Research Article

Crystal Facet-Dependent Intrinsic Charge Separation on Well-Defined Bi₄TaO₈Cl Nanoplate for Efficient Photocatalytic Water Oxidation

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The development of photocatalysts with wide spectral absorption and high charge separation efficiency has always been a pursued objective for photocatalytic solar energy conversion. Herein, we reported a wide-range visible-light-active Bi₄TaO₈Cl (BTOC) single crystal nanoplate with dominating [110] and [001] facets for enhancing the intrinsic charge separation efficiency. In situ selective photodeposition of metals and metal oxides provides evidences of photogenerated electrons and holes spatially separated on [110] and [001] coexposed facets of BTOC, respectively. The intrinsic charge separation efficiency was demonstrated to be closely dependent on the crystal facets, which can be modulated by tuning the coexposed crystal facet ratio. Further surface modification of BTOC with suitable dual cocatalyst Ag and RuOₓ enables remarkable improvement of charge separation efficiency and photocatalytic water oxidation performance. Investigation by comparison between well-defined BTOC nanoplate and BTOC nanoparticles confirmed the significance of coexposed crystal facets for efficient spatial charge separation and the blocking of reverse reaction from Fe²⁺ to Fe³⁺ ions during water oxidation reaction, indicating that rational modulation of exposed crystal facets is significant for controlling the intrinsic charge separation efficiency on Bi₄TaO₈Cl photocatalyst for efficient photocatalytic water splitting.

1. Introduction

Photocatalytic water splitting for converting solar energy into clean and sustainable hydrogen energy is a promising approach to solve energy and environmental problems, while efficient photogenerated charge separation on a semiconductor photocatalyst is the key of the heterogeneous photocatalysis process [1–5]. As it is well known, surface atomic arrangement and coordination of semiconductors significantly affect the physicochemical properties and photogenerated charge separation [6, 7]. Therefore, rational regulation of the exposed crystal facets and surface atomic configurations of semiconductor-based photocatalysts by precisely optimizing the preparation process is essential for modulating the intrinsic charge separation properties [8–11].

Recently, the strategy for enhancing charge separation is focused on spatial charge separation between coexposed anisotropic facets of a low symmetry single crystal semiconductor [12–18]. Realizing spatial charge separation on photocatalysts is dependent on the adopted preparation processes for the construction of crystal facets with dissimilar surface work function [19, 20]. The crystal facet-dependent charge separations have been reported on several photocatalysts, such as BiVO₄, TiO₂, BiOCl, SrTiO₃, BaTaON, and NaTaO₃ [21–26]. Nevertheless, exploring wide-range visible-light-active photocatalysts with excellent charge separation properties and deepening understandings of the relationship between spatial charge separation and coexposed crystal facets are needed for further enhancing intrinsic charge separation efficiency and promoting the development of photocatalysis.
Silleń–Aurivillius perovskite (Bi₄Mo₆OₓX) compounds with narrow band gap are promising for solar water splitting [27–31]. More importantly, their layered structure characteristics are beneficial for constructing anisotropic facets with low symmetry by precisely regulating the preparation procedures [32]. Bismuth tantalum oxychloride (Bi₄TaO₈Cl) as a typical example was recently reported for the preparation of {001} facet-dominated orthorhombic nanoplates [33], and the {001} facets are considered to be the photoactive surface [34]. In addition, Bi₄TaO₈X was also recently reported with improved photocatalytic CO₂ reduction activity due to the surface modification by Ag nanoparticles [35]. Additionally, photoinduced surface modification by generating reactive species on the Bi₄TaO₈Cl surface was also reported [36]. Despite most of the literatures having demonstrated improved photocatalytic activities on Bi₄TaO₈Cl through surface modification [37], or loading of - suitable cocatalyst [38], the relationship between the intrinsic photoreactivity and the exposed facets is still unclear, and there is a lack of in-depth exploration about the crystal facet-dependent charge separation properties of Bi₄TaO₈Cl.

