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Effects of the molar ratio on the photo-generated charge separation behaviors and photocatalytic activities of $(BiO)_2CO_3$-BiOBr composites

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ABSTRACT

The molar ratio of two semiconductors will remarkably influence the photo-induced charge separation behaviors of the composites constructed, thus affecting the corresponding photocatalytic activity. Therefore, it is critical to reveal the relationship between the molar ratio of two semiconductors and the photo-induced charge separation; the information can shed light on the study of nature of surface catalysis. In this work, $(BiO)_2CO_3$-BiOBr composites were facilely fabricated in-situ through a pore impregnating approach using HBr aqueous solution. The samples were studied by BET, XRD, SEM, UV–Vis DRS and surface photovoltage spectroscopy (SPS). The photocatalytic activities of the samples were evaluated by the discoloration of methyl orange (MO) aqueous solution upon the simulated sunlight illumination. The results reveal that the $(BiO)_2CO_3$-BiOBr composite with 3/4 M ratio of $(BiO)_2CO_3$/BiOBr displays the highest photo-induced charge separation rate and photocatalytic activity, the results further manifest that no different electronic transfer property occurs after coupling $(BiO)_2CO_3$ with BiOBr.

1. Introduction

Recently, fabrication of heterojuctions has attracted great interest in photocatalysis research [1,2]. Usually, construction of heterojuctions needs two semiconductors with matched band structures, thus after they contacted with each other, there exists an interfacial electric field between the two semiconductors, and the interfacial electric field can greatly promote the separation of photo-generated electrons and holes on exposure light due to the different energy band structures. Obviously, the photocatalytic efficiency can be benefited from the enhanced separation of photo-induced charge pairs. Therefore, study on the separation properties of the photo-generated charge pairs of heterojunctions during the process of photocatalytic degradation of organic pollutants is not only the core issue of construction and perfection of the high-performance photocatalytic system, but also is of great theoretical and practical significance for understanding the nature of the surface photocatalytic reaction. Commonly, the molar ratio of two semiconductors will greatly influence the photo-induced charge separation behaviors of the composites formed, since the light reached to the interface will be remarkably affected by the molar ratio of two semiconductors. Therefore, it is prerequisite to reveal the relationship between the molar ratio of two semiconductors and the photo-induced charge separation properties (the rate and phase).

As an aurivillius-related oxide and n-type wide bandgap photocatalyst, $(BiO)_2CO_3$ (BOC) has aroused increasing attention owing to its striking layered-structure [3,4]. The photocatalytic activity of BOC has been intensely investigated. However, the photocatalytic efficiency of BOC should be further promoted to meet the practical application [5–7]. Various attempts have been executed to resolve this issue, among the approaches developed; construction of heterostructures is proved to be a simple and effective strategy to boost the photocatalytic performance of BOC [8–12]. Among all the photocatalysts which can couple with BOC, BiOBr is thought to be a favorable and ideal candidate. BiOBr is a p-type photocatalyst with layered-structure similar to BOC, furthermore, BiOBr exhibits photocatalytic activity under visible light illumination and high *anti*-photocorrosion ability [13–15]. However, the photocatalytic

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activity of BiOBr is far from satisfactory for practical applications and it is crucial to enhance the photocatalytic efficiency. Construction of $(BiO)_2CO_3$-BiOBr heterojuctions is expect to elevate the photocatalytic activity of the bare $(BiO)_2CO_3$ and BiOBr owing to the enhanced separation rate of photo-generated electrons and holes as analyzed above. More important, $(BiO)_2CO_3$-BiOBr heterojuctions can be facilely prepared in-situ through using HBr aqueous solution. In fact, $(BiO)_2CO_3$-BiOBr heterostructures has been fabricated and the corresponding photocatalytic performance has been investigated, based on the results of characterization and photocatalytic activities, the photo-generated charge separation mechanism was proposed by Cao and coworkers [16]. However, the effects of the molar ratio of $(BiO)_2CO_3$/BiOBr on the photo-generated charge separation behaviors and photocatalytic activities of the $(BiO)_2CO_3$-BiOBr composites have seldom concerned. In fact, the information can shed light on the nature of the surface photocatalytic reaction.

Methyl orange (MO) was widely applied as a model azo dye in photocatalysis research because of its toxic or carcinogenic [17]. In this paper, MO was used as a probe pollutant to evaluate the photocatalytic activity of $(BiO)_2CO_3$-BiOBr heterostructures.

In the present work, $(BiO)_2CO_3$-BiOBr heterostructures was successfully constructed in-situ via a facile pore impregnating method using HBr aqueous solution. To reveal the effects of the molar ratio of $(BiO)_2CO_3$/BiOBr on the photo-induced charge separation behaviors (separation rate and phase) and the photocatalytic activities of the $(BiO)_2CO_3$-BiOBr composites, the separation behaviors of photo-generated charge pairs were studied by surface photovoltage spectroscopy (SPS). The information is conducive to better understand the effects of the molar ratio of $(BiO)_2CO_3$/BiOBr on the photo-induced charge separation behaviors (separation rate and phase) of the $(BiO)_2CO_3$-BiOBr composites and the corresponding photocatalytic activities.

