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4 **Tuning Electron Transfer by Crystal Facet Engineering of BiVO₄ for Boosting**
5 **Visible-Light Driven Photocatalytic Reduction of Bromate**

6

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28 **ABSTRACT:**

29 Removal of bromate (BrO_3^-) has gained increasing attention in drinking water treatment process.
30 Photocatalysis technology is an effective strategy for bromate removal. During the photocatalytic
31 reduction of bromate process, the photo-generated electrons are reductive species toward bromate
32 reduction and photo-generated holes responsible for water oxidation. In this study, the monoclinic
33 bismuth vanadate (BiVO_4) single crystal was developed as a visible photocatalyst for the effective
34 removal of bromate. The as-synthesized BiVO_4 photocatalyst with optimized $\{010\}$ and $\{110\}$ facets
35 ratio could achieve almost 100% removal efficiency of BrO_3^- driven by visible light with a
36 first-order kinetic constant of 0.0368 min^{-1} . As demonstrated by the electron scavenger experiment
37 and density functional theory (DFT) calculations, the exposed facets of BiVO_4 should account for the
38 high photocatalytic reduction efficiency. Under visible light illumination, the photo-generated
39 electron and holes were spatially transferred to $\{010\}$ facets and $\{110\}$ facets, respectively. The
40 BiVO_4 single crystal photocatalyst may serve as an attractive photocatalyst by virtue of its response
41 to the visible light, spatially charge transfer and separation as well as high photocatalytic activity,
42 which will make the removal of BrO_3^- in water much easier, more economical and more sustainable.

43 *Keywords:* bromate; bismuth vanadate; photocatalysis; crystal engineering

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52 INTRODUCTION

53 Bromate (BrO_3^-) originated from the chlorination or ozonation process in bromide-containing water
54 has attracted the attention of many researchers (Bouland et al., 2005; Chen et al., 2016; Parker et al.,
55 2014, Zhu et al.,). The drinking water standard of BrO_3^- in the European Union and the U.S.
56 Environmental Protection Agency is less than 10 $\mu\text{g/L}$ (Shen et al., 2017; Weinberg et al., 2003; Wu
57 et al., 2013). To overcome this obstacle, considerable progress has been made regarding the
58 transformation of BrO_3^- to Br^- by using various technologies, such as electrochemical reductive
59 treatment (Xie and Shang, 2007), zero-valent iron (Wang et al., 2009; Zhang et al., 2015) and
60 FeOOH catalytic reduction (Nie et al., 2014). Although these already established technologies can
61 remove BrO_3^- effectively, they may suffer from various problems such as high cost, operational
62 complexity, as well as the potential secondary pollution risk induced by metal leaching (Ayoubi-Feiz
63 et al., 2015; Lin et al., 2016; Noguchi et al., 2003).

64 Recently, photocatalysis process was regarded as a superior technology to remove BrO_3^- (Noguchi
65 et al., 2002). Compared with the conventional removal methods mentioned above, photocatalysis
66 shows fascinating potential for bromate removal systems due to its high efficiency, low-cost and
67 environmental benignity (Ayoubi-Feiz et al., 2015; Lin et al., 2016; Noguchi et al., 2003). As the
68 widely used photocatalyst, TiO_2 based photocatalysts had been extensively employed in bromate
69 removal by UV-light driven photocatalysis, whereas the efficient conversion of BrO_3^- to Br^- was
70 contributed to the photo-generated electrons at conduction band (CB) (Li et al., 2016; Liu et al., 2016;
71 Zhang et al., 2005).

72 However, the photocatalytic systems based on TiO_2 -photocatalysis still suffer from some problems
73 for bromate removal: (i) The wide bandgap ($E_g = 3.2 \text{ eV}$) of TiO_2 can only be responsively under UV
74 light irradiation (UV, 3% ratio of solar light). This may cause inconvenience in practical applications
75 (Perry et al., 2009; Williams et al., 2008; Yang et al., 2020a; Yang et al., 2020b). (ii) The reducing
76 agent in the photocatalytic system is photo-generated electrons. It is important to improve the

77 quantum efficiency of photoelectrons to participate in the bromate reduction reaction (Pan and Zhu,
78 2010; Wang et al., 2020a; Yang et al., 2019; Zhu et al., 2020c; Wang et al., 2020b; Wang et al., 2019).
79 (iii) As a redox couple in the reaction depends on generated-electrons and holes, the photocatalytic
80 reduction half-reaction is interdependent to the oxidation half-reaction mediated by photo-generated
81 holes at the valence band (VB). Therefore, there is a growing interest in developing high overall
82 efficiency visible light driving photocatalysts (Zhang et al., 2019; Zhu et al., 2019; Zhu et al.,
83 2020a).

84 In the BrO_3^- reduction system, BrO_3^- acts as an electron acceptor, and the reduction reaction ($1 e^-$
85 process) is not considered as a limiting step for the overall photocatalytic redox reaction. On the
86 other hand, the oxidation of water ($4 e^-$ process) is observed as a bottleneck or the rate-determining
87 step (Zhu et al., 2020b). Based on the above-mentioned points, the premise for effective BrO_3^-
88 reduction is to find a visible photocatalyst with high reductive activity, high selectivity and water
89 oxidation ability.

