Supplementary Information (SI) for Chemical Communications.

Supporting Information

Spontaneous adsorption of iridium chloride complex on oxychloride photocatalysts provides efficient and durable reaction site for water oxidation

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Experimental

Synthesis of Bi-Based Oxyhalides

Bi_4NbO_8Cl was synthesized using the flux method reported in our previous work.[1] A stoichiometric mixture of Bi_2O_3, BiOCl, and Nb_2O_5 was mixed with a flux (NaCl and CsCl; 35:65 molar ratio) at 1 mol% and placed in an alumina crucible. The mixture was heated at 50 ℃ h^{-1} to 650 ℃ and held at this temperature for 10 h. The product was then cooled naturally to room temperature. The resulting product was thoroughly washed with distilled water, filtered, and air-dried. The powder obtained was characterized by X-ray diffraction (XRD), diffuse reflectance spectroscopy, and scanning electron microscope (SEM) and was confirmed to be Bi_4NbO_8Cl (Figure S1).

Bi_4TaO_8Cl was synthesized via a solid-state method following a previously reported procedure.[2] Bi_2O_3, BiOCl, and Ta_2O_5 were mixed in stoichiometric proportions, pelletized, and sealed in a vacuum quartz tube. The quartz tube was heated at 10 ℃ min^{-1} to 800 ℃ and held at this temperature for 20 h. The samples were then allowed to cool naturally to room temperature. The obtained powder was confirmed as Bi_4TaO_8Cl (Figure S10).

Bi_2ErO_4Cl was synthesized using the flux method following a previously reported procedure.[3] Bi_2O_3, BiOCl, and Er_2O_3 (1:2:1.1 molar ratio) were mixed with a flux agent (CsCl). The mixture was placed in an alumina crucible, heated at a rate of 10 ℃ min^{-1} to 800 ℃, and held at this temperature for 20 h. The product was cooled naturally to room temperature and thoroughly washed with distilled water, filtered, and air-dried. The obtained powder was confirmed as Bi_2ErO_4Cl (Figure S10).

$SrBi_3O_4Cl_3$ was synthesized using the flux method, following a previously reported procedure.[4] $SrCO_3$ and BiOCl were mixed in stoichiometric amounts with the flux agents $SrCl_2$ and KCl (50:50 molar ratio). The mixture was placed in an alumina crucible, heated at a rate of 10 ℃ min^{-1} to 700 ℃, and held at this temperature for 12 h. The product was cooled naturally to room temperature and was thoroughly washed with distilled water, filtered, and air-dried. The obtained powder was confirmed as $SrBi_3O_4Cl_3$ (Figure S10).

Loading of Ir-based cocatalysts

Ir-based cocatalysts were deposited using four different methods[5-7]: microwave-assisted (MW), impregnation (IMP), colloidal adsorption (COL), photodeposition (PD), and adsorption (ADS). The loading amount of the Ir was set at 0.5 wt.% relative to the photocatalyst.

For the MW method, 0.3 g of Bi_4NbO_8Cl was suspended in Milli-Q water and an $IrCl_3 \cdot nH_2O$ precursor solution was added. The total volume was adjusted to 15 mL and the mixture was dispersed using an ultrasonic cleaner. Microwave heating was performed at 150 ℃ for 10 min using a Biotage Initiator+ microwave reactor. For the IMP method, 0.3 g of Bi_4NbO_8Cl was suspended in Milli-Q water, and a $Na_2IrCl_6 \cdot nH_2O$ precursor solution was added. The suspension was evaporated in a water bath, and the resulting powder was heated at 450 ℃ in air for 30 min. In the COL method, 0.3 g of Bi_4NbO_8Cl was suspended in Milli-Q water and an Ir colloidal solution, prepared according to a previous report,[6] was added. The total volume was adjusted to 150 mL, and the mixture was dispersed using an ultrasonic cleaner. The suspension was stirred in the dark for 1 h under ambient conditions, after which the powder was recovered by vacuum filtration, thoroughly washed with Milli-Q water, and air-dried. In the PD method, 0.3 g of Bi_4NbO_8Cl was suspended in a 5 mM sodium nitrate aqueous solution (150 mL), and a $Na_3IrCl_6 \cdot nH_2O$ precursor solution was added. The mixture was then dispersed using an ultrasonic cleaner. The suspension was stirred under an Ar atmosphere while being irradiated with visible light (λ > 400 nm) for 5 h using a 300-W Xe lamp. The resulting powder was recovered by vacuum filtration, thoroughly washed with Milli-Q water, and air-dried. In the ADS method, 0.3 g of Bi_4NbO_8Cl was suspended in Milli-Q water, and a $Na_3IrCl_6 \cdot nH_2O$ precursor solution was added. The total volume was adjusted to 150 mL, and the mixture was dispersed using an ultrasonic cleaner. The suspension was stirred in the dark for 5 h under ambient conditions, after which the powder was recovered via vacuum filtration, thoroughly washed with Milli-Q water, and air-dried.

