Solid-state Z-scheme assisted hydrated tungsten trioxide/ZnIn$_2$S$_4$ photocatalyst for efficient photocatalytic H$_2$ production

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Abstract

Efficient water splitting for H$_2$ evolution over semiconductor photocatalysts is highly attractive in the field of clean energy. It is of great significance to construct heterojunctions, among which the direct Z-scheme nanocomposite photocatalyst provides effective separation of photo-generated carriers to boost the photocatalytic performance. Herein, Z-scheme hydrated tungsten trioxide/ZnIn$_2$S$_4$ is fabricated via an in-situ hydrothermal method where ZnIn$_2$S$_4$ nanosheets are grown on WO$_3$·xH$_2$O. The close contact between WO$_3$·0.5H$_2$O and WO$_3$·0.33H$_2$O as well as ZnIn$_2$S$_4$ improve the charge carrier separation and migration in the photocatalyst, where the strong reducing electrons in the conduction band of ZnIn$_2$S$_4$ and the strong oxidizing holes in the valence band of WO$_3$·0.33H$_2$O are retained, leading to enhanced photocatalytic hydrogen production. The obtained WO$_3$·xH$_2$O/ZnIn$_2$S$_4$ shows an excellent H$_2$ production rate of 7200 µmol g$^{-1}$ h$^{-1}$, which is 11 times higher than pure ZnIn$_2$S$_4$. To the best of our knowledge, this value is higher than most of the WO$_3$-based noble metal-free semiconductor photocatalysts. The improved stability and activity are attributed to the formation of the Z-scheme heterojunction, which can markedly accelerate the interfacial charge separation for surface reaction. This work offers a promising strategy towards the design of an efficient Z-scheme photocatalyst to suppress electron–hole recombination and optimize redox potential.

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Keywords: Z-scheme, hydrated tungsten trioxide/ZnIn$_2$S$_4$, hydrogen evolution, photocatalytic

1. Introduction

Hydrogen is a kind of clean, eco-friendly, sustainable, and green energy source, which has a broad development prospect [1–4]. Photocatalytic hydrogen production from water provides a green and sustainable way to convert solar energy to hydrogen [5–9]. Although numerous semiconductor photocatalysts for hydrogen production have been developed, hydrogen evolution is still limited by the low catalytic efficiency [10–13]. Insufficient separation and utilization of charge carriers is one of the critical issues that inhibit the further improvement of photocatalytic performance [14–17]. Therefore, it is important to construct photocatalysts with unique architectures to suppress the rapid recombination of photo-generated electron and hole pairs.
future perspectives

Photocatalytic hydrogen production from water provides a green and sustainable way to convert solar energy to hydrogen. The separation and transfer of charge carriers are highly important for the reaction. Constructing Z-scheme heterojunction nanocomposites can not only promote the charge separation, but also optimize the redox capacity, and thus is one of the most attractive strategies towards efficient hydrogen evolution. All-solid-state Z-scheme photocatalytic systems are especially more attractive for efficient charge separation since they can shorten the electron transfer path and avoid the undesired backward reactions caused by redox couples as compared with the Z-scheme systems with a shuttle redox mediator. Strategies to construct all-solid-state Z-scheme systems with efficient charge separation and transfer efficiency are of great significance to the field of light driven hydrogen evolution.

and extract them to the maximum extent for participation in water reduction.

Heterojunction hybrid structures have received intensive attention, which can steer the charge kinetics by proper selection of the semiconductor materials [18–21]. Among them, Z-scheme heterojunction nanocomposites are of particular importance due to their ability to promote not only the charge separation, but also the redox capacity. In a typical Z-scheme heterojunction nanocomposite, due to the well matched band structure of the components, photo-generated electrons and holes with weak redox capacity recombine with each other, leaving the electrons at the more negative conduction band (CB) and the holes at the more positive valence band (VB) separated, which results in long-lived charge separation and improved redox capacity [22–27]. Compared with the Z-scheme systems with a shuttle redox mediator, the all-solid-state Z-scheme photocatalytic systems with two semiconductors in direct contact are much more attractive for efficient promotion of the charge separation since they can shorten the electron transfer path and avoid the undesired backward reactions caused by the redox couples [28–33]. Although various kinds of all-solid-state Z-scheme photocatalytic systems have been developed, an efficient Z-scheme system for hydrogen production under visible light, a rational selection of semiconductors as well as a delicate synthesis to optimize their interfaces are not easy to achieve. How to make full use of the advantages of a solid-state Z-scheme system while suppressing undesirable potential barriers for charge transfer is still challenging.