90 Monoclinic BiVO_4 has been widely used in photocatalysis or photoelectrochemical process for the
91 water oxidation to produce oxygen due to its efficient and active visible light photocatalytic
92 properties (Nakabayashi et al., 2017; Saison et al., 2015). Therefore, the oxidation reaction would not
93 hamper the reductive half-reaction (bromate reduction reaction). On the premise that BiVO_4 can
94 efficiently oxidize water, the major water oxidation products are oxygen rather than hydroxyl
95 radicals (Nakabayashi et al., 2017; Saison et al., 2015). This can mitigate the problem of the
96 re-oxidation of bromine ions by hydroxyl radicals. Recent associated studies on the preparation of
97 single crystal BiVO_4 photocatalysts have shown that photo-generated carriers could be transferred to
98 different exposed crystal facets (Li et al., 2013; Zhu et al., 2017), the reduction and oxidation
99 reactions were spatially separated with a high reaction extent. Learned from these experiences, the
100 reduction surface (photo-generated electron rich surface) of BiVO_4 can be made by the crystal facet
101 engineering, thus improving the quantum efficiency of photo-generated electrons involved in the

102 bromate reduction reaction.

103 Herein, three kinds of BiVO₄ crystals (BVO-a, b and c) with different exposed facets were
104 prepared and applied to the photocatalytic reduction of bromate under visible light. Additionally, the
105 structure and morphology of BiVO₄ single crystals were characterized using X-ray diffraction (XRD)
106 and field emission scanning electron microscopy (FESEM). Furthermore, the BrO₃⁻ reduction
107 performance was evaluated by calculating the conversion of BrO₃⁻ to Br⁻. Lastly, the optical
108 properties and electron configuration were estimated using density functional theory (DFT), and the
109 bandgap, band position, and effective electron mass were also taken into consideration. The possible
110 photocatalytic reduction mechanisms of BrO₃⁻ by BiVO₄ crystals were proposed.

111 **EXPERIMENTAL SECTION**

112 **Synthesis of the photocatalyst.** BiVO₄ powders were prepared by liquid-solid state reaction. 5
113 mmol of V₂O₅ and 10 mmol of Bi(NO₃)₃·5H₂O were added in 60 mL of DI water. The precursor
114 solution was stirred until a yellow solution was formed. The pH of the solution was regulated to 1.0,
115 0.5 and 0.1 by ammonia solution or dilute nitric acid solution, and then the solution was vigorously
116 stirred at room temperature for 5 days. The obtained BiVO₄ powder was separated by centrifugation,
117 washed with DI water and dried at 60 °C. Moreover, the obtained BiVO₄ powders synthesized at
118 different pH values of 1.0, 0.5 and 0.1 were labeled as BiVO₄-a, BiVO₄-b and BiVO₄-c.

119 **Characterization.** The powder X-ray diffraction (XRD) characterization was conducted on an
120 X-ray diffractometer (Bruker D8 Adv., Germany). The crystalline phase and morphology of the
121 as-prepared BiVO₄ samples were characterized by an X-ray diffractometer (Bruker D8 Adv.,
122 Germany) and a field emission scanning electron microscope (FESEM, Type-4800, Hitachi, Japan),
123 respectively. A spectrophotometer (Type-UV2550, Shimadzu, Japan) recorded the UV-vis diffuse
124 reflectance spectroscopy (DRS) of the powders. The photoelectrochemical measurements were
125 conducted using a CHI760E electrochemical workstation. The photocurrent measurements were
126 carried out under visible light irradiation (300 W Xenon lamp).

127 **Theoretical Calculations.** The optimization of the unit cell of monoclinic scheelite BiVO_4 was
128 performed using the CASTEP code with the projector augmented wave (PAW) pseudopotentials (Liu
129 et al., 2017), and the parameter was set according to the reference (Long et al., 2008). The angle β of
130 monoclinic scheelite BiVO_4 was set to 134.9° for simplification, the detailed parameters can be
131 found in Table S1. The stable crystal configuration of the bulk and the cleavage surface with the
132 optimized lowest energy are shown in Figure S1.

133 **Experimental Setup and Procedures.** The BrO_3^- ions removal performance was tested according
134 to the previous method reported by our team (Liu et al., 2019). Both BrO_3^- and Br^- ions were
135 determined by an ion chromatograph analyzer (LC-10A, Shimadzu, Japan).

136 RESULTS AND DISCUSSION

137 **Characterization of BiVO_4 Photocatalysts.** The XRD patterns of three types of as-synthesized
138 BiVO_4 photocatalysts are presented in Figure 1A. All diffraction patterns of samples (BiVO_4 -a, b and
139 c) showed sharp diffraction peaks and all typical peaks were attributed to monoclinic scheelite
140 BiVO_4 crystal phase (JCPDS No. 14-0688, space group: $C2/c$), evidently suggesting that the BiVO_4
141 photocatalysts have high crystallinity (Liu et al., 2014). Considering the phenomenon that the (121)
142 peak was the highest peak for separated BiVO_4 -a, b and c, the (121) peak was selected as the
143 benchmark to evaluate the possible exposed surface in BiVO_4 crystal qualitatively, i.e., the intensity
144 ratios of the diffraction peak of (040) and (110) compared with (121). The intensity of (040)
145 diffraction peak followed the order of $\text{BiVO}_4\text{-a} > \text{BiVO}_4\text{-b} > \text{BiVO}_4\text{-c}$, while that of (110) diffraction
146 peak showed a reverse order, i.e., $\text{BiVO}_4\text{-c} > \text{BiVO}_4\text{-b} > \text{BiVO}_4\text{-a}$. However, the intensity of (110)
147 diffraction peak of $\text{BiVO}_4\text{-c}$ was stronger than that of $\text{BiVO}_4\text{-b}$ and a ($\text{BiVO}_4\text{-c} > \text{BiVO}_4\text{-b} >$
148 $\text{BiVO}_4\text{-a}$). According to Wang's study, this intensity difference in XRD pattern indicated that the
149 (040) diffraction peak was the dominant peak for $\text{BiVO}_4\text{-a}$, and that for $\text{BiVO}_4\text{-c}$ was (110) (Wang et
150 al., 2011). The FESEM image of $\text{BiVO}_4\text{-a}$ exhibited a sheet-like geometry with a length of 1.5 μm ,
151 width of 400-nm, and thickness of 150-nm, respectively (Figure 1B). The $\text{BiVO}_4\text{-b}$ sample exhibited

