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Efficient Visible-Light Driven Photocatalytic Hydrogen Production by Z-Scheme ZnWO$_4$/Mn$_{0.5}$Cd$_{0.5}$S Nanocomposite without Precious Metal Cocatalyst

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Abstract: How to restrain the recombination of photogenerated electrons and holes is still very important for photocatalytic hydrogen production. Herein, Z-scheme ZnWO$_4$/Mn$_{0.5}$Cd$_{0.5}$S (ZWMCS) nanocomposites are prepared and applied as visible-light driven precious metal cocatalyst free photocatalyst for hydrogen generation. The ZnWO$_4$/Mn$_{0.5}$Cd$_{0.5}$S nanocomposites with 30 wt% ZnWO$_4$ (ZWMCS-2) can reach a photocatalytic hydrogen evolution rate of 3.36 mmol g$^{-1}$ h$^{-1}$, which is much higher than that of single ZnWO$_4$ (trace) and Mn$_{0.5}$Cd$_{0.5}$S (1.96 mmol g$^{-1}$ h$^{-1}$). Cycling test reveals that the ZWMCS-2 nanocomposite can maintain stable photocatalytic hydrogen evolution for seven cycles (21 h). The type of heterojunction in the ZWMCS-2 nanocomposite can be identified as Z-scheme heterojunction. The Z-scheme heterojunction can effectively separate the electrons and holes, so that the hydrogen generation activity and stability of the ZWMCS-2 nanocomposite can be enhanced. This work provides a highly efficient and stable Z-scheme heterojunction photocatalyst for hydrogen generation.

Keywords: hydrogen energy; Z-scheme; nanocomposite; heterojunction

1. Introduction

In order to alleviate the environmental pollution and energy shortage originated from the excessive use of fossil fuels, renewable and clean energy sources are urgently needed to replace the fossil fuels [1,2]. Hydrogen, as an ideal renewable and clean fuel, has attracted extensive attentions [3–5]. Visible light driven photocatalytic hydrogen evolution from water splitting is an efficient and environmentally friendly method to harvest the endless solar energy and turn it into hydrogen energy [6–9]. This method is very helpful to alleviate the environmental and energy issues originated from fossil fuels.

Currently, many photocatalysts are continuously discovered and intensively studied [10,11]. Among them, CdS, as a kind of classical semiconductor material, is widely used in solar energy generation, paints, photocatalysis, as well as other fields. Since CdS has strong absorption of visible light, and its conduction band position is lower than hydrogen evolution potential, it is expected to be an excellent photocatalytic hydrogen evolution photocatalyst [12–15]. However, numerous studies have shown that the actual photocatalytic hydrogen generation performance of CdS is not high, and the main problems are its low separation efficiency of electrons and holes and serious photo-corrosion [16,17]. Fortunately, an increasing number of reports have proposed methods to improve the weakness of CdS, such as modification of nanostructures [18], non-noble metal ion doping [19], construction of heterojunctions [20,21], and introducing surface defects [22].

Recent studies have revealed that introducing other metal ions into CdS can form solid solutions such as Mn$_x$Cd$_{1-x}$S [23], Zn$_x$Cd$_{1-x}$S [24], Cd$_x$In$_{1-x}$S [25], and (Zn$_{0.95}$Cu$_{0.05}$)$_{1-x}$Cd$_x$S [26].
Mn$_x$Cd$_{1-x}$S solid solution can be formed by substitute part of Cd$^{2+}$ in CdS by Mn$^{2+}$. The substitution of Cd$^{2+}$ by Mn$^{2+}$ can effectively enlarge the interlayer spacing of CdS, thus promoting the ionic diffusion kinetic properties [27,28]. By changing the molar ratio of Mn$^{2+}$/Cd$^{2+}$, the band edge position and the band gap width of Mn$_x$Cd$_{1-x}$S can be tuned [29]. So the photocatalytic hydrogen evolution activity of Mn$_x$Cd$_{1-x}$S can be optimized. However, some of the drawbacks of CdS are still retained in Mn$_x$Cd$_{1-x}$S, such as low separation efficiency of carriers [30].

As a typical metal tungstate semiconductor, ZnWO$_4$ has been widely used in the fields of photocatalytic hydrogen generation and organic pollutant degradation due to its non-toxicity, low cost, ultra-wide band gap (3.5 eV) as well as excellent physicochemical stability [31]. However, the problems of rapid recombination of photogenerated electron-hole and weak visible light absorption still hinder the practical usage of ZnWO$_4$ in the field of photocatalysis [32]. Therefore, the study on modification of ZnWO$_4$ is of great significance.