WO3 is one of the potential visible light photocatalysts due to its tunable band gap (2.4–2.8 eV) in the visible region along with its high stability and nontoxicity [34, 35]. Various nanostructures of WO3 have been prepared for different applications. Although rarely studied, hydrated tungsten trioxide is reported to possess better photocatalytic properties than tungsten trioxide itself [36–38]. Inspired by the verified band structures of different hydrated tungsten trioxides, we hypothesize that in-situ synthesis of different hydrated tungsten trioxides in one-pot could possibly construct WO3·xH2O-based heterojunctions with tight interfaces to avoid charge recombination and realize boosted charge separation, which is thus promising as the oxidation counterpart to develop an efficient Z-scheme photocatalyst. Metal sulfides are regarded as good candidates for photocatalytic hydrogen production due to their strong absorption in the visible range. ZnIn2S4 (ZIS), a typical layered structure, is one of the important members in the community of ternary chalcogenides. Its suitable band gap (2.34–2.48 eV), remarkable chemical stability and nontoxicity rank ZIS as an attractive photocatalyst in different applications, such as, organic transformation, CO2 reduction and hydrogen evolution [39–43]. Especially, the use of ZIS for photocatalytic hydrogen evolution from water has received increasing attention. The well matched band structures of both ZIS and WO3·xH2O offer a great opportunity to construct WO3·xH2O/ZIS as a new kind of efficient Z-scheme photocatalyst.

In this study, we report a new design of a solid-state Z-scheme WO3·xH2O/ZIS photocatalytic system with dramatically enhanced photocatalytic H2 evolution. WO3·0.33H2O and WO3·0.5H2O with strong interfacial interaction were obtained by a one-pot hydrothermal reaction, which ensured the fast electron transfer from the CB of WO3·0.33H2O to the VB of ZIS, mediated by WO3·0.5H2O. Thus, the optimized WO3·xH2O/ZIS showed the best photocatalytic performance with a hydrogen evolution rate of 7200 μmol g−1 h−1, which is about 11 times higher than that of pure ZIS. This study provides fresh impetus for designing and developing functional photocatalytic systems for energy conversion.

2. Experimental

2.1. Preparations

All the reagents were of analytical grade and used without further purifications. WO3·0.33H2O–WO3·0.5H2O (denoted as WO3·xH2O) nanocomposites were synthesized according to previous literatures [44] with a slight modification, where 660 mg (1 mmol) sodium tungstate dihydrate and 100 mg polyvinylpyrrolidone (PVP) (Fw = 55 000) were dissolved in 12 ml deionized water and 2 ml acetic acid. The above solution was stirred for 60 min and then transferred into a Teflon-lined stainless steel autoclave (25 ml), followed by heating at 200 °C for 8 h. After cooled down to room temperature, the sample was separated by centrifugation and washed with distilled water and absolute ethanol several times and dried at 60 °C in an oven. To prepare WO3·0.5H2O, 0.5 g Na2WO4·2H2O and 1.35 g NH3CONH2 were dissolved in 2.5 ml water, and 43.0 ml ethanol was slowly added to form a white suspension. After ultrasonication for 10 min, 4.0 ml 3.0 mol l−1 HCl was added into the suspension, which was then maintained at 200 °C for 24 h. For WO3·0.33H2O, 2.2 mmol sodium oleate were dissolved in 20 ml of distilled water at 50 °C and 0.5 g of Na3WO4·2H2O were added. After vigorous stirring for 5 h, the pH value was adjusted to 1 by adding dilute HNO3, and the volume of the suspension was adjusted to 40 ml by adding deionized water. After being stirred for 4 h, the precursor was sealed in a 50 ml Teflon-lined autoclave and heated at 180 °C for 20 h.

To prepare WO3·xH2O/ZIS nanocomposites with different mass ratios, 50 mg WO3·xH2O was dispersed in 30 ml distilled water and sonicated for 60 min. Subsequently, different
amounts of Zn(NO$_3$)$_2$, In(NO$_3$)$_3$ and L-cysteine were added and the suspension was sonicated for several minutes. After that, the resultant suspension was sealed in a Teflon-lined stainless steel autoclave and heated at 180 °C for 18 h. The product was collected by centrifugation, washed with deionized water and ethanol consecutively, and finally dried at 60 °C. The WO$_3$·xH$_2$O/ZIS nanocomposites with different mass ratios are denoted as WO$_3$·xH$_2$O/ZIS-Y, where Y represents different mass ratios of WO$_3$·xH$_2$O and ZIS. For comparison, the WO$_3$·0.33H$_2$O/ZIS and WO$_3$·0.5H$_2$O/ZIS nanocomposites were synthesized following the similar procedures of WO$_3$·xH$_2$O/ZIS. Pure ZIS was synthesized following the similar procedures with the absence of WO$_3$·xH$_2$O.

