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Simultaneous visible-light-induced hydrogen production enhancement and antibiotic wastewater degradation using MoS₂@Zn_xCd_{1-x}S: Solid-solution-assisted photocatalysis

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ABSTRACT

In this study, a Zn_xCd_{1-x}S solid solution was successfully synthesized using a hydrothermal method. MoS₂ serving as a co-catalyst for hydrogen evolution was also prepared through a one-pot hydrothermal method. The structures, morphology, chemical states, and optical properties were characterized using powder X-ray diffraction, scanning electron microscopy, high-angle annular dark field-scanning transmission electron microscopy, elemental mapping, X-ray photoelectron spectroscopy, and UV-Vis diffuse reflection spectroscopy. Visible-light-driven photocatalytic experiments were conducted to simultaneously achieve hydrogen production and amoxicillin antibiotic wastewater degradation. The results indicated 8%MoS₂/Zn_xCd_{1-x}S achieves the best photocatalytic performance. The Zn_xCd_{1-x}S samples illustrated a superior performance to that of CdS, which can be attributed to a thermodynamic improvement. Based on the results of PL and TRPL analyses, the enhancement of the hydrogen production mechanisms can be ascribed to the prolonged separation process of the photocarriers. Furthermore, the degradation results were analyzed using the HPLC method and the possible degradation pathways were determined through the HPLC-MS techniques.

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1. Introduction

Photocatalysis has attracted tremendous attention since it was first reported by Fujishima et al. [1] in 1972. It can be recognized as one of the most potent methods for various applications, such as environmental purification, energy conversation, and the preparation of chemical agents [2–8]. More importantly, the nature of photocatalysis with a green, clean, and environmentally friendly property can be reflected by the light source, which can be obtained directly from solar energy [8]. Under these circumstances, studies on photocatalysis have

become popular in recent years. The photocatalytic hydrogen evolution has received significant interest from scholars [9–15]. Hydrogen energy is regarded as a type of clean energy with a high thermal value. Furthermore, it can also serve as a type of sustainable energy because it only produces water after being burned and can be recycled or generated from water. These excellent properties make hydrogen a green energy source for the future. Therefore, if solar energy can be converted into hydrogen energy through photocatalysis, a hydrogen-based industrial society can be powerfully promoted.

Since the past several years, rapid development of material

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designs for photocatalytic hydrogen evolution has been witnessed, including TiO_2 , polymeric carbon nitride, and sulfide [16–21]. Among them, CdS has provoked the interests of scholars because it has a suitable CB positioned for hydrogen evolution, and the bandgap indicates that it can utilize visible light effectively [22–26]. Many CdS-based photocatalytic systems have been investigated. Among of them, CdS-lactic acid and CdS- $\text{S}^{2-}/\text{SO}_3^{2-}$ systems helped in advancing the industrial application of hydrogen evolution [26,27]. Scientists have devoted themselves to the promotion of the photocatalytic hydrogen evolution performance of CdS. In this regard, the construction of a solid solution has been proven to be an effective strategy [28]. A solid-solution strategy usually involves two or more types of semiconductors. The bandgap of the materials can be effectively regulated through the formation of a solid solution. The aim of a solid-solution strategy is to improve the redox ability of a pristine semiconductor and/or the capacity of the optical absorption, which can be favorable for the photocatalysis. Therefore, numerous photocatalysts with an outstanding performance, such as $\text{GaN}:\text{ZnO}$, $\text{Bi}_x\text{Y}_{1-x}\text{VO}_4$, ZnIn_2S_4 , and $\text{Zn}_x\text{Cd}_{1-x}\text{S}$, have been successfully designed by applying this strategy [28–35].

