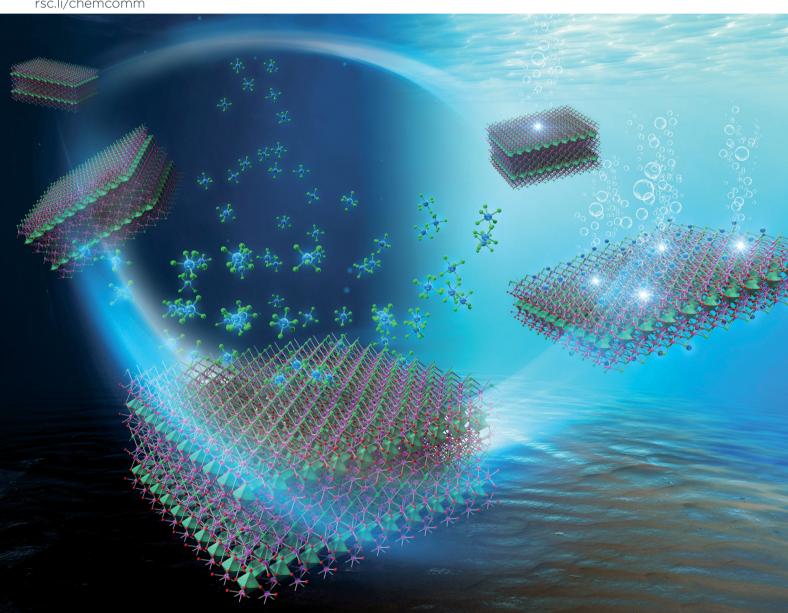
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Spontaneous adsorption of iridium chloride complex on oxychloride photocatalysts provides efficient and durable reaction site for water oxidation†

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The visible-light-driven O2 evolution on oxychloride photocatalysts, such as Bi₄NbO₈Cl, was significantly enhanced by stirring in an aqueous solution containing IrCl₆³⁻ in the dark. Various characterizations indicated that highly dispersed IrOxHvClz-like species spontaneously formed on the oxychloride surface, serving as effective and stable cocatalysts for enhancing O2 evolution.

Water splitting using semiconductor photocatalysts is a promising approach to clean hydrogen production. 1-5 Till now, ultraviolet (UV)-light-driven water splitting with a quantum efficiency of almost 100% has been achieved using SrTiO3based photocatalysts.6 Large-scale photocatalytic hydrogen production tests are also underway.⁷ However, since UV light accounts for only a small fraction of the solar spectrum, developing photocatalysts capable of harvesting visible light, which constitutes nearly half of sunlight, is necessary to achieve practically high efficiencies.

Mixed-anion compounds, such as oxynitrides and oxysulfides, have been developed to address this requirement. 8 These photocatalyst materials have the valence band maximum (VBM) composed of their N-2p or S-3p orbitals hybridized with O-2p. The contribution of these orbitals to the VBM reduces the bandgap and enables visible light absorption. However, these materials often suffer from self-oxidative deactivation by photogenerated holes during water splitting. Recently, Sillén-(-Aurivillius)-type layered oxyhalides, such as Bi₄NbO₈Cl, have emerged as promising photocatalysts for visible-light-driven

Fig. 1 Crystal structures of Sillén(-Aurivillius)-type layered oxyhalide photocatalysts: Bi_4MO_8Cl (M = Nb, Ta), Bi_2REO_4Cl (RE = rare earth), and SrBi₃O₄Cl₃.

water splitting (Fig. 1).^{9,10} These materials feature a unique valence band structure, in which elevated O-2p orbitals primarily contribute to the VBM. This structure enables photogenerated holes to be preferentially consumed by water oxidation, minimizing self-oxidation and providing remarkable stability as O2 evolution photocatalysts in Z-scheme water-splitting systems. 11,12

Previous efforts to enhance photocatalytic activity have included the exploration of related oxyhalide materials and synthetic methods such as flux-assisted synthesis. 13,14 However, further exploration of their surface engineering is needed, particularly for loading effective water oxidation cocatalysts. Unlike the well-studied surfaces of metal oxides, layered oxyhalides possess more complex surfaces with volatile halogen species, requiring innovative surface modification strategies to improve both charge transfer and surface reactions.

