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# Construction of strongly coupled 2D–2D $SnS_2$/CdS S-scheme heterostructures for photocatalytic hydrogen evolution†

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The fabrication of neoteric photocatalysts with high-efficiency charge separation for the solar-driven hydrogen evolution reaction (HER) remains a challenge. The construction of strongly coupled two-dimensional (2D)–2D heterostructures facilitates charge spatial migration due to the regulation of the interlayer forces and electronic structures. In this work, we demonstrate novel 2D–2D $SnS_2$/CdS heterostructures by loading $SnS_2$ nanosheets ($SnS_2$ NSs) onto CdS nanosheets (CdS NSs). The $SnS_2$/CdS heterostructures possess close face-to-face contact and strongly coupled interactions to improve the charge transfer kinetics, and the loading of $SnS_2$ can enhance light absorption and suppress the photocorrosion of CdS. The optimized S-scheme $SnS_2$/CdS heterostructures exhibit excellent photocatalytic hydrogen evolution activity in lactic acid sacrificial solution under visible light ($\lambda \geq 420$ nm), affording the highest hydrogen evolution rate on $SnS_2$/CdS heterostructures with 35 wt% $SnS_2$ (5.18 mmol $g^{-1}$ $h^{-1}$), which is approximately 6-fold higher than that of pure CdS NSs (0.87 mmol $g^{-1}$ $h^{-1}$). In addition, a highest apparent quantum efficiency (AQE) of 59.3% was obtained at 420 nm. When methanol was used as the sacrificial agent, the hydrogen production rate reached 3.27 mmol $g^{-1}$ $h^{-1}$ and methanol was oxidatively reformed into methoxymethanol ($CH_3OCH_2OH$). This work provides a feasible method for designing strongly coupled 2D–2D heterostructure photocatalysts for energy storage and conversion applications.

## 1. Introduction

Due to over-reliance on traditional fossil fuels, there are great concerns regarding environmental pollution and energy shortage.[1] Solar-fuel conversion is one of the best ways to achieve of energy supply revolution and sustainable development.[2] Photocatalytic water splitting powered by solar energy is one of the technologies with the greatest potential to alleviate the above problems by producing green hydrogen energy.[3] Therefore, more attention has been focused on the intensive exploration of photocatalysts with reactive sites and excellent durability for elevating the conversion efficiency of solar-to-hydrogen energy.[4,5]

Among the hydrogen-evolving semiconductors, cadmium sulfide (CdS) is a prominent photocatalyst with a suitable band gap (~2.4 eV) for utilizing visible light and an appropriate conduction band position for reducing protons to hydrogen.[6] However, pure bulk CdS has a series of inherent shortcomings including photocorrosion and inevitable annihilation of photogenerated electron–hole pairs.[7] As a result, it has always been challenging to design outstanding CdS-based photocatalysts with prominent stability for the hydrogen evolution reaction (HER) in water splitting. Compared to bulk CdS, two-dimensional (2D) CdS NSs possess a large specific surface area and more active sites, which are not only conducive to the rapid migration of photogenerated carriers from the bulk phase to the surface but are also beneficial for constructing 2D–2D layered heterostructures with face-to-face contact and plentiful interfacial contact.[8–10] Among the CdS-based heterostructure materials, considerable research efforts have been devoted to designing CdS-based S-scheme photocatalytic systems, such as CdS/$WO_3$,[11] CdS/$TiO_2$,[12] CdS/$CuWO_4$,[13] g-$C_3N_4$/CdS,[14] CdS/$BiVO_4$,[15] CdS/ZnO,[16] FeOOH/CdS,[17] and CdO/CdS,[18] since S-scheme heterostructures have a unique charge transfer path that can suppress the photocorrosion and retain the high reducibility of the photogenerated electrons.[19] Moreover, integration with other conductive materials to construct S-scheme heterostructures is beneficial for improving the photocatalytic hydrogen evolution performance.[20] Thus, the exploration of 2D CdS-based S-scheme photocatalysts with well-defined structures and remarkable activity is of paramount significance. Inspired

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by this, we set out to find another suitable 2D material to fabricate CdS-based heterojunction photocatalysts through a strong electronic coupling effect.[21,22]

Recently, tin disulfide ($SnS_2$) with a narrow band gap energy of 2.2–2.4 eV and promising visible-light response was identified as a conspicuous n-type semiconductor for the photocatalytic reaction.[23,24] Vacancy defect engineering was utilized to design dually modified $MoS_2/SnS_2$ S-scheme heterojunction photocatalysts for the photo-reduction of Cr(VI) and the photodegradation of organic dyes.[25] 2D $SnS_2/TiO_2$ heterostructures with exposed high-energy (001) and low-energy (101) facets were constructed for the enhanced photocatalytic reduction of $CO_2$ into $CH_4$.[26] 2D thin hexagonal $SnS_2$ nanosheets were fabricated on 2D g-$C_3N_4$ nanosheets by simple ultrasonic and calcination methods to generate $SnS_2$/g-$C_3N_4$ heterostructures with tight interface matching between facets and excellent charge separation efficiency, which is beneficial for U(VI) removal under actual sunlight irradiation.[27] So far, there have been few reports about 2D–2D $SnS_2$/CdS heterostructures in the field of the sunlight-driven HER through water splitting. Moreover, according to the literature, it is feasible to construct an S-scheme heterostructure between $SnS_2$ and CdS, since the conduction band and valence band of $SnS_2$ nanosheets match well with those of CdS nanosheets.[28,29]

Guided by the above strategies, herein, we report the construction of a 2D–2D strongly coupled $SnS_2$/CdS heterostructure photocatalyst for enhanced hydrogen evolution in solar-driven water splitting. This unique face-to-face contact effectively promotes charge transfer, and the loading of $SnS_2$ NSs can improve the visible-light absorption and suppress the photocorrosion of the CdS NSs. As a result, the highest hydrogen evolution rate of 5.18 mmol $g^{-1}$ $h^{-1}$ was obtained with lactic acid as the sacrificial agent under visible-light irradiation, with the highest apparent quantum efficiency (AQE) of 59.3% at 420 nm. Furthermore, when methanol was used as the sacrificial agent, the hydrogen production rate was 3.27 mmol $g^{-1}$ $h^{-1}$, where methanol can be transformed into $CH_3OCH_2$-OH. This research may provide an innovative strategy for the design of $SnS_2$ and CdS based photocatalysts with enhanced water-splitting performance under visible-light irradiation.

