Journal of Catalysis 356 (2017) 1–13

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

An environmentally friendly Z-scheme WO_3/CDots/CdS heterostructure with remarkable photocatalytic activity and anti-photocorrosion performance

Jun Zhang [a], Yun Guo [a], Yuhan Xiong [a], Dandan Zhou [b], Shuangshi Dong [a,*]

[a] Key Laboratory of Groundwater Resources and Environment, Ministry of Education, Jilin University, Changchun 130021, Jilin, China
[b] School of Environment, Northeast Normal University, Changchun 130117, Jilin, China

ARTICLE INFO

Article history:
Received 21 July 2017
Revised 21 September 2017
Accepted 26 September 2017

Keywords:
All-solid-state Z-scheme
Nonmetallic electronic mediator
Interface charge transfer
Visible light photocatalyst
Anti-photocorrosion
Biocompatibility
Low cytotoxicity

ABSTRACT

As a representative artificial photosynthetic system, direct Z-scheme WO_3/CdS is a promising photocatalyst system for water purification. However, this system is still limited due to low electron transfer efficiency and serious photocorrosion. Here, we designed and precisely fabricated a novel all-solid-state Z-scheme WO_3/CDots/CdS system. The CDots, as a nonmetallic electron mediator, could promote interfacial charge carrier separation and eliminate photocorrosion with enhanced photocatalytic activity. The phase, morphologies, microstructures, and optical and electrical properties of as-obtained Z-scheme WO_3/CDots/CdS heterojunctions were investigated in detail. The photocatalytic performance of as-prepared catalysts was evaluated by the decomposition of 4-chlorophenol (4-CP), rhodamine B (RhB), and tetracycline hydrochloride (TCH) and the reduction of aqueous Cr(VI) in visible light. The optimized Z-scheme WO_3/CDots/CdS-2 photocatalyst exhibited the highest photocatalytic activity for degrading and mineralizing 4-CP (~70.0% and 48.3% in 7 h, respectively), both of which exceeded the rates observed in WO_3/CdS samples under the same conditions by ~2 times. In addition, the WO_3/CDots/CdS-2 showed excellent stability and reusability with negligible change at ~2.2% difference for 4-CP degradation in eight cycles. The release percentage of SO_4^{2-} (transformed from S^{2-}) and Cd^{2+} was only ~0.77% and 0.79%, respectively, when compared with the initial concentration, which was far less than for the WO_3/CdS system (~5.64% and 5.70%). The results indicated that a thorough and complete Z-scheme charge carrier transfer route was achieved. Toxicity assessment authenticated good biocompatibility and low cytotoxicity of WO_3/CDots/CdS. This study showed that the Z-scheme WO_3/CDots/CdS was a promising photocatalyst for water purification.

© 2017 Elsevier Inc. All rights reserved.

1. Introduction

Semiconductor photocatalyst systems has great potential application in water purification [1]. Over the past decades, numerous semiconductor materials have been used and developed, including TiO_2, ZnO, WO_3, CdS, MoS_2, g-C_3N_4, $BiVO_4$, V_2O_5, BiOX (X = Cl, Br, and I), AgBr, Bi_2WO_6, etc. [1–7]. However, further application is severely limited due to low light utilization efficiency and rapid recombination of photogenerated electron–hole pairs. It has been found that engineered heterojunctions in photocatalysts can enhance photocatalytic activity via the spatial separation of photogenerated electron–hole pairs [8]. Compared with conventional heterostructures (typle-I, typle-II, and p-n heterojunction), the Z-scheme heterojunction could realize spatial separation of electron–hole pairs and ensure strong redox ability simultaneously [9–18].

The direct Z-scheme WO_3/CdS heterostructure is a significant and mature Z-scheme photocatalytic system. It shows effective photocatalytic performance in pollutant degradation, CO_2 reduction, and H_2 evolution in visible light due to its well-matched energy band structures, consisting of the WO_3 photosystem I (PS I) and CdS photosystem II (PS II) [10,19]. Recently, various noble-metal particles (such as Au, Ag, and Pt) have been chosen to act as electron mediators to promote its photoactivity [11,13]. This was attributed to the fact that the noble-metal nanoparticles, as a link to connect WO_3 PS I and CdS PS II (electron mediator), were anchored at the WO_3/CdS interface to increase the effective contact and to accelerate the carrier separation [20,21]. Compared with the direct Z-scheme, the one with solid electron mediators is more favorable in terms of ensuring a continuous flow of electrons between the source and target photosystem due to close contact

---

* Corresponding author.
E-mail address: sdong@jlu.edu.cn (S. Dong).

https://doi.org/10.1016/j.jcat.2017.09.021
0021-9517/© 2017 Elsevier Inc. All rights reserved.

