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Substrate-dependent photoreactivities of BiOBr nanoplates prepared at different pH values

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ABSTRACT

In this study, we showed that BiOBr nanoplates prepared at different pH values have substrate-dependent photocatalytic activities under visible-light irradiation. The BiOBr nanoplates synthesized at pH 1 (BOB-1) degraded salicylic acid more effectively than did those obtained at pH 3 (BOB-3), but the order of their photocatalytic activities in rhodamine B (RhB) degradation were reversed. Electrochemical Mott–Schottky and zeta-potential measurements showed that BOB-1 had a more positive valence band and lower surface charge, leading to superior photocatalytic activity in salicylic acid degradation under visible light. However, BOB-3 was more powerful in RhB degradation because larger numbers of superoxide radicals were generated via electron injection from the excited RhB to its more negative conduction band under visible-light irradiation; this was confirmed using active oxygen species measurements and electron spin resonance analysis. This study deepens our understanding of the origins of organic-pollutant-dependent photoreactivities of semiconductors, and will help in designing highly active photocatalysts for environmental remediation.

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1. Introduction

In recent years, semiconductor photocatalysis has been widely used to remove environmental organic contaminants [1–3]. Visible-light-active bismuth oxybromide (BiOBr), which has a desirable band gap of about 2.7 eV, has attracted increasing interest [4]. BiOBr crystallizes in the tetragonal matlockite layer structure, characterized by $[\text{Bi}_2\text{O}_2]$ slabs interleaved with double slabs of bromide atoms. The internal electric fields between the $[\text{Bi}_2\text{O}_2]$ and bromide atom layers facilitate the separation of photogenerated electron-hole pairs and therefore improve its photocatalytic performance [5–9].

Recently, Ye's group found that the hydrothermal pH did not change the dominant exposed facet of BiOBr single-crystalline nanosheets, but could affect the size, surface area, and band structure; this could affect the photoreactivity of BiOBr rather than the exposed facet [10]. BiOBr with high photocatalytic activity has been widely studied and used in photovoltaic solar energy conversion, photocatalytic water splitting, and environmental pollutant decomposition.

Generally, the environmental remediation performance of a photocatalyst depends mainly on its structural properties such as phase composition, particle size, morphology, and specific surface area. Many reports have established a correlation

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between the structure of a TiO_2 catalyst and its photocatalytic activity in pollutant removal [11–13]. However, the reported photoreactivities of TiO_2 are often contradictory. Chio's group systematically investigated the photocatalytic degradation of 19 substrates in water with eight commercial TiO_2 samples, in terms of their degradation or conversion rates. They found that the activities of the substrates were complex, and showed the substrate-specific nature of TiO_2 photocatalysts [14]. It is expected that non- TiO_2 catalysts may also be substrate specific, but no data are available for BiOBr. It is important to understand the influence of the substrate on the photocatalytic performance of BiOBr because of the increasing need for photocatalysts for environmental applications.

The aim of this study was to determine the substrate-specific effects of BiOBr. We prepared BiOBr nanoplates at different pH values via a hydrothermal method and studied their photocatalytic performances in the degradation of rhodamine B (RhB) and salicylic acid (SA). The mechanisms of the substrate-dependent photoreactivities of BiOBr prepared at different pH values were clarified based on active oxygen species measurements, electron spin resonance (ESR) analysis, and electrochemical Mott–Schottky measurements.

2. Experimental

2.1. Preparation of BiOBr photocatalyst

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and cetyl trimethyl ammonium bromide (CTAB) were obtained from the National Medicines Corporation Ltd., China. All chemicals were analytical grade and used as received without further purification. BiOBr nanoplates were synthesized using a hydrothermal method. In a typical procedure, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1.0 g) and CTAB (1.0 g) were dissolved in deionized water (50 mL); the initial pH of the solution was about 1.0. The resulting solution was stirred for 1 h at room temperature and then transferred to a 100-mL autoclave. The autoclave was heated at 160 °C for 18 h. The precipitate was collected, thoroughly washed with deionized water and ethanol, and dried at 50 °C in air. Another BiOBr sample was obtained by adjusting the solution pH to 3.0 with NaOH (1 mol/L). The BiOBr samples obtained at initial pH values of 1 and 3 were denoted by BOB-1 and BOB-3, respectively.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained using a Philips Xpert System instrument with $\text{Cu } K_\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Scanning electron microscopy (SEM) was performed using a JEOL 6490 instrument. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed using a JEOL JEM-2010 instrument operated at 200 kV. The samples for TEM analysis were prepared by dispersing the final powders in ethanol; the dispersions were then dropped on C–Cu grids. Powders deposited on a Cu grid were also examined using high-resolution (HR) TEM. Ultraviolet-visible (UV-Vis)

diffuse-reflectance (DR) spectra were recorded at room temperature using a Cary 300 spectrometer equipped with an integrated sphere. Nitrogen adsorption-desorption isotherms were measured at –196 °C using a Micromeritics ASAP2010 system after vacuum-drying the samples at 200 °C overnight.

