**Research Article**

**Precise composition modulation for optimizing NiWO₄/Pt/CdS Z-scheme system**

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**Abstract**
A reasonable structure is crucial for the solar-to-chemical conversion process of the integrated Z-scheme system. Composition modulation provides a new dimension for the optimization of Z-scheme system. Herein, a composition modulated NiWO₄/Pt/CdS Z-scheme system is demonstrated for photocatalytic hydrogen generation. Proportions of Ni, W, Cd, and S in NiWO₄/Pt/CdS are precisely tuned through the ion-exchange reaction between NiWO₄ and CdS. Important features of the Z-scheme system in terms of light harvesting, charge separation and charge transfer are optimized accordingly. Bandgap of CdS is tuned continuously from 2.22 to 1.52 eV through controlling the Cd and S contents in NiWO₄/Pt/CdS. The results of photoluminescence spectrometry and photoelectrochemical analyses demonstrate that the NiS generated from ion-exchange reaction increase the charge separation and transfer rates. Furthermore, the molar ratio of NiWO₄ to CdS is regulated to a balance state, leading to the decrease of charge recombination. The optimized NiWO₄/Pt/CdS Z-scheme system delivers the comprehensive performance of excellent light harvesting and charge separation abilities, low charge recombination rate, and suitable energy band structure for water reduction. The hydrogen generation rate is increased to 14.39 mmol h⁻¹ g⁻¹ after the optimization. The optimized method brings a new insight into the rational design of Z-scheme system.

**KEYWORDS**
charge separation, light harvesting, NiWO₄/Pt/CdS, optimization, Z-scheme system

**1 INTRODUCTION**
Traditional fossil fuels raise the increasing crisis of energy shortage and environmental pollution. Transformation of solar energy into clean hydrogen by photocatalysis is an intelligent solution for the problems. In order to increase the performance of photocatalysis for the industry application, researchers connect two photocatalysts to construct a Z-scheme heterojunction. Compared with single photocatalyst, Z-scheme heterojunction can enhance the
FIGURE 1  A, Rational optimization of the solar to energy conversion process of the Z-scheme system is crucial; B, If the charge transfers of photosystem II (PSII) and photosystem I (PSI) in the Z-scheme system reach a balance state, the charge recombination of the system decreases.

The essence of optimization of Z-scheme system is to increase the energy input from solar light and to decrease the energy loss which is induced by the unreasonable system structure. Controlling the bandgap structure of this tandem system is interesting and important for the efficient utilization of solar energy. Although bandgap engineering of single photocatalyst has been realized through size control (induced by quantum effect), exogeneic element doping and vacancy engineering, bandgap engineering for Z-scheme system is still lack to leverage the optoelectronic properties. On the other hand, charge separation rate of a Z-scheme system is theoretically related to the balance of charge transfer rates of PSII and PSI (Figure 1B). If the charge transfer rate of PSI is much lower than that of PSII, some of the photogenerated charge carriers in PSII recombine with each other. Because the Z-type charge transfer passageway is inhabited by the low charge transfer rate of PSI. Similarly, charge recombination occurs in PSI if the charge transfer rate of PSII is much lower than that of PSI. Only when the charge transfer rates of PSII and PSI achieve a balance state (Figure 1B), the energy conversion efficiency of the Z-scheme system reaches the maximum. The control of the molar ratio of PSII to PSI is a way to achieve the charge transfer balance.

During the past decades, the charge transfer efficiency between PSII and PSI are always the focus of researchers. Various effective conductive mediators have been developed for the Z-scheme charge transfer, such as the “graphene-functionalized Bi”, ITO nanoparticles and the dual defects on TiO2/g-C3N4 interface and so on. Moreover, many achievements have been made on the ingenious control of the morphology, crystal facet and band bending of the conductive interface to further enhance the Z-type charge transfer. However, few research concerns about the rational optimization of the integrated Z-scheme system through increasing the light harvesting, charge separation and transfer rates in a unified and consistent way.

In this research, we constructed a NiWO4/Pt/CdS Z-scheme system with additional features of adjustable structure and composition. Proportions of Ni, W, Cd and S elements in the NiWO4/Pt/CdS could be easily adjusted, due to the special ion-exchange reaction between NiWO4/Pt/CdS could be easily adjusted, due to the special ion-exchange reaction between NiWO4 and CdS. Bandgap of CdS was engineered continuously from 2.22 to 1.52 eV, and the light harvesting ability was increased. Moreover, we tuned both Cd cation and S anion of NiWO4/Pt/CdS Z-scheme system, not only to optimize the bandgap but also balance the charge transfer (Figure 1). Photoluminescence (PL) spectrometry and photoelectrochemical analyses demonstrated that the charge separation rate was increased and the radiative charge recombination was decreased by the composition modulation accordingly. Consequently, important characteristics of the Z-scheme system were optimized by the composition modulation, and the photocatalytic hydrogen generation rate
was increased to 14.39 mmol h\(^{-1}\)g\(^{-1}\). The optimized method proposed here brings a new perspective for the rational design of Z-scheme system.

