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2D/2D Z-scheme heterojunction of $CuInS_2$/g-C_3N_4 for enhanced visible-light-driven photocatalytic activity towards the degradation of tetracycline

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ABSTRACT

Photocatalysis is one of the most promising technologies owing to its great potential to relieve energy and environmental issues. Constructing Z-scheme heterojunction photocatalyst with strong redox ability to make for enhanced light absorption and efficient charge separation is extremely attractive but still underdeveloped. Herein, Z-scheme heterojunction of $CuInS_2$/g-C_3N_4 with a "sheet-on-sheet" hierarchical structure showing enhanced photocatalytic performance for the tetracycline (TC) degradation under visible-light irradiation has been developed. This 2D/2D hierarchical structure of $CuInS_2$/g-C_3N_4 composite not only enlarges the contact region in the heterojunction interface but also provides more active reaction sites, as demonstrated by the TEM and BET analyses. Particularly, 50 wt% $CuInS_2$/g-C_3N_4 heterojunction shows the highest photocatalytic activity (20 mg/L; 83.7% degradation within 60 min), which the apparent rate constant is 15 and 11 times higher than that of pure g-C_3N_4 and $CuInS_2$ nanosheets, respectively. The remarkably enhanced photocatalytic activity mainly derives from the synergistic effect between $CuInS_2$ and g-C_3N_4, thereby promoting the charge separation during the photocatalytic reaction. This work is expected to provide a design idea to construct multifunctional 2D/2D nanocomposites for photocatalytic applications.

1. Introduction

The presence of pharmaceutical residues in aqueous solution has endangered ecosystems and human health [1]. Tetracycline (TC), a broad-spectrum antibiotic, is extensively used to prevent human and animal infections [2]. Frustratingly, the TC that enters the human or animal body is only partially metabolized and large fraction of TC is excreted by urine and faeces, which has been detected in various water bodies [3]. What's worse, traditional waste-water treatment plants would not achieve desired effect to address residual antibiotics in water, which is limited by the excessive cost and lengthy process [4]. Therefore, seeking a suitable method with high efficiency, low cost, short period and non-pollution to remove TC from wastewater is even more badly needed. As a promising green and sustainable technique for environmental remediation, semiconductor-based photocatalysis has received much attention owing to its many merits (economy, clean, time saving and high efficiency) [5]. Moreover, it only requires the inexhaustible solar light as a driving force, and a proper semiconductor as a photocatalyst to participate in the catalytic reaction for the removal of TC.

Nowadays, visible-light-active graphitic carbon nitride (g-C_3N_4) organic semiconductor has been extensively used in the field of photocatalysis owing to its facile synthesis, its layered graphite-like structure, a medium bandgap (~2.7 eV), lower systemic toxicity and high photostability [6–8]. Additionally, g-C_3N_4 only consists of two earth-abundant nonmetallic elements (carbon and nitrogen), implying that the precursor originals of as-synthetized g-C_3N_4 are exceptionally abundant and economical, including melamine, dicyandiamide, urea, ammonium thiocyanate, *ect* [9,10]. In terms of degradation of TC, g-C_3N_4 shows efficient photocatalytic activity [11,12]. Though possessing unique physicochemical properties, three intractable issues (fast recombination of photogenerated electron-hole pairs, low visible-light utilization efficiency and low surface area) of single-component g-C_3N_4 severely restrict its practical application in photocatalysis [13–15]. In order to overcome the above-mentioned problems, much work has been made to design and construct the multicomponent g-C_3N_4-based heterostructure photocatalysts to improve the photocatalytic activity of pristine g-C_3N_4. In particular, Z-scheme configurations are considered an effective strategy in the construction of heterojunctions to improve the charge separation efficiency and the redox ability upon photo-

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excitation [16]. In addition, among the heterojunctions with tunable dimensionalities, 2D/2D heterojunctions often provide larger interface contact area and higher charge mobility besides the low charge recombination rates in comparison with 0D/2D and 1D/2D heterojunctions, which can be helpful in offering more surface-active sites further to improve the photocatalytic reaction rate [17]. Therefore, when choosing a suitable semiconductor to couple with g-C_3N_4, the semiconductor should be satisfied with the following three requirements: (i) the respective band structures with a staggered alignment to effectively separate the electron-hole pairs; (ii) processing a 2D layered structure to form 2D/2D g-C_3N_4-based heterojunction, exposing more active sites and increasing the reaction rate of photon-generated carriers on the photocatalyst surface; (iii) a narrow band gap for harvesting broad light-absorption.

Recently, $CuInS_2$, as one of ternary sulfide semiconductors, has been considered as an attractive photocatalyst owing to its high absorption coefficient and excellent solar energy conversion efficiency [18]. Moreover, based on previous reports, the conduction band and valance band of g-C_3N_4 are −1.4 eV and 1.3 eV [19], and conduction band and valance band of $CuInS_2$ are −1.86 eV and −0.11 eV [20]. Theoretically, the energy levels of g-C_3N_4 and $CuInS_2$ are well-matched to construct Z-scheme heterostructure. Recently, the previous work reported that the prominently enhanced H_2 evolution was achieved by the $CuInS_2$/g-C_3N_4 heterostructure photocatalyst in comparison with the individual component [21]. However, little research has been investigated at this point concerning the $CuInS_2$/g-C_3N_4 photocatalyst towards the treatment of the antibiotic wastewater, which is also a challenging issue with the worldwide concern. Therefore, it is appealing and highly anticipated to acquire 2D/2D Z-scheme $CuInS_2$/g-C_3N_4 heterojunction photocatalysts for environmental remediation.

