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Article

ZnIn₂S₄ flowerlike microspheres embedded with carbon quantum dots for efficient photocatalytic reduction of Cr(VI)

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ABSTRACT

Development of efficient heterostructured photocatalysts that respond to visible light remains a considerable challenge. We herein show the synthesis of ZnIn₂S₄/carbon quantum dot hybrid photocatalysts with flowerlike microspheres via a facile solvothermal method. The ZnIn₂S₄/carbon quantum dot flowerlike microspheres display enhanced photocatalytic and photoelectrochemical activity compared with that of pure ZnIn₂S₄. With a content of only 0.5 wt % carbon quantum dots, 93% of Cr(VI) is reduced under visible-light irradiation at 40 min. As a co-catalyst, the carbon quantum dots improve the light absorption and lengthen the lifetime of charge carriers, consequently enhancing the photocatalytic and photoelectrochemical activity.

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1. Introduction

With industrialization and population growth, environmental pollution and energy shortages have become overwhelming problems globally. A growing number of contaminants are being directly discarded from manufacturing processes, causing serious threats to the local environment and human health. For instance, hexavalent chromium, Cr(VI), a common heavy metal pollutant in wastewater, is widely used in electroplating, leather tanning, metal finishing, textile manufacturing, steel fabrication, paint and pigments, and fertilizers. Cr(VI) is highly toxic to

marine organisms and can cause cancer, nasal septum perforation, and kidney damage in human beings [1]. The World Health Organization has recommended that the Cr(VI) concentration in drinking water should not exceed 0.003 mg L⁻¹, and the Environmental Protection Agency has stipulated that it should be less than 0.005 mg L⁻¹. Conventional Cr(VI) removal methods include adsorption, ultrafiltration, reverse osmosis, and coagulation. However, these methods have some drawbacks, such as membrane fouling, high power consumption, and high operation and maintenance costs. There is an urgent global need to develop alternative and renewable energy

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sources for both environmental and economic reasons.

The reduction of Cr(VI) to Cr(III) is considered an efficient strategy because less toxic Cr(III) is readily precipitated as Cr(OH)₃ in aqueous solution [2–4]. Recently, the application of semiconductor photocatalysis for decomposing toxic pollutants, converting carbon dioxide, and splitting water under solar light irradiation has received increasing attention because of its simplicity, low cost, high efficiency, reusability, and potential for using solar energy [5–8]. In the catalytic process, the photocatalyst is excited by photons with an appropriate energy to generate electron-hole pairs, which are then transferred to the surface of the photocatalyst where they participate in a series of oxidation or reduction reactions. If the conduction band (CB) of the photocatalyst is more negative than the Cr(VI)/Cr(III) potential (0.51 V vs. NHE [9]), Cr(VI) can be reduced to Cr(III) by the photoinduced electrons. Various photocatalysts, such as metal oxides, transition metal dichalcogenides, oxynitrides, metal-organic frameworks, perovskites, and elemental semiconductors, have been investigated for Cr(VI) reduction [10–12]. However, their catalytic activities are restricted by narrow light absorption ranges and the rapid recombination of charge carriers. Nevertheless, efficient visible-light photocatalysts that can satisfy industrial requirements are still being pursued [13–18].

