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Article

2D mesoporous ultrathin $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheet: Fabrication mechanism and application potential for photocatalytic H_2 evolution

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ABSTRACT

Two-dimensional mesoporous ultrathin $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets with a thickness of ~ 1.5 nm were fabricated using a multistep chemical transformation strategy involving inorganic–organic hybrid ZnS -ethylenediamine (denoted as $\text{ZnS}(\text{en})_{0.5}$) as a hard template. Inorganic–organic hybrid $\text{ZnS}(\text{en})_{0.5}$, $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$, and $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets were sequentially fabricated, and their transformation processes were analyzed in detail. The fabricated $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets exhibited high photocatalytic hydrogen evolution reaction activity in the presence of a sacrificial agent. The $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets exhibited remarkably high H_2 production activity of $\sim 1395 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ in pure water with no co-catalyst, which is the highest value reported thus far for bare photocatalysts, to the best of our knowledge. The high activity of these nanosheets is attributed to their distinct nanostructure (e.g., short transfer distance of photoinduced charge carriers, large number of unsaturated surface atoms, and large surface area). Moreover, ternary NiCo_2S_4 nanoparticles were employed to facilitate the charge separation and enhance the surface kinetics of H_2 evolution. The H_2 production rate reached ~ 62.2 and $\sim 2436 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ in triethanolamine and pure water, respectively, over the $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ heterojunctions. The result indicated that the Schottky junction was critical to the enhanced activity. The proposed method can be used for fabricating other highly efficient CdZnS -based photocatalysts for solar-energy conversion or other applications.

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1. Introduction

Solar-energy conversion via artificial photosynthesis is a promising and ecofriendly technique for extracting H_2 from water. Over the past few years, two-dimensional (2D) photocatalysts have attracted considerable attention because of their spatially anisotropic crystal structure for charge-carrier migration. They are novel materials that have been adopted to develop efficient artificial photosynthesis systems [1–3]. In par-

ticular, ultrathin 2D structures with large specific surface areas can create abundant fast interfacial channels and large interfacial contacts between photocatalyst and reactant molecules. Furthermore, the predominant exposure of a specific facet endows it with a significant amount of low-coordinated surface atoms, facilitating the adsorption and activation of reactants on the unsaturated surface atoms [4–6]. The aforementioned attractive features make ultrathin 2D photocatalysts promising candidates for the development of highly efficient artificial

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photosynthesis systems. For instance, using a facile polyol-mediated hot-injection method, Zhang et al. fabricated flower-like spherical ZnIn_2S_4 superstructures that comprised ultrathin (2–3 nm thick) nanosheets [7]. These superstructures exhibited higher H_2 evolution activity under visible light than typical flower-like bulk ZnIn_2S_4 microspheres fabricated using the conventional hydrothermal method. Other ultrathin 2D photocatalysts (e.g., BiOX ($X = \text{Cl}, \text{Br}$), TiO_2 , $\text{g-C}_3\text{N}_4$, black phosphorus, and CdS [8–16]) have also been successfully synthesized to achieve a high photocatalytic efficiency. Although significant progress in 2D ultrathin photocatalysts was achieved in the aforementioned studies, a high-quality material with high activity for potential applications is urgently required.

$\text{Cd}_x\text{Zn}_{1-x}\text{S}$ is considered to be the most promising candidate for practical applications owing to its high activity compared with TiO_2 , $\text{g-C}_3\text{N}_4$, and other normal materials [17,18]. However, $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ is always present as agglomerated nano/microspheres, and the drastic aggregation of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ nanoparticles causes surface-area reduction, sluggish charge separation, and slow surface reaction kinetics, limiting the photocatalytic performance [19–22]. The strategies for resolving these issues involve accelerating the diffusion of the reactant and the migration of photoelectrons, as well as increasing the surface area. The construction of ultrathin 2D mesoporous nanostructures are likely to create $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ another realizable route to achieve high activity. Nevertheless, 2D $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ with a well-defined microstructure and chemical composition is extremely difficult to obtain owing to the lack of anisotropic growth driving force, which results from the intrinsic non-layered close-packed crystal structure of the hexagonal wurtzite/zincblende framework. In a previous study, one-dimensional $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ was prepared via a solvothermal process; however, the rational design and synthesis of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ with ultrathin 2D architectures for efficient interparticle or interfacial charge transfer remain technical challenges [23]. The ultrathin 2D structure is likely to retain well-preserved structural frameworks after topotactic transformation via a specific precursor, accompanied by limited lattice variations or the collapse of the few-layer-thick structure. For instance, Zhang et al. [24] fabricated layered TiO_2 nanosheets with a thickness of 4–10 nm by calcining an NH_4TiOF_3 intermediate. In their study, the intercalated molecules were removed, and layered single-crystal TiO_2 with exposed highly reactive (001) facets was fabricated, in which the morphology of the intermediate was maintained. In light of this result, we propose a chemical transformation route for fabricating ultrathin, porous $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets, which can be used as a platform (i.e., substrate) to investigate photocatalytic reactions and develop ultrathin 2D CdZnS -based heterostructures for enhanced solar-energy conversion or other applications.

