

Electronic Supplementary Information

Heterostructures between tin-based intermetallic compound and layered semiconductor for gas sensing

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Experiment section

Materials. Thiourea ($\text{CS}(\text{NH}_2)_2$, 99%) and tin tetrachloride hydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 99.5%) were purchased from Sigma Aldrich. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%) was purchased from J&K chemical. Oleic acid (99.5%) n-octylamine (99.5%), tin dichloride hydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 99.5%), ascorbic acid (99.5%) and platinum acetylacetonate ($\text{Pt}(\text{acac})_2$, 99.5%) were purchased from Aladdin. The gaseous analyses ($\text{C}_3\text{H}_6\text{O}$, NH_3 , CH_2O , C_7H_8 and NO_2) which were diluted with air at concentrations of 1000 ppm were purchased from Nanjing Teqi Co., Ltd. All chemicals were used as received without further purification. The deionized (DI) water was purified using Milli-Q3 System (Millipore, France).

Preparation of SnS_2 nanoplates. In a typical process, 0.25 mmol of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 3.75 mmol of $\text{CS}(\text{NH}_2)_2$ were dissolved in 19.45 mL DI water and stirred for 2 h to form a homogeneous solution. This solution was transferred to a 25 mL Teflon-lined stainless-steel autoclave, heated to 220 °C in an electrical oven and then maintained at this temperature for 12 h before being cooled down naturally to room temperature. The obtained product was centrifuged at 8000 rpm for 10 min, and the precipitate was washed with DI water for three times before further characterization.

Preparation of Pt_3Sn nanoparticles. In a typical process, 15 mg $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 35.6 mg ascorbic acid and 10 mg $\text{Pt}(\text{acac})_2$ were dissolved in a mixture of 1 mL oleic acid and 10 mL n-octylamine to form a homogeneous solution. 4.95 mL of this mixed solution was transferred to a 5 mL Teflon-lined stainless-steel autoclave, heated to 180 °C in an electrical oven and then maintained at this temperature for 6 h before being cooled down naturally to room temperature. The obtained product was centrifuged and the precipitate was washed with ethanol and cyclohexane for three times before further characterization.

Preparation of $\text{SnS}_2/\text{Pt}_3\text{Sn}$ heterostructures. Typically, 1 mL of the as-prepared SnS_2 dispersion (with a concentration of 12 g/L) was centrifuged and washed sequentially

with a mixed solution of ethanol and oleic acid (volume ratio of 1:1) and then a mixed solution of ethanol, oleic acid and n-octylamine (volume ratio of 1:1:1), and finally redispersed in a mixture of 1 mL oleic acid and 10 mL n-octylamine together with 10 mg Pt(acac)₂, 15 mg SnCl₂·2H₂O and 35.6 mg ascorbic acid to form a homogenous solution. 4.95 mL of this solution was then transferred to a 5 mL Teflon-lined stainless-steel autoclave, heated to 180 °C in an electrical oven and then maintained at this temperature for 6 h before being cooled down naturally to room temperature. The obtained product was centrifuged and the precipitate was washed with ethanol for three times before further characterization.

Characterizations. Transmission electron microscope (TEM, JEOL 2100plus, Japan), scanning electron microscope (SEM, JEOL JSM-7800F, Japan), and high-resolution transmission electron microscope (HRTEM, JEOL 2100F, Japan) coupled with energy dispersive X-ray (EDX) spectroscope were used to investigate the compositional, morphological and structural properties of the sample. X-ray diffraction (XRD, Rigaku Smart Lab, Japan) was performed using the CuK α radiation ($\lambda = 1.54 \text{ \AA}$). Ultraviolet photoelectron spectrometer (UPS, PHI 5000 VersaProbe, Japan) measurement was carried out to study the electronic work function of metallic materials.

