Controlled Growth of BiOCl with Large \{010\} Facets for Dye Self-Photosensitization Photocatalytic Fuel Cells Application

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Supporting Information

ABSTRACT: BiOCl with \{010\} facets could be a promising material for photodegradation and energy conversion devices such as dye self-photosensitization photocatalytic fuel cells (DSPFCs). However, the \{010\} facets usually diminish rapidly during the growth process as the result of its high surface energies. In this work, we reported a simple and efficient method to prepare BiOCl with tunable exposed \{010\} facets. It was found that the solvent used in the synthesis process had important roles in the formation of ultrathin construction and the growth of \{010\} facets by controlling the [H+]+. For decreasing the surface energy and promoting the growth of high-active \{010\} facets, the thickness of BiOCl and the areas of \{001\} were reduced in its forming process. We had demonstrated that the enhancement of visible light-harvesting and photosensitization activity of BiOCl was primarily attributed to the decrease of thickness and the growth of \{010\} facets which could provide large surface areas and more active sites for dye absorption and photoelectron transfer. The BiOCl samples with tunable exposed \{010\} areas were evaluated as photoanode materials in DSPFCs. As expected, owing to its strong dye absorption capability and high transfer efficiency of charge carriers, the DSPFC with optimal performance was obtained by employing RhB as fuel when BiOCl possessed the larger areas of \{010\} facets and became a thinner nanosheet structure. Also, the \$J_{sc}\$ and \$V_{oc}\$ of DSPFC were measured to be 0.0058 mA/cm² and 0.689 V, respectively. Meanwhile, approximately 67% color removal was achieved on BiOCl\{010\}-Pt cell by treating 40 mL of 5 mg/L RhB under visible light for 240 min, which was much higher than that of P25-Pt (4%).

KEYWORDS: BiOCl\{010\}, low [H+]+, large surface area, DSPFCs, visible light

INTRODUCTION

Environmental pollution and excessive energy consumption have caused great attention worldwide. Since the discovery of the photocatalytic splitting of water into hydrogen over TiO₂ semiconductor materials under UV light,¹ photo fuel cells (PFCs) have been demonstrated as a promising and potential technique for addressing and relieving the intense pressure between environment and energy.²⁻⁵ In PFC systems, the photoanode utilizes solar energy as impetus and contaminant as fuel to simultaneously achieve energy conversion and pollutant degradation.⁶ Currently, the research of PFC devices assembled with TiO₂ semiconductor materials under UV light,¹ photo fuel cells (PFCs) have been demonstrated as a promising and potential technique for addressing and relieving the intense pressure between environment and energy.²⁻⁵ In PFC systems, the photoanode utilizes solar energy as impetus and contaminant as fuel to simultaneously achieve energy conversion and pollutant degradation.⁶ Currently, the research of PFC devices assembled with TiO₂ semiconductor materials achieved impressive achievement under UV,⁷,⁸ but the limited visible light-harvesting and the presence of surface states seriously impeded their wide application.⁹,¹⁰ Although quantum dots, such as CdS and PbS, can be employed to enhance the visible light absorption capacity and photoelectron transfer efficiency,¹¹,¹² the toxicity of quantum dots¹³ and the instability of CdS¹⁴ are of concern for applications.

The dye self-photosensitization photocatalytic fuel cells (DSPFCs) are developed to fulfill the highly visible light-harvesting and effective photosensitization degradation.¹⁵,¹⁶ Compared to PFCs, the generation of photoelectrons that came from excited dye molecules usually is much easier owing to the wide light absorption region of dye molecules.¹⁷ Moreover, the loss of photoelectrons is small and the recombination rate of charge carriers is low in DSPFCs, because the valence band of the semiconductor is not involved in the process of the photosensitization reaction.¹⁸,¹⁹ BiOCl can be used as a novel promising material for DSPFC application owing to its unique electronic structure and surface properties. Although the BiOCl cannot be photoexcited directly under visible light because of its wide band gap, it was demonstrated that the BiOCl with \{010\} facets exhibited excellent dye self-photosensitization performance. On one hand, the BiOCl layered structure