Numerous studies have indicated that functional modifications are effective for inhibiting rapid charge recombination and enhancing the surface kinetics of bare photocatalysts [25–30]. Recently, multi-elemental metallic compounds have attracted considerable attention owing to their versatility. The partial substitution of host lattice atoms of a certain material

with appropriate guest atoms can enhance the structural and electronic properties, reducing the activation energy of H_2 production and enlarging the active sites. Jin et al. [31] reported that the substitution of S atoms of CoS_2 with P atoms altered the electronic structure and significantly enhanced the hydrogen evolution reaction (HER) performance. Alshareef et al. [32] obtained ternary NiCoP via partial substitution of the Ni of Ni_2P with extrinsic Co atoms. They proved that the ternary NiCoP had a lower Gibbs free energy for the adsorption of reactants (H^+ or H_2O) than Ni_2P . Similarly, ternary cobalt-nickel sulfide (NiCo_2S_4) has been successfully employed for water splitting (electrolysis) owing to its various advantageous properties, including its high electroconductibility ($\sim 1 \times 10^{-3} \mu\Omega^{-1}\cdot\text{cm}^{-1}$ at ambient temperatures), high carrier density ($3.18 \times 10^{22} \text{ cm}^{-3}$ at 2 K), and high architectural controllability, compared with the corresponding oxide or single-metal compounds [33]. Recently, its capability for HER photocatalysis in the presence of a sacrificial agent was demonstrated [34], which is not surprising, as both photocatalytic and electrocatalytic HERs rely on the reversible adsorption and desorption of H_2 on the catalyst surface. Accordingly, the combination of $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ with NiCo_2S_4 is a promising strategy.

In this study, mesoporous ultrathin $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets were fabricated by chemically transforming inorganic–organic hybrid $\text{ZnS}(\text{en})_{0.5}$ into $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ and then transforming the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ into inorganic $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets, which exhibited higher photocatalytic HER activity than the corresponding nanoparticles. The $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets also exhibited excellent H_2 production activity ($\sim 1395 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) in pure water with no co-catalyst or other substance added. Furthermore, NiCo_2S_4 particles were employed to enhance the activity of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets. To the best of our knowledge, the activity of 7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ in the presence of triethanolamine (TEOA) and in pure water exceeded that of most previously reported catalysts. Moreover, for the first time, we report that the inorganic–organic hybrid 2D $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ intermediate exhibited higher photocatalytic HER activity than $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles.

2. Experimental

The procedures for the preparation of the NiCo_2S_4 and $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles and the photocatalytic experiment and characterizations are presented in the Supporting Information.

2.1. Synthesis of inorganic–organic hybrid $\text{ZnS}(\text{en})_{0.5}$ nanosheets

First, 2 mmol of $\text{Zn}(\text{NO}_3)_2$ was dissolved in a mixed solution containing 10 mL of H_2O and 50 mL of ethylenediamine (en). Subsequently, 250 mg of thiourea (Tu) was introduced into the resulting transparent solution. Next, the solution was transferred into a sealed vessel and incubated at 160 °C for 16 h. The resulting white products were washed with ethyl alcohol several times and then dried for use. Additionally, $\text{Zn}(\text{OAc})_2$, ZnCl_2 , and ZnSO_4 were employed to fabricate $\text{ZnS}(\text{en})_{0.5}$, for compari-

son.

2.2. Synthesis of inorganic–organic hybrid $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$

First, 89.3 mg of cadmium chloride was dissolved in 70 mL of ethylene glycol (EG). Second, 100 mg of the prepared $\text{ZnS}(\text{en})_{0.5}$ nanosheets was dispersed in the solution with ultrasonic treatment for 30 min. The resulting suspension was stirred for 15 min and then kept at 160 °C for 8 h. Lastly, the yellow products were harvested and washed with ethyl alcohol, yielding $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$.

2.3. Synthesis of mesoporous $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets and $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ composites

Mesoporous $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets were prepared as follows. First, 100 mg of as-prepared $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ powder was dispersed in 70 mL of H_2O after 20 min of ultrasonic treatment. The resulting yellow suspension was kept at 140 °C for 3 h. Then, the product was centrifuged and washed with deionized water. The preparation procedures for the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles are presented in the Supporting Information.

$\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ heterojunctions were prepared as follows. First, 100 mg of the fabricated $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets and a specific amount of NiCo_2S_4 nanoparticles were dispersed (separately) in 20 mL of absolute ethyl alcohol with ultrasonic treatment for 1 h. Subsequently, the two suspensions were mixed and subjected to evaporation, yielding a dry green powder, which was heated at 200 °C for 1 h in N_2 .

3. Results and discussion

The procedures for fabricating the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets are shown in Fig. 1 (nonporous inorganic–organic hybrid $\text{ZnS}(\text{en})_{0.5} \rightarrow \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ intermediate $\rightarrow$ mesoporous $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets). First, nonporous inorganic–organic hybrid $\text{ZnS}(\text{en})_{0.5}$ was prepared as a hard template based on the solvent coordination molecular template mechanism with en as a soft template. Here, the en acted as a structure-directing molecule incorporated into the ZnS inorganic framework (Eq. 1). Then, the Zn^{2+} in the $\text{ZnS}(\text{en})_{0.5}$ lattice was partially replaced

Fig. 1. Preparation of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets.

with Cd^{2+} via hydrothermal cation exchange in EG (Eq. (2)). Simultaneously, some of the en molecules were dissolved in EG, and an inorganic–organic hybrid $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ intermediate was fabricated. Subsequently, the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ was topologically transformed into $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ with a mesoporous sheet-like morphology by removing the en molecules within its crystal lattice through a second low-temperature hydrothermal treatment in water (Eq. (3)).

