Enhancement of photocatalytic efficiency by in situ fabrication of BiOBr/BiVO₄ surface junctions

Wenzong Yin, Xiang Sun, Wenzhong Wang*

State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China. E-mail: yinwz@nimte.ac.cn

ARTICLE INFO

Article history:
Received 28 September 2016
Revised 31 October 2016
Accepted 5 January 2017
Available online 14 March 2017

Keywords:
Surface junction
Photocatalysis
N-deethylation
Adsorption efficiency
Redox potential

ABSTRACT

Surface junctions between BiOBr and BiVO₄ were synthesized. The BiOBr/BiVO₄ with 1 wt.% of BiOBr exhibited the highest photocatalytic activity in the degradation of RhB under visible-light irradiation. It was found that the highly efficient adsorption of RhB molecules via the electrostatic attraction between Br⁻ and cationic –N(Et)₂ group played a key role for the high photocatalytic activities of BiOBr/BiVO₄. This efficient adsorption promoted the N-deethylation of RhB and thus accelerated the photocatalytic degradation of RhB. Moreover, the metal-to-metal charge transfer (MMCT) mechanism was proposed, which revealed the concrete path paved with Bi–O–Bi chains for the carrier migration in BiOBr/BiVO₄. The interaction between photoexcited RhB* and the Bi³⁺ in BiVO₄ provided the driving force for the migration of photo-generated carriers along the Bi–O–Bi chains. This work has not only demonstrated the important role of efficient adsorption in the photocatalytic degradation of organic contaminants, but also developed a facile strategy to improve the efficiency of photocatalysts.

© 2017 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

INTRODUCTION

Photocatalytic activity in the degradation of contaminants involves two aspects: photocatalytic ability and photocatalytic efficiency. Once a photocatalyst possesses the ability to degrade certain contaminant, the work to improve its photocatalytic efficiency is on the agenda. As photocatalytic degradation of contaminants takes place on the surface of the photocatalysts (Fujishima et al., 2008), it is critical for photocatalysts to contact efficiently with the molecules of contaminants so as to enhance the degradation efficiencies. Recently, Han and coworkers (Han et al., 2009) have improved the photocatalytic efficiency of TiO₂ by exposing the high reactive (001) facets of TiO₂. The (001) facets presents high surface energies and thus exhibits intense adsorption of dye molecules. Wang et al. (2008a), Wang et al. (2008b) have found that the photocatalytic efficiency of TiO₂ was significantly enhanced by surface fluorination using hydrogen fluoride (HF) solution. This fluorination established the substitution of adsorbed OH⁻ with F⁻. The adsorbed F⁻ increased both the saturation amount and the adsorption strength for organic dyes via the interaction with the cationic moiety. However, the adsorbed F⁻ is not stable enough and can be easily washed away. An alternative strategy is to fabricate surface junctions by loading fluoride or other halides onto the surface of photocatalyst and expose the reactive facets of the halides for active adsorption.

Monoclinic BiVO₄ (m-BiVO₄) exhibited photocatalytic activities in the degradation of rhodamine B (RhB) under visible-light irradiation. However, the degradation rates were not satisfying as expected partially because of the inactive adsorption. Meanwhile, BiOBr with exposed (001) facets showed active adsorption of RhB molecules (An et al., 2008). Therefore, the photocatalytic efficiency of m-BiVO₄ is expected to be enhanced by loading...
appropriate amount of BiOBr on its surface to increase the adsorption of RhB molecules. Herein, BiOBr/BiVO₄ surface junctions were fabricated in situ via the reaction between BiOBr and VO₃⁻. The content of BiOBr in the product was tuned by changing the amount of VO₃⁻ (Yin et al., 2010). The surface-loaded BiOBr not only enhanced the adsorption of RhB molecules, but also paved a Bi–O–Bi path for the migration of electrons from photoexcited RhB⁺ to BiVO₄. Thus, the photocatalytic efficiency of m-BiVO₄ in the degradation of RhB was enhanced significantly.

