Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Bi_2S_3/ZnS heterostructures for dark-assisted H_2S sensing: synergy of increased surface-adsorbed oxygen and charge transfer

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Experimental section

Synthesis of Bi_2S_3

Bi_2S_3 was synthesized by an easy solvothermal. Typically, 1 mmol $Bi(NO_3)_3 \cdot 5H_2O$ and 2 mmol $Na_2S \cdot 9H_2O$ were dissolved in 15 mL EG, respectively. $Na_2S \cdot 9H_2O$ solution was added slowly in drops into $Bi(NO_3)_3 \cdot 5H_2O$ solution and stirred continuously for 1 hour. The resulting mixture was then transferred to 50 mL of Teflon-lined stainless-steel autoclaves and heated at 180 °C for 12 hours. After the reaction was completed and cooled down naturally, the black solid product was collected and washed several times with ultra-pure water and anhydrous ethanol, then dried at 60 °C for 5 hours.

Synthesis of Bi_2S_3/ZnS heterostructures

Bi_2S_3/ZnS heterostructures were synthesized by as-prepared Bi_2S_3 through a secondary solvothermal method. The specific process was as follows: firstly, 0.1 mmol Bi_2S_3 was dissolved in 10 mL EG and stirred for 30 minutes. Then, 10 mL $Zn(NO_3)_3 \cdot 6H_2O$/EG and 10 mL $Na_2S \cdot 9H_2O$/EG solutions were added to the above suspension separately followed by magnetic stirring for 30 minutes, in which the molar ratio of zinc and sulfur was 1:1. The mixed solution was then transferred to Teflon-lined stainless-steel autoclaves (50 mL) and reacted at 180 °C for 12 hours. Finally, the obtained precipitate was centrifuged and dried. To further optimize the properties of the composites, Bi_2S_3/ZnS heterostructures with different contents were prepared by modulating the added amount of zinc and sulfur source. For convenience, the samples were labelled as Bi_2S_3/ZnS-1, Bi_2S_3/ZnS-3, Bi_2S_3/ZnS-5, Bi_2S_3/ZnS-10, corresponding to the molar of zinc source (0.001 mmol, 0.003 mmol, 0.005 mmol, 0.010 mmol, respectively).

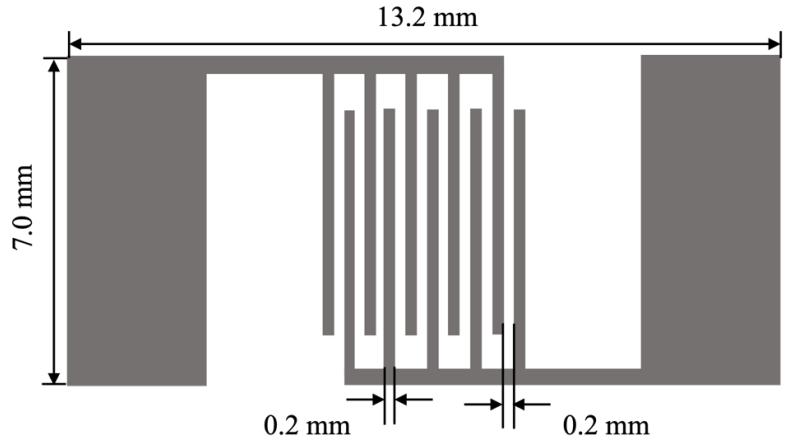

Fig. S1 Schematic diagram of the Ag-Pd interdigital electrode.

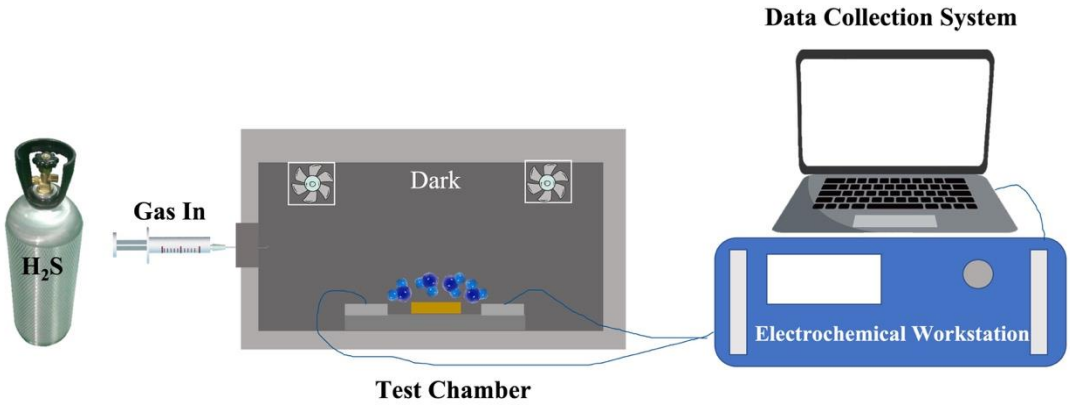

Fig. S2 Schematic diagram of the sensor measurement.

