



Novel Bi₂O₄/BiOBr heterojunction photocatalysts: In-situ preparation, photocatalytic activity and mechanism

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ABSTRACT

Novel Bi₂O₄/BiOBr heterojunctions were fabricated via a chemical etching process. BiOBr nanosheets could be in-situ generated in Bi₂O₄ micro-rods, which greatly improved the interface quality. The photocatalytic performance of samples was evaluated by the degradation of rhodamine B (RhB) and methyl orange (MO) under visible light irradiation. The results showed that Bi₂O₄/BiOBr heterojunctions displayed higher photocatalytic activity than pure Bi₂O₄ and BiOBr, and 99.3% MO could be degraded in 60 min over 0.4BB (~ 33.3 mol% BiOBr) sample. The effective separation and transfer of the photogenerated electrons and holes were believed to be the main factor for the enhanced activity, and the holes (h⁺) and ·O₂⁻ radicals were confirmed to be the main active species. This work offers an effective route to the fabrication of Bi₂O₄/BiOBr heterojunctions with high interface quality for photocatalytic applications.

1. Introduction

Environmental pollution, especially the water pollution, has become the greatest concerns in human society, which seriously affects our daily life. Semiconductor photocatalysis has been accepted as a promising solution to the problem, since it can effectively degrade water pollutant by using abundant and clean solar energy. In the past, most of studies were focused on TiO₂ due to its high chemical stability, low cost and strong redox ability [1–3]. However, TiO₂ can only be activated under UV irradiation due to the wide band gap (3.2 eV), which accounts for less than 7% of solar radiation reaching the earth. Therefore, the development of visible light active materials has become a hot topic in photocatalysis research.

Recently, there is an increasing focus on Bismuth (III)-based semiconductors, which are reported as a class of promising visible light photocatalyst for environmental purification. In these compounds, the overlapping between 6s² orbital of Bi³⁺ ion and O2p orbital can narrow the band gap and widen the valance band width, which is in favor of the enhancement of the photocatalytic performance [4,5]. So far, many bismuth(III)-based photocatalysts such as Bi₂O₃ [6], BiVO₄ [7], Bi₂WO₆ [8], Bi₂O₂CO₃ [9] and BiOX (X = Cl, Br, I) [10–12] have been developed, and all of them exhibit commendable activity. Besides, it was reported that the empty 6s orbital of Bi⁵⁺ in Bi(V)-based compounds could also modify the band gap and support the high photocatalytic activity. For example, NaBiO₃ was reported to have high photo-degradation efficiency towards 4-t-octylphenol and carbamazepine

[13,14]. Recently, bismuth mixed-valence oxide Bi₂O₄ was also reported to possess strong visible light response, which attracted more and more attention. Wang et al. [15] synthesized Bi₂O₄ microrods via the hydrothermal process, and found that they could remove not only color dyes but also colorless aromatic compounds. By the same method, Hu et al. [16] also prepared Bi₂O₄ micro-rods, further confirming their strong mineralizing abilities. Nonetheless, the photocatalytic activity Bi₂O₄ is still at low level, which needs further improvement for the practical applications. To enhance the photocatalytic performance, a feasible strategy is to construct heterojunctions with other semiconductors, in which photogenerated charge carriers can be effectively separated. Various Bi₂O₄-based heterojunctions such as Bi₂O₃/Bi₂O₄ [17] and Fe₃O₄/Bi₂O₄ [18] have been developed and demonstrated to be efficient and stable photocatalysts. BiOBr, as a bismuth(III)-based compound, has been widely studied and is often used as second phase to construct heterojunction photocatalysts. We speculate that the coupling of Bi₂O₄ and BiOBr will help to the enhancement of the photocatalytic activity.

Herein, Bi₂O₄/BiOBr heterojunctions were in-situ prepared via a facile chemical etching process. Their structural and optical properties were characterized by XRD, FE-SEM, TEM, BET, XPS, UV–vis DRS, EIS and photocurrent measurement. The photocatalytic activity of the samples was evaluated by the degradation of RhB and MO, and the corresponding mechanism was investigated and proposed.

