Tunable Bandgap Engineering of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ Solid Solution with Controlled Ratio via a Facile One-Pot Synthesis for Visible-Light Photocatalytic H$_2$ Production

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1. Introduction

Photocatalytic H$_2$ generation proffers a promising way to address energy and environmental issues.[1] The rapid development of visible-light-responsive, high-efficiency, stable, earth-abundant, and low-cost semiconductors is crucial for the practical photocatalytic H$_2$ evolution application.[2] Among the class of metal dichalcogenides, metal selenides have emerged as potential photocatalysts for H$_2$ production from water splitting owing to their narrow bandgap as compared to the corresponding metal oxides/sulfides, but they exhibit sluggish activity and serious photocorrosion.[3]

Several strategies such as controlling morphologies and phases,[4] loading cocatalysts,[5] and constructing heterojunctions[6] have been demonstrated to improve the catalytic activity of metal selenide and other nanostructured semiconductors. Moreover, the formation of metal selenide-based solid solutions can enhance light absorption and charge transfer.[7] Notably, the more negative conduction band (CB) position of semiconductors always leads to a higher reduction power, while the wider bandgap often connotes to weaker absorption ability.[8] In this respect, constructing semiconductor solid-solution nanostructures has been proposed to modulate electrical resistivity, expand the light responses, and provide a suitable CB edge position for the improved photocatalytic H$_2$ evolution.[8,9] Dan et al. constructed a series of novel Cd$_x$In$_{1-x}$S solid solutions through a mild hydrothermal method, which presented an orderly visible-light response range from 550

Metal selenide semiconductors in photocatalysis are limited, owing to their low activity and poor stability. Herein, a facile one-pot solution approach is developed to prepare particulate Zn$_x$Cd$_{1-x}$Se solid solutions with tunable energy band structures. X-ray diffractometer (XRD) patterns demonstrate that the crystal structure of the samples are not changed. The analysis of UV–vis and the photoluminescence spectra exhibits that the bandgap of Zn$_x$Cd$_{1-x}$Se photocatalysts utilizing oleylamine as an organic template can be accurately controlled, which gradually becomes wider from 1.60 to 2.70 eV with increasing Zn/Cd molar ratio. Under visible-light irradiation, the optimal Zn$_{0.5}$Cd$_{0.5}$Se without any cocatalyst exhibits a superior photocatalytic H$_2$ generation rate (438.3 $\mu$mol h$^{-1}$ g$^{-1}$), exceeding that of pristine CdSe and ZnSe by more than 12 and 17 times, an apparent quantum yield of 1.7% at 420 nm and excellent stability. The results are on account of the balance between the bandgap width and the conduction band (CB) potential of Zn$_{0.5}$Cd$_{0.5}$Se, implying the excitation of more photogenerated electrons and faster charge carrier separation efficiency, which could be substantiated by the transient photocurrent response and electrochemical impedance spectroscopy. Therefore, this work provides a straightforward strategy to synthesize metal selenide for diverse photocatalytic applications.

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to 600 nm and remarkable separation performance of charge carriers.[10] In analogy with the traditional Zn$_{x}$Cd$_{1-x}$S solid solutions,[11] the band structures of the corresponding metal selenides (Zn$_{x}$Cd$_{1-x}$Se) can be adjusted by tuning the ratio of Zn/Cd precursors.[6c,12] However, unlike Zn$_{x}$Cd$_{1-x}$S, the Zn$_{x}$Cd$_{1-x}$Se nanostructures were generally prepared by various synthetic routes, such as solid-state reaction,[6c] ion-exchange methods,[13] diethylenetriamine template-assisted,[14] solvothermal,[15] and a multiple-step process.[16] Nevertheless, most of the reported approaches involving Zn$_{x}$Cd$_{1-x}$Se nanostructures suffer from irregular structures and complicated preparation conditions, hindering their practical application. For instance, Yosuke et al. synthesized Zn$_{x}$Cd$_{1-x}$Se particles via a solid-state reaction in a sealed quartz ampoule.[6c] At present, there have been several reports on the relatively facile preparation and photocatalytic applications of nanoscale Zn$_{x}$Cd$_{1-x}$Se.[8,17] Additionally, the Zn$_{x}$Cd$_{1-x}$Se photocatalyst exhibits trace H$_2$ production due to its rapid charge carriers recombination and sluggish surface reactions.[6c] To the best of our knowledge, diethylenetriamine (DETA) generally serving as an organic template is used in complex methods to synthesize Zn$_{x}$Cd$_{1-x}$Se solid solutions.[18] Therefore, developing a simple method to synthesize uniform Zn$_{x}$Cd$_{1-x}$Se nanocrystals with tunable bandgap engineering for highly efficient photocatalytic H$_2$ production performance remains a considerable challenge.

