Heterostructured NiO/ZnO Nanorod Arrays with Significantly Enhanced H\textsubscript{2}S Sensing Performance

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Abstract: H\textsubscript{2}S gas sensors were fabricated using p-n heterojunctions of NiO/ZnO, in which the ZnO nanorod arrays were wrapped with NiO nanosheets via a hydrothermal synthesis method. When the H\textsubscript{2}S gas molecules were adsorbed and then oxidized on the ZnO surfaces, the free electrons were released. The increase in the electron concentration on the ZnO boosts the transport speed of the electrons on both sides of the NiO/ZnO p-n junction, which significantly improved the sensing performance and selectivity for H\textsubscript{2}S detection, if compared with sensors using the pure ZnO nanorod arrays. The response to 20 ppm of H\textsubscript{2}S was 21.3 at 160 \(^{\circ}\)C for the heterostructured NiO/ZnO sensor, and the limit of detection was 0.1 ppm. We found that when the sensor was exposed to H\textsubscript{2}S at an operating temperature below 160 \(^{\circ}\)C, the resistance of the sensor significantly decreased, indicating its n-type semiconductor nature, whereas when the operating temperature was above 160 \(^{\circ}\)C, the resistance significantly increased, indicating its p-type semiconductor nature. The sensing mechanism of the NiO/ZnO heterostructured H\textsubscript{2}S gas sensor was discussed in detail.

Keywords: ZnO; nanorods; NiO; p-n junction; H\textsubscript{2}S gas sensor

1. Introduction

Nanowires \([1–3]\), nanorods (NRs) \([4,5]\), nanobelts \([6,7]\), and nanotubes \([8]\) have shown good electronic or optoelectronic properties due to their special nanostructures, excellent crystallinities and oriented growth, significant quantum size effect, and optical non-linearity \([9]\). Among these, zinc oxide (ZnO) NRs are widely applied in the fields of sensors \([4,10–14]\), photocatalysis \([13]\), solar cells \([15,16]\), UV photodetectors \([17,18]\), and field emission devices \([19]\) due to their wide band gap (3.37 eV), high binding exciton energy (60 meV), excellent electricity properties, and low cost \([20,21]\). Compared with bulk ZnO materials, ZnO nanorod arrays have a large specific surface area and strong electronic transmission capability \([22]\).

Hydrogen sulfide (H\textsubscript{2}S), one of the most common toxic gases, causes serious issues in terms of human health and environmental safety \([23,24]\). The H\textsubscript{2}S concentration that is safe for human beings is about 20–100 ppb \([24]\). The U.S. Scientific Advisory Board on Toxic Air Pollutants recommends that the concentration of H\textsubscript{2}S in human environments should be controlled within <83 ppb \([25]\). Therefore, it is critical to develop a fast, precise, and reliable H\textsubscript{2}S detection method \([23]\). In recent years, the H\textsubscript{2}S gas sensor has received considerable attention for its high sensitivity, good selectivity, good reliability, low cost, and low power consumption. Many H\textsubscript{2}S gas sensors based on Fe\textsubscript{2}O\textsubscript{3}, CuO, ZnO, and CeO\textsubscript{2} semiconductors have been reported \([3,4,26–31]\). Among these metal oxides, ZnO...
nano-material is among the most studied. However, the sensing performance of the nanostructured sensors is strongly dependent on the morphology and structure of sensitive materials. To improve the performance of these nanostructured sensors, an effective method involves using surface modification. For example, Zhao et al. [32] reported that a gas sensor composed of ZnO nanofibers modified with Cu can achieve a response of 18.7 to 10 ppm H\textsubscript{2}S at 230 °C. Compound semiconductor oxides, which can form p-n heterostructures, have also been employed extensively to improve H\textsubscript{2}S sensors’ properties. For example, Kim et al. [33] reported that a gas sensor composed of ZnO NRs modified with CuO showed a response of 890 when exposed to 50 ppm H\textsubscript{2}S at 500 °C. Nickel oxide (NiO), as a typical p-type semiconductor [14], has been extensively researched in optoelectronic devices and sensors due to its ease of formation of a p-n heterojunction together with an n-type semiconductor (such as ZnO), thus achieving excellent physical and chemical properties [18,34,35]. However, few studies of NiO/ZnO p-n heterojunction nanorod arrays have been reported for detecting H\textsubscript{2}S gas.

