# Nanoscale

## REVIEW

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# Enhanced photocatalytic performance of SnS₂ under visible light irradiation: strategies and future perspectives

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Tin(ii) sulfide (SnS₂) has emerged as a promising candidate for visible light photocatalytic materials. As a member of the transition metal dichalcogenides (TMDs) family, SnS₂ features a band gap of approximately 2.20 eV and a layered structure, rendering it suitable for visible light activation with a high specific surface area. However, the application of SnS₂ as a visible light photocatalyst still requires improvement, particularly in addressing the high recombination of electrons and holes, as well as the poor selectivity inherent in its perfect crystal structure. Therefore, ongoing research focuses on strategies to enhance the photocatalytic performance of SnS₂. In this comprehensive review, we analyze recent advances and promising strategies for improving the photocatalytic performance of SnS₂. Various successful approaches have been reported, including controlling the reactive facets of SnS₂, inducing defects in the crystal structure, manipulating morphologies, depositing noble metals, and forming heterostructures. We provide a detailed understanding of these phenomena and the preparation techniques involved, as well as future considerations for exploring new science in SnS₂ photocatalysis and optimizing performance.

## 1 Introduction

The family of transition metal dichalcogenides (TMDs) has garnered significant attention in photocatalytic applications owing to its visible light band gap and layered structure, which provides a high specific surface area.[1,2] However, the traditional utilization of primary TMD materials such as MoS₂, MoSe₂ and WS₂ has predominantly been as supporting photocatalysts alongside other materials like ZnO,[3–6] TiO₂,[7–10] C₃N₄[11] and others, due to their properties akin to graphene.[12,13] In contrast, unlike MoS₂, MoSe₂ and WS₂, SnS₂ has emerged as a promising photocatalyst under visible light irradiation, attributable to its suitable band gap energy for visible light.[14,15]

SnS₂ belongs to the family of layered structure transition metal dichalcogenides (TMDs), characterized as an n-type semiconductor with a band gap ranging from 2.18 to 2.44 eV.[16] In practical applications, SnS₂ has found widespread use

across various fields such as batteries,[17,18] sensors,[19,20] and photocatalysis due to its low cost, low toxicity, excellent stability, and abundant natural reserves.[21] SnS₂ can be synthesized using various techniques, including hydrothermal,[22,23] solvothermal,[24,25] CVD,[26,27] and pulse laser deposition,[28–30] among others. Additionally, SnS₂ can exhibit diverse morphologies, such as flower-like structures, plate-like forms, nanoparticles, and quantum dots, rendering it particularly intriguing for both study and application purposes.

Various reports have shown that SnS₂ can be utilized in numerous photocatalytic applications, such as hydrogen production,[31–34] wastewater treatment,[35–39] antibacterial and antifungal activity,[40–43] and air purification.[44] For example, Yu *et al.*[45] first reported the photocatalytic hydrogen production of SnS₂ nanosheets under solar light simulation with H₂ evolution activity of 1.06 mmol h⁻¹ g⁻¹. In the case of waste water remediation, there are numerous reports for different kinds of waste water such as heavy metals,[46–48] organic dyes,[49,50] and pharmaceutical waste.[51–53] For antibacterial activity, SnS₂ has been applied to inactivate *S. aureus* and *E. coli* as reported by Fakhri *et al.*,[40,41] and for air purification SnS₂ has been reported to be able to remove various VOC gasses such as trichloroethylene[54] and formaldehyde[55] as well as NOₓ gas.[44] Other applications have also been reported by researchers such as CO₂ reduction and nitrogen fixation which make SnS₂ a promising photocatalyst candidate. (For detailed summaries see sub-section 2.2.)

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As a photocatalyst, some characteristics of $SnS_2$ have become key for an excellent performance. These include low recombination and hole rates,[56–59] a high specific surface area,[60,61] high-reactivity facets,[62,63] and good stability.[64,65] Despite the confirmed photocatalytic performance of $SnS_2$, there are still limitations that hinder its efficiency, such as a high recombination of electrons and holes,[66,67] and low specific surface area. Consequently, many researchers have focused on modifying $SnS_2$ to meet the requirements.

Several strategies have been widely adopted to enhance photocatalytic performance, including morphological modification,[68,69] structural engineering,[70,71] and hetero-structure formation.[72–74] Each of these strategies has unique advantages. For instance, morphological modification can alter the surface structure of $SnS_2$, influencing parameters such as surface area and facet arrangement, which are beneficial for improving photocatalytic performance. Structural engineering involves disturbing the crystal structure of $SnS_2$ through various treatments, including vacancy generation, doping addition, and strain engineering. These treatments effectively decrease electron and hole recombination, thereby enhancing photocatalytic performance. Noble metal doping, such as Au, Pt, and Ag, is a well-known method for improving photocatalytic performance due to its ability to act as an electron acceptor, slowing down the recombination of electrons and holes.[75] Meanwhile, heterostructure formation can generate a synergistic effect between one sample and another, effectively improving the photocatalytic performance.[76]

Presently, there are several reports that have reviewed the photocatalytic performance of $SnS_2$. Sharma et al.[77] reviewed the photocatalytic performance of $SnS_2$ related to energy conversion and a heterostructure perspective approach, while Guo et al.[78] reviewed the advancement of the photocatalytic performance of $SnS_2$ by comparing pure $SnS_2$ and $SnS_2$-based composite. While these two reviews have addressed some important aspects of improvement strategies, the detailed explanation and fundamental mechanism of the photocatalytic enhancement of $SnS_2$ have not been thoroughly explored. In this study, we systematically investigate the current advancement strategies for enhancing photocatalytic performance, which can be classified into three categories: structural modification, morphology engineering, and heterojunction formation. We will elucidate the factors from each strategy that have the most significant impact on the photocatalysis of $SnS_2$. Furthermore, we will propose future perspectives for the development of photocatalytic studies on $SnS_2$ based on the existing literature. Fig. 1 illustrates three distinct strategies for enhancing photocatalytic performance across various applications, discussed in this review. The first strategy involves structural modification, encompassing vacancy generation and doping processes. The second strategy focuses on morphological manipulation, featuring a range of morphologies such as nanoflowers, nanoparticles, nanosheets, and quantum dots. The final strategy concerns heterojunction formation, encompassing Schottky junctions, heterojunctions types I and II, p–n junctions, as well as Z-scheme and S-scheme photocatalysts. Additionally, we address current challenges and offer insights into future developments.

## 2  $SnS_2$ properties and photocatalytic applications

### 2.1  Physical properties of $SnS_2$

Tin disulfide ($SnS_2$) belongs to the IV–VI chalcogenide materials and exhibits a golden-yellowish color, resembling the configuration of transition metal dichalcogenide (TMD) materials.[77] The atomic arrangement of $SnS_2$ consists of a Sn atom sandwiched between two hexagonally close-packed sulfur atoms. In layered $SnS_2$, planar threefold layers (TLs) are



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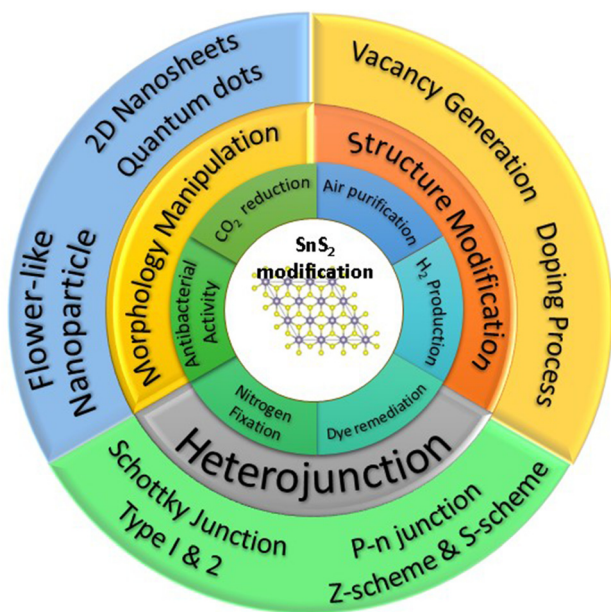
**Fig. 1** Modification strategy of $SnS_2$ for improving photocatalytic performance.

formed, where strong covalent bonding exists in a plane, while weak van der Waals interactions dominate out of plane, as shown in Fig. 2(a).[79] The $SnS_2$ structure belongs to the covalent bonding group of $P\bar{3}m1$ (164) with lattice parameters $a = b = 0.3643$ nm and $c = 1.7683$ nm.[79] Like the other members of the TMD family, $SnS_2$ has a layered structure with several interesting properties such as a high optical absorption coefficient, tunable bandgap, low toxicity, and natural abundance, which makes it very promising for 2D material applications such as photocatalysis, photoanodes,[80] and gas sensors.[20] $SnS_2$ corresponds to an n-type semiconductor that possesses a narrow energy band gap of 2.0–2.4 eV. The band positions of $SnS_2$



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were determined by linear extrapolation of the band edges and secondary electron cut-off, to the baseline, and yielded an ionization potential ($E_{vac} - E_{VBM}$) of 6.44 ± 0.07 eV and an electron affinity ($E_{vac} - E_{CBM}$) of 4.16 ± 0.17 eV. A bandgap ($E_{CBM} - E_{VBM}$) of 2.28 ± 0.15 eV is thus found that corresponds to the indirect band gap as shown in Fig. 2(b). $SnS_2$ also has higher electron mobility (~230 cm$^2$ V$^{-1}$ s$^{-1}$), higher capacitance (645 mA h g$^{-1}$), and lower environmental noxiousness.[81] The photocatalytic reaction process occurs when the band positions of the photocatalyst align with the redox potentials required for specific chemical reactions. For instance, the conversion of $H^+$ to $H_2$ can occur at 0 V *vs.* NHE energy, where electrons in the conduction band with an energy lower than 0 V can reduce $H^+$ to $H_2$. Conversely, the transformation of $OH^-$ to $OH^{\bullet}$ requires 1.93 V *vs.* NHE, necessitating holes with an energy higher than 1.93 *vs.* NHE to oxidize $OH^-$ to $OH^{\bullet}$. In this context, the band positions of $SnS_2$ fulfill both criteria, with the conduction band at −1.5 V *vs.* NHE and the valence band at 2.13 V *vs.* NHE,[82] as illustrated in Fig. 2(c). Various chemical reactions may yield different potential energy requirements, thus influencing the applicability of $SnS_2$ in photocatalysis.

## 2.2 Photocatalytic applications of $SnS_2$

The utilization of $SnS_2$ as a photocatalyst was initially documented in 2007 by He *et al.*[83] who explored the formation of a heterostructure between $SnS_2$ and $TiO_2$ for methyl orange degradation. However, after this initial investigation, research on $SnS_2$ photocatalysis remained limited until 2017, when the number of publications on the subject notably increased, as illustrated in Fig. 3(a). Presently, the total number of publications on $SnS_2$ as a photocatalyst remains at less than 500, significantly lower compared with conventional photocatalysts such as $TiO_2$ or ZnO, and even other transition metal dichalcogenide (TMD) materials like $MoS_2$ and $WS_2$ (based on Scopus data). As a 2D photocatalyst material, $SnS_2$ has found applications across various domains, including air purification,[44,55] wastewater treatment,[47,84–87] hydrogen production,[88–97] and antibacterial purposes,[41] $CO_2$ reduction, and[89,91,98–100] nitrogen fixation.[92,94,101]

According to Scopus data, illustrated in Fig. 3(b), the predominant focus of photocatalytic applications involving $SnS_2$ is wastewater treatment, constituting 66% of the total research publications to date. Following closely, hydrogen production and $CO_2$ reduction make up 21% and 10% of the total publications on $SnS_2$ as a photocatalyst. The least explored applications include nitrogen fixation, antibacterial activity, and air purification. Wastewater treatment represents the most extensively studied application when investigating $SnS_2$ photocatalytic performance. Given the high demand for clean water in our daily lives, the removal of wastewater from water resources is of paramount importance. Various types of wastewater, containing pollutants such as organic dyes, heavy metals, pharmaceutical waste, and even uranium(VI), pose significant threats to our health. Until now (2024 January 10th), based on Scopus data there are 337 publications that have reported the use of $SnS_2$ photocatalyst for wastewater treat-
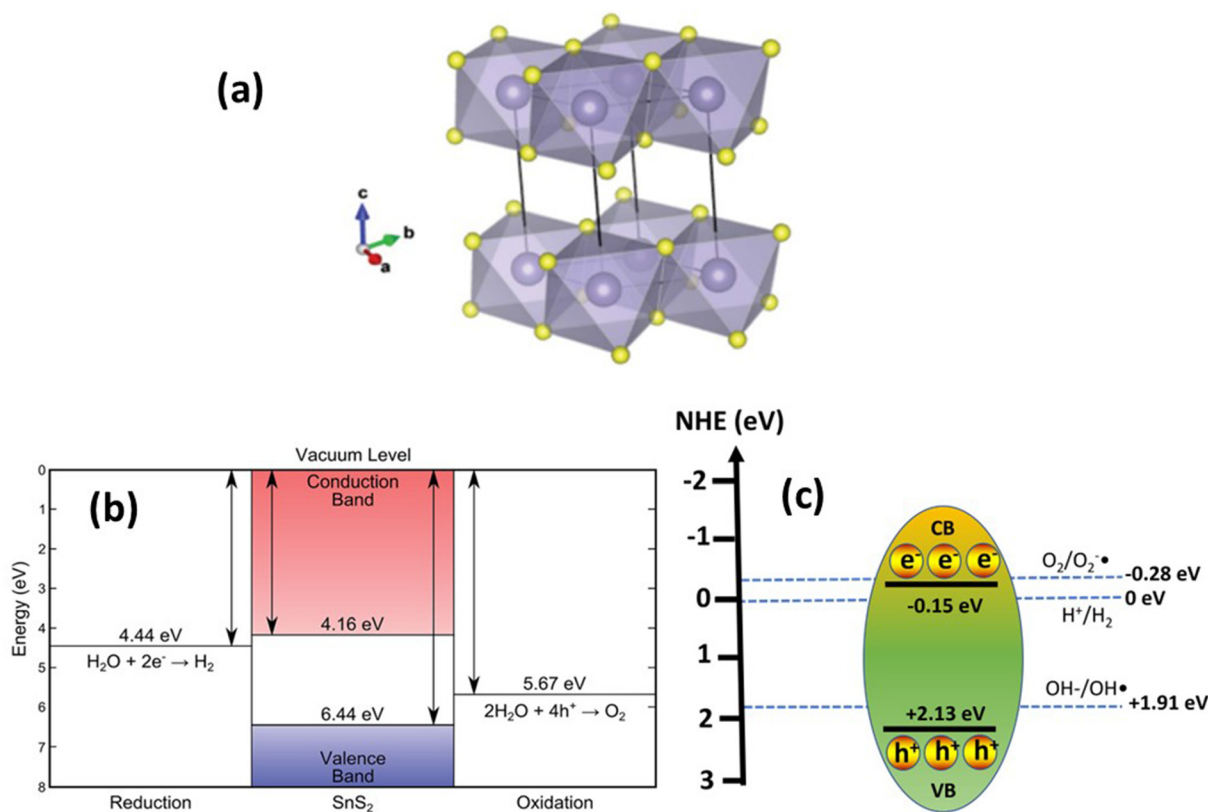
**Fig. 2** (a) Crystal structure and (b) band position of $SnS_2$. (Reproduced from ref. 79 with permission from the Royal Society of Chemistry, copyright 2016.)[79] (c) Band position of $SnS_2$ for photocatalytic reactions.
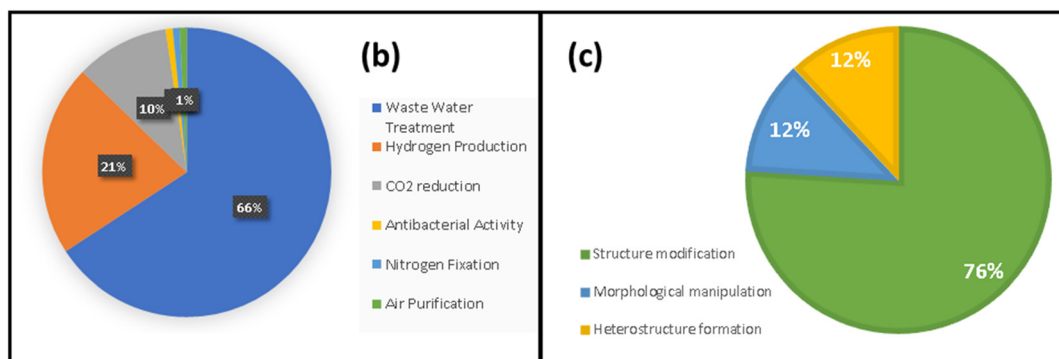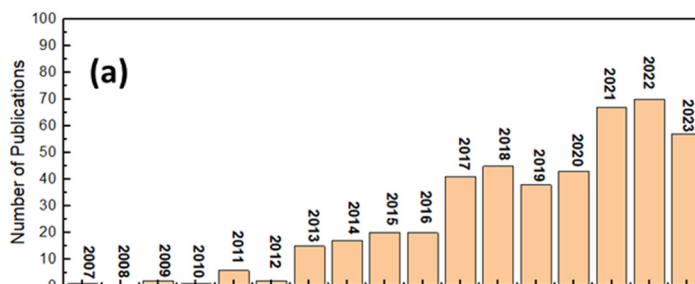


**Fig. 3** (a) Number of $SnS_2$ photocatalytic publications; (b) summary of practical applications of $SnS_2$ photocatalytic. (c) Graphical illustration for photocatalytic improvement strategies for $SnS_2$.

ment under visible light irradiation and 192 of them are about organic dye removal such as methylene blue,[102–104] methyl orange,[105] and rhodamine B (RhB).[49,106] For heavy metals, hexavalent chromium (Cr(VI)) is the most studied waste water model for photocatalytic investigations of $SnS_2$, with 99 publications, which makes $SnS_2$ one of the most promising materials for Cr(VI) reduction under visible light irradiation. In the pharmaceutical waste field, tetracycline is the most studied wastewater, with 11 reports showing a good performance for tetracycline removal by a $SnS_2$ photocatalyst. Table 1 shows the summary of various types of application of $SnS_2$ photocatalysts. It can be seen that the $SnS_2$ photocatalyst exhibits great potential for various types of photocatalytic application.

**2.2.1 $CO_2$ reduction.** Recently, $CO_2$ conversion has attracted considerable attention for photocatalytic results due to its great potential for reducing $CO_2$ pollution alongside producing more valuable products.[107] Sun et al.[108] initiated efforts to reduce $CO_2$ through photocatalytic processes by $SnS_2$ under visible light irradiation. Their research successfully converted $CO_2$ into CO with a yield of approximately 80 ppm after 8 hours of xenon irradiation. Subsequently, Li et al.[109] explored the influence of $SnS_2$ morphology on $CO_2$ reduction via photocatalytic reactions. They examined two distinct morphologies—tablet-like and flower-like—and observed the conversion of $CO_2$ gas into $CH_4$ and CO gases. Notably, each morphology exhibited a unique behavior in $CO_2$ reduction. The flower-like morphology demonstrated a higher $CH_4$ yield at 97.5 μmol $g^{-1}$ compared with CO gas at 75.1 μmol $g^{-1}$, while the tablet morphology showed stronger CO production at 61.6 μmol $g^{-1}$ relative to $CH_4$ gas at 17.2 μmol $g^{-1}$. This underscores the impact of $SnS_2$ morphology on $CO_2$ reduction, which is directly linked to variations in charge separation processes, surface properties, and other factors (further elaborated in the subsequent discussion). Recent endeavors have focused on optimizing and enhancing $CO_2$ reduction through various techniques, including the formation of Z-scheme heterojunctions,[110] type II heterojunctions, vacancy generation,[106] and doping processes.[97] Among these strategies, Z-scheme heterojunctions have shown significant promise in improving the $CO_2$ reduction process. Wang et al. reported the synthesis of a Z-scheme photocatalyst, $SnO_2/SnS_2/Cu_2SnS_3$, which achieved a $CO_2$ reduction to ethanol rate of 28.44 mmol $g^{-1}$ $h^{-1}$ as a byproduct. The fundamental process of $CO_2$ reduction can be described as follows: when subjected to irradiation, electrons and holes are generated. Electrons in the conduction band, possessing a band position more negative than the reduction potential of $CO_2$, participate in reactions that transform $CO_2$ into various chemicals. The specific transformation depends on the suitability of the conduction band energy for reducing $CO_2$ into alternative chemical compounds.

