Short Communication

Novel Bi$_2$S$_3$-sensitized BiOCl with highly visible light photocatalytic activity for the removal of rhodamine B

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1. Introduction

At present, colored organic dyes released in the textile effluents have become a more serious environmental problem. Due to the special nature of synthetic dyes, conventional treatments (such as adsorption, biodegradation and chemical coagulation) have been ineffective for the removal of such organic pollutants and difficult to accord with the more stringent international environmental standards [1–3]. Therefore, developing novel technologies with more efficiency and less cost is of great importance and urgency. Among them, photocatalysis has been regarded as a potential method [4–7].

BiOCl has been widely applied in the fields of catalysis [8,9], photoluminescence materials [10], ferroelectric materials [11] and pigments [12] for many years owing to its unique layered structure and high photocorrosion stability [13–16]. Furthermore, BiOCl has also been well-known as an effectual photocatalyst for decomposing organic compounds in polluted wastewater [17,18]. However, BiOCl with a wide band gap (3.19–3.60 eV) can only absorb ultraviolet light, which is merely about 3% of the solar energy spectrum [19]. The intrinsic property of BiOCl limits its efficient utilization of solar energy as well as photocatalytic activity. Consequently, many attempts have been adopted to enhance its activity by modifying BiOCl with other semiconductors that can absorb visible light, such as BiOCl/Bi$_2$O$_3$ [20], BiOCl/BiOCl [21], Fe$_3$O$_4$/BiOCl [22] and WO$_3$/BiOCl [16]. Besides, bismuth sulfide (Bi$_2$S$_3$) with a typical lamellar-structure has also attracted increasing attentions in the photocatalysis field [23–25]. Due to its narrow band gap (~1.3 eV) [23], Bi$_2$S$_3$ can respond to the whole visible light region, suggesting that it is a potential sensitizer to sensitize BiOCl. Cheng et al. demonstrated that Bi$_2$S$_3$ nanocrystals/BiOCl hybrid architectures displayed highly efficient visible light photoactivities in decontamination of 2,4-dichlorophenol and methyl orange [26], indicating that the Bi$_2$S$_3$/BiOCl heterostructure could be formed and facilitate the separation of photogenerated carriers via the easy chemical conversion from BiOCl to Bi$_2$S$_3$. However, to the best of our knowledge, there are few reports on Bi$_2$S$_3$ as a sensitizer together with the related mechanism study on the degradation pathway of colored organic dye.

The aim of the present work is to investigate the phase structure, morphological and optical properties of Bi$_2$S$_3$-sensitized BiOCl heterostructure prepared through a facile ion exchange method and elucidate the possible origin of highly enhanced photocatalytic performance. Rhodamine B (RhB) is a representative of organic dyes and was used to evaluate the photocatalytic performance of Bi$_2$S$_3$/BiOCl heterostructure under visible light.

2. Experimental

2.1. Materials and preparation

All of the reagents were provided by Sinopharm Chemical Reagent Co., Ltd. (China) except that TiO$_2$ (P25) was purchased from Degussa Co. (Frankfurt, Germany). All reagents were used without further purification. Deionized water was used throughout this study.

BiOCl was prepared in advance. Bi(NO$_3$)$_3$·5H$_2$O (0.03 mol) was dissolved in 400 mL deionized water with pH = 1.96 adjusted by glacial acetic acid. After adding 30 mL of KCl (0.03 mol) aqueous solution, the pH of reaction solution was adjusted to 3.0 by ammonia water and
stirred vigorously for 12 h at 85 °C. Then the white precipitate was collected, washed with deionized water and dried at 80 °C in air.

Bi$_2$S$_3$/BiOCl was synthesized through the ion exchange method between BiOCl and thiocetamide at room temperature; BiOCl (5.76 mmol) was dispersed in 40 mL deionized water and sonicated for 10 min. After adding 10 mL of thiocetamide (1.38 mmol) aqueous solution, the earth yellow mixture was stirred for 5 h, and then collected, washed and dried at 80 °C in air.

For comparison, Bi$_2$S$_3$ was prepared by adding a stoichiometric amount of thiocetamide to Bi-based glycol solution (molar ratio of Bi/S = 2:3) and then black Bi$_2$S$_3$ precipitate was obtained. The sample was continuously washed with water and ethanol, finally dried at 80 °C in air.

