



Article

Enhanced NO₂ Sensing Performance of ZnO-SnO₂ Heterojunction Derived from Metal-Organic Frameworks

Xiaowei Ren, Ze Xu , Zhongtai Zhang and Zilong Tang *

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

* Correspondence: tzl@tsinghua.edu.cn

Abstract: Nitrogen dioxide (NO₂) is the major reason for acid rain and respiratory illness in humans. Therefore, rapid, portable, and effective detection of NO₂ is essential. Herein, a novel and simple method to construct a ZnO-SnO₂ heterojunction is fabricated by pyrolysis of bimetallic metal organic frameworks. The sensitivity of ZnO-SnO₂ heterojunction towards 0.2 ppm NO₂ under 180 °C is 37, which is 3 times that of pure ZnO and SnO₂. The construction of heterojunction speeds up the response-recovery process, and this kind of material exhibits lower detection limit. The construction of heterojunction can significantly improve the NO₂ sensitivity. The selectivity, stability, and moisture resistance of ZnO-SnO₂ heterojunction are carried out. This could enable the realization of highly selective and sensitive portable detection of NO₂.

Keywords: NO₂ gas sensor; ZnO; SnO₂; heterojunction; MOFs derivatives



Citation: Ren, X.; Xu, Z.; Zhang, Z.; Tang, Z. Enhanced NO₂ Sensing Performance of ZnO-SnO₂ Heterojunction Derived from Metal-Organic Frameworks. *Nanomaterials* **2022**, *12*, 3726. <https://doi.org/10.3390/nano12213726>

Academic Editor: Sergei Kulinich

Received: 29 September 2022

Accepted: 17 October 2022

Published: 23 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Air pollution is one of the greatest threaten to environment and human health. Outdoor air pollution produced by human activities, including road traffic, industrial emission and residential heating [1]. Exposure to NO₂ increased the risk of laryngo-tracheo-bronchitis related disease, mostly due to influenza viral infections [2]. According to WHO Global air quality guidelines [3], the thresholds of several major air pollutants are defined, among which, the guideline value of NO₂ is 25 µg/m³ (at standard atmospheric pressure, 20 °C, 25 µg/m³ ≈ 13 ppb). Up to now, it is still a major challenge to achieve rapid detection to ppb level NO₂. Therefore, the development of NO₂ gas sensors that can respond quickly to low concentrations is of great scientific significance and application value.

At present, much research is focused on enhancing the sensitivity and reducing the detection limit, including microstructure design to improve specific surface area, defect regulation to enhance adsorption performance, facet control to increase effective adsorption sites, loading precious metals and constructing heterostructure to promote sensitivity [4–9]. Among these modification methods, combining two sensitive metal oxides to construct n-n or n-p heterojunction has been proved to be an effective way to enhance the sensitivity, due to the abundant sensitive candidate components to choose from [10]. Many methods are reported to synthesize metal oxides heterojunction [6,11], the pyrolysis of bimetallic metal organic frameworks (MOFs) precursors to obtain metal oxides composite structure has recently been regarded as an effective method [12]. MOFs are known as porous coordination polymers, constructed by metal-based nodes bridged with organic ligand [13]. Recently, much research has focused on the preparation of porous nanomaterials by using MOF as self-sacrificing template [14–17]. Woo et al. [18] developed ZnO/CNTF composites by calcination of ZIF-8/CNTF; the fabricated gas sensor exhibited improved NO₂ sensitivity (1.086 towards 20 ppm NO₂ at 100 °C). Deng et al. [19] obtained laminar SnO₂ by pyrolysis of Sn-MOF@SnO₂, as synthesized sensors exhibited excellent formaldehyde sensing properties (10,000 to 10 ppm formaldehyde at 120 °C). Existing research results

have indicated that MOF-derivatives exhibits high specific surface area and connected channel, which can improve gas accessibility and increase active sites. In the field of sensing, extensive work has proved that mixed-MOF exhibit better performance than single metal node MOFs due to the synergetic effect of diverse valence metals [20,21]. It is well known that ZnO and SnO₂ are considered as two typical gas sensitive materials with excellent properties [22,23]. Although plenty of research works have considered bimetallic MOFs derivations, there has been research on those containing tin oxides. Therefore, the construction of ZnO-SnO₂ heterojunction derived from bimetallic MOFs is expected to improve the gas sensing performance.

Herein, we report a simple strategy to obtain metal oxides heterojunction. At first, the Zn/Sn-bimetallic MOFs are directly synthesized by one-pot methods, and the ZnO-SnO₂ heterojunction is obtained by thermal decomposition subsequently. The as-prepared ZnO-SnO₂ composites derived from bimetallic MOFs exhibits excellent sensitivity to ppb-level NO₂. This study provides a new perspective for the design of metal oxides heterojunction.

2. Experimental

2.1. Synthesis of Zn/Sn Bimetallic MOF

Two Zn/Sn bimetallic MOFs with different Zn/Sn ratio were synthesized. At first, 1.2 g Zinc nitrate ($\geq 99\%$, Zn(NO₃)₂•6H₂O, Beijing Modern Oriental Fine Chemistry Co., Ltd., Beijing, China) was dissolved in 40 mL N, N-Dimethylformamide ($\geq 99.5\%$, DMF, HCON(CH₃)₂, Shanghai Titan Scientific Co., Ltd., Shanghai, China). Then Terephthalic Acid (99%, C₈H₆O₄, Shanghai Titan Scientific Co., Ltd., Shanghai, China) with different weight (1 g, 1.334 g) was added to above solution. Tin (II) chloride ($\geq 99\%$, SnCl₂, Shanghai Macklin Biochemical Technology Co., Ltd., Shanghai, China) with different molar ratio to Zinc was added to above solution (2 mM, 4 mM). 1.2 mL Triethylamine (99%, C₆H₁₅N, Shanghai Titan Scientific Co., Ltd., Shanghai, China) was dropped into the solution after 20 min stirring. Precipitate immediately began to appear in the solution. After 40 min stirring, the products were separated by centrifuged with DMF. Finally, the Zn/Sn(II)-MOF was dried in vacuum oven at 80 °C for 16 h.

2.2. Synthesis of Zn-BDC MOF and Sn-BDC MOF

For comparison, the pure Zn-MOF and Sn-MOF were also synthesized by above steps. For Zn-MOF, 1.2 g Zinc nitrate and 0.667 g Terephthalic Acid were added. For Sn-MOF, 0.76 g SnCl₂ and 0.667 g Terephthalic Acid were added. The other steps were the same as above.

2.3. Synthesis of ZnO-SnO₂ Metal Oxides

The two metal oxides were obtained by thermal decomposition of Zn/Sn(II)-MOF. A suitable amount of the precursor was pyrolysis in air at 800 °C for 2 h at a heating rate of 5 °C/min. The final products with good crystallinity were obtained.

2.4. Preparation of Gas Sensor and Sensing Measurements

A volume of 100 μ L methanol was added to the 25 mg sample and the suspension was mixed evenly by ultrasonic for 1 h. Then, the sensing slurry was drop-coated on the Au interdigital electrodes with a spacing of 0.2 mm. After that, the interdigital electrodes were dried at 60 °C overnight.

