In Operando Impedance Spectroscopic Analysis on NiO–WO₃ Nanorod Heterojunction Random Networks for Room-Temperature H₂S Detection

Yale Wang, Arnab Maity, Xiaoyu Sui, Haihui Pu, Shun Mao, Niraj K. Singh, and Junhong Chen

ABSTRACT: The use of metal-oxide sensors for effectively detecting hydrogen sulfide (H₂S) gas at room temperature is currently hindered by their inadequate sensitivity and selectivity. Using a lucid fabrication strategy, we report a room-temperature, highly sensitive, and selective H₂S gas sensor using NiO-modified WO₃ nanorod (one-dimensional–one-dimensional) random networks. The observed improvements in gas-sensing sensitivity stem from the synergistic effects of various contributions inside the sensing heterostructure, such as bulk nanorod, p–n heterojunction at the interface of these two dissimilar oxides, and gas-induced conducting species due to sulfurization (WS₂→ and NiS₁→). An in situ impedance measurement during gas exposure was used to investigate the influence of these effects. The analysis revealed that these contributing factors can be either cooperating or competing and lead to either increased or decreased sensitivity, respectively. The presence of semimetallic species (NiS, WS₂) was further confirmed by in situ X-ray diffraction analysis of the heterostructure nanorod sample with H₂S gas exposure. The related sensing mechanism in the heterostructure is presented with a conduction pathway model. The room-temperature-operated nanorod heterostructure sensors showed a lower detection limit of H₂S at ∼0.5 ppm, which is significantly lower than its toxicity limiting value ∼10 ppm, per the Environmental Protection Agency. The nanorod heterostructure sensors can be used for real-time, low-cost, room-temperature alarms in an H₂S monitoring system.

1. INTRODUCTION

Hydrogen sulfide (H₂S) is a highly toxic and flammable gas that is widely produced in coal mines and oil industries and used in sewerage pipe detection. Upon exposure, this gas affects the human nervous system and can become life threatening at high concentrations. The effects of H₂S exposure at 2 ppm include nausea, headaches, or loss of sleep; at 20 ppm, fatigue and headache; and between 50 and 100 ppm, respiratory tract irritation, digestive upset, and loss of appetite. Therefore, accurately detecting H₂S in both laboratories and human living places is essential.

H₂S typically has a rotten-egg odor, which can be detected by humans at concentrations as low as 0.5 ppb. This odor threshold concentration is much lower than the Occupational Safety and Health Administration ceiling point (20 ppm). But olfactory fatigue occurs at continuous low-concentration inhalation as well as at high concentrations. Because human odor-level detection is not a reliable method for effectively detecting H₂S in atmosphere, there is a demand for a highly efficient, low-cost H₂S gas sensor operable at room temperature for continuous monitoring in various workplaces to ensure employee safety.

Recently, various quasi one-dimensional (1D) metal-oxide semiconductor nanostructures (e.g., nanorods, nanowires, nanotubes, nanobelts) of various binary oxides have been found to be promising materials for gas sensing. Compared with traditional thin-film technology, the advantages of 1D nanostructures include higher surface-to-volume ratio, good stability, excellent crystallinity, and excellent signal transduction in the presence of gaseous species for their less defective structures. It is argued that better sensitivity can be achieved with n-type 1D metal oxides through the modulation of initial resistance in background air. This can be realized when various surface oxygen species (O₂−, O−, O²⁻) have been
adsorbed on a simple oxide surface and depleted the electrons by creating a surface depletion potential width (ΔD). These adsorbed oxygen species further shrink the actual electron conduction diameter (the nondepleted core inside the nanorod, D_{cond} ≈ D − 2ΔD, where D is the actual diameter) due to the surface depletion region. In addition, the heterojunction of two dissimilar oxides with different work functions could create a larger depletion area at the interface of two dissimilar oxides, which eventually enhances the initial resistance. The conduction pathway is modulated by the coverage of second oxides on the surface of the host oxides, catalytic nature, work function difference, and the thickness of the second oxide. In addition, heterostructures can remarkably improve the selectivity by optimizing the mixing ratio between dissimilar oxides.