Characterization

The prepared samples were studied via X-ray absorption fine structure (XAFS) spectroscopy. XAFS measurements were performed at the BL12C beamline of the Photon Factory (High Energy Accelerator Research Organization, Tsukuba, Japan). The X-ray energy was varied using a Si(111) double-crystal monochromator. The reference samples were diluted in boron nitride, compressed to form pellets, and measured in the transmission mode. Cocatalyst-loaded samples were measured in fluorescence mode using a multichannel solid-state detector. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Scientific iCAP 7400 Duo) was performed to determine the amount of Ir loaded onto Bi_4NbO_8Cl. Scanning transmission electron microscopy (STEM) and scanning electron microscopy (SEM) were conducted using a JEM-ARM200CF and Nvision 40 (Zeiss) system, respectively. The loaded Ir species were observed and analyzed via STEM (JEM-ARM200CF, JEOL) and energy-dispersive X-ray spectroscopy (EDX).

Photocatalytic reaction

Photocatalytic reactions were performed using a closed gas-circulating system. The photocatalyst powder (0.1 g) was dispersed in an aqueous $AgNO_3$ solution (8 mM, 100 mL, without pH adjustment) in a Pyrex top-window cell. The photocatalysts were irradiated with visible light (λ > 400 nm) through a cutoff filter (HOYA; L42) from a 300-W Xe-arc lamp (PerkinElmer; Cermax-PE300BF). The quantity of evolved gases was determined using an online gas chromatograph (thermal conductivity detector; molecular sieve with 5 Å column packing; Ar carrier gas). The oxygen evolution reactions using Fe^{3+} and $[SiVW_{11}O_{40}]^{5-}$ as electron acceptors were also conducted in the same setup. For Fe^{3+}, an aqueous solution of $FeCl_3$ (8 mM, pH 2.3–2.4) was used. For $[SiVW_{11}O_{40}]^{5-}$, an aqueous solution of KH_2PO_4 (0.5 M, pH=4.4) and $K_5[SiVW_{11}O_{40}]\cdot 14H_2O$ (0.5 mM) was used.

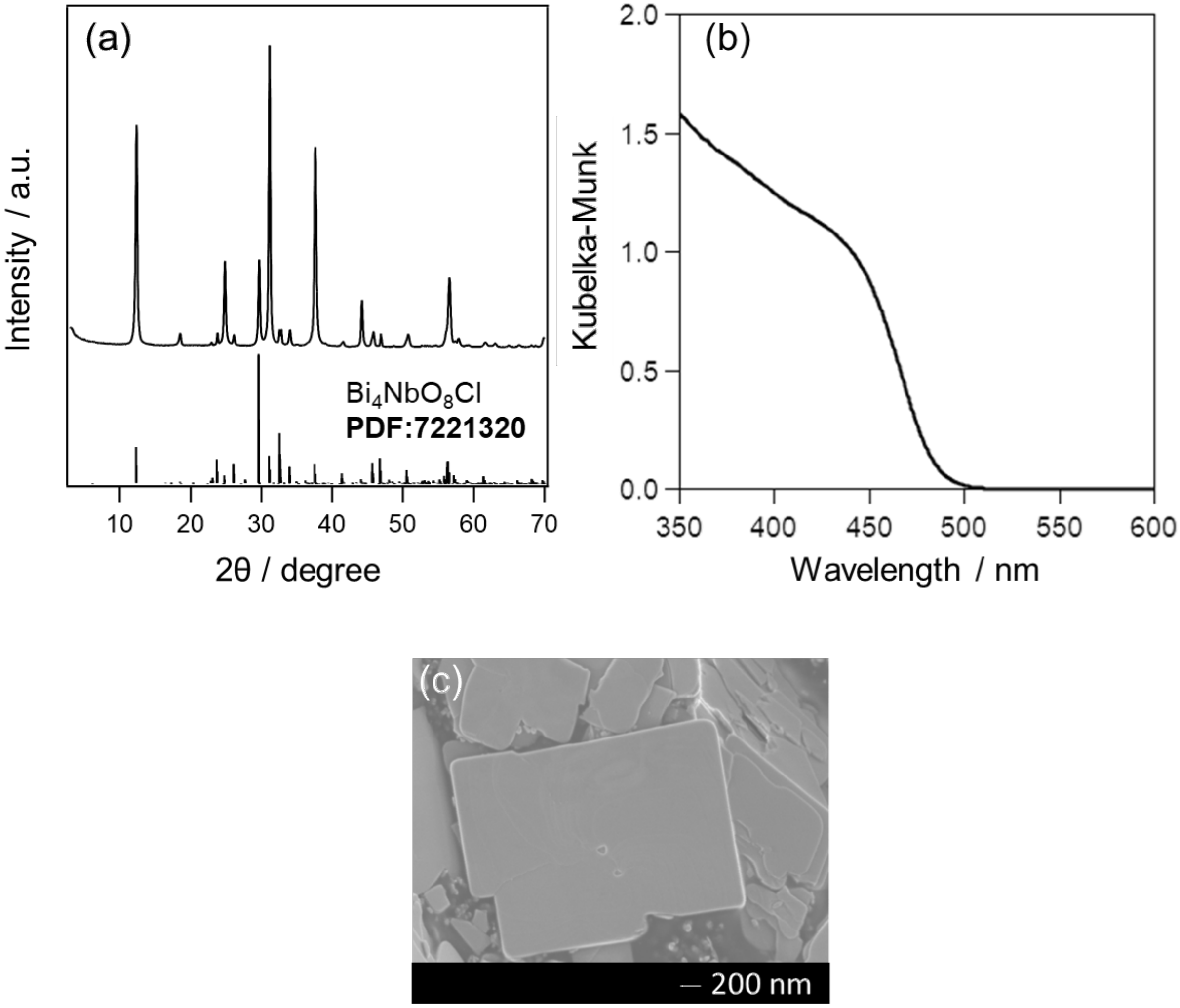

Figure S1. (a) XRD pattern, (b) diffuse reflectance spectrum, and (c) SEM image of Bi_4NbO_8Cl prepared via the flux method.