2.3. Photocatalytic activity evaluation

The photocatalytic degradations of RhB (30 mg/L) or SA (10 mg/L) with BOB-1 and BOB-3 nanoplate photocatalysts were performed at ambient temperature under a 500 W Xe arc lamp with a 420-nm cutoff filter as the light source. Typically, the photocatalyst (0.05 g) was added to 50 mL of RhB or SA aqueous solution in a container. Prior to irradiation, the suspensions were stirred in the dark for 1 h to ensure adsorption-desorption equilibrium. The mixture of RhB or SA solution and the photocatalyst was continuously stirred using a magnetic stirrer during degradation. The photocatalytic reaction was stopped by removing the photocatalyst from the suspension by centrifuging and filtering with a Millipore membrane (220 nm), and then the absorbance of the RhB or SA solution was measured.

2.4. Analytical methods

The RhB concentration was monitored colorimetrically using a Shimadzu UV-2550 UV-Vis spectrometer, and the SA concentration was determined using high-performance liquid chromatography (HPLC; Shimadzu LC-20A, Japan) [15–17]. The HPLC conditions were as follows: an octadecylsilyl reverse-phase column, phosphate buffer solution (pH 3)/deionized water = 20:80 as the mobile phase, column temperature 30 °C, flow rate 0.8 mL/min, and detection wavelength 297 nm. ESR spectroscopy was performed using a Bruker ESR 300E spectrometer, with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a radical spin-trapping agent [18,19]. The DMPO concentration was 0.2 mol/L, and the irradiation source was a 500 W Xe lamp with a cutoff filter ($\lambda > 420 \text{ nm}$).

2.5. Electrochemical measurements

Photoanodes were prepared by mixing a BiOBr sample (50 mg), distilled water (200 μL), and 2.2%–2.6% poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) conductive solution (40 μL) and then grinding for about 10 min [20,21]. The resulting paste was spread on a fluorine-doped tin oxide conducting glass and dried at 160 °C for 10 min. Electrochemical measurements were performed using an electrochemical analyzer (CHI660D, CHI Shanghai, Inc.) in a standard three-electrode system with a saturated calomel electrode (SCE) as the reference electrode, the prepared photoanode (0.5 $\times$ 3 cm^2) as the working electrode, and a platinum wire as the counter electrode, immersed in a 50-mL glass breaker containing 0.5 mol/L Na_2SO_4 electrolyte solution. Mott–Schottky measurements were performed using an independence-potential model. The photocurrent density was measured using an amperometric current–time curve method.

The oxidation potential was measured using cyclic voltammetry to evaluate the band positions of pollutants, using the three-electrode system with the working electrode substituted by a graphite electrode; the electrolyte was RhB (30 mg/L) with 0.5 mol/L Na_2SO_4 aqueous solution or SA (10 mg/L) with 0.5 mol/L Na_2SO_4 aqueous solution.

3. Results and discussion

The XRD patterns provided information on the crystallinities and phase structures of the samples hydrothermally synthesized at pH 1 and 3 (Fig. 1). The XRD patterns of the two samples are different. The BOB-1 peaks can be indexed to a pure tetragonal phase of BiOBr (JCPDS 3-733), and BOB-3 can be indexed to another pure tetragonal phase (JCPDS 73-2061). The cell parameters of BOB-1 are $a = b = 3.915 \text{ \AA}$, $c = 8.076 \text{ \AA}$, and those of BOB-3 are $a = b = 3.923 \text{ \AA}$, $c = 8.0926 \text{ \AA}$. The BOB-3 peaks are stronger than those of BOB-1. The slight structural difference between BOB-1 and BOB-3 may arise from the different pH values of the precursor solution during preparation. The sharp diffraction peaks indicate that the samples are highly crystalline; no impurity peaks were found.

The morphologies of the BiOBr samples obtained at different pH values were investigated using SEM and TEM (Fig. 2). Low-magnification SEM images show that both BOB-1 (Fig. 2(a)) and BOB-3 (Fig. 2(g)) consist of large numbers of irregular nanoplates. High-magnification SEM images show that the BOB-3 nanoplates, obtained at pH 3, are of width 0.6–1.5 μm and thickness 27–44 nm (Fig. 2(h)). The BOB-1 nanoplates, prepared at pH 1, are wider (0.7–2.0 μm) and thicker (50 nm, Fig. 2(b)). TEM images of BOB-1 and BOB-3 are shown in Fig. 2(c) and (i), respectively. The HRTEM images show that the two samples are highly crystalline (Fig. 2(d) and (j)). The clear lattice fringes with interplanar lattice spacings of 0.277 and 0.200 nm correspond to the tetragonal (110) and (020) planes, respectively, of BiOBr, for both BOB-1 and BOB-3 (Fig. 2(e) and (k)). The clear and regular square diffraction spot

Fig. 1. XRD patterns of BOB-1 (1) and BOB-3 (2).

arrays in the SAED patterns show that BOB-1 and BOB-3 are single crystals (Fig. 2(f) and (l)). Fast Fourier transform (FFT) patterns show exposure of the (001) crystal planes for both BOB-1 and BOB-3 (Fig. 2(f) and (l)). The Brunauer-Emmett-Teller surface areas of BOB-1 and BOB-3 are 4.1 and 6.1 m^2/g , respectively. The slightly higher surface area of BOB-3 is attributed to its smaller nanoplates, shown by the SEM and TEM results.

