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Modification of oxyhalide solid-solution photocatalyst with efficient O_2-evolving cocatalyst and electron mediator for two-step photoexcitation overall water splitting

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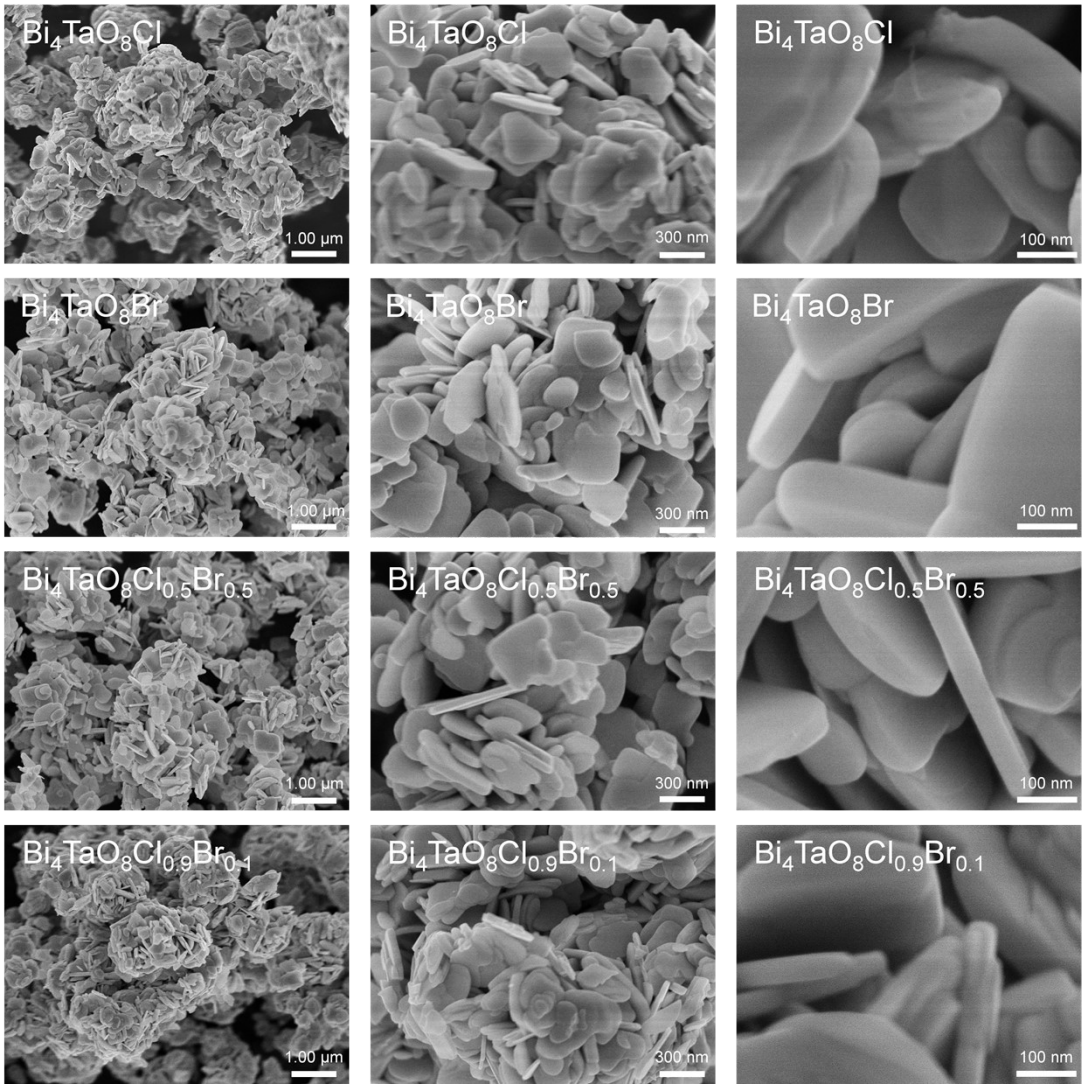

Fig. S1 SEM images of four oxyhalide samples.

