



## Research paper

## Facile fabrication of CdS/ZnAlO heterojunction with enhanced photocatalytic activity for Cr(VI) reduction under visible light

Chao-Rong Chen<sup>a</sup>, Hong-Yan Zeng<sup>a,\*</sup>, Sheng Xu<sup>a</sup>, Jia-Chao Shen<sup>a</sup>, Guo Hu<sup>a</sup>, Run-Liang Zhu<sup>b,\*</sup>, Jin-Ze Du<sup>a</sup>, Yun-Xin Sun<sup>a</sup><sup>a</sup> College of Chemical Engineering, Xiangtan University, Xiangtan, Hunan, 411105, China<sup>b</sup> Key Laboratory of Mineralogy and Metallogeny, Guangdong Provincial Key Laboratory of Mineral Physics and Material Research & Development, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

## ARTICLE INFO

## Keywords:

Photocatalytic  
CdS/ZnAlO composite  
Heterojunction  
Cr(VI) reduction

## ABSTRACT

Cadmium sulfide (CdS) is an excellent visible light responsive material for the appropriate band gap, but the high electron-hole recombination and particle aggregation of CdS seriously limited its practical application in photocatalysis. In this work, the CdS/ZnAlO heterostructures photocatalyst was synthesized via a facile hydrothermal method. The structural characterizations showed that the particles aggregation of CdS and the separation of photogenerated electron-hole pairs were obviously improvement. The CdS/ZnAlO composite showed the highest photocatalytic activity for Cr(VI) reduction under visible light within 120 min. The enhanced photocatalytic activity might be attributed to the synergistic effect of the effective separation of photogenerated electron-hole and the adsorption of Cr(VI) on the interface of the catalyst. In addition, the possible mechanism of Cr(VI) reduction over CdS/ZnAlO was also proposed. The present work is devoted to synthesise a high efficient and stable photocatalyst for Cr(VI) contaminated wastewater treatment.

## 1. Introduction

Chromium is a common and essential material in our daily life, which has been widely used in leather tanning, electroplating, etc. (Jiang et al., 2015; Qu et al. 2017). It exists in nature mainly in two oxidation states namely hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)]. Cr(VI) is extremely toxic and carcinogenic even at very low concentrations, whereas Cr(III) is harmless and is an essential nutrient for sugar and lipid metabolism in humans and animals. Therefore, reducing the Cr(VI) to Cr(III) is considered as a promising approach due to the low toxicity of Cr(III) (Testa et al. 2004; Fellahi et al. 2016; Yang et al. 2018). Many alternative processes such as chemical reduction and photoreduction have been proposed for the reduction of Cr(VI) (Xu et al. 2011; Sarkar et al. 2013). However, conventional chemical reduction methods require massive use of expensive chemical reducing agents. Compared with the conventional methods, photocatalysis method holds great promise due to its simple operation, high efficiency, cost-effective and environment friendly for Cr(VI) reduction (Wang et al. 2009; Wu et al. 2013). Previous studies have demonstrated that semiconductor photocatalysts possessed high efficiency for Cr(VI) reduction (Wei et al. 2016). Significantly, CdS has caused extensive concern because of its suitable band gap and efficient

absorption capacity of visible light (Nasrallah et al. 2011; Yang et al. 2012a; Hu et al. 2013). It has been extensively studied as an excellent photocatalyst for reduction of Cr(VI) in wastewater (Liu et al. 2011; Nasrallah et al. 2011). Nevertheless, the high recombination rate of photogenerated electron-hole pairs and easily aggregation seriously limited the practical application of bare CdS (Li et al. 2011; Xu et al. 2011; Hu et al. 2013).

Layered double hydroxides (LDH), consist of positively charged brucite-like layers with anionic species in the interlayers, forming neutral clay materials. Recently, various forms of the LDH have attracted great attention because a wide variety of elements and ions can be incorporated in this layered structure, making possible for the resulting LDH in achieving novel physical and chemical properties (Wang et al. 2007; Li et al. 2014; Zhang et al. 2014). The mixed oxides obtained by calcining LDH possessed better properties due to more homogeneous interdispersion of the elements and larger specific surface areas (Xu et al. 2015). In particular, ZnAl-LDH is a potential host material for couple with other semiconductor for forming heterogeneous structures because of the large electron energy band gap (Zhang et al. 2013; Baek et al. 2015). The great flexibility in the composition and electronic structure of LDH can effectively prevent the aggregation of CdS particles and facilitate charge transfer on the surface of the

\* Corresponding authors.