1. Experimental

All the reagents (Purchased from Shanghai Chemical Company, China) were of analytical purity and used without further purification. In a typical preparation, 2 mmol of Bi(NO₃)₃·5H₂O was added into de-ionized water under magnetic stirring to form a hydrolyzed white floccule. Meanwhile, appropriate amount of NH₄VO₃ was dissolved into 20 mL of de-ionized water at 96°C and cooled down to room temperature. The NH₄VO₃ solution was then added dropwise into 40 mL of cetyltrimethylammonium bromide (CTAB) solution with the concentration of 0.1 mol/L. The mixture was heated at 80°C for 12 hr. The final product was centrifuged, washed with de-ionized water and absolute ethanol for several times, and dried in air. This series of composite photocatalysts was denoted as CP-x, where x is the mass percentage of loaded BiOBr.

The X-ray diffraction (XRD) patterns of the as-prepared samples were measured with a Rigaku D/Max-2200PC (Rigaku, Japan) diffractometer using monochromatized Cu Kα radiation (λ = 0.15418 nm) at a scanning rate of 8°/min. The diffuse reflectance spectra (DRS) were obtained on a UV–vis spectrophotometer Hitachi U-3010 (Hitachi, Japan) using BaSO₄ as the reference. The conduction band potentials of BiVO₄ and BiOBr was measured via Mott–Scottky method. The Mott–Scottky plots of BiVO₄ and BiOBr was measured via Mott–Scottky method. The Mott–Scottky plots of BiVO₄ and BiOBr were measured with a saturated calomel electrode (SCE) and platinum wire counter electrode, respectively.

The morphology and microstructure of annealed samples were investigated by transmission electron microscopy (TEM) on a JEOL JEM-2100F (JEOL Ltd., Japan). The photocatalytic efficiencies of the BiOBr/BiVO₄ were evaluated by the degradation of RhB under visible-light irradiation. The visible-light was provided by a 500 W Xenon lamp with a 420 nm cutoff filter. Each experiment was performed at room temperature as follows: 0.1 g of photocatalyst was added into 100 mL of RhB solution with a concentration of 10⁻⁵ mol/L. Before illumination, the suspension was stirred in the dark for 12 hr to ensure an adsorption/desorption equilibrium between RhB and the photocatalyst. Then the suspension was stirred and exposed to visible-light irradiation. At given time intervals, 2 mL of the suspensions was taken out and centrifuged to remove the photocatalyst particles. The concentrations of the centrifuged RhB solutions were monitored using a Hitachi U-3010 UV–vis spectrophotometer (Hitachi, Japan). The cycling test of the RhB photodegradation was also performed. Chemical oxygen demand (COD) was estimated before and after the treatment using the K₂Cr₂O₇ oxidation method.

2. Results and discussion

2.1. Phases and photocatalytic activities of the series of CP-x

Fig. 1 displays the XRD patterns of the series of CP-x (x = 0, 1, 2, 4). Only the diffraction peaks of m-BiVO₄ (JCPDS no. 14-0688) are found in the patterns when the content of BiOBr is lower than 4%. But as the content reaches 8% (Fig. S1), diffraction peaks of BiOBr (JCPDS cards no. 09-0393) appear. Given the detection limitation of XRD (~5 wt.%), these results confirm the successful preparation of BiOBr/BiVO₄ composite photocatalysts. Moreover, the relative intensity of (001) facets is significantly higher than the standard (Fig. S1), indicating the preferred exposure of (001) facets. This speculation is further confirmed by the XRD pattern of the pure BiOBr crystals prepared under the same conditions (Fig. S2). Fig. S3 shows the microscopic morphology of BiOBr/BiVO₄ under low magnification, from which tetragonal BiOBr is observed being deposited on the surface of BiVO₄. When the CP-8 was further calcined at 500°C for 2 hr (denoted as CP-8-cal), BiOBr has disappeared (Fig. S4). Instead, Bi₂VO₅.5 has emerged and the BiOBr/BiVO₄ has transformed into Bi₅VO₁₂/BiVO₄. As the Bi₅VO₁₂ or BiVO₄·0.5Bi₂O₃ can be referred as the solid solution of BiVO₄ and Bi₂O₃, it is reasonable to speculate following reactions carried out:

