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## Chemically bonded interface modulated S-scheme charge transfer in $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ core–shell heterostructures for boosted catalytic activity toward nitrogen photofixation†

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The exploration of efficient strategies for nitrogen photofixation driven by visible light at room temperature and atmospheric pressure is still highly desirable but remains a great challenge. In this study, hierarchical  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  core–shell samples were synthesized through a hydrothermal reaction, in which ultrathin  $\text{ZnIn}_2\text{S}_4$  nanosheets were tightly and uniformly wrapped on the surface of  $\text{Sb}_2\text{S}_3$  nanorods. Systematic characterization revealed that the chemically bonded interface in  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  core–shell heterostructures was critical to rapid charge separation, leading to a significant enhancement of photocatalytic performance for nitrogen photofixation. The optimal nitrogen photofixation system, namely,  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75, exhibited excellent performance achieving an ammonia concentration of  $15.96 \pm 0.97 \text{ mg L}^{-1}$  after visible light irradiation for 40 min, which was approximately 1.88 and 7.19 times higher than those of relevant  $\text{ZnIn}_2\text{S}_4$  and  $\text{Sb}_2\text{S}_3$ , respectively. Moreover, an S-scheme charge transfer route on  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  core–shell heterostructures was proposed based on band structure analysis, *in situ* irradiated X-ray photoelectron spectroscopy (ISI-XPS) investigation, noble metal deposition, and density functional theory (DFT) simulation. This work gave a useful insight into the development of efficient photocatalysts for boosted photocatalytic activity toward nitrogen photofixation.

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## Introduction

Ammonia ( $\text{NH}_3$ ), as the basic raw material, is an indispensable fertilizer in agriculture, which is widely used in the manufacture of all nitrogen and nitrogen-containing fertilizers.<sup>1</sup> Besides, due to its high combustion calorific value, ammonia can also be used as an energy source by direct combustion or hydrogen production through its decomposition. Traditional ammonia synthesis has been accomplished at high temperature (300–500 °C) and extreme pressure (200–300 atm) in the presence of iron-based catalysts, namely the Haber–Bosch process, which

consumes 1–2% of the world's energy supply and simultaneously produces more than 300 million tons of carbon dioxide annually.<sup>2–4</sup> In contrast, nitrogen photofixation to ammonia by light irradiation proceeds under ambient conditions without fossil fuel consumption and carbon dioxide emission, which represents a sustainable ammonia synthesis route. However, the catalytic efficiency for ammonia production through the photofixation strategy still cannot meet the requirements of industrial demand.<sup>5</sup> Therefore, it is urgently desired to design and construct efficient photo-driven catalysts with excellent catalytic activity and stability toward nitrogen photofixation.

Antimony sulfide ( $\text{Sb}_2\text{S}_3$ ) is a typical binary transition metal sulfide with strong visible-light harvesting capacity due to its high absorption coefficient and narrow band gap,<sup>6</sup> which has been widely employed in various photocatalytic fields, such as hydrogen evolution from water splitting,<sup>7,8</sup> organic pollutant photodegradation,<sup>9,10</sup> and heavy metal reduction in aqueous solution.<sup>11</sup> But the disordered migration in pure  $\text{Sb}_2\text{S}_3$  greatly accelerates the recombination kinetics of photogenerated charges, leading to low-efficient catalytic activity.<sup>12</sup> For effectively modifying the photocatalytic performance of  $\text{Sb}_2\text{S}_3$ , constructing hybrid heterostructures based on  $\text{Sb}_2\text{S}_3$  has been regarded as the most commonly used and effective tactic.<sup>13–15</sup> Li

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*et al.* constructed a  $\text{Sb}_2\text{S}_3@\text{CdS}$  core–shell heterojunction by *in situ* immobilizing CdS nanoparticles on the surface of  $\text{Sb}_2\text{S}_3$  in a solvothermal environment. Ascribed to the efficient charge separation based on the formation of van der Waals force and Sb–S–Cd bonding throughout the heterogeneous interface between CdS and  $\text{Sb}_2\text{S}_3$ , the resultant  $\text{Sb}_2\text{S}_3@\text{CdS}$  heterostructured sample exhibited highly enhanced activity toward simulated sunlight-driven  $\text{Cr}^{6+}$  reduction and decomplexation of complexed  $\text{Cr}^{3+}$  under weakly acidic conditions.<sup>14</sup> Garg *et al.* fabricated a  $\text{g-C}_3\text{N}_4/\text{Sb}_2\text{S}_3$  heterojunction photocatalyst with varying weight ratios by a hydrothermal reaction. Among the samples, the optimal  $\text{g-C}_3\text{N}_4/\text{Sb}_2\text{S}_3$  composite exhibited the highest photocatalytic performance for tetracycline degradation under natural sunlight because of the rapid charge separation and transfer across the hetero-interface.<sup>15</sup>

Zinc indium sulfide ( $\text{ZnIn}_2\text{S}_4$ ) has the features of excellent optical properties, strong visible-light harvesting ability and highly catalytic stability, making it a promising material for photocatalytic applications.<sup>16–18</sup> Besides,  $\text{ZnIn}_2\text{S}_4$  with a two-dimensional structure possessing a large active surface area could provide sufficient active sites for various photocatalytic reactions.<sup>19,20</sup> More importantly, previous investigations indicated that the integration of  $\text{ZnIn}_2\text{S}_4$  and  $\text{Sb}_2\text{S}_3$  would significantly improve the charge migration efficiency based on the construction of a tightly bonded interface and well-matched band structures between  $\text{ZnIn}_2\text{S}_4$  and  $\text{Sb}_2\text{S}_3$ .<sup>21,22</sup> In recent research, Xiao *et al.* synthesized hierarchical  $\text{Sb}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$  heterostructures using the hydrothermal method, which exhibit highly efficient activities toward both photocatalytic hydrogen production and tetracycline hydrochloride photodegradation.<sup>21</sup> Li *et al.* have also formed a  $\text{ZnIn}_2\text{S}_4@\text{Sb}_2\text{S}_3$  heterojunction with an enhanced photocatalytic hydrogen evolution activity *via* an oil bath method.<sup>22</sup> The above prepared binary heterostructures demonstrate their potential for hydrogen production and pollutant photodegradation. However, the photocatalytic activity, the reaction pathways, and the effect of sulfur vacancies on nitrogen photofixation using  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  core–shell heterostructures are still unclear. Hence, it is still necessary to build chemically bonded interface modulated  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  core–shell heterostructures to achieve highly efficient activity of nitrogen photofixation and simultaneously demystify the charge migration direction and the catalytic mechanism of nitrogen photofixation.

To establish high-quality  $\text{Sb}_2\text{S}_3$  based photocatalytic systems with efficient performance and excellent stability for highly efficient nitrogen photofixation, herein,  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  core–shell heterostructures with interfacial chemical bonds were successfully fabricated by *in situ* growth of  $\text{ZnIn}_2\text{S}_4$  nanosheets onto  $\text{Sb}_2\text{S}_3$  nanorods. A nitrogen photofixation experiment under ambient conditions was conducted to evaluate the catalytic performance of the fabricated  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  photocatalyst by utilizing a Xe lamp as the light source. The results indicated that the optimal  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  photocatalyst with addition of 75 mg of  $\text{Sb}_2\text{S}_3$  nanorods achieved the highest photocatalytic activity for ammonia production from nitrogen, with an activity of 1.88 and 7.19 times higher than those of relevant  $\text{ZnIn}_2\text{S}_4$  and  $\text{Sb}_2\text{S}_3$ , respectively. The obvious activity

improvement in the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  core–shell heterostructures can be attributed to synergistic collaboration of interfacial chemical bonds and an internal electric field, which can greatly accelerate charge transfer across the hetero-interface between  $\text{ZnIn}_2\text{S}_4$  and  $\text{Sb}_2\text{S}_3$ , as evidenced by experimental investigations and density functional theory calculations. The S-scheme charge migration mechanism was verified by electron paramagnetic resonance (EPR), nitroblue tetrazolium (NBT) transformation experiments, *in situ* irradiated X-ray photoelectron spectroscopy (ISI-XPS), and noble metal loading.