Gas sensing measurement was carried out in a computer-controlled evaluation system. The interdigital electrode is placed on the heating table in the test chamber (~ 0.02 L), and the heating table has heating and temperature detection device. The real time dynamic resistance of the fabricated sensors was recorded by a digital multimeter (Agilent 34465A). The dry testing gases involved in this research (10 ppm NO₂, 1000 ppm H₂S, 100 ppm NH₃, 500 ppm CO, 200 ppm C₂H₅OH, all balanced by N₂) were purchased from Beijing AP BAIF Gases Industry Co., Ltd., Beijing, China. The concentration of target gas was controlled by regulating the flow rates of each gas by mass flow controllers (MFC, Beijing Qixing

Co., Ltd., Beijing, China), and total flow rate was settled at 200 mL/min. Specifically, the 10 ppm NO₂ with flow rate of 2 mL/min diluted by 156 mL/min dry N₂ and 42 mL/min dry O₂ was injected to the chamber to obtain the desired concentration of 0.1 ppm NO₂. The gas response was defined as R_g/R_a for oxidizing gas and R_a/R_g for reducing gas, where R_g is the resistance in target gas and R_a is the resistance in air. Humidity tests were measured by passing the flow gas through a quartz flask filled with saturated solutions of K₂CO₃ and pure deionized water to attain the relative humidity (RH) levels of 43% ± 2% and 90% ± 2%, a humidity sensor probe was installed at the outlet of the quartz flask, more testing details described in the Supplementary Materials. Except for the humidity test, other gas performance tests were carried out under dry conditions.

2.5. Characterization

Crystal structure of the samples are recorded by powder X-ray diffraction (XRD, Cu K α , Rigaku D/max-V2500, Rigaku Co., Ltd., Tokyo, Japan). The microstructure and morphology were obtained by using a scanning electron microscope (SEM, Carl Zeiss, Oberkochen, Germany) and transmission electron microscope (TEM, JEOL JEM-2100F, Tokyo, Japan). The elemental valence and surface electronic structure of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, Waltham, MA, USA). The adsorption characteristic was obtained by UV-vis-NIR (Lambda 950, Perkin-Elmer, Waltham, MA, USA) spectrophotometer. Raman spectra were measured by LabRAM HR800 Raman spectrometer under the excitation of 633 nm laser. N₂ adsorption/desorption isotherms at 77 K were carried out by using an American Contador QuadraSorb SI-MP instrument and the specific surface area was calculated from N₂ desorption isotherms by using the Brunauer-Emmett-Teller (BET) method.

3. Results and Discussion

3.1. Material Characterization

The formation of metal oxide heterojunction is illustrated in Figure 1. For simplicity, the samples were abbreviated to S1, S2, S3, and S4, where S1 stands for the metal oxides derived from Zn-MOF, S4 is the derivation of Sn-MOF, S2 and S3 are derivations of Zn/Sn bimetallic MOF with different ratio of Zn to Sn. The structure of the precursors is characterized by XRD, as shown in Figure S1. The diffraction peaks of pure Zn-MOF and Sn-MOF are similar with previous literature [24,25]. The Zn/Sn bimetallic MOF exhibits unique diffraction pattern from Zn-MOF and Sn-MOF, which demonstrated that the bimetallic MOF are not simply mechanically mixed in the material, but have some different arrangements [26]. The contents of zinc element and tin element of sample S2 and S3 are also determined by EDS, as shown in Tables S1 and S2, indicating that sample S2 and S3 are composites of ZnO and SnO₂, and the ratio of Zn to Sn is approximately 1:0.3 and 1:2, respectively.

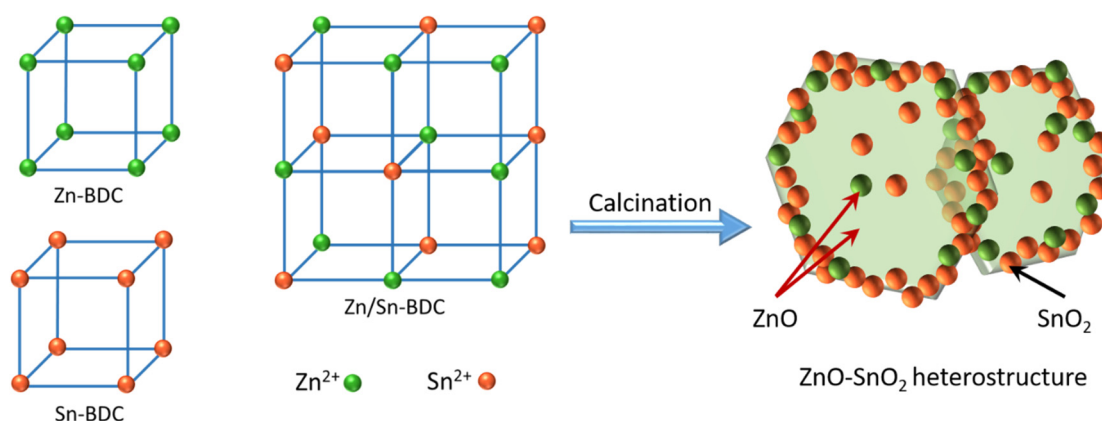


Figure 1. Schematic diagram of heterogeneous bonding of bimetallic oxides.

The X-ray diffraction results of the samples are shown in Figure 2a. The main diffraction peaks of the sample without tin element are well indexed with ZnO (PDF# 99-0111) of wurtzite structure. With the addition of tin element, the diffraction of SnO₂ (PDF# 77-0452) appears in sample S2 and S3. The diffraction peak of sample S4 matches well with the characteristic of SnO₂. The diffraction peaks of all samples match the characteristic peaks contained in either or both ZnO and SnO₂, and no other peaks were observed. Figure 2b exhibits the heterojunction of ZnO-SnO₂ composites. The fringe spacing of grains on both sides of the interface is obviously different. The fringe spacing of the left grain is 2.8 Å, which can only correspond to the (100) plane of ZnO. The fringe spacing of the right grain is 3.4 Å, which can only match with the (110) plane of SnO₂. The well contact of two grains with different composition confirms the existence of heterogeneous structure. Figure 2d is an enlarged image of the red selection in Figure 2c. Nanoparticles grow on the surface of hexagonal nanosheets, the clear lattice interplanar distance of nanoparticles is 3.4 Å, assigned to the (110) plane of tetragonal SnO₂. The hexagonal nanosheets with the lattice fringe of 2.8 Å are consistent with (100) planes of wurtzite ZnO. From the selected area electron diffraction (SAED) pattern in Figure 2e, diffraction rings with (101) and (100) planes of ZnO and (110) and (101) planes of SnO₂ can be observed.

