

ARTICLE

Two-step photocatalytic water splitting into H₂ and O₂ using layered metal oxide KCa₂Nb₃O₁₀ and its derivatives as O₂-evolving photocatalysts with IO₃[−]/I[−] or Fe³⁺/Fe²⁺ redox mediator

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Two-step photoexcitation (Z-scheme) systems that can split water into H₂ and O₂ under UV light were constructed using a layered potassium calcium niobate (KCa₂Nb₃O₁₀) and its derivatives as O₂-evolving photocatalysts, combined with an appropriate H₂-evolving photocatalyst in the presence of iodate/iodide (IO₃[−]/I[−]) or iron(III)/(II) (Fe³⁺/Fe²⁺) as an electron mediator. The original KCa₂Nb₃O₁₀ showed negligibly low activity for photocatalytic water oxidation to O₂ in the presence of IO₃[−] as an electron acceptor, since the anionic IO₃[−] cannot penetrate into the interlayer spaces owing to the strong electrostatic repulsion between IO₃[−] and the negatively charged niobate layers. The rate of O₂ evolution was significantly increased after exfoliation-restack process of KCa₂Nb₃O₁₀, certainly due to much-facilitated access of IO₃[−] to the opened reduction sites of nanosheet surfaces. The loading of RuO_x or PtO_x cocatalysts on the samples significantly increased the rate of O₂ evolution. The electrochemical analysis indicated that these cocatalysts effectively decreased the overpotential of IO₃[−] reduction, which occurs through the 6-electron process. On the other hand, the original layered structure was effective for the photocatalytic O₂ evolution in the presence of Fe³⁺ electron acceptor even without any cocatalysts, suggesting that the interlayer spaces of layered niobate can work as effective reduction sites for cationic Fe³⁺. Finally, simultaneous evolution of H₂ and O₂ was attempted by using these KCa₂Nb₃O₁₀-based materials as O₂-evolving photocatalysts, combined with an appropriate H₂-evolving photocatalyst. By employing the appropriate combination of KCa₂Nb₃O₁₀-based materials with the redox couple, which was suggested by the result of half O₂-evolution reactions, simultaneous evolution of H₂ and O₂ stably proceeded with higher rates.

1. Introduction

Photocatalytic water splitting using semiconductor materials have received much attention due to the potential for clean production of H₂ from water by harvesting abundant solar light. To achieve practically high efficiency of H₂ production under solar light irradiation, both the utilization of wide range of solar light spectrum, especially in visible light region, and the high quantum efficiency in the reaction are undoubtedly indispensable. Water splitting systems based on two-steps photoexcitation, which were inspired by the Z-scheme mechanism of photosynthesis in green plants, have been recently developed and proven as an effective way to utilize wider range of visible light.^{1–13} In this system, the water-splitting reaction is broken up into two stages, one for H₂ evolution and the other for O₂ evolution, and these are

combined by using a shuttle redox couple in the solution. The present author's group have first demonstrated visible-light-induced water splitting into H₂ and O₂ using two different metal oxide semiconductors and an iodate/iodide (IO₃[−]/I[−])¹, and have applied various kinds of semiconductor materials, not only metal oxides but also metal oxynitrides^{2–6} and organic dyes,^{7,8} to the two-steps (Z-scheme) water splitting system. Kudo and his coworkers have also demonstrated Z-scheme type water splitting under visible light using metal oxide photocatalysts with redox couples such as Fe³⁺/Fe²⁺^{9–11} and Co(bpy)₃³⁺/Co(bpy)₃²⁺,¹² or even without any redox couple in the solution (through direct electron transfer between semiconductor particles)¹³.

Cation-exchangeable layered metal oxides such as K₄Nb₆O₁₇ have been studied as promising candidates for efficient photocatalyst materials for water splitting.^{14–33} They

generally consist of 2-dimensional anion layers of metal oxide and the cations such as K^+ that compensate the negative charge of anion layers, thus forming cation-exchangeable layered structures. Efficient photocatalytic reactions are expected to proceed on such cation-exchangeable layered metal oxides, because water molecules, as well as small cations, can generally intercalate into the interlayer spaces of them and efficiently react with the photoexcited carriers, which are generated on the semiconducting 2-dimensional anion layers of metal oxides. Indeed, some cation-exchangeable layered metal oxides such as $K_4Nb_6O_{17}$,²³⁻²⁵ $K_2La_2Ti_3O_{10}$,^{26, 27} $Rb_4Ta_6O_{17}$,²⁸ $RbNdTa_2O_7$,^{29, 30} $A'_2ASrTa_2O_7$ ($A' = H$ or K , $A = La_{2/3}$ or Sr),³¹ 32 $NaCa_2Ta_3O_{10}$ ³³ have been reported as active photocatalyst for efficient water splitting into H_2 and O_2 under UV irradiation. Among them, layered perovskite structure can offer us great variety of semiconducting materials, including visible-light-responsive ones, based on the facile exchange of cations in the A and B sites within the appropriate parameters of tolerance factor.³⁴⁻³⁶ Partial replacement of cations and/or exfoliation of the 2-dimensional layers of these layered perovskite materials have also been extensively studied to enhance the photocatalytic activity. However, such cation-exchangeable layered metal oxides have not been employed as photocatalysts in the Z-scheme water-splitting systems, to the best of our knowledge.

One of the Dion-Jacobson type layered perovskite, $KCa_2Nb_3O_{10}$ has been reported to show significantly high activity for photocatalytic H_2 evolution from an aqueous methanol solution under UV light after exchange of the K^+ cations in the interlayer by protons (H^+), whereas it showed negligibly low activity for O_2 evolution in the presence of Ag^+ ion as sacrificial electron acceptor.³⁷ Ebina *et al.* have reported simultaneous evolution of H_2 and O_2 on derivatives of $KCa_2Nb_3O_{10}$ that were prepared via exfoliation of 2-dimensional layers with a soft-chemical method and following restack process, in which nanoparticles of RuO_x cocatalysts were simultaneously incorporated between the 2-dimensional niobate layers.³⁸ This finding implies that the niobate layers of $KCa_2Nb_3O_{10}$ are potentially capable of oxidation of water efficiently. In the present study, we thus focused on the utilization of $KCa_2Nb_3O_{10}$ and its derivatives as O_2 -evolving photocatalysts in the Z-scheme water-splitting systems with redox mediator such as IO_3^-/I^- or Fe^{3+}/Fe^{2+} . The influences of exfoliation-restack and cocatalysts loading on the activity and selectivity of water oxidation were examined in detail.

2. Experimental

2-1. Preparation of photocatalysts.

