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Article (Special Issue on Photocatalysis in China)

Photocatalytic hydrogen evolution activity over MoS₂/ZnIn₂S₄ microspheres

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ARTICLE INFO

Article history:

Received 9 October 2017

Accepted 31 October 2017

Published 5 December 2017

Keywords:

Composite

Cocatalyst

Photocatalytic hydrogen evolution

Charge carrier

Separation

ABSTRACT

MoS₂/ZnIn₂S₄ composites with MoS₂ anchored on the surface of ZnIn₂S₄ microspheres were synthesized by a two-step hydrothermal process. The obtained samples were characterized by X-ray diffraction, field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, high-resolution transmission electron microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, ultraviolet–visible diffuse reflectance absorption spectroscopy, nitrogen adsorption–desorption measurements, photoluminescence spectroscopy, and photoelectrochemical tests. The influence of the loading of MoS₂ on the photocatalytic H₂ evolution activity was investigated using lactic acid as a sacrificial reagent. A H₂ evolution rate of 343 μmol/h was achieved under visible light irradiation over the 1 wt% MoS₂/ZnIn₂S₄ composite, corresponding to an apparent quantum efficiency of about 3.85% at 420 nm monochromatic light. The marked improvement of the photocatalytic H₂ evolution activity compared with ZnIn₂S₄ can be ascribed to efficient transfer and separation of photogenerated charge carriers and facilitation of the photocatalytic H₂ evolution reaction at the MoS₂ active sites.

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1. Introduction

Photocatalytic H₂ evolution over semiconductors is a promising approach to convert solar energy to clean hydrogen energy [1–4]. A large number of photocatalysts have been developed and investigated for photocatalytic H₂ evolution, CO₂ reduction, and environmental contaminant removal, including metal oxides, sulfides, oxynitrides, and graphitic carbon nitride (g-C₃N₄) [5–34]. Among these photocatalysts, sulfides are excellent candidates for photocatalytic H₂ evolution because of their suitable band gap energies and sites for facilitating the photocatalytic H₂ reaction. Ternary chalcogenide ZnIn₂S₄, a layered structure with a band gap energy of 2.0–2.4 eV, has attracted attention in recent years because of its favorable visible-light harvesting capability, photostability, and low toxicity

[35–41]. However, pure ZnIn₂S₄ usually suffers from rapid recombination of photogenerated electron–hole pairs and a large kinetic barrier for H₂ evolution reaction at the surface sites. As a result, the photocatalytic H₂ evolution performance over pure ZnIn₂S₄ is not satisfactory. To improve the photocatalytic H₂ evolution activity of ZnIn₂S₄, much effort has been made to suppress recombination of charge carriers and promote charge transfer and separation, such as depositing noble metal cocatalysts and combining ZnIn₂S₄ with graphene, carbon nanotubes, carbon quantum dots, and other semiconductors [42–49]. Although loading the precious metal Pt on the surface of ZnIn₂S₄ can enhance the photocatalytic H₂ evolution activity, this strategy has high cost for the photocatalytic reaction and is thus not suitable for practical application. Therefore, it is imperative to discover low-cost, earth-abundant, low-toxicity, and high-effi-

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This work was supported by the National Natural Science Foundation of China (51302200).

DOI: 10.1016/S1872-2067(17)62981-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 12, December 2017

ciency materials to replace noble metals as cocatalysts for the photocatalytic H_2 evolution reaction for practical application [50–52].