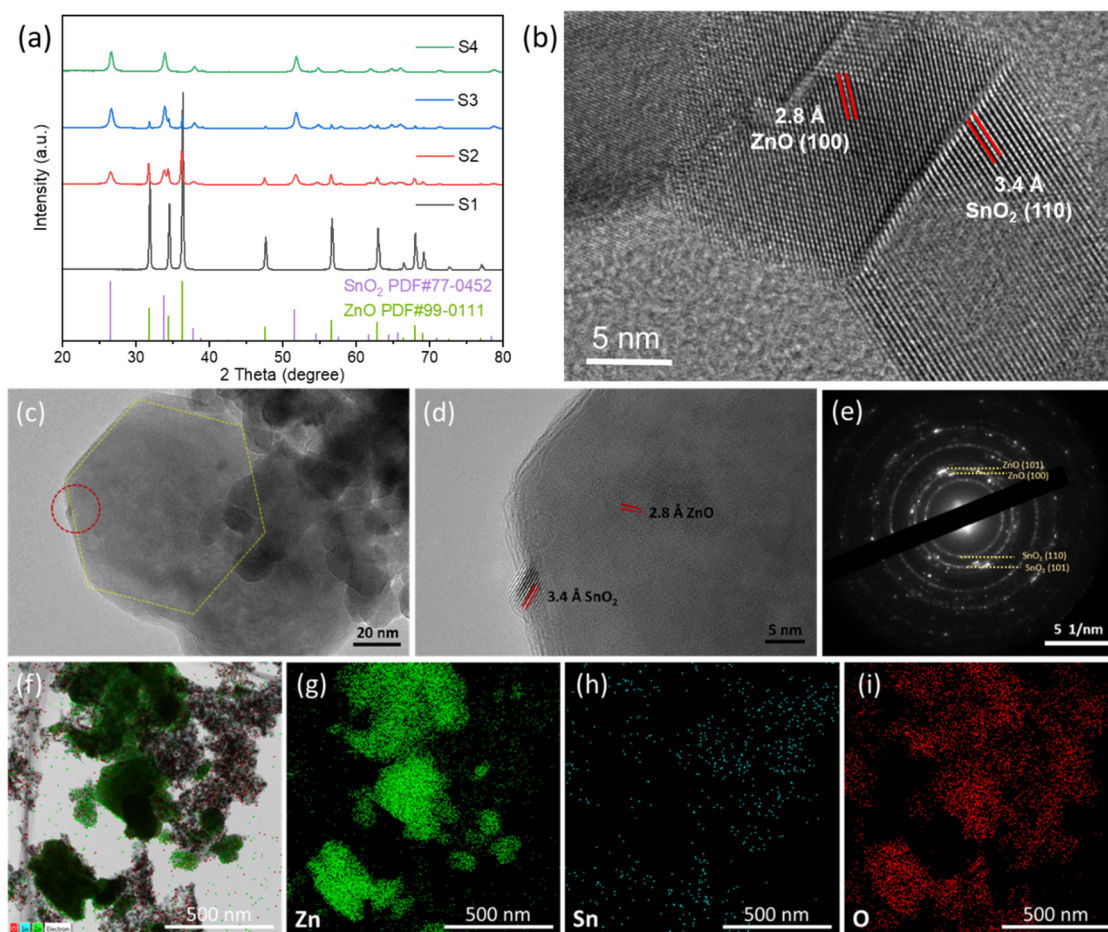


Figure 2. (a) XRD patterns of Zn-Sn bimetallic derivatives. (b–d) HRTEM, (e) SAED images of S2. (f–i) TEM image of S2 and corresponding elemental mapping for Zn, Sn and O elements.

The element distribution of sample S2 can be concluded by EDS map in Figure 2f–i. In agreement with the previous results of XRD and HRTEM, the region with hexagonal sheet structure is dominated by ZnO, small particles attached to the hexagon are ZnO and SnO₂. The results of EDS are in good agreement with XRD results. During the heat treatment, bimetallic MOFs begin to fall apart, and the metal ions are reoriented and

oxidized to two kinds of metal oxides, and the n-n heterojunction structure is eventually formed. TEM and SEM images and corresponding grain size analysis of sample S1–S4 are shown in Figure S2–S5. The mean grain size of S1 is 107 nm. The grain size of sample S2 is heterogeneous, consisting of two grains with different sizes; therefore, the average grain size is calculated according to two different intervals. The mean size of small grain and large grain is 20 nm and 193 nm, respectively. As described above, the large particles in the ZnO-SnO₂ composites are mainly ZnO, and the small particles are mainly SnO₂. The grain size distribution of S3 is similar with S2. In sample S4 (SnO₂), part of large particles condensed into thick sheets after pyrolysis at 800 °C. No clumps of condensation were found in the S2 and S3, indicating that the presence of ZnO inhibits the agglomeration and growth of SnO₂.

X-ray photoelectron spectroscopy is carried out on the sample S1, S2 and S4 to determine the effect of heterojunction on the surface chemical state of Zn, Sn and O. All the peaks are calibrated by C 1s (284.8 eV). The high-resolution spectrum of Zn 2p in sample S1 and S2 exhibited in Figure 3a can be deconvoluted to two characteristic peaks correspond to Zn 2p_{3/2} and Zn 2p_{1/2}, indicating +2 valance of Zn in the samples. Comparing the Zn 2p peaks in S1, the Zn 2p peaks of S2 shift 0.5 eV to low binding energy. The shifts of binding energy could be attributed to the different electronegativity of Zn ions [27], which could be ascribed to the electron transfer between ZnO and SnO₂ in S2. Figure 3b presents the characteristic peaks of Sn 3d_{3/2} and Sn 3d_{5/2} located at 494.8 eV and 486.4 eV, respectively, indicating the +4 valance of Sn. The Sn 3d peaks of S2 shift 0.2 eV to high binding energy compared with S4, which again confirms the electron transfer between ZnO and SnO₂ in S2. As shown in Figure S6b–d, the asymmetric O 1s peak of S1, S2 and S4 can be separated into two peaks, the peak located at 530.2 eV is related to lattice oxygen (O_L), and another located at 531.4–531.6 eV is associated with surface adsorbed oxygen (O_C), including physically-adsorbed, chemisorbed, dissociated, and hydroxy-related oxygen). The latter is usually closely related to the properties of gas-sensitive materials, and the sample S2 has more surface adsorbed oxygen.

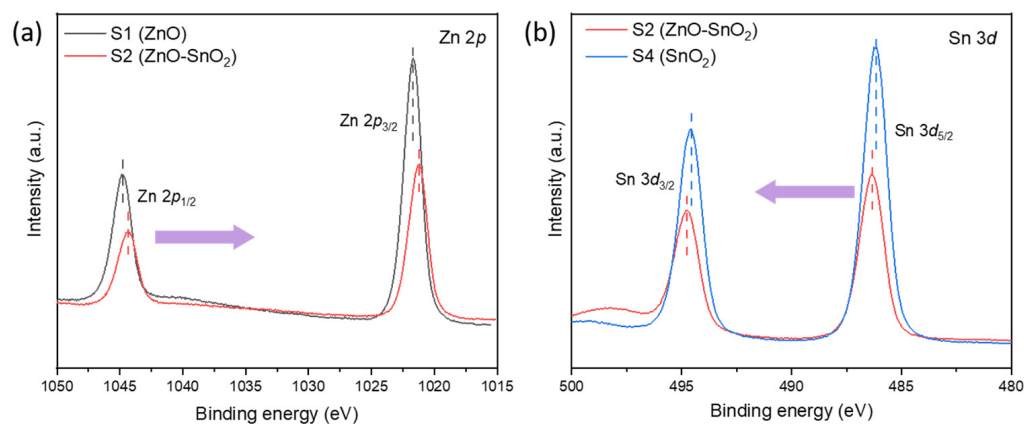


Figure 3. XPS curve of (a) Zn 2p for sample S1 and S2, (b) Sn 3d for sample S2 and S4.

The specific surface area and pore size distribution are critical to gas sensitive materials. The N₂ adsorption/desorption isotherms of sample S1–S4 exhibit in Figure 4a. S2 and S3 exhibit IV type characteristics, demonstrating the mesoporous structure of the material [15]. The BET specific surface area of S1–S4 are 27.03, 29.73, 35.70, 21.92 m²/g, respectively. High specific surface area can expose more active sites, which is conducive to the adsorption of gas molecules.