## RESULTS AND DISCUSSION

### 2.1 Composition modulation of the Z-scheme system

We constructed the NiWO\(_4\)/Pt/CdS Z-scheme system through a three-step method (Table S1). First, NiWO\(_4\) was synthesized by the reaction between Ni\(^{2+}\) and WO\(_4^{2-}\). Second, Pt was deposited on NiWO\(_4\) for the transfer of charge according to the reference.\(^5\) Third, NiWO\(_4\)/Pt precursor was reacted with certain amounts of Cd\(^{2+}\) and S\(^{2-}\) precursor aqueous solutions (0.02 g mL\(^{-1}\) Cd(CH\(_3\)COO)\(_2\)\(\cdot\)2H\(_2\)O and 0.005 g mL\(^{-1}\) CH\(_3\)CSNH\(_2\)) at 180\(^\circ\)C for 5.5 hours, and NiWO\(_4\)/Pt/CdS samples were obtained.

Synthetic conditions of the NiWO\(_4\)/Pt/CdS are listed in Table S1. There are two groups of samples to control the Cd and S contents, which are named as CdS\(_x\) and CdxS\(_y\). Synthetic conditions of CdS\(_x\) are as follow: Cd precursor solutions were kept at 0.9 mL, while S precursor solutions were increased from 1.2 to 2.1, 2.7 and 6.0 mL, and the corresponding samples were named as Cd12S10, Cd10S11, Cd9S19 and Cd9S49, respectively (based on the Cd and S contents within Ni, W, Cd and S, evaluated by EDS, at%). For CdxS\(_y\), the Cd solutions were 0.9, 1.8, 2.7 and 5.4 mL, while the volumes of S solutions were 2.33 times of Cd solutions (S: Cd = 2.07, molar ratio), corresponding samples were named as Cd10S11, Cd15S23, Cd19S33 and Cd28S49 (based on the Cd and S contents, at%).

Elemental compositions of CdS\(_x\) and CdxS\(_y\) obtained by EDS are shown in Figure 2. During the synthesis of NiWO\(_4\)/Pt/CdS, reactions between NiWO\(_4\) and Cd(CH\(_3\)COO)\(_2\), CH\(_3\)CSNH\(_2\) can be described by Equations 1 and 2. CH\(_3\)CSNH\(_2\) first released S\(^{2-}\) at 180\(^\circ\)C and then NiWO\(_4\) reacted with Cd\(^{2+}\) and S\(^{2-}\) to produce NiWO\(_4\)/Pt/CdS. If NiWO\(_4\) and CdS are formed in a stoichiometric ratio, the ratios of Ni to W and Cd to S should be 1:1. However, as shown in Figure 2, Cd content was slightly larger than the stoichiometric ratio for Cd12S10, while S content was larger than the Cd content for other samples. This result reveals that the elemental proportions of Ni, Cd, W and S in the samples are adjustable, through changing the amounts of Cd\(^{2+}\) and S\(^{2-}\) precursor solutions.

\[
\text{CH}_3\text{CSNH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CONH}_2 + \text{S}^{2-} + 2\text{H}^+ \quad (1)
\]

\[
\text{NiWO}_4/\text{Pt} + \text{Cd}^{2+} + \text{S}^{2-} \rightarrow \text{NiWO}_4/\text{Pt}/\text{CdS} \quad (2)
\]

For CdS\(_x\), when the amount of S precursor was increased (Cd precursor solution was 0.9 mL and S precursor solutions were changed from 1.2 to 6.0 mL), Cd and Ni contents in the samples remained almost constant, while the S content dramatically increased from 9.8 to 49.1 at% and W content decreased from 37.9 to 10.4 at% at the same time. The increase of S content and decrease of W content are caused by the anion-exchange reaction (Equation 3): WO\(_4^{2-}\) in NiWO\(_4\) is replaced by S\(^{2-}\) when there is excessive S\(^{2-}\) compared with Cd\(^{2+}\) in the synthetic solution. Similarly, the cation-exchange reaction between the Cd\(^{2+}\) and Ni\(^{2+}\) in NiWO\(_4\) (Equation 4) occurs when there is excessive Cd\(^{2+}\) compared with S\(^{2-}\) (such as Cd12S10). For CdxS\(_y\), when both the amounts of Cd and S precursors were increased
FIGURE 3 XRD patterns of NiWO$_4$/Pt/CdS: CdSx (A) and CdxS (B)

