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Article (Special Issue on Photocatalytic H₂ Production and CO₂ Reduction)**Facile fabrication of ZnIn₂S₄/SnS₂ 3D heterostructure for efficient visible-light photocatalytic reduction of Cr(VI)**

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ABSTRACT

Photocatalytic method has been intensively explored for Cr(VI) reduction owing to its efficient and environmentally friendly natures. In order to obtain a high efficiency in practical application, efficient photocatalysts need to be developed. Here, ZnIn₂S₄/SnS₂ with a three-dimensional (3D) heterostructure was prepared by a hydrothermal method and its photocatalytic performance in Cr(VI) reduction was investigated. When the mass ratio of SnS₂ to ZnIn₂S₄ is 1:10, the ZnIn₂S₄/SnS₂ composite exhibits the highest photocatalytic activity with 100% efficiency for Cr(VI) (50 mg/L) reduction within 70 min under visible-light irradiation, which is much higher than those of pure ZnIn₂S₄ and SnS₂. The enhanced charge separation and the light absorption have been confirmed from the photoluminescence and UV-vis absorption spectra to be the two reasons for the increased activity towards photocatalytic Cr(VI) reduction. In addition, after three cycles of testing, no obvious degradation is observed with the 3D heterostructured ZnIn₂S₄/SnS₂, which maintains a good photocatalytic stability.

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1. Introduction

Currently, serious hexavalent chromium (Cr(VI)) pollution of industrial wastewater due to the growth of the printing, dyeing, and chrome plating industry is threatening the sustainable development of human society [1–4]. In this study, several methods have been employed for treating the Cr(VI) present in waste water, including ion exchange, membrane separation, chemical absorption, etc. [5–8]. However, these methods display the disadvantages of high energy consumption, high cost, and/or incomplete removal of heavy metal ions, which hinder their widespread applications. Photocatalysis as a highly efficient and green method of treating Cr(VI) has been

receiving more and more attention recently [9–11]. After Yoneyama et al. [12] first reported that the reduction of Cr(VI) can be realized by using oxide semiconductor photocatalysts under illumination, it opened up a new pathway for eliminating Cr(VI). Much research focused on the development of different efficient photocatalysts for treating Cr(VI). Among these photocatalysts, TiO₂ is an inexpensive and non-toxic photocatalyst, but it only absorbs ultraviolet light [13–15]. In order to improve the usability of the solar energy, development of visible-light-responsive photocatalysts is essential [16–23]. Metal sulfide semiconductors, which are a superior type of visible-light-driven photocatalysts, are efficient in absorbing visible light [24–30].

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ZnIn₂S₄, as an excellent ternary metal sulfide semiconductor material, exhibits absorption ability in the visible-light range [31–36]. However, the photocatalytic activity of pure ZnIn₂S₄ is inefficient owing to its high charge recombination rate and narrow visible-light-response range [37,38]. In order to solve these issues, constructing a heterojunction is a common and effective method that has been employed [39–42]. Zhang et al. [43] prepared ZnIn₂S₄/CdS composite, which revealed remarkably enhanced photocatalytic Cr(VI) reduction activity under visible-light irradiation. However, CdS contains the toxic Cd element. Xu et al. [44] synthesized heterostructured CaIn₂S₄/ZnIn₂S₄ for the photocatalytic reduction of Cr(VI). However, it is necessary to add ammonium oxalate as a sacrificial agent to obtain a highly efficient photocatalytic reduction performance; this agent may contaminate the water, apart from increasing the cost. Therefore, it is imperative to consider a suitable semiconductor material for constructing the heterojunction. SnS₂ is commonly used for Cr(VI) reduction because it is inexpensive and non-toxic, and displays strong visible-light absorption ability owing to its suitable band gap ($E_g = \sim 2.2$ eV) [45,46]. Therefore, it is feasible to construct ZnIn₂S₄/SnS₂ heterojunction for efficient photocatalytic reduction of Cr(VI).