In recent years, more and more studies tend to construct Z-scheme heterojunction to further promote the photocatalytic hydrogen evolution rate and stability of the photocatalyst [33,34]. For instance, Zuo et al. constructed TiO$_2$-ZnIn$_2$S$_4$ nanoflower with Z-scheme heterostructure, which effectively suppressed the recombination of photogenerated electrons–holes, and improved the photocatalytic H$_2$ generation efficiency and stability [35]. Li and co-workers successfully synthesized a Z-scheme heterostructured NiTiO$_3$/Cd$_{0.5}$Zn$_{0.5}$S photocatalyst with high photocatalytic hydrogen evolution activity and stability relative to constituent materials [36].

In this work, ZnWO$_4$/Mn$_{0.5}$Cd$_{0.5}$S (ZMWCS) nanocomposites with varied Mn$_{0.5}$Cd$_{0.5}$S contents are successfully prepared through a two-step hydrothermal method. Their photocatalytic hydrogen evolution performances are measured under visible light and free of any noble-metal cocatalysts. Among them, the ZMWCS-2 nanocomposite with ZnWO$_4$ mass ratio of 30% shows the optimal photocatalytic hydrogen evolution activity after 21 h cycling test. Through experiments as well as theoretical calculations, the separation method of photogenerated carriers through the heterojunction in ZMWCS-2 nanocomposite is confirmed as Z-scheme. Through the Z-scheme heterojunction, the photogenerated electrons and holes can be effectively separated, thus the hydrogen evolution reaction can be accelerated, and the self-corrosion of Mn$_{0.5}$Cd$_{0.5}$S can be alleviated. The existence of Z-scheme heterojunction lead to the excellent photocatalytic hydrogen evolution activity and stability of the ZMWCS nanocomposites.

2. Results

2.1. Process of Materials Synthesis

As shown in Scheme 1, ZnWO$_4$/Mn$_{0.5}$Cd$_{0.5}$S (ZMWCS) nanocomposites are synthesized via two-step hydrothermal method. First, NaWO$_4$ solution was slowly dropped into Zn(NO)$_3$ solution, and then the mixed solution was heated at 180 °C for 8 h to obtain ZnWO$_4$ nanoparticles. Then, ZnWO$_4$ nanoparticles, Cd(CH$_3$COO)$_2$·2H$_2$O, Mn(CH$_3$COO)$_2$·4H$_2$O, and TAA were added in water, fully dissolved, and heated at 160 °C for 24 h. Through these two steps, ZMWCS nanocomposites were obtained.

2.2. Phase and Morphology Analysis

Figure 1 shows the X-ray powder diffraction (XRD) patterns of Mn$_{0.5}$Cd$_{0.5}$S, ZnWO$_4$ and ZMWCS nanocomposites. The XRD pattern of Mn$_{0.5}$Cd$_{0.5}$S is very similar to that of hexagonal phase CdS (JCPDS 80-0006), except a slight shift in peak positions (Figure S1). The peak shift can be attributed to the partial substitution of Cd$^{2+}$ by Mn$^{2+}$ [37]. The XRD pattern of ZnWO$_4$ is in good agreement with that of monoclinic ZnWO$_4$ (Figure S2, JCPDS No.73-0554). These results confirm the successful preparation of Mn$_{0.5}$Cd$_{0.5}$S and ZnWO$_4$. The ZMWCS nanocomposites (ZMWCS-1, ZMWCS-2, ZMWCS-3, and ZMWCS-4) contain all the characteristic peaks of ZnWO$_4$ and Mn$_{0.5}$Cd$_{0.5}$S, which confirms that both ZnWO$_4$ and Mn$_{0.5}$Cd$_{0.5}$S are contained in ZMWCS nanocomposites. In addition, with the increase
of ZnWO₄ content, the diffraction peak intensity of ZnWO₄ in ZWMCS nanocomposites gradually enhances.