152 a polyhedral box shape (Figure 1C) with an average size of about 1.5 μm . In addition, the $\text{BiVO}_4\text{-c}$
153 with an octahedral shape of about 2 μm was observed in Figure 1D. To further identify the exposed
154 crystal faces, the corresponding HRTEM image for $\text{BiVO}_4\text{-a}$ is given in Figure 1E.

155 The corresponding selected area electron diffraction (SAED) pattern in Figure 1F (inset picture) is
156 taken from the sheet-like $\text{BiVO}_4\text{-a}$ sample (Figure 1E), revealing the growth orientation in
157 accordance with the results of XRD measurements. As determined by XRD result, and with different
158 b axis orientations for different sheets, the d spacings measured from SAED (zone axis [010]) were
159 2.61 \AA , which agreed well with the lattice spacings of (200) monoclinic BiVO_4 (Wang et al., 2011).
160 The growth direction was along the (040) facet, i.e., {010} crystal planes; therefore, the sheet-like
161 $\text{BiVO}_4\text{-a}$ grew along the b axis as seen in the HRTEM images (Figure 1F). Based on these
162 analyses and calculations, a simple schematic illustration of the exposed crystal surface is presented
163 in the insets in Figure 1B, C and D according to the XRD and HRTEM analysis. The XPS spectra of
164 Bi 4f, V 2p and O 1s are illustrated in Figure S2. The Bi 4f consisted of two peaks at the binding
165 energy of 156.3 and 161.5 eV, while the V 2p spectra showed two peaks of 514.0 eV and 521.7 eV,
166 respectively. Moreover, the O 1s spectra was detected at the binding energy of 527.1 eV.

167

168

Figure 1 (A-F)

169

170 **Photocatalytic Reduction of BrO_3^- by BiVO_4 Photocatalysts.** The feasibility of photocatalytic
171 reduction of BrO_3^- using BiVO_4 photocatalysts under visible light irradiation were
172 examined by photocatalytic experiment. No BrO_3^- reduction was observed in the absence of
173 photocatalysts, which excluded the direct visible light driven photolysis of BrO_3^- reduction. As
174 illustrated in Figure 2A, the concentration of BrO_3^- decreased from initial 1000 to 0 $\mu\text{g L}^{-1}$ (below
175 the detection limit) for $\text{BiVO}_4\text{-b}$ after 150 minutes of reaction, which exhibited almost 100% BrO_3^-
176 removal efficiency. However, $\text{BiVO}_4\text{-a}$ and $\text{BiVO}_4\text{-c}$ reduced the initial BrO_3^- concentration (1000

177 $\mu\text{g L}^{-1}$) to 130 and 230 $\mu\text{g L}^{-1}$, respectively. The BrO_3^- removal performance can be well indexed to
178 the first-order reaction $k = 0.0368 \text{ min}^{-1}$ for $\text{BiVO}_4\text{-b}$ (Figure 2B), which was 2.08 and 3.94 times
179 higher than that of $\text{BiVO}_4\text{-a}$ (0.0177 min^{-1}) and $\text{BiVO}_4\text{-c}$ (0.0094 min^{-1}), respectively. (Table S2).
180 These results demonstrated that the $\text{BiVO}_4\text{-b}$ sample showed superior photocatalytic bromate
181 removal performance than that of $\text{BiVO}_4\text{-a}$ and -c samples which might be benefited from the facet
182 effect of BiVO_4 crystal. Moreover, the stability of the BiVO_4 photocatalysts was also evaluated and
183 the result can be seen in Figure S3. during the recycling process, the photocatalytic performance of
184 BiVO_4 was with high stability, amount to 3% activity loss after five-cycles. During the recycling
185 process, the photocatalytic performance of BiVO_4 was of high stability with the activity loss
186 amounting to 3% activity loss after five-cycles

187

188

Figure 2 (A and B)

189

190 **Mechanisms Insight.** To further understand the BrO_3^- reduction mechanism by BiVO_4
191 photocatalyst, the electron scavenger experiments were implemented by adding $\text{S}_2\text{O}_8^{2-}$ (Romão et al.,
192 2015). As a typical electron scavenger, the degradation performance of BrO_3^- was decreased
193 obviously after the introduction of $\text{S}_2\text{O}_8^{2-}$ (Figure S4 and Table S3). Notably, the bromate removal
194 nearly disappeared when 5 mmol of $\text{K}_2\text{S}_2\text{O}_8$ was added. Thus, it could be concluded that the
195 photo-generated electrons were the reactive species during the BrO_3^- photocatalytic reduction
196 process.

