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Construction of CoS₂/Zn_{0.5}Cd_{0.5}S S-scheme heterojunction for enhancing H₂ evolution activity under visible light

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Abstract

In the field of photocatalysis, building a heterojunction is an effective way to promote electron transfer and enhance the reducibility of electrons. Herein, the S-scheme heterojunction photocatalyst ($CoS_2/Zn_{0.5}Cd_{0.5}S$) of CoS_2 nanospheres modified $Zn_{0.5}Cd_{0.5}S$ solid solution was synthesized and studied. The H₂ evolution rate of composite catalyst reached 25.15 mmol·g⁻¹·h⁻¹, which was 3.26 times that of single $Zn_{0.5}Cd_{0.5}S$, while pure CoS_2 showed almost no hydrogen production activity. Moreover, $CoS_2/Zn_{0.5}Cd_{0.5}S$ had excellent stability, and the hydrogen production rate after six cycles of experiments only dropped by 6.19%. In addition, photoluminescence spectroscopy and photoelectrochemical experiments had effectively proved that the photogenerated carrier transfer rate of $CoS_2/Zn_{0.5}Cd_{0.5}S$ was better than CoS_2 or $Zn_{0.5}Cd_{0.5}S$ single catalyst. In this study, the synthesized CoS_2 and $Zn_{0.5}Cd_{0.5}S$ were both n-type semiconductors. After close contact, they followed an S-scheme heterojunction electron transfer mechanism, which not only promoted the separation of their respective holes and electrons, but also retained a stronger reduction potential, thus promoting the reduction of H⁺ protons in photocatalytic experiments. In short, this work provided a new basis for the construction of S-scheme heterojunction in addition to being used for photocatalytic hydrogen production.

Keywords: Photocatalysis; CoS2; Zn0.5Cd0.5S; S-scheme heterojunction

Introduction

Hydrogen energy is a storable clean energy and an energy carrier with extremely low environmental pollution.^[1,2] Studies have found that the use of solar energy to convert water into hydrogen is the most promising technology for obtaining hydrogen energy.^[3,4] Therefore, the construction of visible light-induced semiconductor catalysts is of great significance for improving global environmental degradation and energy shortages.^[5,6] In recent years, many excellent semiconductors have been widely used in the field of photocatalytic H₂ evolution,^[7-10] such as metal oxides, phosphides, metal sulfides, etc. However, the poor stability of semiconductor catalysts, the low utilization of sunlight, and the easy recombination of electrons after being excited by light, which are still problems that need to be solved urgently in this field.^[11-13]

So far, Pt-based catalyst is a catalyst material with strong hydrogen evolution reaction (HER) activity, but its scarcity and high price limit its development in the field of hydrogen production.^[14,15] Therefore, researchers have been working to find low-cost materials with high photocatalytic activity to replace precious metal catalysts. Surprisingly, in recent years, transition metal compounds (for example, $WS_{2,}^{[10]} MoS_{2,}^{[16]} Ni_2P_{i}^{[17]}$ etc.) have been frequently reported due to their excellent H₂ evolution activity in photocatalytic reactions. Among them, cobalt pyrite (CoS₂) has metal-like conductivity and exhibits excellent HER activity. Because of the abundant content of Co element on the earth, CoS₂ is expected to become a low-cost hydrogen evolution catalyst to replace precious metals.^[18,19] However, reports on CoS₂ are more inclined to electrocatalytic hydrogen production, and the research on photocatalytic hydrogen production is not prominent.

As we all know, CdS is one of the representative catalysts for photocatalytic H_2 production reaction,^[20] but the holes generated after CdS are excited by light will oxidize S⁻² in CdS, that is, CdS has a serious photo-corrosion phenomenon, which leads to poor stability in HER.^[21] Based on CdS, the solid solution (Zn_xCd_{1-x}S) of ZnS and CdS formed by doping Zn atoms is widely used for photocatalytic hydrogen production.^[22] Although Zn_xCd_{1-x}S has the stability of ZnS and a band structure similar to CdS, there are still some non-negligible shortcomings, such as the serious agglomeration phenomenon and low carrier separation efficiency of Zn_xCd_{1-x}S.^[23] In order to

improve photocatalytic activity, $Zn_xCd_{1-x}S$ and other semiconductors (for example, NiCo₂S₄,^[22] α -Ni(OH)₂,^[24] CoFe₂O₄,^[25] and MoS₂,^[26]) can be used to construct heterojunction.