In this study, ZnIn₂S₄/SnS₂ 3D heterojunctions were prepared and the photocatalytic reduction efficiencies of Cr(VI) of the photocatalysts were evaluated under visible-light irradiation. Compared with those of pure SnS₂ and ZnIn₂S₄, the reduction efficiency of Cr(VI) over ZnIn₂S₄/SnS₂ 3D heterojunction is significantly improved. Furthermore, the possible mechanism of photocatalytic reduction of Cr(VI) over ZnIn₂S₄/SnS₂ composites is proposed.

2. Experimental

2.1. Synthesis of ZnIn₂S₄ photocatalysts

The ZnIn₂S₄ photocatalysts were prepared by a hydrothermal method. First, ZnCl₂ (0.136 g, 1 mmol), InCl₃·4H₂O (0.586 g, 2 mmol), and thioacetamide (0.46 g, 6 mmol) were successively added to 60 mL distilled water and stirred for 30 min. The mixed solution was then transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 220 °C for 24 h. After cooling to room temperature, solid powders were collected by centrifugation and washed three times using distilled water and ethanol. Finally, the ZnIn₂S₄ powders were vacuum dried at 60 °C for 12 h.

2.2. Synthesis of ZnIn₂S₄/SnS₂ composite photocatalysts

The ZnIn₂S₄/SnS₂ composite photocatalysts were prepared by the hydrothermal method. In a typical synthesis, ZnIn₂S₄ (20 mg) was first dispersed in a 60 mL aqueous solution. SnCl₄·5H₂O (384 mg) and excess L-cysteine were added to the above aqueous solution step by step under vigorous stirring. The mixed solution was then transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 190 °C for 6 h in an electric oven. After the reaction, the ZnIn₂S₄/SnS₂ composite powders were collected via centrifugation and washed

three times with deionized water. Finally, the ZnIn₂S₄/SnS₂ was dried under vacuum for 12 h and named as ZnIn₂S₄+10%SnS₂, in which 10% presents the mass proportion of SnS₂ relative to the mass of ZnIn₂S₄. Other ZnIn₂S₄/SnS₂ composite photocatalysts with different mass ratios of SnS₂ to ZnIn₂S₄ were also synthesized using the same method. For comparison, a pure SnS₂ sample was prepared using the same procedure without adding ZnIn₂S₄.

2.3. Characterization of the photocatalysts

The crystal structures of the photocatalysts were analyzed by an X-ray diffractometer (Bruker D8-AVANCE, Germany) and Raman spectroscopy (LaBRAM HR800, He-Ne laser as the excitation source (532 nm)). The morphologies of the samples were characterized by SEM (JSM-7001F, FEI Co.) and TEM (JEM-2100, Japan). The surface chemical states and the valence band XPS patterns of the samples were obtained by using an X-ray photoelectron spectrometer (Thermo ESCALAB 250Xi). The UV-vis diffuse reflectance spectra (DRS) of the samples were recorded on a UV-vis spectrophotometer (U-3010, Shimadzu). The photoluminescence (PL) spectra of the samples were recorded using a F-7000 FL spectrophotometer with an excitation wavelength of 420 nm. The specific surface areas of the samples were measured through N₂ adsorption-desorption experiments and calculated according to the Brunauer-Emmett-Teller method. The actual SnS₂ contents of the composites were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Optima-7300DV, PE, USA).

2.4. Photoelectrochemical measurements

The photocurrents and the electrochemical impedance spectra of the samples were recorded using an electrochemical workstation (Chenhua CHI660E, China). The photocurrent curves of the samples were recorded using a three-electrode system, in which a Pt wire, a saturated calomel electrode (SCE), and the prepared photoelectrode acted as the counter electrode, reference electrode, and working electrode, respectively. The light source was a 300 W Xe lamp with a 420 nm cut-off filter. Aqueous Na₂SO₄ solution (0.1 mol/L) was employed as the electrolyte. The working photoelectrodes were prepared by dropping the powder-ethanol mixture on FTO substrates several times. Finally, the prepared photoelectrodes were annealed at 300 °C for 1 h under N₂ atmosphere.