While exploring effective cocatalysts and their loading methods to enhance O₂ evolution on the representative oxychloride photocatalyst Bi₄NbO₈Cl, we discovered that highly dispersed

Bi₄MO₈Cl Bi₂REO₄CI SrBi₃O₄Cl₃ (RE=Rare earth)

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 $IrO_xH_vCl_z$ species were spontaneously formed by simply stirring Bi₄NbO₈Cl particles in an aqueous Na₃IrCl₆ solution in the dark. This novel adsorption method significantly enhanced the O₂ evolution rate under visible light irradiation and proved effective for various oxyhalide photocatalysts.

The oxyhalide photocatalyst Bi₄NbO₈Cl was synthesized using the previously reported flux method. 13 X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), and diffuse reflectance spectroscopy confirmed the successful synthesis of single-phase, plate-like particles of Bi₄NbO₈Cl (Fig. S1, ESI \dagger). Initially, various metal oxide species (RuO₂, CoO_x, and IrO2, each with 0.5 wt% metal content) were loaded onto Bi₄NbO₈Cl via a conventional impregnation (IMP) method. The samples were then calcinated at 450 °C in air, and their O₂ evolution activities were evaluated. As summarized in Fig. S2 (ESI†), the loading of IrO₂ provided the highest enhancement, increasing the O2 evolution rate approximately 11-fold compared to unmodified Bi₄NbO₈Cl. RuO₂ and CoO_x also increased the rate to some extent. 13,15 Then, loading of IrO2 cocatalysts was carried out by employing various methods, including colloidal adsorption (COL), microwave-assisted (MW) method, and photodeposition (PD) method, all of which have reportedly been effective for loading IrO2 onto metal oxides and oxynitride photocatalysts. 16-18 Notably, the PD method was proposed to provide IrO₂ species through oxidation of Ir^{III}Cl₆³⁻ precursor to Ir^{IV}O₂ by photogenerated holes on the photocatalyst, accompanied by nitrate ion reduction (e.g., $NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- +$ H₂O) by photoexcited electrons.¹⁸

Additionally, we introduced the simple adsorption (ADS) method as a control test for the PD method. In this approach, the photocatalyst particles were suspended in aqueous Na₃IrCl₆ solution (in the absence of NO₃⁻) in the dark.

Fig. 2 shows the O₂ evolution rates of various Bi₄NbO₈Cl samples (0.1 g) in an aqueous AgNO₃ solution (8 mM, 100 mL) under visible light irradiation ($\lambda > 400$ nm) from a 300-W

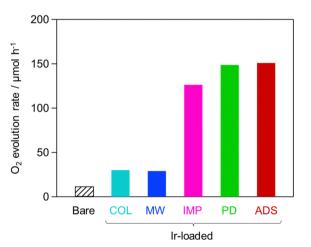


Fig. 2 Initial O₂ evolution rate of Bi₄NbO₈Cl loaded with Ir species via various methods (COL, MW, IMP, PD, and ADS), along with that of bare Bi₄NbO_∞Cl. These reactions were performed in aqueous AqNO_∞ solution (8 mM, 100 mL) containing the photocatalyst powder (0.1 g) under visible light irradiation ($\lambda > 400$ nm) from a 300-W Xe-arc lamp.