Particles of $KCa_2Nb_3O_{10}$ were prepared by calcining a mixture of K_2CO_3 , $CaCO_3$ and Nb_2O_5 ($K:Ca:Nb = 1.1:2:3$) at 1473 K for 12 h. The obtained $KCa_2Nb_3O_{10}$ powder was stirred with 5 M HNO_3 aqueous solution for 72 h to replace K^+ to H^+ , washed with distilled water, and then dried in air at room temperature. The proton-exchanged particles will be denoted as

$H^+/KCa_2Nb_3O_{10}$ hereafter. The $H^+/KCa_2Nb_3O_{10}$ particles (0.4 g) were suspended in 100 mL of aqueous solution, in which equimolar of tetrabutylammonium hydroxide (TBAOH) molecules to that of $H^+/KCa_2Nb_3O_{10}$ (ca. 0.73 mmol, calculated as $HCa_2Nb_3O_{10} \cdot 1.5H_2O$) was added as an initiator of exfoliation. The suspension was continuously shaken at room temperature for 7 days until the $H^+/KCa_2Nb_3O_{10}$ exfoliate into nanosheets.³⁸ The resulting colloidal suspension was added dropwise into 2 M KOH aqueous solution, immediately producing white precipitate. The precipitate was thoroughly washed with water several times and dried in air at room temperature; the obtained sample will be denoted as ex- $Ca_2Nb_3O_{10}/K^+$ hereafter. The TEM images of the exfoliated nano sheets and the ex- $Ca_2Nb_3O_{10}/K^+$ are shown in Fig. S1 in supporting information (SI). Modification of ex- $Ca_2Nb_3O_{10}/K^+$ with cocatalysts was carried out by impregnation of an aqueous solution containing one of ammine complexes of metals such as $[Pt(NH_3)_4](OH)_2$, $[(NH_3)Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5]Cl_6$, $[Ir(NH_3)_6]Cl_3$, $[Rh(NH_3)_6]Cl_3$ and $[Co(NH_3)_6]Cl_3$, followed by heating in air at 773 K for 1 h. Since the dominant valence states of these metal species after the loading procedure were confirmed to be Pt^{2+} , Ru^{4+} , Ir^{4+} , and Rh^{3+} by X-ray photoabsorption spectroscopy (XPS, ULVAC Phai MT-5500), the samples loaded with the cocatalysts will be denoted as PtO, RuO_2 , IrO_2 and Rh_2O_3 -loaded one, respectively. On the other hand, the samples loaded with Co species were confirmed to contain both Co^{2+} and Co^{3+} states, therefore will be denoted as CoO_x -loaded one for simplification. The products will be denoted as $MO_y/ex-Ca_2Nb_3O_{10}/K^+$ ($MO_y = PtO, RuO_2, IrO_2, Rh_2O_3$ and CoO_x). When the protonated forms of these samples are required, the K^+ cations exist in $MO_y/ex-Ca_2Nb_3O_{10}/K^+$ samples were replaced with H^+ by stirring in an aqueous HNO_3 solution (1 M) at room temperature for 24 h (referred to as $MO_y/ex-Ca_2Nb_3O_{10}/K^+/H^+$).

Strontium titanate doped with rhodium species ($SrTiO_3:Rh$)³⁶ was prepared by solid state reaction. A mixture of $SrCO_3$, TiO_2 and Rh_2O_3 ($Sr : Ti : Rh = 1 : 0.99 : 0.01$ to form ideal formula of $SrTi_{0.99}Rh_{0.01}O_{3-\delta}$) was calcined in air at 873 K for 2 h and subsequently at 1273 K for 10 h. Pt cocatalyst was loaded onto $SrTiO_3:Rh$ by impregnation using $H_2PtCl_6 \cdot 6H_2O$ and subsequent heating under a H_2 flow at 573 K for 2 h. In the case of Ru cocatalyst, Ru species were loaded on $SrTiO_3:Rh$ by means of photodeposition method using $RuCl_3 \cdot nH_2O$ as a Ru source, according to the method reported previously.¹¹

2-2. Photocatalytic reactions.

Photocatalytic reactions were carried out using a Pyrex glass reactor connected to a closed gas-circulation system. For the photocatalytic water oxidation (O_2 evolution) in the presence of an electron acceptor (i.e., half reaction of water splitting) catalyst powder (50 or 100 mg) was suspended in 70 mL of an aqueous $NaIO_3$ or $Fe(NO_3)_3$ solution (5 mM) in the reactor by using a set of magnetic stirrer and bar. The pH values of the solutions were controlled by adding aqueous KOH or HNO_3 solution, when needed. Since it was demonstrated that the O_2

evolution in the presence of IO_3^- generally proceeded more efficiently in basic conditions (above pH 9), the original $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ and its derivatives (100 mg) were suspended to $\text{NaIO}_3\text{aq.}$ without proton-exchange. The addition of these K^+ -contain samples spontaneously change the pH of $\text{NaIO}_3\text{aq.}$ (originally ca. 6.8) to higher values up to ca. 9.6 due to the exchange of K^+ with H^+ in the solutions. As for the O_2 evolution in the presence of Fe^{3+} electron acceptor, the reaction must be carried out in acidic condition with pH below ca. 3, because Fe^{3+} cations easily precipitate as $\text{Fe}(\text{OH})_3$ with higher pH values. In order to maintain the pH values below 3 stably through the reactions, the $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ -derivatives were treated by $\text{HNO}_3\text{aq.}$ before the use as described above, and furthermore a small amount of $\text{HNO}_3\text{aq.}$ was added into $\text{Fe}(\text{NO}_3)_3\text{aq.}$ to adjust the pH to 2.5 before reaction.

For the two-step water-splitting reaction with IO_3^-/I^- redox couple, the Pt-loaded $\text{SrTiO}_3\text{:Rh}$ (50 mg) and one of the $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ -derivatives (100 mg) were suspended in an aqueous KI solution (5 mM, 70 mL) as H_2 -evolving and O_2 -evolving photocatalysts, respectively. The pH value of the solution was adjusted to be ca. 12 by adding small amount of aqueous KOH solution. In the case of two-step water splitting with $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple, the Ru-loaded $\text{SrTiO}_3\text{:Rh}$ (50 mg) and one of the proton-exchanged $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ -derivative (500 mg) were suspended in 250 mL of an aqueous $\text{Fe}(\text{ClO}_4)_2$ solution (5 mM), whose pH values were adjusted to ca. 2.5 by adding a small amount of aqueous HClO_4 solution. The suspension was irradiated using 300 W Xe lamp (Cermox LF-300F, $\lambda > 300$ nm) thorough a water filter. The evolved gases were analyzed by on-line gas chromatography (detector; TCD, column packing; molecular sieve 5 A, Ar carrier).

2-3. Electrochemical Measurement.

