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Introduction

Inspired by natural photosynthesis, the use of semiconductors to produce H₂ from water is of great interest and represents a promising approach towards sustainable energy conversion.^{1–5} Among numerous semiconductor photocatalysts, metal chalcogenide materials are a particularly promising class, especially $Zn_xCd_{1-x}S$ solid solutions, which have been extensively studied for photocatalytic H₂ evolution reactions due to their adjustable bandgap and band edge position with the change of Zn/Cd ratio and their extremely high H₂ evolution rate.^{6–10} However, the relatively low photoconversion efficiency and bad stability of traditional $Zn_xCd_{1-x}S$ solid solutions remains the most critical factor restricting practical application.^{11–13} Therefore, inner structural regulation and surface modification of $Zn_xCd_{1-x}S$

Construction of heterojunctions between ReS_2 and twin crystal $\text{Zn}_x\text{Cd}_{1-x}$ S for boosting solar hydrogen evolution[†]

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Facilitating charge separation as well as surface redox reactions is considered to be an efficient way to improve semiconductor-based photocatalytic hydrogen generation. In this study, we developed a highly active and reliable photocatalyst, ReS_2/T -ZCS, by anchoring nanoflower-like ReS_2 particles on the surface of host chalcogenide nanotwins ($Zn_{0.5}Cd_{0.5}S$). By virtue of the in-built driving force from the homojunction with a type-II staggered band alignment in twin crystal $Zn_{0.5}Cd_{0.5}S$ (T-ZCS) and heterojunctions between T-ZCS and ReS₂ on the surface of the photocatalyst, a substantially improved charge separation and transfer property were achieved. Hence, the twin crystal $Zn_{0.5}Cd_{0.5}S$ decorated nanoflower-like ReS₂ exhibits a significantly improved photocatalytic H₂ evolution rate of 112.10 mmol g⁻¹ h⁻¹ and the corresponding apparent quantum efficiency reaches 32.65% at 420 nm, which is 31 times larger than that of pure phase $Zn_{0.5}Cd_{0.5}S$. Our work not only couples the merits of homojunctions and heterojunctions to promote solar energy conversion, but also expands applications of the transition metal dichalcogenide (TMD) family in electrocatalysis, photothermal-catalysis and energy storage.

solid solution for enhancing the separation of electron–hole pairs to improve the photoconversion efficiency is highly desirable for their photocatalytic activity promotion.¹⁴

Recently nano-twin crystal $Zn_xCd_{1-x}S$ (T-ZCS) solid solution has aroused a lot of research interest, in which different crystal phases including zinc blende (ZB) and wurtzite (WZ) segments could form an inner homo-junction.^{15,16} Studies demonstrate that this twin crystal structure can improve the separation of photogenerated electrons and holes due to the "back-to-back" potentials at the homo-junctions.^{17–19} The synchrotron X-ray diffraction and X-ray absorption characterizations revealed the band positions of the homo-junction in twined $Zn_xCd_{1-x}S$ and suggested that photogenerated electrons will transfer from the conduction band (CB) of the ZB phase to the WZ phase, driven by the electrostatic field from the potential energy difference between these two phases.²⁰

Besides the homo-junction formation from inner structural regulation, loading co-catalyst onto host semiconductor photocatalysts can create heterojunctions on the surface, which has proven to be an effective strategy for promoting the separation of photogenerated electron–hole pairs and reducing the activation energy or overpotential for the reaction.^{11,21,22} To date, many researches in this field focus on the study of highly efficient precious metal-free cocatalysts due to scarcity and high cost of noble metals, such as NiS, Cu₃P, CoP, PdP_{~ 0.33}S_{~ 1.67} *etc.*^{17,23–25} Among them, transition metal dichalcogenides (TMDs) such as