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consisting of [Bi₂O₂]³⁺ layers sandwiched between two slabs of halogen ions can induce the formation of internal static electric fields and endow it with an open channel feature, which is beneficial for the photoelectron transfer.₂₅,₂₆ Moreover, the conduction band of BiOCl (−1.1 eV)³¹,₂₂ is more negative than that of TiO₂ (−0.29 eV);₂₅ therefore, the formation of O₂•⁻ active species [E(O₂•⁻/O₂)] (−0.046 eV)]²⁵ on BiOCl is much easier. The O₂•⁻ active species possesses high oxidation activity for further pollutant decomposition. On the other hand, the BiOCl with dominant {010} facets has excellent dye absorption capacity and photosensitization performance due to its large surface areas and more surface active sites, which are favorable for enhancing the light-harvesting.₁₈ The dye absorption capability and mobility of charge carriers are the two major impact factors for DSPFC performance. Therefore, the controlled synthesis of BiOCl with a high percentage of {010} facets has important meaning for obtaining high-performance DSPFCs. Unfortunately, the highly active facets usually diminish rapidly during the growth process as a result of their high surface energies.₂₅,₂₆

In this study, a series of BiOCl materials with tunable exposed {010} facets were synthesized by a facile strategy. The impacts of solvent used in the synthesis process on the nanostructure of BiOCl and the growth of {010} facets were discussed in detail. The experiments on the photodegradation of Rhodamine B contaminant were carried out to assess the photosensitization performance of as-prepared BiOCl and investigate the relationship between {010} facets and photocatalytic activity. Moreover, the photovoltaic performances of DSPFCs assembled with BiOCl photoanodes were researched by employing RhB as fuel. Owing to the strong dye absorption capability and high photoelectron transfer efficiency of {010} facets, the BiOCl with the largest {010} facets exhibited superior photovoltaic and Rhb decomposition performance than P2S and BiOCl[001]. We expect our work to open a new avenue for the wide application of BiOCl in environment protection and energy, and provide new ideas on exploitation and synthesis of photoanodes materials for high-performance DSPFCs.

- EXPERIMENTAL SECTION

Materials. Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), poly(vinyl alcohol) (PVA), sodium chloride (NaCl), ethylene glycol (EG), acetic acid (98%) (AC), nitric acid (36%), sulfuric acid (98%), sodium hydroxide (NaOH), ammonium hydroxide (25%), anhydrous ethanol, Rhodamine B (RhB), and sodium sulfate (Na₂SO₄) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical reagent grade and were used without further purification.

Preparation of Photocatalysts. In a typical procedure, 2.0 g of Bi(NO₃)₃·5H₂O was added to 5 mL of ammonium hydroxide (NH₄OH) at room temperature with continuous ultrasound. After 30 min, 2 mL of solution was added dropwise into 100 mL of anhydrous ethanol that contained 4 mL of saturated sodium chloride solution. Then, the solution turned white, which indicated the formation of BiOCl nanostructure. The mixture solution was allowed to react at room temperature for 24 h under autogenous pressure. After the reaction finished, 20 mL of EG was poured into the white solution with continuous stirring to remove the remaining reagent. After 10 min, the white resulting precipitates were collected, washed with EG and ethanol thoroughly by filtering with a Φ = 0.22 μm organic membrane filter, and dried at 60 °C. The product obtained was denoted BiOCl-NH₄OH. In order to research the role of solvent in the synthesis, other BiOCl samples were also prepared under the same conditions but, instead of using NH₄OH, using (CH₂OH)₂, CH₃COOH, H₂O, and HNO₃ solution as the solvent, respectively. BiOCl[001] with large surface areas was synthesized by the reported method.³⁶

