

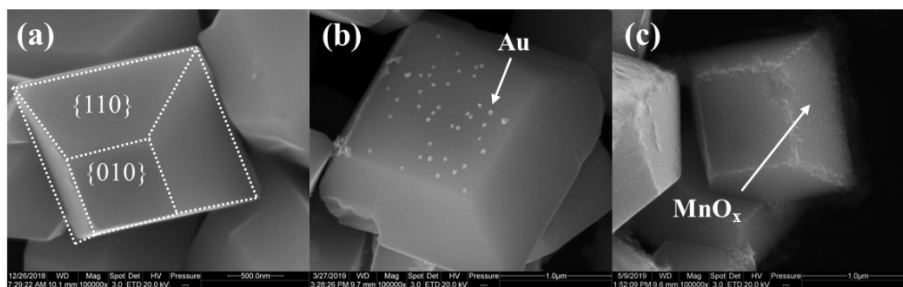
## Supplementary Information

# Surface etching to tune the behaviors of photogenerated charges on decahedron BiVO<sub>4</sub> crystal for efficient photocatalysis

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**Fig. S1** SEM images of (a) BiVO<sub>4</sub>, (b) Au/BiVO<sub>4</sub>, (c) MnO<sub>x</sub>/BiVO<sub>4</sub>.

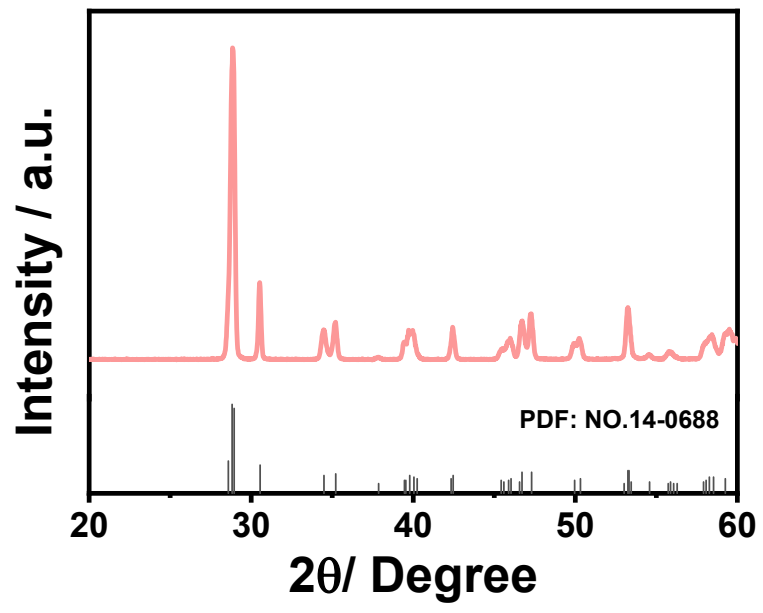


Fig. S2 XRD pattern of BiVO<sub>4</sub> sample.