**2.2.2 Nitrogen reduction.** The exploration of $SnS_2$ photocatalytic applications in nitrogen fixation is still relatively limited, with only four studies investigating its potential in this area. Li et al.[101] reported on the nitrogen fixation capability of $SnS_2$ using nanosheet and nanoplate morphologies. They found that the $NH_4^+$ concentration reached 40.5 μmol $g^{-1}$

and 110.1 μmol $g^{-1}$ on $SnS_2$-plate and $SnS_2$-sheet samples, respectively, after 4 hours, with average reaction rates of 10.1 μmol $g^{-1}$ $h^{-1}$ and 27.5 μmol $g^{-1}$ $h^{-1}$, respectively. These findings highlight the sensitivity of $SnS_2$ photocatalytic performance to particle morphology. Three other reports discussed the nitrogen fixation application of $SnS_2$ in heterostructure forms. For instance, Nie et al.[92] demonstrated the formation of 1D/2D heterojunctions of $SnS_2@MoO_3$ as an efficient catalyst for visible photoelectric nitrogen fixation. Compared with pure $MoO_3$ and $SnS_2$, the nitrogen fixation performance improved by 2.3 and 4.6 times, respectively, and the Faraday efficiency was enhanced by 2.0 and 3.5 times, respectively. Another study by Lan et al.[94] also explored the formation of a Z-scheme heterojunction $Bi/Bi_2S_3/SnS_2$ for nitrogen fixation applications. The results showed that the Z-scheme formation of $Bi/Bi_2S_3/SnS_2$ successfully enhanced $NH_4^+$ production, yielding approximately 96.4 μmol $g^{-1}$ $h^{-1}$, which is 1.9 and 3.0 times higher than that of $SnS_2$ and $Bi/Bi_2S_3$, respectively. The basic mechanism of the nitrogen fixation applications can be explained as follows: upon irradiation, the electrons and holes are generated. After that the photogenerated holes reacted with water to produce $H^+$ ions and in the final reaction $N_2$, $H^+$, and electrons reacted to produce $NH_3$ or $NH_4^+$ ions.[101]

**2.2.3 $H_2$ production.** Hydrogen production has become one of the popular applications for photocatalytic research since the growth of green sources of energy for switching from fossil fuels.[111] Initial investigations into the hydrogen production capabilities of $SnS_2$ were conducted in 2014. Yu et al.[45] prepared monodisperse $SnS_2$ nanosheets for hydrogen production under visible light irradiation, achieving a notable hydrogen production yield of approximately 0.566 mmol $g^{-1}$ $h^{-1}$, which is considerably high for a visible light photocatalyst. The fundamental mechanism of $H_2$ production in photocatalytic reactions involving $SnS_2$ can be elucidated as follows: upon irradiation, the $SnS_2$ semiconductor generates electron–hole pairs. The photoexcited electrons reside in the conduction band and subsequently react with $H^+$ to produce $H_2$ gas. However, for the generation of $H_2$ gas, it is essential that the reduction potential of electrons in the conduction band exceeds the reduction potential of $H^+/H_2$ (0 V). The conduction band position of $SnS_2$ is influenced by various factors such as facet orientation and band gap. Huang et al.[69] demonstrated that the band position of $SnS_2$ is influenced by its facet orientation. Two facet orientations, (100) and (101), exhibit distinct performance characteristics in the photocatalytic production of $H_2$ gas. The (101) facet orientation is more favorable as it possesses a higher conduction band level than the reduction potential of $H^+/H_2$, whereas the dominance of the (100) facet results in a lower reduction potential in the conduction band compared with $H^+/H_2$. These findings suggest that the (101) facet of $SnS_2$ may be more conducive to $H_2$ production. Recent studies have focused on the development of S-scheme and Z-scheme photocatalysts (see Table 1) due to their efficient charge separation and band modulation properties.[112–117]

**Table 1** Photocatalytic data of $SnS_2$ for various types of application

| Sample | Sample | Light source | Photocatalytic result | Additional information | Ref. |
|---|---|---|---|---|---|
| $CO_2$ reduction | Cu-doped $SnS_2$ | 420 nm LED | $CH_3OH$ yield 0.99 mmol $g^{-1}$ | | 97 |
| | S-vacancy $SnS_2$ | 400 W metal halide lamp | CO yield = 2.44 $\mu$mol $g^{-1}$ $h^{-1}$. 1.48 times that of pure $SnS_2$ | | 106 |
| | $SnS_2$ flower-like | 300 W xenon light | CO production rate 8.91 $\mu$mol $g^{-1}$ $h^{-1}$ | | 135 |
| | Z-scheme $SnO_2/SnS_2/Cu_2SnS_3$ | 300 W xenon lamp | Ethanol yield 28.44 mmol $g^{-1}$ $h^{-1}$ 3 times higher than $SnS_2$ | | 110 |
| | $SnS_2/SnO_2$ nanoflower | 300 W xenon lamp | CO yield 60.85 $\mu$mol $g^{-1}$ $h^{-1}$ | | 136 |
| | Partly oxidized $SnS_2$ | 300 W xenon lamp | CO yield 12.28 $\mu$mol $g^{-1}$ $h^{-1}$ | | 67 |
| | Carbon-doped $SnS_2$ | 300 W halogen lamp | $CH_3CHO$ yield 125.66 $\mu$mol per 100 g per 3 h | | 67 |
| | Carbon-doped $SnS_2$ | 150 W halogen lamp | $CH_4$ yield 0.64 $\mu$mol $g^{-1}$ $h^{-1}$ | | 67 |
| | $SnS_2$ QDs/g-$C_3N_4$ | 300 W xenon lamp (420 nm cut-off) | $CH_3OH$ yield 2.3 $\mu$mol $g^{-1}$ $h^{-1}$ | | 137 |
| Hydrogen production | $SnS_2$-nanosheets | 400 W mercury lamp | $H_2$ production rate: 0.566 mmol $g^{-1}$ $h^{-1}$ | | 31 |
| | 2.5 mol% Ni–$SnS_2$ | 400 W mercury lamp | 1429 $\mu$mol $g^{-1}$ $h^{-1}$ | | 138 |
| | $In^{3+}$-doped $SnS_2$ | 300 W xenon lamp | $H_2$ production rate: 470 mmol $g^{-1}$ for 12 h | | 139 |
| | S-scheme $SnS_2/CdS$ | Simulated solar light (100 mW $cm^{-2}$) | 360.75 $\mu$L $h^{-1}$ | | 116 |
| | $SnS_2$/g-$C_3N_4$ | 300 W xenon lamp ($\lambda \geq$ 420 nm) | 1818.8 $\mu$M $g^{-1}$ $h^{-1}$ | | 124 |
| | $SnS_2/CdS/TiO_2$ | 300 W xenon lamp ($\lambda \geq$ 420 nm) | 97.14 $\mu$mol $h^{-1}$ $cm^{-2}$ | | 140 |
| | $SnS_2/BiVO_4$ | 100 mW $cm^{-2}$ xenon lamp, 0.8 V | 900 $\mu$mol $cm^{-2}$ | | 117 |
| | $SnS_2/Cd_{0.5}Zn_{0.5}S$ | 300 W xenon lamp ($\lambda \geq$ 420 nm) | 3.19 mmol $g^{-1}$ $h^{-1}$ | | 141 |
| Air purification | $Bi_4O_5Br_2$–$SnS_2$ | Visible light | 40% $NO_x$ removal | $NO_x$ abatement | 44 |
| | Ni-doped $SnS_2/SnO_2$ | 8 W, 256 nm light | 85% | Trichloroethylene | 54 |
| | $SnS_2/TiO_2$ | 40 W fluorescence lamp | 55% removal | Formaldehyde | 55 |
| Nitrogen fixation | $SnS_2$ nanosheets | 330 W xenon lamp | 27.5 $\mu$mol $g^{-1}$ $h^{-1}$ | | 101 |
| | $SnS_2/MoO_3$ | 300 W xenon lamp | 30.04 $\mu$g $h^{-1}$ $mg^{-1}$ | | 92 |
| | $Bi/Bi_2S_3/SnS_2$ | 300 W xenon lamp | 96.4 $\mu$mol $g^{-1}$ $h^{-1}$ | | 94 |
| Antibacterial activity | $SnS_2$ nanoparticles | 500 W xenon lamp | 75.28 ± 2.3% | S. aureus (ATCC 25923) | 41 |
| | $SnS_2$ nanoparticles | 500 W xenon lamp | 78.95 ± 2.0% | E. coli (ATCC 13534) | 41 |
| | $SnS_2$ nanoparticles | 500 W xenon lamp | 81.22 ± 1.1% | E. coli (ATCC 25922) | 41 |
| | $SnS_2$ | Visible light | 50.39 | E. coli | 43 |
| | Pr-doped $SnS_2$ | Visible light | 71.03 | E. coli | 43 |
| Waste water treatment | $SnS_2$ nanoparticle | 250 W xenon lamp ($\lambda \geq$ 420 nm) | $k_{MO}$: 0.0594 $min^{-1}$ | Methyl orange | 105 |
| | $MoS_2/SnS_2$ | Visible light | $k_{MB}$: 0.0594 $min^{-1}$ | Methylene blue | 122 |
| | $SnS_2$ decorated biochar | Natural sunlight | $k_{MB}$: 0.013 $min^{-1}$ | Methylene blue | 142 |
| | S–Sn–S vacancy $SnS_2$ | 300 W Xe lamp | $k_{RhB}$ = 0.136 $min^{-1}$ | Rhodamine B | 143 |
| | $CdZnS/SnS_2/SnO_2$ | 500 W xenon lamp | $k_{RhB}$ = 0.0267 $min^{-1}$ | Rhodamine B | 49 |
| | Zr-doped $SnS_2$ | Larger than 420 nm | $k_{Cr(VI)}$ = 0.059 $min^{-1}$ | Cr(VI) | 144 |
| | $SnS_2$ nanoparticle | 300 W xenon lamp | $k_{Cr(VI)}$ = 0.00401 $min^{-1}$ | Cr(VI) | 129 |
| | $SnS_2$@$SnO_2$ | 300 W xenon lamp | $k_{Cr(VI)}$ = 0.0907 $min^{-1}$ | Cr(VI) | 129 |
| | $SnS_2/SnS$ | Direct sunlight | $k_{Cr(VI)}$ = 0.086 $min^{-1}$ | Cr(VI) | 145 |
| | $SnS_2/CNTs$ | 300 W xenon lamp ($\lambda \geq$ 420 nm) | $k_{Cr(VI)}$ = 0.07750 $min^{-1}$ | Cr(VI) | 146 |
| | $SnS_2$ nanoplates | Solar irradiance was assumed to be 221 W $m^{-2}$ | $k_{TC}$ = 0.001 $min^{-1}$, $k_{CP}$ = 0.0005 $min^{-1}$ | Tetracycline and ciprofloxacin | 134 |
| | $SnS_2/Bi_2WO_6$ | Solar irradiance was assumed to be 221 W $m^{-2}$ | $k_{TC}$ = 0.027 $min^{-1}$, $k_{CP}$ = 0.024 $min^{-1}$ | Tetracycline and ciprofloxacin | 134 |
| | $SnS_2$ nanoplates | Natural sunlight | $k_{CP}$ = 0.0024 $min^{-1}$ | Ciprofloxacin | 132 |
| | $SnS_2/BiVO_4$ | Natural sunlight | $k_{CP}$ = 0.018424 $min^{-1}$ | Ciprofloxacin | 132 |
| | $SnS_2$ nanoplates | LED light 500 W $m^{-2}$ | $k_{GM}$ = 0.1492 $min^{-1}$ | Gemifloxacin | 37 |
| | Platinum/polypyrrole–carbon black/$SnS_2$ | LED light 500 W $m^{-2}$ | $k_{GM}$ = 0.0429 $min^{-1}$ | Gemifloxacin | 37 |
| | $SnS_2$ nanoparticle | Visible light ($\lambda \geq$ 420 nm) | $k_{TC}$ = 0.00129 $min^{-1}$ | Tetracycline | 38 |
| | $SnS_2/Bi_2MoO_{6-x}$ | Visible light ($\lambda \geq$ 420 nm) | $k_{TC}$ = 0.01245 $min^{-1}$ | Tetracycline | 38 |
| | $SnS_2$ nanoplates | Solar simulator | $k_{NP}$ = 0.014 $min^{-1}$ | Norfloxacin | 147 |

**2.2.4 Antibacterial activity.** The $SnS_2$ photocatalyst has also been explored for antibacterial and antifungal applications. Fakhri et al.[41] demonstrated the removal of S. aureus (ATCC 25923), E. coli (ATCC 13534), and E. coli (ATCC 25922) with removal rates of $75.28 \pm 2.3\%$, $78.95 \pm 2.0\%$, and $81.22 \pm 1.1\%$, respectively. The basic mechanism of antibacterial removal by $SnS_2$ nanoparticles can be elucidated as follows: upon irradiation, electrons and holes are generated, and the photogenerated holes and electrons react with $OH^-$ and $O_2$ to produce $^{\bullet}OH$ and $O_2^{\bullet-}$, respectively. These radical species are then converted into $H_2O_2$, serving as potent oxidative agents for killing bacterial cells. In another study, Fakhri et al.[118] investigated the impact of heterojunction formation of $SnS_2$/$SnO_2$ on antibacterial and antifungal activity. Their results indicate that $SnS_2$/$SnO_2$ exhibits superior bacteria-killing ability compared with pure $SnS_2$ and $SnO_2$, possibly due to the inhibition of the charge carrier separation of electrons and holes. Furthermore, antifungal activity was assessed against pathogenic C. albicans. The largest zones of inhibition for the control, $SnO_2$ nanoparticles, $SnS_2$ nanoplates, and $SnO_2$/$SnS_2$ nanocomposite are 5.89 mm, 13.20 mm, 14.01 mm, and 21.11 mm, respectively. A recent study by Ech-Chergui et al.[43] has corroborated the antibacterial activity of Pr-doped $SnS_2$ for combating E. coli. The Pr-doped $SnS_2$ exhibits enhanced bacteria-killing activity compared with $SnS_2$ alone, attributed to the smaller crystallite size providing more active sites for photocatalytic reactions.

**2.2.5 Air purification.** One of the major environmental issues is the deterioration of air quality due to heavy industry. Various types of air pollutant, including $NO_x$ gas, VOCs, and other gases, are released into our environment, leading to serious health problems. Photocatalytic technology has been acknowledged as one of the solutions to address this issue.[119] In the case of $SnS_2$ photocatalysts, $SnS_2$ has been reported to effectively remove various types of air pollutant, including $NO_x$ gas, formaldehyde, and trichloroethylene, as shown in Table 1. However, the number of reports on the use of $SnS_2$ for air purification is very low, with fewer than 10 publications available. Moreover, all these reports involve heterojunction formation. Therefore, for further development, it is necessary to investigate the use of $SnS_2$ alone for this application.

**2.2.6 Waste-water**

*2.2.6.1 Organic dyes.* Organic dyes are prevalent pollutants in wastewater within our immediate environment, often originating from direct discharge by the textile industry, presenting significant environmental concern. Utilizing photocatalytic wastewater treatment emerges as a promising solution to address this issue, offering notable advantages such as cost-effectiveness, simplicity, and the capability to convert the chemical composition of organic dyes into harmless byproducts such as $CO_2$.[120,121] In the realm of employing $SnS_2$ as a photocatalyst for organic dye degradation, extensive research has been conducted, targeting various dye types including methylene blue,[122] methyl orange,[123] rhodamine B,[124–126] crystal violet,[127] and others. Table 1 depicts the efficacy of $SnS_2$ photocatalysts in removing organic dyes. Notably, the data

demonstrate promising outcomes across all the tested dyes. The underlying mechanism of organic dye degradation can be elucidated as follows: upon irradiation, electron–hole pairs are generated, which subsequently react with $O_2$ and $OH^-$ to yield highly reactive $O_2^{\bullet-}$ and $^{\bullet}OH$ radicals. These radicals possess strong oxidative capabilities, facilitating the decomposition of diverse synthetic dyes into $CO_2$ and water.

*2.2.6.2 Heavy metals.* In addition to organic dyes, the reduction of heavy metals represents a significant area of study in the photocatalytic application of $SnS_2$. Among various heavy metals, hexavalent chromium ($Cr(\text{VI})$) has been extensively researched. Several strategies have been developed to enhance $Cr(\text{VI})$ removal, including vacancy generation,[48] doping formation,[128] and heterostructure formation.[129] The basic mechanism of $Cr(\text{VI})$ reduction involves the generation of electrons and holes upon irradiation, where the photoexcited electrons can directly decompose $Cr(\text{VI})$ ions into $Cr(\text{III})$. The photocatalytic ability of $SnS_2$ depends on the extent to which electrons react with $Cr(\text{VI})$ molecules, which may be attributed to increasing active sites or improving charge carrier separation efficiency. Table 1 presents several studies confirming the degradation of $Cr(\text{VI})$ using $SnS_2$ photocatalysts with varying capabilities. A detailed analysis will be provided in the subsequent section.

*2.2.6.3 Antibiotics.* Pharmaceutical waste, including compounds like tetracycline and others, presents a significant challenge in wastewater management, particularly with many pharmaceutical industries directly discharging their waste into water bodies. Consequently, effective treatment methods are imperative to mitigate the presence of these hazardous chemicals in water. Photocatalysis has emerged as a promising technique for efficiently removing pharmaceutical waste from water. However, the utilization of $SnS_2$ photocatalysts for antibiotic removal remains limited. Only a small number of research papers, fewer than 30, have explored the use of $SnS_2$ photocatalysts for this purpose, with most focusing on the formation of heterojunctions with $SnS_2$, such as Z-scheme and S-scheme configurations.[42,104,130,131] For instance, Kumar et al.[132] demonstrated the effectiveness of Z-scheme $SnS_2$/$BiVO_4$ in removing the antibiotic ciprofloxacin from aqueous solutions. They found that the optimized batch with $0.15SnS_2$/$BiVO_4$ exhibited a significantly higher apparent rate constant ($k = 0.0184$ $min^{-1}$) compared with $BiVO_4$ ($k = 0.0049$ $min^{-1}$) and $SnS_2$ ($k = 0.0024$ $min^{-1}$) alone. This improved performance was attributed to enhanced charge separation efficiency, enabling electrons from $SnS_2$ to directly react with $O_2$ to form $O_2^{\bullet-}$, ultimately degrading ciprofloxacin into $CO_2$ and water.[133] Other antibiotics have also been shown to be degradable by $SnS_2$ photocatalysts. For example, Kumar et al.[134] reported the use of $SnS_2$/$Bi_2WO_6$ for the removal of ciprofloxacin and tetracycline. While $SnS_2$ alone exhibited minimal removal capabilities for these antibiotics, the combination with $Bi_2WO_6$ significantly enhanced the degradation rates. These findings suggest that $SnS_2$ photocatalysts alone are insufficient for effectively decomposing various types of pharmaceutical waste. One of the key limitations is the rapid recombination of electron–hole

pairs, which impedes the reaction of electrons with $O_2$ to generate reactive oxygen species (ROS). Therefore, the development of hybrid photocatalytic systems, combining $SnS_2$ with other materials, holds promise for improving the efficiency of pharmaceutical waste removal from wastewater. Continued research in this area is crucial for advancing sustainable water treatment technologies.