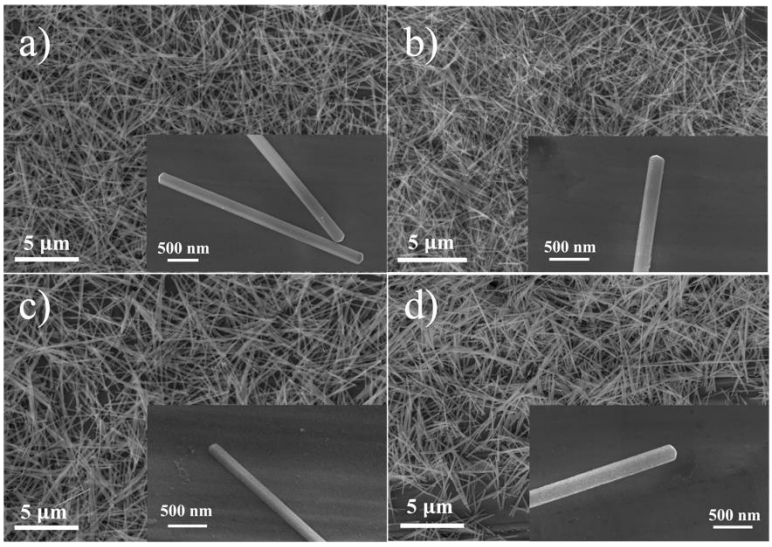

Fig. S3 SEM images of (a) Bi_2S_3; (b) Bi_2S_3/ZnS-1; (c) Bi_2S_3/ZnS-5; (d) Bi_2S_3/ZnS-10.

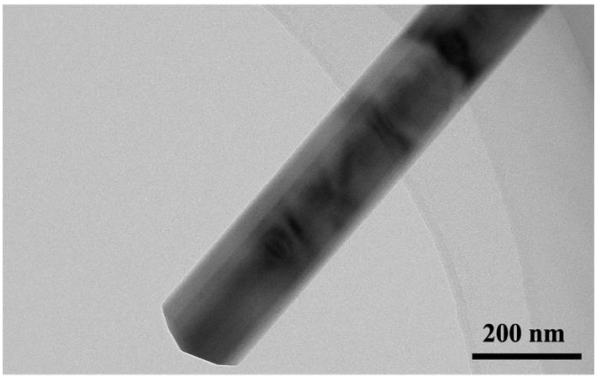

Fig. S4 TEM image of Bi_2S_3.

Table S1 The atomic percentage of the elements in the EDS mapping of Bi_2S_3/ZnS-3 sample.

Elements	Atomic Percentage (%)
S	64.61
Zn	0
Bi	35.39

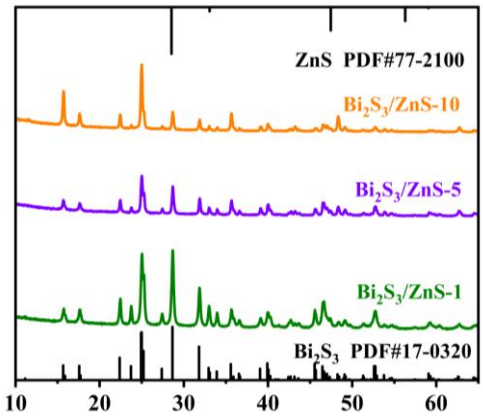

Fig. S5 XRD patterns of Bi_2S_3/ZnS-1, Bi_2S_3/ZnS-5, and Bi_2S_3/ZnS-10.

Table S2 The atomic percentage of the elements in the XPS results of Bi_2S_3/ZnS-3 sample.