2.2. Characterization

X-ray powder diffraction (XRD) patterns of the samples were recorded on a BRUKER D8 ADVANCE X-ray powder diffractometer with Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. The surface composition was determined by X-ray photoelectron spectroscopy (XPS) using a Thermo ESCALAB 250 with Al Kα (1486.6 eV) line at 150 W. Raman spectra were recorded on LABRAM-HR system with laser excitation of 514.5 nm. Fourier transform infrared spectroscopy (FT-IR) was performed using a Nicolet 6700 spectrophotometer (USA). Field emission scanning electron microscope (SEM) images and energy dispersive X-ray spectroscopy (EDS) were obtained on a FEI Sirion200 scanning electron microscope, using a scanning voltage of 5.00 kV (USA). The microstructure and crystallinity of the products were analyzed by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images, and selected area electron diffraction (SAED) on a JEOL-2011 transmission electron microscope with an accelerating voltage of 200 kV (Japan). The Brunauer–Emmett–Teller (BET) surface areas of the samples were investigated on a NOVA 2000e (Quantachrome Instruments, USA) instrument at liquid nitrogen temperature (77.3 K). UV–vis diffuse reflectance spectra (DRS) were collected using a TU-1901 UV–VIS spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) equipped with an integrating sphere attachment. The zeta potential of catalysts was measured with Zetasizer Nano-ZS90 (Malvern Co., United Kingdom).

2.3. Photocatalytic activity evaluation

The photocatalytic activities of as-prepared catalysts were evaluated by degradation of RhB under visible light (λ > 400 nm). The initial concentration of RhB solution was 10 mg/L. In a typical photocatalytic experiment, 0.03 g catalyst was dispersed into 50 mL of RhB solution and stirred magnetically for 60 min in dark to establish an adsorption–desorption equilibrium of RhB on the catalyst surface. Then the suspension was illuminated in a photoreaction apparatus [27] with a 500 W Xe lamp as light source. Light passed through annular quartz tube with running water and a 400 nm cut-off glass filter before entering the reactor. At the given time intervals, about 3 mL of suspension was taken, centrifuged and analyzed by 722s spectrophotometer (Shanghai Youke Instrument. Co., Ltd, China) with deionized water as a reference sample.

3. Results and discussion

3.1. Characterization

To investigate the phase structure of as-prepared catalysts, XRD characterization (Fig. S1) was carried out. However, no diffraction peak of Bi$_2$S$_3$ can be observed in Bi$_2$S$_3$/BiOCl heterostructure, which may be due to the highly dispersed Bi$_2$S$_3$ or low content of Bi$_2$S$_3$ below the XRD detection limit. In addition, no distinct changes were observed for the used Bi$_2$S$_3$/BiOCl compared to the fresh sample (Fig. S2). Therefore, Raman spectra were adopted to further identify the structure of the samples. Fig. 1a shows that the Raman peaks located at 143 and 198 cm$^{-1}$ correspond to A$_{1g}$ and E$_g$ of Bi–X stretching mode in BiOCl, respectively [28]. Bi$_2$S$_3$ has the Raman peak at 100 cm$^{-1}$ and the broad peak regions (200–270 cm$^{-1}$ and 150–170 cm$^{-1}$). As for Bi$_2$S$_3$/BiOCl composite, it possessed not only the typical Raman peaks of BiOCl located at about 143 cm$^{-1}$, but also the typical peaks of Bi$_2$S$_3$ at 100 cm$^{-1}$ and the broad regions (150–170 cm$^{-1}$), indicating that Bi$_2$S$_3$ was really formed in Bi$_2$S$_3$/BiOCl. Furthermore, FT-IR result (Fig. S3) also confirmed the existence of Bi$_2$S$_3$ in Bi$_2$S$_3$/BiOCl.

Fig. 1b displays the DRS spectra of different catalysts. The absorption edge of BiOCl was located at about 370 nm, while Bi$_2$S$_3$ has strong absorption over the whole visible light region. As for the Bi$_2$S$_3$/BiOCl heterostructure, its absorption edge shifts to visible light region with increased intensity compared to that of BiOCl, which displayed the effect of Bi$_2$S$_3$-photosensitization to BiOCl. Based on the absorption spectra, the band gap energy ($E_g$) of BiOCl and Bi$_2$S$_3$ can be determined to be 3.28 and 1.38 eV, respectively (Fig. S4).