Characterization. The powder X-ray diffraction (XRD) patterns measurements were investigated using Rigaku D/max 2500 X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm), the working voltage operated at 40 kV, and 250 mA. The morphologies of the samples were examined by the environment scanning electron microscope (SEM, Hitachi S-4800) from 200 to 800 nm with 5.0 kV scanning voltages. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analysis were conducted on Tecnai G2 F20 at an accelerating voltage of 200 kV. The UV–vis absorption spectrum (DRS) was carried out on a UV–vis spectrophotometer (Hitachi U-4100) from 200 to 800 nm with pure BaSO₄ as the reflectance standard material. A nitrogen-adsorption system (ASAP-2020) was carried out to record the BET specific surface areas of the as-prepared samples through the nitrogen adsorption–desorption isotherms at 77 K. XPS characterization was conducted with the ESCALAB 250 photoelectron spectroscopy system by using Al Kα radiation. For the characterization of RhB/BiOCl, the samples were prepared as follows: 20 mg of the sample was dispersed into 50 mL of 20 mg/L RhB aqueous solution and stirred constantly for 1 h under dark conditions to establish an adsorption–desorption equilibrium, then filtered, and dried at 50 °C for 12 h.

Photocatalytic Measurements. The photocatalytic activity experiments of samples were evaluated by photocatalyzing the Rhodamine B (RhB) under visible light irradiation at ambient temperature using a 300 W Xe arc lamp (CEL-HXF300, Beijing) with a cutoff filter (λ > 420 nm). Briefly, a 0.02 g photocatalyst was added into 100 mL of aqueous solution containing 40 mg/L RhB solution. Prior to irradiation, the suspension was magnetically stirred.
in the dark for 1 h to ensure desorption−adsorption equilibrium. During the procedure of degradation, the analytical samples (about 4 mL) were taken every 5 min and centrifugated at a rate of 8000 rpm to remove the remaining particles. In addition, the RhB concentration was monitored by recording the absorbance of supernatants at maximum absorption wavelength using a UV−vis spectrophotometer (Shimadzu 2550, Japan).

**Photoelectrochemical Measurements.** The photocurrent characterization and electrochemical impedance spectroscopy were carried out on the three electrode quartz cell by the CHI660D workstation. The BiOCl/FTO conductor glass, Ag/AgCl electrode, and platinum foil plate were used as the working electrode, reference electrode, and counter electrode, respectively. The photoanodes were prepared according to a previously reported method.28,29 The FTO substrates were cleaned by ultrasonication in acetone, absolute ethanol, and distilled water for 30 min, respectively. Then, a 10 mg powder sample was dispersed into 100 μL of 25% (W/V) PVA solution under ultrasonication for 1 h to obtain slurries. Afterwards, the as-prepared slurries were spread on FTO substrates, whose edge parts were preprotected by transparent adhesive tape of the size 1 cm × 1 cm. These as-prepared FTO glass electrodes were fired at 80 °C for 12 h. The current density−voltage (J−V) and the current−power (J−P) characteristic were investigated to display the photoelectric performance of BiOCl photoanodes. A 300 W Xe arc lamp (CEL-HXF300, Beijing) was utilized as a light source with a cutoff filter (λ > 420 nm). Na2SO4 (0.05 mol/L) aqueous solution was used as the supporting electrolyte. The initial pH of the solution was adjusted to 2.0 by adding 1 M H2SO4. Prior to irradiation, the photoanode was vertically inserted in dye solution with stirring continuously in the dark for 30 min to absorb the dye molecules.