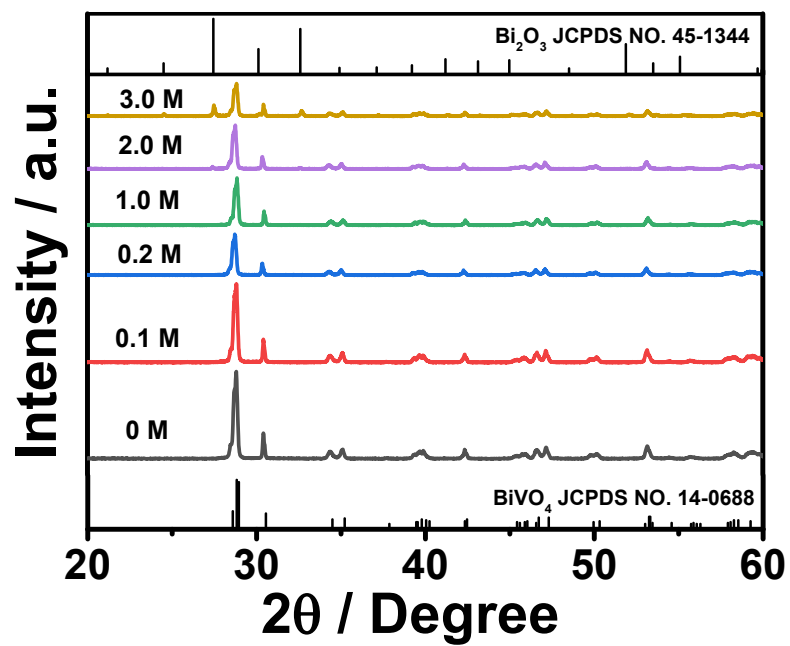
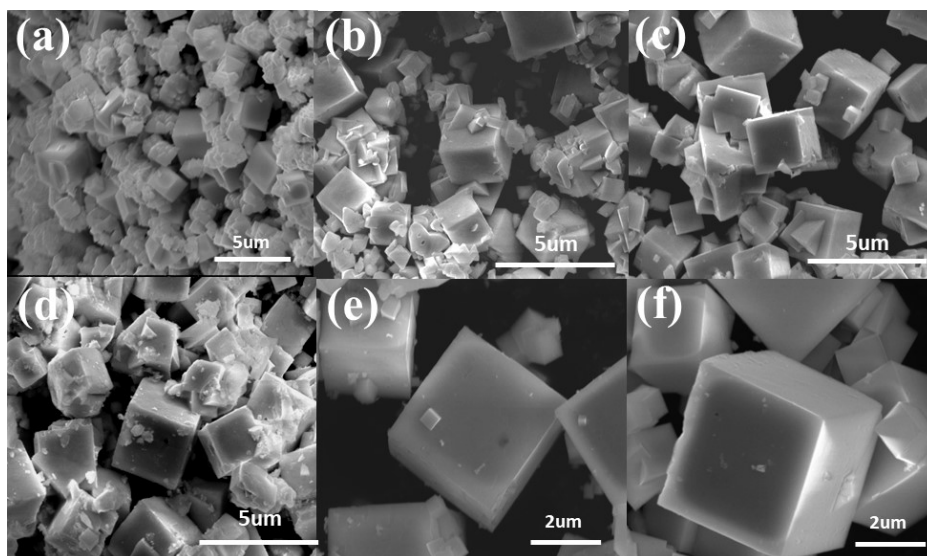


Fig. S3 XRD patterns of BiVO<sub>4</sub> samples etched in NaOH solution with different concentration.



**Fig. S4** SEM images of BiVO<sub>4</sub> samples etched in 4.0 M NaOH solution for (a) 2 h, (b) 3 h, (c) 4 h, (d) 6 h (e) 8 h and (f) 24 h.