The XRD patterns of the prepared samples are shown in Fig. 2(a). The red curve (corresponding to samples prepared with $\text{Zn}(\text{NO}_3)_2$) with sharp diffraction peaks was well indexed to orthorhombic inorganic–organic hybrid $\text{ZnS}(\text{en})_{0.5}$ (in accordance with the literature [35–37]), whose structure has been studied in detail. The $\text{ZnS}(\text{en})_{0.5}$ hybrid comprised an alternating arrangement of layered inorganic ZnS and organic en molecules along the *a*-axis owing to the bonding of Zn and N atoms (Fig. 1). The typical peak associated with the layered structure was observed at 10.46° [38], corresponding to an interlayer spacing of 0.845 nm in the presence of one intercalated en molecule between two ZnS layers. To obtain an inorganic–organic hybrid $\text{ZnS}(\text{en})_{0.5}$ precursor with a desirable shape, $\text{ZnS}(\text{en})_{0.5}$ was fabricated with different Zn salts, i.e., $\text{Zn}(\text{OAc})_2$, ZnCl_2 , and ZnSO_4 . As shown in Fig. 2(a), the XRD patterns of the samples fabricated with ZnSO_4 and ZnCl_2 were significantly different from those of the samples fabricated with $\text{Zn}(\text{NO}_3)_2$

Fig. 2. (a) X-ray diffraction (XRD) patterns of $\text{ZnS}(\text{en})_{0.5}$ prepared with different Zn salts, (b) XRD patterns of $\text{ZnS}(\text{en})_{0.5}$, $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ and $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets.

and $\text{Zn}(\text{OAc})_2$, probably owing to the preferential adsorption of different anions during the crystal growth. Additionally, the scanning electron microscopy (SEM) images were significantly different for these samples (Fig. S1). The samples fabricated with ZnCl_2 and $\text{Zn}(\text{OAc})_2$ appeared to be disordered and unsystematic. When ZnSO_4 was the Zn source, only large bulk $\text{ZnS}(\text{en})_{0.5}$ was observed via SEM. Regular sheet-like $\text{ZnS}(\text{en})_{0.5}$ could be fabricated only when $\text{Zn}(\text{NO}_3)_2$ was employed. The Fourier transform infrared (FT-IR) spectrum of $\text{ZnS}(\text{en})_{0.5}$ prepared with $\text{Zn}(\text{NO}_3)_2$ (red curve in Fig. 3) was inconsistent with that of dissociative en (blue curve) owing to their different chemical states. A similar phenomenon was observed by Li et al. [37], who reported that en molecules were incorporated into the cell of ZnS. The corresponding energy-dispersive X-ray spectroscopy (EDS) and mapping images of $\text{ZnS}(\text{en})_{0.5}$ (Fig. S2) prepared with $\text{Zn}(\text{NO}_3)_2$ indicated that only the four elements Zn, S, C, and N were present, suggesting the purity of the sample and the abundance of en.

After cation exchange with CdCl_2 , although the intensities of the diffraction peaks of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ were significantly reduced, the peaks of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ shown in Fig. 2(b) still fit those of $\text{ZnS}(\text{en})_{0.5}$, except for the peak at 27.0° (marked with a black rhombus) observed in the magnified pattern, which corresponds to the (002) plane of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ [19]. This result indicates that the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ was a novel phase with a different structure from $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$. It had a layered framework similar to that of $\text{ZnS}(\text{en})_{0.5}$, except that some en molecules escaped from the $\text{ZnS}(\text{en})_{0.5}$ framework into the EG during cation exchange [38]. When $\text{Cd}(\text{OAc})_2$ was used for cation exchange, no specific product was achieved, probably owing to the different pH values of the precursor solution. The EDS mapping (Fig. S3) of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ indicated the presence of Zn, Cd, S, C, and N in this intermediate inorganic-organic hybrid, and the molar ratio of Zn:Cd was almost 1:1. As expected, the FT-IR spectrum of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ shown in Fig. 3 is identical to that of $\text{ZnS}(\text{en})_{0.5}$, indicating the presence of numerous en molecules in the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ lattice rather than superficially adsorbed en molecules.

When the en molecules were fully removed from the framework of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ via the second hydrothermal

treatment in pure water, hexagonal wurtzite $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets could be fabricated, as confirmed by the XRD pattern in Fig. 2(b) (black curve). All the peaks for $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ were shifted to lower 2θ values compared with the standard Powder Diffraction File card (01-0677) of hexagonal ZnS, indicating a larger interplanar spacing, which is attributed to the successful introduction of long-radius Cd^{2+} into the unit cell of ZnS [39]. In the FT-IR spectrum of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ (Fig. 3), the peaks corresponding to internal en molecules completely disappeared, and only vibration peaks corresponding to water were observed, indicating the successful conversion process of $\text{ZnS}(\text{en})_x \rightarrow \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x \rightarrow \text{hexagonal wurtzite } \text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$.

The microstructures of the prepared samples were investigated using transmission electron microscopy (TEM) and selected-area electron diffraction (SAED). As shown in Figs. 4(a)–(c), the $\text{ZnS}(\text{en})_{0.5}$ nanosheets had a smooth surface, and the dark rings (marked by the yellow dotted circles) in the observed region resulted from the partial melting of the sample when it was exposed to the electron beam [40]. As shown in Fig. 4(c), further inspection of the $\text{ZnS}(\text{en})_{0.5}$ via high-resolution TEM (HRTEM) revealed numerous anomalous lattice fringes with sufficient obscure edge dislocations and distortions, suggesting that the prepared $\text{ZnS}(\text{en})_{0.5}$ had a grain boundary-rich structure. Similar findings were reported by Liu et al. [36]. The inset SAED pattern in Fig. 4(c) confirms the multi-domain crystallite nature of the $\text{ZnS}(\text{en})_{0.5}$.

