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Preparation of novel p-n heterojunction $Bi_2O_2CO_3$/BiOBr photocatalysts with enhanced visible light photocatalytic activity

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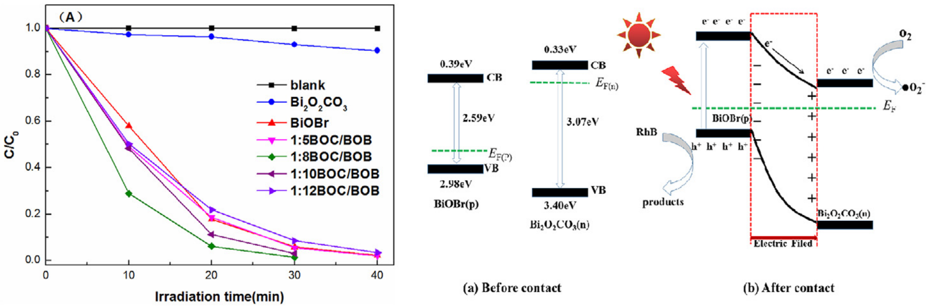
HIGHLIGHTS

- There was no report to investigate the photocatalytic activity of $Bi_2O_2CO_3$/BiOBr p-n heterojunction.
- $Bi_2O_2CO_3$/BiOBr photocatalysts exhibited greatly enhanced photocatalytic activity under visible light.
- The possible mechanism of the enhanced photocatalytic activity was discussed in detail.

GRAPHICAL ABSTRACT

The enhanced photocatalytic activity was derived from the formation of p-n heterojunction of $Bi_2O_2CO_3$/BiOBr.



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ABSTRACT

In this study, a novel $Bi_2O_2CO_3$/BiOBr p-n heterojunction was synthesized via a two-step solvothermal method. The p-n interface was formed by loading $Bi_2O_2CO_3$ nanoparticles on the surface of BiOBr nanosheets. The crystal structure, morphology, and optical property of the as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV–vis diffuse reflectance spectroscopy, respectively. The obtained $Bi_2O_2CO_3$/BiOBr p-n heterojunction composites exhibited the superior photocatalytic activity for the degrading rhodamine B (RhB) under visible light irradiation as compared with $Bi_2O_2CO_3$ and BiOBr. Four times cycling experiments demonstrated that the composites had good photostability and recyclability. The enhanced photocatalytic activity of $Bi_2O_2CO_3$/BiOBr composites was mainly attributed to the formation of p-n heterojunction between $Bi_2O_2CO_3$ and BiOBr, thereby resulting in faster transfer of the photoinduced electron–hole pairs through their interface. Radical trapping experiments confirmed that h^+ and $•O_2^-$ were two main active species in the photocatalytic process. The possible mechanism of the enhanced photocatalytic activity was proposed, which revealed the transfer of the charge carriers and the formation of the active species in photocatalytic process.

1. Introduction

In recent years, photocatalysts used for treating nocuous organic pollutants in air and water have received more and more attention [1,2]. Pollutants can be effectively degraded owing to the gen-

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eration of photoinduced electron-holes in photocatalysts under visible light irradiation. Recently, Bismuth-based oxides with an Aurivillius-layered structure have been the focus point among various photocatalysts, considering its the hybridized valence band by O_{2p} and Bi_{6s} [3]. This type of photocatalyst contains $BiVO_4$ [4–6], $BiWO_6$ [7–9], BiOX (X = Cl, Br, I) [10–12], and so on. Among these photocatalysts, the p-type bismuth oxybromide (BiOBr) is of great research interest, considering its high activity and stability under visible light irradiation [13]. However, pure BiOBr still suffers from the low quantum yield, thereby greatly limiting its practical application. To solve issue, several strategies have been developed, such as ion doping [14], surface decoration (metal deposition or heterojunction) [15,16], and morphology controlled synthesis [17–20]. Meanwhile, constructing heterostructure photocatalyst is effective in enlarging the quantum yield, consequently increasing the photocatalytic efficiency, Such as $g-C_3N_4$/BiOBr [21], $ZnFe_2O_4$/BiOBr [13], Bi_2WO_6/BiOBr [22], and $BiPO_4$/BiOBr [23]. Furthermore, it is not easy to construct an effective heterojunction with increased visible light absorption and efficient separation of photogenerated charge carriers. There are two important factors. Firstly, two semiconductors should have the matched energy level and appropriate molar ratio in order to separate electron-hole pairs efficiently. Secondly, the heterojunction structure between BiOBr and other materials must be compatible to obtain an intimate interface [24,25].