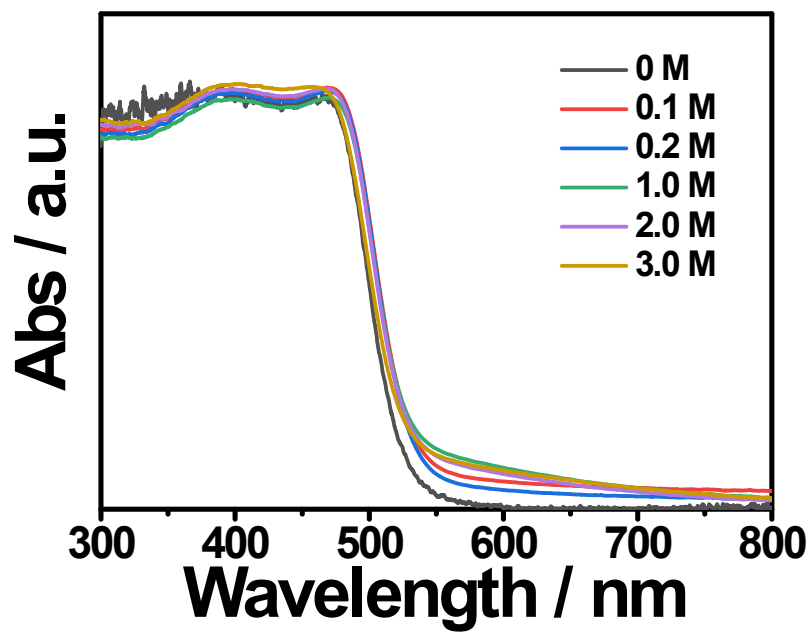
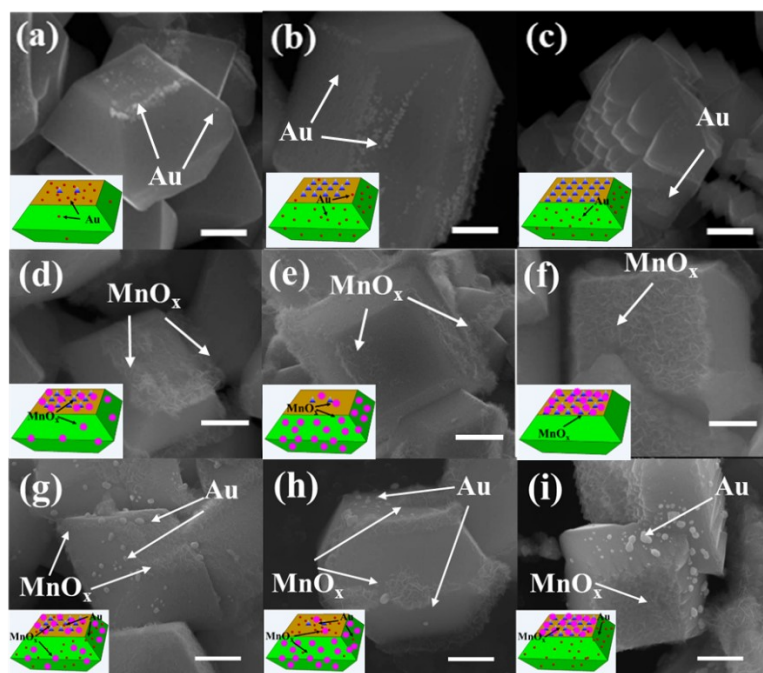
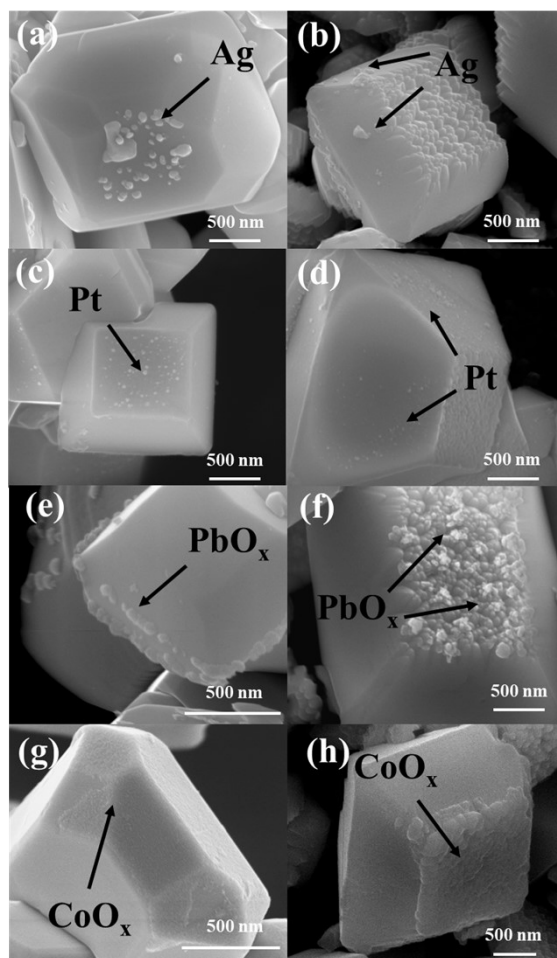


Fig. S5 UV-Vis spectra of BiVO<sub>4</sub> samples etched in NaOH solution with different concentration.