2BiOBr + 1/2O₂ → Bi₂O₃ + Br₂ 

(1)

BiVO₄ + 1/2Bi₂O₃ → Bi₂VO₅.5 

(2)

Fig. 2 shows the photocatalytic activities of the series of CP-x (x = 0, 0.5, 1, 2, 4) in the degradation of RhB. The changing

![Fig. 1 – XRD patterns of CP-0.5 a, CP-1 b, CP-2 c, and CP-4 d. XRD: X-ray diffraction.](image-url)
of \( \frac{C}{C_0} \) during the dark equilibrium was also recorded over different samples (Fig. S5). The major absorption band of RhB is centered at 553 nm and used to monitor the concentration of RhB. It is obvious that the photocatalytic efficiency of BiVO4 is significantly improved by coupling with BiOBr. When the content of BiOBr is lower than 4\%, the CP-1 exhibits the highest degradation efficiency and the perfect stability (Fig. S6). This demonstrates the existence of an optimal content of loaded BiOBr for enhancing the photocatalytic activity of BiVO4. The percentage change of the COD, which reflects the extent of mineralization of an organic species, was studied as a function of irradiation time in the photodegradation of RhB \((10^{-5} \text{ mol/L})\) under visible-light (shown in Fig. S7), in order to further confirm the activity of the photocatalyst from the photocatalysis. If the dye was not degraded completely, the residual organic molecules could be oxidized by \( K_2Cr_2O_7 \), thus the oxygen demand could be more, and the COD would be bigger than that of the completely mineralized dye. The initial COD of the RhB solution is 250.8 mg/L. After visible-light irradiation for 2 hr, the COD decreased markedly to 47.9 mg/L. The significant reduction of COD (81.0\%) further confirms that RhB was truly photodegraded by CP-1% sample. Similar results have been widely reported in other composite photocatalysts (Zong et al., 2008; Lu et al., 2008). Since BiOBr also shows good photocatalytic activities under visible-light, the enhanced photocatalytic activities of the CP-1 might be attributed to the introduction of BiOBr. For further investigation, a mechanically mixed sample with 1\% of BiOBr and 99\% of BiVO4 (denoted as MM-1\%) was prepared. Its photocatalytic efficiency was evaluated by the degradation of RhB under the same conditions (Fig. 2). Only 33.7\% of RhB has been degraded after 60 min of irradiation over the MM-1\%. Such low efficiency not only excludes the sole role of the 1\% BiOBr on the enhanced photocatalytic efficiency, but also indicates a possible heterostructure formed between BiOBr and BiVO4 in CP-1.