## 2. Experimental section

### 2.1 Synthesis of CdS nanosheets

CdS nanosheets (CdS NSs) were synthesized through a hydrothermal method.[30] Specifically, 0.8 g of $Cd(Ac)_2 \cdot 2H_2O$ and 0.87 g of $NH_2CSNH_2$ were dispersed in 30 mL of ethylenediamine under magnetic stirring and then the solution was transferred to a 50 mL Teflon-lined autoclave and maintained at 100 °C for 12 h. After cooling naturally to room temperature, the yellow powder was centrifuged and washed with distilled water, and then dried in air at 60 °C.

### 2.2 Synthesis of 2D–2D $SnS_2$/CdS heterostructures

Different amounts of $SnCl_4 \cdot 5H_2O$ and 1.051 g of citric acid monohydrate were added to 40 mL $H_2O$ under magnetic stirring for 30 min. Next, 0.1 g of the as-prepared CdS NSs and 0.6 g dicyandiamide were added to the above solution under magnetic stirring for 30 min. The solution was transferred to a 100 mL Teflon-lined autoclave and maintained at 180 °C for 12 h. The loading amount of $SnS_2$ nanosheets ($SnS_2$ NSs) was adjusted by changing the amounts of $SnCl_4 \cdot 5H_2O$ added, and these different $SnS_2$/CdS heterostructures were denoted as $SnS_2$/CdS-$x$ ($x = 5, 15, 25, 35, 45$, corresponding to the loadings of 5%, 15%, 25%, 35%, 45% in weight of the $SnS_2$ NSs). For the synthesis of pure $SnS_2$ NSs, the above steps can be performed again without adding pure CdS NSs.

### 2.3 Characterization

A JEM-2100F instrument with 200 kV of accelerating voltage was used to obtain transmission electron microscopy (TEM) images. Powder X-ray diffraction (XRD) data were obtained on a D2 PHASER (AXS) X-ray diffractometer with a Cu Kα radiation source (45.0 kV, 50.0 mA). Raman spectra were collected using a micro-Raman spectroscopy system (Renishaw inVia). The $N_2$ adsorption–desorption isotherms gained from QUADRASORB SI-KR/MP and the surface area of the materials were estimated by Brunner–Emmet–Teller (BET) measurements. X-ray photoelectron spectroscopy (XPS) data was tested by a PHI-5400 ESCA system using an Al Kα radiation source. The standard photoelectron peak of the C 1s at 284.8 eV was used as a reference value to calibrate the binding energy. The Hitachi UH4150 spectrometer was employed to collect the UV-vis absorption spectra. Photoluminescence (PL) spectra were recorded on a PerkinElmer LS 55 spectrometer at an excitation wavelength of 365 nm. The temperature changes and distributions under light illumination were tested by a thermal infrared imager (Fotric 225s, China). The NMR spectra were collected using a Bruker 600 MHz.

### 2.4 Mott–Schottky measurement

To further investigate the process of photocatalytic hydrogen evolution, Mott–Schottky tests were used to calculate and compare the densities of charge carriers ($N_d$).[31] The carrier density was calculated using eqn (1):

$$N_d = \frac{2/e_0\varepsilon\varepsilon_0}{d(1/C^2)/dV} \quad (1)$$

where $e_0$ is the electron charge, $\varepsilon$ is the dielectric constant of the semiconductor, $\varepsilon_0$ is the permittivity of the vacuum, $C$ is the capacitance, and $V$ is the applied bias at the electrode.

### 2.5 Photocatalytic hydrogen production test

Photocatalytic hydrogen production was tested at room temperature in a vacuum-closed gas circulation system (Labsolar 6A, PerfectLight, Beijing, Fig. S1†). Typically, 50 mg of the as-prepared catalyst was dispersed in 100 mL of an aqueous solution containing 10 mL of lactic acid. Before irradiation, the reaction system was vacuum pumped for 30 min, and the yield of hydrogen was detected by gas chromatography (FULI GC9790 II) using Ar as carrier gas. A xenon lamp source of 300 W (PLS-

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SXE300, PerfectLight, Beijing, Fig. S1†) with a cutoff 420 nm filter was fixed 10 cm above the liquid level, and other bandpass filters (365, 420, 550, 700 nm) were used to measure the AQE.[32] The AQE was calculated using eqn (2):

$$\mathrm{AQE} = \frac{2 \times \text{the number of evolved } H_2 \text{ molecules}}{\text{the number of incident photons}} \times 100\% \quad (2)$$

### 2.6 Photoelectrochemical test

The photoelectrochemical measurements were carried out with a standard three-electrode cell on a CHI 660D (CH Instruments, Inc.) electrochemical workstation, with Ag/AgCl as the reference electrode, platinum foil as the counter electrode, and the as-prepared photocatalysts dropped on a fluorine-doped tin oxide (FTO) glass substrate with an effective area of $2 \times 1$ cm$^2$ as the working electrode. The rotating disk electrode was always kept open during the photochemical test. Here, 0.1 M $Na_2SO_4$ was purged with $N_2$ and used as the electrolyte. Visible light (cutoff 420 nm, PLS-SXE300, PerfectLight, Beijing) was used as the light irradiation source.