WO₃ has been investigated as a sensing material for H₂S in recent years. Pure WO₃ films and noble metal-decorated WO₃ nanomaterials have been reported for H₂S sensing. Granqvist and his group produced nanocrystalline WO₃ films using the advanced gas deposition method. After sintering at 750 K, the WO₃ film sensor exhibited extremely high sensitivity toward H₂S at room temperature. This good response is due to the formation of tetragonal phase through sintering, but the detailed sensing mechanism remains unclear.⁴⁻⁶ Kim and his co-worker investigated the CH₄ and H₂S gas-sensing properties of pristine or Au nanoparticles-doped WO₃ nanowires at a high operating temperature. The increased sensitivity was attributed to the catalytic effect of the Au nanoparticles. The slower response time was caused by some delayed reactions in relation to the Au nanoparticles.⁷

One drawback of the traditional metal-oxide semiconductor gas sensor is its high operating temperature, which leads to high power consumption and limits the lifetime of the sensor. Hence, there is a need to investigate sensing performance at room temperature. Sensing performance can be improved when semiconductor metal oxides form heterojunctions with other oxides, especially different types of metal oxides.⁸ These modifications can substantially change the surface properties as well as the electronic properties because they enhance the depletion layer at the heterointerfaces. A heterojunction will form at the boundaries between two dissimilar materials; once the electrical contact at the interface is formed, the electrons at the higher energy level will flow across the interface to the lower-level states to equilibrate the Fermi energy levels.

The H₂S gas-sensing properties of metal-oxide heterostructures have been reported by many researchers over the past few years. Wang et al. synthesized 1D nanosized core–shell CuO–SnO₂ nanomaterials using the hydrothermal method. The p–n junctions are formed from p-type CuO nanoparticles uniformly coated on the n-type SnO₂ nanorods. The gas sensor based on these p–n junction nanomaterials indicated good sensitivity and selectivity against H₂S gas at 60 °C.⁹ Gupta et al. demonstrated an H₂S gas sensor based on randomly distributed nano p–n junction between CuO and WO₃.¹⁰ Modification of a WO₃ thin film with CuO resulted in enhanced sensitivity toward H₂S (sensitivity of 53 400% toward 10 ppm H₂S at 300 °C).

Lee et al. investigated the H₂S sensing properties of CuO-functionalized WO₃ nanowires at 300 °C.¹¹ The enhanced gas-sensing property of these p–n junction nanomaterials is likely the result of two factors: (1) The p–n junctions formed at the grain boundaries of p-type CuO and n-type SnO₂/WO₃ resulted in a potential barrier. The barrier blocked the electrons transporting through the nanomaterials, which increased the initial resistance of the sensors in air. (2) The formation of metallic CuS due to the interaction of CuO with H₂S resulted in a drastic decrease in the resistance of these sensors.

In addition, Zhou et al. prepared CuO–NiO core–shell microspheres using the simple two-step hydrothermal method.¹² At the optimal operating temperature of 260 °C, the gas sensors displayed the highest sensitivity of 460% toward 100 ppm H₂S gas. The improved response is due to the catalytic effect of NiO shell and the formation of heterojunctions at the boundaries between NiO and CuO, which resulted in a higher number of adsorbed oxygen molecules on the surface.

Few studies have explored the sulfurization reaction on the NiO or WO₃ surface during H₂S gas sensing, especially at room temperature. Considering that the work function of NiO is 9.4 eV, which is higher than that of CuO (8.5 eV), the large work function difference between NiO and WO₃ may provide a broader depletion area formed at the heterojunction interface and lead to a larger resistance change during gas sensing. It could be deduced that the combination of 1D NiO and WO₃ nanostructures could potentially boost H₂S gas-sensing performance at room temperature.

In the recent literature, various 1D–1D heterostructures have been reported for efficient gas sensing, including zero-dimensional oxide-coated 1D structures, brush-like 1D–1D composite, and coaxial 1D–1D core–shell oxide composites with various fabrication processes using electrospinning, thermal evaporation, hydrothermal, and atomic layer deposition.¹³⁻¹⁸ These processes are time consuming, expensive, and power hungry, and thus there is a demand to process heterostructures more quickly and less expensively while at the same time maintaining their crystal purity and improved sensing performance. Here, we report a sensor based on NiO–WO₃ nanorod heterostructures synthesized through the facile-solution-based mixing method followed by gentle heat treatment. This process maintains high-quality crystallinity in constituent oxides without the formation of any secondary phase in the composite form. With the use of this heterojunction nanorod composite, enhanced H₂S gas-sensing properties have been realized compared with pure nanorods. The typical sensitivity was 230% toward 10 ppm H₂S, and the lower detection limit could reach the ppb level. This type of gas sensor showed better sensing performance (room-temperature sensitivity, selectivity, and limit of detection (LOD)) when compared with most of the literature reports.