197 As we know, for semiconductor photocatalysis, the optical properties are directly related to the
198 intrinsic electron configuration and thus influence the photocatalytic performance. Figure 3A shows
199 the DRS spectra of BiVO_4 samples with different exposed surfaces. The adsorption properties of the
200 obtained three types of BiVO_4 were all typical visible light-driven photocatalysts with an absorption
201 edge at approximately 536 nm ($E_g = 2.31 \text{ eV}$), which was in line with the previous report (Su et al.,

202 2011). The DFT calculation regarding optical properties was conducted to better understand the
 203 relationship of light absorption with exposed surface. As shown in Figure 3B, there was no obvious
 204 difference in the absorption threshold for polycrystal, {010} and {110} facets BiVO₄, respectively,
 205 which was in accordance with the DRS results. Based on the above DRS and DFT calculation results,
 206 it can be concluded that the optical properties of BiVO₄ samples may not be the major reasons for the
 207 great difference in the photocatalytic removal of bromate.

208

209 **Figure 3 (A and B)**

210

$$211 \quad E_{\text{VB}} = \chi - E^e + \frac{E_{\text{g}}}{2} \quad (1)$$

$$212 \quad E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}} \quad (2)$$

213 Furthermore, the theoretical positions of energy band position of BiVO₄ at pH = pH_{pzc} were
 214 calculated using the following conventional eqn. 1 and 2 (Xu and Schoonen, 2000). E^e is the free
 215 electron energy (4.5 V), E_{g} is the measured band gap. By substituting these absolute
 216 electronegativities of Bi, V and O to eqn. 1 and 2, the E_{VB} of 2.80 V and E_{CB} of 0.49 V (SHE) were
 217 obtained (Cooper et al., 2014). Although the valence band position of BiVO₄ was suitable for
 218 hydroxyl radicals generation, according to the previous literature, BiVO₄ was generally considered as
 219 a highly efficient photocatalyst for water oxidation to produce oxygen rather than hydroxyl radicals,
 220 thus making the reduction of BrO₃⁻ more efficient towards Br⁻ conversion (Nakabayashi et al., 2017;
 221 Saison et al., 2015).

222 As shown in Figure S1, VO₄³⁻ was a stretched tetrahedron. In the stretched BiO₈ dodecahedron, Bi
 223 atoms were surrounded by 8 O atoms, and the four bond lengths were different (2.467, 2.466, 2.471,
 224 and 2.528 Å) (Stoltzfus et al., 2007; Yang et al., 2013). As we know, the dipole moments played an
 225 important role in photocatalysis, especially on the effective separation of carriers. A big dipole

226 moment always means a high driving force makes efficient photo-generated carriers transfer (Li et al.,
 227 2014). In this regard, the absolute numerical value of dipole moment is calculated to be 0.79 and
 228 0.68 D on {010} and {110} facets, respectively. The larger dipole moment of the BiO polyhedrons
 229 for {010} facet demonstrates greater distortion of the {110} surface layer, hence leading to a larger
 230 internal polarization which is conducive to the charge separation and higher activity for the
 231 photocatalytic reduction of BrO_3^- .

232

233

Table 1

234

235 To further understand the electronic configuration of the two exposed crystal facets, the band
 236 structure of BiVO_4 is plotted in Figure 4A. Considering the symmetry of the monoclinic system, the
 237 path selected from the Brillouin zone was along $Z \rightarrow G \rightarrow Y \rightarrow A \rightarrow B \rightarrow D \rightarrow E \rightarrow C$. The DFT
 238 calculated E_g for BiVO_4 was 2.12 eV, close to the experimental value (2.31 eV). The highest band
 239 energy level and lowest energy level were located at different K-points, which indicated the typical
 240 indirect band gap property. Furthermore, we can calculate the effective carrier masses of {010} and
 241 {110} facets based on the curvatures of the bands in the corresponding directions by fitting parabolic
 242 functions to the conduction band minimum (CBM) and valence band maximum (VBM) of BiVO_4 .
 243 According to the Eq. (3) (Li et al., 2014), the effective electron masses can be estimated, where k is
 244 the wave vector, and E_k is the energy corresponding to the wave vector k .

245

$$m^* = \pm h^2 \left(\frac{d^2 E_k}{dk^2} \right)^{-1} \quad (3)$$

246 The calculated results are summarized in Table 1. The effective electron masses were approximately
 247 0.13 m_0 and 0.30 m_0 , and the effective hole masses are estimated to be approximately 0.18 m_0 and
 248 0.57 m_0 for {010} and {110} surfaces, respectively. In the photocatalytic process, lower effective
 249 mass means higher drift velocity, and the photo-generated hole/electron pairs could be transferred to
 250 the surface of photocatalyst (Li et al., 2014). Therefore, the effective electron mass of {010} was

251 0.13 m₀, obviously lower than that of {110} facets making it favorable for the photocatalytic bromate
252 reduction process.

253

254

Figure 4 (A and B)

255

256 According to the dipole moment and charge transport calculation, the presence of {010} facet
257 exposed BiVO₄ was beneficial for the charge separation. As revealed from the photocurrent of
258 BiVO₄-a, BiVO₄-b and BiVO₄-c in [Figure 4B](#), BiVO₄-b possessed a much higher photocurrent than
259 BiVO₄-a and BiVO₄-c. The intense photocurrent generally means a higher hole/electron pairs
260 separation efficiency ([Li et al.](#)). As shown in [Figure 4B](#), the BiVO₄-b sample with {010} facet
261 exposed maintained a high separation efficiency of hole/electron pairs, which was in well agreement
262 with the result of dipole moment calculations.