Recently, the layered MoS_2 structure has received extensive attention as a cocatalyst in the photocatalytic H_2 evolution reaction [53–71]. For example, Ye's group [53] coupled exfoliated MoS_2 monolayers with commercialized CdS to form composites that exhibit significantly enhanced photocatalytic H_2 evolution activities. Zhao et al. [54] synthesized $\text{MoS}_2/\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ composites by a two-step hydrothermal route. They achieved an extremely high H_2 evolution rate of 12.30 mmol/h/g at the optimal loading amount of MoS_2 . Yu et al. [55] used the adsorption in situ transformation method to prepare amorphous $\text{MoS}_x/\text{g-C}_3\text{N}_4$ hybrids. Photocatalytic experimental results showed that the H_2 evolution activity of $\text{g-C}_3\text{N}_4$ is markedly improved compared with pure $\text{g-C}_3\text{N}_4$. Meng's group [56] anchored MoS_2 nanosheets on the surface of ZnIn_2S_4 by the in situ photoassisted deposition method. They achieved a H_2 evolution rate of 8.047 mmol/h/g, which is 28 times higher than that of pure ZnIn_2S_4 under identical conditions. It has been suggested that facilitation of the photocatalytic H_2 evolution using MoS_2 as a cocatalyst originates from the unsaturated edge sulfur atoms acting as active sites to rapidly capture protons from aqueous solution and then promote direct reduction of H^+ to H_2 [57]. Based on the aforementioned reports, designing and loading MoS_2 on the surface of semiconductors could be an effective method to improve the photocatalytic H_2 evolution activity. Herein, a two-step hydrothermal route was used to fabricate $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ composites. A significantly enhanced photocatalytic H_2 evolution activity was achieved in the presence of a small amount of MoS_2 as a cocatalyst compared with pure ZnIn_2S_4 .

2. Experimental

2.1. Preparation

The ZnIn_2S_4 samples were fabricated according to our previously reported method [36]. Typically, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 mmol) and $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ (2 mmol) were dissolved in deionized water (70 mL) and the pH value of the solution was then adjusted to 1.0 by adding hydrochloric acid (1 mol/L). Next, thioacetamide (TAA, 10 mmol) was added to the above solution with intense magnetic stirring. After stirring for 30 min at room temperature, the mixture was transferred to a 100-mL Teflon-lined stainless steel autoclave and heated at 160 °C for 12 h in an electric oven. The mixture was then naturally cooled to room temperature. The obtained light yellow product was collected by centrifugation, washed with deionized water and ethanol three times, and then dried at 60 °C for 12 h.

The $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ composites were synthesized by hydrothermal treatment. The typical procedure using the 1 wt% $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ composite as an example was as follows. As-fabricated ZnIn_2S_4 (0.2 g) was dispersed in deionized water (60 mL) with ultrasonic treatment. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (0.0022 g) and thiourea (0.0041 g) were then added to the above suspension. After stirring for 30 min, the suspension was

transferred to a 100-mL Teflon-lined stainless steel autoclave and kept at 210 °C for 24 h. The resultant product with a theoretical mass ratio of 1 wt% MoS_2 in the $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ composite was washed with deionized water and ethanol several times, and then dried at 60 °C for 12 h. Samples with different theoretical MoS_2 mass ratios (0.5–20 wt%) were fabricated by changing the added amounts of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and thiourea. The pure MoS_2 sample was prepared by the same procedure except that the ZnIn_2S_4 precursor was not added. Pure ZnIn_2S_4 treated by the same second hydrothermal procedure without adding MoS_2 and 1 wt% Pt-loaded ZnIn_2S_4 obtained by the light-assisted reduction method were used as controls.

2.2. Characterization

The crystal phases were analyzed by a Shimadzu XRD-7000 diffractometer operating at 40 kV and 30 mA with $\text{Cu K}\alpha$ irradiation. Morphology analysis and energy dispersive spectroscopy (EDS) were performed with a JSM-7100F field emission scanning electron microscope (FESEM). High-resolution transmission electron microscopy (HRTEM) observation was performed with a JEOL JEM 2100F electron microscope operating at 200 kV accelerating voltage. The X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG Multilab 2000 spectrometer operating at 300 W with an $\text{Al K}\alpha$ source. Raman spectroscopy was performed with a Jobin Yvon LabRAM HR800 spectrometer. The ultraviolet-visible (UV-vis) diffuse reflectance absorption spectra were recorded with a Purkinje General TU-1901 spectrophotometer using BaSO_4 as the reference standard. The Brunauer-Emmett-Teller (BET) specific surface areas of the samples were determined with a Micromeritics ASAP 2020 nitrogen adsorption apparatus. The photoluminescence (PL) spectra were recorded with a PerkinElmer LS55 fluorescence spectrometer at an excitation wavelength of 350 nm. The elemental contents of the samples were determined by a Shimadzu EDX-7000 X-ray fluorescence (XRF) spectrometer with a Cu target in standardless mode.