2.5. Photocatalytic activity measurements

The photocatalytic performances of the ZnIn₂S₄/SnS₂ composite photocatalysts, as well as those of pure SnS₂ and ZnIn₂S₄, were evaluated for the reduction of Cr(VI) under visible-light irradiation. Typically, 50 mg of the catalyst was added into a 100 mL solution with the Cr(VI) concentration of 50 mg/L, which was prepared by dissolving dried K₂Cr₂O₇ in distilled water. Prior to illumination, the reaction solutions were magnetically stirred for 20 min in the dark to reach adsorp-

Fig. 1. (a) XRD patterns and (b) Raman spectra of pure ZnIn₂S₄, SnS₂, and ZnIn₂S₄/SnS₂ composites with different mass ratios of SnS₂ to ZnIn₂S₄.

tion-desorption equilibrium. As the photocatalytic reduction proceeded, 3 mL of the reaction solution was taken out at given time intervals and centrifuged (12000 rpm/10 min) to remove the photocatalyst particles. Finally, the concentrations of Cr(VI) were measured by the standard diphenylcarbazide method ($\lambda_{\max} = 540$ nm) [43]. The kinetic curves were calculated using the pseudo-first-order kinetic model [3,45]:

$$\ln(C_0/C_t) = kt$$

where t is the irradiation time, k is the kinetic rate constant, C_0 is the initial concentration of Cr(VI), and C_t is the concentration of Cr(VI) at time t . In order to demonstrate the stability of the photocatalyst, three recycle experiments were carried out using the ZnIn₂S₄+10%SnS₂ composite sample. After each recycle experiment, the photocatalyst was soaked in nitric acid (1 mol/L) for a certain time to remove the Cr-containing precipitate.

3. Results and discussion

3.1. Characterization of the photocatalysts

Fig. 1(a) shows the XRD patterns of pure ZnIn₂S₄, SnS₂, and ZnIn₂S₄/SnS₂ composites with different mass ratios of SnS₂ to ZnIn₂S₄. For pure ZnIn₂S₄, the six strong diffraction peaks observed at 21.6°, 27.7°, 30.5°, 47.2°, and 52.4° are assigned to the (006), (102), (104), (110), and (116) crystal planes of hexago-

nal ZnIn₂S₄ (JCPDS card no. 65-2023), respectively. As for pure SnS₂, the main peaks are observed at 15.21°, 28.13°, 32.08°, 50.12°, and 52.45°, which can be attributed to the (001), (100), (101), (110), and (111) crystal planes of hexagonal SnS₂ (JCPDS card no. 23-0677), respectively. However, the characteristic diffraction peaks of SnS₂ cannot be obviously observed in the cases of the ZnIn₂S₄/SnS₂ composites. Therefore, the more sensitive Raman spectroscopy was employed to detect the SnS₂ phase, and the results are shown in Fig. 1(b). ZnIn₂S₄ shows four peaks at 72, 112, 245, and 366 cm⁻¹ [47,48], whereas the strong peak at 312 cm⁻¹ is assigned to SnS₂ [45]. As the content of SnS₂ increases, the Raman characteristic peak intensity of SnS₂ at 312 cm⁻¹ becomes stronger for the ZnIn₂S₄/SnS₂ composite photocatalysts. However, it must be mentioned that the characteristic peaks of SnS₂ cannot be obviously observed even in the ZnIn₂S₄ + 30%SnS₂ sample. A possible reason is that the SnS₂ present in the ZnIn₂S₄/SnS₂ composites is of poor crystal quality. ZnIn₂S₄ displays a great influence on the crystal quality of SnS₂ during the hydrothermal process. Fig. 2(a) shows the UV-vis DRS of pure ZnIn₂S₄, SnS₂, and ZnIn₂S₄/SnS₂ composites with different mass ratios of SnS₂ to ZnIn₂S₄. The absorption band edge of pure ZnIn₂S₄ is about 540 nm, corresponding to a band gap of 2.26 eV (see Fig. 2(b)). Pure SnS₂ exhibits an absorption band edge at about 630 nm and the band gap is 1.97 eV (see Fig. 2(b)). The visible-light absorption of ZnIn₂S₄ is slightly enhanced for the ZnIn₂S₄+10%SnS₂ and

Fig. 2. (a) UV-vis absorption DRS of pure ZnIn₂S₄, SnS₂, and ZnIn₂S₄/SnS₂ composites with different mass ratios of SnS₂ to ZnIn₂S₄; (b) Plots of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for pure ZnIn₂S₄ and SnS₂.