(Cd precursor solutions were from 0.9 to 5.4 mL, while S precursor solutions were 2.33 times of Cd precursor solutions), Cd and S contents in the samples increased while Ni and W contents decreased. The decrease of W was quickly than Ni, because the amounts of S precursors were larger than Cd precursors (S:Cd = 2.07, molar ratio).

\[
\text{NiWO}_4 + S^{2-} \rightarrow \text{NiS} + \text{WO}_4^{2-} \quad (3)
\]

\[
\text{NiWO}_4 + \text{Cd}^{2+} \rightarrow \text{CdWO}_4 + \text{Ni}^{2+} \quad (4)
\]

XRD patterns of CdSx are shown in Figure 3A. In general, characterized peaks of NiWO$_4$ (00-015-0755) and CdS (00-010-0454) co-existed in all the samples, while minor peaks of CdWO$_4$ or NiS arose when adjusting the S content. Therefore, main components for every sample are NiWO$_4$ and CdS. In Cd$_{12}$S$_{10}$ which the Cd content was slightly higher than S content, characterized peaks of CdWO$_4$ (00-014-0676) appeared. The presence of CdWO$_4$ gives the evidence of the cation-exchange reaction (Equation 4).

XRD patterns of CdxSy are shown in Figure 3B. Similar to CdSx, the main components for every sample were NiWO$_4$ (00-015-0755) and CdS (00-010-0454). In the Cd$_{10}$S$_{11}$ pattern, characterized peaks of NiS did not exist. When both the Cd and S contents increased, minor peaks of NiS (00-012-0041) arose in Cd$_{15}$S$_{23}$. Further increasing the Cd and S contents induced the increase of NiS peak intensity. Finally, small peaks of NiS$_2$ (00-011-0099) existed in the pattern, indicating that a large excessive amount of S can combine with Ni to produce crystalline NiS. The presence of NiS also proves the anion-exchange reaction (Equation 3).

XRD patterns of CdxSy are shown in Figure 3B. Similar to CdSx, the main components for every sample were NiWO$_4$ (00-015-0755) and CdS (00-010-0454). In the Cd$_{10}$S$_{11}$ pattern, characterized peaks of NiS did not exist. When both the Cd and S contents increased, minor peaks of NiS (00-012-0041) arose in Cd$_{15}$S$_{23}$. Further increasing the Cd and S contents induced the increase of NiS peak intensity. Finally, small peaks of NiS$_2$ (00-011-0099) arose in Cd$_{28}$S$_{49}$. These results also indicate that large excessive S induces to create NiS in crystal state. Still, NiS in doping state also exists in the samples.

Composition modulation of NiWO$_4$/Pt/CdS through ion-exchange reaction is described in Figure 4. When the

FIGURE 4 Composition modulation of NiWO$_4$/Pt/CdS through the ion-exchange reaction
Cd content is close to S content in a stoichiometric ratio, the basic structure is NiWO₄/Pt/CdS. When the Cd content is higher than S content, CdWO₄ is produced by the cation-exchange reaction between NiWO₄ and the excessive Cd²⁺ (Equation 4). Similarly, when the S content is higher than Cd content, NiS is generated through the anion-exchange reaction between NiWO₄ and the excessive S²⁻ (Equation 3). Moreover, when both the Cd and S contents increase equally, molar ratio of CdS to NiWO₄ increases. Therefore, composition modulation of NiWO₄/Pt/CdS is achieved by the ion-exchange reaction. As the physicochemical properties of a multi-component system are determined by its composition, the composition modulation brings an effective strategy for the optimization of Z-scheme system.

 Morphologies of the samples are shown in Figure 5. The SEM images show that the samples were bulk aggregations with nano-particles on the surface. Morphologies of Cd₁₂S₁₀-Cd₉S₉₁, Cd₁₀S₁₁-Cd₁₉S₃₃, Cd₉S₄₉ and Cd₂₈S₄₉ were similar. While for Cd₉S₄₉ and Cd₂₈S₄₉, the size of surfaced nanoparticles became bigger, and the outlines became clear. The change of morphology may be related to the high S content. The FE-TEM images of Cd₁₉S₃₃ show that the aggregations were composed of nano-particles with size of around 10 nm (Figure 5I, J). EDS-mapping images show that the elements of Ni, W, Cd and S were evenly distributed on the bulk aggregation (Figure 5K).