Gas sensing tests. Gas sensors were fabricated based on SnS₂ nanoplates, Pt₃Sn NPs and SnS₂/Pt₃Sn heterostructures respectively for sensing various gases, including C₃H₆O, NH₃, CH₂O, C₇H₈ and NO₂. Typically, a drop of 100 μ L aqueous solution containing 10 mM as-prepared SnS₂, Pt₃Sn or SnS₂/Pt₃Sn was drop-casted onto an Au interdigitated electrode (with 0.1 mm spacing over a 2 \times 1 cm² area, Changchun Mega Borui Technology Co., Ltd) and then dried in an oven at 60 °C. The gas sensing test was performed in an air/N₂-tight chamber with electrical feedthroughs at room temperature (normally 25 °C). A constant current was applied to the sensor electrode, and the variation of the sensor resistance was monitored and recorded with the changes in the gas environment using a data acquisition system (34972A, Agilent) with a 20 channel multiplexer (34901, Agilent). A typical sensing measurement cycle consists of

three sequential steps: (1) an air or N₂ flow was introduced into the chamber to record a baseline resistance (R₀); (2) a target gas, e.g., NO₂, balanced in air was introduced, and the concentration increased with progressive cycles; and (3) after a certain time of exposure, the resistance of the sensor was recorded as R_a, and the target gas was then replaced by air to allow the resistance of the sensor to return to R₀. All gas flows were set at 500 sccm, precisely controlled by using mass-flow controllers. The sensing performance of Pt₃Sn NPs and Pt₃Sn/SnS₂ heterostructures were measured in air to demonstrate their potential for practical use. However, because SnS₂ nanoplates showed very poor conductivity in air whose resistance was beyond our measurement range, gas sensing for SnS₂ was only measured in N₂.

DFT calculations. First-principles calculations based on density functional theory (DFT) were performed with the Cambridge Serial Total Energy Package (CASTEP) in Materials Studio (Version 8.0) of Accelrys Inc.¹ Generalized Gradient Approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) method was used in the approximation of the exchange–correlation part.^{2,3} An ultrasoft pseudopotential was applied and the cut-off energy was set to 300 eV. The Brillouinzone k-point sampling was performed in a 3 × 4 × 1 Monkhorst–Pack scheme. The convergence tolerance criteria for self-consistent field, energy, maximum force, maximum stress, and maximum displacement were set to 2.0 × 10⁻⁶ eV/atom, 2.0 × 10⁻⁵ eV/atom, 0.05 eV/Å, 0.1 GPa and 0.002 Å. To modeling NO₂ adsorption on (001)SnS₂, (100)Pt₃Sn, (110)Pt₃Sn and (111)Pt₃Sn layers, 3×3×2, 2×2×2, 2×2×2 and 2×2×2 supercells were used, respectively.

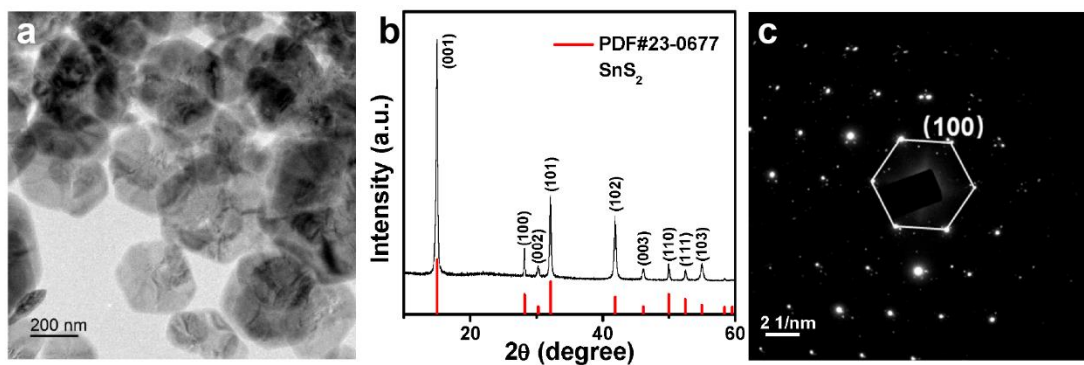


Fig. S1 (a) TEM image, (b) XRD pattern and (c) SAED pattern of SnS₂ nanoplates.