**RESULTS AND DISCUSSION**

The characterization of XRD patterns was carried out to describe the crystal structure of samples. From Figure 1a, all of the diffraction patterns corresponded to the BiOCl tetragonal crystals (JCPDS 06-0249), and no other diffraction peaks were observed. However, the samples prepared in different solvents exhibited distinct differences of diffraction peak intensity on {001} and {010} facets. Compared to the other solvent, the sample obtained in HNO3/ethanol possessed the highest (001) peaks which were the characteristic diffraction peaks of {001} facets. Because the hydrogen ions in solution preferred to absorb on oxygen terminated {001} facets; therefore, the BiOCl with {001} facets was easily formed under high [H+] condition.18 Once the [H+] in solution was controlled by using different solvent, the intensity of (001) peaks became weak gradually, indicating that the growth rate of BiOCl was decayed along the {001} facet direction.30 Furthermore, the (110) peaks, as characteristic diffraction peaks of {010} facets, grew rapidly. For reducing the surface energy and promoting the growth of highly active {010} facets, the thickness of BiOCl became thin, and the areas of {001} also decreased. As clearly shown in Figure 1b, it could be seen that the specific values of the I(110)/I(001) gradually increased with the decrease of {001}. These results suggested that the crystal growth speed was inhibited along the {001} facets and increased along the {010} facets as a result of the preferred orientation under the low [H+]. Different surface properties endow semiconductors with distinctive optical and electronic properties.31,32 The BiOCl with a large percentage area of {010} facets exposed

<table>
<thead>
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<th>solvent</th>
<th>H (nm)</th>
<th>L (nm)</th>
<th>S BET (m² g⁻¹)</th>
<th>k (10⁻² min⁻¹)</th>
<th>k (10⁻⁴ g min⁻¹ m⁻²)</th>
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</thead>
<tbody>
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<td>3030</td>
<td>17.302</td>
<td>0.1</td>
<td>0.578</td>
</tr>
<tr>
<td>H₂O</td>
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<td>523.7</td>
<td>10.16</td>
<td>1.2</td>
<td>11.81</td>
</tr>
<tr>
<td>AC</td>
<td>50.6</td>
<td>454.8</td>
<td>9.2047</td>
<td>1.3</td>
<td>14.12</td>
</tr>
<tr>
<td>EG</td>
<td>27.5</td>
<td>139.4</td>
<td>32.86</td>
<td>3.3</td>
<td>10.04</td>
</tr>
<tr>
<td>NH₄OH</td>
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<td>123.8</td>
<td>63.82</td>
<td>9.6</td>
<td>15.04</td>
</tr>
</tbody>
</table>

“Approximate thickness (nm). “Diameter of BiOCl samples from TEM images (nm). “The degradation rate constant of RhB. “Normalized degradation rate constant of RhB.

**Table 1. Physical Parameter and Photosensitization Degradation Activity of the BiOCl Samples**

**Figure 2.** SEM images of BiOCl samples prepared in different solutions: (a) HNO₃/ethanol, (b) H₂O/ethanol, (c) AC/ethanol, (d) EG/ethanol, and (e) NH₄OH/ethanol.
exhibited superior dye photosensitization activity under visible light.18,19

The typical scanning electron microscopy (SEM) images of BiOCl samples were shown in Figure 2. With the growth of \{010\} faces, the size of BiOCl samples gradually decreased, and the nanostructures changed from the 2D nanosheet to the 3D nanoflower (Figure 2a–e). This change was ascribed to the change of [H+] in ethanol solution. All detailed parameters are displayed in Table 1. During the growth of BiOCl, the hydrogen ions in solution preferred to absorb on oxygen terminated \{001\} facets and increased the crystal growth speed along the \textit{ab} plane. Therefore, the uniform square-shaped BiOCl nanosheets with exposed \{001\} were obtained in a HNO3/ethanol solution. Once \textit{H}2\textit{O} was used as solvent, the hydrogen ions mainly came from the hydrolysis of Bi(NO3)3, and therefore, the [H+] was much lower than HNO3 solution which resulted in the slow crystal growth along the \textit{ab} plane. It was clearly observed that the morphology of BiOCl changed from a uniform nanosheet to nanodiscs. Also, the BiOCl nanodiscs were much thinner and smaller than a nanosheet (Figure 2b). Compared to those of the \textit{H}2\textit{O}/ethanol samples, the size and thickness of BiOCl prepared in \textit{CH}3\textit{COOH}/ethanol became slightly smaller owing to the low degree of ionization of \textit{CH}3\textit{COOH}. In EG/ethanol solution, Bi3+ preferred to absorb on oxygen terminated EG molecule to form a relatively stable complex Bi2(OCH2CH2O)3. Relatively speaking, the stronger dissolving capacity between EG and ethanol solution is beneficial for the formation and growth of BiOCl tiny nuclei. Moreover, the tiny nuclei are not easy to reunite together in ethanol solution during the growth, leading to the final products with small crystal size (Figure 2d). These results corresponded to those from the literature reports.33,34 Finally, the 3D porous nanoflower structure of BiOCl was formed through the Ostwald ripening and self-assembly process.35,36 With a further decrease of [H+], the BiOCl ultrathin nanosheet units were formed in NH4OH/ethanol solution first owing to the growth of \{010\} facets, and then the ultrathin nanosheets aggregated freely into a 3D porous...
nano flower to reduce the surface energy (Figure 2e). The nano flower structure with interlaced ultrathin nanosheets can not only greatly increase the surface areas of photocatalyst, but also enhance the multireflection of light. The decrease of size and change of structure can influence significantly the physical and chemical properties of BiOCl.