[11,20–22]. Even so, the preceding Z-scheme photocatalysts are still limited by the use of expensive noble-metal particles and low photocatalytic activity [11,13]. More importantly, the significant release of cadmium ions in direct Z-scheme WO_3/CdS heterostructures has been considered a huge threat to the environment [20,23] resulting from serious photocorrosion of CdS in photocatalytic processes [8,11,12,20,23]. According to Xu at al. [20], the photocorrosion of CdS can be efficiently prevented by introducing an electron mediator to effectively promote electron transfer and to consume the holes in the valence band (VB) of CdS. Thus, it is imperative to develop an effective nonmetallic electron relaying medium to realize a highly competent and stable Z-scheme system.

Carbon nanodots (CDots), as a novel zero-dimensional nanocarbon material with size below 10 nm, possess low toxicity, low cost, chemical stability, ecofriendliness, excellent optical properties, and unique photoinduced electron-transfer and electron-reservoir properties [24,25]. CDots have been widely employed as a co-catalyst to modify semiconductors with enhanced photocatalytic activities, such as TiO_2, ZnO, CdS, WO_3, Bi_2WO_6, BiOX (X = Cl, Br, and I), Ag_3PO_4, $ZnFe_2O_4$, and g-C_3N_4 [6,26–31]. The conjugated π structure of CDots played a key role in these composites [26,32]. Kang et al. [33] proved that the CDots could act as an electron transfer intermediary (electron transporters and acceptors) to significantly improve the photoelectric conversion efficiency. Based on this, inserting CDots into the WO_3/CdS interface and coupling the three above to generate an all-solid-state Z-scheme heterostructure (WO_3/CDots/CdS) would efficiently reduce the recombination of photogenerated electron–hole pairs and enhance the photocatalytic activity. In this way, a complete and vectorial Z-scheme charge carrier transfer route may be realized, and thus the serious photocorrosion in previous literature may be eliminated [20].

The extensive use of nanomaterials has caused considerable harm to the environment, health, and safety in recent years [29]. It has been confirmed that some prevalent catalyst nanoparticles affect gene expression in zebrafish embryos, inhibited seedling growth of different *Arabidopsis thaliana* [29,34], showed cytotoxicity to human lung cells ($\sim$80 μg mL^{-1}) [35], and decreased the cell proliferation and viability of human keratinocytes [36]. Thus, the potentially harmful effects of nanomaterials should be properly evaluated prior to their use.

Here, for the first time, we designed and precisely constructed a novel all-solid-state Z-scheme WO_3/CDots/CdS system, in which CDots were used as a solid-state nonmetallic electron mediator to promote interfacial charge carrier separation and transport and to eliminate photocorrosion in order to enhance photocatalytic activity. The photocatalytic performance of as-prepared catalysts was evaluated by measuring the decomposition of 4-CP, RhB, and TCH and the reduction of aqueous Cr(VI) in visible light. Especially, we further investigated the photocorrosion of WO_3/CDots/CdS by observing the change in content of SO_4^{2-} (transformed from S^{2-}) and Cd^{2+} in eight cyclic 4-CP degradation tests. Subsequently, a vectorial Z-scheme charge carrier transfer mechanism of the WO_3/CDots/CdS heterostructure was proposed and elucidated. The toxicity of WO_3/CDots/CdS nanocomposites toward *Staphylococcus aureus* and *Escherichia coli* was also evaluated.

2. Experimental

2.1. Photocatalyst preparation

All reagents were used as received without further purification. The CDots and WO_3 nanorods were prepared via a typical electrochemical method and a facile hydrothermal method, respectively. The detailed synthesis procedures were described in our previous study [26].