![Scheme 1. Schematic diagram for the synthesis of ZnWO₄/Mn₀.₅Cd₀.₅S (ZWMCS) nanocomposites.](image)

Figure 2 shows the scanning electron microscopy (SEM) images of Mn₀.₅Cd₀.₅S, ZnWO₄ and ZWMCS-2 nanocomposite. In Figure 2a, Mn₀.₅Cd₀.₅S presented nanoparticle morphology (~50 nm). In Figure 2b, ZnWO₄ exhibits rod-like morphology. In Figure 2c, numerous Mn₀.₅Cd₀.₅S and ZnWO₄ are attached to each other to form the ZWMCS-2 nanocomposite. Figure 2d–f shows the energy dispersive spectroscopy (EDS) spectra of Mn₀.₅Cd₀.₅S, ZnWO₄ and ZWMCS-2 nanocomposite. It reveals that Mn₀.₅Cd₀.₅S, ZnWO₄, and ZWMCS-2 nanocomposite only contain the respective constituent prime peaks and no impurity peaks, which indicates the purity of the synthesized samples. The EDS mapping images in Figure 2g confirm that the constituent elements of ZWMCS-2 nanocomposite are well distributed, which further indicates the composition of the ZWMCS-2 nanocomposite.
The two peaks at 651.56 and 639.96 eV (Figure 4b) correspond to Mn 2p. The elemental mapping images for the EDS mapping images of Cd, Mn, S, Zn, W, and O elements can be clearly seen in the XPS survey spectrum. The two peaks at 411.07 and 404.33 eV belong to Cd 3d, Mn 2p, S 2p, Zn 2p, W 4f, and O 1s elements, respectively. In Figure 4a, the two peaks at 411.07 and 404.33 eV belong to Cd 3d, Mn 2p, S 2p, Zn 2p, W 4f, and O 1s elements, respectively. In Figure 4a, the two peaks at 411.07 and 404.33 eV belong to Cd 3d, Mn 2p, S 2p, Zn 2p, W 4f, and O 1s elements, respectively. In Figure 4a, the two peaks at 411.07 and 404.33 eV belong to Cd 3d, Mn 2p, S 2p, Zn 2p, W 4f, and O 1s elements, respectively. In Figure 4a, the two peaks at 411.07 and 404.33 eV belong to Cd 3d, Mn 2p, S 2p, Zn 2p, W 4f, and O 1s elements, respectively. In Figure 4a, the two peaks at 411.07 and 404.33 eV belong to Cd 3d, Mn 2p, S 2p, Zn 2p, W 4f, and O 1s elements, respectively.

The morphology of the material can be further observed by transmission electron microscopy (TEM). As shown in Figure 3a, Mn0.5Cd0.5S presents nanoparticles with a diameter of about 50 nm. In Figure 3b, ZnWO4 takes on short nanorods morphology with a diameter in the range of 5–50 nm. Figure 3c shows the morphology of ZWMCS-2 nanocomposite. Mn0.5Cd0.5S, and ZnWO4 cluster together to form the nanocomposite. Figure 3d shows a HRTEM image of ZWMCS-2 nanocomposite, the lattice fringe spacing of Mn0.5Cd0.5S is 0.293 nm, corresponding to the (112) crystal plane of ZnWO4, and the lattice fringe spacing of Mn0.5Cd0.5S is 0.173 nm, corresponding to the (112) crystal plane of ZnWO4. The lattice distortion appears at the junction between them, which indicates the formation of heterojunction. The presence of heterojunctions indicates the successful formation of composites between ZnWO4 and Mn0.5Cd0.5S.

2.3. X-ray Photoelectron Spectroscopy (XPS) and Elemental Analysis

The chemical state and elemental composition of ZWMCS-2 nanocomposite are analyzed by X-ray photoelectron spectroscopy (XPS). As shown in Figure S3, the characteristic peaks of Cd, Mn, S, Zn, W, and O elements can be clearly seen in the XPS survey spectrum of ZWMCS-2 nanocomposite. Figure 4a–f shows the high-resolution XPS spectra of Cd 3d, Mn 2p, S 2p, Zn 2p, W 4f, and O 1s elements, respectively. In Figure 4a, the two peaks at 411.07 and 404.33 eV belong to Cd 3d3/2 and Cd 3d5/2, respectively [23,30]. The two peaks at 651.56 and 639.96 eV (Figure 4b) correspond to Mn 2p1/2 and Mn 2p3/2, respectively [23,30]. In Figure 4c, the peaks at 161.95 and 160.69 eV correspond to S 2p3/2 and S 2p1/2, respectively [23,30]. The peaks at 1044.08 and 1021.06 eV (Figure 4d) represent Zn 2p3/2 and Zn 2p1/2, respectively [31,38]. As shown in Figure 4e, the two peaks at 36.98 and 34.84 eV belong to W f5/2 and W f7/2, respectively [31,38]. In the high-resolution...
XPS spectra of O 1s (Figure 4f), the peaks located at 530.72 and 529.48 eV represent the characteristic peaks of lattice oxygen in ZnWO₄ [31,38].