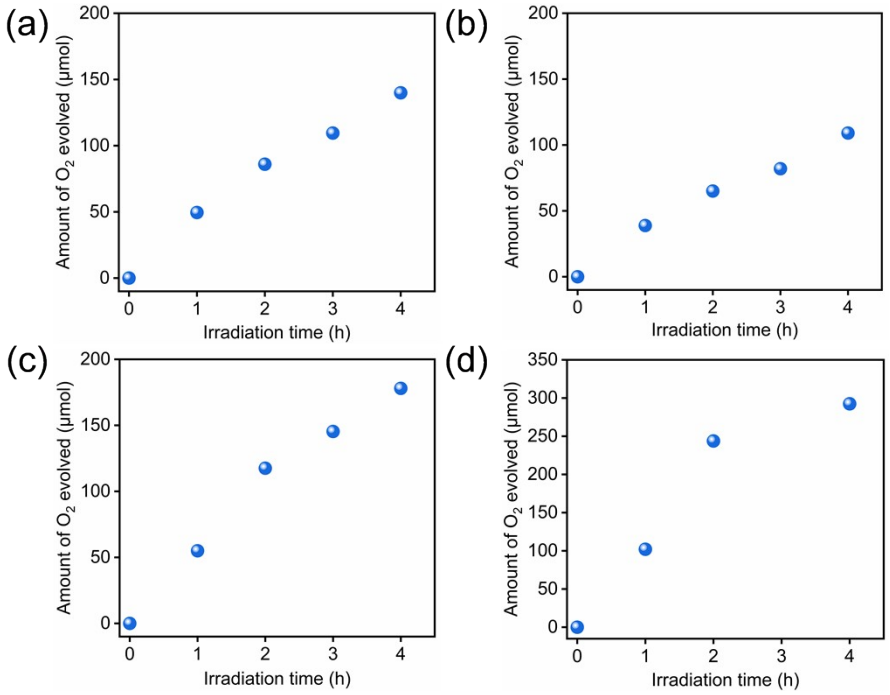

Fig. S2 Time course of photocatalytic O_2-evolution activity on (a) Pt-modified Bi_4TaO_8Cl, (b) Pt-modified Bi_4TaO_8Br, (c) Pt-modified $Bi_4TaO_8Cl_{0.5}Br_{0.5}$ and (d) Pt-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ from an aqueous $Fe(NO_3)_3$ solution. Conditions: photocatalyst, 100 mg; cocatalyst, 0.3 wt% Pt; 10 mM aqueous $Fe(NO_3)_3$ solution, 150mL; light source, 300 W Xenon lamp ($\lambda \geq 420$ nm).

