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Article

Constructing low-cost Ni_3C /twin-crystal $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ heterojunction/homojunction nanohybrids for efficient photocatalytic H_2 evolution

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ABSTRACT

The development of low-cost semiconductor photocatalysts for highly efficient and durable photocatalytic H_2 evolution under visible light is very challenging. In this study, we combine low-cost metallic Ni_3C cocatalysts with twin nanocrystal $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (ZCS) solid solution homojunctions for an efficient visible-light-driven H_2 production by a simple approach. As-synthesized $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ -1% Ni_3C (ZCS-1) heterojunction/homojunction nanohybrid exhibited the highest photocatalytic H_2 -evolution rate of $783 \mu\text{mol h}^{-1}$ under visible light, which is 2.88 times higher than that of pristine twin nanocrystal ZCS solid solution. The apparent quantum efficiencies of ZCS and ZCS-1 are measured to be 6.13% and 19.25% at 420 nm, respectively. Specifically, the homojunctions between the zinc blende and wurtzite segments in twin nanocrystal ZCS solid solution can significantly improve the light absorption and separation of photogenerated electron-hole pairs. Furthermore, the heterojunction between ZCS and metallic Ni_3C NP cocatalysts can efficiently trap excited electrons from ZCS solid solution and enhance the H_2 -evolution kinetics at the surface for improving catalytic activity. This study demonstrates a unique one-step strategy for constructing heterojunction/homojunction hybrid nanostructures for a more efficient photocatalytic H_2 evolution compared to other noble metal photocatalytic systems.

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1. Introduction

Since Fujishima and Honda first reported photoelectrochemical water splitting into H_2 and oxygen over TiO_2 photoe-

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electrodes under UV light in 1972 [1], photocatalytic H₂ evolution has been considered as a promising approach to produce H₂ by converting solar energy to chemical energy. Therefore, various types of semiconductor photocatalysts have been developed for efficient photocatalytic H₂ evolution from water in the past decades [2,3]. Among them, CdS and Zn_xCd_{1-x}S solid solutions have attracted significant attention owing to their narrow bandgaps (absorbing light at extended wavelengths) and energy band positions with greater driving forces [4–7]. However, the fast recombination of photogenerated electron-hole pairs and significant photocorrosion resulted in unsatisfactory photoactivity, thereby limiting their practical applications [8]. Generally, the recombination of photogenerated carriers can be classified into bulk and surface recombination. It is still a significant challenge to suppress both the bulk and surface recombination of photogenerated electron-hole pairs in photocatalytic H₂ generation.

As generally perceived, nanostructured sulfide-based photocatalysts, such as zero-dimensional nanoparticle (NP)/nanocrystals, one-dimensional (1D) nanowire/nanorods, two-dimensional nanoplates/nanosheets [9], and three-dimensional nanoflowers/nanospheres [10,11] can significantly shorten the migration distance of carriers, facilitate an efficient charge transfer, and reduce recombination in crystals [12,13]. Therefore, they have been regarded as promising for decreasing bulk recombination in semiconductors. Recently, Zn_xCd_{1-x}S solid solution with a twin crystal structure has attracted research interest owing to the successful formation of homojunctions between different crystal phases [14–17]. The homojunctions can improve the photocatalytic H₂ evolution activity of pristine sulfite photocatalysts through an enhanced separation efficiency of photogenerated electron-hole pairs without any cocatalyst [14–18]. For example, Liu et al. synthesized twin-induced 1D homojunction Zn_{0.5}Cd_{0.5}S (ZCS) nanorods with a type-II staggered band alignment and achieved an improved charge separation. The quantum efficiency reached 62% without requiring a noble-metal cocatalyst. Therefore, twin crystal Zn_xCd_{1-x}S solid solutions have been considered as superior visible-light-responsive photocatalysts for H₂ evolution from water, owing to the effectively suppressed bulk recombination of photogenerated electron-hole pairs [19]. However, several disadvantages should be resolved for further enhancing the photocatalytic H₂-evolution activities over the twin crystal Zn_xCd_{1-x}S solid solution owing to the fast surface charge recombination and insufficient number of surface reactive sites [15].

Several modification strategies, including loading cocatalysts [9,20], heteroatom doping [21,22], constructing heterojunctions [23–25], coupling with nanocarbons [26], and constructing Z-scheme systems have been investigated considerably to decrease the surface recombination in sulfide-based semiconductors. Among them, loading cocatalysts has been considered as one of the most effective strategies for accelerating H₂-evolution kinetics and promoting surface charge separation. Previous studies have confirmed that noble metals, such as Pt, Ag, and Au, could efficiently improve the H₂ evolution activity of semiconductor photocatalysts [27,28]. However, the high cost and scarcity of these noble metals significantly limited