$\text{Zn}_x\text{Cd}_{1-x}\text{S}$ series materials have received significant interest for use in the photocatalytic hydrogen evolution. Such materials have a suitable bandgap to respond to visible light and have taken a suitable position as a CB for hydrogen evolution [31–35]. Recently, an internal quantum efficiency of $\sim 100\%$ at 425 nm for photocatalytic H_2 production from a $\text{Zn}_x\text{Cd}_{1-x}\text{S}-\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ system was reported [27]. Subsequently, the group also designed a CPC reactor for photocatalytic hydrogen evolution through a $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}-\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ system. The results showed that hydrogen can be obtained at a rate of 2.9 and 4.0 L/h each day in spring and summer in China, respectively [36]. This striking achievement has brought the photocatalytic hydrogen evolution closer to industrialization. However, a co-catalyst has also played an important role in the hydrogen evolution. Usually, a noble metal and its oxides can be selected as a co-catalyst. In recent years, owing to its potential to reduce the cost of a catalyst, the non-noble metal, MoS_2 , has become popular [24,32–34]. In particular, MoS_2 can accelerate the electron transfer thus promoting the separation of the photocarriers [20]. These unique properties have made MoS_2 a superior co-catalyst when coupled with $\text{Zn}_x\text{Cd}_{1-x}\text{S}$.

Typically, a sacrificial reagent will act as an electron donor, affording more H^+ to participate in the photocatalytic hydrogen evolution. Different from typical water splitting, however, the addition of a sacrificial reagent will also change the Gibbs free energy of the water splitting, which is normally much less than 237 kJ/mol, and will be thermodynamically beneficial for the hydrogen evolution. As a result, the photocatalytic hydrogen evolution always involves the consumption of a sacrificial reagent. Although the existence of a sacrificial agent, such as $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$, can allow more electrons to participate in the hydrogen generation, more studies are needed to investigate whether the use of a sacrificial agent to produce hydrogen is economically suitable. In addition, some organic sacrificial reagents, such as methanol, ethanol, and lactic acid, can be re-

garded as a type of energy or fuel. Therefore, the probing of a cheap sacrificial agent as well as an effective system has been an area of focus. Since 2016, many groups have reported that photocatalytic hydrogen can be generated from waste, such as waste wood, paper, sawdust, antibiotic wastewater, and waste gases [37–40]. Such studies have regarded waste materials as a sacrificial reagent during photocatalytic hydrogen generation, which has inspired the consideration of energy waste.

In recent years, the wide use of antibiotic drugs has been a significant concern because it can contribute to drug-resistant genes. Furthermore, the formation of cross- and multiple-resistances in organisms, originating from the abuse of antibiotic drugs, is a threat to humans lives [41–43]. Our group initially reported the use of amoxicillin, which has been one of the most widely used antibiotic drugs in the past decades, as a sacrificial reagent for the photocatalytic hydrogen evolution [44]. However, the degradation efficiency when using Bi metal-doped polymeric carbon nitride and MoS_2/CdS is low.

Based on our previous studies, photocatalytic hydrogen can be simultaneously achieved with the degradation of amoxicillin antibiotic wastewater. However, the degradation efficiency is low. Under an anaerobic environment, to improve the photocatalytic degradation, enhancing the oxidation of the photocatalyst is a possible method. Therefore, in this study, $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ samples using MoS_2 as a co-catalyst were successfully synthesized. MoS_2 was initially applied simultaneously to hydrogen evolution and degradation of antibiotic wastewater. The results indicate that hydrogen can be achieved through $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ after doping with MoS_2 . In addition, the degradation efficiency is also improved under visible light as compared with our previous studies.

2. Experimental

2.1. Materials

All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The reagents were of analytic grade and used as-received without further purification. Ultrapure water with a resistivity of 18.2 Ω was also used throughout the experiments.

2.2. Synthesis of photocatalysts

The samples were synthesized using a one-pot hydrothermal method. Typically, 36 mmol of thiourea was dissolved in 60 mL of ultrapure water. Subsequently, x mmol of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $(2.4-x)$ mmol of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ($x = 0, 0.48, 1.20, 1.92, 2.40$) were introduced after stirring for 1 h, and y mmol ($y = 0, 0.240, 0.384, 0.480, 0.720$) $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was added into the aforementioned solution to form a mixture after continuous stirring for 6 h. The precursor solution was then transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated to 473 K for 24 h in an air-blown-driven oven. The particles obtained were washed using ultrapure water and absolute ethanol three times through a centrifugation process. After drying at 80 $^\circ\text{C}$ in a vacuum oven for 12 h, the

samples were obtained and denoted as $y\%$ $\text{MoS}_2@\text{Zn}_x\text{Cd}_{1-x}\text{S}$ ($x = 0, 0.2, 0.5, 0.8, 1$; $y = 0, 5, 8, 10, 15$).

