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Easy synthesis of high (110) facet-exposed BiOCl microspheres with excellent visible light degradation capability towards RhB

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Abstract

A novel BiOCl microsphere with high (110) facets exposure is successfully synthesized via a one-step solvothermal process in the presence of ethylene glycol without any other surfactant. The percentage of exposed (110) facets can be easily controlled by reactant concentration. The obtained BiOCl microsphere exhibited excellent photocatalytic efficiency for degradation of Rhodamine B (Rhb). Under visible light irradiation, 100 ml 20 mg l\(^{-1}\) Rhb can be completely decomposed in only 45 min. The excellent performance can be attributed to the efficient separation of photogenerated electrons and holes benefited from the special electronic structure of BiOCl microspheres. The (110) crystal facets are beneficial for holes transfer while the electrons migrate in [001] direction which is perpendicular to the (110) facet, thus extending the lifetime of photoinduced charges. This study may open more possibilities for the rational design and controllable synthesis of visible light photocatalysts with excellent performance.

1. Introduction

Semiconductor photocatalysis has attracted widespread attention since 1972, when Fujishima and Honda produced hydrogen and oxygen from water under ultraviolet light irradiation by using TiO\(_2\) as catalyst [1]. Photocatalysts can convert solar energy into chemical energy and thus contribute to the treatment of environmental pollutants [2], CO\(_2\) reduction [3], H\(_2\) generation from water splitting [4, 5] and nitrogen fixation [5] etc. For a long time, TiO\(_2\) has been thought as one of the best photocatalyst with excellent overall performance due to its high activity, considerable stability, low price and non-toxicity [6, 7]. However, the wide band gap (3.2 eV) and high photoinduced-charges recombination efficiency of TiO\(_2\) impede its practical application. To improve the utilization of sunlight, various photocatalysts with better visible light photoresponse have been extensively studied.

BiOX (X = F, Cl, Br, I) is one kind of the most potential visible-light-driven photocatalyst [8–11]. It possesses an anisotropic layered structure, in which the X\(^-\) ions can easily insert into the [Bi\(_2\)O\(_2\)]\(^{2+}\) layers and thereby constructing an internal electric field along the [001] direction [12, 13]. Moreover, BiOX is one of the indirect band gap semiconductors, which means that the photoinduced electrons must pass through a certain k-space distance before they reach the conduction band [12, 14]. Accordingly, these features of BiOX inhibit the recombination of photogenerated electrons and holes, hence improving the photocatalytic activity.

In view of the existence of the internal electric field along [001] direction, many efforts have been devoted to synthesize the BiOX photocatalysts dominated with (001) facets. For example, Wu et al fabricated BiOBr nanosheets with dominantly exposed (001) facets via a solvothermal reaction by adding HNO\(_3\), and the percentage of exposed (001) facets could be successfully controlled by HNO\(_3\) concentration [15]. The obtained BiOBr photocatalysts display improved abilities for reducing CO\(_2\) only into CO not CH\(_4\), which demonstrates a high selectivity. Similar to BiOBr, BiOCl nanosheets with exposed (001) facets also possess superior photocatalytic performance [16]. However, Yu et al presented that BiOBr with dominantly exposed (010) facets can behave better performance than (001) facets, they thought that (010) facets possess open channels for...
organic pollutants accommodation, providing significantly improved adsorption and photocatalytic performance [13]. Li et al proposed that the (001) facets and (010) facets are orthogonal to each other, which make them different in the length and direction of charge transfer [17]. Compared to (001) facet, the (010) facet of BiOBr has better charge transfer efficiency and preferably improves the interfacial charge separation [17, 18]. Thus, the (010)-dominated BiOX can more efficiently restrain the recombination of photogenerated holes and electrons.

Due to the (110) facet is also vertical to (001) facet, it can similarly provide an alternative charge separation path to improve the photocatalytic performance. Very recently, Yang et al prepared BiOX with selectively exposed (110) facet using PVP as the structure directing agent [19]. The theoretical calculations confirmed that highly exposed (110) facets can generate free electrons and holes more easily due to it higher electron and hole density, therefore, it profits to generate more -OH and -O2· active radicals etc. Moreover, the electrons prefer to migrate to the (001) facets while the holes travel to the (110) planes. Thus, the higher (110)-exposed BiOCl demonstrated much higher dye degradation rate [19]. Liu et al synthesized BiOCl/TiO2 heterojunctions with selectivly grown (110) facets, it indicated that the photogenerated holes could transfer from TiO2 to BiOCl along the (110) facet while the electrons move from BiOCl to TiO2 in the [001] direction, which significantly enhances the photodegradation of PFOA [20]. Up to now, to obtain highly (110)-exposed facets, surfactants with large molecular weight or binary composite system are needed, developing simple strategy to synthesize BiOX with highly exposed (110) facet is still a challenge.