TEM images of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ intermediate are presented in Figs. 4(d)–(f). As shown, the sheet-like feature of $\text{Zn}_{0.5}\text{S}(\text{en})_{0.5}$ was well maintained after the cation exchange. The AFM image in Fig. S4 indicates that the thickness of this $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ intermediate was ~ 5.7 nm. Interestingly, a strip edge composed of numerous nanoparticles appeared along the edge of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ nanosheets, appearing to be thicker than the interior observed via TEM. Furthermore, the marked lattice spacing located at the edge of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ in Fig. 4(f) matches the (002) plane of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanocrystal. To elucidate this finding, $\text{ZnS}(\text{en})_{0.5}$ was used individually with identical procedures in EG, in the absence of CdCl_2 . Surprisingly, the sheet-like feature of the $\text{ZnS}(\text{en})_{0.5}$ was well maintained, and the strip edge was still observed in the treated $\text{ZnS}(\text{en})_{0.5}$ (Fig. S5). This indicates that the partial dissolution of intercalated en into the EG during the cation exchange was primarily responsible for this phenomenon. Because the ion-exchange reaction occurred very rapidly (within 15 min; XRD pattern is shown in Fig. S6), when $\text{ZnS}(\text{en})_{0.5}$ was solvothermally treated with a non-amine solvent, the internal en molecules located at the edge of the nanosheets quickly escaped from the bulk into the solvent under the thermal effect. Simultaneously, the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ intermediate was formed at the edge of the nanosheet. As the reaction continued, the edge was decomposed, forming $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles, which reduced the surface energy and enhanced the thermodynamic stability, explaining the (002) peak in the XRD pattern for the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ intermediate. Additionally, the surface of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ was rough, and numerous nanocrystals were observed, in contrast to the fresh $\text{ZnS}(\text{en})_{0.5}$. The following three reasons are suggested for this [37,38,40,41]: (1) partial dissolution of en

Fig. 3. FT-IR spectra of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets, $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$, $\text{ZnS}(\text{en})_{0.5}$, and dissociative en molecules.

Fig. 4. TEM images of $\text{ZnS(en)}_{0.5}$ prepared with $\text{Zn(NO}_3)_2$ (a–c), $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S(en)}_x$ (d–f), and $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ (g–i) nanosheets; (j) EDS line scanning pattern and the corresponding elemental composition of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets; (k) Atomic force microscopy (AFM) image of the prepared $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets.

from the $\text{ZnS(en)}_{0.5}$ lattice into the EG during the hydrothermal treatment resulted in lattice distortion, accompanied by lattice contraction, leading to the formation of a rough surface and porous structures. (2) Numerous point defects (e.g., S vacancies) were formed owing to the different in-and-out diffusion rates of Zn^{2+} and Cd^{2+} during the cation exchange. The migration and accumulation of these point defects eventually produced volume defects of voids, leading to thermodynamic stability. (3) The radii of Zn^{2+} and Cd^{2+} differed. Tensile-stress-induced lattice cracking occurred when a large amount of Cd^{2+} quickly accessed the $\text{ZnS(en)}_{0.5}$ lattice. Moreover, regardless of whether $\text{ZnS(en)}_{0.5}$ was directly treated in pure water at 140 °C for 3 h or by the same conditions as fabricating $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets, the structure collapsed, and numerous nanoparticles were clearly observed (Fig. S7).

When the en was completely removed from the unit cell of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S(en)}_x$, the mesoporous feature of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets was more clearly observed (Figs. 4(g)–(i)), which was related to $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S(en)}_x$. When the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S(en)}_x$ underwent solvent-assisted thermal treatment in pure water, the en molecules were released from the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S(en)}_x$ lattice via hydrolysis, forming hexagonal $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$, during which lattice mismatches between the orthorhombic $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S(en)}_x$ and the hexagonal wurtzite $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ induced the formation of voids, accompanied by the shrinkage of the unit cell [40,42]. Nevertheless, as indicated by the HRTEM image and SAED pattern in Fig. 4(j), the prepared $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets exhibited a typical pseudo-single-crystal characteristic. The preferential exposed

surface lattice spacing was 0.326 nm, corresponding to the (002) plane of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$. Jang et al. [38] reported that owing to the self-healing process of planar defects during hydrothermal treatment, defects (e.g., stacking faults and twin boundaries) eventually vanished. Thus, a superstructure with a high degree of crystallographic orientation was obtained via nonclassical crystallization routes; it was evolved from a fusion of the primary nanocrystals, as shown in Figs. 4(d)–(f). AFM measurements (Fig. 4(k)) indicated that the thickness of the prepared $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets was only ~1.5 nm, which was far greater than that of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S(en)}_x$ for the removal of interlayered en molecules. This reveals that the distance for charge transportation was reduced and that the density of active unsaturated surface atoms very high, making the dissociative adsorption of the reactants more efficient owing to the small atomic coordination numbers of the exposed atoms compared with the bulk counterpart [1,2,43]. The zigzag curve obtained from the AFM measurements indicated the mesoporous property of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets. Their high crystallinity and ultrasmall thickness significantly enhanced their activity by reducing the bulk recombination, accelerating the migration of charge carriers from the interior to the surface-adsorbed reactants and facilitating the absorption of surface reactants [44,45]. Moreover, the porosity created microchannels and new active sites, which not only facilitated mass transfer but also stimulated charge migration during the reaction. The EDS line scanning pattern in Fig. 4(j) indicates that the mole ratio of Zn:Cd was well maintained after the second hydrothermal treatment of

Fig. 5. High-resolution XPS spectra of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets and $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$.

$\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$. It also indicates that the elemental compositions of the interiors and edges of the sheets were identical. The mole ratio of Zn: Cd in $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ was regulated by adding CdCl_2 and $\text{ZnS}(\text{en})_{0.5}$ at different mole ratios, as shown in Fig. S8, indicating great potential for the fabrication of 2D ultrathin CdZnS -based heterojunctions.