Transition metal dichalcogenides have attracted considerable attention owing to their unique structures, outstanding electronic and optical properties, and wide variety of applications [19]. In our previous works, MoSe₂, MoS₂, and Ni₃S₂-based hybrid materials have been reported to possess excellent catalytic activities for the reduction of Cr(VI). Encouragingly, MoSe₂-carbon quantum dot (CQD) and CuS-graphene composites can respond to the entire solar light spectrum, from UV to visible and even NIR energy, and show good Cr(VI) reduction activities under light radiation over the full spectrum [20,21]. Furthermore, ternary metal chalcogenide semiconductors have aroused particular interest owing to their unique optoelectronic properties and catalytic activities [22,23]. As an important ternary metal chalcogenide semiconductor, ZnIn₂S₄, which has a narrow bandgap (2.34–2.48 eV), is regarded as a potential candidate for visible-light photocatalytic evolution of hydrogen and degradation of organic pollutants [24]. Unfortunately, ZnIn₂S₄ fails to achieve a satisfactory activity owing to poor adsorption and short charge carrier lifetimes [25]. Numerous attempts have been made towards achieving higher visible-light catalytic activity by controlling morphology doping with noble metals, and constructing heterostructured composites [26,27]. Recent results have demonstrated that ZnIn₂S₄-based composites, such as ZnIn₂S₄/In₂S₃, CuInS₂, CdS, MoS₂, ZnFe₂O₄, Ni(OH)₂, graphene, and g-C₃N₄, exhibit excellent catalytic activities owing to their synergistic effects under visible-light irradiation. Despite this progress, few efforts have been reported on the application of ZnIn₂S₄ for photocatalytic reduction of Cr(VI) [28–31].

Constructing 0D–3D heterostructures is a quite effective method for enhancing the catalytic activity of pure ZnIn₂S₄. Currently, CQDs have been applied as matrices to support semiconductors for improved catalytic activity [32]. Kang et al. [32]

reported a series of CQD-based composites, including Fe₂O₃/CQDs, TiO₂/CQDs, ZnO/CQDs, SiO₂/CQDs, and Cu₂O/CQDs, with excellent catalytic activities. CQDs play an important role in enhancing the catalytic activity of pure semiconductors. CQDs can act as an electron-acceptor material to promote the transfer of photoinduced electrons, thus hindering recombination and lengthening the lifetimes of charge carriers owing to electronic interactions between the semiconductors and CQDs [33]. In addition, CQDs with light-converting properties can convert longer wavelength light to shorter wavelength light, which can excite the pure photocatalyst to form more electron-hole pairs. The light-converting properties of CQDs improve the effectiveness of solar light usage by CQD-based composites, consequently enhancing their catalytic activities. Therefore, it is highly desirable to fabricate ZnIn₂S₄/CQD (ZC) hybrid photocatalysts with flowerlike 3D microspheres, which can efficiently increase visible-light absorption and charge carrier separation, resulting in improved catalytic activity. However, to the best of our knowledge, ZC hybrid photocatalysts have not been explored, especially for the photocatalytic reduction of Cr(VI).

Herein, we report ZC hybrid photocatalysts with flowerlike microspheres, synthesized via a hydrothermal method, for Cr(VI) reduction. To the best of our knowledge, this is the first investigation of ZC hybrids with flowerlike microspheres for Cr(VI) reduction under visible-light irradiation.

2. Experimental

The experimental details are described in the Electronic Supplementary Information (ESI†). ZC hybrids with 0.25, 0.5, 1, and 2 wt % CQDs were named as ZC-0.25, ZC-0.5, ZC-1, and ZC-2, respectively. Owing to the synergistic effect between the components, ZC hybrids show remarkably improved catalytic activities for the reduction of Cr(VI) compared with pure ZnIn₂S₄.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the powder XRD patterns of pure ZnIn₂S₄ and

Fig. 1. XRD patterns of pure ZnIn₂S₄, ZC-0.25, ZC-0.5, ZC-1, and ZC-2.

the ZC hybrids. All the samples exhibit similar XRD patterns, in which all diffraction peaks can be assigned to the crystal phase of hexagonal ZnIn_2S_4 (JCPDS 65-2023) [34]. The results demonstrate that the introduction of CQDs does not cause the development of new crystal orientations or changes in the preferential orientations of ZnIn_2S_4 . No additional impurities, such as ZnS or In_2S_3 , were detected in any of the XRD patterns, demonstrating the phase purity of the as-prepared samples. In addition, no characteristic diffraction peaks corresponding to CQDs appear in the ZC hybrids, which may be due to the low amounts of CQDs.