In this study, a series of Zn$_{x}$Cd$_{1-x}$Se solid solutions with tunable band structures and well-distributed nanoparticle morphology with a size of 5–11 nm were prepared via a facile one-pot method, which utilized oleylamine as an organic template. The absorption edges of Zn$_{x}$Cd$_{1-x}$Se vary in the range of 460–775 nm by adjusting the Zn/Cd ratio. Notably, the Zn$_{0.5}$Cd$_{0.5}$Se sample presents the optimal H$_2$ generation rate of 438.3 μmol h$^{-1}$ g$^{-1}$ in the absence of noble-metal cocatalysts under visible light ($\lambda > 420$ nm), along with superior stability during cycled photocatalytic reactions. Based on various characterizations, the optimal Zn$_{0.5}$Cd$_{0.5}$Se solid solution possesses a suitable bandgap of 1.82 eV and the CB level (–0.82 V vs RHE), which is favorable for optimizing the electronic structure and improving carrier dynamics. This work highlights the advantages of controllable band structures in the preparation of photocatalysts with enhanced H$_2$ evolution activity, paving the way for further exploration of the novel ternary selenide solid-solution-based photocatalysts with superior photocatalytic activity.

2. Results and Discussion

The uniform Zn$_{x}$Cd$_{1-x}$Se solid solutions with different Zn/Cd ratios were prepared through a simple one-pot solution-phase approach (Figure 1). Typically, zinc acetate dihydrate (Zn (OAc)$_2$·2H$_2$O) was used as the Zn ions source and cadmium acetate dihydrate (Cd (OAc)$_2$·2H$_2$O) was regarded as the source of Cd ions. The samples were synthesized through a three-necked glass flask by means of oleylamine as a template with a certain amount of selenium (Se) powder as the Se ions source, which is equal to the total molar of Zn (OAc)$_2$·2H$_2$O and Cd (OAc)$_2$·2H$_2$O.

As illustrated by the X-ray diffractometer (XRD) patterns in Figure 2, it can be seen that all the diffraction peaks of all the samples are less sharp and broader, which indicates that the Zn$_{x}$Cd$_{1-x}$Se solid solution has small crystal sizes.[19] Furthermore, several peaks at 25.4°, 42.1°, and 53.7° can be well-indexed with the (111), (220), and (311) planes of cubic phase of CdSe (JCPDS no. 88-2346), respectively. For ZnSe, three
Zn
nescence (PL) spectra of ZnSe, CdSe, and Zn_{0.5}Cd_{0.5}Se were
absorption edges of Zn. It exhibits a continuous shift toward shorter wavelengths in the
460 nm can be observed in pristine CdSe and ZnSe, respectively. The shifts of the XRD peaks toward a higher degree
(220), and (311) planes of cubic ZnSe (JCPDS no. 88-2345),
respectively. The shifts of the XRD peaks toward a higher degree
when increasing the Zn contents. This indicates that the direc-
tions, demonstrating that the synthesized samples are
apparent peaks at 27.2°, 45.4°, and 53.6° correspond to the (111),
(220), and (311) planes of cubic ZnSe (JCPDS no. 88-2345),
respectively. The shifts of the XRD peaks toward a higher degree
are ascribed to the replacement of the larger Cd^{2+} (0.74 Å) with
the smaller Zn^{2+} (0.97 Å), which makes the crystal cell shrink,
illustrating the formation of Zn_{x}Cd_{1−x}Se solid solutions. In
addition, a pronounced shift toward a higher angle and close
to the corresponding diffraction peaks of pure ZnSe is observed
when increasing the Zn contents. This indicates that the direc-
tion of the crystal plane of the samples has not changed, and the
crystal structure remains constant. To explore the effect of Zn concentration on the morphology,
the Zn_{x}Cd_{1−x}Se solid solutions were analyzed by transmission
electron microscope (TEM). It can be seen from Figure 4 that
the morphology of the samples prepared by changing the Zn/
Cd molar ratio is consistent with the morphology of pure
CdSe (Figure S2a, Supporting Information) and ZnSe
(Figure S3a, Supporting Information), exemplifying a large
number of uniformly dispersed nanospheres. The diameters of the
aggregated nanoparticles of Zn_{x}Cd_{1−x}Se are mainly distributed
in the narrow range of 5–11 nm. As depicted in Table S1,
Supporting Information, the average crystallite sizes of the samples
were calculated with the full width at half of maximum intensity (FWHM). The calculation data was in accord with the results of TEM. This indicates that the morphology of samples
does not change in Zn_{x}Cd_{1−x}Se solid solutions. As depicted
in Figure 4a,b, one group of lattice fringes can be observed in the
HRTEM image of Zn_{0.5}Cd_{0.5}Se. The lattice spacing of 0.338 nm
is between the homologous lattice spacing of pure CdSe
(0.350 nm in Figure S2b, Supporting Information) and ZnSe
(0.327 nm in Figure S3b, Supporting Information), which corre-
sponds to the (111) plane. With the addition of Zn concentration
in the Zn_{x}Cd_{1−x}Se solid, the fringe lattice distance is reduced
due to the larger radius of Cd^{2+} (0.74 Å) than that of the
Zn^{2+} (0.97 Å). As such, it further confirms the result obtained