To evaluate the catalytic ability of metal oxides (PtO , RuO_2 , IrO_2 , Rh_2O_3 , and CoO_x) used as cocatalysts, these particles were prepared on conductive glass substrate (FTO) via basically same procedure to that on $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ -derivatives as follows. Small amount (50 μL) of $[\text{Pt}(\text{NH}_3)_4](\text{OH})_2$, $[(\text{NH}_3)_4\text{Ru}-\text{O}-\text{Ru}(\text{NH}_3)_4-\text{O}-\text{Ru}(\text{NH}_3)_5]\text{Cl}_6$, $[\text{Ir}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ or $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ aqueous solution (10 mM) was dropped on a FTO substrate, and the substrates were dried in air at room temperature and subsequently calcined at 773 K for 1 h. XPS analysis confirmed that the valence states of the loaded metal cations were basically same as to those loaded on the $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ -derivatives. The electrochemical cell used for the experiments consisted of a prepared MO_x/FTO electrode as the working electrode, a Pt wire as the counter electrode, and a Ag/AgCl as the reference electrode. The potential of the working electrode was controlled using a potentiostat (VersaSTAT3, Princeton Applied Research Co., Ltd.). The overpotentials for IO_3^- and Fe^{3+} reduction over the MO_x/FTO electrodes were estimated by means of cyclic voltammetry (CV) in a 0.5 M Na_2SO_4 aqueous solution (40 mL) in the absence and presence of NaIO_3 or $\text{Fe}(\text{NO}_3)_3$ with different concentrations. The overpotentials for water oxidation were

estimated based on the CV profiles of the MO_x/FTO electrodes in a dehydrated acetonitrile (40 mL) solutions containing tetrabutylammonium perchlorate (0.1 M) and different amounts of distilled water (0, 72, 360, 720 μL).

3. Results and discussion

3-1. Characterizations of samples before and after exfoliation-restack process.

Fig. 1 shows XRD patterns of the prepared samples. Both the original $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ and its proton-exchanged form ($\text{H}^+/\text{HCa}_2\text{Nb}_3\text{O}_{10}$) exhibited strong and sharp diffraction peaks corresponding to (00*n*) facets as reported^{39, 40}, indicating well-regulated stacking of niobate layers along with c-axis. The (00*n*) diffraction peaks shifted to lower angles after the proton-exchange due to the spontaneous hydration of interlayer space, forming average formula of $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$.⁴⁰ As seen in the SEM images (see Fig. 2-a and b), both the original $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ and $\text{H}^+/\text{HCa}_2\text{Nb}_3\text{O}_{10}$ consist of aggregation of plate-like primary particles with grain sizes of several micrometers; these samples exhibit quite small surface area (ca. 0.5 m^2/g) as described in the SEM images. Because the probe N_2 molecule cannot intercalate into quite-narrow space of interlayers, only the outermost part of particles are measured as specific surface area. The intensity of peaks corresponding to (00*n*) was significantly decreased along with obvious broadening in the peak width after the exfoliation-restack process (see Fig. 1-c for $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ sample). The change in the (00*n*) diffraction peaks indicated that the niobate sheets once exfoliated were randomly restacked by the static attraction between the negatively charged niobate sheet and the positive charge of K^+ cations added into the solution, forming loosely

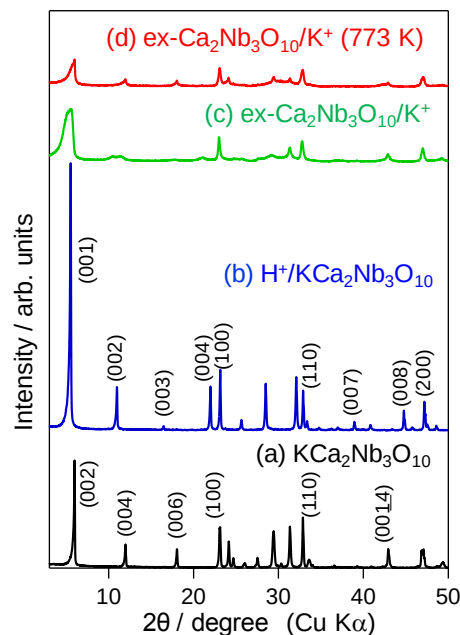


Fig.1 XRD patterns of (a) $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, (b) $\text{H}^+/\text{KCa}_2\text{Nb}_3\text{O}_{10}$, (c) $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ and (d) $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ (773 K).

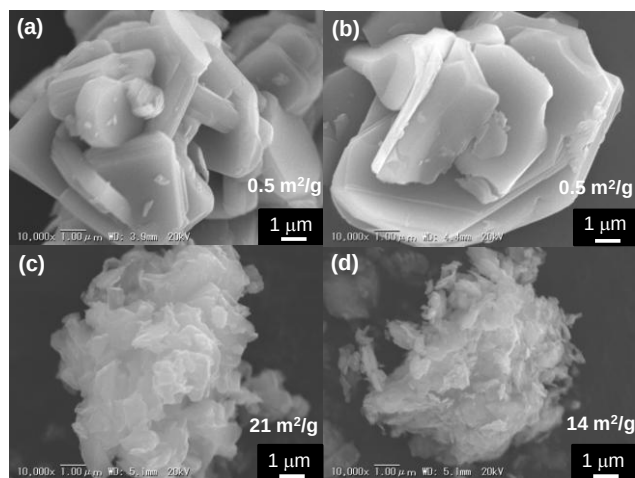


Fig. 2 SEM images of (a) $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, (b) $\text{H}^+/\text{KCa}_2\text{Nb}_3\text{O}_{10}$, (c) $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$, (d) $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ (773 K) particles.

bounded layered structures (see Fig. S1 for TEM image of exfoliated nano sheet and re-stacked one). As shown in Fig. 2-c, the $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ sample indeed consisted of randomly stacked thin plates with much smaller size (several hundred nanometers) compared to the original one. Through the exfoliation-restack process, the specific surface area of sample significantly increased (from ca. 0.5 to 21 m^2/g , see the values shown in SEM images). This significant increase indicated the increased fraction of outermost layer *via* the exfoliation-restack process and also suggested the formation of pore or voids between the niobate sheets, to which N_2 probe molecules can penetrate. Both the broadening and the shift of (00 n) peaks toward lower angles in $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ strongly suggested that the interlayer spaces contained larger amounts of water molecules than in the $\text{H}^+/\text{KCa}_2\text{Nb}_3\text{O}_{10}$ sample, possibly along with a small amount of bulky TBA^+ cations that were incorporated during the restack process. While the (00 n) peaks of the $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ sample became shaper after calcinations of at 773 K in air certainly due to the elimination of water and TBA^+ molecules from the interlayer spaces, they were readily broadened again by exposing to moisture condition as shown in Fig. S2, indicating facile hydration nature of the interlayer spaces of samples obtained *via* the exfoliation-restack process. On the other hand, the diffraction peaks corresponding to (1 m 0), such as (100) or (110), are clearly remained even after the exfoliation-restack process, while the intensity decreased to be about half of the originals. The clear presence of peaks corresponding to (1 m 0) indicated that the planer structures of niobate sheets themselves were retained to some extent, while the size of sheets was reduced during the exfoliation process, as clearly observed in the SEM and TEM images of $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ (Fig. 2-c and Fig.S1-b).