FESEM images of pure ZnIn_2S_4 and the ZC hybrids are shown in Fig. 2(a)–(e). Pure ZnIn_2S_4 displays flowerlike microspheres that consist of numerous interweaving petals (Fig. 2(a)). The morphologies of the ZC hybrids are similar to that of pure ZnIn_2S_4 (Fig. 2(b)–(e)), and the sizes of the ZC flowerlike microspheres decrease with increasing CQD content, indicating that the introduction of CQDs affects the growth of ZnIn_2S_4 crystallites. It can be observed from Fig. 2(b)–(e) that CQDs are well dispersed on the surfaces of ZnIn_2S_4 flowerlike microspheres in the ZC hybrids, forming good contact that favors the fast transport of charge carriers in catalytic reaction processes. Moreover, with increasing CQD content, the amount of CQDs deposited on the ZC hybrids increases gradually. The composition of a ZC hybrid (ZC-0.5) was identified by energy-dispersive X-ray spectroscopy (EDS) coupled with FESEM, as shown in Fig. 2(f). The existence of ZnIn_2S_4 and CQDs in the ZC hybrid photocatalysts is confirmed by the peaks corresponding to C, Zn, In, and S in the EDS spectrum of ZC-0.5.

A more detailed structural analysis of the ZC hybrids was conducted using HRTEM. Fig. 3 shows low- and high-magnification HRTEM images of ZC-0.5. It can be found that ZC flowerlike microspheres are self-assembled from

Fig. 2. FESEM images of pure ZnIn_2S_4 (a), ZC-0.25 (b), ZC-0.5 (c), ZC-1 (d), and ZC-2 (e); (f) EDS spectrum of ZC-0.5.

Fig. 3. Low (a)- and high (b)-magnification HRTEM images of ZC-0.5.

ZnIn_2S_4 petals, and CQDs are embedded in the ZnIn_2S_4 petals, which is beneficial to the catalytic process. The lattice interplanar spacing was measured as 0.41 nm, corresponding to the (006) plane of hexagonal ZnIn_2S_4 (JCPDS 65-2023). The lattice fringe connected to ZnIn_2S_4 was ascribed to the (002) plane of graphitic carbon [35].

Fig. 4 shows the Raman spectra of pure ZnIn_2S_4 and the ZC hybrid photocatalysts. For pure ZnIn_2S_4 , the four characteristic Raman bands observed at 72, 123, 300, and 345 cm^{-1} can be assigned to F_{2g} , LO_1 , TO_2 , and LO_2 , respectively [36–38]. All the characteristic Raman bands observed for the ZC hybrids are similar to those of pure ZnIn_2S_4 . No characteristic peaks corresponding to CQDs appear in the Raman spectra of the ZC hybrids, which may be due to the low amounts of CQDs.

The chemical status and surface chemical composition of ZC-0.5 were characterized by XPS. Fig. 5 shows the high-resolution XPS spectra for Zn 2p, In 3d, S 2p, and C 1s. As shown in Fig. 5(a), the Zn 2p spectrum exhibits two peaks at 1021.6 and 1044.7 eV, corresponding to $\text{Zn } 2p_{3/2}$ and $\text{Zn } 2p_{1/2}$, respectively, which is similar to those reported in the literature [39,40]. For the In 3d spectrum, the two peaks located at 444.8 and 452.3 eV are associated with $\text{In } 3d_{5/2}$ and $\text{In } 3d_{3/2}$ of ZnIn_2S_4 , respectively [41]. The S 2p spectrum in Fig. 5(c) can be deconvoluted into two peaks at 160.9 and 162.1 eV, which are assigned to $\text{S } 2p_{3/2}$ and $\text{S } 2p_{1/2}$, respectively [39]. The C 1s spectrum can be deconvoluted into three peaks located at 284.5, 286.6, and 289.2 eV, which are ascribed to C–C, C–O, and O–C=O bonds, respectively [42,43]. Furthermore, the intensities of the C–O and C=O peaks are very weak, demonstrating the complete

Fig. 4. Raman spectra of pure ZnIn_2S_4 , ZC-0.25, ZC-0.5, ZC-1, and ZC-2.

