi₂O₃/WO₃ sensors. (d) Transient plots of pure WO₃ and Bi₂O₃/WO₃ sensors to ppm-level TEA. (e) Relationship between sensor response and TEA concentration. The inset shows the corresponding dilogarithm curve. (f) Changes in response and recovery time for Bi₂O₃/WO₃ sensor along with TEA concentration.

from the background level. When the criterion for gas detection was set to $R_0/R_g > 1.5$, the theoretical $D_L$ of the 0.4-Bi₂O₃/WO₃ sensor was calculated to be 32 ppb, suggesting that the composite materials have the advantage for detecting the low-concentration TEA. With the increase of the TEA concentration, the response and recovery time basically presents a downward trend at the initial stage and remained unchanged thereafter (Fig. 5(f)), which may be the result of the nonuniform gas concentration after injection at the initial stage.

It is generally known that the gas-sensing performance of the semiconductor materials is critically influenced by relative humidity (RH). Herein, the humidity-dependent experiments of the Bi₂O₃/WO₃ sensor to 50 ppm TEA were conducted under different RHs in the range of 11%–97% RH (Fig. S8 in the ESM). As summarized in Fig. 6(a), the sensor response slightly declines about 11% along with the increase of the RH from 11% to 97%, which is apparently smaller than those reported in Refs. [15,30,38,42]. In addition, the anti-interference performance of the Bi₂O₃/WO₃ sensor was tested under three mixed gases of isopropanol, triethanolamine, and TEA (I—10 ppm: 10 ppm; II—20 ppm: 20 ppm; and III—50 ppm: 50 ppm). As shown in Fig. 6(b), the sensor response decreases negligibly in the presence of the interfering molecules (triethanolamine and isopropanol), demonstrating the superiority of the Bi₂O₃/WO₃ sensor in the mixed gas detection. The long-term stability and reproducibility were also measured to evaluate the sensor performance, as shown in Figs. 6(c) and 6(d), respectively. No obvious variations in the response are observed during the test period of nearly 30 d and after running for 10 cycles, suggesting excellent stability and reproducibility of the Bi₂O₃/WO₃ gas sensor.

The synergistic effect between WO₃ and Bi₂O₃ plays a crucial role in improving the performance of the Bi₂O₃/WO₃ sensor. Firstly, the conductivity change of the composite upon the oxygen adsorption and gas reaction is believed to be a primary reason for the gas-sensing behavior. The band gaps of WO₃ and Bi₂O₃ are 2.78 and 2.83 eV, respectively. When they are in contact with each other, free electrons will flow from Bi₂O₃ to WO₃ to equate the Fermi levels, creating an electron depletion layer and an electron accumulation layer on the Bi₂O₃ side and WO₃ side, respectively (Fig. 7). When the sensor is exposed to an air atmosphere, the oxygen molecules are easily adsorbed on the surface.
Fig. 6 (a) Response values of Bi$_2$O$_3$/WO$_3$ sensor to 50 ppm TEA under various RHs. (b) Response curves of Bi$_2$O$_3$/WO$_3$ sensor to mixed gas of isopropanol, triethanolamine, and TEA. Mixed gas I—isopropanol : triethanolamine : TEA = 10 ppm : 10 ppm : 10 ppm; mixed gas II—isopropanol : triethanolamine : TEA = 20 ppm : 20 ppm : 20 ppm; mixed gas III—isopropanol : triethanolamine : TEA = 50 ppm : 50 ppm : 50 ppm. (c) Long-term stability and (d) reproducibility of Bi$_2$O$_3$/WO$_3$ sensor to 50 ppm TEA.

Fig. 7 Energy-band diagrams and depletion layer changes of sensor based on Bi$_2$O$_3$/WO$_3$ composite when exposed to air and TEA. Note: $E_c$, $E_F$, and $E_v$ represent the energies at conduction band, Fermi level, and valence band, respectively.

of the Bi$_2$O$_3$/WO$_3$ composite to generate the oxygen-ion species (predominantly exist in the form of O$^-$), which increases the thickness of the depletion layer. Upon exposure to the TEA gas at 140 °C, the trapped electrons are released to the composite by the reaction between the TEA molecules and chemisorbed oxygen species ($C_6H_{15}N + O^- \rightarrow CO_2 + N_2 + H_2O + e^-$), which decreases the electron depletion layer and results in a sharp decline in the resistance as observed. Secondly, the reactive sites are relatively increased by
the defects in the composite (Fig. 3), which accelerates the electron transfer and uplifts band bending for the electrons to pass through the electron depletion layer. Additionally, the rational design of a hierarchical structure guarantees abundant channels for the gas adsorption and desorption. The as-formed slit-like pores efficiently increase the contact region, facilitate the gas molecules to diffuse and interact with the composite, and thus advance the sensor performance.

4 Conclusions

In summary, the advanced Bi$_2$O$_3$/WO$_3$ composite has been successfully synthesized through a combination of the hydrothermal–ultrasonic procedure followed by the thermal treatment. Owing to the formation of the heterojunctions, the composite possesses decreased band gap and increased defect content, which is confirmed by the UV–Vis and PL analysis, respectively. Benefiting from the abundant slit-like pores, desirable defect features, and amplification effect of the heterojunctions between WO$_3$ and Bi$_2$O$_3$, the composite sensor shows a distinctive response of 0.5–2.8 ppm TEA, which meets up with the threshold value of toxic TEA concentration established by the OSHA. As compared with pristine WO$_3$ sensor, the composite sensor demonstrates faster response/recovery time (1.7-fold/1.2-fold), higher response (2.1-fold), and lower power consumption (30 °C decrement). In addition, the composite sensor exhibits the long-term stability, reproducibility, and negligible response towards the interfering molecules, indicating the promising potential of the Bi$_2$O$_3$/WO$_3$ heterojunction in real applications. The novel design of the Bi$_2$O$_3$/WO$_3$ composite in this work shows great promise for rationally designing the advanced semiconductor gas sensors by utilizing the interfacial energy barriers of the hierarchical metal oxides.

Author contributions

Mingxin Zhang: investigation, data curation, visualization, formal analysis, writing original draft, and writing—review & editing. Kai Liu: investigation, validation, and writing-review & editing. Xingmin Zhang: data curation. Bingbing Wang: resources and writing—review & editing. Xinru Xu: investigation. Xinxin Du: resources and investigation. Chao Yang: methodology and writing—review & editing. Kewei Zhang: conceptualization, methodology, resources, writing—review & editing, supervision, and funding acquisition.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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