2. Experimental section

2.1. Preparation

$(BiO)_2CO_3$ was prepared by a facile parallel flaw precipitation approach using $Bi(NO_3)_3 \cdot 5H_2O$ and Na_2CO_3 aqueous solution as the method given in Ref [18]. $(BiO)_2CO_3$ -BiOBr composites with different molar ratios of $(BiO)_2CO_3$/BiOBr were constructed in-situ by a pore impregnating approach using HBr aqueous solution, the procedure was same as that described in the literature [18]. The molar ratio of $(BiO)_2CO_3$/BiOBr is 2/1, 3/4 and 1/8 by adjusting the concentration of HBr aqueous solution. BiOBr was also synthesized by the above method. The samples with different molar ratios of $(BiO)_2CO_3$/BiOBr were denoted as 2/1, 3/4 and 1/8, respectively.

2.2. Characterization

A SSA-4200 automatic surface analyzer was employed to measure the Brunauer-Emmett-Teller (BET) surface area of the samples. X-ray diffraction patterns of the samples were recorded by a DX-2600 X-ray diffractometer (Cu Kα = 0.15406 nm) at room temperature. The UV–Vis diffuse reflection spectra were conducted on a UV–Vis spectrophotometer (TU-1907) using $BaSO_4$ as the reflectance sample. Scanning electron microscopy (SEM) images were taken on a JSM-7500F scanning electron microscope operating at 5 kV. The results of SPS were obtained according to the procedure described in Ref [19].

2.3. Photocatalytic activity evaluation

Photocatalytic experiments were performed in a Pubchem III photochemical reactor as the procedure given in Ref [20]. 50 mg of sample was dispersed into 50 mL of MO aqueous solution (10 mg L^{-1}) under intense magnetic stirring. The light source was a 500 W Xenon lamp and the initial pH of MO solution was controlled at 6.85. At regular interval, 5 mL of the suspension was sampled and centrifuged; the concentration of MO was measured and analyzed by Lambert-Beer law.

3. Results and discussion

3.1. Results of photocatalyst characterization

The S_{BET} of samples was exhibited in Table 1. The results demonstrate that S_{BET} of the samples drops gradually as the content of BiOBr increasing. Commonly, the relative high S_{BET} can provide more active sites for the photocatalytic reaction, adsorbing more MO molecular on the catalysts. The result can be further certificated by the adsorption of MO on the samples surface.

Fig. 1 shows the XRD patterns of the samples. All the peaks of BOC accord well with the standard tetragonal phase (JCPDS No. 41-1488). The peaks of BiOBr can be readily indexed to tetragonal phase (JCPDS No. 09-0393). For the 2/1, 3/4 and 1/8 samples, the peaks of BOC and BiOBr were simultaneously observed. The diffraction intensity of BiOBr gradually increases, at the meantime, the diffraction intensity of BOC decreases as the content of BiOBr increasing, demonstrating that BOC gradually transforms into BiOBr by acid etching using HBr aqueous solution. The results support that $(BiO)_2CO_3$ and BiOBr coexist in the composites, fitting well with the results reported by Cao and coworkers [16].

Fig. 2 shows the SEM images of BOC, 3/4 and BiOBr. Three samples display similar irregular plate-like morphology, which may attribute to the similar layered-structure of BiOBr and BOC. Furthermore, seldom pores were observed for these three samples, resulting in low specific surface area, which agrees well with the results exhibited in Table 1.

Fig. 3 a shows the UV–Vis DRS of BOC, 3/4 and BiOBr. Compared to the pure BOC, the 3/4 sample appears red-shift, which is due to the presence of BiOBr in the composites, as BiOBr is a visible light driven-photocatalyst. The bandgap of BOC and BiOBr can be estimated by following the Kubelka-Munk function, $\alpha h\nu = A\,(h\nu\text{-}Eg)^{n/2}$, where α, h, v, Eg and A are absorption coefficient, Plank constant, light frequency, band gap energy, and a constant, respectively. For $(BiO)_2CO_3$ and BiOBr, the values of n are 4 and 4, respectively [21,22]. As shown in Fig. 3 b, the band gap of BOC and BiOBr is around 3.22 eV and 2.71 eV, respectively. The conduction band (CB) and valence band (VB) potentials can be further calculated using the following equations.

$$E_{VB} = X - E^c + 0.5\ Eg$$

$$E_{CB} = E_{VB} - Eg$$

Where E_{VB} represents the VB edge potential, E_{CB} stands for the CB edge potential, X is the electronegativity of the semiconductor, E^c is about 4.5 eV for the energy of free electrons on the hydrogen scale, Eg is defined as the band gap. X is 6.332 and 6.178 eV for BOC and BiOBr, respectively. The VB and CB of BOC were calculated to be 3.44 eV and 0.22 eV, respectively. Similarly, the VB and CB of BiOBr

Table 1
S_{BET} of photocatalysts prepared.

Catalyst	BOC	2/1	3/4	1/8	BiOBr
S_{BET}	10.0	9.3	9.0	7.4	6.3