

Highly dispersed Fe-Ru dual cocatalyst derived from Prussian blue analogue for boosting O₂ evolution on an oxyiodide photocatalyst

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Iron hexacyanoruthenate, a Prussian blue analogue, was employed as a precursor to load highly dispersed Fe and Ru dual cocatalysts on an oxyiodide Ba₂Bi₃Nb₂O₁₁I, resulting in significantly enhanced activity for non-sacrificial O₂ evolution with Fe³⁺ electron acceptor under visible light.

Water splitting employing semiconductor photocatalysts has garnered attention as a promising technology for clean hydrogen (H₂) production, and extensive research has been conducted in this field owing to its significant potential for addressing energy and environmental challenges.^{1–5} Cocatalysts loaded on photocatalysts play a crucial role in enhancing the efficiency of water splitting by facilitating charge separation at the heterointerface with the photocatalyst and accelerating surface redox reactions via the provision of active sites exhibiting low activation energy. Single-metal (oxide) cocatalysts—such as Pt and Rh for H₂ evolution and RuO_x and IrO_x for O₂ evolution—are widely utilized in photocatalytic water-splitting systems. Additionally, multimetal cocatalysts have emerged as highly efficient and/or multifunctional alternatives to single-component systems.^{6,7}

Iron-ruthenium dual oxide (Fe,Ru)O_x has been reported to be an effective cocatalyst for oxygen evolution photocatalysts, including layered oxyhalides, in various Z-scheme water-splitting systems.^{8–12} This cocatalyst promotes both the reduction of redox species and water oxidation in a bifunctional manner, resulting in improved O₂ evolution compared with its

single component (i.e., FeO_x or RuO_x).⁸ For example, the loading of (Fe,Ru)O_x on a promising oxyiodide photocatalyst Ba₂Bi₃Nb₂O₁₁I substantially enhanced the O₂ evolution rate in an aqueous solution with Fe³⁺ electron acceptor.¹² However, conventional impregnation method using mixed precursor solutions (e.g., Fe(acac)₃ and Ru(acac)₃ in acetone) resulted in partial segregation of Fe and Ru species as well as aggregation of particles, which probably hindered catalytic performance¹¹.

These limitations motivated us to develop a more uniform and highly dispersed Fe-Ru-based cocatalyst on the photocatalyst surface, aiming to increase the intrinsic activity and the number of active sites available for surface reactions. In this study, we employed iron hexacyanoruthenate (KFe[Ru(CN)₆], hereafter denoted as “FeHCRu”) as a precursor for the loading of Fe-Ru dual cocatalyst. FeHCRu, a Prussian blue analogue, is a coordination polymer in which cyano ligands alternately bridge Fe and Ru, enabling atomic-level mixing of the two metals. While this material has been applied in electrocatalysis,^{13,14} electrochromism,¹⁵ and biosensing,^{16,17} its use as a cocatalyst or cocatalyst precursor in combination with a photocatalyst has, to the best of our knowledge, not been reported. Herein, FeHCRu was impregnated onto Ba₂Bi₃Nb₂O₁₁I and subsequently calcined under argon (Ar) flow, resulting in a significant enhancement of O₂ evolution activity in a Z-scheme water splitting system.

Following previous studies, Ba₂Bi₃Nb₂O₁₁I and FeHCRu were synthesized via the flux and coprecipitation methods, respectively.^{12,18} X-ray diffraction (XRD) and other measurements validated the successful synthesis of the target compounds (Figures S1 and S2). We evaluated the photocatalytic O₂ evolution activity of Ba₂Bi₃Nb₂O₁₁I samples loaded with FeHCRu at different calcination temperatures, denoted as Ba₂Bi₃Nb₂O₁₁I (FeHCRu-*T* °C), under visible light in the presence of the reversible electron acceptor Fe³⁺ (Figure 1). The samples calcined at temperatures exceeding 400 °C exhibited significantly higher activity than those calcined at