Elements	Atomic Percentage (%)
C	20.12
O	5.79
Bi	7.90
Zn	7.40
S	58.79

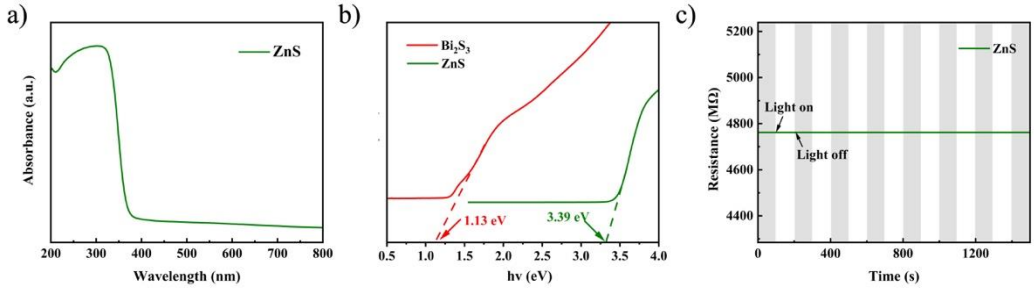

Fig. S6 (a) UV-vis DRS of ZnS. (b) The plot of $(\alpha h\nu)^2$ vs photo energy ($h\nu$) for Bi_2S_3 and ZnS. (c) The unchanged resistance of ZnS tested by periodically turning on and off 160 mW/cm^2 white light source for seven cycles.

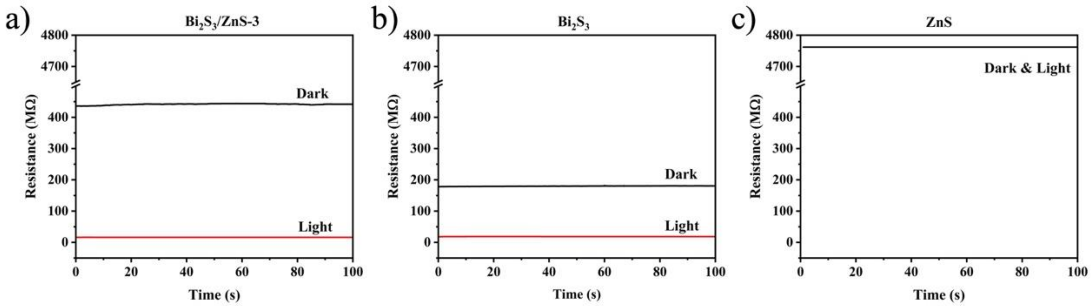

Fig. S7 The baseline curves of devices based on (a) Bi_2S_3/ZnS-3, (b) Bi_2S_3 and (c) ZnS before and after light irradiation.

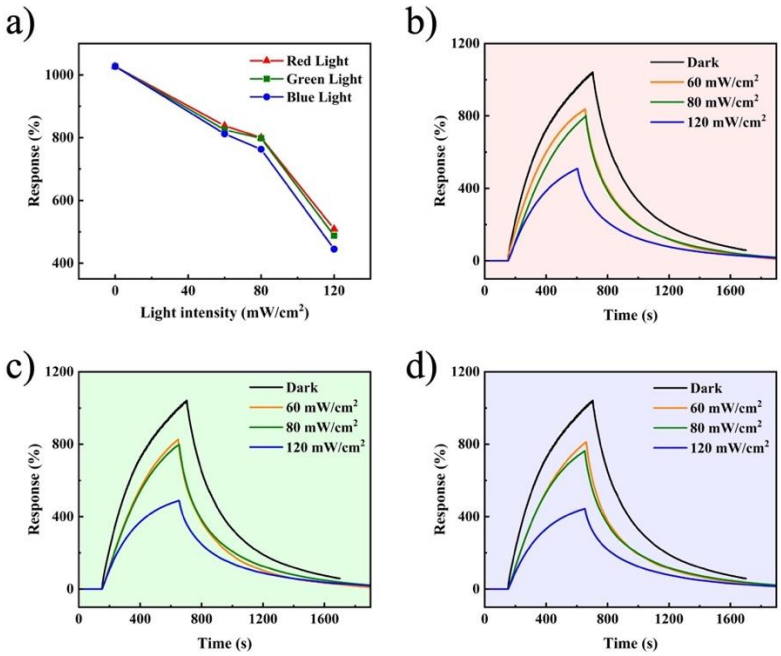

Fig. S8 (a) Summarized sensing responses of Bi_2S_3/ZnS-3 sensor to 500 ppb H_2S in dark and under different light illumination. Response and recovery curves based on Bi_2S_3/ZnS-3 sensor toward 0.5 ppm H_2S under different (b) red, (c) green, and (d) blue light intensity.