Figure 2. XRD patterns of Zn_{x}Cd_{1−x}Se samples.

![Image](image1)

Figure 3. a) UV–vis diffuse reflectance spectra and b) Tauc plots of Zn_{x}Cd_{1−x}Se samples.

![Image](image2)
from XRD. The high-angle annular dark-field (HAADF) image and elemental mapping analysis of Zn$_{0.5}$Cd$_{0.5}$Se (Figure 4c–f) exhibited the homogeneous spread of Zn, Cd, and Se elements, which further revealed that Zn$_{x}$Cd$_{1-x}$Se solid solutions were successfully synthesized.

The surface area and porous structures of pristine CdSe, ZnSe, and Zn$_{0.5}$Cd$_{0.5}$Se samples were explored using nitrogen adsorption–desorption and corresponding pore size distribution curves. As displayed in Figure 5, all three photocatalysts clearly exhibited type-IV adsorption-desorption isotherms according to the Brunauer–Deming–Deming–Teller classification with a distinct IUPAC-H2 type hysteresis loop, suggesting that the well-ordered pores with interconnecting channels present in CdSe, ZnSe, and Zn$_{0.5}$Cd$_{0.5}$Se.[24] The inset of Figure 5 illustrates the intensive peaks that occurred at ~2–40 nm in the pore size distribution curves of the three samples, which further testified the presence of mesopores.[25] Additionally, Table S2, Supporting Information, exhibited the BET surface area, average pore diameter, and pore volume of these photocatalysts. The consistent average pore diameters between 6 and 7 nm of all samples demonstrate CdSe, ZnSe, and Zn$_{0.5}$Cd$_{0.5}$Se possess mesoporous structures. It can be observed that only slight differences exist in BET surface area (57.3371 m$^2$/g of CdSe, 59.1672 m$^2$/g of Zn$_{0.5}$Cd$_{0.5}$Se, 63.7806 m$^2$/g of ZnSe) and pore volume (0.1188 cm$^3$/g of CdSe, 0.1160 cm$^3$/g of Zn$_{0.5}$Cd$_{0.5}$Se, 0.1245 cm$^3$/g of ZnSe), which are attributed to the similar morphology, structure and particle distribution. Therefore, these results implied that the BET surface area should not be crucial factors boosting the photocatalytic H$_2$ evolution efficiency.

