## Supporting Information

Improved water oxidation under visible light on oxyhalide  $Bi_4MO_8X$  (M = Nb, Ta; X = Cl, Br) photocatalysts prepared using excess halogen precursors

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Fig. S1 Lattice constants of the prepared BMOX samples calcined at various temperatures between 973 and 1173 K.



Fig. S2 XRD patterns and photographic images of the residual crystals formed on the inner walls of the quartz silica-tubes.



Fig. S3 SEM images of the BNOB samples calcined at (a) 973 K, (b) 1073 K, and (c) 1173 K, and the ex-BNOB samples calcined at (d) 1073 K and (e) 1173 K.



Fig. S4 SEM images of the BTOC samples calcined at (a) 973 K, (b) 1073 K, and (c) 1173 K, and the ex-BTOC samples calcined at (d) 1073 K and (e) 1173 K.



Fig. S5 SEM images of the BTOB samples calcined at (a) 973 K, (b) 1073 K, and (c) 1173 K, and the ex-BTOB samples calcined at (d) 1073 K and (e) 1173 K.

Table S1 Initial rates of  $O_2$  evolution and atomic ratios determined by XPS and EDX for the BTOC samples prepared using different excesses of BiOCl and calcined at 1073 K

	Initial rate of O <sub>2</sub>	Atomic ratio	
<b>BiOX Excess</b>	evolution	CI/Bi	CI/Bi
	(µmol h⁻¹)	(XPS)	(EDX)
0 mol%	17.5	0.24	0.24
5 mol%	69.1	0.25	0.26
10 mol%	62.5	0.25	0.26
15 mol%	56.0	0.25	0.26



Fig. S6 Time course of O<sub>2</sub> evolution from ex-BTOC in an aqueous AgNO<sub>3</sub> solution (5 mM) under visible light irradiation ( $\lambda > 400$  nm). The induction period should be due to diffusion of the product for detection.



Fig. S7 Initial rates of O<sub>2</sub> evolution from the BTOX samples prepared using a stoichiometric precursor ratio in the presence of excess (5 mol%) KX (X = Cl, Br), (5 mol%) BiOX (X = Cl, Br), or (2.5 mol%) Bi<sub>2</sub>O<sub>3</sub> and calcined at 1073 K. The photocatalytic reaction was carried out in an aqueous AgNO<sub>3</sub> solution (5 mM) under visible light irradiation ( $\lambda$  > 400 nm).