Unique $\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}$ and $\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$ Z-scheme photocatalysts for efficient visible-light-induced H_2 evolution

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ABSTRACT Artificial Z-scheme photocatalytic systems have received considerable attention in recent years because they can achieve wide light-absorption, high charge-separation efficiency, and strong redox ability simultaneously. Nevertheless, it is still challenging to exploit low-cost and stable Z-scheme photocatalysts with highly-efficient H_2 evolution from solar water-splitting so far. Herein, we report a novel all-solid-state Z-scheme photocatalyst $\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}$ consisting of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanorods coated with oxygen-deficient WO_{3-x} amorphous layers. The $\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}$ exhibits an outstanding H_2 evolution reaction (HER) activity as compared with Pt-loaded $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and most WO_3 - and CdS -based photocatalysts, due to the generation of stronger reducing electrons through the appropriate Zn-doping in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and the enhanced charge transfer by introducing oxygen vacancies (W^{5+}/OVs) into the ultrathin WO_{3-x} amorphous coatings. The optimal HER rate of $\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}$ is determined to be $21.68 \text{ mmol h}^{-1} \text{ g}^{-1}$, which is further raised up to $28.25 \text{ mmol h}^{-1} \text{ g}^{-1}$ (about 12 times more than that of Pt/ $\text{Cd}_{1-x}\text{Zn}_x\text{S}$) when $\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}$ is hybridized by CoO_x and NiO_x dual cocatalysts ($\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$) through *in-situ* photo-deposition. Moreover, the corresponding apparent quantum yield (AQY) at 420 nm is significantly increased from 34.6% for $\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}$ to 60.8% for $\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$. In addition, both $\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}$ and $\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$ demonstrate good stability towards HER. The results displayed in this work will inspire the rational design and synthesis of high-performance nanostructures for photocatalytic applications.

Keywords: Z-scheme charge transfer, photocatalytic H_2 evolu-

tion, $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solutions, oxygen-deficient WO_{3-x} amorphous layers, CoO_x and NiO_x dual cocatalysts

INTRODUCTION

The development of new renewable energy has currently been extremely urgent due to the limited reserves and depletion of fossil fuels, as well as the associated environmental problems [1–5]. Recently, the sustainable hydrogen (H_2) production based on solar photocatalytic water splitting has attracted great attention, owing to the renewability of solar energy, the abundance of water resources, and the cleanliness and high-energy-density of H_2 energy [6–8]. For photocatalysis, the desirable catalysts should satisfy the following factors: wide light absorption, good stability, efficient charge-separation, and strong redox ability. However, single-component photocatalysts are unsuitable for practical applications because of their high charge recombination and incompatibility between the wide light absorption and strong redox ability [9]. In this regard, numerous hybrid photocatalytic systems are properly designed and constructed to overcome the drawbacks of single-component photocatalysts [10–14]. Nevertheless, in conventional heterojunction-type systems, the redox ability of photogenerated electrons and holes is weakened after charge transfer, which is unfavorable to the photocatalytic activity. This impels a new-type photocatalytic system, the artificial heterogeneous Z-scheme photocatalysts mimicking the natural photosynthesis process, which can achieve the spatial isolation of charge carriers and the strong redox ability

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simultaneously. Among them, all-solid-state Z-scheme photocatalysts consisting of narrow-bandgap semiconductors with proper band structures have become the focus of current frontier research, due to their feasibility to meet the aforementioned criterions of desirable photocatalysts [15,16]. Among various semiconducting photocatalysts, CdS has attracted great interest for H₂ evolution reaction (HER) due to its effective sunlight absorption and suitable conduction band potential [17–19]. However, CdS alone exhibits a poor HER capability as a result of the rapid charge carrier recombination and photocorrosion. On the other hand, narrow-bandgap WO₃ shows high carrier mobility and good chemical stability by comparison with other photocatalysts [20,21]. Moreover, the relatively positive valence band potential of WO₃ endows it with good oxidation capacity [22]. Therefore, CdS and WO₃ were selected as the components for constructing Z-scheme hybrid, which was expected to present a highly efficient H₂ evolution activity based on photocatalytic water-splitting. The previously reported Z-scheme WO₃/CdS system is usually composed of WO₃ nanorods or hierarchical spheres/urchins loaded with a small amount of CdS nanoparticles [23,24]. As the main part of these WO₃/CdS composites is WO₃, the overall HER performance is not high because WO₃ is not active for H₂ evolution [25]. Although conductors such as Pt, Au, and Ag have been employed to form the known Ohmic contact to facilitate the charge transfer and increase the activity of these WO₃/CdS composites [25–28], the high cost [29,30] and complexity of material preparation hinder their massive applications. As is well known, the solid-solid contact interface is easily aggregated with abundant defects, which enables it to display quasi-continuous energy levels and form Ohmic contact as well. Moreover, the solid-solid contact interface can be optimized to show lower electrical resistance for enhanced charge transfer through the introduction of some defects such as oxygen vacancies [20,31]. In addition, appropriate Zn-doping in CdS has been demonstrated as an effective way to raise the conduction band level, which is in favor of producing stronger reducing electrons to increase the HER property [32]. Furthermore, recent research shows that [33], the photocatalytic activity can be significantly improved *via* selective photo-deposition of reduction and oxidation cocatalysts with the photocatalyst possessing spatially isolated redox sites. Consequently, novel efficient Z-scheme photocatalytic systems toward H₂ production from water splitting can be expected by depositing appropriate cocatalysts with the spatially separated photogenerated electrons and holes

under illumination.

In this work, a novel all-solid-state Z-scheme photocatalytic system Cd_{1-x}Zn_xS@WO_{3-x} was prepared with an ethanediamine-assisted solvothermal method followed by a facile hydrolysis oxidation process under ambient conditions. Interestingly, the conduction band potential of Cd_{1-x}Zn_xS solid solutions becomes more negative with the increasing Zn content, which is beneficial to the formation of stronger reducing electrons for HER. Moreover, the oxygen vacancies in amorphous WO_{3-x} coatings facilitate the Z-scheme charge transfer through lowering the interfacial electrical resistance. Therefore, under visible-light illumination, Cd_{1-x}Zn_xS@WO_{3-x} demonstrates an excellent HER activity as compared with Pt-decorated Cd_{1-x}Zn_xS, individual Cd_{1-x}Zn_xS and WO₃. In addition, after Cd_{1-x}Zn_xS@WO_{3-x} is hybridized by CoO_x and NiO_x nanoparticles through *in-situ* photo-deposition, the HER performance is further improved, owing to the efficient Z-scheme charge separation and selective charge trapping by the reduction and oxidation dual cocatalysts.

EXPERIMENTAL SECTION

Chemicals

The chemicals present in this work were purchased from Shanghai Adamas-Beta Reagent Co., Ltd. (China), which can be listed as follows: Cd(NO₃)₂·4H₂O, Zn(NO₃)₂·6H₂O, Ni(CH₃COO)₂·4H₂O, Co(CH₃COO)₂·4H₂O, WCl₄, Na₂S·9H₂O, Na₂SO₃, S powder, ethanediamine, triethanolamine (TEOA), ethylene glycol (EG), *N,N*-dimethylformamide (DMF), thioacetamide, lactic acid, ethanol, and HNO₃ (68 wt%). All the reagents were of analytical grade and used as received.

Synthesis of one-dimensional (1D) Cd_{1-x}Zn_xS solid solutions

The synthesis of 1D Cd_{1-x}Zn_xS solid solutions was carried out according to the ethanediamine-assisted solvothermal method reported in our recent work [34].

Synthesis of WS₂ and WO₃ nanosheets

WS₂ nanosheets were prepared by a solvothermal method, where DMF served as the solvent. Briefly, 1 mmol WCl₄ and 6 mmol thioacetamide were dissolved in 30 mL DMF through agitation for 30 min, which was then transferred into a 50-mL autoclave and sealed before heating at 200°C for 24 h. After reaction, the black precipitate was washed with ethanol by centrifugation thrice, and dried at 80°C for 5 h to get WS₂ nanosheets.

The WO_3 nanosheets were synthesized through the chemical oxidation of WS_2 nanosheets followed by a calcination process. Specifically, 0.45 g WS_2 nanosheets were dispersed into 100 mL HNO_3 aqueous solution (4 mol L^{-1}) by ultrasonication, which was then refluxed at 50°C for 48 h to complete the oxidation process. In the next step, the yellow precipitate was rinsed with water for several times until it was neutral. After that, the precipitate was dried at 80°C for 5 h before roasting at 450°C for 2 h to form WO_3 nanosheets.

Synthesis of 1D $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}$ composites

In a routine preparation, 0.6 g $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ was first dispersed in 7.5 mL EG by sonication and agitation, and then this suspension was mixed with 7.5 mL EG solution dissolved with different amounts of WCl_4 . Following this step, the above suspension was further stirred for 30 min to carry out the ion-absorption process. After that, the greenish precipitate was separated by centrifugation and washed with ethanol once and water twice. At last, the precipitate was dried at 80°C in an oven and the $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}$ composites were obtained. For simplicity, the $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}$ hybrids are abbreviated as $\text{CZ}_x\text{S-YW}$, where x is the ratio of Zn in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and Y represents the concentration (mol L^{-1}) of WCl_4 reaction solution.

