p–n Heterojunction Photocatalyst Mn$_{0.5}$Cd$_{0.5}$S/CuCo$_2$S$_4$ for Highly Efficient Visible Light-Driven H$_2$ Production

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ABSTRACT: It is highly important to develop efficient and cheap photocatalysts for hydrogen production. Herein, a series of p–n heterojunction Mn$_{0.5}$Cd$_{0.5}$S/CuCo$_2$S$_4$ has been successfully synthesized for the first time by the hydrothermal impregnation method. Mn$_{0.5}$Cd$_{0.5}$S/CuCo$_2$S$_4$ loading with 12 wt % CuCo$_2$S$_4$ shows the highest H$_2$ evolution rate of 15.74 mmol h$^{-1}$ g$^{-1}$ under visible light ($\lambda \geq 420$ nm) irradiation, which is about 3.15 and 15.28 times higher than that of bare Mn$_{0.5}$Cd$_{0.5}$S (4.99 mmol h$^{-1}$ g$^{-1}$) and CuCo$_2$S$_4$ (1.03 mmol h$^{-1}$ g$^{-1}$), respectively. In addition, it shows a relatively good stability during the five recycle tests, with about 20% loss of reaction rate compared to that of the first cycle. The superior photocatalytic performance is attributed to the effective separation and transfer of photogenerated charge carriers because of the formation of the p–n junction. The samples are systematically characterized by X-ray diffraction, ultraviolet–visible (UV–vis), diffuse reflectance spectroscopy, scanning electron microscopy, transmission electron microscopy (TEM), high-resolution TEM, X-ray photoelectron spectroscopy, photoluminescence, EIS, and so on. UV–vis and EIS show that CuCo$_2$S$_4$ can effectively improve the visible light response of Mn$_{0.5}$Cd$_{0.5}$S/CuCo$_2$S$_4$ and promote the electron transfer from CuCo$_2$S$_4$ to the conduction band of Mn$_{0.5}$Cd$_{0.5}$S so as to improve the photocatalytic efficiency. This study reveals that the p–n heterojunction Mn$_{0.5}$Cd$_{0.5}$S/CuCo$_2$S$_4$ is a promising photocatalyst to explore the photocatalysts without noble metals.

1. INTRODUCTION

Because of the consumption of fossil fuels and serious environmental pollution, ecological damage and energy shortage seriously threaten the sustainable development of society. Much attention has been drawn to develop clean and green energy to address global challenges. Hydrogen energy is considered as an ideal energy resource because of its high conversion efficiency, environmental friendliness, and recyclability. Photocatalytic water splitting has been considered to be a promising technology, which can convert solar energy into chemical energy. It can also promote the energy transformation, environmental protection, and construction of a low-carbon society. So far, a large number of semiconductor materials, including oxides, sulﬁdes, and nitrogen oxides, have been used for photocatalytic hydrogen production from water reduction. Among these, metal sulﬁdes, such as Mn$_x$Cd$_{1-x}$S, have shown promising hydrogen production performances because of wide solar response and suitable band edge positions. However, the H$_2$ evolution rate of Mn$_x$Cd$_{1-x}$S is still unsatisﬁed because of the rapid recombination of photogenerated electron–hole pairs. To solve these problems, several strategies, including metal doping, cocatalyst modiﬁcation, morphological tailoring, and construction of a heterojunction, have been developed to further improve the photocactivity of Mn$_x$Cd$_{1-x}$S. Among these approaches, cocatalyst modiﬁcation and construction of a heterojunction can be considered as ideal approaches because of the accelerated charge separation. Besides, the cocatalyst can provide low activation potentials and abundant active sites. However, up to now, the most effective cocatalyst is still based on noble metals, such as Pt, Ag, Au, and so on. Kumar et al. have designed a Ag/Fe$_2$O$_3$ bridged SrTiO$_3$/g-C$_3$N$_4$ composite to improve the H$_2$ evolution rate. Liu et al. have prepared a new Mn$_{0.5}$Cd$_{0.5}$S/WO$_3$/Au ternary heterostructure to boost the photocatalytic activity. However, it is diﬃcult to achieve industrial application because of high cost. Therefore, developing an eﬃcient, stable, and earth-abundant cocatalyst is of great signiﬁcance for Mn$_{0.5}$Cd$_{0.5}$S solid solution systems. Recently, transition metal sulﬁdes, such as MoS$_2$, CoS$_2$, NiS, CuS, and so forth, have been widely used in photocatalytic hydrogen evolution because of their high efﬁciency, stability,
and low cost. For example, Liu et al.19 have synthesized a novel Mn$_{0.5}$Cd$_{0.5}$S/RGO-MoS$_2$ ternary heterojunction, which exhibits a higher H$_2$ production efficiency compared to that of bare Mn$_{0.5}$Cd$_{0.5}$S. Wang et al.20 found that MoS$_2$ modification via a one-pot solvothermal process could significantly improve the photocatalytic performance of Mn$_{0.5}$Cd$_{0.5}$S/MnS. Zhai and coworkers21 have successfully synthesized a series of transition metal sulﬁde XS (X = Mo, Cu, and Pd)-supported Mn$_{0.5}$Cd$_{0.5}$S composites. The results showed that XS can improve the H$_2$ production activity of Mn$_{0.5}$Cd$_{0.5}$S.