Herein, aiming to explore the crystal facet-dependent photoreactivity and modulate the intrinsic charge separation through regulation of highly exposed facets, Bi₄TaO₈Cl (BTOC) was chosen as a visible-light-active photocatalyst for water oxidation. Well-defined BTOC nanoplates with exposed {110} side facets and {001} top facets were synthesized using a facile flux method. The BTOC nanoplate displays the capacity of spatial charge separation proven by in situ photochemical deposition, where photogenerated electrons and holes are selectively accumulated on the {110} facets and {001} facets, respectively. The BTOC-0.8 displays a higher charge separation efficiency and AQE for photocatalytic O₂ evolution than BTOC-0.5, BTOC-2.1, and BTOC-2.5, which may be due to the modulation of the coexposed crystal facet ratio. Furthermore, the charge separation efficiency and photocatalytic activity of BTOC-0.8 were further improved by loading dual cocatalysts Ag and RuO₂, and the reverse oxidation of Fe³⁺ to Fe²⁺ ions was also blocked owing to spatial charge separation between coexposed facets.

2. Materials and Methods

2.1. Chemicals. Bismuth oxide (Bi₂O₃) with 99.99% purity was purchased from Aladdin, BiOCl (99.99%) from Sigma-Aldrich, and Ta₂O₅ (99.99%) from Ameresco Chemical, and NaCl (99.5%) and KCl (99.5%) were purchased from Sinopharm Chemical. All chemicals used were of analytical grade and were used without further purification unless otherwise stated.

2.2. Synthesis of Samples. BTOC well-defined photocatalyst crystal samples, BTOC-0.5, BTOC-0.8, BTOC-2.1, and BTOC-2.5, were prepared using flux method. In a typical synthesis, a sample BTOC-0.5 was prepared by weighing stoichiometric ratios of Bi₂O₃, BiOCl, and Ta₂O₅ in the ratio of 5:4:2 in mmol with the eutectic mixture of NaCl:KCl (10 mmol:10 mmol) as flux agents; the mixture was thoroughly mixed using mortar and pestle. Thereafter, the obtained mixture was transferred into a high-temperature stable evacuated silica crucible and calcined at 973 K for 3 h in a temperature-programmed oven. Afterward, the obtained cooled yellow product was washed several times with deionized water and dried in the oven at 353 K overnight. Likewise, sample BTOC-0.8 was prepared by weighing stoichiometric ratios of Bi₂O₃, BiOCl, and Ta₂O₅ (5:4:2 in mmol) with eutectic mixture of NaCl and KCl (36 mmol:36 mmol) of the precursor as flux agents and following suit. Similarly, samples BTOC-2.1 and BTOC-2.5 were prepared using a similar preparation process, except that the precursor concentration was adjusted. Samples BTOC-2.1 and BTOC-2.5 were prepared by weighing stoichiometric ratios of Bi₂O₃, BiOCl, and Ta₂O₅ (2:1.5:0.8 in mmol) and Bi₂O₃, BiOCl, and Ta₂O₅ (1.5:1:0.5 in mmol) with eutectic mixture of NaCl and KCl (1:1) as flux agents, respectively. The precursors were thoroughly mixed together using mortar and pestle for each sample; thereafter, the obtained mixture was transferred into a high-temperature stable evacuated silica crucible and calcined at 1023 K for 3 h in a temperature-programmed oven to obtain samples BTOC-2.1 and BTOC-2.5. The obtained cooled yellow powder was washed several times with deionized water and dried in the oven at 353 K.

2.3. Characterizations. The as-prepared BTOC sample crystal structure was characterized using scanning electron microscopy (SEM, Quanta 200 FEG, FEI) and high-resolution transmission electron microscopy (HRTEM, JEM-F200). X-ray diffraction (XRD) was recorded on Rigaku D/Max-2500/PCXRD, and UV-visible (UV-vis) diffuse reflectance spectra were measured on a UV-vis spectrophotometer (JASCO V-550). Transient photocurrent response and photochemical impedance spectroscopy were measured using an electrochemical workstation and VersaStudio CV (CHI-760D, Chenhua Instruments Co., Ltd.). Mott-Schottky measurements were carried out on a Princeton Applied Research PARSTAT 2273, and the frequency and amplitude of AC potential used were 1 kHz and 100 mV, respectively.