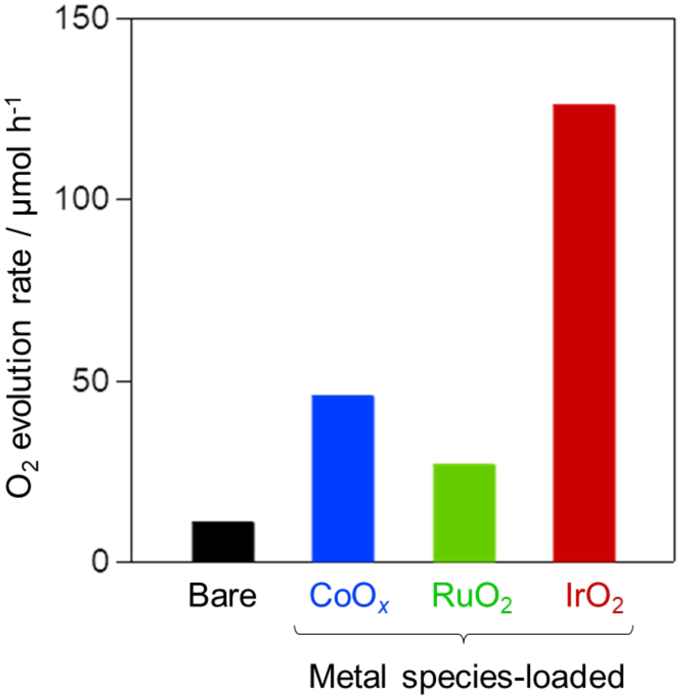

Figure S2. Initial O_2 evolution rate of Bi_4NbO_8Cl loaded with various metal species via the IMP method, along with that of bare Bi_4NbO_8Cl. $Co(NO_3)_2{\cdot}6H_2O$ and $RuCl_3{\cdot}nH_2O$ were used as Co and Ru species precursors, respectively.

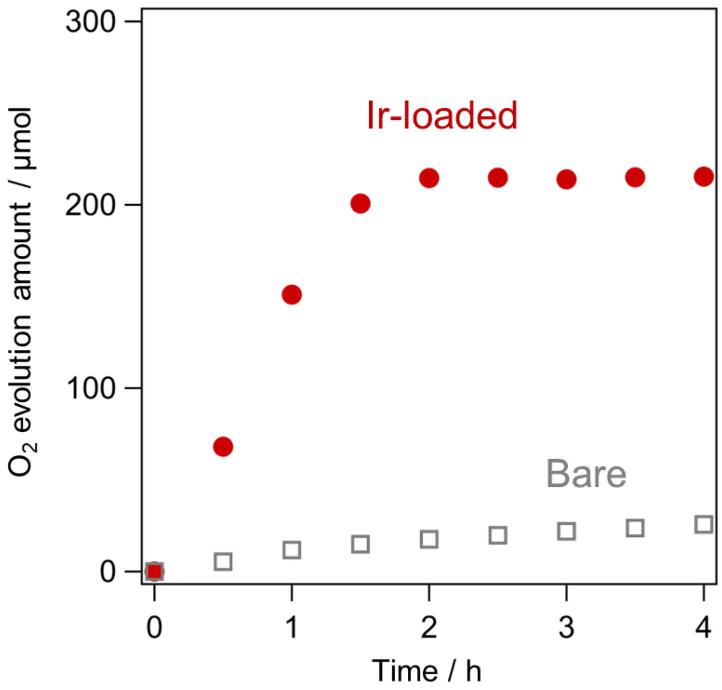

Figure S3. Time course of O_2 evolution on Bi_4NbO_8Cl loaded with Ir species via ADS method. The reaction was performed in aqueous $AgNO_3$ solution (8 mM, 100 mL) under visible light irradiation ($\lambda > 400$ nm). If all the introduced Ag^+ ions are reduced to Ag metal by photoexcited electrons, 200 µmol of O_2 would be generated according to the following equations.

$$Ag^+ + e^- \rightarrow Ag \qquad (1)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (2)$$