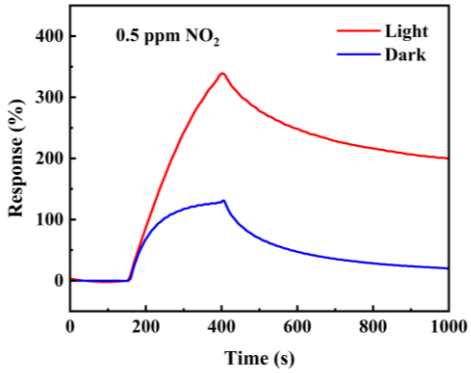

Fig. S9 Comparison of Bi_2S_3/ZnS-3 sensor to 500 ppb NO_2 under light and in dark.

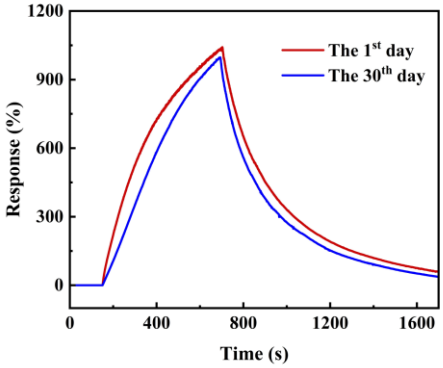

Fig. S10 Comparison of response curves to 500 ppb H_2S in dark on 1st and 30th day.

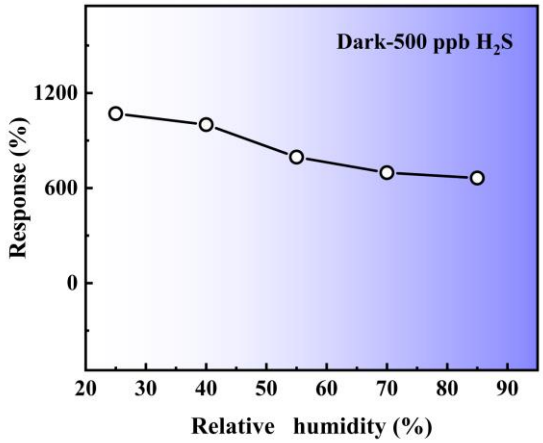

Fig. S11 The sensing response of Bi_2S_3/ZnS-3-based sensor toward 500 ppb H_2S in different relative humidity in dark.

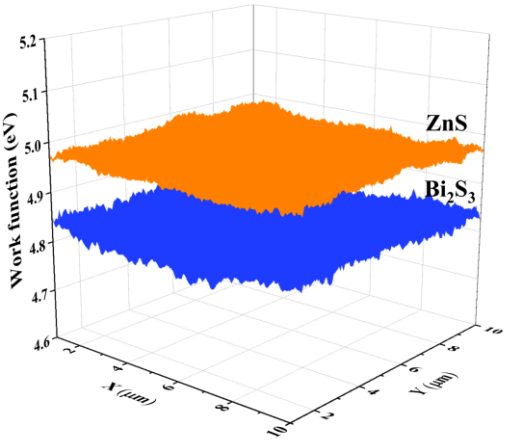

Fig. S12 Work functions of Bi_2S_3 and ZnS measured by KPFM.

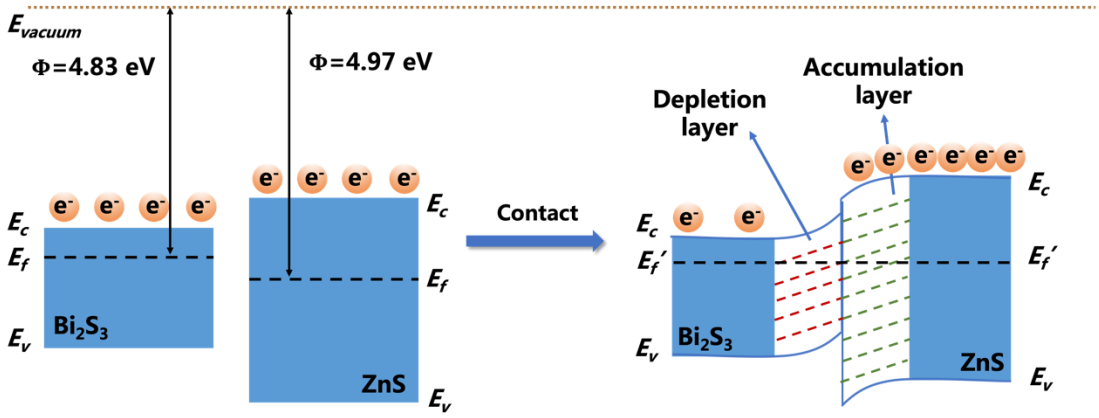

Fig. S13 The energy band diagram of the Bi_2S_3/ZnS heterostructure before and after equilibrium.