The detailed conduction mechanisms of pure and heterostructure oxides have been investigated through in operando impedance spectroscopy analysis and equivalent circuit modeling. In addition to the adsorption–desorption mechanism, a unique surface sulfurization process during H₂S gas exposure is responsible for destroying the p–n junction effect by creating various quasi-metallic byproducts (NiS, W₅S₇−). This leads to a larger decrease in resistance from initial high base resistance, signifying the formation of the p–n heterojunction of certain composites. The sulfurization phenomena are only unique toward H₂S, thereby improving the selectivity against other reducing or oxidizing gases. The crystal phase formation of these quasi-metallic species on the surface has been further confirmed by in situ X-ray diffraction (XRD) analysis. Impedance analysis revealed that the contributing resistive components inside the heterostructures...
from grain, grain boundary, p–n junction, and metallic species could be either cooperating or compensating, depending on the specific molar ratio of individual oxides and the overall conduction nature (p–n-type) of the oxides. It is argued that by selecting a specific optimized molar ratio between constituent WO3 and NiO nanorods, it is possible to minimize the compensating conduction components (decreasing response) and maximize the cooperating conduction (enhancing response) to develop a room-temperature, high-performance, alarm-based H2S gas detector.

2. RESULTS AND DISCUSSION

2.1. Morphology and Crystal Structure. Scanning electron microscopy (SEM) images of the WO3, W3N1, W1N1, W1N3, and NiO are shown in Figure 1a(i)–(v), respectively. It can be observed that the diameters of the pure WO3 and NiO are around 300 and 60 nm, respectively. The length of the WO3 is around 1–3 μm. Figure 1a(i) shows an SEM image of a typical WO3 nanowire bridging a pair of Au electrode fingers in a sensor device. From Figure 1a(i)–(v), the ratio of WO3 and NiO in the images matches the molar ratio calculated before, suggesting the formation of uniform dispersion. The XRD patterns for WO3, NiO, and NiO–WO3 nanoheterostructures are shown in Figure 1b. The peaks from pure NiO are weak and broad, suggesting that the crystallinity of the NiO nanowires is not very good. The XRD patterns of pure WO3 can be indexed to cubic phase (JCPDS card 75-2187). There are no obvious peak shifts or any trace of other phases, besides pure NiO and WO3, from other nanostructures. Therefore, the crystal structure of the three nanoheterostructures is considered to have originated primarily from the mixture of cubic NiO and WO3 with separate phases. The X-ray photoelectron spectroscopy (XPS) spectra of different samples were studied to further investigate valence chemistry and binding energy of constituent elements of the as-prepared metal-oxide heterostructure samples. The carbon peak is reset as 285.0 eV. The O 1s XPS spectra of various samples are enlarged in Figure 1c. The XPS spectra of O 1s core-level electrons measured from pure NiO and WO3 both display three peaks. The binding energies of 529.1 eV in NiO and 530.6 eV in WO3 correspond with the lattice oxygen in crystalline NiO and WO3. Here, O 1s signals present shoulders located at the high binding energy (532.0–534.7 eV) side of each main peak for every sample, which can be attributed to the OH species on the surface. The O 1s peaks at 530.9 eV in NiO and 531.9 eV in WO3 belong to the deficient or chemisorbed oxygen. Note that because of the different chemical environments of O in heterostructure oxides, each characteristic peak has some shifts in the three mixed heterostructure samples. Table 1 lists the corresponding binding energies and atomic ratios for different characteristic peaks of O 1s in these five oxide samples. The ratio of lattice oxygen increases gradually with the increase of WO3 content in three heterostructure samples, suggesting that more surface oxygen vacancies had formed.
the pure NiO, the Ni 2p signal could be dissolved into four peaks. The peaks at 855.4 eV and 861.3 eV are attributed to Ni 2p3/2, and the peaks at 873.1 and 879.1 eV are attributed to Ni 2p1/2. The Ni 2p peaks of samples W1N3, W1N1, and W3N1 can also be separated into four peaks. Compared with pure NiO, the spectrum of sample W3N1 exhibits an overall shift to higher binding energy. The shift of Ni 2p peaks to higher binding energy is about 1.5 eV. This phenomenon can be explained by the strong interaction between WO3 and NiO nanowires in sample W3N1, which implies the formation of p−n junctions and leads to the increased surface activity of WO3 nanorods.