More details about the crystal structure and morphology of BiOCl were obtained from the transmission electron microscopy (TEM) images. The square-shaped BiOCl nano-sheet structure was acquired in HNO3/ethanol, with diameter and thickness 3 and 0.25 μm (Figure 3a). A clear lattice spacing of 0.275 nm and the interfacial angle of 90° were observed (Figure 3b), which corresponded to the (110) lattice planes. When the [H+] was controlled, the size of BiOCl became small, and the morphology changed to nanodiscs. The thicknesses of samples were estimated to be 61.5, 50.6, and 27.5 nm by using H2O, CH3COOH, and (CH 2OH)2 as solvent, respectively (Figure 3c−e). Also, the nano flower structure of BiOCl was presented in Figure 3f. It was clearly observed that the BiOCl nano flower was composed of a large amount of interlaced ultrathin nanosheets with 15 nm thickness. As mentioned previously, the solvents have a significant effect on the morphology and thickness of BiOCl samples. The surface areas of BiOCl can be enlarged greatly owing to the reduction of nanosized species and the formation of a nano flower structure, which can provide a larger space for dye molecule absorption and chemical reaction. Moreover, the predominant defect on the surface of BiOCl would be changed from VBi‴ to VBi‴VO••VBi‴ with the decrease of thickness. The negatively charged VBi‴VO••VBi‴ preferred to absorb molecular cationic dye. Clear and continuous lattice fringes with a lattice spacing of 0.37 nm were determined by high-resolution TEM (HRTEM) images (Figure 3g), that corresponded to the {002} atomic planes. The physical and chemical performance of semiconductor materials is closely related to its surface properties and geometric structure.

The XPS characterization was carried out to record the surface chemical properties and composition of as-prepared BiOCl. As shown in Figure 4a, bismuth, oxygen, and chloride elements were included in the sample. The elements’ molar ratio was estimated to be 1:1.42:0.93 corresponding with the stoichiometric molar ratio in BiOCl. The peaks of binding energies for the Bi(4f) core level were located at 164.78 and 159.48 eV, which belonged to Bi(4f5/2) and Bi(4f7/2), respectively (Figure 4b). Also, the positions of characteristic peaks were the same in BiOCl-HNO3 and BiOCl-NH4OH. These results suggested that the bismuth ions in BiOCl samples were in a trivalence chemical state. The binding energies of O1s in different BiOCl samples were presented in Figure 4c. It could be clearly seen that the O1s peak position in BiOCl-NH4OH had a slight shift (0.31 eV) along low binding energy orientation. This suggested that the BiOCl-NH4OH surface had more negative charge than BiOCl-HNO3, which could be attributed to the decrease of the BiOCl thickness. With the

Figure 4. XPS spectra of BiOCl samples: (a) survey, (b) Bi4f, (c) O1s.
growth of \{010\}, the thickness of BiOCl decreased gradually, leading to the change of predominant defects on the surface of BiOCl from V_{Bi}^{‴} \rightarrow V_{Bi}^{‴}V_{O}^{•}V_{Bi}^{‴}. The negative charge of V_{Bi}^{‴}V_{O}^{•}V_{Bi}^{‴} defects is favorable for cationic dye adsorption.38