Based on the above discussion, a new $CoS_2/Zn_{0.5}Cd_{0.5}S$ composite was prepared in this paper and used for hydrogen evolution reaction with 10 vol% lactic acid solution as sacrifice agent. Experiments showed that $CoS_2/Zn_{0.5}Cd_{0.5}S$ had very excellent HER activity, and its H₂ evolution rate reached 25.15 mmol·g⁻¹·h⁻¹, which was much higher than other materials containing $Zn_xCd_{1-x}S$. This was not only attributable to the successful coupling of CoS_2 and $Zn_{0.5}Cd_{0.5}S$ to improve the serious agglomeration of $Zn_{0.5}Cd_{0.5}S$, but also to the close contact between CoS_2 and $Zn_{0.5}Cd_{0.5}S$, formed an S-scheme heterojunction. The heterojunction retained a strong hydrogen reduction potential. The study of $CoS_2/Zn_{0.5}Cd_{0.5}S$ photocatalyst will provide a new strategy for the use of CoS_2 in the field of hydrogen production and the construction of S-scheme heterojunction.

Experimental section

Materials

NaOH (sodium hydroxide, 96.0%), Cd(Ac)₂·2H₂O (cadmium acetate dihydrate, 99.0%), Zn(Ac)₂·2H₂O (Zinc acetate dihydrate, 99.0%), Na₂S₂O₃·5H₂O (sodium thiosulfate, 99.5%), C₂H₅NS (thioacetamide, 99.0%), Co(NO₃)₂·6H₂O [Cobalt nitrate hexahydrate, 99.9%], absolute ethanol (AE, 99.7%) and L-lactic acid (85%).

Synthesis of CoS₂

Added Na₂S₂O₃·5H₂O and Co(NO₃)₂·6H₂O with a molar ratio of 2:1 into the beaker, as well as 30 mL of AE and 40 mL of deionized water (DW). Then the mixed solution was continuously stirred for 1 h. After the solution was uniformly mixed, it was transferred to a 100 mL polytetrafluoroethylene (PTFE) reactor and maintained at 180°C for 12 h. Finally, it was washed several times with DW and AE, and then the prepared CoS₂ was dried for 8 h at 60 °C.

Synthesis of Zn_{0.5}Cd_{0.5}S

Weighed 12.5 mmol C₂H₅NS, 5 mmol Cd(Ac)₂·2H₂O and 5 mmol Zn(Ac)₂·2H₂O, added them to a beaker containing 75 mL DW, stirred for 1 h, added 0.8 g NaOH during stirring, and then transferred to a PTFE reactor of 100 mL, heated for 24 h at 180 °C. After cooling, the products were washed and dried as before. The synthesis method of other $Zn_xCd_{1-x}S$ pure substances was

the same as above, only the molar ratio of $Zn(Ac)_2 \cdot 2H_2O$ and $Cd(Ac)_2 \cdot 2H_2O$ was changed. The quality of the required drugs was shown in Table S1 (Supporting Information).

Synthesis of CoS₂/Zn_{0.5}Cd_{0.5}S (CZCS-y, y=1,2,3,4,5)

Taking CZCS-3 as an example, added 40 mg of CoS₂ powder to a beaker containing 30 mL of AE and 0.1 g of Zn_{0.5}Cd_{0.5}S. After ultrasonic treatment for 20 min, it was heated and stirred in a water bath at 80 °C until it became viscous, then dried in a thermostat for 12 h at 60°C, and finally ground to obtain CZCS-3 powder. Scheme 1 was a preparation process of CZCS-3 composite catalyst. The same method was used to prepare a composite catalyst with a mass ratio of $Zn_xCd_{1-x}S$ (x=0.3, 0.4, 0.6, 0.7) and CoS_2 of 1:0.4. The required mass and catalyst abbreviation were shown in Table S2 and Table S3 (Supporting Information).



Scheme 1: Preparation process of CZCS-3 composite catalyst.

Characterization

Characterization methods and instruments were recorded in detail in the Supporting Information.

Photocatalytic hydrogen production experiments

Added 12 mg of photocatalyst powder and 30 mL of 10 vol% L-lactic acid aqueous solution into a 65 mL quartz bottle equipped with a sealing rubber sheet, and then ultrasonicated for 5 min and stirred for 15 min. Filled the flat-bottomed quartz bottle with N₂, kept it for 15 min. Then put the flat-bottomed quartz reactor into a multichannel photocatalytic reaction system, and conducted a hydrogen evolution experiment for 5 h under simulated visible light (5W LED lamp, $\lambda \ge 420$ nm), and the amount of hydrogen precipitated was detected by a gas chromatograph (SP-2100, 13X column, TCD, N₂ carrier). In addition, the apparent quantum efficiency (AQE) of the CZCS-3 sample was studied. The hydrogen production data required for the CZCS-3 at different wavelengths was measured by using a 300 W Xe lamp as the light source and matching

monochromatic light cut-off filters of different wavelengths. The photon flux of the incident light at different wavelengths was detected by the strong light optical power meter (CEL-NP2000). Formula (1) was the calculation formula of AQE.^[27]

$$AQE(\%) = \frac{2 \times the \ number \ of \ evolved \ hydrogen \ molecules}{the \ number \ of \ incident \ photon} \times 100\%$$
(1)

Electrochemical measurement

In this part, an electrochemical workstation (VersaSTA4-400) was used to measure photoelectrochemical characteristics such as linear sweep voltammetry (LSV) and photocurrent response (I-T) curve. The electrodes and electrolyte solutions used were detailed in the Supporting Information. The photocurrent response curve test also required a 300 W Xe lamp ($\lambda \ge 420$ nm) to provide the light source.