2.3. Photocatalytic H_2 evolution experiments

The photocatalytic H_2 evolution experiments were performed in a 300-mL Pyrex glass reactor. A 300 W Xe lamp (PLS-SXE300, Beijing Trusttech Co. Ltd., China) with a 420-nm cut-off filter was used as the light source. In a typical photocatalytic H_2 evolution experiment, the photocatalyst (80 mg) was dispersed in an aqueous solution (80 mL) containing lactic acid (10 mL) by ultrasonic treatment. Before irradiation, the reactor was thoroughly evacuated to remove air. During irradiation, continuous magnetic stirring was performed to maintain the photocatalyst in suspension. After irradiation for 1 h, 100 μL of the gas was intermittently sampled and the amount of hydrogen was detected by a gas chromatograph (SP7820, thermal conductivity detector, X13 molecular sieve column, N_2 carrier gas).

The apparent quantum efficiency (AQE) for H_2 evolution was determined in a 75-mL Pyrex glass reactor. Differing from the above experiments, 20 mg of the photocatalyst was dis-

persed in 20 mL aqueous solution containing 2 mL lactic acid. The other photoreaction conditions were the same as the above experiments except that a band-pass filter ($\lambda = 420$ nm) was used instead of the cut-off filter. The average intensity and area of irradiation were determined to be 22.8 mW/cm² and 9.62 cm², respectively. The AQE for H₂ evolution was determined by

$$\text{AQE} = \frac{2 \times \text{the number of evolved H}_2 \text{ molecules}}{\text{the number of inducent photons}} \times 100\%$$

2.4. Photoelectrochemical measurements

Electrochemical impedance spectroscopy (EIS) and the photocurrent tests were performed using an electrochemical system (CHI 760D, China) with a three-electrode cell. The working electrodes were prepared as follows. A certain amount of the photocatalyst was mixed with ethanol (1 mL) and Nafion aqueous solution (1 mL, 5 wt%) by ultrasonic treatment. The mixture (0.1 mL) was then dropped on indium tin oxide (ITO) glass (1 cm × 1 cm). After evaporation of ethanol in air, the photocatalyst was attached to the ITO glass surface. A platinum plate and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Na₂SO₄ solution (0.1 mol/L) was used as the electrolyte. A 300-W Xe lamp with a 420 nm cut-off filter acted as the light source.

3. Results and discussion

3.1. XRD and XRF analysis

The crystal phases of the samples were identified by XRD. As shown in Fig. 1, pure ZnIn₂S₄ shows characteristic diffraction peaks of the (006), (102), (110), (116), and (202) crystal planes, which can be indexed to the hexagonal phase of ZnIn₂S₄ (JCPDS No. 65-2023) [36]. For MoS₂, the diffraction peaks located at $2\theta = 14^\circ, 33^\circ, 39^\circ$, and 59° are assigned to the (002), (100), (103), and (110) crystal planes of MoS₂ (JCPDS No. 37-1492) [58]. The XRD patterns of the MoS₂/ZnIn₂S₄ composites with MoS₂ mass ratios of 0.5–10 wt% are similar to pure ZnIn₂S₄, which may be because of the low contents and high dispersion of MoS₂ in the composites. In contrast, the diffrac-

tion peaks of the (002) and (100) crystal planes ascribed to MoS₂ are observed in the XRD pattern of the 20 wt% MoS₂/ZnIn₂S₄ composite. The above results suggest that loading MoS₂ on the surface of ZnIn₂S₄ by hydrothermal treatment does not influence the crystal phase of ZnIn₂S₄. To accurately determine the MoS₂ contents in the MoS₂/ZnIn₂S₄ composites, XRF spectroscopy was performed. The mass ratios of MoS₂ in the 0.5, 1, 3, 5, 10, and 20 wt% MoS₂/ZnIn₂S₄ composites are estimated to be 0.47, 0.67, 2.46, 4.23, 8.89, and 17.52 wt%, respectively, which are close to the theoretical contents.