263 The intrinsic reason for the separation of photo-generated carriers on the {010} and {110} of
264 BiVO₄ crystal facets was evaluated by the DFT calculation method ([Pan et al., 2011](#)). [Figure 5A](#)
265 shows the density of states (DOS) calculation results (where Fermi energy was set as 0 eV). We can
266 ascertain the conduction band edge and valence band edge from [Figure 5A](#), where the conduction
267 band edge for {110} facets was 1.33 eV, and that for {010} was 2.15 eV. Thus, the energy differences
268 for conduction bands (Δ_{CB}) between {010} and {110} facets was about 0.82 eV. Similarly, we could
269 calculate the Δ_{VB} by analyzing the DOS curves and the result is about 0.20 eV between {010} and
270 {110} facets. The existed difference well demonstrated that the transfer trend of photo-generated
271 electron was from {110} to {010} facets in the thermodynamic view. Within this context, the
272 electrons were accumulated on {010} facets, whereas the holes were enriched on {110} facets. Based
273 on the calculated results obtained in [Figure 5A](#), the schematic diagram of spatial photo-generated
274 carriers separation between {110} and {010} facets is schematic shown in [Figure 5B](#). Furthermore,
275 the Work function (W) calculation results are shown in [Figure 5C](#) and [5D](#). The W of {010} and {110}

276 facets was 6.2 eV and 4.5 eV, respectively. The W value of {010} facets is obvious bigger than that
277 of {110} facets, which makes the {010} facets have a higher electron capture ability (Gao et al.,
278 2011). The results were in line with the density of state (DOS) analysis, where the photo-generated
279 electrons were separated spatially with the photo-generated holes during photocatalytic process to
280 form electron-rich {010} facets and hole-rich {110} facets.

281
282 **Figure 5 (A, B, C and D)**

283
284 For a practical photocatalytic reaction, reduction reactions were accompanied by oxidation
285 reactions. To achieve a high photocatalytic efficiency (in this study, is photocatalytic reduction of
286 bromate), high oxidation reactions involved by photo-generated holes must be considered. To
287 clarify the mechanism deeply, the test of BiVO₄ photocatalyst utilized in water oxidation under
288 visible light irradiation of O₂ evolution with BrO₃⁻ as electron sacrificial agent (NaBrO₃, 0.1 mol L⁻¹)
289 was conducted, and the photocatalytic O₂ evolution performance is shown in Table S4. As shown in
290 Table S4, the BiVO₄-b exhibited the highest oxygen production with the rate of 11.70 μmol h⁻¹, and
291 the order of oxygen production rate was BiVO₄-b (11.70 μmol h⁻¹) >> BiVO₄-a (2.30 μmol h⁻¹) >
292 BiVO₄-c (1.50 μmol h⁻¹). The results evidently confirmed that the BiVO₄-b showed the highest water
293 oxidation, as an overall reaction, the photo-reduction performance was correlated with the oxidation
294 ability. Therefore, the BiVO₄-b sample with an optimized exposure ratio of the {010} and {110}
295 surfaces exhibited the highest photocatalytic bromate reduction activity. The conceivable intrinsic
296 mechanisms are schematically showed in Figure 6. Under the irradiation of visible light,
297 photo-generated carriers were separated toward different surfaces for the polyhedral box shape
298 BiVO₄ photocatalyst, i.e., the photo-generated electrons (thermodynamic potential of 0.49 V, SHE)
299 and photo-generated holes (2.80 V, SHE) were transferred to different facets of BiVO₄ crystal. As
300 shown in Figure 6, the {010} facets were the electron-rich surfaces, whereas the holes were

301 accumulated on the {110} surfaces. The electron with a redox potential of 0.49 V was a robust
302 reductive for bromate reduction ($\text{BrO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Br}^- + 3\text{H}_2\text{O}$, $E^\ominus = 1.423 \text{ V}$). And
303 photo-generated hole with a high redox potential of 2.80 V could decompose H_2O to produce oxygen
304 efficiently ($2\text{H}_2\text{O} - 4\text{e}^- \rightarrow \text{O}_2 + 4\text{H}^+$, $E^\ominus = 1.23 \text{ V}$). In this manner, BrO_3^- could be regarded as the
305 electron acceptor and *in-situ* reduced at {010} facets, while the water oxidation reaction was
306 occurred at {110} surfaces to produce O_2 . The photo-generated electron-hole pairs were spatially
307 separated, and the oxidation and reduction reactions occurred at different crystal facets; thus, a high
308 bromate reduction efficiency and selectivity on BiVO_4 single crystal with optimized {010} and {110}
309 ratio could be achieved. Besides, a systemic comparison with conventional photocatalyst of TiO_2 ,
310 traditional bulk BiVO_4 or Bi_2MoO_6 documented from literature is summarized in [Table S5](#). The
311 BiVO_4 -b sample with active exposed facets ratio could remove almost 100% of BrO_3^- , whose kinetic
312 constant was significantly higher than that of other conventional photocatalysts.

313

314

Figure 6

315

316 **Conclusions.** To achieve efficient removal of BrO_3^- , we herein developed single crystal
317 photocatalysts BiVO_4 with different exposed facets. The {010} facets are exposed electron-rich
318 surfaces with a higher dipole moment and a lower effective mass of electrons/holes, which is more
319 favorable for the photocatalytic bromate reduction reaction. Under visible light illumination, the
320 photo-generated reductive electrons and oxidative photo-generated holes are spatially transported to
321 {010} and {110} facets, respectively. During the bromate photocatalytic removal process, water acts
322 as an electron donor, thus avoiding the risk of secondary pollution, making the BrO_3^- removal of
323 high efficiency. This investigation provides a simple and effective strategy for enhanced degradation
324 of bromate without complicated preparation procedure, which makes the bromate removal more
325 efficient and sustainable, and also gives a guideline for the development of single crystal

326 photocatalyst for bromate photocatalytic reduction.

