Supporting Information

SnS$_2$/SnS p-n heterojunctions with an accumulation layer for ultrasensitive room-temperature NO$_2$ detection

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Fig. S1. Schematic diagram of the sensor measurement.

Fig. S2. SEM images of (a) SnS$_2$/SnS-6 and (b) SnS$_2$/SnS-1.

Table S1. EDS elemental analysis of SnS$_2$/SnS-1, SnS$_2$/SnS-3, and SnS$_2$/SnS-6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S (%)</th>
<th>Sn (%)</th>
<th>S/Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnS$_2$/SnS-1</td>
<td>55.56</td>
<td>44.44</td>
<td>1.15</td>
</tr>
<tr>
<td>SnS$_2$/SnS-3</td>
<td>61.13</td>
<td>38.87</td>
<td>1.59</td>
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<tr>
<td>SnS$_2$/SnS-6</td>
<td>63.51</td>
<td>36.49</td>
<td>1.74</td>
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Fig. S3. TEM (top) and HRTEM (bottom) images of SnS$_2$/SnS heterostructures with different molar ratios of Sn/S in the precursors, (a) (b) SnS$_2$/SnS-6, (c) (d) SnS$_2$/SnS-3, and (e) (f) SnS$_2$/SnS-1.

Fig. S4. SEM images of (a) pristine SnS$_2$ and (b) pristine SnS.
**Fig. S5.** Survey XPS spectrum of the hierarchical SnS$_2$/SnS-3 heterostructures.

**Fig. S6.** (a) UV-vis diffuse reflectance spectra (DRS) and (b) digital graphs of SnS, SnS$_2$/SnS-3, and SnS$_2$. In Fig. S6a, SnS$_2$ shows a significant increase in the absorption at wavelengths shorter than 500 nm. While SnS shows a wide absorption range with absorbance peak around 800 nm. For SnS$_2$/SnS-3, the curve reflects the combination of spectral response of SnS$_2$ and SnS: it has two absorbance peaks located at around 450 nm and 800 nm, corresponding to the bandgaps of SnS$_2$ and SnS. Moreover, the heterostructure of SnS$_2$/SnS-3 is also implied by the sample color (Fig. S6b), which is between yellow of SnS$_2$ and black of SnS.
Fig. S7. Dynamic response-recovery curve of the SnS$_2$/SnS-3 sensor exposure to 4 ppm NO$_2$ with sensing time of 1000 s.

Fig. S8. Cross-sectional-view SEM images of the SnS$_2$/SnS-3 sensor with different thickness: (a) ~20 μm, (b) ~14 μm, (c) ~6 μm, and their sensing response curves toward 1 ppm NO$_2$ at room temperature (d).
**Fig. S9.** I-V curve of the SnS$_2$/SnS-3 sensor with different thickness.

**Table S2.** The recovery time of the SnS$_2$/SnS-3 sensor toward various concentrations of NO$_2$ at room temperature. The recovery time is calculated by the time difference between reaching the final response point and the 90% recovery point.

<table>
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<tr>
<th>Conc. (ppm)</th>
<th>0.125</th>
<th>0.25</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
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<tr>
<td>Response time (s)</td>
<td>391</td>
<td>370</td>
<td>375</td>
<td>300</td>
<td>328</td>
<td>365</td>
<td>369</td>
<td>373</td>
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<tr>
<td>Recovery time (s)</td>
<td>1567</td>
<td>1579</td>
<td>1590</td>
<td>1379</td>
<td>1332</td>
<td>1216</td>
<td>1065</td>
<td>997</td>
</tr>
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</table>

**Fig. S10.** The response of the SnS$_2$/SnS-3 sensor to 0.075, 0.100, and 0.125 ppm NO$_2$ at room temperature.
**Fig. S11.** The response and recovery curve of the SnS$_2$/SnS-3 sensor after aging 0.5 month and 4 months to 4 ppm NO$_2$ at room temperature.

**Fig. S12.** Work functions of SnS$_2$ (5.07 eV), SnS/SnS$_2$-3 (4.89 eV), and SnS (4.79 eV) measured by Kelvin probe based on 218 data points.

**Fig. S13.** Working resistance of the SnS$_2$, SnS$_2$/SnS-6, SnS$_2$/SnS-3, SnS$_2$/SnS-1, and SnS sensors.
Fig. S14. *I-V* curve of the pristine SnS$_2$, SnS$_2$/SnS-6, SnS$_2$/SnS-3, SnS$_2$/SnS-1, and pristine SnS sensors.

Fig. S15. Nitrogen adsorption/desorption isotherms of (a) SnS$_2$/SnS-1, (b) SnS$_2$/SnS-3, (c) SnS$_2$/SnS-6, (d) pristine SnS$_2$, and (e) their corresponding Brunauer-Emmett-Teller (BET) surface area.