3.2. Morphology and EDS analysis

FESEM images of pure ZnIn₂S₄, pure MoS₂, and the 1 wt% MoS₂/ZnIn₂S₄ composite are shown in Fig. 2(a)–(c). Pure ZnIn₂S₄ forms relatively uniform spheres (average diameter 3 μm) composed of a large number of interleaving flakes (Fig. 2(a)). Pure MoS₂ forms micrometer-sized sheets. MoS₂ aggregation is greatly inhibited for the 1 wt% MoS₂/ZnIn₂S₄ composite. There are some agglomerated sheets with sizes of 0.1–0.5 μm distributed on the surface of ZnIn₂S₄. The size and morphology of ZnIn₂S₄ are not obviously affected by the second hydrothermal process. HRTEM was performed to reveal the structure of the MoS₂/ZnIn₂S₄ composite (Fig. 2(d)). The MoS₂/ZnIn₂S₄ composite is composed of microsized ZnIn₂S₄ spheres and nanosized MoS₂ agglomerates, which agrees with the SEM observations. HRTEM was also performed to clearly identify the structure of the 1 wt% MoS₂/ZnIn₂S₄ composite (Fig. 2(e)). A distinct heterostructure interface is observed, indicating that MoS₂ is in close contact with ZnIn₂S₄. The lattice spacing of 0.63 nm corresponds to the (002) plane of MoS₂, whereas the lattice spacing of 0.32 nm corresponds to the (102) plane of ZnIn₂S₄. The elemental composition of the composite was determined by EDS measurements (Fig. 2(f)). The composite is composed of Zn, In, Mo, and S. The above results confirm coexistence of MoS₂ and ZnIn₂S₄ in the composite.

3.3. XPS analysis

To determine the chemical composition and the valence states of the constituent species, XPS was performed. Fig. 3(a) shows the XPS survey spectra of pure ZnIn₂S₄ and the 1 wt% MoS₂/ZnIn₂S₄ composite. In the survey spectrum of the 1 wt% MoS₂/ZnIn₂S₄ composite, there is a weak Mo 3p peak, indicating that the composite contains little Mo. The Zn 2p spectra are shown in Fig. 3(b). In the high-resolution Zn 2p XPS spectrum of ZnIn₂S₄, the peaks at binding energies of 1045 and 1022 eV can be attributed to Zn 2p_{1/2} and Zn 2p_{3/2}, respectively. The Zn 2p peaks are slightly shifted in the spectrum of the 1 wt% MoS₂/ZnIn₂S₄ composite. Fig. 3(c) shows the high-resolution In 3d XPS spectra. The peaks at about 445.0 and 452.5 eV are assigned to In 3d_{5/2} and In 3d_{3/2}. Compared with pure ZnIn₂S₄, the In 3d XPS peaks for the 1 wt% MoS₂/ZnIn₂S₄ composite are shifted toward higher binding energy. The high-resolution Mo 3d XPS spectra are shown in Fig. 3(d). The peaks at 229.6 and 233.1 eV are attributed to Mo 3d_{5/2} and Mo 3d_{3/2}, in accordance with a previous report [56]. The high-resolution S 2p XPS spec-

Fig. 1. XRD patterns of ZnIn₂S₄, MoS₂, and MoS₂/ZnIn₂S₄ composites with different mass ratios.