Fig. 3. SEM images of (a and b) pure ZnIn_2S_4 and (d and e) $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ composite. (c) TEM image of pure SnS_2 and (f) HRTEM image of $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ sample.

$\text{ZnIn}_2\text{S}_4+20\%\text{SnS}_2$ samples owing to the relatively low contents of SnS_2 . The visible-light absorption of ZnIn_2S_4 is obviously improved when the amount of SnS_2 increases to 30 wt%.

The morphologies of pure ZnIn_2S_4 , SnS_2 , and $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ composite are shown in Fig. 3. Pure ZnIn_2S_4 exhibits a flower-like microsphere structure with a particle diameter of about 7 μm ; this structure is composed of nanosheets with the thickness of about 20 nm (see Fig. 3(a) and 3(b)). Pure SnS_2 also displays a nanosheet structure with a lateral size of about 100 nm (see Fig. 3(c)). The nanosheet structure will provide a large surface area for the absorption and reduction of Cr(VI) . In Fig. 3(d) and 3(e), after the hydrothermal reaction, the SnS_2 nanosheets are dispersed on the surface of ZnIn_2S_4 and the microsphere structure of ZnIn_2S_4 does not

collapse. In Fig. 3(f), the lattice spacing of 0.33 nm corresponds to the (102) plane of ZnIn_2S_4 . On the other hand, the lattice fringes with the spacing of 0.29 nm observed can be attributed to the (101) crystal plane of SnS_2 . The EDS elemental mapping images of Zn, In, S, and Sn of the $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ sample are shown in Fig. S1. The elements Zn, In, S, and Sn are uniformly distributed in the $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ composite. These results suggest that the $\text{ZnIn}_2\text{S}_4/\text{SnS}_2$ heterostructure has been successfully synthesized.

The surface chemical states of the $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ composite sample were also investigated, and the results are shown in Fig. 4. In Fig. 4(a), the high-resolution Zn 2p spectrum displays two peaks at 1021.47 and 1044.53 eV, which correspond to Zn 2p_{3/2} and Zn 2p_{1/2} binding energies, respectively, which confirm the existence of Zn^{2+} . As shown in Fig. 4(b), the two binding energy values of In 3d_{5/2} and In 3d_{3/2} at 444.69 and 452.25 eV can be attributed to In^{3+} . Fig. 4(c) shows two peaks at 161.58 and 162.43 eV, which correspond to S 2p_{3/2} and S 2p_{1/2} binding energies, respectively. In addition, two strong peaks at 486.47 and 494.95 eV that correspond to the Sn 3d_{5/2} and Sn 3d_{3/2} binding energies, respectively, of Sn^{4+} are also observed (see Fig. 4(d)) [45,49]. A small peak appears close to each of the main binding energy peaks of In 3d and Sn 3d in the case of the $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ sample, which indicates a positive binding energy shift of about 2 eV (see Fig. 4(b) and 4(d)). However, no small peaks can be observed for the pure ZnIn_2S_4 and SnS_2 samples (see Fig. S2(c) and S2(d)). The small peaks of the twin peaks may be caused by the introduction of additional O during the hydrothermal process. The binding energies of In

Fig. 4. High-resolution XPS spectra of (a) Zn 2p, (b) In 3d, (c) S 2p, and (d) Sn 3d of $\text{ZIS}+10\%\text{SnS}_2$ composite.