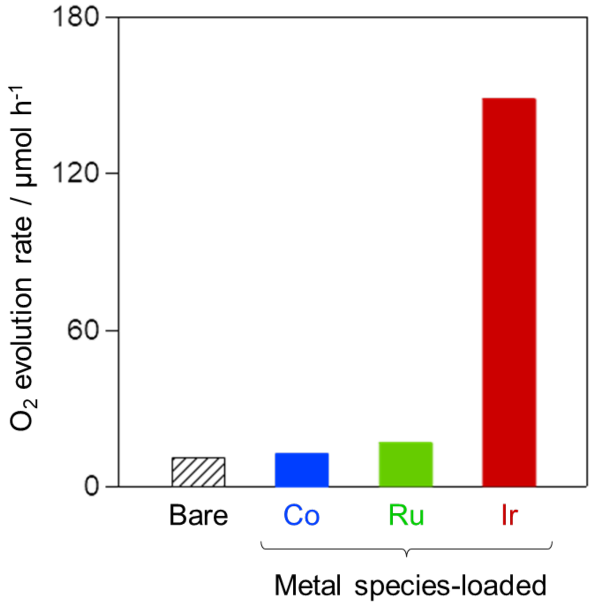

Figure S4. Initial O_2 evolution rate of Bi_4NbO_8Cl loaded with various metal (Co, Ru, and Ir) species via adsorption (ADS) method, along with bare Bi_4NbO_8Cl. $CoCl_2 \cdot 6H_2O$ and $RuCl_3 \cdot nH_2O$ were used as Co and Ru species precursors, respectively.

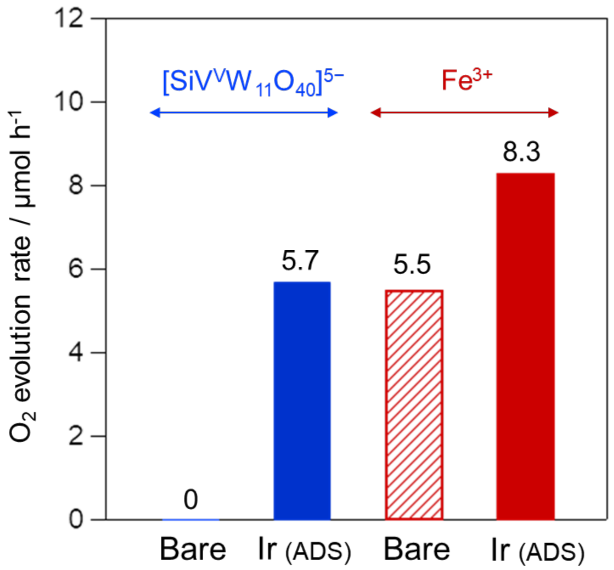

Figure S5. Initial O_2 evolution rate over bare Bi_4NbO_8Cl and Bi_4NbO_8Cl loaded with Ir species via ADS method from aqueous $[SiV^{V}W_{11}O_{40}]^{5-}$ or Fe^{3+} solution under visible light irradiation ($\lambda > 400$ nm).

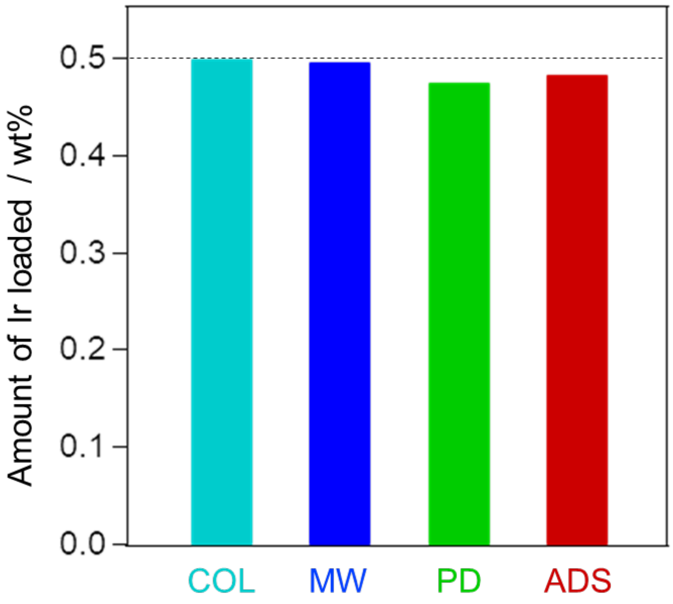

Figure S6. Amount of Ir loaded on Bi_4NbO_8Cl via various methods (COL, MW, PD, and ADS), determined by ICP measurements. The loading amounts of Ir species for the ADS and PD samples were slightly smaller, while most of the introduced Ir species (0.5 wt.% metal content) were successfully loaded onto the surface of Bi_4NbO_8Cl, regardless of the loading method.

