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Supporting Information

Thermally Induced Oxygen Vacancies in BiOCl Nanosheets and Their Impact on Photoelectrochemical Performance**

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Supporting information

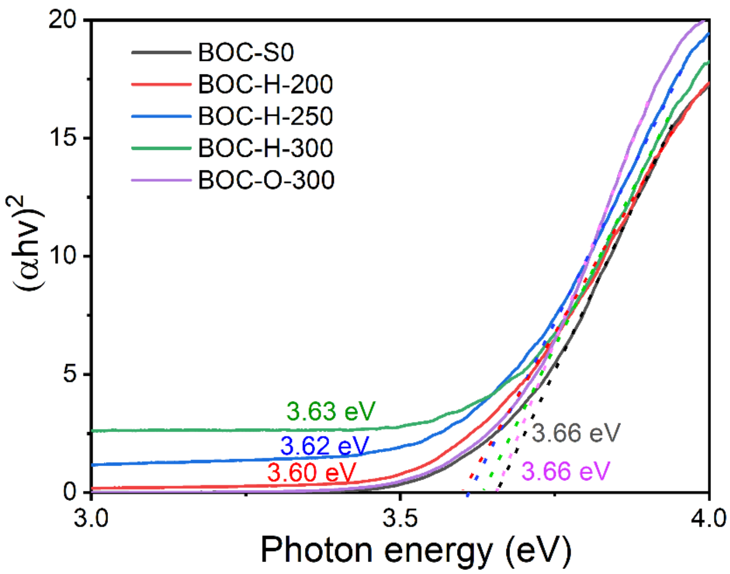

Fig. S1. Tauc plots of as-prepared BiOCl samples assuming direct band gaps. Their bandgaps of direct optical absorption are determined at around 3.6 eV.