In order to investigate more detailed structure information, Raman spectroscopy was carried out to characterize the structure information and molecular vibrations of the materials. As shown in Figure 4b, the characteristic peaks of ZnO centered at around 334, 381 and 439 cm^{−1} [28], corresponding to the vibration modes of E₂ (high) – E₂ (low), A_{1T}, and E₂ (high), respectively. The peaks at 635 and 778 cm^{−1} corresponds to A_{1g} and B_{2g}

modes, respectively, which are attributed to the stretching of Sn–O bonds [29]. The main peaks of all samples can correspond to the characteristic peaks of ZnO or SnO₂, which is consistent with previous analysis. Furthermore, the spectrum of Raman mapping was obtained by a 50 × 50 µm area as shown in Figure S7, providing the spatial information of ZnO and SnO₂ phases in micro level.

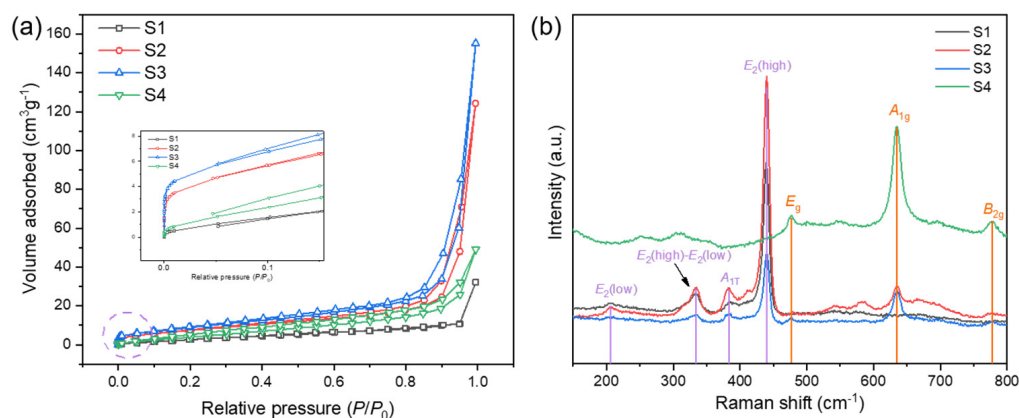


Figure 4. (a) The nitrogen adsorption/desorption isotherm of S1–S4 and the curve at low pressure zone (inset) (b) Raman spectrum of all samples (purple letters represent characteristic peaks of ZnO and orange represents SnO₂).

The variation of optical absorption characteristic and band gap energies of S1, S2, and S4 samples were analyzed by UV–vis diffuse reflectance spectroscopy in the wavelength range 250–800 nm. As shown in Figure 5a, the sample ZnO exhibits an intense adsorption edge around $\lambda < 380$ nm assigned by the intrinsic wide band gap. The absorption edge of SnO₂ is approximately located at 300 nm. Two absorption bands can be observed in S2. The band gap energies of S1, S2 and S4 were determined by Tauc-plot methods [30]. According to previous study, materials involved in this paper are direct band gap [31,32]. The estimated band gaps were 3.19, 3.22, and 3.63 eV for S1, S2 and S4, respectively. The appearance of two absorption bands and the calculated band gap energy of S2 confirmed that the combination of ZnO and SnO₂. Based on the analysis result of TEM, XRD, Raman, XPS and UV–vis, the formation of ZnO–SnO₂ heterojunction was confirmed, which could have a particular influence on the physical and chemical properties of the materials.

3.2. Gas Sensing Properties

For metal oxides semiconductors, the adsorption characteristic of gas on the surface of materials are strongly affected by temperature. Firstly, the sensing performance of all samples was carried out to 0.2 ppm NO₂ at different working temperature, as shown in Figure 6a. The sensitivity firstly increases to optimal value and then decreases with the increase of temperature. NO₂ molecules do not have enough activation energy to react with the adsorbed oxygen species at low temperature. Rising temperature can promote the physical and chemical adsorption of NO₂. The desorption rate accelerates when the temperature rises to a certain extent, leading to the decrease of response value. The resistance was too large to measure for sample S3 contacted with NO₂ at 160 °C. Although S3 sample has the highest response value at 180 °C, the excessive resistance is not conducive to practical application, hence, sample S2 is selected as the research object. Compared with pure ZnO (S1) or SnO₂ (S4), the samples combined with ZnO and SnO₂ exhibit better NO₂ sensing performance. For sample S2, the NO₂ sensing sensitivity is about 37 at 180 °C, which is 3 times that of ZnO (S1) and SnO₂ (S4). This demonstrating the proper combination of ZnO and SnO₂ can improve the NO₂ sensing performance. Figure 6b illustrates the reproducibility of S2 to 0.2 ppm NO₂ at 180 °C under dry condition, demonstrating the stability and the n-type semiconducting conduction characteristic of the as fabricated gas sensor. Figure 6c exhibits the dynamic resistance curve towards 0.02–5 ppm NO₂ under

180 °C, resistance increases with the increase of NO₂ concentration. The actual response value is 1.21 towards 20 ppb NO₂, which means the gas sensors fabricated in this paper has a very low detection limit, the dynamic resistance towards 20–50 ppb NO₂ was shown in Figure S8. The fabricated gas sensor exhibits a significant response to ppb-level NO₂. The relationship of response value and NO₂ concentration are exhibited in Figure S9, blue line is the fitting curve, and there are different fitting curves at low concentration and high concentration. Figure 6d presents the baseline resistance as a function of temperature for all samples. With the increase of temperature, the baseline resistance decreases. At 180 °C, baseline resistance (R_a) is ranked from low to high: S1 < S2 < S3 < S4. S4 exhibits the highest resistance, indicating the greatest activation energy is required, and S3 is next. With the increase of Sn content, the activation energy increases. In addition, the baseline resistance also influenced by the grain size and contact interface. The resistance increase in S2 and S3 can be ascribed to the increase of heterogeneous interface. From Figure 6e it can be concluded that the combination of ZnO and SnO₂ greatly improve the NO₂ sensitivity and accelerate the response-recovery time. The response values of S1, S2, S3, and S4 towards 0.1–5 ppm NO₂ at 180 °C are exhibited in Figure 6f. The NO₂ sensitivity of S2 and S3 is much higher than the single component either ZnO or SnO₂.