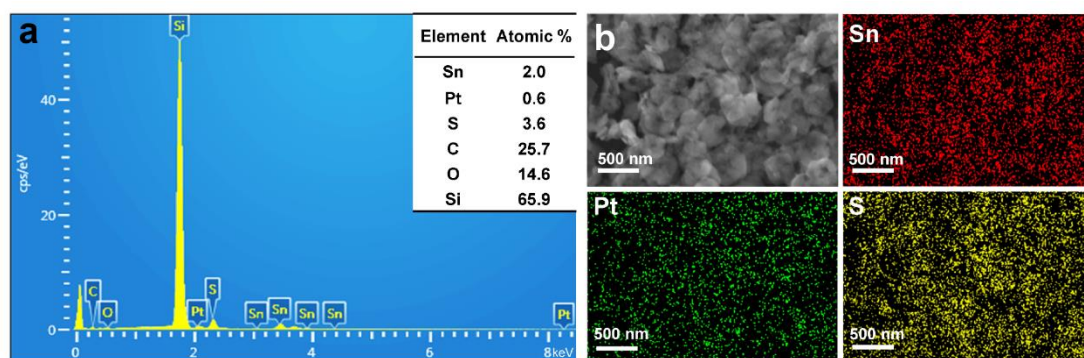


Fig. S2 (a) EDS spectrum and (b) EDS mapping of as synthesized SnS₂/Pt₃Sn heterostructures.

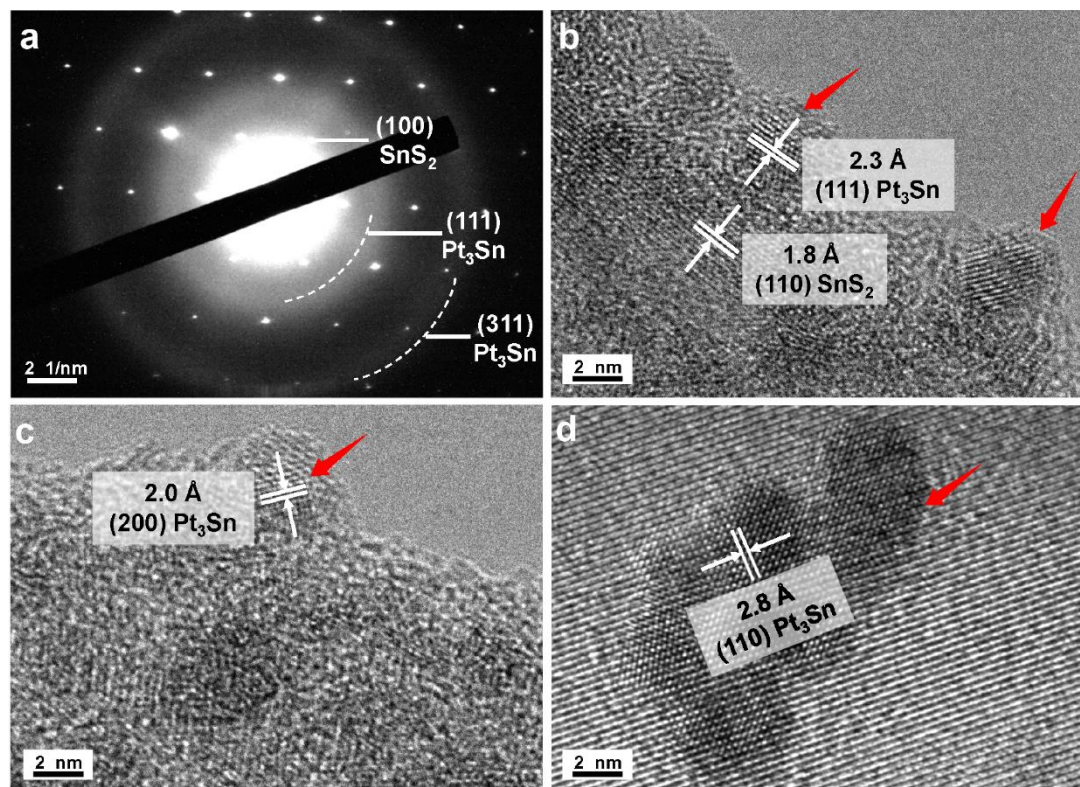


Fig. S3 (a) SAED pattern of a SnS₂/Pt₃Sn heterostructure and (b-d) HRTEM images of SnS₂/Pt₃Sn

heterostructure, revealing some Pt₃Sn particles with lattice fringes corresponding to (111), (200) and (110) planes. Arrows are used to point out Pt₃Sn NPs.