2.2. Characterizations

The crystal structures of as-prepared samples were determined by Bruker D8 ADVANCE x-ray diffraction with Cu Kα radiation ($l = 0.15418$ nm), which was operated at 40 kV and 40 mA. The morphologies of the samples were obtained by a field emission scanning electron microscopy (JSM-6700F). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy images were obtained in a JEOL model JEM 2010 EX instrument with an accelerating voltage of 200 kV. To prepare the TEM sample, the sample powder suspension was sonicated in ethanol and a drop of it was dripped on a 3 mm-diameter fine mesh copper grid mounted with a carbon film. X-ray photoelectron spectra (XPS) was obtained by a Thermo Scientific ESCA Lab 250 system, with a monochromatic Al $Kα$ as the x-ray source and a hemispherical analyzer. Ultraviolet-visible diffuse reflectance spectroscopy (UV–vis DRS) of as-synthesized materials was recorded at the wavelength range of 250–800 nm. BaSO$_4$ was used as a reflectance standard in the UV–vis diffuse reflectance experiment. Electrochemical impedance spectroscopy (EIS) and transient photocurrent responses were measured on an electrochemical analyzer (CHI760) in a stagnant nitrogen gas. Electrochemical impedance spectroscopy (EIS) and transient photocurrent responses were measured on an electrochemical analyzer (CHI760) in a stagnant nitrogen gas.

3. Results and discussion

The XRD pattern of the obtained WO$_3$·xH$_2$O nanocomposite shows a mixture of WO$_3$·0.5H$_2$O (JCPDS 4-0363) and WO$_3$·0.33H$_2$O (JCPDS 35-1001) (figure 1(a)). The well preserved XRD patterns of WO$_3$·xH$_2$O in WO$_3$·xH$_2$O/ZIS nanocomposites revealed the unaffected crystalline phase during the hybridization process. The two diffraction peaks at 20.7° and 47.7° correspond to the (102) and (108) crystallographic planes of hexagonal ZIS phase, respectively (JCPDS 49-1562), indicating the successful hybridization of ZIS with WO$_3$·xH$_2$O. The peak intensities of ZIS gradually become stronger as the concentration of the ZIS precursor is increased, indicating the formation of WO$_3$·xH$_2$O/ZIS-Y (figure 1(b)).

The morphology of the WO$_3$·xH$_2$O/ZIS was examined by FESEM. As shown in figure 2(a), pure WO$_3$·xH$_2$O shows the stacking of nanosheets with smooth surfaces. Flower-like ZIS nanosheets are tightly integrated on the surface of WO$_3$·xH$_2$O as observed in WO$_3$·xH$_2$O/ZIS-0.7, confirming the successful hybridization instead of simple physical mixing (figure 2(b)). The strong interconnection between ZIS nanosheets and WO$_3$·xH$_2$O is further confirmed by TEM (figure 2(c)). Interplanar spacings of 0.312, 0.295, and 0.324 nm are observed, which correspond to the d-spacings of (200) plane of WO$_3$·0.33H$_2$O, (222) plane of WO$_3$·0.5H$_2$O and (012) plane of ZIS, respectively (figure 2(d)). In addition, clear boundaries between the above three components can be observed, indicating intimate contacts formed in the ternary heterojunctions.

The surface chemical composition and electronic state of WO$_3$·xH$_2$O/ZIS nanocomposites are studied by XPS analyses, in comparison with ZIS and WO$_3$·xH$_2$O (figure 3). The XPS spectrum of WO$_3$·xH$_2$O/ZIS-0.7 in the W 4 f region shows peaks at 35.0 eV (4 f$_{5/2}$) and 37.2 eV (4 f$_{7/2}$), which correspond to the typical binding energies of W$^{6+}$ states (figure 3(a)). Compared with WO$_3$·xH$_2$O, the binding energies of W$^{6+}$ in WO$_3$·xH$_2$O/ZIS-0.7 shift slightly to higher values, indicating decreased electron density around W [45]. Meanwhile, the characteristic binding energies of In$^{3+}$ 3d (444.4 and 452.0 eV) in WO$_3$·xH$_2$O/ZIS-0.7 slightly to lower binding energies as compared with pure ZIS, while there are no changes for Zn$^{2+}$ 2p (1021.4 and 1044.7 eV) and S$^{2-}$ 2p (161.3 eV and 162.6 eV) (figures 3(b)–(d)). The shift of the
binding energies of W$^{6+}$ and In$^{3+}$ in different directions suggests the strong electronic interaction between WO$_3$·xH$_2$O and ZIS in the WO$_3$·xH$_2$O/ZIS nanocomposites [30, 46]. Given the well matched band structures of WO$_3$·xH$_2$O and ZIS and their strong electronic interaction, we expect that the ternary heterojunction structured WO$_3$·xH$_2$O/ZIS could show excellent photocatalytic performance.