The nitrogen adsorption−desorption isotherm analysis was conducted to survey the special surface area of BiOCl samples. With the growth of \{010\} facets, the surface areas of BiOCl reduced first and then increased, which was attributed to the change in its nanostructure (Figure 5a). The large special surface area can offer more active sites and open space for molecular dye absorption. The BiOCl prepared in NH_{4}OH/ethanol solution possessed the largest surface area than the others due to its 3D interlaced nanoflower structure. All of these detailed parameters are displayed in Table 1. The RhB adsorption curves over the as-prepared samples under dark conditions for 60 min were shown in Figure 5b. As light receptors and electron donor, the adsorption efficiency of photosensitizer is an important influencing factor on the generation of photoelectrons and light-harvesting. In comparison, the RhB adsorption capability of BiOCl-NH_{4}OH is larger than that of the others, which is primarily ascribed to its large surface area and thin nanosheet structure. Although the BiOCl prepared in HNO_{3} had a relatively large surface area (17.302 m^{2} g^{-1}), the RhB adsorption capability was lower than that of the others, revealing that the physical performance of BiOCl was closely related with \{010\} facets. The \{010\} facets could provide more active sites for cationic RhB molecule adsorption. For DSPFCs, the large special surface areas play a vital role in enhancing the harvest of visible light and dye absorption capability.39

The DRS was employed to analyze the optical absorption properties of the BiOCl samples as shown in Figure 6a. Generally, the energy gap of a photocatalyst directly determines its optical absorption performance. This is the conversion formula40

\[ \alpha h \nu = A(\nu - E_g)^{1/2} \]

where \(\alpha\), \(h\), \(\nu\), and \(E_g\) are the absorption constant, Planck constant, light frequency, and band gap, respectively. Therefore, the band gaps of BiOCl and BiOCl-RhB were estimated to be 3.25 and 3.12 eV (Figure 6b). For the wide band gap, the BiOCl samples had no visible light absorption range from 400 to 800 nm. Once the dye molecule was adsorbed on the surface of BiOCl, its absorption intensity for visible light improved significantly. Moreover, the band gap of BiOCl/RhB samples was slightly smaller than that of BiOCl. The reasons that the visible light absorption capacity of BiOCl/RhB improved and its band gap became slightly more narrow were primarily attributed to the dye photosensitization performance of BiOCl{010} and the defective energy levels. On one hand, the RhB molecules adsorbed on the \{010\} surface by the dye self-photosensitization process can greatly enhance the visible light absorption due to the narrow band gap of RhB (\(E_g = 2.37\) eV).41 On the other hand, the thickness of BiOCl reduced with the growth of \{010\} activity facets, which resulted in the change of the predominant defect on the surface of BiOCl from V_{Bi}^{‴} \rightarrow V_{Bi}^{‴}V_{O}^{•}V_{Bi}^{‴}. The existence of oxygen vacancy defects could induce a new energy level to form within the forbidden band of BiOCl and RhB. The new energy level would decrease the band...
From Figure 6a, it was clearly seen that the visible light absorption intensity of BiOCl enhanced gradually with the growth of {010} facets. That was because the {010} facets could provide large surface area and more active sites for RhB absorption, which was favorable for the enhancement of visible light absorption. The results can be proven by the SEM image of RhB/BiOCl in Figure S1 (Supporting Information). The peak at 567 nm was the absorbance of RhB. These results have indicated that the visible light absorption of BiOCl can be enhanced by controlling the growth of {010} facets. The high harvest of visible light is beneficial for improving the photovoltaic performance of DSPFCs.