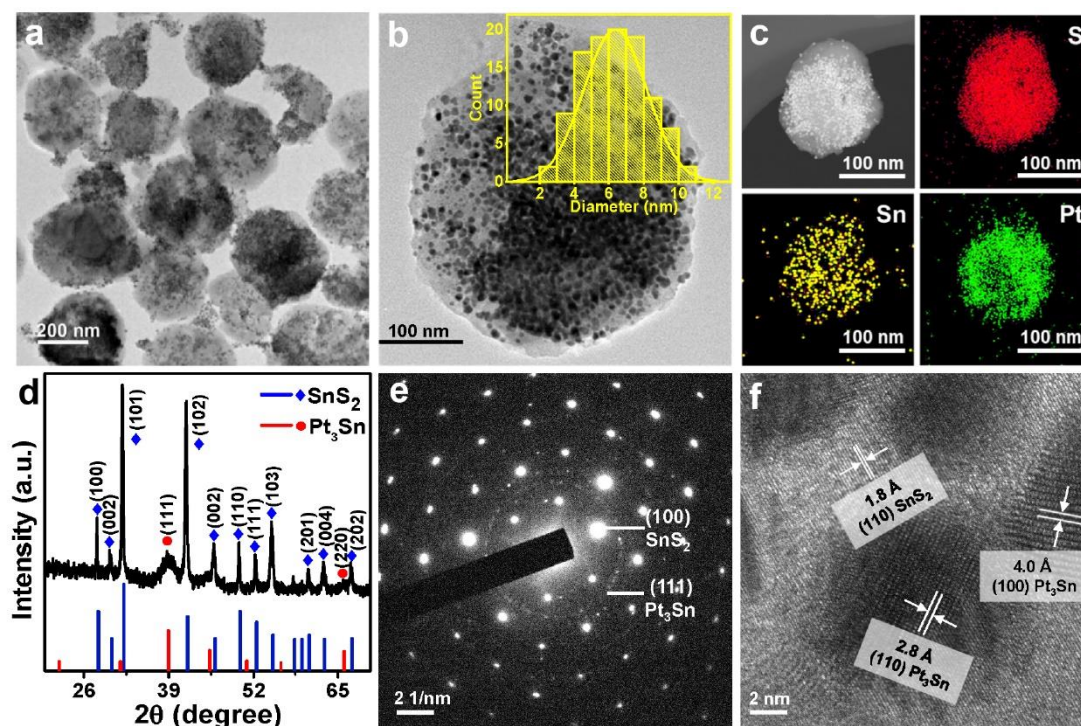


Fig. S4 Morphology, composition and crystal structure analyses of SnS₂/Pt₃Sn heterostructures prepared when SnCl₂·2H₂O was not introduced to the growth solution of Pt₃Sn. (a) Representative TEM image of SnS₂/Pt₃Sn heterostructures. (b) An enlarged TEM image of a SnS₂/Pt₃Sn heterostructure. Inset: size distribution of Pt₃Sn NPs. (c) EDS mapping of a typical SnS₂/Pt₃Sn heterostructure. (d) XRD pattern of the SnS₂/Pt₃Sn heterostructures. (e) SAED pattern of a SnS₂/Pt₃Sn heterostructure along the [001] SnS₂ zone axis. (f) HRTEM image of a small area of a SnS₂/Pt₃Sn heterostructure.

