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Double Z-scheme system of silver bromide@bismuth tungstate/tungsten trioxide ternary heterojunction with enhanced visible-light photocatalytic activity

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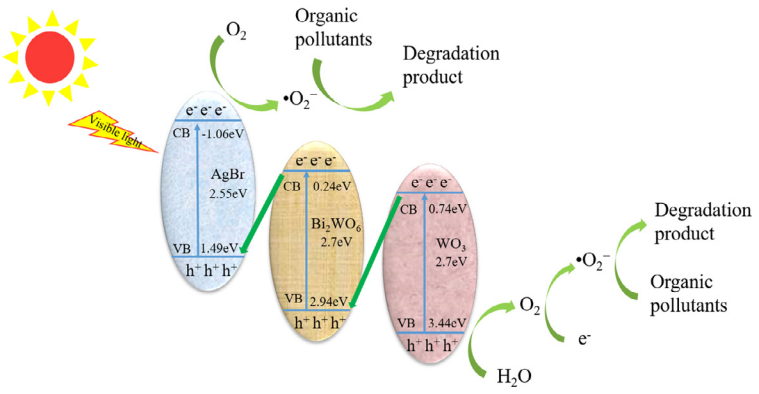
HIGHLIGHTS

- $AgBr@Bi_2WO_6/WO_3$ exhibited greatly enhanced photocatalytic activity.
- The $AgBr@Bi_2WO_6/WO_3$ composite is a novel ternary system.
- The increased photocatalytic activity of the double Z-scheme system was discussed in detail.

GRAPHICAL ABSTRACT

The enhanced photocatalytic performance was ascribed to the atypical double Z-scheme system of $AgBr@Bi_2WO_6/WO_3$.



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ABSTRACT

The ternary heterojunction of silver bromide@bismuth tungstate/tungsten trioxide ($AgBr@Bi_2WO_6/WO_3$) was designed and synthesised by hydrothermal and deposition–precipitation approaches. The composites were characterised by X-ray diffraction, transmission electron microscopy and X-ray photoelectron spectroscopy (XPS). The photoabsorption range and bandgaps of the photocatalysts were analysed by ultraviolet-visible diffuse reflectance spectroscopy (UV–vis DRS). Compared with Bi_2WO_6/WO_3 or AgBr alone, the $AgBr@Bi_2WO_6/WO_3$ composites displayed higher visible-light photocatalytic performance for degrading rhodamine B (RhB). $AgBr@Bi_2WO_6/WO_3$ with 40% AgBr concentration was optimum for photocatalytic activity. Radical-trapping experiments revealed that superoxide anion radicals ($\cdot O_2^-$) and holes (h^+) were the active species during photocatalytic degradation and that $\cdot O_2^-$ was the dominant active species. Therefore, the increased photocatalytic activity of $AgBr@Bi_2WO_6/WO_3$ was attributed to the atypical double Z-scheme system, which effectively improved the transfer and separation of electron–hole pairs in ternary heterojunction structures.

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1. Introduction

Semiconductor photocatalysis has reached considerable advances since Fujishima and Honda (1972) discovered that solar energy can drive water splitting by using TiO_2 [1–4]. However, pure TiO_2 can absorb only ultraviolet (UV) irradiation (ì < 380 nm) because of its wide bandgap (3.2 eV for anatase structures), thereby preventing its widespread application [5–7]. In recent years, researchers have proposed various visible-light-driven semiconductor photocatalysts that can efficiently utilise solar energy [8,9]. These photocatalysts include Bi_2MoO_6 [10], Fe_2O_3 [11], Cu_2O [12] and $Ag_2V_4O_{11}$ [13]. In particular, Bi_2WO_6, has exhibited a suitable bandgap (2.7 eV) and promising visible-light photocatalytic performance in degrading organic pollutants [14]. Nevertheless, the recombination of photogenerated electrons and holes for Bi_2WO_6 was too rapid, and photoabsorption was limited, thereby hindering the practical application of Bi_2WO_6 [15].

Thus, the fabrication of heterojunction was proposed developed to modify the Bi_2WO_6 semiconductor and consequently improve photocatalytic performance. To date, several Bi_2WO_6-based composites, such as MoS_2/Bi_2WO_6 [16], Bi_2O_3/Bi_2WO_6 [17], SnS/Bi_2WO_6 [18] and Bi_2WO_6/WO_3 [19], have been utilised in managing organic pollutants because of the excellent photocatalytic activity of these composites. Previous reports have suggested that the introduction of WO_3 into Bi_2WO_6 could boost photocatalytic property. Gui et al. demonstrated that compared with sole Bi_2WO_6 and WO_3, the Bi_2WO_6/WO_3 photocatalyst exhibited a substantially higher photocatalytic performance in degrading rhodamine B (RhB) [20]. However, the visible-light response of Bi_2WO_6/WO_3 is less than 450 nm.