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WS₂, MoS₂, and WSe₂ have been found to have good electrical conductivity and stability for the application of photocatalysis and electrocatalysis.²⁶⁻²⁹ Molybdenum disulfide (MoS₂) is the most prominantly reported TMD cocatalyst for promoting photocatalytic activity.^{30,31} B. Hinnemann *et al.*³² reported that MoS₂ has the potential for efficient hydrogen production, owing to its hydrogen bonding Gibbs free energy being zero based on density functional theory calculation. Zou et al.33 proved that the 2D/2D heterojunction between black phosphorus and MoS₂ can accelerate charge transfer and separation in the photocatalytic process. Compared with widely reported MoS₂, ReS_2 is an emerging new member of the two-dimensional (2D) TMD family which has recently attracted significant attention in the catalysis, electronic, and optoelectronic fields.³⁴ ReS₂ usually possesses a distorted 1T crystal structure, leading to more exposed unsaturated edge sites.^{35,36} The two-dimensional (2D) morphology provides a larger surface area and transmission channels for the rapid diffusion of reaction ions and photogenerated charge transfer.^{27,37} Moreover, the weak interlayer coupling endows ReS2 with layer-independent photoelectric characters.^{38,39} These advantages endow ReS₂ with considerable potential for enhancing photocatalytic performance.^{40,41} However, to our knowledge, previous studies mainly focus on ReS₂ alone or the optoelectronic property. The study of ReS2 based composites in photocatalytic applications is at the initial stage of development. In particular, the role of ReS₂ in the twin crystal chalcogenide photocatalyst remains unexplored.

Based on the information mentioned above, we constructed a photocatalyst with nano-twin crystal $Zn_xCd_{1-x}S$ solid solution and ReS₂ (ReS₂/T-ZCS) by using a two-step hydrothermal method. This catalyst has homojunctions within T-ZCS, and heterojunctions between T-ZCS and ReS₂ on the surface. The resulting ReS₂/T-ZCS presents an excellent photocatalytic hydrogen evolution rate of 112.10 mmol h⁻¹ g⁻¹ under visible light irradiation and apparent quantum efficiency of 32.65% at 420 nm, which is about 31 times higher than that of pure phase ZCS solid solution under the same conditions. The inner homo-junction of the twin crystal $Zn_xCd_{1-x}S$ solid solution and the heterojunction between $Zn_xCd_{1-x}S$ and loaded ReS₂ nanoflowers synergistically enhance the transfer and separation efficiency of photogenerated charge carriers.

Results and discussion

Preparation and structure analysis of the ReS₂/T-ZCS nanocomposite

The synthetic process of the ReS₂/T-ZCS hybrid photocatalyst is illustrated in Scheme 1 and the detailed procedures are described in the Experimental Section. Twin crystal ZCS was first prepared by a hydrothermal method according to our previous work.^{15,17} It should be noted that the introduction of NaOH plays an important role in forming the twin crystal phase by controlling the crystallization rate of zinc blende (ZB) and wurtzite (WZ).²⁰ Then, the prepared twin crystal ZCS was added to the solution of NH₄ReO₄, CH₄N₂S and HONH₃Cl with



magnetic stirring. After secondary hydrothermal treatment at 220 $^{\circ}$ C for 48 h, ReS₂/T-ZCS hybrid photocatalysts were obtained in which ReS₂ nanoflowers were loaded on the surface of the twined ZCS.

The crystal structure of the obtained samples was measured by X-ray diffraction (XRD) patterns. As shown in Fig. 1a, diffraction peaks at both $2\theta = 14.6^{\circ}$ and 32.8° for the ReS₂ sample are in accordance with the (002) and (020) planes of the triclinic phase of ReS2 (JCPDS No. 89-0341).42 P-ZCS without adding NaOH shows characteristics of cubic phase (JCPDS No. 05-0566).43,44 The diffraction peaks of the as-prepared twin crystal T-ZCS display a clear left-shift compared to standard cubic ZnS (JCPDS No. 05-0566) and right-shift compared to standard hexagonal CdS (JCPDS No. 41-1049), which is due to the formation of $Zn_{0.5}Cd_{0.5}S$ solid solution. Moreover, the sharp diffraction prominent peaks at 31.83° and 48.61° can be assigned to the diffraction of (111) and (220) crystal planes, respectively, which are in good accordance with the diffraction pattern of cubic phase Zn_{0.5}Cd_{0.5}S, and peaks at 2θ values of 25.15°, 27.41°, 28.66°, 45.52° and 54.02° can be indexed to the (100), (002), (101), (110) and (112), respectively, which match well with the hexagonal phase Zn_{0.5}Cd_{0.5}S.^{17,45} This diffraction pattern of the Zn0.5Cd0.5S nanocrystals suggests the presence of both hexagonal phase and cubic phase. All ReS2/T-ZCS samples with different amounts of ReS₂ exhibit diffraction peaks of twin crystal ZCS but without the appearance of diffraction peaks of ReS₂ (Fig. S1, ESI[†]), which should be related to the small particle size and relatively uniform dispersion of ReS₂ (see the TEM results).42,46