## Experimental section

### Preparation of materials

**Synthesis of  $\text{Sb}_2\text{S}_3$  nanorods.**  $\text{Sb}_2\text{S}_3$  nanorods were prepared by a solvothermal reaction according to the method described in previous literature.<sup>11</sup> Typically,  $\text{SbCl}_3$  (3 mmol, 0.684 g) and thiourea (18 mmol, 1.370 g) were added into 80 mL ethylene glycol (EG) to obtain a clear solution by magnetic stirring for 30 min. Then, the above solution was poured into a 100 mL Teflon-lined autoclave and reacted at 180 °C for 10 h. The resultant black precipitate was washed with deionized water two times and absolute ethanol three times.

**Synthesis of the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  heterostructured catalyst.**  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  nanocomposites with core–shell heterostructures were synthesized by *in situ* growth of  $\text{ZnIn}_2\text{S}_4$  nanosheets onto  $\text{Sb}_2\text{S}_3$  nanorods. Typically, a certain amount of as-synthetic  $\text{Sb}_2\text{S}_3$  nanorods was suspended in a mixed solvent consisting of 32 mL deionized water and 8 mL glycerol. Then,  $\text{ZnCl}_2$  (1 mmol, 0.136 g),  $\text{In}(\text{NO}_3)_3$  (2 mmol, 0.602 g), and thiourea (6 mmol, 0.451 g) were gradually dissolved in the above suspension. Subsequently, the mixture was transferred to a 50 mL Teflon-lined autoclave and reacted at 120 °C for 2 h. After naturally cooling down to room temperature, the powdery precipitate was washed with absolute ethanol three times. Finally, the as-obtained  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  precipitate was dried at 60 °C for 6 h. According to the added amount of  $\text{Sb}_2\text{S}_3$  nanorods, the heterostructured samples were denoted as  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4\text{-}x$  ( $x$  represents the added amount of  $\text{Sb}_2\text{S}_3$ , *viz.*, 25, 50, 75, and 100 mg). For comparison, pure  $\text{ZnIn}_2\text{S}_4$  was prepared under the same reaction condition just without the addition of  $\text{Sb}_2\text{S}_3$  nanorods.

### Characterization

A powder X-ray diffractometer (XRD, Bruker D2 Phaser Diffractometer) equipped with a monochromatic  $\text{Cu K}\alpha$  generator was used to examine crystalline structures. Field-emission scanning electron microscopy (FESEM, ZEISS GeminiSEM 300), transmission electron microscopy (TEM, FEI Titan Cubed Themis G2 300), and high-angle annular dark field scanning TEM (HAADF-STEM, FEI Titan Cubed Themis G2 300) were carried out to observe the morphologies, structures, and elements. Nitrogen adsorption–desorption measurements (Micromeritics ASAP 2460) were performed to record Brunauer–Emmett–Teller (BET) surface areas and pore-diameter distribution. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) and *in situ*

irradiated XPS (ISI-XPS, ESCALAB 250Xi) with monochromatic Al K $\alpha$  radiation were conducted to analyze the element compositions and electron transfer in the measured samples. Fourier transform infrared (FT-IR) spectra of samples were recorded using a Thermo Fisher Nicolet IS50 infrared spectrometer. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS, U-4100) were recorded to acquire optical properties with BaSO<sub>4</sub> as a reference. Electron paramagnetic resonance (EPR) was measured on a Bruker A300 EPR spectrometer. The photoluminescence (PL) and time-resolved PL (TRPL) spectra were recorded on an F-4600 fluorescence spectrophotometer at room temperature. The photoelectrochemical measurements including transit photocurrent response and electrochemical impedance spectra (EIS) were performed in Na<sub>2</sub>SO<sub>4</sub> aqueous solution (0.5 M) under irradiation of a 300 W Xe lamp on a CHI760E electrochemical workstation using a three-electrode electrochemical system, in which a Pt wire and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. The details about the theoretical calculations are shown in the ESI<sup>†</sup> and the atomic structure diagram used in the calculation could be found in Fig. S1.<sup>†</sup>

### Photocatalytic activity

Photocatalytic activity toward ammonia production by nitrogen photofixation was performed in a homemade catalytic system at room temperature and atmospheric pressure under irradiation of a 300 W Xe lamp (PerfectLight). Typically, 50 mg photocatalyst was ultrasonically dispersed in 50 mL deionized water including 1 mL methanol as the hole scavenger. Prior to the catalytic reaction, the suspension was bubbled for 30 min by nitrogen at a flow rate of 100 mL min<sup>-1</sup>. At given irradiation time intervals, the irradiated suspension was extracted and separated using a polyether sulfone filter to obtain the supernatant. The concentration of produced ammonia was quantitatively analyzed using Nessler's reagent with a UV-visible absorption spectrophotometer (UVmini-1280, Shimadzu). The produced NH<sub>3</sub> was further verified by ion chromatography (Thermo Scientific Aquion) coupled with an NH<sub>3</sub>-selective electrode (Bante 931-NH<sub>3</sub>).

## Results and discussion

The fabrication of Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> core–shell heterostructures involved two steps, that is, solvothermal synthesis of Sb<sub>2</sub>S<sub>3</sub> nanorods and the construction of a heterogeneous interface by *in situ* growth of ZnIn<sub>2</sub>S<sub>4</sub> nanosheets on Sb<sub>2</sub>S<sub>3</sub> nanorods (Fig. 1a). First, under a solvothermal environment, the precursor in EG gradually nucleated and then crystallized to generate Sb<sub>2</sub>S<sub>3</sub> nanorods by orientation growth. The morphology of the resultant Sb<sub>2</sub>S<sub>3</sub> nanorods was revealed using a field-emission scanning electron microscope (FESEM). Fig. 1b depicts the one-dimensional structure of the as-prepared Sb<sub>2</sub>S<sub>3</sub> sample with a smooth surface and its length irregularly varied within several microns. Then, through a solvothermal process, the produced ZnIn<sub>2</sub>S<sub>4</sub> crystal nucleus tended to immobilize on the Sb<sub>2</sub>S<sub>3</sub> surface and further grew into nanosheets;

simultaneously ZnIn<sub>2</sub>S<sub>4</sub> nanosheets grew along the surface of the Sb<sub>2</sub>S<sub>3</sub> nanorods to form a tight heterogeneous interface between Sb<sub>2</sub>S<sub>3</sub> nanorods and ZnIn<sub>2</sub>S<sub>4</sub> nanosheets, namely, the fabrication of Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> core–shell heterostructures. The successful decoration of ZnIn<sub>2</sub>S<sub>4</sub> nanosheets on Sb<sub>2</sub>S<sub>3</sub> nanorods could be observed by FESEM. As shown in Fig. 1d and S2a–c,<sup>†</sup> all the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> samples exhibited core–shell heterostructures with a rough surface, which clearly proved that the Sb<sub>2</sub>S<sub>3</sub> nanorods with a smooth surface were tightly covered by ZnIn<sub>2</sub>S<sub>4</sub> nanosheets. These close heterogeneous contacts would act as high-speed channels to promote the separation of photogenerated electrons and holes, thus improving the photocatalytic activity. It is worth noting that, when a small amount (25 mg) of Sb<sub>2</sub>S<sub>3</sub> nanorods was introduced into the reaction system, some of the ZnIn<sub>2</sub>S<sub>4</sub> nanosheets would agglomerate to form microsphere-like assemblies due to the lack of enough Sb<sub>2</sub>S<sub>3</sub> nanorods to act as supporting carriers (Fig. S2a<sup>†</sup>). With the increase of the added amount of Sb<sub>2</sub>S<sub>3</sub> nanorods, the ZnIn<sub>2</sub>S<sub>4</sub> nanosheet assembly gradually disappeared, leaving only the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> core–shell heterostructures. Therefore, it is important to optimize the added amount of Sb<sub>2</sub>S<sub>3</sub> nanorods to acquire suitable Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> core–shell heterostructures.

