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Article

Ultrathin Ni(OH)₂ nanosheets decorated with Zn_{0.5}Cd_{0.5}S nanoparticles as 2D/0D heterojunctions for highly enhanced visible light-driven photocatalytic hydrogen evolution

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ABSTRACT

Designing and fabricating highly efficient photocatalysts for water splitting is a promising strategy to address energy and environmental issues. Cadmium sulfide (CdS) has received significant interest as a photocatalyst for visible-light-induced hydrogen (H₂) generation. However, the severe photocorrosion, high overpotential, rapid charge recombination, and sluggish surface reaction kinetics drastically hinder its practical application in water splitting. Herein, uniform zinc cadmium sulfide (Zn_{0.5}Cd_{0.5}S) nanoparticles were anchored on ultrathin Ni(OH)₂ nanosheets *via* a facile solution-phase approach to form an intimate two-dimensional (2D)/zero-dimensional (0D) heterojunction. Under visible light irradiation, the 7%Ni(OH)₂/Zn_{0.5}Cd_{0.5}S composite exhibited the highest H₂ production rate of 6.87 mmol·h⁻¹·g⁻¹ with an apparent quantum yield of 16.8% at 420 nm, which is almost 43 times higher than that of pristine Zn_{0.5}Cd_{0.5}S and considerably higher than that of the Pt/Zn_{0.5}Cd_{0.5}S photocatalyst. The high photoactivity of the 2D/0D Ni(OH)₂/Zn_{0.5}Cd_{0.5}S heterojunction can be ascribed to its unique and robust structure, wherein the ultrathin Ni(OH)₂ nanosheets not only provide an excellent platform for the incorporation of Zn_{0.5}Cd_{0.5}S nanoparticles but also serve as an effective cocatalyst to promote photoinduced electron transfer and offer more active sites for photocatalytic H₂ generation. This work paves the way toward the development of versatile, low-cost, and highly efficient 2D/0D heterojunction photocatalysts for solar energy conversion.

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1. Introduction

H₂ is widely considered as an emerging alternative to fossil fuels, owing to its high energy capacity and environmental friendliness [1]. Semiconductor-based photocatalytic water splitting has proven to be a promising avenue for so-

lar-to-chemical fuel conversion [2–4]. To date, enormous efforts have been devoted to the design and development of efficient semiconductor-based photocatalysts for H₂ evolution. However, some conventional semiconductors (e.g., TiO₂) have limited visible light absorbance, which greatly limits their practical applications [5]. CdS has received growing attention as a

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visible light photocatalyst for H_2 production, owing to its appropriate electronic band structure, morphology, and structural diversity [6,7]. Nevertheless, CdS still suffers from obvious drawbacks such as severe light-induced photocorrosion, low chemical stability, and fast recombination of photoexcited charge carriers, which generally result in poor photoactivity for H_2 production [6–10]. To address these issues, the formation of multicomponent CdS-based solid solutions has turned out to be an efficient approach, because of the controllable band structure, relatively high stability, and superior photocatalytic activity of these systems [11,12]. Recently, significant progress has been made in the utilization of CdS-based solid solutions such as ternary $Mn_xCd_{1-x}S$ [13,14] and $Zn_xCd_{1-x}S$ [11,15,16], which exhibited enhanced photocatalytic H_2 generation performance compared to their CdS counterparts.

Ternary $Zn_xCd_{1-x}S$ solid solutions have received particular attention because of their tunable band structure by changing the Zn/Cd ratio, visible light absorption, and superior chemical stability [17,18]. However, $Zn_xCd_{1-x}S$ still suffers from rapid recombination of photogenerated electron-hole pairs and insufficient number of active sites, which can severely limit its photocatalytic H_2 production activity, practical application, and further development [14,19–21]. Many recent research efforts have been devoted to improving the photocatalytic performance of $Zn_xCd_{1-x}S$, for instance by optimizing its structure and morphology [17,22–24], developing semiconductor-based Z-scheme photocatalytic systems [25,26], and achieving hybridization with cocatalysts [27–29]. Among these strategies, cocatalyst modification has been reported as a general method to facilitate interfacial charge transfer, reduce the activation potential, and provide more effective active sites for the H_2 evolution reaction [30]. $Zn_xCd_{1-x}S$ composites modified with noble metal Pt cocatalysts displayed extraordinary photocatalytic activity, owing to their high activity and low overpotential for proton reduction [31–33]. However, the scarcity and high cost of Pt severely limit its wide application. To date, numerous noble-metal-free cocatalysts such as reduced graphene oxide (RGO) [27,34], $1T-Li_xMoS_2$ [29], WO_3 [35], MoS_2 [36,37], $Cu_2(OH)_2CO_3$ [38], and CoP [20,39] have proven to be effective for modifying $Zn_xCd_{1-x}S$ solid solutions and improving the photocatalytic performance. However, the identification of suitable and efficient cocatalysts decorated with particular $ZnCdS$ nanostructures [such as zero-dimensional (0D) nanoparticles] for photocatalytic H_2 evolution is challenging.