Fig. 5. Zn 2p (a), In 3d (b), S 2p (c), and C 1s (d) XPS spectra for ZC-0.5.

removal of most of the oxygen-containing functional groups [42,44]. All the results are consistent with the formation of ZC hybrids.

Fig. 6 shows the UV-Vis spectra of pure ZnIn_2S_4 and the ZC hybrids. Pure ZnIn_2S_4 shows excellent absorption in the visible-light region owing to its narrow bandgap. The ZC hybrids have better absorption properties than pure ZnIn_2S_4 . With increasing CQD content, the absorption of the ZC hybrids increases. In addition, the introduction of CQDs leads to a red shift in the bandgap of the ZC hybrids owing to chemical bonding between the semiconductor and the CQDs, as also observed for other reduced-graphene-oxide-based composites [45]. All these characteristics are beneficial for improving the catalytic

activities of ZC hybrids.

3.2. Photocatalytic activity and photocurrent response

It is known that during photocatalysis, charge transportation and separation are crucial factors that determine catalytic activity, which can be demonstrated by the photocurrent response. Fig. 7 shows the photocurrent responses of pure ZnIn_2S_4 and the ZC hybrids under visible-light irradiation. The photocurrent quickly decreases to zero when the light is switched off, indicating the recombination of photoinduced electron-hole pairs. The transient photocurrent responses of all

Fig. 6. UV-Vis spectra of pure ZnIn_2S_4 , ZC-0.25, ZC-0.5, ZC-1, and ZC-2.

Fig. 7. Photocurrent responses of pure ZnIn_2S_4 , ZC-0.25, ZC-0.5, ZC-1, and ZC-2 under visible-light irradiation.

the samples are reversible and relatively stable at light on and light off. The ZC hybrids show higher photocurrents than pure ZnIn_2S_4 . With increasing CQD content, the photocurrent first increases and then decreases. The ZC-0.5 hybrid exhibits the highest photocurrent, suggesting more efficient charge-transfer processes and longer lifetimes of electron-hole pairs.

The photocatalytic activities of pure ZnIn_2S_4 and the ZC hybrids were investigated for the reduction of Cr(VI) under visible-light irradiation. The photoreduction activity in a Cr(VI) solution was examined using UV-Vis absorption spectroscopy. The temporal changes in Cr(VI) concentration were monitored by recording the variations in the maximum absorption of Cr(VI) at 365 nm. Fig. 8(a) shows the time-dependent reduction rates of Cr(VI) by pure ZnIn_2S_4 , ZC-0.25, ZC-0.5, ZC-1, and ZC-2 under visible-light irradiation. It can be observed that the variation in Cr(VI) concentration is negligible without a photocatalyst under visible-light irradiation. For pure ZnIn_2S_4 , a high reduction rate of 84% was observed after irradiation for 40 min owing to the good visible-light absorption of this catalyst. Nevertheless, the catalytic activity can still be further enhanced because charge recombination is quick in pure ZnIn_2S_4 . When CQDs are introduced into ZnIn_2S_4 to form hybrid photocatalysts, the Cr(VI) reduction rates are gradually improved. The