The composition of the prepared $\text{ReS}_2/\text{T-ZCS}$, pure phase P-ZCS, twin crystal T-ZCS and ReS_2 were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) experiments. As shown in Fig. 1b, the atomic ratio of Zn to



Fig. 1 (a) XRD patterns of pure phase P-ZCS, twin crystal T-ZCS, ReS_{2} , standard hexagonal CdS and cubic ZnS. (b) The composition of P-ZCS, T-ZCS, pure ReS_2 and $\text{ReS}_2/\text{T-ZCS}$ samples based on ICP-AES.

Cd in both the P-ZCS and T-ZCS samples is about 1:1, which agrees with the stoichiometric ratio of the $Zn_{0.5}Cd_{0.5}S$ solid solution. Pure ReS₂ sample exhibits the atomic ratio of Re to S with 1:2 and ReS₂/T-ZCS also keeps a similar atomic ratio of Zn to Cd with the $Zn_{0.5}Cd_{0.5}S$ solid solution. According to the practical atomic percentage of ReS₂ in the ReS₂/T-ZCS sample, the calculated weight percentage of ReS₂ is about 9.76%, which is very close to the stoichiometric weight percentage of ReS₂ in the 10% ReS₂/T-ZCS sample.

Morphological structure

The microstructures and morphologies of ReS_2 , pure phase P-ZCS, twin crystal T-ZCS and 10% $\text{ReS}_2/\text{T-ZCS}$ samples were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM image of the ReS_2 sample in Fig. 2a presents flower-like nanospheres with an average diameter of approximately 500 nm. TEM images in Fig. 2b and c show that the flower-like nanospheres are composed of uniformly dispersed ReS_2 nanosheets. The lattice fringes of 0.60 nm in Fig. 2d are assigned to the (002) planes of ReS_2 (JCPDS No. 89-0341), which is consistent with the results of XRD.

Meanwhile, SEM and TEM images show that the average diameters of twin crystal T-ZCS particles are 55 \pm 5.0 nm (Fig. 2e, f and Fig. S6, ESI[†]). The WZ/ZB boundaries of the twin crystal structure can be identified in the HRTEM image as shown in Fig. 2h. The lattice spacing of 0.330 nm belongs to the (111) diffraction plane of Zn_{0.5}Cd_{0.5}S and the corresponding fast Fourier transform (FFT) image further suggests the presence of twin crystal structure for ZCS.^{15,17} In comparison, pure phase P-ZCS exhibits only a set of lattices with a periodic spacing of 0.33 nm that are assigned to cubic Zn_{0.5}Cd_{0.5}S(111) lattice planes (Fig. S2, ESI[†]), without the appearance of the twin crystal boundary.

As for the ReS₂/ZCS sample, SEM and TEM images (Fig. 2i–k and Fig. S3b, ESI[†]) show that several ReS₂ nanoparticles were attached on the surface of bulk ZCS. The interfacial area between ZCS and ReS₂ was examined by HRTEM in Fig. 2m and Fig. S3c (ESI[†]), in which the lattice spacing of 0.61 nm and 0.330 nm corresponds to the (002) plane of ReS₂ and (111) crystal plane of ZCS nanoparticles, respectively. It is noted that



Fig. 2 SEM, TEM and HRTEM images of ReS₂ (a–d), twin crystal T-ZCS (e–h) and 10% ReS₂/T-ZCS (i–k and m).

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the size of ReS₂ nanoparticles that were loaded on the surface of twined ZCS is about 8-15 nm (Fig. 2m and Fig. S3c, ESI[†]), which is much smaller than that of pure ReS₂ flower-like particles (~ 500 nm). The SEM and TEM results display the intimate contact between ReS₂ and ZCS, which demonstrates the heterojunction formation by the hydrothermal method. The elemental mapping images and corresponding EDS spectrum (Fig. S4 and S5, ESI[†]) clearly present the existence and distribution of Zn, Cd, Re and S elements.

