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# A novel Z-Scheme $CdS/Bi_3O_4Cl$ heterostructure for photocatalytic degradation of antibiotics: Mineralization activity, degradation pathways and mechanism insight

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ABSTRACT

A novel Z-Scheme $CdS/Bi_3O_4Cl$ heterostructure photocatalysts are fabricated by a facile surfactant-free method, and the visible-light-driven photocatalytic activity has been investigated for degradation of ciprofloxacin (CIP) and tetracycline (TC). For degradation of CIP, the Z-Scheme $CdS/Bi_3O_4Cl$-50 heterostructure displays the optimal rate constant ($k_{app}$ = 0.0151 $min^{-1}$), which is about 10.63 and 1.97 times higher than that of pure $Bi_3O_4Cl$ ($k_{app}$ = 0.00142 $min^{-1}$) and CdS ($k_{app}$ = 0.00764 $min^{-1}$), respectively. Meanwhile, as expected, the rate constant of Z-Scheme $CdS/Bi_3O_4Cl$-50 heterostructure also displays the highest (0.0643 $min^{-1}$) for degradation of TC, which is 2.14 times and 4.34 times as high as those of the bare CdS (0.0301 $min^{-1}$) and $Bi_3O_4Cl$ (0.0148 $min^{-1}$), respectively. The enhancement of phototcatalytic activity is ascribed to the significant improved transfer and separation of charge carriers, which are proved by photocurrent and electrochemical impedance spectra (EIS) measurements. The possible degradation pathway for CIP and TC are proposed based on the HPLC-MS analysis. Compared with pure CdS nanospheres and $Bi_3O_4Cl$ nanosheets, the Z-Scheme $CdS/Bi_3O_4Cl$ heterostructures exhibit the excellent mineralization ability towards the CIP and TC molecules degradation through the analysis of the total organic carbon (TOC) tests. Moreover, the photocatalytic mechanism over Z-Scheme $CdS/Bi_3O_4Cl$ heterostructure under visible light irradiation is investigated by active species trapping experiments and ESR technology. The present work provides a new approach to construct Z-Scheme heterojunction photocatalysts and a deeper insight for the mineralization activity, possible degradation pathways and photocatalytic mechanism.


## 1. Introduction

Antibiotics, particularly ciprofloxacin (CIP) and tetracycline (TC), have been frequently detected in the aquatic environment because of inappropriate use in human and animals [1–5]. More importantly, the corresponding wastewater is seriously threatening to the human health and ecosystem, even with low residual activity and at a concentration as low as nanograms per liter [6–8]. Thereby, it is strongly desired to develop efficient and cost-effective technology to remove antibiotics from aqueous environment. In recent years, comparing with many traditional methods, semiconductor photocatalysis has been considered as a promising and green technology for degradation of organic pollutants, because it can degrade the pollutants into small molecules or mineralize them into $CO_2$ and $H_2O$ under mild reaction conditions [9,10].

Recently, bismuth oxyhalides (BiOX, X = Cl, Br, and I), as a class of layered semiconductor materials, have attracted much attention due to its unique and excellent electrical property, suitable energy band positions and high-efficiency photocatalytic activity [11–13]. Especially, $Bi_3O_4Cl$ possesses the special open crystalline structure characterized by a Sillén related oxide-structure consisting of $[Bi_3O_4]$ layers sandwiched between two slabs of [Cl] ions [14,15]. The unique crystalline structure can make itself self-built internal static electric field in $Bi_3O_4Cl$ to prompt the separation and transportation of photo-generated electrons and holes, which is beneficial for enhancing the photocatalytic performance [16]. Nevertheless, the photocatalytic activity of single $Bi_3O_4Cl$ is limited due to the poor visible light utilization and low rate of charge transfer [17]. To overcome the above disadvantages and further improve photocatalytic performance of $Bi_3O_4Cl$ under visible light irradia-