Although there are many publications about photocatalytic performance with different applications, we can categorize their strategies into three different categories.

(1) **Structural modification**: This strategy involves altering the structure of $SnS_2$ to enhance its photocatalytic properties. This could include changes in the composition, arrangement of atoms, or other structural aspects.

(2) **Morphological manipulation**: Morphological manipulation focuses on changing the physical shape or form of $SnS_2$ to improve its photocatalytic performance. This might involve controlling the particle size, shape, or surface structure.

(3) **Heterostructure formation**: This approach involves creating composite materials by combining $SnS_2$ with other materials, possibly forming interfaces or layered structures. The high percentage suggests that researchers find this strategy particularly effective or promising for enhancing photocatalytic performance.

Based on these three classifications, the quantitative analysis has been made and plotted in Fig. 3(c) based on the Scopus data until now. The structural modification and morphological manipulation $SnS_2$ strategies are just 12% each of the total of publications of $SnS_2$ photocatalytic. On the other hands, the heterostructure formation exceeded more than 75%, which indicates, at the current stage, that the heterostructure formation of $SnS_2$ is the most popular strategy for improving strategies, which probably attributed to the unique characteristics of composite structures which imply to the better performance.

# 3 Photocatalytic improvement strategies

## 3.1 Structural modification

Structural modification is a valuable strategy for enhancing photocatalytic performance. By adjusting the structural properties of the photocatalyst, it is possible to improve its electronic and surface characteristics for a range of photocatalytic applications, including optimizing light utilization, enhancing charge transfer kinetics, and creating additional active sites.[148,149] Several established techniques can be employed to modify the structure of the photocatalyst, including vacancy generation and doping. These methods can increase the photocatalyst's charge separation efficiency and surface reactivity by raising the adsorption energy.

### 3.1.1 Vacancy generation. 
Vacancies in 2D materials, such as graphene and transition metal dichalcogenides (TMDs), have garnered significant attention due to their easy formation in these materials. In addition to expediting the charge separ-

ation, the generation of vacancies in 2D materials like $SnS_2$ can increase the number of active sites, facilitating reactant adsorption and thereby implying photocatalytic improvements. In the case of $SnS_2$, sulfur vacancies have been well established as effective methods for modifying its structure in photocatalytic applications.

The synthesis of sulfur vacancy-generating $SnS_2$ was reported by Qiang et al.,[48] prepared via hydrothermal reaction for Cr(VI) reduction under visible light irradiation. They observed that adjusting the molar ratio between the Sn and S precursors during synthesis is crucial for controlling the defect concentration on $SnS_2$ nanoparticles. A higher Sn to S ratio indicates a higher defect content, confirmed by EPR analysis (Fig. 4(a)). An intense resonance signal from EPR analysis for the sample with a Sn to S ratio of five was observed, indicating a higher defect concentration compared with the sample with a lower Sn to S ratio due to sulfur vacancy. Photocatalytic Cr(VI) reduction also demonstrated that the sample with a high defect content exhibits the best photocatalytic ability (Fig. 4(b)). This phenomenon was attributed to the prolonged charge carrier lifetime of the sulfur vacancy sample, as demonstrated in the photocurrent analysis of all the prepared samples (Fig. 4(c)). $SnS_2$ nanosheets with an optimal amount of sulfur vacancies exhibited a superior photoreduction rate of Cr(VI) (100% in 20 min), roughly 18.09 times higher than that of pure $SnS_2$ (Table 2), indicating vast prospects for photocatalytic wastewater treatment. The presence of sulfur vacancies in the crystal structure of $SnS_2$ serves to create an electron trap between the valence band and conduction band, effectively slowing down the recombination of electrons and holes. In that case the trapped electrons are still able to generate chemical reactions with Cr(VI) ions to change into less hazardous ions (Cr(III)).

Sulfur vacancy generation is not only suitable for Cr(VI) reduction but also for other applications, including $CO_2$ reduction and phenol degradation. In a recent publication, Zhang et al.[150] employed a synthesis method using L-cystine as the sulfur precursor to generate S-vacancies in $SnS_2$ for $CO_2$ reduction (see Fig. 4(d)). Their investigation demonstrated a significant enhancement in the $CO_2$ reduction efficacy of $SnS_2$ with S-vacancies, showcasing a 14.3-fold improvement compared with commercially available $SnS_2$ products. Their objective was to elucidate the underlying mechanism of $CO_2$ reduction and discern the role of $Sn^0$ atoms in $CO_2$ adsorption. Through DFT analysis, it was observed that the $CO_2$ molecule approached the surface of $Sn/SnS_2$, where the $S_x^{2-}$ ions in proximity transferred photogenerated electrons to the oxygen atom of the $CO_2$, thereby activating the $CO_2$ molecule and facilitating adsorption. $Sn^0$ particles functioned as electron transport bridges, enabling the further transfer of photogenerated electrons to the $S_x^{2-}$ ions, consequently reducing the adsorption energy barrier and accelerating the reaction rate. In a parallel investigation, Li et al.[106] explored variations in the Sn precursor's valence state ($Sn^{2+}$ and $Sn^{4+}$) to induce S-vacancies in the crystal structure. Based on their investigation, the $Sn^{2+}$ precursor yielded a higher S-vacancy content than the $Sn^{4+}$ precur-
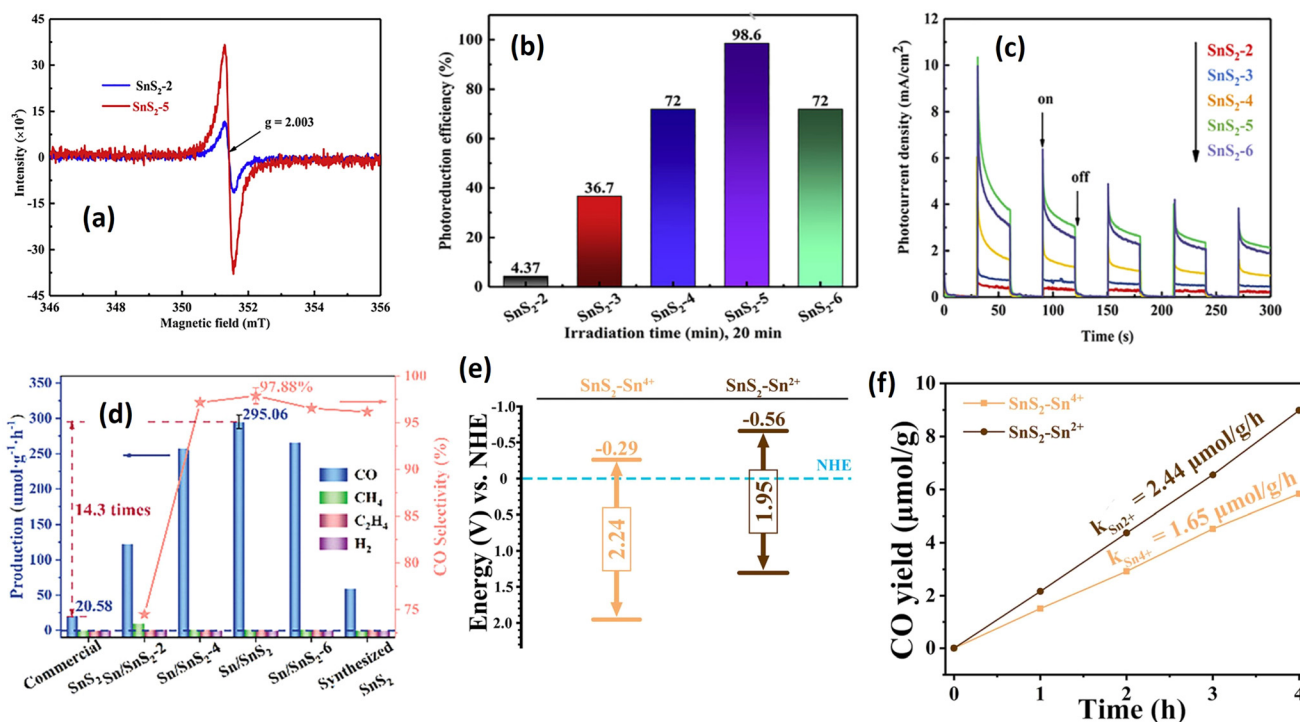
**Fig. 4** (a) Room-temperature EPR spectra of $SnS_2$-2 and $SnS_2$-5. (b) Comparison of Cr(VI) photoreduction over $SnS_{2-X}$ (X = 2, 3, 4, 5, 6) under visible light irradiation. (c) Photocurrent response of $SnS_{2-X}$ (X = 2, 3, 4, 5, 6).[48] (Reproduced from ref. 48 with permission from Elsevier, copyright 2020.) (d) Photocatalytic $CO_2$ reduction performance of vacancy generated $SnS_2$ prepared at different L-cystine concentrations (−1, −2, −4, −6 mol).[150] (Reproduced from ref. 150 with permission from Wiley, copyright 2023.) (e) Energy band of $SnS_2$–$Sn^{4+}$ and $SnS_2$–$Sn^{2+}$. (f) $CO_2$ reduction of $SnS_2$–$Sn^{4+}$ and $SnS_2$–$Sn^{2+}$.[106] (Reproduced from ref. 106 with permission from Elsevier, copyright 2023.)

sor, with a determined vacancy ratio (*via* EPR analysis) of 4 : 1 for $Sn^{2+}$ : $Sn^{4+}$. This increase in S-vacancy quantity resulted in a band position shift, as illustrated in Fig. 4(e), leading to a more potent $CO_2$ reduction capability. Photocatalytic $CO_2$ reduction revealed a 1.47 times enhancement with the $Sn^{2+}$ precursor compared with $Sn^{4+}$, attributed to the heightened S-vacancy concentration (see Fig. 4(f)). The enhanced photocatalytic performance following an increase in S-vacancy concentration can be attributed to several factors, including improved light absorption and increased efficiency in the separation of photogenerated charge carriers. Beyond S-vacancies, other vacancy types, such as Sn–S vacancies and S–Sn–S vacancies, may exist, imparting distinct effects on the physical properties and photocatalytic performance of $SnS_2$. Guo *et al.*[143] addressed these defects by introducing a specific amount of 2,2′-bipyridine during the hydrothermal reaction. Their research has confirmed several phenomena directly correlated with the improvements in photocatalysis. The presence of S-vacancies and S–Sn–S vacancies could decrease the band gap energy, resulting in an upward shift of the valence and conduction bands. This shift facilitates a stronger reduction ability, enabling more efficient reactions with $O_2$ molecules. Furthermore, the S–Sn–S vacancy demonstrates the highest adsorption energy, followed by Sn–S and S vacancies, respectively. This trend is also reflected in the electron transfer ability, with the S–Sn–S vacancy exhibiting an electron transfer

ability 4.7 times higher than that of S vacancy. These findings suggest that the presence of S–Sn–S vacancies is more favorable for improving photocatalytic performance, a conclusion also supported by Guo *et al.*[143] for phenol decomposition (Table 2).

**3.1.2 Doping $SnS_2$.** Doping is widely recognized as an effective method for altering the structure of photocatalysts to improve their photocatalytic performance. In the case of $SnS_2$, the doping process involves the replacement of one or more $SnS_2$ atoms with other atoms, including cations or anions. Transition metal elements such as Cu,[97,151] Ce,[152] Zr,[144] and others have been successfully integrated into the $SnS_2$ structure. For instance, Liu *et al.*[153] demonstrated the doping of Cu onto the $SnS_2$ layer *via* a hydrothermal reaction for $H_2$ production applications under visible light irradiation. They varied the Cu concentration from 0 to 10% to determine the optimal concentration. The results indicated that a 5% Cu concentration represented the optimal condition for water-splitting photocatalytic reactions, exhibiting a sixfold increase compared with 0% Cu, as depicted in Fig. 5(a). Interestingly, the Cu doping process induces defects in the crystal structure of $SnS_2$, as investigated by EPR analysis, as depicted in Fig. 5(b). The electron paramagnetic resonance (EPR) signal for Cu-doping exhibits a stronger signal than undoped $SnS_2$, confirming the presence of a vacancy defect originating from the S-vacancy. This result indicates that a S-vacancy can be gener-

**Table 2** Summary of photocatalytic performance through vacancy engineering and doping formation of $SnS_2$

| Vacancy type | Light source | Photocatalytic testing | Photocatalytic performance | Ref. |
|---|---|---|---|---|
| S-vacancy $SnS_2$ | 500 W Xe lamp | 50 mg $L^{-1}$ Cr(VI) reduction | Degradation efficiency (100% in 20 min), roughly 18.09 times that of pure $SnS_2$ | 48 |
| S-vacancy $SnS_2$ | 400 W metal halide lamp | $(1 \times 10^{-5}$ M) rhodamine B (RhB) degradation | $k_{RhB}$ = 0.0102 $min^{-1}$ for S-vacancy $SnS_2$, ~2.1 times that of $SnS_2$ | 106 |
| S-vacancy $SnS_2$ | 400 W metal halide lamp | $CO_2$ reduction (1 atm) | CO yield = 2.44 μmol $g^{-1}$ $h^{-1}$. 1.48 times that of pure $SnS_2$ | 106 |
| S–Sn-vacancy $SnS_2$ | 300 W Xe lamp | RhB, and methylene blue (MB) degradation | $k_{RhB}$ = 0.054 $min^{-1}$ (3.17 times that of pure $SnS_2$), $k_{MB}$ = 0.043 $min^{-1}$ (3.07 times that of pure $SnS_2$) | 143 |
| S–Sn–S-vacancy $SnS_2$ | 300 W Xe lamp | RhB and MB degradation | $k_{RhB}$ = 0.136 $min^{-1}$ (8.00 times that of pure $SnS_2$), $k_{MB}$ = 0.116 $min^{-1}$ (8.28 times that of pure $SnS_2$) | 143 |
| C-doped $SnS_2$ | Visible light | $CO_2$ reduction (acetaldehyde formation) | Acetaldehyde formation: 1256.6 μmol $g^{-1}$ (228.47 times that of $SnS_2$) | 67 |
| Cu-doped $SnS_2$ | 420 nm LED | $CO_2$ reduction ($CH_3OH$ production) | Cu-doped $SnS_2$: 0.99 mmol $g^{-1}$ $h^{-1}$ (2.06 times that of $SnS_2$) | 97 |
| Cu-doped $SnS_2$ | 300 W xenon lamp | Hydrogen evolution | Cu-doped $SnS_2$: 1.37 mmol $g^{-1}$ $h^{-1}$ far exceeding 6 times that of pure $SnS_2$ | 153 |
| Ce-doped $SnS_2$ | Solar irradiation | 10 and 20 ppm of methyl orange (MO) | $k_{MO}$ = 0.096 and $k_{MO}$ = 0.080 for 10 ppm and 20 ppm. $SnS_2$: $k_{MO}$ = 0.045 and $k_{MO}$ = 0.035 for 10 and 20 ppm | 87 |
| Zr-doped $SnS_2$ | Larger than 420 nm | 40 mg $L^{-1}$ Cr(VI) reduction | $k_{Cr(VI)}$ = 0.059 $min^{-1}$ nearly 2.2 times that of $SnS_2$ | 144 |
| $In^{3+}$-doped $SnS_2$ | White LED 48 W | 20 ppm Cr(VI) reduction | $k_{Cr(VI)}$ = 0.123 $min^{-1}$. 39.4 times that of $SnS_2$ | 128 |
| $In^{3+}$-doped $SnS_2$ | 300 W xenon lamp | Hydrogen evolution | $H_2$ production rate: 470 mmol $g^{-1}$ for 12 h. 1.95 times higher than $SnS_2$ | 139 |
| Sr-doped $SnS_2$ | 250 W xenon lamp | 10 ppm RhB degradation | $k_{RhB}$ = 0.00721 $min^{-1}$ (1.55 times that of $SnS_2$) | 154 |

ated not only by controlling the S-source but also through the doping process. Moreover, the average electron lifetime of Cu-$SnS_2$ is longer than $SnS_2$, as shown in Fig. 5(c). The average lifetime of Cu-doped $SnS_2$ is 0.358 s, which is slower than $SnS_2$, with 0.341 s, indicating that defects caused by the S-vacancy act as electron acceptors, preventing electron and hole recombination. Upon exposure to visible light irradiation, electrons transition from the valence band to the conduction band. As defects are introduced, these electrons migrate to defect levels and promptly engage in reactions with adsorbed $H_2O$, rather than undergoing recombination with holes in the valence band. Additionally, compared with pristine $SnS_2$, Cu doping enables a broader range of visible light absorption, suggesting increased electron involvement in the redox reaction. Furthermore, due to the vacancies generated by Cu doping, the crystallinity decreases, and surface area increases. These factors are also beneficial for enhancing the photocatalytic reaction. Another study by Govindan et al.[87] conducted successful cation doping, introducing Ce atoms into the $SnS_2$ structure using a microwave-assisted method. In their research, they observed the formation of Sn-vacancies instead of S-vacancies. Additionally, alongside S-vacancy formation, they noted an increase in strain on the crystal structure of $SnS_2$ after Ce doping, measuring approximately $3.5 \times 10^{-3}$, which was higher than without Ce doping ($2.3 \times 10^{-3}$). This behavior can be attributed to the higher atomic radius of $Ce^{3+}/Ce^{4+}$ (0.102 nm) compared with $Sn^{4+}$ (0.07 nm). The modification of the $SnS_2$ structure with Ce doping was confirmed to enhance the photocatalytic performance, demonstrated by conducting methyl orange degradation under solar irradiation. The results indicate that Ce-doped $SnS_2$ improved the degradation of

methyl orange twice as fast as pristine $SnS_2$ (Table 2). The higher photocatalytic performance of Ce-doped $SnS_2$ could be attributed to the decreased crystallite size resulting from significant strain and a greater quantity of Sn vacancies. These factors facilitate a greater number of photon pathways within the $SnS_2$ host structure, consequently enhancing the photocatalytic activity for decomposing methyl orange molecule into $CO_2$ and water. In contrast to the above analysis, Park et al.[128] proposed a different mechanism to explain the doping behavior of $In^{3+}$-doped $SnS_2$. They proposed that instead of the S-vacancy serving as an electron acceptor, the $In^{3+}$ ions serve as electron acceptors, effectively improving the charge carrier separation efficiency as shown in Fig. 5(d). The photocurrent analysis of $In^{3+}$-$SnS_2$ shows strong photoelectron excitation compared with $SnS_2$, which is directly correlated with the luminescence analysis in Fig. 5(e), indicating a slower recombination of electrons and holes after $In^{3+}$ doping. The photocatalytic activity of $In^{3+}$-doped $SnS_2$ tested for Cr(VI) reduction (Fig. 5(f)) shows a superior performance compared with $SnS_2$ and standard P-25 under visible light irradiation, providing clear evidence of the effect of $In^{3+}$ in enhancing photocatalytic performance through extending the electron–hole lifetime. However, the effect of $In^{3+}$ has been strengthened by Li et al.[139] who proposed that $In^{3+}$ is responsible for S-vacancy generation, acting as an electron trap to improve hydrogen generation, with a hydrogen production rate of about 470 μmol $g^{-1}$ for 12 h as shown in Table 2.