Recently, $Ni(OH)_2$ was shown to be a promising cocatalyst for the photocatalytic H_2 generation reaction [28,40–46]. For instance, Wang *et al.* reported that the $TiO_2-Ni(OH)_2/CNT/CdS$ composite exhibited high H_2 production photoactivity, with $Ni(OH)_2$ serving as a cocatalyst for trapping photoelectrons and providing active reaction sites for the proton reduction to H_2 [47]. Previous studies have reported that $Ni(OH)_2$ nanoparticles can also serve as cocatalyst to improve the H_2 production over modified g- C_3N_4 photocatalysts [48,49]. Furthermore, the decoration of $Ni(OH)_2$ on metal-sulfide-based systems such as CdS [50], $Zn_xCd_{1-x}S$ [28,51], $ZnIn_2S_4$ [52], and $ZnIn_2S_4/g-C_3N_4$ [53] enhanced the photocatalytic H_2 evolution performance. However, most of the previous studies have focused on 0D

$Ni(OH)_2$ nanoparticles, whereas 2D $Ni(OH)_2$ nanosheets hybridized with semiconductors have rarely been investigated. 2D nanosheet-like structures have the advantages of facilitating the transfer of photoexcited carriers and providing more active reaction sites [54]. Therefore, the rational preparation of a novel 2D/0D heterojunction photocatalyst with ultrathin $Ni(OH)_2$ nanosheets is a promising strategy for H_2 evolution from water splitting.

In this study, $Zn_{0.5}Cd_{0.5}S$ nanoparticles were prepared by a facile one-pot solvothermal approach and subsequently anchored onto ultrathin $Ni(OH)_2$ nanosheets to form 2D/0D $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ heterojunctions *via* a solution-phase method. The structural characteristics, physicochemical properties, and H_2 evolution activity of the resulting 2D/0D $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ hybrids were systematically investigated. The optimized $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ photocatalyst exhibited a much higher photocatalytic H_2 evolution efficiency under visible light than the pristine $Zn_{0.5}Cd_{0.5}S$ and $Pt/Zn_{0.5}Cd_{0.5}S$ photocatalysts. A possible mechanism for the enhanced photocatalytic H_2 evolution of the $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ heterojunction photocatalyst was proposed. This unique 2D/0D metal hydroxide/ternary metal sulfide heterojunction may provide an effective strategy for designing extremely efficient noble-metal-free photocatalysts.

2. Experimental

2.1. Preparation

Preparation of $Zn_{0.5}Cd_{0.5}S$ nanoparticles. Typically, 4 mmol of zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$), 4 mmol of cadmium acetate dihydrate ($Cd(OAc)_2 \cdot 2H_2O$), 10 mmol of thioacetamide (TAA), and 85 mL of triethylene glycol (TEG) were added to a flask with continuous stirring for 30 min. After that, the reaction solution was transferred to a 100 mL Teflon-lined autoclave and heated at 200 °C for 12 h. Thereafter, the yellow product was washed with ethanol several times before vacuum drying at 60 °C for 12 h.

Preparation of $Ni(OH)_2$ nanosheets. Ultrathin $Ni(OH)_2$ nanosheets were synthesized according to a previously reported method [55]. Typically, 2 mmol of nickel acetate dihydrate ($Ni(OAc)_2 \cdot 2H_2O$) was dissolved in 5 mL of deionized water. Then, sodium carboxymethyl cellulose solution (20 mL, 1 g/L) was dropped into the mixture under continuous stirring. After that, 10 mL of dilute ammonia (ammonia/deionized water = 1:9) was added dropwise to the above mixture. The mixture was then sealed in a 50 mL Teflon-lined autoclave and heated at 80 °C for 12 h. The resulting $Ni(OH)_2$ nanosheets were washed several times with deionized water and ethanol *via* centrifugation, followed by drying at 60 °C under vacuum overnight.