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tion, constructing of semiconductor heterojunction with appropriate band is a good choice. For instance, Ning et al. reported that the $Bi_3O_4Cl$/BiOCl heterojunction exhibited higher photocatalytic activity than pure $Bi_3O_4Cl$ and BiOCl for the degradation of Orange II under visible light, which is attributed to the efficient separation of photoinduced electrons and holes [18]. Huang et al. synthesized the AgCl/$Bi_3O_4Cl$ heterojunction to promote the specific surface area, light absorption performance and the separation efficiency of electron–hole pairs, which ultimately obtained excellent photocatalytic activity for degradation Rhodamine [19]. However, the shortcoming of ordinary heterojunction is the redox ability of photogenerated electrons and holes general becoming weaker after charge transfer [20–22]. Considering the importance of photo-induced carriers transfer, the construction of Z-Scheme heterojunction has become a hot topic because it can not only inhibit the electron–hole recombination, but also can keep excellent redox ability [23,24].

Cadmium sulfide (CdS), as an important II–VI semiconductor, has been considered as a promising material for photocatalytic reactions because of its narrow band gap of 2.21 eV, wide visible light response range and high photocatalytic performance [25,26]. Up to now, a number of CdS-based Z-Scheme heterojunction have been successfully established to improve the photocatalytic activity, such as BiOCl/Au/CdS [27], CdS/$BiVO_4$ [28], g-$C_3N_4$/Au/CdS [29], CdS/BiOI [30], CdS/Ag/$Bi_2MoO_6$ [31], Pt/CdS-TNTAs [32], $Bi_2WO_6$/Au/CdS [33] and CdS/Au/$TiO_2$ [34]. To the best of our knowledge, the suitable band gap edge of CdS ($E_{CB} = -0.50$ eV, $E_{VB} = 1.71$ eV) can match well with ($E_{CB} = 0.55$ eV, $E_{VB} = 3.26$ eV) of $Bi_3O_4Cl$ to form the Z-Scheme heterojunction system, which can enhance the charge carrier separation effectively and improve the photocatalytic activity.

In the present study, the Z-Scheme CdS/$Bi_3O_4Cl$ heterostructures are firstly synthesized and investigated in photocatalytic degradation of CIP and TC. Compared to bare CdS and $Bi_3O_4Cl$, the as-synthesized Z-Scheme CdS/$Bi_3O_4Cl$ heterostructures could remarkably improve photocatalytic performance. Meanwhile, charge separation and migration behaviors of the as-fabricated samples are assessed by photocurrent and EIS tests. The possible degradation pathway for CIP and TC are proposed based on the HPLC-MS analysis. The Z-Scheme CdS/$Bi_3O_4Cl$ heterostructure exhibits the excellent mineralization ability towards the CIP and TC molecule degradation through the analysis of the total organic carbon (TOC) tests. Moreover, the possible enhancing photocatalytic mechanism is discussed in depth based on the active species trapping experiments and ESR technique.

## 2. Experimental section

### 2.1. Preparation of CdS nanospheres

All the reagents are analytically grade and used without further purification. Typically, 0.426 g (1.6 mmol) of $Cd(Ac)_2 \bullet 2H_2O$ and 3.0448 g (40 mmol) of thiourea were dissolved in 40 mL deionized water and stirred for 30 min to obtain a clear solution. Then the obtained solution was transferred into a 50 mL Teflon-lined stainless steel autoclave at 140 °C for 5 h. The as-obtained product was collected by adding ethanol into the solution and centrifuged and subsequently dried in an oven at 60 °C overnight.