To better elucidate the *in situ* growth of ZnIn<sub>2</sub>S<sub>4</sub> nanosheets on Sb<sub>2</sub>S<sub>3</sub> nanorods and the construction of Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> core–shell heterostructures, transmission electron microscope (TEM), high-resolution TEM (HRTEM) and high-angle annular dark field scanning TEM (HAADF-STEM) characterization of the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75 was performed to obtain the microstructure information. The TEM images revealed that the ZnIn<sub>2</sub>S<sub>4</sub> nanosheets exhibited a sheet-like morphology, and the heterogeneous structures were observed throughout these ultrathin nanosheets tightly decorated on the Sb<sub>2</sub>S<sub>3</sub> nanorods (Fig. 1e and f). The above results confirmed that the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> heterostructures were heterogeneous hybrid systems with tight interface contacts as opposed to the physical mixtures of the individual Sb<sub>2</sub>S<sub>3</sub> and ZnIn<sub>2</sub>S<sub>4</sub> phases. The HRTEM image (Fig. 1g) showed clear lattice fringes with the interplanar distances of 0.278 and 0.412 nm, belonging to the (006) crystal plane of hexagonal ZnIn<sub>2</sub>S<sub>4</sub> and the (221) crystal plane of orthotropic stibnite Sb<sub>2</sub>S<sub>3</sub>, respectively. Fig. 1h illustrates the HAADF image of the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75 sample. It was worth noting that ultrathin ZnIn<sub>2</sub>S<sub>4</sub> nanosheets were evenly dispersed and hierarchically wrapped on the surface of Sb<sub>2</sub>S<sub>3</sub> nanorods to build core–shell catalytic systems. The elemental mapping images of the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75 sample (Fig. 1i–l) clearly reveal that all the elements with uniform distribution corresponded to the measured sample region, revealing the successful construction of the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> hybrid sample. The microstructure observation demonstrated that Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> core–shell heterostructures effectively established good interfacial contacts through obvious morphological changes of ZnIn<sub>2</sub>S<sub>4</sub> from assembly to ultrathin nanosheets. These ultrathin nanosheets decorated on the contacted interfaces between Sb<sub>2</sub>S<sub>3</sub> and ZnIn<sub>2</sub>S<sub>4</sub> could not only facilitate the rapid separation of photogenerated hole–electron pairs, but also cause more exposure of additional active sites and this improves the reaction sites,

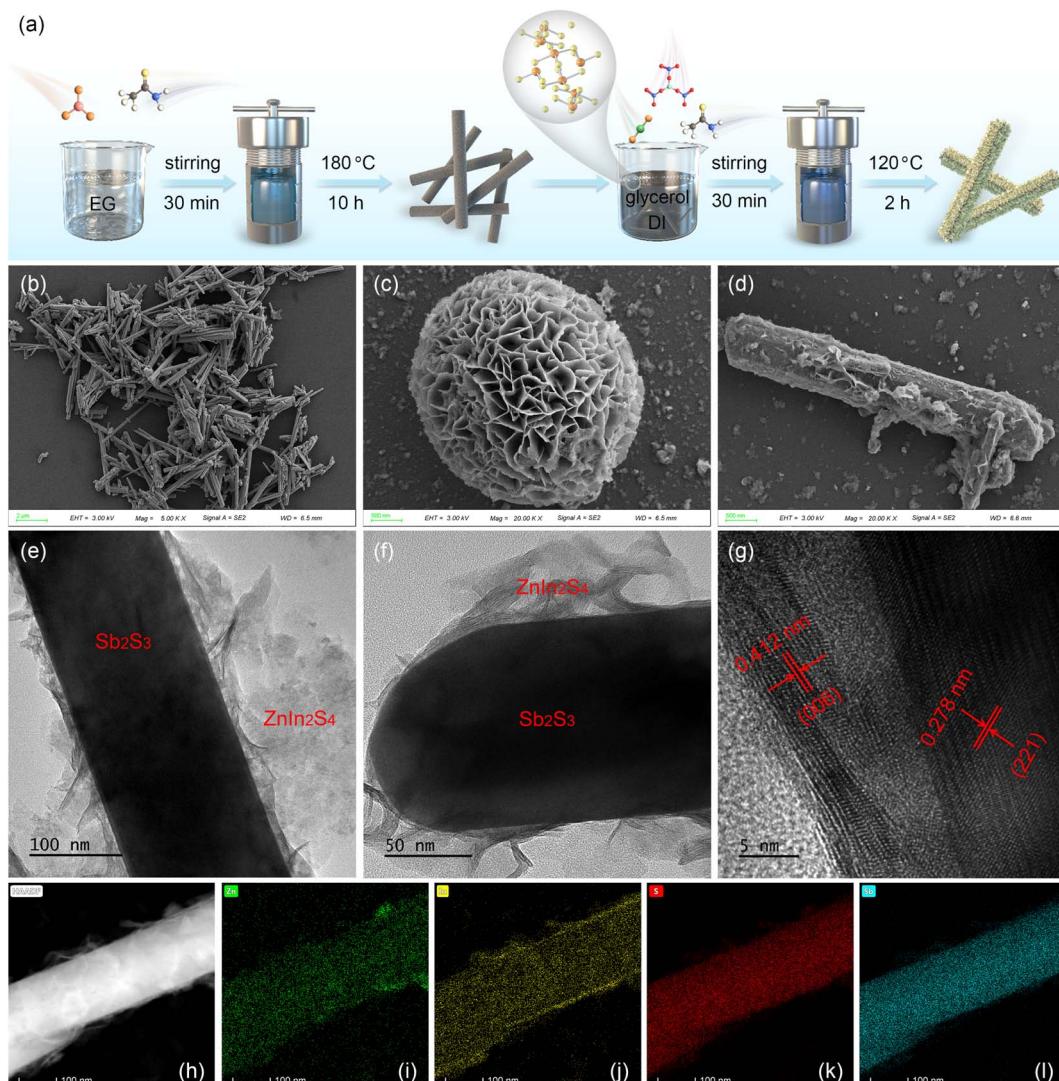
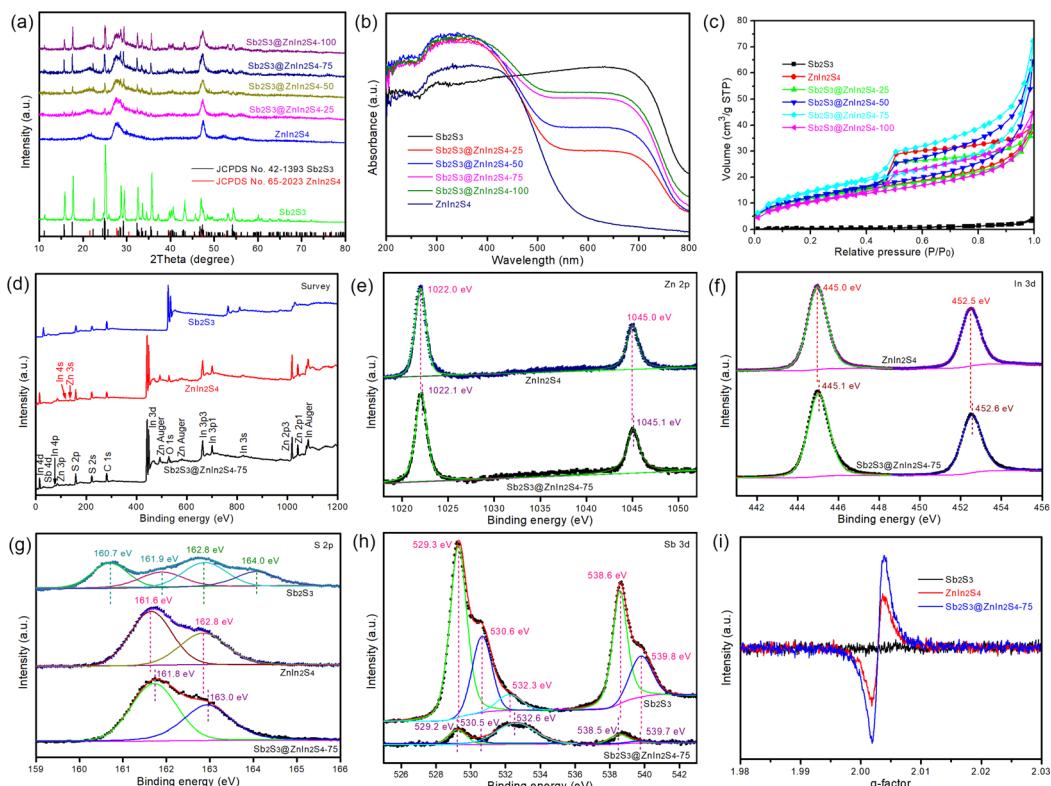