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100 °C. The O₂ evolution activity followed a volcano-shaped trend with respect to calcination temperature, increasing up to 500 °C and then decreasing at 550 °C. Importantly, calcination at any of these temperatures did not alter the bulk crystal structure of Ba₂Bi₃Nb₂O₁₁I or negatively affect its intrinsic O₂ evolution activity (Figures S3, S4, and Table S1). The volcano-shaped trend resembled that observed when (Fe,Ru)O_x was applied using acac-based precursors, although the optimal temperature differed (500 °C for FeHCRu and 450 °C for (Fe,Ru)O_x),¹² likely due to the different thermal decomposition behaviors of their respective precursor ligands. The optimized Ba₂Bi₃Nb₂O₁₁I (FeHCRu-500 °C) sample exhibited approximately 2.5 times higher O₂ evolution activity than a previously reported Ba₂Bi₃Nb₂O₁₁I sample loaded with (Fe,Ru)O_x using acac-based precursors at its optimal temperature (hereafter referred to as Ba₂Bi₃Nb₂O₁₁I (acac-450 °C)). Consistently, the apparent quantum efficiency (AQE) for O₂ evolution over Ba₂Bi₃Nb₂O₁₁I (FeHCRu-500 °C) was 0.6% (at 405 nm), which is twice as high as that over Ba₂Bi₃Nb₂O₁₁I (acac-450 °C) (0.3% at 405 nm)¹².

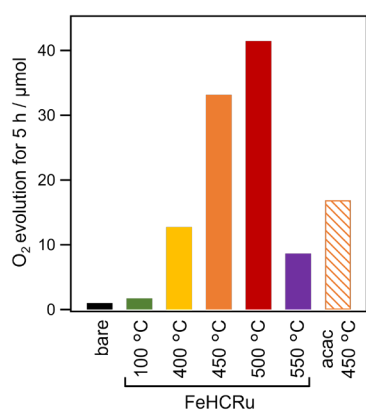


Figure 1. Amounts of O₂ evolved over 5 h reaction for unmodified Ba₂Bi₃Nb₂O₁₁I, Ba₂Bi₃Nb₂O₁₁I (FeHCRu-*T* °C), or Ba₂Bi₃Nb₂O₁₁I (acac-450 °C) in Fe(NO₃)₃ (aq) (8 mM) under visible light ($\lambda > 400$ nm) irradiation.

Annular dark-field scanning transmission electron microscopy (ADF-STEM) images and STEM equipped with energy-dispersive X-ray spectroscopy (STEM-EDS) elemental maps of Ba₂Bi₃Nb₂O₁₁I (acac-450 °C) and Ba₂Bi₃Nb₂O₁₁I (FeHCRu-500 °C) are shown in Figure 2. As reported previously,¹¹ for Ba₂Bi₃Nb₂O₁₁I (acac-450 °C), FeO_x was loaded as large particles exhibiting diameters of several tens of nanometers, while RuO_x was distributed either on the surface of FeO_x or in Fe-deficient regions. In contrast, for Ba₂Bi₃Nb₂O₁₁I (FeHCRu-500 °C), both Fe and Ru species were highly dispersed, most appearing smaller than 10 nm, and positioned close to each other. To further evaluate the cocatalyst dispersion, the electrochemically active surface area (ECSA) was estimated through electrochemical measurements. Cocatalyst precursors were spin-coated onto conductive fluorine-doped tin oxide (FTO) substrates, calcined under an Ar flow, and subsequently subjected to cyclic voltammetry (CV). The results indicated that FeHCRu calcined at 500 °C exhibited higher dispersion than (Fe,Ru)O_x prepared at 450 °C using acac-based precursors (Figure S5). These findings strongly suggest that the improved loading state—characterized by closely spaced, highly dispersed Fe and Ru

species without forming separate aggregates—increased the number of active sites, thereby enhancing the O₂ evolution activity of the oxydide photocatalyst.

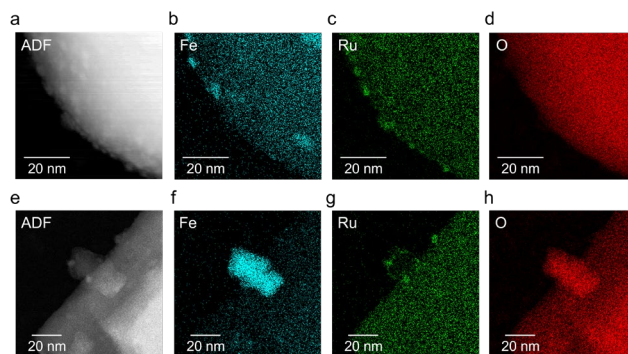


Figure 2. ADF-STEM images of (a) Ba₂Bi₃Nb₂O₁₁I (FeHCRu-500 °C) and (e) Ba₂Bi₃Nb₂O₁₁I (acac-450 °C), along with the STEM-EDS elemental maps of Fe, Ru, and O for Ba₂Bi₃Nb₂O₁₁I (FeHCRu-500 °C) (b-d) and Ba₂Bi₃Nb₂O₁₁I (acac-500 °C) (f-h).