Preparation of $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ heterostructures. The 2D/0D $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ composites were fabricated *via* a facile solution-phase approach. Briefly, 100 mg (total mass) of $Zn_{0.5}Cd_{0.5}S$ and $Ni(OH)_2$ was dispersed in 40 mL of anhydrous ethanol and ultrasonicated for 60 min. After stirring the above mixture for 12 h, the product was collected by centrifugation

and dried in vacuum. The calculated mass ratios of $\text{Ni}(\text{OH})_2$ in the 2D/0D $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites were 3%, 5%, 7%, 9%, and 11%. For comparison, 0D $\text{Ni}(\text{OH})_2$ nanoparticles were incorporated into the as-obtained $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles to prepare 0D/0D $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanocomposites using a general approach [50].

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded using a Smartlab-3KW (Rigaku Ltd., Japan) diffractometer. Scanning electron microscopy (SEM) images were obtained using a Hitachi SU8220 electron microscope. Transmission electron microscopy (TEM), High resolution TEM (HRTEM), and elemental mapping images were acquired on a Titan G260-300 transmission electron microscope. Ultraviolet-visible (UV-vis) absorption spectra were recorded on a UV-3600 (Shimadzu, Japan) spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo Fisher Scientific K_α system. Time-resolved photoluminescence (TRPL) spectra were recorded using a FL3C-111 (HORIBA Instruments, Inc.) spectrophotometer.

2.3. Photocatalytic measurements

Photocatalytic H_2 generation tests were carried out using a closed-circulation apparatus. Typically, 40 mg of photocatalyst was added to 60 mL of 0.35 M/0.25 M Na_2S - Na_2SO_3 aqueous solution, and the mixture was irradiated using a 300 W Xe lamp (CEL-HXF300, Beijing Aulight Co., Ltd) with a UV cut-off filter ($\lambda > 400$ nm). The generated H_2 was measured by gas chromatography (GC-7920, using high-purity N_2 as a carrier gas) by using with a 5 Å molecular sieve column and a thermal conductivity detector (TCD). The 3%Pt/ $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample was prepared by an *in situ* photodeposition approach, using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ as the precursor. For the photocatalytic H_2 evolution cycling experiments, the system was evacuated to remove residual gas before the cycling tests.

2.4. Photoelectrochemical (PEC) measurements

PEC tests were carried out using a VSP-300 multi-channel potentiostat (Bio-Logic, France) in a three-electrode configuration, with a Ag/AgCl (in 3.5 M KCl solution) electrode as the reference electrode and a piece of Pt sheet as the counter electrode. A 0.1 M Na_2SO_4 solution was used as the electrolyte. To prepare the working electrodes, 6 mg of photocatalyst and 3 mL of ethanol were mixed by ultrasonication for 20 min, dropped onto a 1 cm × 2 cm carbon paper, and then dried at 120 °C under vacuum for 5 h. A 0.1 M Na_2SO_4 aqueous solution was employed as the electrolyte. The transient photocurrent was collected by applying a potential of 0.4 V under several light on-off cycles. Electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range of 10^{-1} to 10^5 Hz, by applying a 0.4 V bias vs. Ag/AgCl. Linear sweep voltammetry (LSV) profiles were recorded at a scanning rate of 20 mV/s.

3. Results and discussion

3.1. Synthesis and characterization

The crystallinity and structure of the pristine $\text{Ni}(\text{OH})_2$ nanosheets, $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles, and $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites were investigated using XRD. As shown in Fig. 1, the XRD patterns of the $\text{Ni}(\text{OH})_2$ nanosheets displayed several characteristic peaks that could be systematically matched with the hexagonal phase of $\text{Ni}(\text{OH})_2$ (JCPDS PDF#03-0177). Similarly, the diffraction peaks of the pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles were assigned to the hexagonal $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ solid solution (JCPDS PDF#89-2943). No diffraction peaks from other impurities were detected in the XRD pattern, indicating that both the pristine $\text{Ni}(\text{OH})_2$ and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ samples had high purity and crystallinity. The $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite exhibited similar patterns to the pure $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample, except for several weak diffraction peaks that were ascribed to hexagonal $\text{Ni}(\text{OH})_2$. In addition, the intensities of the diffraction peaks of $\text{Ni}(\text{OH})_2$ slightly increased with increasing $\text{Ni}(\text{OH})_2$ content, indicating the successful hybridization of $\text{Ni}(\text{OH})_2$ and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ in the $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ photocatalyst. Furthermore, the weight percentage of $\text{Ni}(\text{OH})_2$ calculated through ICP-AES analysis showed good agreement with the initial $\text{Ni}(\text{OH})_2$ content (Table S1).