### 2.7 Computational methods

All density functional theory (DFT) calculations were performed on the Vienna *Ab initio* Simulation Package (VASP) by using the PBE exchange-correlation function. The interaction between valence electrons and the ionic core was described by the PAW pseudo-potential. Geometry optimization was conducted with a cutoff energy of 400 eV. We considered the GGA+U approach and the van der Waals forces were considered using the DFT-D3 method. The three layers of atoms on the surface were allowed to relax until the magnitude of all residual forces was less than 0.02 eV. Ionic relaxations were carried out under conventional energy ($10^{-5}$ eV). The Monkhorst–Pack *k*-point mesh of $3 \times 3 \times 1$ was used to calculate the geometry optimization.

## 3. Results and discussion

The strongly coupled 2D–2D $SnS_2$/CdS heterostructures with enhanced photocatalytic hydrogen evolution performance were fabricated *via* a hydrothermal method (Fig. 1a). The optical images of pure CdS NSs, $SnS_2$/CdS heterostructures, and pure $SnS_2$ NSs are shown in Fig. S2,† where the color changed from light yellow to orange. The prepared CdS nanoflowers were composed of ultrathin CdS NSs (Fig. 1b) and the 2D–2D $SnS_2$/CdS heterostructures were constituted by $SnS_2$ NSs inserted into the lacuna of CdS NSs assemblies to form the face-to-face strong contact (Fig. 1c). As shown in Fig. 1d, the CdS NSs mainly exposed (002) crystal planes with a spacing of 0.332 nm, and the mainly exposed crystal face of $SnS_2$ NSs was the (100) plane with a spacing of 0.313 nm.[33] Furthermore, the selected area electron diffraction (SAED) pattern (Fig. 1e) verified that $SnS_2$ NSs were strongly coupled on the surface of CdS NSs, and suggested that CdS and $SnS_2$ NSs exposed their (002) and (100) crystal faces, respectively. Moreover, the elemental mappings (Fig. 1f–i) exhibited that the Cd, Sn, and S elements were uniformly

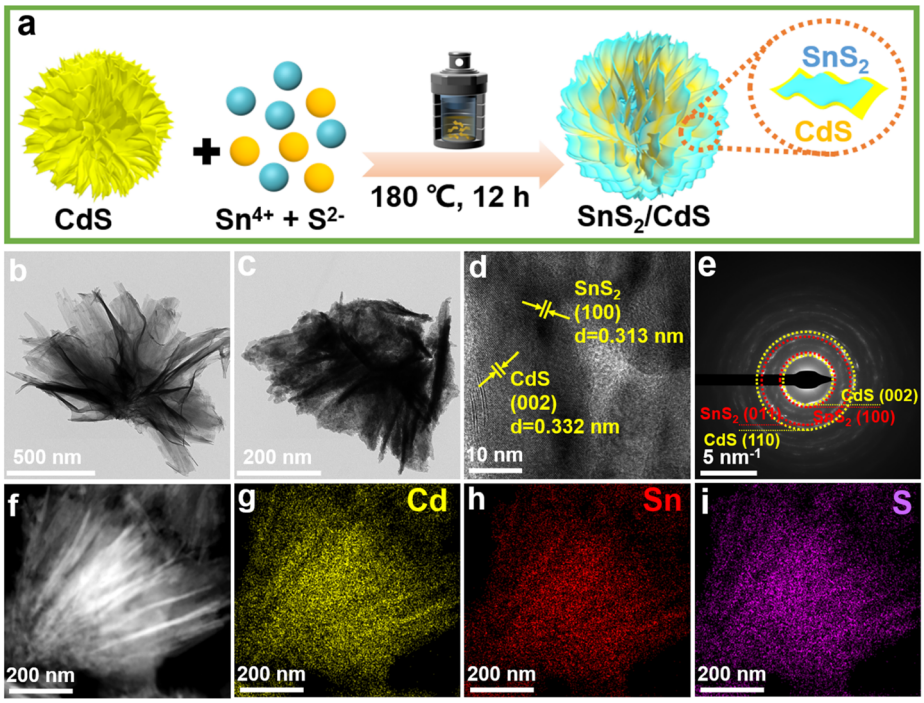


Fig. 1 (a) Schematic representation of the preparation process of 2D–2D $SnS_2$/CdS heterostructures. (b and c) TEM images of CdS NSs and 2D–2D $SnS_2$/CdS heterostructures. (d) HRTEM images, (e) SAED pattern, and (f–i) the corresponding EDX mapping images of 2D–2D $SnS_2$/CdS heterostructures.

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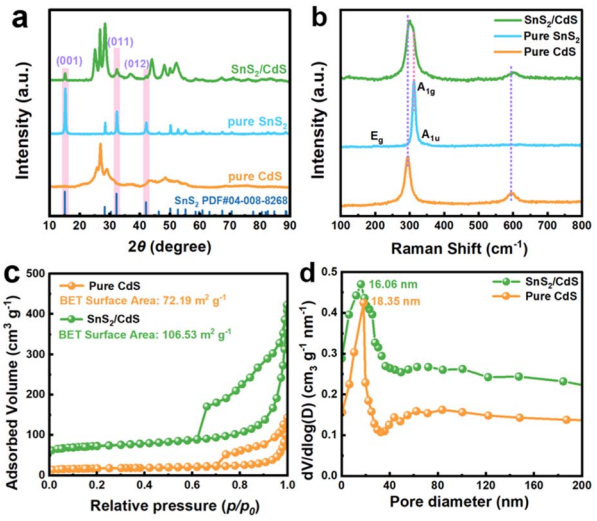


Fig. 2 (a) XRD patterns, (b) Raman spectra, (c) nitrogen sorption–desorption isotherms and (d) the corresponding pore size distribution plots of the pure CdS and 2D–2D $SnS_2$/CdS heterostructures.