Surface areas and pore size distributions

The textural properties of the samples were elucidated by N₂ adsorption–desorption isotherms and the corresponding pore size distribution curves. As shown in Fig. S7 (ESI[†]), N₂ adsorption–desorption isotherms of P-ZCS, T-ZCS, and ReS₂/T-ZCS samples exhibit type IV characteristics with H3 hysteresis loops in the high pressure range. P-ZCS and T-ZCS show approximately equal specific surface area (11.96 m² g⁻¹ vs. 13.16 m² g⁻¹). When ReS₂ nanoparticles were loaded onto T-ZCS, the surface area increases and the maximum value reached 34.72 m² g⁻¹ for the 10% ReS₂/T-ZCS samples compared with P-ZCS and T-ZCS may be attributed to the coverage of flower-like ReS₂ nanoparticles, which could provide more active sites for photocatalytic reaction.

XPS analysis

X-ray photoelectron spectra (XPS) were measured to investigate the elemental composition and surface chemical states of P-ZCS, T-ZCS, ReS₂ and 10% ReS₂/T-ZCS samples. The binding energy is calibrated by taking the C 1s peak at 284.6 eV as a reference. Fig. S8 (ESI†) compares the high resolution XPS spectra of Cd 3d and Zn 2p of P-ZCS and T-ZCS samples, which split into Cd 3d_{5/2}, Cd 3d_{3/2}, Zn 2p_{3/2} and Zn 2p_{1/2} respectively due to spin orbit coupling.^{18,47} It is shown that both Cd 3d and Zn 2p peaks of the T-ZCS sample appear at lower binding energies than those of P-ZCS, indicating the increased electron density on the surface of T-ZCS and the surface Cd and Zn oxidation state of T-ZCS is lower than that of P-ZCS. This phenomenon demonstrates that the surface environment of twin crystal ZCS is more suitable for the reduction reaction.

In addition, twin crystal ZCS in Fig. 3 shows that binding energies of Cd 3d are found at 404.87 and 411.60 eV, Zn 2p at 1021.85 and 1044.87 eV, and S 2p signals at 161.22 and 162.35 eV, which can be attributed to Cd²⁺, Zn²⁺ and S²⁻ species according to the literature. $^{\rm 48-50}$ Pure $\rm ReS_2$ exhibits two peaks with binding energies of 44.55 eV and 42.11 eV, which were assigned to Re 4f_{7/2} and Re 4f_{5/2}, respectively.⁵¹ The binding energies of Cd 3d_{5/2} and Cd 3d_{3/2} in the ReS₂/T-ZCS sample shifted to 411.89 eV and 405.10 eV, which positively shifted by 0.29 and 0.23 eV, in comparison with twin crystal T-ZCS, respectively. Similarly, the XPS peaks of both Zn 2p_{3/2} and S 2p_{3/2} observed for the ReS₂/T-ZCS nanocomposite shifted to higher binding energies at 1021.99 eV and 162.76 eV, compared with those of twin crystal T-ZCS, respectively. Furthermore, the binding energies of Re $4f_{7/2}$ (43.90 eV) and Re $4f_{5/2}$ (41.46 eV) in the ReS₂/T-ZCS nanocomposite are negatively shifted in comparison



Fig. 3 High-resolution XPS spectra of (a) Cd 3d, (b) Zn 2p, (c) Re 4f and (d) S 2p of T-ZCS, ReS_2 and 10% ReS_2/T -ZCS samples.

with those in pure ReS₂. These positive energy shifts of Cd 3d, Zn 2p and S 2p imply the decreased electron density of ZCS in the ReS₂/T-ZCS sample, while the negative energy shift of Re 4f indicates increased electron density of ReS₂ in the ReS₂/T-ZCS sample. These results illustrate the presence of strong interactions at the interface between ReS₂ and twin crystal ZCS within the ReS₂/T-ZCS nanocomposite,^{43,52} which drives the photogenerated electron transfer from the conduction band (CB) of T-ZCS to the CB of the ReS₂ nanoparticles. All these binding energy shifts suggested that ReS₂ has been deposited on twin crystal ZCS to form a heterojunction rather than a simple physical mixture.