The UV-Vis DR spectra of BOB-1 and BOB-3 display similar broad absorbances in the visible-light region (Fig. 3), as confirmed by their pale-yellow color (insets in Fig. 3). The BiOBr nanoplates can therefore respond to a wide range of solar spectrum wavelengths. The absorption edges of BOB-1 and BOB-3 are at about 430 nm. The BiOBr band gap was estimated from the tangent line in the plot of the square root of the Kubelka-Munk function against the photon energy, as shown in the inset in Fig. 3. The calculated band gap of BOB-1 is 2.72 eV, i.e., close to that of 2.73 eV for BOB-3. The slightly larger band gap energy of BOB-3 can be attributed to its small size [22].

Fig. 2. SEM images (a, b), TEM image (c), HRTEM images (d, e), and FFT pattern (f) of BOB-1. SEM images (g, h), TEM image (i), HRTEM images (j, k), and FFT pattern (l) of BOB-3.

Fig. 3. (a) UV-Vis spectra of BOB-1 and BOB-3. (b) Plots of $(\alpha h\nu)^{1/2}$ vs. photon energy ($h\nu$), and the bottom inset shows photographs of BOB-1 (a') and BOB-3 (b').

Fig. 4. (a) Time profiles of RhB adsorption over BOB-1 and BOB-3. (b) Photocatalytic activities of RhB degradation with BOB-1 and BOB-3 under visible-light irradiation ($\lambda > 420$ nm). (c) Time profiles of SA adsorption over BOB-1 and BOB-3. (d) Photocatalytic activities of SA degradation with BOB-1 and BOB-3 under visible-light irradiation ($\lambda > 420$ nm).

The photocatalytic activities of the BOB-1 and BOB-3 nanoplates were evaluated using RhB (30 mg/L) and SA (10 mg/L) as probe molecules under visible-light irradiation ($\lambda > 420$ nm). The adsorptions of RhB and SA on BOB-1 and BOB-3 before photodegradation were examined. RhB and SA were not efficiently adsorbed by BOB-1 (Fig. 4(a)); only 0.8% of RhB and

0.2% of SA, respectively, were adsorbed. However, 9.1% of RhB and 12.7% of SA were adsorbed on the surfaces of BOB-3 samples (Fig. 4(c)). If we assume that the adsorption follows a pseudo-first-order model, the rate constants of RhB adsorption over BOB-1 and BOB-3 were 0.005 and 0.059 min^{-1} , respectively, and those of SA were 0.01 and 0.063 min^{-1} ,

respectively. Further investigation showed that the surface-area-normalized pseudo-first-order adsorption rate constants for BOB-3 ($0.01 \text{ g min}^{-1} \text{ m}^{-2}$ for RhB and $0.01 \text{ g min}^{-1} \text{ m}^{-2}$ for SA) were still several times those for BOB-1 ($0.001 \text{ g min}^{-1} \text{ m}^{-2}$ for RhB and $0.003 \text{ g min}^{-1} \text{ m}^{-2}$ for SA), indicating that the adsorption difference was caused not only by the larger specific surface area of BOB-3, but also by other factors induced by the different pH values of the precursor solutions. In the absence of a photocatalyst, RhB did not self-degrade under visible-light irradiation ($\lambda > 420 \text{ nm}$). The photodegradation efficiencies of RhB over the BOB-1 and BOB-3 were about 35% and 92% in 25 min, respectively (Fig. 4(b)). The apparent reaction rate (k) for BOB-3 was higher than that for BOB-1 (inset in Fig. 4(b)). The degradation constant of RhB over BOB-3 was $9.85 \times 10^{-2} \text{ min}^{-1}$, six times that over BOB-1 (0.0165 min^{-1}). The surface-area-normalized apparent reaction rate constant for BOB-3 (k' , $16.1 \text{ g min}^{-1} \text{ m}^{-2}$) was also still much higher than that for BOB-1 ($4.0 \text{ g min}^{-1} \text{ m}^{-2}$), suggesting that the activity of BOB-3 in RhB degradation is higher than that of BOB-1.