The photocatalytic performance of BiOCl{010} was evaluated by RhB photosensitization degradation under visible light. From Figure 7a, it could be clearly observed that the RhB photosensitization degradation efficiency significantly improved with the growth of {010} facets. Obviously, the BiOCl with large areas of {010} facets possessed strong dye absorption capability, which can greatly enhance the light-harvesting. The large amounts of photoelectrons could be directly injected from the excited dye molecule into the conduction band of BiOCl and were captured by dissolved O$_2$ by the more negative BiOCl conduction band ($-1.1$ eV) than $E_{O_2/O_2^-}$ ($-0.046$ eV), the photoelectrons were more easily transferred to the BiOCl conduction band. Thus, the $O_2^{2-}$ oxidation activity species could be generated for dye decomposition. The Mott–Schottky plot for BiOCl-NH$_4$OH had been conducted to elucidate its semiconductor properties. As shown in Figure S2 (Supporting Information), the flat band potential ($V_B$) of BiOCl-NH$_4$OH was approximately determined to be $-1.26$ V versus Ag/AgCl. That is to say, the conduction band of BiOCl-NH$_4$OH is around $-1.1$ V versus standard hydrogen electrode (SHE). It was surprising to find that the $100$ mL of the $40$ mg/L RhB solution decomposed completely after $25$ min under visible light irradiation when $20$ mg of the BiOCl photocatalyst prepared in the NH$_4$OH/ethanol solution was used. In order to accurately describe the photocatalytic performance, the initial reaction rate of photocatalytic degradation was investigated. From Figure 7b, it was clearly seen that the reaction rate constant ($k$) and that normalized by the surface area ($k'$) on RhB photosensitization degradation were closely related to the area of {010} facets. These detailed data are displayed in Table 1. The effects of pH on the RhB adsorption and photosensitization degradation are shown in Figure 7c. With the increase of pH, the RhB adsorption was decreased after continuous stirring for $60$ min. Moreover, the RhB photosensitization degradation efficiency had no obvious distinction in the pH variation from $2.0$ to $6.0$, but it decreased quickly when the pH changed to $10.0$. Because the RhB molecules preferred to aggregate with each other to form a larger molecule with the increased pH value, and these large molecules were hardly absorbed on the surface of BiOCl{010} facets, the RhB photosensitization degradation efficiency decrease was sharp. In conclusion, the dye photosensitization degradation performance would be enhanced at pH = 2.0 and hindered at a higher pH value. The RhB characteristic absorption peak centered at $553$ nm decreased quickly with the extension of visible light irradiation time, and the color removal reached up to $100\%$ after $25$ min (Figure 7d). The XRD and XPS before and after light irradiation had also been conducted to elucidate the stability of photocatalyst. As shown in Figure S3 (Supporting Information), there was no significant change in the data of XRD and XPS, which suggested the as-prepared BiOCl photocatalyst was stable.
indicates that the BiOCl with large percentage of \{010\} areas could be a promising material for DSPFCs.

The transient photocurrent responses were employed to analyze the formation and transfer of photoelectrons on the surface of BiOCl. As displayed in Figure 8, there had been no photocurrent generation under visible light irradiation on the BiOCl/FTO electrode. Because of its high light excitation energy, the photoinduced charge carriers failed to be generated on the surface of BiOCl. However, a high photocurrent signal appeared under visible light after the BiOCl/FTO electrode was inserted into RhB solution for 30 min, which suggested that a large number of electrons were generated and transferred on the surface of the electrodes. Moreover, as the larger \{010\} facets were exposed, the higher photocurrent was generated on the surface of BiOCl. The \{010\} facets can offer a large surface area and more active sites for RhB molecule adsorption which is beneficial for the formation of photoelectrons. In order to further prove that the \{010\} facets were vital to the photosensitization property, BiOCl samples with a large surface area and nearly 100% exposed \{001\} facets were prepared.27