### 2.2 Bandgap engineering and light harvesting enhancing of the Z-scheme system

UV-vis spectra of CdSₓ and CdxSᵧ are shown in Figure 6A, B, respectively. Light absorption edges at the wavelength of approximately 500 nm are attributed to the bandgap of CdS.[14] The absorbance from approximately 500 to 800 nm increased with the increase of S content. This can be attributed to the NiS, because NiS shows strong absorbance in the visible light region.[5,15]

CdS is a direct semiconductor,[12,16] the bandgap values of CdS in the samples can be evaluated by the inter-
section point between the extension lines of Tauc plot \((\alpha h\nu)^2 - h\nu\) curve and the X axis.\(^{[17]}\) \((\alpha h\nu)^2 - h\nu\) curves of CdSx and CdxSy are shown in Figure 6C, D, respectively. The bandgap of CdS in the Cd12S10 (2.22 eV) was almost equal to that of pure CdS (2.21 eV). The CdS bandgap of CdSx decreased quickly from 2.22 to 1.52 eV when the S content was increased. By contrast, the CdS bandgap of CdxSy decreased slowly from 2.04 to 1.80 eV, when both the Cd and S contents were increased. As the S content regions of CdSx and CdxSy were similar (All the S contents were approximately 10-49 at%), while the Cd contents of CdxSy (Cd: 10-28 at%) were higher than those of CdSx (Cd: 9-12 at%). The different bandgap values should be attributed to their different Cd contents. This result indicates that both the S and Cd contents in NiWO\(_4\)/Pt/CdS have important influences on the CdS bandgap. Figure S2 shows that the bandgap of CdS only slightly decreased when the CdS powder was physical mixed with equivalent NiWO\(_4\) and CdWO\(_4\) or NiS powder. Accordingly, NiWO\(_4\), CdWO\(_4\) and NiS powders hardly affects the measurement of CdS bandgap. The sharp decrease of the CdS bandgap of the samples (from 2.22 to 1.52 eV) is attributed to the NiS doping. The relationship between CdS bandgap and \((S-Cd)/Cd\) is shown in Figure 7. \((S-Cd)/Cd\) represents the excessive amount of S compared with Cd, which is related to the amount of NiS due to the anion-exchange reaction (Equation 3). While the Cd content represents the amount of CdS. Thus, the \((S-Cd)/Cd\) ratio gives an index of the ratio of NiS to CdS. As the Figure S1 proves that the change of CdS bandgap is induced by NiS doping, the \((S-Cd)/Cd\) ratio is related to the CdS bandgap. Interestingly, the relationship
between CdS bandgap and (S–Cd)/Cd of CdSx and CdxSy flows the fitting curve of $y = 0.0604x^2 - 0.399x + 2.1037$, and the correlation coefficient $R^2$ is 0.972. This result demonstrates that the ratio of NiS to CdS is the determining factor for the bandgap of CdS.

As the radii of Ni$^{2+}$ is similar to that of Cd$^{2+}$, Ni$^{2+}$ can dope into the structure of CdS, which induces the decrease of CdS bandgap. Chen et al. revealed that Ni$_x$Cd$_{1-x}$S bandgap decreased from 2.45 to 2.42 eV when increasing the ratio of Ni to Cd$^{12}$ Sahu et al. reported that the bandgap of Cd$_{(1-x)}$Ni$_x$S can be reduced to 1.7 eV when the ratio of Ni to Cd increased,$^{13}$ Ubale et al. showed that the bandgap of CdS in (CdS)$_{(1-x)}$(NiS)$_x$ composite decreased from 2.2 to 1.65 eV when the ratio of NiS to CdS increased.$^{16}$ These researches suggest that the CdS bandgap in NiS/CdS composition decreases as the ratio of NiS to CdS increases, which are consistent with the results in this research. This work achieves continuous bandgap engineering of CdS in NiWO$_4$/CdS Z-scheme system through controlling the index of (S–Cd)/Cd. High (S–Cd)/Cd value implies high ratio of NiS to CdS, which provides more excessive NiS available for doping. Accordingly, the doping degree of NiS increases with the increase of (S–Cd)/Cd, leading to the decrease of CdS bandgap.

VB and CB potentials ($E_{VB}$ and $E_{CB}$) of CdS versus the normal hydrogen electrode (NHE) are evaluated by the Equations 5 and 6.$^{18}$ $E_\text{e}$ is 4.5 eV versus NHE, $\chi$ is the Sanderson electronegativity of CdS, which is determined by the geometric average of the Cd and S atoms.

$$E_{CB} = \chi - E_\text{e} - 0.5E_g \quad (5)$$

$$E_{VB} = E_{CB} + E_g \quad (6)$$

Energy band potentials of the samples are shown in Figure S3. When only S content increased, bandgap and $E_{CB}$ of PSI decreased quickly (CdSx, left side); when both Cd and S contents increased, bandgap and $E_{CB}$ of PSI decreased slowly (CdxSy, right side). Interestingly, control the Cd and S contents of NiWO$_4$/CdS composition brings an easy and effective way for continuously adjusting the bandgap and band potential. The light harvesting of the Z-scheme system increases through the bandgap engineering.