3-2. Photocatalytic water oxidation on $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ -based samples using IO_3^- as electron acceptor

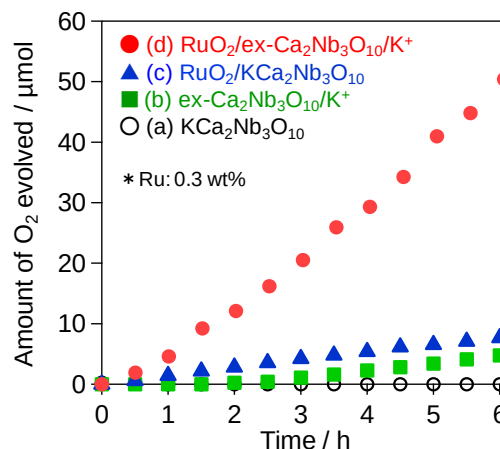
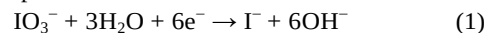


Fig. 3 Time courses of O_2 evolution over 100 mg of (a) $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, (b) $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$, (c) $\text{RuO}_2/\text{KCa}_2\text{Nb}_3\text{O}_{10}$, (d) $\text{RuO}_2/\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ in 5 mM NaIO_3 aqueous solution under UV light irradiation ($\lambda > 300$ nm, Xe lamp).

Fig. 3 shows the time courses of O_2 evolution from water on $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ -based samples using iodate (IO_3^-) as an electron acceptor under UV light irradiation. Although O_2 evolution on the original $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ sample was negligible, the $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ was found to generate appreciable amount of O_2 with steady rate. The proton-exchanged form ($\text{H}^+/\text{KCa}_2\text{Nb}_3\text{O}_{10}$) also showed negligibly low activity for O_2 evolution, while the $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ sample treated with acid ($\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+/\text{H}^+$) generated appreciable amount of O_2 (see Fig. S3). Since the IO_3^- anion cannot penetrate into the interlayer spaces of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ (or $\text{H}^+/\text{KCa}_2\text{Nb}_3\text{O}_{10}$) owing to both the larger size of IO_3^- anions and the electrostatic repulsion between IO_3^- and the negatively charged niobate layers, i.e., $(\text{Ca}_2\text{Nb}_3\text{O}_{10})^-$; the reduction of IO_3^- by the photoexcited electrons must occur at the outermost layer or at the edge of niobate layers of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ (or $\text{H}^+/\text{KCa}_2\text{Nb}_3\text{O}_{10}$). Therefore the rate of IO_3^- reduction on $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ is undoubtedly limited by the small amount of the active sites, resulting in the negligibly low rate of water oxidation, due to the fast recombination between electrons and holes. It is reasonable to consider that the O_2 evolution on $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ sample was enhanced by the increased number of active sites for IO_3^- reduction, based on the fact that the exfoliation-restacking process obviously increased the number of outermost layer and edges of niobate sheets as proven by the increased specific surface area and the SEM images of $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$. The loading of RuO_2 cocatalyst on the surface of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ particles also increased the rate of O_2 generation (see Fig. 3-c), probably due to the enhanced IO_3^- reduction *via* 6-electron process (eq. 1) on the RuO_2 cocatalysts as reported in the O_2 generation on WO_3 photocatalysts with IO_3^- electron acceptor.⁴¹



Combination of the exfoliation-restack process and the loading of RuO_2 cocatalyst drastically increased the rate of O_2 evolution

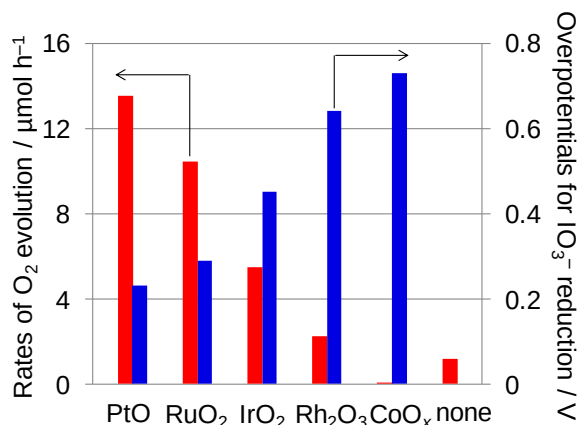


Fig. 4 Rates of O₂ evolution over ex-Ca₂Nb₃O₁₀/K⁺ loaded with 0.3 wt% of various metal oxides (PtO, RuO₂, IrO₂, Rh₂O₃, CoO_x) in 5 mM NaIO₃ aqueous solution under UV light irradiation ($\lambda > 300$ nm, Xe lamp) and overpotentials for IO₃⁻ reduction on each catalyst.

(see Fig. 3-d). This significant increase in O₂ evolution rate is undoubtedly due to the much further enhanced IO₃⁻ reduction at large number of active sites, i.e., the RuO₂ cocatalysts loaded on the surface of niobate sheets, to which IO₃⁻ anion can readily access.

The O₂ evolution on ex-Ca₂Nb₃O₁₀/K⁺ samples loaded with other metal oxides (MO_y) was also evaluated in the presence of IO₃⁻ as an electron acceptor. The rates of O₂ evolution in the steady state were summarized in Fig. 4 as red bars (see Fig. S4 for the time courses). Although the loading of CoO_x was detrimental to the O₂ evolution, all the other cocatalysts were found to increase the rate of O₂ evolution on the ex-Ca₂Nb₃O₁₀/K⁺ samples. The O₂ evolution rate increased in the following order; Rh₂O₃ < IrO₂ < RuO₂ < PtO. The role of cocatalysts loaded on semiconductor photocatalyst is generally understood as facilitator of the surface redox reactions in

reductive and/or oxidative processes, i.e., reduction of IO₃⁻ and/or oxidation of water in the present reaction system. In order to clarify which process was more facilitated by the effective cocatalysts, electrochemical measurements were carried out on the MO_y particle, which were loaded on conductive glass electrode (FTO) via basically same procedure to that on the ex-Ca₂Nb₃O₁₀/K⁺ samples. Fig. 5 shows CV profiles of FTO substrates loaded with various MO_y, along with unmodified one, in the presence of IO₃⁻ (10 mM). Although the loading of CoO_x on FTO had almost no effect, the loading of other MO_y, specifically PtO and RuO₂, drastically increased the cathodic current, suggesting the catalytic activity of these MO_y for IO₃⁻ reduction. Since it was quite difficult to standardize the effective surface area of MO_y particles loaded on FTO, which undoubtedly affects the current value, the catalytic activity of each material was compared by estimating the overpotential for IO₃⁻ reduction. To estimate the overpotentials for IO₃⁻ reduction on each catalyst, CV profiles were examined in the absence and in the presence of different concentrations of IO₃⁻. As shown in Fig. 6 for example, the onset of cathodic current for IO₃⁻ reduction on RuO₂/FTO was observed at around 0.79 V vs. RHE. The apparent overpotential on RuO₂/FTO was thus estimated to be ca. 0.30 V from the difference between the onset potential (indicated by the solid line) and the standard redox potential ($E(\text{IO}_3^-/\text{I}^-) = 1.085$ V at pH 6.8, as indicated by the dotted line in Fig. 6). As summarized in Fig. 4 as blue bars, the overpotential decreased in the following order; CoO_x > Rh₂O₃ > IrO₂ > RuO₂ > PtO. Clearly, the rate of O₂ evolution on ex-Ca₂Nb₃O₁₀/K⁺ samples loaded with these MO_y cocatalysts increased with the decreased overpotentials for IO₃⁻ reduction on the MO_y. On the other hand, clear relationship could not be observed between the O₂ evolution rate and the overpotentials for water oxidation on the MO_y (see Fig. S5). These results indicate that the determining step in this reaction system is the reduction of IO₃⁻ and thus the activation of this step is key to