3. Results

3.1. Structural and Morphological Characterization. Bismuth tantalum oxychloride Bi₄TaO₈Cl (BTOC) was prepared using flux preparation method. Firstly, the precursor ratio and the synthesis temperature were extensively studied to determine the optimal synthesis conditions. For BTOC samples prepared using different ratios of Bi₂O₃, BiOCl, and Ta₂O₅, the X-ray diffraction (XRD) results show no significant difference and the diffraction peaks of all samples were indexed to Bi₄TaO₈Cl with orthorhombic phase symmetry, and the UV-visible absorption patterns also exhibit similar optical properties (Figure S1). In addition, the SEM images show that all samples are nanoplate-like in shape except for thickness differences that affect the proportion of exposed facets (Figure S2). To investigate the validity of precursor ratio regulation, photocatalytic water oxidation was conducted on the BTOC samples using Fe(NO₃)₃ as electron scavengers (Figure S3). It was observed that photocatalytic water oxidation activity varied significantly with the precursor.
ratio, and the BTOC prepared using a precursor ratio of 5:4:2 for Bi₂O₃, BiOCl, and Ta₂O₅, respectively, shows the highest photocatalytic activity, showing that accurate precursor concentration plays an important role in preparation of BTOC photocatalyst. Furthermore, different BTOC samples were prepared using the same precursor ratio of 5:4:2 for Bi₂O₃ : BiOCl : Ta₂O₅, respectively, under different temperatures. The XRD peak intensity of the as-prepared samples increases gradually with the increase of temperature, indicating the enhancement of crystallinity (Figure S4a). In addition, UV-visible absorption spectra display similar absorption band edges with exception of the sample at 600°C (Figure S4b). SEM images exhibit that the apparent shape of the as-prepared BTOC changes from regular nanoplates to nanoparticles over temperatures ranging from 900°C to 600°C (Figure S5). Therefore, the flux temperature has significant effect on the growth of BTOC nanoplates crystal. Similarly, the photocatalytic water oxidation activity was conducted, and the BTOC synthesized at 700°C show the highest photocatalytic O₂ evolution activity (Figure S6).

In order to further explore the reasons for the differences in photoreactivity of different BTOC nanoplates, several typical BTOC samples were selected for a more detailed characterization and analysis. For convenient identification, these samples are named BTOC-0.5, BTOC-0.8, BTOC-2.1, and BTOC-2.5, according to the diffraction peak intensity ratios of (004) and (220) crystal facets that reflect the modulation of the coexposed facet ratio to some extent. Figure 1(a) shows that there is no obvious difference in the XRD patterns, and they were indexed to the BTOC with orthorhombic phase symmetry. SEM images of BTOC-0.5, BTOC-0.8, BTOC-2.1, and BTOC-2.5 show a square nanoplate-like shape with difference in the thickness (Figure S7), which further shows the diversity in the exposed ratio of the top and lateral surfaces. To identify the corresponding exposed facets, high-resolution transmission electron microscopy (HRTEM) analysis was performed on the BTOC-0.8 (Figure 1(c)). Selected-area electron diffraction (SAED) pattern gives a diffraction spot with identified (220) and (004) planes of orthorhombic BTOC (Figure 1(d)). HRTEM image conducted on the top facet shows the lattice fringe spacing of 0.387 nm and 0.274 nm indexes to (110) and (020) planes of BTOC, respectively (Figure 1(e), Figure S8). Therefore, given the orthorhombic BTOC phase symmetry, the highly exposed facets of the as-prepared BTOC samples can be recognized as [001] top facets and [110] side facets; the difference of these samples is the variation in the exposed facet ratio.

**Figure 1:** Structural and morphological characterization of BTOC samples. (a) XRD patterns of BTOC-0.5, -0.8, -2.1, and -2.5 (the values represent the ratio of the diffraction peak intensities of the (004) and (220) crystal facets); (b) SEM images of sample BTOC-0.5, -0.8, -2.1, and -2.5; (c–e) TEM image, corresponding SAED pattern, and HRTEM image of BTOC-0.8 nanoplate with (110) and (001) facets; (f) schematic illustration of BTOC nanoplate structure.
3.2. Optical Properties. Figure 2(a) shows the arrangement and coordination of Bi, Ta, O, and Cl atoms along the (001) top facet and (110) side facet. UV-vis diffuse reflectance spectra (DRS) and the Mott-Schottky measurement were conducted to investigate the optical absorption band structure. As shown in Figure 2(b), BTOC-0.5, BTOC-0.8 BTOC-2.1, and BTOC-2.5 display a comparable light absorption edge except that BTOC-2.1 and BTOC-2.5 exhibit higher extinction coefficient in the short wavelength range than BTOC-0.5 and BTOC-0.8. According to the plots of \((\alpha h\nu)^{1/2}\) versus photon energy \((h\nu)\), the band gap energies \((E_g)\) of BTOC-0.5, BTOC-0.8, BTOC-2.1, and BTOC-2.5 were determined to be 2.40 eV. The positive slope of the Mott-Schottky plots reveals the n-type characteristics while the flat band potentials were determined to be between -0.10 V and -0.17 V (vs. RHE) (Figure 2(c)). Combining these results, the electronic band structures of BTOC-0.5, BTOC-0.8, BTOC-2.1, and BTOC-2.5 are shown in Figure 2(d), and the band positions are comparable.