Similarly, pure MoS_2 was synthesized using the same procedure mentioned above without the addition of either $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ or $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. The amount of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ was determined at 0.720 mmol.

2.3. Physicochemical analyses

Powder X-ray diffraction (XRD) patterns of the as-prepared samples were investigated on a D8 Advance (Bruker) diffractometer using $\text{Cu-K}\alpha$ radiation under 40 kV and 40 mA. The scan range is from 10° to 80° , and the scan speed is $12^\circ/\text{min}$. X-ray photoelectron spectroscopy (XPS) was conducted using a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer with $\text{Mg-K}\alpha$ as an X-ray source. The morphology of the catalysts was carried out by scanning electron microscopy (SEM, JSM-6700) and high-resolution transmission electron microscopy (HRTEM; FEI Talos F200X). A high-angle annular dark field-scanning transmission electron microscope was selected to reveal the components of the catalysts. A Raman microscope (Senterra R200-L/Senterra R200-L) was utilized with an excitation wavelength of 520 nm to characterize the properties of the catalysts. The UV-Vis diffuse reflection spectroscopy (UV-Vis DRS) was performed using a UV-Vis spectrophotometer (Shimadzu, Japan) with BaSO_4 as a reference. The reflectance spectrum was converted into the absorption intensity based on the Kubelka-Munk method. The amoxicillin concentration and photocatalytic degradation by-products were determined by high-performance liquid chromatography (HPLC, Agilent 1260) as well as high liquid chromatography and linear ion trap quadrupole mass spectrometry (HPLC1260 and LTQ XL, Ag-

ilent, USA; Thermo-fisher, USA, respectively).

2.4. Photocatalytic activity measurements

The photocatalytic hydrogen generation and amoxicillin degradation experiments were conducted in a 300 mL Pyrex glass cell connected to a closed gas circulation and evacuation system. A 300 W Xe lamp was used as the visible light source equipped with a 420 nm cutoff optical filter. Mainly, 0.04 g of $\text{MoS}_2@\text{Zn}_x\text{Cd}_{1-x}\text{S}$ was added to an aqueous solution with a certain concentration of amoxicillin (80 mL) and then ultrasonically dispersed for 20 min. Magnetic stirring was applied throughout the entire procedure. Before irradiation, the reaction system was pumped to a vacuum state to remove gases in the system. The amount of produced H_2 was measured every hour through online gas chromatography (Huaai, GC9160, China, MS-5A) using Ar as a carrier gas.

3. Results and discussion

3.1. Physical phase analysis

The structure and phase of the as-prepared samples were initially explored based on the XRD characterizations, as listed in Fig. 1. It was determined that all peaks of the pristine CdS can be searched in the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ with a low ZnS concentration. Simultaneously, the characteristic peaks of ZnS in the solid solution materials were not clear until the amount of ZnS was increased. This was reflected by the peaks of $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{S}$. The narrow-range XRD patterns indicate that the main characteristic peaks of CdS show a slight migration after coupling with ZnS to form the solid solution catalysts. The structures of all samples

Fig. 1. XRD patterns of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ (a and b), $5\%\text{MoS}_2@\text{Zn}_x\text{Cd}_{1-x}\text{S}$ (c), $8\%\text{MoS}_2@\text{Zn}_x\text{Cd}_{1-x}\text{S}$ (d), $10\%\text{MoS}_2@\text{Zn}_x\text{Cd}_{1-x}\text{S}$ (e), and $15\%\text{MoS}_2@\text{Zn}_x\text{Cd}_{1-x}\text{S}$ ($x = 0, 0.2, 0.5, 0.8$ and 1) (f).

Fig. 2. SEM images of 8%MoS₂/Zn_{0.5}Cd_{0.5}S (a–d), MoS₂/CdS (e), CdS (f), ZnS (g), and MoS₂/ZnS (h).

showed a hexagonal phase as based on the XRD results. Fig. 1 (c)–(f) shows the structure of the samples after doping with the MoS₂ as a co-catalyst prepared using a one-pot method. The XRD pattern of single MoS₂ is also shown in Fig. S1. It can be clearly seen that the main structure did not undergo any evident changes after MoS₂ doping. Furthermore, the intensity of the (100) facet decreased, which can be ascribed to the increase in the ZnS concentration. However, there were no obvious characterization peaks of the MoS₂ in any of the MoS₂@Zn_xCd_{1-x}S samples.