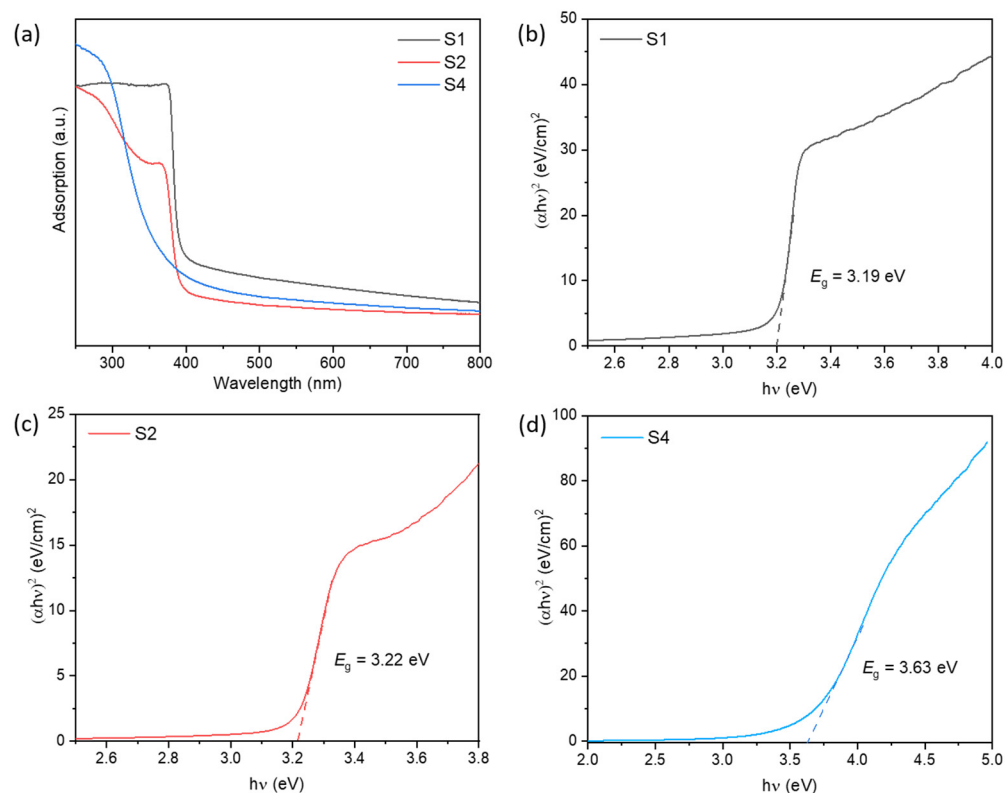


Figure 5. (a) UV-vis diffuse reflectance spectra of S1, S2 and S4. The energy band gap of (b) S1, (c) S2 and (d) S4 calculated by Tauc-plot methods.

Stability is another important index for evaluating gas sensors. Figure 7a illustrates that the fabricated gas sensor exhibits excellent repeatability after several days, even if no degradation can be observed, which may be due to the stability of the microstructure of the materials after high temperature heat treatment. The effect of humidity on the NO₂ sensing response was investigated under 43% RH and 90% RH condition, as shown in Figure 7b. In the presence of water molecules, the sensor presented better response-recovery characteristic. The response value to NO₂ decreased, indicating that water molecules will hinder the adsorption of NO₂ gas molecules.

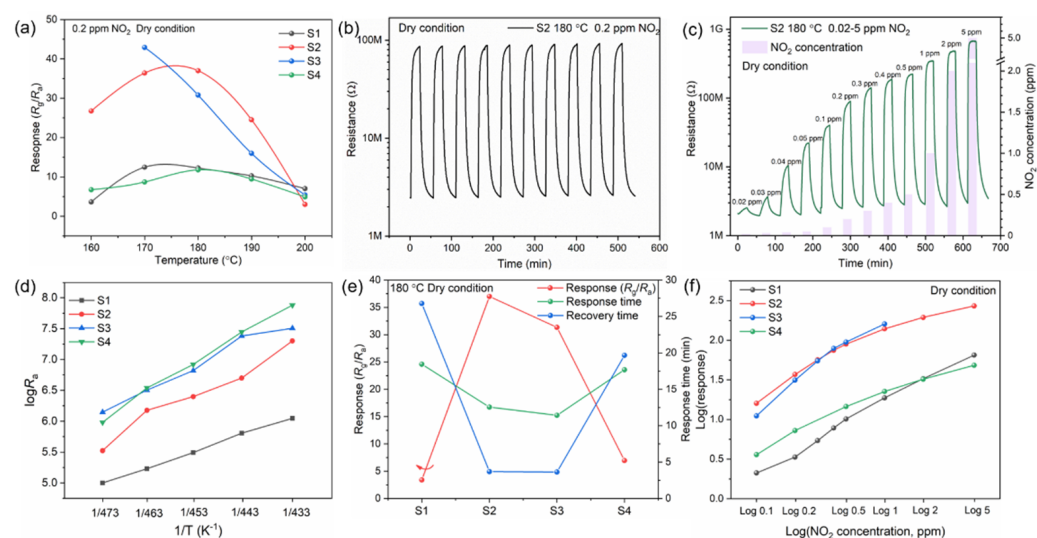


Figure 6. (a) Response value of the sensors towards 0.2 ppm NO₂ at different working temperature. (b) Reproducibility of S2 to 0.2 ppm NO₂ at 180 °C. (c) Dynamic response of S2 to 0.02–5 ppm NO₂ at 180 °C. (d) R_a of the sensors at different operating temperature. (e) Response value and response and recovery time of sample S1, S2, S3 and S4 towards 0.2 ppm NO₂ at 180 °C. (f) Response value of all samples to 0.1–5 ppm NO₂ at 180 °C. (Double logarithmic coordinate axis was used).

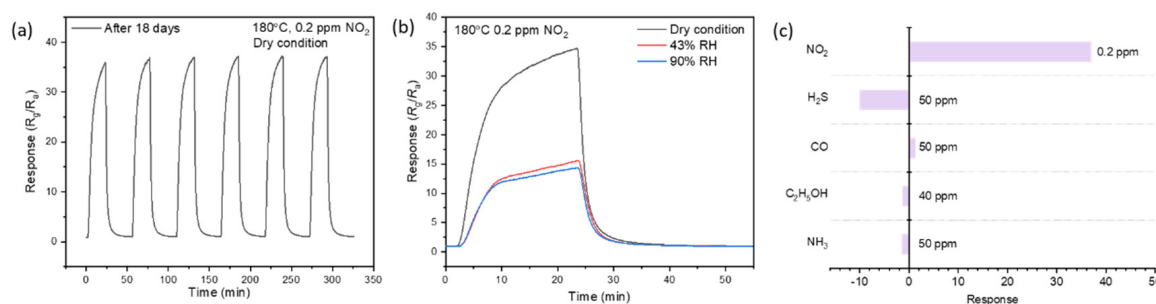


Figure 7. (a) Cyclic response curve of S2 after 18 days. (b) Response curve of S2 to 0.2 ppm NO₂ under dry and humidity condition. (c) The response value of S2 to 0.2 ppm NO₂ and 40–50 ppm other gases at 180 °C under dry condition (Negative values represent p-type responses).

Figure 7c illustrates the sensitivity of fabricated gas sensor towards 0.2 ppm NO₂ and other higher concentration gases (50 ppm H₂S, 50 ppm CO, 40 ppm C₂H₅OH, 50 ppm NH₃) at 180 °C. The selectivity of NO₂ on sensing materials is affected by several reasons, including electron affinity of target gas and the amount of adsorbed gas molecules on the surface of sensing materials under optimal working temperature, as well as surface defect species [33,34]. The mechanism of the selective detection of ZnO-SnO₂ composition to NO₂ over other gases can be summed up to three points. Firstly, the electron affinity of NO₂ molecules is higher than other interfering gases, which means NO₂ is more inclined to grab electrons from the conduction band of material. Secondly, operating temperature also has a significant influence on the selective adsorption of gas. The work temperature in this paper is around 180 °C, which may be suitable for NO₂ adsorption. Thirdly, it has been proved that ZnO and SnO₂ are two typical NO₂ adsorption material, the combination of the two sensitive materials will produce a synergistic effect and enhance the NO₂ sensitive characteristics [35].

To further understand the practicality of the gas sensor fabricated by ZnO-SnO₂ in this study, the NO₂ sensing performance were compared with ZnO-based, SnO₂-based and ZnO-SnO₂ sensors reported recently. As shown in Table 1, sample S2 exhibits relatively sensitive performance towards NO₂.

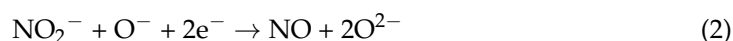
Table 1. NO₂ sensing performance of the materials synthesized in this study and other materials in the reported literature.