As a bimetallic sulﬁde, CuCo$_2$S$_4$ has high conductivity because of the low electronegativity of sulfur. However, there are few reports on the application of CuCo$_2$S$_4$ toward photocatalytic H$_2$ production. In this study, Mn$_{0.5}$Cd$_{0.5}$S and CuCo$_2$S$_4$ were successfully synthesized by a simple one-step hydrothermal method, separately. Moreover, Mn$_{0.5}$Cd$_{0.5}$S/CuCo$_2$S$_4$ nanocomposites were prepared by the hydrothermal impregnation method for the first time. Mn$_{0.5}$Cd$_{0.5}$S and CuCo$_2$S$_4$ can form a p–n heterojunction, which shows excellent photocatalytic activity for hydrogen evolution (15.74 mmol h$^{-1}$ g$^{-1}$) under visible light. This work may provide a suitable suggestion for the synthesis of p–n heterojunction composite materials without noble metals to improve H$_2$ production activity and broaden the synthetic application of hydrogen-producing materials.

2. RESULTS AND DISCUSSION

2.1. X-ray Diffraction Analysis. The phase structure of as-prepared Mn$_x$Cd$_{1-x}$S CCS and CMS/yCCS nanocomposites was investigated by X-ray diffraction (XRD). In Figure 1a, the diffraction peaks of the Mn$_x$Cd$_{1-x}$S products are shifted toward higher diffraction angles from CdS (PDF#89-0440) to MnS (JCPDS#72-1534) with the increase in the x value from 0.1 to 0.5. The continuous shifts of XRD patterns show that the samples are not the mixture of CdS and MnS but Mn$_x$Cd$_{1-x}$S (0.1 $\leq$ x $\leq$ 0.5) solid solution. This implies that Cd$^{2+}$ with a larger ionic radius (0.97 Å) than Mn$^{2+}$ (0.46 Å) incorporates into the lattice of the MnS crystal, which increases the fringe lattice distance and leads to the formation of a solid solution.

With the increase in the x value ($x > 0.5$) in the Mn$_x$Cd$_{1-x}$S, some diffraction peaks of MnS appear; the characteristic peaks at about 34.2, 49.1, and 61.2° are ascribed to the (200), (220), and (222) planes of MnS (PDF#72-1534), respectively, indicating that the MnS exists in the samples. The XRD pattern of the as-prepared CCS sample is shown in Figure 1c. The peaks at 26.6, 31.3, 37.9, 46.9, 49.9, and 54.8° are ascribed to the cubic CCS (PDF#42-1450). There are no impurity peaks, indicating the synthesis of the pure-phase CCS. In Figure 1c, pure CMS and all CMS/yCCS composites exhibit the similar diffraction peaks, meaning the good dispersion of CCS nanoparticles in the surface of CMS, and the deposition of CCS does not affect the crystalline structure of CMS.

In order to further clarify the composition of CMS/yCCSs, the inductively coupled plasma-optical emission spectroscopy test was carried out. It can be seen from Table S1 that the actual molar ratio of Mn/Cd/S in CMS/12CCS is 0.46:0.54:1, which is very close to 0.5:0.5:1. The actual loading amount of CCS is 11.9%, which is close to the theoretical 12%. These results indicate that the CMS/yCCS composite has been successfully synthesized.

2.2. Scanning Electron Microscopy, Energy-Dispersive Spectrometer, and Transmission Electron Microscopy Analysis. The surface morphologies of as-prepared CMS and CMS/12CCS composites were investigated by scanning electron microscopy (SEM) and the results are shown in Figure 2. It can be observed that the morphology of the CMS/12CCS nanocomposite consists of some irregular particles with an average size of 50–60 nm. It is similar to that of pure CMS, indicating that CCS loading has no effect on the morphology of CMS. The bright field micrograph in Figure 3 shows that the average particle size of the CMS/12CCS nanocomposite is 50–60 nm, which is consistent with the SEM results. The high-resolution transmission electron microscopy (HRTEM) image in Figure 3c shows three different kinds of lattice fringes. The lattice fringe with a spacing of about 0.328 nm can be assigned to the (002) crystal plane of CMS. The lattice fringes with a spacing of 0.533 and 0.285 nm are assigned to the (111) and (113) crystal plane of CCS, respectively. Therefore, CCS is in tight contact with the host material CMS, which can promote the transfer rate of photoinduced carriers between CMS and CCS. Moreover, Mn, Cd, Cu, Co, and S elements are all detected using an energy-dispersive spectrometer, demonstrating again that CCS is well dispersed in the surface of CMS. In Figure 4a–f, the EDS element mapping of CMS/12CCS displays the homogeneous distribution of Mn, Cd, S, Cu, and Co elements in the sample. All of these results confirm that there is an intimate interfacial contact between CMS and CCS. Such an intimate heterojunction can provide more active sites and promote the effective separation of photogenerated carriers, thus improving the activity of H$_2$ evolution.