3.3. Photogenerated Charge Distribution. The photogenerated charge distribution on the coexposed {001} and {110} facets of the as-prepared BTOC samples was further explored by in situ photochemical deposition of metal oxides and metals [22]. As depicted in Figure 3, after photooxidation reactions taking Mn²⁺ and Pb²⁺ ions as precursors and IO₃⁻ ion as electron scavenger, MnOₓ and PbO₂ particles were found mainly deposited on the top {001} surface, showing that photogenerated holes are specifically selectively accumulated on the {001} facets (Figures 3(b) and 3(c), Figure S9). Also, after photoreduction reactions of metals in the presence of methanol (CH₃OH) as the hole scavenger, it is revealed that Au, Ag, and Pd particles were...
specifically deposited on the {110} lateral facets and not on the {001} top facets, suggesting that {110} facets are more favorable for accumulating photogenerated electrons on the BTOC (Figures 3(d)–3(f), Figure S9). To further corroborate the selectively spatial separation of electrons and holes between the coexposed {110} and {001} facets, simultaneous photodeposition of Au and MnOₓ was conducted. After photodeposition reaction, Au and MnOₓ particles were found selectively aggregated on the {110} and {001} facets, respectively, showing precisely that, spatial separation of photogenerated electrons and holes on the coexposed facets of BTOC was achieved (Figure S9). As schematically demonstrated in Figure 3(g), photogenerated electrons and holes are spatially separated on the {110} and {001} coexposed facets of BTOC nanoplates, respectively. These results confirm that precisely controlled exposure of anisotropic crystal facets could achieve effective spatial charge separation by properly optimizing the synthesis parameters during BTOC sample preparation.

3.4. Charge Separation Efficiency. To investigate the intrinsic charge separation efficiency of BTOC-0.5, BTOC-0.8, BTOC-2.1, and BTOC-2.5 samples, photocatalytic reaction was conducted in the presence of CH₃OH as hole scavengers and Fe³⁺ ions as electron acceptors under visible light (λ ≥ 420 nm). Noticeably, BTOC-0.8 displays much higher charge separation efficiency than BTOC-0.5, BTOC-2.1, and BTOC-2.5 (Figure 4(a), Figure S10), although electrons and holes are spatially separated onto different coexposed facets for all samples, indicating that charge separation and migration from the bulk to the surface in BTOC are largely affected by the difference in the coexposed facet ratio. Furthermore, photocatalytic water oxidation and the corresponding apparent quantum efficiency (AQE) tests were conducted to explore the effect of charge separation property on photocatalytic water oxidation performance. The results show that BTOC-0.8 still displays the higher photocatalytic O₂ evolution activity than other samples regardless of whether AgNO₃ and Fe(NO₃)₃ are electron acceptors (Figure 4(b), Figure S11) and achieves the highest AQE for photocatalytic water oxidation (Figure S11). This is consistent with the results of charge separation efficiency, indicating that the variation of photocatalytic activity between BTOC samples mainly originates from the difference of charge separation properties. Moreover, photovoltaic (PEC) measurement was also performed to corroborate the above results, and the BTOC-0.8 shows a markedly higher photocurrent density than others, a result comparable with the charge separation efficiency trend (Figure 4(c)). Also, electrochemical impedance spectroscopy (EIS) analysis was adopted to explore the charge transfer process (Figure 4(d), Table S1). It is shown that the BTOC-0.8 possess the smaller charge transfer resistance indicating faster charge separation and transfer. The above results specifically confirm that charge separation is readily available on these samples, but the difference in charge carrier dynamics owing to the different coexposed facet ratio led to the observed significant difference in the photocatalytic performance between the as-prepared samples.