For comparison, $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}$ was also prepared with a solvothermal method. Generally, 0.6 g $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ was dispersed in 30 mL DMF by ultrasonication to form a suspension at first, into which 0.0276 g WCl_4 and 0.0382 g thioacetamide were then dissolved after stirring for 30 min. Next, the suspension was sealed into a 50-mL autoclave and maintained at 200°C for 24 h. After reaction, the product was rinsed with ethanol thrice and dried at 80°C in a vacuum oven. The fabricated $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}$ is denoted as $\text{CZ}_x\text{S-WO}$, where x stands for the proportion of Zn in $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solutions.

Synthesis of 1D $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$ through photo-deposition

The $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$ was prepared by an *in-situ* photo-deposition strategy. Specifically, 30 mg $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}$ was first dispersed in 100 mL aqueous solution containing 20 vol% lactic acid by ultrasonication, and a certain amount of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was subsequently dissolved into the above suspension. Then, the photo-deposition for the suspension was conducted using the Labsolar-6A online H_2 evolution and detection system (PerfectLight, Beijing Co., Ltd.). Before illumination by a 300-W Xe lamp

equipped with a 420-nm cutoff filter, the suspension was stirred and vacuumized. The photo-deposition process was carried out for 3 h under the reaction temperature of 6°C as controlled by a circulating water pump. Finally, the $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$ was obtained after the product was rinsed with ethanol thrice and dried at 80°C under vacuum.

Characterization

X-ray diffraction (XRD) patterns of the photocatalysts were measured on a Rigaku D/max 2500 PC X-ray diffractometer using the Cu K α radiation (40 kV, 150 mA). Scanning electron microscopy (SEM) images were collected by a ZEISS MERLIN Compact scanning electron microscope. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), dark-field scanning TEM (STEM), and energy-dispersive X-ray spectroscopy (EDX) elemental mapping tests were performed with a FEI Tecnai G2 F20 S-TWIN microscope. X-ray photoelectron spectroscopy (XPS) measurements were conducted by a Thermo Fisher ESCALAB 250 Xi spectrometer. Electron paramagnetic resonance (EPR) spectra were measured at room temperature by a Bruker A300 spectrometer. Ultraviolet-visible (UV-vis) absorption spectra tests were carried out on a Shimadzu UV 3600 spectrometer. Photoluminescence (PL) emission spectra were tested with an Edinburgh FLS980 fluorescence spectrophotometer employing the excitation light of 325 nm. The inductively coupled plasma emission spectroscopy (ICP) data were obtained by an Agilent 730 ICP-OES machine. Brunauer-Emmett-Teller (BET) specific surface areas and corresponding pore-size distributions were examined by a Micromeritics TriStar II 3020 automatic adsorption instrument.

Photocatalytic H_2 evolution reactions

The photocatalytic H_2 evolution activities of photocatalysts were evaluated with a Labsolar-6A online H_2 evolution and detection system manufactured by PerfectLight, Beijing Co., Ltd. Before each test, 30 mg photocatalyst was first dispersed into 100 mL aqueous lactic acid solution (20 vol%) by ultrasonication to get a uniform suspension, which was then filled into the reactor and vacuumized for use. The light irradiation for H_2 evolution was ensured by a 300-W Xe lamp (PLS-SXE 300D) equipped with a 420-nm cutoff filter. Meanwhile, the reaction temperature was maintained at 6°C by a homeothermic circulating pump. The generated H_2 was detected once an hour by a gas chromatograph installed with a thermal-conductivity detector. To study the in-

fluence of hole scavenger on the photocatalytic H₂ evolution activity, lactic acid solution was replaced by TEOA (20 vol%) and 0.35 mol L⁻¹ Na₂S/0.25 mol L⁻¹ Na₂SO₃ aqueous solution with the same volume. The apparent quantum yield (AQY) of H₂ formation for the photocatalysts was measured by using a 420-nm bandpass filter, which can be determined according to the equation below:

$$\begin{aligned}\text{AQY} &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% \\ &= \frac{2 \times \text{number of evolved H}_2 \text{ molecules}}{\text{number of incident photons}} \times 100\% \\ &= \frac{2 \times n_{\text{H}_2}}{n_p} \times 100\% \\ &= \frac{2 \times n_{\text{H}_2}}{\frac{P \times t \times \lambda}{h \times c}} \times 100\%.\end{aligned}$$

In this equation, n_{H_2} and n_p are the number of H₂ molecules and photons, respectively; P denotes the light power; $t = 3600$ s stands for the illumination time; $\lambda = 420$ nm is the incident light wavelength; $h = 6.63 \times 10^{-34}$ J s represents the Planck constant; and $c = 3.0 \times 10^8$ m s⁻¹ is the light speed.

Electrochemical and photoelectrochemical measurements

The electrochemical and photoelectrochemical properties of photocatalysts were measured on a CHI 660E electrochemical workstation utilizing a three-electrode setup, in which Pt plate and Ag/AgCl were the counter-electrode and reference electrode, respectively. The working electrode was prepared by coating the catalyst ink in PEG aqueous solution onto fluorine doped tin oxide (FTO) glass, which was then dried and calcined at 450°C for 1 h under N₂ atmosphere. Mott-Schottky curves were recorded using 0.5 mol L⁻¹ Na₂SO₄ aqueous solution as the electrolyte. The amplitude and frequency were 0.005 V and 500 Hz, respectively. For electrochemical impedance spectroscopy (EIS), the electrolyte was 0.5 mol L⁻¹ Na₂SO₄ aqueous solution. The data were collected at open circuit potential employing the amplitude of 0.005 V and frequency of 0.1–10⁴ Hz. Transient photocurrent measurement was performed in 20 vol% lactic acid aqueous solution applying the bias potential of 0.5 V. A 300-W Xe lamp equipped with a 420-nm cutoff filter was used to ensure the visible-light irradiation, in which both the lighting and dark time were fixed as 20 s.

RESULTS AND DISCUSSION

Cd_{1-x}Zn_xS solid solutions possess much increased pho-

tocatalytic HER activities owing to their higher conduction band levels compared with pristine CdS [32,35]. Therefore, Cd_{1-x}Zn_xS is a suitable photocatalyst for efficient HER. For the as-prepared Cd_{1-x}Zn_xS ($0 \leq x \leq 0.15$, Fig. S1), the bandgaps based on the UV-vis absorption spectra and corresponding Kubelka-Munk plots are 2.42, 2.45, 2.47, and 2.49 eV for CdS, Cd_{0.95}Zn_{0.05}S (CZ_{0.05}S), Cd_{0.90}Zn_{0.10}S (CZ_{0.10}S), and Cd_{0.85}Zn_{0.15}S (CZ_{0.15}S), respectively (Fig. S2). It is well known that, the bandgap of ZnS (~3.7 eV) is much larger than that of CdS (~2.4 eV) [18,36]. Therefore, the bandgap of Cd_{1-x}Zn_xS solid solution enlarges with the increase of Zn-doping amount, leading to the blue-shift of absorption edge of Cd_{1-x}Zn_xS (Fig. S2a) and displaying a decreased light absorption range. The conduction band minimum (CBM) potential (E_{CBM}) of Cd_{1-x}Zn_xS solid solutions relative to the normal hydrogen electrode (NHE) potential can be calculated as follows [37]: $E_{\text{CBM}} = \chi - E_c - 0.5E_g$, where χ is the electronegativity of a semiconductor, which is defined as the geometric mean of absolute electronegativity of the constituent atoms. E_g represents the bandgap of semiconductor, while E_c (4.50 eV) is the energy of free electrons on the hydrogen scale. Consequently, the E_{CBM} is estimated to be -0.520, -0.532, -0.538, and -0.545 V vs. NHE for CdS, CZ_{0.05}S, CZ_{0.10}S, and CZ_{0.15}S, respectively. Although the light absorption range is decreased, the E_{CBM} of Cd_{1-x}Zn_xS becomes more negative with the increase of Zn ratio, which is conducive to generating stronger reducing electrons to promote HER. Moreover, the BET surface area of Cd_{1-x}Zn_xS is increased with the increase of Zn content (Fig. S3 and Table S1), which contributes more active sites to boost the HER performance. Therefore, with the increase of Zn-doping, the enhanced reducing power of photogenerated electrons (due to more negative E_{CBM}) and increased active sites (due to enlarged BET surface area) are responsible for the improved HER activity of Cd_{1-x}Zn_xS solid solutions (Fig. S4). After doping, the CZ_{0.15}S exhibited the highest H₂ formation rate (Fig. S4b), and hence, CZ_{0.15}S nanorods were chosen as the active component to construct high-performance hybrid photocatalysts.

The synthesis of Cd_{1-x}Zn_xS@WO_{3-x} and Cd_{1-x}Zn_xS@WO_{3-x}/CoO_x/NiO_x nanorods is schematically illustrated in Fig. 1. Firstly, the 1D Cd_{1-x}Zn_xS solid solutions with different aspect ratios were prepared by an ethylenediamine-directing solvothermal strategy [34]. Subsequently, the Cd_{1-x}Zn_xS was ultrasonically dispersed in EG solution containing different concentrations of WCl₄, which was then stirred for 30 min before it was rinsed with ethanol and water and dried in an oven to produce

Figure 1 Schematic process for the synthesis of $\text{Cd}_{1-x}\text{Zn}_x\text{S}@WO_{3-x}$ and $\text{Cd}_{1-x}\text{Zn}_x\text{S}@WO_{3-x}/\text{CoO}_x/\text{NiO}_x$ nanorods.