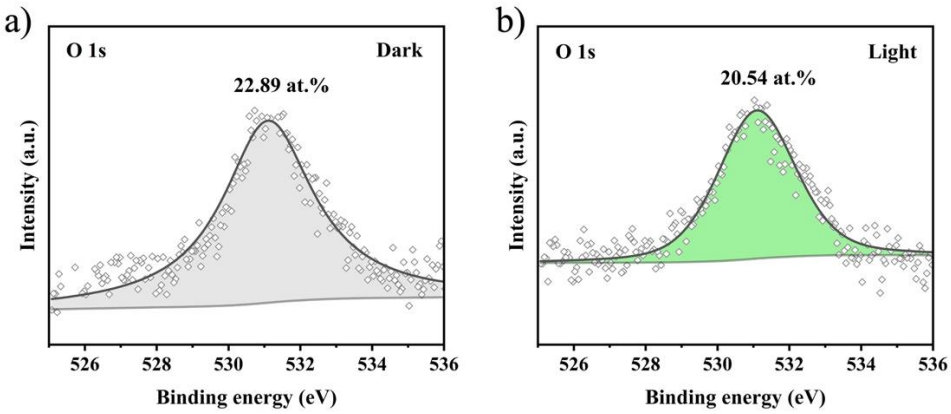

Fig. S14 The in-situ O 1s XPS spectra of Bi_2S_3/ZnS heterostructures: (a) in dark and (b) under green light illumination.

The in-situ XPS test was performed on the ESCLAB 250 Xi instrument. Firstly, the chemical state of the sample was recorded under dark conditions, maintaining a stable test environment during the whole process. Then, green light was irradiated on the sample surface through the observation window, simultaneously the chemical state of the sample surface under light condition was measured. At last, the variation of O_2^- contents adsorbed on material surface under dark and light conditions was analyzed.

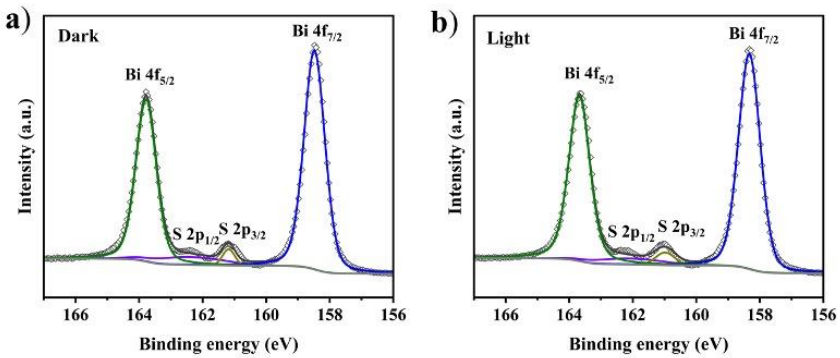

Fig. S15 The Bi 4f XPS spectra of Bi_2S_3/ZnS-3 (a) in dark and (b) under light illumination.

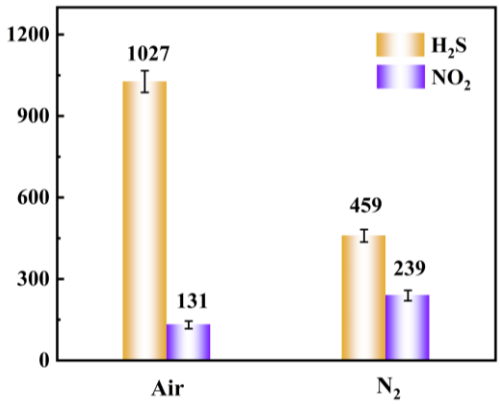

Fig. S16 The sensing response of Bi_2S_3/ZnS-3 to 500 ppb H_2S and NO_2 in different test condition: Air and N_2 as the background gases in dark.