Fig. 2. FESEM images of ZnIn₂S₄ (a), MoS₂ (b), and 1 wt% MoS₂/ZnIn₂S₄ (c). TEM image (d), HRTEM image (e), and EDS (f) of the 1 wt% MoS₂/ZnIn₂S₄ composite.

trum of ZnIn₂S₄ can be fitted as two peaks (Fig. 3(e)). The peaks at binding energies of 161.8 and 162.9 eV are associated with S 2p_{3/2} and S 2p_{1/2}, respectively. Similar to the Zn 2p and In 3d peaks, the S 2p peaks in the MoS₂/ZnIn₂S₄ composite are also shifted to higher values. These shifts are indicative of electronic interaction and transfer between ZnIn₂S₄ and MoS₂, which is in agreement with a previous report [59]. The XPS results confirm close contact between ZnIn₂S₄ and MoS₂.

3.4. Raman analysis

Raman spectroscopy is a useful technique to investigate the microscopic structures of samples. Fig. 4 shows the Raman spectra of ZnIn₂S₄ and the 1 wt% MoS₂/ZnIn₂S₄ composite. For

ZnIn₂S₄, there are five characteristic peaks at 121, 243, 294, 343, and 367 cm⁻¹, which is consistent with a previous report. The strong peak at 121 cm⁻¹ confirms the layered structure of ZnIn₂S₄, and the other four peaks are related to the LO₁, TO₂, LO₂, and A_{1g} modes of ZnIn₂S₄ [37]. For the 1 wt% MoS₂/ZnIn₂S₄ composite, the Raman peaks corresponding to ZnIn₂S₄ are present in the spectrum. The Raman peaks of MoS₂ are also present at about 382 and 408 cm⁻¹, which can be attributed to the E_{2g} and A_{1g} modes of MoS₂ [53]. In the spectrum of the 1 wt% MoS₂/ZnIn₂S₄ composite, the representative peaks of ZnIn₂S₄ have shifted from 121 to 128 cm⁻¹ and from 294 to 304 cm⁻¹ compared with the spectrum for ZnIn₂S₄. These red shifts indicate the strong interaction between ZnIn₂S₄ and MoS₂, which is in agreement with the XPS investi-

Fig. 3. XPS spectra of ZnIn₂S₄ and the 1 wt% MoS₂/ZnIn₂S₄ composite. (a) XPS survey; (b) Zn 2p; (c) In 3d; (d) Mo 3d; (e) S 2p.

Fig. 4. Raman spectra of ZnIn_2S_4 and the 1 wt% $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ composite.

gation.

3.5. UV-vis diffuse reflectance absorption spectroscopy analysis

UV-vis diffuse reflectance absorption spectroscopy was performed to investigate the optical absorption properties of the samples (Fig. 5). Pure ZnIn_2S_4 exhibits a strong absorption band edge at about 525 nm, which is related to the intrinsic band gap absorption. Using the equation $E_g = 1240/\lambda$, where E_g and λ are the band gap energy and absorption band edge of the semiconductor, the band gap energy of ZnIn_2S_4 is about 2.36 eV. Notably, the $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ composite shows enhanced absorption intensity in the visible region compared with pure ZnIn_2S_4 . Furthermore, the absorption intensity increases with increasing mass ratio of MoS_2 in the composite, which is consistent with the color of the samples changing from light yellow to black.

3.6. BET analysis

The BET surface areas and pore size distribution curves of

Fig. 5. UV-vis diffuse reflectance absorption spectra and optical photographs of ZnIn_2S_4 (a), 0.5 wt% $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ (b), 1 wt% $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ (c), 3 wt% $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ (d), 5 wt% $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ (e), 10 wt% $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ (f), and MoS_2 (g).

pure ZnIn_2S_4 , MoS_2 , and the 1 wt% $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ composite were obtained by nitrogen adsorption-desorption measurements (Fig. 6). The three isotherms are very similar and type IV according to the Brunauer-DeMing-DeMing-Teller classification. Furthermore, the shapes of the hysteresis loops in the range 0.5–1.0 P/P_0 are type H3, which indicates formation of porous structures in the samples. The BET specific surface areas of pure ZnIn_2S_4 , MoS_2 , and the 1 wt% $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ composite are estimated to be 56.0, 48.9, and 49.9 m^2/g , respectively. The pore size distribution curves indicate that the samples exhibit wide pore size distributions (20 to 300 nm), verifying the presence of mesopores and macropores in the samples.