Doping in $SnS_2$ structures, not only within the transition metal family but also through carbon infusion, has been demonstrated to markedly enhance photocatalytic efficacy. In a study by Shown et al.,[67] carbon-doped $SnS_2$ was investigated
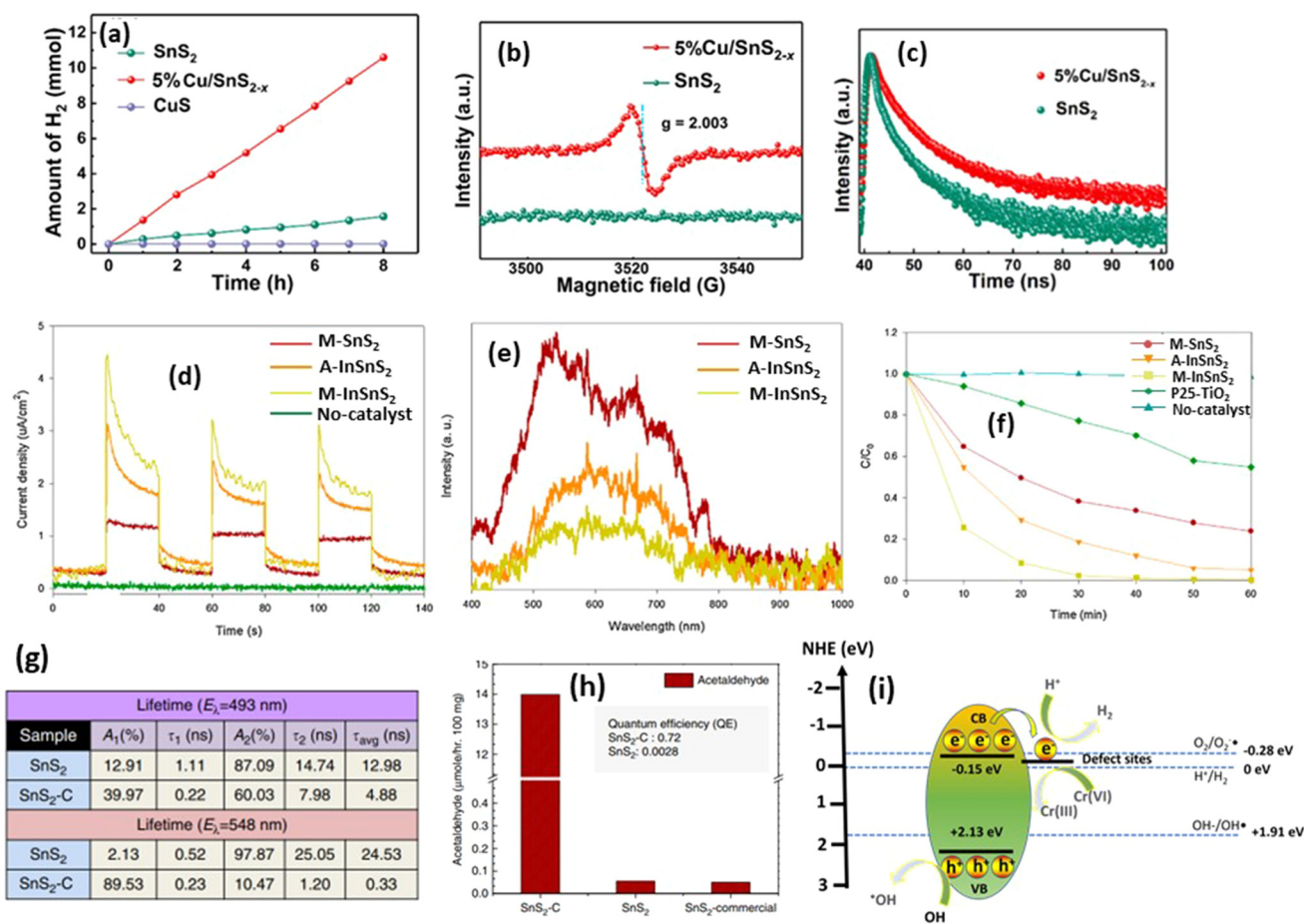
**Fig. 5** (a) Photocatalytic water reduction capability of $SnS_2$, CuS, and Cu-doped $SnS_2$. (b) EPR spectra of $SnS_2$ and Cu-$SnS_2$, and (c) time-resolved photoluminescence spectra of $SnS_2$ and Cu-doped $SnS_2$.[97] (Reproduced from ref. 97 with permission from the Royal Society of Chemistry, copyright 2023.) (d) Photocurrent measurements of $In^{3+}$-doped $SnS_2$. (e) Photoluminescence measurement of $In^{3+}$-doped $SnS_2$. (f) Cr(VI) photodegradation by using $In^{3+}$-doped $SnS_2$.[128] (Reproduced from ref. 128 with permission from Elsevier, copyright 2017.) (g) Charge life-time of C-doped $SnS_2$. (h) Photocatalytic $CO_2$ reduction into acetaldehyde by using carbon-doped $SnS_2$.[67] (Reproduced from ref. 67 with permission from Springer Nature, copyright 2018.) (i) Photocatalytic reaction mechanism of S-vacancy on the $SnS_2$ structure.

for its capacity to catalyze $CO_2$ reduction to acetaldehyde gas under 300 W halogen irradiation. The carbon doping regimen involved the use of L-cystine as both a sulfur and carbon source. The results revealed that carbon doping induced macrostrain within the $SnS_2$ lattice, leading to distinct photophysical properties. Moreover, carbon doping facilitated the adsorption of $CO_2$ molecules on the surface, with a relatively low dissociation barrier observed. In Fig. 5(g), the observed average lifetimes for $SnS_2$–C are 4.88 and 0.33 ns, markedly shorter than the 12.98 and 24.53 ns for $SnS_2$ at 493 and 548 nm, respectively. This decrease in lifetime in $SnS_2$–C implies the presence of a nonradiative pathway, characterized by the delocalization of electrons from $SnS_2$ to C, thereby facilitating effective carrier separation. Additionally, the resulting carbon-doped $SnS_2$–C exhibited smaller nanosheets composed of only a few atomic layers, thereby reducing the charge diffusion times compared with pure $SnS_2$. These findings collectively underscore the exceptional quantum efficiency of carbon-doped $SnS_2$, which demonstrated an improvement of

over 257 times compared with pristine $SnS_2$. This enhanced quantum efficiency manifested as a remarkable increase in acetaldehyde production on carbon-doped $SnS_2$, outperforming pure $SnS_2$ by 228.47 times (Fig. 5(h)).

Based on the results, structural modification can enhance photocatalytic performance by several factors including S-vacancy generation, strain engineering, and ion trapping which successfully impeded the recombination of electrons and holes through an electron trap. However, since the majority of the publications state that the S-vacancy was the most responsible species for improving the photocatalytic reaction, therefore the photocatalytic mechanism of $SnS_2$'s structural modification can be generally explained as follows (Fig. 5(i)): upon exposure to light, electrons from the valence band become excited to the conduction band of $SnS_2$. Without a vacancy state, the electron would easily recombine with holes in the valence band. However, due to the presence of a vacancy state below the conduction band of $SnS_2$, electrons tend to be trapped, providing sufficient time to initiate photocatalytic

reactions. These reactions have potential applications in various fields, including hydrogen production, wastewater treatment, and many others.

All these structural modification strategies exhibit varying degrees of improvement in photocatalytic applications, as summarized in Table 2. Among these strategies, the carbon doping of $SnS_2$ emerges as one of the most promising approaches, showing an enhancement ability over 228.47 times greater than pristine $SnS_2$ in the reduction of CO to acetaldehyde.[67] Additionally, $In^{3+}$ doping in the $SnS_2$ structure demonstrates a superior photocatalytic performance for wastewater treatment, exhibiting an improvement degree approximately 39.4 times higher than pristine $SnS_2$.[128] This suggests that $In^{3+}$ doping enhances the charge separation efficiency more effectively than other cation doping methods and direct S-vacancy formation. However, the underlying mechanisms of this phenomenon remain unclear, as each doping process generates S-vacancies in the system, and the role of the dopant itself is not fully understood. Therefore, one plausible explanation for this phenomenon may lie in the variation in vacancy content and surface properties of the $SnS_2$ after doping, including an increased surface area and other factors.

## 3.2 Morphological manipulation

Beyond the structural factor, the photocatalytic activity of $SnS_2$ is also influenced by its surface properties. These properties are intricately linked to changes in morphology, impacting the surface area, the active facets, and the reaction process for photocatalytic reactions. Researchers have explored various $SnS_2$ morphologies, each demonstrating distinct photocatalytic performances. These morphologies encompass flower-like structures, nanosheets, nanoparticles, quantum dots, and more.

### 3.2.1 Flower-like.

The flower-like morphology of $SnS_2$ is one of the most common shapes observed. It is formed due to the arrangement of several hexagonal shapes, creating a flower-like structure, as shown in Fig. 6(a).[155] This shape is typically prepared through a direct hydrothermal reaction without additional surfactants. The size of the flower can be adjusted by varying the reaction conditions, such as reaction time, temperature, and precursor amounts. One advantage of the flower-like morphology is the abundance of active sites on the crystal structure's edges.[156] Sengodu et al.[157] have successfully synthesized three distinct morphologies of $SnS_2$: nano-
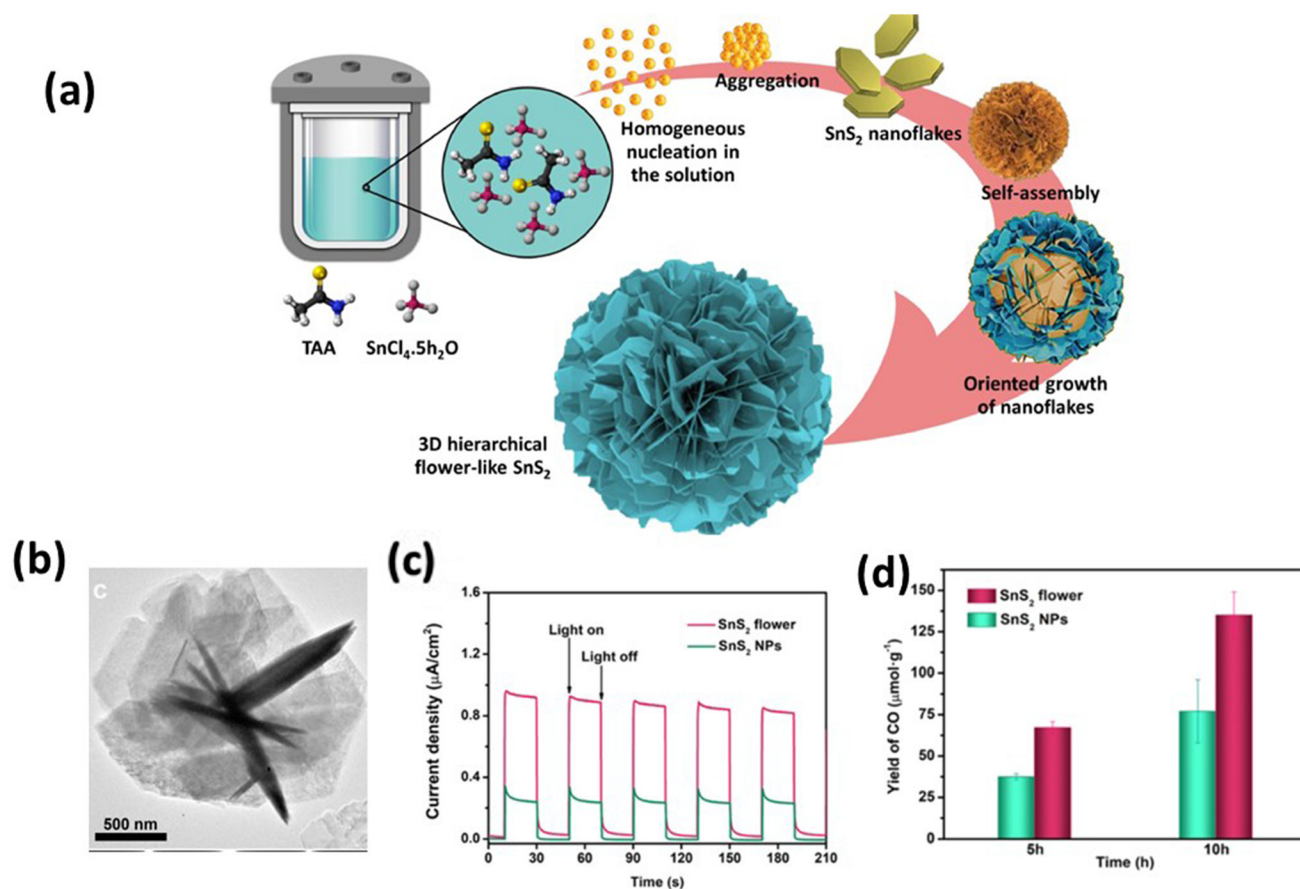


**Fig. 6** (a) Formation of $SnS_2$ rose flower-like morphology.[155] (Reproduced from ref. 155 with permission from Elsevier, copyright 2021.) (b) TEM images of an individual $SnS_2$ flower. (c) Transient photocurrent and (d) comparative CO formation yield of the $SnS_2$ flower and $SnS_2$ NPs within the reaction times of 5 and 10 h, respectively.[135] (Reproduced from ref. 135 with permission from the American Chemical Society, copyright 2021.)

particles, nanoflowers (flower-like), and nanoplates, each exhibiting unique specific surface areas. Notably, the nanoflower morphology stands out with the highest specific surface area recorded, at 127.04 $m^2 g^{-1}$, surpassing the values for nanoplates and nanoparticles, which are 96.40 and 69.4 $m^2 g^{-1}$, respectively. Mondal et al.[158] corroborated the superior photocatalytic performance of the flower-like morphology, emphasizing its potential for environmental applications. Their study revealed that controlling the sulfur source precursor, particularly employing 0.06 g thioacetamide, led to the formation of nanoflowers, while 0.1 g thioacetamide resulted in a distinct nano-yarn morphology. Moreover, the nanoflower morphology of $SnS_2$ exhibited a markedly higher specific surface area than the nano-yarn, proving advantageous for enhanced photocatalytic Cr(VI) reduction under visible light irradiation. Upon photocatalytic reactions, the nanoflower with a high specific surface area can absorb more molecules onto the surface, increasing the likelihood of reaction occurrence. Moreover, the higher specific surface area enhanced light absorption leading to a more efficient generation of electron and holes for reducing C(VI) into Cr(III). Another report from You et al.[135] has investigated the advantages of a flower-like morphology over nanoparticles. They observed that the flower-like structures prepared by the hydrothermal reaction have an average size of 2.39 ± 0.26 μm and a thickness of around 20 nm, which is favorable for carrier transport to the catalyst surface (Fig. 6(b)). The flower-like morphology has a surface area around 20.11 $m^2 g^{-1}$ which is higher than for the nanoparticle, at 12.99 $m^2 g^{-1}$. Hence, $SnS_2$ flowers can supply more surface-active sites, leading to higher adsorption and photocatalysis. The flower-like structure also can absorb more light, as illustrated in Fig. 6(c), due to the scattering and reflection of light within the three-dimensional structure. Also, a thin sheet structure can shorten the transmission path, promoting more carriers to migrate to the surface of the photocatalyst.[135] The photocatalytic $CO_2$ reduction performance is undoubtedly directly correlated with the properties, as shown in Fig. 6(d). The $CO_2$ reduction performance of the flower-like morphology is 135.13 μmol $g^{-1}$ which is 1.75 times higher than $SnS_2$ nanoparticles.

### 3.2.2 2D nanosheets.
Two-dimensional (2D) layered morphologies can be defined as morphologies with a large two-dimensional ratio and a low vertical ratio. Due to their unique physicochemical properties, 2D material-based photocatalysts are expected to offer intriguing features such as porous structures, high specific surface areas, good crystallinity, a rich variety of host–guest species, better charge carrier separation, and abundant surface-active sites.[159] As mentioned earlier, the TMD family exhibits 2D properties, providing an advantage for photocatalytic applications. In the case of the $SnS_2$ photocatalyst, several reports have successfully demonstrated the preparation of 2D layered structures for photocatalytic applications.[45,71,160–163] Yu et al.[45] have reported monodisperse $SnS_2$ nanosheets for hydrogen generation photocatalysis. Fig. 7 (a and b) shows the $SnS_2$ hexagonal nanosheets of 0.8–1 μm with a thickness of about 22 nm. The nanosheets are

assembled by ca. 35–38 hexagonal $SnS_2$ layers (the experimental value of single-layer $SnS_2$ is determined to be 0.61 nm). Yu et al.[45] prepared the $SnS_2$ nanosheets using a hydrothermal method with polyvinyl pyrrolidone (PVP) as a controlling agent. PVP can act in aggregation prevention during the hydrothermal reaction, preventing the $SnS_2$ layers from stacking into flower-like morphologies. Moreover, the monodisperse $SnS_2$ layers can also be achieved in an ethanol solution. The photocurrent measurement indicates that $SnS_2$ nanosheets have high electron mobility, which is beneficial for the $H_2$-production reaction compared with the P-25 standard (Fig. 7(c)). The $H_2$-production testing result shows various morphologies that have been compared with $SnS_2$ nanosheets, including nanoplates and sphere particles. The $H_2$ production yield for the nanosheet sample is much higher than for nanoplates, and spheres, as well as P-25 (Fig. 7(d)). The enhanced photocatalytic activity of $SnS_2$ nanosheets may be attributed to their low thickness, which provides more active sites. Additionally, their short and convenient approach allows photogenerated electrons and holes to migrate efficiently to the reaction sites on the surface, thereby decreasing the recombination probability and enhancing the photocatalytic efficiency.[45]

