Enhanced Photocatalytic Hydrogen Evolution by Loading Cd$_{0.5}$Zn$_{0.5}$S QDs onto Ni$_2$P Porous Nanosheets

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Abstract

Ni$_2$P has been decorated on CdS nanowires or nanorods for efficient photocatalytic H$_2$ production, whereas the specific surface area remains limited because of the large size. Here, the composites of Cd$_{0.5}$Zn$_{0.5}$S quantum dots (QDs) on thin Ni$_2$P porous nanosheets with high specific surface area were constructed for noble metal-free photocatalytic H$_2$ generation. The porous Ni$_2$P nanosheets, which were formed by the interconnection of 15–30 nm-sized Ni$_2$P nanoparticles, allowed the uniform loading of 7 nm-sized Cd$_{0.5}$Zn$_{0.5}$S QDs and the loading density being controllable. By tuning the content of Ni$_2$P, H$_2$ generation rates of 43.3 μM h$^{-1}$ (1 mg photocatalyst) and 700 μM h$^{-1}$ (100 mg photocatalyst) and a solar to hydrogen efficiency of 1.5% were achieved for the Ni$_2$P-Cd$_{0.5}$Zn$_{0.5}$S composites. The effect of Ni$_2$P content on the light absorption, photoluminescence, and electrochemical property of the composite was systematically studied. Together with the band structure calculation based on density functional theory, the promotion of Ni$_2$P in charge transfer and HER activity together with the shading effect on light absorption were revealed. Such a strategy can be applied to other photocatalysts toward efficient solar hydrogen generation.

Keywords: Ni$_2$P, Cd$_{0.5}$Zn$_{0.5}$S, Nanosheet, Quantum dot, Hydrogen evolution

Background

As an efficient strategy to produce H$_2$ by utilizing solar energy, photocatalytic hydrogen production has attracted extensive attention since TiO$_2$ was reported as a photocatalyst in 1972 [1]. Compared with TiO$_2$, Cd$_x$Zn$_{1-x}$S shows excellent visible-light driven catalytic activity because of the narrower band gap and good photochemical stability. A H$_2$ production rate as high as 1097 μM h$^{-1}$ g$^{-1}$ has been achieved by using Cd$_{0.5}$Zn$_{0.5}$S as photocatalyst [2], which composition has been proven to be the optimum for photocatalytic property. To decrease carrier recombination and prompt carrier separation for hydrogen evolution reaction (HER), noble metals such as Pt, Co-Pt, Ru, Au, and Pd have been used as co-catalysts [3–8]. For example, when co-catalyzed with Co-Pt, the photocatalytic H$_2$ generation rate of Cd$_{0.5}$Zn$_{0.5}$S quantum dots (QDs) could be increased by 4.7-folds [4]. A H$_2$ production as high as ~ 6.3 mM h$^{-1}$ mg$^{-1}$ was achieved when CdZnS was combined with Au [9]. However, the high cost of noble-metals greatly limits the future application in large scale, which makes the non-precious co-catalysts to be good candidates of precious ones for photocatalytic H$_2$ generation.

Among the various non-noble co-catalysts including carbon family (graphene, carbon nanotubes, reduced grapheme oxide, carbon nanodots) [10–15], phosphides [16–22], and TiO$_2$ [23, 24] and sulfides [25–32], Ni$_2$P and CoP have been extensively composited with CdS nanowires and/or nanorods for efficient photocatalytic H$_2$ production [16–18, 33–36]. In these composites, one-dimensional (1D) CdS was always decorated by smaller phosphides' nanoparticles or nanosheets with HER activity, and carrier recombinations can be greatly reduced because of the long carrier diffusion length of the 1D structure and its well-defined hetero-interface with the co-catalysts. Considering the advantages of QDs such as its high solar energy to fuel conversion...
efficiency, low fabrication costs [37, 38], and HER mainly occurs at co-catalyst/electrolyte interface, it is rational to construct hetero-nanostructures with plenty of specific surface area of active sites while still maintaining fast carrier separation. In this case, a reverse structure with photocatalysts loaded onto co-catalysts was reported for efficient photocatalytic H2 generation [10, 13]. For instance, hydrogen generation rates of 2.08 and ~33.4 mM h−1 mg−1 were established by loading Cd0.5Zn0.5S QDs onto onion-like carbon and 2D graphitic carbon nitride (g-C3N4) microribbons, respectively. These make it highly expectable for photocatalytic H2 generation if phosphide nanostructures were decorated by Cd0.5Zn0.5S QDs. However, such a reverse structure has been rarely reported up to now.