3.7. Photocatalytic H_2 evolution activity

The photocatalytic H_2 evolution activities of the samples with different mass ratios of MoS_2 were evaluated under visible light irradiation using lactic acid as a sacrificial reagent. For comparison, photocatalytic H_2 evolution experiments of pure ZnIn_2S_4 treated by the second hydrothermal procedure (denoted as the reference sample) and 1 wt% Pt-loaded ZnIn_2S_4 were also performed under the same reaction conditions. The results are shown in Fig. 7. Pure ZnIn_2S_4 and ZnIn_2S_4 treated by the second hydrothermal procedure show poor photocatalytic H_2 evolution activity with H_2 evolution rates of 23 and 45 $\mu\text{mol}/\text{h}$, respectively, which can be ascribed to fast recombination of the photogenerated electron-hole pairs and the deficiency of reactive active sites. The slight enhancement of the photocatalytic H_2 evolution activity for ZnIn_2S_4 treated by the second hydrothermal procedure may be because of the increase of the crystallinity of ZnIn_2S_4 . When a small amount of MoS_2 is added to ZnIn_2S_4 to form a composite, the photocatalytic H_2 evolution activity markedly improves. With increasing MoS_2 content, the photocatalytic activity initially increases and then decreases. When the MoS_2 amount in the composites is about 1 wt%, the H_2 evolution rate reaches the highest value of 343 $\mu\text{mol}/\text{h}$, corresponding to an AQE of about 3.85% at 420 nm monochromatic light. The 1 wt% $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ composite has a 14.9 times faster H_2 evolution rate than pure ZnIn_2S_4 un-

Fig. 6. Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves of ZnIn_2S_4 , MoS_2 , and the 1 wt% $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ composite.

Fig. 7. Comparison of the photocatalytic H_2 evolution rates of different samples.

der visible light illumination. The H_2 evolution rate decreases with increasing amount of MoS_2 above 1 wt%. This may be because MoS_2 covers the active sites on the surface of $ZnIn_2S_4$ and shields light absorption of $ZnIn_2S_4$, which might influence excitation of $ZnIn_2S_4$. As a control, the photocatalytic H_2 evolution rate of 1 wt% Pt-loaded $ZnIn_2S_4$ is only 120 $\mu\text{mol/h}$ under the same conditions, which is lower than that of the 1 wt% $MoS_2/ZnIn_2S_4$ composite. This indicates that MoS_2 is a suitable substitute for Pt in cocatalysts for the photocatalytic H_2 evolution reaction.

The photocatalytic stability of a semiconductor is crucial for its practical application. The photostability of $ZnIn_2S_4$ and the 1 wt% $MoS_2/ZnIn_2S_4$ composite were investigated in three consecutive runs with a total time of 15 h with the sacrificial reagent solution periodically replaced in each run (Fig. 8). The photocatalytic H_2 evolution rate decreases because of consumption of the sacrificial reagent in each run. When the sacrificial reagent solution is changed, the photocatalytic H_2 evolution activity recovers. In the third run, the photocatalytic H_2 evolution activity of the $MoS_2/ZnIn_2S_4$ composite exhibits a slight decrease, indicating that photocorrosion occurs. The crystal phase of the recycled 1 wt% $MoS_2/ZnIn_2S_4$ composite after 15 h photocatalytic reaction was determined by XRD (Fig.

Fig. 8. Stability of photocatalytic H_2 evolution over $ZnIn_2S_4$ and the 1 wt% $MoS_2/ZnIn_2S_4$ composite.

Fig. 9. XRD patterns of the fresh and used 1 wt% $MoS_2/ZnIn_2S_4$ composite.

9). The intensities of the diffraction peaks in the XRD pattern of the used sample decrease compared with those before the reaction, suggesting that photocorrosion occurred during the photocatalytic reaction.

