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Visible-light photocatalytic degradation of multiple antibiotics by AgI nanoparticle-sensitized Bi_5O_7I microspheres: Enhanced interfacial charge transfer based on Z-scheme heterojunctions

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ABSTRACT

The development of efficient visible light photocatalysts for refractory organic pollutant degradation has gained considerable attention in wastewater treatment. Here, close-connected AgI/Bi_5O_7I (AI/BOI) heterojunctions were successfully synthesized by a facile deposition–precipitation approach. Multiple antibiotics, including tetracycline, deoxytetracycline, oxytetracycline, and ciprofloxacin, were employed as target pollutants to evaluate the visible light photoactivity of the prepared samples. The obtained AI/BOI-5 exhibited optimal photocatalytic activity and photoelectric property, which was 8.62 times (tetracycline degradation rate) and 12.44-fold (photocurrent intensity) than those of bare BOI, respectively. The strengthened visible light absorption and effective separation and transfer of the photoinduced electrons and holes should be responsible for the improvement of photocatalytic performance. The mineralization ability comparison was explored by total organic carbon and three-dimensional excitation–emission matrix fluorescence spectra measurements. The AI/BOI-5 also revealed good adaptability to higher initial contaminant concentrations and desired photodegradation stability in practical applications. By the studies of reactive species trapping, electron spin resonance and nitroblue tetrazolium agent of $\cdot O_2^-$ transformation experiments verified that $\cdot O_2^-$, h^+, and ·OH were all produced in AI/BOI photocatalytic systems, while only $\cdot O_2^-$ and h^+ worked during BOI photolysis. A possible Z-scheme heterojunction mechanism can be ascribed to the enhanced photocatalytic degradation of multiple antibiotics induced by AI/BOI. This work gives deep insight into heterostructured photocatalysis and provides a novel way to construct and design highly efficient photocatalysts for water purification.

1. Introduction

Since the advent of penicillin production in 1929, antibiotics have been widely used to improve human and animal health and to strengthen plant viability and agricultural harvests [1–3]. However, the long-term and extensive utilization of antibiotics in human beings and veterinary medicines can cause the emergence and potential spread of resistance genes [4–9]. More importantly, anthropogenic activities and unreasonable antibiotic disposal in wastewater treatment plants (WWTPs) lead to the continuous discharge of pharmaceutical residues into aquatic environments. Accumulated antibiotics in seawater, surface water, groundwater, and even drinking water increase the difficulty of pollutant degradation (even secondary pollution), pose a serious threat to ecosystem function, and disrupt the endocrine systems of living beings [10–13]. Hence, it is urgent to develop an environment-friendly and efficient approach to antibiotic removal in wastewater treatment.

Advanced oxidation processes (AOPs) have been demonstrated to be one of the best recommended technologies for refractory and toxic organic pollutant removal from wastewater [6,14]. As a new type of AOP technology, semiconductor-based photocatalysis is an ideal chemical process for antibiotic degradation, due to its cost-effectiveness and satisfactory catalytic efficiency. From the viewpoint of energy conservation and environment protection, the development of photocatalysts that utilize solar energy efficiently for the decomposition of hazardous pollutants has become a hot spot in photocatalysis [14,15].

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Recently, Bi-based photocatalysts have displayed perfect photocatalytic activity under visible light and have been widely investigated, such as BiOI [16], $BiVO_4$ [17], BiOBr [18,19], BOI [20], Bi_2O_4 [21], and Bi_2WO_6 [22]. Among them, BOI is a new photocatalyst with a moderate band gap of (~2.90 eV) [23], which possesses a special layered crystal structure and can be employed in organic pollutant degradation under visible light irradiation. Yang et al. successfully fabricated rodlike BOI via a facile precipitation transformation method and utilized it in rhodamine degradation. Er^{3+}/Fe^{3+} co-doped porous BOI microspheres were synthesized by Liu and his co-workers, and their prominent visible-light photoactivity in the decomposition of colorless target phenols was discussed [24]. Nevertheless, pure BOI still suffers from several disadvantages, such as its insufficient light absorption and lower photoinduced electron–hole pair separation and photocatalytic efficiency [25]. Construction of heterojunctional structures by combining BOI with another appropriate semiconductor had been verified as a constructive and instructive strategy. For instance, in Liu's report, distinctly enhanced photocatalytic and photoelectrochemical properties were achieved by the introduction of g-C_3N_4 to construct the heterostructured photocatalyst BOI/g-C_3N_4 [26]. Zhao et al. also developed an Ag/AgBr/BOI heterojunction through Ag/AgBr nanoparticles tightly bound to BOI, resulting in efficient charge transfer at the heterojunction interface [27]. For long-term development and in-depth investigation, more BOI-based heterostructured photocatalysts should be developed and used for refractory pollutant degradation.