In this work, we successfully prepared BiOCl three-dimensional microspheres with selectively exposed (110) facets by a one-pot solvothermal reaction without any other surfactants. The as-synthesized BiOCl microspheres exhibit significantly enhanced photocatalytic decomposition ability towards RhB under visible light (λ > 420 nm), RhB can be completely decomposed in only 45 min.

2. Experimental section

2.1. Synthesis of BiOCl microspheres

The 3D BiOCl microspheres were synthesized via a simple one-pot solvothermal reaction as follows: 1.455 g Bi(NO3)3 and 0.224 g KCl were sequentially dissolved in 30 ml ethylene glycol. The resulted transparent solution was transferred to a stainless-steel autoclave (100 ml), after being heated at 160 °C for 12 h in an oven, the obtained precipitates were washed with deionized water/ethanol and dried at 80 °C. In order to compare BiOCl prepared at different reactant concentration, 0.05, 0.075, 0.1, 0.15 and 0.2 mol L⁻¹ Bi(NO3)3 and KCl were also respectively used under the same conditions. The final products were marked as BiOCl-0.05, BiOCl-0.075, BiOCl-0.1, BiOCl-0.15, BiOCl-0.2, respectively.

2.2. Materials characterization

The crystal phase information of the product was obtained via a Bruker D2 Phaser diffractometer. Scanning electron microscopy (SEM, Thermo Scientific Apreo 2C and Phenom Pro-SE) and transmission electron microscopy (TEM, FEI Talos F200s Super-X) equipped with elemental mapping were used to observe the morphology, size and composition of synthesized samples. Diffuse reflectance spectroscopy (DRS) was measured with a UV-Vis spectrophotometer (PE Lambda 750S). The photoluminescence (PL) spectroscopy was measured on a fluorescence spectrophotometer (Edinburgh FLs1000) at room temperature with excitation wavelength of 320 nm. The total organic carbon (TOC) testing was conducted on a TOC analyzer (Vario TOC Select, Elementar Analysensysteme GmbH, Germany).

2.3. Photocatalytic measurements

The photocatalytic performance of the synthesized products was estimated by degrading the Rhodamine B (RhB) in the aqueous solution at room temperature. Typically, 30 mg photocatalyst was added into the aimed solution (RhB: 20 mg L⁻¹, 100 ml). To obtain the adsorption-desorption equilibrium of RhB on the BiOCl microspheres, the suspensions were firstly stirred in the dark environment for 1 h. Then the suspensions were irradiated with a Xe lamp (300 W), and the visible light irradiation (λ > 420 nm) were obtained by a filter plate. Finally, 5 ml RhB solution was sampled and centrifuged at 15 min intervals, the dye concentration was determined using a UV-Vis spectrophotometer (UV1101).

2.4. Trapping experiments

To analyze the reactive species in the photodegradation process, ethylenediaminetetraacetic acid (EDTA), p-Benzoinone (BQ), tert-butyl alcohol (t-BuOH), and dimethyl sulfoxide (DMSO) were employed as reactive spec scavengers for h⁺, O2·-, -OH and e⁻, respectively. For each trapping experiment, 0.2 M scavenger was added into the suspensions before the photocatalysis reaction.
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3. Results and conclusions
Figure 1 shows the XRD patterns of products prepared at different reactant concentrations. All samples match to
the tetragonal BiOCl (ICPDS No. 06–0249) well. The diffraction peaks at 12.0°, 25.9°, 32.5°, 33.4°, 40.9° and
46.6° match (001), (101), (110), (102), (112) and (200) crystal planes of BiOCl, respectively. It indicates that pure
BiOCl was successfully synthesized. It is obvious that the signals of (110) plane in all as-synthesized samples
exhibit much higher relative strength than that in standard card, which confirms that the (110) facets are highly
dominated. The relative intensity of (110) peak can corresponds to the exposure ratio of (110) facet [21], it
obviously changed with the increasing Bi(NO₃)₃/KCl concentration. The (112) peak of all samples are relatively
close, so it was selected to compare with (110). The intensity ratios of peak 110/peak 112 are 2.634, 3.517, 2.931,
2.275 and 1.820 for BiOCl-0.05, BiOCl-0.075, BiOCl-0.1, BiOCl-0.15, BiOCl-0.2, respectively. It is obvious that
the BiOCl-0.075 exhibits the highest and sharpest (110) peak, indicating the exposure extent of (110) facet could be
well tuned by simply adjusting the reactant concentration.