To investigate the cation-exchange process, the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets and the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ intermediate were analyzed via X-ray photoelectron spectroscopy (XPS) to determine whether the external Cd^{2+} was substituted at the Zn^{2+} sites in the $\text{ZnS}(\text{en})_{0.5}$ matrix or the other sites. As shown in Fig. 5(a), only two peaks were observed for both $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ and $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$, corresponding to $\text{S } 2p_{3/2}$ (161.91 eV for $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ nanosheets, 162.67 eV for $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$) and $\text{S } 2p_{1/2}$ (164.03 eV for $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets, 165.04 eV for $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$). Thus, neither sample contained bonds other than metal-S [19,46]. The two strong peaks at 1021.5 and 1044.6 eV in the high-resolution $\text{Zn } 2p$ XPS spectrum of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ originated from S-Zn bonds. The two small peaks at 1025.0 and 1047.9 eV correspond to Zn-N bonds in the [S-Zn-en] group, where one Zn atom was bonded with three S atoms and coordinated with one N atom of en (Fig. 5(b)) [36,43]. In agreement with the spectrum of Zn, two small peaks were observed in the Cd 3d spectrum of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ (Fig. 5(c)), indicating the presence of Cd-N bonds in the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$. No other peaks were observed in high-resolution spectrum of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets, except for that corresponding to Cd-S bonds. The foregoing results confirm that the Cd^{2+} substitution occurred at Zn sites in the $\text{ZnS}(\text{en})_{0.5}$ matrix (rather than other sites), indicating that the solvothermal treatment was completely responsible for the escape of en molecules from the unit cell of $\text{ZnS}(\text{en})_{0.5}$ and the reduced intensities of the diffraction peaks after the cation exchange.

To fully exploit the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets as a platform photocatalyst, they were integrated with ternary NiCo_2S_4 nanoparticles via sample physical mixing. The XRD peaks of NiCo_2S_4 at 26.8° , 31.52° , 38.28° , 50.45° , and 55.33° , corresponding to the (220), (311), (400), (511), and (440) planes, respectively, were not observed for the composite, owing its low NiCo_2S_4 content and low crystallinity (Fig. S9) [47]. The TEM images of 7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ in Fig. S10(a)–(c) reveal that $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets were in contact with aggregated Ni-

Co_2S_4 , whose diameter was approximately 30–50 nm. The lattice fringes marked in the high-resolution image correspond to the (111) and (220) facets of the NiCo_2S_4 nanoparticles, indicating the successful fabrication of the binary composite. The mapping images and energy-dispersive X-ray spectrum in Fig. S11 indicate the presence of the required elements at the stoichiometric ratio. The high-resolution X-ray photoelectron spectrum in Fig. S12 confirms that the chemical states of the five elements were well maintained, except that the binding energies shifted to a lower or higher position under the interaction of electrons with the heterogeneous interfaces, indicating that a binary heterojunction was formed.

N_2 adsorption-desorption isotherm and pore-size distribution (based on the Barrett-Joyner-Halenda model) measurements were performed for the prepared samples, as shown in Fig. 6. The distinct feature of type IV isotherms with an H1 hysteresis loop was observed for the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets and 7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$. This indicates that the mesopores were uniformly cylindrical and that the introduction of NiCo_2S_4 did not alter the mesoporous feature of the nanosheets [48,49]. Nevertheless, the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles exhibited typical H3 curves, similar to other aggregated particles. For the intermediates, a remarkable capillary condensation step in the P/P_0 range of 0.3–0.8 was observed in the isotherm, which is attributed to the presence of radial mesochannels [49,50]. As expected, $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ exhibited the largest Brunauer-Emmett-Teller (BET) surface area ($121.6 \text{ m}^2/\text{g}$) in the presence of interlayer en molecules, and the pore-size distribution was centered at 7.2 nm. After the complete removal of en, the BET surface area of the fresh $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets was significantly reduced (to $62.4 \text{ m}^2/\text{g}$), and the pore diameter was increased from ~7 to ~21 nm owing to the self-healing process of planar defects and the shrinkage of the unit cell [38]. The $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets exhibited a significantly larger BET sur-

Table 1
 N_2 adsorption-desorption results.

Samples	Specific surface area (m^2/g)	Pore diameter (nm)
$\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ particles	35.1	4.6
$\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets	62.4	20.6
$\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$	121.6	7.2
7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$	65.9	19.8

Fig. 6. N_2 adsorption-desorption isotherms and pore-size distributions.

face area than the $Cd_{0.5}Zn_{0.5}S$ nanoparticles ($35.1 \text{ m}^2/\text{g}$; TEM images are shown in Fig. S13), and their surface area was very close to that of 7%- $NiCo_2S_4/Cd_{0.5}Zn_{0.5}S$ ($65.9 \text{ m}^2/\text{g}$). The pore-size distribution of 7%- $NiCo_2S_4/Cd_{0.5}Zn_{0.5}S$ was centered at $\sim 20 \text{ nm}$. The distribution was narrow and similar to that of the pure $Cd_{0.5}Zn_{0.5}S$ nanosheets, indicating that the meso-structure was well preserved. As mentioned previously, we consider that these pores facilitated the diffusion of reactants and products by providing numerous effective transport pathways, enhancing the photocatalytic performance of the material.