In this paper, a p-n heterojunction structure composed of NiO nanosheets (NSs) and ZnO NRs was prepared using a hydrothermal synthesis method. It was used as a sensitive material to fabricate a gas sensor on an Al\textsubscript{2}O\textsubscript{3} ceramic tube. Excellent H\textsubscript{2}S sensing performance was attained, and the sensing mechanism was discussed in detail.

2. Experiment

All the chemicals used were analytical grade reagents and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the standard gases used were purchased from NIMTT Measurement and Testing Technology Co. Ltd. (Chengdu, China). The crystalline phase of samples was characterized by X-ray diffractometer (XRD, Dmax-2500, Rigaku, Tokyo, Japan) and transmission electron microscope (TEM, JEM-2200FS, Jeol, Tokyo, Japan). The morphologies and element contents of the samples were observed using scanning electron microscope (SEM, Inspect F50, ThermoFisher, Hillsboro, OR, USA) and energy dispersive spectrometer (EDS, Inspect F50, ThermoFisher, Hillsboro, OR, USA). UV–visible spectrophotometer (UV-2600, Shimadzu, Kyoto, Japan) was used to study the band-gap energies of the samples. X-ray photoelectron spectroscopy (XPS, XSAM800, Kratos, Manchester, UK) was measured to analyze valence states of the elements in the samples.

2.1. Growth of ZnO NRs

A hydrothermal synthetic method was used to grow ZnO NRs. The typical procedure was described below: 1.646 g (7.5 mmol) zinc acetate dihydrate of was dissolved into 25 mL 2-methoxyethanol, and then 0.45 mL ethanolamine was added. The above solution was stirred for 1 h at 60 °C to achieve a sol, which was then uniformly coated onto the cleaned Al\textsubscript{2}O\textsubscript{3} tubes and annealed at 300 °C for 10 min. The process was repeated twice and annealed at 450 °C for 1 h to form ZnO seeds layer on the Al\textsubscript{2}O\textsubscript{3} tubes. We mixed 40 mL (5 mM) zinc nitrate aqueous solution and 40 mL (5 mM) hexamethylenetetramine, and then the solution was placed in a Teflon-lined stainless steel autoclave. The Al\textsubscript{2}O\textsubscript{3} tubes covered by the ZnO seeds layer were also placed in the autoclave. After hydrothermal reaction at 90 °C for 5 h, a ZnO NR layer formed on the Al\textsubscript{2}O\textsubscript{3} tubes. Finally, the sample was rinsed three times in deionized water and dried in an oven at 80 °C.

2.2. Preparation of NiO/ZnO Heterostructures

Nickel acetate tetrahydrate (1.866 g; 7.5 mmol) and 0.45 mL ethanolamine were added into 25 mL 2-methoxy ethanol, then a uniform sol was obtained by stirring for 3 h at room temperature. The sol was uniformly coated onto the ZnO NRs’ surfaces, and then annealed at 300 °C for 10 min. The process was repeated again and then annealed at 450 °C for 1 h to obtain a NiO seeds layer. Nickel nitrate (40 mL; 5 mM) and hexamethylenetetramine (40 mL; 5 mM) were mixed into a uniform solution and transferred into the Teflon-lined stainless steel autoclave, and the Al\textsubscript{2}O\textsubscript{3} tubes with ZnO NRs were also placed in the autoclave, which was heated at 90 °C for 3 h. The Al\textsubscript{2}O\textsubscript{3} tubes were removed and rinsed three times in deionized water and dried in the oven at 80 °C to obtain a NiO/ZnO heterostructure sample.
3. Results and Discussion

3.1. Characterizations of Pure ZnO Nanorods and NiO/ZnO Heterostructures

SEM images of pure ZnO NRs and NiO/ZnO heterostructures are shown in Figure 1. ZnO NRs are uniform with an average diameter of about 150 nm, as shown in Figure 1a. The quasi-hexagonal cross-section of ZnO NRs indicates that ZnO NRs are preferentially oriented in a direction of [0001], indicating a wurtzite crystal structure. The SEM images of the NiO/ZnO heterostructures sample shown in Figure 1b,c indicate that the NiO NSs shows a netlike morphology on the top of ZnO NRs, and fills some gaps between ZnO nanorods, which facilitated the formation of p-n heterostructures at their interfaces. Figure 1d depicts the EDS spectrum of NiO/ZnO heterostructures, based on which the atomic content of nickel was estimated to be 2.41%.