$\text{Cd}_{1-x}\text{Zn}_x\text{S}@WO_{3-x}$. It is proposed that, the dissolved W-containing precursor was adsorbed by $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ at first *via* electrostatic interactions with nitrogenous species remaining on the surface [38], which was then hydrolyzed and oxidized into oxygen-deficient WO_{3-x} amorphous layers coating on $\text{Cd}_{1-x}\text{Zn}_x\text{S}$, under heating condition with the presence of H_2O and O_2 . Finally, under irradiation, 1D $\text{Cd}_{1-x}\text{Zn}_x\text{S}@WO_{3-x}/\text{CoO}_x/\text{NiO}_x$ hybrids were obtained through the *in-situ* photo-deposition of CoO_x and NiO_x nanoparticles onto $\text{Cd}_{1-x}\text{Zn}_x\text{S}@WO_{3-x}$.

X-ray diffraction (XRD) patterns of $\text{CZ}_{0.15}\text{S}$ nanorods, WO_3 nanosheets, and $\text{CZ}_{0.15}\text{S}@WO_{3-x}$ nanorods with different concentrations of WO_{3-x} are displayed in Fig. 2. Obviously, the diffraction peaks of $\text{CZ}_{0.15}\text{S}$ nanorods can be indexed as the wurtzite phase of CdS (JCPDS card No. 80-0006), while the signals of WO_3 nanosheets are consistent with that of triclinic WO_3 (JCPDS card No. 20-1323). For the $\text{CZ}_{0.15}\text{S}@WO_{3-x}$ hybrids with different amounts of WO_{3-x} , except the diffraction signals of $\text{CZ}_{0.15}\text{S}$, no visible WO_{3-x} signal can be found in the XRD pattern of composite even having a higher WO_{3-x} content ($\text{CZ}_{0.15}\text{S}-0.11\text{W}$), which may be due to the weak crystallinity and high dispersion of the involved WO_{3-x} .

TEM image of individual $\text{CZ}_{0.15}\text{S}$ is presented in Fig. 3a, which consists of many uniform nanorods with smooth surface. Based on the fast Fourier transform (FFT) result (Fig. 3b) of one lying $\text{CZ}_{0.15}\text{S}$ nanorod oriented in [100], the top and bottom planes of the nanorod could be determined as {100} facets, while the growth direction parallels to $\langle 001 \rangle$, i.e., *c*-axis. Meanwhile, HRTEM analysis of the nanorod in Fig. 3c also reveals that, the nanorod lattices stretch preferentially along the *c*-axis. By considering the symmetry of wurtzite structure, the $\text{CZ}_{0.15}\text{S}$ nanorods are surrounded by six equivalent {100} facets and they grow along the *c*-axis. The dark-field STEM image and corresponding EDX elemental mapping results (Fig. 3d) disclose that, Cd, Zn, and S are uniformly distributed all over the whole nanorod. The $\text{CZ}_{0.15}\text{S}@WO_{3-x}$ hybrid nanorods were formed after $\text{CZ}_{0.15}\text{S}$ was coated by WO_{3-x} amorphous layers. As shown in Fig. 3e, the $\text{CZ}_{0.15}\text{S}-0.08\text{W}$ sample prepared after air-drying is

Figure 2 XRD patterns of $\text{CZ}_{0.15}\text{S}$ nanorods, WO_3 nanosheets, and the $\text{CZ}_{0.15}\text{S}@WO_{3-x}$ hybrid nanorods with different WO_{3-x} contents.

featured by the rod-like morphology similar to that of pristine $\text{CZ}_{0.15}\text{S}$. Further, HRTEM measurement (Fig. 3f) indicates that, $\text{CZ}_{0.15}\text{S}-0.08\text{W}$ possesses a unique core-sheath structure comprising the $\text{CZ}_{0.15}\text{S}$ nanorod enwrapped by ultrathin WO_{3-x} layers (highlighted by the yellow dashed lines). The amorphous WO_{3-x} layers coating on the $\text{CZ}_{0.15}\text{S}$ nanorod can be unambiguously observed as demonstrated in Fig. 3g. Moreover, the STEM and corresponding EDX elemental mapping results of $\text{CZ}_{0.15}\text{S}-0.08\text{W}$ (Fig. 3h) confirm the homogeneous distribution of Cd, Zn, W, and S throughout the entire nanorod. Furthermore, the influence of synthesis parameter on the structure of product was investigated. It can be seen from Fig. S5 that the $\text{CZ}_{0.15}\text{S}-0.08\text{W}$ fabricated with vacuum-drying owns an analogous structure to that prepared after air-drying (Fig. 3e–g). Additionally, when the concentration of WCl_4 reaction solution was increased to 0.11 mol L^{-1} , besides WO_{3-x} layers, many small WO_{3-x} nanoparticles were also formed on the surface of product ($\text{CZ}_{0.15}\text{S}-0.11\text{W}$, Fig. S6).

XPS tests were performed to identify the surface compositions and related chemical valence states of $\text{CZ}_{0.15}\text{S}$ -

Figure 3 (a) TEM, (b, c) HRTEM, and (d) dark-field STEM and EDX elemental mapping images of CZ_{0.15}S nanorods. (e–h) The corresponding results of CZ_{0.15}S-0.08W nanorods.

0.08W nanorods. For CZ_{0.15}S nanorods, the electron binding energies of Cd 3d (404.7 and 411.5 eV, Fig. 4a) and Zn 2p (1022.1 and 1045.3 eV, Fig. 4b) could be assigned to the Cd²⁺ and Zn²⁺ species, respectively [39–41]. In comparison with CZ_{0.15}S, both the Cd²⁺ and Zn²⁺ of CZ_{0.15}S-0.08W exhibit a blue-shift of binding energies, suggesting the interaction between CZ_{0.15}S and the coated WO_{3-x} [42]. Besides, the valence state of W in CZ_{0.15}S-0.08W was carefully studied as presented in Fig. 4c, where the data of pure WO₃ and WS₂ are also given for reference. We can see that, the WO₃ and WS₂ possess the doublets locating at 35.5–37.6 eV and 32.3–34.5 eV, which correspond to W⁶⁺ and W⁴⁺ ions, respectively [43,44]. It is evident that, both the W spectra of CZ_{0.15}S-0.08W prepared after vacuum-drying (CZ_{0.15}S-0.08W-vacuum) and air-drying (CZ_{0.15}S-0.08W-air) contain the component stemming from W⁶⁺. Meanwhile, a small peak around 33.5 eV (between the peaks of 32.3 and 34.5 eV

for W⁴⁺) is found for CZ_{0.15}S-0.08W-air, which could be attributed to the W⁵⁺ species [45,46]. Noticeably, the CZ_{0.15}S-0.08W-vacuum is endowed with a much weakened W⁵⁺ signal compared with CZ_{0.15}S-0.08W-air, which may result from the different hydrolysis and oxidation processes under these two drying conditions. In our synthesis, the WCl₄ was dissolved into EG at first to form the W-EG complexes [47], which were then adsorbed onto the surface of Cd_{1-x}Zn_xS nanorods *via* electrostatic interactions. After being rinsed with ethanol and water, the remained W-EG complexes on Cd_{1-x}Zn_xS nanorod surface would be hydrolyzed and oxidized into WO_{3-x} during the subsequent drying processes. As the heating rate in air atmosphere is significantly higher than that in vacuum condition, the hydrolysis and oxidation processes for W-EG complexes could be very fast in air atmosphere, which results in the formation of more oxygen vacancies (W⁵⁺/OVs) in the WO_{3-x} species. In

Figure 4 (a) Cd 3d, (b) Zn 2p XPS spectra of $\text{CZ}_{0.15}\text{S}$ and $\text{CZ}_{0.15}\text{S-0.08W}$ nanorods. (c) W 4f spectra of WS_2 , WO_3 , and $\text{CZ}_{0.15}\text{S-0.08W}$ prepared under different drying conditions. (d) O 1s spectra of WO_3 , $\text{CZ}_{0.15}\text{S}$, and $\text{CZ}_{0.15}\text{S-0.08W}$ obtained after air-drying.

addition, the O 1s spectra of WO_3 , $\text{CZ}_{0.15}\text{S}$, and $\text{CZ}_{0.15}\text{S-0.08W-air}$ were analyzed and compared. As shown in Fig. 4d, all these three samples are in possession of the components at 531.5 and 533.2 eV, originating from the O in hydroxyl and bound H_2O of hydration, respectively [48,49]. Moreover, different from $\text{CZ}_{0.15}\text{S}$, the $\text{CZ}_{0.15}\text{S-0.08W-air}$ displays a new signal around 530.2 eV, which belongs to the O in W–O bonds of WO_{3-x} [50]. Therefore, one can conclude from the above results that, the coated W species on $\text{CZ}_{0.15}\text{S-0.08W-air}$ are WO_{3-x} which contain a certain amount of oxygen vacancies (W^{5+}/OVs). To directly confirm the formation of oxygen vacancies, EPR measurements were carried out. As shown in Fig. 5, the $\text{CZ}_{0.15}\text{S-0.08W}$ obtained after drying in air atmosphere exhibits a sharp signal at $g = 2.003$, which can be attributed to the electrons trapped on oxygen vacancies [23,51]. In contrast, no detectable EPR signal can be found in the $\text{CZ}_{0.15}\text{S-0.08W}$ prepared after vacuum-drying, indicating the absence of oxygen vacancies in this sample. The EPR data are in good agreement with the XPS results (Fig. 4).