EIS tests were performed to investigate interfacial charge transfer and the separation efficiency over pure $ZnIn_2S_4$ and the 1 wt% $MoS_2/ZnIn_2S_4$ composite. As shown in Fig. 10(a), the diameter of the Nyquist circle for the 1 wt% $MoS_2/ZnIn_2S_4$ composite is less than that for pure $ZnIn_2S_4$, indicating that the composite has more rapid interfacial charge transfer and effective charge separation, which is beneficial for improvement of the photocatalytic H_2 evolution activity. Transient photocurrent response measurements were also performed to verify effective charge transfer and separation in the $MoS_2/ZnIn_2S_4$ composite. Generally, the photocurrent is caused by diffusion of

Fig. 10. EIS Nyquist plots (a) and transient photocurrent responses (b) of $ZnIn_2S_4$ and the 1 wt% $MoS_2/ZnIn_2S_4$ composite.

photogenerated electrons to the back contact and photogenerated hole capture by electron donors in the electrolyte [60]. In Fig. 10(b), the photocurrent density of the 1 wt% MoS₂/ZnIn₂S₄ composite is higher than that of pure ZnIn₂S₄, which suggests that the MoS₂/ZnIn₂S₄ composite undergoes more effective charge transfer and separation than ZnIn₂S₄. PL spectroscopy was also performed to investigate the separation efficiency and recombination of photogenerated charge carriers (Fig. 11). The 1 wt% MoS₂/ZnIn₂S₄ composite exhibits a lower PL peak intensity than pure ZnIn₂S₄, indicating that the charge carrier recombination rate of the MoS₂/ZnIn₂S₄ composite is suppressed under visible light irradiation. These results confirm that coupling MoS₂ with ZnIn₂S₄ to form a composite can facilitate separation of photogenerated electron–hole pairs.

Based on the above results, a possible mechanism for the improvement in the photocatalytic H₂ evolution activity is shown in Fig. 12. The conduction band (CB) and valence band (VB) potentials of ZnIn₂S₄ were estimated by the empirical equation $E_{CB} = \chi - E^c - 0.5E_g$, where E_{CB} is the CB potential, χ is the electronegativity of the semiconductor, which is the geometric mean of the electronegativities of the constituent atoms, and E^c is the energy of free electrons on the hydrogen scale (about 4.5 eV). For ZnIn₂S₄, the calculated χ and E_g values are 4.82 and 2.36 eV, respectively [45]. Thus, the E_{CB} value of

ZnIn₂S₄ is estimated to be −0.86 eV. Using the equation $E_{VB} = E_{CB} + E_g$, the VB potential $E_{VB} = 1.50$ eV. For MoS₂, $E_{CB} = -0.12$ eV and $E_g = 1.8$ eV versus the normal hydrogen electrode potential [54,58]. Under visible light irradiation, the photogenerated electrons are easily excited from the VB to the CB of ZnIn₂S₄. Because of the matched energy band positions of ZnIn₂S₄ and MoS₂, the photoexcited electrons can easily transfer from ZnIn₂S₄ to MoS₂, which promotes separation and suppresses recombination of the photogenerated electron–hole pairs. MoS₂ then acts as active sites to reduce H⁺ to H₂. The holes in the VB of ZnIn₂S₄ would be consumed by the sacrificial reagent to generate the oxidation products. Therefore, this coupled system is not only favorable for separation of photogenerated electron–hole pairs, but it also improves the photocatalytic H₂ evolution activity.

4. Conclusions

MoS₂/ZnIn₂S₄ composites have been fabricated by a two-step hydrothermal process and applied to photocatalytic H₂ evolution with lactic acid as a sacrificial reagent. A remarkable improvement in photocatalytic H₂ evolution activity is achieved by adding a small amount of MoS₂ to ZnIn₂S₄, which can be attributed to efficient transfer and separation of photogenerated electron–hole pairs. Among the composites, the 1 wt% MoS₂/ZnIn₂S₄ composite shows the highest photocatalytic H₂ evolution rate of 343 $\mu\text{mol/h}$ under visible light irradiation, which is even higher than that of 1 wt% Pt-loaded ZnIn₂S₄. The corresponding AQE is about 3.85% at 420 nm monochromatic light. This work provides an approach to prepare high-performance MoS₂-based photocatalysts for many potential applications.