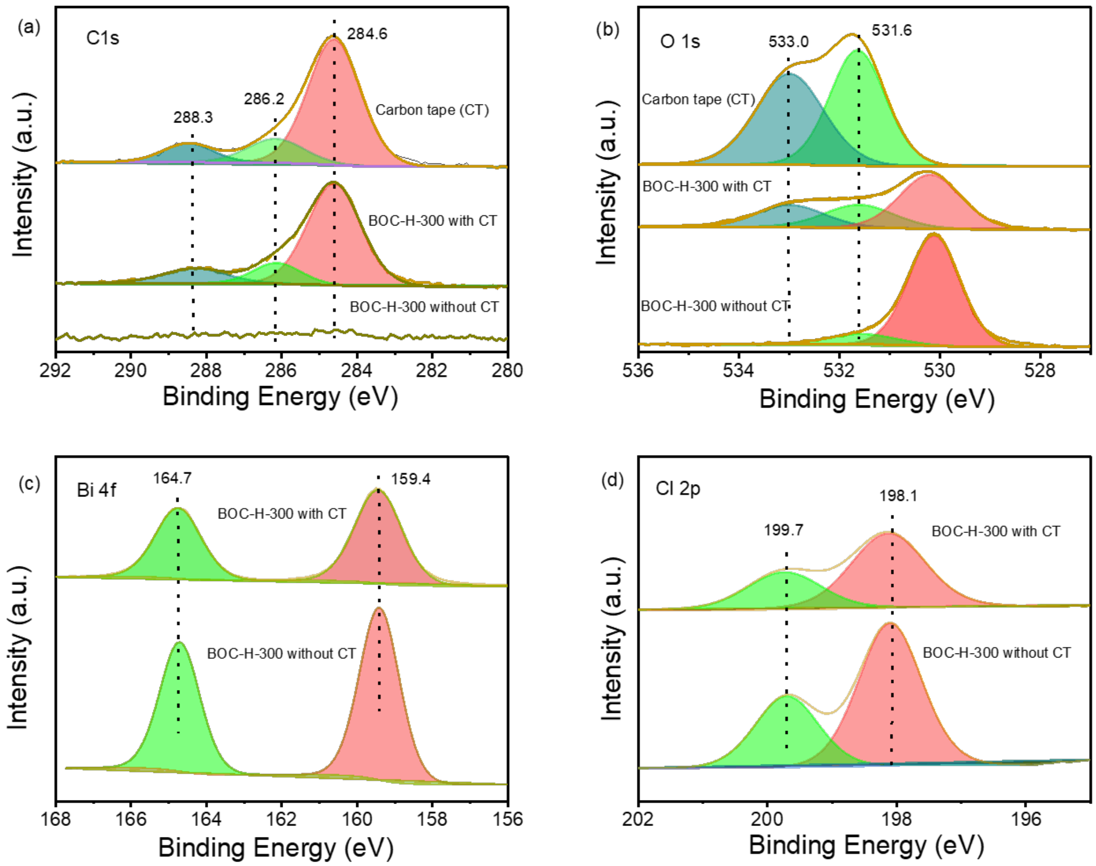

Fig. S2. C 1s, O 1s, Bi 4f and Cl 2p high resolution XP spectra of carbon tape and BOC-H-300, measured at 298 K. As shown in (a), C 1s peaks of BOC-H-300 are completely originated from conductive carbon tape (CT). O 1s peaks at 531.6 eV and 533.0 eV which is attributed to absorbed oxygen species are dominantly resulted from signals of CT(b), while no shifts are discovered in Bi 4f (c) and Cl 2p spectra (d).

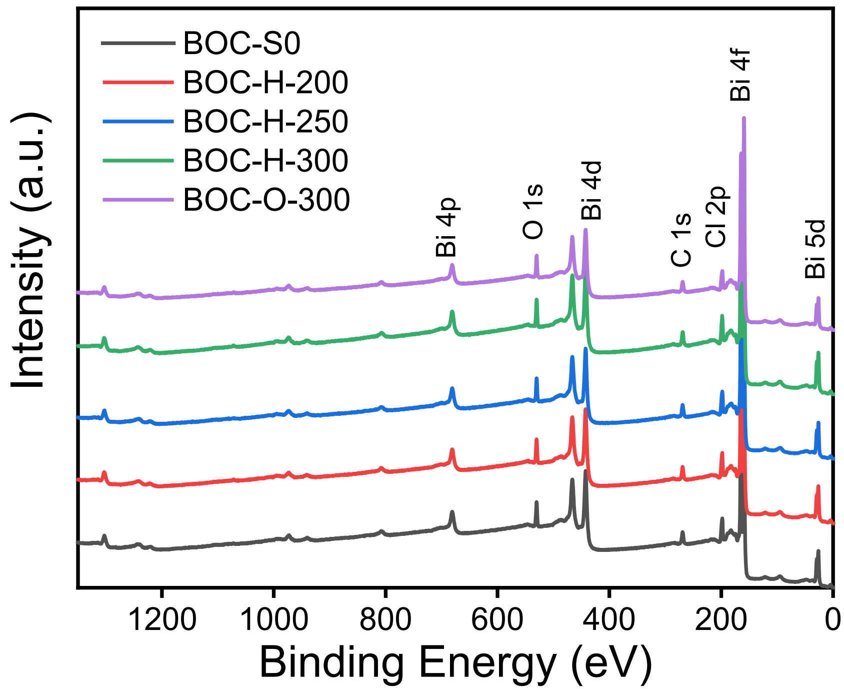

Fig. S3. Survey XP spectra of BiOCl samples.