The photocatalytic degradations of SA over the two types of BiOBr nanoplates under visible-light irradiation were further compared. The SA degradation efficiencies over BOB-1 and BOB-3 were about 10% and 33%, respectively, in 180 min under visible-light irradiation (Fig. 4(d)). The SA degradation rate constant for BOB-1 was 0.033 min^{-1} , which was 2.3 times that of BOB-3 (0.0143 min^{-1} ; inset in Fig. 4(d)). The surface-area-normalized apparent reaction rate constant for BOB-1 (k' , $8.05 \text{ g min}^{-1} \text{ m}^{-2}$) was 3.44 times that for BOB-3 ($2.34 \text{ g min}^{-1} \text{ m}^{-2}$). The SA degradation activity of BOB-1 was clearly higher than that of BOB-3, contrary to the case for RhB degradation.

We determined the pH values of the BiOBr suspensions to clarify the different RhB and SA degradation trends of BiOBr nanoplates obtained at different pH values. The pH values of the BOB-1 and BOB-3 suspensions were 5.6 and 7.1 respectively; this difference might be related to differences between their surface hydroxyl groups, which are known to affect the surface structure of a catalyst [23]. We then measured the zeta potentials of BOB-1 and BOB-3 aqueous

Fig. 5. Zeta potentials of BOB-1 and BOB-3 suspensions in water with mass concentrations of 0.1% as a function of pH.

suspensions with mass concentrations of 1% as a function of pH from 3.0 to 10.3 (Fig. 5). The isoelectric points for BOB-1 and BOB-3 were 5.1 and 9.8, respectively. The high zeta potential of BOB-3 suggests that it has a higher surface charge, as a result of the presence of a larger number of surface hydroxyl groups [24]. This result is consistent with the pH measurement results. It is reasonable to suppose that BOB-3, with more surface hydroxyl groups, could form hydrogen bonds with RhB and SA, resulting in better adsorption. As shown in Fig. 4, SA adsorption on BOB-3 ($0.0027 \text{ g min}^{-1} \text{ m}^{-2}$) was better than RhB adsorption ($0.012 \text{ g min}^{-1} \text{ m}^{-2}$), because SA contains both carboxyl and hydroxyl groups, whereas RhB has only carboxyl groups. The differences between the surface structures of BOB-1 and BOB-3 could therefore explain the different SA and RhB adsorption performances of BiOBr nanoplates obtained at different pH values (Fig. 4); this might influence the separation of photogenerated electron-hole pairs, and thus affect the photoreactivities of the BiOBr nanoplates.

Radical- and hole-trapping experiments were performed to investigate the different photodegradation trends of RhB and SA over BOB-1 and BOB-3 [25,26]. A series of scavengers, i.e., KI for holes, $\text{K}_2\text{Cr}_2\text{O}_7$ for electrons, $\text{K}_2\text{Cr}_2\text{O}_7/\text{argon}$ for $\bullet\text{O}_2^-$, and

Fig. 6. (a) Photodegradation of SA over BOB-1 in presence of different scavengers and (b) photodegradation of RhB over BOB-3 in presence of different scavengers; $0.5 \text{ mmol/L K}_2\text{Cr}_2\text{O}_7$, $10 \text{ mmol/L iso-propanol}$, and KI.

isopropanol for $\bullet\text{OH}$, were used to quench these photoinduced active species (Fig. 6). As shown in Fig. 6(a), $\bullet\text{OH}$ contributed slightly to the photodegradation (12.3%) of SA over BOB-1, but the contributions of photogenerated electrons (2.5%) and $\bullet\text{O}_2^-$ (2.9%) to SA degradation with BOB-1 were negligible. In contrast, the addition of KI strongly suppressed the degradation of SA with BOB-1, indicating that photogenerated holes (87.6%) mainly accounted for SA degradation (Table 1). The specific reactive species involved in the photocatalytic degradation of RhB over BOB-3 were also investigated (Fig. 6(b)). We found that the addition of KI and $\text{K}_2\text{Cr}_2\text{O}_7/\text{argon}$ seriously inhibited RhB degradation; their inhibition efficiencies were 82.2% and 65.9%, respectively (Table 1). This shows that photogenerated holes and $\bullet\text{O}_2^-$ both play important roles in RhB degradation with BOB-3. This was confirmed by the lower RhB photodegradation inhibition (38.7%) by $\text{K}_2\text{Cr}_2\text{O}_7$ compared with those by KI (82.2%) and $\text{K}_2\text{Cr}_2\text{O}_7/\text{argon}$ (65.9%). We therefore concluded that both photogenerated holes and $\bullet\text{O}_2^-$ were responsible for RhB oxidation with BOB-3. Because $\bullet\text{O}_2^-$ radicals can be generated via the reaction of photogenerated electrons and molecular oxygen ($\text{O}_2 + e^- \rightarrow \bullet\text{O}_2^-$), and photogenerated electrons only accounted for 38.7% of RhB degradation, which is much lower than the contribution of $\bullet\text{O}_2^-$ radicals (65.9%), we deduced that another $\bullet\text{O}_2^-$ radical generation pathway occurred in addition to that by direct visible-light-driven electrons on the conduction band (CB) during RhB degradation over BOB-3. This additional $\bullet\text{O}_2^-$ radical generation pathway is thought to be related to the RhB dye sensitization process.