To further investigate the electronic interactions in Zn$_{x}$Cd$_{1-x}$Se catalysts, the surface chemical state of the elements was obtained (Figure S4–S6, Supporting Information). Figure S4–S5, Supporting Information, presented that the peaks at 411.8 and 405.0 eV can be attributed to Cd 3d$_{3/2}$ and Cd 3d$_{5/2}$ of Cd$^{2+}$ in CdSe, while the peaks at 1044.8 and 1021.7 eV identify Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$ of Zn$^{2+}$ in ZnSe, respectively. Moreover, the binding energy of the two peaks recorded in the Se 3d region shows a similar location at 54.5 and 53.7 eV, which can be ascribed to Se 3d$_{3/2}$ and Se 3d$_{5/2}$.[26] As demonstrated in Figure 6a,b, the high-resolution X-ray photoelectron spectroscopy (XPS) spectrum of Zn 2p and Cd 3d in the Zn$_{0.5}$Cd$_{0.5}$Se
matches well with pristine ZnSe and CdSe, except a slight shift toward lower energy in Cd 3d and higher energy in Zn 2p. Thus, this infers that the Zn concentration can change the Cd core level electrons due to the chemical interaction. Additionally, the apparent shifts in Zn 2p and Cd 3d signified the redistribution of charges between Zn and Cd atoms. Figure 6c exhibits that the XPS spectrum of Se 3d of Zn$_x$Cd$_{1-x}$Se, in which the 54.5 and 53.7 eV peak positions belong to Se 3d$_{3/2}$ and Se 3d$_{5/2}$, is consistent with the Se 3d of Zn$_{0.5}$Cd$_{0.5}$Se. As illustrated in Figure 6d, the VB spectra of Zn$_{0.5}$Cd$_{0.5}$Se sample is 1.00 eV, and based on Figure 3, the corresponding conduction band position could be calculated. Apart from Zn$_{0.5}$Cd$_{0.5}$Se, the high-resolution XPS spectra of other Zn$_x$Cd$_{1-x}$Se nanocrystals are presented in Figure S6, Supporting Information. Overall, the aforementioned results indicate that Zn$_x$Cd$_{1-x}$Se solid solution has been successfully synthesized, which is in agreement with the XRD and HRTEM analyses.

A comparison of the hydrogen generation of the Zn$_x$Cd$_{1-x}$Se ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9,$ and $1.0)$ samples is depicted in Figure 7a. Under simulated visible light, the pristine CdSe displays a photocatalytic H$_2$ evolution rate of 33.9 μmol g$^{-1}$ h$^{-1}$. As the Zn concentration increases, the H$_2$ evolution of Zn$_x$Cd$_{1-x}$Se becomes higher and up to 438.3 μmol g$^{-1}$ h$^{-1}$ for the Zn$_{0.5}$Cd$_{0.5}$Se ($x = 0.5$) sample with an apparent quantum yield (AQY) of 1.7% at 420 nm, exceeding that of pure CdSe by more than 12 times. Table S3, Supporting Information, depicts the comparison of our present H$_2$ evolution reaction results compared to other published literature on the metal selenide photocatalysts. Nevertheless, the photocatalytic performance gradually deteriorates with a further increase in Zn concentration in the Zn$_x$Cd$_{1-x}$Se solid solution ($x = 0.7, 0.9,$ and $1$). Surprisingly, the pure ZnSe shows the lowest activity with an H$_2$ production rate of 25.4 μmol g$^{-1}$ h$^{-1}$. Typically, the pristine CdSe exhibits negligible properties due to its narrow bandgap, which leads to the fast recombination of photogenerated carriers. Contrarily, the pure ZnSe sample cannot absorb more photons stemming from its large bandgap even if it possesses a prominent ability of H$^+$ reduction. Unlike the aforementioned two binary sulfide samples, the Zn$_{0.5}$Cd$_{0.5}$Se solid solution demonstrates a balance between an excellent light-absorption capacity and an appropriate band gap that leads to the ameliorated H$_2$ production efficiency. As depicted in Figure 7b, no significant reduction in H$_2$ evolution was detected through four experimental cycles, suggesting that Zn$_{0.5}$Cd$_{0.5}$Se solid solution possesses high photocatalytic stability. Furthermore, the crystal structure of the recovered Zn$_{0.5}$Cd$_{0.5}$Se sample was studied. Figure S7 and S8, Supporting Information, demonstrate no peak position change after irradiation as evidenced in the XRD patterns and XPS spectra, testifying that there is no distinct structural alteration and chemical state change appearing at the Zn$_{0.5}$Cd$_{0.5}$Se solid solution. The TEM characterization (Figure S9, Supporting Information) further confirms that Zn$_{0.5}$Cd$_{0.5}$Se possesses excellent stability in morphology.