Cr(VI) reduction rates depend on the CQD content in the ZC hybrid. The Cr(VI) reduction rates were 86%, 93%, 72%, and 66% for ZC-0.25, ZC-0.5, ZC-1, and ZC-2, respectively, after irradiation for 40 min. These results indicate that increasing the CQD content causes the Cr(VI) reduction rate to first increase and then decrease. The total Cr, Cr(VI), and Cr(III) concentrations after the visible-light-driven photocatalytic reaction using pure ZnIn_2S_4 and the ZC hybrids were also investigated, as shown in Fig. S1. Cr(III) is observed to appear during the visible-light photocatalytic reaction process, indicating the successful reduction of Cr(VI). Furthermore, the total Cr, Cr(VI), and Cr(III) concentrations are lowest for ZC-0.5, which demonstrates that higher total Cr and Cr(VI) removal rates can be achieved by using ZC hybrid composites under visible-light irradiation. The kinetic data for Cr(VI) reduction were fit well by a pseudo-first-order kinetic equation, as shown in Fig. S2. The rate constants for the Cr(VI) reduction process were 0.045, 0.049, 0.064, 0.031, and 0.026 min^{-1} for pure ZnIn_2S_4 , ZC-0.25, ZC-0.5, ZC-1, and ZC-2, respectively. The ZC hybrids with appropriate CQD contents exhibit better catalytic activities for Cr(VI) reduction than pure ZnIn_2S_4 . The ZC-0.5 hybrid shows the best Cr(VI) reduction activity under visible-light irradiation. These results indicate that the introduction of CQDs has im-

Fig. 8. (a) Photocatalytic reduction of Cr(VI) by pure ZnIn_2S_4 , ZC-0.25, ZC-0.5, ZC-1, and ZC-2 under visible-light irradiation; (b) Photostability of ZC-0.5 as indicated by its photocatalytic activity over three cycles; (c) Photocatalytic degradation of MO and RhB by ZC-0.5 under visible-light irradiation; (d) Photocatalytic reduction of Cr(VI) by ZC-0.5 in the presence of electron scavengers under visible-light irradiation.

portant effects on the catalytic activities of ZC hybrids.

The photostability of an as-prepared photocatalyst is very important for practical applications. Therefore, the photostability of a ZC hybrid (ZC-0.5) was studied by repeating the photocatalytic Cr(VI) reduction experiment three times under visible-light irradiation. As shown in Fig. 8(b), the Cr(VI) reduction rate did not decrease significantly after three cycles. Furthermore, the surface chemical composition, morphology, and structure of the ZC-0.5 hybrid after the photocatalytic reaction were characterized by XPS, FESEM, and XRD (Figs. S3 and S4). The results indicate that the binding energies of Zn, In, S, and C did not change obviously before and after the photocatalytic reaction. Moreover, the morphology and structure of the ZC-0.5 hybrid after the catalytic reaction were similar to those before the catalytic reaction. Therefore, the as-prepared ZC hybrids have good stability and durability, and can be regarded as promising visible-light photocatalysts for practical applications.

The photocatalytic degradation of methyl orange (MO) and rhodamine B (RhB) by a ZC hybrid (ZC-0.5) was also investigated under visible-light irradiation, as shown in Fig. 8(c). The degradation rates were 96% and 95% for MO and RhB, respectively. Similarly, the other ZC hybrids also displayed excellent catalytic activities for the degradation of MO and RhB. The final products after photocatalytic degradation of MO and RhB were determined by high-resolution mass spectrometry using a Bruker micrOTOF-Q II spectrometer, as shown in Fig. S5. The results indicate that some degradation byproducts are present after the photocatalytic degradation of MO and RhB. As shown in Fig. S5(a), before light irradiation, the MO sample shows two m/z peaks. The first at $m/z = 328$ corresponds to the parent dye molecule and the second at $m/z = 306$ is attributed to the loss of one methyl group from the nitrogen atom of the amino group. After irradiation for 90 min, the intensities of these peaks reach minimums close to zero. However, m/z peaks corresponding to the main byproducts were observed at 213 ($[M-H-SO_2]^-$), 257 ($[M-H-SO_2]^-$), 292 (monohydroxylated), 308 (anion of MO), and 338 (anion of MO) (Fig. S5(b)). Similar results were obtained after the photocatalytic degradation of RhB. As shown in Fig. S5(d), the main byproducts with m/z peaks at 115 and 274 correspond to maleic acid and the decarboxylation product of RhB. The m/z peak at 318 corresponds to the intermediate at m/z 387 (de-ethylated intermediate) after losing a fragment of 74 mass units $\{(C_2H_5)_2NH\}$.