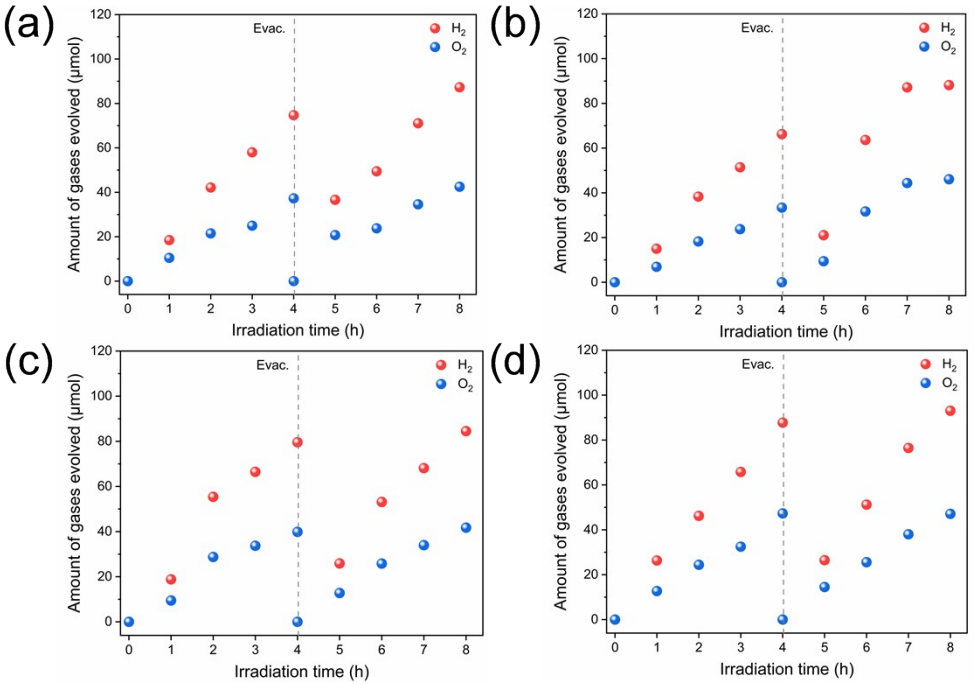

Fig. S3 Time course of photocatalytic activity for two-step excitation overall water splitting reaction using (a) RGO and CoO_x modified Bi_4TaO_8Cl, (b) RGO and CoO_x modified Bi_4TaO_8Br, (c) RGO and CoO_x modified $Bi_4TaO_8Cl_{0.5}Br_{0.5}$ and (d) RGO and CoO_x modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ as OEP. Conditions: $Ru/SrTiO_3$:Rh as HEP, 50 mg; OEP (CoO_x, 0.5 wt% as Co; RGO, 0.5 wt%), 50 mg; 150 mL H_2O, pH = 4; light source, 300 W Xenon lamp ($\lambda \geq 420$ nm).

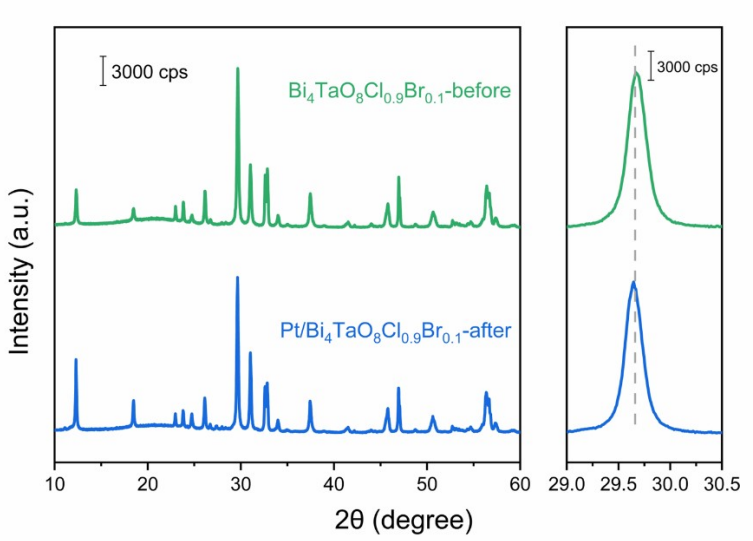

Fig. S4 XRD patterns of $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ sample before photocatalytic reaction and Pt-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ sample after photocatalytic reaction.

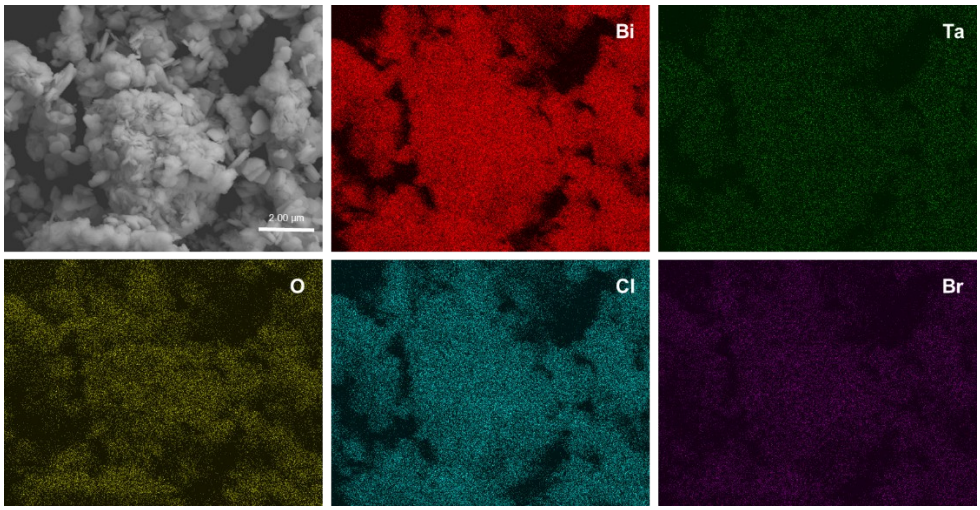

Fig. S5 EDS elemental mapping of Pt-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ sample after photocatalytic reaction.