2.3. X-ray Photoelectron Spectroscopy Analysis. X-ray photoelectron spectroscopy (XPS) was further used to investigate the surface chemical status of CMS/12CCS. In Figure 5a, Mn, Cd, Cu, Co, and S elements can be detected obviously, which is in good agreement with the EDS results. Figure 5b–f shows the homologous high-resolution XPS spectra of Mn, Cd, S, Cu, and Co, respectively. Compared to pure CMS, slight shifts toward higher binding energies can be observed from the high-resolution spectra of CMS/12CCS in Figure 4b–d, suggesting that the binding energies of the core-level electrons of these metal and sulfur ions are affected because of the possible chemical bonding actions among the...
composite components. Compared to the pristine CMS, the binding energies of Cd 3d and Mn 2p in the CMS/12CCS slightly shift toward a high value, which suggests the presence of strong chemical and electronic coupling between CMS and CCS. In the Mn 2p XPS spectrum (Figure 5b), the peaks at 652.3 and 640.7 eV correspond to 2p1/2 and 2p3/2 of Mn2+, respectively. In Figure 5c, the Cd 3d spectrum displays two binding energy peaks at 411.6 and 404.8 eV, which are corresponding to Cd 3d5/2 and Cd 3d3/2 of Cd2+, respectively. The binding energy peaks of S 2p in Figure 5d are located at 162.2 and 161.1 eV, which can be attributed to 2p1/2 and 2p3/2 of S2− in CMS/12CCS nanocomposites, respectively. The Cu 2p peaks can be divided into two peaks, including Cu 2p1/2 (952.2 eV) and Cu 2p3/2 (932.3 eV) (Figure 5e), which indicates that the oxidation state of copper was +1. The Co 2p peak displayed in Figure 5f can be divided into four peaks. The peaks at 782.1 and 797.2 eV are the satellite peaks, indicating that the Co element exists in the form of Co3+ and Co2+. All these results indicate the presence of chemical bonds between CCS and CMS rather than a simple physical mixture.

2.4. BET Surface Areas. The Brunauer–Emmett–Teller (BET) specific surface areas (SBET) of pure CMS, CCS, and the as-prepared CMS/CCS composites were measured by nitrogen adsorption and are summarized in Table S2. The BET specific surface areas of the pristine CMS and CCS are 25.95 and 35.62 m² g⁻¹, respectively. Although CMS/12CCS has the smallest area (18.76 m² g⁻¹), it shows the highest activity. Consistent with Bao’s work, SBET is not a key factor to restrict the H₂ production rate of CMS/CCS. The different H₂ evolution rate of CMS/CCS should be attributed to other factors, such as their crystal structure and band structure, because the separation of photogenerated electron–hole pairs and the proceeding of H₂ evolution rate will be determined by these structures.

2.5. Photocatalytic H₂ Evolution Activity and Stability. The photocatalytic H₂ evolution activities of all samples were evaluated under visible light irradiation (λ ≥ 420 nm) using Na₂S (0.35 M) and Na₂SO₃ (0.25 M) as sacrificial agents. Figure 6a shows the photocatalytic H₂ evolution efficiency of MnₓCd₁−ₓS with different Mn/Cd ratios. The results show that the H₂ evolution efficiency has enhanced with the increase in Mn content (x < 0.5). However, when x is more than 0.5, the H₂ evolution efficiency of MnₓCd₁−ₓS decreases with a further increase in the x value. When x = 0.5, Mn₀.₅Cd₀.₅S has the highest H₂ evolution activity (4.99 mmol h⁻¹ g⁻¹). Figure 6c,d shows the photocatalytic H₂ evolution rate of CMS/yCCS composites with different contents of CCS. Almost no H₂ is detected for bare CCS, suggesting its poor photocatalytic activity for H₂ evolution. CMS exhibits a low H₂ evolution rate of 4.99 mmol h⁻¹ g⁻¹, probably because of the high recombination of photogenerated electron–hole pairs. However, after loading CCS as a cocatalyst, H₂ evolution performance of CMS/yCCS improved obviously, indicating...
that CCS is an effective cocatalyst for CMS. The H$_2$ evolution performance enhances with the increased amount of CCS from 3 to 12 wt %. The optimal CCS loading amount is 12 wt %, with the highest H$_2$ evolution rate of 15.74 mmol h$^{-1}$ g$^{-1}$, which is about 3.15 times and 2.89 times higher than that of CMS and Mn$_{0.5}$Cd$_{0.5}$S/3 wt % Pt (marked as CMS/3Pt), respectively. The photocatalytic H$_2$ evolution activities of all samples were also evaluated under the same conditions, except that the 420 nm cutoff filter was replaced with a 510 nm cutoff filter. It can be seen from Figure S3 that when the wavelength is more than 510 nm, the H$_2$ production rate of CMS/12CCS is 1.26 mmol h$^{-1}$ g$^{-1}$, which is 2.17 times that of a pure CMS (0.58 mmol h$^{-1}$ g$^{-1}$). The AQE of CMS/12CCS was calculated to be 41.48% at 420 nm. The hydrogen production and AQE of Mn$_{x}$Cd$_{1-x}$S-based catalysts are listed in Table S3. It can be seen from Table S3 that CMS/12CCS has a high hydrogen evolution rate and the highest AQE. However, with the further increase in CCCS, the H$_2$ evolution performance drops. The reason can be ascribed to the shielding effect that the excessive black CCCS will partially block the light absorption of CMS.$^9$ Besides, the active sites for H$_2$ evolution can be covered by excessive CCCS, thus blocking the effective contact between the active sites and reactants. Therefore, the overmuch amount of CCCS can act as the recombination centers of photon-generated carriers and reduce the light absorption of CMS. What is more, to confirm the photostability of CMS/12CCS, five cycle tests have been carried out under the same conditions for 20 h. As shown in Figure 6f, after five cycle tests, the H$_2$ evolution rate is 12.62 mmol h$^{-1}$ g$^{-1}$, which is 19.82% lower than the 15.74 mmol h$^{-1}$ g$^{-1}$ in the first cycle. Although the photocatalytic H$_2$ evolution activity shows a little decrease after five-round cycles, it still maintains good stability. For the CMS/12CCS, XPS test was performed after the reaction. It can be seen from Figure S2 that the XPS spectra shift to higher binding energy after the photocatalytic reaction; however, no obvious changes are found in XRD and SEM before and after reaction (Figure S1), indicating that CMS/12CCS has good stability. We have synthesized five batches of CMS/CCS by the same method, and the activity test was carried out under the same conditions. As shown in Figure S4, the average H$_2$ evolution rate of CMS/12CCS is basically stable at 15.7 mmol h$^{-1}$ g$^{-1}$,
with certain repeatability. The results indicate that the CMS/12CCS photocatalyst is stable for photocatalytic H₂ evolution.