2.2. Gas-Sensing Performance. Hydrogen sulfide is a colorless, toxic, and flammable reducing gas. Figure 2a shows the dynamic responses of pure WO3, pure NiO, and NiO−WO3 nanoheterostructures toward 10 ppm H2S measured at room temperature. The bare NiO nanowires do not indicate any response against 10 ppm H2S, just as reported in our previous study.21 The sensitivity was enhanced significantly for W3N1, as discussed later in greater detail.

The NiO−WO3 nanoheterostructures show n-type gas-sensing behavior toward reducing H2S gas due to the conductance difference in WO3 and NiO. The band gap of WO3 (2.8 eV) is smaller than that of NiO (3.8 eV), which means that the conductance of WO3 is better; this made the WO3 more dominant in sensing signal variation. The sensitivity decreases as the molar ratio of NiO increases further. This can be explained as the spillover effect caused by the nonresponsive insulating layer of NiO on the surface of WO3. Figure 2b indicates the dynamic response of the W3N1 gas sensor exposed to different concentrations of H2S at room temperature. The selectivity and sensitivity toward hydrogen sulfide were significantly higher than toward other gases, as shown in Figure 2d,e, possibly due to the lower dissociation energy of H2S. The dissociation energy of the hydrogen sulfide (91.2 kcal/mol) is less than those of carbon monoxide (256.3 kcal/mol), benzene (112 kcal/mol), and ammonia (107.6 kcal/mol); as a result, the sensing response perfectly matches the dissociation energy ranking of these four gases.

Table 2 briefly summarizes the gas-sensing performance of various metal-oxide-based sensors toward H2S at room temperature. The sensitivity of our NiO−WO3 nanoheterostructures is comparable with that reported in the literature. It is worth noting that the synthesis method of our work is less expensive compared with others reported in the literature (listed in Table 2).

2.3. Sensing Mechanism. When the Fermi level (EF) of one semiconductor material is different from that of another (i.e., due to the work function difference), the electrons flow across the grain boundary after the contact between these two semiconductors until the Fermi energies have equilibrated at the interface. For the contact between p- and n-type semiconductors, as illustrated in Figure 3, the major carrier (holes and electrons for p- and n-type semiconductors, respectively) flows across the boundary, leading to a change in the electrical conductance of the sensor.

Table 2. Comparison of the Room-Temperature-Sensing Performance of Various Metal-Oxide-Based Gas Sensors toward H2S

| material          | method                  | concn (ppm) | sensitivity (%) | response/recovery time(s) | LOD (ppb) | ref |
|-------------------|-------------------------|-------------|-----------------|---------------------------|-----------|-----|
| In2O3             | carbothermal method      | 10          | 40              | ~60/~7200                  | 200       | 22  |
| Zn/ZnO            | thermally evaporated deposition | 8           | 60              | ~270/~750                  | 1000      | 23  |
| Cu/SWCNTs         | spin-coating            | 20          | 30              | 10/20                      | 24        |
| CuO/SWCNTs        | drop-casting            | 10          | 45              |                           | 100       | 25  |
| SnO2 multitube arrays |                       | 5           | 50              | 14/30                      | 5000      | 26  |
| SnO2/CNT          | CVD                     | 50          | 30              | ~60/~60                    | 9000      | 27  |
| quasi-2D CuO/SnO2 | electrochemical deposition | 50          | 80              | 180/500                    | 500       | 28  |
| CeO2              | tube film coating       | 10          | 60              | 50/75                      | 50        | 29  |
| CuO2/FGS          | syringe dispensing      | 0.1         | 40              | 120/300                    | 5         | 30  |
| NiO−WO3           | drop-casting            | 10          | 230             | 270/~7200                  | 200       | this work |