The visible-light-induced photocatalytic H_2 evolution

activities of $\text{CZ}_{0.15}\text{S@WO}_{3-x}$ nanorods with different WO_{3-x} concentrations were compared. As shown in Fig. 6a and Fig. S7, the WO_3 nanosheets (Fig. S8) are inert for HER and both $\text{CZ}_{0.15}\text{S}$ and Pt-loaded $\text{CZ}_{0.15}\text{S}$ ($\text{CZ}_{0.15}\text{S-Pt}$) nanorods possess lower activities toward H_2 formation. In contrast, $\text{CZ}_{0.15}\text{S@WO}_{3-x}$ hybrid nanorods prepared after air-drying show significantly improved HER activity, among which $\text{CZ}_{0.15}\text{S-0.08W}$ exhibits the maximum H_2 evolution rate of $21.68 \text{ mmol h}^{-1} \text{ g}^{-1}$, about 12 times that of individual $\text{CZ}_{0.15}\text{S}$. In addition, some comparative experimental results are also demonstrated. For instance, the photocatalytic activity of $\text{CZ}_{0.15}\text{S-WO}$ prepared by a solvothermal method was evaluated, which was inferior to that of $\text{CZ}_{0.15}\text{S-0.05W}$ having a close WO_{3-x} content. Regarding the preparation of $\text{CZ}_{0.15}\text{S-WO}$, the W-containing species grown on $\text{CZ}_{0.15}\text{S}$ nanorods varied with the concentration of reactant (WCl_4 , thioacetamide) solution. At a lower reactant concentration (2.83 and $16.98 \text{ mmol L}^{-1}$ for WCl_4 and thioacetamide, respectively), WO_3 nanocrystals (ca. 3 wt%) were produced on the surface of $\text{CZ}_{0.15}\text{S}$ nanorods ($\text{CZ}_{0.15}\text{S-}$

Figure 5 EPR spectra of CZ_{0.15}S-0.08W obtained after drying in air atmosphere and vacuum condition.

WO, Fig. S9). When the WCl₄ and thioacetamide concentrations were increased respectively to 5.15 and 30.90 mmol L⁻¹, WS₂ nanosheets (ca. 6 wt%) started to appear on the CZ_{0.15}S nanorod surface (CZ_{0.15}S-WS, Fig. S10). Under solvothermal conditions, thioacetamide decomposed to generate S²⁻ anions, which then combined with W⁴⁺ cations to form WS₂. However, if a low concentration of WCl₄ and thioacetamide solution was used, the produced WS₂ species might be unstable due to their small amount, which could react with the dissolved oxygen or water and transform into WO₃ during the following reaction processes. It is common to see that, the WS₂ nanosheets obtained by chemical synthesis were usually accompanied by the formation of some WO₃ clusters [52,53]. The TEM and HRTEM images of CZ_{0.15}S-WO in Fig. S9 indicate that, WO₃ nanocrystals with a big size were loaded on the surface of CZ_{0.15}S nanorods. Besides, negligible W⁵⁺ signals can be found in the XPS spectrum of CZ_{0.15}S-WO (Fig. S10), which suggests the deficiency of oxygen vacancies in this sample. Compared with CZ_{0.15}S-WO with big WO₃ nanoparticles, CZ_{0.15}S-0.05W consists of CZ_{0.15}S nanorods coated by ultrathin oxygen-deficient WO_{3-x} amorphous layers (similar to that of CZ_{0.15}S-0.08W). Therefore, more heterostructure interfaces can be formed in CZ_{0.15}S-0.05W to retard the recombination of charge carriers. Moreover, the oxygen vacancies in CZ_{0.15}S-0.05W could reduce the interfacial electric resistance to facilitate the transfer of photogenerated electrons and holes. As a result, benefiting from the above advantages, CZ_{0.15}S-0.05W demonstrates a much better HER performance than CZ_{0.15}S-WO (Fig. 6a). Besides, when WCl₄ was replaced by different

proportions of MoCl₅, the products were all provided with degraded HER performances (Fig. S11). On the other hand, the influence of hole scavenger on the H₂ evolution activity (Fig. S12) was explored, which uncovered that lactic acid contributed to promoting the HER significantly compared with the Na₂S/Na₂SO₃ and TEOA. Interestingly, after CZ_{0.15}S-0.08W was co-deposited with CoO_x and NiO_x (CZSW-CoO_x/NiO_x) through illumination, the HER rate further increased to 28.25 mmol h⁻¹ g⁻¹, exceeding that of most WO₃- and CdS-based photocatalysts (Table S2) [27,54–58]. The effect of CoO_x/NiO_x photo-deposition on the HER activity of CZ_{0.15}S-0.08W was investigated accordingly. Fig. S13a and S13c disclose that, the optimal HER property of CZSW-CoO_x/NiO_x was obtained at the deposition amount of 2.5 wt%. What's more, under the identical loading concentration (2.5 wt%), the CZ_{0.15}S-0.08W supported with CoO_x and NiO_x (CZSW-CoO_x/NiO_x) is much more active than the counterparts consisting solely of CoO_x (CZSW-CoO_x) or NiO_x (CZSW-NiO_x) (Fig. S13b and S13d). Therefore, the above results suggest that, the HER activity of CZ_{0.15}S-0.08W increases after photo-deposition and the co-deposition with CoO_x and NiO_x.

It is well known that, the electron-hole pair recombination of photocatalyst could give rise to PL emission. Hence, the PL emission spectra (excited at 365 nm) of WO₃, CZ_{0.15}S, and CZ_{0.15}S-0.08W were measured to study their separation abilities for charge carriers, as the latter was a critical factor determining the photocatalytic efficiency [59]. As exhibited in Fig. 6b, the PL signals at ~477 and 524 nm are related to the excitonic and trap-state recombination, respectively [60,61]. As expected, compared with pure WO₃ and CZ_{0.15}S, CZ_{0.15}S-0.08W displays the lowest emission intensity indicating that the former is endowed with a much better capability for charge separation than the latter two [57]. The decreased PL emission of CZ_{0.15}S-0.08W could result from the heterostructure formed between WO_{3-x} and CZ_{0.15}S, which significantly suppresses the recombination of photogenerated electrons and holes, responsible for the superior HER activity of CZ_{0.15}S-0.08W. The visible-light-induced photocurrent responses of WO₃, CZ_{0.15}S, and CZ_{0.15}S-0.08W were also compared as presented in Fig. 6c. The CZ_{0.15}S-0.08W shows a much higher photocurrent density than WO_{3-x} and CZ_{0.15}S, suggesting that the charge carriers are separated more efficiently by the former [62], which agrees well with the PL emission results. Moreover, the charge-transfer process occurring under illumination was investigated by the EIS tests. The Nyquist plots in Fig. 6d evidence that CZ_{0.15}S-0.08W has

Figure 6 (a) Photocatalytic H₂ evolution rates of WO₃, CZ_{0.15}S, CZ_{0.15}S-Pt, CZ_{0.15}S-0.08W@CoO_x/NiO_x (CZSW-CoO_x/NiO_x), and CZ_{0.15}S@WO_{3-x} hybrids with varying WO_{3-x} contents. (b) PL spectra, (c) photocurrent responses, and (d) EIS Nyquist plots of WO₃, CZ_{0.15}S, and CZ_{0.15}S-0.08W. (e) Apparent quantum yield calculation curves and (f) long-term photocatalytic H₂ evolution stability of CZ_{0.15}S-0.08W and CZSW-CoO_x/NiO_x nanorods.

the smallest semicircular arc, indicating its minimum charge-transfer resistance compared with WO₃ and CZ_{0.15}S [63]. The reduced charge-transfer resistance of CZ_{0.15}S-0.08W can be attributed to the facilitated separation and transfer of photoexcited charge carriers [64,65], consistent with the photocurrent and PL emission results. Furthermore, the AQY of HER for CZ_{0.15}S-

0.08W and CZSW-CoO_x/NiO_x were measured using the illumination of 420 nm monochromatic light. We can see from Fig. 6e that, the CZ_{0.15}S-0.08W achieves an AQY of 34.6%, which is dramatically increased to 60.8% when the reaction is triggered by CZSW-CoO_x/NiO_x.

The stability of the as-prepared samples was investigated as it was critical for widespread photocatalytic

applications. Firstly, the durability of $\text{CZ}_{0.15}\text{S}-0.08\text{W}$ and $\text{CZSW-CoO}_x/\text{NiO}_x$ towards long-term H_2 production was measured as shown in Fig. 6f, indicating that the H_2 evolution of both samples were steady during a 12 h uninterrupted testing. In addition, the cycling stability of $\text{CZSW-CoO}_x/\text{NiO}_x$ composite was also evaluated. As shown in Fig. S14, there was no obvious activity decay after 5 cycle measurements using the same photocatalyst and testing conditions. These results show that $\text{CZ}_{0.15}\text{S}-0.08\text{W}$ and $\text{CZSW-CoO}_x/\text{NiO}_x$ are endowed with outstanding stability towards H_2 production for photocatalytic water splitting. It is worth mentioning that, the HER activity of $\text{CZ}_{0.15}\text{S}-0.08\text{W}$ with oxygen-deficient WO_{3-x} layers was maintained well after being stored for

seven weeks (Fig. S15).