Transient photocurrent response is commonly used to explore the charge separation efficiency upon visible light irradiation. As depicted in Figure 8a, pure CdSe and ZnSe show relatively low
photocurrent intensity, revealing the inferior performance of effective electron transfer. Moreover, for the Zn$_x$Cd$_{1-x}$Se solid solutions, an increased photocurrent intensity illustrates that the appropriate ratio of Zn/Cd dictates a predominant factor to facilitate the migration of electrons. Among all, Zn$_{0.5}$Cd$_{0.5}$Se exhibits a higher photocurrent density, which demonstrates that appropriate band structure of Zn$_{0.5}$Cd$_{0.5}$Se could accelerate the charge carriers transfer and inhibit the recombination of photoinduced electron–hole pairs to the most extent. Electrochemical impedance spectroscopy (EIS) was performed to analyze the transfer of electrons in Zn$_x$Cd$_{1-x}$Se solid solutions. Zn$_{0.5}$Cd$_{0.5}$Se sample presents a quenched arc radius compared with pristine CdSe and ZnSe (Figure 8b), highlighting superior electron transfer efficiency.\cite{28} Figure 9 illustrates the photocatalytic H$_2$ generation activity at different monochromatic light. For Zn$_{0.5}$Cd$_{0.5}$Se solid solution, H$_2$ evolution rate decreases with increasing wavelength, implying that the wavelength-dependent photocatalytic H$_2$ production performance variation trend is approximately identical to the UV–vis absorbance spectrum. The aforementioned results revealed that the proper band structures effectively boost the photo-response and the transformation of the photo-induced electron.

To unravel the band structures, the VBs of the as-synthesized Zn$_x$Cd$_{1-x}$Se solid solutions were observed by XPS valence band spectra in Figure S10, Supporting Information. The bandgap and CB of Zn$_x$Cd$_{1-x}$Se can be adjusted by changing Zn concentrations. As shown in Figure 10, the CB for Zn$_{0.5}$Cd$_{0.5}$Se shifts more negative potential when the Zn/Cd molar ratio increases. Generally, the higher positions of CB in Zn$_x$Cd$_{1-x}$Se imply
the faster transfer efficiency of electrons and excellent performance toward the H₂ evolution. Despite the fact that Zn₀.₅Cd₀.₅Se (x = 0.7, 0.9, and 1.0) presents more negative CB levels than Zn₀.₅Cd₀.₅Se, the photocatalytic H₂ production activity is lower. Notably, the Zn₀.₅Cd₀.₅Se sample possesses the balance between optical absorption capacity and recombination of photogenerated carriers, which exhibits a significant promotion in the H₂ generation.¹⁰ Hence, a suitable bandgap and auspicious CB position result in the absorption of more photons and the efficient transmission of photogenerated electrons for reducing water to H₂ (Figure 10).

3. Conclusion

To sum up, a simple method has been explored to design active ZnₓCd₁₋ₓSe solid solutions for noble-metal-free photocatalytic H₂ evolution. When the Zn/Cd molar ratio is 1:1, the Zn₀.₅Cd₀.₅Se sample without any cocatalysts exhibits the optimal H₂ production rate of 320.6 μmol g⁻¹ h⁻¹ at 420 nm (AQY = 1.7%), which is 9 times and 12 times higher than those of pristine CdSe and pristine ZnSe, respectively. The aforementioned result is attributed to the balance between the bandgap width and the CB edge position of the Zn₀.₅Cd₀.₅Se sample, hence revealing the excitation of more photogenerated electrons and the faster separation efficiency of charge carriers. It is further evidenced by the analyses of electrochemical impedance spectroscopy and transient photocurrent characterization. As a whole, this research paves a new direction towards the synthesis of ZnₓCd₁₋ₓSe nanostructured materials with controlled ratio and tunable bandgap engineering toward improved H₂ generation. This investigation offers new insights into unveiling the mechanism of visible light absorption and boosted photoactivity for ZnₓCd₁₋ₓSe solid solutions.