The morphologies and structures of the pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and $\text{Ni}(\text{OH})_2$ samples were characterized by SEM and TEM. As shown in Figs. S1 and 2(a), $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ shows a uniform particle-like morphology with an average particle size of approximately 14 nm. As shown in Fig. 2(b), the HRTEM image of an individual $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticle displays a lattice spacing of 0.321 nm, assigned to the (002) plane of hexagonal $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$. The SEM (Fig. S2) and TEM (Fig. 2(c)) images of the $\text{Ni}(\text{OH})_2$ nanosheets clearly show an ultrathin 2D sheet-like structure with rolled edges. The thickness of the ultrathin $\text{Ni}(\text{OH})_2$ nanosheets was estimated to be approximately 1.6 nm from the measured length of the rolled edges. Moreover, as shown in Fig. 2(d), the HRTEM image displays lattice fringes of approximately 0.232 nm, which were attributed to the (002) crystal plane of hexagonal $\text{Ni}(\text{OH})_2$.

Fig. 1. XRD patterns of pristine $\text{Ni}(\text{OH})_2$, $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, and $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites with different contents of $\text{Ni}(\text{OH})_2$ nanosheets.

Fig. 2. TEM (a) and HRTEM (b) images of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles; TEM (c) and HRTEM (d) images of $\text{Ni}(\text{OH})_2$ nanosheets.

The morphology, structure, and heterojunction interface between the $\text{Ni}(\text{OH})_2$ nanosheets and the $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles of the hybrid photocatalyst (7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample) were determined through SEM, TEM, and HRTEM. As shown in the SEM (Fig. 3(a)) and TEM (Fig. 3(b)) images, the 0D $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles are fully anchored onto the 2D $\text{Ni}(\text{OH})_2$ nanosheets. The HRTEM image (Fig. 3(c)) shows lattice fringes with interplanar spacings of 0.321 and 0.156 nm, corresponding to the $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (002) and $\text{Ni}(\text{OH})_2$ (110) planes, respectively, and reveals that the individual $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles were strongly attached to the 2D $\text{Ni}(\text{OH})_2$

Fig. 3. SEM (a), TEM (b), and HRTEM (c,d) images of 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$.

Fig. 4. HADDF-STEM image (a) of 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample and corresponding STEM-EDX elemental mapping images (b–f) for Zn, Cd, S, Ni, and O, respectively.

nanosheets. Similarly, the lattice spacings of several $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles and $\text{Ni}(\text{OH})_2$ nanosheets were clearly observed and respectively attributed to the crystal phases of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and $\text{Ni}(\text{OH})_2$ (Fig. 3(d)), further confirming the presence of well-defined heterointerfaces between $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles and ultrathin $\text{Ni}(\text{OH})_2$ nanosheets in the nanohybrids. The corresponding scanning TEM (STEM) (Fig. 4(a)) and EDS elemental mapping images (Figs. 4(b)–(f)) of the 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample show a homogeneous distribution of Ni and O in the $\text{Ni}(\text{OH})_2$ matrix, while the Zn, Cd, and S elements were present only in the $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles. These results indicate the coexistence of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and $\text{Ni}(\text{OH})_2$ as well as their intimate 2D/0D heterojunction, which are crucial for their photocatalytic performance.

The absorbance spectra of the as-synthesized $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, $\text{Ni}(\text{OH})_2$, and 2D/0D $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites were measured by UV-vis diffuse reflectance spectroscopy. As shown in Fig. 5, the pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample exhibited an absorption edge of 515 nm, corresponding to a band gap of approximately 2.41 eV. On the other hand, the absorption spectrum of pristine $\text{Ni}(\text{OH})_2$ displays two wide absorptions in the ranges of 380–400 and 650–750 nm. All the $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ compo-

Fig. 5. UV-vis diffuse reflectance spectra of as-synthesized pristine $\text{Ni}(\text{OH})_2$, $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, and $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites.

sites exhibited absorption features similar to those of pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, indicating that $\text{Ni}(\text{OH})_2$ was not doped in the lattice sites of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, in agreement with previous studies on $\text{Ni}(\text{OH})_2$ -modified semiconductor photocatalysts [40,48]. Furthermore, the absorbance intensities of the $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites showed slight changes with increasing amounts of $\text{Ni}(\text{OH})_2$, which could be attributed to the intense absorption of $\text{Ni}(\text{OH})_2$ nanosheets and the color change from orange to light yellow (Fig. S3).