Fig. 1 (a) Schematic diagram of the synthetic process of Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> core–shell heterostructures. SEM images of (b) Sb<sub>2</sub>S<sub>3</sub>, (c) ZnIn<sub>2</sub>S<sub>4</sub>, and (d) Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75. (e and f) TEM, (g) HRTEM, (h) HAADF, and (i–l) elemental mapping images of the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75 sample.

which is beneficial for improving the photocatalytic performance toward nitrogen photofixation.

The powder X-ray diffraction (XRD) technique was used to analyze the phase structures of the different samples, as shown in Fig. 2a. The characteristic diffraction peaks of Sb<sub>2</sub>S<sub>3</sub> agreed well with the standard card of the orthorhombic phase (JCPDS No. 42-1393).<sup>11</sup> The XRD patterns of ZnIn<sub>2</sub>S<sub>4</sub> were in good accordance with those of the hexagonal phase (JCPDS No. 65-2023).<sup>23</sup> After solvothermally decorating ZnIn<sub>2</sub>S<sub>4</sub> nanosheets on the Sb<sub>2</sub>S<sub>3</sub> surface, the synthesized Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> core–shell heterostructures with different amounts of Sb<sub>2</sub>S<sub>3</sub> added exhibited integrated XRD patterns of Sb<sub>2</sub>S<sub>3</sub> and ZnIn<sub>2</sub>S<sub>4</sub>. The diffraction intensity belonging to Sb<sub>2</sub>S<sub>3</sub> increased obviously with increasing amount of Sb<sub>2</sub>S<sub>3</sub> added into the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> core–shell heterostructures, further proving the coexistence and successful combination of Sb<sub>2</sub>S<sub>3</sub> and ZnIn<sub>2</sub>S<sub>4</sub>. The above results well supported the conclusion of SEM/TEM observation. No other impurities were observed, revealing the high purity of the

synthesized samples. The optical absorption ability of pure ZnIn<sub>2</sub>S<sub>4</sub>, bare Sb<sub>2</sub>S<sub>3</sub> and their Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> core–shell heterostructures was checked by ultraviolet–visible diffuse reflectance spectroscopy (UV-vis DRS), as shown in Fig. 2b. Noticeably, pure ZnIn<sub>2</sub>S<sub>4</sub> exhibited a certain light absorption capacity with an absorption threshold of around 560 nm, while bare Sb<sub>2</sub>S<sub>3</sub> had a strong light absorption ability and could absorb most of the irradiated light throughout the ultraviolet to visible light region. Such an excellent optical absorption ability of Sb<sub>2</sub>S<sub>3</sub> signified that it could probably be utilized to improve the light harvesting ability of ZnIn<sub>2</sub>S<sub>4</sub>. Indeed, after the construction of Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> samples, all the core–shell heterostructures showed improved light absorption intensity in the measured range with increasing Sb<sub>2</sub>S<sub>3</sub> content. Moreover, compared to pure ZnIn<sub>2</sub>S<sub>4</sub>, all Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> core–shell heterostructures had a slight red shift toward the longer wavelength region upon the introduction of Sb<sub>2</sub>S<sub>3</sub>, which revealed that a certain interaction between Sb<sub>2</sub>S<sub>3</sub> and ZnIn<sub>2</sub>S<sub>4</sub> was



**Fig. 2** (a) XRD patterns, (b) UV-vis DRS, and (c)  $N_2$  adsorption/desorption curves of pure  $ZnIn_2S_4$ , bare  $Sb_2S_3$  and their  $Sb_2S_3@ZnIn_2S_4$  heterostructures. XPS data: (d) survey spectra, (e) Zn 2p, (f) In 3d, (g) S 2p, and (h) Sb 3d. (i) EPR spectra of pure  $ZnIn_2S_4$ , bare  $Sb_2S_3$  and the  $Sb_2S_3@ZnIn_2S_4$ -75 heterostructures.

formed due to the surface coverage of  $Sb_2S_3$  nanorods with  $ZnIn_2S_4$  nanosheets. The improved light harvesting efficiency of  $ZnIn_2S_4$  in the measured region by coupling with  $Sb_2S_3$  meant that more photogenerated charges were produced and then participated in the photocatalytic reaction, giving rise to the activity enhancement of nitrogen photofixation.

The specific surface area and porosity of pure  $ZnIn_2S_4$ , bare  $Sb_2S_3$  and their  $Sb_2S_3@ZnIn_2S_4$  core–shell heterostructures were studied through  $N_2$  adsorption/desorption tests. As shown in Fig. 2c, the isotherms of the measured samples were characteristic of type IV, with a type H3 adsorption hysteresis loop, indicating the presence of mesoporous structures.<sup>24,25</sup> Additionally, the macroporous structures in the samples were also recorded as indicated by pore size distributions (Fig. S3†), which could probably be ascribed to the slit holes formed between  $ZnIn_2S_4$  nanosheets. The Brunauer–Emmett–Teller (BET) specific surface areas (SSAs) of pure  $ZnIn_2S_4$  and bare  $Sb_2S_3$  were determined to be  $45.34$  and  $2.01\text{ m}^2\text{ g}^{-1}$ , respectively. As shown in Table S1,† after the  $ZnIn_2S_4$  nanosheets were anchored on the  $Sb_2S_3$  nanorods, the BET SSA and total pore volume gradually increased for the  $Sb_2S_3@ZnIn_2S_4$  core–shell heterostructures with increasing  $Sb_2S_3$  addition until the addition amount of  $Sb_2S_3$  reached  $75$  mg. Further increasing the amount of  $Sb_2S_3$  nanorods added would lead to a decrease in the BET SSA. The large SAA of the  $Sb_2S_3@ZnIn_2S_4$ -75 heterostructure usually provided more surface active sites and probably increased the photocatalytic reactivity.

To investigate the chemical states and interfacial interaction between  $Sb_2S_3$  and  $ZnIn_2S_4$ , X-ray photoelectron spectroscopy (XPS) tests were conducted. As observed in Fig. 2d, the XPS survey spectrum of the  $Sb_2S_3@ZnIn_2S_4$ -75 heterostructure revealed the existence of Zn, In, S, and Sb elements, providing evidence of coupling between  $Sb_2S_3$  and  $ZnIn_2S_4$ . As shown in Fig. 2e and f, the pure  $ZnIn_2S_4$  sample had two characteristic binding energies centered at  $1022.0$  and  $1045.0$  eV in Zn 2p and  $445.0$  and  $452.5$  eV in In 3d, belonging to the Zn  $2p_{3/2}$  and Zn  $2p_{1/2}$  states of  $Zn^{2+}$  and the In  $3d_{5/2}$  and In  $3d_{3/2}$  states of  $In^{3+}$ , respectively.<sup>26,27</sup> From the high-resolution spectrum of S 2p (Fig. 2g), the asymmetric S 2p peak of bare  $Sb_2S_3$  could be deconvoluted into four peaks located at  $160.7$ ,  $161.9$ ,  $162.8$ , and  $164.0$  eV. The first two peaks located at  $160.7$  and  $161.9$  eV were probably ascribed to S bonded with Sb in a double bond. The two remaining peaks centered at  $162.8$  and  $164.0$  eV were assigned to S bonded with Sb by a single bond. Pure  $ZnIn_2S_4$  also exhibited two peaks with binding energies of  $161.6$  and  $162.8$  eV, which corresponded to S  $2p_{3/2}$  and S  $2p_{1/2}$ , respectively.<sup>28,29</sup> After the coupling of  $ZnIn_2S_4$  with  $Sb_2S_3$ , the core level of Zn, In, and S species in the  $Sb_2S_3@ZnIn_2S_4$ -75 heterostructure obviously moved in the high binding energy direction. The slight positive shift of these peaks was also attributed to the interfacial charge transfer of  $ZnIn_2S_4$  and  $Sb_2S_3$ . Bare  $Sb_2S_3$  was fitted with five peaks (Fig. 2h). The peaks at  $529.3$  eV (Sb  $3d_{5/2}$ ),  $538.6$  eV (Sb  $3d_{3/2}$ ),  $530.6$  eV (Sb  $3d_{5/2}$ ) and  $539.8$  eV (Sb  $3d_{3/2}$ ) represented the different bonding states of Sb with S.<sup>30</sup> There