2.3 The charge separation and transfer mechanisms of the Z-scheme system

PL spectra of NiWO$_4$/Pt, CdS, NiWO$_4$/Pt/CdWO$_4$, NiWO$_4$/Pt/NiS and NiWO$_4$/Pt/CdS (Cd19S33) are shown in Figure 8. Emission peak with maximum at approximately 360-380 nm existed in all the samples, which is attributed to the charge recombination of NiWO$_4$.$^{5,19}$ The PL intensity provides an index to evaluate the radiative charge recombination rate. Charge recombination rates of NiWO$_4$/Pt and CdS were high. Recombination rate of NiWO$_4$/Pt/CdWO$_4$ was slightly lower than that of NiWO$_4$/Pt, indicating that CdWO$_4$ has minor effect on the charge separation of NiWO$_4$/Pt. Similarly, the charge recombination of NiWO$_4$/Pt was reduced by NiS to some extent. In comparison, the charge recombination rate of NiWO$_4$/Pt/CdS (Cd19S33) was much lower than those of NiWO$_4$/Pt, CdS, NiWO$_4$/Pt/CdWO$_4$ and NiWO$_4$/Pt/NiS. Namely, the combination of NiWO$_4$/Pt and CdS largely decreases the recombination. The decrease of charge recombination is attributed to the efficient charge transfer between NiWO$_4$ and CdS, which promote the photocatalytic reaction. Therefore, the photocatalytic process should be highly related to NiWO$_4$/Pt/CdS structure directly.

The charge transfer paths between NiWO$_4$ (p-type)$^{20}$ and CdS (n-type) are discussed in Figure S4. In theory, there are two possible charge transfer paths: pn-junction and Z-scheme system. However, charge transfer as pn-junction is difficult because $E_{CB}$ and $E_{VB}$ of NiWO$_4$ are much lower than those of CdS. Charge barriers are formed at the interface due to the large potential differences (the band bending of a pn-diode is only 0.3-0.4 eV), which prohibiting the charge transfer. Clearly, the “pn-type” charge transfer path and its band alignment is unfavorable for the charge transfer and the hydrogen generation. In contrast, as the excellent conductor Pt can create an ohmic contact at the interface,$^{21,22}$ electrons in NiWO$_4$ CB tend to transfer to CdS VB with the assistance of conductive Pt. Figure S5 shows that the PCA of NiWO$_4$/CdS was much lower...
FIGURE 9 Effect of S–Cd content on PCA and PL intensities (from Figure S7a,b at 382.2 nm) of CdSx and CdxSy. The PCA tests were taken in a homedepot photoelectrolytic reactor (see details in the experimental section).

than that of NiWO₄/Pt/CdS, which proves that Pt plays an important role in the charge transfer process. Accordingly, the “Z-type” charge transfer through the conductive Pt largely increases the PCA. As the “Z-type” charge transfer path matches well with the experimental results of PL (Figure 8) and PCA (Figure 9 and S5), the charge transfer of NiWO₄/Pt/CdS mainly follows the “Z-type” path.

Figure S5 also shows that the hydrogen generation rate of NiWO₄/CdS was higher than that of pure CdS. Figure 8 shows that the charge recombination rate of NiWO₄/Pt/CdS (Cd19S33) was much lower than that of pure CdS. Hence, in the Cd19S33 Z-scheme system, Z-type charge transfer path largely reduces the charge recombination rate, which provides more charge carriers for photocatalytic hydrogen generation. The SEM images and XRD patterns of Cd19S33 and CdS are shown in Figure S6a,b. SEM images show that the morphology of Cd19S33 was bulk aggregation, while that of CdS was nano-particles with size of 20-50 nm. It is generally accepted that the PCA of separated nano-particles is higher than that of bulk aggregations. XRD patterns (Figure S6b) show that pure CdS was the mixed crystals with hexagonal and cubic structure, and Cd19S33 was mostly cubic. It is reported that PCA of CdS in hexagonal crystal is higher than that in cubic crystal. Consequently, performance of Cd19S33 Z-scheme system may be further increased if its morphology and crystal structure are optimized in the future work.

2.4 Composition modulation for optimizing the performance of the Z-scheme system

Effects of S–Cd content on the PCA of CdSx and CdxSy are shown in Figure 9.

S–Cd content is an index of NiS content. When the S–Cd content was near zero, PL intensities of Cd12S10 and Cd9S11 were similar. When the S–Cd content increased, PL intensities of both CdSx and CdxSy decreased, suggesting that the increase of NiS content reduces the charge recombination rate.