The morphologies of BiOCl samples prepared at different reactant concentrations were investigated by SEM. As shown in figure 2, all BiOCl products have a microsphere-shaped morphology. The average diameters of
BiOCl microspheres obtained under different conditions are all about 1 μm, which indicates that the reactant
concentration do not influence the size of microspheres. However, with the increasing reactant concentration,
the sphericity and integrity of the BiOCl microspheres were gradually improved, and the surface also becomes
smoother and denser. Based on the magnified images (figure 2(c) and inset of figures 2(a), (d)–(f)), it is obvious that
the BiOCl microspheres consist of various tiny nanoflakes. It is reasonable that BiOCl nanoflakes prefer to
forming microsphere by self-assembly in the presence of high viscosity EG [22–24]. The hierarchical
nanostructures can provide the photocatalyst more active sites, which is beneficial for better adsorption and
photocatalytic performance.

Figure 3(a) displays the TEM image of a single BiOCl-0.075 microsphere, it confirms that the product are
uniform solid microspheres, and some flake-like tiny nanoparticles can be clearly observed on the surface. Two
sets of lattices with fringe spacings of 0.273 nm and 0.368 nm can be observed in the HRTEM images of single
nanoflake (figure 3(b) and (c)), corresponding to (110) and (002) planes of BiOCl, respectively. The selected area
electron diffraction (SAED) pattern (figure 3(d)) displays a typical polycrystalline ring pattern, (101), (110) and
(200) planes of tetragonal BiOCl can be observed clearly. Figures 3(e)–(h) present the corresponding element
mapping of a single BiOCl-0.075 microsphere, indicating the uniform distribution of all Bi, Cl, and O elements
in the microsphere. Combining previous XRD, SEM, TEM and EDS analysis, it identifies that the BiOCl
microspheres with high (110)-exposed facets has been successfully synthesized via a simple solvothermal
process.

Figure 4(a) compares the UV–vis diffuse reflectance spectra of all as-synthesized photocatalysts. All BiOCl
microspheres exhibit strong absorption in the UV light region while display different performance in the visible
light region (λ > 400 nm). The visible light absorbance of BiOCl microspheres increases with the increasing
reactant concentration and BiOCl-0.2 displays the strongest visible light harvest ability. The band gap (Eg) of the

3.

![Figure 1. XRD patterns of BiOCl prepared at different reactant concentrations.](image-url)
samples can be evaluated based on the onset of the absorption edge [22, 25]. Figure 4(b) demonstrates the plot of transformed Kubelka-Munk function (versus the energy of light) of different BiOCl microspheres, it displays a continuous $E_g$ decrease companying increasing reactant concentration, the decrease of band gap is beneficial to improve the light absorption and enhance the photocatalytic efficiency.

Figure 5 shows the photoluminescence (PL) spectra of different BiOCl samples. It is obvious that BiOCl-0.075 demonstrates the weakest emission. The higher PL intensity means higher recombination rate and shorter lifetime of photoinduced charges [26], thus, the separation efficiency of photogenerated electrons and holes should be: BiOCl-0.075 > BiOCl-0.1 > BiOCl-0.05 > BiOCl-0.15 > BiOCl-0.2, which is consistent with the exposed (110) facets ratio of different samples (figure 1). It confirms that the increased exposed ratio of (110) facets is conducive to enhance the separation efficiency of photogenerated electrons and holes and extend the lifetime of photogenerated carriers.