![Figure 3. TEM images of (a) Mn₀.₅Cd₀.₅S, (b) ZnWO₄, and (c) ZWMCS-2 nanocomposite; (d) HRTEM images of the ZWMCS-2 nanocomposite.](image)

![Figure 4. XPS spectra of the as-prepared samples: (a) Cd 3d; (b) Mn 2p; (c) S 2p; (d) Zn 2p; (e) W 4f; (f) O 1s.](image)

2.4. BET Surface Area Analysis

Figure 5a,b show the N₂ adsorption–desorption isotherms of Mn₀.₅Cd₀.₅S, ZnWO₄ and ZWMCS nanocomposites. It can be seen from the figure that all samples have hysteresis loops, corresponding to Type IV isotherms [35,39]. Figure 5c shows the BET surface areas of each sample (specific values are shown in Table 1), and the specific surface area of ZWMCS nanocomposites are gradually elevated with the increase of the content of ZnWO₄.
The linear conversion of absorption curves of Mn\(_{0.5}\)Cd\(_{0.5}\)S, ZnWO\(_4\), and ZWMCS nanocomposites. (a) Mn\(_{0.5}\)Cd\(_{0.5}\)S, ZnWO\(_4\), and ZWMCS-2 nanocomposite; (b) ZWMCS nanocomposites; (c) the BET surface area for Mn\(_{0.5}\)Cd\(_{0.5}\)S, ZnWO\(_4\), and ZWMCS nanocomposites.

Figure 5. N\(_2\) adsorption–desorption isotherms of (a) Mn\(_{0.5}\)Cd\(_{0.5}\)S, ZnWO\(_4\), and ZWMCS-2 nanocomposite and (b) ZWMCS nanocomposites; (c) the BET surface area for Mn\(_{0.5}\)Cd\(_{0.5}\)S, ZnWO\(_4\), and ZWMCS nanocomposites.

Table 1. The BET surface areas and H\(_2\) evolution rate of the Mn\(_{0.5}\)Cd\(_{0.5}\)S, ZnWO\(_4\), and ZWMCS nanocomposites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET Surface Area (m(^2) g(^{-1}))</th>
<th>H(_2) Evolution Rate (mmol g(^{-1}) h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(<em>{0.5})Cd(</em>{0.5})S</td>
<td>6.29</td>
<td>1.96</td>
</tr>
<tr>
<td>ZWMCS-1</td>
<td>9.48</td>
<td>1.20</td>
</tr>
<tr>
<td>ZWMCS-2</td>
<td>13.34</td>
<td>3.36</td>
</tr>
<tr>
<td>ZWMCS-3</td>
<td>15.52</td>
<td>2.28</td>
</tr>
<tr>
<td>ZWMCS-4</td>
<td>16.91</td>
<td>1.89</td>
</tr>
<tr>
<td>ZnWO(_4)</td>
<td>24.24</td>
<td>0.06</td>
</tr>
</tbody>
</table>