![Figure 1](image-url)

**Figure 1.** SEM images of (a) pure ZnO NRs, (b,c) NiO/ZnO heterostructures and (d) EDS of NiO/ZnO heterostructures.

XRD pattern of pure ZnO NRs is shown in Figure 2. The ZnO NRs are in a hexagonal wurtzite crystal structure with lattice constants $a = 3.252 \, \text{Å}$ and $c = 5.201 \, \text{Å}$ (JCPDS file No. 36-1451). The three main peaks are at (0 0 2), (1 0 1), and (1 0 3). As the (0 0 2) diffraction peak is the strongest, we conclude that ZnO NRs grow preferentially along this direction with high crystallinity. For the NiO/ZnO heterostructures, no peaks corresponding to NiO are detected and the XRD peak positions of ZnO do not shift because the quantity of NiO is less than the XRD detection limit, estimated to be at 5%.
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Figure 2. XRD patterns of ZnO NRs.

TEM analysis was used to further investigate the NiO/ZnO heterostructures. Figures 3a–d show the TEM bright-field image of NiO/ZnO heterostructures and elemental mappings of Zn, Ni, and O. Zn is concentrated on the ZnO NRs and Ni is diffused over the interfaces of the ZnO NRs network, which means that the gaps and surfaces of ZnO NRs are covered with NiO NSs.

Figure 3. (a) TEM bright-field image of NiO/ZnO heterostructures and (b–d) elemental mapping of NiO/ZnO heterostructures.

Figure 4a shows the survey XPS spectrum of NiO/ZnO heterostructures, which indicates the existence of Zn, Ni, and O. Figure 4b shows the high resolution Zn 2p peak, which has been deconvoluted into peaks at 1021.4 eV and 1044.6 eV corresponding to Zn 2p\(_{3/2}\) and Zn 2p\(_{1/2}\), respectively. The results reveal the existence of Zn\(^{2+}\) in ZnO [18,36]. Figure 4c shows the Ni 2p spectrum of NiO/ZnO heterostructures. The peaks at the binding energies of 855.6 eV and 873.2 eV correspond to Ni 2p\(_{3/2}\) and Ni 2p\(_{1/2}\) of NiO, respectively. Apart from these, two satellite peaks located at the binding energies of 861.5 eV and 879.3 eV reflect Ni 2p\(_{3/2}\) and Ni 2p\(_{1/2}\), respectively, which proves the existence of...
Ni$^{2+}$ [18]. The O 1s XPS spectrum of the NiO/ZnO heterostructures is shown in Figure 4d. The two peaks that deconvoluted at 530.8 eV and 532.3 eV correspond to the metal oxides (Zn-O bonds and Ni-O bonds) and the chemisorbed hydroxyl (O-H bonds) on the surface of NiO/ZnO heterostructures, respectively [37,38].

Figure 4. XPS spectra of (a) full spectrum, (b) Zn 2p, (c) Ni 2p, and (d) O 1s.

Figure 5 shows the UV-visible absorption spectra of ZnO NRs, NiO NSs, and NiO/ZnO heterostructures at room temperature. The band gap is calculated using Equation (1) [39]:

$$\alpha h\nu = C(h\nu - E_g)^{1/2}$$  (1)

where $\alpha$ is the absorption coefficient, $C$ is a constant, and $E_g$ is the band gap of the semiconductors.

Figure 5. (a) UV-visible absorption spectra and (b) plot of $(\alpha h\nu)^2$ vs. $h\nu$ of ZnO NRs, NiO NSs, and NiO/ZnO heterostructures.
The band gap energy absorption edges of ZnO NRs and NiO NSs are 385 nm and 317 nm, which correspond to their band gaps of 3.20 eV and 3.91 eV, respectively. For the NiO/ZnO heterostructures, due to the coupling of ZnO and NiO, more electrons are freely transferred from NiO with a higher Fermi level to ZnO with a lower level, which promotes the separation of holes and electrons and then effective heterojunctions are formed. Therefore, the band gap of NiO/ZnO heterostructures decreases to 3.05 eV, and the absorption edge showed a red shift from 385 nm to 406 nm [40].

3.2. Gas Sensing Properties

The sensors were placed in a four-liter chamber to test their sensing performance, and the test bias voltage was fixed during the gas sensing process. To allow the sensors to work at different operation temperatures, a heating wire was placed inside the ceramic tube. The response (R) of the sensors was defined as the ratio of R_a to R_g (when the resistance is reduced after the sensor is exposed to the target gas) or R_g to R_a (when the resistance is increased after the sensor is contacted with the targeted gas), where R_a is the resistance of the sensor measured in air and R_g is the resistance of the sensor when it contacts the gas detected.