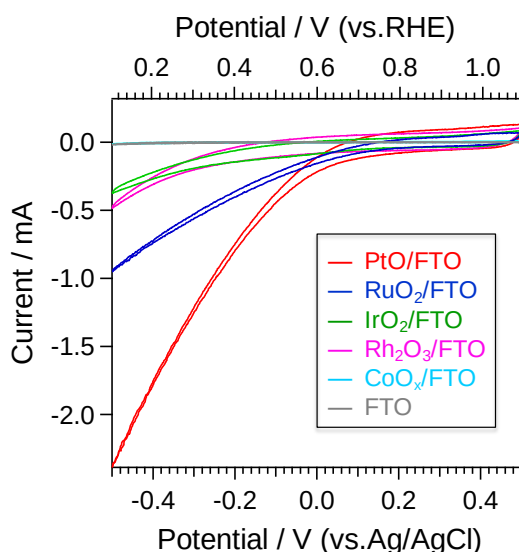


Fig. 5 CV profiles of FTO substrates loaded with various metal oxides in the presence of IO₃⁻ (10 mM, pH 6.8).

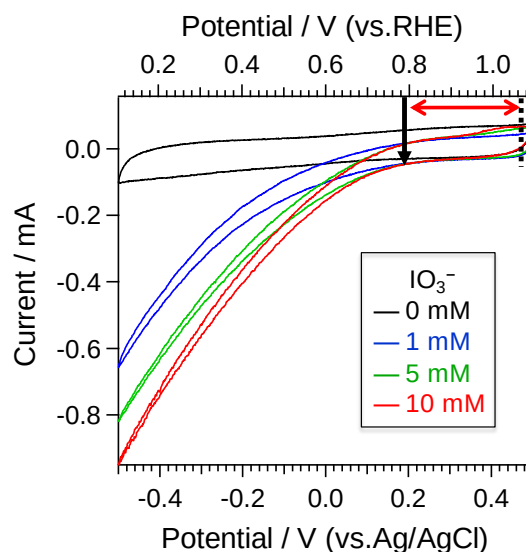


Fig. 6 CV profiles of RuO₂/FTO in the presence of different concentration of IO₃⁻ (0, 1, 5, 10 mM, pH 6.8).

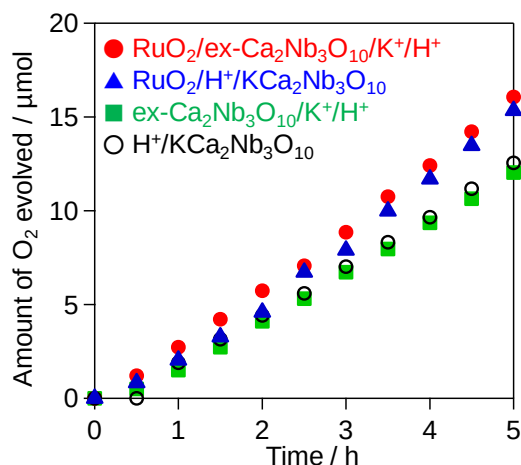


Fig. 7 Time courses of O₂ evolution over 50 mg of H⁺/KCa₂Nb₃O₁₀, ex-Ca₂Nb₃O₁₀/K⁺/H⁺, RuO₂/H⁺/KCa₂Nb₃O₁₀, RuO₂/ex-Ca₂Nb₃O₁₀/K⁺/H⁺ in Fe(NO₃)₃ aqueous solution (5 mM, pH2.3) under UV light irradiation (λ > 300 nm, Xe lamp).

achieve efficient O₂ evolution on the ex-Ca₂Nb₃O₁₀/K⁺ photocatalysts similar to the case of WO₃ photocatalysts,⁴¹ while one cannot exclude the possibility that these MO_y cocatalysts partially affected the oxidation of water to O₂.

3-3. Photocatalytic water oxidation on KCa₂Nb₃O₁₀-based samples using Fe³⁺ as electron acceptor

Photocatalytic O₂ evolution on these KCa₂Nb₃O₁₀ derivatives was also examined using Fe³⁺ as an electron acceptor, instead of IO₃⁻. In this case, the reaction must be carried out in acidic condition with pH below ca. 3, because Fe³⁺ cations easily precipitate as Fe(OH)₃ with higher pH. Thus, the KCa₂Nb₃O₁₀-derivatives were treated by HNO₃aq. before the use to replace K⁺ by H⁺, as well as the addition of an appropriate amount of HNO₃aq. into Fe(NO₃)₃aq. for pH adjustment (from 1.5 to 2.5) before each reaction as needed. Fig. 7 shows the time courses of O₂ evolution over H⁺/KCa₂Nb₃O₁₀, ex-Ca₂Nb₃O₁₀/K⁺/H⁺, and RuO₂-loaded samples under UV light irradiation. Contrary to the case of reactions with IO₃⁻ acceptor, the layered H⁺/KCa₂Nb₃O₁₀ sample, which was prepared from KCa₂Nb₃O₁₀ via simple proton exchange, showed appreciable O₂ evolution in the presence of Fe³⁺. The rate of O₂ evolution on ex-Ca₂Nb₃O₁₀/K⁺/H⁺ sample, which was prepared via exfoliation-restack process and following proton-exchange, was almost same as that on the original H⁺/KCa₂Nb₃O₁₀, in spite of the marked increase in the specific surface areas (0.5 and 20 m²/g). These findings strongly suggested that the interlayer spaces of the original H⁺/KCa₂Nb₃O₁₀ can work as effective reaction sites for reduction of Fe³⁺ because there is possibility that cationic species such as Fe³⁺ are able to intercalate into the interlayer spaces via ion-exchange with H⁺. The loading of RuO₂ cocatalyst on both the H⁺/KCa₂Nb₃O₁₀ and ex-Ca₂Nb₃O₁₀/K⁺/H⁺ samples obviously increased the rate of O₂ generation compared to the original ones; however the

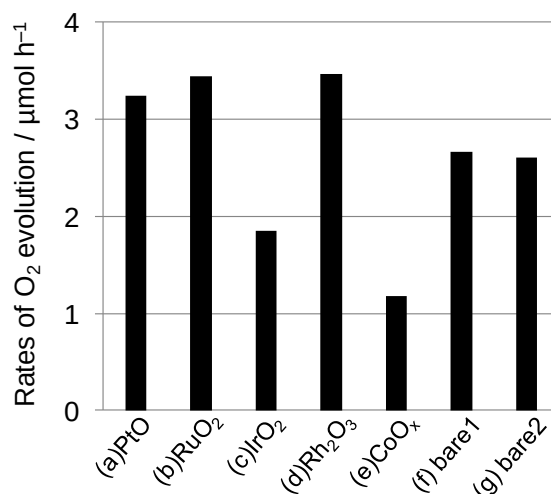


Fig. 8 Rates of O₂ evolution over ex-Ca₂Nb₃O₁₀/K⁺/H⁺ loaded with 0.5 wt% of various metal oxides (PtO, RuO₂, IrO₂, Rh₂O₃, CoO_x) (a~e) and unloaded samples, (f) ex-Ca₂Nb₃O₁₀/K⁺/H⁺ and (g) H⁺/KCa₂Nb₃O₁₀ in 5 mM Fe(NO₃)₃ aqueous solution under UV light irradiation (λ > 300 nm, Xe lamp).