3.5. Photocatalytic Activity. As the reduction and oxidation cocatalysts has been widely demonstrated to promote surface reaction, we further optimized the photocatalytic activity by loading appropriate cocatalysts. BTOC is modified by means of in situ photodeposition of Ag and RuOₓ as a single and or dual cocatalyst, and the photocatalytic water oxidation performance was tested in the present of Fe(NO₃)₃ as electron scavengers. As shown in Figure 5(a), the cocatalyst-modified BTOC-0.8 show higher photocatalytic activity regardless of single or dual cocatalyst modification than the pristine BTOC-0.8, especially the sample loaded with a dual cocatalyst (Ag/RuOₓ/BTOC-0.8); the photocatalytic activity almost doubled. In addition, (Fe,Ru)Oₓ as dual cocatalyst was also demonstrated to enhance the photocatalytic activity as shown in Figure S12 [39]. Moreover, the improved surface reaction in turn further promotes the enhancement of charge separation efficiency (Figure 5(b)), which indicates that the loading of the cocatalyst significantly accelerates the extraction and utilization of photogenerated charges. Finally,
the AQE of photocatalytic oxygen evolution improved to ~10% at 420 nm (Figure 5(b)). As it has been demonstrated previously that achieving spatial charge separation between coexposed facets on well-defined particulate photocatalysts could inhibit the reverse oxidation reaction from Fe$^{2+}$ to Fe$^{3+}$ due to the existence of coulomb repulsion force between the Fe$^{2+}$ ions and positively charged facets [40, 41], time-dependent photocatalytic water oxidation was conducted in the presence of the Fe$^{3+}$/Fe$^{2+}$ shuttle to corroborate the effect of spatial charge separation on blocking of reverse reaction. Notably, Fe$^{3+}$ ions formed during the photocatalytic water oxidation could reach the theoretical value of Fe$^{3+}$ ions in the original solution, regardless of the initial concentration of Fe$^{3+}$ (Figure 5(c), Figure S13), and the cocatalysts promoted the water oxidation reaction rate and accelerated the consumption of Fe$^{3+}$ ions (Figure 5(d)). This illustrates that the oxidation reverse reaction, from Fe$^{2+}$ to Fe$^{3+}$, was completely blocked by the achievement of spatial charge separation, which was also observed in BTOC-2.1 (Figure S14). In order to further confirm the significant role of spatial charge separation between coexposed facets in improving photocatalytic water oxidation activity, BTOC nanoparticle was prepared under the same reaction conditions and explored for photocatalytic water oxidations (Figure S15–S16). The results clearly show that BTOC nanoparticles display a very poor photocatalytic activity

![Figure 4](image-url)
compared to the well-defined BTOC nanoplates, indicating that the spatial charge separation within BTOC nanocrystals plays a substantial role on the intrinsic charge separation efficiency and photocatalytic performance (Figure S17).

4. Discussion

In summary, we have synthesized well-defined Bi$_4$TaO$_8$Cl (BTOC) nanoplates with {110} and {001} dominant facets as a visible-light-active semiconductor. We demonstrated that the BTOC nanoplates possess the capacity of spatial charge separation, where photogenerated electrons and holes prefer to accumulate on the {110} facets and {001} facets, respectively. The intrinsic charge separation efficiency was demonstrated to be closely dependent on the crystal facets, which can be modulated by tuning the coexposed crystal facet ratio. The BTOC-0.8 displays a significant high charge separation efficiency and AQE for photocatalytic water oxidation, owing to the modulation of the coexposed crystal facet ratio. The photocatalytic water oxidation activity was further improved by loading dual cocatalysts Ag and RuO$_x$, and the oxidation reverse reaction of Fe$^{2+}$ to Fe$^{3+}$ ions was totally blocked owing to spatial charge separation between coexposed facets. Our work unravels the crystal facet-dependent intrinsic photoreactivity, which provides a feasible strategy to fabricate semiconductor-based photocatalyst for solar energy conversion.

Data Availability

All data presented in the paper and the supporting information are available from the corresponding author upon reasonable request.
Conflicts of Interest

The authors declare no conflict of interest.

Authors’ Contributions

R.L. conceived the idea and revised the manuscript. A.A. and M.S. designed and performed most of the experiments and data analysis. X.T., Y.Z., and B.Z. contributed to the photocatalysis test and analysis. N.T. contributed to the HRTEM analysis. All authors discussed the results and contributed to the manuscript. Abraham Adenle and Ming Shi contributed equally to this work.

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Supplementary Materials

Figures S1–S17 and Tables S1 show the SEM, XRD, UV-vis absorption spectra, photocatalytic activity results, HRTEM, and SAED patterns. (Supplementary Materials)

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