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Fabrication of visible-light-driven silver iodide modified iodine-deficient bismuth oxyiodides Z-scheme heterojunctions with enhanced photocatalytic activity for *Escherichia coli* inactivation and tetracycline degradation

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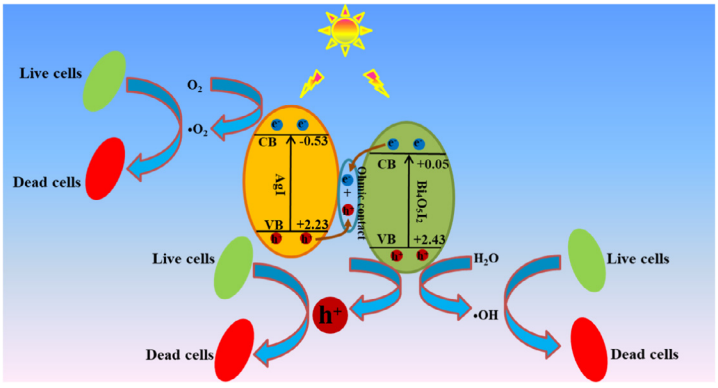
GRAPHICAL ABSTRACT



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ABSTRACT

At present, various organic pollutants and pathogenic microorganisms presented in wastewater have severely threatened aquatic ecosystem and human health. Meanwhile, semiconductor photocatalysis technology for water purification has attracted increasingly significant attention. Herein, we successfully constructed a series of novel visible-light-driven (VLD) $Bi_4O_5I_2$/AgI hybrid photocatalysts with different AgI amounts. Compared with pristine AgI and $Bi_4O_5I_2$, $Bi_4O_5I_2$/AgI with the optimal AgI contents exhibited remarkably enhanced photocatalytic performance in probe experiment for *Escherichia coli* (*E. coli*) disinfection and tetracycline (TC) degradation. The efficiency for TC degradation and *E. coli* inactivation reached 82% and 100% in 30 min, respectively. The enhanced electron-hole separation efficiency was responsible for improved photocatalytic activity. In addition, the destruction process of the chemical structure of TC molecules was further investigated by three-dimensional excitation-emission matrix fluorescence spectra (3D EEMs). The activity and crystal phase of the catalysts did not change significantly after four cycles, demonstrating their excellent recyclability and stability of catalysts. The Ag^+ ion leaking experiments, radical trapping experiments and ESR tests demonstrated that $\cdot OH$, $\cdot O_2^-$ and h^+ were the main active species in photocatalytic disinfection processes. Furthermore, the photocatalytic mechanism of $Bi_4O_5I_2$/AgI nanomaterials was discussed in detail in conjunction with the energy band structure, and a

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reasonable Z-scheme interfacial charge transfer mechanism was proposed. This work is expected to provide an efficient water disinfection method.

1. Introduction

In the past few decades, the rapid development of industry has brought about serious environmental pollution while bringing benefits to mankind. Organic pollutants and pathogenic microorganisms contained in industrial wastewater are regarded as two major pollution sources that need to be urgently addressed [1–3]. Specifically, Tetracycline (TC), a class of antibiotics that was widely used in the medical field, has caused serious environmental issues due to their poor biodegradability but high production [4,5]. Besides, adverse effect of bacteria in aquatic ecosystems cannot be ignored either. For instance, as one kind of pathogenic microorganism, *Escherichia coli* (*E. coli*) can cause many intestinal diseases [6,7]. Therefore, removing these contaminants and microorganism from wastewater will contribute to improving the aquatic environment. Some conventional water treatment methods, such as chlorination, ozonization, microbial degradation, adsorption and filtration technologies have achieved corresponding effects in controlling water pollution [8,9]. Meanwhile, they also inevitably produced noxious disinfection by-products and caused secondary pollution. Therefore, seeking an efficient, environmentally friendly water disinfection method is urgent. Recently, semiconductor photocatalysis was considered as one of the green and sustainable technologies for the removal of contaminants from wastewater [10–12]. Especially for the VLD photocatalysis, it not only solved the problem that traditional semiconductor materials (such as TiO_2) cannot utilize visible light, but also met the development demand for cost-saving. Hence, developing eco-friendly, narrow band gaps and efficient visible-light-driven (VLD) photocatalysts has become a tendency for water purification.