3.2. Morphology analysis

The morphologies of the samples were revealed through SEM images, as shown in Figs. 2 and S2. The CdS showed the morphology of a ball cluster, which was composed of small-particle CdS with a hexagonal phase. The ZnS also depicted a non-uniform particle size. The Zn_{0.5}Cd_{0.5}S exhibited a hexagonal morphology composed of CdS and ZnS, as shown in Fig. 2(b). The morphology could be preserved after the MoS₂ doping.

To prove the existence of the MoS₂, HRTEM analysis was conducted, the results of which are demonstrated in Fig. 3. The (110) and (004) facets with an interplanar crystal distance of 0.207 and 0.168 nm are well matched with the hexa-CdS (PDF:65-3414), respectively. Similarly, the ZnS can also be determined as a hexahedron phase because (1130) facets can be searched (PDF:12-0688). The hexa-CdS and hexa-ZnS appeared

in the same region, indicating the formation of Zn_{0.5}Cd_{0.5}S. In conclusion, HRTEM further confirmed the hexagonal phase of ZnS and CdS in the solid solution, which corresponds with the XRD results. Moreover, the presence of MoS₂ can also be reflected based on the relative results. As shown in Fig. 3(b), the (201) crystal facet of MoS₂, with a distance of 0.136 nm, corresponds well with the results. The intimate contact between the MoS₂ and Zn_{0.5}Cd_{0.5}S, which can be seen in Fig. 3(b), suggests that a heterojunction can be formed.

The morphology and structure can also be confirmed through TEM and the element mapping method, as indicated in Fig. 4. The hexagonal and quadrangular shapes of the projection can be ascribed to the hexagonal polyhedron irradiated with different angles of the electron beam. The STEM element mapping clearly indicates the distribution of each element in the structure of the 8%MoS₂/Zn_{0.5}Cd_{0.5}S.

3.3. Chemical state analysis

An XPS analysis is favorable for providing information on the chemical state of the samples. Fig. 5(a)–(e) shows the relative results of CdS, ZnS, Zn_{0.5}Cd_{0.5}S, and MoS₂@Zn_{0.5}Cd_{0.5}S. The movement of the peaks can be ascribed to the change in the chemical state of the element. This indicates that the combination of CdS and ZnS was mainly through the formation of a solid solution, and not merely a physical hybrid.

In the Mo 3d spectra, as is widely known, the peaks located at approximately 226.0 and 229.0 eV in MoS₂@Zn_{0.5}Cd_{0.5}S and

Fig. 3. HRTEM images of Zn_{0.5}Cd_{0.5}S (a) and MoS₂/Zn_{0.5}Cd_{0.5}S (b).

Fig. 4. TEM images and element mapping results of 8%MoS₂/Zn_{0.5}Cd_{0.5}S.

pure MoS₂ can be ascribed to the interference of S 2s, respectively. Interestingly, the Mo 3d spectra in MoS₂@Zn_{0.5}Cd_{0.5}S shows a significant migration with a decreasing trend compared with the pure MoS₂, which also demonstrates that the Mo element has a trend of accepting electrons. This is not surprising because the Mo will also bind with the S in Zn_{0.5}Cd_{0.5}S. This suggests that Mo³⁺ can be combined with S²⁻ from Zn_{0.5}Cd_{0.5}S through a chemical bond. This result can be reflected by the Mo 3d XPS spectra, which show that the binding energy decreased. To the best of our knowledge, if the element accepts the negative electrons, the binding energy shown in the XPS will correspondingly decrease, and vice versa. This also illustrates that the chemical environment of MoS₂@Zn_{0.5}Cd_{0.5}S has largely changed compared with the pure MoS₂. It can be inferred that the chemical state of S in MoS₂ and Zn_{0.5}Cd_{0.5}S is different. The Mo 3d has four peaks, which can be determined at 1T-MoS₂ and

2H-MoS₂ in pure MoS₂ (232.3 and 235.4 eV for the 1-T phase, and 233.6 and 236.8 eV for 2H). The phase of Zn_{0.5}Cd_{0.5}S can be determined during the hexagonal phase based on XRD and HRTEM analyses. The difference among the crystal phase might cause a different chemical state of S. As a result, a large migration in the Mo 3d XPS spectra appeared. However, further study is needed to determine the structure of the MoS₂, particularly the corresponding composition of the 1T and 2H phase MoS₂, respectively. Raman spectra further provided evidence of MoS₂ in the MoS₂@Zn_{0.5}Cd_{0.5}S samples. The peaks at 373 and 401 cm⁻¹ can be attributed to the vibration modes of E_{2g} and A_{1g}, respectively, as exhibited in Fig. 5(f) [45].