The photocatalytic degradation towards RhB under visible light irradiation is used to evaluate the photocatalytic performance of the as-prepared photocatalysts. Figure 6(a) compares the RhB photodegradation performance of different BiOCl microsphere. During the dark period, photocatalysts could reach the adsorption-desorption equilibrium after 30 min BiOCl-0.05, BiOCl-0.075 and BiOCl-0.1 display stronger adsorption ability towards RhB, which can be attributed to their looser microstructure. After being irradiated
with visible light, the dye removal rate of all BiOCl photocatalysts reach 99% in 90 min, especially, BiOCl-0.05 and BiOCl-0.075 exhibit more excellent photocatalytic performance, the removal rate reaches 99.5% and 99.7% in 45 min, respectively. Figure 6(b) compares the photodegradation kinetic of several samples, and the calculated rate constants of all photocatalysts are also labeled in Figure 6(b). The linear relationship between \(\ln\left(C_t/C_0\right)\) and \(t\) indicates the degradation of dye follows the pseudo first-order reaction kinetics. The calculated rate constant of BiOCl-0.075 under visible light is about \(4.953 \times 10^{-2} \text{ min}^{-1}\), indicating its high photocatalytic activity and rapid degradation rate. Interestingly, BiOCl-0.2 with highest visible light harvest capacity has the worst degradation performance, which can be precisely attributed to its lowest (110) facets exposure. High (110)-exposed facets can significantly decrease the recombination efficiency of photoinduced electrons and holes \([19, 27]\), the more (110)-exposed facet and stronger dye adsorption ability endue BiOCl-0.075 the best photocatalytic performance.

Figure 7(a) shows the temporal UV–vis absorption spectra of RhB during the degradation process in the presence of BiOCl-0.075. 22.5% of RhB can be adsorbed by BiOCl-0.075 microspheres in the darkness. After being irradiated by visible light, the concentration of RhB solution rapidly decreased and the color of the suspension changed from red to colorless quickly, 99.7% of RhB was removed in 45 min, indicating the excellent dye-degradation performance of BiOCl-0.075. It is worth noting that an obvious blue-shift of RhB absorption peak can be observed with extending irradiation time, which is closely related to the generation of smaller and smaller intermediates based on a stepwise de-ethylation process of RhB \([28]\). This phenomenon also verifies the

**Figure 4.** (a) UV–vis diffuse reflectance spectra, (b) the plot of transformed Kubelka-Munk function (versus the energy of light) of BiOCl microspheres prepared at different reactant concentrations.

**Figure 5.** Photoluminescence spectra (\(\lambda_{\text{exc}}=320\,\text{nm}\)) of BiOCl microspheres prepared at different reactant concentrations.
photodegradation of RhB molecules under visible light in the presence of BiOCl microsphere with high (110) exposed facet. Figure 7(b) compares the performance of BiOCl-0.075 and commercial P25. No degradation is observed in the absence of photocatalysts, P25 do not have the adsorption abilities and its photodegradation under visible light is almost negligible, and BiOCl-0.075 microspheres can completely remove RhB in 45 min.

To further investigate the mineralization degree of RhB, TOC curves of RhB aqueous solution degraded by BiOCl-0.075 have been analyzed. As shown in figure 8, the TOC removal efficiency displays the same rule as the absorption and photodegradation ratio of RhB (figure 6(a)). After visible light irradiation for 45 min, the TOC removal percentage is 78.2%, and it further reached 89.8% after 90 min photodegradation. The result confirms the high degree mineralization of RhB in the photocatalysis process and indicates that BiOCl-0.075 can serve as the efficient photocatalyst for organic pollutants degradation.

The used BiOCl microsphere can be easily recycled. After separating and simply washing, the used photocatalyst can basically restore the original adsorption and degradation ability. Figure 9(a) displays the RhB-removing performance of recycled BiOCl-0.075. After five cycles of photodegradation, there is almost no change in the adsorption ability, and only a slight decrease in photodegradation efficiency can be observed, possibly due to the loss of sample during the collection and decontamination process, it demonstrates that BiOCl microspheres have extraordinary stability and reusability.

To further understand the photocatalytic degradation process of BiOCl towards RhB, the active species trapping experiments were carried out to evaluate the contribution of different active species. DMSO, BQ, t-BuOH and EDTA were employed as the quencher of $e^{-}$, $O_2^{•-}$, -OH and $h^{•+}$ [29–31], respectively. Figure 9(b) shows the result of active species trapping experiments, the addition of BQ causes the dramatically decrease of
RhB degradation rate, indicating the $\cdot O_2^-$ radicals should be the key roles in RhB photodegradation process, whereas $e^-$ and $\cdot OH$ are not the main reactive species. Owing to the existence of the internal electric field, the photo-generated electrons would migrate in the direction of [001] and then react with $O_2$ to form $\cdot O_2^-$, while the holes rapid transfer along the exposed (110) facets, with the oxidation of $\cdot O_2^-$ and $h^+$, the RhB molecules could be decomposed into $CO_2$ and $H_2O$ etc. small molecules.