PL intensities of CdxSy were lower than those of CdSx (Figure 9) even if the S–Cd contents were similar, indicating that there should be another factor affecting the charge recombination besides NiS. The affected factor is the charge transfer balance between NiWO₄ and CdS. The molar ratio between PSII and PSI has an important influence on the charge transfer balance of the Z-scheme system (Figure 1). The limiting step of the charge transfer rate of the CdSx Z-scheme system is CdS, due to the low molar ratio of CdS to NiWO₄ (the Cd contents of CdSx were only around 10 at%). By contrast, for CdxSy when both Cd and S contents are increased at a proper ratio, the amounts of NiS and CdS increase. The increase of CdS content also enhances the charge transfer rate of PSII, leading to a charge transfer balance state between PSII (NiWO₄) and PSI (CdS). Therefore, the charge recombination rates of the CdxSy are lower than those of CdSx.

Zhang et al. reported that WO₃/CdS Z-scheme system showed the best performance when the CdS content was 20 wt%.[21] Wu et al. reported that for the BiVO₄/CdS/CdS Z-scheme system, the proper mass ratio of BiVO₄/CdS was 50%;[24] Wang et al. reported that, the appropriated amount of CdS in the ZnO/CdS Z-scheme system was 30.9 wt%.[25] These researches suggest that the ratio of PSII to PSI have an important influence on the performance of Z-scheme system. Our work further demonstrates that the ratio of PSII to PSI affects the charge recombination of the Z-scheme system. A proper ratio of PSII to PSI creates a charge transfer balance state, which largely increases the charge separation rate and reduces the recombination.

Effect of S–Cd content on the PCA of CdSx and CdxSy is shown in Figure 9. PCA of both CdSx and CdxSy first increased and then decreased with the increase of S–Cd content. The change of PCA should be related to the bandgap structure, charge separation and transfer processes. The increase of S–Cd enhanced the PCA at the beginning. This is because the increase of S–Cd content induces the decrease of CdS bandgap, which enhances the light harvesting. Furthermore, the charge separation and transfer rates were also increased with the increase of S–Cd content (due to the positive effects of NiS), leading to the decrease of charge recombination and thus increases the PCA. However, the increase of S–Cd content to high levels inhabits the charge transfer process (such as Cd28S49), leading to the decrease of PCA.

Figure 9 also shows that the PCA of CdxSy were higher than those of CdSx. This is because the charge
recombination rates of CdxSy are lower than those of CdSx. Moreover, compared with the low $E_{CB}$ of CdSx (Cd9S19, –0.18 V; Cd9S49, –0.07 V), $E_{CB}$ of CdxSy are at the levels which higher than the hydrogen generation potential (Cd15S23, –0.26 V; Cd19S33, –0.27 V; Cd28S49, –0.21 V). The higher $E_{CB}$ of CdxSy provides stronger reduction ability for the hydrogen generation (Figure S3).

Photocatalytic performance of Cd19S33 is the best among the samples, indicating that it has the appropriate composition for hydrogen generation. As shown in Figure 10, Cd12S10 (CdS content is low, without NiS) Cd19S33 (CdS content is medium, contains NiS) and Cd28S49 (CdS content is high, contains a lot of NiS) were selected to discuss how the composition modulation affects the charge separation and transfer process of the Z-scheme system. The PL spectra in Figure 10B shows that the charge recombination rates of Cd19S33 and Cd28S49 were much lower than that of Cd12S10. Figure 10C shows the photocurrents of Cd19S33 and Cd28S49 were much higher than that of Cd12S10. While Figure 10D shows that the EIS semicircular arcs of Cd19S33 and Cd28S49 Nyquist plots were much larger than that of Cd12S11. As previously mentioned, the high CdS content in Cd19S33 and Cd28S49 brings the Z-scheme system to a charge transfer balance state, which decreases the charge recombination. Moreover, the NiS of Cd19S33 and Cd28S49 significantly increases the separation efficiency as well as the conductivity and mobility of the photo-generated charge [15,26] in the Z-scheme system, leading to the low charge recombination rates and high photocurrents. The PCA of Cd28S49 was a little lower than that of Cd19S33 (Figure 9) even if it has lower charge recombination rate and higher photocurrent. The reason may be the excessive NiS induces the decrease of $E_{CB}$(CdS) (Figure S3) and the decompose of NiWO4 in Cd28S49 (Figure 10A), leading to the decrease of redox potentials and the increase of charge transfer resistance.

The ratio of (Ni+W) to (Cd+S) for the Cd19S33 was approximately 1:1 (Figure 10A), while the S content was slightly higher than Cd content. This composition has many excellent features for the photocatalytic hydrogen generation, such as the suitable band structure for efficient light harvesting and water reduction, excellent charge separation and transfer abilities, and low charge recombination rate. Therefore, the optimization of NiWO4/Pt/CdS Z-scheme system has been achieved through the composition modulation. The hydrogen generation rate of the optimized Cd19S33 reached 14.39 mmol h⁻¹g⁻¹ (Figure 11), which is relatively high when compared with other CdS based photocatalytic Z-scheme systems (Table S2). The apparent quantum efficiency (AQE) was 2.54% at 365-nm wavelength.
FIGURE 11  Long-term photocatalytic hydrogen generation over the optimized Cd19S33. The average hydrogen generation rate was calculated from the reaction from the first to the tenth hour. The PCA test was taken in the photocatalytic reactor equipped with a quartz window (see details in the experimental section).