### 2.2. Synthesis $Bi_3O_4Cl$ nanosheets

The $Bi_3O_4Cl$ nanosheets were prepared according to a similar literature [35]. In a typical case, 1 mmol (0.485 g) $Bi(NO_3)_3 \bullet 5H_2O$ was dispersed in 10 mL of ethylene glycol under magnetic stirring for 10 min to form a suspension. Meanwhile, 0.33 mmol (0.018 g) of $NH_4Cl$ was added to 25 mL of distilled water with vigorously stirred for 5 min and slowly added into above suspension. Then, the precursor was transferred into a 50 mL Teflon-lined stainless autoclave at 160 °C for 12 h. The resulting powder was collected by centrifugation and washed with distilled water and alcohol several times, dried at 80 °C for 6 h. Then, the solid powder was calcined in the muffle furnace at 500 °C for 5 h with a heating rate of 5 °C min.

### 2.3. Synthesis Z-Scheme CdS/$Bi_3O_4Cl$ heterostructure

The Z-Scheme CdS/$Bi_3O_4Cl$ heterostructures were prepared by a simple hydrothermal method. Typically, certain amount of as-prepared of $Bi_3O_4Cl$ nanosheets were added in 1 mL (0.2 g $mL^{-1}$) of PVP at room temperature, and then certain amount of CdS nanospheres were dispersed in 10 mL of alcohol with vigorously stirred for 30 min and slowly added into above suspension. The mixture was transferred into a Teflon-lined autoclave (50 mL) and was kept at 160 °C for 6 h. In this manner, different mass ratios of the $Bi_3O_4Cl$ to CdS samples (abbreviated as CdS/$Bi_3O_4Cl$-30, CdS/$Bi_3O_4Cl$-50, CdS/$Bi_3O_4Cl$-70, and CdS/$Bi_3O_4Cl$-100) were obtained.

### 2.4. Characterization of the as-prepared samples

The crystalline phases of the samples were determined by powder X-ray diffraction (XRD, D/MAX-2500 diffractometer, Rigaku, Japan). The morphologies of as-prepared samples were examined by scanning electronic microscopy (SEM) on an S-4800 field emission SEM (SEM, Hitachi, Japan). The transmission electron microscopy (TEM), high-resolution TEM (HRTEM) were examined by transmission electron microscopy (Tecnai G2; FEI Co) using an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was obtained by Thermo ESCALAB 250X (America) electron spectrometer using 150 W Al K$\alpha$ radiations. UV–Vis absorption spectra were obtained using a UV–Vis spectrophotometer (UV-3600, Shimadzu, Japan) at room temperature. Photocurrent and electrochemical impedance spectra tests were carried out using CHI 660 C and CHI 760E (Chenhua Instruments Co. Shanghai china) electrochemical workstation, respectively. Total organic carbons were measured on a multi N/C 2100 (AnalytikJena AG, Germany) TOC analyzer.

### 2.5. Photocatalytic activity measurement

The photocatalytic performance of as-prepared photocatalysts were evaluated by degradation of CIP and TC under visible ($\lambda > 420$ nm) irradiation. The light source was provided by a 250 W xenon lamp with a 420 nm cutoff filter. The intensity of visible light was determined to be 150 mW $cm^{-2}$ by the CEL-NP2000 optical power densitometer. The photocatalytic experiments were performed as the following: 50 mg of as-synthesized catalyst powder was placed in 100 mL of 10 mg $L^{-1}$ CIP aqueous solution or TC aqueous solution, and then the suspension was vigorously stirred in the dark for 30 min to achieve the adsorption–desorption equilibrium. Furthermore, the condensed water was introduced to make the temperature of photochemical reactor at 25 °C. At given irradiation time intervals, the suspension of 5 mL was sampled and separated by centrifuge, then analyzed according to the absorbance at $\lambda_{max} = 277$ nm (CIP) and $\lambda_{max} = 357$ nm (TC) by UV–vis spectrophotometer.

### 2.6. Active species trapping and $\bullet O_2^-$ quantification experiments

In order to investigate the active species generated in Z-Scheme CdS/$Bi_3O_4Cl$ heterostructure system, 1, 4-benzoquinone (BQ, 1 mM), ethylenediamine tetraacetic acid disodium salt (EDTA-2Na, 1 mM) and tert-butyl alcohol (TBA, 1 mM) were used as the

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