2.5. UV-Vis Diffuse Reflectance Spectroscopy and Band Gap Analysis

Figure 6a shows the UV-vis diffuse reflectance spectroscopy (DRS) of Mn\(_{0.5}\)Cd\(_{0.5}\)S, ZnWO\(_4\), and ZWMCS-2 nanocomposite. The absorption edges of Mn\(_{0.5}\)Cd\(_{0.5}\)S and ZnWO\(_4\) are at 578.15 and 358.76 nm, respectively. This result indicates that ZnWO\(_4\) is a typical invisible light excitation semiconductor material, while Mn\(_{0.5}\)Cd\(_{0.5}\)S has good visible light absorption ability. Figure 6a shows that ZWMCS-2 nanocomposite also has good light absorption ability. These results indicate that the ZWMCS-2 nanocomposite formed by Mn\(_{0.5}\)Cd\(_{0.5}\)S and ZnWO\(_4\) retains the good visible light absorption ability of Mn\(_{0.5}\)Cd\(_{0.5}\)S. The linear conversion of absorption curves of Mn\(_{0.5}\)Cd\(_{0.5}\)S and ZnWO\(_4\) (Figure 6b) shows that the band gap (\(E_g\)) of Mn\(_{0.5}\)Cd\(_{0.5}\)S and ZnWO\(_4\) are 2.24 and 3.68 eV, respectively. According to (Supporting Information Equations (S2) and (S3)) [39,40], the \(E_{VB}\) of Mn\(_{0.5}\)Cd\(_{0.5}\)S and ZnWO\(_4\) are 1.63 and 3.65 eV, respectively, and the \(E_{CB}\) of Mn\(_{0.5}\)Cd\(_{0.5}\)S and ZnWO\(_4\) are \(-0.61\) and \(-0.03\) eV, respectively. Therefore, the conduction and valence band positions of Mn\(_{0.5}\)Cd\(_{0.5}\)S are interlaced with those of ZnWO\(_4\), the type of heterojunction formed between Mn\(_{0.5}\)Cd\(_{0.5}\)S and ZnWO\(_4\) in ZWMCS-2 nanocomposite can be Type-II or Z-scheme.

2.6. Photocatalytic H\(_2\) Evolution Performance and Electrochemical Analysis

Figure 7a shows the photocatalytic hydrogen evolution rate of each photocatalyst under visible light and without cocatalyst conditions. Among them, the photocatalytic hydrogen evolution rate of Mn\(_{0.5}\)Cd\(_{0.5}\)S is 1.96 mmol g\(^{-1}\) h\(^{-1}\), which is significantly higher than that of CdS (trace). This indicates that Mn\(^{2+}\) doping can significantly increase the photocatalytic hydrogen evolution activity of CdS. The ZWMCS nanocomposites synthesized by combining ZnWO\(_4\) and Mn\(_{0.5}\)Cd\(_{0.5}\)S together have improved photocatalytic hydrogen evolution activity than the single material. Among them, the ZWMCS-2 nanocomposite has the highest photocatalytic hydrogen evolution rate of 3.32 mmol g\(^{-1}\) h\(^{-1}\), which is much higher than that of Mn\(_{0.5}\)Cd\(_{0.5}\)S. Cycling test shows that the ZWMCS-2 nanocomposite still maintains good photocatalytic activity after seven cycles (21 h) of photocatalytic hydrogen evolution test (Figure 7b).
2.7. Photocatalytic H₂ Evolution Performance and Electrochemical Analysis

Figure 7a shows the photocatalytic hydrogen evolution rate of each photocatalyst under visible light and without cocatalyst conditions. Among them, the photocatalytic hydrogen evolution rate of Mn₀.₅Cd₀.₅S is 1.96 mmol g⁻¹ h⁻¹, which is significantly higher than that of CdS (trace). This indicates that Mn²⁺ doping can significantly increase the photocatalytic hydrogen evolution activity of CdS. The ZWMCS nanocomposites synthesized by combining ZnWO₄ and Mn₀.₅Cd₀.₅S together have improved photocatalytic hydrogen evolution activity than the single material. Among them, the ZWMCS-2 nanocomposite has the highest photocatalytic hydrogen evolution rate of 3.32 mmol g⁻¹ h⁻¹, which is much higher than that of Mn₀.₅Cd₀.₅S. Cycling test shows that the ZWMCS-2 nanocomposite still maintains good photocatalytic activity after seven cycles (21 h) of photocatalytic hydrogen evolution test (Figure 7b).