Figure 8 in Supporting Information showed the comparison of transient photocurrent responses of BiOCl-001 and BiOCl-NH4OH. It could be clearly observed that a higher transient photocurrent was generated on the BiOCl-NH4OH photoanode. Therefore, more photoelectrons could be obtained from the current–voltage \((J−V)\) and current–power \((J−P)\) characteristics. The photovoltaic performance comparison of BiOCl in dye self-photosensitization photocatalytic fuel cells (DSPFCs). In the DSPFC system, the BiOCl photoanode used the molecular dye as fuel to generate electrons under visible light irradiation. The electron could be spontaneously transferred through an external circuit from photoanode to cathode to generate electricity. Therefore, the high photoelectric conversion efficiency could be obtained when massive photoelectrons were generated and transferred effectively on the surface of the photoanode. The short-circuit current density \(I_{sc}\), the open-circuit potential \(V_{oc}\), and fill factor \(FF\) of the cell with different BiOCl photoanodes are displayed in Table 2. The fill factor was determined by the following formula:

\[
FF = \frac{P_{max}}{J_{sc} \times V_{oc}} = \frac{I_{max} \times V_{max}}{J_{sc} \times V_{oc}}
\]

Here, \(I_{max} \times V_{max}\) is the maximum power of the BiOCl-Pt cell obtained from the current–power curve. \(J_{sc} \times V_{oc}\) is the highest possible power maximum of the cell. The fill factor, that directly reflects the performance of fuel cell, is denoted by the specific value of the maximum power and the highest possible maximum power of the cell. In DSPFCs, the \(J_{sc}\) was 0.0012 mA cm\(^{-2}\) with the absence of RhB and increased from 0.0017 to 0.0033, 0.0041, 0.0049, and 0.0058 mA cm\(^{-2}\) with the growth of \{010\} facets (Figure 9a). The increase of \(J_{sc}\) was primarily attributed to the \{010\} facets that provided large surface areas for RhB adsorption and an open channel for photoelectron transfer. The photovoltaic performance comparison of DSPFCs assembled with BiOCl-NH4OH, BiOCl[001], and P25 photoanodes, respectively, was carried out (Figure S6 in Supporting Information). It could be clearly observed that a higher photocurrent was generated on the BiOCl-NH4OH
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Figure S8 (Supporting Information), the RhB degradation performance of BiOCl-NH4OH in photocatalytic fuel cells, the large areas of {010} facets and interlaced ultrathin structure exhibited excellent photocatalytic activity and photoelectric performance. Therefore, our study will open an avenue for the wide application of BiOCl in environment protection and energy.

■ CONCLUSION

In conclusion, BiOCl materials with tunable exposed {010} facets were successfully synthesized by using different solvents. The growth of {010} facets was controlled by the [H+] in the solution. The sample prepared in NH4OH solution possessed the largest area of {010} facets and surface area among these samples. For a decrease in the surface energy to support the growth of highly active {010} facets, the thickness of BiOCl was reduced and the structure changed from nanoplates to nanoflowers. The photosensitization degradation activity of RhB enhanced with the growth of {010} facets, which was attributed to the large surface area and open channel performance of {010} facets. The excellent photovoltaic performance was obtained on the BiOCl-NH4OH photoanode by employing RhB as fuel whose color removal efficiency was achieved on the BiOCl{010}-Pt cell by treating 40 mL of 5 mg/L RhB under visible light for 240 min, which was much higher than P25-Pt (4%). Moreover, the DSPFCs still exhibited high photocatalytic activity after four consecutive cycles. For all we know, this strategy that investigates the effect of different crystal structures on chemical properties is also appropriate for other semiconductor materials, such as TiO2 and Ag3PO4, which is beneficial for promoting the development of PFCs and DSPFCs. We expect our work to open a new avenue for the wide application of BiOCl in environment protection and energy, and provide new ideas on exploitation and synthesis of photoanode materials for high-performance DSPFCs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b03150.

Additional characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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- Figure 9. Current–voltage (J–V) plots and power–voltage (J–P) plots for a BiOCl-Pt cell with different BiOCl photoanodes under visible light irradiation. C_{RhB} = 10 mg/L, 0.05 M Na2SO4 aqueous solutions, pH = 2.0.
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