TEM image of $\text{CZSW-CoO}_x/\text{NiO}_x$ is shown in Fig. 7a, which displays that the hybrid is composed of nanorods deposited with small nanoparticles. In Fig. 7b, the interplanar spacing (0.297 nm) of the nanoparticle anchored on $\text{CZ}_{0.15}\text{S}$ nanorod (marked in Fig. 7a) is in consistence with the $\{110\}$ planes of cubic NiO (JCPDS No. 02-1216). Moreover, according to the HRTEM analyses of Fig. 7c, the nanoparticle (Fig. S16) loaded on amorphous WO_{3-x} coating-layer possesses the lattices of 0.246 nm, assigned to the $\{111\}$ planes of cubic CoO (JCPDS No. 01-1227). In addition, the existence of Cd, Zn, W, Co, Ni, S, and O elements in $\text{CZSW-CoO}_x/\text{NiO}_x$ hybrid is demonstrated by the STEM and corresponding EDX elemental mapping by the STEM and corresponding EDX elemental mapping

Figure 7 (a) TEM, (b, c) HRTEM, (d) dark-field STEM and EDX elemental mapping, and (e, f) Ni 2p and Co 2p XPS results of $\text{CZSW-CoO}_x/\text{NiO}_x$ nanorods.

results (Fig. 7d). Furthermore, the valence states of nickel and cobalt species in CZSW-CoO_x/NiO_x photo-deposited with Na₂S/Na₂SO₃ solution were analyzed by XPS measurements. As indicated by Fig. 7e, the Ni 2p peaks located at 852.8–871.5 eV can be attributed to the Ni⁰ species [66,67], while the Ni 2p doublet at 855.9–873.7 eV is related to the Ni²⁺ ions in NiO [68]. For Co 2p spectrum (Fig. 7f), the signals with binding energies of 780.3 and 795.6 eV are identified, which belong to the Co²⁺ ions in CoO [69]. Therefore, the XPS data are in good agreement with the HRTEM results.

After HER test, the CZSW-CoO_x/NiO_x was also characterized by HRTEM and XPS tests. As shown in Fig. S17a, the nanoparticle on WO_{3-x} amorphous layer displays the structure of cubic CoO (JCPDS No. 01-1227). Meanwhile, based on the HRTEM image in Fig. S17b, the nanoparticle anchored on CZ_{0.15}S nanorod is identified as the cubic NiO (JCPDS No. 02-1216). On the other hand, the Ni 2p XPS spectrum in Fig. S17c indicates that, Ni and NiO still exist in the CZSW-CoO_x/NiO_x hybrid after reaction. Moreover, the presence of CoO species is confirmed by the Co 2p peaks in Fig. S17d. The HRTEM and

XPS results of the used CZSW-CoO_x/NiO_x are similar to that before reaction (Fig. 7), which suggests that the catalyst structure after photocatalytic reaction is maintained, demonstrating a favorable stability of the CZSW-CoO_x/NiO_x composite.

The photocatalytic H₂ evolution activities of CZ_{0.15}S-0.08W and CZ_{0.15}S-0.10W prepared under different drying conditions were compared. As indicated in Fig. 8a, the HER performance of CZ_{0.15}S-0.08W-air is superior to that of CZ_{0.15}S-0.08W-vacuum. Similarly, in comparison with CZ_{0.15}S-0.10W-vacuum, the CZ_{0.15}S-0.10W-air displays a much enhanced capability towards H₂ production (Fig. 8b). Hence, we can see that, the HER activities of CZ_{0.15}S@WO_{3-x} synthesized by air-drying are much better than that of the counterparts fabricated after vacuum-drying, which suggests that the oxygen vacancies (W⁵⁺/OVs) formed in CZ_{0.15}S-0.08W (Fig. 4) plays a critical role in the enhancement of photocatalytic activity. One can notice that, the CZ_{0.15}S@WO_{3-x} hybrid shows a middle light-absorption as compared with pure CZ_{0.15}S and WO₃ (Fig. S18); however, the HER activity of CZ_{0.15}S@WO_{3-x} is much higher than that of the other two

Figure 8 (a, b) Comparison of H₂ formation activities of CZ_{0.15}S-0.08W and CZ_{0.15}S-0.10W prepared after drying under different conditions. (c) Mott-Schottky curves of CdS, CZ_{0.15}S, and WO₃. (d) The Z-scheme interfacial charge transfer between WO_{3-x} and CZ_{0.15}S.

(Fig. 6a and Fig. S7). To uncover the reason for the enhanced photocatalytic activity of $\text{CZ}_{0.15}\text{S}@ \text{WO}_{3-x}$, the electronic band structures of $\text{CZ}_{0.15}\text{S}$ and WO_{3-x} were studied accordingly. On the basis of the Kubelka-Munk theory [53], the bandgaps of $\text{CZ}_{0.15}\text{S}$ and WO_3 are determined to be 2.49 eV (direct band gap) and 2.48 eV (indirect band gap), respectively (Figs S2 and S19). In Fig. 8c, the Mott-Schottky curves show that the flat band potentials of CdS, $\text{CZ}_{0.15}\text{S}$, and WO_3 are found to be -0.71 , -0.92 , and -0.45 V vs. Ag/AgCl, corresponding to -0.11 , -0.32 , and 0.15 V vs. RHE, respectively. The positive slopes of Mott-Schottky profiles confirm that these three samples all belong to the n-type semiconductor [70]. It is commonly acknowledged that, the conduction band bottom of n-type semiconductor is about 0.1 V more negative than its flat band potential [71]. Therefore, the conduction band minimum (CBM) potentials of CdS, $\text{CZ}_{0.15}\text{S}$, and WO_3 are estimated to be -0.21 , -0.42 , and 0.05 V vs. RHE, respectively. The more negative CBM potential of $\text{CZ}_{0.15}\text{S}$ than CdS indicates that Zn-doping affects the CBM level of CdS, which is beneficial to the formation of stronger reducing electrons for HER [72]. Integrating the bandgaps of $\text{CZ}_{0.15}\text{S}$ and WO_3 with their CBM potentials, the corresponding band alignments can be fixed (Fig. 8d). Furthermore, for $\text{CZ}_{0.15}\text{S}@ \text{WO}_{3-x}$ hybrid, the photogenerated charge transfer between $\text{CZ}_{0.15}\text{S}$ and WO_{3-x} was thoroughly analyzed. According to the heterostructure-type charge transfer pathway [73], under illumination, the photo-induced electrons in the conduction band (CB) of $\text{CZ}_{0.15}\text{S}$ will migrate into the CB of WO_{3-x} through the conjoint interfaces, while the holes will move from the valence band (VB) of WO_{3-x} to the VB of $\text{CZ}_{0.15}\text{S}$. However, in this case, the photogenerated electrons in the CB of WO_{3-x} cannot reduce H^+ into H_2 due to the positive CB potential of WO_{3-x} (Fig. 8d), which is not in agreement with the photocatalytic HER results (Fig. 6a). In contrast, the charge transfer should follow the Z-scheme mechanism.

According to previous studies [74,75], the Fermi level of WO_{3-x} is lower than that of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$. Thus, after WO_{3-x} was coated onto $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ to form $\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}$ heterostructure, the electrons will flow from $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ to WO_{3-x} until their Fermi levels are aligned [25], which leads to the establishment of space-charge region and built-in electric field at the interfaces [76,77] with the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and WO_{3-x} being positively and negatively charged near the surface, respectively. As shown in Fig. 4a and b, both the Cd 3d and Zn 2p signals in $\text{Cd}_{1-x}\text{Zn}_x\text{S}@ \text{WO}_{3-x}$ hybrid shift to higher binding energies as compared with that in individual $\text{Cd}_{1-x}\text{Zn}_x\text{S}$, indicating