Compared with binary heterojunction, ternary heterojunction can more efficiently separate photogenerated carriers and increase the scope of light absorption. Various heterojunction products have been fabricated, such as $BiOBr@WO_3/Bi_2WO_6$ [21], $FeWO_4@ZnWO_4/ZnO$ [22] and $g\text{-}C_3N_4@WO_3/Bi_2WO_6$ [23,24]. Although these ternary heterojunction structures can efficiently promote the transfer and separation of photo-induced carriers, their practical application is still hindered by certain limitations. The mechanism underlying Bi_2WO_6/WO_3-based photocatalysts for enhancing photocatalytic performance remains to be elucidated. Given its unique structure and excellent properties, silver bromide is a promising visible-light photocatalyst for degrading organic compounds and is typically loaded onto other semiconductor materials to enhance their photocatalytic activities [25–29]. Wang et al. synthesised a $AgBr/Bi_2WO_6$ composite photocatalyst, which performed well in degrading methylene blue under visible-light irradiation [30]. Cao et al. designed $AgBr/WO_3$ nanocomposites, which enhanced photocatalytic activity for degrading methylene orange [31]. Therefore, decorating Bi_2WO_6/WO_3 composites with AgBr ($AgBr@Bi_2WO_6/WO_3$) might result in a high-efficiency photocatalyst that has not yet been reported to our knowledge.

In this work, $AgBr@Bi_2WO_6/WO_3$ ternary heterojunction was synthesised by hydrothermal and deposition–precipitation methods. Compared with binary Bi_2WO_6/WO_3 and AgBr, this composite exhibited improved activities for degrading RhB, of which 99% was photodegraded by 40%-$AgBr@Bi_2WO_6/WO_3$ after 80 min of visible-light irradiation. The results revealed that the ternary heterojunction structure accelerated the separation and transfer of electron–hole pairs as well as extend the absorption range of visible light. A possible reason is the photocatalytic mechanism of the atypical double Z-scheme system of ternary heterojunction.

2. Experimental methods

2.1. Materials

Bismuth nitrate pentahydrate (analytical reagent, AR), silver nitrate (AR), sodium bromide (AR), isopropanol (AR) and RhB were supplied by Sinopharm Chemical Reagent Co., Ltd. Sodium tungstate dihydrate (AR), sodium oxalate (AR), nitric acid (AR) and sodium hydroxide (AR) were supplied by Guangdong Xilong Chemical Co., Ltd. Anhydrous ethanol (AR) and benzoquinone (chemically pure) were supplied by Beijing Chemical Inc. Deionised water was used throughout this study. All chemicals were as received without further purification.

2.2. Synthesis of Bi_2WO_6/WO_3

Bi_2WO_6/WO_3 nanosheets were prepared by one-step hydrothermal method. $Bi(NO_3)_3{\cdot}5H_2O$ (4 mmol) was dissolved in 10 mL of 4 mol L^{-1} HNO_3 solution and stirred for 10 min. The solution was then dropwise added with $Na_2WO_4{\cdot}2H_2O$ (2.4 mmol) dissolved in deionised water. The suspension was stirred for 12 h at room temperature and transferred into a 100 mL stainless autoclave. The autoclave was heated to 180 °C and maintained for 24 h, after which it was left to naturally cool to room temperature. Finally, the products were washed with distilled water and ethanol several times and dried at 80 °C for 8 h.

2.3. Synthesis of $AgBr@Bi_2WO_6/WO_3$ composites

$AgBr@Bi_2WO_6/WO_3$ composites were synthesised by a simple deposition–precipitation approach. Proportionate amounts of NaBr, $AgNO_3$ and Bi_2WO_6/WO_3 were weighed according to the percentage of the mass ratio of AgBr and Bi_2WO_6/WO_3 ($AgBr:Bi_2WO_6/WO_3$ = 0.2, 0.3, 0.4, 0.5). Subsequently, the as-prepared Bi_2WO_6/WO_3 (0.2 g) was added to deionised water (20 mL). The solution was sonicated for 10 min and added with a stoichiometric amount of NaBr aqueous solution. After sonication for 10 min, an aqueous solution of $AgNO_3$ (mole ratio of Ag:Br, 1:1.2) was slowly added dropwise into the suspension. The resulting suspensions were stirred vigorously for 12 h at room temperature. Finally, the precipitates were filtered, washed with distilled water and pure ethyl alcohol and then dried at 80 °C.

2.4. Characterisation of photocatalysts

The crystalline phases of the samples were recorded by X-ray diffraction (XRD) (D/MAXRB, Rigaku, Japan). The diffraction patterns were determined in the 2θ = 20–90° range with a Cu Kα source (λ = 0.15405) running at 40 kV and 30 mA. Both the transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of the samples were recorded by a transmission electron microscope (F-20, FEI, USA). X-ray photoelectron spectroscopy (XPS) measurements were performed on an X-ray photoelectron spectrometer (ESCALAB 250Xi) using Al Kα radiation. The UV–visible (UV–Vis) diffuse reflectance spectra of the samples were recorded at room temperature by a UV–Vis spectrophotometer (T9s; Persee, China) equipped with an integrating sphere. $BaSO_4$ was used as reference. Photoelectrochemical measurements were recorded by an electrochemical workstation in a traditional three-electrode system (5060F; RST, China), as described in our previous study [32].