E-mail addresses: [hyzeng@xtu.edu.cn](mailto:hyzeng@xtu.edu.cn) (H.-Y. Zeng), [zhurl@gig.ac.cn](mailto:zhurl@gig.ac.cn) (R.-L. Zhu).

photocatalyst (Guo et al. 2005). Therefore, by combining CdS and LDH to constitute a CdS/ZnAlO heterojunction photocatalyst both can enhance visible light absorption and decrease the recombination rate of photogenerated electron-hole pairs, thus resulting in the improvement of photocatalytic activity.

In this work, we fabricated CdS/ZnAlO heterogeneous structures via a facile hydrothermal technique and an in situ sulfuration method. One advantage of this synthesis route is that the CdS species were dispersed homogeneously on the surface of the ZnAlO nanosheets. The as-prepared materials were characterized using XRD, SEM, TEM, XPS, UV–vis DRS and PL. On the other hand, the photocatalytic performance of the CdS/ZnAlO composite for Cr(VI) reduction under visible light irradiation was also investigated. Combining with the characterization and experimental results, a possible mechanism of photocatalytic reduction was also proposed.

## 2. Experimental section

### 2.1. Materials and reagents

Thiourea ( $\text{CH}_4\text{N}_2\text{S}$ ) was purchased from Nanjin Chemical Reagent Co., Ltd., China. Urea ( $\text{CH}_4\text{N}_2\text{O}$ ), zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) were purchased from Tianjin Damao Chemical Reagent Factory, China. All the chemical reagents were of analytical grade and used without further purification, and all the solutions were made with deionized water, where  $0.1 \text{ mol}\cdot\text{L}^{-1}$  NaOH and HCl solutions were used for pH adjustment.

### 2.2. Sample preparation

ZnAl LDH (molar ratio of  $\text{Zn}^{2+}/\text{Al}^{3+} = 3.0$ ) was prepared through urea method (Zhang et al., 2014a). In a typical process, the solution containing  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $0.15 \text{ mol}\cdot\text{L}^{-1}$ ),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  ( $0.05 \text{ mol}\cdot\text{L}^{-1}$ ) and urea (molar ratio of urea/ $\text{NO}_3^- = 4.0$ ) were placed into a three-neck flask heated at  $105^\circ\text{C}$  for 12 h under vigorous stirring, then the resulting reactant was aged at  $80^\circ\text{C}$  for another 12 h. The precipitates were centrifuged and washed with deionized water for several times, and subsequently dried at  $80^\circ\text{C}$  overnight, which was denoted as LDH.

CdS/LDH composite was prepared by the following process: the solutions containing  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (molar ratio of Zn/Al/Cd = 3:1:1) and urea (molar ratio of urea/ $\text{NO}_3^- = 4.0$ ) were dissolved in deionized water using ultrasonic dispersion for 30 min. Subsequently, the mixture was maintained at  $105^\circ\text{C}$  for 12 h under stirring. The obtained solids were aged, centrifuged and washed thoroughly. The obtained products were dispersed in the solution containing  $\text{CH}_4\text{N}_2\text{S}$  with an excess of 10% Cd content in the product. After stirring for 12 h, the precipitates were collected by centrifugation and dried at  $80^\circ\text{C}$ , which was denoted as CdS/LDH. Part of the CdS/LDH was calcined at  $500^\circ\text{C}$  for 4 h to obtain CdS/ZnAl mixed metal oxides (namely CdS/ZnO/ZnAl<sub>2</sub>O<sub>4</sub>). For convenient, the product was denoted as CdS/ZnAlO. Meanwhile, the pure CdS was synthesized by mixing a certain amount of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  with urea and stirred for 12 h to form  $\text{Cd}(\text{OH})_2$ , after that the precipitation was put into the solution containing  $\text{CH}_4\text{N}_2\text{S}$  and stirred for another 12 h.