Another report from Liu et al.[163] reported the formation of 2D nanosheets by the sonication of $SnS_2$/n-propylamine in $HNO_3$ solution to exfoliate the bulk $SnS_2$ into $SnS_2$ nanosheets, as shown in Fig. 7(e). The exfoliation of inorganic ($SnS_2$)–organic hybrids that are composed of few- or single-layered inorganic targeting slabs sandwiched by a single-layer organic molecule via coordinated bonds. The inserting organic molecule can be removed by the ion exchange method. In this research, they also confirmed the improvement of the charge carrier lifetime investigated by photocurrent measurement compared with bulk materials as shown in Fig. 7(f). Moreover, the charge carrier lifetime was observed to be around 0.78 ns which is almost 10 times higher than bulk $SnS_2$. The Cr(VI) removal under visible light irradiation shows a significant improvement compared with bulk $SnS_2$ (Fig. 7(g)) with a degradation rate about 0.01436 $min^{-1}$ which is 6 times higher than $SnS_2$ bulk materials. It indicates that the improvement of charge carrier separation from $SnS_2$ nanosheets has a direct correlation with the photocatalytic performance. Moreover, since $SnS_2$ nanosheets are a layered structure, the heterostructure of $SnS_2$ with other 2D materials was also interesting and has been explored by many researchers. For example, Zhang et al.[162] have prepared a 2D heterojunction $SnS_2$/$MoS_2$ photocatalyst for methylene blue degradation. In this work, they prepared two-step hydrothermal reactions, as shown in Fig. 7(h). At the initial stage the nanolayer of $SnS_2$ was prepared, and the $MoS_2$ layers grew on the $SnS_2$ surface using a hydrothermal reaction. The formation of a 2D heterostructure of $SnS_2$/$MoS_2$ nanosheets can increase the charge separation efficiency, which leads to an increase in the photocurrent signal, as shown in Fig. 7(i). The photocurrent density of $SnS_2$/$MoS_2$ was 15.20 mA $cm^{-2}$ in the stable second cycle, which exhibited an 8.8 times enhancement compared with that of $SnS_2$ (~1.55 mA $cm^{-2}$) and a 23.1 times improvement com-
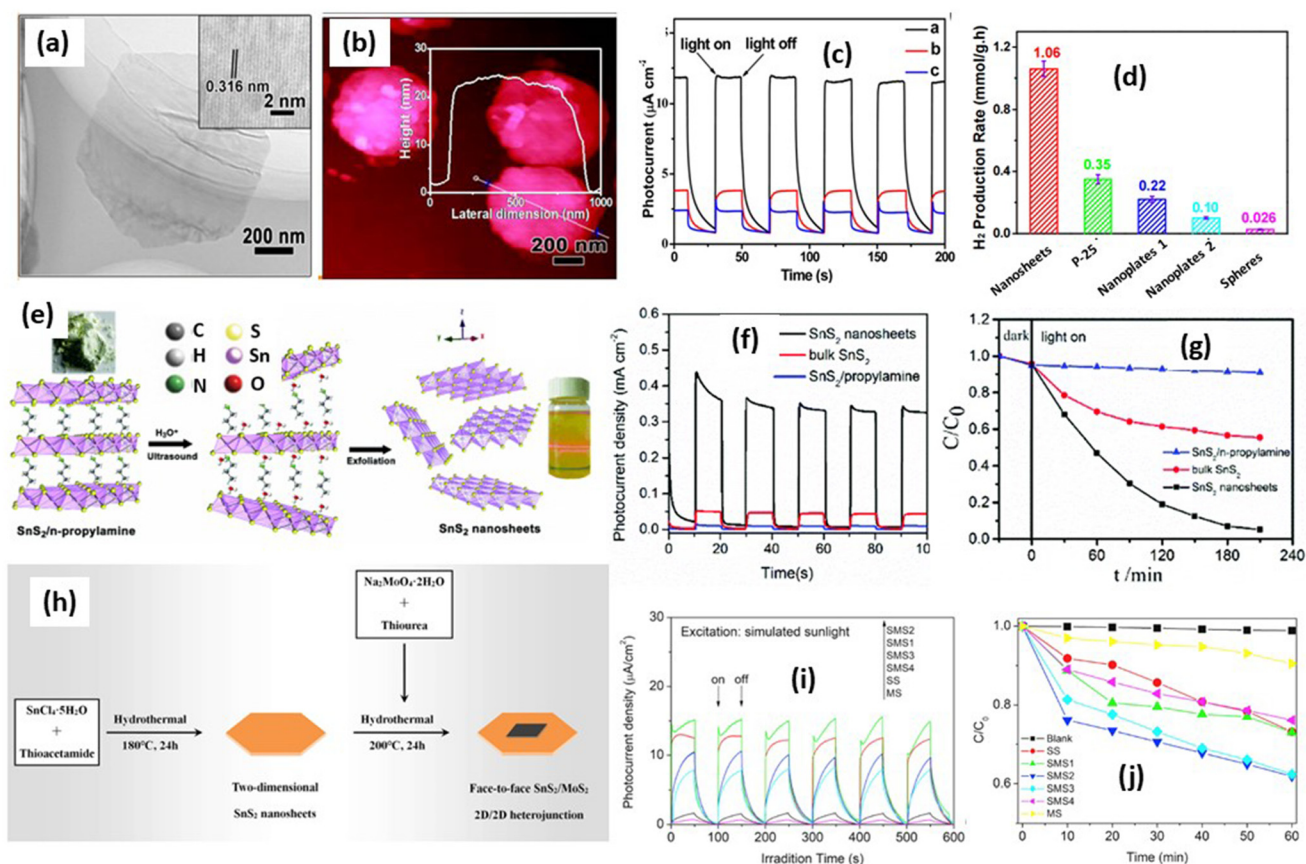
**Fig. 7** (a) TEM image of an individual nanosheet. Inset is an HRTEM image. (b) High-magnification AFM image and corresponding height profile.[45] (c) The photoelectrochemical response of the samples at 0.8 V *versus* SCE electrode under 300 W Xe lamp illumination ($\lambda$ > 420 nm). (Reproduced from ref. 45 with permission from the American Chemical Society, copyright 2014.) (d) Comparison of the photocatalytic hydrogen production rate of the samples. (e) Schematic illustration of the exfoliation of bulk $SnS_2$/n-propylamine into few-layer $SnS_2$ nanosheets. (f) Chronoamperometry at 0.6 V *vs.* $Hg/Hg_2SO_4$. (g) Photocatalytic reduction of 100 mg $L^{-1}$ Cr(VI) with (1) the bulk $SnS_2$/n-propylamine hybrid, (2) bulk $SnS_2$, and (3) $SnS_2$ nanosheets.[163] (Reproduced from ref. 163 with permission from the Royal Society Chemistry, copyright 2019.) (h) A schematic drawing of the synthetic process of $SnS_2$/$MoS_2$. (i) Photocurrent and (j) photocatalytic activities of SS ($SnS_2$), SMS1 ($SnS_2$/$MoS_2$ (Mo : Sn = 1%)), SMS2 ($SnS_2$/$MoS_2$ (Mo : Sn = 2.5%)), SMS3 ($SnS_2$/$MoS_2$ (Mo : Sn = 5%)), SMS4 ($SnS_2$/$MoS_2$ (Mo : Sn = 75%)) and MS ($MoS_2$) for methylene blue decomposition under UV-vis irradiation.[162] (Reproduced from ref. 162 with permission from Elsevier, copyright 2019.)

pared with that of $MoS_2$ (~0.63 mA $cm^{-2}$). This phenomenon occurred due to the improvement of the charge separation efficiency due to the charge transfer between $MoS_2$ and $SnS_2$, which can prolong the charge carrier lifetimes. The photocatalytic activity is also directly correlated with the photocurrent result as shown in Fig. 7(j). The best sample $SnS_2$/$MoS_2$ demonstrated an enhanced photocatalytic rate of 81% compared with $SnS_2$.

**3.2.3 Nanoparticles.** Nanoparticles can be defined as particles with a diameter of less than 100 nm in size, offering numerous advantages over bulk-size materials, including an increased specific surface area, higher defect density, and improved dispersibility. Several reports have highlighted the photocatalytic performance of $SnS_2$ nanoparticles.[16,25,41,105,164–167] Fakhri *et al.*[41] reported the formation of $SnS_2$ nanoparticles by a hydrothermal reaction with the addition of 5 vol% acetic acid and 0.005 mol $SnCl_4·5H_2O$ and 0.02 mol thioacetamide. The produced nanoparticle was

about 20–30 nm as shown in Fig. 8(a) and (b). They conducted a photocatalytic investigation for ENRO degradation under 500 W xenon irradiation, revealing a degradation rate of approximately 0.0296 $min^{-1}$ using $SnS_2$ nanoparticles as catalyst (Fig. 8(c)).

Zhang *et al.*[105] conducted a more detailed investigation into $SnS_2$ nanoparticle formation and its photocatalytic ability. They controlled the particle diameter and specific surface area of the $SnS_2$ particle by adjusting parameters such as sulfur source concentration and reaction temperature during the hydrothermal process. Increasing the reaction temperature resulted in larger particle sizes, as depicted in Fig. 8(d) and (e). For instance, particles prepared at 180 °C had an average size of around 142 nm, while those from the 120 °C hydrothermal reaction were about 23 nm in size. Conversely, higher sulfur source concentrations led to smaller particle sizes, illustrated in Fig. 8(e) and (f). For instance, the particle size decreased to 46 nm when the sulfur source concentration was
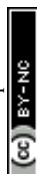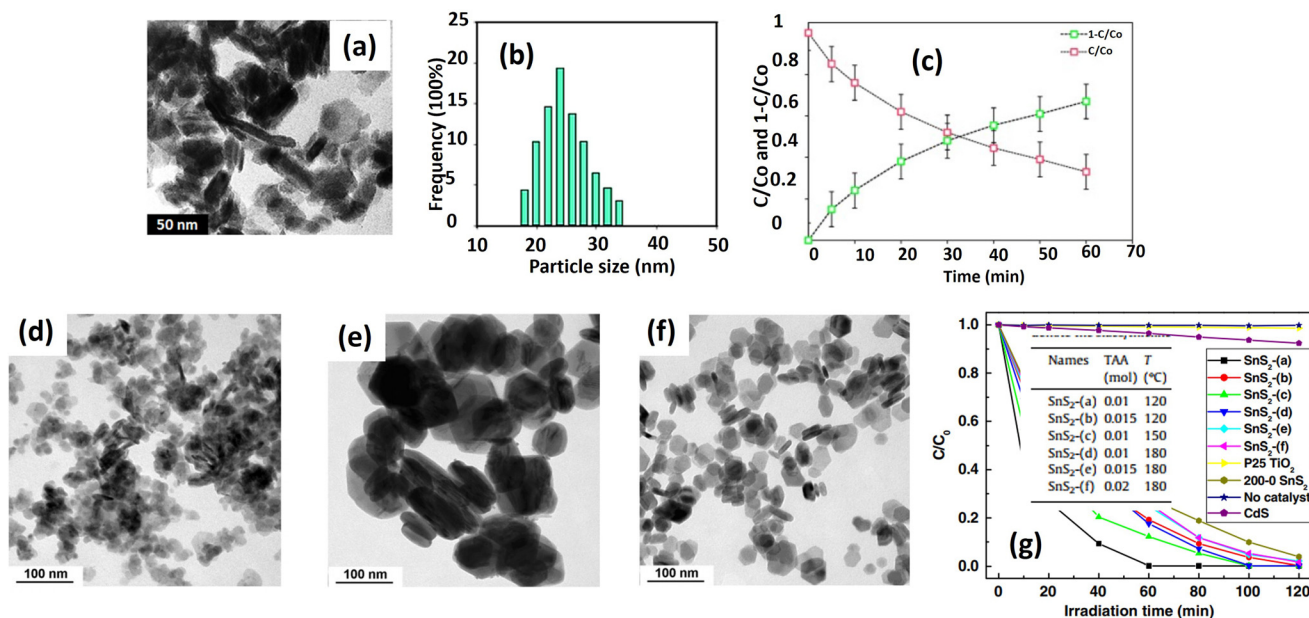
**Fig. 8** (a) TEM image and (b) particle size distribution of SnS₂ NPs; (c) the photodegradation of ENRO by SnS₂ NPs under visible light.[41] (Reproduced from ref. 41 with permission from Elsevier, copyright 2015.) TEM images of SnS₂ prepared with (d) 0.01 mol of TAA at 120 °C; (e) 0.01 mol of TAA at 180 °C; and (f) 0.02 mol of TAA at 180 °C; (g) photocatalytic activities of SnS₂, flower-like CdS and P25 TiO₂ in degrading MO in distilled water under visible light (420 nm) irradiation.[105] (Reproduced from ref. 105 with permission from Elsevier, copyright 2011.)

increased from 0.01 mol to 0.02 mol. Higher reaction temperatures promote lower viscosity and enhance the diffusion of constituent $Sn^{4+}$ and $S^{2-}$ ions. Moreover, they accelerate Ostwald ripening rates, resulting in larger particle sizes.[105]

On the other hand, increasing the initial amount of thioacetamide from 0.01 to 0.02 mol releases more $S^{2-}$ ions, saturating the reaction solution further. Consequently, a greater number of SnS₂ crystal nuclei form in the initial stages, reducing the available $Sn^{4+}$ for subsequent crystal growth during the hydrothermal reaction and resulting in smaller particle sizes. Photocatalytic degradation of methyl orange reveals that SnS₂ synthesized at 120 °C exhibits superior performance compared with the sample prepared at 180 °C (Fig. 8(g)). The variation in particle size accounts for the observed differences, significantly influencing the available surface area and creating additional active sites to facilitate photocatalytic reactions. Furthermore, smaller particle sizes commonly lead to defect formation, serving as electron traps that prolong the lifetime of electrons and holes, thus promoting the photocatalytic degradation of methyl orange.

**3.2.4 Quantum dots.** Among other morphologies, quantum dots are one of the most unique morphologies regarding their physical properties. Quantum dots can be defined as particles of less than 10 nm. The uniqueness of these quantum dots is their properties, which are significantly affected by size, called the quantum size effect. Quantum dots are also recognized as having a high surface-to-volume ratio, which is comparable with larger two-dimensional nanosheets.[168] In the case of SnS₂, several reports have successfully synthesized SnS₂ quantum dots using various

methods.[47,127,168–172] Zhao et al.[169] have reported the size-control of SnS₂ quantum dots using the sonication method with PEG400 as a solvent. They controlled the quantum dot size by varying the heating times after the sonication process. Fig. 9(a–d) shows the TEM images of SnS₂ quantum dots prepared by different heating times of 4, 8, 12, and 16 h, respectively. The particle size distribution of each sample plotted in the inset of each figure indicates the increase in the size with the increase of heating time from 5 to 10 nm.

Interestingly, the UV-Vis absorbance of SnS₂ quantum dots largely shifted to the larger wavelength, indicating the narrower band gap value after increasing the particle size (Fig. 9(e)). This behavior is a typical characteristic of quantum dot particles where the band gap energy is greatly affected by size. Quantum-sized particles have a higher surface area-to-volume ratio, which increases the probability of photon absorption; moreover, quantum-sized particles often exhibit higher charge carrier mobility due to their unique electronic structure and reduced dimensionality. Enhanced mobility facilitates the efficient separation and migration of photogenerated electron–hole pairs, which are essential for driving redox reactions in photocatalysis. The luminescence analysis (Fig. 9(f)) has also confirmed the emission shift because of electron excitation. The significant shift in the band gap with a slight increase in size is one of the unique features of quantum dots due to the quantum confinement effect, which is beneficial for luminescence applications. On the other hand, Wang et al.[173] reported the fabrication of a Si-photoanode incorporating SnS₂ quantum dots for the hydrogen evolution reaction. In Fig. 9(g), the TEM image displays the par-
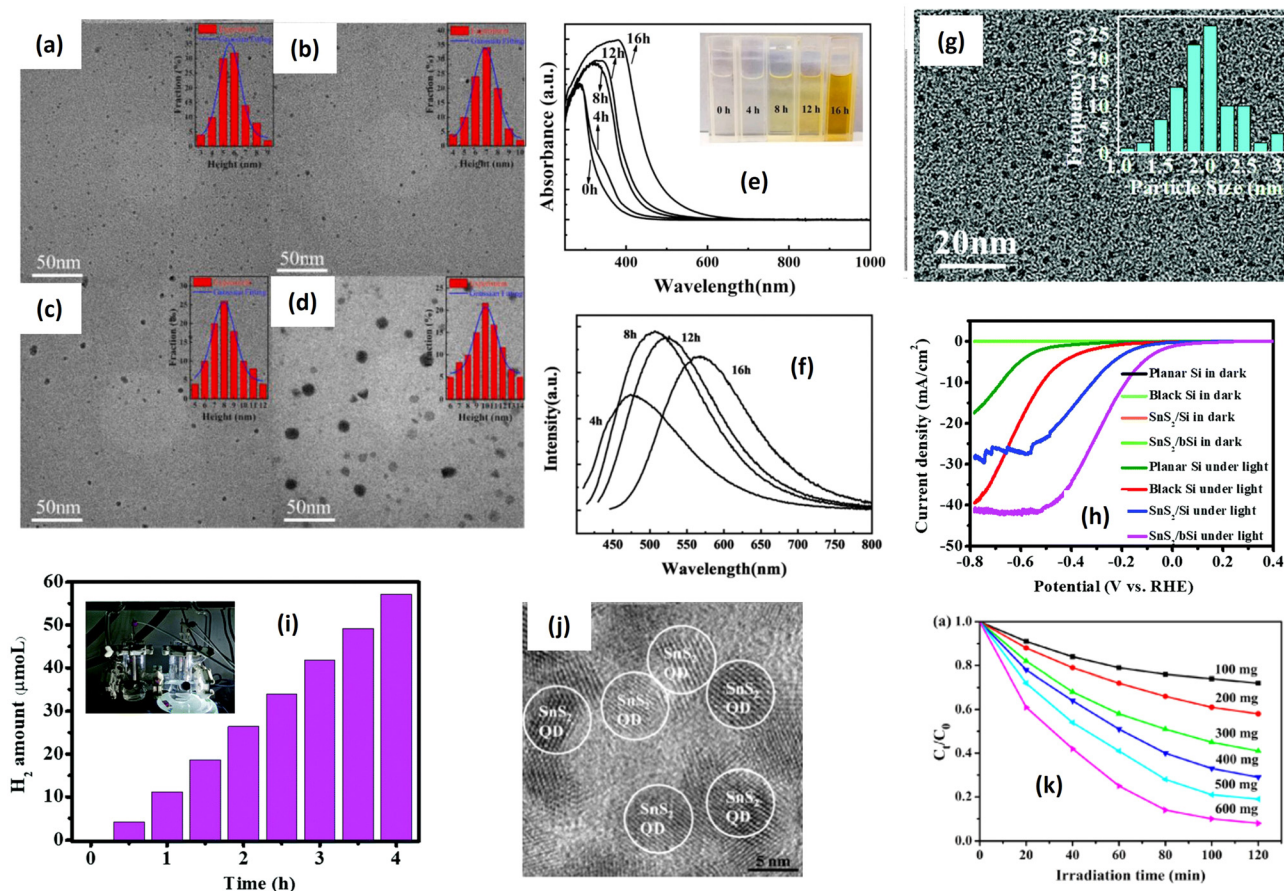
**Fig. 9** TEM (inset: size distribution) images of SnS$_2$ QDs after heating for (a) 4 h; (b) 8 h; (c) 12 h; and (d) 16 h. (e) Absorption spectra of SnS$_2$ QDs with different heating times. (f) Luminescence analysis of SnS$_2$ QDs with different heating times.[169] (Reproduced from ref. 169 with permission from Elsevier, copyright 2023.) (g) TEM images of as-synthesized SnS$_2$ QDs. (h) Lateral size distribution of SnS$_2$ QDs;[173] (reproduced from ref. 173 with permission from the Royal Society of Chemistry, copyright 2019). (i) The calculated photocurrent density under various wavelengths; (j) HR-TEM images of SnS$_2$ QDs; (k) effect of the dosage of the SnS$_2$ QD photocatalyst on the photocatalytic reduction of 100 mg L$^{-1}$ Cr(vi) under visible-light irradiation ($\lambda$ = 420 nm).[47] (Reproduced from ref. 47 with permission from Elsevier, copyright 2016.)

ticle distribution of SnS$_2$ quantum dots, with an average size of approximately 2 nm. Fig. 9(h) illustrates the polarization curves of planar Si, SnS$_2$/pSi, black Si, and SnS$_2$/bSi samples. All the Si electrodes exhibit noticeable current responses under illumination, contrasting with dark conditions. Additionally, the SnS$_2$/bSi photocathode demonstrates a maximum photocurrent of ~41 mA cm$^{-2}$ at approximately −0.51 V, attributed to the light-harvesting nanostructure of black Si and the active sites of the SnS$_2$ catalyst. The hydrogen evolution reaction (Fig. 9(i)) indicates a hydrogen amount of about 55 μmol L$^{-1}$ after irradiation. The photocatalytic performance of SnS$_2$ quantum dots has been also reported by Tu *et al.*[47] for Cr(vi) reduction under visible light irradiation. The quantum size SnS$_2$ has been successfully prepared for hydrothermal reaction with L-cystine as a particle-controlling agent. SnS$_2$ quantum dots with a size of 6.32 nm have been obtained, as shown in Fig. 9(j). The photocatalytic performance of SnS$_2$ quantum dots also shows good potential for wastewater treatment (Fig. 9(k)). Comparing various morphologies, it is anticipated that the most suitable morphology for photocatalytic

applications can be identified. Different morphologies can be achieved by adjusting several parameters during the synthesis process. As shown in Table 3, diverse morphologies, including flower-like structures, nanolayers, nanoparticles, and quantum dots, have been synthesized using different methods. Upon evaluating the apparent rate constants derived from the catalytic activities, it becomes evident that the flower-like structure exhibits the most effective photocatalytic reaction, with a degradation rate of approximately 0.0692 min$^{-1}$, followed by the nanoparticle morphology with the highest observed degradation rate of about 0.0594 min$^{-1}$. The superior photocatalytic performance of the flower-like morphology is attributed to its large specific surface area, excellent interfacial contact, and rapid electron transfer.[157] The enhanced photocatalytic properties of the flower-like structure can be elucidated as follows: the abundant petal-like structures provide more surface area for photochemical reactions to occur upon irradiation and interaction with chemicals, while the arrangement of flower-like structures traps light, thereby increasing electron–hole generation.[174] Furthermore, the open and porous nature of