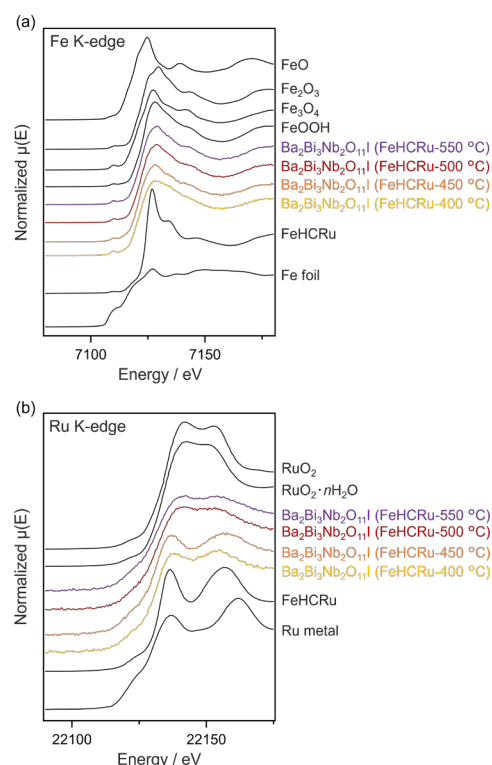


Figure 3. (a) Fe K-edge and (b) Ru K-edge XANES spectra for Ba₂Bi₃Nb₂O₁₁I (FeHCRu-*T* °C).

The chemical states of Fe and Ru in Ba₂Bi₃Nb₂O₁₁I (FeHCRu-*T* °C) were investigated by analyzing X-ray absorption fine structure (XAFS). The Fe K-edge X-ray absorption near-edge structure (XANES) spectra across all calcination temperatures (400–550 °C) resembled those of Fe₂O₃ and FeOOH, suggesting that Fe existed in an oxidized state (Figure 3a). This assignment is consistent with the Fe K-edge extended XAFS (EXAFS) spectra, which show the presence of Fe–O bond (Figure S6a). In contrast, the Ru K-edge XANES spectra changed with increasing temperature, indicating a gradual transformation into a mixture of metallic Ru and (hydrous) Ru oxide species (Figure 3b). This interpretation is corroborated by the corresponding Ru K-edge

EXAFS spectra, which reflect the coexistence of these species (Figure S6b). Such transformation is likely associated with the release of cyanide groups, as evidenced by the gradual weight loss observed in the thermogravimetric–differential thermal analysis (TG-DTA) of FeHCRu under a nitrogen atmosphere (Figure S2c). The IR spectra of the FeHCRu-loaded sample calcined at or below 500 °C retained a peak attributed to the stretching vibration of cyano groups ($\sim 2100\text{ cm}^{-1}$) (Figure S7). However, this peak disappeared in the sample calcined at 550 °C. These results indicate that the Fe–N bonds are relatively weak and dissociate at temperatures as low as 400 °C, whereas the Ru–C bonds are more robust, with the cyano ligands gradually dissociating but partially persisting up to 500 °C.

Additional spectroscopic and photocatalytic investigations were conducted to evaluate the stability of the O_2 evolution activity and gain insights into the underlying cocatalyst behavior. XAFS analysis of $\text{Ba}_2\text{Bi}_3\text{Nb}_2\text{O}_{11}\text{I}$ (FeHCRu-500 °C) after the O_2 evolution reaction revealed that the Fe K-edge spectrum remained largely unchanged, indicating that the oxidation state of Fe was maintained throughout the reaction (Figure S8a). In contrast, the Ru K-edge spectrum showed evidence of partial reduction of Ru species during the reaction (Figure S8b)—such a reduction behavior is also observed in a previous study on (Fe,Ru) O_x using acac-based precursors.¹² This result suggests that a fraction of the Ru species accepted photogenerated electrons and facilitated the reduction of Fe^{3+} . Indeed, time-resolved microwave conductivity (TRMC) measurement of $\text{Ba}_2\text{Bi}_3\text{Nb}_2\text{O}_{11}\text{I}$ (FeHCRu-500 °C) suggests that both electrons and holes transfer to the cocatalyst (Figure S9). Furthermore, electrochemical investigations support that the reduced Ru species (Ru metal) exhibit a high activity for Fe^{3+} reduction (Figure S10). The three-cycle test (Figure S11) demonstrated that the O_2 evolution activity did not decrease following the first cycle; notably, it improved in the second cycle. This result implies that the change in the chemical state of Ru did not have a negative effect on the photocatalytic performance and may have even enhanced it. The $\text{Ba}_2\text{Bi}_3\text{Nb}_2\text{O}_{11}\text{I}$ (FeHCRu-500 °C) sample generated 97.2 μmol of O_2 for 9 hours (Figure S11). Since water oxidation is a four-electron process, this corresponds to the involvement of 389 μmol of electrons and holes contributing to this reaction. This value is substantially larger than the amount of Fe and Ru in FeHCRu loaded (3.6 μmol), confirming that the loaded Fe–Ru species functioned as a cocatalyst on the O_2 evolution photocatalyst. The stability of both the photocatalyst and the cocatalyst was validated by XRD, EDX, and TEM measurements of the $\text{Ba}_2\text{Bi}_3\text{Nb}_2\text{O}_{11}\text{I}$ (FeHCRu-500 °C) sample after the repeatability test (Figures S12 and S13).