The surface chemical composition and states of the as-synthesized photocatalysts were further investigated by XPS analysis. Fig. 6(a) displays the XPS survey profiles of 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, and $\text{Ni}(\text{OH})_2$, further confirming the coexistence of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles and $\text{Ni}(\text{OH})_2$ nanosheets in the $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite. Based on Fig. 6(b)–(d), the Zn 2p (1021.5 eV for Zn 2p_{3/2} and 1044.6 eV for Zn 2p_{1/2}), Cd 3d (404.8 eV for Cd 3d_{5/2} and 411.6 eV for Cd 3d_{3/2}), S 2p (161.5 eV for S 2p_{3/2} and 162.6 eV for S

2p_{1/2}) binding energies for the 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample were approximately the same as those of pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$. Figs. 6(e)–(f) show the high-resolution XPS profiles of Ni 2p and O 1s levels for the 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite and pristine $\text{Ni}(\text{OH})_2$. The obvious peaks located at 855.7 and 873.4 eV for the $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite in Fig. 6(e) (855.6 and 873.3 eV for $\text{Ni}(\text{OH})_2$) were attributed to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively, indicating the presence of Ni²⁺ in the $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and $\text{Ni}(\text{OH})_2$ samples [56]. Moreover, the binding energies at 531.4 and 532.7 eV in the O 1s spectrum of 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ shown in Fig. 6(f) (531.0 and 532.7 eV for $\text{Ni}(\text{OH})_2$) were assigned to hydroxide species bound to $\text{Ni}(\text{OH})_2$ and adsorbed water on the catalyst surface, respectively [57]. Therefore, the XPS results further confirmed that the 2D/0D hybrids were successfully fabricated by hybridizing $\text{Ni}(\text{OH})_2$ nanosheets with $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles. Moreover, the valence band (VB) XPS spectrum in Fig. S4 shows that the VB of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ was located at approximately 1.55 eV. Ac-

Fig. 6. XPS survey scans (a) of pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, $\text{Ni}(\text{OH})_2$, and 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite. High-resolution XPS profiles of Zn 2p (b), Cd 3d (c), and S 2p (d) levels in $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$. High-resolution XPS profiles of Ni 2p (e) and O 1s (f) levels in $\text{Ni}(\text{OH})_2$ and 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$.

cording to the UV-vis results, the conduction band (CB) minimum energy was estimated to be -0.86 eV.

3.2. Photocatalytic and PEC properties

Photocatalytic H_2 generation experiments of as-synthesized $Zn_{0.5}Cd_{0.5}S$ nanoparticles, $Ni(OH)_2$ nanosheets, and $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ composite photocatalysts with different $Ni(OH)_2$ contents were conducted under visible light. As shown in Fig. 7(a), the average photocatalytic H_2 evolution rate of pristine $Zn_{0.5}Cd_{0.5}S$ was 0.16 $mmol \cdot h^{-1} \cdot g^{-1}$. It is evident that the $Ni(OH)_2$ nanosheets exhibited no activity for photocatalytic H_2 generation, implying that they mainly served as cocatalysts in the 2D/0D $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ hybrids. Impressively, the incorporation of 3 wt% $Ni(OH)_2$ led to a H_2 evolution rate of 2.69 $mmol \cdot h^{-1} \cdot g^{-1}$, which was much higher than that of pristine $Zn_{0.5}Cd_{0.5}S$ and 3%Pt/ $Zn_{0.5}Cd_{0.5}S$ (0.85 $mmol \cdot h^{-1} \cdot g^{-1}$), indicating that the modification with $Ni(OH)_2$ nanosheets could promote the H_2 generation activity of $Zn_{0.5}Cd_{0.5}S$. Upon further increasing the $Ni(OH)_2$ nanosheet loading up to 7 wt%, the composite exhibited the highest H_2 evolution rate, which can be mainly ascribed to the optimal incorporation of $Ni(OH)_2$ nanosheets, serving as substrates for the water reduction reaction. However, the photocatalytic H_2 generation rate constantly decreased when the amount of $Ni(OH)_2$ nanosheets increased (9 wt% and 11 wt%), which can be attributed to the unavoidable mask effect caused by the excessive amount of $Ni(OH)_2$ nanosheets. The optimal $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ composition exhibited an excellent photocatalytic H_2 evolution rate of 6.87 $mmol \cdot h^{-1} \cdot g^{-1}$, which was about 43 and 8 times higher than that of the $Zn_{0.5}Cd_{0.5}S$ and 3%Pt/ $Zn_{0.5}Cd_{0.5}S$ photocatalysts, respectively. This indicates that the incorporation of $Ni(OH)_2$ in $Zn_{0.5}Cd_{0.5}S$ can be a promising strategy to reduce the costs and enhance the photocatalytic H_2 evolution efficiency. Furthermore, the 7% $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ sample exhibited a high apparent quantum yield (AQY) of 16.8% at 420 nm. The photocatalytic H_2 evolution performance of 7% $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ was comparable to that of most $Zn_{0.5}Cd_{0.5}S$ -based photocatalysts (Table S2). To determine the crystalline structure of the hybrids after the photocatalytic reaction, we measured the XRD pattern of