was an extra peak at 532.3 eV, which was ascribed to oxygen-containing functional groups absorbed on the surface of the sample. The abovementioned Sb species belonging to Sb 3d<sub>5/2</sub> and Sb 3d<sub>5/2</sub> shifted toward the lower binding energy region upon fabricating the heterostructure.<sup>31</sup> The above results verified the M-S-Sb (M = Zn and In) bond formed at the heterogeneous interface of Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>, which induced strong interfacial interaction between these two components with free electron migration from ZnIn<sub>2</sub>S<sub>4</sub> to Sb<sub>2</sub>S<sub>3</sub>. This strong interface interaction and charge redistribution between ZnIn<sub>2</sub>S<sub>4</sub> and Sb<sub>2</sub>S<sub>3</sub> probably induce the formation of an internal electric field within Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> heterostructures. As shown in Fig. 2i, both ZnIn<sub>2</sub>S<sub>4</sub> and Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75 had a Lorentzian line shape emerging at  $g = 2.002$ , verifying the formation of sulfur vacancies in these two samples.<sup>32</sup>

The photocatalytic performance of bare Sb<sub>2</sub>S<sub>3</sub>, pure ZnIn<sub>2</sub>S<sub>4</sub>, and the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> samples toward nitrogen photofixation was investigated by adding methanol as a sacrificial agent to capture photogenerated holes under visible light irradiation, as shown in Fig. 3a. Control experiments under different experimental conditions were carried out with the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75 sample (Fig. S4 and S5†). There was no NH<sub>4</sub><sup>+</sup> produced in the absence of the visible light, indicating that the light irradiation was the essential driving force for the nitrogen photofixation. Notably, the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75 sample exhibited significantly decreased activity toward nitrogen photofixation when N<sub>2</sub> was replaced with Ar, confirming that N<sub>2</sub> was indeed the N source of the photofixation reaction. Without the introduction of methanol, the catalytic activity toward nitrogen photofixation was greatly suppressed because added methanol into the catalytic system as a scavenger of photogenerated holes could effectively inhibit the recombination of photogenerated holes and

electrons and actively improve the utilization rate of photo-generated electrons for the nitrogen reduction reaction. Apparently, bare Sb<sub>2</sub>S<sub>3</sub> nanorods exhibited low ammonia production activity due to low charge migration efficiency. By contrast, ZnIn<sub>2</sub>S<sub>4</sub> exhibited suitable photocatalytic nitrogen photofixation activity and it reached 8.51 ± 1.29 mg L<sup>-1</sup> for ammonia production after visible light irradiation for 40 min. The photocatalytic performance toward nitrogen photofixation dependence on the Sb<sub>2</sub>S<sub>3</sub> content was in-depth explored. After the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> core-shell heterostructures were constructed, all Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> hybrid samples possessed improved photocatalytic activity. The improvement of the photocatalytic performance of Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> hybrid samples was probably due to the efficient charge migration across the heterogeneous interface between Sb<sub>2</sub>S<sub>3</sub> and ZnIn<sub>2</sub>S<sub>4</sub>. Notably, photocatalytic ammonia production activity first increased and then decreased in the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> hybrid systems with the increase of Sb<sub>2</sub>S<sub>3</sub> content. Among all the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> hybrid samples, the optimized Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75 sample showed the highest photocatalytic activity, and an ammonia concentration of 15.96 ± 0.97 mg L<sup>-1</sup> could be produced after 40 min of visible light irradiation, which was around 7.19 and 1.88 times higher than those of bare Sb<sub>2</sub>S<sub>3</sub> and pure ZnIn<sub>2</sub>S<sub>4</sub>, respectively. The produced NH<sub>3</sub> over Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75 was further verified by ion chromatography coupled with an NH<sub>3</sub>-selective electrode. The concentrations from ion chromatography and the NH<sub>3</sub>-selective electrode were determined to be 9.30 and 8.50 mg L<sup>-1</sup>, respectively. A higher Sb<sub>2</sub>S<sub>3</sub> content in the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-100 sample resulted in the decrease of photocatalytic ammonia production activity, which was probably due to the decreased concentration of interfacial contacts and active sites as evidenced by SEM observation and BET measurement. Yang *et al.*

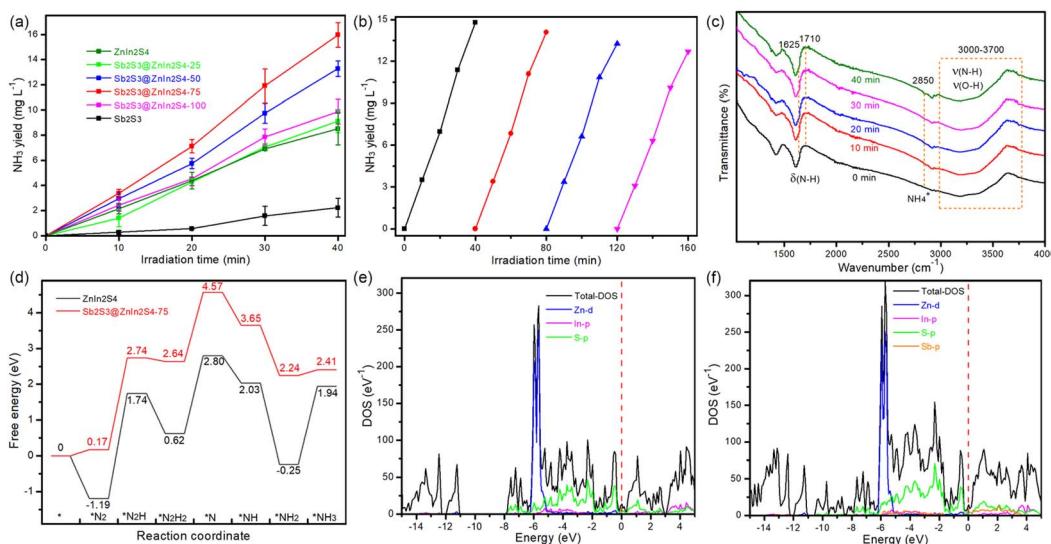


Fig. 3 (a) Photocatalytic ammonia production activity over bare Sb<sub>2</sub>S<sub>3</sub>, pure ZnIn<sub>2</sub>S<sub>4</sub>, and the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> samples with the addition of methanol as the sacrificial agent under visible light irradiation. (b) Recycling runs toward N<sub>2</sub> photofixation for ammonia production over the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75 sample. (c) FTIR spectra during the N<sub>2</sub> photofixation process over the Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75 sample. (d) Gibbs free energy diagrams of the main reactions during N<sub>2</sub> photofixation over ZnIn<sub>2</sub>S<sub>4</sub> and Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub>-75 samples. Density of states (DOS) of (e) ZnIn<sub>2</sub>S<sub>4</sub> and (f) Sb<sub>2</sub>S<sub>3</sub>@ZnIn<sub>2</sub>S<sub>4</sub> samples.