The ultraviolet-visible (UV-vis) absorption spectra of the $Cd_{0.5}Zn_{0.5}S$ nanosheets and the inorganic-organic intermediate are presented in Fig. 7. The absorption edge of the $Cd_{0.5}Zn_{0.5}S$ nanosheets was located at 530 nm . The curve of $Cd_{0.5}Zn_{0.5}S(en)_x$ exhibited an obvious blue shift and a larger bandgap compared with that of the $Cd_{0.5}Zn_{0.5}S$ nanosheets. This is similar to the phenomena previously observed by Zhang et al. [51,52] for a $g\text{-}C_3N_4/\text{ethanediamine}$ inorganic-organic composite. The inset Kubelka-Munk plots indicate that the optical bandgaps of the $Cd_{0.5}Zn_{0.5}S$ nanosheets and $Cd_{0.5}Zn_{0.5}S(en)_x$ were 2.45 and 2.53 eV , respectively. For the binary composites (Fig. 7b), the optical absorption coefficients in the visible region ($500\text{--}800 \text{ nm}$) increased with the mass fraction of $NiCo_2S_4$, owing to the robust visible-light response of $NiCo_2S_4$. However,

in the UV region, the light-absorption coefficients of all the binary composites were nearly identical to that of the pristine $Cd_{0.5}Zn_{0.5}S$ nanosheets. Although the enhanced visible light cannot drive the production of electrons and holes that can be directly consumed by surface reactants, the photons that accumulate on the surface of the $NiCo_2S_4$ exert a local heating effect, forming a local heat field, which increases the surface redox efficiency.

3.1. Photocatalytic H_2 evolution

As shown in Fig. 8(a), the photocatalytic performance of the samples was initially enhanced in a 20% TEOA ($\text{pH} = 9.5$) aqueous solution under illumination from a 300-W Xe lamp (wavelength range: $350\text{--}780 \text{ nm}$; $344 \text{ mW}/\text{cm}^2$). Relatively low activity with an H_2 evolution rate of $8.5 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ was observed over $Cd_{0.5}Zn_{0.5}S$ nanoparticles. The H_2 evolution rate of the $Cd_{0.5}Zn_{0.5}S$ nanosheets reached $\sim 19.1 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which was 2.2 times higher than that of the $Cd_{0.5}Zn_{0.5}S$ nanoparticles. As discussed previously, the high activity resulted from the special microstructure, which were extremely conducive to the diffusion of reactants and products, the charge-carrier transport, and the activation of the reactants. The inorganic-organic hybrid $Cd_{0.5}Zn_{0.5}S(en)_x$ intermediate also exhibited enhanced activity ($\sim 13.5 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) compared with the

Fig. 7. UV-vis absorption spectra of the prepared samples.

Fig. 8. (a) Photocatalytic performance of the Cd_{0.5}Zn_{0.5}S nanoparticles and Cd_{0.5}Zn_{0.5}S(en)_x and Cd_{0.5}Zn_{0.5}S nanosheets. (b) H₂ production over various NiCo₂S₄/Cd_{0.5}Zn_{0.5}S heterojunctions. (c, d) Wavelength-dependent photocatalytic H₂ production over 7%-NiCo₂S₄/Cd_{0.5}Zn_{0.5}S. (e) H₂ production over the samples under visible-light irradiation. (f) H₂ production in pure water over Cd_{0.5}Zn_{0.5}S nanoparticles, Cd_{0.5}Zn_{0.5}S nanosheets, and 7%-NiCo₂S₄/Cd_{0.5}Zn_{0.5}S.

Cd_{0.5}Zn_{0.5}S nanoparticles, whereas its activity was significantly inferior to that of the inorganic Cd_{0.5}Zn_{0.5}S nanosheets. Zhang et al. [51] attributed the enhanced activity of such an inorganic-organic hybrid to its improved hydrophilia in the presence of numerous interlayer amino groups, which currently appears to be untenable. It is more rational that the interlayer amino groups function as pseudo-sacrificial agents during illumination owing to their low reducibility, similar to molecular co-catalysts.

The results for H₂ evolution over various NiCo₂S₄/Cd_{0.5}Zn_{0.5}S heterostructures are presented in Fig. 8(b). A typical volcanic plot was observed with the increasing mass proportion of NiCo₂S₄, indicating that the HER activity of 7%-NiCo₂S₄/Cd_{0.5}Zn_{0.5}S reached a maximum value of ~62.2 mmol·h⁻¹·g⁻¹. This value was 7.3 and 3.3 times higher than those for the Cd_{0.5}Zn_{0.5}S nanoparticles and Cd_{0.5}Zn_{0.5}S nanosheets, respectively. Moreover, the 7%-NiCo₂S₄/Cd_{0.5}Zn_{0.5}S and fresh Cd_{0.5}Zn_{0.5}S nanosheets both exhibited high stability over 9 h (3 cycles) of measurement in a TEOA solution (Fig. S14). To the best of our knowledge, this efficiency in the TEOA aqueous solution is higher than those of most previously reported catalysts. Additionally, the apparent quantum yields (AQYs) of 7%-NiCo₂S₄/Cd_{0.5}Zn_{0.5}S at various wavelengths were determined, as shown in Figs. 8(c) and (d). The average H₂ evolution rate reached ~5.45 mmol·h⁻¹·g⁻¹ under irradiation with a wavelength of 365 ± 5 nm, and the corresponding AQY was calculated as 40.3%. This suggests the efficient regulation of the directed spatial separation of electron-hole pairs by the NiCo₂S₄/Cd_{0.5}Zn_{0.5}S heterostructures, as discussed below. For comparison, single-metal CoS_x-modified Cd_{0.5}Zn_{0.5}S nanosheets

were examined under identical conditions (a structural analysis is presented in the Supporting Information). As predicted, the activity of 7%-CoS_x/Cd_{0.5}Zn_{0.5}S was ~42.3 mmol·h⁻¹·g⁻¹, which was lower than that of 7%-NiCo₂S₄/Cd_{0.5}Zn_{0.5}S. This is reasonable, as numerous studies have theoretically and experimentally confirmed that the amount of active sites can be increased and the Gibbs free energy of reactant adsorption can be reduced by introducing a second ion into a specific material (e.g., NiCoP_x and CoMoS_x). The result here further highlighted the substitution effect of Co site by Ni atoms [25,32,34,53,54].