Figure 2. (a) Dynamic response and recovery curve of NiO−WO3 nanoheterostructures. (b) Dynamic response of the W3N1 heterostructures to 0.2, 0.5, 1, 5, and 10 ppm H2S gas at room temperature. (c) Sensitivity variation of the W3N1 sensor as a function of H2S concentration. (d) Dynamic response of W3N1 against 10 ppm H2S, CO, NH3, and C6H6. (e) Comparative performance for W3N1 toward 10 ppm H2S, CO, C3H8, and NH3.
respectively) diﬀuses across the interface, leading to its depletion and the band bending across the interface. For the metal-oxide-based field-effect transistor sensors, O2 molecules can adsorb on their surface upon exposure to air and thus extract electrons from the conduction band ($E_{CB}$) in the metal oxides, turning into oxygen ions residing on the surface. Physically, both the molecular (O$_2^-$) and atomic (O$^-$, O$_2^-$) oxygen ions can be formed, whereas the coverage of the latter will increase at elevated temperatures.$^{31}$ The p–n junction formation on the nanoheterostructure surface will decrease the barrier for electrons transfer from metal oxide to the adsorbed O$_2$, which will lead to the formation of molecular oxygen ions (O$_2^-$) at room temperature. For the nanowire materials, this p–n junction formation will make the major carrier transfer channel narrower.

From the gas-sensing performance, it was found that the W and W3N1 samples show n-type behavior, whereas W1N1, W1N3, and NiO samples indicate p-type behavior. This suggests that the gas-sensing performances for these two types are predominantly controlled by the relative amounts of the W and N sites. It is also evident from the microstructure that the NiO nanowires are sequentially percolating the WO$_3$ nanorods with the increased NiO content; a generalized grain distribution model of these two typical heterostructures (W3N1 and W1N3) is shown in Figure 4a,b, respectively. For the W3N1 samples (Figure 4a), the current is predominantly controlled by the W sites, whereas the N sites control the rest of the heterostructure sensors (W1N1 and W1N3). For all of the sensing materials, W3N1 exhibits maximum sensing performance.

**Figure 3.** Schematic illustration of the formation of p–n junction between n-type WO$_3$ and p-type NiO.

**Figure 4.** Schematic conduction pathway model during H$_2$S gas exposure for (a) W3N1 and (b) W1N3.
In general, three major factors play a role in enhancing sensing performance. The $\text{H}_2\text{~S}$ sensing mechanism for metal-oxide sensors can be ascribed by two different mechanisms, adsorption–desorption and sulfurization–desulfurization. Due to the room-temperature operation, the adsorbed oxygen gas species on the oxide surface is molecular oxygen ions ($\text{O}_2^-$).

Thus, the adsorption–desorption mechanism becomes

$$2\text{H}_2\text{~S} + 3\text{O}_2^- \leftrightarrow 2\text{H}_2\text{O} + 2\text{SO}_2 + 3\text{e}^- \quad (1)$$

whereas for the sulfurization mechanism, the NiO and WO$_3$ grain surfaces can show the following set of reactions

$$\text{NiO} + \text{H}_2\text{~S} \rightarrow \text{NiS}_{(1-x)} + \text{H}_2\text{O} \quad (2)$$

$$\text{WO}_3 + \text{H}_2\text{~S} \rightarrow \text{WS}_{(2-x)} + \text{H}_2\text{O} \quad (3)$$

where $x$ stands for the stoichiometric ratio.

Due to first the reaction by reaction 1 (adsorption), the resistance of the pure WO$_3$ decreases as the number of majority carriers (electrons) increases, whereas for p-type NiO, the resistance increases due to the electron–hole recombination-induced reduction of the majority carrier (hole). For sulfurization reactions (reactions 2 and 3), due to the formation of semimetallic (narrower band gap materials) NiS$_{(1-x)}$ and WS$_{(2-x)}$, a much more conducting path can be created on the surface of the sensors upon $\text{H}_2\text{~S}$ gas exposure. Physically, both mechanisms can simultaneously occur in pure metal-oxide samples.

