Spontaneous Adsorption of Iridium Chloride Complex on oxychloride photocatalysts Provides Efficient and Durable Reaction Site for Photocatalytic Water Oxidation

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Significance and Relevance

Sillén(-Aurivillius)-type layered oxyhalides, such as Bi_4NbO_8Cl, have been reported to function as stable O_2-evolution photocatalysts in Z-scheme water splitting systems. While investigating effective cocatalysts and their loading methods to enhance O_2 evolution on the representative oxychloride photocatalyst Bi_4NbO_8Cl, we discovered for the first time that highly dispersed $IrO_xH_yCl_z$ species, spontaneously formed by simply stirring Bi_4NbO_8Cl particles in an aqueous Na_3IrCl_6 solution in dark, significantly enhanced the O_2 evolution rate. Moreover, this novel adsorption method proved effective for various oxyhalide photocatalysts.

Preferred and 2nd choice for the topic: "Photocatalysis and photoelectrocatalytic approaches, solar energy utilization" preferred or "H_2 storage and transportation, green H_2 production, hydrogen vectors"
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Sillén(-Aurivillius)-type layered oxyhalides (e.g., oxychlorides) such as Bi_4NbO_8Cl have emerged as promising photocatalysts for visible-light-driven water splitting (Figure 1).[1] Along with exploring related oxyhalide materials, their synthetic methods such as flux-assisted synthesis have been studied to improve their photocatalytic activities.[2] On the other hand, there is still plenty room for exploring their surface engineering, such as loading effective cocatalysts for water oxidation.

Results and Discussion

The oxyhalide photocatalyst Bi_4NbO_8Cl was synthesized using the flux method previously reported.[2] The loading of IrO_2 cocatalysts was carried out via various methods such as the colloidal adsorption (COL), microwave-assisted (MW) method, and photodeposition (PD) method, all of which have been reported as effective for loading IrO_2 on metal oxide and oxynitride photocatalysts.[3-5] Note that, the PD method was proposed to provide IrO_2 species through the oxidation of a Ir precursor $Ir^{III}Cl_6^{3-}$ to $Ir^{IV}O_2$ by photogenerated holes on the photocatalyst accompanied by the reduction of nitrate ions (e.g., $NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + 2H_2O$) by photoexcited electrons.[5] In addition to the above methods, herein we introduced a simple adsorption (ADS) method, which was originally carried out as one of the control tests of the above mentioned PD method. In particular, the photocatalyst particles were just suspended in an aqueous Na_3IrCl_6 solution (in the absence of NO_3^-) in dark.

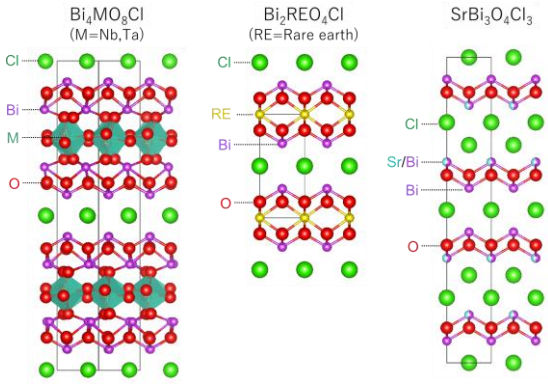

Figure 1 Crystal structures of layered oxyhalide photocatalysts: Bi_4MO_8Cl (M=Nb, Ta), Bi_2REO_4Cl (RE=Rare Earth), and $SrBi_3O_4Cl_3$.

Figure 2 shows the O_2 evolution rates on each Bi_4NbO_8Cl sample (0.1 g) in an aqueous $AgNO_3$ solution (8 mM, 100 mL) under visible light irradiation ($\lambda > 400$ nm) from a 300-W Xe-arc lamp. The PD

method afforded higher rate than IMP, whereas COL and MW ones resulted in slightly higher than bare one but much lower than IMP. Surprisingly, newly attempted ADS method provided almost same rate to PD one, in other words, the highest O_2 evolution rate.