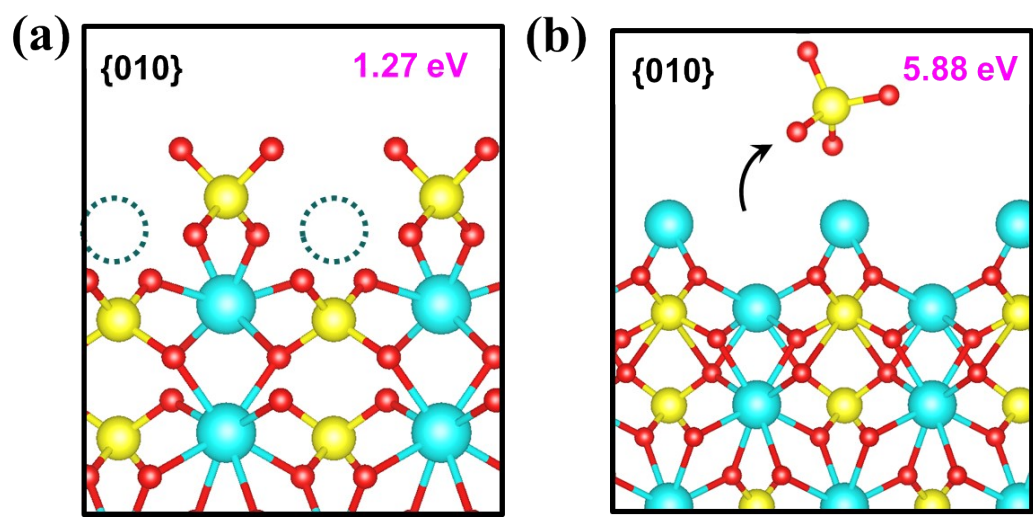
**Fig. S6** SEM images of etched  $\text{BiVO}_4$  crystals with photoreduction-deposition of Au (a) 0.2 M; (b) 1.0 M; (c) 3.0 M. SEM images of etched  $\text{BiVO}_4$  crystals with photooxidation-deposition of  $\text{MnO}_x$  (a) 0.2 M; (b) 1.0 M; (c) 3.0 M. SEM images of etched  $\text{BiVO}_4$  crystals with photo-deposition of Au and  $\text{MnO}_x$  (a) 0.2 M; (b) 1.0 M; (c) 3.0 M. The contents of the deposited Au and  $\text{MnO}_x$  are 0.5 wt.% and 2.0 wt.%, respectively. Scale bar, 500 nm.



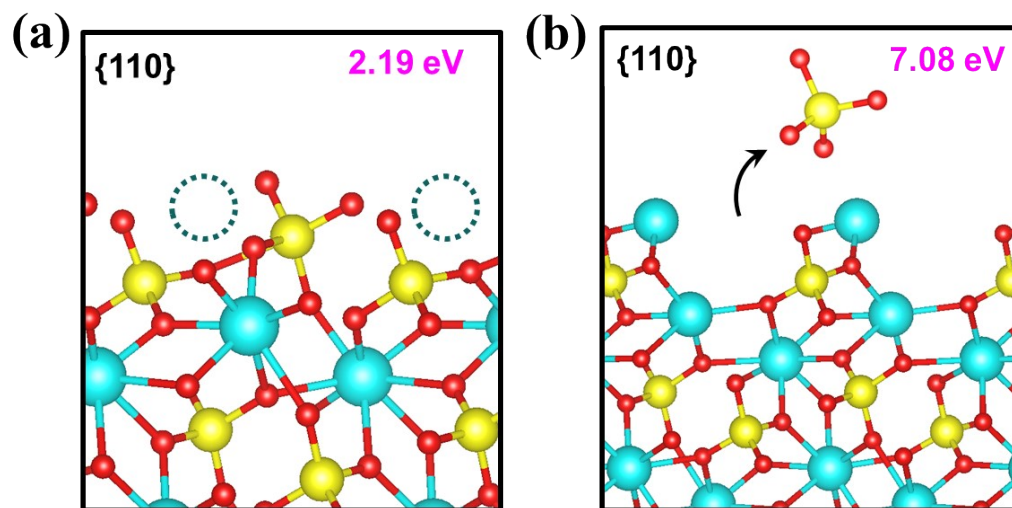
**Fig. S7** SEM images of decahedron  $\text{BiVO}_4$  crystals (a,c,e,g) and etched  $\text{BiVO}_4$  crystals (b,d,e,f) with photoreduction-deposition of Ag, Pt,  $\text{PbO}_x$  and  $\text{CoO}_x$ . The contents of the deposited Ag, Pt,  $\text{PbO}_x$  and  $\text{CoO}_x$  are 0.5 wt.%.

Ag and Pt particles were selectively deposited on  $\{010\}$  facets of decahedron  $\text{BiVO}_4$ , while deposited on  $\{110\}$  facets after surface etching, indicating that photogenerated electrons selectively accumulate on  $\{010\}$  facets of decahedron  $\text{BiVO}_4$ , while transferring to  $\{110\}$  facets after surface etching. In addition,  $\text{PbO}_x$  and  $\text{CoO}_x$  species were selectively deposited on  $\{110\}$  facets of decahedron  $\text{BiVO}_4$ , while deposited on the etched region, indicating that photogenerated holes selectively accumulate on  $\{110\}$  facets of decahedron  $\text{BiVO}_4$ , while transferring to etched region after surface etching.