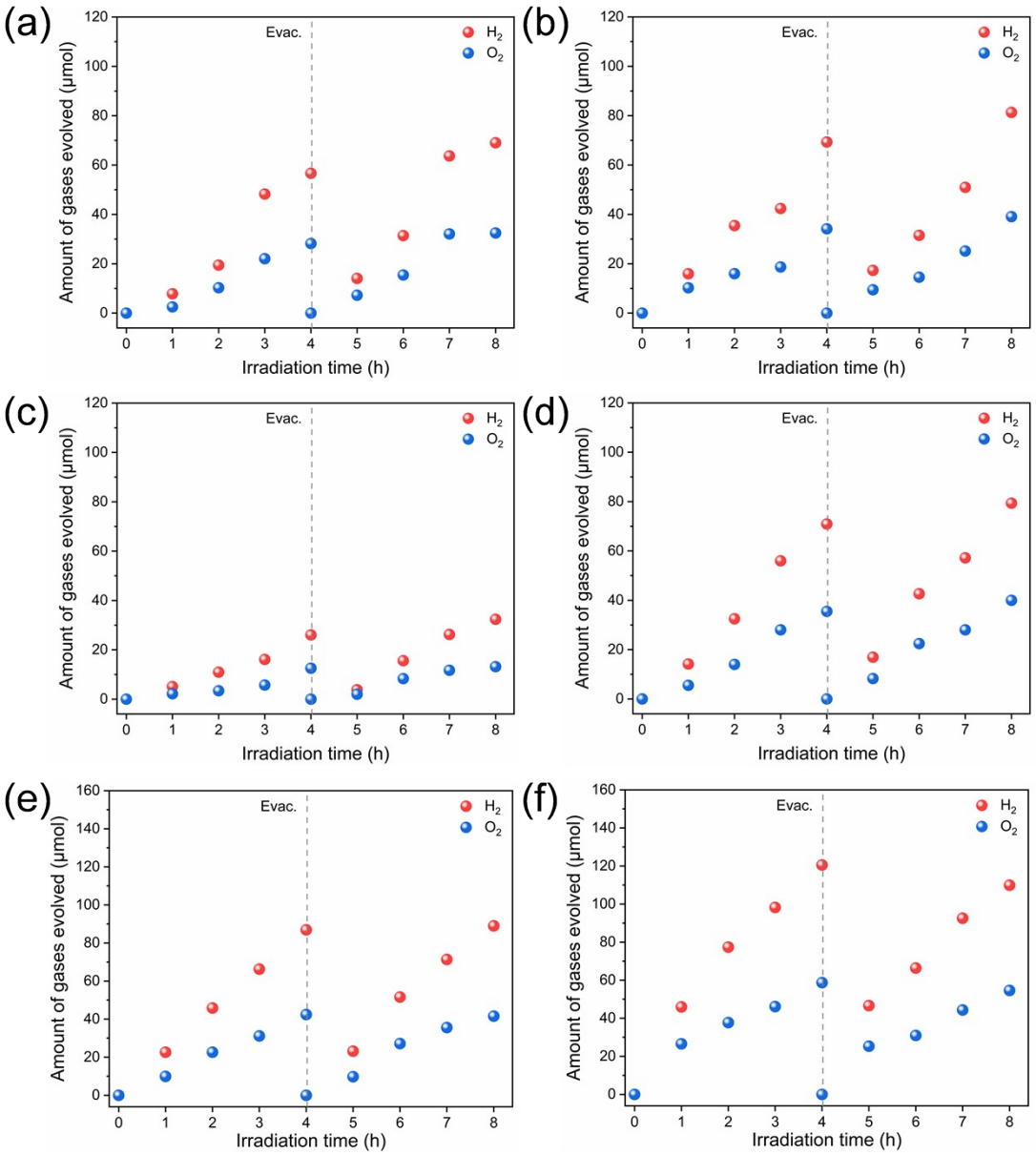

Fig. S6 Time course of photocatalytic activity for two-step excitation overall water splitting reaction using $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ as OEP modified with (a) IrO_x calcined at 573 K, (b) RuO_x calcined at 573 K, (c) PtO_x calcined at 573 K, (d) CoO_x calcined at 573 K, (e) RuO_x calcined at 773 K, and (f) CoO_x calcined at 773 K. Conditions: $Ru/SrTiO_3$:Rh as HEP, 50 mg; surface-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ (IrO_x, RuO_x, PtO_x or CoO_x, 0.5 wt% as Ir, Ru, Pt or Co; RGO, 0.5 wt%), 50 mg; 150 mL H_2O, pH = 4; light source, 300 W Xenon lamp ($\lambda \geq 420$ nm).