enhancement was not so significant compared to that in the case of IO₃⁻ acceptor (see Fig. 3). The effect of MO_y cocatalyst on the O₂ evolution was also examined on the ex-Ca₂Nb₃O₁₀/K⁺/H⁺ samples in the presence of Fe³⁺ electron acceptor. As summarized in Fig. 8, the loading of PtO and Rh₂O₃ appreciably enhanced the rate of O₂ evolution, while the enhancement was not so remarkable. The electrochemical measurement on these MO_y loaded on FTO was also carried out to evaluate the catalytic activity for reduction of Fe³⁺. Although the cathodic current obviously increased on all the metal oxides except for CoO_x (see Fig. S6), the onset potentials for Fe³⁺ reduction were observed at similar potentials at around 0.5 V vs. Ag/AgCl; suggesting that the overpotentials for Fe³⁺ reduction on these materials are quite small. Because the reduction of Fe³⁺ to Fe²⁺ is one-electron process, this reaction is expected to proceed with relatively-high efficiency even without effective cocatalysts, i.e., even on the bare surface and/or in the interlayers of H⁺/KCa₂Nb₃O₁₀ based materials. Indeed, the unmodified samples such as ex-Ca₂Nb₃O₁₀/K⁺/H⁺ showed relatively high rate of O₂ evolution with steady rate (see Fig. 7). Thus, the loading of cocatalysts had a limited effect for enhancing O₂ evolution on the ex-Ca₂Nb₃O₁₀/K⁺/H⁺ photocatalysts with Fe³⁺ acceptor.

3-4. Z-scheme type water splitting using KCa₂Nb₃O₁₀ derivatives as O₂-evolving photocatalysts coupled with a H₂-evolving photocatalyst in the presence of IO₃⁻/I⁻ or Fe³⁺/Fe²⁺ redox

Overall water splitting (i.e., simultaneous evolution of H₂ and O₂) was attempted by combining the KCa₂Nb₃O₁₀ derivatives with an appropriate H₂-evolving photocatalyst in the presence of IO₃⁻/I⁻ or Fe³⁺/Fe²⁺ redox. In the present study, strontium titanate (SrTiO₃) doped with Rh species (denoted as SrTiO₃:Rh)

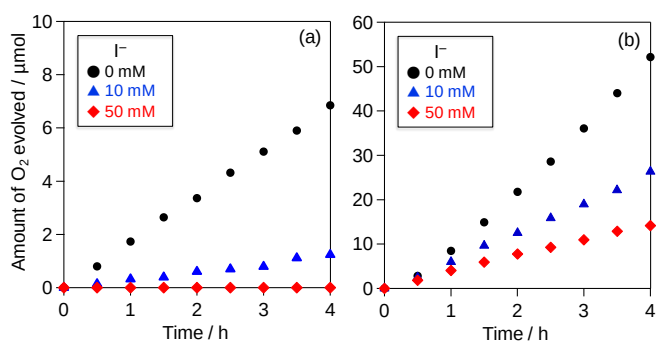


Fig. 9 Time courses of O_2 evolution over (a) $\text{PtO}(0.5 \text{ wt\%})/\text{KCa}_2\text{Nb}_3\text{O}_{10}$, (b) $\text{PtO}(0.5 \text{ wt\%})/\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$, in the solution containing different concentration of I^- (0 – 50 mM) and a fixed concentration of IO_3^- (5 mM) at pH 9.6.

was used as the H_2 -evolution photocatalyst, which had been first reported by Kudo *et al.* to show reasonable activity for H_2 -evolution in the presence of Fe^{2+} electron donor under visible light.⁹ We also confirmed that the $\text{SrTiO}_3:\text{Rh}$ loaded with Pt cocatalysts can generate H_2 from aqueous solution containing I^- as an electron donor both under UV and visible light irradiation (see Fig. S7); no O_2 generation was observed even under UV light irradiation. Before constructing Z-scheme systems for simultaneous evolution of H_2 and O_2 , the selectivity for water oxidation on the $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ derivatives was evaluated in the coexistence of an electron acceptor (i.e., IO_3^- or Fe^{3+}) and an electron donor (i.e., I^- or Fe^{2+}). Although high concentration of electron donor is generally required for achieving efficient H_2 generation on H_2 -evolving photocatalyst, it adversely decrease the rate of O_2 evolution on O_2 -evolving photocatalyst primary due to the occurrence of competitive backward reaction, i.e., the oxidation of the electron donor in place of oxidation of water.^{42–44} Thus, high selectivity for water oxidation, i.e., the capability of O_2 evolution even in the presence of considerable concentration of electron donor (I^- or Fe^{2+}), is required for the O_2 -evolving photocatalysts that are employed in Z-scheme water splitting systems.

Fig. 9 shows the rates of O_2 evolution over $\text{PtO}/\text{ex-}$

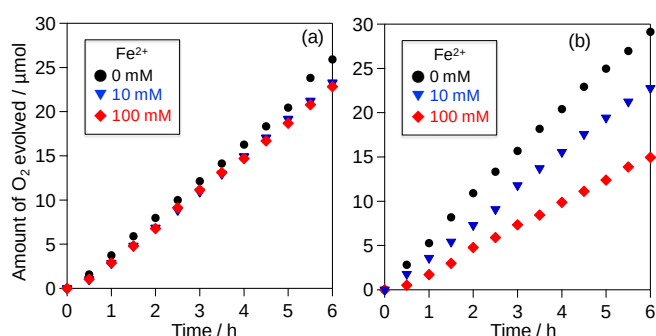


Fig. 11 Time courses of O_2 evolution over (a) $\text{H}^+/\text{KCa}_2\text{Nb}_3\text{O}_{10}$, (b) $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+/\text{H}^+$ in the solution containing different concentration of Fe^{2+} (0 – 100 mM) and a fixed concentration of Fe^{3+} (5 mM) at pH 1.5.