Here, a reverse structure of Cd0.5Zn0.5S QDs on Ni2P nanosheet arrays was synthesized by thermal solution method for enhanced photocatalytic H2 generation. A hydrogen generation rate of 700 μM h−1 (with 100 mg feeding catalyst) and a solar to hydrogen efficiency (STH) of 1.5% were achieved at 1.5 wt% of Ni2P. The effect of Ni2P on the H2 generation rate, optical, and electrochemical property of the composite was systematically studied. Moreover, the band structure of Ni2P was calculated based on density functional theory, together with the photo-electrochemical property, the detailed role of Ni2P for the H2 generation was revealed.

Methods/experimental
Synthesis of Co-catalyst
Firstly, 20 mL deionized water containing 2.61 g nickel nitrate and 2.52 g hexamethylenetetramine was transferred to a Teflon autoclave and heated at 120 °C for 10 h for the formation of NiOOH. After cooled down to room temperature, the NiOOH product was washed by alcohol and deionized water respectively for three times. By weighing the final product (dispersed in 5 mL ethanol) over 4 cm2 area FTO substrate and dried at 70 °C for 5 h. The frequency range was kept within 0.1 Hz ~ 100 kHz, and E(vs RHE) = E(vs Ag/AgCl) + EAg/AgCl (ref) + 0.0591 V × pH, where (EAg/AgCl (ref) = 0.1976 V vs NHE (normal hydrogen electrode) at 25 °C) [39]. Electrochemical impedance spectra (EIS) measurements were conducted in 1 M NaOH electrolyte (pH = 14) in an electrochemical work station (CHI 760E, CH Instruments) with a typical three-electrode configuration. A Pt foil and a saturated Ag/AgCl were used as the counter and reference electrode, respectively. The potentials were converted to those vs reversible hydrogen electrode (RHE) by the equation E(vs RHE) = E(vs Ag/AgCl) + EAg/AgCl (ref) + 0.0591 V × pH, where (EAg/AgCl (ref) = 0.1976 V vs NHE (normal hydrogen electrode) at 25 °C) [39]. Electrochemical impedance spectra (EIS) measurements were carried out in darkness at 0.5 V vs RHE with an amplitude of 5 mV and the electrolyte of 0.35 M Na2SO3 and 0.25 M Na2S aqueous solution by using a similar three-electrode system. The working electrode was made via spreading ~2 mg product (dispersed in 5 mL ethanol) over 4 cm2 area FTO substrate and dried at 70 °C for 5 h. The frequency range was kept within 0.1 Hz ~ 100 kHz, and
the spectra were analyzed by the Z-View program (Scribner Associates Inc.).

**Photocatalytic (PC) H₂ Generation**

Before H₂ production, the photocatalysts with different mass (1, 5, and 10 mg) were dispersed in a sealed quartz reactor (volume 40 mL, 5 cm × 5 cm × 1.6 cm) with 15 mL 0.75 M Na₂S and 1.05 M Na₂SO₃ aqueous solution. After degassing for 30 min by nitrogen, the photocatalytic experiment was performed under the irradiation of a 300 W Xe (PLS-SXE300/300UV, Perfect Light) lamp with a cut-off filter of 420 nm and an incident power of 300 mW/cm². The catalytic solution was kept continually stirring during the whole PC experiment. In every hour, 1-mL gas production was collected and analyzed by a gas chromatograph (GC-2018, Shimadzu, Japan, TCD). Further cycling stability experiment was performed under the same condition. Paralleling experiments with the feeding dosage of photocalysts from 15 to 100 mg were conducted in 100 mL electrolyte of Na₂S and Na₂SO₃ in a larger reactor (volume 150 mL) under the same illumination. The solar to hydrogen efficiency (STH) was calculated by the flowing equation:

\[
\text{STH}\% = \frac{\text{energy of generated H}_2}{\text{light energy onto the surface of solution}} \times 100\%
\]

\[
= \frac{237 \text{kJ/mole} \times \text{moles of H}_2 \text{produced}}{300 \text{mW/cm}^2 \times \text{area of solution been irradiated}} \times 100\%
\]

**Computational Methods**

The energy and electronic properties of bulk Ni₂P were calculated using density functional theory (DFT) method. Vienna Ab-initio Simulation Package (VASP) [40] was adopted during the calculations with the projector augmented wave pseudo potentials (PAW) [41], and the Perdew-Burke-Ernzerhof type (PBE) generalized gradient approximation (GGA) [42] exchange–correlational functional methods. A Brillouin zone with a 9 × 9 × 9 Monkhorst–Pack Γ point grid [43], a kinetic energy cut off with 450 eV, and an energy criterion of 10⁻⁶ eV were
applied for geometric optimization until the residual forces were converged to less than 0.01 eV/Å. The bulk model of hexagonal Ni$_2$P with P-62M symmetry was taken into account. After fully structure optimized, the lattice parameter of Ni$_2$P ($a = b = 5.86918$ Å, and $c = 3.37027$ Å) can be obtained, which is well consistent with the reported values [44].