the $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ composite after 4 h of photocatalytic H_2 evolution reaction. Similar to the primary composites, Fig. S5 shows diffraction peaks corresponding to $Ni(OH)_2$, whose intensities slightly increased with increasing amount of $Ni(OH)_2$ nanosheets.

To further evaluate the H_2 generation reproducibility and stability of the $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ composites, recycling tests were performed on the optimal 7% $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ sample. As shown in Fig. 7(b), the photocatalytic H_2 evolution performance of 7% $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ only showed a slight decrease after 20 h (4 cycles). Moreover, we investigated the phase and micromorphology of the recycled 7% $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ composite. As illustrated by the XRD (Fig. S6), TEM (Fig. S7(a)), and HRTEM (Fig. S7(b)) results, the spent 7% $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ sample showed no evident structural and morphological changes, reflecting the strongly coupled interface between $Ni(OH)_2$ and $Zn_{0.5}Cd_{0.5}S$ in the hybrid system. Furthermore, the XPS analysis in Fig. S8 reveals that the $Zn_{0.5}Cd_{0.5}S$ and $Ni(OH)_2$ phases were retained after the repeated photocatalytic reaction. These results highlight the high stability of the $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ photocatalyst during the long-term H_2 production reaction. In addition, 0D $Ni(OH)_2$ nanoparticles were incorporated into $Zn_{0.5}Cd_{0.5}S$ nanoparticles to prepare the 0D/0D $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ photocatalyst. As shown in Figs. S9 and S10, structural characterization through SEM, TEM, HRTEM, HAADF-STEM, and EDS elemental mapping indicated the formation of 0D/0D $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ nanohybrids. For comparison, the photocatalytic H_2 generation activity of 0D/0D 7% $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ was also investigated under identical conditions. As shown in Fig. S11, the H_2 production capacity of the 0D/0D $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ composite was clearly lower than that of the 2D/0D $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ photocatalyst.

To gain deeper insight into the effect of the ultrathin $Ni(OH)_2$ nanosheets on the enhanced catalytic H_2 generation performance, PEC analysis was used to study the interfacial charge transfer between $Ni(OH)_2$ nanosheets and $Zn_{0.5}Cd_{0.5}S$ nanoparticles. Fig. 8(a) displays the photocurrent response of the pristine $Zn_{0.5}Cd_{0.5}S$ and 7% $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$ electrodes. Pristine $Zn_{0.5}Cd_{0.5}S$ exhibited a low photocurrent density, owing to its relatively rapid recombination of photoexcited charge

Fig. 7. (a) Photocatalytic H_2 production activities of $Zn_{0.5}Cd_{0.5}S$, $Ni(OH)_2$, $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$, and 3%Pt/ $Zn_{0.5}Cd_{0.5}S$; ND = not detected. (b) Recycling tests of photocatalytic H_2 generation over 7% $Ni(OH)_2/Zn_{0.5}Cd_{0.5}S$.

Fig. 8. (a) Transient photocurrent response curves of pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$; (b) EIS Nyquist plots of pristine $\text{Ni}(\text{OH})_2$, $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, and 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ samples.

carriers. By incorporating $\text{Ni}(\text{OH})_2$, the photocurrent density of the 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ hybrids was markedly enhanced, reflecting the efficient charge separation and improved electron transfer in the $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite. EIS Nyquist plots of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, $\text{Ni}(\text{OH})_2$, and 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ electrodes under dark and visible light conditions were obtained to study their charge transfer resistance. As shown in Fig. 8(b), the $\text{Ni}(\text{OH})_2$ electrode showed a much smaller arc radius than the $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ ones under dark conditions; moreover, the arc radius remained unchanged after visible light irradiation, implying that $\text{Ni}(\text{OH})_2$ served as cocatalyst and had higher conductivity than the $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite samples. As such, $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ exhibited a smaller arc radius than $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, while the 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite displayed a smaller arc radius under visible light than $\text{Ni}(\text{OH})_2$; this indicates that the charge transfer resistance was substantially decreased, facilitating charge separation in the $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites [58,59]. The EIS results were in good agreement with the improved photocurrent, low overpotential, and enhanced photocatalytic H_2 generation activity

discussed above.