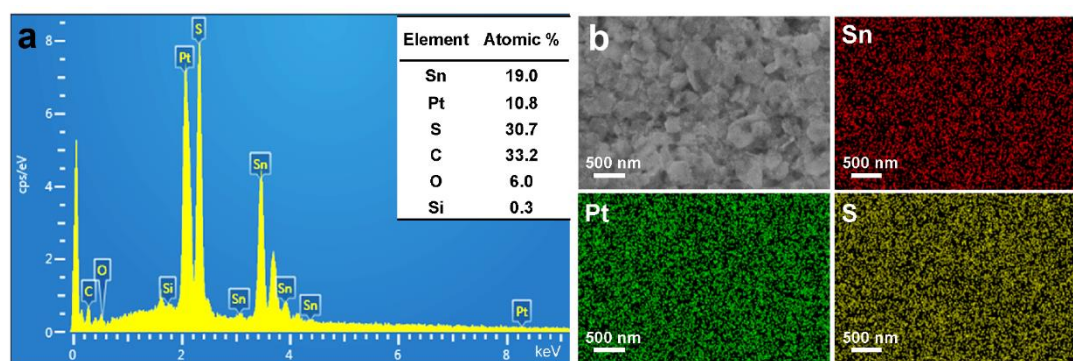


Fig. S5 EDS analysis of the SnS₂/Pt₃Sn heterostructures when SnCl₂·2H₂O was not introduced to the growth solution of Pt₃Sn. Based on the stoichiometric ratios of Pt₃Sn (Pt:Sn = 3:1) and SnS₂ (Sn:S = 1:2), their content ratio in the heterostructure can be estimated as Pt₃Sn : SnS₂ = 3.6:15.4 or

1:4.3.



Fig. S6 Photograph of an interdigitated electrode with deposited SnS₂/Pt₃Sn for gas sensing.

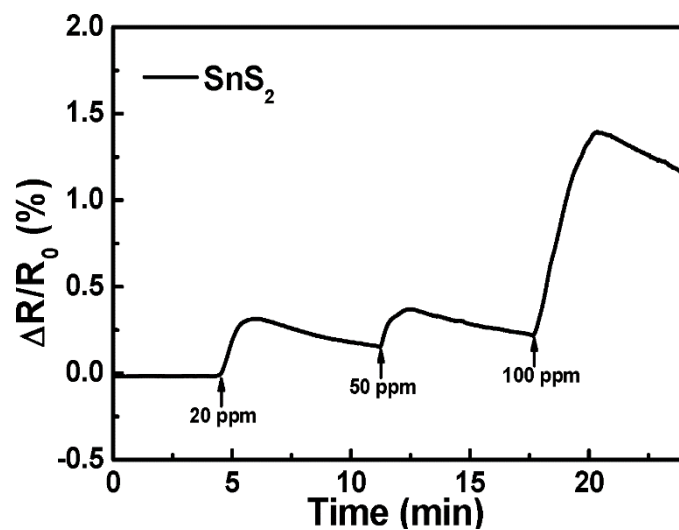


Fig. S7 Dynamic sensing performance of a NO₂ sensor fabricated based on SnS₂ nanoplates.

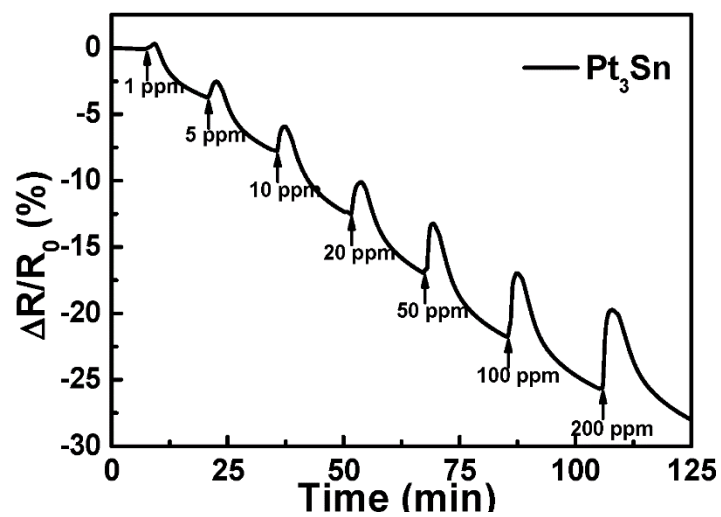


Fig. S8 Dynamic sensing performance of a NO₂ sensor fabricated based on Pt₃Sn NPs.