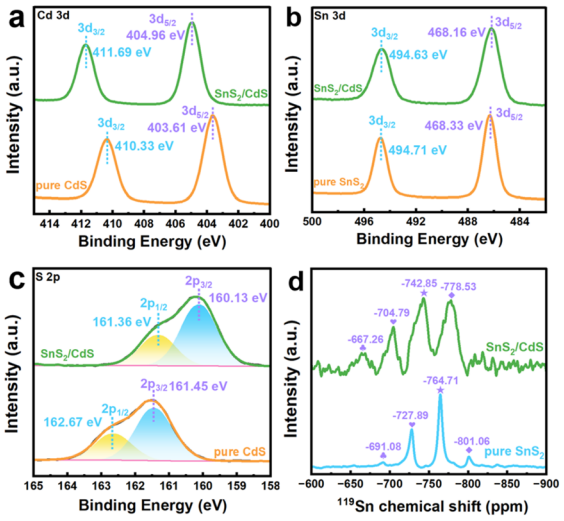


Fig. 3 (a) Cd 3d XPS peaks, (b) Sn 3d XPS peaks, (c) S 2p XPS peaks of the pure CdS NSs and 2D–2D $SnS_2$/CdS heterostructures, and (d) $^{119}$Sn MAS NMR spectra of pure $SnS_2$ and $SnS_2$/CdS heterostructures.

distributed. For pure $SnS_2$, the nanosheets tended to manifest into hexagonal structures (Fig. S3†).

X-ray diffraction (XRD) patterns of pure CdS, $SnS_2$/CdS heterostructures, and pure $SnS_2$ are shown in Fig. 2a. For pure CdS NSs, the diffraction peaks can be indexed to the hexagonal CdS phase (PDF# 01-070-2553).[34] Compared with pure CdS and $SnS_2$ NSs, the diffraction peaks of $SnS_2$/CdS heterostructures at 15.13, 28.45, and 42.22° are ascribed to the (001), (011), and (012) crystal faces of $SnS_2$ (PDF# 04-008-8268).[35] From Raman spectra (Fig. 2b), the characteristic peaks of $SnS_2$/CdS heterostructures were slightly blue-shifted compared with those of pure CdS NSs, which is powerful evidence for the formation of strongly coupled contact between $SnS_2$ and CdS. For pure $SnS_2$ NSs, the out-of-plane $A_{1g}$ mode at ~314 cm$^{-1}$ is the most prominent, while the peaks of $E_g$ and $A_{1u}$ modes are extremely weak.[36] Notably, the Raman band of $SnS_2$/CdS heterostructures around 300 cm$^{-1}$ became broadened, which proved the existence of $SnS_2$ NSs. The $N_2$ sorption–desorption isotherms are typical type-IV isotherms. The Brunauer–Emmett–Teller (BET) surface areas of CdS NSs, $SnS_2$/CdS heterostructures, and $SnS_2$ NSs are 72.19, 106.53, and 132.18 m$^2$ g$^{-1}$, and the Barrett–Joyner–Halenda (BJH) pore sizes (Fig. 2d and S4†) of the three are 16.06, 18.35, and 23.62 nm, respectively. This morphology change of $SnS_2$/CdS heterostructures is helpful to provide more active sites for photocatalysis.[37,38]

X-ray photoelectron spectroscopy (XPS) measurements were performed to study the elemental compositions and chemical environments of the samples. Compared with pure CdS NSs, there were characteristic peaks of the Sn element in the $SnS_2$/CdS heterostructures from the full-spectrum scan (Fig. S5 and S6†), which implies the loading of $SnS_2$ NSs on the CdS NSs. In detail, the Cd 3d peaks of $SnS_2$/CdS heterostructures (Fig. 3a) shifted from 410.33 and 403.61 eV to 411.69 and 404.96 eV as compared to pure CdS NSs, indicating that the electron density of CdS NSs decreased with the decoration of the $SnS_2$ NSs.[39] Analogously, the Sn 3d peaks of $SnS_2$/CdS heterostructures (Fig. 3b) shift from 494.71 and 468.33 eV to 494.63 and 468.16 eV, which imply a strong interaction between $SnS_2$ and CdS.[40] Moreover, as exhibited in Fig. 3c, the peaks at 161.36 and 160.13 eV affiliated with S 2p1/2 and S 2p3/2 of $SnS_2$/CdS heterostructures moved to lower binding energies as compared with pure CdS NSs, further substantiating the formation of heterostructures.[41]

The solid-state $^{119}$Sn NMR tests were also carried out to reveal the chemical structure of $SnS_2$/CdS heterostructures (Fig. 3d). The characteristics of the main line indicate that the Sn atoms in pure $SnS_2$ and $SnS_2$/CdS heterostructures have different atomic environments at the NMR scale, that is, a slight disorder exists in $SnS_2$/CdS heterostructures. Pure $SnS_2$ NSs exhibited four characteristic peaks at −691.08, −727.89, −764.71, and −801.06 ppm, corresponding to the Sn(IV)–S bonds.[42,43] The four peaks clearly show the presence of the four distinct Sn sites in the materials. For $SnS_2$/CdS heterostructures, the Sn(IV) peaks were slightly shifted to up-field with lower chemical shifts, suggesting that the electron density around the Sn atom increased. It is worth noting that the intensities of the peaks at −667.26 ppm and −778.53 ppm in the $SnS_2$/CdS heterostructures were significantly stronger than those in pure $SnS_2$, indicating that there was strong interfacial interaction between CdS and $SnS_2$, resulting in increased Sn(IV) content.[44–47] In addition, in the $SnS_2$/CdS heterostructures, the peak width of the four characteristic peaks was significantly wider than those of pure $SnS_2$, which is because the Sn sites act as the connecting anchors at the interface between CdS and $SnS_2$. The above results reveal that there is strong coupling between $SnS_2$ and CdS.