2.6. Optical Absorption. Ultraviolet−visible (UV−vis) diffuse reflectance spectra of samples are shown in Figure 7. As can be seen, the pure CMS sample displays an absorption edge at about 525 nm, corresponding to a band gap of 2.46 eV (Figure S5a). Pure CCS has a strong light response in the whole visible light region because of its narrow band gap of 1.75 eV (Figure S5b). For the CMS/γCCS composite, with the increase in CCS content from 3 to 15 wt %, the absorption edge of the composite displays an obvious red shift and enhanced absorption in the visible light region, which is attributed to the contribution of CCS on the surface of CMS. It is believed that the enhanced light absorption of CMS/γCCS composites is favorable to generate more available photo-generated electrons for participating in the photocatalytic reaction toward H₂ evolution.

2.7. Photoluminescence Spectra and Photoelectrochemical Measurements. In order to study the processes of charge transfer, separation, and recombination in the CMS/CCS, the photoluminescence (PL) emission spectrum was measured under an excitation wavelength of 330 nm (Figure 8a). The lower the PL peak intensity, the lower the recombination rate of photogenerated electron−hole pairs. Obviously, CMS/12CCS has the lowest PL peak intensity compared to other samples, indicating that the formation of a heterojunction between the CMS solid solution and CCS can promote the photogenerated charge transfer/separation at the interface. To further evaluate the interface charge separation efficiency, the transient photocurrent for the pure CMS and CMS/CCS under visible light irradiation is measured (Figure 8b). The bare CMS shows a relatively low photocurrent density because of the rapid recombination of photoinduced carriers. After loading of the CCS cocatalyst, with the increase of the CCS (γ ≤ 12), the sample shows an enhanced photocurrent intensity, suggesting that the separation of the photogenerated charge carriers is obviously promoted. When CCS is overloaded (γ > 12), the photocurrent intensity of the sample decreases. Nyquist impedance spectroscopy of CMS and CMS/CCS is displayed in Figure 8c. The CMS/12CCS composite exhibits a smaller arc radius than other samples,
indicating that the charge in CMS/12CCS has less resistance during the transportation process. These results indicate that the superior photocatalytic performance of CMS/12CCS is attributed to the effective separation and transfer of photo-generated charge carriers.

2.8. Proposed Mechanism. On the basis of the Results and Discussion mentioned above, a proposed photocatalysis mechanism over CMS/12CCS nanocomposites has been carried out. The detailed band structures, valence band (VB), and conduction band (CB) of CCS and CMS are studied to investigate the charge-transfer process and direction and the photocatalytic mechanism.

According to the equations

\[ E_{VB} = X - E^o + 0.5E_g \]

\[ E_{CB} = E_{VB} - E_g \]

where \( E_{VB} \) and \( E_{CB} \) are the VB and CB of semiconductors, respectively. \( X \) is the electronegativity of the semiconductor. \( E^o \) is the energy of free electrons on the hydrogen scale (4.5 eV). \( E_g \) is the band gap energy of the semiconductor. The \( X \) value of CMS is 4.996, so the \( E_{VB} \) and \( E_{CB} \) of CMS are calculated to be 1.73 and \(-0.73\) eV, respectively (\( E_g \) of CMS is 2.46 eV). The \( X \) value of CCS is 5.32 eV, so the \( E_{VB} \) and \( E_{CB} \) of CCS are 1.69 and \(-0.06\) eV, respectively (\( E_g \) of CCS is 1.75 eV). According to Figure S6a, the Mott–Schottky plots of CMS have a positive slope, showing that it is an n-type semiconductor. In contrast, the Mott–Schottky plots of CCS have a negative slope, corresponding to a p-type semi-

![Figure 8](https://dx.doi.org/10.1021/acsomega.0c05106)  
Figure 8. (a) PL spectra of CMS, CMS/CCS, and CCS; (b) transient photocurrent responses; and (c) EIS spectra.