Scheme 1. Proposed photocatalytic mechanism for ZC hybrid photocatalysts under visible-light irradiation.

3.3. Possible photocatalytic mechanism

A possible photocatalytic mechanism for the reduction of Cr(VI) is proposed, as shown in Scheme 1. Under visible-light irradiation, the valence band (VB) electrons of $ZnIn_2S_4$ can be excited to generate electron-hole pairs. Subsequently, the electrons and holes migrate to the surface of the photocatalyst to participate in redox reactions. Meanwhile, the electrons and holes may recombine in the bulk and at the surface of the photocatalyst. In the photocatalytic Cr(VI) reduction process, Cr(VI) can be reduced to Cr(III) by photoinduced electrons because the Cr(VI)/Cr(III) potential (0.51 V vs. NHE [9]) is more positive than the CB of $ZnIn_2S_4$ (−1 V vs. NHE). Fig. S6 shows the high-resolution Cr 2p XPS spectrum of ZC-0.5 after the photocatalytic reaction. The two peaks located at 577.3 and 586.9 eV correspond to Cr 2p_{1/2} and Cr 2p_{3/2}, respectively, which are attributed to Cr(VI) and Cr(III). This result demonstrates that Cr(VI) can be reduced to Cr(III) during the catalytic reaction process. The Cr(III) species will precipitate on the surface of the photocatalyst as Cr_2O_3 or $Cr(OH)_3$, as reported for similar systems [46,47]. The deposited Cr(III) species can be removed via simple washing of the sample with deionized water or NaOH.

To demonstrate the role of photoinduced electrons, a trapping experiment was performed (Fig. 8(d)). The results indicate that the addition of an electron scavenger leads to a rapid decrease in the catalytic activity, demonstrating that the photoinduced electrons play an important role in the catalytic Cr(VI) reduction process. The spin-trapping electron paramagnetic resonance (EPR) technique was also used to demonstrate the generation and reactivity of photoinduced electrons. EPR spectra were collected at ambient temperature under visible-light irradiation using a JEOL JES-FA200 EPR spectrometer. The light source was a 500-W Xe arc lamp equipped with a UV cutoff filter ($\lambda > 420$ nm). Purified TEMPO was added to a solution containing ZC-0.5 and Cr(VI). The mixture was irradiated for 10 min and then immediately subjected to EPR measurements. As shown in Fig. S7, the distinct EPR signals of TEMPO were observed in the dark. However, the intensity of the EPR signals was reduced under visible-light irradiation, demonstrating that TEMPO is reduced to TEMPOH by photoinduced electrons [48]. The EPR spectra of a sample containing TEMPO and ZC-0.5 further confirmed the presence of photoinduced electrons during the Cr(VI) reduction process. Furthermore, photoinduced holes can oxidize H_2O to form O_2 , as demonstrated by gas chromatography measurements in our previous work [49]. The major reaction steps can be summarized as follows:

To evaluate the effect of the active species during the photocatalytic degradation of MO and RhB, the EPR technique was used to probe the relevant active species, as shown in Fig. S8. Purified DMPO was added to a solution containing ZC-0.5 and MO or RhB. The mixture was irradiated for 10 min and then immediately subjected to EPR measurements. No signals were observed when the ZC-0.5 suspension was in the dark. However,

Fig. 9. Nyquist plots (a) and nitrogen adsorption-desorption isotherms (b) of pure ZnIn₂S₄, ZC-0.25, ZC-0.5, ZC-1, and ZC-2. The inset in (a) shows the corresponding equivalent circuit model.

er, under visible-light irradiation, the four characteristic peaks of DMPO- $\cdot$ OH adducts (intensity: 1:2:2:1) were observed in the solutions containing MO or RhB, indicating the formation of $\cdot$ OH radicals during photocatalytic degradation of MO and RhB [50].