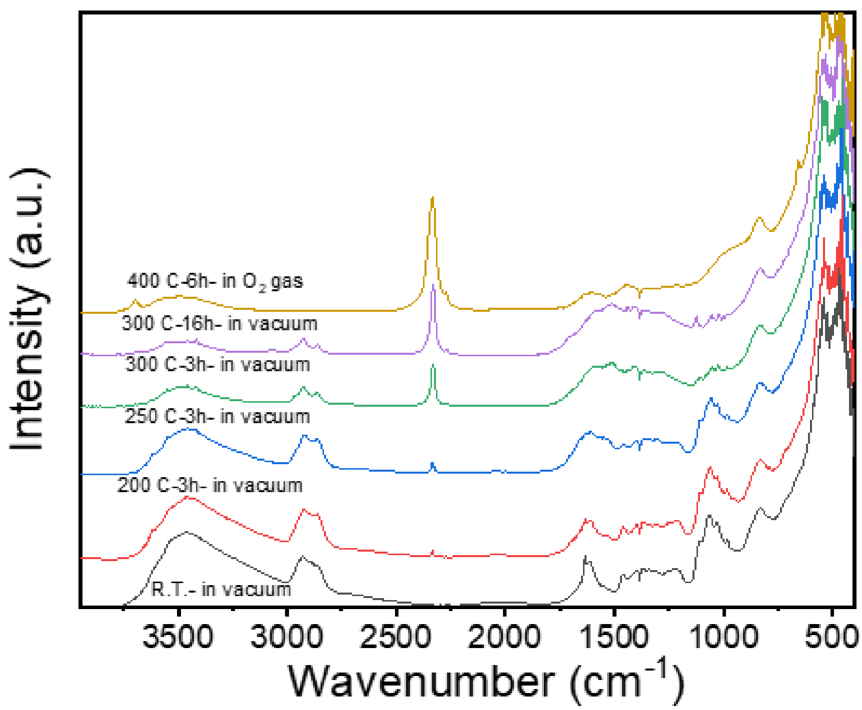

Fig. S4. Full *in-situ* DRIFTS of pristine BOC-S0 sample after heat treatment, measured in static vacuum (< 1 mbar) at 298 K.

Calculation of donor densities using the Mott-Schottky equation.

According to the classical Mott-Schottky relationship, the equation can be written as [1]:

$$\frac{1}{C_{sc}} = \frac{2}{e\varepsilon_0\varepsilon_r N_D \cdot A^2}(V - V_{fb} - \frac{kT}{e})$$

C_{sc} is the space charge layer capacitance of the semiconductor, N_D is the donor density, e is elementary charge 1.60 × 10^{-19} C, ε_0 is the dielectric constant in vacuum which is equal to 8.85 × 10^{-14} F cm^{-1}, ε_r is relative dielectric constant of the material with ε_r(BiOCl) = 6.74 [2]. A is the actual surface area which can be calculated from the mass and the BET data of the used material, V_{fb} is the flat band potential, k Boltzmann constant, T temperature in Kelvin.

From the Mott-Schottky formula, the donor density can be obtained as follows:

$$N_D = \frac{2}{e\varepsilon_0\varepsilon_r \cdot slope \cdot A^2}$$

For instance, the slope of sample BOC-S0 is 18.5 ×10^{10} F^{-2} V^{-1}, the BET specific surface area is 19.5 m^2 g^{-1}, 100 mg sample is used for preparation of 2.2 mL slurry solution. 100 µL of that is taken out and dropped onto 2×2 cm^2 glasses. The effective irradiation area is 0.283 cm^2. Herein, the actual (i.e., PEC active) mass of BOC-S0 on the photoelectrode can be calculated.

$$m_a = \frac{100\ mg \times 100\ \mu L \times 0.283\ cm^2}{2200\ \mu L \times 2\ cm \times 2\ cm} = 0.322\ mg$$

The actual BET derived surface area $A = 0.322\ mg \times 19.5\ m^2\ g^{-1} = 62.7\ cm^2$

From this follows the donor density of sample BOC-S0

$$N_D = \frac{2}{1.6\ \times 10^{-19}\ C \times 8.85 \times 10^{-14}\ F\ cm^{-1} \times 6.74 \times 18.5\ \times 10^{10}\ F^{-2}\ V^{-1} \times 62.7^2\ cm^4}$$
$$= 2.88 \times 10^{16}\ cm^{-3}$$

References

[1] B. Bera, A. Chakraborty, T. Kar, P. Leuaa, M. Neergat, *J. Phys. Chem. C* **2017,** 121, 20850-20856.

[2] L. Zhao, X. Zhang, C. Fan, Z. Liang, P. Han, *Physica B: Condensed Matter* **2012,** 407, 3364-3370.