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Fig. 11. PL spectra of ZnIn₂S₄ and the 1 wt% MoS₂/ZnIn₂S₄ composite.

Fig. 12. Proposed photocatalytic H₂ evolution mechanism of the MoS₂/ZnIn₂S₄ composite.

Graphical Abstract

Chin. J. Catal., 2017, 38: 2067–2075 doi: 10.1016/S1872-2067(17)62981-4

Photocatalytic hydrogen evolution activity over MoS₂/ZnIn₂S₄ microspheres

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A MoS₂/ZnIn₂S₄ composite with MoS₂ anchored on the surface of ZnIn₂S₄ microspheres was synthesized by a two-step hydrothermal process. The marked improvement in photocatalytic H₂ evolution activity compared with pure ZnIn₂S₄ can be ascribed to efficient transfer and separation of photogenerated charge carriers and facilitation of the photocatalytic H₂ evolution reaction at the MoS₂ active sites.

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MoS₂修饰ZnIn₂S₄微米球复合光催化剂的制备及光催化制氢活性增强研究

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摘要: 开发高效、稳定的半导体光催化材料是太阳能光催化制氢领域的研究热点, ZnIn₂S₄因其合适的能隙、带边电势位置以及稳定、低毒等优点而受到广泛关注. 但在实际应用中, 单纯的ZnIn₂S₄光催化制氢活性仍较低, 主要原因是ZnIn₂S₄受激产生光生电子-空穴对后, 载流子的传输、分离效果不理想, 易在体相或表面复合; 再者是单一的ZnIn₂S₄表面缺少催化反应产氢的活性位点. 为提高催化活性, 通常在催化剂的表面负载一定量的贵金属作为助催化剂, 但由于贵金属成本高和稀缺性, 限制了其实际应用. 因此, 开发低成本、储量丰富、高效的非贵金属助催化剂来增强ZnIn₂S₄的光催化制氢活性具有显著意义.

最近研究表明, 具有层状结构的MoS₂可被作为一种非贵金属助催化剂应用于光催化制氢, 且已取得了优异的光催化制氢效果. 理论计算得出, 暴露在MoS₂边缘的不饱和S原子具有与质子H⁺很强的键合作用, 从而使其能够作为活性位点便利地产生氢气. 因而将MoS₂负载于ZnIn₂S₄的表面, 可进一步提高ZnIn₂S₄的光催化制氢活性.

本文采用二步水热法制备了MoS₂负载于ZnIn₂S₄微球表面的MoS₂/ZnIn₂S₄复合光催化剂. 采用X-射线衍射、场发射扫描电子显微镜、透射电子显微镜、X射线光电子能谱、Raman光谱、紫外-可见漫反射吸收光谱、氮气吸附-脱附测试和荧光光谱等技术对所得样品进行了表征. 以乳酸作为牺牲试剂考察了MoS₂负载量对光催化制氢活性的影响. 结果显示, 当MoS₂含量为1 wt%时, MoS₂/ZnIn₂S₄复合光催化剂的光催化产氢活性最高, 达343 μmol/h, 是单纯ZnIn₂S₄的14.9倍. 此外, 对1 wt% MoS₂/ZnIn₂S₄样品进行光催化制氢的长效循环测试表明, 该样品在可见光下能够保持稳定、有效的光催化制氢性能. 据此提出一个可能的增强光催化制氢活性机理: 适量的MoS₂可以促进ZnIn₂S₄表面光生载流子的有效传输和分离, 从而延长载流子的寿命.

关键词: 复合物; 助催化剂; 光催化产氢; 电荷载流子; 分离

收稿日期: 2017-10-09. 接受日期: 2017-10-31. 出版日期: 2017-12-05.

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基金来源: 国家自然科学基金(51302200).

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