their commercial development and application [8]. Therefore, non-noble-metal H₂-evolution cocatalysts must be developed for efficient photocatalytic activities. Thus far, various Earth-abundant noble metal-free cocatalysts, such as MoS₂ [9,20,29,30], Ni(OH)₂ [31], NiS_x [26,32–34], Co₃O₄ [35], CoP_x [36–38], Mo₂C [39], and Ni₂P [40,41], have been studied as cocatalysts to enhance the charge carrier separation and H₂-evolution kinetics on the surfaces of CdS and Zn_xCd_{1-x}S solid solutions. Additionally, transition metal carbides with high electronic conductivities [42], including WC [43], Ni₃C [44], Mo₂C [39], and Ti₃C₂ MXene [45], have served as promising cocatalysts for efficient photocatalytic H₂ evolution in acidic or basic media. In our previous study, Ni₃C NPs exhibited superior photocatalyst H₂-evolution activities over CdS nanosheets in Na₂S–Na₂SO₃ solution [44]. Jiang et al. [46] used Ni₃C as a cocatalyst to modify Zn_{0.3}Cd_{0.7}S nanorods. However, the activity and stability of Zn_{0.3}Cd_{0.7}S nanorods were unsatisfactory. Additionally, homojunctions in CZS solid solution can effectively separate bulk electron-hole pairs. Meanwhile, CZS solid solution homojunctions show stable photocatalytic performance under visible light. Therefore, the synergistic effects between the ZCS homojunctions and the Ni₃C cocatalyst are expected to yield better photocatalytic performance. Based on previous studies, the promising and low-cost Ni₃C NPs should be employed as cocatalysts for improving photocatalytic H₂ evolution instead of the twin nanocrystal ZCS solid solution to simultaneously achieve suppressed bulk and surface charge separation and improved H₂-evolution kinetics.

For the first time, we designed an effective photocatalytic system composed of a twin nanocrystal ZCS solid solution and low-cost Ni₃C NPs. In this study, we prepared the twin nanocrystal ZCS solid solution by a precipitation-hydrothermal method [14]. Subsequently, Ni₃C/twin nanocrystal Zn_{0.5}Cd_{0.5}S composites were successfully synthesized by a facile grinding method. The homojunctions between the zinc blende and wurtzite segments in the twin nanocrystal ZCS solid solutions could significantly improve the separation of photogenerated electron-hole pairs, thereby leading to an improved H₂ evolution performance. Previous studies have proven that Ni₃C NPs could serve as a cocatalyst to increase visible-light absorption and the number of HER active sites, promote charge separation and transfer, and accelerate surface H₂-evolution kinetics [44]. Therefore, the enhanced photocatalytic performance of Ni₃C/twin nanocrystal Zn_{0.5}Cd_{0.5}S composites might be attributed to the synergistic effects between the ZCS homojunctions and the Ni₃C cocatalyst. The possible mechanism for improving the photocatalytic activity of Ni₃C/twin nanocrystal Zn_{0.5}Cd_{0.5}S composite photocatalysts is further analyzed and proposed according to the following experimental results. This study suggests that the combination of homojunctions and Earth-abundant transition metal carbide cocatalysts is a promising method to fabricate effective photocatalytic systems.

2. Experimental

2.1. Preparation of photocatalysts

2.1.1 Synthesis of twin nanocrystal ZCS solid solution

Twin nanocrystal ZCS solid solutions were prepared by a simple precipitate/hydrothermal method [14]: 15 mL of 4 M NaOH aqueous solution was added into an aqueous solution (60 mL) containing 15 mmol of $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ and 15 mmol of $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$; next, 37.5 mmol of thioacetamide was dispersed into the above solution containing a mixture of $\text{Cd}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$. The entire experiment was performed under constant magnetic stirring. The suspension was further stirred for 30 min. Next, the reacting mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 24 h. After cooling to room temperature, a yellow product was collected by centrifugation and then washed several times with deionized water and ethanol, separately. Finally, it was dried at 60 °C for 12 h in a vacuum oven.

A twin nanocrystal $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ solid solution with adjusted Zn/Cd molar ratios can be synthesized using the method above.

2.1.2 Synthesis of Ni_3C NPs

Ni_3C NPs were synthesized using a previously reported method, 2 mmol of $\text{Ni}(\text{Ac})_2$ and 14.1 mL of oleylamine were mixed into a 100 mL three-neck round-bottom flask. The mixture was stirred magnetically under nitrogen flow. Next, it was heated to 250 °C and maintained at this temperature for 2 h. Furthermore, 30 mL of acetone was added into the mixture after cooling to room temperature. The resulted Ni_3C NPs were collected by centrifugation (5000 rpm, 15 min) and washed eight times with deionized water and ethanol, separately. Next, the black products were dried at 60 °C for 10 h in an oven. Finally, the Ni_3C NPs were dispersed in hexane for long-time storage.

2.1.3 Synthesis of $\text{Ni}_3\text{C}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites

$\text{Ni}_3\text{C}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites were prepared as follows: 200 mg of prepared ZCS powders and 1 mL of Ni_3C NPs dispersed in hexane (2 mg mL^{-1}) were ground together in an agate mortar. Next, the mixed solid powders were redispersed by adding 2 mL of ethanol and ground again. Finally, the $\text{Ni}_3\text{C}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites were dried in an oven at 60 °C for 10 h.

The obtained composite powder with 1 wt% Ni_3C NPs was represented as ZCS-1. The other composites with different contents of Ni_3C were prepared using the same method. The other $\text{Ni}_3\text{C}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites with Ni_3C NP percentages of 0.5 wt%, 1.5 wt%, and 2 wt% were denoted as ZCS-0.5, ZCS-1.5, and ZCS-2, respectively.