Herein, we develop a 2D/2D Z-scheme heterojunctions of $CuInS_2$/g-C_3N_4 and demonstrate their excellent visible-light-driven photocatalytic performance toward the degradation of TC. The results reveal that 50 wt% $CuInS_2$/g-C_3N_4 heterojunction shows the highest photocatalytic activity (20 mg/L; 83.7% degradation within 60 min), which the apparent rate constant is 15 and 11 times higher than that of pure g-C_3N_4 and $CuInS_2$ nanosheets, respectively. The original of the enhanced photoactivity of g-C_3N_4/$CuInS_2$ in this work is attributed to the Z-scheme mechanism, which is identified by the reactive species trapping experiment.

2. Experimental section

2.1. Synthesis of g-C_3N_4 powders

The general process for the fabrication of g-C_3N_4 is based on the previous report [22]. 10 g urea powder was placed in a covered alumina crucible, heated to 550 °C in a muffle furnace at a speed of 0.5 °C/min, and kept at this temperature for 3 h. The obtained bulk g-C_3N_4 products were grinded into powders after cooling down to room temperature. Next, 400 mg bulk g-C_3N_4 obtained as above was placed in an open ceramic container and heated to 500 °C with a ramp rate of 2 °C/min, and maintained at this temperature for 2 h. A light yellow powder of g-C_3N_4 nanosheets was finally obtained.

2.2. Synthesis of $CuInS_2$ and $CuInS_2$/g-C_3N_4 composites

Briefly, 100 mg of CuCl, 221 mg $InCl_3$ and 160 mg sulfur powder were mixed in 30 mL of triethylene glycol. Then, homogeneous precursor was transferred into 40 mL Teflon-lined stainless-steel autoclave, and kept at 200 °C for 48 h. After cooling to room temperature, the product was collected, washed and dried. For the $CuInS_2$/g-C_3N_4 composites, the g-C_3N_4 nanosheets with different weight ratios (15 wt %, 30 wt%, 50 wt% and 70 wt%) were added to the fabricated process of $CuInS_2$, which were abbreviated as 15% CIS-CN, 30% CIS-CN, 50% CIS-CN and 70% CIS-CN, respectively. In addition, pure g-C_3N_4 and $CuInS_2$ were labelled as CN and CIS, respectively.

2.3. Characterization

X-ray diffraction (XRD) patterns of materials were recorded using an X'Pert-ProMPD (Holand) D/max-γA X-ray diffractometer with Cu Kα radiation (λ = 0.154178 nm). Transmission electron microscope (TEM), high-resolution TEM (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-SEM) were performed with a FEI-Tecnai F20 microscope operating at 200 kV, respectively. X-ray photoelectron spectroscopy (XPS) Valence band X-ray photoelectron spectra (VBXPS) were carried out on a KRATOS Axis ultra-DLD X-ray photoelectron spectrometer with a monochromatized Al Kα X-ray source. UV–vis absorption spectra of the samples were recorded on a Lambda 750 (Perking Elmer) spectrophotometer in the tested range of 200–800 nm. The Brunauer-Emmett-Teller (BET) specific surface areas and pore volumes were characterized by a Micromeritics ASAP-2050 porosimeter. Photoluminescence (PL) spectra of the as-prepared samples were detected by Fluorolog-TCSPC Luminescence Spectrometer. The total organic carbon (TOC) was measured by automatic total organic carbon analyzer (TOC-V, Shimadzu, Japan).

2.4. Photocatalytic activity measurement

In the photocatalytic degradation process of tetracycline (TC), visible light was obtained by using 300 W xenon lamp with a 420 nm cut off filters. In each test, 50 mg photocatalyst was suspended in 100 mL of 10 mg/L TC. The solution was stirred for 30 min in dark to ensure the establishment of adsorption equilibrium. At certain time intervals, 3 mL aliquots were extracted and centrifugated in the reaction process, then analyzed on UV–vis spectrophotometer at the max absorbed wavelength of 357 nm.

2.5. Active species capturing experiment

Sacrificial agents (1 mmol), including 2-propanol (IPA), disodium ethylenediamine tetra acetic acid (EDTA) and 1,4-benzoquinone (BQ), were added into the preceding photocatalytic test to capture hydroxyl radicals ($^{\cdot}OH$), holes (h^+) and superoxide radicals ($^{\cdot}O_2^-$), respectively.

3. Results and discussion

The XRD patterns of as-prepared CN, CIS and 50% CIS-CN samples are displayed in Fig. 1. For pure CN, two characteristic peaks at 13.1° and 27.6° are detected, which correspond to an in-plane structural packing motif and the interlayer stacking peak of aromatic systems,

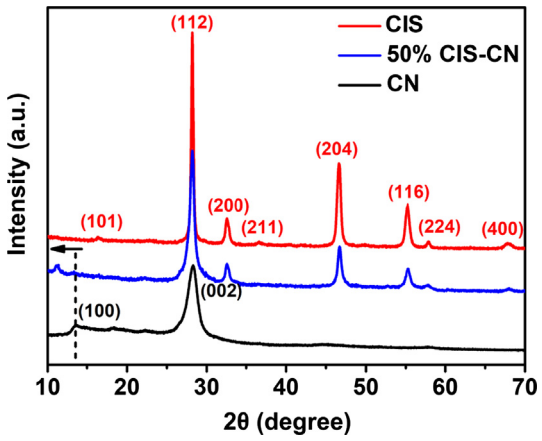

Fig. 1. XRD patterns of as-prepared samples.