The photoelectric properties of the as-synthesized ZIS, WO$_3$·xH$_2$O and WO$_3$·xH$_2$O/ZIS nanocomposite are examined by UV–vis DRS as shown in figure S1. Pure WO$_3$·xH$_2$O shows an absorption edge at about 400 nm. Incorporation of the visible light responsive ZIS onto WO$_3$·xH$_2$O obviously results in enhanced absorption in the visible range, which increases with increasing amount of ZIS incorporated, in agreement with the observed color change of the samples.

The photocatalytic hydrogen production activity is evaluated in a closed gas circulation system with lactic acid as the sacrificial agent under visible light irradiation. Figure 4(a) compares the photocatalytic H$_2$ production rates of the whole set of samples. In consistent with previous reports, ZIS is
active for the visible light induced hydrogen evolution but with low activity of 660 µmol g⁻¹ h⁻¹, owing to its poor charge separation capability. Hybridization of WO₃·xH₂O and ZIS results in significantly improved hydrogen evolution activity. Increasing the loading amount of ZIS onto WO₃·xH₂O first leads to an increase and then a decrease in the hydrogen evolution rate, with a surprisingly high activity of 7200 µmol g⁻¹ h⁻¹ achieved over WO₃·xH₂O/ZIS-0.7, which is about 11 times that of pure ZIS (figures 4(a) and (b)). It is noteworthy that this hydrogen evolution rate value is higher than most of the WO₃-based noble metal-free photocatalysts (table S1 and figure 5(a)). Moreover, the AQY for the WO₃·xH₂O/ZIS-0.7 reaches 9.3% at 420 nm. The decreased hydrogen evolution rate of WO₃·xH₂O/ZIS at higher loading amount of ZIS is probably due to the shielding of excess amount of ZIS over the nanocomposite, which acts as charge recombination center. The photocatalytic stability of WO₃·xH₂O/ZIS-0.7 was investigated by intermittent...
evacuation and exposure to atmospheric conditions every 4 h for four times. As shown in figure 5(b), WO$_3$:H$_2$O/ZIS-0.7 can be reused for at least four times without obvious loss of the hydrogen evolution activity. In addition, the recycled WO$_3$:xH$_2$O/ZIS-0.7 shows similar XRD patterns and morphology with the fresh one (figure S2), further confirming the high stability of WO$_3$:xH$_2$O/ZIS-0.7 for the photocatalytic hydrogen evolution.

To explore the underlying mechanism of the enhanced hydrogen evolution activity of WO$_3$:xH$_2$O/ZIS hybrids, the hydrogen evolution performance of WO$_3$:xH$_2$O alone is investigated. As expected, pure WO$_3$:xH$_2$O has hardly any photocatalytic H$_2$ evolution activity due to its weak visible light absorption and its CB being more positive than the hydrogen evolution potential. Therefore, the synergistic effect between WO$_3$:xH$_2$O and ZIS is regarded to be a crucial factor for the excellent photocatalytic activity observed in WO$_3$:xH$_2$O/ZIS. In addition, since WO$_3$:xH$_2$O exists in different crystalline phases and may have great influence on the photocatalytic performance, we study the photocatalytic activities of heterojunctions formed between single phase WO$_3$ hydrate and ZIS (that are, WO$_3$:0.5H$_2$O/ZIS-0.7 and WO$_3$:0.33H$_2$O/ZIS-0.7) to understand the role played by the WO$_3$:xH$_2$O hybrid. As shown in figure 4(b), both samples are active for hydrogen evolution, but are much inferior to WO$_3$:xH$_2$O/ZIS-0.7. These results reveal that the Z-scheme nanostructured ternary heterojunctions formed among WO$_3$:0.5H$_2$O, WO$_3$:0.33H$_2$O and ZIS in the WO$_3$:xH$_2$O/ZIS-0.7 nanocomposites are indispensable for the excellent photocatalytic activity, which help promote efficient interfacial charge separation and transportation.