In addition, XPS spectra of the ReS₂/T-ZCS composite under light irradiation were carried out to directly monitor the change of surface chemical state. As shown in Fig. S9 (ESI[†]), in comparison with ReS₂/T-ZCS without light irradiation, the binding energies of Re $4f_{7/2}$ and $4f_{5/2}$ shifted to negative energy values of 43.51 eV and 41.06 eV, which indicates the enhanced density of an electron cloud under light irradiation. At the same time, the XPS peaks of both Zn 2p and Cd 3d for ReS₂/T-ZCS with light irradiation shifted to higher binding energies. It can be seen that the shifted direction of the Re 4f XPS peak is opposite to that of the Zn 2p and Cd 3d peaks under light irradiation. This result directly reflects that the photogenerated electrons transfer from T-ZCS to ReS₂, resulting in the accumulated electrons on the surface of ReS₂.

UV-vis DRS analysis and Mott-Schottky plots

UV-vis diffuse reflectance spectra (DRS) measurements were carried out to investigate the optical absorption properties of the as-prepared samples. As shown in Fig. 4a, twin crystal ZCS exhibits an absorption edge at approximately 520 nm, which is consistent with previously reported works.⁴⁵ The pristine ReS_2 shows a very broad and strong absorption across the entire visible region from 300 to 800 nm, indicating that it possesses strong light harvesting capability in both the UV and visible



Fig. 4 (a) UV-vis diffuse reflection spectra and (b) corresponding Tauc plots of P-ZCS, T-ZCS, ReS₂ and ReS₂/T-ZCS samples; (c) Mott–Schottky plots and (d) band structure diagrams of T-ZCS and ReS₂ samples.

regions.³⁴ All the ReS₂/T-ZCS composites manifested a similar absorption edge. In addition, compared with T-ZCS, the absorption intensities of the ReS₂/T-ZCS composites in the visible light region increased with increasing ReS₂ content, matching the color of the as-prepared samples changing from light yellow to dark grey (inset Fig. 4a).

The band gap of a single semiconductor was evaluated through the Tauc plot.43 As shown in Fig. 4b, based on the equation $\alpha h\nu = A(h\nu - E_{\alpha})^{n/2}$, where h, α , ν , E_{α} , and A are the Planck constant, absorption coefficient, light frequency, energy of band gap, and proportionality constant, respectively.^{34,53} The band gap is calculated to be 2.58 eV and 1.44 eV for pure ZCS and ReS2, respectively. Mott-Schottky plots were constructed to define the types of conductivity and band potential for semiconductors. The positive slopes in Fig. 4c indicate that both twin crystal ZCS and ReS₂ are n-type semiconductors.⁵⁴ The determined flat band potentials from the x-intercepts in the corresponding M-S plots for T-ZCS and ReS₂ are -0.642 and -0.303 V vs. Hg/HgCl₂ (saturated calomel electrode, SCE), respectively. The calculated flat-band potentials of T-ZCS and ReS_2 were estimated to be -0.401 V and -0.062 V vs. NHE, respectively (detailed calculation process in ESI[†]). It is known that the conduction band potential (E_{CB}) for n-type semiconductors is more negative by about -0.1 or -0.2 V than its flat band potential.^{12,55} Therefore, the $E_{\rm CB}$ values for T-ZCS and ReS₂ are roughly reckoned to be -0.501 V and -0.162 V vs. NHE. Using the formula $E_g = E_{VB} - E_{CB}$, the valence band (VB) potentials of T-ZCS and ReS2 were calculated to be 2.079 Vand 1.278 V, respectively. Therefore, type I heterojunctions are formed in the ReS₂/T-ZCS composites, and the detailed information of the band structure is displayed in Fig. 4d.

Photocatalytic activity and stability

The photocatalytic hydrogen evolution measurements were carried out in 100 mL aqueous solution with 0.35 M Na₂S and

