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Construction of highly efficient and stable ternary AgBr/Ag/PbBiO$_2$Br Z-scheme photocatalyst under visible light irradiation: Performance and mechanism insight

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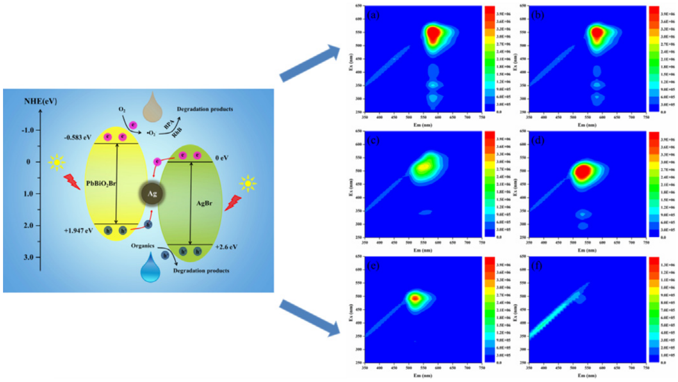
GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the novel ternary AgBr/Ag/PbBiO$_2$Br Z-scheme photocatalysts were synthesized via a CTAB-assisted calcination process. The AgBr/Ag/PbBiO$_2$Br composites were employed for the degradation of rhodamine B (RhB) and antibiotic bisphenol A (BPA) under visible light irradiation. Results showed that the obtained AgBr/Ag-3/PbBiO$_2$Br displayed optimal photocatalytic performance, which could remove almost all RhB within 25 min and effectively decompose 82.3% of BPA in 120 min. Three-dimensional excitation-emission matrix fluorescence spectra (3D EEMs) were utilized for the purposes of fully grasping the behaviors of RhB molecules during the reaction process. Meanwhile, the effects of initial RhB concentration and co-existent electrolytes were investigated from the viewpoint of practical application. In addition, there was no obvious loss in degradation efficiency even after four cycles. The enhanced photocatalytic performances of AgBr/Ag/PbBiO$_2$Br could be credited to the accelerated interfacial charge transfer process and the improved separation of the photogenerated electron-hole pairs. The existence of a small amount of metallic Ag played a significant role in preventing AgBr from being further photocorroded, resulting in the formation of a stable Z-scheme photocatalyst system. This study demonstrated that using metallic Ag as an electron mediator to construct Z-scheme photocatalytic system provided a feasible strategy in promoting the stability of Ag-based semiconductors.

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1. Introduction

Over the past few decades, environmental crisis has become increasingly rigorous with the rapid development of industrial civilization. In particular, the wastewater discharged from industrial plants usually contains dyes, heavy metal ions, antibiotics, pathogenic microorganisms and other refractory contaminants, which poses a serious threat to the flora and fauna in aquatic ecosystems [1]. Semiconductor photocatalysis, as a promising technology, has been well applied to deal with these emerging problems. In the process of photocatalysis development, TiO_2 and ZnO have been deeply investigated due to their chemical stability and superior reactivity [2–5]. But unfortunately, their wide band gaps only allow them to be excited by ultraviolet light, which have kept them away from practical application. Thus, in order to make full utilization of solar energy, considerable efforts have been made to exploit novel and effective visible light driven photocatalysts.

In recent years, bismuth-based photocatalysts have been verified to be a new kind of candidates due to their distinct electron structure and extraordinary visible light response capacity. A group of bismuth materials, such as Bi_2WO_6, $BiVO_4$, Bi_2O_3, BiOBr, $PbBiO_2X$ (X = Cl, Br, I) [6–9], were deeply investigated for their excellent photocatalytic activities. Among them, $PbBiO_2Br$ is a promising photocatalyst with suitable band gap (~2.47 eV) and has received gradual concern in the degradation of organic pollutants [10]. For examples, Xiao et al. have fabricated the hierarchical $PbBiO_2Br$ structure assembled by ultrathin nanosheets through a facile solvothermal method, and the obtained sample showed excellent photocatalytic performance towards the degradation of methyl orange (MO) [11]. Another kind of porous $PbBiO_2Br$ microsphere was successfully achieved by a solvothermal process, where ion liquid was introduced as template, reactant and solvent. Then both organic dyes and antibacterial agents were adopted to investigate its photocatalytic activity under visible light irradiation [12]. Nonetheless, the photocatalytic property of individual $PbBiO_2Br$ is still constrained by the rapid recombination of internal electron-hole pairs. To overcome this inherent drawback of $PbBiO_2Br$ and improve the degradation efficiency, combining $PbBiO_2Br$ with another suitable semiconductor to fabricate a heterojunction has been demonstrated to be a feasible and effective method. To date, several pioneer attempts, such as $NbSe_2$/$PbBiO_2Br$ [13], $PbBiO_2Br$/BiOBr [14], $PbBiO_2Br$/UiO-66-NH_2 [15], g-C_3N_4/$PbBiO_2Br$ [16], have been made, and the highly efficient heterogeneous photocatalysts were obtained. Therefore, in order to further investigate the application of $PbBiO_2Br$ in photodegradation, more $PbBiO_2Br$-based photocatalysts are expected to be designed.