However, the formation of the heterojunction between the NiO and WO$_3$ induced by the electrons from the WO$_3$ side diffusing to the NiO side and the holes from the NiO side toward the WO$_3$ site, leads to a large potential barrier and especially a very high initial resistance of W3N1 samples in the air compared with other samples. This is consistent with similar work reported in the literature about the formation of $\text{p}–\text{n}$ junctions.$^{32,33}$ In the presence of $\text{H}_2\text{~S}$ gas, this large potential barrier decreases due to the adsorption–desorption mechanism but drastically collapses due to the surface sulfurization (formation of WS$_{(2-x)}$) process; both effects, in turn, cause a large decrease in resistance. Therefore, for the W3N1 samples, the sensing mechanism is enhanced by the collapse of heterojunction, which decreases the resistance considerably.

For the p-type W1N1 and W1N3 heterostructures (Figure 4b), the sensing performance is dominantly controlled by the smaller NiO grains, since the WO$_3$ grains are segregated from the electrode. Similarly, due to the adsorption–desorption mechanism, the resistance of the NiO grain–grain boundary should be increased, whereas the resistance decrease in the grain surface is also possible from the sulfurization process. As a result, the total change in resistance in $\text{H}_2\text{~S}$ gas exposure depends on which of these two competing processes (opposite change in resistance) is dominant. For the W3N1 heterostructure, the NiO-coated WO$_3$ nanorods can easily interconnect with finger electrodes and thus enhance the sensitivity by the same direction change in resistance from the adsorption–desorption mechanism, heterojunction effect, and sulfurization process, whereas the sensitivity decreases for W1N1, W1N3, and NiO samples due to the opposite compensation effect.

To further confirm the sulfurization process, in situ XRD analyses were performed with the samples after exposure to $\text{H}_2\text{~S}$. Figure 5a–c shows the XRD plot of all of the tested sensors before and after injection of the $\text{H}_2\text{~S}$ gas. Significantly, the new intense peaks for WS$_{(2-x)}$ were confirmed for the W and W3N1 samples, but the NiS peaks were weaker for rest of the samples. From the literature, Gibbs free energies of NiS and WS$_3$ formation are found as $-61.6$ and $-232.1$ kJ/mol, respectively.$^{19,34}$ Therefore, the propensity of the sulfurization reaction of NiO is weaker than WO$_3$. Thus, a good combination and the same direction changes due to the adsorption–desorption mechanism, heterojunction effect, and sulfurization process enabled the W3N1 sample to achieve higher sensitivity than any other samples.

**2.4. Impedance Spectroscopy Analysis.** To further confirm these cooperating and competing effects and to visualize the individual effects, in situ alternating current impedance analysis (amplitude 10 mV) was performed before and after gas exposure for all pure and heterostructure sensors. Figure 6a–e shows the measured the Nyquist plot for the sensor in air and in 10 ppm $\text{H}_2\text{~S}$ gas. The electrical equivalent circuit model is adopted from the contribution of nanorod grain, interboundary, or junction among nanorods. These can be expressed as a set of resistor–capacitor (RC) parallel circuit components. For n-type materials, major contributions for sensing come from nanorod grain and grain boundary, and they can be expressed as a set of RC (RC$_{\text{grain}}$ and RC$_{\text{grain boundary}}$) circuits (shown in Figure 7a). For p-type material, the situation is different: when the electrons are adhered by adsorbed molecular oxygen ($\text{O}_2^-$) from a p-type
An NiO–WO3 nanorod p–n heterojunction random network structure was fabricated using the facile, sonication-based solution mixing method for different volume ratios, followed by a gentle low-temperature annealing (200 °C). The XRD data shows the phase purity of constituent oxides in discreet and composite form is maintained well. SEM images showed that shorter NiO nanorod distributed around relatively longer WO3 nanorod (1D–1D structure) and formed nanojunction coating. The exhibited heterojunction effect is maximally observed for W3N1 (75 mol % WO3–25 mol % NiO) and confirmed by observation of the increase in resistance due to the formation of diode-like p–n nanojunction at the WO3–NiO interface.