Results and discussion

The phase structure of the prepared samples were identified and confirmed by X-ray diffractometer (XRD). It could be found from the XRD pattern of Figure 1a that compared with the standard cards of cubic phase CdS (PDF#65-2887) and cubic phase ZnS (PDF#65-1691), the position of the diffraction peak of $Zn_{0.5}Cd_{0.5}S$ was continuously shifted to a certain extent. The characteristic peaks corresponded to the (311), (220), (200) and (111) crystal planes of the $Zn_{0.5}Cd_{0.5}S$ sample were between the main diffraction peaks of cubic CdS and ZnS.^[28] That was, the diffraction peak of Zn_{0.5}Cd_{0.5}S shifted to a small-angle compared to ZnS as a whole, and shifted to a large-angle compared to CdS as a whole. This could be explained as the synthesis of $Zn_{0.5}Cd_{0.5}S$ solid solution instead of simple mixture of CdS and ZnS, this was consistent with previous reports.^[21,29] Comparing the XRD patterns of CZCS-3 and Zn_{0.5}Cd_{0.5}S, it could be seen that CZCS-3 contained the characteristic peak of Zn_{0.5}Cd_{0.5}S without change, indicating that the lattice structure of Zn_{0.5}Cd_{0.5}S did not change after coupling with CoS₂. In Figure 1b, the characteristic peaks of the CoS_2 sample corresponded well to the diffraction peaks of the CoS_2 standard card (PDF#89-1492), indicating that a single CoS2 catalyst had also been successfully synthesized. And the characteristic peaks of the CZCS-3 sample at 32.3°, 36.2°, 39.7°, 54.9° and 60.2° corresponded to CoS2.^[30] Except for the diffraction peaks of CoS2 and Zn0.5Cd0.5S, the CZCS-3 sample did not contain other impurity peaks, indicating that the synthesized composite sample had high purity. (Deposition Number(s) 1646235 (for CoS₂), 1605240 (for CdS), 1666388

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(for ZnS) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.)



Figure 1. XRD pattern: (a) Comparison between $Zn_{0.5}Cd_{0.5}S$ and CZCS-3, (b) comparison between CoS_2 and CZCS-3.

The morphology of the catalyst is an important characterization for studying the catalytic performance of the sample, and it is also a side verification of the successful synthesis of the catalyst. Figures 2a-c were the scanning electron microscope (SEM) images of Zn_{0.5}Cd_{0.5}S, CoS₂ and CZCS-3 samples respectively. It could be seen that $Zn_{0.5}Cd_{0.5}S$ exhibited uneven smaller particles and had serious agglomeration. The particle size distribution diagram of Zn0.5Cd0.5S (Figure S1, Supporting Information) was obtained from Figure 2a by SEM particle size analysis method. It could be seen that most of the particles of $Zn_{0.5}Cd_{0.5}S$ were distributed in 45-75 nm, mainly concentrated in 45 nm, and the average particle size was 59.9 nm. However, CoS₂ was a stacked structure of spheres with uneven sizes of about 0.2-2 µm. As could be seen from the SEM of CZCS-3 (Figure 2c), a large number of Zn_{0.5}Cd_{0.5}S particles uniformly loaded on the surface of CoS₂, which not only retained the spherical accumulation structure of CoS₂, but also broke the agglomeration state of $Zn_{0.5}Cd_{0.5}S$ particles. This structure can provide more active sites to promote the photocatalytic H₂ production capacity under visible light. Figure 2d was a transmission electron microscope (TEM) image of the CZCS-3 sample. The irregular spherical shape with a light-colored outline was CoS_2 . It could be seen more clearly that a large amount of Zn_{0.5}Cd_{0.5}S was covered on the surface of CoS₂, and the size was basically the same as estimated in SEM. The high-resolution TEM (HRTEM) of the CZCS-3 sample was magnified (Figure 2e), and the clear lattice fringes with different orientations could be seen. The measured interplanar

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spacing d of 0.247 nm and 0.324 nm corresponded to the (210) facet of CoS_2 and the (111) facet of $Zn_{0.5}Cd_{0.5}S$, respectively.^[31,32] Figures 2f-g were the energy dispersive X-ray (EDX) spectrum and element mapping of the CZCS-3 sample. It could be seen that CZCS-3 was composed of Cd, Zn, Co, and S elements, and the distribution of each element was relatively uniform.