revealed that the nitrogen reduction reaction could generate more reactive intermediates to induce photocatalytic urea production by the activation and oxidation of  $\text{CH}_3\text{OH}$  over the Pt cluster-decorated  $\text{TiO}_2$  catalyst.<sup>33</sup> To reveal the possibility of the photocatalytic urea production, the produced concentration of urea was measured by the diacetyl monoxime method through UV-vis absorption spectroscopy at a characteristic wavelength of 525 nm (Fig. S6†). No obvious improvement of absorption intensity could be observed with extended irradiation time, indicating that the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 sample cannot produce urea although methanol was added into the reaction system during the nitrogen photofixation process. The photocatalytic stability of the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  heterostructures was evaluated through recycling runs toward  $\text{N}_2$  photofixation for ammonia production over the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 sample (Fig. 3b). During the recycling runs, the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 sample displayed a slight decrease in activity. After four consecutive recycling reactions, the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 sample still retained 79.6% of initial activity, indicating relatively good stability for practical applications. Furthermore, FT-IR spectra of the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 sample with different irradiation times are shown in Fig. 3c. These broad absorption bands within 3000–3700  $\text{cm}^{-1}$  from different  $\text{N}_2$  photofixation times could be ascribed to the stretching mode of O–H and N–H functional groups.<sup>34</sup> The characteristic absorption peak at 2850  $\text{cm}^{-1}$  is due to the stretching vibration of  $\text{NH}_4^+$ .<sup>35</sup> Notably, this absorption peak at 2850  $\text{cm}^{-1}$  is only observed in the irradiated samples, which revealed that  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 exhibited visible-light driven catalytic activity towards  $\text{N}_2$  photofixation. The absorption peaks at 1625 and 1710  $\text{cm}^{-1}$  verify the presence of N–H bending mode.<sup>36</sup> The above results indicate that the  $\text{N}_2$  photofixation reaction can be successfully achieved by  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 under visible-light irradiation. Moreover, to further reveal the catalytic mechanism of  $\text{N}_2$

photofixation, hydrazine, as an important intermediate product during the  $\text{N}_2$  photofixation process, was detected by the Watt–Chrissp method (Fig. S7†).<sup>37</sup> Obviously, no by-product hydrazine in the residual solutions was detected. The above results indicated that the  $\text{N}_2$  photofixation pathways toward ammonia production were most likely to follow the associative distal mechanism because of the presence of a N–H bond and  $\text{NH}_4^+$  but the absence of  $\text{N}_2\text{H}_4$ . To further reveal the pathways of  $\text{N}_2$  photofixation, the corresponding Gibbs free energies ( $\Delta G$ ) for each step of the  $\text{N}_2$  photofixation process were calculated, as shown in Fig. 3d. Notably, the  $^* \text{N}_2\text{H}_2$  to  $^* \text{N}$  step exhibited a high energy barrier, indicating that this was the rate-limiting step in the  $\text{N}_2$  photofixation. In addition, the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  samples exhibited a smaller energy barrier than  $\text{ZnIn}_2\text{S}_4$ , which was beneficial for  $\text{N}_2$  photofixation for ammonia production. The observed phenomenon can be attributed to the increase in the number of DOS peaks near the Fermi level on the right side for  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ , primarily originating from the contribution of the p orbitals of Sb, as shown in Fig. 3e and f. This increase enhances the conductivity, thereby facilitating the activation of  $\text{N}_2$ . Consequently, the energy barrier for the conversion of  $\text{N}_2$  to  $\text{NH}_3$  is significantly reduced for  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ .

To explore the origin of the boosted photocatalytic performance of  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  heterostructures, the migration behaviors of photogenerated charges were systematically investigated. First, the Mott–Schottky (M–S) curves were recorded to reveal the conduction band potential ( $E_{\text{CB}}$ ) of the semiconductors. In Fig. 4a and b, the M–S curves revealed that both  $\text{Sb}_2\text{S}_3$  and  $\text{ZnIn}_2\text{S}_4$  possessed positive slopes, indicating n-type semiconductor features.<sup>38,39</sup> The flat-band potential ( $E_{\text{fb}}$ ) of  $\text{Sb}_2\text{S}_3$  and  $\text{ZnIn}_2\text{S}_4$  was appropriately  $-0.75$  and  $-1.43$  V *versus* Ag/AgCl, respectively. As the  $E_{\text{fb}}$  of n-type semiconductors is about 0.1 V positive compared to  $E_{\text{CB}}$ , the CB positions of  $\text{Sb}_2\text{S}_3$  and  $\text{ZnIn}_2\text{S}_4$  were determined to be  $-0.25$  and  $-0.83$  V *versus*

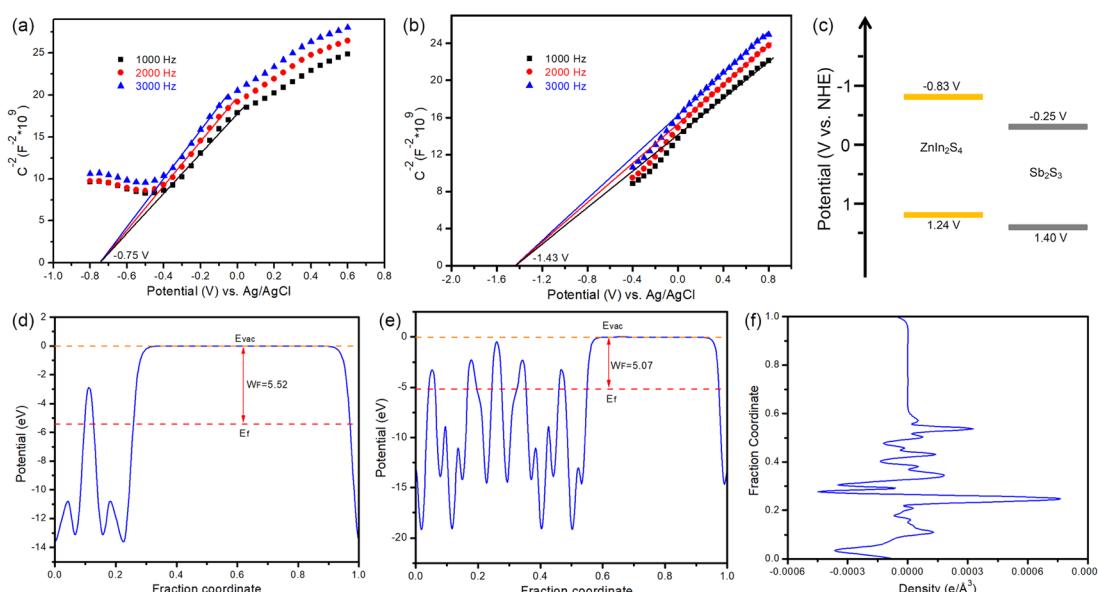


Fig. 4 Mott–Schottky curves of (a)  $\text{Sb}_2\text{S}_3$  and (b)  $\text{ZnIn}_2\text{S}_4$ . (c) Band structures of  $\text{Sb}_2\text{S}_3$  and  $\text{ZnIn}_2\text{S}_4$ . Calculated average potential profile along the Z axis of (d)  $\text{Sb}_2\text{S}_3$  and (e)  $\text{ZnIn}_2\text{S}_4$ . (f) Plane average electron density difference of  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ .