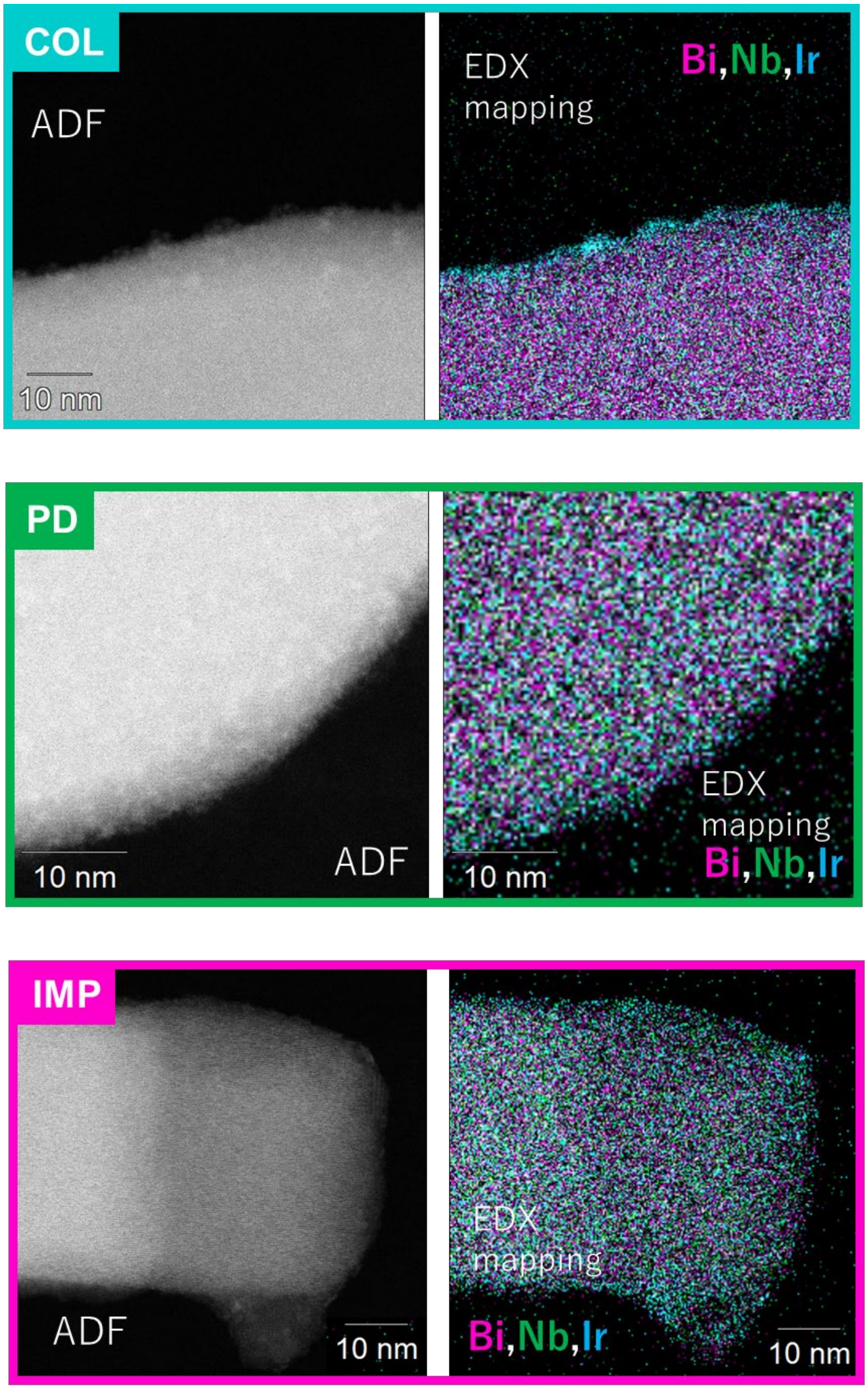

Figure S7. STEM images of Bi_4NbO_8Cl loaded with Ir species via various methods (COL, PD, and IMP).

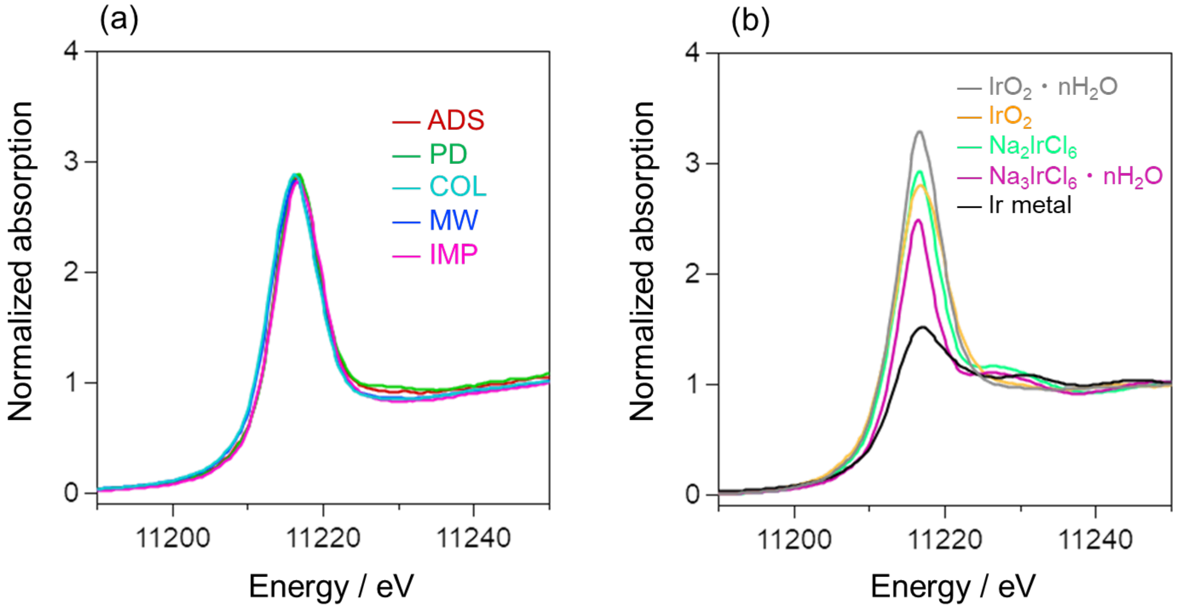

Figure S8. Ir L3-edge XANES spectra of (a) Bi_4NbO_8Cl loaded with Ir species via various methods (COL, MW, IMP, PD, and ADS), along with those of the (b) reference samples.