2.2 Characterization

Similar instruments and methods were used to measure the powder X-ray patterns, X-ray photoelectron spectra, N_2 adsorption/desorption isotherms, UV-vis diffuse reflectance spectra, photoluminescence (PL) spectra, and time-resolved decay curves [47–51].

2.3 Photocatalytic H_2 experiments

The photocatalytic H_2 -evolution reaction was performed in

a 100 mL three-neck flat-bottom Pyrex flask, under the irradiation of a 300 W Xe lamp (PLS-SXE300, Beijing Perfect light Technology Co. Ltd. China) with a UV cutoff filter ($\lambda \geq 420$ nm, ca. 160 mW cm^{-2}). For detailed testing, 50 mg of photocatalyst was dispersed in 80 mL of a mixture solution comprising Na_2S (0.25 M) and Na_2SO_3 (0.25 M). The volume of the evolved gas was recorded after 1 h of irradiation under visible light.

The apparent quantum efficiency (QE) was measured under similar photocatalytic reaction conditions, 50 mg of the photocatalyst was dispersed in 80 mL of a sacrificial reagent aqueous solution (0.25 M Na_2S - Na_2SO_3) with constant stirring and an ultrasonic bath. The QE was measured using a 300 W Xe lamp and a 420 nm band pass filter. Finally, it was calculated according to the following equation:

$$\begin{aligned} \text{QE} (\%) &= \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} * 100\% \\ &= \frac{\text{Number of hydrogen molecules}}{\text{Number of incident photons}} * 100\% \\ &= (M * N_A * 2) / ((I * A * t) / (E_g * J)), \end{aligned}$$

where M represents the amount of H_2 generation; N_A represents the Avogadro constant; I is the light intensity; A is the light incident area; t is the light incident time; E_g and J are fixed constants.

2.4 Electrochemical tests

All the electrochemical tests, including the photocurrent-time curves (I - t curves), electrochemical impedance spectroscopy (EIS), and electrocatalytic H_2 evolution, were performed according to our previously reported methods [44,47–52].

3. Results and discussion

3.1 Morphology, structure, and composition characterization

The structures and morphologies of the photocatalysts were investigated using transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). As shown in Fig. 1(A), (B), (D) and (E), the as-prepared twin nanocrystal ZCS solid solution exhibits a lateral dimension in the range of 50–100 nm, which is in accordance with that obtained in previous studies [14,18]. Black and white strips can be clearly identified from Fig. 1(B) and (E), indicating the existence of strip-like structures on the surface of the nanocrystal. In the HRTEM image (Fig. 1(C)), boundaries, wurtzite phase, and zinc-blende phase in the twin nanocrystal can be distinguished, indicating the existence of homojunctions between the zinc blende (ZB) and wurtzite (WZ) segments in twin nanocrystal ZCS solid solution [15]. Furthermore, the fast Fourier transform (FFT) pattern confirms the coherent twin boundaries (Fig. 1(F)) [14]. The TEM and HRTEM images proved that the obtained ZCS solid solution exhibits a twin crystal structure.

As shown in Fig. 2(A), the average grain diameter of the Ni_3C NPs was approximately 50 nm. As shown in Fig. 2B, the strip-like structure is consistent with the structure of the twin

Fig. 1. (A, B, D, E) TEM images of twin nanocrystal ZCS solid solution, (C) HRTEM image of twin nanocrystal ZCS solid solution, (F) FFT pattern indicating that the twins in each grain are parallel to each other in (111) planes.

nanocrystal ZCS solid solution. Some smaller NPs were uniformly distributed on the surface of the twin nanocrystal ZCS solid solution, which were Ni_3C NPs. The HRTEM image shows that the twin nanocrystal ZCS solid solution was intimately coupled with the loaded Ni_3C NPs (Fig. 2(C)). It is well known that the intimate contact interface could provide charge transfer and channel trapping for improving carrier separation efficiency. Meanwhile, as shown in the HRTEM image (Fig. 2(C)), the lattice spacing value of 0.20 nm corresponded to the (113) diffraction plane of hexagonal Ni_3C [53]. The interplanar spacing of 0.31 nm corresponded to the (111) diffraction plane of ZCS. The corresponding EDX elemental mapping of ZCS-1 composite in Fig. 2(E)–(I) further proved the co-existence of Zn, Cd, S, Ni, and C elements in the sample. Zn and Cd elements were uniformly distributed in the same area, implying the formation of a solid solution between ZnS and CdS .

Because the Zn/Cd ratio in the solid solution was important for photocatalytic H_2 -evolution activity, the element composition of ZCS-1 was investigated using the electron dispersive spectrum (EDS). As shown in Table 1. The experiment results indicated that the Zn/Cd ratio in the composite was approximately 0.5/0.5, which agreed well with the initial raw material ratio in the synthetic procedure. The C content in the experiment data was considerably high, which might be due to the unavoidable adventitious carbon on the surfaces of the sample and the carbon film. According to the Ni content, the

Fig. 2. (A) TEM image of Ni_3C NPs; TEM (B) and HRTEM (C) images of ZCS-1; (E–I) Corresponding elemental mapping of ZCS-1.

loading content of the Ni_3C NPs was calculated to be 0.95%, which was close to the initial proportion (1%). All the analysis results proved that the twin nanocrystal ZCS solid solution, Ni_3C NPs, and Ni_3C /ZCS composites were synthesized successfully. The successfully synthesized CZS-1 can be further confirmed by the following XRD patterns.