3.4. Optical analysis

The optical ability of the samples can be studied through the UV-vis diffuse reflectance spectra, as exhibited in Fig. 6(a). Compared with the pristine CdS, the increased concentrations of ZnS could be responsible for the decreased visible light absorption ability after the formation of the Zn_xCd_{1-x}S. Consequently, the higher concentration of Zn is, the lower the visible light absorption ability.

The energy band gap (E_g) of Zn_xCd_{1-x}S ($x = 0, 0.2, 0.5, 0.8, 1$) can be investigated based on Eq. (1) [6]:

$$ah\nu = k(h\nu - E_g)^{1/n} \quad (1)$$

where k represents a constant, and a , h , ν , and E_g are the absorption coefficient, Plank constant, light frequency, and band gap, respectively [6]. The value of n is 2 for direct-type semiconductors and 1/2 for indirect-type semiconductors, which can be determined based on the type of the optical transition. CdS, ZnS, and Zn_xCd_{1-x}S ($x = 0, 0.2, 0.5, 0.8, 1$) are direct-type semiconductors, and thus n is 2 in the present study. The bandgap values of CdS, Zn_{0.2}Cd_{0.8}S, Zn_{0.5}Cd_{0.5}S, Zn_{0.8}Cd_{0.2}S, and

Fig. 5. XPS spectra of S 2p (a, d), Zn 2p (b, e) and Mo 3d (c) as well as Raman spectra analysis (f) of the samples.

Fig. 6. UV-vis spectrum and calculated band energy results of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ ($x = 0, 0.2, 0.5, 0.8, \text{ and } 1$).

ZnS were calculated to be 2.25, 2.33, 2.39, 2.55, and 3.68 eV, respectively, as illustrated in Fig. 6(b). As a result, the values of the bandgap showed a positive relationship with the increased ZnS concentrations. The wide bandgap will be thermodynamically beneficial for the enhanced redox ability of the photocatalysts. Furthermore, the UV-vis spectra of the samples after MoS₂ doping and the pure MoS₂ are exhibited in Fig. S3. For the ZnS samples, it is evident that the light absorption ability was enhanced from 350 to 700 nm after MoS₂ doping. This can be attributed to the existence of MoS₂. Other samples also exhibited a similar trend, and the enhanced light-absorption range was located within visible light range, namely, 550 to 800 nm.

However, it seems that the MoS₂ doped $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ ($x = 0, 0.2, 0.5, 0.8, 1$) does not correspond highly to the pristine $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ samples. It can be speculated that the MoS₂ will affect the synthesis procedure of the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ in this one-pot synthesis method.

3.5. Photocatalytic performance

The photocatalytic performance evaluation was investigated based on the simultaneous photocatalytic hydrogen evolution and the degradation of amoxicillin antibiotic wastewater under visible light ($\lambda > 420 \text{ nm}$). As can be seen from Fig. 7, $\text{Zn}_x\text{Cd}_{1-x}\text{S}$

Fig. 7. Photocatalytic hydrogen evolution performance in an amoxicillin solution with a concentration of 0.1 g/L using $y\%$ MoS₂@ $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ ($x = 0, 0.2, 0.5, 0.8, 1; y = 5, 8, 10, 15$) samples.

Fig. 8. Enhanced mechanisms of hydrogen production: PL spectrum (a) excited at a wavelength of 360 nm and TRPL spectrum (b) excited at a wavelength of 360 nm with emissions at 440 nm.