![Figure 9](https://dx.doi.org/10.1021/acsomega.0c05106)  
Figure 9. Proposed mechanism of the photocatalytic \( \text{H}_2 \) reduction over CMS/12CCS under visible light irradiation.
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4. CONCLUSIONS

In summary, we have synthesized a series of CMS/γCCS photocatalysts via the hydrothermal impregnation method. CMS/12CCS loading with 12 wt % CCS exhibits the best \( \text{H}_2 \) production efficiency of 15.74 mmol h\(^{-1}\) g\(^{-1}\) under visible light (\( \lambda \geq 420 \) nm) irradiation, which is about 3.15 times and 15.28 times higher than that of bare CMS (4.99 mmol h\(^{-1}\) g\(^{-1}\)) and CCS (1.03 mmol h\(^{-1}\) g\(^{-1}\)), respectively. Additionally, CMS/12CCS shows an excellent AQE of 41.48% at 420 nm and good photostability over 20 h. The significant photocatalytic performance can be attributed to the effective separation and transfer of photogenerated charge carriers because of the formation of the p–n junction. This work reveals that the heterojunction between CMS and CCS can improve the photocatalytic hydrogen evolution and provides a suitable suggestion for the synthesis of composite materials without noble metals to improve \( \text{H}_2 \) production activity.

4. EXPERIMENTAL SECTION

4.1. Materials. Manganese acetate tetrahydrate (Mn\((\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}\)), cadmium nitrate tetrahydrate (Cd(NO\(_3\))\(_2\cdot 4\text{H}_2\text{O}\)), thioacetamide, ethylenediamine (EDA), copper nitrate trihydrate (Cu(NO\(_3\))\(_3\cdot 3\text{H}_2\text{O}\)), cobalt nitrate hexahydrate (Co(NO\(_3\))\(_2\cdot 6\text{H}_2\text{O}\)), tertiary butanol (TBA), ammonia water (\(\text{NH}_3\cdot \text{H}_2\text{O}\)), sodium sulfide nonahydrate (Na\(_2\text{S}\cdot 9\text{H}_2\text{O}\)), and sodium sulfite (Na\(_2\text{SO}_3\)) are analytic reagents and used without further purification.

4.2. Synthesis. 4.2.1. Synthesis of Mn\(_x\)Cd\(_{1-x}\)S. Mn\(_x\)Cd\(_{1-x}\)S solid solutions were synthesized through a hydrothermal method. First, 2x mmol Mn\((\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}\), 2(1 – x) mmol Cd(NO\(_3\))\(_2\cdot 4\text{H}_2\text{O}\) and excessive amounts of thioacetamide were dissolved in 60 mL of EDA under continuous stirring. Then, the mixture was stirred for 30 min and ultrasonicated for another 30 min. Finally, the mixture was transferred into a 100 mL Teflon-lined autoclave and kept at 180 °C for 24 h. After cooling to room temperature naturally, Mn\(_x\)Cd\(_{1-x}\)S solid solutions were obtained by washing with ethanol and deionized water alternately several times and then dried at 60 °C for 6 h. The obtained Mn\(_x\)Cd\(_{1-x}\)S sample was marked as CMS.

4.2.2. Synthesis of CuCo\(_2\)S\(_4\). A total of 1 mmol Cu(NO\(_3\))\(_2\)· 3H\(_2\)O, 2 mmol Co(NO\(_3\))\(_2\)·6H\(_2\)O, and 6 mmol thiourea (\(\text{CH}_4\text{N}_2\text{S}\)) were dissolved in 60 mL of deionized water. Then, 15 mL of TBA and 2.5 mL of ammonia water were added into the abovementioned mixed solution and stirred for 1 h. Next, the mixture was transferred to a 100 mL Teflon-lined autoclave and kept at 180 °C for 10 h. After cooling naturally, a black precipitate was obtained by filtration and washed with ethanol and deionized water several times. The collected powder was denoted as CCS.

4.2.3. Preparation of the Mn\(_{0.5}\)Cd\(_{0.5}\)S/CuCo\(_2\)S\(_4\) Composite. The Mn\(_{0.5}\)Cd\(_{0.5}\)S/CuCo\(_2\)S\(_4\) nanocomposite was prepared by the hydrothermal impregnation method. In a typical process, 0.1 g of Mn\(_{0.5}\)Cd\(_{0.5}\)S was dispersed in 50 mL of absolute ethanol. After ultrasonic treatment for 1 h, the quantitative CuCo\(_2\)S\(_4\) was added into the abovementioned solution and ultrasonicated for another 1 h. Finally, the mixture was stirred overnight and dried in an oven at 80 °C. The mass ratio of CuCo\(_2\)S\(_4\) to Mn\(_{0.5}\)Cd\(_{0.5}\)S was 3, 7, 10, 12, and 15 wt %. The total preparation process is shown in Scheme 1. The final products were marked as CMS/γCCS (\( y \) is the mass percentage of CCS, \( y = 3, 7, 10, 12, \) and 15).