The crystal phases of the prepared samples were investigated using their XRD patterns. As shown in Fig. 3(A), the crystal phases of the as-prepared ZnS and CdS samples correspond well to the cubic phase ZnS (PDF# 05-0566) and hexagonal phase CdS (PDF# 41-1049), respectively. However, the diffraction patterns of the twin nanocrystal $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ solid solution with different Zn/Cd molar ratios exhibit multiphase characteristics, indicating that increasing the amount of zinc will transform the crystal phases of the twin nanocrystal $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ solid solution from hexagonal-phase CdS to cubic-phase ZnS . In Fig. 3(B), the six peaks at 2θ values of 39.55° , 41.92° , 44.95° , 58.91° , 71.75° , and 78.74° correspond to the (110), (006), (113), (116), (300), and (119) planes of the hexagonal-phase Ni_3C (PDF# 72-1467), respectively. The analysis results suggested that the twin nanocrystal ZCS solid solution and the Ni_3C NPs were fabricated successfully using the reported methods [54]. Furthermore, these results agreed well with the results of TEM and HRTEM analyses. However, no characteristic peaks of Ni_3C were identified in the XRD patterns of $\text{Ni}_3\text{C}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites, which might be caused by the low contents and high dispersion of Ni_3C NPs within the composites.

XPS analysis was performed to obtain a deeper insight into the surface elemental compositions of the prepared nanomaterials. Fig. 4 shows the XPS profile of ZCS-1 sample. The binding energy scales were referenced by calibrating the C 1s peak to 284.8 eV. The fully scanned spectra in Fig. 4(A) indicate the existence of Zn, Cd, S, Ni, and C in the ZCS-1 composite photocatalyst. The oxidation states of the elements were confirmed via the high-resolution XPS profile of Zn 2p, Cd 3d, S 2p, Ni 2p,

Table 1
Experimental data of EDS of ZCS-1.

Sample	Atomic fraction (at%)					Weight fraction (wt%)				
	Zn	Cd	S	Ni	C	Zn	Cd	S	Ni	C
ZCS-1	15.33	15.58	30.54	0.56	37.99	23.68	41.47	23.23	0.79	10.83

Fig. 3. XRD patterns of the twin nanocrystal $\text{Zn}_{1-x}\text{Cd}_x\text{CdS}$ solid solution with different Zn/Cd molar ratios (A), ZCS-X composites and Ni_3C (B).

Fig. 4. XPS survey profile (A) and high-resolution XPS profile of Zn 2p (B), Cd 3d (C), S 2p (D), Ni 2p (E), and C 1s (F) of the ZCS-1 sample.

and C 1s (Fig. 4(B)–(F)). The binding energies of 1021.9 eV ($2p_{3/2}$) and 1045 eV ($2p_{1/2}$) with a peak separation of 23.1 eV are typically assigned to Zn^{2+} (Fig. 4(B)) [55]. The binding energies of Cd $3d_{5/2}$ and Cd $3d_{3/2}$ for the twin nanocrystal ZCS solid solution were 405.2 and 411.9 eV, respectively, which confirmed the dominant oxidation state of Cd^{2+} (Fig. 4(C)) [56]. The results confirmed the co-existence of Zn^{2+} and Cd^{2+} in ZCS. In addition, S 2p peaks appeared at binding energies of 161.4 and 162.6 eV, which could be attributed to the S $2p_{3/2}$ and S $2p_{1/2}$ levels, respectively (Fig. 4(D)). The XPS characteristic peaks of Ni $2p_{3/2}$ and Ni $2p_{3/2}$ satellites were located at 856.4 and 861.8 eV, further confirming the presence of Ni^{+} in Ni_3C (Fig. 4(E)). As shown in Fig. 4(F), three peaks are clearly observed in the C 1s XPS profile. The peak at 284.3 eV could be assigned to Ni–C bonds, with a second peak at 286.2 eV assigned to the C–O functional group. Between these two peaks, a third peak at 284.8 eV could be attributed to sp^2 hybridized carbon atoms in C–C bonds. All the results confirmed the formation of a Ni_3C -modified twin nanocrystal ZCS solid solution.

3.2. Textural and optical properties

The textural properties of the prepared twin nanocrystal ZCS solid solution and ZCS-1 were measured by N_2 adsorption-desorption isotherms and the corresponding pore size distribution curves. As shown in Fig. 5(A), a well-defined step at P/P_0 of 0.8–1.0 was obtained from the N_2 adsorption-desorption isotherms of two samples, which corresponded to type-IV adsorption-desorption isotherms. Meanwhile, the mean pore size distributions were at approximately 75 nm (Fig. 5(A) inset). The BET surface areas and pore volumes of ZCS and ZCS-1 are further summarized in Fig. 5(B). It is evident that the BET surface area and pore volume of ZCS-1 are larger than those of the twin nanocrystal ZCS solid solution, which may be caused by the coverage of the Ni_3C NPs. All the results suggested that the improved catalytic activity of ZCS-1 was partially related to the changes in the specific surface area.