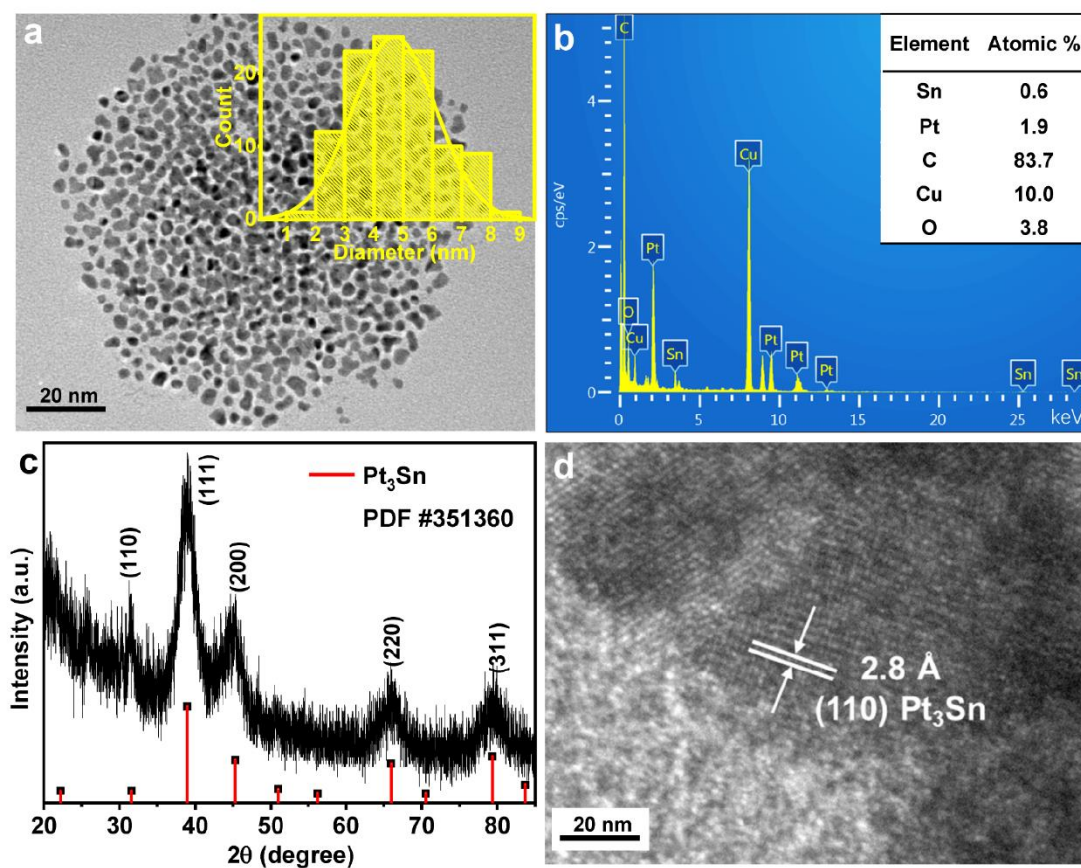


Fig. S9 (a) TEM image, (b) EDS spectrum, (c) XRD pattern and (d) HRTEM image of Pt₃Sn NPs. The TEM image shows that the NPs have an average diameter of ~4.8 nm. The EDS analysis result indicates that the atomic ratio of Pt and Sn is about 3:1. The XRD pattern of the NPs matches with the standard pattern for Pt₃Sn (JCPDS NO.35-1360). The observed lattice spacing of 0.28 nm in the HRTEM image can be assigned to the (110) planes of Pt₃Sn.

