Facile synthesis of a visible light $\alpha$-Fe$_2$O$_3$/BiOBr composite with high photocatalytic performance

Xiao-Ju Wen, Chang Zhang, Cheng-Gang Niu, Lei Zhang, Da-Wei Huang, Xiao-Yu Wang, Xue-Gang Zhang and Guang-Ming Zeng

Novel $\alpha$-Fe$_2$O$_3$/BiOBr composites were synthesized by a simple in hydrolysis method for the first time, and were fully characterized by X-ray diffraction patterns (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and UV-vis diffuse reflectance spectra (DRS). The $\alpha$-Fe$_2$O$_3$/BiOBr composite showed much higher visible-light-driven (VLD) photocatalytic activity than pure $\alpha$-Fe$_2$O$_3$ and BiOBr for rhodamine B (RhB) degradation. Specifically, the 10Fe/100Bi composite showed the highest photocatalytic activity for the degradation of dyes under visible light irradiation. The stability of the photocatalyst is found to be satisfying, which gives it potential in practical applications. The high photocatalytic activity could be attributed to the enhanced light absorption and the improved separation of photogenerated charge carriers, due to the formation of a p–n heterojunction between $\alpha$-Fe$_2$O$_3$ and BiOBr.

1. Introduction

Semiconductor photocatalysis offers an effective strategy for organic pollutant remediation and water splitting. TiO$_2$, the key photocatalyst for convenient wastewater treatment and other essential cleaning processes, nevertheless, suffers from problems such as ineffective sunlight capture and conversion due to its wide band gap (about 3.2 eV). Thus, it is urgent and necessary to develop highly efficient visible-light-driven photocatalysts for pollutants degradation.

$\alpha$-Fe$_2$O$_3$, a n-type semiconductor with a narrow band gap of 2.2 eV, has been intensely used as a material for electrochemical electrodes, photocatalysts, and gas sensors due to its sufficient stability and absorption capability in the visible light region. Its abundant raw materials, environmentally friendliness, excellent conductivity (high discharge and charge current rates) and stability are preferable features for large-scale production and applications. Recently, the hierarchical structured $\alpha$-Fe$_2$O$_3$/Bi$_2$WO$_6$ was reported and exhibited much enhanced photocatalytic activity in degradation of acid red G dye and RhB dye under visible-light irradiation.

a $\alpha$-Fe$_2$O$_3$/BiOBr p–n heterojunctions with high photocatalytic activity for the degradation of mixture dyes under visible light was synthesized. Therefore, the combining of $\alpha$-Fe$_2$O$_3$ and another semiconductor with a suitable valence band and conduction band positions is a promising strategy.

Up to now, bismuth-based photocatalytic materials such as Bi$_2$O$_3$, BiOBr, BiVO$_4$, BiOCl, BiOI etc. have aroused great interest in the scientific community due to their intriguing electronic structures. Among them, BiOBr has stimulated researcher intensive interest for its visible light response and higher stability. Although pure BiOBr samples was synthesized by different methods with various architectures, it is still imperative to further improve its photocatalytic activity for practical applications. Fabrication of a heterojunction composite containing BiOBr has been turned out an attractive strategy for enhancing the photocatalytic activity of BiOBr. Recently, BiOBr–ZnFe$_2$O$_4$ heterojunctions were reported and exhibited excellent ability for the degradation of organic dyes under visible light irradiation. What’s more, enhanced photocatalytic activities have also been studied over BiOBr–AgBr and BiOBr–bismuth oxyhydrate composite materials. These results motivated us to design $\alpha$-Fe$_2$O$_3$/BiOBr heterojunctions that are expected to be ideal for improving photocatalytic activity.

Herein, a series of $\alpha$-Fe$_2$O$_3$/BiOBr composites were prepared by a simple in hydrolysis method. We have investigated the activities of the catalysts at different molar ratios of Fe$_2$O$_3$ to BiOBr. Furthermore, the mechanism of the enhanced photocatalytic efficiency of the composite was discussed.

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*College of Environmental Science Engineering, Key Laboratory of Environmental Biology Pollution Control, Ministry of Education, Hunan University, Changsha 410082, China. E-mail: cgniu@hnu.edu.cn; cgniu@hotmail.com; Tel: +86-731-88823820

South China Institute of Environmental Sciences, Ministry of Environmental Protection of PRC, Guangzhou 510655, China. E-mail: huangdawei@scies.org
2. **Experimental**

2.1. **Fe(OH)₃ precursor preparation**

All the chemicals are of analytical reagent grade and were used without further purification. Distilled water was used in all our experiments. The α-Fe₂O₃/BiOBr composite was synthesized via a hydrothermal process, using Fe(OH)₃ as precursor. Briefly, Fe(OH)₃ precursor was firstly obtained by mixing Fe(NO₃)₃·9H₂O and 0.1 M NaOH aqueous solutions. After being rinsed with deionized water, the precipitation was sonicated for 30 min to disperse in deionized water completely.