the normal hydrogen electrode (NHE), respectively.<sup>40</sup> Combined with their band gap ( $E_g$ ) values (Fig. S8†), the band structure diagrams of  $\text{Sb}_2\text{S}_3$  and  $\text{ZnIn}_2\text{S}_4$  are shown in Fig. 4c. Apparently, the staggered and matched band alignment between  $\text{Sb}_2\text{S}_3$  and  $\text{ZnIn}_2\text{S}_4$  was established, which was conducive to fabricating type II or S-scheme heterostructures. Subsequently, the work function ( $\Phi$ ), a key physical parameter to determine free electron transfer within the heterojunction, was calculated by DFT. The  $\Phi$  of  $\text{Sb}_2\text{S}_3$  was about 5.52 eV (Fig. 4d), which was obviously bigger than that of  $\text{ZnIn}_2\text{S}_4$  (5.07 eV) (Fig. 4e). Therefore, upon the construction of  $\text{Sb}_2\text{S}_3@{\text{ZnIn}_2\text{S}_4}$  heterostructures, the free electrons in  $\text{ZnIn}_2\text{S}_4$  with a high Fermi level would spontaneously diffuse to  $\text{Sb}_2\text{S}_3$  with a low Fermi level through the heterogeneous interface between  $\text{Sb}_2\text{S}_3$  and  $\text{ZnIn}_2\text{S}_4$  to equilibrate the Fermi level of these two components.<sup>41</sup> This free electron redistribution cause heterogeneous interface near the sides of  $\text{Sb}_2\text{S}_3$  and  $\text{ZnIn}_2\text{S}_4$  forming an electron accumulation layer with negative charge and an electron depletion layer with positive charge, respectively, as evidenced by the charge density difference (Fig. 4f and S9†). As a result, this interfacial charge distribution led to the formation of an internal electric field

pointing from  $\text{ZnIn}_2\text{S}_4$  to  $\text{Sb}_2\text{S}_3$ , which effectively promoted rapid migration of photogenerated charges across the heterogeneous interfaces and thus improved catalytic performance toward  $\text{N}_2$  photofixation.<sup>42</sup>

To prove the migration direction of photogenerated charges within  $\text{Sb}_2\text{S}_3@{\text{ZnIn}_2\text{S}_4}$  heterostructures, systematical characterization studies, including electron paramagnetic resonance (EPR), nitroblue tetrazolium (NBT) transformation experiments, *in situ* irradiated X-ray photoelectron spectroscopy (ISI-XPS), and noble metal loading, were carried out. As shown in Fig. 5a, the EPR signal of DMPO- $\cdot\text{O}_2^-$  was detected in the suspension of  $\text{Sb}_2\text{S}_3@{\text{ZnIn}_2\text{S}_4}$ -75 under visible light irradiation and its intensity gradually increased with extended irradiation time, indicating that the  $\text{Sb}_2\text{S}_3@{\text{ZnIn}_2\text{S}_4}$ -75 sample was capable of producing  $\cdot\text{O}_2^-$ .<sup>43</sup> The produced  $\cdot\text{O}_2^-$  was further analyzed through NBT transformation experiments (Fig. 5b). Apparently, the absorption spectral intensity of NBT decreased as the radiation time increased when the  $\text{Sb}_2\text{S}_3@{\text{ZnIn}_2\text{S}_4}$ -75 sample was introduced, indicating that  $\cdot\text{O}_2^-$  indeed appeared in irradiated  $\text{Sb}_2\text{S}_3@{\text{ZnIn}_2\text{S}_4}$ -75 and simultaneously NBT was successfully consumed by the produced  $\cdot\text{O}_2^-$ .<sup>44</sup> Interestingly, the  $E_{\text{CB}}$  of

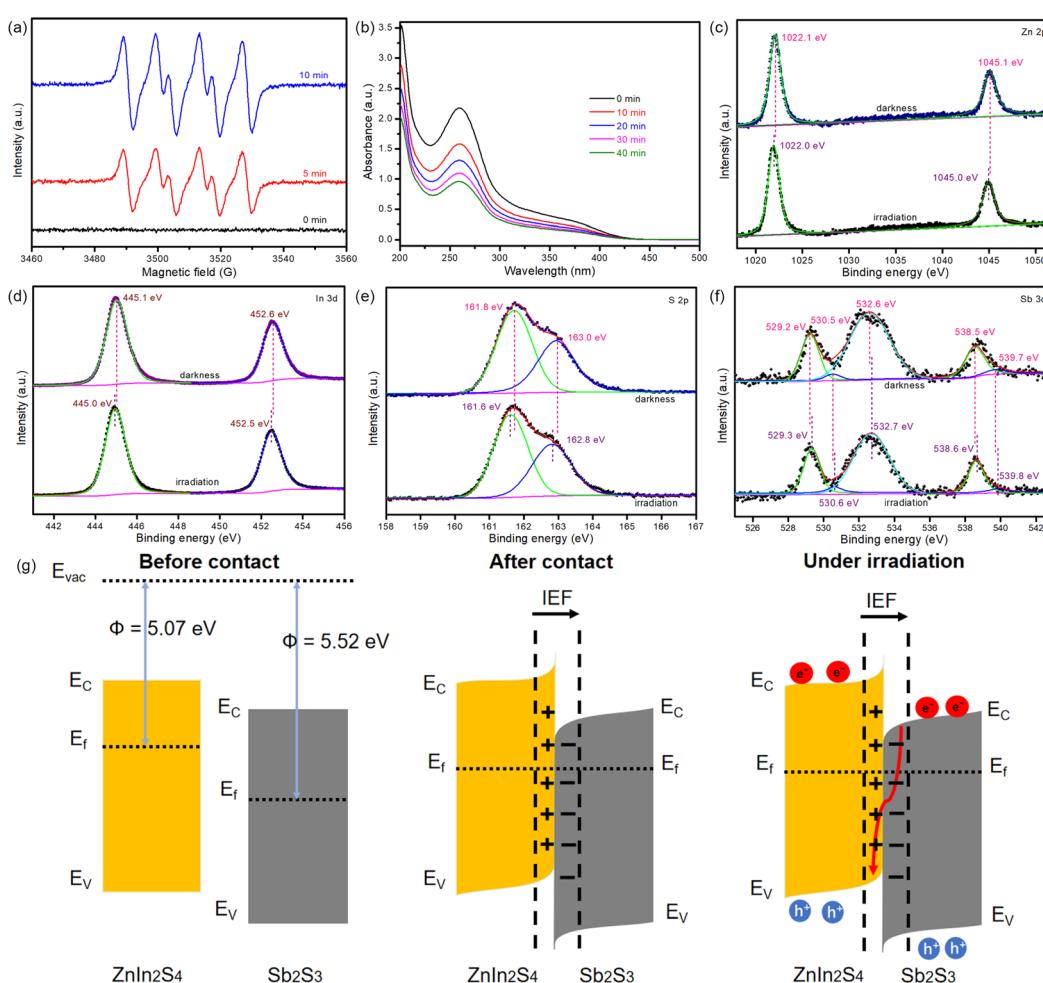


Fig. 5 (a) EPR spectra and (b) time-dependent absorption peak of NBT over the  $\text{Sb}_2\text{S}_3@{\text{ZnIn}_2\text{S}_4}$ -75 sample. ISI-XPS data: (c) Zn 2p, (d) In 3d, (e) S 2p, and (f) Sb 3d. (g) Schematic illustration of internal electric field formation and the S-scheme charge transfer pathway at the interface of  $\text{Sb}_2\text{S}_3@{\text{ZnIn}_2\text{S}_4}$  under light irradiation.

$\text{Sb}_2\text{S}_3$  does not meet the conversion requirements of  $\text{O}_2/\text{O}_2^-$  ( $-0.33$  V),<sup>45</sup> suggesting that  $\text{O}_2^-$  does not originate from the oxygen reduction reaction between  $\text{O}_2$  and  $E_{\text{CB}}$  of  $\text{Sb}_2\text{S}_3$ . Therefore, based on the above results and analyses, we could draw the conclusion that the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  sample followed an S-scheme rather than a type II charge separation mechanism. ISI-XPS was performed to directly verify the S-scheme charge separation mechanism within the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  sample. As shown in Fig. 5c–f, the results from ISI-XPS indicated that  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 exhibited smaller binding energy in the regions of  $\text{Zn}$  2p,  $\text{In}$  3d, and  $\text{S}$  2p and bigger binding energy in  $\text{Sb}$  3d when exposed to light irradiation than those in the darkness. These results indicated that the photogenerated electrons in the CB of  $\text{Sb}_2\text{S}_3$  were injected into  $\text{ZnIn}_2\text{S}_4$ , further verifying the S-scheme charge migration mechanism.<sup>46,47</sup> Such a charge migration path, driven by the internal electric field between  $\text{Sb}_2\text{S}_3$  and  $\text{ZnIn}_2\text{S}_4$ , convincingly confirms the successful formation of S-scheme heterostructures (Fig. 5g). The migration direction of photogenerated charge was traced by the noble metal deposition method.<sup>48</sup> It could be noticed that noble Au was tightly loaded onto the surface of  $\text{ZnIn}_2\text{S}_4$  when the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 sample was used as the photocatalyst (Fig. S10†), revealing that the S-scheme charge migration mechanism was achieved within  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  samples and photogenerated electrons were accumulated in the CB of  $\text{ZnIn}_2\text{S}_4$ .