The optical properties of the as-prepared samples were evaluated using UV-vis absorption spectroscopy (Fig. 6). As shown, the absorption edges appeared at approximately 510 nm for all samples (Fig. 6(A)). Compared to ZCS, no distinct absorption edge shift could be identified in the composite samples, suggesting that the Ni_3C NPs were not doped into the pure twin nanocrystal ZCS solid solution. It is evident that the ab-

Fig. 5. (A) N₂ adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) of ZCS and ZCS-1. (B) BET surface areas and pore volumes of ZCS and ZCS-1.

Fig. 6. (A) UV-vis absorption spectra of as-prepared samples and optical images of samples (inset); (B) Tauc plots of the UV-vis spectra.

sorbance in the visible-light region (> 500 nm) enhanced significantly with increasing number of Ni₃C NPs. Meanwhile, the colors of the composite samples changed from light yellow to dark green, which was consistent with the changes in absorbance (Fig. 6(A) inset). These results indicated that loading Ni₃C NPs on the surface of twin nanocrystal ZCS solid solution could effectively increase the absorbance in the visible light range, thereby yielding a more efficient utilization of light. To further discuss the optical properties of the samples, the bandgap energies of ZCS and ZCS-1 were estimated using the following equation [56]:

$$a = A(h\nu - E_g)^{n/2}/h\nu,$$

where a , A , h , ν , and E_g are the absorption coefficient, proportionality constant, Planck's constant, frequency of the incident light, and band energy, respectively. n is equal to 1 for a direct transition. The Tauc plots of the UV-vis spectra for the twin nanocrystal ZCS solid solution and ZCS-1 are exhibited in Fig. 6(B). The corresponding bandgaps of the twin nanocrystal ZCS solid solution and ZCS-1 were estimated to be 2.33 and 2.27 eV, respectively. The band energy of ZCS-1 was slightly narrower than that of the twin nanocrystal ZCS solid solution, which might be caused by the interfacial contact between the twin nanocrystal ZCS solid solution and the Ni₃C NPs. It is thought that the enhanced absorbance of the Ni₃C/Zn_{0.5}Cd_{0.5}S samples in visible light range might be beneficial for enhancing the photocatalytic H₂-evolution activity.

3.3. Photocatalytic H₂ evolution activity and stability

The photocatalytic H₂-evolution activities of all the prepared photocatalysts were evaluated under 300 W xenon lamp irradiation ($\lambda \geq 420$ nm) using a 0.25 M Na₂S-Na₂SO₃ aqueous solution as a sacrificial agent (Fig. 7). As shown in Fig. 7(A), the time courses of H₂ evolution over all the samples increased steadily with time during the photocatalytic reactions, suggesting the relatively excellent photostability under visible-light irradiation. To further investigate the H₂-evolution activity, the average H₂-evolution rates over various samples were calculated, as shown in Fig. 7(B) and 7(C). No H₂ evolution could be detected when bare Ni₃C was used as the photocatalyst. Furthermore, the twin nanocrystal ZCS solid solution exhibited better H₂-evolution activity (272 $\mu\text{mol h}^{-1}$) compared to Zn_{1-x}Cd_xS solid solutions with different Zn/Cd ratios (Fig. 7(C)). The corresponding QE at 420 nm was calculated to be 6.13%. These data indicate that the Ni₃C NPs significantly affect the determination of photocatalytic activity. Loading a small percentage of Ni₃C NPs (0.5–4 wt%) resulted in a significant increase in the H₂-evolution rates of Ni₃C/Zn_{0.5}Cd_{0.5}S composites. When the percentage was 1.0 wt% (ZCS-1), the highest H₂-evolution rate reached 783 $\mu\text{mol h}^{-1}$ with a QE of 19.25% at 420 nm, which was approximately 2.88 and 3.14 times higher than those of ZCSs. However, the photocatalytic activity of ZCS-1 was still much lower than that of ZCS-1%Pt, suggesting that the interfacial contact between Ni₃C and the twin nanocrystal ZCS must be further improved. These results indicated that the Ni₃C NPs could effectively decrease the recombination of photogenerated electron-hole pairs. Clearly, excess Ni₃C cocatalyst on the twin nanocrystal ZCS solid solution could

Fig. 7. Time courses (A) and average rates (B) of H₂ evolution over different composite photocatalysts. (C) Comparison of H₂ evolution activities of Ni₃C, twin nanocrystal Zn_{1-x}Cd_xS solid solutions with different Zn/Cd ratios, ZCS-1 composite, and ZCS-1%Pt. (D) Wavelength dependence of the apparent quantum efficiencies for the ZCS-1 sample. Reaction conditions: 50 mg of catalyst; 80 mL of 0.25 M Na₂S-Na₂SO₃ aqueous solution; xenon lamp (300 W) light source with a UV cutoff filter ($\lambda \geq 420$ nm).

cause a relative decrease in the photocatalytic H₂-evolution activity, owing to the incident-light shielding of the active sites on the ZCS twinned nanocrystal surface.