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Table List

Table 1 Summary of the effective masses

	{010}/m ₀	{110}/m ₀
m _h [*]	0.18	0.57
m _e [*]	0.13	0.30

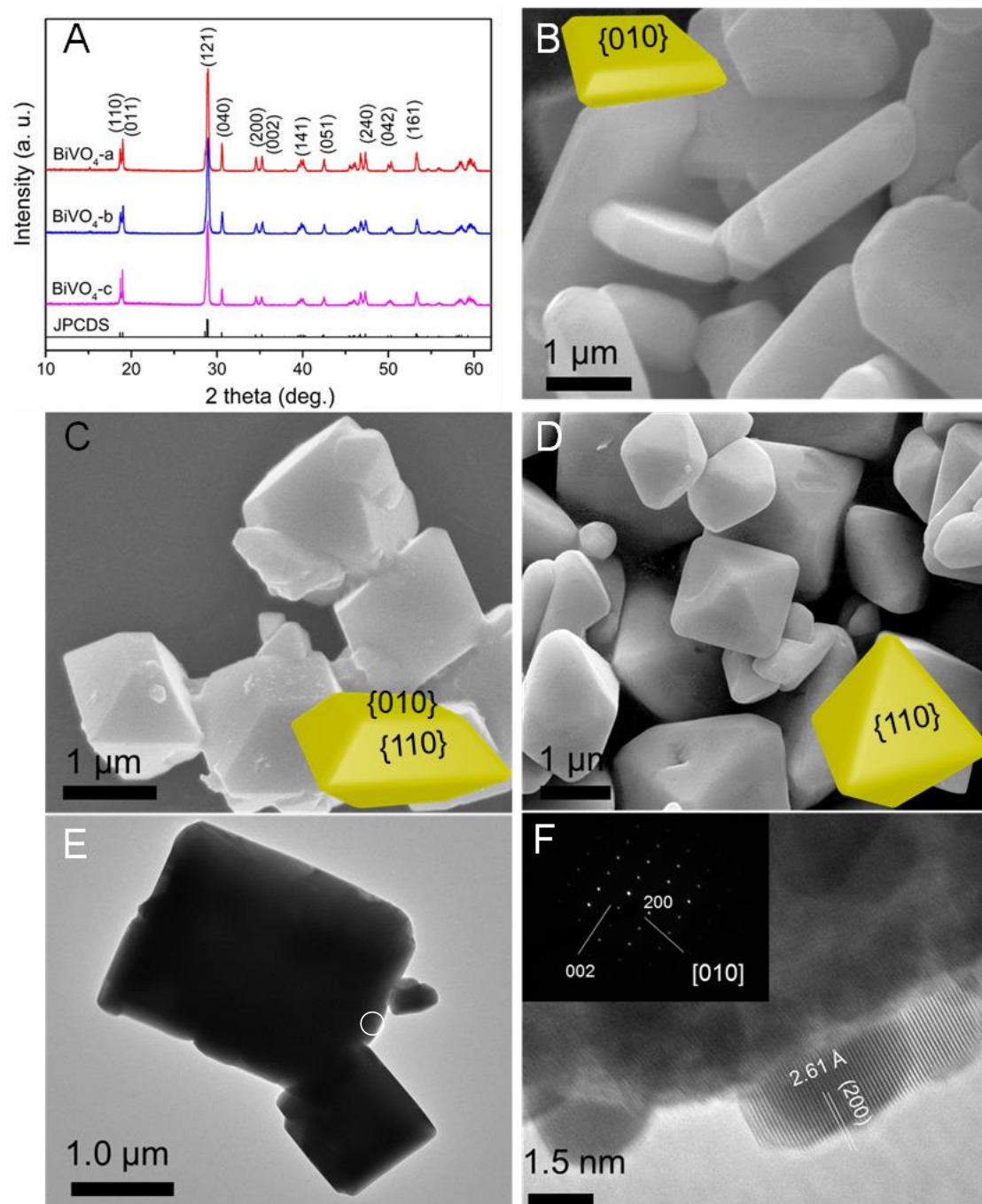


Figure 1 XRD patterns of (A) BiVO₄ samples, SEM pictures of (B) BiVO₄-a, (C) BiVO₄-b, (D) BiVO₄-c, (E) TEM and HRTEM (F) pictures of BiVO₄-a.