We then determined the amounts of active oxygen species generated over BOB-1 and BOB-3 under visible-light irradiation using ESR spin-trapping with DMPO (Fig. 7). Fig. 7(a) shows that BOB-1 did not induce $\bullet\text{O}_2^-$ production under visible-light irradiation; however, an $\bullet\text{O}_2^-$ signal was observed in the BOB-3 system. In addition, $\bullet\text{OH}$ radical signals were not detected over BOB-1 or BOB-3 under visible-light irradiation (Fig. 7(b)), confirming that $\bullet\text{OH}$ was not the major active species in RhB and SA degradation during photocatalysis with BiOBr. These observations are in good agreement with the data in Table 1.

Table 1

Summary of inhibition efficiencies for degradations of RhB/SA by BOB-1 and BOB-3 with addition of various scavengers.

Scavenger	Inhibition efficiency (%)	
	BOB-1 (SA)	BOB-3 (RhB)
<i>iso</i> -propanol	12.3	–7
$\text{K}_2\text{Cr}_2\text{O}_7$	2.5	38.7
$\text{K}_2\text{Cr}_2\text{O}_7/\text{argon}$	2.9	65.9
KI	87.6	82.2

Reaction conditions: 0.5 mmol/L $\text{K}_2\text{Cr}_2\text{O}_7$, 10 mmol/L of *iso*-propanol and KI.

We measured the oxidation potentials of RhB and SA using cyclic voltammetry to clarify the substrate dependence of pollutant degradation during BiOBr photocatalysis. The oxidation potentials of SA were about 1.45 V vs. SCE and 1.70 V vs. the normal hydrogen electrode (NHE) in 0.5 mol/L Na_2SO_4 and 10 mg/L SA aqueous solution as the electrolyte, and those of RhB were about 0.98 V vs. SCE and 1.23 V vs. NHE in 0.5 mol/L Na_2SO_4 and 30 mg/L RhB aqueous solution as the electrolyte (Fig. 8(a) and (b)). Clearly, RhB, which has a lower oxidation potential, is easier to oxidize than SA. We estimated the band positions of BOB-1 and BOB-3 based on Mott–Schottky plots (Fig. 8(c)). The flat band potentials of BOB-1 and BOB-3 were -0.47 V vs. SCE (~ -0.22 V vs. NHE) and -0.59 V vs. SCE (~ -0.34 V vs. NHE), respectively (Fig. 8(d)). The bottom of the CB was more negative by ~ -0.1 V than the flat band potential, therefore the CBs of BOB-1 and BOB-3 were estimated to be -0.32 and -0.44 V vs. NHE, respectively (Fig. 8(d)). The reduction potential of $\text{O}_2/\bullet\text{O}_2^-$ is -0.33 V vs. NHE, therefore BOB-1 cannot initiate molecular oxygen activation, but BOB-3, which has a more negative CB, can effectively reduce molecular oxygen to generate $\bullet\text{O}_2^-$ under visible-light irradiation, in agreement with the above results. The valence bands (VBs) of BOB-1 and BOB-3 were estimated to be about 2.41 and 2.30 V, respectively, suggesting that BOB-1, which has a more positive VB, would have a larger number of photogenerated holes for SA oxidation. This result is consistent with those shown in Figs. 4 and 6, and confirms that the pH values of the precursor solutions affect the band structures of the BiOBr nanoplates, and therefore influence active species

Fig. 7. (a) DMPO spin-trapping ESR spectra of BOB-1 and BOB-3 methanol dispersions, for DMPO- $\text{O}_2\bullet^-$ detection. (b) DMPO spin-trapping ESR spectra of BOB-1 and BOB-3 in aqueous dispersions, for DMPO- $\bullet\text{OH}$ detection.

Fig. 8. Oxidation potentials of SA (0.5 mol/L Na₂SO₄ and 10 mg/L SA aqueous solution) (a) and RhB (0.5 mol/L Na₂SO₄ and 30 mg/L RhB aqueous solution) (b). Determined using cyclic voltammetry. (c) Mott-Schottky plots of BOB-1 and BOB-3 electrodes. (d) Estimated band positions for BOB-1 and BOB-3, oxidation potentials of RhB and SA, and reduction potentials of $O_2/\bullet O_2^-$.

generation, resulting in substrate-dependent photocatalytic activity of BiOBr.