Materials	NO ₂ (ppm)	Operating Temperature (°C)	Response (R _g /R _a or R _a /R _g)	Ref.
ZnO nanoneedles	5	195	6	[36]
SnO ₂ -Sn ₃ O ₄ heterostructure	0.2	150	11	[37]
ZnO@rGO	10	RT	6.77	[38]
MXene sphere/ZnO	100	RT	1.72	[39]
Sputtered SnO ₂ /ZnO	5	100	26.4	[40]
ZnO-SnO ₂ hetero-nanowires	0.25	150	17	[41]
ZnO-SnO ₂ composite	1	350	21.5	[42]
ZnO nanorod/SnO ₂ film	50	300	1.37	[43]
SnO ₂ @ZnO	1	150	25	[44]
ZnO-SnO ₂ heterojunction	0.2	180	37	this work

The definitions are the same in this article, and some values were read from the figures in references, which may not be very accurate.

3.3. NO₂ Sensing Mechanism

After the above analysis of the structure and gas sensitive performance of ZnO, SnO₂ and ZnO-SnO₂ samples, it can be concluded that the construction of ZnO-SnO₂ heterojunction can significantly improve the gas sensitivity of NO₂, the n-n heterojunction plays a vital role in the sensing properties. Figure 8 illustrates the band structure of ZnO-SnO₂ heterojunction. The band structures of ZnO and SnO₂ that were previously in contact with each other are exhibited in Figure 8a. The ϕ (work function) and E_g (band gap) of ZnO are 5.2 eV, 3.19 eV, respectively, and those value of SnO₂ are 4.55 eV, 3.63 eV, respectively. The heterojunction formed at the interface between ZnO and SnO₂. The electrons will flow from SnO₂ to ZnO owing to the lower work function of SnO₂ compared with ZnO [45], leading to the increasing number of free electrons on the surface of ZnO. The Fermi levels will become equal when a dynamic equilibrium is established between ZnO and SnO₂. Therefore, the electron depletion layer formed at the SnO₂ side, and electron accumulation layer formed at the ZnO side. The shift of binding energy in XPS analysis confirmed the different electronegativity of the elements. Besides, NO₂ is an oxidizing gas. The formation of electron accumulation layer will further promote NO₂ to grab electrons from the conduction band of ZnO. In addition, increasing number of electrons will facilitate more oxygen species adsorbed on the surface of ZnO and further reacts with NO₂ simultaneously. The corresponding equation is shown below [46]:



Generally, the sensing performance of metal oxides semiconductors can be affected by potential barriers. The interfaces between ZnO-ZnO, ZnO-SnO₂, and SnO₂-SnO₂ may have an important influence on the sensing performance [41]. The smaller particles of SnO₂ in ZnO-SnO₂ composition are facilitates NO₂ adsorption. Therefore, the excellent NO₂ sensing performance can contribute to the increased free electrons, larger number of adsorption sites, and the interfaces effect of ZnO-SnO₂ heterojunction.

A high performance gas sensor fabricated by sensitive materials will be widely used in environmental monitoring, artificial intelligence, the Internet of Things, and wearable devices in the future [47–49].

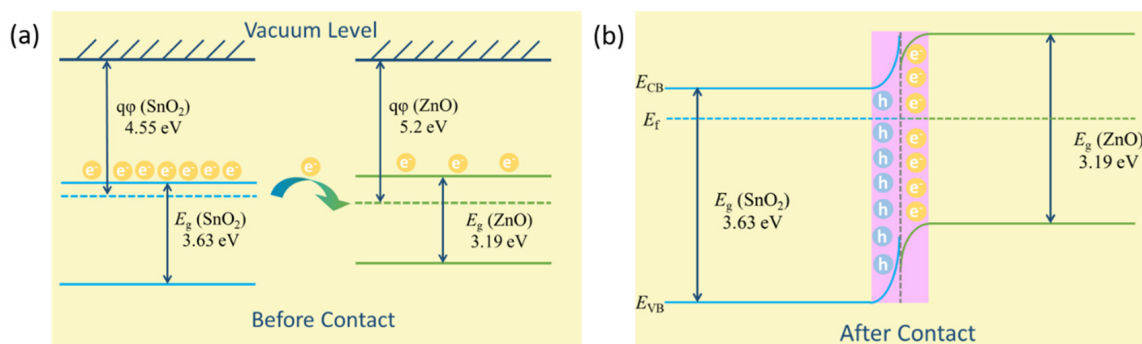


Figure 8. Schematic diagram for the band structure of ZnO-SnO₂ (a) before contact, (b) after contact.

4. Conclusions

In summary, bimetallic MOFs were synthesized by direct solution methods, and the ZnO-SnO₂ metal oxides heterojunction structure was obtained after subsequent heat treatment. The size of SnO₂ nanoparticles is 5–30 nm, and the diameter of ZnO hexagonal nanoparticles are 0.1–2 μ m. The construction of ZnO-SnO₂ heterojunction greatly enhanced the NO₂ sensing performance. When the molar ratio of ZnO to SnO₂ is 1:0.3, the response value of ZnO-SnO₂ heterostructures is 37 towards 0.2 ppm NO₂ at 180 $^{\circ}$ C, which is 3 times higher than pure ZnO and SnO₂ made by the same methods. Furthermore, ZnO-SnO₂ heterostructures could detect NO₂ as low as 20 ppb. Moreover, the ZnO-SnO₂ heterostructure exhibits excellent selectivity to NO₂. The outstanding NO₂ sensing performance of ZnO-SnO₂ heterostructure can be attributed to the synergistic effect of n-n heterojunction between ZnO-SnO₂.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano12213726/s1>, Table S1. EDS element result of S2, Table S2. EDS element result of S3, Figure S1. XRD of the precursor, Figures S2–S5. TEM, SEM images and corresponding grain size analysis of S1–S4. Figure S6. XPS curve of (a) O 1s for sample S1, S2 and S4; (b–d) O 1s peak area fitting results of S1, S2 and S4. Figure S7. Raman mapping and spectra of ZnO-SnO₂. The intensity of Raman peak (a) E_2 (high), (b) A_{1g} . (c) I_{E_2 (high)}/ $I_{A_{1g}}$. (d) Raman spectra of ZnO-SnO₂, Figure S8. The real time resistance of sample S2 towards 20–50 ppb NO₂, Figure S9. The correlation between response value and NO₂ concentration and the fitting curve.

Author Contributions: X.R.: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Validation, Visualization, Writing—original draft preparation, Writing—review & editing, Validation. Z.X.: Conceptualization, Formal analysis, Writing—review & editing. Z.Z.: Supervision. Z.T.: Resources, Writing—review & editing, Project administration, Funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financially supported by the National Natural Science Foundation of China (Nos. 51772163 and 51472137).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest: We declare that we have no conflict of interest.