Figure 2. SEM images of (a) Zn_{0.5}Cd_{0.5}S, (b) CoS₂ and (c) CZCS-3. (d) TEM, (e) HR-TEM, and (f) EDX energy spectrum of CZCS-3. (g-k) EDS mapping images of Cd, Zn, Co and S in CZCS-3.

In order to further study the valence states of the elements contained in the CZCS-3 composite catalyst, CZCS-3 was scanned by X-ray photoelectron spectroscopy (XPS). Figure 3a was the full spectrum of the CZCS-3 sample, Cd, Co, S and Zn elements were all detected, which were consistent with the previous EDX spectrum and element mapping results. In Figure 3b, the characteristic peak of Zn $2p_{3/2}$ was located at 1022.1 eV, and the characteristic peak of Zn $2p_{1/2}$ was founded at 1045.1 eV. For Cd 3d (Figure 3c), similar to Zn 2p, two characteristic peaks belonged to Cd $3d_{3/2}$ (411.8 eV) and Cd $3d_{5/2}$ (405.1 eV) could be observed. This showed that both Zn and Cd elements in CZCS-3 existed in the +2 valence state.^[33,34] From the XPS spectrum of S 2p (Figure 3d), it could be seen that the two peaks at the binding energy of 162.8 eV and 161.6 eV corresponded to S $2p_{1/2}$ and S $2p_{3/2}$, respectively, indicated the presence of S²⁻ in CZCS-3.^[24] Figure 3e showed the peak area of Co 2p. The two peaks at 781.9 eV and 798.1 eV corresponded to Co $2p_{3/2}$ and Co $2p_{1/2}$ (the two peaks at 803.5 eV and 786.5 eV were satellite peaks), this was

consistent with our previous report.^[30] Figure S2 (Supporting Information) was the comparison of the XPS spectra of CoS₂, Zn_{0.5}Cd_{0.5}S and CZCS-3. It was worth noting that compared with pure Zn_{0.5}Cd_{0.5}S, the binding energy of Zn 2p in CZCS-3 showed a slight positive shift in the absence of light illumination. This phenomenon was further confirmed in the XPS spectra of Cd 3d and S 2p, which means that Zn_{0.5}Cd_{0.5}S would lose electrons after being in close contact with CoS₂.^[35] Compared with CoS₂, the XPS spectra of Co 2p and S 2p in CZCS-3 both shifted to the direction of lower binding energy. The obvious shift of the fine spectrum of each element indicated that there was a strong interaction between Zn_{0.5}Cd_{0.5}S and CoS₂, forming an effective heterojunction structure.^[22] These results also indicated that before CZCS-3 was illuminated, electrons transferred from Zn_{0.5}Cd_{0.5}S to CoS₂, resulting in an internal electric field at the interface of the two materials.^[36] Except for the shift of the fine spectrum of the element, the peak shape of each fine spectrum had almost no change, which indicated that the construction of the heterojunction had no effect on the chemical valence of the element.



Figure 3. XPS spectra: (a) Full spectrum of CZCS-3; (b) Zn 2p; (c) Cd 3d; (d) S 2p; (e) Co 2p.

Ultraviolet visible diffuse reflectance spectroscopy (UV-Vis DRS) can be used to study the photoresponse performance of the photocatalyst. As shown in Figure 4a, the CoS_2 sample showed strong light absorption between 250-800 nm, while $Zn_{0.5}Cd_{0.5}S$ had an inherent light absorption edge around 500 nm. Compared with $Zn_{0.5}Cd_{0.5}S$, the CZCS-3 sample had an upward tail absorption phenomenon in the region > 500 nm, which could indicate that a mixed interface structure was formed between $Zn_{0.5}Cd_{0.5}S$ and CoS_2 .^[37] It could also be explained that, compared

with a single sample of $Zn_{0.5}Cd_{0.5}S$, the addition of CoS_2 improved the light response performance of CZCS-3 in the 500-800 nm region. Figures 4b-d were the sample band gap (E_g) value determined according to Tauc formula: $\alpha hv = A(hv - E_g)^{n}$.^[22] The E_g values of CoS₂, Zn_{0.5}Cd_{0.5}S and CZCS-3 were 2.47 eV, 2.35 eV and 1.87 eV, respectively, and the E_g values of the two pure substances were consistent with previous reports.^[31,33] Among them, the E_g value of CZCS-3 was the smallest, indicating that in the CZCS-3 sample, the mixed interface structure formed between Zn_{0.5}Cd_{0.5}S and CoS₂ made CZCS-3 easier to be excited by light to generate electrons, which was beneficial to the photocatalytic H₂ evolution reaction.