We also examined the transient photocurrent responses of BOB-1 and BOB-3 catalyst film electrodes in different solutions (Fig. 9). As shown in Fig. 9(a), both electrodes promptly generated photocurrents with reproducible responses to on/off cycles. The photocurrent for the BOB-3 film was higher than that for the BOB-1 film electrode in 0.5 mol/L Na₂SO₄ solution, indicating more efficient photoinduced charge separation and transfer in BOB-3 under visible light; this is consistent with the results of the band structure measurements. As expected, the photocurrents of BOB-1 and BOB-3 increased in the presence of RhB (30 mg/L) in Na₂SO₄ electrolyte (Fig. 9(b)), because of RhB dye sensitization under visible-light irradiation. In contrast, the presence of SA (10 mg/L) only slightly increased the photocurrent for BOB-1 in Na₂SO₄ electrolyte, and significantly decreased the photocurrent for the BOB-3 electrode (Fig. 9(c)). Table 2 summarizes the photocurrent densities for BOB-1 and BOB-3 in different electrolytes in the absence or presence of RhB or SA. The presence of RhB increased the photocurrent densities for the BOB-1 and BOB-3 electrodes by factors of 5.1 and 2.0, respectively, compared with those in pure Na₂SO₄ electrolyte. These photocurrent density enhancements confirmed electron

injection via RhB sensitization under visible light. The presence of SA did not significantly change the photocurrent density for BOB-1, but sharply decreased the photocurrent density for the BOB-3 electrode to one-fifth of the initial value ($1.65 \mu\text{A}/\text{cm}^2$). These different changes in the presence of SA are thought to arise because surface-adsorbed SA would inhibit the separation of photogenerated electron-hole pairs [27], and much more SA was adsorbed on BOB-3 than on BOB-1, leading to weaker SA degradation activity of BOB-3.

On the basis of the above results and discussion, we propose a possible mechanism to explain the substrate-dependent photocatalytic activities of BOB-1 and BOB-3 nanoplates prepared at different pH values in the degradation of RhB and SA (Fig. 10). Under visible-light irradiation, both BOB-1 and BOB-3 can be excited to generate electrons in the CB, leaving holes in the VB. RhB can be excited during degradation under visible light and then inject electrons into the CBs of BOB-1 and BOB-3 (Fig. 10(a)). A larger amount of RhB adsorbed on BOB-3 increases the amount of injected electrons to the CB. As shown in Fig. 8, the CB of BOB-1 (-0.32 V vs. NHE) is more positive than the reduction potential of $O_2/\bullet O_2^-$ (-0.33 V vs. NHE), but BOB-3 has a more negative CB (-0.44 V vs. NHE); therefore, only the abundant CB electrons of BOB-3 can reduce molecular oxygen to generate $\bullet O_2^-$ under visible-light irradiation. The

Fig. 9. (a) Photocurrent responses of BOB-1 and BOB-3 in 0.5 mol/L Na_2SO_4 solution. (b) Photocurrent responses of BOB-1 and BOB-3 in 0.5 mol/L Na_2SO_4 and 30 mg/L RhB solution. (c) Photocurrent responses of BOB-1 and BOB-3 in 0.5 mol/L Na_2SO_4 and 10 mg/L SA solution.

generated $\cdot\text{O}_2^-$ and photogenerated holes therefore contribute to the higher visible-light photocatalytic RhB degradation performance of the BOB-3 catalyst compared with that of BOB-1. In the degradation of colorless SA, which has a high oxidation potential (Fig. 10(b)), BOB-3, which has a less positive VB (2.41 V vs. NHE), cannot efficiently oxidize SA by its photogenerated holes. The adsorbed SA inhibits the separation of photogenerated electron-hole pairs of BiOBr, therefore a larger amount of SA adsorbed on BOB-3 results in fewer photogenerated holes for SA oxidation with BOB-3. These two factors account for the poor SA degradation photoreactivity of BOB-3.

4. Conclusions

Two types of BiOBr nanoplates, BOB-1 and BOB-3, were prepared at pH 1 and 3, respectively, via a hydrothermal route. BOB-1 did not degrade RhB more effectively than BOB-3 did, but it was more powerful in SA degradation than BOB-3 under visible-light irradiation. These substrate-dependent photoreactivities of BiOBr nanoplates were related to their band potentials and pollutant molecule adsorption abilities, as well as the properties of the pollutant molecules. Determination of the active oxygen species and ESR analysis showed that photogenerated holes and $\cdot\text{O}_2^-$ were both responsible for RhB degradation, but photogenerated holes mainly accounted for SA degradation. Because of the RhB dye sensitization effect, the photocatalytic activity of BOB-3 was better than that of BOB-1, as a result of its better adsorption performance and more negative CB, which promoted

superoxide radical generation via electron injection from the excited RhB under visible-light irradiation. In the case of colorless SA, which inhibited the separation of photogenerated electron-hole pairs, BOB-3 was less powerful than BOB-1, because of the larger amount of SA adsorbed on the surface and the less positive VB of BOB-3, which greatly lowered SA oxidation by holes photogenerated by BOB-3. The results of this study increase our understanding of the origin of the organic-pollutant-dependent photoreactivities of

Fig. 10. (a) Possible mechanism of photocatalytic degradation of RhB over BOB-1 and BOB-3 under visible-light irradiation ($\lambda \geq 420$ nm). (b) Possible mechanism of photocatalytic degradation of SA over BOB-1 and BOB-3 under visible-light irradiation ($\lambda \geq 420$ nm).

