### Supplementary Information

## Improving the Photo-oxidative Capability of BiOBr via

# **Crystal Facet Engineering**

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Fig. S1 XPS spectra of BiOBr-010 and BiOBr-001 for; (a) Bi 4f, (b) Br 3d and (c) O 1s regions.



Fig. S2 Photocatalytic activities of as-prepared BiOBr samples (a) photocatalytic water oxidation in the presence of AgNO<sub>3</sub>, photocatalyst loading = 150 mg, suspension volume = 150 mL; (b) aqueous phase formic acid photo-oxidation, photocatalyst loading = 50 mg, suspension volume = 50 mL.



Fig. S3 Plot of photocurrent versus time for (a) BiOBr-001 and (b) BiOBr-010. Inset: theoretical amounts of  $H_2$  and  $O_2$  evolved based on the photocurrent densities.



Fig. S4 (a) Raman spectra and (b) Bi 4f spectra of BiOBr-001 and BiOBr-010. The Raman band at 90 cm<sup>-1</sup> and peaks at ~163.0 eV and ~157.5 eV in the Bi 4f spectra (indicated by the black arrows) demonstrate the presence of oxygen vacancies in the two materials.

### Apparent quantum yield of formic acid degradation

#### **Materials**

Potassium trisoxalatoferrate (III) ( $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ ) crystals used for the actinometric measurements were synthesized by reacting aqueous iron (III) chloride (FeCl<sub>3</sub>) and potassium oxalate ( $K_2C_2O_4 \cdot H_2O$ ) as described elsewhere.<sup>1</sup>

A standard Fe(II) stock solution of known concentration (0.001137 mol·L<sup>-1</sup>) for calibration purposes was prepared from Mohr's salt ( $(NH_4)_3Fe(SO_4)_2 \cdot 6H_2O$ ) dissolved in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution and kept in the dark after preparation.

In addition, a 1.0 M sodium acetate (CH<sub>3</sub>COONa), a 0.50 M and 0.05 M H<sub>2</sub>SO<sub>4</sub> mixed and a 0.05 M 1,10-phenanthroline ligand stock solution were prepared.

#### **Calibration of Fe(II)**

Different concentrations of a Fe(II) standard solution were prepared as follows: certain volumes of Fe(II) stock solution in water (650  $\mu$ L in total), 1150  $\mu$ L of 1.0 M sodium acetate, 750  $\mu$ L of 0.50 M H<sub>2</sub>SO<sub>4</sub> and 25  $\mu$ L ligand solution were prepared as standards for the calibration curve. The UV-vis absorbance curves of the calibration and analytical samples were recorded by a Shimadzu UV 3600 spectrophotometer. The calibration curve (Fig. S5) was obtained from the absorbance values at 510 nm, which is where the absorption maxima is located.



Fig. S5 Calibration curve of Fe(II) for actinometric experiments.

### **Actinometric measurements**

For the actinometic measurements, 26.6 mg of the as-prepared  $K_3[Fe(C_2O_4)_3].3H_2O$  crystals was dissolved in 50 mL of 0.05 M H<sub>2</sub>SO<sub>4</sub> solution and then transferred into the spiral reactor used for the formic acid degradation experiments. After 10 mins light irradiation, 50 µL of irradiated sample was removed and mixed with the stock solution as described above. Based on the calibration curve and measured absorbance value, the concentration of Fe(II) formed during illumination was estimated, thus, the number of incident photons was determined.

The number of absorbed photons was determined on the basis of the following equation:

 $2[Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow 2[Fe(C_2O_4)_2]^{2-} + 2CO_2 + C_2O_4^{2-}$ 

In this process, the photoreduction of  $[Fe(C_2O_4)_3]^3$ -occurs whereby one Fe-complex can absorb a photon of light to form Fe(II).<sup>2</sup>

#### References

- 1. C. Hatchard and C. A. Parker, 1956.
- 2. I. P. Pozdnyakov, O. V. Kel, V. F. Plyusnin, V. P. Grivin and N. M. Bazhin, *The Journal of Physical Chemistry A*, 2008, **112**, 8316-8322.