Figure 4. (a) UV-vis DRS of CoS₂, Zn_{0.5}Cd_{0.5}S and CZCS-3; Band gap plots for (b) CoS₂, (c) Zn_{0.5}Cd_{0.5}S, and (d) CZCS-3.

Figure 5a was the N₂ adsorption-desorption isotherm (77K) of CoS₂, Zn_{0.5}Cd_{0.5}S and CZCS-3. It could be seen that these catalysts were all type IV curves with H3 type hysteresis loop, it had obvious mesoporous characteristics. And from the pore diameter distribution of the three catalysts in Figure 5b and the average pore size in Table 1, the pore diameter of the sample was distributed between 0-50 nm. According to the definition of IUPAC, the pore size structure in this range was divided into micropores and mesopores.^[38] In Table 1, the S_{BET} (specific surface area) of CoS₂, Zn_{0.5}Cd_{0.5}S and CZCS-3 were 18.57, 7.78 and 14.14 m²·g⁻¹, respectively. The S_{BET} of CZCS-3 was between the two simple substances, the density difference between Zn_{0.5}Cd_{0.5}S and CoS₂ and their

 S_{BET} per unit mass were the main reasons for the S_{BET} change of the final composite material.^[39] It further showed that there was a mixed interface structure between $Zn_{0.5}Cd_{0.5}S$ and CoS_2 , and the good synergy could help improve the performance of photocatalytic H₂ evolution reaction.



Figure 5. (a) N_2 adsorption-desorption curves of CoS_2 , $Zn_{0.5}Cd_{0.5}S$ and CZCS-3 and (b) pore size distribution curves.

Catalyst	$S_{BET}(m^2 \cdot g^{-1})$	Pore volume(cm ³ ·g ⁻¹)	Average pore size (nm)
Zn _{0.5} Cd _{0.5} S	18.57	0.18	35.60
CoS_2	7.78	0.02	13.03
CZCS-3	14.14	0.08	23.93

Table 1. The physical arameters of CoS₂, Zn_{0.5}Cd_{0.5}S and CZCS-3.

In order to prove the superiority of the $CoS_2/Zn_{0.5}Cd_{0.5}S$ photocatalyst, under the condition of L-lactic acid solution (10 vol%) as the sacrificial agent, the H₂ evolution rate of the prepared photocatalyst was measured and compared. It could be found from Figures 6a-b and Figure S3a (Supporting Information) that pure CoS₂ basically did not exhibit hydrogen evolution activity in lactic acid solution, and the H₂ evolution amount was negligible. The H₂ evolution amount of a single Zn_{0.5}Cd_{0.5}S in the fifth hour was 463.51 µmol. However, among the composite catalysts, CZCS-3 had the highest hydrogen production, reaching 1508.91 µmol (the hydrogen production rate had reached 25.15 mmol·g⁻¹·h⁻¹), which was about 3.26 times the H₂ evolution of pure Zn_{0.5}Cd_{0.5}S. On the one hand, it showed that after the addition of CoS₂, the CoS₂/Zn_{0.5}Cd_{0.5}S heterojunction was formed, and the good interface contact and synergy between CoS₂ and Zn_{0.5}Cd_{0.5}S were beneficial to photocatalytic H₂ evolution reaction. On the other hand, it showed that the mass ratio of CoS₂ and Zn_{0.5}Cd_{0.5}S during the preparation of the composite catalysts had an

important influence on the activity of HER. This may be because when the mass of CoS_2 in the $CoS_2/Zn_{0.5}Cd_{0.5}S$ photocatalyst was small, the agglomeration phenomenon of $Zn_{0.5}Cd_{0.5}S$ was still serious. A large amount of $Zn_{0.5}Cd_{0.5}S$ covered the surface of CoS_2 , which masked the active sites of CoS_2 or blocked the absorption of light by CoS_2 , thereby reducing the electron concentration of CoS_2 , and the photocatalytic activity also decreases.

Figure 6c and Figure S3b (Supporting Information) showed the effect of the ratio of Cd to Zn in $Zn_xCd_{1-x}S$ on the composite photocatalyst on the basis of keeping the mass ratio of $Zn_xCd_{1-x}S$ to CoS_2 at the optimal ratio ($Zn_xCd_{1-x}S$: $CoS_2=1$: 0.4). Obviously, the ratio of Zn to Cd had a great influence on the H₂ evolution reaction activity of the composite photocatalyst, which could be attributed to the different energy band structure and photosensitive strength of $Zn_xCd_{1-x}S$ materials with different mass ratios of Zn to Cd,^[22] this was also reflected in the H₂ evolution of pure $Zn_xCd_{1-x}S$ with different mass ratios of Zn to Cd (Figure S4, Supporting Information).