Table 2

Photocurrent densities for BOB-1 and BOB-3 electrodes in different electrolytes.

Electrolyte	Photocurrent density ($\mu\text{A}/\text{cm}^2$)	
	BOB-1	BOB-3
Na_2SO_4	0.45	1.65
Na_2SO_4 and RhB	2.30	3.35
Na_2SO_4 and SA	0.50	0.36

Reaction conditions: Na_2SO_4 solution 0.5 mol/L, RhB solution 30 mg/L, SA solution 10 mg/L.

Graphical Abstract

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Substrate-dependent photoreactivities of BiOBr nanoplates prepared at different pH values

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BiOBr prepared at pH 1 more efficiently oxidized salicylic acid via photogenerated holes, because of its more positive valence band and poor adsorption ability. BiOBr prepared at pH 3 had superior rhodamine B degradation activity because of its more negative conduction band and better adsorption ability, which enhanced $\bullet\text{O}_2^-$ generation.

semiconductors and will help in the design of highly active photocatalysts for environmental remediation.

References

- [1] Yu C L, Wang Q Z, Yu J C, Liu H, Wei L F. *Chin J Catal* (余长林, 周晚琴, 余济美, 刘鸿, 魏龙福. 催化学报), 2014, 35: 1609
- [2] Li J D, Yu C L, Fang W, Zhu L H, Zhou W Q, Fan Q Z. *Chin J Catal* (李家德, 余长林, 方稳, 朱丽华, 周晚琴, 樊启哲. 催化学报), 2015, 36: 987
- [3] Wang X T, Li Y M, Liu X, Gao S M, Huang B B, Dai Y. *Chin J Catal* (王潇彤, 李延敏, 刘新, 高善民, 黄伯杨, 戴瑛. 催化学报), 2015, 36: 389
- [4] Wang J L, Yu Y, Zhang L Z. *Appl Catal B*, 2013, 136–137: 112
- [5] Zhang X, Ai Z H, Zhang L Z. *J Phys Chem C*, 2008, 112: 747
- [6] Deng Z T, Chen D, Peng B, Tang F Q. *Cryst Growth Des*, 2008, 8: 2995
- [7] Huang W L, Zhu Q S. *J Comput Chem*, 2008, 30: 183
- [8] Li R, Gao X Y, Fan C M, Zhang X C, Wang Y W, Wang Y F. *Appl Surf Sci*, 2015, 355: 1075
- [9] Liu C B, Zhao W W, Huang Y, Wang H M, Zhang B. *Tetrahedron*, 2015, 71: 4344
- [10] Ye L Q, Su Y R, Jin X L, Xie H Q, Cao F P, Guo Z. *Appl Surf Sci*, 2014, 311: 858
- [11] Cheng H F, Huang B B, Dai Y. *Nanoscale*, 2014, 6: 2009
- [12] Zhang J, Fu W, Xi J H, He H, Zhao S C, Liu H W, Ji Z G. *J Alloys Comp*, 2013, 575: 40
- [13] Lee J S, Choi W Y. *J Phys Chem B*, 2005, 109: 7399
- [14] Ryu J G, Choi W Y. *Environ Sci Technol*, 2008, 42: 294
- [15] Venema D P, Hollman P C H, Janssen K P L T M, Katan M B. *J Agric Food Chem*, 1996, 44: 1962
- [16] Paterson J R, Srivastava R, Baxter G J, Graham A B, Lawrence J R. *J Agric Food Chem*, 2006, 54: 2891
- [17] Matsuda H, Kaburagi K, Matsumoto S, Kurihara K, Tochigi K, Tomono K. *J Chem Eng Data*, 2009, 54: 480
- [18] Sun M, Li D Z, Chen Y B, Chen W, Li W J, He Y H, Fu X Z. *J Phys Chem C*, 2009, 113: 13825
- [19] Sun M, Li D Z, Zheng Y, Zhang W J, Shao Y, Chen Y B, Li W J, Fu X Z. *Environ Sci Technol*, 2009, 43: 7877
- [20] Ishikawa A, Takata T, Kondo J N, Hara M, Kobayashi H, Domen K. *J Am Chem Soc*, 2002, 124: 13547
- [21] Zhang J S, Chen X F, Takanabe K, Maeda K, Domen K, Epping J D, Fu X Z, Antonietti M, Wang X C. *Angew Chem Int Edt*, 2010, 49: 441
- [22] Bruda C, Chen X B, Narayanan R, El-Sayed M A. *Chem Rev*, 2005, 105: 1025
- [23] Suttiponparnit K, Jiang J K, Sahu M, Suvachittamont S, Charinpanitkul T, Biswas P. *Nanoscale Res Lett*, 2011, 6: 1
- [24] Chen S Y, Wang L W. *Chem Mater*, 2012, 24: 3659
- [25] Ge S X, Zhang L Z. *Environ Sci Technol*, 2011, 45: 3027
- [26] Yin M C, Li Z S, Kou J H, Zou Z G. *Environ Sci Technol*, 2009, 43: 8361
- [27] Linsebigler A L, Lu G Q, Yates J T. *Chem Rev*, 1995, 95: 735