Steady and transient PL analyses are performed to reveal photophysical characteristics of the photogenerated electron–hole pairs. As shown in figure 6(a), pure WO$_3$:xH$_2$O, ZIS and WO$_3$:xH$_2$O/ZIS-0.7 show PL emission at around 355 nm, with WO$_3$:xH$_2$O/ZIS-0.7 demonstrating the lowest PL intensity, indicating suppressed recombination of the charge carriers and hence suppressed radiative emission [47]. In addition, the time-resolved transient PL decay spectra show that WO$_3$:xH$_2$O/ZIS-0.7 exhibits shorter emission lifetimes ($t_1 = 0.9$ ns, $t_2 = 1.1$ ns) as compared with ZIS ($t_1 = 1.0$ ns, $t_2 = 9$ ns) and WO$_3$:xH$_2$O ($t_1 = 1.0$ ns, $t_2 = 10$ ns). The average emission lifetime, which reflects the overall emission decay behavior [48], of WO$_3$:xH$_2$O/ZIS-0.7 (1.0 ns) is much shorter than that of ZIS (7.2 ns) and WO$_3$:xH$_2$O (8.5 ns) (figure 6(b)). This is probably because that the strong interfacial contact in the local heterostructure accelerates the charge transfer across the interfaces. The promoted charge transfer process is also revealed by the transient photocurrent responses and the EIS, in which the WO$_3$:xH$_2$O/ZIS-0.7 electrode shows the highest photocurrent intensity and the smallest semicircle radius (figures 6(c) and (d)).

To get more insight into the enhanced charge flow process, band structure study is performed. The band gap energies ($E_g$) of WO$_3$:0.33H$_2$O and WO$_3$:0.5H$_2$O are reported to be approximately 2.63 and 2.95 eV, respectively [49, 50]. We use Mott-Schottky method to further determine their VB and CB edges. As shown in figures S3(a) and (b), the flat band energy ($E_{fb}$) values are determined from the linear intercept of the axis, which are −0.35 and −0.25 eV vs. NHE at pH = 7 for WO$_3$:0.33H$_2$O and WO$_3$:0.5H$_2$O, respectively. Therefore, based on the experimental results of photocatalytic H$_2$ production, the possible charge transfer process across the ternary WO$_3$:xH$_2$O/ZIS heterojunction under visible light is proposed and illustrated in figure 7. Under the light irradiation, electrons are excited to the CB and holes are left in the VB of WO$_3$:0.33H$_2$O in the WO$_3$:xH$_2$O/ZIS ternary structure. The tight contact between WO$_3$:0.33H$_2$O and WO$_3$:0.5H$_2$O provides a short migration path of the photogenerated carriers, which increases the opportunity of photoinduced electrons in the CB of WO$_3$:0.33H$_2$O to migrate through WO$_3$:0.5H$_2$O and then recombine with the holes in the VB of ZIS. The migration of charge carriers can promote the electron accumulation in the CB of ZIS, and the holes are retained in the VBs of WO$_3$:0.33H$_2$O, which are consumed by the sacrificial electron donor. Therefore, the photocatalytic reaction of the as-prepared WO$_3$:xH$_2$O/ZIS nanocomposites follows a direct solid-state Z-scheme mechanism, which not only accelerates the separation and transfer of photogenerated charges but also retains the electrons with strong redox ability for efficient photocatalytic H$_2$ production. It can be concluded that the enhanced photocatalytic activity of the as-prepared WO$_3$:xH$_2$O/ZIS nanocomposites can be ascribed to the enhanced visible-light harvesting and highly effective charge-separation resulting from the solid-state Z-scheme junction in the ternary structure.
4. Conclusion

In summary, a novel Z-scheme WO$_3$·xH$_2$O/ZIS ternary heterojunction has been constructed for photocatalytic H$_2$ production. The close-contact between WO$_3$·0.33H$_2$O and WO$_3$·0.5H$_2$O provides a short migration path in the material interfaces from the CB of WO$_3$·0.33H$_2$O to the VB of ZIS, mediated by WO$_3$·0.5H$_2$O, which effectively accelerates the separation of the charge carriers. Benefiting from the unique spatial structure and charge migration path (enhanced separation efficiency of photo-generated electron–hole pairs), the obtained WO$_3$·xH$_2$O/ZIS nanocomposites exhibit more efficient photocatalytic performance for photocatalytic H$_2$ production than pure WO$_3$·xH$_2$O and ZIS under visible light irradiation. This Z-scheme nanostructured heterojunction shows great potential to realize more efficient H$_2$ production.

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