### 2.2. Mechanisms for the enhanced photocatalytic efficiency of the CP-1

As reported in Ref. (Hu et al., 2006), RhB dye is zwitterionic and can be degraded in two different pathways: N-deethylation and direct cleavage of conjugated chromophore structure. The former one can be characterized by the shift of the maximum absorption band \( \lambda_{\text{max}} \) of RhB while the latter one by the change in the absorption maximum \( A_{\text{max}}/A_{\text{max}}^0 \). These two procedures usually take place simultaneously in the presence of photocatalyst under irradiation. As a result, it is a cooperative effect that results in the decrease of absorbance at the wavelength of 553 nm with the irradiation time prolonged. Furthermore, Wang and coworkers (Wang et al., 2008a; Wang et al., 2008b) revealed that the two degradation pathways of RhB depended greatly on the adsorption modes of zwitterionic RhB on the surface of photocatalysts. If the adsorption performed via the cationic moiety (\( -N(Et)_2 \) group), N-deethylation predominated in the degradation pathways before destruction of the chromophore structure. When adsorbed through the carboxylic (\( -COOH \) group), however, RhB experienced direct cleavage of chromophore structure. To clarify the degradation pathway of RhB over the CP-1, the hypsochromic shifts of \( \lambda_{\text{max}} \) and the decrease of \( A_{\text{max}}/A_{\text{max}}^0 \) were investigated respectively (Fig. 3). After irradiated for 20 min, \( \lambda_{\text{max}} \) shifted from 553 nm to 501 nm. This value is very close to the \( \lambda_{\text{max}} \) (498 nm) of the fully-deethylated RhB (rhodamine), indicating that deethylation was nearly accomplished. In contrast, \( A_{\text{max}}/A_{\text{max}}^0 \) decreases by 95\% even after 60 min of irradiation. These characteristics are demonstrated in Fig. 4a. The above results reveal that N-deethylation has predominated in the degradation of RhB over the CP-1. In this case, it can be speculated that most RhB molecules were adsorbed on the CP-1 via the cationic \(-N(Et)_2\) moiety. Considering the high electronegativity of Br\(-\) it might be the Br\(-\) in BiOBr that facilitates the adsorption. To testify this proposition, the CP-1 was calcined at 500°C to remove the Br\(-\) and the degradation pathway of RhB over the as-prepared CP-1-cal was investigated. The results are shown in Fig. 3. It takes 50 min for \( \lambda_{\text{max}} \) to shift from 553 nm to 501 nm in the degradation over the CP-1-cal while 20 min over the CP-1. In other word, the N-deethylation rate over the CP-1 is 2.5 times
faster than that over the CP-1-cal. This drastically decline in N-deethylation rate is clearly displayed in Fig. 4b. The rate of the cleavage of conjugated chromophore structure was evaluated with the reaction constant \( k \) determined by the plots of \( \ln(A_{\text{max}}/A_{0,\text{max}}) \) vs irradiation time \( t \). The \( k \) values of the cleavage process are 0.042 and 0.041 min\(^{-1}\) for the degradation over the CP-1 and CP-1-cal, respectively (Fig. S8).

Among the three steps, Reaction (4) is critical for the photocatalytic degradation because it involves the interaction between excited RhB\(^*\) and photocatalysts. To clarify the interaction process, we investigated the generation, transfer and release of the photo-generated holes.

Here, the photo-generated holes have two possible sources: BiOBr and BiVO\(_4\). As the MM-1 and CP-2 both exhibit far lower degradation rates than the CP-1, it could exclude the BiOBr as the source of the photo-generated holes. Alternatively, these holes should originate predominantly from BiVO\(_4\).

Since the excited RhB\(^*\) molecules were adsorbed on BiOBr, it is necessary to clarify the way in which the photo-generated holes on BiVO\(_4\) surface migrate to interact with the excited RhB\(^*\) molecules. Concretely, it involves two issues: (1) the origination of the driving force for the carrier migration and (2) the path paved for the migration of photo-generated carrier.

The first issue could be addressed from the viewpoint of photoelectrochemistry. When irradiated by visible-light, RhB was excited into RhB\(^*\) and the redox potential \( \phi \) of RhB\(^*\) is \(-1.09 \text{ V vs. NHE}\) (Hu et al., 2006). Meanwhile, holes are generated in the VB of the BiVO\(_4\). The \( \phi \) value of these holes is the same 2.68 V (vs. NHE) as that of the VB (Fujishima et al., 2000), which is more positive than the 2.0 V of \( \phi (\text{Bi}^{5+/\text{Bi}^{3+}}) \) (Qin and Wang, 2000). As a result, Bi\(^{3+}\) in the surface BiVO\(_4\) could be oxidized into Bi\(^{5+}\) by the photoinduced holes. In this case, an electric field with the potential of 3.09 V is set up between the RhB\(^*\) and Bi\(^{5+}\). With this potential, electrons

\[ \text{dye} \rightarrow \text{dye}^* \]  
\[ \text{dye}^* + h^+ \rightarrow \text{dye}^+ \]  
\[ \text{dye}^+ \rightarrow N - \text{deethylation} \]
could be driven to migrate from RhB* to Bi\textsuperscript{5+} and holes from Bi\textsuperscript{5+} to RhB* (Scheme 1). Nevertheless, the latter migration could not work out from the viewpoint of heterojunction.

