Supporting Information

Defect engineering in atomically-thin bismuth oxychloride towards photocatalytic oxygen evolution

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The details of density functional theory (DFT) calculations

Code: GPAW

Method: projector-augmented wave (PAW)

Basis: Plane wave

Pseudopotential: PBE

Convergence criterion:

Energy: 0.0005, # eV / electron

Density: 1.0e-4,

Eigenstates: 4.0e-8, # eV^2 / electron

Bands: occupied,

Forces: float('inf')) # eV / Ang Max

k-points:

bulk material: 12*12 *12 f

(001) 2d surface 12 *12 *1

(110) 1d surface 1*12 *1

Defect rich surface 1*12 *1
Figure S1. AFM images of (a) BiOCl materials and (b) defect-rich BiOCl ultrathin nanosheets.

Figure S2. XPS spectra of BiOCl and defect-rich BiOCl materials, (a) Survey of the sample, (b) Bi 4f, (c) O 1s, (d) Cl 2p.
Figure S3. XPS valence band spectra of BiOCl and defect-rich BiOCl.

Figure S4. $(\alpha E_{\text{photon}})^{1/2}$ vs. $E_{\text{photon}}$ curves of the as-prepared BiOCl and defect-rich BiOCl sample.
Figure S5. Steady-state photoluminescence (PL) spectra of the BiOCl and defect-rich BiOCl materials.

Figure S6. Electrochemical impedance spectroscopy (EIS) of BiOCl and defect-rich BiOCl materials.
Figure S7. (a) Crystal structure of defects-rich BiOCl, (b) DOS diagrams from first-principles simulations for defects-rich BiOCl (001) and defects-rich (110) facets.

Figure S8. Calculated DOS of atomically-thin BiOCl nanosheets and defect-rich BiOCl, (a) (001) and (b) (110) facets.
**Figure S9.** Characterizations of bulk BiOCl. (a) XRD pattern and (b) TEM image.

**Figure S10.** Photocatalytic degradation of ENR in the presence of BiOCl and defect-rich BiOCl materials under light irradiation.
Figure S11. ESR spectra of the DMPO-O$_2$$^\cdot$ adducts and DMPO-·OH recorded with (a, b) BiOCl and (c, d) defect-rich BiOCl under UV light irradiation.