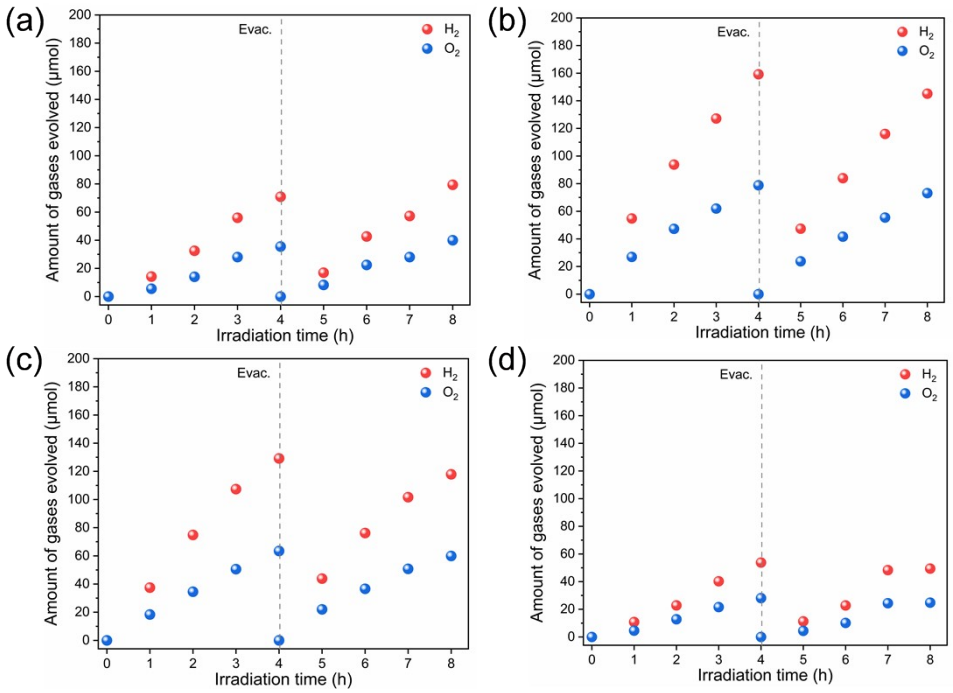

Fig. S7 Time course of photocatalytic activity for two-step excitation overall water splitting reaction using CoO_x-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ as OEP calcined at (a) 573 K, (b) 673 K, (c) 773 K, (d) 873 K. Conditions: $Ru/SrTiO_3$:Rh as HEP, 50 mg; surface-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ (CoO_x, 0.5 wt% as Co; RGO, 0.5 wt%), 50 mg; 150 mL H_2O, pH = 4; light source, 300 W Xenon lamp ($\lambda \geq 420$ nm).