Figure 6d was the comparative experimental data obtained by changing the amount of CZCS-3 photocatalyst in the H_2 production experiment. It could be seen that when 12 mg of CZCS-3 sample was added to 30 mL of sacrificial agent, the photocatalytic H_2 evolution rate was the highest, indicating that in the photocatalytic HER, it was not that the more photocatalyst was added, the better the hydrogen production rate. The AQE of the CZCS-3 sample under different wavelengths of monochromatic light was shown in Figure 6e, a high AQE of 6.74% was obtained at 420 nm. Figure 6f studied the hydrogen production rate of the CZCS-3 sample under long-term illumination (20 h). The hydrogen production rate of the CZCS-3 sample dropped slightly after the tenth hour. This might be because the reaction time was too long, the pressure in the hydrogen production bottle increased, which inhibited the progress of the hydrogen evolution reaction or a small amount of gas leaked. However, with the prolongation of the illumination time, the hydrogen production still showed an increasing trend, which showed that the CoS₂/Zn_{0.5}Cd_{0.5}S heterojunction has excellent light stability.



Figure 6. Photocatalytic H₂ evolution comparison of (a) CoS_2 , $Zn_{0.5}Cd_{0.5}S$, CZCS-3, (b) CZCS-Y (Y=1, 2, 3, 4, 5), (c) CZ₃CS-3, CZ₄CS-3, CZ₆CS-3, CZ₆CS-3, and CZ₇CS-3, and (d) by changing the quality of CZCS-3 catalyst; (e) AQE of H₂ evolution for CZCS-3 under different wavelength irradiation; (f) Hydrogen production test of CZCS-3 for 20 h.

In order to further confirm that the CoS₂/Zn_{0.5}Cd_{0.5}S photocatalyst had excellent cycle stability, the cycle hydrogen production of CZCS-3 and two single catalysts were tested. Surprisingly, the cycle hydrogen production rate of the CZCS-3 sample within 30 h did not change significantly (Figure 7a). Compared with the first round, the H₂ production of the sixth round of stability experiment only decreased by 6.19%, while the hydrogen production of Zn_{0.5}Cd_{0.5}S had a significant downward trend, indicating that there was a photo-corrosion phenomenon similar to CdS. Compared with Zn_{0.5}Cd_{0.5}S, the stability of the CZCS-3 sample was enhanced. This was attributed to the construction of the heterojunction structure between CoS₂ and Zn_{0.5}Cd_{0.5}S solid solution. Figure 7b compared the XRD patterns of the CZCS-3 sample before and after the hydrogen evolution reaction. Obviously, the XRD diffraction peaks of the CZCS-3 catalyst after the HER were basically the same as those before the reaction, indicating that the prepared CZCS-3 catalyst did not undergo a phase change after participating in the catalytic reaction. The SEM of the CZCS-3 catalyst after H₂ production (Figure S5, Supporting Information) and before H₂ production also did not change significantly, which can further illustrate that the constructed CoS₂/Zn_{0.5}Cd_{0.5}S heterojunction photocatalyst had a high degree of stability.



Figure 7. (a) Cycle test of CoS_2 , $Zn_{0.5}Cd_{0.5}S$ and CZCS-3 photocatalyst; (b) XRD patterns before and after CZCS-3 reaction.

As shown in Figure 8a, in order to study the electron-hole recombination rate of the prepared sample, the Photoluminescence (PL) spectrum of the samples were measured under the condition of an excitation wavelength of 350 nm. Photoluminescence was hardly observed with pure CoS₂, while $Zn_{0.5}Cd_{0.5}S$ and CZCS-3 had similar fluorescence emission peaks at the excitation wavelength of 469 nm.^[23] Moreover, the fluorescence quenching effect of CZCS-3 was better than that of $Zn_{0.5}Cd_{0.5}S$ alone. On the one hand, the added CoS₂ had no photoluminescence effect at this excitation wavelength.^[22] On the other hand, it was because the electrons in CZCS-3 could be transferred quickly, the electron-hole recombination was inhibited. Figure 8b was the time-resolved fluorescence (TRPL) decay curve of the sample obtained by triple exponential decay fitting, the average life (Tav) calculated through fitting was shown in Table 2.^[40] The average lifetime of pure $Zn_{0.5}Cd_{0.5}S$ was 0.37 ns, while the average lifetime of the CZCS-3 sample was reduced to 0.07 ns. This indicated that the formation of CoS₂/Zn_{0.5}Cd_{0.5}S heterojunction effectively inhibited the recombination of photogenerated electrons and holes in Zn_{0.5}Cd_{0.5}S, and made the transfer of photogenerated electrons easier.^[35] Therefore, CZCS-3 showed better photocatalytic H₂ evolution performance than Zn_{0.5}Cd_{0.5}S.