**Results and Discussion**

Figure 1a, b show the morphology of Ni$_2$P before and after the composition with Cd$_{0.5}$Zn$_{0.5}$S QDs (Ni$_2$P wt%: 1.5%). Pure Ni$_2$P has a flower-like morphology which is composed of many crossed nanosheets with the thickness less than 20 nm and planar size from several tens nanometer to micrometer scope. From the XRD pattern of pure Ni$_2$P in Fig. 1c, diffraction peaks of (111), (201), (210), and (300) planes can be clearly observed at 40.7°, 44.6°, 47.4°, and 54.2°, respectively, which correspond to hexagonal Ni$_2$P (JCPDF no. 89-2742). After loaded by Cd$_{0.5}$Zn$_{0.5}$S QDs, the surface of the nanosheets become rather rough, and plenty of nanoparticles with size less than 10 nm can be distinguished on the pristine Ni$_2$P skeleton. At the same time, the XRD refraction peaks of Cd$_{0.5}$Zn$_{0.5}$S (JCPDF no. 89-2943) (100), (002), (101), and (110) planes can be clearly found at 26.0°, 27.8°, 29.6°, and 45.9°, respectively [6, 45], while the diffraction signal of Ni$_2$P is greatly depressed because of the low weight ratio (1.5 wt%) of Ni$_2$P to Cd$_{0.5}$Zn$_{0.5}$S. The coexistence of Cd$_{0.5}$Zn$_{0.5}$S and Ni$_2$P was demonstrated by the X-ray photoelectron spectrometer (XPS) fine and survey spectra in Fig. 1d–f. Except the oxygen and carbon signals arising from the air absorption, only Ni, P, Cd, Zn, and S can be detected, which rules out the possibility of other impurities. The peaks at 855.5 and 873.9 eV can be assigned to Ni 2P$_{3/2}$ and 2P$_{1/2}$, respectively, and the peak of P 2P$_{3/2}$ can be found at 133.6 eV [16, 46]. Concurrently, the doublet peaks of Zn 2p, Cd 3d, and S 2p suggest the bivalent Zn$^{2+}$, Cd$^{2+}$, and S$^{2-}$ from Cd$_{0.5}$Zn$_{0.5}$S QDs [3, 34, 47]. In brief, the growth of Cd$_{0.5}$Zn$_{0.5}$S on Ni$_2$P nanosheets has been established for the formation of Ni$_2$P-Cd$_{0.5}$Zn$_{0.5}$S nanocomposites.

The microstructure and elemental composition of the samples were further investigated by TEM-related techniques. From the different magnification TEM images of pure Ni$_2$P (Fig. 2a, b), the nanosheets are porous and composed of cross-linked irregular nanoparticles with size less than 15–30 nm. The selected area electron diffraction pattern (SAED) in Fig. 2c shows the diffraction ring of Ni$_2$P (111), (201), (210), and (300) planes. The diffractive signals of high-index planes such as (222), (402), and (211) can be observed. The high-angle annular dark field (HAADF)-STEM image, and h–l the corresponding EDX mappings of Ni$_2$P-Cd$_{0.5}$Zn$_{0.5}$S composite.
and (420) can also be detected due to the strong multi-scattering of the high-energy electrons. After composited with Cd$_{0.5}$Zn$_{0.5}$S, the intercrossed Ni$_2$P nanosheets were covered by plenty of smaller nanoparticles with size of ~7 nm (Fig. 2d). The EDX spectra (inset, Fig. 2f) clearly shows the signal of Ni, P, Cd, Zn, and S, indicative of the coexistence of Ni$_2$P and Cd$_{0.5}$Zn$_{0.5}$S. From the SAED pattern (Fig. 2f), strong diffractive rings of Cd$_{0.5}$Zn$_{0.5}$S (002), (110), and (200) planes (denoted by yellow dash lines) can be clearly distinguished along with the weak signals of Ni$_2$P (300), (402), and (420) (marked by white dash lines), suggesting the good composition of Ni$_2$P with QDs. The high-resolution TEM image of Ni$_2$P-Cd$_{0.5}$Zn$_{0.5}$S sample in Fig. 2e further shows the lattice fringes with spacing of 0.34 and 0.22 nm, which corresponds to the Cd$_{0.5}$Zn$_{0.5}$S (002) and Ni$_2$P (111) crystal planes, respectively. The elemental EDX mappings (Fig. 2h–l) taken from the region shown by the high-angle annular dark field (HAADF) image (Fig. 2g) exhibit that Ni, P, Cd, Zn, and S are distributed uniformly among the sample, further demonstrating the successful composition of Cd$_{0.5}$Zn$_{0.5}$S QDs with the porous Ni$_2$P nanosheets.