Xe-arc lamp. Among the tested methods, PD achieved the highest O2 evolution rate, outperforming the IMP method. The COL and MW methods showed slightly higher rates than the bare sample but considerably lower values than IMP. Notably, the newly introduced ADS method, in which Bi₄NbO₈Cl particles were stirred in an aqueous Na₃IrCl₆ solution under dark conditions, achieved a rate comparable to that of PD, the highest among all the methods. The O₂ evolution rate of the ADS sample remained steady until the Ag⁺ ions in the solution were completely consumed (Fig. S3, ESI†). Attempts to apply the ADS method with other metal species (e.g., Ru and Co) did not significantly enhance the O2 evolution rates (Fig. S4, ESI†), indicating that the enhancement is unique to the Ir species. The ADS sample also exhibited higher activity than the bare sample, not only with the sacrificial electron acceptors (Ag⁺) but also with the reversible electron acceptors (Fe³⁺ and polyoxometalate $[SiV^VW_{11}O_{40}]^{5-}$) (Fig. S5, ESI†). These findings highlight the potential of such modified oxyhalide photocatalysts in Z-scheme water-splitting systems with redox mediators.

The Ir species loaded via ADS and other methods were characterized using various techniques. Inductively coupled plasma (ICP) spectroscopy measurements indicated that most of the introduced Ir species (0.5 wt% metal content) were successfully loaded onto the surface of Bi₄NbO₈Cl, regardless of the loading method (Fig. S6, ESI†). The driving force for the spontaneous adsorption of Ir species is likely related to the electrostatic attraction between the Bi₄NbO₈Cl particles and the $IrCl_6^{3-}$ precursor. The pH of the solution during the ADS method was measured to be around 5. At pH 5, the Bi₄NbO₈Cl particles are positively charged,19 suggesting that the electrostatic attraction between them possibly promotes the adsorption of Ir species. Fig. 3 and Fig. S7 (ESI†) show scanning transmission electron microscope (STEM) images of each Bi₄NbO₈Cl sample. For the ADS sample (Fig. 3), identifying the Ir species was almost impossible, suggesting highly dispersed, fine particles or clusters on the surface. Alternatively, Ir species are distinctly evident in the MW sample but are indistinguishable in the PD sample, as shown in Fig. S7 (ESI†). The IMP sample exhibited much smaller Ir species compared to those from the MW and COL methods. These observations imply that Ir species with high dispersion and small size are critical for enhancing O2 evolution on Bi4NbO8Cl photocatalysts.

The X-ray absorption fine structure (XAFS) results are shown in Fig. 4 and Fig. S8 (ESI†). The X-ray absorption near-edge structure (XANES) spectra (Fig. S8, ESI†) revealed that the loaded Ir species predominantly existed in the +4 oxidation state across all loading methods. In the extended XAFS (EXAFS) spectra (Fig. 4), the Ir species loaded using the COL, MW, and IMP methods showed only Ir-O bonds in the first coordination shell, indicating that the Ir species existed as oxides or hydroxides, as previously reported. In contrast, the samples prepared via ADS and PD methods exhibited both Ir-O and Ir-Cl bonds, indicating the formation of $IrO_xH_yCl_z$ species, which are effective cocatalysts for O2 evolution. The PD method was originally proposed to deposit IrO2 on a photocatalyst through the oxidation of IrCl₆³⁻ by photogenerated holes, accompanied by the ChemComm Communication

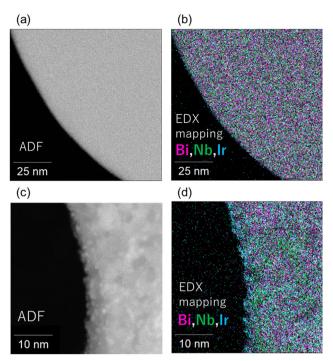


Fig. 3 (a) and (c) STEM image and (b) and (d) EDX mapping of Bi₄NbO₈Cl loaded with Ir species via ADS (a) and (b) and MW (c) and (d) method.