**Table 3** Photocatalytic activities of morphologically modified $SnS_2$

| Morphology type | Light source | Synthesis method | Photocatalytic testing | Photocatalytic result | Ref. |
|---|---|---|---|---|---|
| $SnS_2$-flower-like | 300 W xenon lamp | Hydrothermal (at 180 °C, 9 h) 80 mL 0.01 M $SnCl_4\cdot5H_2O$ and L-cysteine | 100 mg L$^{-1}$ rhodamine B degradation | Degradation rate: 0.0251 min$^{-1}$ | 50 |
| $SnS_2$ flower-like | 300 W xenon lamp | Solvothermal in ethanol, (180 °C, 12 h) 2 mmol $SnCl_4\cdot5H_2O$ and 5 mmol $CH_3CSNH_2$ (thioacetamide) | 10 ppm rhodamine B degradation | Degradation rate: 0.0692 min$^{-1}$ | 36 |
| $SnS_2$ flower-like | 400 W metal halide lamp | Hydrothermal (200 °C, 24 h) 10 mmol $SnCl_4\cdot5H_2O$, and 3.04 g (40 mmol) thiourea | 10 ppm methylene blue degradation | Degradation rate: 0.0179 min$^{-1}$ | 176 |
| $SnS_2$ flower-like | 300 W xenon lamp | Hydrothermal (180 °C, 3 days) 100.0 mg $SnO_2$ hollow multi-shelled microspheres and 1.0 g thioacetamide | $CO_2$ reduction | CO production rate 8.91 μmol g$^{-1}$ h$^{-1}$ | 135 |
| $SnS_2$-nanosheets | 300 W xenon lamp | Solvothermal in ethanol with acetic acid (180 °C, 12 h) 0.25 mmol $SnCl_4\cdot5H_2O$, 0.625 mmol of thioacetamide | Nitrogen fixation | $NH_4^+$ yield: 27.5 μmol g$^{-1}$ h$^{-1}$ | 101 |
| $SnS_2$-nanosheets | 300 W xenon lamp | Sonication in an ice-water bath for 1 h | 50 mg L$^{-1}$ Cr(VI) reduction | $k_{Cr(VI)} = 0.01436$ min$^{-1}$ | 163 |
| $SnS_2$-nanosheets | 300 W xenon lamp 320 nm filter | Solvothermal in triethylene glycol (220 °C, 12 h). 1 mmol $SnCl_2\cdot2H_2O$, 2 mmol TAA and 0.5 g PVP | Hydrogen generation | $H_2$ production rate: 1.06 mmol g$^{-1}$ h$^{-1}$ | 45 |
| $SnS_2$-nanosheets | 400 W mercury lamp | Hydrothermal with ethylenediamine (200 °C, 24 h). 3.5 g (10 mmol) of stannic(IV) chloride and 3.04 g (40 mmol) of thiourea | Hydrogen generation | $H_2$ production rate: 0.566 mmol g$^{-1}$ h$^{-1}$ | 31 |
| $SnS_2$-nanosheets | 400 W mercury lamp | Hydrothermal with ethylenediamine (200 °C, 24 h). 3.5 g (10 mmol) of stannic(IV) chloride and 3.04 g (40 mmol) of thiourea | Methylene blue degradation | $k_{MB}$: 0.0178 min$^{-1}$ | 31 |
| $SnS_2$-nanoparticle | 250 W xenon lamp 420 nm filter | Hydrothermal (130–170 °C). 5 mmol $SnCl_4\cdot5H_2O$, 10 mmol thioacetamide | 50 mg L$^{-1}$ Cr(VI) reduction | $k_{Cr(VI)}$: 0.0394 min$^{-1}$ | 164 |
| $SnS_2$-nanoparticle | 250 W xenon lamp 420 nm filter | Hydrothermal (140–180 °C). 5 mmol $SnCl_4\cdot5H_2O$, 10 mmol thioacetamide | 20 mg L$^{-1}$ methyl orange degradation | $k_{MO}$: 0.0594 min$^{-1}$ | 105 |
| $SnS_2$-nanoparticle | 500 W xenon lamp | Hydrothermal + acetic acid (130–170 °C, 12 h). 0.005 mol $SnCl_4\cdot5H_2O$ and 0.01–0.02 mol thioacetamide | 10 mL of log phase culture's antibacterial reaction | The bacteria killing ability of 0.11 g mL$^{-1}$ NPs: 75.28 ± 2.3% for *S. aureus* (ATCC 25923), 78.95 ± 2.0% for *E. coli* (ATCC 13534), 81.22 ± 1.1% for *E. coli* (ATCC 25922) | 41 |
| $SnS_2$ quantum dots | 300 W Xe lamp equipped with a cut-off filter ($\lambda > 420$ nm) | Hydrothermal at (160 °C, 16 h) Sn source: $SnCl_4\cdot5H_2O$ S source: L-cystine modifier | 100 mg L$^{-1}$ of Cr(VI) reduction | Degradation ability: 92% for 2 h | 47 |

flower-like structures facilitates a better mass transfer of reactants and products,[175] enhancing accessibility to active sites and promoting more effective contact between the photocatalyst and target pollutants in the surrounding environment.

## 3.3 Heterostructure formation

Heterostructure photocatalysts have garnered widespread acceptance as a highly promising technique for the development of high-performance photocatalysts. The heterostructures can be defined as the combination of photocatalysts with other materials (other photocatalysts or co-catalysts). The key advantage of heterostructure formation lies in the synergistic effects between the different materials, wherein each component mutually reinforces the other, thereby enhancing the overall photocatalytic performance.[177,178] As illustrated in Fig. 3(b), the current literature demonstrates that approxi-

mately 75% of published works on $SnS_2$-based photocatalysts involve heterostructure formation. Diverse materials, including semiconductors, metals, and 2D materials such as graphene and its derivatives, have been combined with $SnS_2$ and exhibit a significant impact on the photocatalytic properties, such as the improvement of specific surface area, heightened light sensitivity, and enhanced reactivity. Furthermore, a crucial aspect is its ability to mitigate the recombination of electrons and holes through the formation of heterojunctions. A heterojunction is an electrical transfer between two or more materials resulting from differing electronic states and band positions. This phenomenon extends the lifetimes of electrons and holes, providing them with more time to promote redox reactions for photocatalytic reactions. To date, various types of heterojunction formation exhibit distinct characteristics and effects on photocatalytic reactions, including type I, type II, p–

n junction, Schottky junction, and Z-scheme, as illustrated in Fig. 10.[179]

**3.3.1 Schottky junction and surface plasmon resonance.** A Schottky junction typically forms during the interaction between a metal and a semiconductor. Upon contact, electrons from the semiconductor tend to flow towards the metal until a Fermi equilibrium is reached. Subsequently, a barrier potential arises, hindering the further flow of electrons into the metal unless they overcome this potential barrier. The Schottky barrier effectively acts as an electron trap, preventing the electrons from flowing back into the semiconductor. This characteristic turns the metal into an electron sink for the photoinduced electrons. The Schottky barrier serves to impede the recombination of electron–hole pairs, thereby extending the lifespan of electrons for the photoreaction.[180]

The exploration of Schottky junction processes in $SnS_2$ photocatalysts remains limited in the existing literature, with only a few reports delving into this phenomenon with different types of noble metal including Pt,[37] Au,[181] and Ag.[182] Among other noble metals, gold (Au) has emerged as one of the extensively studied supports for $SnS_2$ photocatalysts. Feng et al.[183] reported the deposition of Au on $SnS_2$ nanoflowers prepared via hydrothermal synthesis for methylene blue degradation under visible light irradiation. The transmission electron microscopy (TEM) images in Fig. 11(a and b) reveal a 20 nm size of Au deposition on 3 μm size $SnS_2$ nanoflowers, indicating intimate contact between the Au and $SnS_2$, which enhances the charge transfer efficiency. Fig. 11(c) demonstrates the methylene blue degradation ability of Au-deposited $SnS_2$ with varying Au concentrations, showcasing a significant enhancement in degradation after Au deposition. Specifically, the degradation rate of Au–$SnS_2$ was approximately 3.91 times higher than that of $SnS_2$ nanoflowers alone (Table 4). The pronounced improvement in methylene blue degradation post-Au deposition can be attributed to the enhanced charge carrier efficiency facilitated by the Schottky junction formation between Au and $SnS_2$ (Fig. 11(d)). As the Fermi level of Au is lower than that of $SnS_2$, electron transfer from $SnS_2$ to Au occurs, effectively preventing electron–hole recombination. This allows the generation of radicals necessary for methylene blue molecule dissociation. Charge separation efficiency, typically reflected in the number of mobile electrons on the surface, was assessed through photocurrent measurement (Fig. 11(e)). Mondal et al.[184] endeavored to decompose benzylamine using Au–$SnS_2$ nanosheets under solar irradiation. Synthesized via a hydrothermal reaction followed by gold photoreduction using a 400 W xenon lamp, Au-deposited $SnS_2$ nanosheets achieved a conversion rate of approximately 98%
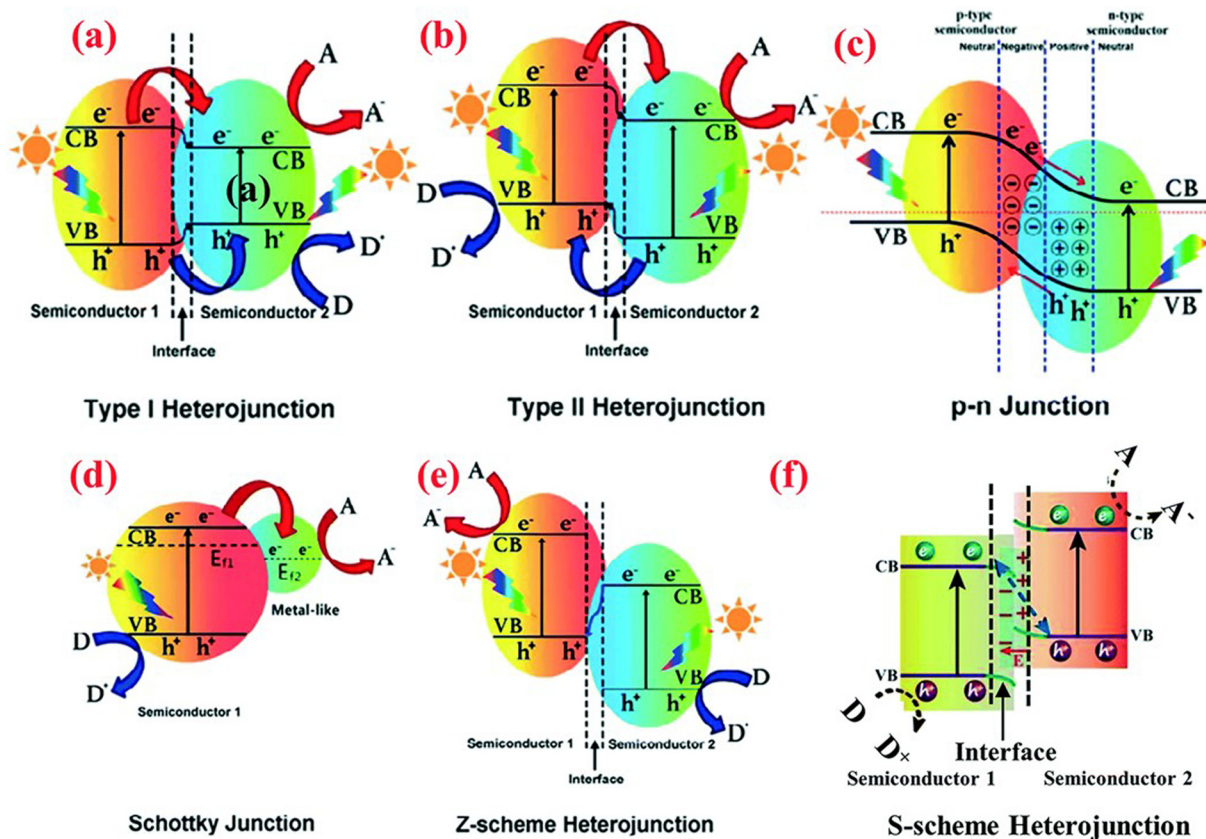


**Fig. 10** Band structure of various types of heterojunction in a photocatalytic hybrid nanocomposite: (a) type I heterojunction; (b) type II heterojunction; (c) p–n junction; (d) Schottky junction; (e) Z-scheme heterojunction; and (f) S-scheme heterojunction.[179] (Reproduced from ref. 179 with permission from the Royal Society of Chemistry, copyright 2021.)
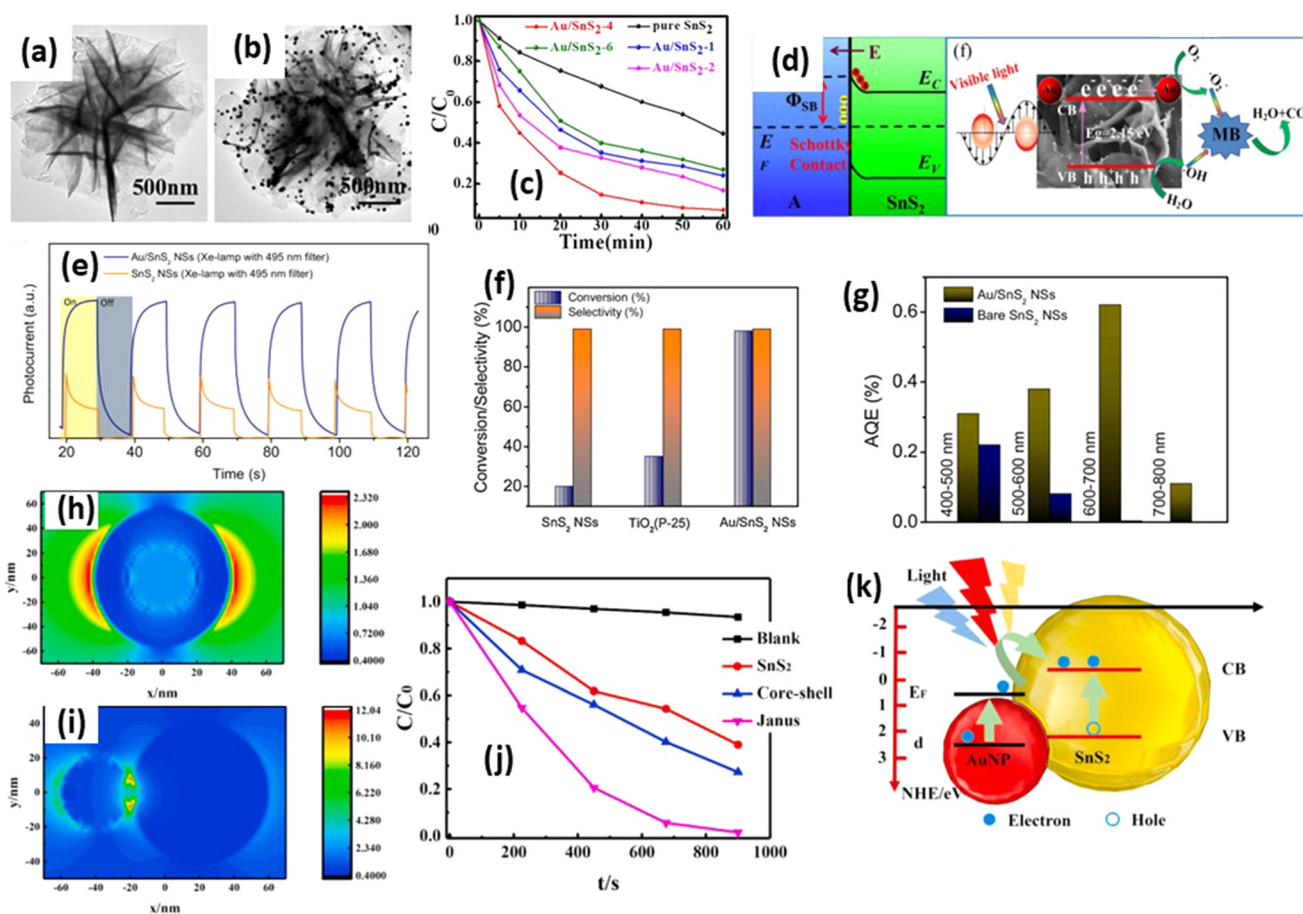
**Fig. 11** TEM images of (a) SnS$_2$ and (b) Au/SnS$_2$. (c) Methylene blue degradation by Au/SnS$_2$. (d) Illustration of the band alignment formed at the interface between the SnS$_2$ and Au NPs.[183] (Reproduced from ref. 183 with permission from Elsevier, copyright 2019.) (e) Transient photocurrent recorded on bare SnS$_2$ and Au/SnS$_2$ NSs using a 400 W Xe lamp (with an attached 495 nm cut-off filter). (f) Comparison plots of benzylamine oxidation efficiency with different catalysts under natural sunlight and ambient conditions for 2 h in open air. (g) Plot of AQE at different wavelength ranges under LED illumination in air at room temperature for bare SnS$_2$ and Au/SnS$_2$.[184] (Reproduced from ref. 184 with permission from Elsevier, copyright 2021.) (h) The near-field distribution of the core–shell structure and the (i) Janus structure with Au nanoparticle s, respectively. (j) Degradation curves of methyl orange under visible light. (k) The schematic diagram of the LSPR-enhanced visible light catalysis of SnS$_2$ and the heterostructures with Au nanoparticles.[186] (Reproduced from ref. 186 with permission from Elsevier, copyright 2021.)

under solar light (Fig. 11(f)), surpassing SnS$_2$ and standard P-25 conversion rates of about 20% and 35%, respectively (Table 4).