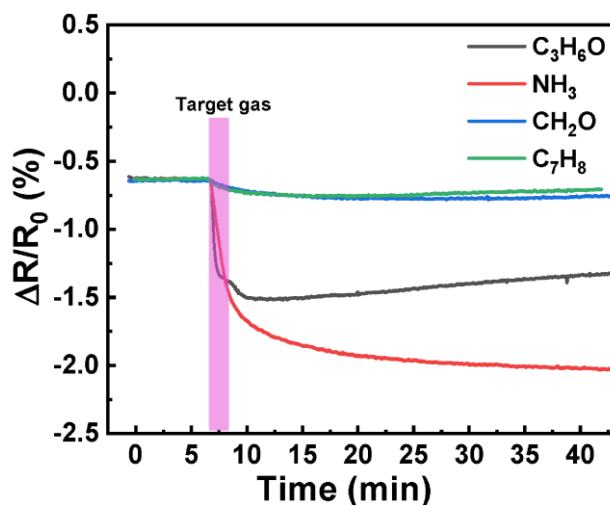


Fig. S10 The response of SnS₂/Pt₃Sn based sensor to NO₂ and other several gas species such as C₃H₆O, NH₃, CH₂O, C₇H₈, NO₂ at a concentration of 50 ppm at room temperature (the target gas was introduced for 2 min).

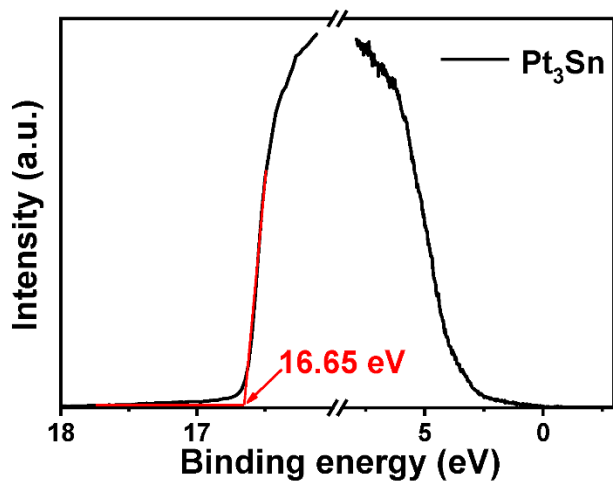


Fig. S11 UPS analysis of the work function (ϕ) of Pt₃Sn, which is determined as 4.55 eV.

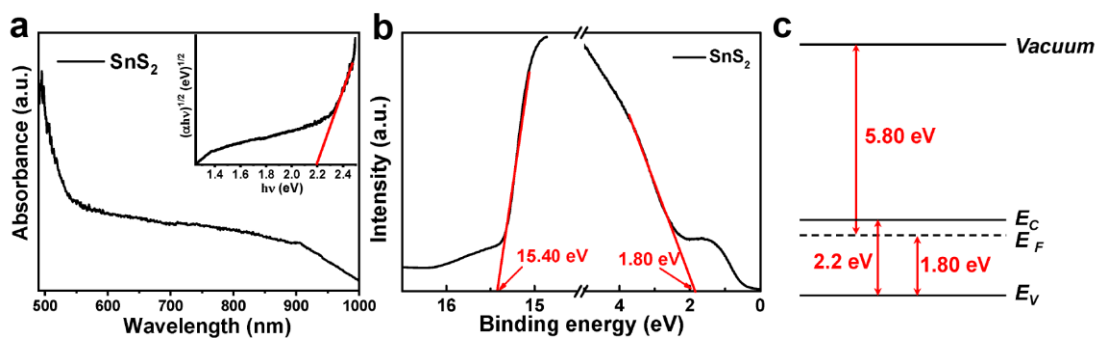


Fig. S12 (a) UV-Vis absorption spectrum of SnS₂ nanoplates. (b) UPS analysis of SnS₂, whose work function (ϕ) is estimated as 5.80 eV. (c) The diagrams of SnS₂ conduction and valence band position.