References

- Kim, D.; Chen, Z.; Zhou, L.F.; Huang, S.X. Air pollutants and early origins of respiratory diseases. *Chronic Dis. Transl. Med.* **2018**, *4*, 75–94. [CrossRef] [PubMed]
- Schwartz, J.; Spix, C.; Wichmann, H.E.; Malin, E. Air pollution and acute respiratory illness in five german communities. *Environ. Res.* **1991**, *56*, 1–14. [CrossRef]

3. WHO. WHO Global Air Quality Guidelines: Particulate Matter (PM_{2.5} and PM₁₀), Ozone, Nitrogen Dioxide, Sulfur Dioxide and Carbon Monoxide; World Health Organization: Geneva, Switzerland, 2021.
4. Yang, X.; Zhang, Y.; Hao, X.; Song, Y.; Liang, X.; Liu, F.; Liu, F.; Sun, P.; Gao, Y.; Yan, X.; et al. Nafion-based amperometric H₂S sensor using Pt-Rh/C sensing electrode. *Sens. Actuators B* **2018**, *273*, 635–641. [[CrossRef](#)]
5. Hsueh, T.-J.; Wu, S.-S. Highly sensitive Co₃O₄ nanoparticles/MEMS NO₂ gas sensor with the adsorption of the Au nanoparticles. *Sens. Actuators B* **2021**, *329*, 129201. [[CrossRef](#)]
6. Miller, D.R.; Akbar, S.A.; Morris, P.A. Nanoscale metal oxide-based heterojunctions for gas sensing: A review. *Sens. Actuators B* **2014**, *204*, 250–272. [[CrossRef](#)]
7. Alenezi, M.R.; Henley, S.J.; Emerson, N.G.; Silva, S.R. From 1D and 2D ZnO nanostructures to 3D hierarchical structures with enhanced gas sensing properties. *Nanoscale* **2014**, *6*, 235–247. [[CrossRef](#)]
8. Yuan, H.; Aljneibi, S.; Yuan, J.; Wang, Y.; Liu, H.; Fang, J.; Tang, C.; Yan, X.; Cai, H.; Gu, Y.; et al. ZnO nanosheets abundant in oxygen vacancies derived from metal-organic frameworks for ppb-level gas sensing. *Adv. Mater.* **2019**, *31*, e1807161. [[CrossRef](#)]
9. Zhou, L.; Hu, Z.; Wang, P.; Gao, N.; Zhai, B.; Ouyang, M.; Zhang, G.; Chen, B.; Luo, J.; Jiang, S.; et al. Enhanced NO₂ sensitivity of SnO₂ SAW gas sensors by facet engineering. *Sens. Actuators B* **2022**, *361*, 131735. [[CrossRef](#)]
10. Cheng, L.; Li, Y.; Cao, G.; Sun, G.; Cao, J.; Wang, Y. Boosting TEA sensing performance of ZnO porous hollow spheres via in situ construction of ZnS-ZnO heterojunction. *Sens. Actuators B* **2022**, *364*, 131883. [[CrossRef](#)]
11. Liu, W.; Gu, D.; Li, X. Ultrasensitive NO₂ detection utilizing mesoporous ZnSe/ZnO heterojunction-based chemiresistive-type sensors. *ACS Appl. Mater. Interfaces* **2019**, *11*, 29029–29040. [[CrossRef](#)]
12. Yang, Z.; Zhang, D.; Chen, H. MOF-derived indium oxide hollow microtubes/MoS₂ nanoparticles for NO₂ gas sensing. *Sens. Actuators B* **2019**, *300*, 127037. [[CrossRef](#)]
13. Burtch, N.C.; Heinen, J.; Bennett, T.D.; Dubbeldam, D.; Allendorf, M.D. Mechanical properties in metal-organic frameworks: Emerging opportunities and challenges for device functionality and technological applications. *Adv. Mater.* **2017**, *30*, 1704124. [[CrossRef](#)]
14. Dong, X.; Su, Y.; Lu, T.; Zhang, L.; Wu, L.; Lv, Y. MOFs-derived dodecahedra porous Co₃O₄: An efficient cataluminescence sensing material for H₂S. *Sens. Actuators B* **2018**, *258*, 349–357. [[CrossRef](#)]
15. Ren, X.; Xu, Z.; Liu, D.; Li, Y.; Zhang, Z.; Tang, Z. Conductometric NO₂ gas sensors based on MOF-derived porous ZnO nanoparticles. *Sens. Actuators B* **2022**, *357*, 131384. [[CrossRef](#)]
16. Guo, L.; Shen, Z.; Ma, C.; Ma, C.; Wang, J.; Yuan, T. Gas sensor based on MOFs-derived Au-loaded SnO₂ nanosheets for enhanced acetone detection. *J. Alloys Compd.* **2022**, *906*, 164375. [[CrossRef](#)]
17. Tan, J.; Hussain, S.; Ge, C.; Wang, M.; Shah, S.; Liu, G.; Qiao, G. ZIF-67 MOF-derived unique double-shelled Co₃O₄/NiCo₂O₄ nanocages for superior gas-sensing performances. *Sens. Actuators B* **2020**, *303*, 127251. [[CrossRef](#)]
18. Woo, S.; Jo, M.; Lee, J.-S.; Choi, S.-H.; Lee, S.; Jeong, H.S.; Choi, S.-J. Metal-organic frameworks-driven ZnO-functionalized carbon nanotube fiber for NO₂ sensor. *J. Sens. Sci. Technol.* **2021**, *30*, 369–375. [[CrossRef](#)]
19. Deng, Z.; Zhang, Y.; Xu, D.; Zi, B.; Zeng, J.; Lu, Q.; Xiong, K.; Zhang, J.; Zhao, J.; Liu, Q. Ultrasensitive formaldehyde sensor based on SnO₂ with rich adsorbed oxygen derived from a metal organic framework. *ACS Sens.* **2022**, *7*, 2577–2588. [[CrossRef](#)]
20. Song, Y.; Xu, M.; Li, Z.; He, L.; Hu, M.; He, L.; Zhang, Z.; Du, M. A bimetallic CoNi-based metal-organic framework as efficient platform for label-free impedimetric sensing toward hazardous substances. *Sens. Actuators B* **2020**, *311*, 127927. [[CrossRef](#)]
21. Long, L.; Liu, X.; Chen, L.; Wang, S.; Liu, M.; Jia, J. MOF-derived 3D leaf-like CuCo oxide arrays as an efficient catalyst for highly sensitive glucose detection. *Electrochim. Acta* **2019**, *308*, 243–252. [[CrossRef](#)]
22. Kumar, M.; Bhatt, V.; Abhyankar, A.C.; Kim, J.; Kumar, A.; Yun, J.-H. Modulation of structural properties of Sn doped ZnO for UV photoconductors. *Sens. Actuators A Phys.* **2018**, *270*, 118–126. [[CrossRef](#)]
23. Yang, X.; Zhang, S.; Yu, Q.; Zhao, L.; Sun, P.; Wang, T.; Liu, F.; Yan, X.; Gao, Y.; Liang, X.; et al. One step synthesis of branched SnO₂/ZnO heterostructures and their enhanced gas-sensing properties. *Sens. Actuators B* **2019**, *281*, 415–423. [[CrossRef](#)]
24. Ghosh, A.; Das, G. Green synthesis of Sn(II)-BDC MOF: Preferential and efficient adsorption of anionic dyes. *Microporous Mesoporous Mater.* **2020**, *297*, 110039. [[CrossRef](#)]
25. Li, J.; Cheng, S.; Zhao, Q.; Long, P.; Dong, J. Synthesis and hydrogen-storage behavior of metal-organic framework MOF-5. *Int. J. Hydrogen Energy* **2009**, *34*, 1377–1382. [[CrossRef](#)]
26. Wang, Q.; Li, Z.; Banares, M.A.; Weng, L.T.; Gu, Q.; Price, J.; Han, W.; Yeung, K.L. A novel approach to high-performance aliovalent-substituted catalysts-2D bimetallic MOF-derived CeCuOx microsheets. *Small* **2019**, *15*, e1903525. [[CrossRef](#)]
27. Qin, S.; Tang, P.; Feng, Y.; Li, D. Novel ultrathin mesoporous ZnO-SnO₂ n-n heterojunction nanosheets with high sensitivity to ethanol. *Sens. Actuators B* **2020**, *309*, 127801. [[CrossRef](#)]
28. Song, Y.; Zhang, S.; Zhang, C.; Yang, Y.; Lv, K. Raman spectra and microstructure of zinc oxide irradiated with swift heavy ion. *Crystals* **2019**, *9*, 395. [[CrossRef](#)]
29. Zhao, Q.; Ju, D.; Deng, X.; Huang, J.; Cao, B.; Xu, X. Morphology-modulation of SnO₂ hierarchical architectures by Zn doping for glycol gas sensing and photocatalytic applications. *Sci. Rep.* **2015**, *5*, 7874. [[CrossRef](#)]
30. Makula, P.; Pacia, M.; Macyk, W. How to correctly determine the band gap energy of modified semiconductor photocatalysts based on UV-vis spectra. *J. Chem. Lett.* **2018**, *9*, 6814–6817. [[CrossRef](#)]
31. Chen, X.; Shen, Y.; Zhou, P.; Zhong, X.; Li, G.; Han, C.; Wei, D.; Li, S. Bimetallic Au/Pd nanoparticles decorated ZnO nanowires for NO₂ detection. *Sens. Actuators B* **2019**, *289*, 160–168. [[CrossRef](#)]