Figure 3a shows the H$_2$ evolution rate of Ni$_2$P-Cd$_{0.5}$Zn$_{0.5}$S nanocomposites varied with the content of Ni$_2$P at the feeding dosage of 1 mg in a 40 mL reactor. Pure Cd$_{0.5}$Zn$_{0.5}$S shows a photocatalytic H$_2$ evolution rate of 12.6 μM h$^{-1}$ mg$^{-1}$, and pure Ni$_2$P shows negligible hydrogen generation. With the addition of Ni$_2$P, the photocatalytic activity of the Ni$_2$P-Cd$_{0.5}$Zn$_{0.5}$S composites has been obviously enhanced and reaches the highest value of 43.3 μM h$^{-1}$ mg$^{-1}$ at 1.5 wt% Ni$_2$P, nearly 3.4 times higher than pure Cd$_{0.5}$Zn$_{0.5}$S. Further addition of Ni$_2$P (≥3 wt%) will result in fast degradation of property, and the H$_2$ evolution rate is less than pure Cd$_{0.5}$Zn$_{0.5}$S when Ni$_2$P increases to 5 wt%. Such a nonlinear behavior suggests that there exist an optimum Ni$_2$P content, namely, an appropriate loading density of Cd$_{0.5}$Zn$_{0.5}$S on Ni$_2$P for the photocatalytic property. At the same time, the stability of 1.5 wt% Ni$_2$P-Cd$_{0.5}$Zn$_{0.5}$S was studied by cycling test (Fig. 3b). During four successive cycles that lasted for totally 16 h, the H$_2$ generation maintained relatively stable with negligible degradation, indicating the good photocatalytic stability of the composite.

The effect of the amount of catalyst on STH efficiency and H$_2$ generation was systematically studied (Fig. 3c–d).
for 1.5 wt% Ni$_2$P-Cd$_{0.5}$Zn$_{0.5}$S sample. Two typical reactors with volume of 40 and 150 mL were adopted at the same illumination power density. When tested in the smaller reactor (40 mL), though both the STH and H$_2$ generation rate increase with the catalyst's dosage from 1 to 10 mg, the increased step is far less than that of the dosage. The STH and H$_2$ generation rate are only 0.45% and 166 $\mu$M h$^{-1}$ when the dosage of the catalyst increased to 10 mg, nearly 3.8 times of the 1 mg sample. For the larger reactor (150 mL), distinct increase in STH and H$_2$ generation can be found with the dosage increased from 15 to 100 mg, and a 1.53% STH and a 700 $\mu$M h$^{-1}$ of H$_2$ generation can be achieved at the dosage of 100 mg, nearly 3.1 times of the 15 mg catalyst. Considering that the incident light has longer path when it passes through a deeper reactor, such a result shows that larger reactor will be more beneficial for the utilization of the incident light. However, the STH efficiency will be saturated once the dosage increased to about 100 mg, suggesting there exists an optimum dosage for the light utilization. The optimum H$_2$ generation rate is superior than CdZnS QDs-2D g-C$_3$N$_4$ microribbons (H$_2$ generation rate 33.4 mM h$^{-1}$ g$^{-1}$) [10], Cd$_{0.1}$Zn$_{0.9}$S nanoparticles-carbon nanotubes (rate: 1563 $\mu$M h$^{-1}$ g$^{-1}$) [11], a sandwich-structured C$_3$N$_4$/Au/CdZnS photocatalyst (rate 6.15 mM h$^{-1}$ g$^{-1}$) [9], and CdS QDs-sensitized Zn$_{1-x}$Cd$_x$S solid solutions (rate 2128 $\mu$M h$^{-1}$ g$^{-1}$) [48].