Figure 8. (a) Steady-state fluorescence of $Zn_{0.5}Cd_{0.5}S$, CZCS-3, and CoS₂; (b) Time-resolved fluorescence (TRPL) decay curves of $Zn_{0.5}Cd_{0.5}S$ and CZCS-3.

Systems	Lifetime <\u03c7>(ns)	Pre-exponential factors A/%	Average lifetime,< _{[av>} (ns)	χ^2
ZnCdS	т1=2.51 т2=11.80 т3=0.18	A ₁ =41.37 A ₂ =12.37 A ₃ =46.26	0.37	1.79
CZCS-3	τ1=2.17 τ2=9.29 τ3=0.05	$A_1=24.73$ $A_2=9.73$ $A_3=65.54$	0.07	1.34

Table 2. Fluorescence lifetime parameters of Zn_{0.5}Cd_{0.5}S and CZCS-3 samples.

In addition to PL spectra, photoelectrochemical experiments were used to further study the transfer and separation efficiency of generated photoelectrons in the catalyst. Figure 9a recorded the I-T curves of CoS_2 , $Zn_{0.5}Cd_{0.5}S$, and CZCS-3 samples. All three samples had obvious photocurrent response intensity under four switching cycles of illumination. Generally, the stronger the photocurrent response intensity, the higher the electron transfer rate in the catalyst, and the longer the electron lifetime.^[41] The comparison showed that the CZCS-3 composite catalyst exhibits the strongest photocurrent response. This indicated that the coupling effect between CoS_2 and $Zn_{0.5}Cd_{0.5}S$ accelerated the migration of electrons and prolonged the life of electrons, so that the photocatalytic activity of the CZCS-3 complex was better than that of the two pure substances.

Figure 9b showed the LSV polarization curve of the sample. Generally, the photocatalytic

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hydrogen evolution reaction activity is highly dependent on the over-potential of the reaction.^[42] Obviously, under the same voltage, the overpotential of the sample was CoS_2 , $Zn_{0.5}Cd_{0.5}S$, and CZCS-3 in descending order. It further showed that the CZCS-3 sample had good photocatalytic activity and was a promising material for photocatalytic hydrogen production.

Electrochemical impedance spectroscopy (EIS) is an effective way to further study the electron migration and recombination in materials. Theoretically, the greater the radius of the arc of the Nyquist curve, the greater the impedance during electron transfer.^[12] In Figure 9c, The arc radius of CZCS-3 material was the smallest, which effectively verified the increase in the charge transfer rate, which was consistent with the H₂ evolution rate of the CZCS-3 material.



Figure 9. (a) I-T curves, (b) LSV polarization curves and (c) EIS spectra of Zn_{0.5}Cd_{0.5}S, CZCS-3, CoS₂.

In order to determine the flat band potential (E_{fb}) and semiconductor type of the CoS₂ and Zn_{0.5}Cd_{0.5}S two single catalysts, the Mott-Schottky curve of the materials were measured in the photoelectrochemical experiment. The results were shown in Figures 10a and 10c. The slope of the Mott-Schottky curve was positive, indicating that the measured substance is an n-type semiconductor.^[43,44] Both CoS₂ and Zn_{0.5}Cd_{0.5}S were n-type semiconductors, the same as the previous report.^[22,31] One of the conditions for the formation of S-type heterojunction was the coupling of two n-type semiconductors.^[45] In addition, the E_{fb} of CoS₂ and Zn_{0.5}Cd_{0.5}S were -0.45 eV and -0.68 eV (vs. saturated calomel electrode (SCE)), respectively. Generally, the relationship between the conduction band potential (E_{CB}) of an n-type semiconductor and the E_{fb} is: $E_{CB} = E_{fb} - 0.10 \text{ V}_{25}^{[25]}$ and there is also a certain conversion relationship between the SCE electrode and the standard hydrogen electrode (NHE), namely: $E_{NHE} = E_{SCE} + 0.241 \text{ V}_{24}^{[46]}$ Through these two relations, the E_{CB} values of pure CoS₂ and Zn_{0.5}Cd_{0.5}S relative to NHE relationship between the substance is also a certain conversion.

10d.



were 2.16 eV and 1.81 eV, respectively. The detailed band structure was shown in Figures 10b and

Figure 10. (a) (c) Mott-Schottky curves of CoS_2 and $Zn_{0.5}Cd_{0.5}S$; (b) (d) Energy band structure diagram of CoS_2 and $Zn_{0.5}Cd_{0.5}S$.