0.25 M Na₂SO₃ as a hole sacrificial reagent under visible light $(\lambda > 420 \text{ nm})$ irradiation. No appreciable H₂ evolution is detected in the absence of either light irradiation or photocatalyst. Fig. S11 (ESI⁺) summarizes the H₂ evolution amount of pure phase P-ZCS, twin crystal T-ZCS and different ratios of ReS₂/T-ZCS nanocomposites within 3 h. The corresponding photocatalytic H₂ evolution rates of these samples are also shown in Fig. 5a. Pure phase P-ZCS displays extremely low activity for hydrogen evolution with the rate of 3.6 mmol $g^{-1} h^{-1}$. while the photocatalytic hydrogen evolution rate greatly increases to 30.29 mmol g^{-1} h⁻¹ when a twin crystal phase is formed. Combining theoretical calculation and spectrum characterization (detailed calculation process was shown in Fig. S10 of the ESI[†]), the band energy position of T-ZCS was determined to be -0.47 eV(CB) and +2.10 eV(VB) for the ZB phase, as well as -0.27 eV (CB) and +2.3 eV (VB) for WZ phase, respectively. The band structure alignment of twin T-ZCS satisfies the requirement of reducing H₂ evolution.⁵⁶ The electrostatic repulsion effect could not hinder the continuous transfer of electrons across the heterojunction according to the suppressed PL emission intensity (Fig. S19, ESI⁺). The formation of a heterojunction between the ZB and WZ phase in T-ZCS facilitates the electron transfer from ZB to CB of WZ and improves the charge separation efficiency. Moreover, loading ReS₂ nanoparticles on the surface of T-ZCS could further substantially improve the hydrogen evolution activity. It is noted that the H₂ evolution rate gradually increases as the ReS₂ content increased from 2% to 15%. However, a decreased H₂ evolution rate can be observed when the ReS₂ content in the ReS₂/T-ZCS composite was further increased to 10%. The optimal ReS2/T-ZCS composites exhibit the highest H₂-evolution rate of 112.10 mmol h^{-1} g⁻¹ without the use of any additional co-catalysts (such as noble metal, noble metal



Fig. 5 Photocatalytic H₂ evolution rate under visible light irradiation for 3 h over (a) pure phase P-ZCS, twin crystal T-ZCS and 10%ReS₂/T-ZCS catalysts and (b) ReS₂/T-ZCS with different ReS₂ contents. (c) Recycling experiments of the 10% ReS₂/ZCS sample and (d) wavelength dependence of the quantum hydrogen evolution efficiency for the ZCS and 10% ReS₂/ZCS sample.

complex), which is approximately 31 times higher than pure phase P-ZCS and 3.7 times higher than that of twin crystal T-ZCS.

For comparison, a physical mixture of ReS₂ (10 wt%) and T-ZCS (denoted as 10% ReS2/T-ZCS-Mix) was also investigated for photocatalytic H₂ evolution under the same conditions (see Fig. S12, ESI[†]). Obviously, the heterojunction 10% ReS₂/ZCS nanocomposite exhibited considerably enhanced H₂ evolution activity than the physical mixture 10% ReS₂/T-ZCS-Mix. This suggests that the strong interfacial interaction between the ReS₂ nanoflower structure and T-ZCS is extremely beneficial for the photogenerated charge transfer. Moreover, the apparent quantum yield (AQY) of 10% ReS2/T-ZCS under several monochromic lights was measured to be 32.65%, 27.72%, 5.7%, 4.1% and 3.7% at the wavelength of 420, 450, 520, 550 and 600 nm, respectively. It is observed that the wavelength-dependent hydrogen evolution efficiency was in good agreement with the light absorption capacity of T-ZCS, but not with that of the 10% ReS₂/T-ZCS composite (Fig. 5d), it can be deduced that the photogenerated electrons come from T-ZCS, and the 10% ReS₂ composite serves as a co-catalyst for trapping the electron to catalyze the evolution of H₂.⁵⁷ The photostability of the optimal 10% ReS₂/T-ZCS composite was evaluated through the photocatalytic H₂ evolution reaction in the presence of prolonged visible light irradiation of 12 h, and the H₂ evolution rate for every 3 h reaction was calculated (Fig. 5c). The result shows that the photocatalytic hydrogen evolution rate of the 10% ReS₂/ T-ZCS sample has no obvious change in four recycling experiments. The SEM and TEM images of the used ReS₂/ T-ZCS sample in Fig. S13 (ESI[†]) show that the morphology and size of the used ReS2/T-ZCS sample don't change obviously in comparison with the fresh ReS₂/T-ZCS sample, which maintains the morphology of T-ZCS loading ReS2 nanoparticles and the average size of 55 nm. The HRTEM image of the used ReS₂/T-ZCS sample exhibits a clear lattice spacing of the (002) plane of ReS_2 and (111) crystal plane of ZCS, which is consistent with the fresh sample. XRD and XPS characterizations show that the corresponding characteristic peaks are wellmaintained, and the peak position did not obviously shift (Fig. S14 and S15, ESI[†]). The absorption property of the recycled ReS₂/T-ZCS kept a similar absorption edge to the fresh sample (Fig. S16, ESI⁺). These characterization results indicate that ReS₂/T-ZCS composites are stable.