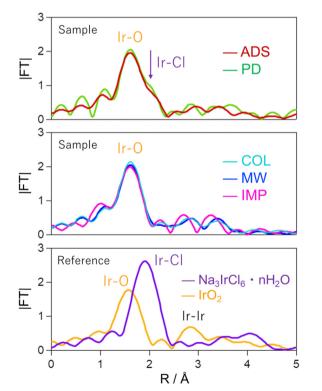


Fig. 4 Fourier-transformed Ir L₃-edge EXAFS spectra of Bi₄NbO₈Cl loaded with Ir species via various methods (COL, MW, IMP, PD, and ADS), along with those of reference samples.

reduction of NO₃⁻ by photoexcited electrons under light irradiation.18 However, the present ADS method achieved

comparably high activity than the PD method without light or electron acceptor. Additionally, the states of the Ir species loaded via ADS and PD were almost identical, as confirmed by STEM and XAFS measurements. Thus, for both methods, the IrO_rH_vCl_z species are probably loaded on the oxyhalide through the partial hydrolysis of $IrCl_6^{3-}$ in water. 20,21 Notably, the EXAFS spectrum of the ADS-loaded sample post-photocatalytic O2 evolution still showed Ir-Cl bonds, indicating stability under the photocatalytic reaction conditions (Fig. S9, ESI†). These findings indicate that active Ir species were spontaneously formed from IrCl₆³⁻ on the Bi₄NbO₈Cl surface during stirring in the dark, for both the PD and ADS methods.

We applied this novel ADS method to other oxychloride photocatalysts, including Bi₄TaO₈Cl, Bi₂ErO₄Cl, and SrBi₃O₄Cl₃ (Fig. 1 and Fig. S10, ESI†). Fig. 5 shows the O₂ evolution rates of these oxyhalide photocatalysts with Ir species loaded using the ADS method. The time course of O₂ evolution is shown in Fig. S11 (ESI†). Ir loading significantly improved the O2 evolution rates for both Sillén-type (Bi₂ErO₄Cl and SrBi₃O₄Cl₃) and Sillén-Aurivillius-type (Bi₄NbO₈Cl and Bi₄TaO₈Cl) oxychlorides. In contrast, applying the ADS method to oxide-based (BiVO₄ and WO₃) and oxynitride-based (TaON) photocatalysts negligibly improved the O2 evolution (Fig. S12, ESI†). This distinction indicates that the IrCl₆³⁻ complex possibly interacts with the surface of oxychlorides, facilitating the formation of highly active Ir species and/or enabling efficient charge transfer, thereby significantly enhancing O2 evolution rates. As shown in Fig. S13 (ESI†), using Na₂IrCl₆ significantly enhances O₂ evolution similar to Na₃IrCl₆ on Bi₄NbO₈Cl, whereas Ir(acac)₃ without Cl anions yields less pronounced improvement. These findings underscore the critical role of surface Cl interactions on oxychlorides. Further investigation is required to elucidate the mechanisms underlying this activity enhancement. Nonetheless, the novel ADS method is a mild, simple, and versatile method for loading active and stable Ir species, significantly enhancing the O2 evolution rates of various oxychloride photocatalysts.

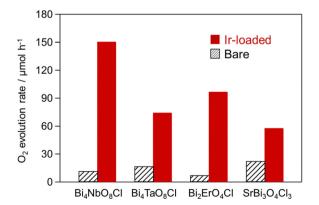


Fig. 5 Initial O₂ evolution rate of oxyhalides loaded with or without Ir species via ADS method. These reactions were performed in aqueous AgNO₃ solution (8 mM, 100 mL) containing the photocatalyst powder (0.1 g) under visible light irradiation ($\lambda > 400$ nm) from a 300-W Xe-arc lamp.

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In summary, this study demonstrated the potential of the novel ADS method as a simple, mild, and versatile approach for enhancing the visible-light-driven O2 evolution activity of oxyhalide photocatalysts by loading highly dispersed and active Ir species. This method effectively improved the performance of not only a representative oxyhalide Bi₄NbO₈Cl but also of various other oxyhalide photocatalysts through simple stirring in an aqueous Ir precursor solution. The success of the ADS method, particularly with oxyhalides rather than with conventional oxides and oxynitrides, suggests the importance of Clmediated interactions in facilitating effective cocatalyst deposition and/or charge transfer. These findings provide valuable insights for the development of tailored cocatalysts and their loading techniques to optimize the photocatalytic efficiency of mixed-anion photocatalysts.

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Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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