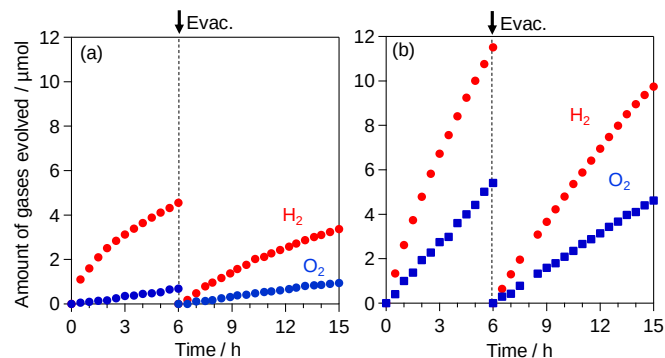


Fig. 10 Time courses of H_2 and O_2 evolution using a mixture of $\text{Pt}(0.5 \text{ wt\%})/\text{SrTiO}_3:\text{Rh}$ and $\text{PtO}(0.5 \text{ wt\%})/\text{KCa}_2\text{Nb}_3\text{O}_{10}$ (a) or $\text{PtO}(0.5 \text{ wt\%})/\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ (b) KI aqueous solution (5 mM, pH 12.0) under UV light irradiation ($\lambda > 300 \text{ nm}$, Xe lamp).

$\text{Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ and $\text{PtO}/\text{KCa}_2\text{Nb}_3\text{O}_{10}$ samples from the solution containing different concentration of I^- (0 – 50 mM) and a fixed concentration of IO_3^- (5 mM). On the both samples, the O_2 evolution rates significantly decrease with increasing concentration of I^- in the solution, undoubtedly due to the occurrence of backward reaction (the oxidation of I^-) instead of oxidation of water to O_2 . The O_2 evolution rate on $\text{PtO}/\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ sample was reduced to about one-half by the addition of 10 mM of I^- to the solution, while that on $\text{PtO}/\text{KCa}_2\text{Nb}_3\text{O}_{10}$ was reduced to almost one-fifth of that in the absence of I^- . These findings indicated that $\text{PtO}/\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+$ sample possess relatively high selectivity for water oxidation, and therefore can be used as O_2 -evolving photocatalyst with an appropriate concentration of I^- electron donor lower than 10 mM, while the original $\text{PtO}/\text{KCa}_2\text{Nb}_3\text{O}_{10}$ sample should be used with much lower concentration of I^- below 1 mM.

Then, simultaneous evolution of H_2 and O_2 was attempted by combining these $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ derivatives with the $\text{SrTiO}_3:\text{Rh}$ loaded with Pt cocatalysts in an aqueous KI solution (5 mM). The concentration of KI (5 mM) was chosen based on the fact that the rate of H_2 evolution on $\text{Pt}/\text{SrTiO}_3:\text{Rh}$ photocatalyst increased with the increasing concentration up to

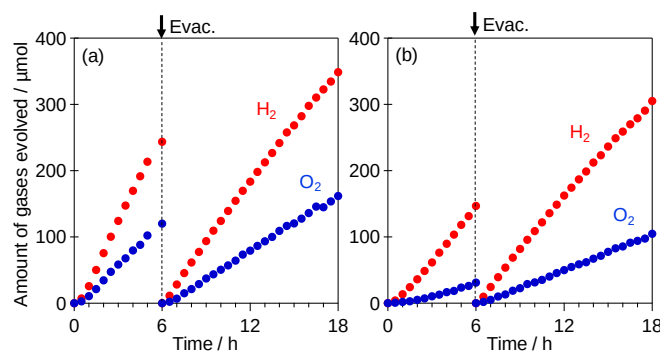


Fig. 12 Time courses of H_2 and O_2 evolution using a mixture of $\text{Ru}(0.7 \text{ wt\%})/\text{SrTiO}_3:\text{Rh}$ and $\text{H}^+/\text{KCa}_2\text{Nb}_3\text{O}_{10}$ (a) or $\text{ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+/\text{H}^+$ (b) in $\text{Fe}(\text{ClO}_4)_2$ aqueous solution (5 mM, pH 2.5) under UV light irradiation ($\lambda > 300 \text{ nm}$, Xe lamp).

5 mM and almost saturated at higher concentrations. As shown in Fig. 10a, the combination of PtO/ex-Ca₂Nb₃O₁₀/K⁺ and Pt/SrTiO₃:Rh resulted in simultaneous and stable evolution of H₂ and O₂ in the stoichiometric ratio (2:1). Such simultaneous evolution was not observed when the each photocatalyst was singly irradiated under same condition. No steady gas evolution proceeded in the absence of I⁻. These findings indicated that the water splitting into H₂ and O₂ proceeded through two-step photoexcitation between these two different photocatalysts. Although the use of PtO/KCa₂Nb₃O₁₀ with Pt/SrTiO₃:Rh resulted in simultaneous evolution of H₂ and O₂ as seen in Fig. 10b, the amount of O₂ was obviously lower than the stoichiometric value expected by the amount of H₂ generated. This deviation is certainly due to both the low activity and selectivity for water oxidation of PtO/KCa₂Nb₃O₁₀ sample, as indicated by the result shown in Fig. 9.

The construction of Z-scheme water splitting system with Fe³⁺/Fe²⁺ redox was also attempted using the KCa₂Nb₃O₁₀ derivatives as O₂-evolving photocatalysts. To suppress the precipitation of Fe³⁺ into Fe(OH)₃ under higher pH condition than ca. 3, the KCa₂Nb₃O₁₀ derivatives were used after exchanging the K⁺ cations by H⁺ as described in a previous section. Fig. 11 shows the rates of O₂ evolution over H⁺/KCa₂Nb₃O₁₀ and ex-Ca₂Nb₃O₁₀/K⁺/H⁺ samples from the solution containing different concentration of Fe²⁺ (0 – 100 mM) and a fixed concentration of Fe³⁺ (5 mM). Because the aqueous solutions containing high concentration of Fe(ClO₄)₂ themselves exhibit pH values below 2, all the pH values of the reaction solution (containing catalyst particles) were adjusted to 1.5 by adding appropriate amounts of HClO₄aq. to minimize the influence of pH difference on the O₂ evolution. Interestingly, the rate of O₂ evolution on H⁺/KCa₂Nb₃O₁₀ was rarely affected by the increasing concentration of Fe²⁺ electron donor in the solution, indicating the high selectivity for water oxidation on this sample. On the other hand, the rate of O₂ evolution on ex-Ca₂Nb₃O₁₀/K⁺/H⁺ sample appreciably decreased with increasing concentration of Fe²⁺, strongly suggesting the occurrence of backward reaction (oxidation of Fe²⁺) on this catalyst. One of the most likely reasons for the selective oxidation of water on the original H⁺/KCa₂Nb₃O₁₀ sample even in the presence of considerable amount of Fe²⁺ will be the preferential intercalation of Fe³⁺ cations instead of Fe²⁺ into the active interlayer spaces. Considering the size of Fe³⁺ and Fe²⁺ cations, the larger size of Fe²⁺ certainly makes it difficult for the Fe²⁺ cations to stay in the narrow interlayer spaces, resulting in the elimination of them from the interlayers, whereas smaller Fe³⁺ can be there. In that case, the photoexcited electrons generated on 2-dimensional niobate sheet can efficiently reduce Fe³⁺ cations that are intercalated into the interlayer space, whereas the photogenerated holes can selectively oxidize water in the interlayer space where the Fe²⁺ cations are excluded. Although the clear clues for preferential intercalation of Fe³⁺ rather than Fe²⁺ could not be obtained in the present materials mainly due to the competitive exchange with H⁺ cations in the acidic condition, such preferential intercalation probably can be

an effective way to achieve highly efficient O₂ evolution in the two-step water splitting systems with Fe³⁺/Fe²⁺ redox couple.