4.3. Characterizations. The crystal structure of the samples was characterized using a Rigaku SmartLab X-ray diffractometer using Cu Kα radiation. The surface morphologies of the samples were evaluated using a scanning electron microscope (FEI Inspect F50), transmission electron microscope (JEOL model JEM-2010F), and high-resolution transmission electron microscope (JEM-2010F). The XPS measurement was carried out to identify the elemental composition and chemical state of the samples. UV–vis diffuse reflectance absorption spectra of the samples (with BaSO\(_4\) as a reference) were studied using a Shimadzu UV 2401 spectrophotometer. The PL was analyzed on an F-7100 fluorescence spectrometer.
Nitrogen adsorption data obtained on a NOVA Surface Area Analyzer Station A were used to calculate the BET surface area. The photoelectrochemical tests were obtained using a CHI model 618C electrochemical analyzer and a standard three-electrode system; the Ag/AgCl (saturated KCl) and Pt foil were used as the reference electrode and counter electrode, respectively. A 300 W Xe lamp with a 420 nm cutoff filter was used as the light source. Mott–Schottky measurements were evaluated in a 0.5 mol/L Na2SO4 electrolyte (pH = 6.2) at a frequency of 1 kHz in the dark. The preparation method of the working electrode is as follows: a total of 30 mg of the samples was dispersed in absolute ethanol and grinded for 30 min and the suspension was spin-coated on cleaned FTO glass and dried at 80 °C for 1 h.

4.4. Photocatalytic Test. The photocatalytic H2 production experiment was completed in the photocatalytic activity evaluation system. In a typical process, 20 mg of the sample was well dispersed in a 100 mL mixed solution containing Na2S (0.35 M) and Na2SO3 (0.25 M) as sacrificial agents. The system was evacuated using a vacuum pump to drive away the dissolved gases. A 300 W Xe lamp with a 420 nm filter (λ ≥ 420 nm) was used as the visible light source. The temperature of the reaction system was maintained at about 6 °C. Before irradiation, the photoreactor was evacuated for 30 min to thoroughly exhaust the air. The produced hydrogen amount was detected on line by gas chromatography (GC-7920) every 1 h. The total reaction time was 4 h. The irradiation area was thoroughly exhaust the air. The produced hydrogen amount was detected on line by gas chromatography (GC-7920) every 1 h. The total reaction time was 4 h. The irradiation area was 19.6 cm² and the average energy density is 59.506 mW/cm². The AQE for H2 evolution was measured under the same conditions, except that the UV cutoff filter was replaced by a 420 nm band-pass filter. The AQE was calculated using the following equation

\[
\text{AQE} = \frac{2 \times \text{the number of evolved hydrogen}}{\text{the number of incident photons}} \times 100\%
\]

4. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05106.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the Key Research Projects of Science and Technology Department of Sichuan Province (2020YJ0260).

■ REFERENCES

(1) Dawood, F.; Anda, M.; Shafiullah, G. M. Hydrogen production for energy: An overview. Int. J. Hydrogen Energy 2020, 45, 3847–3869.

(2) Nicita, A.; Maggio, G.; Andaloro, A. P. F.; Squadrito, G. Green hydrogen as feedstock: Financial analysis of a photovoltaic-powered electrolysis plant. Int. J. Hydrogen Energy 2020, 45, 11395–11408.

(3) Wang, J.; Zhang, Y.; Wang, X.; Su, W. Simultaneous enhancements in photoactivity and anti-photocorrosion of Z-scheme Mn0.5Cd0.5S/WO3 for solar water splitting. Appl. Catal., B 2020, 268, 118444.

(4) Kojima, Y.; Yamaguchi, M. Ammonia storage materials for nitrogen recycling hydrogen and energy carriers. Int. J. Hydrogen Energy 2020, 45, 10233–10246.

(5) Xiang, Z.; Nan, J.; Deng, J.; Shi, Y.; Zhao, Y.; Zhang, B.; Xiang, X. Uniform CdS-decorated carbon microsheets with enhanced photocatalytic hydrogen evolution under visible-light irradiation. J. Alloys Compd. 2019, 770, 886–895.

(6) Liu, Y.; Gong, Z.; Lv, H.; Ren, H.; Xing, R. Rational design of Au decorated Mn0.5Cd0.5S/WO3 step-scheme heterostructure with multi-channel charge transfer and efficient H2 generation. Appl. Surf. Sci. 2020, 526, 146734.

(7) Zhai, H.; Liu, X.; Wang, P.; Huang, B.; Zhang, Q. Enhanced photocatalytic H2 production of Mn0.5Cd0.5S solid solution through loading transition metal sulfides XS (X = Mo, Cu, Pd) cocatalysts. Appl. Surf. Sci. 2018, 430, S15–S22.