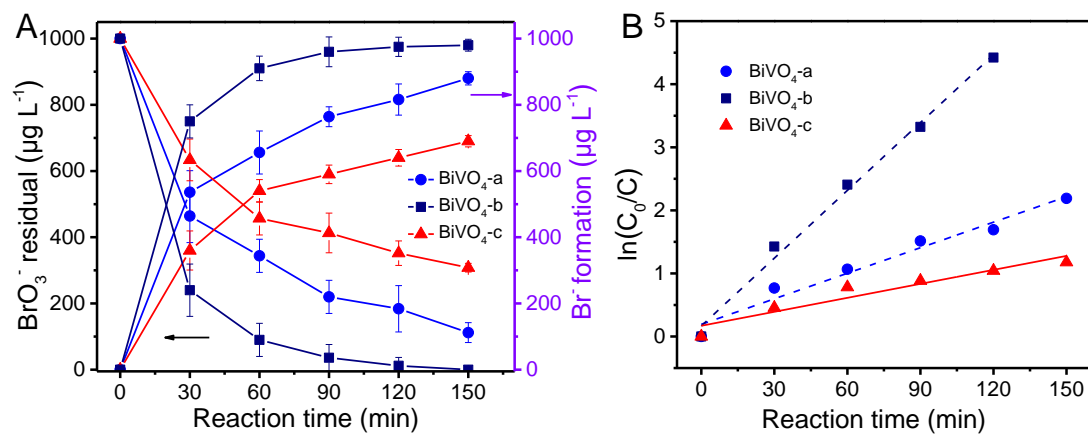


Figure 2 Time course of (A) photocatalytic reduction of BrO_3^- by BiVO_4 photocatalysts under visible light irradiation at $\text{pH } 7.1 \pm 0.4$, (B) the corresponding kinetics rate constants derived from A.

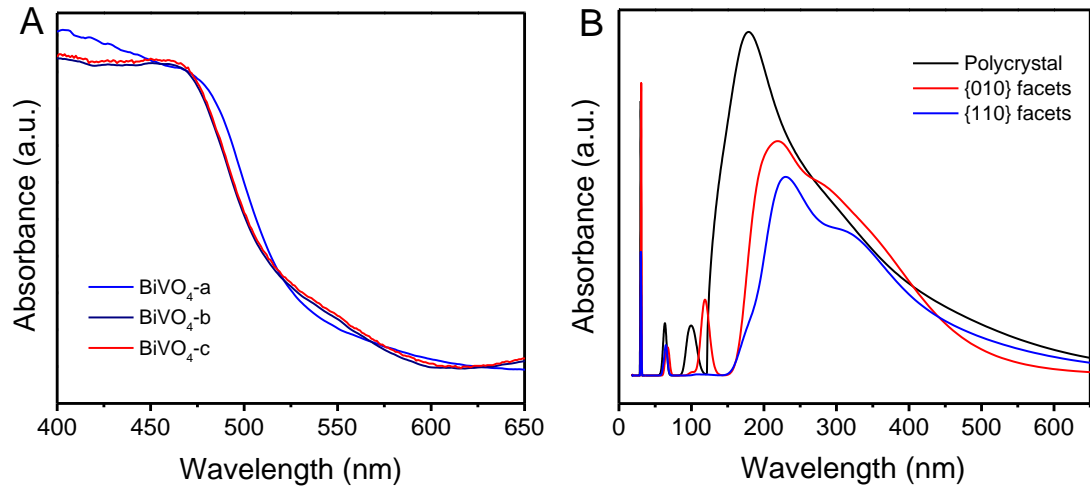


Figure 3 (A) The experimental diffuse reflectance spectra of BiVO₄ samples, (B) calculated absorption coefficient of polycrystal BiVO₄, {010} and {110} facets exposed BiVO₄.

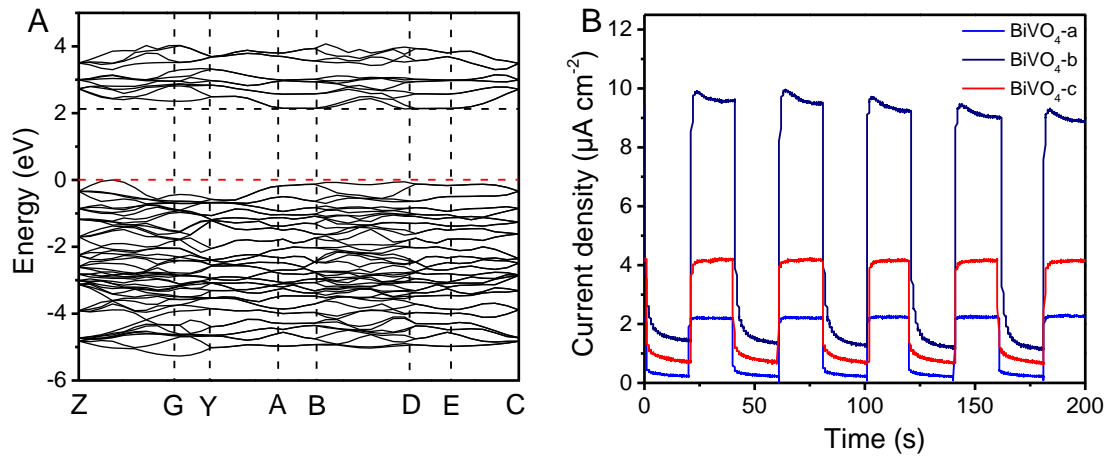


Figure 4 The band structure (A) of BiVO₄ crystal and (B) photocurrent-time curve of BiVO₄ samples.