The efficient charge migration within  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  heterostructures was explored by photoelectrochemical tests,

photoluminescence (PL), time-resolved PL (TRPL), and surface photovoltage (SPV) measurements, as shown in Fig. 6. Compared with bare  $\text{Sb}_2\text{S}_3$  and pure  $\text{ZnIn}_2\text{S}_4$ , the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 sample with a higher photocurrent intensity (Fig. 6a) and smaller semicircle (Fig. 6b) indicated higher charge transfer and separation efficiency and smaller electrical resistance upon the formation of the heterogeneous interface.<sup>49,50</sup> As shown in Fig. S11,† PL tests revealed  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 could produce lower PL intensity in comparison with pure  $\text{ZnIn}_2\text{S}_4$ , indicating either a faster migration process with a shorter lifetime or a slower recombination process with a longer lifetime for the photogenerated electrons.<sup>51</sup> Then, TRPL spectra of the  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 heterostructure and pure  $\text{ZnIn}_2\text{S}_4$  were further recorded to investigate the migration dynamics behavior of photogenerated charge (Fig. 6c). Both  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 and pure  $\text{ZnIn}_2\text{S}_4$  could be fitted with a double exponential function and the corresponding fitting parameters are described in Table S2.† Apparently, the average PL lifetime of  $\text{ZnIn}_2\text{S}_4$  was prolonged from  $4.81$  to  $5.48$  ns after coupling with  $\text{Sb}_2\text{S}_3$ . As we know, the short lifetime components ( $\tau_1$ ) represented the nonradiative recombination of the photogenerated electrons captured by the surface defects, and the long lifetime components ( $\tau_2$ ) resulted from the recombination of the free excitons.<sup>52</sup> The increased PL lifetime and decreased PL intensity jointly revealed that the radiative recombination of photogenerated electrons on the excited states of  $\text{ZnIn}_2\text{S}_4$  was significantly suppressed due to the existence of  $\text{Sb}_2\text{S}_3$  in  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 that could inject photogenerated electrons and

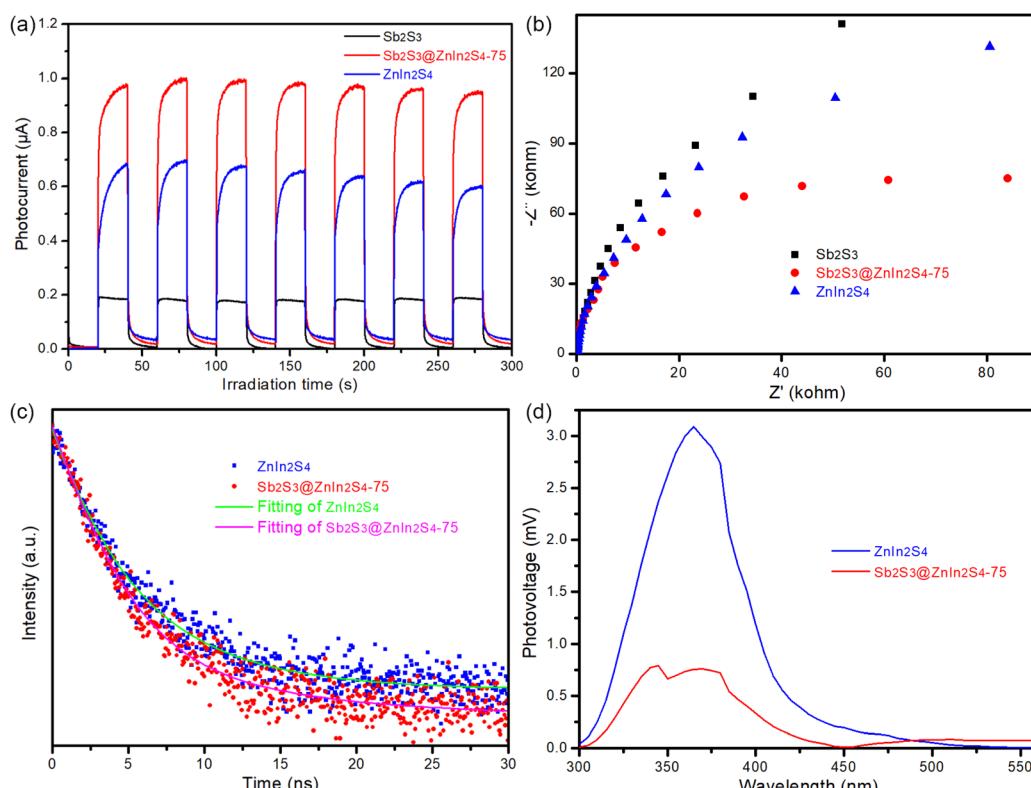


Fig. 6 (a) Photocurrent response, (b) electrochemical impedance spectroscopy (EIS), (c) TRPL, and (d) SPV spectra of the sample.

react with photogenerated holes on the VB of  $\text{ZnIn}_2\text{S}_4$ .<sup>53</sup> Fig. 6d shows the SPV spectra of pristine  $\text{ZnIn}_2\text{S}_4$  and  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75. Compared with pure  $\text{ZnIn}_2\text{S}_4$ , the SPV signal of  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 was obviously decreased, which indicated that more photogenerated holes on  $\text{ZnIn}_2\text{S}_4$  were recombined with injected photogenerated electrons from  $\text{Sb}_2\text{S}_3$  and thus more photogenerated electrons moved to the surface.<sup>54,55</sup> According to the results, we reached a conclusion that the S-scheme charge transfer gave rise to efficient charge migration across the heterogeneous interface between  $\text{Sb}_2\text{S}_3$  and  $\text{ZnIn}_2\text{S}_4$ .

## Conclusion

In conclusion, herein we reported a hydrothermal reaction to synthesize S-scheme  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  hybrid systems by anchoring  $\text{ZnIn}_2\text{S}_4$  on the  $\text{Sb}_2\text{S}_3$  surface, which display significant enhancement of photocatalytic activity towards nitrogen photofixation under visible light irradiation. The optimized photocatalytic ammonia production activity of  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$  samples was successfully achieved by modulating the addition amount between  $\text{Sb}_2\text{S}_3$  and  $\text{ZnIn}_2\text{S}_4$ . The photocatalytic experiment indicated that the optimal  $\text{Sb}_2\text{S}_3@\text{ZnIn}_2\text{S}_4$ -75 sample possessed the highest photocatalytic activity with an ammonia production rate of  $15.96 \pm 0.97 \text{ mg L}^{-1}$  after visible light irradiation for 40 min, which was about 1.88 and 7.19 times higher than those of relevant  $\text{ZnIn}_2\text{S}_4$  and  $\text{Sb}_2\text{S}_3$ , respectively. Such high efficiency in photocatalytic ammonia production was ascribed to faster charge separation originating from S-scheme charge separation. We hoped that our current investigation could provide some insights into the design and application of direct S-scheme hybrid systems for highly efficient photocatalytic activity towards nitrogen photofixation.

## Data availability

The data supporting the findings of this study are available within the references, article and its ESI.†

## Author contributions

C. J. Z. performed the experiments. C. Z. and H. X. Y. assisted with the  $\text{N}_2$  photofixation experiments. T. C. and J. Z. carried out the characterization of materials. Z. H. and W. C. designed the research work. W. M. and G. L. carried out the theoretical calculations. W. C. wrote the manuscript. All authors discussed the results and commented on the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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