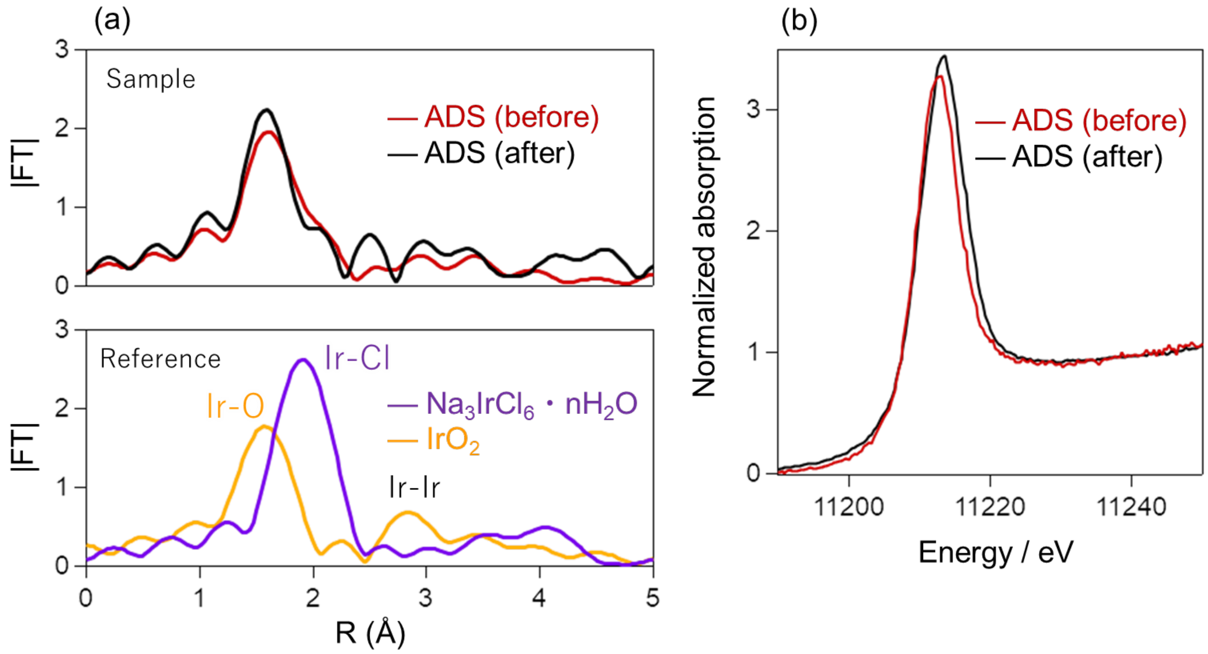

Figure S9. Ir L3-edge (a) EXAFS and (b) XANES spectra of Bi_4NbO_8Cl loaded with Ir species via ADS method before and after O_2 evolution reaction.