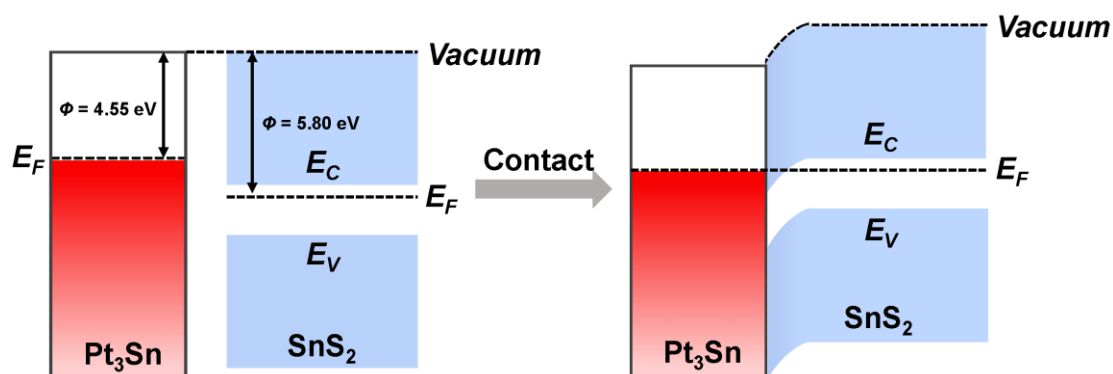


Fig. S13 Schematic illustration showing the band diagram of SnS₂/Pt₃Sn before and after contact at equilibrium.

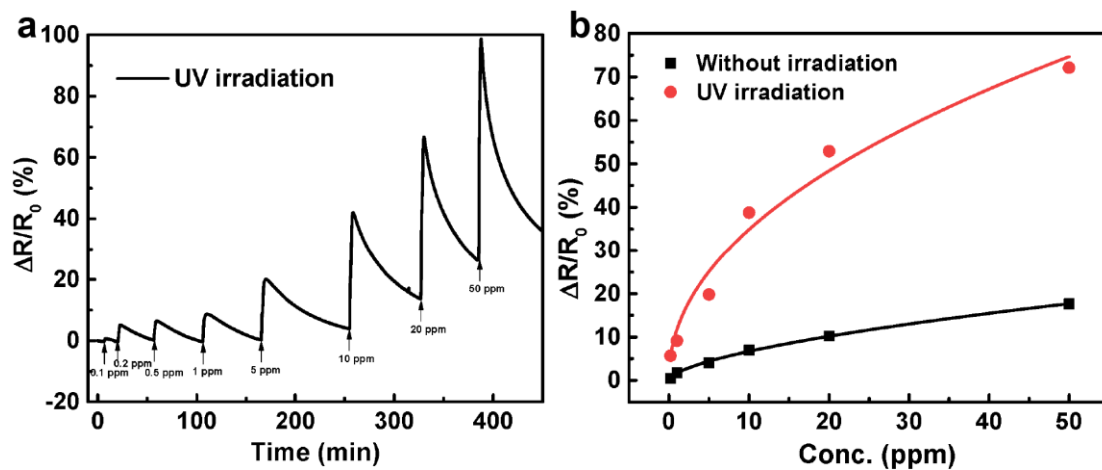


Fig. S14 (a) Dynamic sensing performance of a NO_2 sensor fabricated based on $\text{SnS}_2/\text{Pt}_3\text{Sn}$ heterostructure under UV irradiation (365 nm). (b) Change of resistance of $\text{SnS}_2/\text{Pt}_3\text{Sn}$ based sensors under UV irradiation and without UV irradiation.

Table S1 Comparison of the room temperature sensing performance of the SnS₂/Pt₃Sn heterostructures and some other previous reports.

Materials	Operating conditions	Limit of detection (ppb)	Response ($\Delta R/R_0$)	Ref.
SnS₂/Pt₃Sn	RT	25	0.4% @ 0.2 ppm 0.8% @ 0.5 ppm 1.8% @ 1 ppm 4.1% @ 5 ppm	This work
MoS ₂ /SnO ₂	RT	n.a.	0.6% @ 0.5 ppm	4
g-C ₃ N ₄ /GaN	RT and 392 nm light	n.a.	17.0% @ 5 ppm	5
NbS ₂	RT	241	1.53% @ 0.5 ppm	6
MoS ₂	RT	n.a.	0.2% @ 0.1 ppm	7
WS ₂	RT	n.a.	10.6% @ 0.8 ppm	8
Pt-ZnO/PRGO	RT	n.a.	43.8% @ 5 ppm	9
CuO/rGO	RT	n.a.	400.8% @ 5 ppm	10
Cu ₂ O/rGO	60 °C	n.a.	4.8% @ 0.02 ppm	11
MoS ₂ /graphene	120 °C	n.a.	29.8% @ 1 ppm	12

n.a. means not available.

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