Fig. 8(e) presents the results for the photocatalytic HER with the Cd_{0.5}Zn_{0.5}S nanosheets, Cd_{0.5}Zn_{0.5}S nanoparticles, and 7%-NiCo₂S₄/Cd_{0.5}Zn_{0.5}S irradiated by visible light (420–780 nm). Unexpectedly, the average HER rate of the Cd_{0.5}Zn_{0.5}S nanoparticles was only ~3.2 mmol·h⁻¹·g⁻¹, which was significantly lower than that of the Cd_{0.5}Zn_{0.5}S nanosheets (~5.9 mmol·h⁻¹·g⁻¹). This indicates the advantages of the mesoporous microstructure of the Cd_{0.5}Zn_{0.5}S nanosheets, as discussed previously. The binary NiCo₂S₄/Cd_{0.5}Zn_{0.5}S composite exhibited higher activity under visible light (~12.7 mmol·h⁻¹·g⁻¹) than the Cd_{0.5}Zn_{0.5}S nanoparticles and nanosheets. However, a comparison with the efficiency under the full light exposure range (350–780 nm) revealed that the enhanced visible-light harvesting capacity contributed little to its overall HER performance, primarily owing to the sluggishness of Cd_{0.5}Zn_{0.5}S.

Given the economy of the catalyst in the sacrificial system and the inevitable ultraviolet light in practical applications, the aforementioned samples were also tested in ultrapure water (Fig. 8(f)) without any co-catalyst or pH regulation. For the Cd_{0.5}Zn_{0.5}S nanoparticles, almost no H₂ was identified by GC

owing to the degraded charge separation and surface kinetics of the nanoparticles in the absence of sacrificial agents. Interestingly, the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets exhibited an average H_2 evolution rate of $\sim 1395 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ after 3 h of the reaction. To the best of our knowledge, this is the highest value of a bare single photocatalyst for the photocatalytic H_2 evolution in pure water and is higher than those of numerous binary or ternary photocatalytic systems, as shown in Table S1. The average efficiency of 7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ was $2436 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ under identical conditions. This enhanced activity indicates that the separation efficiency and surface redox kinetics of the $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ heterojunction benefited from the NiCo_2S_4 . Nevertheless, no O was detected regardless of whether the nanosheets or binary composite were employed, owing to the favorable kinetics and thermodynamics of the reverse reaction of water splitting. Unfortunately, the activity of the samples was continuously attenuated over the 3 h of measurement; this problem should be solved in a future study.

To investigate the functionalization of the NiCo_2S_4 nanoparticles, photoelectrochemical and optical analyses were conducted. Fig. 9(a) indicates that the bare $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets exhibited a relatively low photocurrent density ($156 \mu\text{A}\cdot\text{cm}^{-2}$), whereas the higher transient photocurrent density ($245 \mu\text{A}\cdot\text{cm}^{-2}$) for 7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ indicates the rapid separation of electron-hole pairs and the enriched surface electrons of the $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ heterojunction [55,58]. Furthermore, electrochemical impedance spectroscopy revealed a smaller radius of the Nyquist plot semicircle for the composite (Fig. 9(b)), indicating the enhanced kinetics charge-carrier transfer between the heterogeneous interfaces. As expected, the HER polarization curves of the two samples indicated that

7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ had a higher cathodic current density and lower overpotential (Fig. 9(c)) [56,60,62]. By plotting the overpotential with respect to the logarithm of the current ($\log i$), the kinetic parameters of the HER were obtained (Fig. 9(d)), suggesting faster H_2 evolution kinetics over 7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$, whereas the adsorption and activation of water remained the rate-limiting step of the entire reaction [54]. Alshareef et al. [33] reported that NiCo_2S_4 behaves as a metal with high conductivity (several orders of magnitude higher than that of the corresponding oxide). Thus, the results of the present study suggest that the high property of the $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ heterojunction benefited from the synergetic contribution of the high conductivity and the enriched surface sites of NiCo_2S_4 . Hence, the heterojunction may function as an electron collector and a reduction site for adsorbed H^+ [61].

Subsequently, the band alignments of NiCo_2S_4 and $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ were investigated to confirm the directed transfer of photoelectrons from $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ to NiCo_2S_4 . Figs. 10(a) and (b) show the X-ray photoelectron VB and UV photoelectron spectra of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets, indicating that the VB potential and work function were +2.05 eV (vs. standard hydrogen electrode (SHE)) and 4.27 eV, respectively. The conduction-band (CB) potential was calculated to be -0.40 eV (vs. SHE). Furthermore, the UV photoelectron spectrum of NiCo_2S_4 was investigated. As shown in Fig. 10(b), the work function was 4.53 eV ($21.12 - 16.69 = 4.53$ eV) for prepared NiCo_2S_4 [25]. The foregoing results certify the up-bending band of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ when they contact and the thermodynamic feasibility of photoelectrons from the CB of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets to NiCo_2S_4 .

A photoluminescence (PL) analysis was performed to qualitatively determine the $\cdot\text{OH}$ concentrations ($E_{(\cdot\text{OH}/\text{OH}\cdot)} = +1.99$ eV

Fig. 9. Photocurrent density-time curves (a), Nyquist plots (b), HER polarization curves (c), and Tafel plots (d) for the two samples.