The catalytic activity of each Fe–Ru species cocatalyst was evaluated via electrochemical measurements. Electrodes, prepared similarly to those utilized for ESCA measurements, were subjected to linear sweep voltammetry (LSV) (Figure 4). FeHCRu calcined at 100 °C exhibited negligible catalytic activity for both water oxidation and Fe^{3+} reduction, whereas calcination at temperatures exceeding 400 °C significantly enhanced the catalytic activity, with the highest activity

observed at 500 °C (Figure 4). This temperature-dependent trend in catalytic activity corresponds with the temperature dependence observed for O_2 evolution activity of $\text{Ba}_2\text{Bi}_3\text{Nb}_2\text{O}_{11}\text{I}$ (FeHCRu- T °C) (Figure 1). The emergence of catalytic activity at temperatures above 400 °C is probably related to the decomposition of FeHCRu. The decrease in catalytic activity above 500 °C is likely attributed to the aggregation of the catalyst particles, as shown by ECSA measurements (Figure S5), which suggest that increasing the calcination temperature reduces the number of active sites. The progression of aggregation with increasing calcination temperature was also observed in TEM images of $\text{Ba}_2\text{Bi}_3\text{Nb}_2\text{O}_{11}\text{I}$ (FeHCRu- T °C) (Figure S14). The trade-off between favorable progress in the decomposition of FeHCRu and unfavorable aggregation of cocatalyst at elevated temperatures likely explains the volcano-type dependence of O_2 evolution activity on the loading temperature for $\text{Ba}_2\text{Bi}_3\text{Nb}_2\text{O}_{11}\text{I}$ (FeHCRu- T °C) (Figure 1). The previously reported (Fe,Ru) O_x prepared at 450 °C using acac-based precursors¹² or chloride-based precursors⁸ exhibited lower catalytic activity for both water oxidation and Fe^{3+} reduction than FeHCRu calcined even at the same temperature (Figure 4). Note that (Fe,Ru) O_x prepared using chloride-based precursors exhibits higher catalytic activity than that derived from acac-based ones in electrode evaluations; however, when deposited onto $\text{Ba}_2\text{Bi}_3\text{Nb}_2\text{O}_{11}\text{I}$, chlorine–iodine substitution occurs, resulting in lower photocatalytic activity compared with the acac-derived sample.¹² Although the FeHCRu-derived species exhibited higher catalytic activity for the desired reactions, it also exhibited higher catalytic activity for Fe^{2+} oxidation, i.e., the reverse electron transfer reaction (Figure S15), which is also supported by the photocatalytic reaction in the presence of both Fe^{2+} and Fe^{3+} (Figure S16). These results indicate that the FeHCRu-derived cocatalyst promotes both the forward and reverse reactions; however, its pronounced enhancement of the forward reaction plays a key role in improving O_2 evolution on $\text{Ba}_2\text{Bi}_3\text{Nb}_2\text{O}_{11}\text{I}$.