Based on the DSR analysis (figure 4), the optical band edges of as-synthesized BiOCl-0.05 and BiOCl-0.075 microspheres are 3.25 and 3.16 eV respectively, which indicate that it cannot directly adsorb visible light theoretically, the visible light-response of BiOCl microspheres could be attributed to the indirect sensitization effect of the dye [19, 27, 32]. The characteristic UV–vis absorption peak of RhB is at about 550 nm (figure 7(a)), and BiOCl microspheres (especially BiOCl-0.075) exhibit certain degree of adsorption capacity towards RhB (figure 6(a)), which is much better than that of P25 (figure 7(b)), these factors finally contribute to the occurrence of dye sensitization. Based on the above experimental results, a possible photocatalytic mechanism of BiOCl microspheres with highly exposed (110) facets could be proposed. After being excited by visible light irradiation, the RhB molecules adsorbed on the surface of BiOCl microspheres can produce excited state electrons and injected it into the conduction band of BiOCl [19], furthermore, the exposed (110) facets of BiOCl increased the separation efficiency of photogenerated carriers by migrating $e^-$ and $h^+$ in different directions [19, 20]. After trapping the photogenerated $e^-$, the adsorbed $O_2$ molecules on the surface of catalyst were
Table 1. The photocatalytic performance for RhB degradation of some recently reported BiOCl photocatalysts.

| Photocatalyst                                      | Dye concentration (mg l$^{-1}$) and volume (ml) | Photo-catalyst dosage (mg) | Time (min) | Removal (%) | Degradation efficiency (mg·g$^{-1}$·min$^{-1}$)$^{a}$ | References (year) |
|---------------------------------------------------|-------------------------------------------------|---------------------------|------------|-------------|--------------------------------------------------------|-------------------|
| (110) exposed BiOCl                                | 20 mg l$^{-1}$ 1 00 ml                          | 30                        | 45         | 99.7%       | 1.4770                                                 | This work         |
| (110) exposed BiOCl prepared with PVP              | 10 mg l$^{-1}$ 50 ml                            | 100                       | 30         | 95%         | 0.1583                                                 | [19] (2020)       |
| (001) exposed BiOCl                                | 5 mg l$^{-1}$ 1 00 ml                           | 100                       | 8          | 99.9%       | 0.6244                                                 | [33] (2020)       |
| BiOCl with (001)/(110) facet heterojunction        | Unknown concentration 100 ml                    | 100                       | 30         | 90%         | /                                                      | [34] (2020)       |
| B-doped BiOCl with exposed (001) facets            | 50 ml 10 mg l$^{-1}$                            | 10                        | 100        | 81.5%       | 0.4075                                                 | [35] (2019)       |

$^{a}$ The degradation efficiency is calculated by the following formula:
reduced to $-O_2^-$ with strong reaction activity [27], which could decompose the organic pollutants into H$_2$O and CO$_2$ rapidly. Thus, the as-synthesized 3D BiOCl microspheres exhibit good light response and photocatalytic degradation performance towards RhB in the region of visible light.

Table 1 compares some recently reported BiOCl photocatalysts with different dominated facets and its photocatalytic degradation capability towards RhB. The BiOCl microspheres with highly exposed (110) facets display obviously enhanced photocatalytic performance.

$$Q_{\text{mt}} = \frac{(1 - C_f) V}{m t},$$

where $Q_{\text{mt}}$ means the average degradation amount of RhB for per unit of mass of photocatalyst and in unit time; $C_f$ (mg L$^{-1}$) represents the concentration of RhB after the removal; $V$ (L) represents the volume of dye solution; $m$ (g) is the amount of photocatalyst; $t$ (min) is the photocatalytic degradation time.

4. Conclusion

In summary, a novel BiOCl microsphere photocatalyst dominated with (110) facets was synthesized via a simple solvothermal method without using any other surfactants. The BiOCl microsphere exhibits extraordinary photodegradation performance towards RhB under visible light, it can completely remove RhB in only 45 min. Highly exposed (110) facet is beneficial to separate the traveling path of $h^+$ and $e^-$, so enhanced photocatalytic activity can be obtained because of the inhibited recommendation of photo-induced charges. The BiOCl microspheres with excellent photocatalytic degradation ability and stability would be a promising photocatalyst for practical water pollutants treatment.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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