In Fig. 7(D), the wavelength-dependent apparent quantum yields (AQY) of ZCS-1 photocatalyst are shown in a 0.25 M Na₂S-Na₂SO₃ aqueous solution under different monochromatic light irradiations. The AQYs at 405, 420, 475, 520, and 550 nm were evaluated to be 20.41%, 19.25%, 8.78%, 2.84%, and 2.39%, respectively. The variation trend of the AQYs exhibited a closely coincident relationship with the UV-vis absorption spectrum of the ZCS-1 sample, further confirming that visible light absorption is important in the realization of photocatalytic H₂ evolution.

The long-term photostability of the photocatalyst is an important parameter for its practical application. In this study, the photostability experiment of ZCS-1 and ZCS samples for four reaction cyclic runs was performed (Fig. 8). For ZCS, only a 6%

activity loss was recorded after a 12 h visible light irradiation. However, the experimental data indicated that the composite sample lost 23% of the original photocatalytic H₂-evolution activity after 12 h of visible light irradiation, which might be caused by the gradual fall-off of the Ni₃C NPs from the twin nanocrystal ZCS solid solution. The result confirmed that the Ni₃C/Zn_{0.5}Cd_{0.5}S composites were relatively stable for the photocatalytic H₂ evolution from water under visible light irradiation.

3.4. Charge separation and transfer mechanism

In addition, the surface reaction processes, including the photoexcited energy, electron transfer, and recombination over the twin nanocrystal ZCS solid solution and the ZCS-1 photocatalysts were further verified by photoluminescence (PL) analysis under an excitation wavelength of 230 nm. As dis-

Fig. 8. Repeated time courses of photocatalytic H₂ evolution on ZCS-1 (A) and ZCS (B) samples. Reaction conditions: 50 mg of catalyst; 80 mL of 0.25 M Na₂S-Na₂SO₃ aqueous solution; xenon lamp (350 W) light source with a UV cutoff filter ($\lambda \geq 420$ nm).

Fig. 9. PL spectra (A) transient photocurrent responses (I - t curves) (B), electrochemical impedance spectroscopy Nyquist plots (C), and Mott-Schottky (MS) plots (D) of ZCS and ZCS-1 photocatalysts.

played in Fig. 9(A), all samples exhibited similar emission trends, which could be attributed to the recombination of photogenerated electron-hole pairs in the twin nanocrystal ZCS solid solution. Furthermore, the ZCS-1 composite photocatalyst exhibited a much lower PL intensity compared to the pure twin nanocrystal ZCS solid solution, suggesting the efficient transfer of photogenerated electrons and longer lifetime of photogenerated charge carriers in the composite photocatalyst. This result is consistent with the enhancement in the photocatalytic activity. The experimental results further indicated that the existence of Ni_3C as cocatalysts could efficiently improve the separation and transfer of photogenerated charge carriers in the composite.

To further investigate the improved separation efficiency of the photogenerated charge carriers, the transient photocurrent responses (I - t curves) of the pure twin nanocrystal ZCS solid solution and ZCS-1 composite photocatalysts were tested in a 0.1 M Na_2SO_4 aqueous solution under visible light irradiation at 0.1 V vs. Ag/AgCl. As shown in Fig. 9(B), the photocurrent density of the ZCS-1 samples was higher (approximately thrice) than that of the pure twin nanocrystal ZCS solid solution under the same experimental condition, suggesting the effective charge transfer and separation in the $\text{Ni}_3\text{C}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ system. The enhanced photocurrent might have contributed to the enhancement in the photocatalytic H_2 -evolution activity, according to previous reports [44].

EIS is one of the most powerful characterization techniques to investigate the interfacial charge transfer resistance. The arc radius on the EIS Nyquist plots of the samples are shown in Fig. 9(C), which can be simulated well using an equivalent circuit diagram. The Nyquist plot of ZCS-1 shows a smaller arc radius compared to that of the twin nanocrystal ZCS solid solution, suggesting that the loading of Ni_3C can significantly reduce the transfer resistances across the solid-liquid interface. This promotes the interfacial separation of photogenerated charge car-

riers significantly. Therefore, this result indicates that Ni_3C is pivotal in improving the charge transfer and separation efficiency, which can enhance the photocatalytic H_2 -evolution activity.

The Mott-Schottky (MS) plot was used to study the effect of Ni_3C on the flat-band (V_{fb}) edge positions of the ZCS-1 photocatalyst; the V_{fb} value is the difference between the Fermi level and the water-reduction potential [47]. In Fig. 9(D), the positive slopes demonstrate the n-type semiconductor properties of the samples. The decreasing slope indicates that loading Ni_3C can increase the carrier density of the composite, thereby improving the photocatalytic H_2 evolution performance [57,58]. The flat band potentials for the twin nanocrystal ZCS solid solution and ZCS-1 were estimated to be -1.25 and -1.17 V (vs. Ag/AgCl), respectively. The evident positive shift proved the strong interaction between the twin nanocrystal ZCS solid solution and the Ni_3C , which further promoted photogenerated electron transfer.

The separation and transfer processes of the photogenerated charge carriers were further revealed by fluorescence lifetime measurements. The average lifetime can be calculated using the following equation [59]:

$$\langle t \rangle = (A_1 t_1^2 + A_2 t_2^2) / (A_1 t_1 + A_2 t_2)$$

As shown in Fig. 10, the average lifetimes of ZCS and ZCS-1 were 4.6939 and 3.2492 ns, respectively. This observed shortening of emission lifetime indicated the emergence of a nonradiative pathway from the electronic interaction between Ni_3C and ZCS [59,60], thereby resulting in efficient photogenerated electrons between ZCS and Ni_3C .