To investigate the photocatalytic enhancement in Au–SnS$_2$ nanosheets, the apparent quantum efficiency (AQE) was examined at different wavelengths (400–500 nm, 500–600 nm, 600–700 nm, 700–800 nm) (Fig. 11(g)). Compared with SnS$_2$ nanosheets, Au–SnS$_2$ exhibited a 1.2 to 3 times higher AQE at 400–500 nm and 500–600 nm wavelengths, attributed to improved electron–hole separation mediated by Au nanoparticles (Fig. 11(g)). Notably, at 600–700 nm, where SnS$_2$ excitation is minimal, Au-deposited SnS$_2$ exhibited a strong AQE, indicating an efficient 'hot-electron' injection mechanism from Au nanoparticles to SnS$_2$ nanosheets.[185] Furthermore, the formation of Au–SnS$_2$ is influenced by Au positioning relative to the SnS$_2$ photocatalyst. Fu *et al.*[186] investigated different composite structures of Au–SnS$_2$ for methyl orange degra-

dation under visible light. Two structures were examined: core–shell and Janus structures. Near-field distribution analysis (Fig. 11(h and i)) revealed a low light enhancement effect in the core–shell structures, leading to diminished photocatalytic ability. Conversely, Janus structures exhibited a significant near-field enhancement, resulting in superior methyl orange degradation (Fig. 11(j)). Among the images, the Janus structures exhibit the highest reaction rate ($4.0 \times 10^{-3}$ s$^{-1}$), followed by the core–shell structures ($1.2 \times 10^{-3}$ s$^{-1}$). A significant increase in photocatalytic activity, approximately four times greater than that of sole SnS$_2$ nanoparticles ($1.0 \times 10^{-3}$ s$^{-1}$), is observed in the Janus structures. This enhancement is attributed to the improved extinction effect. Photoluminescence lifetime analysis revealed longer electron lifetimes in nanoparticle structures (1.74 ns) than Janus structures (1.53 ns) compared with core–shell structures (1.16 ns), indicating an enhanced photocatalytic efficiency. Fig. 11(k) illustrates the proposed

**Table 4** Photocatalytic performance of heterojunction formation of $SnS_2$

| Materials | Heterojunction type | Light source | Photocatalytic testing | Photocatalytic performance | Ref. |
|---|---|---|---|---|---|
| Au–$SnS_2$ | Schottky junction | 330 W xenon lamp | 100 mg L$^{-1}$ rhodamine B degradation | $k_{RhB}$: 0.0514 min$^{-1}$. 3.91 times that of $SnS_2$ | 183 |
| Au–$SnS_2$ | Schottky junction | 400 W xenon lamp | Benzylamine oxidation | Conversion: 98%, 4.9 times that of $SnS_2$ | 184 |
| Au–$SnS_2$ | Schottky junction | 250 W xenon lamp | 50 mg L$^{-1}$ Cr(VI) reduction | $k_{Cr(VI)}$: 0.0234 min$^{-1}$. 2.07 times that of $SnS_2$ | 73 |
| BiFeO$_3$/$SnS_2$ | p–n junction | 250 W mercury lamp | 15 mg L$^{-1}$ methylene blue degradation | $k_{MB}$: 0.0428 min$^{-1}$. 7.50 times that of $SnS_2$ | 188 |
| BiOI/$SnS_2$ | p–n junction | UV-vis (385–740 nm) | 10 mg L$^{-1}$ rhodamine B degradation | $k_{RhB}$ 100% within 30 min 3 times that of $SnS_2$ | 187 |
| TiO$_2$/$SnS_2$ | Type I heterojunction | Xe lamp, 100 mW cm$^{-2}$ | Hydrogen evolution reaction (HER) | H$_2$ yield: 652.4 μmol g$^{-1}$ h$^{-1}$ 7.51 times that of $SnS_2$ | 190 |
| ZnIn$_2$S$_4$/$SnS_2$ | Type II heterojunction | 300 W xenon lamp | 50 mg L$^{-1}$ Cr(VI) reduction | $k_{Cr(VI)}$: 0.01273 min$^{-1}$ 2.2 times that of $SnS_2$ | 196 |
| ZnWO$_4$/$SnS_2$ | Type II heterojunction | Solar hotspot 5 kW h m$^{-2}$ day$^{-1}$ | 50 mg L$^{-1}$ Cr(VI) reduction | $k_{Cr(VI)}$ = 0.061 min$^{-1}$ 3.58 times that of $SnS_2$ | 104 |
| ZnWO$_4$/$SnS_2$ | Type II heterojunction | Solar hotspot 5 kW h m$^{-2}$ day$^{-1}$ | 20 mg L$^{-1}$ tetracycline | $k_{TC}$ = degradation rate: 0.023 min$^{-1}$ 3.28 times that of $SnS_2$ | 104 |
| In$_2$S$_3$/$SnS_2$ | Type II heterojunction | 300 W xenon lamp | 10 mg L$^{-1}$ rhodamine B degradation | $k_{RhB}$: 0.11716 min$^{-1}$. 15.3 times that of $SnS_2$ | 192 |
| Ag$_3$PO$_4$/$SnS_2$ | Z-scheme | A 500 W xenon-arc lamp | 10 mg L$^{-1}$ methylene blue | $k_{MB}$ = 0.063 min$^{-1}$ 7.08 times that of $SnS_2$ | 201 |
| Bi$_2$WO$_4$/$SnS_2$ | Z-scheme | Sunlight | 20 mg L$^{-1}$ tetracycline degradation | $k_{TC}$ = 0.027 min$^{-1}$ 27 times that of $SnS_2$ | 134 |
| BiOBr/$SnS_2$ | Z-scheme | 400 W xenon lamp | 10 mg L$^{-1}$ rhodamine B degradation | $k_{RhB}$ = 0.1203 min$^{-1}$ 75 times that of $SnS_2$ | 197 |
| SnO$_2$/$SnS_2$ | S-scheme | 500 W xenon lamp | 10 mg L$^{-1}$ methyl orange degradation | $k_{MO}$: 0.01182 min$^{-1}$. 2.19 times that of $SnS_2$ | 199 |
| ZnIn$_2$S$_4$/$SnS_2$ | S-scheme | 300 W xenon lamp | H$_2$ production | H$_2$ yield: 1.113 mmol g$^{-1}$ h$^{-1}$ 16.14 times that of ZnIn$_2$S$_4$ | 200 |
| CdS/$SnS_2$ | S-scheme | 300 W xenon lamp | H$_2$ production | H$_2$ yield: 5.18 mmol g$^{-1}$ h$^{-1}$ 5.95 times that of CdS | 198 |

mechanism of surface resonance analysis of Janus Au–$SnS_2$; due to the near-field enhancement, electron excitation becomes more pronounced in $SnS_2$ nanoparticles, significantly enhancing photocatalysis. Besides the enhanced optical fields, the localized surface plasmon resonance (LSPR) induces electron injection from AuNPs to the conduction band edge of $SnS_2$, further contributing to the photocatalytic process. Among these mechanisms, the excited electrons in the conduction band edge of the $SnS_2$ nanoparticles facilitate the generation of reactive oxygen radicals, including superoxide, hydroxyl, and singlet oxygen, through a series of oxidation–reduction processes in the solution. These oxygen radicals exhibit high activity and play a crucial role in degrading methyl orange molecules.[186]

**3.3.2 p–n junction.** The p–n junction arises from electronic interactions driven by differences in the majority carriers of semiconductors. In n-type semiconductors, electrons predominate as majority carriers, whereas in p-type semiconductors, holes are prevalent. Electrons flow from n-type to p-type, while holes migrate oppositely, impeding electron–hole recombination. $SnS_2$, an n-type semiconductor, is frequently combined with various p-type semiconductors like as BiOI,[187] BiFeO$_3$,[188] NiS,[189] and SnS nanoparticles[16] to create p–n junction photocatalysts.

Wang *et al.*[187] confirmed the p–n junction formation between BiOI and $SnS_2$ for rhodamine B degradation under visible light irradiation, as illustrated in Fig. 12(a). Notably, $SnS_2$ has a layered morphology, while BiOI comprises the nanoparticles that disperse on the top of the $SnS_2$ layer. The conduction band of $SnS_2$ is situated at −0.96 V, with a valence band at 1.5 V. Conversely, BiOI exhibits a valence band at +0.53 V and a conduction band at −1.29 V. Upon electrical contact, band alignment ensues, facilitating electron and hole transfer between the BiOI and $SnS_2$ until equilibrium is attained, with the Fermi level equalized. Upon irradiation, electron–hole pairs form in the conduction and valence bands of $SnS_2$ and BiOI. Due to the p–n junction, electrons readily transfer from BiOI to $SnS_2$, while holes undergo the reverse process. This reaction process enhances electron mobility and correlates directly with photocatalytic efficiency. Photocurrent analysis (Fig. 12(b)) demonstrates increased electron densities of BiOI/$SnS_2$ heterostructures compared with BiOI and $SnS_2$. The active electrons in the conduction band react with O$_2$ to form O$_2^{\bullet-}$, while the holes react with OH$^-$ to produce OH$^{\bullet}$, facilitating rhodamine B degradation. Rhodamine B degradation analysis (Fig. 12(c)) indicates a significant improvement after p–n junction formation, three times higher than that observed with $SnS_2$ alone (Table 4), a finding consistent with the photocurrent analysis.

**3.3.3 Type I and II heterojunctions.** Fig. 13(a) illustrates a type I heterojunction within a photocatalytic reaction. Type I heterojunctions manifest when a semiconductor with a rela-
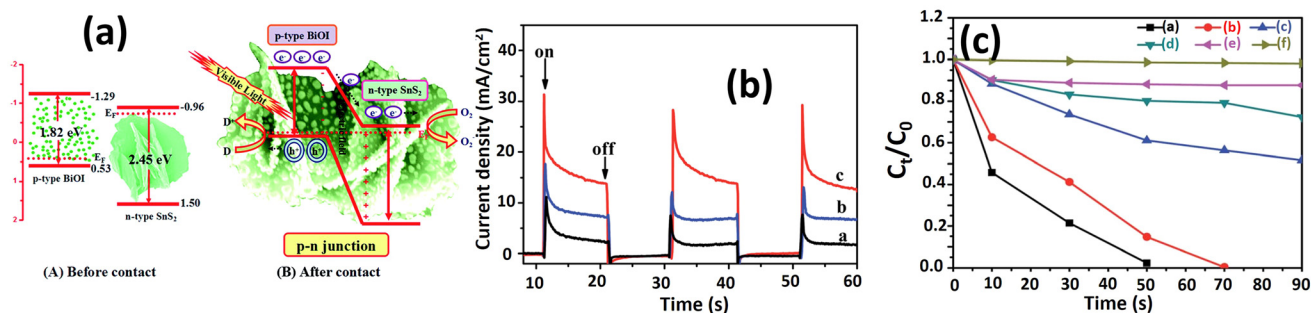
**Fig. 12** (a) Schematic diagrams illustrating the energy bands of p-BiOI and n-SnS$_2$ before contact, the formation of a p–n junction, and the equilibrium energy band diagram. Additionally, the transfer of photoinduced electrons from p-BiOI to n-SnS$_2$ under visible-light irradiation is depicted; (b) comparison of the transient photocurrent response of SnS$_2$ (black), BiOI (blue), and BiOI/SnS$_2$ (red) in 0.1 M Na$_2$SO$_4$ aqueous solution under visible-light irradiation; (c) visible-light photocatalytic activities: (black) BiOI/SnS$_2$, (red) BiOI, (blue) SnS$_2$, (green) P25, (violet) adsorption in the dark, and (yellow) degradation of 10 mg rhodamine B without photocatalyst under visible light ($\lambda$ > 420 nm) irradiation.[187] (Reproduced from ref. 187 with permission from the Royal Society of Chemistry, copyright 2015.)
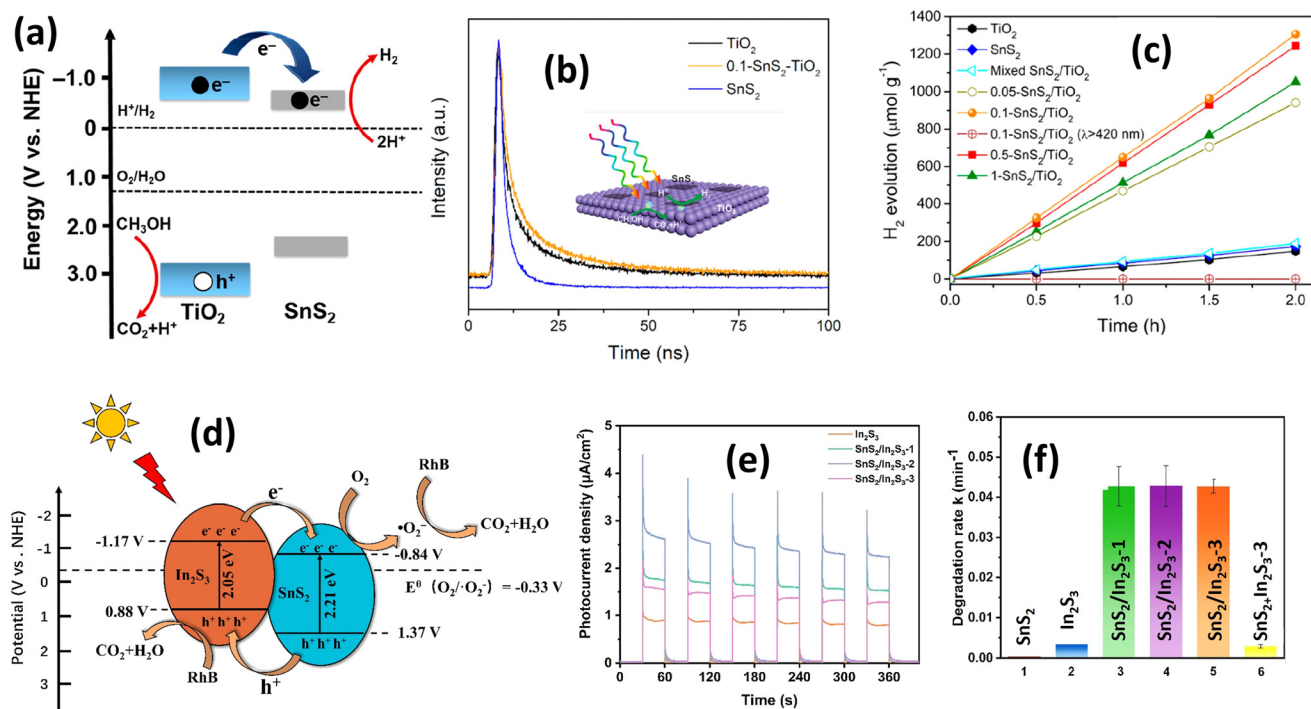


**Fig. 13** (a) Corresponding band energy diagrams and charge transfer path; (b) time-resolved photoluminescence decay spectra of TiO$_2$, SnS$_2$, and 0.1-SnS$_2$/TiO$_2$; (c) photocatalytic H$_2$ evolution curves with different catalysts.[190] (Reproduced from ref. 190 with permission from Elsevier, copyright 2019.) (d) Schematic diagram of the possible photocatalytic degradation mechanism of RhB by the SnS$_2$/In$_2$S$_3$ heterostructure under visible light irradiation; (e) transient photocurrent responses of In$_2$S$_3$ and SnS$_2$/In$_2$S$_3$ heterostructures; (f) the apparent rate constants of SnS$_2$/In$_2$S$_3$.[192] (Reproduced from ref. 192 with permission from Elsevier, copyright 2022.)

tively large band gap energy, such as TiO$_2$, interfaces with another semiconductor possessing a smaller band gap energy. The valence band and conduction band positions are intermediary between those of materials with larger band gaps. In this context, following photoexcitation, electrons and holes migrate from the large band gap photocatalyst to the smaller band gap photocatalyst, thereby facilitating reduction–oxidation reactions crucial for photocatalytic processes. Sun *et al.*[190] provide an exemplar of a type I heterojunction with a

SnS$_2$ photocatalyst, detailing the formation of SnS$_2$/TiO$_2$ heterostructures. Fig. 13(a) elucidates the catalytic reaction process of type I heterojunction formation between SnS$_2$ and TiO$_2$. Under these reaction conditions, they propose that photoelectrons from the conduction band of TiO$_2$ migrate into the conduction band, reducing H$^+$ ions into hydrogen gas. Meanwhile, holes react with methanol to yield hydrogen gas. This heterojunction reaction prolongs the decay time of electrons, estimated at around 4.4 ns compared with TiO$_2$ (2.8 ns)

and $SnS_2$ (1.8 ns) as shown in Fig. 13(b). The hydrogen evolution reaction, as depicted in Fig. 13(c), showcased a remarkable enhancement facilitated by the 0.1-$SnS_2$/$TiO_2$ compared with $SnS_2$ and $TiO_2$ individually. The 0.1-$SnS_2$/$TiO_2$ nanohybrid exhibited an impressive hydrogen production rate, reaching 652.4 $\mu$mol h$^{-1}$ g$^{-1}$, surpassing the rates observed with pure $TiO_2$ and $SnS_2$ by approximately 8 times. However, a further increase in the amount of $SnS_2$ in the hybrid resulted in a slight decline in $H_2$ production activity, with values of 621.5 and 526.7 $\mu$mol h$^{-1}$ g$^{-1}$ for 0.5-$SnS_2$/$TiO_2$ and 1-$SnS_2$/$TiO_2$, respectively. This phenomenon can be attributed to the excess $SnS_2$ hindering the absorption of incident light and the generation of excited carriers by $TiO_2$. Additionally, an abundance of $SnS_2$ may act as charge recombination centers, leading to a reduced photocatalytic performance. Another type I heterojunction formation has been reported by Liu et al.[191] investigating the formation of $SnS$/$SnS_2$ for the electrochemical water splitting process. They found that the energy gap of $SnS_2$ is 2.15 eV, while $SnS$ has an energy gap of 1.1 eV. The conduction band (CB) and valence band (VB) positions of $SnS_2$ are −0.08 eV and 2.08 eV, respectively, whereas those of $SnS$ are 0.12 eV and 1.22 eV, respectively. Given that the VB of $SnS_2$ is more positive while the CB is more negative, electrons and holes tend to migrate to $SnS$ after electron excitation, effectively retarding electron and hole recombination. The photocurrent analysis revealed that the current density under irradiation for the $SnS_2$/$SnS$ heterojunction is five times higher than that of $SnS$ and ten times higher than that of $SnS_2$, confirming the charge carrier efficiency.

Differing from type I heterojunctions, type II heterojunctions involve semiconductor photocatalysts where two types of semiconductor exhibit distinct band structure levels. One semiconductor possesses a more positive valence band, while the other semiconductor has a more negative conduction band. In this arrangement, electrons flow from the semiconductor with the more negative conduction band position, while holes flow from the semiconductor with the more positive valence band. This electrical transfer scheme helps prevent electron and hole recombination. An example of a type II heterojunction formation of $SnS_2$ was reported by Zhang et al.[192] investigating the formation of $SnS_2$ with $In_2S_3$. Fig. 13(d) illustrates the catalytic reaction mechanism of the $SnS_2$/$In_2S_3$ heterostructure for rhodamine B degradation under visible light irradiation. Upon irradiation, electron transfer occurs from the conduction band of $In_2S_3$ to the conduction band of $SnS_2$ due to the more negative level of the conduction band position of $In_2S_3$, while hole transfer operates oppositely due to the greater positivity of the valence band level of $SnS_2$. Similar to a heterojunction type I, this charge transfer process between $In_2S_3$ and $SnS_2$ significantly enhances charge mobility efficiency, as demonstrated in Fig. 13(e); the photocurrent of the $In_2S_3$/$SnS_2$ heterostructure is 3–4 times higher than $In_2S_3$ only, which shows a marked improvement in current density after heterojunction formation. RhB degradation testing indicates a significant enhancement in RhB degradation by conducting $In_2S_3$/$SnS_2$ heterojunction formation (Fig. 13(f)),

where the degradation rate was 99 times and 15 times higher than with $SnS_2$ and $In_2S_3$ alone, respectively. The theoretical explanation of the $In_2S_3$/$SnS_2$ heterojunction as type II heterojunction formation was confirmed by Wang et al.[193] through EPR analysis for detecting superoxide radicals. The lower intensity of the EPR signal of $In_2S_3$/$SnS_2$ compared with $In_2S_3$ indicates electron transfer from $In_2S_3$ to $SnS_2$, confirming type II heterojunction formation. Other materials have also formed type II heterojunctions combined with $SnS_2$, such as g-$C_3N_4$,[194] $ZnWO_4$,[104] $SnO_2$,[195] and $ZnIn_2S_4$.[196]

**3.3.4 Z-scheme and S-scheme photocatalyst.** However, based on above existing heterostructure systems there is still an issue regarding the reducing of the oxidation and reduction ability of the photocatalyst. To address this issue, scientists have pioneered the development of Z-scheme and S-scheme photocatalysts. These novel configurations offer superior reduction and oxidation capabilities compared with conventional type I and type II heterojunction formations. To date, Z-scheme and S-scheme heterojunctions have emerged as the most investigated heterostructures for $SnS_2$-based photocatalysts. Notably, the direct Z-scheme photocatalyst for $SnS_2$ holds considerable promise for future advancements, as it obviates the need for a metal mediator to facilitate Z-scheme reactions.