The loaded Ir species via APD were characterized using multiple techniques. ICP measurements indicated that most of the Ir species introduced (0.5 wt% as metal) were successfully loaded on the surface of Bi_4NbO_8Cl, regardless of the loading methods. STEM observations of ADS one showed that identifying the Ir species is nearly impossible. This suggests that the ADS method successfully deposited highly dispersed Ir species on the surface, likely in the form of extremely small particles or cluster-like structures. In the EXAFS spectra (Figure 3), the Ir species loaded by the COL, MW, and IMP methods show only Ir-O bond in the first coordination shell, suggesting that the Ir species exist as oxides or hydroxides. In contrast, the Ir-loaded samples prepared by the ADS and PD methods exhibit not only Ir-O bond but also the bond attributed to Ir-Cl, strongly suggesting that Ir species represented as $IrO_xH_yCl_z$ contributed to the enhanced O_2 evolution.

We applied this novel ADS method to other oxychloride photocatalysts: Bi_4TaO_8Cl, Bi_2ErO_4Cl, and $SrBi_3O_4Cl_3$ (Figure 1). Figure 4 shows the O_2 evolution rates for the oxyhalide photocatalysts onto which Ir species were loaded using the ADS method. The O_2 evolution rates were significantly improved by loading Ir species for both Sillén-type (Bi_2ErO_4Cl, and $SrBi_3O_4Cl_3$) and Sillén-Aurivillius-type (Bi_4NbO_8Cl and Bi_4TaO_8Cl) oxychlorides. As demonstrated above, the novel ADS method was found for the first time to be a mild, simple, and versatile method for loading active and stable Ir species that can significantly enhance the O_2 evolution rates on various oxychlorides photocatalysts.

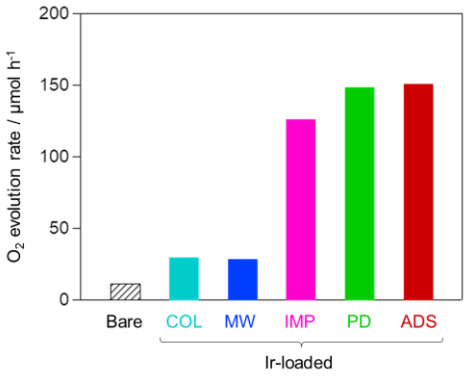

Figure 2. Initial O_2 evolution rate of Bi_4NbO_8Cl loaded with Ir species *via* various methods.

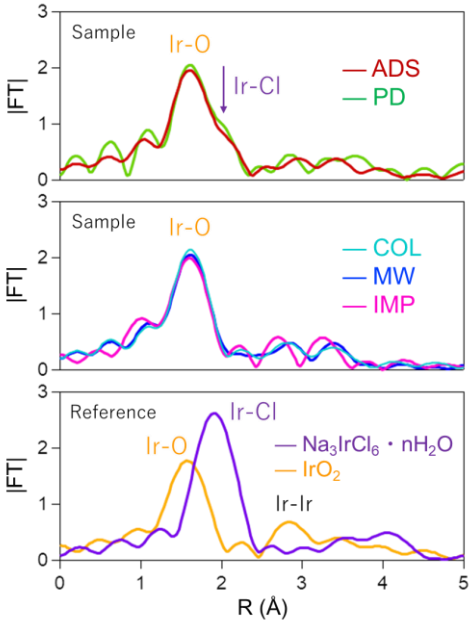

Figure 3. Fourier-transformed Ir L3-edge EXAFS spectra of Bi_4NbO_8Cl loaded with Ir species *via* various methods.

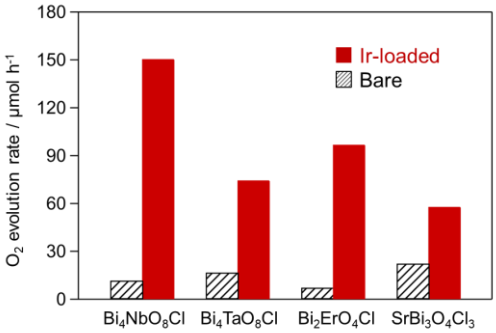

Figure 4. Initial O_2 evolution rate of oxyhalides loaded with or without Ir species *via* adsorption (ADS) method.

References

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Acknowledgements

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