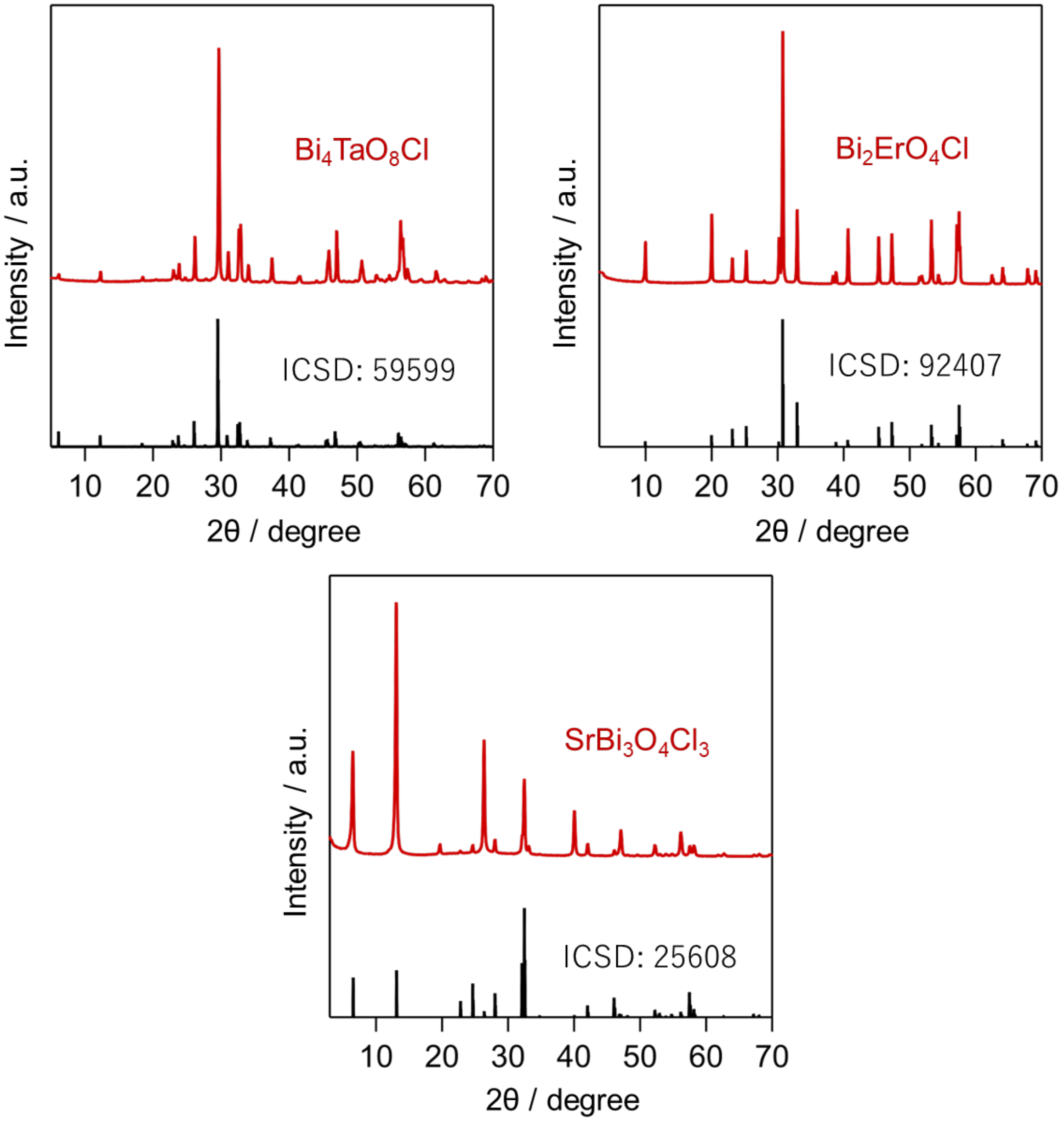

Figure S10. XRD patterns of Bi_4TaO_8Cl, Bi_2ErO_4Cl, and $SrBi_3O_4Cl_3$.

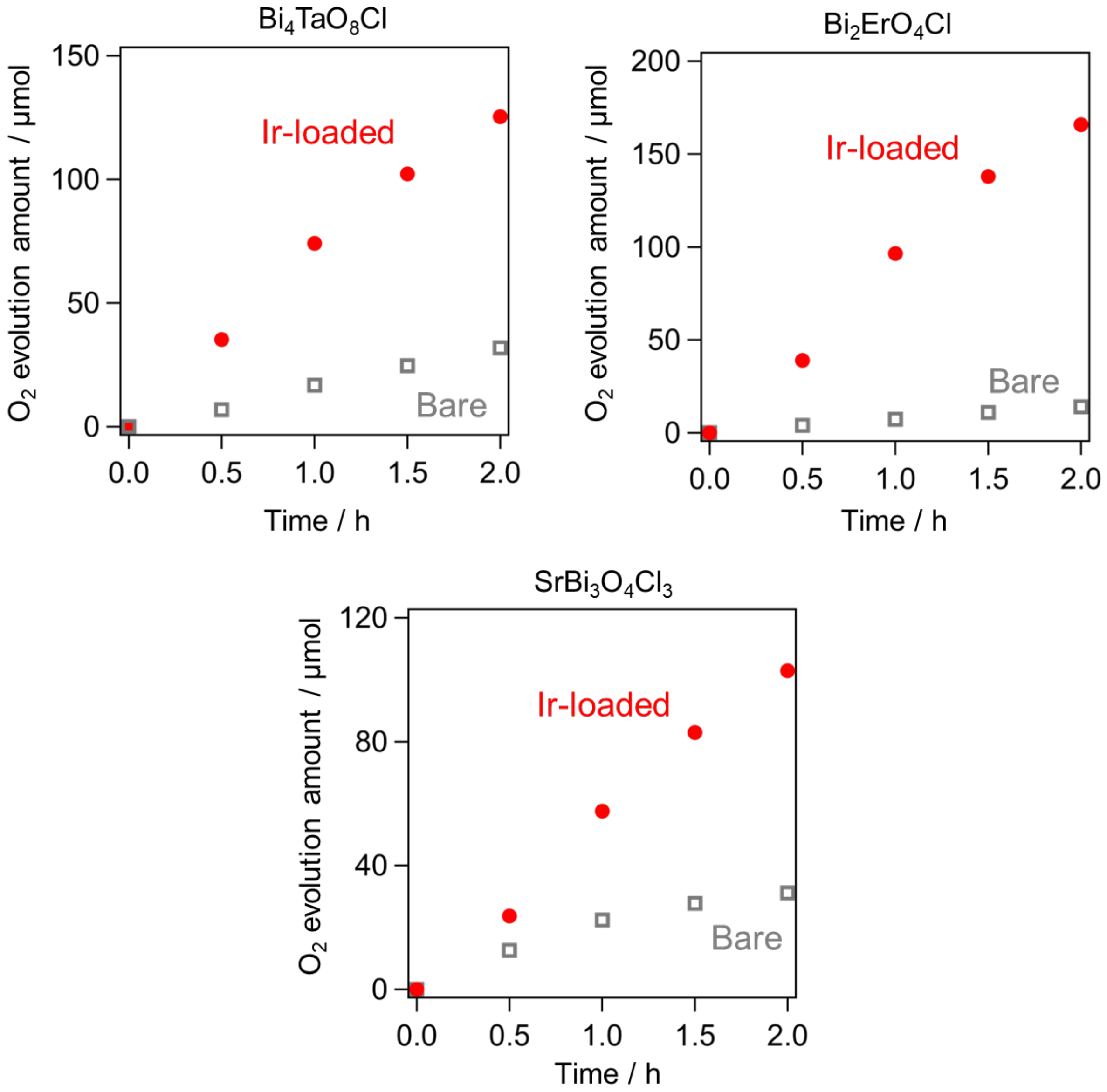

Figure S11. Time course of O_2 evolution on oxyhalides (Bi_4TaO_8Cl, Bi_2ErO_4Cl, and $SrBi_3O_4Cl_3$) loaded with Ir species via ADS method.