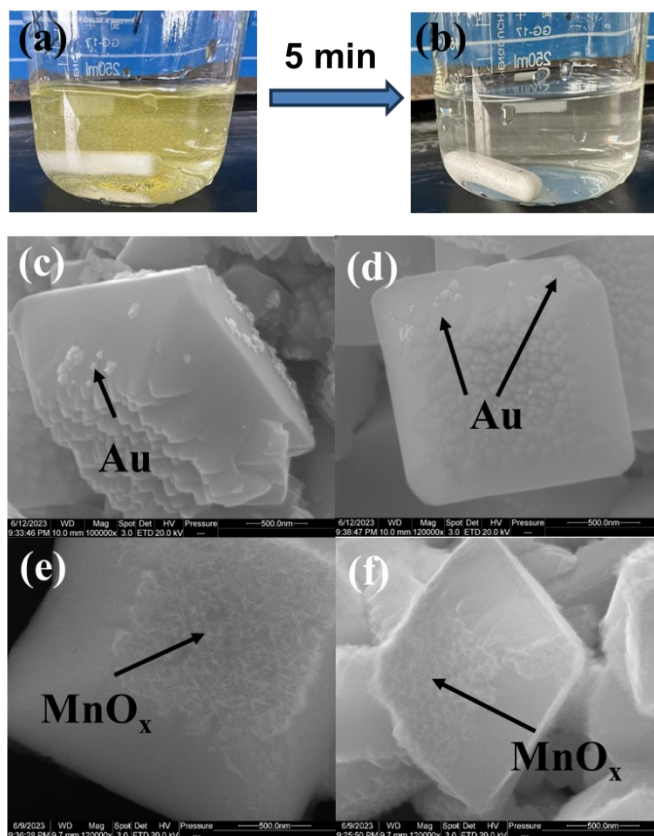




**Fig. S8** The simulated structure of  $\{010\}$  facets of decahedron  $\text{BiVO}_4$  with (a) Bi vacancies and (b)  $\text{VO}_4$  defects.



**Fig. S9** The simulated structure of  $\{110\}$  facets of decahedron  $\text{BiVO}_4$  with (a) Bi vacancies and (b)  $\text{VO}_4$  defects.



**Fig. S10** The images of Bi<sub>2</sub>O<sub>3</sub> (a) before and (b) after treated in 0.1 M HNO<sub>3</sub> solution. SEM images of etched BiVO<sub>4</sub> crystals treated in 0.1 M HNO<sub>3</sub> with photoreduction-deposition of (c,d) Au, (e,f) MnO<sub>x</sub>. The contents of the deposited Au and MnO<sub>x</sub> are 0.5 wt.% and 2.0 wt.%, respectively.

The Etched BiVO<sub>4</sub> crystal was treated in 0.1 M HNO<sub>3</sub> solution for 5 minutes, and ultrapure water for 3 times and dried at 353 K overnight. Then the obtained etched BiVO<sub>4</sub> particles were re-suspended in the solution and followed by photodeposition of Au and MnO<sub>x</sub>. Au particles were selectively deposited on {110} facets of the etched BiVO<sub>4</sub> crystal after treated in 0.1 M HNO<sub>3</sub> solution, while MnO<sub>x</sub> species were selectively deposited on the etched region of BiVO<sub>4</sub> crystal.