Bismuth subcarbonate ($Bi_2O_2CO_3$), as a typical member of the Aurivillius-related oxide family, has become the hotspot in photocatalysis for degrading organic dyes [26]. Unfortunately, pure $Bi_2O_2CO_3$ photocatalyst has wide band gap which limits its environmental application. Therefore, an enormous amount of research effort has been focused on coupling $Bi_2O_2CO_3$ with other photocatalysts to improve its photocatalytic activity. For instance, the $Bi_2O_2CO_3$/BiOI heterojunction showed a good photocatalytic activity in photo cleaning of wastewater containing RhB, methylene blue (MB) and crystal violet under visible light irradiation [27]. The $Bi_2O_2CO_3$/BiOCl heterojunction exhibited higher photocatalytic activity than that of its single components for degrading RhB under visible light irradiation [28]. The heterojunction formed by coupling $Bi_2O_2CO_3$ with BiOI or BiOCl might be attributed to their similar structures. $Bi_2O_2CO_3$, BiOI, and BiOCl belong to the layered Aurivillius-related oxide family, consisting of $[Bi_2O_2]^{2+}$ layers (X-Bi-O-Bi-X) sandwiched between two slabs of X ions, atoms or groups (where $X = CO_3^{2-}$, I^-, and Cl^-). Therefore, the similar structures of different photocataltsts can contribute to forming heterojunction. Based on the above consideration, if n-type $Bi_2O_2CO_3$ with a higher band gap of ~3.5 eV couple with p-type BiOBr with a lower band gap of ~2.4 eV, an efficient heterojunction between $Bi_2O_2CO_3$ and BiOBr can be formed, thereby resulting in the formation of an internal electric field in the interface with its field direction from the n-type to the p-type semiconductor [29,30]. This internal electric field can lead to improving separation efficiency of photo-induced charges via the potential difference at the p-n heterojunction interface [31]. To the best of our knowledge, there are no existing reports on the preparation and investigation of p-BiOBr/n-$Bi_2O_2CO_3$ system. Therefore, we synthesize p-BiOBr/n-$Bi_2O_2CO_3$ heterojunction and explore the process of charge separation and transfer at the surface or interface in detail.

Herein, we report novel heterojunction of p-type BiOBr and n-type $Bi_2O_2CO_3$ constructed by loading amounts of $Bi_2O_2CO_3$ nanoparticles on the surface of BiOBr nanosheets via a two-step solvothermal method. The photocatalytic activity of the $Bi_2O_2CO_3$/BiOBr p-n heterojunction photocatalysts was evaluated by degrading RhB under visible light irradiation. Furthermore, the possible mechanism for the enhanced photocatalytic activity was also proposed based on trapping experiments and calculating band-edge potential positions.

2. Experimental

2.1. Synthesis of the photocatalysts

All the chemical was analytical grade and used without further purification. The preparation of $Bi_2O_2CO_3$ photocatalyst was as follows: 2.99 g Na_2CO_3 and 0.5 g CTAB (hexadecyl trimethyl ammonium bromide) were dissolved in 90 mL deionized water. Subsequently 10 mL HNO_3 (1 mol L^{-1}) containing 1.71 g $Bi(NO_3)_3 \cdot 5H_2O$ was added dropwise into previous solution with constant stirring. The mixture solution was stirred for 2 h at room temperature. Then the products were separated by centrifugation, washed with deionized water and absolute alcohol. The obtained sample dried at 60 °C for several hours.

The preparation of $Bi_2O_2CO_3$/BiOBr (BOC/BOB) composites were as follows: Firstly, 0.51 g $Bi_2O_2CO_3$ and KBr (C/Br molar ratios being 1:5, 1:8, 1:10, 1:12, respectively) were added to 20 mL deionized water with constant stirring 30 min 20 mL ethylene glycol solutions containing $Bi(NO_3)_3 \cdot 5H_2O$ (the mole ratio of Br/Bi = 1) was slowly added to the previous solution dropwise under constant stirring. The mixture was heated at 80 °C for 3 h in a water bath under magnetic stirring. The obtained BOC/BOB composites were separated, washed with deionized water several times and absolute alcohol. The obtained samples dried at 60 °C for several holes. In addition, pure BiOBr was prepared under same conditions without $Bi_2O_2CO_3$.

2.2. Characterization of photocatalysts

The crystalline phases of samples were determined using X-ray diffraction (XRD) (D/MAX-RB, Rigaku, Japan). The diffraction patterns were recorded in the $2\theta = 10–70°$ range with a Cu Kα source (λ = 0.15405) running at 40 kV and 30 mA. The morphology of the samples was measured by using an emission scanning microscopy (SEM, S-4800, Hitachi, Japan). The transmission electron microscopy (TEM) and the high-resolution TEM (HRTEM) images were recorded on a transmission electron microscopy (F-20, FEI, USA) at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on an X-ray photoelectron spectrometer (AXIS ULTRA^{DLD}, Kratos, Japan) using the Mg Kα radiation. The UV–vis diffuse reflectance (DRS) spectra of the samples were recorded at room temperature in the 300–800 nm range using a UV–vis spectrophotometer (U-3900H, Hitachi, Japan) equipped with an integrating sphere. $BaSO_4$ was used as the reference. The photoluminescence (PL) spectra were recorded by a fluorescence spectrophotometer (F-4500, Hitachi, Japan) with a Xe lamp as the excitation light source.

2.3. Photocatalytic experiments

The photocatalytic activity of as-prepared samples was evaluated by the degradation of RhB (10 mg L^{-1}) under visible-light irradiation (λ ≧ 420 nm, 400 W Xe lamp). The experiments were performed at ambient temperature as follows: 20 mg as-prepared photocatalyst was dispersed in 40 mL RhB solution. the suspensions were stirred for 120 min in the dark to achieve an adsorption-adsorption equilibrium between the photocatalysts and RhB before light irradiation. During the irradiation, 4 mL reaction solution was taken at intervals of every 10 min and centrifuged. the centrifuged solution was recorded using a UV–vis spectrophotometer (U-3900H, Hitachi, Japan) at its maximum absorption wavelength of 554 nm.

2.4. Photocurrent measurement

Measurement of the photocurrent was carried out with an electrochemical workstation (5060F, RST, China) in a standard