Current density-voltage characterization curves of pure ZnO NRs, pure NiO NSs, and NiO/ZnO heterostructures were measured at 160 °C, and the results are shown in Figure 6a. All the data exhibit Ohmic behavior, and current density-voltage characteristics display linear patterns.

Figure 6. (a) Current density-voltage characteristics at 160 °C and (b) responses of NiO/ZnO-heterostructures-based sensor to 1 ppm of H_2S at different operating temperatures.

To investigate the optimum working temperatures of the gas sensor, we conducted the sensing process from room temperature to 300 °C. Figure 6b shows the responses of the NiO/ZnO-heterostructures-based sensor when exposed to 1 ppm of H_2S at different working temperatures. As temperature increased, the response increased first and then decreased. The response value (R = 5) reached a maximum at 160 °C. Therefore, we concluded that for NiO/ZnO-heterostructures-based sensors, the optimal temperature is ~160 °C.

Figure 7 shows the dynamic response curves of the sensors for detecting H_2S at 160 °C. When the concentration of H_2S is 20 ppm, the response of pure ZnO NRs-based sensor is 2.7, whereas the response of NiO/ZnO-heterostructures-based sensor shows an improved response of 21.3. When the concentration of H_2S is reduced to 0.1 ppm, the NiO/ZnO sensor still has an obvious response of 1.9, whereas the pure ZnO NRs-based sensor has almost no response. Apart from this, the pure NiO NSs-based sensor was also tested at 160 °C in 20 ppm H_2S, and the response was only ~1.4, as shown in Figure 7d. This indicates that the enhancement of sensor’s performance is mainly due to the formation of NiO/ZnO heterostructures.
Figure 7 shows the dynamic response curves of the sensors for detecting H$_2$S at 160 °C. When the concentration of H$_2$S is 20 ppm, the response of pure ZnO NRs-based sensor is 2.7, whereas the response of NiO/ZnO-heterostructures-based sensor shows an improved response of 21.3. When the concentration of H$_2$S is reduced to 0.1 ppm, the NiO/ZnO sensor still has an obvious response of 1.9, whereas the pure ZnO NRs-based sensor has almost no response. Apart from this, the pure NiO NSs-based sensor was also tested at 160 °C in 20 ppm H$_2$S, and the response was only ~1.4, as shown in Figure 7d. This indicates that the enhancement of sensor’s performance is mainly due to the formation of NiO/ZnO heterostructures.

Figure 7. Dynamic response curves upon exposure to H$_2$S with different concentrations at 160 °C exhibited by sensors based on: (a) pure ZnO NRs and (b) NiO/ZnO, and (c) responses histogram of sensors and (d) pure NiO NSs.

Based on the literature search, the performance of the H$_2$S gas sensor based on different semiconductor materials or composite materials with various nanostructures are listed in Table 1. The NiO/ZnO heterostructures synthesized in this work showed a good response for H$_2$S at a lower temperature, and its limit of detection is as low as 0.1 ppm.

Table 1. Comparison of the H$_2$S gas sensors based on various semiconductors.

<table>
<thead>
<tr>
<th>Material</th>
<th>Detection Limit (ppm)</th>
<th>Gas Conc. (ppm)</th>
<th>T (°C)</th>
<th>Response ($R_a/R_g$ or $R_g/R_a$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO Nanorods</td>
<td>-</td>
<td>100</td>
<td>23</td>
<td>23</td>
<td>[26]</td>
</tr>
<tr>
<td>CuO-ZnO Nanorods</td>
<td>-</td>
<td>100</td>
<td>39</td>
<td>39</td>
<td>[41]</td>
</tr>
<tr>
<td>NiO Thin film</td>
<td>1</td>
<td>50</td>
<td>92</td>
<td>20.6</td>
<td>[25]</td>
</tr>
<tr>
<td>Au-NiO Yolk-shell</td>
<td>1.25</td>
<td>5</td>
<td>400</td>
<td>44.2</td>
<td>[42]</td>
</tr>
<tr>
<td>CuO-NiO Microspheres</td>
<td>10</td>
<td>100</td>
<td>260</td>
<td>47.6</td>
<td>[43]</td>
</tr>
<tr>
<td>CuO-ZnSnO$_3$ Nanowires</td>
<td>25</td>
<td>100</td>
<td>100</td>
<td>2.2</td>
<td>[44]</td>
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<tr>
<td>NiO/ZnO Heterostructures</td>
<td>0.1</td>
<td>20</td>
<td>160</td>
<td>21.3</td>
<td>This work</td>
</tr>
</tbody>
</table>