Recently, silver halides (AgX, X = Cl, Br, I) have been demonstrated as promising photocatalysts due to their outstanding photocatalytic property. Among these materials, AgBr owns a relatively small band gap (~2.6 eV) [17], which makes it conducive to the absorption of visible light. But similar to other Ag-based materials, pure AgBr faces the challenge of serious photocorrosion effect. When exposed to light, the interstitial Ag^+ could be reduced to metal Ag by photogenerated electrons, and as the irradiation time prolonged, excess metallic Ag cluster would form on the surface of AgBr, leading to a severe deterioration in its photocatalytic activity. Thus, the practical application of pure AgBr is greatly restricted [18]. To prevent the photocorrosion process efficiently, it is reasonable to believe that if the photoinduced electrons could be efficiently transferred away from AgBr before they combined with the interstitial Ag^+, the stability of AgBr would be ultimately improved. Fortunately, previous studies have demonstrated that construction of AgBr-based heterojunction [19–21] and decoration of co-catalysts (such as Fe(III) [22], grapheme oxide [23], Ag [24], Au [25] and reduced grapheme oxide [26]) were available strategies. In particular, numerous investigations have confirmed that when a small amount of metallic Ag were co-existed on the surface of AgBr, the photostability of AgBr could be significantly promoted [24,27,28]. Accordingly, it is expected that coupling AgBr, metallic Ag and another suitable semiconductor to form a proper heterojunction might acquire a more stable AgBr-based photocatalyst.

Moreover, recent progress in construction of the Z-scheme photocatalytic system has aroused great interest due to its unique superiority in separating the photogenerated charge carriers. A typical Z-scheme photocatalytic system is usually made up of two band-matched semiconductors and an electron mediator, in which the electron mediator plays an important role in boosting the interfacial recombination between less reactive holes and electrons on different semiconductors [29,30]. Among these electron mediators, owing to the superior electron conductivity, metallic Ag has been demonstrated to be an ideal candidate for the fabrication of Z-scheme photocatalysts [31–34]. Inspired by this special feature of Z-scheme system and the unique role of Ag played in Z-scheme photocatalysts, if a Z-scheme photocatalyst consisting of AgBr, Ag and $PbBiO_2Br$ could be rationally fabricated, allowing the photogenerated electrons on the conduction band (CB) of AgBr to transfer into metallic Ag and combine with the holes migrated from the valence band (VB) of $PbBiO_2Br$. As a consequence, the stability of AgBr would be improved and a highly efficient photocatalyst could be obtained.

In this study, the novel ternary AgBr/Ag/$PbBiO_2Br$ Z-scheme photocatalysts were well-designed through a CTAB-assisted calcination procedure. Intrinsic properties including crystal phase, morphology structure, optical and electrochemical characteristics were systematically investigated to fully recognize the as-prepared samples. The enhanced photocatalytic performances of the as-prepared heterojunctions were reflected by the degradation of RhB and BPA under visible light irradiation. The results of cycling experiments and characterization of the recovered photocatalysts indicated that the stability was well-maintained. Based on the theoretical analysis and the experimental results, a reasonable Z-scheme mechanism was proposed for better comprehending the possible behaviors of the intrinsic charge carriers.

2. Experimental

2.1. Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$), lead nitrate ($Pb(NO_3)_2$), cetyltrimethylammonium bromide (CTAB), sodium hydroxide (NaOH), sliver nitrate ($AgNO_3$), aqueous ammonia (25 wt% of $NH_3 \cdot H_2O$), poly (vinyl alcohol) (PVA), sodium sulfate (Na_2SO_4), isopropyl alcohol (IPA), p-benzoquinone (BQ), sodium oxalate ($Na_2C_2O_4$), rhodamine B (RhB), and bisphenol A (BPA) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytical grade and were used without further purification. Deionized water was employed throughout all experiments.

2.2. Synthesis of the catalysts

2.2.1. Preparation of $PbBiO_2Br$

The $PbBiO_2Br$ nanosheet was synthesized via a hydrothermal method [11,14]. Typically, 1.5 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ was added into 60 mL of deionized water containing stoichiometric amounts of CTAB and $Pb(NO_3)_2$ with continuous stirring to form a homogeneous suspension, and then the pH value of the mixture was adjusted to 14 by the addition of NaOH solution (2 M). After stirring for 30 min, the suspension was transferred into a