Among numerous photocatalysts, bismuth oxyiodides ($Bi_xO_yI_z$), as a class of visible-light-responsive photocatalysts, has been widely used in environmental decontamination. The outstanding photocatalytic property was related to their unique layered structures characterized by $[Bi_2O_2]^{2+}$ slabs and double layers of I^- [13]. The unique layered structures could provide large specific surface areas with more active sites and also generate an internal static electric field to induce the separation of photogenerated charge carriers. As a member of the $Bi_xO_yI_z$ family, BiOI has been reported to exhibit significant photocatalytic antibacterial activity due to the proper band gap (~1.8 eV) [14,15]. However, the practical applications of BiOI nanomaterial were still limited due to the low position of conduction band and high recombination efficiency of photogenerated electron-hole pairs [16]. It was proved that I- deficient strategy may be feasible to adjust the band structure to enhance photocatalytic activity of BiOI [17]. For instances, by I-deficient strategy, $Bi_4O_5I_2$ [18], Bi_5O_7I [19] and $Bi_7O_9I_3$ [20] demonstrated higher photocatalytic activity than that of BiOI. Especially, $Bi_4O_5I_2$ has attracted great attention due to its strong oxidizing property, unique electrical and optical properties [21]. For example, Xiao reported that a novel $Bi_4O_5I_2$ nanomaterial exhibited superior photocatalytic and mineralization efficiency for the degradation of 4-*tert*-butylphenol [22]. However, high recombination efficiency of photo-generated charge carriers severely limited the applications of $Bi_4O_5I_2$ [23]. So far, some modified methods, such as doping, constructing heterojunctions, noble-metal deposition have been adopted to improve the photocatalytic activity of $Bi_4O_5I_2$. Among them, the fabrication of heterojunction structures for $Bi_4O_5I_2$ with other semiconductor materials was considered as a good strategy. Bai reported that g-C_3N_4/$Bi_4O_5I_2$ heterojunction with I_3^-/I^- redox mediator improved photocatalytic CO_2 conversion [24]. Numerous studies have reported that $Bi_4O_5I_2$ has excellent photocatalytic activity in the removal of organic pollutants and reduction of CO_2. Nevertheless, the applications of $Bi_4O_5I_2$ in bacterial disinfection have been rarely reported so far. Considering that the layered structure of $Bi_4O_5I_2$ was similar to BiOI, it is expected that $Bi_4O_5I_2$ also has corresponding antibacterial activity.

Nowadays, silver iodide (AgI), reported as a class of promising photosensitizers, has been widely used in the field of photocatalytic disinfection and organic pollutant degradation [25]. However, due to the photosensitizing effect, the structure of pristine AgI is unstable. Since AgI possessed high position of conduction band, it was often used to combine with other semiconductor materials to construct a heterojunction structure to enhance photocatalytic activity, in which AgI was used as photosensitizer. Thence, AgI particles were widely used to modify VLD photocatalysts [26]. It has been reported that Bi_2MoO_6 modified with AgI could inactivate 5.0×10^7 CFU/mL of *E. coli* and *S. aureus* cells within 30 min and 90 min, respectively, exhibiting stronger photocatalytic antibacterial activity than that of pure Bi_2MoO_6 [27]. Furthermore, composite photocatalyst such as $BiVO_4$/AgI [28], BiOI/AgI [29], Ag/AgI [30] etc, exhibited improved antibacterial activity under visible light irradiation. Based on the above analysis and the matched band structure between $Bi_4O_5I_2$ and AgI, the heterojunction system of $Bi_4O_5I_2$/AgI is expected to exhibit excellent photocatalytic degradation and antibacterial activity. As far as we know, $Bi_4O_5I_2$ modified with AgI was never manufactured and applied in degradation of organic contaminants and bacterial disinfection.

In this study, a novel $Bi_4O_5I_2$/AgI nanocomposite was prepared by deposition-precipitation method. The crystal phase, morphology structure and chemical composition of the prepared photocatalysts were systematically characterized. *E. coli* inactivation and TC degradation were selected as probe reactions to evaluate the photocatalytic properties of $Bi_4O_5I_2$/AgI composites. The degradation process of TC molecules was further studied by 3D EEMs technology. For bacterial disinfection experiments, the effects of inorganic anions and initial *E. coli* concentrations on the antibacterial activity were also studied. Besides, the contribution of released Ag^+ ion to the inactivation of *E. coli* was evaluated. Radical trapping experiments and electron spin resonance measurements determined the main active species for photocatalytic bacterial inactivation. Finally, a reasonable Z-scheme mechanism was proposed to explain the enhanced photocatalytic activity of $Bi_4O_5I_2$/AgI nanomaterial.

2. Material and method

2.1. Materials

Bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), silver nitrate ($AgNO_3$), potassium iodide (KI), ethylene glycol (EG), sodium oxalate ($Na_2C_2O_4$), 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL), isopropyl alcohol (IPA), ethanol (C_2H_5OH), ferrous chloride ($FeCl_2$) were analytical grade and received without further purification, and were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Deionized water obtained from a Millipore system (18.25 MΩ cm) was used in all experiments.