2.2. **α-Fe₂O₃/BiOBr composite sample preparation**

The α-Fe₂O₃/BiOBr composite was synthesized via a hydrothermal process, using Fe(OH)₃ as precursor. In a typical procedure, 2 mmol Bi(NO₃)₃·5H₂O and 2 mmol KBr were dissolved in 30 mL and 10 mL deionized water, respectively. After that, these two solutions were mixed together and stirred for 30 min until a white suspension was formed. Then different volume (5.0, 10.0, 15.0 and 20.0 mL) of the Fe(OH)₃ suspension was added dropwise to the mixture in order to obtain the dark red suspension with a Fe/Bi molar ratio of 0.05, 0.10, 0.15 and 0.20, respectively. After stirring for 30 min, the reaction mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave, kept at 160 °C for 10 h, followed by natural cooling to room temperature. The product was collected by centrifugation, washed thoroughly with deionized water and alcohol several times, and then dried at 60 °C overnight. According to Fe/Bi molar ratio, the as-prepared composite photocatalysts were marked as 5Fe/100Bi, 10Fe/100Bi, 15Fe/100Bi, and 20Fe/100Bi, respectively.

For comparison, the pure BiOBr sample and α-Fe₂O₃ was also prepared via the same hydrothermal process as described above.

2.3. **Characterization**

The photodegradation activities of the samples were evaluated by the degradation of RhB aqueous solution under visible light irradiation. A 300 W Xe lamp (CEL-HXF300, Beijing) lamp with a 420 nm cutoff filter was used as the light source. The experiments were performed at room temperature as follows: 0.10 g of the as prepared catalyst was added into 100 mL RhB aqueous solutions (20 mg L⁻¹). Prior to illumination, the suspensions were stirred for 30 min in the dark to reach an adsorption–desorption equilibrium of dye molecules on the surface of the photocatalyst. Afterward the suspension was exposed to visible light irradiation while the temperature of the solution was kept unchanged by cooling water. At certain time intervals, 4 mL suspensions were sampled and centrifuged by TGL-16 G centrifuge (Shanghai Anting Scientific Instrument Factory, China) at 8000 rpm for 5 min to remove the remaining particles. The upper clear liquid was analyzed by recording the maximum absorption band (553 nm for RhB) and UV-vis spectra of dyes using an UV-vis spectrophotometer (Shimadzu 2550, Japan).

The stability of the α-Fe₂O₃/BiOBr composite catalyst was evaluated by reusing the catalyst for four runs for the decomposition of RhB under the same conditions. After each run, the catalyst was separated by a simple precipitation procedure and was reused.

3. **Result and discussion**

3.1. **Characterization of samples**

3.1.1. **XRD analysis.** The crystal structure of the products was investigated by the XRD method, as shown in Fig. 1a. As can be seen, all the characteristic peaks in Fig. 1a could be indexed to the tetragonal phase of BiOBr (JCPDS card no. 09-0393).²⁸ Compared with the pure BiOBr, some diffraction peaks were detected in the XRD patterns of 10Fe/100Bi samples (Fig. 1), the peaks at 2θ = 24.15°, 35.63°, 54.07°, 64.00° (marked with ▲) were indexed to [012], [110], [116] and [300] planes of Fe₂O₃ (JCPDS file no. 87-1165).²⁹,³⁰,³¹ respectively. The diffraction peaks of Fe₂O₃ are not observed for the 10Fe/100Bi sample, which may be due to the overlap of some α-Fe₂O₃ diffraction peaks with those of BiOBr (e.g. the diffraction peaks at 33.16° and 62.44° are missing). And iron compounds tend to fluoresce under the X-ray beam, reducing the intensity of their signal. Moreover, the small size and small amount of α-Fe₂O₃ on the BiOBr nanoflakes also results in decreased peak intensities. Fig. 1b shows the XRD patterns of the different Fe/Bi mole ratio samples; compared with BiOBr, the diffraction peak positions of BiOBr in the xFe/yBi samples are not shifted, indicating that Fe₂O₃ was not inserted into the lattice of BiOBr. The diffraction peaks of Fe₂O₃ are observed in addition to those of BiOBr. Moreover, the peak intensity of Fe₂O₃ increases gradually with increasing Fe₂O₃ content. The XRD results showed that α-Fe₂O₃ should only be deposited on the surface of the BiOBr instead of iron being incorporated into the crystal lattice of the photocatalyst.