(8) Wang, J.; Luo, J.; Liu, D.; Chen, S.; Peng, T. One-pot solvothermal synthesis of Mo5S7-modified Mn0.5Cd0.5S/MnS hetero-junction photocatalysts for highly efficient visible-light-driven H2 production. Appl. Catal., B 2019, 241, 130–140.

(9) Wang, Q.; Zhang, Y.; Liao, J.; Li, L.; Liu, H.; Meng, J.; Zhu, Z.; Cao, Y.; Yao, H.; Li, H.; Yang, Y. A novel Mn0.5Cd0.5S/SiO2 derived MnO2/SiO2 nanowires modified by Co3P nanoparticles for efficient photocatalytic H2 evolution under visible light irradiation. Appl. Catal., B 2018, 237, 689–698.

(10) Ikeue, K.; Shinmura, Y.; Machida, M. Ag-doped Mn−Cd sulfide as a visible-light-driven photocatalyst for H2 evolution. Appl. Catal., B 2012, 123–124, 84–88.

(11) Liu, Y.; Ren, H.; Lv, H.; Gong, Z.; Cao, Y. An insight into the trifunctional roles of Cu2(OH)3CO3 cocatalyst in boosting the photocatalytic H2 evolution activity over Zn0.5Cd0.5S nanoparticles. Appl. Surf. Sci. 2019, 484, 1061–1069.

(12) Liu, H.; Meng, J.; Zhang, J. Self-assembled three-dimensional flowerlike Mn0.5Cd0.5S microspheres as efficient visible-light-driven photocatalysts for H2 evolution and CO2 reduction. Catal. Sci. Technol. 2017, 7, 3802–3811.
(13) Huang, Q.; Wang, J.-C.; Ye, L.-Q.; Zhang, Q.; Yao, H.-C.; Li, Z.-J. A novel p–n heterojunction Mn0.25 Cd0.75 S/C/SiO3 for highly efficient photocatalytic H2 evolution under visible light irradiation. J. Taiwan Inst. Chem. Eng. 2017, 80, 570–577.

(14) Liu, H.; Xu, Z.; Zhang, Z.; Ao, D. Novel visible-light driven Mn0.5Cd0.5S/g-C3N4 composites: Preparation and efficient photocatalytic hydrogen production from water without noble metals. Appl. Catal. A 2016, 518, 150–157.

(15) Yang, J.; Wang, D.; Han, H.; Li, C. Roles of Cocatalysts in Photocatalysis and Photoelectrocatalysis. Acc. Chem. Res. 2013, 46, 1900–1909.

(16) Kumar, A.; Rana, A.; Sharma, G.; Naushad, M.; Al-Muhtaseb, A.; Guo, C.; Iglesias-Juez, A.; Stadler, F. J. High-Performance Photocatalytic Hydrogen Production and Degradation of Levofloxacin by Wide Spectrum-Responsive Ag/Fe2O3 Bridged SrTiO3/g-C3N4 Plasmonic Nanojunctions: Joint Effect of Ag and Fe2O3. ACS Appl. Mater. Interfaces 2018, 10, 40474–40477.

(17) Jin, J.; Wang, C.; Ren, X.-N.; Huang, S.-Z.; Wu, M.; Chen, L.-H.; Hasen, T.; Wang, B.-J.; Li, Y.; Su, B.-L. Anchoring ultrathin metallic and oxidized Pt nanoclusters on yolk-shell TiO2 for unprecedentedly high photocatalytic hydrogen production. Nano Energy 2017, 38, 118–126.

(18) Pan, B.; Luo, S.; Su, W.; Wang, X. Photocatalytic CO2 reduction with H2O over LaPbO3 nanorods deposited with Pt cocatalyst. Appl. Catal., B 2015, 168–169, 458–464.

(19) Liu, Y.; Gong, Z.; Xie, Y.; Lv, H.; Zhang, B. Revealing the synergetic effects of graphene and MoS2 on boosted photocatalytic H2 production of Mn0.5Cd0.5S photocatalyst. Appl. Surf. Sci. 2020, 505, 144637.

(20) Liu, X.; Liang, X.; Wang, P.; Huang, B.; Qin, X.; Zhang, X.; Dai, Y. Highly efficient and noble metal-free NiS modified Mn0.5Cd0.5S solid solutions with enhanced photocatalytic activity for hydrogen evolution under visible light irradiation. Appl. Catal., B 2017, 203, 282–288.

(21) Liao, L.; Zhu, J.; Bian, X.; Zhu, L.; Scanlon, M. D.; Girault, H. H.; Liu, B. MoS2 Formed on Mesoporous Graphene as a Highly Active Catalyst for Hydrogen Evolution. Adv. Funct. Mater. 2013, 23, 5326–5333.

(22) Bisroju, R. K.; Das, D.; Sharma, R.; Pal, S.; Mawlong, L. P. L.; Bhorkar, K.; Giri, P. K.; Singh, A. K.; Narayanan, T. N. Hydrogen Evolution Reaction Activity of Graphene–MoS2 van der Waals Heterostructures. ACS Energy Lett. 2017, 2, 1355–1361.