($x = 0, 0.2, 0.5, 0.8, 1$) with different amounts of MoS₂ samples was selected as the photocatalyst. Compared with a single MoS₂@CdS, the performance of the photocatalytic hydrogen evolution first increased and then decreased with the increase in the concentration of ZnS. This is interesting but not unusual because the visible light absorption ability was decreased after the formation of the solid solutions, as proved by the UV-vis results. Simultaneously, the Zn_xCd_{1-x}S solid solutions were more favorable for the hydrogen evolution. Taking the two reasons mentioned above into consideration, the Zn_{0.5}Cd_{0.5}S series samples exhibited the best performances when the doping amount of MoS₂ was less than 10%. Because it can affect the absorption ability of the catalysts, the amount of MoS₂ was also another important factor considered.

In the 15% MoS₂@Zn_xCd_{1-x}S samples, therefore, the Zn_{0.2}Cd_{0.8}S demonstrated a superior result compared with the other catalysts. This can be attributed to the higher content of the MoS₂, which will inhibit the Zn_xCd_{1-x}S from being irradiated. Therefore, to ensure that more visible light can be absorbed and utilized efficiently, CdS with a higher concentration than that of ZnS will be beneficial for an enhanced hydrogen production. If the concentration of ZnS continues to increase, the visible light absorption ability of the samples will be weakened. The hydrogen evolution will thus be largely decreased. Consequently, in the 15% MoS₂ doped Zn_xCd_{1-x}S materials, the Zn_{0.2}Cd_{0.8}S, and not Zn_{0.5}Cd_{0.5}S, exhibited the best performance. As discussed above, the 8% MoS₂@Zn_{0.5}Cd_{0.5}S samples therefore manifested a superior performance compared with all other photocatalysts among the hydrogen evolution types considered in this study.

Through this exploration, the pure Zn_xCd_{1-x}S ($x = 0, 0.2, 0.5, 0.8, 1$) samples demonstrated nearly no hydrogen evolution in this system, which can be ascribed to the rapid recombination of the photocarriers. The results of the photocatalytic hydrogen

evolution using pure MoS₂ and Zn_{0.5}Cd_{0.5}S are listed in Fig. S4. It can be concluded that no hydrogen can be measured for MoS₂, and approximately 10 μ mol of hydrogen can be obtained each hour. Although the thermodynamic driving force can be improved after the formation of a solid solution, the separation of the photogenerated electrons and holes also needs to be enhanced. The MoS₂ plays a significant role in the separation process of the photogenerated carriers. The PL and the time-resolved fluorescence spectra (TRPL) results are evidence of this inference. As listed in Fig. 8(a), Zn_{0.5}Cd_{0.5}S and 8% MoS₂@Zn_{0.5}Cd_{0.5}S were selected as the model samples in this study. The PL results revealed that the emission peak shows an evident decrease after the MoS₂ was coupled. The appearance of the maximum emission peak can be caused by a recombination of the photoelectrons and holes. The lower intensity of the PL peaks should be responsible for the longer life of the photogenerated carriers [18]. Further illustration of the prolonged photocarriers can also be verified based on the TRPL results. The lifetime of the photocarriers in Zn_{0.5}Cd_{0.5}S and 8% MoS₂@Zn_{0.5}Cd_{0.5}S can be calculated after being fitted. The decay curves of the fluorescence can be fitted based on the kinetic function principle: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where A_1 and A_2 represent the amplitudes, and τ_1 and τ_2 can be defined as the corresponding emission lifetimes, respectively. In addition, to value the actions of the recombination of the photocarriers, the average lifetime (τ_{ave}) can also be determined through the following equation: $\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$. In this study, the values of A_1 , A_2 , τ_1 , τ_2 , and τ_{ave} were calculated and are summarized in Table 1. As a conclusion, the lifetime of the photocarriers in Zn_{0.5}Cd_{0.5}S and 8% MoS₂@Zn_{0.5}Cd_{0.5}S were 2.504 and 3.346 ns, respectively, which indicates an enhanced separation process prolonging the lifetime of the photocarriers [44].

The degradation efficiency of the samples illustrating the

Table 1

Lifetime (τ_i) and amplitudes (A_i) of the transient absorption decay signal regions for pure Zn_{0.5}Cd_{0.5}S and 8% MoS₂@Zn_{0.5}Cd_{0.5}S.