3.5. The proposed photocatalytic mechanism

A polarization curve was employed to further investigate the function of Ni_3C cocatalysts in enhancing the photocatalytic H_2 evolution performance. Fig. 11 shows the polarization

Fig. 10. Time-resolved transient PL decay of twin nanocrystal ZCS solid solution (A) and ZCS-1 (B).

Fig. 11. Polarization curves of the photocatalysts were measured at a scan rate of 5 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ solution (A) and $0.25 \text{ M Na}_2\text{S-Na}_2\text{SO}_3$ aqueous solution (B).

curves of the pure twin nanocrystal ZCS solid solution, ZCS-1, and Ni_3C samples in different electrolytes. As displayed in Fig. 11(A), the cathodic current ranging from -0.6 to -1.1 V vs. NHE can be attributed to the electrocatalytic H_2 evolution. Compared to that of the pure twin nanocrystal ZCS solid solution, the cathodic current densities of the ZCS-1 and Ni_3C electrodes exhibited significant enhancements. All samples exhibited the same changing trend of cathodic current densities in the $0.25 \text{ M Na}_2\text{S-Na}_2\text{SO}_3$ aqueous solution (Fig. 11(B)), indicating that Ni_3C

NPs could accelerate the electrocatalytic H_2 -evolution kinetics and decrease the activation energy barrier for H_2 evolution.

As displayed in Fig. 12(A) and (B), the valence band maximum positions (VBM) for ZCS and ZCS-1 were estimated to be 1.49 and 1.40 V (vs. NHE), respectively. According to the bandgap energy and VBM position, the corresponding CBM position could be calculated to be -0.84 and -0.87 V (vs. NHE), respectively. The electronic band structures of the two samples are shown in Fig. 12(C). It was observed that loading Ni_3C as

Fig. 12. Valence-band XPS profile of twin nanocrystal ZCS solid solution (ZCS) (A), ZCS-1 (B), corresponding bandgap structures (C) of two photocatalysts.

the cocatalyst could slightly increase the CB energy of $\text{Ni}_3\text{C}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites, which could improve the reduction ability of photogenerated electrons, thereby enhancing the photocatalytic activity. In addition, loading Ni_3C NPs could effectively narrow the bandgap of the twin nanocrystal ZCS solid solution for increasing visible-light absorbance, which was beneficial for increasing the photocatalytic H_2 -evolution activity.

According to previous reports together with the analyses above, the possible photocatalytic H_2 -evolution reaction mechanism over the $\text{Ni}_3\text{C}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites under visible light irradiation is presented in Scheme 1. Under visible light irradiation, the electrons were excited rapidly from the valence band (VB) to the conduction band (CB) and then reacted with H^+ ions to form H_2 . In the $\text{Ni}_3\text{C}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite, compared to that of zinc blende segments, the up-shift of both the CB and VB energy levels in the wurtzite segment could result in an efficient separation of both the bulk and surface recombination of photogenerated electron-hole pairs. The intimate contact at the atomic level for the homojunctions between two phases is posited to promote the separation and transfer of photogenerated charge carriers. Owing to the energy level difference of the wurtzite-zinc homojunction, the photogenerated electrons on the CB of the wurtzite segments will transfer to the CB of the zinc blende segments. On the contrary, the photogenerated holes will be transferred and fixed in the WZ region regardless of their generation site. Subsequently, the photogenerated electrons from either the wurtzite or zinc blende segment will be transferred to the Ni_3C NPs for H_2 evolution because of its high electrical conductivity and low electrocatalytic H_2 -evolution overpotential, which further improves the separation and transfer efficiency of the photogenerated charge carriers. Moreover, the holes localized in the WZ region with strong oxidation ability can be quickly removed by the $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ mixed aqueous solution, thereby further enhancing the photocatalytic H_2 -evolution activity. Therefore, it is evident that the excellent synergistic effects of the homojunctions and the Ni_3C cocatalyst can improve the separation efficiency of the photogenerated electron-hole pairs and accelerate the H_2 evolution

kinetics to achieve a significant enhancement in photocatalytic H_2 -evolution activity in $\text{Ni}_3\text{C}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites.

4. Conclusions

In summary, $\text{Ni}_3\text{C}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite photocatalysts were successfully synthesized via a facile grinding method, which exhibited superior photocatalytic activities for H_2 evolution from water under visible light irradiation using sacrificial reagents. Under the optimal photocatalytic conditions, the as-synthesized ZCS-1 sample exhibited the highest photocatalytic H_2 -evolution rate of $783 \mu\text{mol h}^{-1}$ in $0.25 \text{ M Na}_2\text{S}-\text{Na}_2\text{SO}_3$ aqueous solution, which was 2.88 times higher than that of the pristine twin nanocrystal ZCS solid solution. The measured QE values of the twin nanocrystal ZCS solid solution and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}-1\%\text{Ni}_3\text{C}$ were 6.13% and 19.25% at 420 nm, respectively. According to a previous study [61], the homojunctions between the zinc blende and wurtzite segments in a ZCS twinned nanocrystal could significantly improve the separation of photogenerated electron-hole pairs, thereby enhancing the photocatalytic H_2 -evolution activity significantly. All the experimental results suggested that the Ni_3C NPs cocatalysts on the surface of the twin nanocrystal ZCS solid solution could effectively increase visible-light absorption, promote charge separation and transfer, and enhance surface H_2 -evolution kinetics. Therefore, the synergistic effects of the homojunctions and the Ni_3C cocatalyst could promote the separation of photogenerated electron-hole pairs to achieve a significant enhancement in photocatalytic H_2 -evolution activity. This study could provide invaluable insights for the modification of sulfide photocatalysts to enhance photocatalytic H_2 evolution.