The long-term photocatalytic hydrogen generation over Cd19S33 is shown in Figure 11. The hydrogen generation rate decreased from 16.8 mmol h\(^{-1}\)g\(^{-1}\) (2-4 hours) to 13.1 mmol h\(^{-1}\)g\(^{-1}\) (8-10 hours). As is known to all, CdS are photo-corroded easily in the presence of lactic acid. Interestingly, for the NiWO\(_4\)/Pt/CdS Z-scheme system, a part of NiWO\(_4\) was decomposed while the CdS stayed almost the same after the photocatalytic reaction (Refer to the EDS and XRD results which are shown in Figure S8). The reason is that the Z-type charge transfer path changes the oxidation reaction site of lactic acid from the VB of CdS to that of NiWO\(_4\), which protects the CdS from photocorrosion (Figure S4). Accordingly, this result provides the evidence of Z-type charge transfer path of NiWO\(_4\)/Pt/CdS Z-scheme system.

Controlling the composition is significant for engineering the physicochemical properties of the multiple component system. In this research, composition modulation takes effects on the NiWO\(_4\)/Pt/CdS Z-scheme system through the following three aspects: (1) the NiS generated from the ion-exchange reaction brings a doping effect on CdS, leading to the decrease of its bandgap and the increase of light harvesting; (2) the generated NiS facilitates the charge separation and transfer processes; (3) the molar ratio of NiWO\(_4\) (PSII) to CdS (PSI) as well as their charge transfer rates are regulated to a balance state, leading to the decrease of charge recombination. Consequently, the light harvesting, charge separation and transfer processes of NiWO\(_4\)/Pt/CdS Z-scheme system are optimized through the simple composition modulation.

Besides NiWO\(_4\)/Pt/CdS, CoWO\(_4\)/Pt/CdS and ZnWO\(_4\)/Pt/CdS Z-scheme systems were also investigated (the synthetic method is shown in Supporting Information). As shown in Figure S9, PCA of CoWO\(_4\)/Pt/CdS was close to NiWO\(_4\)/Pt/CdS, while that of ZnWO\(_4\)/Pt/CdS was relatively low. The low PCA of ZnWO\(_4\)/Pt/CdS is related to the large bandgap of ZnWO\(_4\) (5.85 eV).\(^{[27]}\) This result demonstrates the possibility of extending this fabrication method to other metal tungstate/metal sulfide Z-scheme system.

3  CONCLUSION

In summary, this research provides a simple composition modulation method for optimizing NiWO\(_4\)/Pt/CdS Z-scheme system to enhance the solar-to-chemical conversion efficiency. After an ingenious control of the proportions of Ni, W, Cd and S elements in the NiWO\(_4\)/Pt/CdS through the ion-exchange reaction, the light harvesting, charge separation and transfer abilities of the Z-scheme system were increased. The bandgap of CdS in NiWO\(_4\)/Pt/CdS was adjusted continuously from 2.22 to 1.52 eV. The decrease of bandgap is induced by NiS doping. The charge recombination was largely reduced through a control of both Cd and S contents. The low recombination of the optimized NiWO\(_4\)/Pt/CdS is attributed to the NiS and appropriate molar ratio of CdS to NiWO\(_4\). The hydrogen generation rate was increased to 14.39 mmol h\(^{-1}\)g\(^{-1}\) after the system optimization. The research insights reveal that the Z-scheme system should be recognized as an integrated system. The efficiency can achieve the maximum only when all the light harvesting, charge generation, separation and transfer processes operated in full synergy with the whole Z-scheme system.

4  EXPERIMENTAL SECTION

Chemical reagents: Ni(NO\(_3\))\(_2\)·6H\(_2\)O (98%), Zn(NO\(_3\))\(_2\)·6H\(_2\)O (99%), Co(NO\(_3\))\(_2\)·6H\(_2\)O (98%), Cd(CH\(_3\)COO)\(_2\)·2H\(_2\)O (99.9%), Na\(_2\)WO\(_4\)·2H\(_2\)O (99-100.5%), CH\(_3\)CSNH\(_2\) (98%), NaBH\(_4\) (95.0%), H\(_2\)PtCl\(_6\)·6H\(_2\)O (98.5%), lactic acid (85.0-92.0%) were purchased from Wako Chemical.