Compared with pure ZnIn₂S₄, the ZC hybrids show enhanced catalytic activities under visible-light irradiation owing to a synergistic effect. The CQDs can act as an electron-acceptor material to promote the transfer of photoinduced electrons, thus lengthening the lifetimes of charge carriers, which could be evaluated by electrochemical impedance spectroscopy (EIS) under visible-light irradiation. Typical Nyquist plots for pure ZnIn₂S₄ and the ZC hybrids are shown in Fig. 9(a). The semicircle is associated with the charge-transfer resistance (R_{ct}) and the constant phase element (CPE) at the photocatalyst/electrolyte interface. The inclined line corresponds to the ion diffusion process in the electrolyte, arising from the Warburg impedance (Z_w). The corresponding equivalent circuit is shown in the inset of Fig. 9(a). A smaller semicircle radius indicates that the transfer of charge carriers is more efficient. It can be observed that the semicircle radius of the ZC hybrids is smaller than that of pure ZnIn₂S₄, demonstrating that the introduction of CQDs can inhibit the recombination of charge carriers, in accordance with the photocurrent response results. The EIS and photocurrent response results demonstrate that the ZC-0.5 hybrid shows the highest separation efficiency of charge carriers, in agreement with the results of the photocatalytic experiments.

In addition to the recombination of charge carriers, adsorption is also a crucial factor in the photocatalytic process, which was evaluated using nitrogen adsorption-desorption isotherms (Fig. 9(b)). Pure ZnIn₂S₄ and the ZC hybrids all displayed type IV isotherms with H₂ and H₃ hysteresis loops, indicating the presence of mesopores. The Brunauer-Emmett-Teller specific surface areas, pore volumes, and average pore size of pure ZnIn₂S₄ and the ZC hybrids are listed in Table S1. It can be observed that the specific surface areas of the ZC hybrids are not consistent with the results of the photocatalytic experiments. Therefore, the specific surface area does not play a crucial role

in the catalytic Cr(VI) reduction process.

Based on the above results, an enhancement mechanism is proposed for the ZC hybrids. During the catalytic process, the photoinduced electrons can transfer from ZnIn₂S₄ to the CQDs owing to their synergistic effect, which can improve the separation efficiency and prolong the lifetimes of photoinduced charge carriers, as supported by EIS and the photocurrent responses, thus enhancing the catalytic activity. Furthermore, the CQDs, which have light-converting properties, can convert longer wavelength light to shorter wavelength light, allowing the excitation of ZnIn₂S₄ to form more photoinduced electron-hole pairs, consequently enhancing the catalytic activity. The introduction of CQDs has important effects on the light absorption and charge-transfer behavior of the ZC hybrids, which inevitably further affect the catalytic activity. Therefore, the enhanced catalytic activities of the ZC hybrids arise from the excellent light absorption properties, the reduced recombination of charge carriers, and the light-converting effect with the introduction of CQDs. Moreover, photoinduced electrons dominant the Cr(VI) reduction process.

4. Conclusions

In summary, a series of ZC hybrids with flowerlike microspheres were prepared via a facile solvothermal method for photocatalysis. The results indicate that the ZC hybrid photocatalysts display excellent catalytic activities owing to their synergistic effect. A 0.5 wt % CQD content increases the Cr(VI) reduction rate to 93% after 40 min of visible-light irradiation. The enhancement of catalytic activity is ascribed to excellent light absorption, good interfacial charge transfer, and the light-converting effect of the CQDs. It is expected that our work could provide valuable information for the design of CQD-based composites with further desirable properties.

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Graphical Abstract

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ZnIn₂S₄/carbon quantum dot hybrid photocatalysts display excellent visible-light catalytic activity for the reduction of Cr(VI) with a reduction rate of 93%.