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Scheme 1. Proposed photocatalytic H_2 evolution and charge transfer mechanisms in the $\text{Ni}_3\text{C}/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite photocatalyst under visible light irradiation.

Graphical Abstract

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Constructing low-cost Ni₃C/twin-crystal Zn_{0.5}Cd_{0.5}S heterojunction/homojunction nanohybrids for efficient photocatalytic H₂ evolution

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The noble metal-free Ni₃C cocatalysts could significantly enhance the photocatalytic H₂ evolution over the twin nanocrystal Zn_{0.5}Cd_{0.5}S solid solution homojunctions.

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构建低成本的Ni₃C/孪晶Zn_{0.5}Cd_{0.5}S异质结/同质结纳米杂化体系来实现高效的光催化分解水产氢

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摘要: 开发低成本的半导体光催化剂以实现可见光下高效、持久的光催化分解水产氢化是一个非常具有挑战性的课题。近年来, 具有孪晶结构的Zn_xCd_{1-x}S (ZCS)固溶体引起了人们的研究兴趣, 这主要是由于孪晶相之间形成了同质结, 同质结可以通过提高体相光生电子-空穴对的分离效率, 从而提高原始硫化物光催化剂的光催化分解水产氢活性。但由于孪晶ZCS固溶体表面超快载流子复合以及活性位点不足, 进一步提高其光催化析氢活性还需解决这些不足。负载助催化剂被认为是加速产氢动力学和促进表面光生电子空穴分离最有效策略之一。因此, 我们将低成本的类金属Ni₃C助催化剂与孪晶ZCS固溶体通过简单的研磨方法结合来实现高效的可见光催化分解水产氢。合成的Zn_{0.5}Cd_{0.5}S-1% Ni₃C (ZCS-1)异质结/同质结最高的可见光光催化分解水产氢速率可达783 μmol h⁻¹, 是纯ZCS的2.88倍。在420 nm时, ZCS和ZCS-1的表观量子效率分别为6.13%和19.25%。这是由于孪晶ZCS固溶体中闪锌矿段和纤锌矿段的同质结连接可以显著提高光生电子空穴对的体相转移和分离。同时, ZCS与金属Ni₃C助催化剂间的异质结可以有效地增加孪晶ZCS固溶体的光捕获及表面载流子分离, 增强产氢活性位, 从而提高催化活性。

本文以乙酸镉、乙酸锌和氢氧化钠为原料合成了CdZn(OH), 后者与硫代乙酰胺水热合成了孪晶CZS, 并用超声研磨方法合成CZS-Ni₃C。在可见光下进行了产氢测试, 实验结果证实了优化的ZCS-1在Na₂S·9H₂O和Na₂SO₃的水溶液中光催化析氢活性最高。经过4次连续的循环反应, ZCS-1二元复合体系展现出良好的稳定性。为深入探讨高效产氢机制, 对纳米级ZCS复合材料的光催化物化性能及载流子分离机制进行了表征。通过X射线衍射确定了ZCS和ZCS-1的晶体结构。用高分辨电子显微镜和X射线光电子能谱证实合成了ZCS和Ni₃C助催化剂的成功复合。用紫外-可见漫反射光谱法对制备的ZCS和ZCS-1复合样品的光吸收特性进行了表征。结果表明, 在ZCS上负载Ni₃C以后, 样品的可见光吸收能力显著提升。利用稳态及瞬态荧光光谱研究了ZCS-1光催化剂的电荷载流子复合和转移行为。进一步对纯ZCS和ZCS-1复合光催化剂的瞬态光电流响应(*I-t*曲线)进行了研究, 确定了光生载体的分离效率。阻抗是深入研究电荷载流子迁移和界面转移的最有力技术, 利用阻抗技术证实ZCS-1界面高效的载流子分离性能。极化曲线结果表明, 加入Ni₃C可以降低ZCS的产氢过电势, 因此加速表面产氢动力学。

由此可见, 本文所构建的ZCS同质结与Ni₃C助催化剂的协同作用可以明显促进体相及表面光生电子空穴对的分离, 从而显著增强光催化分解水产氢活性。该文所采用基于ZCS纳米孪晶与异质助催化剂耦合策略可以作为一种通用策略扩展到各种传统半导体的改性, 从而极大地推进高效光催化产氢材料的持续进步。

关键词: 可见光光催化产氢; Zn_{0.5}Cd_{0.5}S固溶体; 孪晶; 同质结异质结; 廉价Ni₃C助催化剂

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