The light-harvesting performances (Fig. 4a and S7a†) of pure CdS NSs and $SnS_2$/CdS heterostructures were tested by UV-vis absorption spectroscopy. The $SnS_2$/CdS heterostructures showed enhanced light absorption from 700 to 800 nm as

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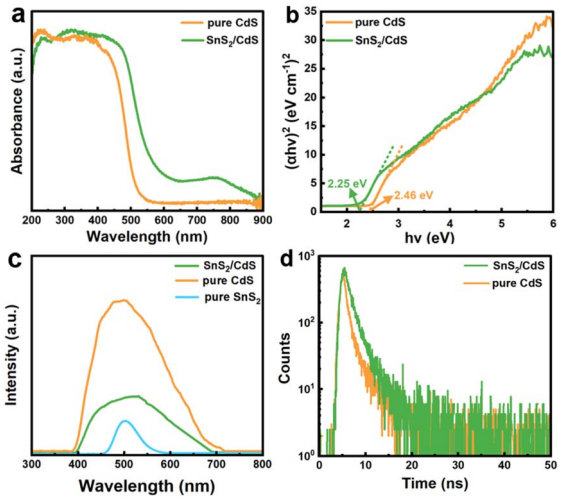


Fig. 4 (a) UV-vis absorption spectra, (b) optical band gaps, (c) photoluminescence spectra, and (d) time-resolved transient photoluminescence decay spectra of the pure CdS NSs and 2D–2D $SnS_2$/CdS heterostructures.

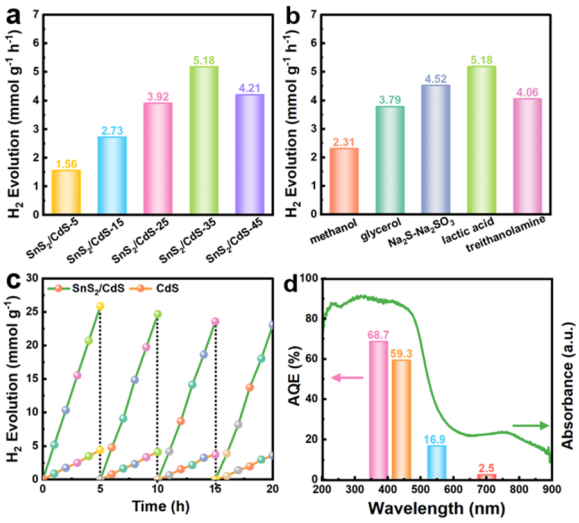


Fig. 5 (a) $H_2$ evolution rates of $SnS_2$/CdS heterostructures with different amounts of $SnS_2$ NSs; (b) a comparison of photocatalytic hydrogen production activities with different sacrificial agents; (c) cycling tests of photocatalytic $H_2$ evolution under visible light ($\lambda \geq 420$ nm); (d) UV-vis light absorption and the corresponding wavelength-dependent AQE of $SnS_2$/CdS heterostructures.

compared with pure CdS NSs. The optical bandgaps of pure CdS NSs and $SnS_2$/CdS heterostructures were calculated from linear transformations of absorption curves (Fig. 4b). Since the pure $SnS_2$ NSs possess a narrow band gap (Fig. S7b†), the band gap of $SnS_2$/CdS heterostructures decreased to 2.25 eV, lower than that of pure CdS NSs (2.46 eV), which may substantially enhance the utilization of solar energy and elevate the photocatalytic activity.[48,49] Photoluminescence spectroscopy (PL) was carried out to study the separation ability of photogenerated electron–hole pairs (Fig. 4c). The PL intensities of $SnS_2$/CdS heterostructures were lower as compared to pure CdS NSs because pure $SnS_2$ NSs have very low PL intensity, suggesting that $SnS_2$/CdS heterostructures have a higher carrier separation efficiency.[50] Furthermore, to study the migration dynamics of the carriers, the time-resolved transient photoluminescence (TRPL) decay spectra (Fig. 4d and S8†) were employed. Table S1† records the relevant data, where $\tau$ is the lifetime and $A$ is the corresponding magnitude. Accordingly, the pure $SnS_2$ NSs have the longest positron lifetime (27.94 ns), and the positron lifetime of $SnS_2$/CdS heterostructures (2.12 ns) is longer than that of pure CdS NSs (1.80 ns), verifying that the introduction of $SnS_2$ NSs can elevate the separation efficiency of photogenerated carriers and prolong the lifetime of electrons.[51]

The photocatalytic hydrogen evolution performances were firstly measured in deionized (DI) water with lactic acid as a scavenger under visible-light irradiation ($\lambda \geq 420$ nm). Benefiting from the tight face-to-face contact between $SnS_2$ NSs and CdS NSs, the $SnS_2$/CdS heterostructures with a strong electronic coupling effect showed outstanding photocatalytic performance. The hydrogen evolution rate of $SnS_2$/CdS heterostructures with different loading amounts of $SnS_2$ showed a volcano shape (Fig. 5a). With 35 wt% $SnS_2$ NSs loaded, the hydrogen production rate of $SnS_2$/CdS heterostructures can reach up to 5.18 mmol $g^{-1}$ $h^{-1}$, which is approximately 5.95-fold that of pure CdS NSs (0.87 mmol $g^{-1}$ $h^{-1}$). Moreover, the $SnS_2$/CdS heterostructures exhibited remarkable photocatalytic HER performance with different sacrificial agents (Fig. 5b), fully certifying that constructing strongly coupled contacts can provide more active sites and improve the separation efficiency of photogenerated electrons and holes. Particularly, the $SnS_2$/CdS heterostructures can maintain photocatalytic stability after 20 hours of cycling tests (Fig. 5c), indicating that loading $SnS_2$ NSs can also favor the suppression of the photocorrosion of CdS. XRD and XPS analyses (Fig. S9†) were carried out on the $SnS_2$/CdS heterostructures after 20 hours of cycling tests, and there was no change in the valence state of $SnS_2$/CdS heterostructures. Fig. 5d shows the wavelength-dependent AQE of the 35 wt% $SnS_2$/CdS heterostructures irradiated at different wavelengths (365, 420, 550, and 700 nm), suggesting that the photocatalytic hydrogen evolution is driven by absorption and photoexcitation. Notably, the highest apparent quantum efficiency (AQE) of $SnS_2$/CdS heterostructures was 59.3% at 420 nm, which is higher than that of most CdS-based photocatalysts (Table S2†). Based on the above results, the 35 wt% $SnS_2$/CdS heterostructure not only possessed remarkable photocatalytic performance under ultraviolet light ($AQE_{365\ nm}$ = 68.7%), but also exhibited promising activity under visible light irradiation ($AQE_{420\ nm}$ = 59.3%), proving that loading $SnS_2$ NSs can promote the light absorption capacity of CdS.