To reveal the mechanism for the enhanced photocatalytic property and detailed role of Ni$_2$P, both the optical and electrochemical property of pure Ni$_2$P, Cd$_{0.5}$Zn$_{0.5}$S, and the composites were studied by Fig. 4. From the absorption spectra (Fig. 4a), pure Cd$_{0.5}$Zn$_{0.5}$S exhibits an absorption edge at 506 nm, corresponding to the band gap of 2.45 eV [13, 49]. For pure Ni$_2$P (the inset), wide absorption over the whole visible range can be found. After the composition, besides the absorption in range < 506 nm, obvious tails over the visible wavelength > 506 nm can be found, which can be attributed to the contribution from Ni$_2$P. As the visible absorption in longer wavelength increases with Ni$_2$P, the composite shows reduced absorption of Cd$_{0.5}$Zn$_{0.5}$S (< 506 nm). At the same time, the photoluminescence spectra (Fig. 4b) exhibit that pure Cd$_{0.5}$Zn$_{0.5}$S has intensive band edge luminescence at ~ 620 nm when excited at the wavelength of 400 nm. After composition, it will be degraded gradually with the addition of Ni$_2$P. Considering that higher content of Ni$_2$P will induce more Ni$_2$P/Cd$_{0.5}$Zn$_{0.5}$S interfaces which help to enhance charge transfer and suppress charge recombination, the decrease of PL intensity can be understood by the reduced carrier recombination and enhanced charge transfer at the Ni$_2$P/Cd$_{0.5}$Zn$_{0.5}$S interface.

The effective role of Ni$_2$P in prompting charge transfer can also be reflected by the EIS spectra depending on Ni$_2$P content (Fig. 4c). As shown by the equivalent circuit model, the increase of Ni$_2$P content will lead to the decrease of the charge transfer resistance ($R_t$), resulting in the increase of the electron transfer rate and the decrease of the charge recombination rate ($R_c$). The decrease of the charge transfer resistance ($R_t$) is beneficial for the enhancement of the photocatalytic property, while the decrease of the charge recombination rate ($R_c$) is beneficial for the stability of the photocatalytic property. The LSV curve and EIS (inset) spectrum of pure Ni$_2$P is shown in Fig. 4d.
circuit (inset, Fig. 4c), the charge transfer resistance (Rct) at catalyst/electrolyte interface can be evaluated by the semicircle radius of the Nyquist plots based on R-C equivalent circuit. The equivalent series resistance (ESR) can be obtained from the intersection of the curve and the real resistance (Z') axis, while the charge-transfer resistance (Rct) corresponds to the width of the semicircle plotted at higher frequencies. The Rct of pure Cd0.5Zn0.5S is 17,320 Ω, indicative of its semiconductor nature. After the composition with 1, 1.5, and 3 wt% Ni2P, Rct decreases gradually to 8432, 7721, and 5473 Ω, respectively, suggesting the enhancement of Ni2P in the electrical conductivity. Indeed, Ni2P has been considered as a good electrocatalyst toward HER [44, 50, 51]. From the LSV curve of pure Ni2P on Ni foam shown in Fig. 4d, the Ni2P has good HER activity with overpotentials of 84 mV and 201 mV to attach the current density of 10 and 50 mA/cm² (without iR-correction), respectively. The EIS spectrum (inset Fig. 4d) exhibits that Ni2P has a very low Rct (~ 7.3 Ω), indicating the metallic character of Ni2P, which agrees well with the above EIS result. This indicates that the photoelectrons are mainly attributed to the photo-excitation of Cd0.5Zn0.5S rather than Ni2P. Moreover, the Fermi level of Ni2P (obtained from out car file) locates at 1.03 V vs. NHE, much lower than the conductive band minimum (CBM) level (~ 1.04 V vs NHE) of Cd0.5Zn0.5S QDs [13].

Accordingly, the schematic mechanism was demonstrated for the photocatalytic H2 evolution of the composite by Fig. 5c. The location of Fermi level of Ni2P makes it energetically favorable for the transfer of photo-generated electrons from Cd0.5Zn0.5S to Ni2P, then prompts the separation of photo-excited electrons and holes at the interface, resulting in the depression of charge recombination. Concurrently, H2 will evolve efficiently at the active sites of Ni2P due to the good HER.