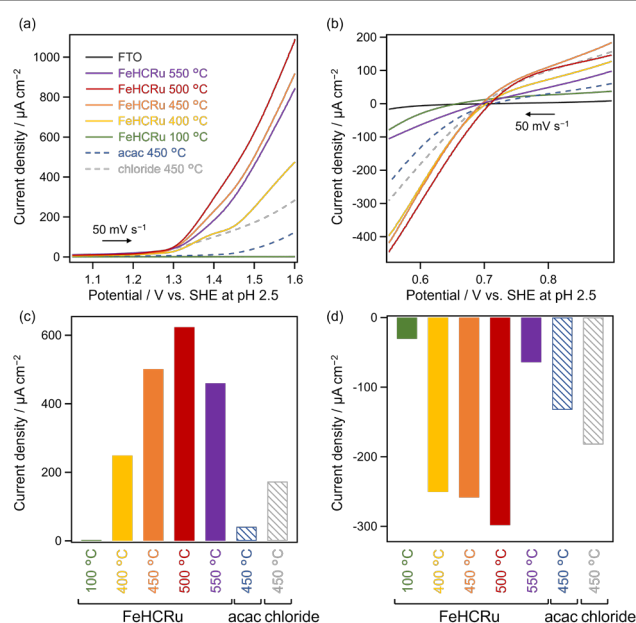


Figure 4. LSV results for electrodes prepared using FeHCRu, acac (chloride)-based precursors in aqueous Na₂SO₄ solution (a) in the absence and (b) in the presence of Fe³⁺ electron acceptor. The catalytic activity for water oxidation was evaluated in (a), and that for Fe³⁺ reduction in (b). The current densities at 1.5 V and 0.6 V in (a) and (b) are summarized in (c) and (d), respectively.

The optimized Ba₂Bi₃Nb₂O₁₁I (FeHCRu-500 °C) was utilized as the O₂ evolution photocatalyst, and RuO_x-loaded Rh-doped SrTiO₃ (SrTiO₃:Rh; characterization in Figure S17) was used as the H₂ evolution photocatalyst in the Z-scheme water splitting system in the presence of the Fe³⁺/Fe²⁺ redox couple (Figure 5). As the reaction proceeded, the concentration of Fe³⁺/Fe²⁺ reached equilibrium, and H₂ and O₂ were steadily produced in a stoichiometric ratio of 2:1. The gas evolution rate of the system employing Ba₂Bi₃Nb₂O₁₁I (FeHCRu-500 °C) was higher than that of the previously reported system using Ba₂Bi₃Nb₂O₁₁I (acac-450 °C).¹² Therefore, loading the Fe-Ru dual cocatalyst onto Ba₂Bi₃Nb₂O₁₁I using FeHCRu under optimal conditions maximized the O₂ evolution rate, thereby improving overall water splitting performance.

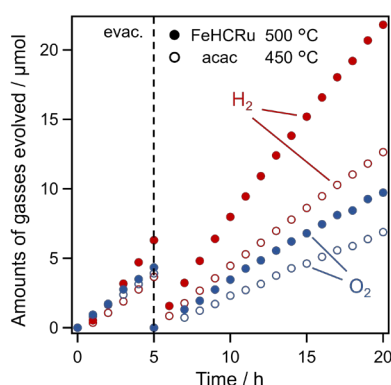


Figure 5. Time courses of H₂ and O₂ evolution over a mixture of Ba₂Bi₃Nb₂O₁₁I (FeHCRu-500 °C) or Ba₂Bi₃Nb₂O₁₁I (acac-450 °C) and RuO_x-loaded SrTiO₃:Rh in Fe(NO₃)₃ (aq) (2 mM) at pH 2.4 under visible light.

In summary, iron hexacyanoruthenate (FeHCRu), a Prussian blue analogue, was employed as a precursor for a Fe-Ru dual cocatalyst on the oxyiodide photocatalyst Ba₂Bi₃Nb₂O₁₁I. Loading FeHCRu onto Ba₂Bi₃Nb₂O₁₁I at 500 °C under Ar flow yielded highly dispersed Fe and Ru species on the photocatalyst surface, thereby significantly enhancing O₂ evolution in the presence of Fe³⁺ as a reversible electron acceptor. Compared with conventional (Fe,Ru)O_x cocatalysts prepared using acac-based precursors, the FeHCRu-derived cocatalyst more effectively accelerated O₂ evolution on Ba₂Bi₃Nb₂O₁₁I and consequently enhanced overall Z-scheme water splitting, primarily owing to the increased number of active sites. These findings highlight that Prussian blue analogues are promising precursors for constructing highly dispersed mixed-metal compound cocatalysts, offering a viable strategy to boost the efficiency of photocatalytic water splitting.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information.

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