that the electron cloud densities of Cd and Zn atoms are decreased after the hybridization of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and WO_{3-x} . The reduced electron cloud densities of Cd and Zn atoms imply that, the electrons are transferred from $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ to WO_{3-x} after they are combined together, which is in agreement with the above statements. Then, the interfacial electric field could cause the depletion or accumulation of charge carrier near the semiconductor surface in contrast to the bulk. As a result, the energy band edges of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ with high Fermi level are bended upward continuously towards the interface, oppositely, the energy band edges of WO_{3-x} with low Fermi level display a downward bending towards the interface [77]. The downward band bending enables the electrons to flow out swimmingly but impedes the transmission of holes, while the upward band bending is beneficial to the movement of holes rather than electrons. As a result, the photo-induced electrons in WO_{3-x} will recombine with the holes in $\text{CZ}_{0.15}\text{S}$, and the stronger reducing electrons in the CB of $\text{CZ}_{0.15}\text{S}$ and oxidizing holes in the VB of WO_{3-x} are well spatially isolated, resulting in significantly decreased charge recombination and highly efficient H_2 evolution activity of $\text{CZ}_{0.15}\text{S}@ \text{WO}_{3-x}$. It is worth mentioning that, the oxygen defects in WO_{3-x} could engender a set of quasi-continuous energy levels to reduce the interfacial electric resistance and realize ohmic contact for $\text{CZ}_{0.15}\text{S}@ \text{WO}_{3-x}$ [9,31], which facilitates the transfer of charge carriers through the Z-scheme and improves the HER performance effectively. Therefore, after drying in air, the synthesized $\text{CZ}_{0.15}\text{S}@ \text{WO}_{3-x}$ having more W^{5+}/OVs exhibits a much higher HER activity than the one obtained after vacuum-drying (Fig. 8a and b). What's more, based on the separation of photo-excited electrons in $\text{CZ}_{0.15}\text{S}$ and holes in WO_{3-x} , NiO_x and CoO_x which have been proven to be good cocatalysts in serving as the traps to capture electrons and holes respectively [78–80] are photo-deposited onto $\text{CZ}_{0.15}\text{S}@ \text{WO}_{3-x}$ to form $\text{CZ}_{0.15}\text{S}@ \text{WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$ hybrid (Fig. 6 and Fig. S12), for which the photocatalytic activity is further notably increased (Fig. 6a). Hence, the excellent H_2 evolution performance of $\text{CZ}_{0.15}\text{S}@ \text{WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$ could be attributed to the highly efficient Z-scheme charge separation and selective charge trapping by NiO_x and CoO_x redox cocatalysts.

The strategy through introducing oxygen vacancies into the artificial Z-scheme photocatalytic systems to enhance their photocatalytic HER activity is universal. And the validity of this strategy has been confirmed by various photocatalytic systems reported recently. For example, the rich oxygen vacancies in Z-scheme g- $\text{C}_3\text{N}_4/\text{OD-ZnO}$

heterojunction play dual-function roles in improving visible-light absorption and mediating the efficient charge separation, leading to enhanced photocatalytic degradation of 4-chlorophenol and H_2 evolution [81]. Another example is that the oxygen vacancies in direct Z-scheme BCN-TiO₂ heterostructures enhanced the visible-light absorption and the transfer of photogenerated carriers, which improved the photocatalytic activity for H_2 production significantly [82]. As for Cd_{1-x}Zn_xS, it has the similar effect when it forms a Z-scheme composite with other oxygen-defective semiconductor oxides. For example, the oxygen vacancies in direct Z-scheme ZnO_{1-x}/Zn_{0.2}Cd_{0.8}S heterostructures increased photocatalytic hydrogen production by enhancing visible-light harvesting significantly [83]. Besides, when CdS or ZnS was used to construct Z-scheme hybrid photocatalysts, this strategy is also practicable. For instance, in the CdS/CdWO₄ and CdS/ZnO Z-scheme heterostructures comprising oxygen-defected CdWO₄ or ZnO, the oxygen vacancies helped to form ohmic contact and broaden light absorption, resulting in improved photocatalytic hydrogen evolution [84,85]. While in double Z-scheme ZnO/ZnS/g-C₃N₄ ternary structure, the oxygen vacancies together with sulfur vacancies boosted photo-activity through enhancing the visible-light absorption and facilitating the separation and transfer of charge carriers [86].

CONCLUSIONS

In summary, a novel Z-scheme Cd_{1-x}Zn_xS@WO_{3-x} nano-hybrid photocatalyst consisting of Cd_{1-x}Zn_xS nanorods coated with oxygen-deficient WO_{3-x} amorphous layers was prepared for the first time. The HER measurements indicate that, Cd_{1-x}Zn_xS@WO_{3-x} exhibits a superior activity as compared with Pt-decorated Cd_{1-x}Zn_xS and individual Cd_{1-x}Zn_xS and WO₃. It is revealed that, the excellent HER performance of Cd_{1-x}Zn_xS@WO_{3-x} results from the generation of stronger reducing electrons after appropriate Zn-doping in Cd_{1-x}Zn_xS which increases the CB level, and the facilitated charge transfer caused by the introduction of oxygen vacancies into WO_{3-x} which decreases the interfacial electrical resistance. Specifically, CZ_{0.15}S-0.08W demonstrates an outstanding HER rate of 21.68 mmol h⁻¹ g⁻¹, which is further increased to 28.25 mmol h⁻¹ g⁻¹ after photo-deposition with CoO_x and NiO_x redox cocatalysts (CZSW-CoO_x/NiO_x). Moreover, the AQY at 420 nm of CZSW-CoO_x/NiO_x (60.8%) is much improved in comparison with that of CZ_{0.15}S-0.08W (34.6%). Moreover, both the CZ_{0.15}S-0.08W and CZSW-CoO_x/NiO_x present good HER stability under long-term irradiation. The results demonstrated in this

work will facilitate the development of photocatalysts with highly-efficient solar conversion and utilization.

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- 1 Xiao M, Wang Z, Lyu M, *et al.* Hollow nanostructures for photocatalysis: advantages and challenges. *Adv Mater*, 2018, 315: 1801369
- 2 Zhao K, Zhao S, Gao C, *et al.* Metallic cobalt-carbon composite as recyclable and robust magnetic photocatalyst for efficient CO₂ reduction. *Small*, 2018, 14: 1800762
- 3 Wang J, Cui Y, Wang D. Design of hollow nanostructures for energy storage, conversion and production. *Adv Mater*, 2018, 20: 1801993
- 4 Wang L, Wan J, Zhao Y, *et al.* Hollow multi-shelled structures of Co₃O₄ dodecahedron with unique crystal orientation for enhanced photocatalytic CO₂ reduction. *J Am Chem Soc*, 2019, 141: 2238–2241
- 5 Wei Y, Wang J, Yu R, *et al.* Constructing SrTiO₃-TiO₂ heterogeneous hollow multi-shelled structures for enhanced solar water splitting. *Angew Chem Int Ed*, 2019, 58: 1422–1426
- 6 Huang ZF, Song J, Li K, *et al.* Hollow cobalt-based bimetallic sulfide polyhedra for efficient all-pH-value electrochemical and photocatalytic hydrogen evolution. *J Am Chem Soc*, 2016, 138: 1359–1365
- 7 Yuan YP, Ruan LW, Barber J, *et al.* Hetero-nanostructured suspended photocatalysts for solar-to-fuel conversion. *Energy Environ Sci*, 2014, 7: 3934–3951
- 8 Han T, Chen Y, Tian G, *et al.* Hydrogenated TiO₂/SrTiO₃ porous microspheres with tunable band structure for solar-light photocatalytic H₂ and O₂ evolution. *Sci China Mater*, 2016, 59: 1003–1016
- 9 Zhou P, Yu J, Jaroniec M. All-solid-state Z-scheme photocatalytic systems. *Adv Mater*, 2014, 26: 4920–4935
- 10 Xiang Q, Yu J, Jaroniec M. Graphene-based semiconductor photocatalysts. *Chem Soc Rev*, 2012, 41: 782–796
- 11 Rahman MZ, Zhang J, Tang Y, *et al.* Graphene oxide coupled carbon nitride homo-heterojunction photocatalyst for enhanced hydrogen production. *Mater Chem Front*, 2017, 1: 562–571
- 12 Lingampalli SR, Rao CNR. Remarkable improvement in visible-light induced hydrogen generation by ZnO/Pt/Cd_{1-x}Zn_xS heterostructures through substitution of N and F in ZnO. *J Mater Chem A*, 2014, 2: 7702–7705
- 13 Lingampalli SR, Gautam UK, Rao CNR. Highly efficient photocatalytic hydrogen generation by solution-processed ZnO/Pt/CdS, ZnO/Pt/Cd_{1-x}Zn_xS and ZnO/Pt/CdS_{1-x}Se_x hybrid nanostructures. *Energy Environ Sci*, 2013, 6: 3589–3594
- 14 Du H, Liu YN, Shen CC, *et al.* Nanoheterostructured photocatalysts for improving photocatalytic hydrogen production. *Chin J Catal*, 2017, 38: 1295–1306
- 15 Zhu M, Sun Z, Fujitsuka M, *et al.* Z-scheme photocatalytic water splitting on a 2D heterostructure of black phosphorus/bismuth vanadate using visible light. *Angew Chem Int Ed*, 2018, 57: 2160–2164
- 16 Zhang Z, Huang J, Fang Y, *et al.* A nonmetal plasmonic Z-scheme photocatalyst with UV- to NIR-driven photocatalytic protons reduction. *Adv Mater*, 2017, 29: 1606688
- 17 Cheng L, Xiang Q, Liao Y, *et al.* CdS-based photocatalysts. *Energy*