Transient photocurrent response, EIS and PL spectra

To investigate the separation-recombination efficiency of photogenerated charge of these ReS₂/T-ZCS composites, photo/electrochemical properties were characterized. As illustrated in Fig. 6a, photocurrent was measured in a 0.5 M Na₂SO₄ solution with an interval time of on-off switches at about 20 s. P-ZCS, T-ZCS and all of these ReS₂/T-ZCS composites exhibited reproducible photocurrent responses for each illumination period, and the photocurrent dropped rapidly in the dark during four on-off cycles of light irradiation. All of these ReS₂/T-ZCS composites exhibited stronger photoresponse and current density than that of P-ZCS and T-ZCS. P-ZCS shows weak photocurrent responses and the current density is only 1.0×10^{-6} A cm⁻² under visible light



Fig. 6 (a) Transient photocurrent response curves and (b) EIS Nyquist plots of P-ZCS, T-ZCS and ReS₂/T-ZCS samples. (c) Photoluminescence (PL) spectra and (d) decay curves of ZCS, T-ZCS and 10% ReS₂/T-ZCS samples excited at 375 nm.

irradiation, which is much lower than T-ZCS. The photocurrent responses further improve when ReS2 nanoflowers dispersed on the surface of T-ZCS. Among them, the 10% ReS₂/T-ZCS composite displayed the highest photocurrent responses under visible light irradiation. These results demonstrate that these $\text{ReS}_2/\text{T-ZCS}$ composites possess excellent charge separation efficiency in comparison with pure phase P-ZCS and T-ZCS. The interfacial charge transfer properties were measured via electrochemical impedance spectroscopy (EIS). The diameter of the semicircle in the Nuquist plot corresponds to the charge transfer resistance in the electrolyte solution.⁵⁸ As shown in Fig. 6b and Fig. S18 (ESI†), ReS₂/T-ZCS composites had a smaller semicircle and notably lower charge transfer resistance value than that for pure phase P-ZCS and twin crystal T-ZCS. This implies the faster electron transfer in the ReS₂/T-ZCS composites, which is consistent with the photocatalytic activity.

Photoluminescence (PL) experiments were further performed to study the behaviour of photoinduced charge carriers of the materials. Fig. 6c shows that pure phase P-ZCS exhibits a much stronger emission peak than twin crystal T-ZCS and the PL intensity of T-ZCS further quenches after introducing ReS2. The 10% ReS₂/T-ZCS composite shows the lowest emission peak among the ReS₂/T-ZCS samples. The absolute fluorescence quantum yield (inset of Fig. 6c and Table S2, ESI[†]) displays that 10% ReS₂/T-ZCS (0.44%) has a much smaller absolute fluorescence quantum yield than P-ZCS (6.70%) and T-ZCS (5.50%). The reduced PL intensity and smaller absolute fluorescence quantum yield indicate that the recombination of electrons and holes is effectively suppressed in the ReS2/T-ZCS nanocomposites.59 Apart from the emission spectra, time-resolved fluorescence (TRPL) decay curves were also measured and fitted as shown in Fig. 6d and Table S2 (ESI[†]). P-ZCS, T-ZCS and all ReS₂/ZCS composites present two radiative lifetimes with different percentages. Theoretically, the short lifetime (τ_1) component



Scheme 2 Diagram of the photocatalytic mechanism for the flower-like ReS_2/ZCS systems.

is ascribed to a surface-related nonradiative recombination process (the trapping of electrons to defects), and the long lifetime (τ_2) component is attributed to the recombination of free excitons in the semiconductor.60 Compared with pure phase P-ZCS, twin crystal T-ZCS exhibits a quick decay process, in which both τ_1 and τ_2 are much smaller than P-ZCS. This demonstrates that the formation of twin crystals in the ZCS solid solution could effectively suppress the radiative charge recombination. Furthermore, the introduction of ReS₂ nanoparticles accelerates fluorescence quenching, which is supported by the shorter average radiative lifetime (τ_{ave}) of 10% ReS₂/T-ZCS in comparison with that of P-ZCS, T-ZCS and other ReS₂/T-ZCS samples. This is because the radiative charge recombination had been suppressed and should be related to the effective trapping of photogenerated electrons by ReS2 and more efficient electron injection from twin crystal ZCS to ReS₂.