3d and Sn 3d usually show shifts toward higher values when the In and Sn elements couple with O [50,51]. The increased content of O in the $\text{ZnIn}_2\text{S}_4+10\% \text{SnS}_2$ sample is also confirmed by EDS characterization (see Table S1). For comparison, the XPS patterns of the pure ZnIn_2S_4 , SnS_2 , and $\text{ZnIn}_2\text{S}_4+10\% \text{SnS}_2$ samples were also obtained, and the results are shown in Fig. S3. Compared with that of pure ZnIn_2S_4 , the Zn 2p binding energy of the $\text{ZnIn}_2\text{S}_4+10\% \text{SnS}_2$ sample shows a shift towards lower values (see Fig. S3(a)). On the other hand, the Sn 3d binding energy of the $\text{ZnIn}_2\text{S}_4+10\% \text{SnS}_2$ sample slightly shifts to a higher value, compared with the case of pure SnS_2 (see Fig. S3(b)). These results indicate that there is a strong interfacial chemical interaction between ZnIn_2S_4 and SnS_2 , which will promote the interfacial charge transfer. On the basis of the above results, it can be concluded that $\text{ZnIn}_2\text{S}_4/\text{SnS}_2$ 3D heterostructures have been fabricated. The actual contents of SnS_2 in the $\text{ZnIn}_2\text{S}_4+10\% \text{SnS}_2$, $\text{ZnIn}_2\text{S}_4+20\% \text{SnS}_2$, and $\text{ZnIn}_2\text{S}_4+30\% \text{SnS}_2$ samples were measured by ICP-AES. The mass proportions of SnS_2 relative to the mass of ZnIn_2S_4 are 7.97%, 17.37%, and 24.31% for the $\text{ZnIn}_2\text{S}_4+10\% \text{SnS}_2$, $\text{ZnIn}_2\text{S}_4+20\% \text{SnS}_2$, and $\text{ZnIn}_2\text{S}_4+30\% \text{SnS}_2$ samples, respectively.

3.2. Photocatalytic reduction of Cr(VI)

The Cr(VI) reduction efficiencies of pure ZnIn_2S_4 , SnS_2 , and $\text{ZnIn}_2\text{S}_4/\text{SnS}_2$ composites with different mass ratios of SnS_2 to ZnIn_2S_4 were evaluated, and the results are shown in Fig. 5. In Fig. 5(a), the concentration of Cr(VI) reveals no change in the

absence of a photocatalyst. After the addition of the photocatalyst, the concentration of Cr(VI) decreases obviously. These results suggest that the reduction of Cr(VI) can occur only as a photocatalytic reaction. Bare ZnIn_2S_4 and SnS_2 show low photocatalytic reduction activities. An enhanced photocatalytic reduction efficiency is observed by using $\text{ZnIn}_2\text{S}_4/\text{SnS}_2$ 3D heterostructure composites. $\text{ZnIn}_2\text{S}_4+10\% \text{SnS}_2$ exhibits the highest photocatalytic reduction efficiency of 80.2% after 120 min of the reaction. The $\text{ZnIn}_2\text{S}_4/\text{SnS}_2$ 3D heterojunction facilitates the photogenerated charge carrier separation, thus improving the photocatalytic reduction activity. Upon increasing the amount of SnS_2 further, the photocatalytic reduction activity decreases, because of the poor activity of SnS_2 . To quantitatively analyze the photocatalytic performances, the kinetic curves of the photocatalytic Cr(VI) reduction carried out with the different photocatalysts were obtained, as shown in Fig. 5(b). The kinetic rate constant (k value) of the $\text{ZnIn}_2\text{S}_4+10\% \text{SnS}_2$ sample is 0.01273, which is 1.43 and 2.28 times higher than those of pure ZnIn_2S_4 (0.00893) and SnS_2 (0.00558), respectively. The amount of photocatalyst has an important impact on the reduction efficiency of Cr(VI). Therefore, the effect of $\text{ZnIn}_2\text{S}_4+10\% \text{SnS}_2$ sample dosage on the degradation activity of Cr(VI) was investigated, and the results are presented in Fig. 5(c). As the amount of photocatalyst increases, the reduction efficiencies of Cr(VI) are remarkably improved. The reduction efficiency reaches 100% after 120 min of the reaction when the amount of $\text{ZnIn}_2\text{S}_4+10\% \text{SnS}_2$ sample is 75 mg. If the photocatalyst dosage is further increased, the reduction efficiency can reach 100% in a shorter time. The kinetic rate constants are

Fig. 5. (a) Efficiencies and (b) kinetic curves of Cr(VI) reduction over pure ZnIn_2S_4 , SnS_2 , and $\text{ZnIn}_2\text{S}_4/\text{SnS}_2$ composites with different mass ratios of SnS_2 to ZnIn_2S_4 . Initial Cr(VI) concentration: 50 mg/L; photocatalyst dosage: 50 mg. (c) Efficiencies and (d) kinetic curves of Cr(VI) reduction over different amounts of $\text{ZnIn}_2\text{S}_4+10\% \text{SnS}_2$ sample. (e and f) UV-vis absorption spectra of aqueous Cr(VI) after photocatalytic reduction over different amounts of $\text{ZnIn}_2\text{S}_4+10\% \text{SnS}_2$ sample.