- Environ Sci*, 2018, 11: 1362–1391
- 18 Chen J, Wu XJ, Yin L, *et al.* One-pot synthesis of CdS nanocrystals hybridized with single-layer transition-metal dichalcogenide nanosheets for efficient photocatalytic hydrogen evolution. *Angew Chem Int Ed*, 2015, 54: 12110–12114
- 19 Du H, Xie X, Zhu Q, *et al.* Metallic MoO₂ cocatalyst significantly enhances visible-light photocatalytic hydrogen production over MoO₂/Zn_{0.5}Cd_{0.5}S heterojunction. *Nanoscale*, 2015, 7: 5752–5759
- 20 Huang ZF, Song J, Pan L, *et al.* Tungsten oxides for photocatalysis, electrochemistry, and phototherapy. *Adv Mater*, 2015, 27: 5309–5327
- 21 Li H, Zhao F, Zhang J, *et al.* A g-C₃N₄/WO₃ photoanode with exceptional ability for photoelectrochemical water splitting. *Mater Chem Front*, 2017, 1: 338–342
- 22 Yang C, Chen JF, Zeng X, *et al.* Enhanced photochemical performance of hexagonal WO₃ by metal-assisted S–O coupling for solar-driven water splitting. *Sci China Mater*, 2018, 61: 91–100
- 23 Yousaf AB, Imran M, Zaidi SJ, *et al.* Highly efficient photocatalytic Z-scheme hydrogen production over oxygen-deficient WO_{3-x} nanorods supported Zn_{0.3}Cd_{0.7}S heterostructure. *Sci Rep*, 2017, 7: 6574
- 24 Jin J, Yu J, Guo D, *et al.* A hierarchical Z-scheme CdS-WO₃ photocatalyst with enhanced CO₂ reduction activity. *Small*, 2015, 11: 5262–5271
- 25 Zhang LJ, Li S, Liu BK, *et al.* Highly efficient CdS/WO₃ photocatalysts: Z-scheme photocatalytic mechanism for their enhanced photocatalytic H₂ evolution under visible light. *ACS Catal*, 2014, 4: 3724–3729
- 26 Liu Z, Wu J, Zhang J. Quantum dots and plasmonic Ag decorated WO₃ nanorod photoanodes with enhanced photoelectrochemical performances. *Int J Hydrogen Energy*, 2016, 41: 20529–20535
- 27 Yin XL, Liu J, Jiang WJ, *et al.* Urchin-like Au@CdS/WO₃ micro/nano heterostructure as a visible-light driven photocatalyst for efficient hydrogen generation. *Chem Commun*, 2015, 51: 13842–13845
- 28 Tian B, Yang B, Li J, *et al.* Water splitting by CdS/Pt/WO₃-CeO_x photocatalysts with assisting of artificial blood perfluorodecalin. *J Catal*, 2017, 350: 189–196
- 29 Roy A, Lingampalli SR, Nassar IM, *et al.* Effectiveness of NiO in replacing Pt in the photochemical generation of hydrogen by (TiO₂)_{1-x}(NiO)_x/Cd_{0.8}Zn_{0.2}S heterostructures. *Solid State Commun*, 2016, 243: 1–6
- 30 Du H, Liang K, Yuan CZ, *et al.* Bare Cd_{1-x}Zn_xS ZB/WZ heterophase nanojunctions for visible light photocatalytic hydrogen production with high efficiency. *ACS Appl Mater Interfaces*, 2016, 8: 24550–24558
- 31 Xiao F, Zhou W, Sun B, *et al.* Engineering oxygen vacancy on rutile TiO₂ for efficient electron-hole separation and high solar-driven photocatalytic hydrogen evolution. *Sci China Mater*, 2018, 61: 822–830
- 32 Li Q, Meng H, Zhou P, *et al.* Zn_{1-x}Cd_xS solid solutions with controlled bandgap and enhanced visible-light photocatalytic H₂-production activity. *ACS Catal*, 2013, 3: 882–889
- 33 Li R, Zhang F, Wang D, *et al.* Spatial separation of photogenerated electrons and holes among {010} and {110} crystal facets of BiVO₄. *Nat Commun*, 2013, 4: 1432
- 34 Lin H, Sun B, Wang H, *et al.* Unique 1D Cd_{1-x}Zn_xS@OMoS₂/NiO_x nanohybrids: Highly efficient visible-light-driven photocatalytic hydrogen evolution *via* integrated structural regulation. *Small*, 2019, 15: 1804115
- 35 Zhang X, Zhao Z, Zhang W, *et al.* Surface defects enhanced visible light photocatalytic H₂ production for Zn-Cd-S solid solution. *Small*, 2016, 12: 793–801
- 36 Xu X, Hu L, Gao N, *et al.* Controlled growth from ZnS nanoparticles to ZnS-CdS nanoparticle hybrids with enhanced photoactivity. *Adv Funct Mater*, 2015, 25: 445–454
- 37 Su Y, Zhang Z, Liu H, *et al.* Cd_{0.2}Zn_{0.8}S@UiO-66-NH₂ nanocomposites as efficient and stable visible-light-driven photocatalyst for H₂ evolution and CO₂ reduction. *Appl Catal B-Environ*, 2017, 200: 448–457
- 38 Liu B, Yao H, Song W, *et al.* Ligand-free noble metal nanocluster catalysts on carbon supports *via* “soft” nitriding. *J Am Chem Soc*, 2016, 138: 4718–4721
- 39 Wang H, Naghadeh SB, Li C, *et al.* Enhanced photoelectrochemical and photocatalytic activities of CdS nanowires by surface modification with MoS₂ nanosheets. *Sci China Mater*, 2018, 61: 839–850
- 40 Chao Y, Zhou P, Li N, *et al.* Ultrathin visible-light-driven Mo incorporating In₂O₃-ZnIn₂Se₄ Z-scheme nanosheet photocatalysts. *Adv Mater*, 2019, 31: 1807226
- 41 Tian FY, Hou D, Tang F, *et al.* Novel Zn_{0.8}Cd_{0.2}S@g-C₃N₄ core-shell heterojunctions with a twin structure for enhanced visible-light-driven photocatalytic hydrogen generation. *J Mater Chem A*, 2018, 6: 17086–17094
- 42 Jiang B, Tian C, Pan Q, *et al.* Enhanced photocatalytic activity and electron transfer mechanisms of graphene/TiO₂ with exposed {001} facets. *J Phys Chem C*, 2011, 115: 23718–23725
- 43 Zhao ZG, Liu ZF, Miyauchi M. Tailored remote photochromic coloration of *in situ* synthesized CdS quantum dot loaded WO₃ films. *Adv Funct Mater*, 2010, 20: 4162–4167
- 44 Gopannagari M, Kumar DP, Reddy DA, *et al.* *In situ* preparation of few-layered WS₂ nanosheets and exfoliation into bilayers on CdS nanorods for ultrafast charge carrier migrations toward enhanced photocatalytic hydrogen production. *J Catal*, 2017, 351: 153–160
- 45 Song J, Huang ZF, Pan L, *et al.* Oxygen-deficient tungsten oxide as versatile and efficient hydrogenation catalyst. *ACS Catal*, 2015, 5: 6594–6599
- 46 Chen TY, Chang YH, Hsu CL, *et al.* Comparative study on MoS₂ and WS₂ for electrocatalytic water splitting. *Int J Hydrogen Energy*, 2013, 38: 12302–12309
- 47 Li Y, Zhao KQ, Feng C, *et al.* Ethyleneglycol tungsten complexes of calix[6 and 8]arenes: synthesis, characterization and ROP of ϵ -caprolactone. *Dalton Trans*, 2014, 43: 13612–13619
- 48 Zhou P, Xu Q, Li H, *et al.* Fabrication of two-dimensional lateral heterostructures of WS₂/WO₃-H₂O through selective oxidation of monolayer WS₂. *Angew Chem*, 2015, 127: 15441–15445
- 49 Ratcliff EL, Meyer J, Steirer KX, *et al.* Evidence for near-surface NiOOH species in solution-processed NiO_x selective interlayer materials: Impact on energetics and the performance of polymer bulk heterojunction photovoltaics. *Chem Mater*, 2011, 23: 4988–5000
- 50 Wang L, Tsang CS, Liu W, *et al.* Disordered layers on WO₃ nanoparticles enable photochemical generation of hydrogen from water. *J Mater Chem A*, 2019, 7: 221–227
- 51 Fang Z, Jiao S, Wang B, *et al.* Synthesis of reduced cubic phase WO_{3-x} nanosheet by direct reduction of H₂WO₄·H₂O. *Mater Today Energy*, 2017, 6: 146–153
- 52 Mahler B, Hoepfner V, Liao K, *et al.* Colloidal synthesis of 1T-WS₂ and 2H-WS₂ nanosheets: Applications for photocatalytic hydrogen evolution. *J Am Chem Soc*, 2014, 136: 14121–14127