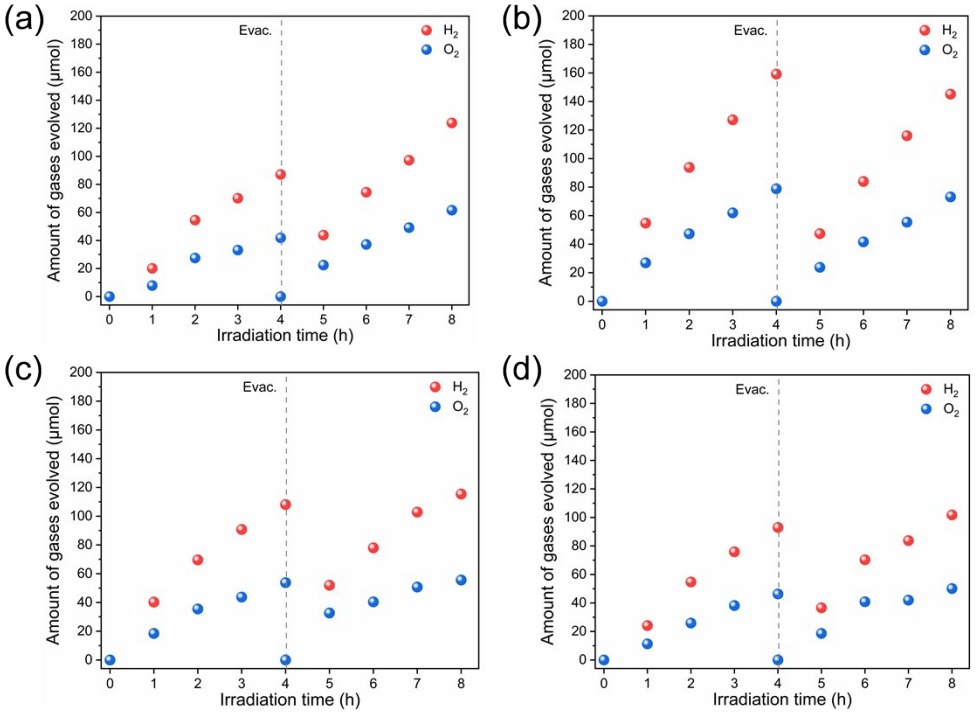

Fig. S8 Time course of photocatalytic activity for two-step excitation overall water splitting reaction using CoO_x-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ at 673 K as OEP with Co contents of (a) 0.3 wt%, (b) 0.5 wt%, (c) 0.8 wt%, (d) 1 wt%. Conditions: $Ru/SrTiO_3$:Rh as HEP, 50 mg; surface-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ (RGO, 0.5 wt%), 50 mg; 150 mL H_2O, pH = 4; light source, 300 W Xenon lamp ($\lambda \geq 420$ nm).

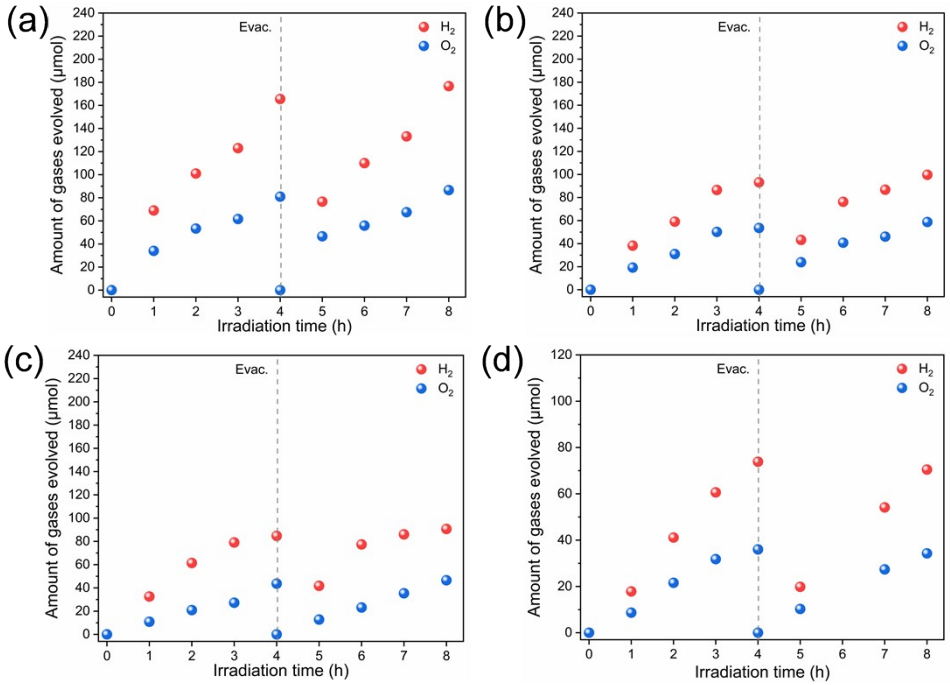

Fig. S9 Time course of photocatalytic activity for two-step excitation overall water splitting reaction using CoO_x-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ as OEP with different electron mediators (a) RGO, (b) Ir, (c) Au, (d) Fe^{3+}/Fe^{2+}. Conditions: $Ru/SrTiO_3$:Rh as HEP, 50 mg; surface-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ (CoO_x, 0.5 wt% as Co; RGO, Ir or Au as mediator, 0.3 wt%), 50 mg; 150 mL H_2O (150 mL of 2mM $Fe(NO_3)_3$ solution for (d)), pH = 4 (pH = 2.4 for (d)); light source, 300 W Xenon lamp ($\lambda \geq 420$ nm).