Samples	A_1	Weighting Factor of A_1	τ_1 (ns)	A_2	Weighting factor of A_2 (%)	τ_2 (ns)	τ_{ave} (ns)	R^2
Zn _{0.5} Cd _{0.5} S	0.878	89.87	0.758	0.099	10.13	4.90	2.504	0.994
8% MoS ₂ @ Zn _{0.5} Cd _{0.5} S	0.863	83.62	1.369	0.169	16.38	5.75	3.346	0.995

Fig. 9. Photocatalytic degradation of amoxicillin through 5%MoS₂@Zn_{0.5}Cd_{0.5}S (a), 8%MoS₂@Zn_{0.5}Cd_{0.5}S (b), 10%MoS₂@Zn_{0.5}Cd_{0.5}S (c), and 15%MoS₂@Zn_{0.2}Cd_{0.8}S (d), and degradation efficiency (e) after 5 h of reaction.

best hydrogen evolution was achieved through the HPLC method, as demonstrated in Fig. 9. The results indicate that the degradation efficiency was decreased with an increase in the MoS₂ concentration after a 5 h reaction. It can be seen that MoS₂, which was doped on the surface of Zn_{0.5}Cd_{0.5}S, occupied the center of the catalysis reaction. As a result, the degradation efficiency showed an opposite trend with an increase in the MoS₂. Furthermore, 15%MoS₂@Zn_{0.2}Cd_{0.8}S shows a higher efficiency than those of both the 8%MoS₂@Zn_{0.5}Cd_{0.5}S and 10%MoS₂@Zn_{0.5}Cd_{0.5}S samples, which was attributed to the higher CdS content, as discussed above.

The degradation processes were also important in this study. As is well known, the photocatalytic hydrogen evolution is conducted in an anaerobic environment. If the degradation process also occurs under the same condition, the products may be different compared with under an aerobic environment. The explorations on the degradation pathway were conducted using the HPLC-MS method, as described in Figs. S5 and S6. A possible pathway can be proposed based on the results of HPLC-MS, as depicted in Fig. 10. The small molecules could be tested, thus excluding the idea that the decreased concentration of the amoxicillin antibiotic wastewater was merely caused by the adsorption procedure.

Recycled photocatalysis experiments were conducted to test the stability of the photocatalysts. The results showed a slight decrease in stability, as indicated in Fig. S7. The reason for this can mainly be ascribed to two aspects: the chemical adsorption between catalysts and amoxicillin and the photocorrosion. Because the sulfides tend to undergo photocorrosion, the stability of the samples is important. Therefore, the chemical state and

the phase of 8%MoS₂@Zn_{0.5}Cd_{0.5}S before and after the photocatalytic experiment were studied based on the XPS and XRD

Fig. 10. Possible degradation pathway of the amoxicillin under vacuum conditions.

Fig. 11. XPS (a–e) and XRD patterns (f) of 8%MoS₂@Zn_{0.5}Cd_{0.5}S before and after the photocatalytic experiment.

patterns, as demonstrated in Fig. 11, respectively. The results illustrate that there were no obvious changes in its structure after the reaction, which suggests a stable structure of the samples in this photocatalytic system and excludes photocorrosion as the reason. Therefore, the reduced hydrogen evolution performance can be attributed to the chemical adsorption on the photocatalysts, which occupied the photocatalytic active sites and affected the hydrogen evolution reaction. Furthermore, the simultaneous processes of the photocatalytic hydrogen evolution and amoxicillin wastewater degradation are schematically described in Fig. 12. The entire process is as follows: when $y\%$ MoS₂@Zn_xCd_{1-x}S ($x = 0, 0.2, 0.5, 0.8, 1$; $y = 5, 8, 10, 15$) is irradiated with visible light, the photogenerated electrons and holes will appear in pairs and migrate to the surface of the photocatalyst. The amoxicillin is oxidized by the holes, which will be favorable for more electrons participating in the photocatalytic

Fig. 12. Schematic illustration of photocatalytic hydrogen evolution simultaneously with the degradation of amoxicillin.

hydrogen evolution. The MoS₂, which accelerates the transfer of the photoelectrons, is beneficial for the separation of the photogenerated electrons and holes. Consequently, an enhanced hydrogen evolution and the degradation of the amoxicillin antibiotic wastewater can be achieved through this dual-functional photocatalysis system.