Fig. 10. (a) X-ray photoelectron valence-band (VB) spectra of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets. (b) UV photoelectron spectrum of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets. (c) UV photoelectron spectrum of the NiCo_2S_4 nanoparticles.

vs. SHE) of the two samples in an alkaline terephthalic acid aqueous solution (Figs. 11(a) and (b)) [19,57]. The 7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ exhibited strong signals, whereas the signals of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets were relatively weak after 60 min of exposure, indicating that the oxidizing capacity of the holes of 7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ was not degraded and that more $\cdot\text{OH}$ was generated in the case of 7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$. Additionally, it was found that the rapid separation of charge carriers benefited from the high conductivity of mixed-metallic NiCo_2S_4 . Notably, the signal of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets decreased within 60 min of irradiation owing to their poor photostability. However, the peak intensity for 7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ was steadily enhanced, indicating the rectified photostability. As shown in Figs. 11(c) and (d), the results of *in situ* electron paramagnetic resonance (EPR) spectroscopy agreed with those of the PL analysis. The foregoing findings indicate that the holes of the binary composites were well maintained in the VB of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets under light irradiation. The PL quenching of 7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ observed in the steady-state PL spectrum in Fig. 11(e) confirms that the recombination rate was significantly limited owing to

the directed migration of photoelectrons in the CB of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$. Thus, a Schottky contact might have been developed. The directed transfer of charge carriers is schematically illustrated in Fig. 11(f) [59]. The excited electrons of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ flowed into NiCo_2S_4 owing to its low energy level, and the holes left behind in the VB of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ induced another half-reaction in the aqueous solution.

4. Conclusions

Ultrathin mesoporous $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets (thickness of ~ 1.5 nm) were successfully fabricated via the multistep chemical transformation of inorganic-organic hybrid $\text{ZnS}(\text{en})_{0.5}$. The prepared nanosheets exhibited enhanced photocatalytic HER activity in the presence of a sacrificial agent. Additionally, they exhibited high H_2 production performance $\sim 1395 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ in pure water with no co-catalyst or other substance added, which is better than that of many previously reported catalysts. Moreover, ternary NiCo_2S_4 was combined with $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheets via mechanical mixing to enhance the photocatalytic H_2 evolution performance. The activity of

Fig. 11. PL spectra after $\cdot\text{OH}$ detection (a, b) and *in situ* EPR spectra (c, d) of the samples, (e, f) PL spectra of the samples and the charge-transfer route of the binary composites.

Graphical Abstract

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2D mesoporous ultrathin $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanosheet: Fabrication mechanism and application potential for photocatalytic H_2 evolution

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Efficient photocatalytic H_2 evolution over NiCo_2S_4 nanoparticle-modified 2D $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ ultrathin mesoporous nanosheets and corresponding charge transfer between interfaces.

7%- $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ reached $\sim 62.2 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ in TEOA and $\sim 2436 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ in pure water within 3 h of irradiation. A Schottky junction was formed over the binary heterojunctions. Furthermore, the 2D inorganic–organic hybrid $\text{Cd}_{0.5}\text{Zn}_{0.5}(\text{en})_x$ intermediate exhibited higher photocatalytic HER activity ($\sim 13.5 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) than the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles under the same conditions. This study provides an effective technique for fabricating highly efficient CdZnS-based photocatalyst.

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二维介孔超薄 $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ 纳米片：形成机制及光催化分解水制氢性能

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摘要: 太阳光驱动的光催化分解水产氢是一种绿色制氢技术, 并以氢为载体可实现太阳能向化学能的转化。目前开发高效、稳定的可见光催化剂仍是本领域的研究热点。在各类光催化材料中, $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ 固溶体比 TiO_2 及 $\text{g-C}_3\text{N}_4$ 具有更优异的光催化产氢活性, 但它一般为团聚了的纳米颗粒或纳米微球, 表面积小, 比表面反应迟缓, 从而限制了其实际应用。通常, 超薄多孔二维结构光催化剂具有高比表面积, 能够为反应物分子与催化剂之间提供大量接触界面并促进传质, 此外, 特定晶面暴露赋予了其大量不饱和配位表面原子, 使反应物分子更容易在催化剂表面吸附活化, 提升表面催化反应动力学。本文首先采用乙二醇与水的混合溶液制备了无机有机杂化的硫化锌-乙二醇(记为: $\text{ZnS}(\text{en})_{0.5}$)。随后, 分别以 $\text{ZnS}(\text{en})_{0.5}$ 为硬模板、以乙二醇为反应介质、氯化镉为镉源, 通过溶剂热阳离子交换得到了无机有机杂化的 $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ 中间产物。最后, 将 $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ 在纯水中进行水热反应脱除晶格内乙二醇分子得到了2D介孔超薄 $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ 纳米片。TEM测试发现, 纳米片表面存在大量孔洞, 其主要源于 $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}(\text{en})_x$ 的相变过程及其晶格内乙二醇分子的逃逸导致的晶格畸变。AFM观察结果表明, 最终产物 $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ 纳米片厚度约为1.5 nm; 其比表面积可达63.5 m^2/g , 几乎是相应纳米颗粒的两倍。以三乙醇胺(TEOA)为牺牲剂时, $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ 纳米片的产氢速率达到19.1 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, 是相应纳米颗粒的两倍多。即使在纯水中, $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ 纳米片产氢速率仍可达到1395 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, 超过了目前所报道的未加修饰的光催化剂的活性。其优异的活性源于其独特的结构优势, 包括载流子迁移距离的缩短、表面不饱和原子及比表面积的增加。但在纯水中其严重的光腐蚀仍然亟待克服。此外, 为进一步增强其活性, 通过机械复合的方法得到了 $\text{NiCo}_2\text{S}_4/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ 二元复合光催化剂, 其在TEOA为牺牲剂时制氢速率可达62.2 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, 在纯水制氢速率达到2436 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ 。电化学、UPS及EPR分析表明, NiCo_2S_4 与 $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ 纳米片间形成了肖特基接触, 进一步促进了载流子分离能力, 提高了复合物的产氢活性。以本工作为基础, 还可制备其他高活性的CdZnS-基功能光催化材料用于太阳能转化或其他领域。

关键词: 介孔; 超薄; $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ 纳米片; 光催化; 产氢

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