Fig. 6. (a) Cyclic performance of ZnIn₂S₄+10%SnS₂ sample in the photocatalytic reduction of Cr(VI). Initial Cr(VI) concentration: 50 mg/L; photocatalyst dosage: 100 mg. (b) XRD patterns of ZnIn₂S₄+10%SnS₂ sample before and after the cyclic test.

consistent with the reduction efficiencies, indicating that a higher photocatalyst dosage results in a larger kinetic rate constant (see Fig. 5(d)). From Fig. 5(e) and 5(f), the absorption peak of aqueous Cr(VI) is located at about 540 nm [52]. As the photocatalytic reaction time increases, the intensity of the absorption peak decreases. The intensity decreases faster for a higher photocatalyst dosage. A comparison of the reduction efficiencies obtained when using ZnIn₂S₄ or SnS₂ photocatalyst with similar dosages is shown in Table S2. The ZnIn₂S₄/SnS₂ 3D heterostructure is advantageous for the photocatalytic reduction of Cr(VI). The stability of the photocatalyst is an important factor for practical application. Cyclic experiments were conducted, and the results are shown in Fig. 6(a). The reduction rate of Cr(VI) does not obviously decrease after three cycles, which indicates the stability of ZnIn₂S₄/SnS₂ composite. The XRD patterns of the ZnIn₂S₄+10%SnS₂ sample before and after the cyclic test are displayed in Fig. 6(b). There is no obvious change in the XRD pattern, which further confirms that the ZnIn₂S₄/SnS₂ composite is relatively stable.

3.3. Mechanism of the enhanced photocatalytic performance of ZnIn₂S₄/SnS₂ 3D heterostructure

In order to reveal the mechanism of how the ZnIn₂S₄/SnS₂ 3D heterostructure enhances its photocatalytic performance, the PL spectra of the pure ZnIn₂S₄, ZnIn₂S₄+10%SnS₂, and ZnIn₂S₄+20%SnS₂ samples were recorded, and the results are shown in Fig. 7. The PL peak of ZnIn₂S₄ is located at 545 nm, which corresponds to the absorption band edge [43]. The PL peak of pure ZnIn₂S₄ is the strongest, which suggests that fast charge recombination occurs in ZnIn₂S₄. The PL intensity of the ZnIn₂S₄+10%SnS₂ sample is much lower than that of pure ZnIn₂S₄, which suggests that the charge separation efficiency is enhanced as a result of the construction of the 3D heterostructure [49]. In addition, the PL intensity of the ZnIn₂S₄+10%SnS₂ sample is slight lower than that of the ZnIn₂S₄+20%SnS₂ sample, which indicates a superior charge separation efficiency in the case of the former. The PL results are in good agreement with the reduction efficiency of Cr(VI). Fig. 8(a) shows the photocurrents of the pure ZnIn₂S₄, SnS₂, ZnIn₂S₄+10%SnS₂, and