To further explore how $\text{Ni}(\text{OH})_2$ nanosheets can act as high-efficiency cocatalysts for $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, LSV measurements of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ were carried out under dark and visible light conditions. As shown in Fig. 9(a), the cathodic current density of pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ was rather low at a high applied voltage, and subsequently increased under visible light. Furthermore, the $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite exhibited a much higher current density and lower overpotential than pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, particularly under visible light irradiation, further demonstrating that $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composites can significantly reduce the overpotential and boost the H_2 production activity [60]. To gain further insight into the effect of the ultrathin 2D $\text{Ni}(\text{OH})_2$ nanosheet matrix on the charge carrier separation of 0D $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles, TRPL decay spectra were obtained for bare $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$. As shown in Fig. 9(b) and the corresponding fitted data (Table S3), the average lifetimes of pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ were 12.70 and 13.37 ns, respectively. Obviously, the $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite exhibited a longer PL lifetime than the pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ sample, suggesting

Fig. 9. LSV curves (a) and TRPL spectra (b) of 7% $\text{Ni}(\text{OH})_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$.

Fig. 10. Schematic illustration of charge transfer process in $\text{Ni(OH)}_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ system during photocatalytic H_2 evolution.

that the intimate 2D/0D $\text{Ni(OH)}_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ heterointerface is more beneficial for the photoexcited charge transfer [61,62]. As shown in Fig. S12, the Mott-Schottky curve of pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ displayed a positive slope, suggesting that $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ is a typical *n*-type semiconductor. Moreover, the *n*-type semiconductor properties of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ were retained after hybridization with Ni(OH)_2 nanosheets. Impressively, the flat-band potential (E_{fb}) was positively shifted from -0.87 V for pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ to -0.66 V for $\text{Ni(OH)}_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, which can be ascribed to the improved electrical conductivity and lower overpotential of Ni(OH)_2 during the electrochemical analysis [63,64].

Based on the experimental results discussed above, we can propose a possible mechanism for the markedly improved photocatalytic H_2 generation performance of the $\text{Ni(OH)}_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ heterostructures. As shown in Fig. 10, under visible light irradiation, photogeneration of electron-hole pairs readily occurs in 0D $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles. This can be attributed to the appropriate band structure of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, in which the VB electrons are photoexcited to the CB, whereas holes in the VB of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ are quenched by S^{2-} and SO_3^{2-} and generate SO_4^{2-} and $\text{S}_2\text{O}_3^{2-}$. At the same time, the photoexcited electrons of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ can be rapidly transferred to the strongly attached Ni(OH)_2 nanosheets. These migrated photo-generated electrons contribute to efficient proton reduction for H_2 production. Hence, the presence of 2D Ni(OH)_2 nanosheets in the $\text{Ni(OH)}_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ heterojunction can favor the separation of photogenerated electron-hole pairs, reduce the overpotentials, and provide abundant active sites for H_2 production, thus achieving a greatly enhanced photoactivity for H_2 generation.

4. Conclusions

In summary, we have developed a facile solvothermal method for the preparation of uniform $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles. The $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles were strongly coupled to ultrathin 2D Ni(OH)_2 nanosheets through a facile solu-

tion-phase hybridization approach. By optimizing the amount of Ni(OH)_2 nanosheets, the optimal 7% $\text{Ni(OH)}_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ composite photocatalysts achieved a superior photocatalytic H_2 evolution rate of $6.87 \text{ mmol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ under visible light, along with a high AQY of 16.8% (420 nm), which was approximately 43 and 8 times higher than that of pristine $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and Pt-modified $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ photocatalysts, respectively. Such marked enhancement in the photocatalytic H_2 generation activity can be ascribed to the formation of a stable 2D/0D $\text{Ni(OH)}_2/\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ heterojunction; in this structure, the ultrathin Ni(OH)_2 nanosheets serve as efficient noble-metal-free cocatalysts and excellent substrates to host uniform $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ nanoparticles, promote photoinduced electron transfer, reduce the overpotential, and provide sufficient active sites for the photocatalytic H_2 evolution reaction. This work will assist the design of precious-metal-free and high-efficiency 2D-0D heterojunction photocatalysts, paving the way to explore and expand photochemical catalysis, energy conversion, and other applications.