4. Conclusions

In conclusion, a series of materials, $y\text{MoS}_2@\text{Zn}_x\text{Cd}_{1-x}\text{S}$ ($x = 0, 0.2, 0.5, 0.8, 1$), have been successfully synthesized using a one-pot hydrothermal method. The photocatalytic hydrogen evolution simultaneously with the degradation of amoxicillin was achieved. The results show that 8%MoS₂@Zn_{0.5}Cd_{0.5}S possesses the best performance among the photocatalysts. The maximum amount of hydrogen can reach 630 μmol after a 5 h reaction. Approximately 30% of amoxicillin antibiotic wastewater can be degraded under visible light. These results demonstrate that both the hydrogen evolution and the degradation efficiency are superior to those found in our previous study. However, more materials still need to be explored and the degradation needs to be further improved. The relationship between hydrogen and degradation is also extremely interesting, which deserves exploration in our next study.

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Graphical Abstract

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Simultaneous visible-light-induced hydrogen production enhancement and antibiotic wastewater degradation using $\text{MoS}_2@\text{Zn}_x\text{Cd}_{1-x}\text{S}$: Solid-solution-assisted photocatalysis

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Simultaneous photocatalytic hydrogen evolution and degradation of amoxicillin can be achieved under visible light using $\text{MoS}_2@\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$. The solid solution strategy will be favorable for both the hydrogen evolution and antibiotic wastewater degradation.

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MoS₂@Zn_xCd_{1-x}S增强可见光诱导产氢性能同时降解抗生素废水： 固溶体策略助力光催化

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摘要: 随着工业化进程的加快, 能源的需求亦随之增长。以传统不可再生的化石燃料为主体的能源结构, 虽然可以满足日常能源需求, 但是使用后其排放的氮氧化物、硫氧化物以及CO₂温室气体将会对人类的环境造成污染。因此, 开发清洁可持续的新型能源成为重要的研究方向之一。氢能作为一种可持续能源, 具有高热值、零排放等优点, 而光催化粉末体系制氢则具有低成本、低污染等优势。因此, 光催化制氢有望成为未来氢能重要的生产方式之一。然而, 由于目前关于光催化制氢的研究大多集中于牺牲剂体系, 例如醇类及醇胺类体系。传统牺牲剂体系作为探索光催化制氢的作用机制是很有效的, 但是具体到未来工业化进程中, 其经济性还需进一步的提高, 且其中甲醇、乙醇等本身也可作为一种燃料使用。因此, 开发廉价的牺牲剂体系, 也成了未来工业化进程中的一个重要方面。本文选用MoS₂@Zn_xCd_{1-x}S作为催化剂, 以抗生素废水作为牺牲剂, 在可见光照射下实现产氢的同时, 降解阿莫西林抗生素废水, 相比于单独的MoS₂@ZnS及MoS₂@CdS体系, 性能明显的提高。通过扫描电镜与元素分布测试证明了各个元素的存在及分布。XRD结果表明, MoS₂@Zn_xCd_{1-x}S是以固溶体形式存在, 并非简单地物理混合。随后HRTEM进一步证实所形成的固溶体催化剂呈六方晶相。采用XPS和Raman分析了元素的化学环境, 发现固溶体与MoS₂可能是通过Mo-S-Cd/Zn键而结合; 而MoS₂表现出1-T与2-H的混相结构。材料的吸光性能通过紫外可见漫反射测试。我们发现, 随着ZnS含量的不断增加, 固溶体在可见光区域的吸收不断减弱, 同时吸收带边向着紫外光区移动。而光催化制氢性能测试实验表明, Zn_{0.5}Cd_{0.5}S体系呈现出最佳的性能, 这可能是因为当Cd:Zn=1:1时, 固溶体策略对于CdS在热力学与动力学方面的提升均达到最佳。而MoS₂量的增加, 产氢效果也呈现出“火山峰”似的规律, 过多的MoS₂将会吸收主要的入射光, 从而使Zn_{0.5}Cd_{0.5}S不能被有效地激发进而参与到反应中去。液相色谱-质谱联用技术表明阿莫西林的降解不仅仅是由于吸附所致, 光催化也存在一定的贡献。而反应前后的XRD与XPS结果则表明了催化剂结构稳定。

关键词: 光催化; 氢能; 抗生素废水; 降解; 协同

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