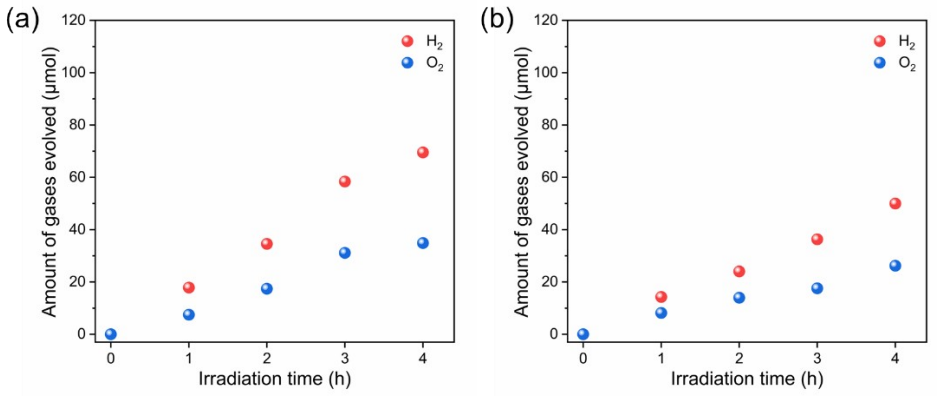

Fig. S10 (a) Time course of gas evolution during two-step photoexcitation water splitting reaction under visible light ($\lambda \geq 420$ nm). Conditions: $Ru/SrTiO_3$:Rh as HEP, 50 mg; CoO_x-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ as OEP (CoO_x, 0.5 wt% as Co), 50 mg; 150 mL H_2O, pH = 4; light source, 300 W Xenon lamp ($\lambda \geq 420$ nm). (b) Time course of gas evolution during two-step photoexcitation water splitting reaction under visible light ($\lambda \geq 420$ nm). Conditions: $Ru/SrTiO_3$:Rh as HEP, 50 mg; CoO_x-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ as OEP (CoO_x, 0.5 wt% as Co), 50 mg; GO, 0.3 wt% of OEP; 150 mL H_2O, pH = 4; light source, 300 W Xenon lamp ($\lambda \geq 420$ nm).

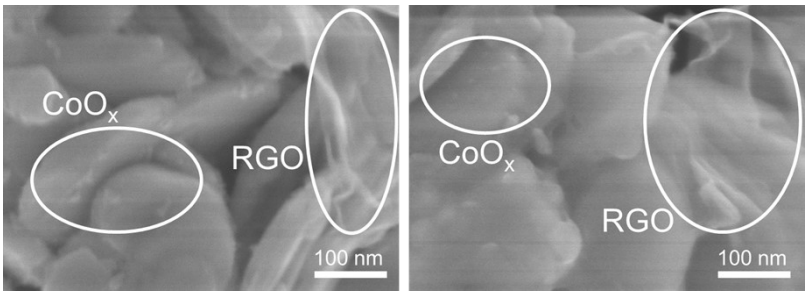

Fig. S11 SEM images of RGO and CoO_x co-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$.