To study the sensors’ selectivity, the dynamic response curves of a NiO/ZnO sensor exposed to H$_2$S and other gases (such as NH$_3$, C$_2$H$_4$O, NO$_2$, and CO) for the same concentration of 20 ppm were measured at 160 °C. The results are shown in Figure 8a. For the NiO/ZnO-heterostructures-based sensor, if compared with the responses of 21.3 obtained when testing with H$_2$S, the responses of several other gases were negligible. Therefore, the NiO/ZnO-heterostructures-based sensor has an excellent selectivity toward H$_2$S.
Figure 9. Schematic model for sensors exposed to H$_2$S: (a) pure ZnO and (b) NiO/ZnO heterostructures.
As the surface of ZnO NRs are modified by the NiO NSs, their responses to H\textsubscript{2}S are enhanced significantly. The reasons for this can be explained as follows: (1) The network-like structure increases the adsorption areas of oxygen ions. (2) The low valence Ni\textsuperscript{2+} can be oxidized easily to the high valence Ni\textsuperscript{3+} \cite{13, 48, 49}; thus, oxygen ions are quickly adsorbed onto the sensor’s surface. (3) Due to the good contact between NiO and ZnO, a concentration difference is generated between holes and electrons at their interfaces. This concentration difference causes carrier diffusion, thus causing the energy band to bend in the depletion layer. When the carrier diffusion achieves an equilibrium condition, a space charge region is formed at their interfaces and a uniform Fermi level (EF) was obtained, as shown in Figure 10.

![Figure 10. Energy band structure of p-NiO/n-ZnO heterostructures.](image)

When the NiO/ZnO-heterostructures-based sensor is in contact with H\textsubscript{2}S gas molecules at 160 °C, H\textsubscript{2}S is mainly oxidized by the oxygen ions absorbed on the surface of ZnO NRs, releasing electrons into ZnO and increasing the concentration of the majority carrier (electrons). Therefore, the resistance of the sensor is reduced. For the semiconductor material, the holes decrease with the increase in electrons since \( n_0 \times p_0 = n_i^2 \), where \( n_0 \) is the electron concentration, \( p_0 \) is the holes’ concentration, and \( n_i \) is the intrinsic carrier concentration. Therefore, the increase in electrons enhances the fast transport of electrons across the p-n junction. The electrons move to recombine with the holes, thus reducing the thickness of the depletion layer at the interfaces between NiO and ZnO \cite{13, 14}. Therefore, the resistance of sensor decreases and its conductivity increases. The schematic model for the sensing mechanism is shown in Figure 9b.

Figure 11 shows the resistance variation of NiO/ZnO-heterostructures-based sensor to 1 ppm H\textsubscript{2}S at 160 °C and 240 °C. Note that the resistance variation of NiO/ZnO-heterostructures-based sensor to 1 ppm H\textsubscript{2}S at 160 °C and 240 °C shows a completely opposite trend of dynamic responses at the lower and higher temperatures, with the critical boundary temperature being 160 °C.
When the temperature is higher than 160 °C, H₂S mainly reacts with the oxygen ions (O²⁻) on the surface of NiO NSs [50], thus releasing electrons into the NiO. Electrons recombine with holes, thus leading to a reduction in the majority carriers (holes) of NiO. The decrease in holes restrains the movement of electrons on both sides of the p-n junction. Therefore, the conductivity of the sensor is reduced. Besides, the dissociation of the reducing gas (e.g., H₂S) causes the formation of crystal defects and deteriorates the conductive three-dimensional network structure. Consequently, the resistance of the sensor is increased. At higher temperatures, sulfur atoms are also decomposed from H₂S molecules, which are then diffused into ZnO NRs and form ZnS [4,51]. Therefore, random structures of the n-p-n-type junction can be formed at the interfaces among ZnS, NiO, and ZnO, which leads to the increased barrier energy and also the sensor’s resistance.

4. Conclusions

A H₂S semiconductor gas sensor based on NiO/ZnO heterostructures was fabricated and tested and its key sensing mechanisms were investigated. Comparing with the pure ZnO NRs, the sensing performance of the NiO/ZnO-heterostructures-based sensor was improved significantly within the concentration range of 0.1 to 20 ppm. The sensor has very good selectivity toward H₂S compared to NH₃, C₂H₄O, NO₂, and CO, which can be attributed to the formation of p-n junction effects at the interfaces between NiO and ZnO. When the sensor is exposed to H₂S at temperatures above 160 °C, the performance of the NiO/ZnO-heterostructures-based sensor changes from n-type semiconductor to p-type, and a sensing mechanism based on the p-n junctions was proposed.

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