32. Liu, Q.; Zhan, H.; Huang, X.; Song, Y.; He, S.; Li, X.; Wang, C.; Xie, Z. High visible light photocatalytic activity of SnO_{2-x} nanocrystals with rich oxygen vacancy. *Eur. J. Inorg. Chem.* **2021**, 2021, 4370–4376. [\[CrossRef\]](#)
33. Yang, T.; Jin, W.; Liu, Y.; Li, H.; Yang, S.; Chen, W. Surface reactions of CH₃OH, NH₃ and CO on ZnO nanorod arrays film: DFT investigation for gas sensing selectivity mechanism. *Appl. Surf. Sci.* **2018**, 457, 975–980. [\[CrossRef\]](#)
34. Wen, Z.; Tian-mo, L. Gas-sensing properties of SnO₂–TiO₂-based sensor for volatile organic compound gas and its sensing mechanism. *Phys. B Condens. Matter* **2010**, 405, 1345–1348. [\[CrossRef\]](#)
35. Xuan, J.; Zhao, G.; Sun, M.; Jia, F.; Wang, X.; Zhou, T.; Yin, G.; Liu, B. Low-temperature operating ZnO-based NO₂ sensors: A review. *RSC Adv.* **2020**, 10, 39786–39807. [\[CrossRef\]](#)
36. Gonzalez-Chavarri, J.; Parellada-Monreal, L.; Castro-Hurtado, I.; Castaño, E.; Mandayo, G.G. ZnO nanoneedles grown on chip for selective NO₂ detection indoors. *Sens. Actuators B* **2018**, 255, 1244–1253. [\[CrossRef\]](#)
37. Zeng, W.; Liu, Y.; Mei, J.; Tang, C.; Luo, K.; Li, S.; Zhan, H.; He, Z. Hierarchical SnO₂–Sn₃O₄ heterostructural gas sensor with high sensitivity and selectivity to NO₂. *Sens. Actuators B* **2019**, 301, 127010. [\[CrossRef\]](#)
38. Gao, R.; Gao, L.; Zhang, X.; Gao, S.; Xu, Y.; Cheng, X.; Guo, G.; Ye, Q.; Zhou, X.; Major, Z.; et al. The controllable assembly of the heterojunction interface of the ZnO@rGO for enhancing the sensing performance of NO₂ at room temperature and sensing mechanism. *Sens. Actuators B* **2021**, 342, 130073. [\[CrossRef\]](#)
39. Yang, Z.; Jiang, L.; Wang, J.; Liu, F.; He, J.; Liu, A.; Lv, S.; You, R.; Yan, X.; Sun, P.; et al. Flexible resistive NO₂ gas sensor of three-dimensional crumpled MXene Ti₃C₂Tx/ZnO spheres for room temperature application. *Sens. Actuators B* **2021**, 326, 128828. [\[CrossRef\]](#)
40. Sharma, B.; Sharma, A.; Joshi, M.; Myung, J.-h. Sputtered SnO₂/ZnO heterostructures for improved NO₂ gas sensing properties. *Chemosensors* **2020**, 8, 67. [\[CrossRef\]](#)
41. Zhao, S.; Shen, Y.; Maboudian, R.; Carraro, C.; Han, C.; Liu, W.; Wei, D. Facile synthesis of ZnO–SnO₂ hetero-structured nanowires for high-performance NO₂ sensing application. *Sens. Actuators B* **2021**, 333, 129613. [\[CrossRef\]](#)
42. Phuoc, P.H.; Viet, N.N.; Thong, L.V.; Hung, C.M.; Hoa, N.D.; Duy, N.V.; Hong, H.S.; Hieu, N.V. Comparative study on the gas-sensing performance of ZnO/SnO₂ external and ZnO–SnO₂ internal heterojunctions for ppb H₂S and NO₂ gases detection. *Sens. Actuators B* **2021**, 334, 129606. [\[CrossRef\]](#)
43. Bai, M.; Chen, M.; Li, X.; Wang, Q. One-step CVD growth of ZnO nanorod/SnO₂ film heterojunction for NO₂ gas sensor. *Sens. Actuators B* **2022**, 373, 132738. [\[CrossRef\]](#)
44. Zhang, Z.; Xu, M.; Liu, L.; Ruan, X.; Yan, J.; Zhao, W.; Yun, J.; Wang, Y.; Qin, S.; Zhang, T. Novel SnO₂@ZnO hierarchical nanostructures for highly sensitive and selective NO₂ gas sensing. *Sens. Actuators B* **2018**, 257, 714–727. [\[CrossRef\]](#)
45. Tharsika, T.; Haseeb, A.S.; Akbar, S.A.; Sabri, M.F.; Hoong, W.Y. Enhanced ethanol gas sensing properties of SnO₂-core/ZnO-shell nanostructures. *Sensors* **2014**, 14, 14586–14600. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Oh, E.; Choi, H.-Y.; Jung, S.-H.; Cho, S.; Kim, J.C.; Lee, K.-H.; Kang, S.-W.; Kim, J.; Yun, J.-Y.; Jeong, S.-H. High-performance NO₂ gas sensor based on ZnO nanorod grown by ultrasonic irradiation. *Sens. Actuators B* **2009**, 141, 239–243. [\[CrossRef\]](#)
47. Zan, G.; Wu, T.; Zhu, F.; He, P.; Cheng, Y.; Chai, S.; Wang, Y.; Huang, X.; Zhang, W.; Wan, Y.; et al. A biomimetic conductive super-foldable material. *Matter* **2021**, 4, 3232–3247. [\[CrossRef\]](#)
48. Zan, G.; Wu, T.; Dong, W.; Zhou, J.; Tu, T.; Xu, R.; Chen, Y.; Wang, Y.; Wu, Q. Two-level biomimetic designs enable intelligent stress dispersion for super-foldable C/NiS nanofiber free-standing electrode. *Adv. Fiber Mater.* **2022**, 4, 1177–1190. [\[CrossRef\]](#)
49. Jeong, S.Y.; Kim, J.S.; Lee, J.H. Rational design of semiconductor-based chemiresistors and their libraries for next-generation artificial olfaction. *Adv. Mater.* **2020**, 32, e2002075. [\[CrossRef\]](#)