3.1.2. **SEM and TEM analysis.** Fig. 2a and b shows an SEM image of a typical BiOBr sample. The pristine BiOBr shows uniquely layered structures which are composed of dozens of irregular plates with smooth surfaces and a plate thickness of 70–110 nm. α-Fe₂O₃, large amounts of nanoclusters diameter of 20–50 nm were deposited on the surface of BiOBr, resulting in the formation of a heterostructure (Fig. 2c–f). With increasing...
Fe/Bi mole ratio, more Fe$_2$O$_3$ nanoclusters have agglomerated and even separated from the surface of BiOBr (Fig. 2e and f).

The morphology and microstructure of $\alpha$-Fe$_2$O$_3$/BiOBr photocatalyst was further characterized by TEM. The TEM image (Fig. 3a and b) shows that the nanoclusters with an average dimension of about 30 nm attached on the surface of the BiOBr flakes, which is identified with the observed in the SEM images. Fig. 3c and d presents the HRTEM image of the $\alpha$-Fe$_2$O$_3$/BiOBr composite. The clear lattice fringes show that the as-prepared composites are highly crystallized. It is clear that the interplanar spacing of the distinct lattice fringes (Fig. 3c) is about 0.2286 nm and 0.2517 nm, which coincide with the planes of BiOBr (112) and Fe$_2$O$_3$ (110), respectively. It can also be found some other lattice fringes (Fig. 3d), the spacing of the lattice is 0.2629 nm and 0.2517 nm corresponding to the planes of BiOBr (111) and Fe$_2$O$_3$ (110), respectively. The above results further strongly demonstrate that the $\alpha$-Fe$_2$O$_3$/BiOBr nanocrystal heterojunction formed in the composite is in well agreement with the results of the XRD analyses.

3.1.3. Optical absorption properties. The UV-vis diffuse reflection spectra of the pristine BiOBr and the $\alpha$-Fe$_2$O$_3$/BiOBr catalyst are shown in Fig. 4. From the Fig. 4, the pure BiOBr presents the photoabsorption property from the UV light region to visible light shorter than 450 nm. Compared with the pristine BiOBr, the obtained $\alpha$-Fe$_2$O$_3$/BiOBr composite samples exhibited a wide visible-light absorption in the range of 400–650 nm.

Fig. 1  (a) XRD patterns of BiOBr, 10Fe/100Bi; (b) XRD patterns of the different Fe/Bi mole ratio samples.

Fig. 2  SEM images of (a) and (b) BiOBr; (c) 5Fe/100Bi; (d) 10Fe/100Bi; (e) 15Fe/100Bi; (f) 20Fe/100Bi.

Fig. 3  HRTEM images of the 10Fe/100Bi composite under (a) low; (b) medium; (c) and (d) high magnifications.
Fe₂O₃/BiOBr composites were evaluated for the degradation of absorption coefficient from 0.05 to 0.20 due to the narrow band gap and large gradually increased when the molar ratio of Fe/Bi increased had no ability to decompose RhB under visible light irradiation. The photocatalytic activity of the photocatalyst. It may be that a higher Fe/Bi ratio causes more Fe₂O₃ nanoparticles to agglomerate and even separate from the surface of BiOBr. Furthermore, the photogenerated electron–hole pairs of Fe₂O₃ were reported to easily recombine. Thus, the photocatalytic degradation efficiencies of the xFe/yBi samples decrease when the amount of Fe₂O₃ is higher. In addition, pure BiOBr has a higher photocatalytic activity than pure Fe₂O₃. α-Fe₂O₃ has a short diffusion length of photogenerated holes compared to BiOBr, which has a layered structure that favors the separation of photogenerated carriers.