Considering that the addition of Ni2P decreased the absorption at wavelength < 506 nm, it is necessary to demonstrate whether the light absorption of Ni2P can be utilized to generate hydrogen. The band structure of Ni2P was then studied by DFT calculation. Figure 5a, b presents the ball and stick model of bulk Ni2P and the calculated band structure. From Fig. 5b, no band gap can be detected, suggesting the metallic characteristic of Ni2P, which agrees well with the above EIS result. This indicates that the photoelectrons are mainly attributed to the photo-excitation of Cd0.5Zn0.5S rather than Ni2P. Moreover, the Fermi level of Ni2P (obtained from out car file) locates at 1.03 V vs. NHE, much lower than the conductive band minimum (CBM) level (~ 1.04 V vs NHE) of Cd0.5Zn0.5S QDs [13].

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![Fig. 5](image-url) The band diagram and charge separation and transfer mechanism for the photocatalytic H2 evolution. a Top views of the ball and stick model of (001) surface-terminated bulk Ni2P. b Calculated band structure of Ni2P where the red dash line represents Fermi level. c Schematic mechanism illustrating the charge separation and transfer for the photocatalytic H2 generation.
activity and large specific surface area of the composites. The positive roles of Ni$_2$P in charge transfer and HER activity will dominate at the lower content of Ni$_2$P ($\leq$ 1.5 wt%). When the content surpasses 1.5 wt%, the shading effect of Ni$_2$P in light absorption will overcome the positive aspect, leading to the degradation of H$_2$ generation. An optimum photocatalytic property will be achieved at 1.5 wt% Ni$_2$P when the two effects reach a balance.

**Conclusions**

A reverse structure of Cd$_{0.5}$Zn$_{0.5}$S QDs on Ni$_2$P porous nanosheets were fabricated for efficient photocatalytic H$_2$ production. The Ni$_2$P porous nanosheets were composed of 15–30-nm-sized nanoparticles that allows the effective loading of 7-nm-sized Cd$_{0.5}$Zn$_{0.5}$S QDs. As the charge separation and transfer property is enhanced with the addition of Ni$_2$P from 0 to 5 wt%, a competitive shading effect that unfavorable for the light absorption of Cd$_{0.5}$Zn$_{0.5}$S is induced. An optimum photocatalytic H$_2$ generation of 43.3 μM h$^{-1}$ (dosage 1 mg) will be achieved at 1.5 wt% Ni$_2$P. Based on the optimum content, the photocatalytic dependence on feeding dosage of catalyst shows that the STH efficiency will reach the highest value of 1.5% at the dosage of 100 mg. The high HER activity and band structure of Ni$_2$P were revealed, confirming the effective role of Ni$_2$P in prompting photocatalytic H$_2$ evolution dynamics from both experimental and theoretical aspects. The heterostructure of Cd$_{0.5}$Zn$_{0.5}$S QDs–Ni$_2$P porous nanosheets can not only help to prompt the photo-excited charge separation and transfer, but also speed up the dynamics of hydrogen evolution reaction via the co-catalytic role of Ni$_2$P, thus enhances the photocatalytic hydrogen generation property. Such a method can be applied to other catalysts toward efficient photocatalytic property.

**Abbreviations**

CBM: Conductive band minimum; DFT: Density functional theory; EDX: Energy dispersive X-ray spectroscopy; EIS: Electrochemical impedance spectra; FESEM: Field emission scanning electron microscopy; FTO: Fluorine-doped tin oxide; GGA: Generalized gradient approximation; HER: Hydrogen evolution reaction; LSV: Linear sweep voltammetry; NHE: Normal hydrogen electrode; PBE: Perdew-Burke-Ernzerhof type; PC: Photocatalytic; PL: Photoluminescence; QDs: Quantum dots; RHE: Reversible hydrogen electrode; STEM: Scanning transmission electron microscopy; STH: Solar to hydrogen; TEM: Transmission electron microscopy; VASP: Vienna Ab-initio Simulation Package; XPS: X-ray photoelectron spectroscopy; XRD: X-ray diffraction

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**Availability of Data and Materials**

The datasets supporting the conclusions of this article are included within the article.

**Authors’ Contributions**

XNW carried out the experimental design and the experimental data analysis. LFX prepared the Cd$_{0.5}$Zn$_{0.5}$S and Ni$_2$P–Cd$_{0.5}$Zn$_{0.5}$S samples and performed the XRD, SEM, XPS characterization and performed the LSV, EIS, PC, and stability tests. TS and ZW carried out the theoretical calculations. KZ, XNP, and YBH performed the PL measurements. QL performed the TEM characterization. All authors read and approved the final manuscript.

**Competing Interests**

The authors declare that they have no competing interests.

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