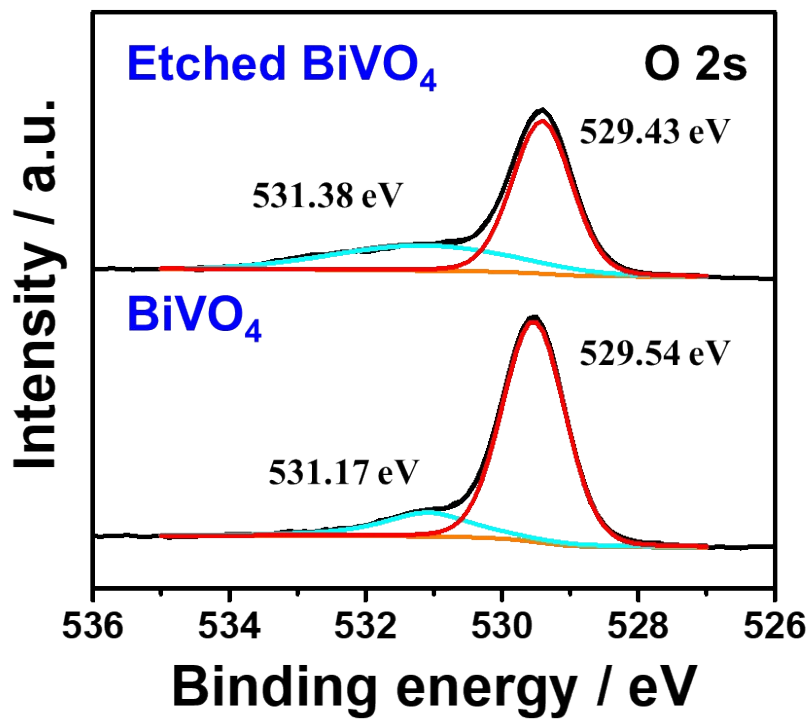


Fig. S11 XPS spectra of BiVO<sub>4</sub> and etched BiVO<sub>4</sub>.

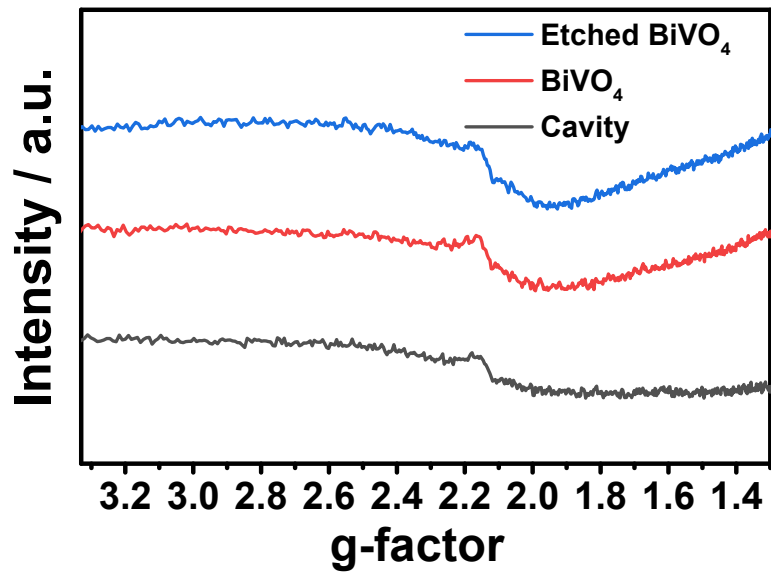
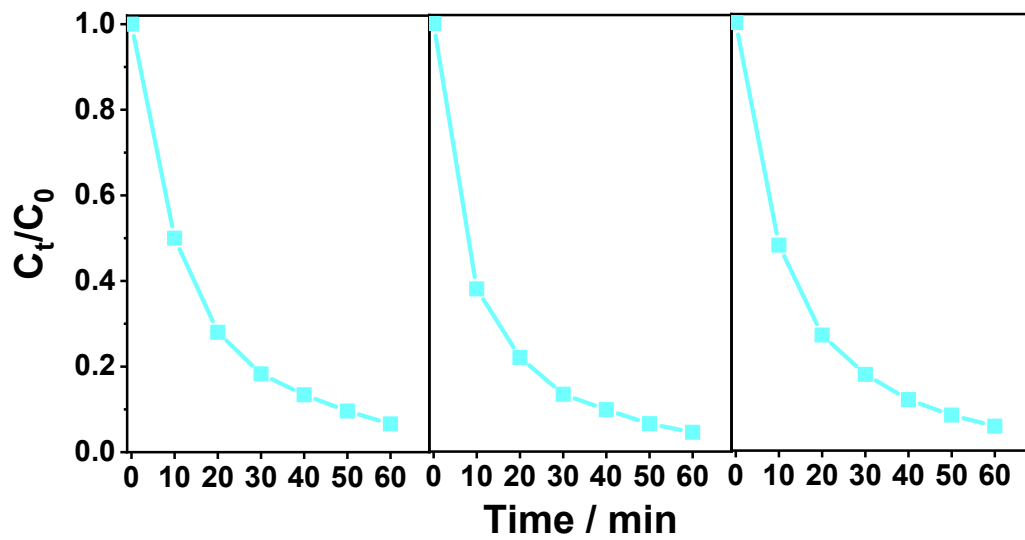
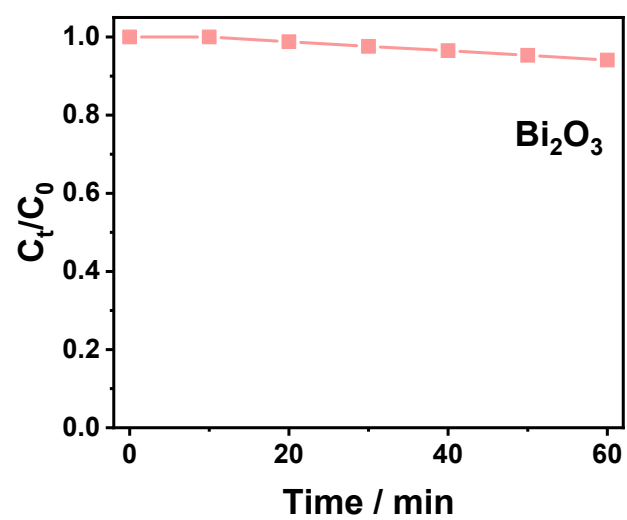