The oxidative reforming of methanol is also an important chemical reaction. Here, when methanol is used as the sacrificial agent, both $H_2$ and carbon-containing products can be obtained. Fig. 6a shows the hydrogen production rate of $SnS_2$/CdS heterostructures with methanol as the sacrificial agent, and the hydrogen production rate can reach 3.27 mmol $g^{-1}$ $h^{-1}$. Moreover, the catalytic activity can remain stable after 20 hours of cycling tests. NMR analysis was used to investigate the types

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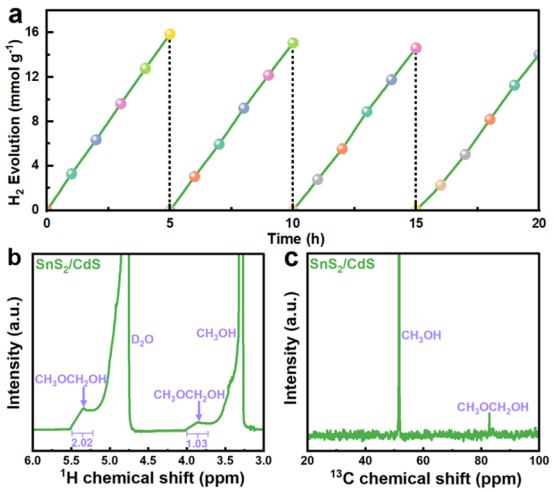


Fig. 6 (a) $H_2$ evolution rates of $SnS_2$/CdS heterostructures with methanol as the sacrificial agent. (b) $^1$H NMR and (c) $^{13}$C NMR spectra of the products of photocatalytic reaction with methanol as the sacrificial agent.

of carbon-containing products when methanol was used as a sacrificial agent. From the $^1$H NMR spectrum (Fig. 6b), there are two characteristic peaks at 3.85 and 5.85 ppm corresponding to $CH_3OCH_2OH$.[52] Similarly, the peak at 82.8 ppm can also be attributed to $CH_3OCH_2OH$ in the $^{13}$C NMR spectrum (Fig. 6c). Therefore, methanol was oxidized to $CH_3OCH_2OH$ along with the photocatalytic hydrogen evolution reaction.

The photoelectrochemical properties can reflect more information about photogenerated carriers. The electrochemical impedance spectroscopy (EIS) Nyquist plots are exhibited in Fig. 7a. The arc radii of $SnS_2$/CdS heterostructures are smaller than those of pure CdS with and without light irradiation, demonstrating that $SnS_2$/CdS heterostructures

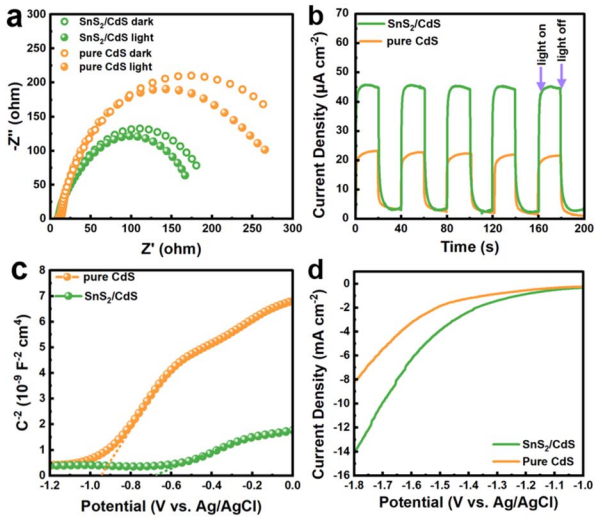


Fig. 7 (a) EIS Nyquist plots, (b) chronoamperometry curves, (c) Mott–Schottky plots, and (d) linear sweep voltammogram curves of pure CdS and $SnS_2$/CdS heterostructures.

possess smaller interfacial resistance for charge separation.[53] The chronoamperometric curves at an applied constant voltage of 0.6 V in 0.1 M $Na_2SO_4$ solution under light and dark conditions are displayed in Fig. 7b. In detail, the photocurrent density of $SnS_2$/CdS heterostructures under visible light (~45 μA cm$^{-2}$) is twice that of pure CdS, demonstrating that constructing strongly coupled face-to-face contact is conducive to charge separation and migration.[54] Note that the chronoamperometric responses of both $SnS_2$/CdS heterostructures and pure CdS maintained stability for several cycles. The carrier density of these photocatalysts can be reflected in the slope of the Mott–Schottky (M–S) curves in Fig. 7c. The $SnS_2$/CdS heterostructures displayed a smaller slope than that of pure CdS, implying that the $SnS_2$/CdS heterostructures possessed higher carrier density and the establishment of 2D–2D strong coupled contact can favour the transfer of carriers.[55] From the linear sweep voltammogram (LSV) curves (Fig. 7d), the $SnS_2$/CdS heterostructures have a smaller overpotential for the hydrogen evolution reaction compared with pure CdS and $SnS_2$ (Fig. S10†), suggesting that loading $SnS_2$ NSs can improve the proton reduction ability.[56]