In order to further explore the photogenerated electron hole separation efficiency of each photocatalyst, their photocurrent responses are tested, and the results are shown in Figure 8. The curve of ZnWO₄ is almost a straight line, which indicates that the photocurrent response of ZnWO₄ under visible light is very weak. Unlike ZnWO₄, Mn₀.₅Cd₀.₅S show obvious photocurrent response under visible light. Compared with Mn₀.₅Cd₀.₅S, the ZWMCS-2 nanocomposite has obvious higher photocurrent. This indicates that the ZWMCS-2 nanocomposite has higher photogenerated electron-hole separation efficiency. The excellent electron-hole separation efficiency of the ZWMCS-2 nanocomposite is conducive to the photocatalytic hydrogen evolution reaction.
The calculation results reveal that the surface work functions of Mn_{0.5}Cd_{0.5}S (112) and ZnWO_4 (111) are 4.29 and 5.07 eV, respectively. So, the fermi level of ZnWO_4 (111) is significantly lower than that of Mn_{0.5}Cd_{0.5}S (112). When ZnWO_4 and Mn_{0.5}Cd_{0.5}S are combined together, a built-in electric field is formed between ZnWO_4 and Mn_{0.5}Cd_{0.5}S, and the electron movement direction is from Mn_{0.5}Cd_{0.5}S to ZnWO_4. The continuous movement of electrons in the built-in electric field and the continuous accumulation of holes make the bands of Mn_{0.5}Cd_{0.5}S and ZnWO_4 gradually bend, forming Z-scheme heterojunction, as shown in Figure 9c [40]. It should be noted that the heterojunction herein cannot be Type-II. According to Type-II mechanism (Figure S4), the effective valence band of the ZWMCS-2 nanocomposite is only 1.63 eV, which is much lower than the potential of H_2O/OH (2.27 eV) [39], so the ·OH radical cannot be generated. However, the ZWMCS-2 nanocomposite is found to have a significant ·OH signal by EPR test (Figure 9d). Therefore, the separation mechanism of electrons–holes through the heterojunction in ZWMCS-2 nanocomposite does not belong to Type-II. Following the Z-scheme mechanism (Figure 9e), the effective valence band of the ZWMCS-2 nanocomposite is 3.68 eV, which is much higher than the H_2O/OH potential (2.27 eV), and ·OH can be generated. As revealed by Figure 9d, obvious signals of ·OH can be detected in ZWMCS-2 nanocomposite by EPR. Therefore, the type of heterojunction in ZWMCS-2 nanocomposite is determined to be Z-scheme.

The photocatalytic hydrogen evolution mechanism of the ZWMCS-2 nanocomposite can be described as following. After irradiated by visible light, ZWMCS-2 nanocomposite generates electron-hole pairs. Due to the existence of Z-scheme heterojunction, the photogenerated electrons in the conduction band of ZnWO_4 are transferred to the valence band of Mn_{0.5}Cd_{0.5}S, and then recombines with the photogenerated holes there. Through this process, the holes in the valence band of Mn_{0.5}Cd_{0.5}S are consumed, avoiding the recombination with electrons, so that a large number of photogenerated electrons are collected in the conduction band of Mn_{0.5}Cd_{0.5}S. The effective conduction band of the ZWMCS-2 nanocomposite is −0.61 eV, which is higher than the H^+/H_2 potential (0 eV) [33,34]. Therefore, the photogenerated electrons in the conduction band of Mn_{0.5}Cd_{0.5}S can reduce hydrogen ions in water to hydrogen. At the same time, the holes in the valence band of ZnWO_4 are consumed by the sacrificial agents (S^{2−} and SO_3^{2−}). The existence of Z-scheme heterojunction promotes the effective separation of photogenerated electrons and holes, and

![Figure 8. Photocurrent density–time curves of Mn_{0.5}Cd_{0.5}S, ZnWO_4, and ZWMCS-2 nanocomposite.](image-url)
promotes the performance of photocatalytic hydrogen evolution. Therefore, the ZWMCS-2 nanocomposite has excellent photocatalytic activity and stability for hydrogen production.

![Figure 9. Electrostatic potentials and optimized models of (a) Mn$_{0.5}$Cd$_{0.5}$S (112) facet and (b) ZnWO$_4$ (111) facet. (c) The Z-scheme formation process of Mn$_{0.5}$Cd$_{0.5}$S (112) and ZnWO$_4$ (111) facet. (d) DMPO spin trapping EPR spectra of Mn$_{0.5}$Cd$_{0.5}$S, and ZWMCS-2 nanocomposite. (e) The photocatalysis mechanism of ZWMCS-2 nanocomposite under visible light illumination.](image)

### 3. Materials and Methods

#### 3.1. Synthesis of ZnWO$_4$ Nanoparticles

Solution A was obtained by dissolving 1.65 g of NaWO$_4$·2H$_2$O in 15 mL of distilled water. Solution B was obtained by dissolving 1.49 g of Zn(NO)$_3$·6H$_2$O in 15 mL distilled water. Under continuous stirring, solution A was slowly dropped into solution B. The mixed solution was stirred for 1 h, then it was transferred to a 50 mL reaction kettle, heated at 180 °C for 8 h. After cooling to room temperature, the sample was collected by centrifugation, washed repeatedly with distilled water, and freeze-dried for 18 h.