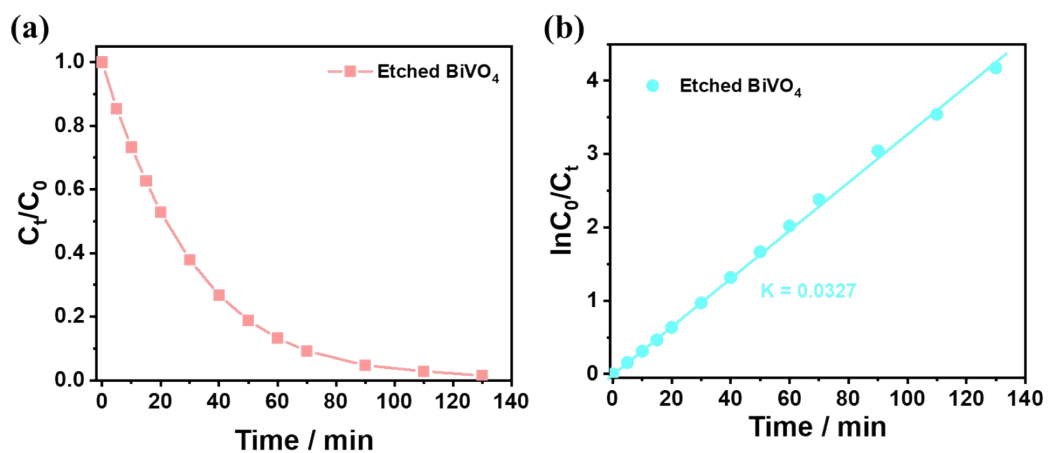
Fig. S12 EPR spectra of BiVO<sub>4</sub> and etched BiVO<sub>4</sub> samples.



**Fig. S13** The cycling tests for photocatalytic degradation of methyl blue over etched  $\text{BiVO}_4$ . Reaction conditions: catalyst, 200 mg;  $10.0 \text{ mg L}^{-1}$  methyl blue, 100 mL; light source, Xe lamp (300 W).



**Fig. S14** Photocatalytic degradation of methyl blue over  $\text{Bi}_2\text{O}_3$  crystal. Reaction conditions: catalyst, 200 mg;  $10.0 \text{ mg L}^{-1}$  methyl blue, 100 mL; light source, Xe lamp (300 W).  $\text{Bi}_2\text{O}_3$  crystal was prepared by treating  $\text{BiVO}_4$  in 4.0 M NaOH for 24 h.



**Fig. S15** (a) Photocatalytic degradation of m-cresol over etched BiVO<sub>4</sub> crystal. (b) Corresponding rate constants of m-cresol degradation from (a). Reaction conditions: catalyst (the BiVO<sub>4</sub> particles treated in 2.0 M NaOH solution for 2.5 hours), 200 mg; 5.0 mg L<sup>-1</sup> m-cresol, 100 mL; light source, Xe lamp (300 W).



**Table S1** The atomic ratios of  $O_L$  and  $O_B$  in etched  $\text{BiVO}_4$  and pristine  $\text{BiVO}_4$  calculated according to XPS patterns.

<b>Sample</b>	<b><math>V_L</math></b>	<b><math>V_B</math></b>
<b><math>\text{BiVO}_4</math></b>	83.2%	16.8%
<b>Etched <math>\text{BiVO}_4</math></b>	67.9%	32.1%