According to semiconductor theory, the heterojunctions can set up a built-in electric field at the interface and thus promote the separation of photo-generated electron–hole pairs (Long et al., 2006; Zhang et al., 2009). The positions of conduction band (CB) and valence band (VB) for monoclinic BiVO\textsubscript{4} and BiOBr have been calculated according to the method in Ref. (Wang et al., 2008a; Wang et al., 2008b). The CB of BiOBr (−0.26 eV) is positioned higher than that of BiVO\textsubscript{4} (0.35 eV) before the two crystals are coupled. But the VB of BiOBr (2.46 eV) is lower than that of BiVO\textsubscript{4} (2.77 eV). The Fermi levels of the two crystals lie at about the middle of their respective band gap (Sun et al., 2003). When BiVO\textsubscript{4} is coupled with BiOBr and the heterojunctons reach a thermodynamic equilibrium, their Fermi levels line up. The renewed energy band positions are displayed in Fig. 6. The CB potentials of BiOBr are more negative than that of BiVO\textsubscript{4} (Sun et al., 2003). When BiVO\textsubscript{4} is irradiated by visible-light, Reaction (6) took place and metal M\textsubscript{2} was oxidized by M\textsubscript{1}. The oxidized M\textsubscript{2} could further oxidize degradable organics. Thus, photo-generated holes are transferred from M\textsubscript{1} to M\textsubscript{2} and then to the organics. Analogically, the transfer of photo-generated carriers during the degradation of RhB over the CP-1 can be explained as follows presuming M\textsubscript{1} = M\textsubscript{2} = Bi.

As a typical bismuth oxyhalide, BiOBr is of matlockite structure. This structure can be characterized by [Bi\textsubscript{2}O\textsubscript{2}] slabs interleaved with double slabs of bromium atoms (Zhang et al., 2008a; Zhang et al., 2008b). In [Bi\textsubscript{2}O\textsubscript{3}] slabs, Bi\textsuperscript{5+} ions are bridged through oxygen atoms and thus form Bi–O–Bi chains (Scheme 1). BiVO\textsubscript{4} crystals are perovskite-structured and composed of V–O tetrahedra and Bi–O octahedral (Walsh et al., 2009). The Bi–O octahedra link through corners (O) and the hybridization of Bi 6s and O 2p in BiVO\textsubscript{4} forms a largely delocalized VB that promotes the transfer of photo-generated electrons through bridged BiOBr from RhB* to BiVO\textsubscript{4}, rather than hole transfer from BiVO\textsubscript{4} to RhB*.

Although the above discussion verifies that the potential between RhB* and BiVO\textsubscript{4} works as the driving force for the migration of photoinduced carriers, it does not depict the concrete path for carrier migration and what the path paved with. Recently, the metal-to-metal charge transfer (MMCT) theory has been proposed (Lin and Frei, 2005a, 2005b) and developed for the preparation of oxo-bridged hetero-bimetallic complex with photocatalytic activities under visible-light (Nakamura et al., 2007; Nakamura and Frei, 2006). This theory has also found applications in explanation of the photocatalytic activities for Fe-doped SrTiO\textsubscript{3} (Xie et al., 2008), Cr\textsuperscript{III}-grafted TiO\textsubscript{2} (Irie et al., 2008), coupled CuO–TiO\textsubscript{2} nanocomposites (Li et al., 2008) and Sr\textsuperscript{2+}–M\textsubscript{n}O\textsubscript{3} solid solutions (Sun and Lin, 2009). The photocatalytic reactions involved in the MMCT theory can be generally described as:

\[
M_{1}^{(m_{1}+n_{1})} + O - M_{2}^{(m_{2})} + h_{\nu} \rightarrow M_{1}^{m_{1}} - O - M_{2}^{(m_{2}+n_{1})}
\]

