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Article

# $ZnIn_2S_4$ 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 $ZnIn_2S_4$/carbon quantum dot hybrid photocatalysts with flowerlike microspheres via a facile solvothermal method. The $ZnIn_2S_4$/carbon quantum dot flowerlike microspheres display enhanced photocatalytic and photoelectrochemical activity compared with that of pure $ZnIn_2S_4$. 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.



## 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, $MoSe_2$-, $MoS_2$-, and $Ni_3S_2$-based hybrid materials have been reported to possess excellent catalytic activities for the reduction of Cr(VI). Encouragingly, $MoSe_2$-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, $ZnIn_2S_4$, 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, $ZnIn_2S_4$ 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 $ZnIn_2S_4$-based composites, such as $ZnIn_2S_4/In_2S_3$, $CuInS_2$, CdS, $MoS_2$, $ZnFe_2O_4$, $Ni(OH)_2$, graphene, and g-$C_3N_4$, 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 $ZnIn_2S_4$ for photocatalytic reduction of Cr(VI) [28–31].

Constructing 0D–3D heterostructures is a quite effective method for enhancing the catalytic activity of pure $ZnIn_2S_4$. 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 $Fe_2O_3$/CQDs, $TiO_2$/CQDs, ZnO/CQDs, $SiO_2$/CQDs, and $Cu_2O$/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 covert 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 $ZnIn_2S_4$/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 $ZnIn_2S_4$.

## 3. Results and discussion

### 3.1. Characterization

Fig. 1 shows the powder XRD patterns of pure $ZnIn_2S_4$ and

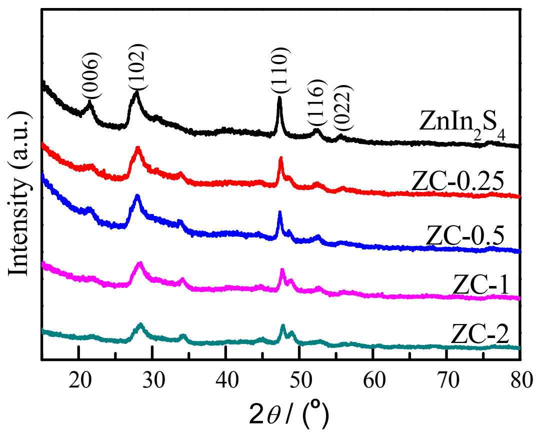


**Fig. 1.** XRD patterns of pure $ZnIn_2S_4$, ZC-0.25, ZC-0.5, ZC-1, and ZC-2.