Water splitting into H₂ and O₂ was attempted by combining these O₂-evolving photocatalyst with SrTiO₃:Rh loaded with Ru cocatalyst¹¹ in an aqueous Fe(ClO₄)₂ solution (5 mM, pH 2.5) under UV and visible light irradiation ($\lambda > 300$ nm). As shown in Fig. 12a, the combination of H⁺/KCa₂Nb₃O₁₀ and Ru/SrTiO₃:Rh generated H₂ and O₂ with the stoichiometric rate quite stably for long time. On the other hand, the use of ex-Ca₂Nb₃O₁₀/K⁺/H⁺ sample resulted in the smaller amount of O₂ than stoichiometric amount as seen in Fig. 12b, undoubtedly due to the occurrence of backward reaction (oxidation of Fe²⁺) on ex-Ca₂Nb₃O₁₀/K⁺/H⁺ as demonstrated in the half reactions (Fig. 11). These findings indicate the potential availability of cation-exchangeable layered materials as efficient O₂-evolving photocatalysts for achieving efficient water splitting in the Fe³⁺/Fe²⁺ redox mediator.

4. Conclusions

In the present study, we attempted to apply a cation-exchangeable layered semiconductor KCa₂Nb₃O₁₀ and its derivatives as O₂-evolving photocatalyst in Z-scheme type water splitting systems with redox mediators, IO₃⁻/I⁻ and Fe³⁺/Fe²⁺. The optimum form of the photocatalyst materials was found to strongly depend on the redox couples combined. When IO₃⁻ was used as an electron acceptor for O₂ evolution, combination of the exfoliation-restacking process and the loading of appropriate cocatalysts such as PtO were quite effective to increase the rate of O₂ evolution. The former one can effectively increase the numbers of the opened active sites where the large and anionic IO₃⁻ can access, and the later one significantly catalyzes the reduction of IO₃⁻, which proceed via 6-electrons process. On the other hand, the original layered structure of H⁺/KCa₂Nb₃O₁₀ sample, which was obtained via simple proton exchange of KCa₂Nb₃O₁₀, was effective for achieving efficient and selective water oxidation to O₂ in the presence of Fe³⁺ electron acceptor; the exfoliation-restacking process adversely lowered the selectivity. These findings strongly suggested that the cation-exchangeable interlayer spaces could work as effective reaction sites for reduction of Fe³⁺. Simultaneous and stoichiometric evolutions of H₂ and O₂ with were indeed demonstrated under UV light irradiation by employing the optimum KCa₂Nb₃O₁₀-based material as an O₂-evolving photocatalyst combined with a H₂-evolving photocatalyst with an appropriate redox couple. The present results indicated potential availability of cation-exchangeable metal oxides as efficient photocatalysts materials affording high selectivity for water reduction and/or oxidation in Z-scheme type water splitting systems with redox couple.

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Supporting Information

Two-step photocatalytic water splitting into H₂ and O₂ using layered metal oxide KCa₂Nb₃O₁₀ and its derivatives as O₂-evolving photocatalysts with IO₃⁻/I⁻ or Fe³⁺/Fe²⁺ redox mediator

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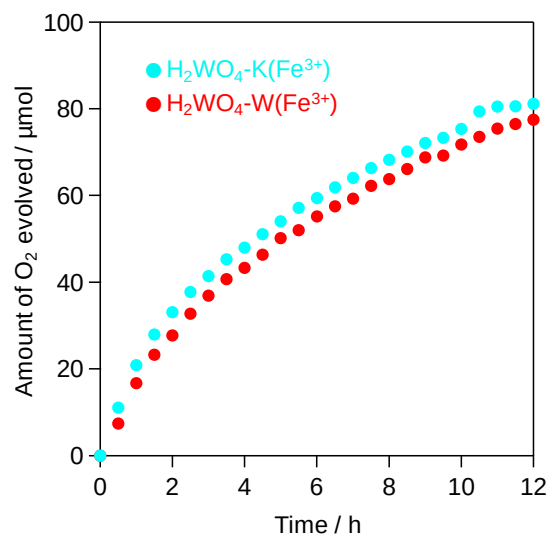


Fig. S1 Time courses of O₂ evolution over H₂WO₄-W and H₂WO₄-K in Fe(ClO₄)₃ aqueous solution (5 mM, pH2.3) under visible light irradiation (λ > 400 nm, Xe lamp).

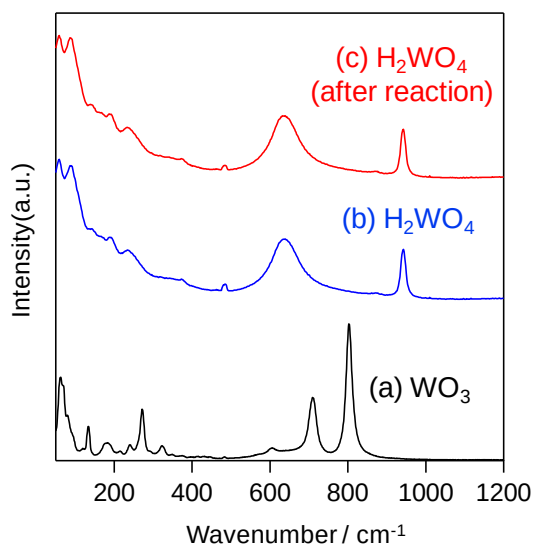


Fig. S2 Raman spectra of (a)WO₃ and (b,c) H₂WO₄ before and after O₂ evolution from Fe(ClO₄)₃ aqueous solution.

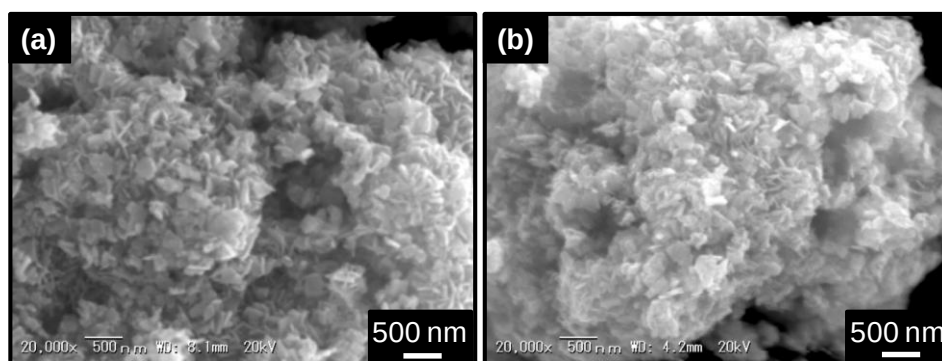


Fig. S3 SEM image of H₂WO₄ (a) before and (b) after O₂ evolution from Fe(ClO₄)₃ aqueous solution .