ZnIn₂S₄+20%SnS₂ samples. Bare SnS₂ and ZnIn₂S₄ display lower photocurrents. After the construction of the 3D heterojunction, the photocurrents of the ZnIn₂S₄/SnS₂ composites are significantly enhanced. Among them, ZnIn₂S₄+10%SnS₂ composite exhibits the highest photocurrent. The results suggest that the charge transfer is improved through the development of the 3D heterojunction [33]. To reveal the interfacial charge transfer process, the electrochemical impedance spectra of the pure ZnIn₂S₄, SnS₂, ZnIn₂S₄+10%SnS₂, and ZnIn₂S₄+20%SnS₂ samples were measured, and the results are exhibited in Fig. 8(b). The Nyquist arc radii of the ZnIn₂S₄/SnS₂ composites are smaller than those of pure SnS₂ and ZnIn₂S₄. Moreover, the Nyquist arc radius of ZnIn₂S₄+10%SnS₂ composite is the minimum. These results suggest that the ZnIn₂S₄+10%SnS₂ sample displays the minimum interface resistance, which is beneficial for the interfacial charge transfer [53]. ZnIn₂S₄/SnS₂ heterojunction with a suitable amount of SnS₂ facilitates charge separation and transfer. However, more SnS₂ on the surface of ZnIn₂S₄ will inhibit the charge separation and transfer because SnS₂ displays a poorer activity than ZnIn₂S₄. Similar results are observed for other composite heterojunctions [41,43]. Therefore, the ZnIn₂S₄+10%SnS₂ sample shows a lower PL intensity, higher photocurrent, and smaller Nyquist arc radius than the ZnIn₂S₄+20%SnS₂ sample, which is consistent with the photo-

Fig. 7. PL spectra of pure ZnIn₂S₄, ZnIn₂S₄+10%SnS₂, and ZnIn₂S₄+20%SnS₂ samples.

Fig. 8. (a) Transient photocurrent responses and (b) electrochemical impedance spectra of pure ZnIn_2S_4 , SnS_2 , and $\text{ZnIn}_2\text{S}_4/\text{SnS}_2$ composites with different mass ratios of SnS_2 to ZnIn_2S_4 .

catalytic performances. The surface areas and pore sizes of the pure ZnIn_2S_4 , SnS_2 , and $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ composite samples were investigated by N_2 adsorption-desorption experiments, and the results are shown in Fig. S4. The surface areas of pure ZnIn_2S_4 , SnS_2 , and $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ are 89.3, 80.9, and 41.9 m^2/g , respectively. The pore sizes of ZnIn_2S_4 , SnS_2 , and $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ are 3.8 nm, 16.3 nm, and 3.8 nm, respectively. The surface area of the $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ sample is slightly lower than that of pure ZnIn_2S_4 . The pore sizes of the ZnIn_2S_4 and $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ samples are the same. However, the photocatalytic activity of the $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ sample is much higher than that of pure ZnIn_2S_4 , which suggests that the surface area and pore size do not contribute to the improved photocatalytic performance. According to the above discussion, it can be confirmed that the enhanced charge separation and the light absorption are the two reasons for the improved photocatalytic Cr(VI) reduction performance.

Fig. 9 shows the valence band XPS spectra of pure ZnIn_2S_4 and SnS_2 . The energy gaps between the Fermi levels and the valence band positions are 1.30 and 1.62 eV for ZnIn_2S_4 and SnS_2 , respectively. The flat band potentials of ZnIn_2S_4 and SnS_2 are $-0.06 V_{\text{RHE}}$ and $-0.05 V_{\text{RHE}}$, respectively (see Fig. S5). The band gaps of ZnIn_2S_4 and SnS_2 are 1.97 V_{RHE} and 2.26 V_{RHE} , respectively (see Fig. 2(b)). Based on the above calculations, the conduction band and valence band positions of ZnIn_2S_4 are

Fig. 9. Valence band XPS spectra of pure ZnIn_2S_4 and SnS_2 .

$-1.02 V_{\text{RHE}}$ and 1.24 V_{RHE} , respectively, whereas the conduction band and valence band positions of SnS_2 are $-0.40 V_{\text{RHE}}$ and 1.57 V_{RHE} , respectively. Therefore, a type II heterojunction forms between ZnIn_2S_4 and SnS_2 , which favors charge separation [54]. A schematic illustration of the photocatalytic reduction of Cr(VI) over $\text{ZnIn}_2\text{S}_4/\text{SnS}_2$ 3D heterostructure is presented in Fig. 10. Under visible-light irradiation, the photogenerated electrons tend to transfer from ZnIn_2S_4 to SnS_2 , whereas the holes move from SnS_2 to ZnIn_2S_4 , because of the match in the band structures at the heterojunction. Finally, $\text{Cr}_2\text{O}_7^{2-}$ is reduced to Cr(III) by the photoelectrons, and the photogenerated holes oxidize H_2O .