Furthermore, the photodegradation process of RhB with the photocatalysts accorded well with the pseudo-first-order reaction (Fig. 6a). The integrated rate equation was expressed as below:

\[ \ln(C/C_0) = kt \]  

where, \( k \) is the pseudo-first-order rate constant (min⁻¹). The apparent rate constant \( k \) was calculated to be 0.0204, 0.0280, 0.0635, 0.0314, 0.0279, and 0.0009 min⁻¹ for the 0Fe/100Bi catalyst, the 5Fe/100Bi catalyst, the 10Fe/100Bi catalyst, the 15Fe/100Bi catalyst, the 20Fe/100Bi catalyst and the 100Fe/0Bi catalyst, respectively (Fig. 6b). That is, the photocatalytic activity of the 10Fe/100Bi catalyst is about 3.1 times higher than that of the pure BiOBr. This result clearly indicates that the combination of BiOBr and α-Fe₂O₃ significantly enhances the photocatalytic activity of BiOBr.

Fig. 7 displays the absorption spectra of the RhB aqueous solution during the photocatalytic degradation process by the 10Fe/100Bi catalyst. The characteristic absorption band of RhB at 554 nm diminished quickly, accompanied by slight concomitant blueshift from 554 to 494 nm of the maximum absorption. The result indicates that the α-Fe₂O₃/BiOBr catalyst possess excellent visible-light photocatalytic activity.

The photocatalytic activity of as prepared α-Fe₂O₃/BiOBr heterojunctions was compared to the previously reported visible-light activity of various BiOBr heterojunctions as shown in Table 1. From Table 1, it is clear that the α-Fe₂O₃/BiOBr heterojunctions show enhanced visible-light activity compared to the previously reported other heterojunctions.

The recyclability of sample is one of the most significant parts for the practical application; the recycle experiment of 10Fe/100Bi for photocatalytic reaction under the same reaction condition was carried out to evaluate the optical stability of the catalyst. As shown in Fig. 8a, about 90% of RhB is still degraded after four runs, indicating that the composite still showed high photocatalytic activity after four reaction cycles. The apparent rate constant \( k \) was calculated to be 0.0635, 0.0618, 0.0609, and 0.0597 min⁻¹ for each runs, respectively (Fig. 8b). The results...
validate that the α-Fe2O3/BiOBr composite is a kind of active and stable photocatalyst in favor of the long-term practical application.

3.3. Photocatalytic mechanism

In order to investigate the possible photodegradation mechanism, different scavengers were employed to detect the active species formed in the 10Fe/100Bi photocatalytic system by a trapping experiment. In this work, three typical chemicals, isopropanol (IPA, a quencher of ·OH), sodium oxalate (Na2C2O4, a quencher of h+) and benzoquinone (BQ, a quencher of ·O2−) with the amount of 10 mmol L−1 were adopted as the scavengers. The results are illustrated in Fig. 9, the degradation efficiency of RhB in the presence of BQ was obviously suppressed and the photodegradation rates were only 18%. Furthermore, the addition of IPA and Na2C2O4 acted as ·OH and h+ trapping agent presented slight influence on the photodegradation of RhB. It can be elucidated that h+ and ·O2− were generated in the photodegradation process, and ·O2− was acted as the dominant active species responsible for the photocatalytic degradation of RhB under visible light irradiation.

In a hybrid composite, the band positions of individual components are crucial to affect the process of excitation, migration and recombination of the photogenerated electrons and holes, which is also important to understand the mechanism of the dye photodegradation.45

Table 1 Comparison of visible-light degradation rate (%) of RhB over previously reported BiOBr heterojunctions and α-Fe2O3/BiOBr heterojunction

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Degradation rate (%)</th>
<th>The initial concentration of RhB</th>
<th>Irradiation time (min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOBr-g-C3N4</td>
<td>99</td>
<td>10 mg L−1</td>
<td>40</td>
<td>37</td>
</tr>
<tr>
<td>MoS2/BiOBr</td>
<td>100</td>
<td>10 mg L−1</td>
<td>170</td>
<td>38</td>
</tr>
<tr>
<td>BiOBr/montmorillonite</td>
<td>98.96</td>
<td>40 mg L−1</td>
<td>120</td>
<td>39</td>
</tr>
<tr>
<td>BiOCl-BiOBr</td>
<td>99</td>
<td>10 mg L−1</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>Fe-doped BiOBr</td>
<td>73</td>
<td>10 mg L−1</td>
<td>30</td>
<td>41</td>
</tr>
<tr>
<td>α-Fe2O3/BiOBr</td>
<td>95</td>
<td>20 mg L−1</td>
<td>40</td>
<td></td>
</tr>
</tbody>
</table>
The band gap energies \( (E_g) \) of the samples were determined by the formula\(^{46} \) based on the DRS results:

\[
A (h \nu - E_g)^2 = a h \nu
\]  