pH调控合成溴氧铋纳米片的底物依赖光催化特性

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摘要: 近年来, 半导体光催化技术已广泛用于去除水中有机污染物. 在各类光催化剂中, 具有合适禁带宽度的溴氧铋(BiOBr, 2.7 eV)材料吸引了众多研究者兴趣. 通常情况下, 半导体光催化降解有机污染物性能主要与光催化材料的结构性性质, 如物相组成、颗粒粒径、材料表面结构等相关. 研究已经证实了 TiO_2 光催化降解有机污染物具有底物依赖的特性, 但是BiOBr的有机物降解特性与底物性质的关系研究尚未见文献报道. 为发展高效的BiOBr太阳光催化污染净化技术, 研究有机底物与BiOBr光催化降解性能的关系具有重要意义.

本文分别在 $\text{pH} = 1$ 和 $\text{pH} = 3$ 条件下采用水热法合成了BiOBr纳米片(BOB-1和BOB-3), 并通过X射线粉末衍射(XRD), 扫描电子显

显微镜(SEM), 透射电子显微镜(TEM), 紫外-可见漫反射(DRS)等技术表征了所制备半导体光催化材料. 结果表明, 在不同pH条件下均能合成具有高结晶度的四方相BiOBr, BOB-1和BOB-3均由不规则的纳米片组成, BOB-3纳米片宽度大约为0.6–1.5 μm , 厚度大约27–44 nm, 而BOB-1纳米片宽度大约为0.7–2.0 μm , 厚度大约50 nm. 选区电子衍射观察到了BOB-1和BOB-3清晰的晶格条纹, 晶格间距为0.20和0.28 nm, 分别对应着四方晶系的(020)面和(110)面.

选取罗丹明B(RhB)和水杨酸(SA)为典型有机底物分子, 研究了BOB-1和BOB-3纳米片的底物依赖光催化特性. 结果表明, BOB-1吸附SA和RhB 1 h后, 吸附率分别仅为0.2%和0.8%, 而BOB-3对SA和RhB的效率分别可达9.1%和12.7%; 光催化降解两种底物分子的结果表明, BOB-1和BOB-3降解RhB的速率分别为4.00以及16.10 $\text{g}\cdot\text{min}^{-1}\cdot\text{m}^{-2}$, 而降解SA的速率分别为2.35 $\text{g}\cdot\text{min}^{-1}\cdot\text{m}^{-2}$. 可见, BOB-1显示了高效降解SA的能力, 而, BOB-3则表现出更强的降解RhB活性. 电化学Mott-Schottky和电动电位测试结果表明, BOB-1比BOB-3有更正的价带电位和更低的表面电荷. 捕获实验(KI捕获空穴, $\text{K}_2\text{Cr}_2\text{O}_7$ 捕获电子, 氙气捕获超氧负离子, 异丙醇捕获羟基自由基)表明光生空穴与超氧负离子是BOB-3降解RhB的主要活性物种, 而BOB-1降解SA主要是光生空穴作用, 电子顺磁共振(ESR)测试进一步证实了以上结果. 光电流密度测试结果表明, 可见光作用下RhB可被激发到RhB*, 导致BOB-3的电子空穴对分离效率高; 而当电解质中存在SA时, 催化剂的表面羟基与SA形成氢键, 致使光生电子与空穴分离效果变差, 因而光电流减少.

本文提出了pH调控合成溴氧铋纳米片的底物依赖光催化降解RhB和SA机理, 与BiOBr导带电位、底物分子吸附量、底物分子物理化学性质相关. BOB-1和BOB-3纳米片催化剂在可见光激发下能产生光生导带电子和价带空穴, 这些光生载流子可迁移到催化剂表面. 染料分子RhB在可见光作用下能发生光敏化作用生成激发态RhB*, RhB*可以将电子注入BOB-3催化剂的导带, 导带上的光生电子与RhB*注入电子与吸附在其表面的氧气共同作用生成更多的超氧负离子, 从而高效降解RhB. 由于BOB-1比BOB-3有更正导带电势, 导带电子无法直接还原氧气生成超氧负离子, 仅能依靠光生空穴直接氧化RhB, 导致BOB-1表现出降解RhB性能弱; 对于无色的底物SA, 吸附较多SA的BOB-3催化剂上的表面羟基与SA之间形成氢键作用, 抑制了光生电子与空穴对的分离, 导致BOB-3在可见光光催化降解SA活性弱, 而BOB-1表面吸附SA较少, 同时BOB-1有更负的价带电位, 利用光生空穴与吸附在催化剂表面的SA反应, 从而表现出高效降解SA的性能.

关键词: 降解; 可见光; 底物依赖光催化活性; 溴氧铋纳米片; 罗丹明B; 水杨酸

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