According to the XPS of pure CdS and pure $SnS_2$, their valence band (VB) positions can be extracted (Fig. S11a and b†). Combining with the optical band gaps, their conduction band (CB) positions can be calculated. Two possible electron transfer mechanisms of $SnS_2$/CdS heterostructures are shown in Fig. 8a and b. To drive the photocatalytic water splitting reaction, the reduction potential of the bottom of the conduction band must be more negative than that of hydrogen ion to hydrogen (−0.414 V *vs.* NHE at pH = 7). If the $SnS_2$/CdS heterostructures conform to the type-II electron transfer mechanism, the hydrogen evolution reaction will occur on the $SnS_2$ conduction band. The conduction band potential of $SnS_2$ is more positive than the reduction potential of $H^+/H_2$, and the hydrogen evolution reaction cannot occur on the conduction band of $SnS_2$, so the $SnS_2$/CdS heterostructures do not conform to the type-II electron transfer mechanism. In terms of the work function calculated by DFT (Fig. 9a–c), the electron is always transferred from the high Fermi level to the low Fermi level, until the Fermi levels of the two are in equilibrium. From Fig. 8c, the conduction band position of CdS is higher than that of $SnS_2$, so it can be considered that the electrons at the interface should be transferred from the CdS to $SnS_2$ until the Fermi levels of the two phases reach equilibrium at the interface. This kind of electron transfer will lead to a decrease in electron density at the interface of CdS and an increase in electron density at the interface of $SnS_2$, resulting in the potential difference between the two phases and the formation of the built-in electric field at the interface (the direction of the electric field is from CdS to $SnS_2$).[57] Moreover, the VB of CdS bends upward and the CB of $SnS_2$ bends downward. Under visible light irradiation, the built-in electric field can induce electron transfer from the $SnS_2$ conduction band to the CdS valence band. Therefore, the S-scheme heterostructures between CdS and $SnS_2$ were established. The band bending can weaken the energy barrier, which is beneficial for enhancing the proton reduction ability of the CB of the CdS for the photocatalytic hydrogen evolution reaction. Simultaneously, the holes were

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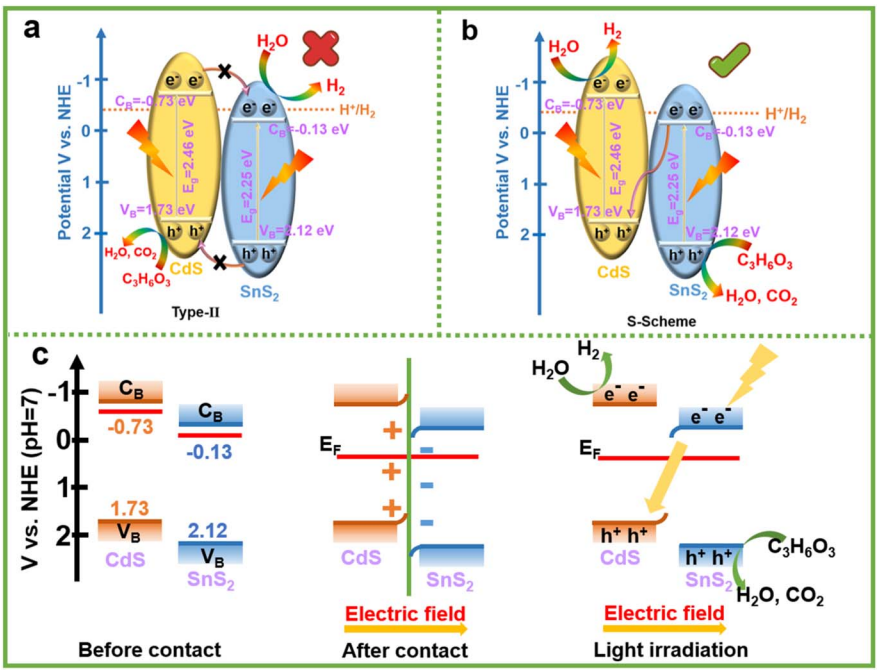


Fig. 8 (a) Type-II and (b and c) S-scheme illustration of the possible charge transfer processes in the $SnS_2$/CdS heterostructures.