4. Conclusions

$\text{ZnIn}_2\text{S}_4/\text{SnS}_2$ 3D heterojunction was successfully prepared by a simple hydrothermal method. The $\text{ZnIn}_2\text{S}_4/\text{SnS}_2$ composites show stronger photocatalytic abilities toward Cr(VI) reduction than pure ZnIn_2S_4 and SnS_2 . Furthermore, the $\text{ZnIn}_2\text{S}_4+10\%\text{SnS}_2$ composite sample displays excellent cycle stability. The 3D heterostructure promotes charge transfer and inhibits the recombination of the photogenerated electrons and holes, thereby enhancing the photocatalytic activity towards Cr(VI) reduction. The $\text{ZnIn}_2\text{S}_4/\text{SnS}_2$ 3D heterojunction also provides an efficient and environmentally friendly way of photo-

Fig. 10. Schematic illustration of the photocatalytic reduction of Cr(VI) over $\text{ZnIn}_2\text{S}_4/\text{SnS}_2$ 3D heterostructure.

catalytically reducing Cr(VI) for waste water treatment.

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Graphical Abstract

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Facile fabrication of ZnIn₂S₄/SnS₂ 3D heterostructure for efficient visible-light photocatalytic reduction of Cr(VI)

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The charge separation and visible-light absorption efficiencies of ZnIn₂S₄ are promoted by constructing the ZnIn₂S₄/SnS₂ 3D heterostructure. A superior photocatalytic ability for Cr(VI) reduction is obtained over the ZnIn₂S₄/SnS₂ 3D heterostructure.

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ZnIn₂S₄/SnS₂ 3D异质结的制备及其在可见光下高效还原Cr(VI)的应用

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摘要: 随着印染、纺织和镀铬等行业的不断发展, 含有六价铬(Cr(VI))工业废水的大量排放造成严重的环境污染, 威胁着人类健康. 在过去的几十年中, 废水中Cr(VI)去除的方法有很多, 其中包括离子交换、膜分离、化学沉淀和吸附等. 然而, 这些传统的方法存在成本高、能耗高、效率低或者去除不彻底等缺点, 阻碍了其广泛应用. 在此背景下, 光催化还原作为一种高效、绿色、有应用前景的Cr(VI)废水处理方法, 受到越来越多科学家的关注. 开发高效可见光响应光催化剂是实现光催化还原Cr(VI)应用的关键. ZnIn₂S₄是一种三元硫化物半导体材料, 具有较强可见光吸收能力. 但纯ZnIn₂S₄光生载流子复合严重以及可见光响应范围较窄导致其光催化性能较低. 为了解决这一问题, 构建异质结是一种常见的有效方法. SnS₂具有合适的带隙(~2.2 eV), 价格低廉, 无毒且可见光吸收能力强. 因此, 构建ZnIn₂S₄/SnS₂异质结有望实现高效可见光催化还原Cr(VI).

本文通过简单的水热法成功制备了ZnIn₂S₄/SnS₂三维(3D)异质结, 并在可见光照射下对催化剂还原Cr(VI)性能进行了评价. 实验结果显示, ZnIn₂S₄/SnS₂ 3D异质结光催化活性随着SnS₂含量增加呈现先增加后减少的趋势. 当SnS₂与ZnIn₂S₄的质量比为1:10时, ZnIn₂S₄/SnS₂ 3D异质结催化还原Cr(VI)效率最高. 可见光照射下反应70 min, Cr(VI) (50 mg/L)的还原效率达到100%, 远高于纯ZnIn₂S₄和SnS₂. 荧光光谱分析(PL)和紫外-可见吸收光谱(UV-Vis)显示, 光生载流子分离效率和光吸收效率的增强是还原Cr(VI)性能增加的两个原因. 此外, 经过三个周期的循环实验, ZnIn₂S₄/SnS₂ 3D异质结催化还原Cr(VI)效率没有明显降低, 表现出较好的光催化稳定性.

关键词: ZnIn₂S₄/SnS₂三维异质结; 光催化还原Cr(VI); 可见光响应; 电荷分离; 光催化稳定性

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