Based on the above characterization analysis and experimental results, the photocatalytic hydrogen production mechanism of CZCS-3 composite material was inferred. Figure 11a was a schematic diagram of the relative energy levels before the two pure substances were in contact. Compared to the valence band (VB) and conduction band (CB) positions of CoS₂ and Zn_{0.5}Cd_{0.5}S, it was not difficult to see that the CB position of Zn_{0.5}Cd_{0.5}S was more negative (with stronger reducibility), and the VB position of CoS_2 was more positive (with stronger oxidizing property). If the electron transfer followed the type-II heterojunction mode, the overall redox capability of the heterojunction was weakened. In addition, the latest report claimed that the existence of electrostatic repulsion made it difficult to realize the electron transfer mode of type-II heterojunction.^[47] Here, we speculated that the CZCS-3 composite material was an S-scheme heterojunction photocatalyst. As we all know, the Fermi energy of n-type semiconductors is close to the conduction band.^[48,49] It was not difficult to know that compared with CoS_2 , $Zn_{0.5}Cd_{0.5}S$ had a larger Fermi energy and a smaller work function. Therefore, as shown in Figure 11b, when Zn_{0.5}Cd_{0.5}S was in contact with CoS₂, the electrons of Zn_{0.5}Cd_{0.5}S were spontaneously dispersed on CoS_2 until the Fermi level was aligned to the same level, and the energy band of $Zn_{0.5}Cd_{0.5}S$ bended upwards and the energy band of CoS₂ bended downwards. At the same time, an internal

electric field from $Zn_{0.5}Cd_{0.5}S$ to CoS_2 was formed.^[47,50] This was consistent with the results of XPS characterization. When irradiated by visible light (Figure 11c), CoS_2 and $Zn_{0.5}Cd_{0.5}S$ were excited by light to generate electrons (e⁻) and transition from their respective VB to CB, leaving oxidizing holes (h⁺) on the VB. The e⁻ on the CB of CoS_2 and the h⁺ on the VB of $Zn_{0.5}Cd_{0.5}S$ were affected by the three factors of Coulomb attraction, internal electric field and energy band bending, and recombined at the contact interface, that was, a stepped (S-scheme) transfer path was formed.^[51,52] Thus, the electrons in $Zn_{0.5}Cd_{0.5}S$ CB, which were relatively strong reduction, were retained for the reduction of hydrogen. In the meantime, the h⁺ in the VB of CoS_2 and the L-lactic acid sacrificial agent underwent an oxidation reaction and were consumed, which further inhibited the recombination of the electrons and holes, and the photocatalytic activity was also enhanced.



Figure 11. Proposed mechanism of H_2 production: (a) CoS_2 and $Zn_{0.5}Cd_{0.5}S$ before contact, (b) CoS_2 and $Zn_{0.5}Cd_{0.5}S$ after contact, (c) S-scheme electron transfer mechanism after visible light irradiation.

Conclusion

From the results of XRD, XPS and TEM, it was found that CoS_2 nanospheres and $Zn_{0.5}Cd_{0.5}S$ solid solution were successfully supported together, and a new photocatalytic composite material was prepared. Among them, when the mass ratio of $Zn_{0.5}Cd_{0.5}S$ to CoS_2 was 1:0.4 (CZCS-3), the composite material had the most excellent hydrogen production performance, and the H₂ production rate in the fifth hour could reach 25.15 mmol·g⁻¹·h⁻¹. Moreover, $CoS_2/Zn_{0.5}Cd_{0.5}S$ had excellent stability, and the hydrogen production rate of the sixth repeated experiment was only 6.19% lower than that of the first. From the PL spectroscopy and electrochemical characterization analysis, it was known that the good contact between CoS_2 and $Zn_{0.5}Cd_{0.5}S$ made the electron transfer of CZCS-3 easier, which benefited from the construction of the $CoS_2/Zn_{0.5}Cd_{0.5}S$ S-scheme heterojunction. This S-scheme electron transfer mechanism formed between two n-type

semiconductors retained a stronger redox potential, thereby effectively promoting the photocatalytic hydrogen production activity.

Conflicts of interest

The authors declare that they have no competing interests.

Acknowledgments

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Table of Contents entry



In this study, $Zn_{0.5}Cd_{0.5}S$ and CoS_2 formed an S-type heterojunction, the mixed interface structure between them provided a new hydrogen-producing active center for each. In addition, the S-type heterojunction electron transfer mechanism not only promoted the separation of electrons (e⁻) and holes (h⁺) between $Zn_{0.5}Cd_{0.5}S$ and CoS_2 , but also retained electrons with strong reducibility, thereby promoting the photocatalytic hydrogen evolution reaction. (In the figure: CB is the conduction band, VB is the valence band, hv is the photon energy).