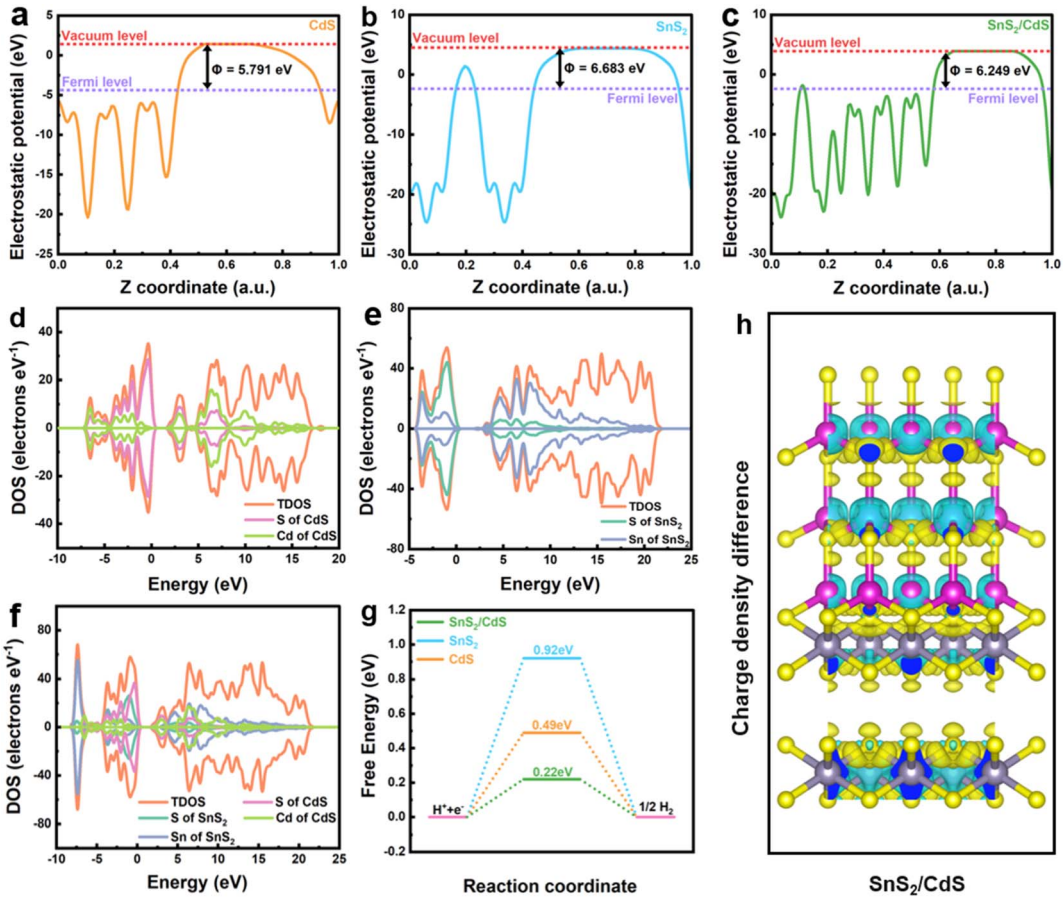


Fig. 9 (a–c) Work function and (d–f) density of state plots, (g) hydrogen adsorption free energy diagram of CdS (002), $SnS_2$ (100), and $SnS_2$/CdS heterostructures interface, and (h) charge density difference diagram for $SnS_2$/CdS heterostructures.

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consumed by reacting with the sacrificial agent in the valence band of $SnS_2$, which helps inhibit the photocorrosion phenomenon of CdS. Therefore, the charge transfer mechanism of the S-scheme heterostructure endowed the $SnS_2$/CdS with a higher reducing capacity for the photocatalytic hydrogen evolution.

To deeply analyse the transfer direction of electrons in the $SnS_2$/CdS heterostructures, the work function ($\Phi_{DFT}$), density state of density (DOS), hydrogen adsorption free energy ($\Delta G_{H*}$) and differential charge density of CdS, $SnS_2$, $SnS_2$/CdS heterostructures were calculated by density functional theory (DFT) (Fig. 9). The work function of the CdS (002), $SnS_2$ (100), and $SnS_2$/CdS models (Fig. S12†) was calculated by the first-principles simulation using the equation $\Phi_{DFT} = E_{vac} - E_F$.[58] According to the crystal models, the work functions of CdS (002), $SnS_2$ (100), and the $SnS_2$/CdS interface were calculated to be 5.791, 6.683, and 6.249 eV, respectively. This is consistent with the distribution of the conduction and valence band potentials of CdS and $SnS_2$ measured by experiments, which once again proved that $SnS_2$/CdS heterostructures conform to the S-scheme electron transfer mechanism. From the DOS calculation results of $SnS_2$/CdS heterostructures, it can be seen that the density of states near the Fermi level is mainly composed of the Cd element in CdS. Meanwhile, CdS is more involved in the photocatalytic hydrogen evolution reaction, and the S element in CdS is the main catalytically active site.[59,60] On comparing the PDOS of the $SnS_2$/CdS heterostructures and pure CdS, the density of states below the Fermi level (valence band) of the S element of CdS in the $SnS_2$/CdS heterostructures was significantly higher than that of the S element in pure CdS, indicating that CdS gained electrons from $SnS_2$. Similarly, compared with the density of Sn states in $SnS_2$ of $SnS_2$/CdS heterostructures and pure $SnS_2$, the density of Sn states above the Fermi level (conduction band) of Sn elements in $SnS_2$ of the $SnS_2$/CdS heterostructures is lower than that of Sn elements in pure $SnS_2$, which proves that the empty orbital composition of $SnS_2$ increases and electrons are transferred outward to CdS. Based on the above results, the electrons in the $SnS_2$/CdS heterostructures are transferred from the conduction band of $SnS_2$ to the valence band of CdS under the action of the built-in electric field. To evaluate the activity of photocatalysts, the hydrogen adsorption free energy ($\Delta G_{H*}$) as an important index was calculated.[61] The closer the $\Delta G_{H*}$ value is to zero, the easier for H* to be adsorbed on the surface of the catalyst, which is beneficial for $H_2$ evolution. The $\Delta G_{H*}$ value of the $SnS_2$/CdS heterostructures is closer to zero as compared with those of pure CdS and $SnS_2$, suggesting that constructing 2D–2D strongly coupled heterostructures is a feasible method for improving the hydrogen evolution performance of photocatalysts. In addition, according to the charge density difference diagram (Fig. 9h and S13†) and charge density diagram (Fig. S14†) of CdS (002), $SnS_2$ (100), and $SnS_2$/CdS heterostructures,[62] the S element in CdS at the interface of $SnS_2$/CdS gain the most electrons, which further indicates that the S site in CdS is the main active site of the hydrogen evolution reaction.

# 4. Conclusions

In summary, strongly coupled 2D–2D $SnS_2$/CdS S-scheme heterostructures were constructed by a hydrothermal method. The $SnS_2$ NSs were uniformly inserted into the lacunas of CdS NSs to form tight face-to-face contact. Benefiting from the abundant active sites and high-efficiency charge separation, the obtained $SnS_2$/CdS S-scheme heterostructures exhibited excellent photocatalytic performance and remarkable stability. Moreover, the large contact area and strongly coupled interplay elevated the charge kinetics. With lactic acid as the sacrificial agent, the highest hydrogen evolution rate of $SnS_2$/CdS heterostructures was 5.18 mmol $g^{-1}$ $h^{-1}$, and the corresponding AQE was 59.3% at 420 nm. When the sacrificial agent was changed from lactic acid to methanol, a hydrogen production rate of 3.27 mmol $g^{-1}$ $h^{-1}$ was obtained, and the methanol was oxidized to $CH_3OCH_2OH$. Combining the detailed analyses of XPS valences and optical band gaps, the carrier transfer mechanism of the S-scheme heterostructure is well explained. This work offers an effective strategy for constructing strongly coupled 2D–2D S-scheme heterostructures to accelerate charge transfer for solar-driven reactions.

# Conflicts of interest

There are no conflicts to declare.

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