The Z-scheme WO_3/CDots/CdS heterostructure was synthesized using a two-step synthesis method. First, the WO_3/CDots nanocomposites were prepared via an oil bath reflux. A quantity of 0.1 g prepared WO_3 nanorods was uniformly dispersed in 80 mL of CDots aqueous solution with vigorous stirring. The mixture was then heated in the oil bath at 90 °C for 3 h. After naturally cooling to room temperature, the resulting samples were washed three times with ultrapure water and dried overnight at 60 °C to obtain the WO_3/CDots nanocomposites. Second, the CdS was introduced via a simple precipitation method. A quantity of 0.5 g as-prepared WO_3/CDots powder was dissolved in 100 mL of ultrapure water, followed by the successive and dropwise addition of 0.1 M $Cd(NO_3)_2$ and 0.05 M NaS with vigorous stirring for 1 h at room temperature. The ratio of the volumes of $Cd(NO_3)_2$ and NaS solutions was kept at 1:2. Z-scheme WO_3/CDots/CdS precipitates were collected and rinsed three times with ultrapure water before being dried at 60 °C. For comparison, the different molar ratios of Cd^{2+} to WO_3/CDots were controlled (1, 2, and 3 mol.%), and the obtained samples accordingly denoted as WO_3/CDots/CdS-X (X = 1, 2, and 3) for simplicity, which was used to investigate the effect of the contents of CdS on the photocatalytic performance. The corresponding pure CdS and WO_3/CdS nanocomposites were also prepared via the same precipitation approach by adding nothing and WO_3 nanorods, respectively, to the mixture of $Cd(NO_3)_2$ and NaS solution. In the process of precipitation, Cd^{2+} can be adsorbed quickly onto the surfaces of WO_3 and CDots due to their negative surface charge, and then the CdS grow in situ [10]. Compared with WO_3, the CDots have more negative surface charge [30], which was conductive to adsorbing Cd^{2+} from $Cd(NO_3)_2$. In this way, a heterogeneous interface can form accurately between CDots and CdS.

2.2. Characterization

The morphology and crystal structure of prepared samples were investigated via scanning electron microscopy (SEM, JEOL JSM-7001F) with an energy-dispersive X-ray spectroscope (EDS), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM, via a 200 kV FEI-Tecnai F20, USA) measurements. X-ray diffraction (XRD) patterns were used to determine the phase composition of the samples, which was obtained via a Bruker D8 powder X-ray diffractometer (Germany) with CuKα (λ = 0.15406 nm) radiation at a scan rate 2θ of 0.02° s^{-1}. X-ray photoelectron spectroscopy (XPS) was performed via a VG ESCALAB210 (Thermo Fisher Scientific, USA) XPS system with an Al*K*α (h = 1486.6 eV) radiation excitation source. All obtained spectra were normalized by referring to the adventitious carbon at 284.6 eV. UV–vis diffuse reflection spectra (DRS) were collected on a UV-2550 spectrophotometer (Shimadzu, Japan) equipped with a Labsphere diffuse reflectance accessory in which $BaSO_4$ was employed as a reflectance reference over the range 300–800 nm. Fourier transform infrared (FT-IR) spectra were investigated via a VERTEX 70 spectrophotometer (Bruker, Germany) within the range of 3500–500 cm^{-1} using pressed KBr discs. Raman spectra were recorded on a T64000 Raman spectrometer (Horiba Jobin Yvon, France) with laser excitation at 514 nm. Photoluminescence (PL) spectra were measured by a luminescence spectrometer (Cary Eclipse, Varian Medical Systems, USA) with an excitation wavelength of 300 nm. Transient time-resolved photoluminescence decay measurements were carried out by a FL920 luminescence spectrometer with an excitation wavelength of 337 nm. Electron spin resonance (ESR) spectra were obtained on a Bruker model ESR JES-FA200 spectrometer using the spin-trap reagent DMPO (5,5-dimethyl-1-pyrroline N-oxide, Sigma Chemical Co.) in water (for hydroxyl radicals) and methanol (for superoxide radicals). The measurement was carried

Download English Version:

https://daneshyari.com/en/article/6526914

Download Persian Version:

https://daneshyari.com/article/6526914

Daneshyari.com