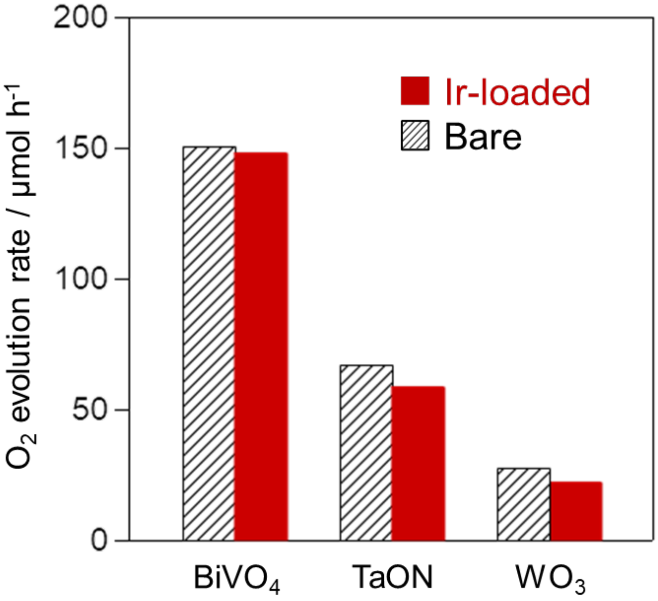

Figure S12. Initial O_2 evolution rate of $BiVO_4$, TaON, and WO_3 loaded with or without Ir species via ADS method.

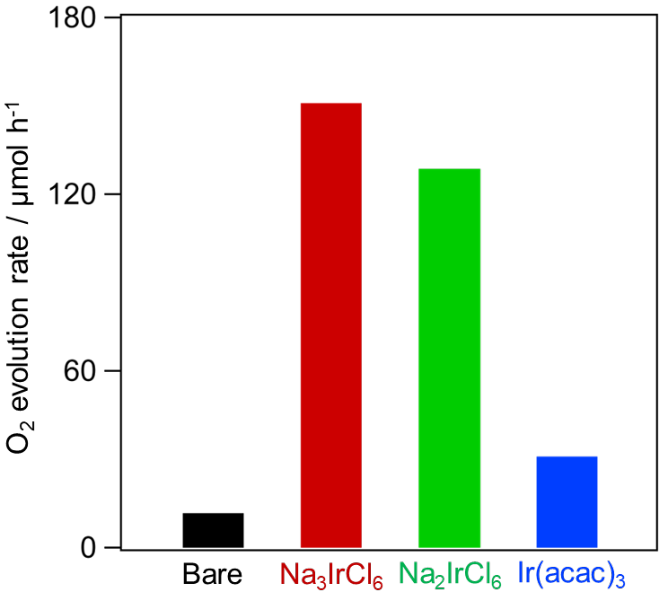

Figure S13. Initial O_2 evolution rate of Bi_4NbO_8Cl loaded with Ir species via ADS method using various Ir precursors (Na_3IrCl_6, Na_2IrCl_6, and $Ir(acac)_3$).

References

1. K. Ogawa, A. Nakada, H. Suzuki, O. Tomita, M. Higashi, A. Saeki, H. Kageyama and R. Abe, *ACS Appl. Mater. Interface*, 2019, **11**, 5642-5650.
2. H. Kunioku, A. Nakada, M. Higashi, O. Tomita, H. Kageyama and R. Abe, *Sustain. Energy Fuels*, 2018, **2**, 1474-1480.
3. A. Nakada, D. Kato, R. Nelson, H. Takahira, M. Yabuuchi, M. Higashi, H. Suzuki, M. Kirsanova, N. Kakudou, C. Tassel, T. Yamamoto, C. M. Brown, R. Dronskowski, A. Saeki, A. Abakumov, H. Kageyama and R. Abe, *J. Am. Chem. Soc.*, 2021, **143**, 2491-2499.
4. Y. Ishii, H. Suzuki, K. Ogawa, O. Tomita, A. Saeki and R. Abe, *Sustain. Energy Fuels*, 2022, **6**, 3263-3270.
5. K. Chen, J. Xiao, J. J. M. Vequizo, T. Hisatomi, Y. Ma, M. Nakabayashi, T. Takata, A. Yamakata, N. Shibata and K. Domen, *J. Am. Chem. Soc.*, 2023, **145**, 3839-3843.
6. K. Maeda and K. Domen, *Angew. Chem. Int. Ed.*, 2012, **51**, 9865-9869.
7. A. Iwase, H. Kato and A. Kudo, *Chem. Lett.*, 2005, **34**, 946-947.