4. Experimental Section

Materials Synthesis: In a typical procedure, 2 mmol of Se and a total of 2 mmol of Zn (OAc)₂·2H₂O and Cd (OAc)₂·2H₂O were added into a three-necked glass flask, heated, and stirred with a magnetic stirrer until it was completely dissolved. The mixture was heated to 280 °C for 1 h, and nitrogen was introduced into the whole reaction process. At the end of the procedure, the samples were naturally cooled to room temperature. The precipitates were collected by centrifugal tube after cleaning with hexane 3 times. The precipitates were dried in an oven at 60 °C for 8 h. The dried sample was ground into fine powder. To remove the oleylamine on the surface of the sample, 10 mL toluene and 10 mL 10% 3-mercaptopropionic acid (MPA) solution were added and stirred with the fine powder for 4 h. Through centrifugal cleaning, drying, and grinding, the target sample was successfully obtained. The ZnₓCd₁₋ₓSe solid solutions were prepared by changing the molar ratio of Zn/Cd, where x was 0.1, 0.3, 0.5, 0.7, and 0.9. Besides, CdSe and ZnSe were synthesized according to the above method without adding Zn (OAc)₂·2H₂O or Cd (OAc)₂·2H₂O, respectively.

Characterization: The crystal phases of the photocatalysts were determined in the range of 10–80 ° (2θ) by using a powder XRD, Smartlab-3KW. The crystallite size was estimated according to the Scherrer formula, in which λ is the wavelength of incident X-ray radiation, β is the FWHM and θ is Bragg’s diffraction angle. UV-vis spectra of the samples were recorded by a PerkinElmer, Lambda 750. Transmission electron microscope (TEM) images were conducted with a TECNAI F-30 microscope. Specific surface area and distribution of pore diameter were carried out on a Micromeritics TriStar II 3020 apparatus. The samples were degassed at 200 °C for 3 h before the BET-BJH measurements. The instrument employed for XPS analysis and valence band XPS spectra were carried out on the ESCALAB 250Xi spectrometer with Al Kα (hν = 1486.6 eV) as an excitation source. The difference between the measured value and the reference value (C 1s level at 284.8 eV) was taken as the charge correction value to correct the binding energy of other elements in the spectrum. The photoluminescence (PL) spectra were performed using an FL3C-111 (HORIBA Instruments Inc.).

Photocatalytic Measurements: The amount of H₂ was measured using gas chromatography (GC-7920). The photocatalytic H₂ evolution experiments were prepared through a closed-circulation apparatus.
First, 40 mg of the as-prepared photocatalyst was dispersed in 60 mL of 0.2 M Na₂S/0.35 M Na₂SO₃ aqueous solution. Afterward, the mixture was vertically irradiated with a 300 W Xe lamp (CEL-HXF300, Beijing Alight Co., Ltd., λ > 420 nm) under magnetic conditions. The AQY, which is defined in the following formula, was measured under the same conditions, but utilized a 420 nm bandpass filter with an FWHM of 10 nm.

\[
\text{AQY} = \frac{2 \times \text{the number of the evolved } \text{H}_2 \text{ molecules}}{\text{The number of emitted photons}} \times 100\% \quad (1)
\]

**Photoelectrochemical (PEC) Measurements:** For the photoelectrochemical (PEC) measurements, transient photocurrent responses and electrochemical impedance spectroscopy (EIS) were measured with a Bio-Logic VSP-300 potentiostat in a 0.1M Na₂SO₄ solution under visible light irradiation through a 300 W Xe lamp (CEL-HXUV300, Beijing Alight Co., Ltd.). The working electrode was prepared as below: 5 mg of photocatalyst powder was dispersed in 0.5 mL of ethanol and 10 μL of nafion solution followed by sonicnation for 4 h. After that, the slurry was distributed uniformly on the 1 × 2 cm ITO glass, which served as the working electrode after being vacuum-dried at 150 °C for 2 h. Meanwhile, Pt sheet and Ag/AgCl were used as the counter electrode and reference electrode, respectively. The transient photocurrent response was collected by implementing several light on-off cycles under a constant potential of 0.4 V. EIS was characterized by applying 0.4 V bias versus Ag/AgCl over a frequency range of 10⁻¹–10⁰ Hz.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

controllable band structures, metal selenide, photocatalytic hydrogen generation, ternary solid solutions, water splitting

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