To further detect the chemical compositions of Bi$_2$S$_3$/BiOCl, XPS analysis was conducted. The typical XPS survey spectrum (Fig. 2a) shows that Bi$_2$S$_3$/BiOCl was composed of Bi, O, Cl, and S elements (C 1s peak can be ascribed to the adventitious hydrocarbon from XPS instrument itself). Furthermore, the high-resolution XPS spectrum of S 2s (the inset of Fig. 2a) as well as those of Bi 4f, O 1s, Cl 2p in Fig. 2b–d confirmed the coexistence of Bi$_2$S$_3$ and BiOCl in Bi$_2$S$_3$/BiOCl composite. The elemental ratio of Bi, S, O and Cl was calculated to be 26.53%, 1.16%, 30.93% and 18.82%, respectively.

The morphology and microstructure of samples were studied by SEM, TEM and HRTEM. The SEM image of single BiOCl in Fig. 3a shows that BiOCl exhibits a roselike flower superstructure assembled by plenty of plates (the inset of Fig. 3a). After the ion exchange process, the
obtained Bi$_2$S$_3$/BiOCl (Fig. 3b) shows anomalous plate structure with average diameter approximately less than 1.5 μm. The enlarged image in Fig. 3b clearly shows that the surfaces of plates are stuck with some tiny and thin flakes. In the reaction process, the BiOCl superstructure split into anomalous plate morphology. EDS displays that Bi, O, Cl, and S elements existed in Bi$_2$S$_3$/BiOCl (Fig. 3c). TEM image (Fig. 3d) further reveals the anomalous plate-like microstructure of Bi$_2$S$_3$/BiOCl. And the SAED pattern (Fig. 3e) suggests the good crystallinity of Bi$_2$S$_3$ in Bi$_2$S$_3$/BiOCl. Moreover, the interface of Bi$_2$S$_3$ and BiOCl was observed by HRTEM (Fig. 3f). The fringe spacing of 0.174 nm corresponded to the (351) planes of Bi$_2$S$_3$ while that of 0.174 nm agreed well with the (212) lattice planes of BiOCl, further confirming the existence of Bi$_2$S$_3$ and the heterojunction formed between Bi$_2$S$_3$ and BiOCl. In addition, the BET surface areas of BiOCl, Bi$_2$S$_3$ and Bi$_2$S$_3$/BiOCl were measured to be 73.88, 277.65 and 15.44 m$^2$/g, respectively. The possible reason for the obvious decrease of surface area for Bi$_2$S$_3$/BiOCl is due to the morphology changes from roselike flower structure of single BiOCl to aggregation structure of anomalous plate of Bi$_2$S$_3$/BiOCl.

3.2. Photocatalytic activity

The photocatalytic activities of as-prepared catalysts were evaluated by degradation of RhB (pH = 6.07) under visible light (λ > 400 nm). Before irradiation, the dark adsorption equilibrium was established for 60 min. Fig. 4a shows the concentration changes of RhB over different catalysts with the irradiation time. It can be seen that the Bi$_2$S$_3$/BiOCl heterostructure degraded 98.0% of RhB within 120 min. Since BiOCl and TiO$_2$ (P25) cannot respond to visible light, BiOCl and TiO$_2$ could only degrade about 45.3% and 8.3% of RhB respectively due to their dye-sensitized photocatalysis. However, almost no RhB was photodegraded by single Bi$_2$S$_3$ during the same irradiation time, which may be ascribed to the fast recombination of electron–hole pairs of Bi$_2$S$_3$ with narrow band gap. For comparison, the direct photolysis of RhB without photocatalyst was carried out and not observed. These results show that Bi$_2$S$_3$/BiOCl heterostructure exhibited the highest visible light photocatalytic activity for the RhB degradation.

In addition, the effect of pH on the photodegradation of RhB over Bi$_2$S$_3$/BiOCl and P25 was also investigated. Fig. S5 shows that the initial pH of solution plays a distinct effect on the degradation of RhB over Bi$_2$S$_3$/BiOCl. Bi$_2$S$_3$/BiOCl displayed the best photocatalytic activity in acidic condition, which may be correlated to the easy generation of •OH compared to the neutral and alkaline solution (Supplementary Data). As for TiO$_2$, the effect of pH on RhB degradation was not obvious.