(23) Ghasemi, Z.; Abdi, V.; Sourinejad, I. Green fabrication of Ag/AgCl@TiO2 superior plasmonic nanocomposite: Biosynthesis, characterization and photocatalytic activity under sunlight. J. Alloys Compd. 2020, 841, 155593.

(24) Liang, Q.; Zhang, C.; Xu, S.; Zhou, M.; Li, Z. Nanocomposites based on 3D honeycomb-like carbon nitride with Cd5Zn9S6 dots for efficient photocatalytic hydrogen evolution. Int. J. Hydrogen Energy 2019, 44, 29964–29974.

(25) Zheng, X.; Guo, Y.; Tian, J.; Sun, B.; Liang, Z.; Xu, X.; Cui, H. Controllable growth of MoS2 nanosheets on novel Cu2S snowflakes with high photocatalytic activity. Appl. Catal., B 2018, 232, 355–364.

(26) Moosavinard, S. E.; Fani, S.; Rahmanian, M. Hierarchical CuCo2S4 hollow nanoneedle arrays as novel binder-free electrodes for high-performance asymmetric supercapacitors. Chem. Commun. 2016, 52, 4517–4520.

(27) Jin, R.; Cui, Y.; Gao, S.; Zhang, S.; Yang, L.; Li, G. CNT@NC@CuCo2S4 nanocomposites: An advanced electrode for high performance lithium-ion batteries and supercapacitors. Electrochim. Acta 2018, 273, 43–52.

(28) Bao, N.; Shen, L.; Takata, T.; Domen, K.; Gupta, A.; Yanagisawa, K.; Grimes, C. A. Facile cd-thiourea complex thermolysis synthesis of phase-controlled Cds nanocrystals for photocatalytic hydrogen production under visible light. J. Phys. Chem. C 2007, 111, 17527–17534.

(29) Liu, X.; Wang, W.; Liu, Y.; Huang, B.; Dai, Y.; Qin, X.; Zhang, X. In situ synthesis of Bi2S3/Bi23SO4 heterojunction photocatalysts with enhanced visible light photocatalytic activity. RSC Adv. 2015, 5, 55957–55963.

(30) Zhong, Y.; Yuan, J.; Wen, J.; Li, X.; Xu, Y.; Liu, W.; Zhang, S.; Fang, Y. Earth-abundant NiS co-catalyst modified metal-free mpg-C3N4/CNT nanocomposites for highly efficient visible-light photocatalytic H2 evolution. Dalton Trans. 2015, 44, 18260–18269.

(31) Zhou, W.; Jia, J.; Lu, J.; Yang, L.; Hou, D.; Li, G.; Chen, S. Recent developments of carbon-based electrocatalysts for hydrogen evolution reaction. Nano Energy 2016, 28, 29–43.

(32) Liu, X.; Liu, Q.; Wang, P.; Liu, Y.; Huang, B.; Rozhkova, E. A.; Zhang, Q.; Wang, Z.; Dai, Y.; Lu, J. Efficient photocatalytic H2 production via rational design of synergistic spatially-separated dual cocatalysts modified Mn0.5Cd0.5S photocatalyst under visible light irradiation. Chem. Eng. J. 2018, 337, 480–487.

(33) Li, L.; Xu, J.; Ma, J.; Liu, Z.; Li, Y. A bimetallic sulfide CuCo2S4 with good synergistic effect was constructed to drive high performance photocatalytic hydrogen evolution. J. Colloid Interface Sci. 2019, 552, 17–26.

(34) Li, H.; Wang, Z.; He, Y.; Meng, S.; Xu, Y.; Chen, S.; Fu, X. Rational synthesis of Mn0.5Cd0.5S for enhanced photocatalytic H2 evolution: Effects of S precursors and the feed ratio of Mn/Cd on its structure and performance. J. Colloid Interface Sci. 2019, 535, 469–480.

(35) Zhang, D.; Tang, Y.; Qiu, X.; Yin, J.; Su, C.; Pu, X. Use of synergistic effects of the co-catalyst, p-n heterojunction, and porous structure for improved visible-light photocatalytic H2 evolution in porous MnOx/Mn0.5Cd0.5S/Cu2P@Cu2S. J. Alloys Compd. 2020, 845, 155569.

(36) Li, X.; Yu, J.; Low, J.; Fang, Y.; Xiao, J.; Chen, X. Engineering heterogeneous semiconductors for solar water splitting. J. Mater. Chem. A 2015, 3, 2485–2534.

(37) Kronik, L.; Shapiro, Y. Surface photovoltage phenomena: theory, experiment, and applications. Surf. Sci. Rep. 1999, 37, 1–206.

(38) Jiang, J.; Zhang, X.; Sun, P.; Zhang, L. ZnO/BiO1 Heterostructures: Photoinduced Charge-Transfer Property and Enhanced Visible-Light Photocatalytic Activity. J. Phys. Chem. C 2011, 115, 20555–20564.