Silver halides (AgX) are employed as photosensitive materials in photographic film industries [7,28–30]. As a member of AgX, AI possesses a strong visible light absorption ability attributable to its relatively narrow band gap (~2.77 eV [8]). Nevertheless, the micro-sized agglomerates and lack of close connection with the original supports over pure AI phases lead to decreased photogenerated carrier separation efficiency [31]. Consequently, a good substrate chosen to disperse AI nanoparticles could commendably improve both the photoactivity and photostability of bare AI; successful cases are AI/BiOI [32], AI/$Bi_2O_2CO_3$ [33], AI/TiO_2 [34], AI/WO_3 [35], and so on. Furthermore, the corresponding conduction band (−0.42 eV) is more negative than that of $O_2/{\cdot}O_2^-$ (−0.33 eV vs. NHE), which was advantageous for more ${\cdot}O_2^-$ species production and enhancement of photooxidation ability. Based on this analysis, it can be expected that the modification of BOI with AI to form AI/BOI heterojunctions could effectively resolve the existing problems in two bare semiconductors.

In this work, AI nanoparticle-decorated BOI microspheres were fabricated by an in situ deposition–precipitation method at room temperature. The properties of AI/BOI composites, such as crystal structure, morphology, optical properties, and electrochemical characteristics, were systematically characterized by the corresponding technologies. The photocatalytic activity was evaluated for multiple antibiotics including tetracycline (TC), deoxytetracycline (DTC), oxytetracycline (OTC), and ciprofloxacin (CIP) degradation. The predominant active species were determined by trapping experiments, electron spin resonance (ESR) tests, and nitroblue tetrazolium (NBT) agent of ${\cdot}O_2^-$ transformation. The recyclability and stability of the catalysts was also discussed in detail. A reasonable degradation mechanism was brought up through a series of theoretical and experimental data analyses.

2. Experimental

2.1. Materials and reagents

Bismuth nitrate hydrate ($Bi(NO_3)_3{\cdot}5H_2O$, ≥99.0%), potassium iodide (KI, ≥99.0%), silver nitrate ($AgNO_3$, ≥99.0%), ethylene glycol (EG, ≥99.0%), ethanol (CH_3CH_2OH, ≥99.7%), tetracycline (TC, ≥99.0%), deoxytetracycline (DTC, ≥98.0%), oxytetracycline (OTC, 95.0–105%), and ciprofloxacin (CIP, ≥99.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd. All the reagents were analytical grade and were used without further purification, and deionized water was used throughout this study.

2.2. Preparation of BOI microspheres

The BOI samples were prepared using BiOI microspheres as the templates. Briefly, 2.765 g of $Bi(NO_3)_3{\cdot}5H_2O$ and 1.020 g of KI were separately dissolved in 50 mL EG with 30 min ultrasonic processing. Afterward, the KI solution was added slowly into the $Bi(NO_3)_3{\cdot}5H_2O$-containing solution with constant stirring. After being stirred for 2 h, the mixture was transferred into a Teflon-lined stainless steel autoclave and maintained at 160 °C for 12 h. The formed BiOI microspheres were filtered, washed with ethanol and deionized water, and dried at 60 °C for 12 h. Last, the BiOI microspheres were placed in a ceramic crucible and then loaded into the region of a muffle furnace, heated to 450 °C at a rate of 3 °C/min, and maintained at 450 °C for 2 h. After natural cooling, BOI microspheres were obtained and collected for following applications.

2.3. Preparation of AI/BOI composites

The AI/BOI heterojunctions were synthesized by an in situ dep osition–precipitation method. In a typical synthesis procedure, 0.500 g of BOI microspheres was ultrasonically dispersed into 100 mL of deionized water. After that, 0.215 mL of KI solution (0.1 M) was added dropwise into the suspension with vigorous stirring for 30 min. Then $AgNO_3$ (0.1 M, 0.215 mL) was slowly added into the mixture. The theoretical mass ratio AI/(AI + BOI) was 1 wt.%, denoted as AI/BOI-1 for simplicity. The products were obtained after 3 h room dark reaction, collected by filtration, washed, and dried at 60 °C overnight. Similarly to the above preparation method, bare AI, AI/BOI-5, AI/BOI-10, and AI/BOI-20 were also fabricated; the mass ratios of AI in these composites were 100, 5, 10, and 20 wt.%, respectively.

2.4. Characterization

The XRD patterns were recorded in a range of 10°–70° on a Rigaku D/max 2500v/pc X-ray diffractometer using CuKα radiation at a scan rate of 0.1° $2\theta\ s^{-1}$. A field emission scanning electron microscope (FESEM, Hitachi S-4800) was used for the basic morphology analysis. TEM) characterization was performed on a FEI Tecnai G20 operated at 200 kV. The UV–vis absorption spectra were obtained by a UV–vis spectrometer (UV-4100, Shimada). The XPS was performed on a Thermo ESCALAB 250XI spectrometer with an Al*K*α source. Photoluminescence (PL) spectra were monitored using a transient fluorescence spectrometer (Edinburgh FLsp920). Three-dimensional excitation–emission matrix fluorescence spectra (3D EEMs) were detected with an F-4500 spectrofluorimeter. ESR signals of spin-trapped radicals were examined on a Bruker ER200-SRC spectrometer under visible light irradiation ($\lambda > 420$ nm). The photocurrent density and EIS were carried out on a CHI660C electrochemical workstation using a standard three-electrode system under visible light illumination. Sodium sulfate electrolyte solution (0.5 M) was adopted as the electrolyte in all electrochemical tests.

2.5. Photocatalytic evaluation

The photocatalytic activity was evaluated by examining the decomposition of four refractory pollutants, TC, DTC, OTC, and