- 53 Liu Z, Li N, Su C, *et al.* Colloidal synthesis of 1T' phase dominated WS₂ towards durable electrocatalysis. *Nano Energy*, 2018, 50: 176–181
- 54 Zhang H, Zhang P, Qiu M, *et al.* Ultrasmall MoO_x clusters as a novel cocatalyst for photocatalytic hydrogen evolution. *Adv Mater*, 2018, 113: 1804883
- 55 Zhao Z, Xing Y, Li H, *et al.* Constructing CdS/Cd/doped TiO₂ Z-scheme type visible light photocatalyst for H₂ production. *Sci China Mater*, 2018, 61: 851–860
- 56 Chang K, Li M, Wang T, *et al.* Drastic layer-number-dependent activity enhancement in photocatalytic H₂ evolution over nMoS₂/CdS ($n \geq 1$) under visible light. *Adv Energy Mater*, 2015, 5: 1402279
- 57 Zhuang TT, Liu Y, Sun M, *et al.* A unique ternary semiconductor-(semiconductor/metal) nano-architecture for efficient photocatalytic hydrogen evolution. *Angew Chem Int Ed*, 2015, 54: 11495–11500
- 58 Zong X, Yan HJ, Wu GP, *et al.* Enhancement of photocatalytic H₂ evolution on CdS by loading MoS₂ as cocatalyst under visible light irradiation. *J Am Chem Soc*, 2008, 130: 7176–7177
- 59 Prusty G, Guria AK, Mondal I, *et al.* Modulated binary-ternary dual semiconductor heterostructures. *Angew Chem Int Ed*, 2016, 55: 2705–2708
- 60 Yin XL, Li LL, Jiang WJ, *et al.* MoS₂/CdS nanosheets-on-nanorod heterostructure for highly efficient photocatalytic H₂ generation under visible light irradiation. *ACS Appl Mater Interfaces*, 2016, 8: 15258–15266
- 61 Simon T, Bouchonville N, Berr MJ, *et al.* Redox shuttle mechanism enhances photocatalytic H₂ generation on Ni-decorated CdS nanorods. *Nat Mater*, 2014, 13: 1013–1018
- 62 Ruan Q, Luo W, Xie J, *et al.* A nanojunction polymer photoelectrode for efficient charge transport and separation. *Angew Chem Int Ed*, 2017, 56: 8221–8225
- 63 Kim ES, Nishimura N, Magesh G, *et al.* Fabrication of CaFe₂O₄/TaON heterojunction photoanode for photoelectrochemical water oxidation. *J Am Chem Soc*, 2013, 135: 5375–5383
- 64 Chang X, Wang T, Zhang P, *et al.* Enhanced surface reaction kinetics and charge separation of p–n heterojunction Co₃O₄/BiVO₄ photoanodes. *J Am Chem Soc*, 2015, 137: 8356–8359
- 65 Li K, Han M, Chen R, *et al.* Hexagonal@cubic CdS core@shell nanorod photocatalyst for highly active production of H₂ with unprecedented stability. *Adv Mater*, 2016, 28: 8906–8911
- 66 Yang H, Jin Z, Liu D, *et al.* Visible light harvesting and spatial charge separation over the creative Ni/CdS/Co₃O₄ photocatalyst. *J Phys Chem C*, 2018, 122: 10430–10441
- 67 Biesinger MC, Payne BP, Grosvenor AP, *et al.* Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Appl Surf Sci*, 2011, 257: 2717–2730
- 68 Wang M, Hu Y, Han J, *et al.* TiO₂/NiO hybrid shells: p–n junction photocatalysts with enhanced activity under visible light. *J Mater Chem A*, 2015, 3: 20727–20735
- 69 Tan BJ, Klabunde KJ, Sherwood PMA. XPS studies of solvated metal atom dispersed (SMAD) catalysts. Evidence for layered cobalt-manganese particles on alumina and silica. *J Am Chem Soc*, 1991, 113: 855–861
- 70 He J, Wang J, Chen Y, *et al.* A dye-sensitized Pt@UiO-66(Zr) metal–organic framework for visible-light photocatalytic hydrogen production. *Chem Commun*, 2014, 50: 7063–7066
- 71 Lin R, Wan J, Xiong Y, *et al.* Quantitative study of charge carrier dynamics in well-defined WO₃ nanowires and nanosheets: Insight into the crystal facet effect in photocatalysis. *J Am Chem Soc*, 2018, 140: 9078–9082
- 72 Pan J, Liu G, Lu GQM, *et al.* On the true photoreactivity order of {001}, {010}, and {101} facets of anatase TiO₂ crystals. *Angew Chem*, 2011, 123: 2181–2185
- 73 Tian J, Hao P, Wei N, *et al.* 3D Bi₂MoO₆ nanosheet/TiO₂ nanobelt heterostructure: Enhanced photocatalytic activities and photoelectrochemistry performance. *ACS Catal*, 2015, 5: 4530–4536
- 74 Kröger M, Hamwi S, Meyer J, *et al.* Role of the deep-lying electronic states of MoO₃ in the enhancement of hole-injection in organic thin films. *Appl Phys Lett*, 2009, 95: 123301
- 75 Liu G, Schulmeyer T, Brötz J, *et al.* Interface properties and band alignment of Cu₂S/CdS thin film solar cells. *Thin Solid Films*, 2003, 431–432: 477–482
- 76 Wang H, Zhang L, Chen Z, *et al.* Semiconductor heterojunction photocatalysts: design, construction, and photocatalytic performances. *Chem Soc Rev*, 2014, 43: 5234–5244
- 77 Huang ZF, Song J, Wang X, *et al.* Switching charge transfer of C₃N₄/W₁₈O₄₉ from type-II to Z-scheme by interfacial band bending for highly efficient photocatalytic hydrogen evolution. *Nano Energy*, 2017, 40: 308–316
- 78 Chen X, Chen W, Gao H, *et al.* *In situ* photodeposition of NiO_x on CdS for hydrogen production under visible light: enhanced activity by controlling solution environment. *Appl Catal B-Environ*, 2014, 152–153: 68–72
- 79 Xin Y, Huang Y, Lin K, *et al.* Self-template synthesis of double-layered porous nanotubes with spatially separated photoredox surfaces for efficient photocatalytic hydrogen production. *Sci Bull*, 2018, 63: 601–608
- 80 Chen X, Chen W, Lin P, *et al.* *In situ* photodeposition of nickel oxides on CdS for highly efficient hydrogen production *via* visible-light-driven photocatalysis. *Catal Commun*, 2013, 36: 104–108
- 81 Wang J, Xia Y, Zhao H, *et al.* Oxygen defects-mediated Z-scheme charge separation in g-C₃N₄/ZnO photocatalysts for enhanced visible-light degradation of 4-chlorophenol and hydrogen evolution. *Appl Catal B-Environ*, 2017, 206: 406–416
- 82 Xing X, Zhang M, Hou L, *et al.* Z-scheme BCN-TiO₂ nanocomposites with oxygen vacancy for high efficiency visible light driven hydrogen production. *Int J Hydrogen Energy*, 2017, 42: 28434–28444
- 83 Guo HL, Du H, Jiang YF, *et al.* Artificial photosynthetic Z-scheme photocatalyst for hydrogen evolution with high quantum efficiency. *J Phys Chem C*, 2017, 121: 107–114
- 84 Jia X, Tahir M, Pan L, *et al.* Direct Z-scheme composite of CdS and oxygen-defected CdWO₄: An efficient visible-light-driven photocatalyst for hydrogen evolution. *Appl Catal B-Environ*, 2016, 198: 154–161
- 85 Xie YP, Yang Y, Wang G, *et al.* Oxygen vacancies promoted interfacial charge carrier transfer of CdS/ZnO heterostructure for photocatalytic hydrogen generation. *J Colloid Interface Sci*, 2017, 503: 198–204
- 86 Dong Z, Wu Y, Thirugnanam N, *et al.* Double Z-scheme ZnO/ZnS/g-C₃N₄ ternary structure for efficient photocatalytic H₂ production. *Appl Surf Sci*, 2018, 430: 293–300

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Supplementary information Supporting data are available in the online version of the paper.

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Z-机制光催化剂 $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}$ 和 $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$ 及其高效可见光解水产氢活性研究

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摘要 人工Z-机制光催化剂因其同时具有光吸收范围宽、电荷分离效率高以及载流子氧化还原能力强等优势受到了研究者的广泛关注。然而,设计和制备能够利用太阳能进行高效光解水产氢的低成本、高稳定性非贵金属Z-机制光催化剂仍具有挑战性。本文报道了一种新颖的全固态Z-机制光催化剂 $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}$ 。该催化剂纳米结构是由氧缺陷 WO_{3-x} 非晶层包覆 $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ 纳米棒组成。研究表明,由于适量的Zn掺杂使得 $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ 具有更强的产生还原性电子能力,同时, WO_{3-x} 超薄非晶层中引入的氧空位(W^{5+}/OVs)有效地促进了电荷的分离,使得该Z-机制 $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}$ 光催化材料具有优异的光催化产氢反应(HER)活性,且显著高于贵金属Pt负载的 $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ 纳米棒($\text{Pt}/\text{Cd}_{1-x}\text{Zn}_x\text{S}$)及绝大多数 WO_3 和CdS基光催化剂。优化后的 $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}$ 复合光催化剂的HER速率可达 $21.68 \text{ mmol h}^{-1} \text{ g}^{-1}$ 。进一步通过原位光沉积负载 CoO_x 和 NiO_x 双共催化剂, $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$ 复合材料的活性高达 $28.25 \text{ mmol h}^{-1} \text{ g}^{-1}$,约为 $\text{Pt}/\text{Cd}_{1-x}\text{Zn}_x\text{S}$ 的12倍。计算结果表明, $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}$ 在420 nm激发光下的HER表观量子产率(AQY)为34.6%,而负载 CoO_x 和 NiO_x 双共催化剂后的 $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$ 的AQY提高到了60.8%。此外, $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}$ 和 $\text{Cd}_{1-x}\text{Zn}_x\text{S@WO}_{3-x}/\text{CoO}_x/\text{NiO}_x$ 均表现出了良好的长时间HER稳定性。该工作将为理性设计和制备高效光解水产氢催化剂提供新视角。