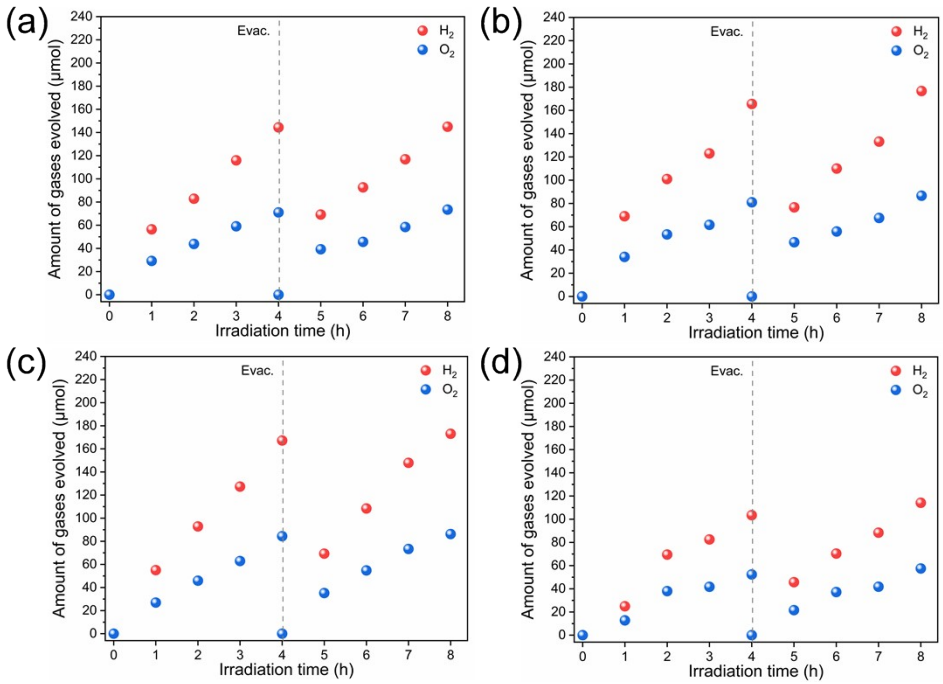

Fig. S12 Time course of photocatalytic activity for two-step excitation overall water splitting reaction using CoO_x-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ as OEP with RGO contents of (a) 0.1%, (b) 0.3%, (c) 0.5%, (d) 0.7%. Conditions: $Ru/SrTiO_3$:Rh as HEP, 50 mg; surface-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$ (CoO_x, 0.5 wt% as Co), 50 mg; 150 mL H_2O, pH = 4; light source, 300 W Xenon lamp ($\lambda \geq 420$ nm).

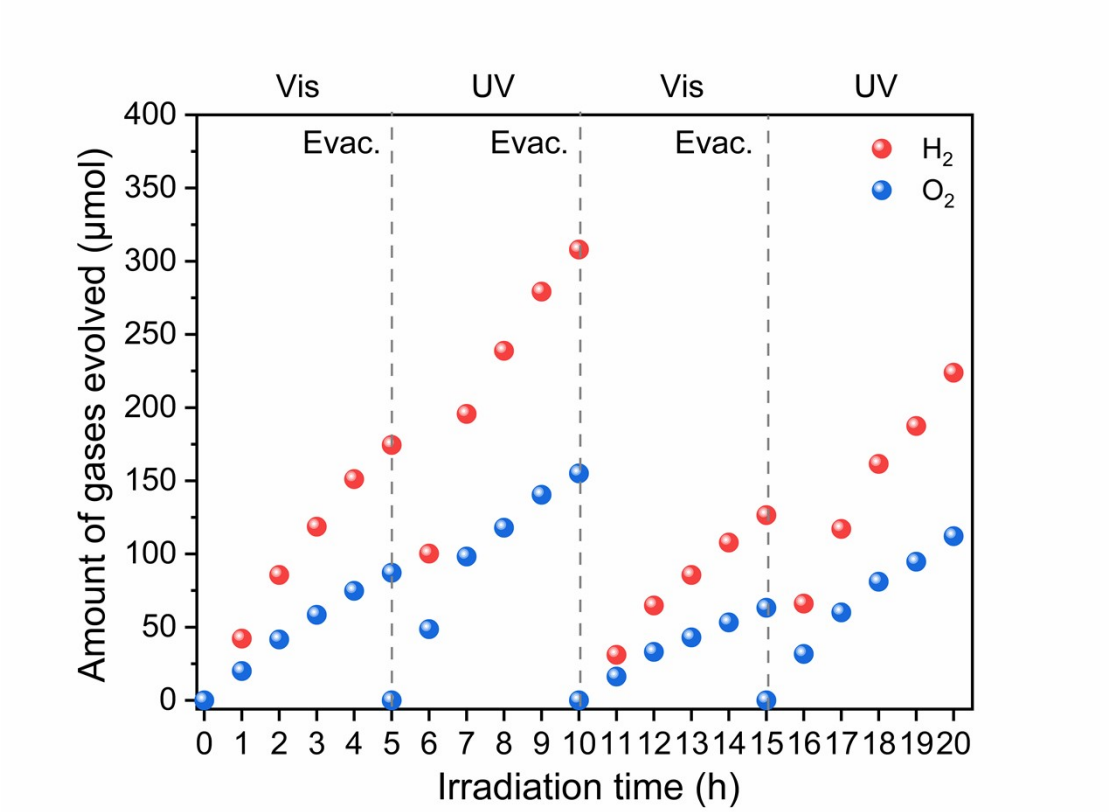

Fig. S13 Time courses of gas evolution during two-step photoexcitation water splitting reaction under visible light ($\lambda \geq 420$ nm) and ultraviolet light ($\lambda \geq 300$ nm) irradiation. Conditions: Ru/$SrTiO_3$:Rh, 50 mg; RGO and CoO_x co-modified $Bi_4TaO_8Cl_{0.9}Br_{0.1}$, 50 mg; 150 mL H_2O, pH=4; light source, 300 W Xenon lamp.