(2)

where \( A \), \( h \), \( \nu \), \( \alpha \) and \( E_g \) are constant, Planck constant, light frequency, absorption coefficient, and band gap energy, respectively. Among them, \( n \) is determined from the type of optical transition of a semiconductor (\( n = 1 \) for direct transition and \( n = 4 \) for indirect transition).\(^{47} \) For BiOBr, the values of \( n \) is of 4.\(^{29,48} \) According to eqn (2), the \( E_g \) of BiOBr was determined from a plot of \( (a h \nu)^{1/2} \) versus \( (h \nu) \) (Fig. 10) and were estimated to be 2.71 eV. Furthermore, the conduction band (CB) and valence band (VB) potentials of BiOBr were calculated by the following empirical formulas:\(^{49} \)

\[
E_{CB} = X - E_C - 0.5E_g
\]

(3)

\[
E_{VB} = E_{CB} + E_g
\]

(4)

where \( E_{CB} \) is the CB edge potential, \( E_{VB} \) is the VB edge potential, \( E_C \) is the energy of free electrons on the hydrogen scale (about 4.5 eV), \( X \) is the electronegativity of the semiconductor, \( E_g \) is the band gap energy of the semiconductor. The \( X \) value for BiOBr was 6.17 eV.\(^{48} \) Thus, the calculated \( E_{CB} \) and \( E_{VB} \) of BiOBr were separately estimated to be 0.32 and 3.03 eV; what’s more, according to previous research, the \( X \) value, the band gap energy of \( \alpha \)-Fe\(_2\)O\(_3\) is 4.78 and 2.2.\(^{31} \) So \( E_{CB} \) and \( E_{VB} \) of \( \alpha \)-Fe\(_2\)O\(_3\) were separately calculated to be \(-0.82\) eV and 1.38 eV.

On the basis of characterization and photocatalytic data, a possible visible light photocatalytic mechanism of the \( \alpha \)-Fe\(_2\)O\(_3\)/BiOBr heterojunctions was proposed, as schematically...
depicted in Fig. 11. BiOBr is a p-type semiconductor whose Fermi level is located close to the valence band, whereas Fe$_2$O$_3$ is a typical n-type semiconductor whose Fermi energy level lies close to the conduction band. The p-type BiOBr and n-type Fe$_2$O$_3$ can thus form a p–n heterojunction, causing a rise in the Fermi level and the energy of the whole band of BiOBr while reducing those of Fe$_2$O$_3$. The electrons can then diffuse from Fe$_2$O$_3$ into BiOBr, resulting in an accumulation of negative charge in the BiOBr region near the junction. Holes can then diffuse from the BiOBr region to the Fe$_2$O$_3$ region, creating a positive section in the region of Fe$_2$O$_3$ in the vicinity of the junction. When the Fermi levels of BiOBr and Fe$_2$O$_3$ reach equilibrium, where the reformed conduction band (CB) edge of BiOBr exceeds that of the latter, and an internal electric field directed from n-Fe$_2$O$_3$ to p-BiOBr is simultaneously created to stop the charge diffusing from Fe$_2$O$_3$ into BiOBr. So, when irradiated with visible light, BiOBr could be excited to generate electron–hole pairs. These electrons can further reduce O$_2$ to form ‘O$_2$’ species. As a consequence, the ‘O$_2$’ as dominant active species are responsible for the degradation of pollutants. The analyses were concordant with the experiment results upon the influence of various radical scavengers.

4. Conclusion

A series of novel $\alpha$-Fe$_2$O$_3$/BiOBr composite was prepared by a one-step hydrothermal route. Compared with BiOBr and $\alpha$-Fe$_2$O$_3$, the $\alpha$-Fe$_2$O$_3$/BiOBr composite photocatalyst exhibited much enhanced photocatalytic activity in degradation of RhB dye under visible light irradiation. In all the as prepared samples, the component 10Fe/100Bi exhibited optimal photocatalytic efficiency, which could remove 95% RhB within 40 min, where the photocatalytic activity did not show a significant decrease after four cycles of reuse. The high photocatalytic activity of the heterojunction materials could be attributed to the p–n heterojunction between $\alpha$-Fe$_2$O$_3$ and BiOBr, which facilitated interfacial charge transfer and inhibited electron–hole recombination. Moreover, the UV absorption edge of the $\alpha$-Fe$_2$O$_3$/BiOBr composite showed a slight red-shift compared to that of the pure BiOBr. These novel heterojunction materials may have potential applications in pollutant removal as highly efficient photocatalysts.

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