The optimal room-temperature H2S gas sensing with excellent selectivity was observed for the W3N1 sensor, which exhibited a sensitivity of ~230% for 10 ppm H2S, this is 1–2 orders of magnitude higher than individual oxides and other composite samples. The excellent sensing performance for W3N1 is attributed to the p–n junction effect, sulfurization by H2S (formation of WS2-like and NiS1-like), and the ideal ratio of the NiO component in the composite. The formation of reactive semimetallic products due to sulfurization was confirmed by XRD analyses for H2S exhibited on the sensor’s surface.

Further investigations from in situ impedance measurement and RC equivalent circuit analyses during gas sensing were performed to evaluate the grain–grain boundary or the contributing effect of the p–n junction in sensing performance. It was found that for the pure WO3 and W3N1 samples, these contributing effects are in the same direction, resulting in a cooperating and highly sensitive performance, whereas for other samples (W1N1, W1N3, and N), the samples exhibited competitive influences, resulting in low sensitivity. The W3N1 sensor also exhibited good selectivity to H2S compared with other interfering gases, such as CO, C2H6, and NH3. This could be explained by additional semimetallic conducting effects from H2S-mediated sulfurization and lower dissociation energy of H2S.

This simple, economic, and energy-saving method could be potentially attractive for the development of various 1D–1D p–n junction composite sensors for room-temperature, low-cost, alarm-based gas sensors to detect various toxic gases, inflammable compounds, and explosives.
4. EXPERIMENTAL SECTION

4.1. Materials Synthesis and Sensor Fabrication. The WO$_3$ and NiO nanowires (denoted as W and N, respectively) were provided by Sigma Aldrich (product number 774548, 774537). To prepare the xWO$_3$-(1-x)NiO (where 0 ≤ x ≤ 1) heterojunction, the individual nanowire samples were prepared at the same concentration (0.01 M), with deionized water as the solvent. Then, the samples were mixed separately in three different volume ratios, such as 3:1 (WO$_3$/NiO), 1:1, and 1:3, denoted as W3N1, W1N1, and W1N3, respectively. Finally, the nanoheterostructure dispersions were obtained after 30 min ultrasonication. Interdigitated Au electrodes were fabricated using e-beam lithography on a silicon substrate with an SiO$_2$ thin top layer. A tiny drop of the nanowire dispersion was drop-casted on the Au electrode, and the metal-oxide nanowires bridged the Au fingers after solvent evaporation. After deposition, the pure metal-oxide nanowire sensors were annealed at 200 °C for 1 h in Ar flow (1 lpm) to improve the contacts among the sensing materials and between the sensing materials and the Au electrodes.

4.2. Characterization and Gas-Sensing Measurement. The morphologies and crystal structures of the WO$_3$ and NiO and all of the nanoheterostructures were studied using scanning electron microscopy (SEM) (Hitachi S4800) and X-ray diffraction (XRD) spectroscopy. The surface chemical composition was characterized by X-ray photoelectron spectroscopy (XPS) (HP 5930A).

For in situ XRD detection, those five powder samples were deposited onto the sample holder for X-ray scanning. For confirmation of sulfurization, the sensor chips containing sensing materials were directly placed on the sample holder for XRD analysis immediately after exposure to H$_2$S. The background signals of gold electrodes and silicon substrate of nanowires were provided by Sigma Aldrich (product number 774548, 774537).

The sensing test was performed in an air-tight chamber. A constant dc voltage was applied to the electrode gap bridged by nanowires or nanowire heterostructures. The electrical resistance was measured by a Keithley 2602 source meter. A typical gas-sensing test cycle consisted of three continuous steps: (1) compressed dry air was introduced into the sensing chamber as the baseline. (2) A target gas diluted in the background signals of gold electrodes and silicon substrate of nanowires was injected to generate the sensing signal; the exposure time for the target gas was 5 min. (3) Clean air was introduced again for sensor recovery. The sensor sensitivity ($S$) was defined as

\[ S = \frac{I_{\text{g}} - I_0}{I_0} \times 100\% \]  

where $I_0$ and $I_g$ are the currents measured in specific gas and in the air, respectively.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: jhchen@uw.edu.

ORCID
Shun Mao: 0000-0003-3319-4203
Junhong Chen: 0000-0002-2615-1347

Author Contributions
Y.W. and A.M. contributed equally to this work.

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