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2. Experimental

2.1. Synthesis of samples

All the chemicals were purchased from Sinopharm Chemical Reagent Co, Ltd. (China) and used as received without further purification. Bi_2O_4 micro-rods were fabricated by a hydrothermal process: 8 mmol of $\text{NaBiO}_3 \cdot 2\text{H}_2\text{O}$ was dispersed into 80 mL of deionized water under vigorous magnetic stirring. The resultant turbid liquid was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 6 h. The product was collected by centrifugation, washed for 3 times with distilled water, and then dried at 80 °C for 24 h.

$\text{Bi}_2\text{O}_4/\text{BiOBr}$ heterojunctions were prepared by the chemical etching process of Bi_2O_4 micro-rods. First, 1 mmol Bi_2O_4 was dispersed in 20 mL of HNO_3 aqueous solution (0.1 M). Then, a certain amount of KBr were added to the above suspension and stirred for 60 min. The final products were washed with deionized water and dried at 80 °C for 24 h. The obtained sample was named as xBB, where x means the amount of substance of KBr ($x = 0.1, 0.2, 0.4$ and 0.6 unit: mmol). The content of BiOBr in 0.1BB, 0.2BB, 0.4BB and 0.6BB can be calculated as ~ 9.5 mol%, 18.1 mol%, 33.3 mol% and 46.1 mol%, respectively. In addition, pure BiOBr was also prepared by the same method with the addition of 2 mmol of KBr.

2.2. Characterization

The phase compositions and crystal structures of the samples were determined by X-ray diffractometer (XRD, Bruker D8 Advance). The morphologies were investigated by field emission scanning electron microscopy (SEM, Quanta 250). The transmission electron microscopy (TEM) and high resolution electron microscopy (HRTEM) images were taken with a FEI, Tecnai G2 F20 electron microscope. XPS data was collected on a thermo ESCALAB 250XI X-ray photoelectron spectrometer. N_2 sorption was used to determine the specific surface area and the pore size distribution. The optical properties of the samples were analyzed by UV–vis diffuse reflectance spectra (DRS, Varian Cary 300). Electrochemical measurements were completed via an electrochemical workstation (CHI660B, China), which were carried out in 0.5 M Na_2SO_4 aqueous solution by using a three-electrode system.

2.3. Photocatalytic measurements

Photocatalytic performance of the samples was evaluated by the

degradation of rhodamine-B (RhB) and methyl orange (MO) under visible light irradiation. A 500 W xenon lamp with a cutoff filter ($\lambda > 420$ nm) was used as the light source. The catalytic experiments were carried out as follows: 0.1 g of the photocatalyst was added into 100 mL of pollutant solution (initial concentration $C_0 = 1.0 \times 10^{-5}$ mol/L). Before the irradiation, the mixed solution was magnetically stirred for 20 min to reach the adsorption-desorption equilibrium. The temperature of the reaction system was kept at ~ 25 °C. Aliquots of 3 mL of the reactant solution was taken in a given time interval and separated by centrifugation. The concentration evolution of RhB and MO was analyzed by UV–vis spectrophotometry at their characteristic wavelengths of 554 and 464 nm, respectively.

3. Results and discussion

3.1. Crystal structure and phase analysis

Fig. 1a shows the XRD patterns of pure Bi_2O_4 , BiOBr and $\text{Bi}_2\text{O}_4/\text{BiOBr}$ composites. All the diffraction peaks of Bi_2O_4 are readily indexed into that of monoclinic Bi_2O_4 (PDF#83-0410), which implies that the pristine Bi_2O_4 is synthesized successfully. After treatment with KBr in acidic condition, an obvious change in XRD pattern can be observed for xBB samples. Besides the diffraction peaks of Bi_2O_4 , some new ones located at $2\theta = 10.9^\circ, 25.2^\circ, 31.7^\circ, 32.2^\circ, 39.4^\circ,$ and 46.2° appear, which match well with the (001), (101), (102), (110), (112) and (200) crystal planes of tetragonal BiOBr (JCPDS 09-0393). With increasing x value, the peaks for BiOBr become stronger and stronger, corresponding to the formation of more BiOBr. Nonetheless, it is worth noting that, the acidic condition is essential for the formation of BiOBr in Bi_2O_4 [19]. In the absence of HNO_3 , no diffraction peaks of BiOBr can be found even etched with 0.6 mmol of KBr (Fig. 1b).