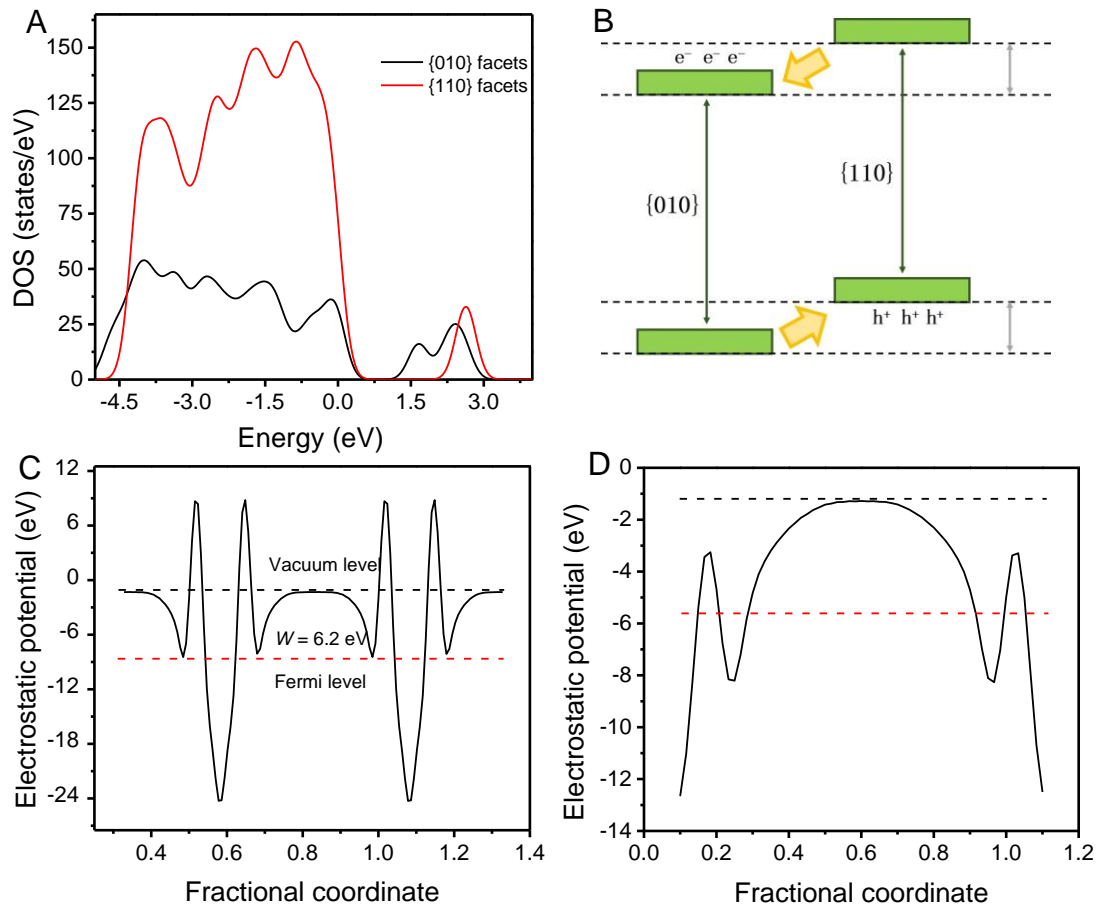


Figure 5 (A) The differences of the energy levels in conduction bands (Δ_{CB}) for {010} and {110} facets, (B) the scheme of carrier separation between {010} and {110} facets, (C) the workfunction (W) of {010} surface and (D) {110} surface.

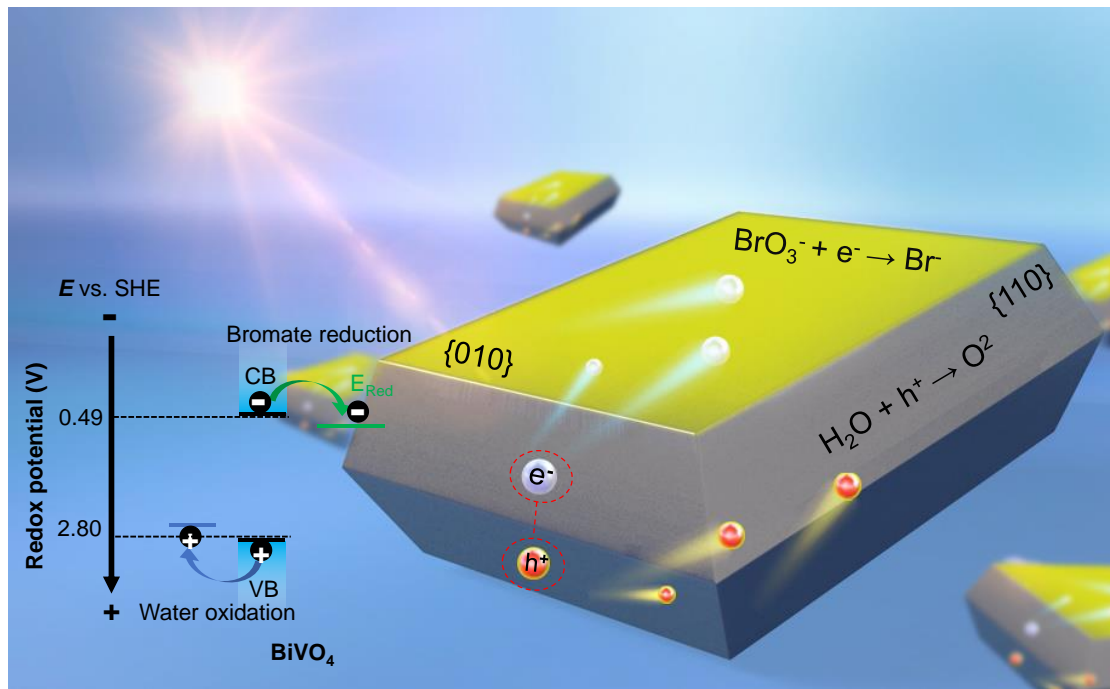


Figure 6 Schematic illustration of photocatalytic reduction of BrO_3^- by $BiVO_4$ -b.