Electronic supporting information

Supporting information is available in the online version of this article.

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Graphical Abstract

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Ultrathin Ni(OH)₂ nanosheets decorated with Zn_{0.5}Cd_{0.5}S nanoparticles as 2D/0D heterojunctions for highly enhanced visible light-driven photocatalytic hydrogen evolution

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Ultrathin two-dimensional (2D) Ni(OH)₂ nanosheets serve as efficient cocatalysts and excellent substrates to host uniform zero-dimensional (0D) Zn_{0.5}Cd_{0.5}S nanoparticles, achieving a considerable improvement in the photocatalytic H₂ evolution.

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超薄Ni(OH)₂纳米片修饰Zn_{0.5}Cd_{0.5}S纳米颗粒作为二维/零维异质结构光催化剂 可见光下光催化制氢

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摘要: 设计与制备高效的光解水催化剂是解决能源问题和环境问题的策略之一。硫化镉因其可在可见光引发下分解水制氢而受到广泛关注, 然而光腐蚀严重, 过电势高, 载流子复合快速以及表面反应动力学缓慢等缺点极大地限制了其在光解水反应中的实际应用。本文采用简单液相法将均匀的Zn_{0.5}Cd_{0.5}S纳米颗粒锚定在超薄Ni(OH)₂纳米薄片上, 构建紧密的二维/零维异质结构。通过调控Ni(OH)₂纳米片的含量, 制备出不同Ni(OH)₂质量比(3%, 5%, 7%, 9%, 11%)的二维/零维Ni(OH)₂/Zn_{0.5}Cd_{0.5}S复合材料, 并考察其可见光激发的光催化分解水制氢性能。

在可见光照射下, Ni(OH)₂/Zn_{0.5}Cd_{0.5}S复合材料的光催化性能要大幅度地优于未修饰的Zn_{0.5}Cd_{0.5}S纳米颗粒, 甚至远高于贵金属Pt修饰的Zn_{0.5}Cd_{0.5}S。在不同Ni(OH)₂含量的纳米复合材料中, 7%Ni(OH)₂/Zn_{0.5}Cd_{0.5}S具有最高效的产氢性能, 产氢速率可达6.87 mmol·h⁻¹·g⁻¹, 且在波长为420 nm的表观量子产率为16.8%。在同等条件下, 二维/零维7%Ni(OH)₂/Zn_{0.5}Cd_{0.5}S复合光催化剂的光催化分解水产氢速率分别约为纯Zn_{0.5}Cd_{0.5}S纳米颗粒和Pt/Zn_{0.5}Cd_{0.5}S光催化剂的43倍和8倍, 甚至要高于零维/零维7%Ni(OH)₂/Zn_{0.5}Cd_{0.5}S纳米复合材料。7%Ni(OH)₂/Zn_{0.5}Cd_{0.5}S复合光催化剂具有优异的光催化产氢循环性能, 通过循环反应后样品的X射线衍射, X射线光电子能谱和透射电子显微镜等表征, 结果表明Ni(OH)₂/Zn_{0.5}Cd_{0.5}S在经过20 h的使用后, 其晶体结构、表面化学成分和形貌结构未发生明显改变。通过研究样品的时间分辨荧光光谱, 线性扫描伏安响应, 光电流性能及电化学交流阻抗等, 发现二维Ni(OH)₂纳米片的修饰能一定程度降低Zn_{0.5}Cd_{0.5}S的过电势, 还能有效促进Zn_{0.5}Cd_{0.5}S的光生电子-空穴的分离和光生电子的转移。

本文认为二维/零维Ni(OH)₂/Zn_{0.5}Cd_{0.5}S光催化活性的大幅提升主要由于Zn_{0.5}Cd_{0.5}S与Ni(OH)₂之间独特且牢固的纳米结构, 在该过程中超薄Ni(OH)₂纳米片不仅能为Zn_{0.5}Cd_{0.5}S纳米颗粒的负载提供平台, 而且作为一种高效的助催化剂, 促进光生电子的转移以及为制氢反应提供更多的活性位点。本文可为多功能、高效及低成本的二维-零维异质结构光催化剂的制备及在太阳能转化方面的应用提供一定借鉴。

关键词: 氢氧化镍纳米片; Zn_{0.5}Cd_{0.5}S纳米颗粒; 助催化剂; 二维/零维纳米异质结构; 光催化制氢

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