Several studies have confirmed the formation of direct Z-scheme photocatalysts. For instance, Luo et al.[15] initiated Z-scheme formation by integrating $SnS_2$ with $Ag_3PO_4$ for methyl orange degradation under visible light irradiation. The schematic representation in Fig. 14(a) illustrates the Z-scheme formation of the $SnS_2$/$Ag_3PO_4$ heterostructure. The realization of a direct Z-scheme photocatalyst depends on the band positions of each constituent material. In the case of the $SnS_2$/$Ag_3O_4$ heterostructure, the Z-scheme configuration is inferred from the disparate band positions of the $SnS_2$ and $Ag_3PO_4$.

The formation of a direct Z-scheme photocatalyst relies on the band positions of each material. In the case of the $SnS_2$/$Ag_3PO_4$ heterostructure, the existence of the Z-scheme can be inferred from the disparate band positions of each material. The valence band (VB) maximum and conduction band (CB) minimum of $SnS_2$ are about 1.21 eV and −0.89 eV, respectively, while the VB and CB potentials of $Ag_3PO_4$ are about 2.62 eV and 0.30 eV, respectively. The CB position of $Ag_3PO_4$ is more positive than the standard reduction potential of $O_2$/$O_2^{\bullet-}$ (0.13 eV). The electron from $Ag_3PO_4$ is unable to reduce $O_2$ into $O_2^{\bullet-}$ and instead reacts with the hole of the $SnS_2$. Consequently, recombination is prevented, leading to a more efficient charge separation process, as demonstrated by photocurrent analysis. This correlation directly corresponds to the observed improvements in photocatalytic activity (see Fig. 14(b and c)). As mentioned earlier, the Z-scheme can be generated if one of the conduction bands (CBs) of the sample position is more positive than the reduction potential of $O_2$/$O_2^{\bullet-}$ (0.13 eV), thereby preventing the reduction reaction. Other reports also confirm the same understanding about the Z-scheme formation, such as Qiu et al.,[197] Li et al.,[49] and Kumar et al.[134]

Slightly different from the Z-scheme, the S-scheme can be generated through the inner electric field phenomenon. This
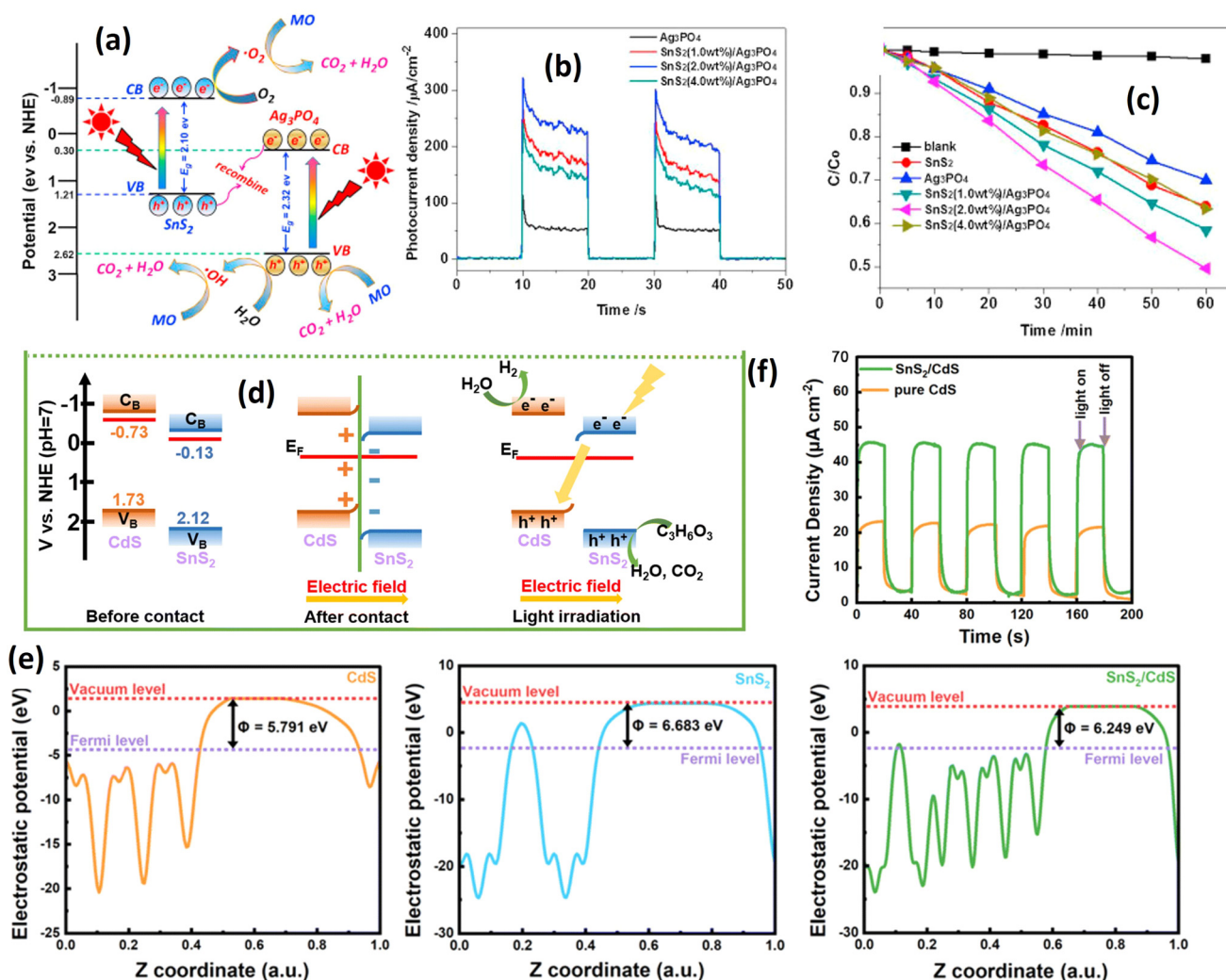
**Fig. 14** (a) Schematic diagram of the possible photoinduced electron–hole pair separation process and direct Z-scheme photodegradation mechanism of methyl orange over the $SnS_2/Ag_3PO_4$ heterojunction photocatalyst under visible light irradiation. (b) Photocurrent response over the as-prepared samples under visible light irradiation. (c) Photocatalytic degradation curves for the photodegradation of MO.[15] (Reproduced from ref. 15 with permission from Elsevier Ltd.) (d) S-scheme illustration of the possible charge transfer processes in the $SnS_2/CdS$ heterostructures; (e) work function analysis of CdS, $SnS_2$ and $SnS_2/CdS$. (f) Photocurrent analysis of CdS and $SnS_2/CdS$.[198] (Reproduced from ref. 198 with permission from the Royal Society of Chemistry.)

electric field emerges when a charge moves between semiconductors, creating a field within each semiconductor due to differing Fermi energies. Fig. 14(d) illustrates an instance of S-scheme formation between $SnS_2$ and CdS nanoparticles.[198] Before contact, $SnS_2$ and CdS exhibit different Fermi energy levels; CdS registers at 5.791 eV (Fig. 14(e)), while $SnS_2$ is at 6.683 eV. Upon interaction, Fermi energy alignment occurs until an equilibrium is established. In this state, the electron density at the $SnS_2$ interface surpasses that of CdS, generating an inner electric field. Consequently, the valence band of CdS bends, and the conduction band of $SnS_2$ shows observable curvature. Upon light irradiation, both $SnS_2$ and CdS generate electron–hole pairs, and the inner electric field facilitates electron transfer from $SnS_2$ to CdS, enhancing the charge separation efficiency. This improvement is supported by photo-

current analysis (Fig. 14(f)). The photocatalytic activity of the S-scheme $SnS_2/CdS$ photocatalyst for $H_2$ production, summarized in Table 4, yields 5.18 mmol $g^{-1}$ $h^{-1}$ of hydrogen, 5.95 times higher than that of CdS alone. Similar S-scheme $SnS_2$-based photocatalysts have been reported for other materials, including BiOBr,[197] $SnO_2$,[199] $ZnIn_2S_4$.[200]

Table 4 presents various reports on the photocatalytic performance of $SnS_2$ heterojunction formations. Different strategies yield varying degrees of improvement compared with $SnS_2$ alone. According to current data, Au/$SnS_2$ demonstrates a 3.91-fold enhancement over $SnS_2$. Among the p–n junction formations, $BiFeO_3/SnS_2$ exhibits the most significant improvement, with a degradation rate approximately 7.50 times higher than $SnS_2$. Similarly, heterojunctions of type I and type II show comparable enhancement, boasting 7.51 times improvements
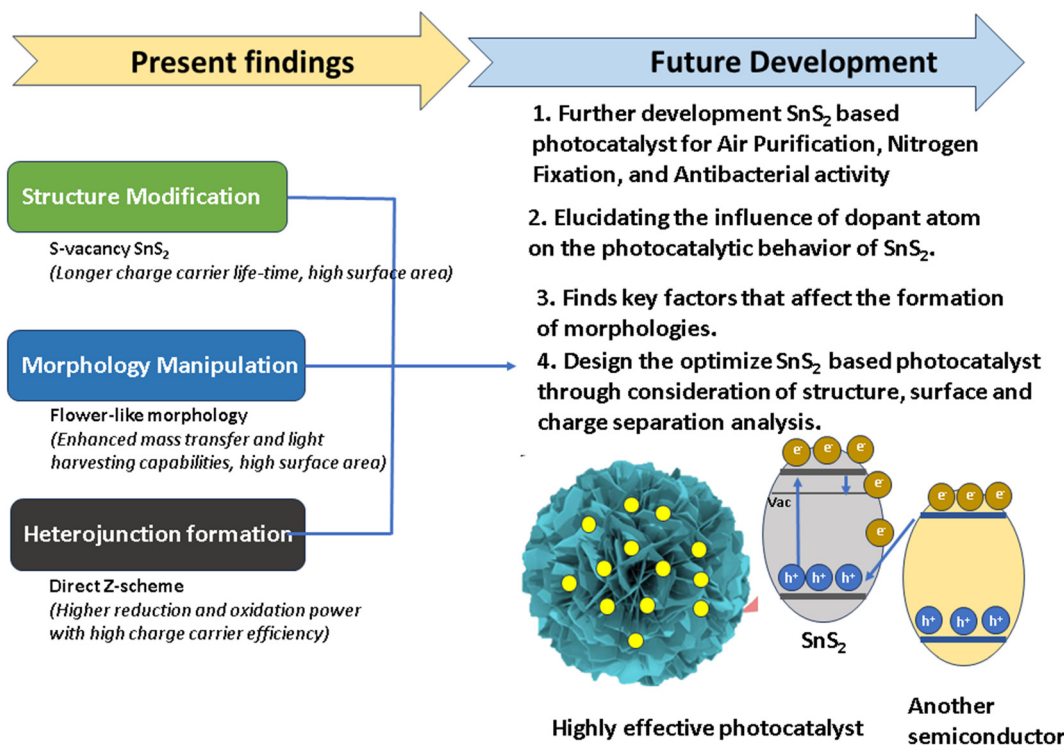
**Fig. 15** Current findings and future research direction for $SnS_2$ photocatalytic research.

over $SnS_2$. Notably, Z-scheme configurations outperform other heterojunction types, with $BiOBr/SnS_2$ achieving the highest improvement, nearly 75 times higher than $SnS_2$ alone. This superior enhancement in Z-scheme heterojunctions is attributed to enhanced charge separation efficiency and stronger reduction and oxidation capabilities, resulting in accelerated degradation rates, and increased photochemical reaction yields.

## 4 Future perspectives

The current strategies for modifying $SnS_2$ have been thoroughly examined, encompassing structural modification, morphological manipulation, and heterojunction formation. Despite the comprehensive elucidation of each photocatalytic advancement mechanism and synthesis technique in this review, challenges persist, hindering the further advancement of $SnS_2$ photocatalysts.

In terms of structural modification, it is established that S-vacancies play a pivotal role in enhancing the photocatalytic performance, primarily by improving electron–hole separation efficiency. While the authors attribute this enhancement to electron traps between the valence and conduction bands, empirical evidence remains elusive. Future research endeavors should focus on elucidating the mechanism of the S-vacancy effect on mid-gap formation to substantiate this claim. Additionally, the role of dopants in photocatalytic reactions remains unclear due to their concurrent generation with

S-vacancy formation during doping processes. To advance research in this area, techniques minimizing the impact of S-vacancies in doping must be developed to gain a comprehensive understanding of doping phenomena for photocatalytic enhancement.

In morphology engineering, the flower-like morphology has emerged as the most suitable structure for various photocatalytic applications, including wastewater treatment and hydrogen production. Enhanced mass transfer and light harvesting capabilities are key attributes contributing to the photocatalytic performance of flower-like structures. However, challenges in material preparation persist, particularly in hydrothermal synthesis methods, which remain dominant in $SnS_2$ flower-like morphology production. Although hydrothermal synthesis is known for producing flower-like morphologies, it is important to note that other morphologies can also be generated using the same method and precursor. This variability may hinder further development, as precise control over flower-like morphology parameters such as size, petal-like dimensions, and facet arrangements are essential for further research development of the morphological effect on the photocatalytic performance of $SnS_2$. Therefore, for future development, it is necessary to find the key factors which control the growth of morphology through hydrothermal reactions encompassing the precursor, solvent, temperature control, and other factors.

While the proliferation of heterojunction formation is widespread, it does not guarantee a comprehensive understanding of photocatalytic mechanisms. Heterostructure formation, con-

sidered one of the most extensively studied systems for $SnS_2$ photocatalysts, relies on the synergistic effects of its constituent materials. Various types of heterostructure have been reported, each with unique characteristics. Among these, the Z-scheme exhibits significant promise for enhancing photocatalytic performance due to its capacity to augment oxidation and reduction potentials for photocatalytic reactions. However, several considerations must be addressed for the optimal utilization of Z-scheme heterojunction photocatalysts. Beyond the reliance on electronic properties for photocatalytic enhancements, factors such as particle interaction and surface optimization are also pivotal. Particle interaction hinges on the specific facets of each particle, as different facets exhibit distinct electronic and adsorption behaviors. Theoretical investigations, particularly those utilizing density functional theory (DFT) calculations, are essential to fully comprehend these interactions. Additionally, optimizing the surface properties of Z-scheme particles for specific applications, including increasing the surface area and modifying the charge, is imperative for optimizing the adsorption process and enhancing active sites for photocatalytic reactions. To address these issues, for future research directions, it is interesting to employ the comprehensive investigation of photocatalyst design while considering the structural design alongside surface optimization and Z-scheme heterojunction formation.

We have thoroughly discussed the current results and outlined future perspectives for three distinct strategies. Building on this understanding, future research endeavors will focus on integrating these strategies into a unified photocatalyst system. The S-vacancy $SnS_2$, characterized by a prolonged charge carrier lifetime, can be elaborately engineered into a flower-like morphology with enhanced mass transfer, light harvesting capabilities, and a large surface area. Concurrently, nanoparticles with suitable band gaps, such as CdS and $Ag_3VO_4$, can be selectively deposited atop the flower-like $SnS_2$ system for generating a Z-scheme photocatalyst, as illustrated in Fig. 14. The successful amalgamation of these components is anticipated to yield a photocatalyst system of exceptional performance, aligning with industrial standards.

Furthermore, it is imperative to address a critical aspect pertaining to the chemical stability of $SnS_2$ itself, given its susceptibility to sulfur atom replacement by oxygen upon exposure to air. Factors influencing stability, including the synthesis process and the photocatalyst environment, necessitate meticulous examination. Such analysis assumes paramount importance for practical applications, wherein long-term stability is imperative for industrial viability.

## 5 Summary

For summarizing this review, Fig. 15 was used for understanding the current findings and future directions. In this review, we have summarized recent strategies for improving the photocatalytic performance of $SnS_2$, focusing on three fundamental approaches: crystal structure engineering, morphology engin-

eering, and heterojunction formation. $SnS_2$-based photocatalysts have been utilized in various applications, including $CO_2$ reduction, $H_2$ production, nitrogen fixation, antibacterial activity, air purification, and wastewater treatment technologies.

At the current stage, the structural engineering of $SnS_2$ has been carried out through two methods: vacancy generation and doping processes. These approaches have successfully increased the photocatalytic performance of $SnS_2$. The fundamental phenomenon observed in S-vacancy generation and doping processes is the ability to decrease the recombination of electrons and holes, thereby facilitating redox reactions. Additionally, altering crystal structures results in a decrease in the crystallite size of $SnS_2$, which is beneficial for increasing the surface area and the number of active sites for chemical reactions.

Various morphologies of $SnS_2$, such as flower-like structures, nanoparticles, nanosheets, and quantum dots, exhibit distinct effects on the photocatalytic performance. Flower-like structures, with their high specific surface area and unique morphology, demonstrate superior light harvesting ability and increased active sites compared with nanosheet and nanoparticle morphologies. Although nanosheets have a smaller surface area than flower-like structures, they facilitate the efficient migration of photogenerated electrons and holes to reaction sites, thereby enhancing the photocatalytic efficiency. Conversely, nanoparticle morphology is influenced by the size of the nanoparticles; smaller nanoparticles also contribute to an improved specific surface area, thereby enhancing photocatalytic activity.

Heterojunction formation is by far the most effective strategy for improving photocatalytic reactions, as it enables the generation of synergistic effects between $SnS_2$ and other materials, significantly enhancing the photocatalytic efficiency. Among various types of heterojunction, Z-scheme photocatalytic reactions are the most promising strategy for improving the photocatalytic performance of $SnS_2$. This is due to their stronger oxidation and reduction capabilities, coupled with highly efficient charge carrier separation efficiency.

For further development, several aspects are still limited in current literature. Firstly, there is a lack of research on the application of $SnS_2$ for antibacterial activity, $N_2$ fixation, and air purification. Therefore, future research should focus more on investigating these types of photocatalytic application. Secondly, there is uncertainty regarding the effect of dopants on vacancy generation. Since the doping process directly leads to vacancy formation, the individual impact of each dopant is not well understood. To address this issue, both synthesis processes and theoretical approaches should be conducted simultaneously to comprehensively understand the doping effect on improving charge carrier separation in $SnS_2$. Moreover, the growth of morphology is not well understood. Therefore, for future development, it is necessary to find the key factor which controls the growth of morphology through hydrothermal reactions encompassing precursor, solvent, temperature control, and other factors.

However, one of the most crucial areas of research is the design of the ideal photocatalyst based on the aforementioned findings. Developing a Z-scheme $SnS_2$-based photocatalyst with a high specific surface area and efficient charge carrier separation is essential. One promising technique is to combine $SnS_2$ flower-like structures with very small nanoparticles, allowing the particles to attach to the flower-like structures, thereby improving the light harvesting process and charge carrier separation efficiency. Lastly, the stability of $SnS_2$ is a critical consideration. Since $SnS_2$ is prone to oxidation, stability studies must be conducted to meet industrial standards.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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