Synthetic methods of CdSx and CdSs: We constructed NiWO\(_4\)/Pt/CdS Z-scheme system in the following. Synthetic method of NiWO\(_4\)/Pt precursor is the same with that in the paper.\(^{[5]}\) In short, NiWO\(_4\) was synthesized by the reaction between Ni\(^{2+}\) and WO\(_4^{2-}\). Pt was deposited on NiWO\(_4\) by using NaBH\(_4\) as a reducing agent (in the synthetic solution, Pt:NiWO\(_4\) = 1.18 at%) for the transfer of the charge. NiWO\(_4\)/Pt/CdS was further prepared. 0.09 g of NiWO\(_4\)/Pt precursor was first placed in the PTFE lining of an autoclave, and certain amount of water was added to keep the total volume of the solution at 30 mL. Cd\(^{2+}\) and
S\textsuperscript{2–} precursor solutions (Cd(CH\textsubscript{3}COO)\textsubscript{2}⋅2H\textsubscript{2}O 0.02 g mL\textsuperscript{−1} and CH\textsubscript{3}CSNH\textsubscript{2} 0.005 g mL\textsuperscript{−1}) were added in the lining. After sonication for 5 minutes, the PTFE lining was sealed up into the autoclave, and the suspension was reacted at 180°C for 5.5 hours. The suspension was filtered and dried in vacuum for one night, and the sample was collected. Synthetic conditions of the NiWO\textsubscript{4}/Pt/CdS are controlled that are listed in Table S1.

Photocatalytic activity tests: Photocatalytic activity (PCA) tests of CdSx and CdxSy were done by a homemade photocatalytic reactor as follow: 50 mg sample and approximately 130 mL aqueous solution of lactic acid (as the sacrificial agent, V\textsubscript{Lactic acid}:V\textsubscript{Water} = 10 vol.%) were put in the reactor and sonicated for 5 minutes. Then the reactor was illuminated by a 550 W Xenon lamp (KXL–552HPF, Wacom). The illuminated area was 12.56 cm\textsuperscript{2}. The AQE was evaluated by a photocatalytic reactor equipped with a quartz window (Zhonghua Instrument Company) as follow: 40.6 mg of CdI\textsubscript{9}S\textsubscript{33} and 65 mL aqueous solution of lactic acid were put in the reactor. The solution was bubbled with nitrogen gas for 15 minutes. Then the reactor was illuminated by a 300 W Xenon lamp (PLS-XSE300D Beijing Perfectlight Technology Co., Ltd.) equipped with a 365-nm bandpass filter (DT365, Perfect light company) for 3 hours. The light intensity was 100 mW cm\textsuperscript{−2}, and the illuminated area was 4.52 cm\textsuperscript{2}. The generated gas was analyzed by a gas chromatography equipped with a TCD detector (GC–9790 plus, FULI company). The AQE was calculated according to the reference.\textsuperscript{[26]} The stability and hydrogen generation rate of CdI\textsubscript{9}S\textsubscript{33} were evaluated by the same photocatalytic reactor. The amount of sample was 20.3 mg, the light intensity was 370 mW cm\textsuperscript{−2}, and the illuminated area was 320-780 nm. Other experiment parameters were the same with those of AQE evaluation mentioned above.

Characterization: Morphology of the samples was shown by a scanning electron microscopy (SEM, SU-8000, Hitachi). Elemental composition was evaluated by the SEM-EDS through the average of five different regions. The SEM and EDS were operated at 30 kV and 10 µA. Morphology of the CdI\textsubscript{9}S\textsubscript{33} was further shown by a Field emission transmission electron microscope (FE-TEM, Thermo Talos F200X, FEI). Crystal structure was examined by an X-ray diffractometry (XRD, Rigaku) operating at 40 kV and 20 mA (Cu K radiation). Bandgap was estimated by a UV-vis diffuse reflectance spectrometry (UV-vis DRS, U–3300 Hitachi). Charge recombination property was analyzed by a photoluminescence spectrometry (PL, F–7000 High Tech, Hitachi). The excitation wavelength was 200 nm, while the photovoltage was 700 V. The transient photocurrent response and electrochemical impedance spectroscopy (EIS) were performed in a three-electrode system on an electrochemical workstation (Bio-Logic Science Instrument Company). The working electrodes were prepared as follows: 1.5 mg of sample was dispersed in 1.5 mL Nafion/ethanol solutions (V\textsubscript{Nafion}:V\textsubscript{Ethanol} = 0.3 vol.%), and sonicated for 30 minutes. Then, 20 µL of the mixed solution was dropped onto a Fluorine-Tin-Oxide (FTO) glass with an area of 1 cm\textsuperscript{2}. After dry naturally, the drop-casting was repeated for another four times until a uniform thin film was formed. The counter electrode was a Pt foil, the reference electrode was an Ag/AgCl electrode and the electrolyte was 0.5 M Na\textsubscript{2}SO\textsubscript{4} aqueous solution.

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DATA AVAILABILITY STATEMENT
Research data are not shared.

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