3.3. Mechanism

To make the reaction mechanism clear, tert-butyl alcohol (TBA) [29], ammonium oxalate (AO) [30] and benzoquinone (BQ) [29] were respectively introduced as the scavengers of hydroxyl radicals (•OH), active holes (h$^+$) and superoxide radicals (•O$_2^-$) to examine the effects of reactive species in photodegradation processes of RhB. The final concentrations of TBA, AO and BQ in the reaction system were 10 mmol/L, 1.0 mmol/L and 1.0 mmol/L, respectively [27,31]. Fig. 4b shows that both BQ and AO lead to a strong suppression on the photodegradation of RhB while TBA showed a comparatively weak effect. It confirms that h$^+$ and •O$_2^-$ played a more important role than •OH for the photodegradation of RhB. In addition, the N$_2$ purging experiment shows the degradation rate of RhB decreased obviously, confirming dissolved oxygen acted as an efficient electrons trap is responsible for the direct generation of •O$_2^-$ over Bi$_2$S$_3$/BiOCl system.

Moreover, photoluminescence (PL) technique with terephthalic acid as a probe molecule [32] also testified the generation of •OH (Fig. 4c) since the PL signal at about 425 nm increased with the irradiation time after irradiating Bi$_2$S$_3$/BiOCl.
Based on the band gap structure of Bi$_2$S$_3$/BiOCl (Supplementary Data) as well as the effects of reactive species, a possible pathway for RhB photocatalytic degradation was proposed (Scheme 1). Under visible light, Bi$_2$S$_3$ will be activated while BiOCl will be not. Consequently, the electrons on the conduction band (CB) of Bi$_2$S$_3$ could migrate easily to the valence band (VB) of BiOCl and then react with O$_2$ adsorbed on the surface of Bi$_2$S$_3$/BiOCl to produce •O$_2^-$ and •OH, further decomposing RhB. In addition, the holes stayed on the VB of Bi$_2$S$_3$ would degrade RhB directly because the VB potential of Bi$_2$S$_3$ (1.47 eV) was more negative than the standard reduction potential of H$_2$O/•OH/H$^+$ (2.72 eV) [31]. Thus the recombination rate of photogenerated electrons and holes was decreased largely.

Except for the above photocatalytic process, photosensitization process for BiOCl via RhB should also be considered because RhB can be degraded over BiOCl with wide band gap (Fig. 4a). According to the previous reports [21,33], it is reasonable to believe that the electrons on the highest occupied molecular orbital (HOMO) of RhB molecules could be excited up to the lowest unoccupied molecular orbital (LUMO) under visible light, and subsequently would be injected to the CB of BiOCl to react with O$_2$ to produce •O$_2^-$ and •OH, further participating in the degradation of RhB.

Therefore, we propose that the mechanism of decomposing of RhB in this system includes two collaborative processes: a photocatalytic process and a photosensitization process.

The photocatalytic process:

\[
catalyst + hv \rightarrow e^- + h^+ \tag{1}
\]

\[
e^- + O_2 \rightarrow O_2^- \tag{2}
\]

\[
2e^- + O_2^- + 2H^+ \rightarrow \text{OH} + \text{OH}^- \tag{3}
\]

\[
\text{RhB} + \cdot O_2^- (h^+, \cdot \text{OH}) \rightarrow \text{products} \tag{4}
\]

The photosensitization process:

\[
\text{RhB} + hv \rightarrow \text{RhB}^* \tag{5}
\]

\[
\text{RhB}^* + \text{BiOCl} \rightarrow \text{RhB}^* + \text{BiOCl}(e^-) \tag{6}
\]

\[
\text{BiOCl}(e^-) + O_2 \rightarrow \text{BiOCl} + \cdot O_2^- \tag{7}
\]

\[
\text{BiOCl}(e^-) + \cdot O_2^- + 2H^+ \rightarrow \text{OH} + \text{OH}^- \tag{8}
\]

\[
\text{RhB} + \cdot O_2^-(\cdot \text{OH}) \rightarrow \text{products} \tag{9}
\]

4. Conclusions

In summary, Bi$_2$S$_3$-sensitized BiOCl composite with Bi$_2$S$_3$–BiOCl heterostructure prepared by an ion exchange method was studied as a novel efficient photocatalyst. Bi$_2$S$_3$/BiOCl exhibited superior enhanced visible light photocatalytic activity and 98.0% of RhB was degraded after 120 min of visible light irradiation. This result could be attributed to the good visible light absorption of sensitizer Bi$_2$S$_3$ and the efficient
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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.05.025.

References