The surface elemental composition and chemical states of related elements of Bi_2O_4 and 0.4BB were analyzed by using XPS. Compared with Bi_2O_4 , the XPS survey spectra of 0.4BB explicitly show the existence of Br element besides Bi and O elements (Fig. 2a). Fig. 2b provides the high-resolution Bi 4f spectra of Bi_2O_4 and 0.4BB. They can both be de-convoluted into two bimodal peaks at binding energy of 158.5 and 159.1 eV (or at 163.7 and 164.3 eV), which correspond to Bi (III) and Bi(V), respectively [20]. However, it is worth noting that the $\text{Bi}^{3+}/\text{Bi}^{5+}$ atomic ratio for Bi_2O_4 is about 1.05, very close to the stoichiometric formula of $\text{Bi}_2\text{O}_4(\text{Bi}^{3+}\text{Bi}^{5+}\text{O}_4)$ [15], while it is as high as 1.68 for 0.4BB sample, implying more Bi^{3+} -contained component. Fig. 2c shows the typical bimodal peaks of Br3d at 68.6 and 69.6 eV for 0.4BB sample, which can be attributed to Br $3d_{5/2}$ and $3d_{3/2}$,

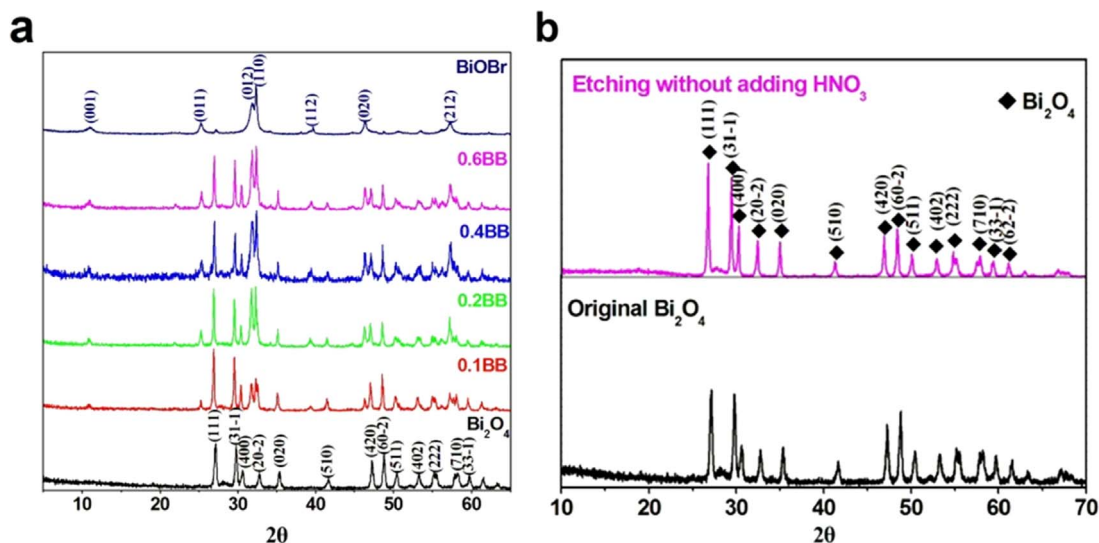


Fig. 1. XRD patterns of (a) as-prepared samples and (b) Bi_2O_4 before and after etched by 0.6 mmol of KBr without HNO_3 .

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