### 2.3. Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Japan Rigaku D/max 2550PC ( $\lambda = 1.5405 \text{ \AA}$ ) with Cu K $\alpha$  irradiation. The scan step was  $0.02 (2\theta)$  with a filament intensity of 30 mA and a voltage of 40 kV. The morphology and microstructure of the samples were characterized by scanning electron microscopy (SEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, FEI Talos F200S) coupled with an energy dispersive X-ray spectroscopy (EDS). X-ray

photoelectron spectroscopy (XPS) analyses were carried out using a Thermo Fisher Scientific K-Alpha spectrometer. The C1s peak from the adventitious carbon based contaminant with a binding energy of 284.8 eV was used as the reference for calibration. UV–visible diffuse reflectance spectra (UV–vis DRS) were measured using a UV–visible spectrophotometer (Shimadzu UV-2550, Kyoto, Japan). The photoluminescence (PL) spectra were carried out at room temperature on a fluorescence spectrophotometer (F-4600, Hitachi, Japan). The scanning speed was 1200 nm/min and the width of the emission slit was 5.0 nm.

### 2.4. Photocatalytic activity test

The photocatalytic performance of the as-prepared photocatalysts was tested for Cr(VI) reduction under visible light irradiation. To simulate the visible spectrum, a 300 W xenon lamp was applied as the light source with a 420 nm cutoff filter, and the filter was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket. In the photocatalytic activity evaluation experiments,  $0.4 \text{ g}\cdot\text{L}^{-1}$  catalyst was added to the synthetic wastewater containing the Cr(VI) concentration of  $50 \text{ mg}\cdot\text{L}^{-1}$ . All experiments were carried out under constant stirring to ensure good dispersion of the catalysts in pH 3.0 at room temperature. Prior to irradiation, the suspension was stirred in dark for 30 min to establish an adsorption/desorption equilibrium. During the photocatalytic process, 2 mL suspensions were sampled at given time intervals and filtered immediately with  $0.45 \mu\text{m}$  membrane filters. The concentrations of Cr(VI) were determined by the 1,5-diphenylcarbazide colorimetric method (Wang et al. 2013; Jin et al. 2014). At the same time, a blank reaction without catalyst as control was also carried out under the same conditions. The photocatalytic activity was evaluated by the reduction efficiency ( $\eta$ ) of Cr(VI) after experiment, where  $C_0$  was the initial concentration and  $C_t$  was the concentration of Cr(VI) after the reaction time (t).

$$\text{Reduction efficiency } (\eta) = (1 - C_t/C_0) \times 100\%$$

## 3. Results and discussion

### 3.1. Structure and morphology analyses

The crystalline structure of the virgin LDH, pure CdS, CdS/LDH, and CdS/ZnAlO samples were investigated by powder XRD pattern (Fig. 1). For the pure CdS, there were six sharply diffraction peaks observed at  $2\theta = 24.80^\circ$ ,  $26.48^\circ$ ,  $43.74^\circ$ ,  $47.82^\circ$  and  $51.94^\circ$ , which correspond to the (100), (111), (101), (220), (103) and (331) crystal planes of hexagonal wurtzite structure, respectively (Zhang et al. 2010; Yang et al. 2012b). The pure LDH sample exhibited characteristic peaks of (003), (006), (009), (110) and (113), confirming the formation of

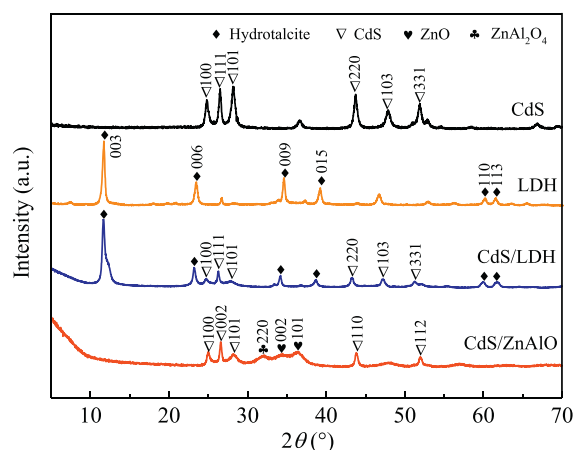


Fig. 1. XRD patterns of the virgin LDH, pure CdS, CdS/LDH and CdS/ZnAlO.

Download English Version:

<https://daneshyari.com/en/article/11007137>

Download Persian Version:

<https://daneshyari.com/article/11007137>

[Daneshyari.com](https://daneshyari.com)