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花状微球 ZnIn_2S_4 /碳量子点复合物用于光催化还原 Cr(VI)

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摘要: 六价铬 Cr(VI) 是废水中常见的重金属污染物, 广泛应用于电镀、皮革制造、金属表面处理、纺织制造等领域. 传统的处理方法有吸附、超滤、反渗透和凝固等. 但是, 这些方法均具有一定的缺陷, 比如膜污染、高功耗、高运行和维护成本. Cr(III) 有较低毒性且易在水溶液中沉淀形成 Cr(OH)_3 , 因此, 将 Cr(VI) 还原为 Cr(III) 被认为是一种有效去除 Cr(VI) 的策略. 近年来, 半导体光催化技术广受关注, 被用于去除有毒污染物、还原二氧化碳和分解水, 并在光催化还原 Cr(VI) 领域取得一系列进展. 但是, 探索开发可见光响应的高效光催化剂仍是挑战. 三元金属硫属元素化合物半导体具有独特的光电特性和催化活性, 备受关注. 尤其是窄带 ZnIn_2S_4 被认为是一种有潜力的可见光催化剂. 但是, 由于其较窄的光响应范围以及光生载流子短的寿命, 使得它的催化活性很低. 研究表明, 控制形貌、掺杂贵金属和构筑异质结复合物能够提高 ZnIn_2S_4 的光催化活性. 不幸的是, 有关 ZnIn_2S_4 在光催化还原 Cr(VI) 中的应用还鲜有报道. 本文通过构筑花状微球 ZnIn_2S_4 和碳量子点(CQDs)异质结, 合成 $\text{ZnIn}_2\text{S}_4/\text{CQDs}$ 复合物, 获得高效光催化还原 Cr(VI) 活性的复合光催化剂.

扫描电子显微镜和高分辨投射电子显微镜结果显示, $\text{ZnIn}_2\text{S}_4/\text{CQDs}$ 复合物是由花瓣自组装的花状微球结构, CQDs分散在 ZnIn_2S_4 花瓣上, 形成很好的界面接触, 有利于光催化过程的进行. 紫外可见吸收光谱结果表明, $\text{ZnIn}_2\text{S}_4/\text{CQDs}$ 复合物在可见光区域展现了很好的吸收. 随着CQDs含量的增加, $\text{ZnIn}_2\text{S}_4/\text{CQDs}$ 复合物的光吸收能力增加, 有利于提高其催化活性. 电化学阻抗谱、光电流响应曲线和原位电子顺磁共振谱结果表明, CQDs可以作为电子受体材料, 促进光生载流子的转移, 抑制其复合, 从而延长光生载流子的寿命.

通过光催化还原 Cr(VI) 的实验发现, 与纯 ZnIn_2S_4 相比, $\text{ZnIn}_2\text{S}_4/\text{CQDs}$ 复合物具有增强的光催化活性, 并且与CQDs的掺杂比例有关. 在可见光照射40 min后, 当CQDs的掺杂比例为0.5 wt%时, $\text{ZnIn}_2\text{S}_4/\text{CQDs}$ 复合物对 Cr(VI) 的还原率达到93%. $\text{ZnIn}_2\text{S}_4/\text{CQDs}$ 复合物优异的催化活性归因于其优异的光吸收, 良好的界面电荷转移, 和CQDs的下转换特性. 另外, 光催化还原 Cr(VI) 实验被循环3次后发现, Cr(VI) 的还原率没有明显降低. 同时, X射线衍射、扫描电子显微镜和光电子能谱结果表明, 催化反应之后的 $\text{ZnIn}_2\text{S}_4/\text{CQDs}$ 复合物的结构、形貌和组分均未发生变化, 说明 $\text{ZnIn}_2\text{S}_4/\text{CQDs}$ 复合物具有良好的稳定性. 本工作以期为进一步设计具有理想功能的CQDs基复合材料提供有价值的信息.

关键词: ZnIn_2S_4 ; 碳量子点; 花状微球; 助催化剂; 光电化学

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