Photocatalytic mechanism

Based on the aforementioned experimental results, the possible mechanism of photocatalytic reaction over twin crystal $Zn_xCd_{1-x}S$ solid solution supported ReS₂ nanoflowers under visible light excitation is depicted in Scheme 2. At the interface between the ZB and WZ segment in the twin crystal Zn_{0.5}Cd_{0.5}S solid solution, the CB and VB energy levels of the ZB segment upshifted a bit with respect to those of the WZ segment. Photogenerated electrons could transfer from the ZB segment to the WZ segment and the transport direction of photogenerated holes is the opposite (Scheme 2). This is the first spatial separation process in twin crystal Zn_{0.5}Cd_{0.5}S solid solution.^{15,20} At the same time, the CB potential of twined ZCS (-0.501 V vs. NHE) is more negative than that of ReS_2 (-0.162 V vs. NHE) and the VB potential of twined ZCS (+2.079 V vs. NHE) is more positive than that of ReS₂ (+1.278 V vs. NHE), which indicates the formation of a type-I heterojunction between ReS2 and T-ZCS. Photogenerated electrons from twined ZCS are extracted by the ReS₂ nanoflowers, where the reduction of H⁺ takes place. Holes also transferred to the VB of ReS_2 and react with the surrounding S^{2-} and SO_3^{2-} . The reaction equations of Na2S and Na2SO3 can be represented as follows (eqn (1)-(4))

$$SO_3^{2-} + H_2O + 2h^+(VB) \rightarrow SO_4^{2-} + 2H^+$$
 (1)

$$2S^{2-} + 2h^{+}(VB) \rightarrow S_{2}^{2-}$$
(2)

$$S_2^{2^-} + SO_3^{2^-} \to S_2O_3^{2^-} + S^{2^-}$$
 (3)

$$SO_3^{2-} + S^{2-} + 2h^+(VB) \rightarrow S_2O_3^{2-}$$
 (4)

The presence of a sacrificial reagent could effectively alleviate the serious photo-corrosion during the reaction process (see XPS spectra of the used $\text{ReS}_2/\text{T-ZCS}$ in Fig. S15, ESI†) and corresponding photoinduced electrons have priority for the reduction reaction to form H₂. The second charge separation is achieved. Benefitting from the homojunctions with a type-II staggered band alignment in twin crystal $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (T-ZCS) and heterojunctions between T-ZCS and ReS₂, photogenerated electrons and holes achieve continuous transfer and spatial separation in the ReS₂/T-ZCS composite. As a result, the ReS₂/ T-ZCS composite exhibits highly efficient hydrogen evolution activity with a rate 31 times larger than that of P-ZCS.

Conclusions

A hybrid photocatalyst composed of twin crystal Zn_{0.5}Cd_{0.5}S and flower-like ReS2 was successfully prepared via a two-step hydrothermal method. The formation of the twin crystal structure and the introduction of nanoflower ReS2 remarkably promoted the hydrogen evolution rate of the $Zn_xCd_{1-x}S$ solid solution. The photocatalytic hydrogen evolution rate of the optimal 10% ReS₂/ T-ZCS nanocomposite is about 31 times and 3.37 times higher than that of pure phase P-ZCS and twinned T-ZCS, respectively. The corresponding apparent quantum efficiency is 32.65% under light irradiation at 420 nm. Moreover, the 10% ReS2/T-ZCS photocatalyst displayed outstanding stability in recycling experiments. The excellent photocatalytic performance benefits from the synergistic effect of phase junctions in the twin crystal structure and heterojunctions between T-ZCS and the uniformly dispersed flower-like ReS2 on the ZCS surface, which acts as the electron pool and provides active sites for photocatalytic reactions. This study exhibits that the flower-like ReS2 could act as a promising co-catalyst and improve the photocatalytic activity of ZCS significantly. Using flower-like ReS2 as a co-catalyst to form a heterojunction should be a promising approach to design efficient photocatalysts for solar hydrogen production.

Conflicts of interest

There are no conflicts to declare.

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