where, M\textsubscript{1} and M\textsubscript{2} are two metal ions with variable valence and matched redox potentials, m\textsubscript{1}, m\textsubscript{2}, and n are integers depicting the metal valence, O is oxygen element, dash represents the bond between oxygen and metals, \(h_{\nu}\) is the energy of photons from the incident light. When photocatalysts were excited by visible-light, Reaction (6) took place and metal M\textsubscript{2} was oxidized by M\textsubscript{1}. The oxidized M\textsubscript{2} could further oxide degradable organics. Thus, photo-generated holes are transferred from M\textsubscript{1} to M\textsubscript{2} and then to the organics. Analogically, the transfer of photo-generated carriers during the degradation of RhB over the CP-1 can be explained as follows presuming M\textsubscript{1} = M\textsubscript{2} = Bi.

As a typical bismuth oxyhalide, BiOBr is of matlockite structure. This structure can be characterized by [Bi\textsubscript{2}O\textsubscript{2}] slabs interleaved with double slabs of bromium atoms (Zhang et al., 2008a; Zhang et al., 2008b). In [Bi\textsubscript{2}O\textsubscript{3}] slabs, Bi\textsuperscript{5+} ions are bridged through oxygen atoms and thus form Bi–O–Bi chains (Scheme 1). BiVO\textsubscript{4} crystals are perovskite-structured and composed of V–O tetrahedra and Bi–O octahedral (Walsh et al., 2009). The Bi–O octahedra link through corners (O) and the hybridization of Bi 6s and O 2p in BiVO\textsubscript{4} forms a largely delocalized VB that promotes the transfer of photo-generated holes via the Bi–O–Bi path (Oshikiri et al., 2002). Since BiVO\textsubscript{4} was derived from BiOBr, the Bi–O–Bi chains could match well with the Bi–O octahedra on BiVO\textsubscript{4} surface. This match paves the Bi–O–Bi path for photoinduced carriers to transfer from RhB* to BiVO\textsubscript{4} or vice versa. When irradiated by visible-light, Bi\textsuperscript{5+} could be derived via the oxidation of Bi\textsuperscript{3+} by photo-generated holes. Meanwhile, RhB was excited into RhB* and efficiently adsorbed on the surface of BiOBr via the electrostatic attraction between Br\textsuperscript{−} and cationic –N(Et\textsubscript{2})\textsuperscript{+} group. The potential between Bi\textsuperscript{5+} and RhB* provided the driving force for the carrier transfer. The electrons could transfer across BiOBr from RhB* to BiVO\textsubscript{4} via the Bi–O–Bi chains (Scheme 1). The built-in electric field at the interface between BiVO\textsubscript{4} and BiOBr also facilitates this electron transfer. However, the electric field prohibits the holes on BiVO\textsubscript{4} surface to migrate through the interface. Hence, photoinduced holes could only transfer on BiVO\textsubscript{4} surface. In other words, the photoinduced electrons from RhB* could react with the holes from BiVO\textsubscript{4} either at the interface or on the surface of BiVO\textsubscript{4}, which results in the N-deethylation of RhB.
3. Conclusions

BiOBr/BiVO₄ surface junctions were in situ fabricated by co-synthesis method. The CP-1 exhibited the highest activities when the content of BiOBr was lower than 4%. The loaded BiOBr on BiVO₄ surface efficiently adsorbed the RhB molecules via the electrostatic attraction between Br⁻ and cationic –N(Et)₂ group. This efficient adsorption promoted the N-deethylation of RhB and thus accelerated the photocatalytic degradation of RhB. The potential of ca. 3.09 V between RhB* and Bi⁵⁺ provided the driving force for the migration of photoinduced carriers in BiOBr/BiVO₄. Furthermore, the Bi–O–Bi chains in BiOBr/BiVO₄ paved the concrete path for the carrier migration.

Acknowledgments

This work was supported by National Basic Research Program (973) of China (No. 2013CB933200), the National Natural Science Foundation of China (Nos. 21671197, 51472260), and the Research Grant (No. 16ZR1440800) from Shanghai Science and Technology Commission.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.12.024.

REFERENCES