#### 3.2. Synthesis of ZnWO$_4$/Mn$_{0.5}$Cd$_{0.5}$S Nanocomposites

First, 0.0992 g of ZnWO$_4$, 0.2451 g of Mn (CH$_3$COO)$_2$·4H$_2$O, 0.2665 g of Cd (CH$_3$COO)$_2$·2H$_2$O, and 0.1503 g of TAA were dissolved in 35 mL distilled water. After continuous
agitation for 1 h, the mixed suspension was transferred to a 50 mL reaction kettle and heated at 160 °C for 48 h. After cooling to room temperature, the sample was collected by centrifugation, washed repeatedly by distilled water, and freeze-dried for 18 h. This sample was named as ZWMCS-2. Other ZnWO₄/Mn₀.₅Cd₀.₅S nanocomposites and Mn₀.₅Cd₀.₅S nanoparticles were synthesized by similar method with different mass contents of ZnWO₄. Table 2 lists the abbreviations of the as-synthesized samples.

Table 2. The amounts of raw materials for preparing the ZnWO₄/Mn₀.₅Cd₀.₅S nanocomposites.

<table>
<thead>
<tr>
<th>Samples</th>
<th>ZnWO₄ (g)</th>
<th>Mn(CH₃COO)₂·4H₂O (g)</th>
<th>Cd(CH₃COO)₂·2H₂O (g)</th>
<th>TAA (g)</th>
<th>Content of ZnWO₄ (%)</th>
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<tr>
<td>Mn₀.₅Cd₀.₅S</td>
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<td>0.2451</td>
<td>0.2665</td>
<td>0.1503</td>
<td>0</td>
</tr>
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<td>ZWMCS-1</td>
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<td>0.2451</td>
<td>0.2665</td>
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<td>20</td>
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<tr>
<td>ZWMCS-2</td>
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<td>0.2665</td>
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<td>ZWMCS-3</td>
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<td>0.2665</td>
<td>0.1503</td>
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</tr>
<tr>
<td>ZWMCS-4</td>
<td>0.2313</td>
<td>0.2451</td>
<td>0.2665</td>
<td>0.1503</td>
<td>50</td>
</tr>
</tbody>
</table>

3.3. Photocatalytic Measurements

Photocatalytic measurements were performed in a 250 mL three-necked flask sealed by rubber stopper. The visible light source is a 300 W Xenon lamp with a λ ≥ 420 nm filter. In a typical photocatalytic hydrogen production process, 0.05 g of catalyst, 8.40 g of Na₂S·9H₂O, and 3.15 g of Na₂SO₃ were dissolved in 100 mL distilled water in the flask, and then N₂ gas was passed into the flask for 30 min to remove air. The flask was illuminated by the Xenon lamp. At an interval of one hour, the gases in the flask was collected by a 1 mL syringe, and was measured by gas chromatography.

3.4. Characterizations

All the characterization equipment and their working parameters are given in the supporting information.

4. Conclusions

ZnWO₄/Mn₀.₅Cd₀.₅S nanocomposites are prepared through a two-step hydrothermal method. Under visible light irradiation, and without the help of any noble metal cocatalyst, the ZWMCS-2 nanocomposite exhibits a high hydrogen evolution rate of 3.36 mmol g⁻¹ h⁻¹, and does not show obvious deterioration after 21 h cycling test. Moreover, the photocatalytic hydrogen evolution activity of the ZWMCS-2 nanocomposite is significantly higher than that of the constituent materials. Through experimental analysis and theoretical calculation, it is confirmed that the type of the heterojunction in the ZWMCS-2 nanocomposite is Z-scheme. The Z-scheme heterojunction can effectively separate the photogenerated electrons and holes, reduce the photo-corrosion of the single material, and maximize the photocatalytic hydrogen evolution.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12121527/s1. Figure S1: (a) XRD patterns of as-prepared CdS, MnS, and Mn₀.₅Cd₀.₅S (S1. (b) is an enlarged view of the dotted box area.). Figure S2: XRD patterns of as-prepared ZnWO₄. Figure S3: XPS survey spectra of ZWMCS-2 nanocomposite. Figure S4: The schematic diagrams of charge transfer in supposed Type-II heterojunction.

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