Two-step photocatalytic water splitting into H\textsubscript{2} and O\textsubscript{2} using layered metal oxide KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} and its derivatives as O\textsubscript{2}-evolving photocatalysts with IO\textsubscript{3}\textsuperscript{−}/I\textsuperscript{−} or Fe\textsuperscript{3+}/Fe\textsuperscript{2+} redox mediator

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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 RuO₂ or PtO₂ 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. 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⁻), and have applied various kinds of semiconductor materials, not only metal oxides but also metal oxinitrides and organic dyes, 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⁺ and Co(bpy)₃³⁺/Co(bpy)₃²⁺, or even without any redox couple in the solution (through direct electron transfer between semiconductor particles). Cation-exchangeable layered metal oxides such as K₂Nb₆O₁₇ have been studied as promising candidates for efficient photocatalyst materials for water splitting.
generally consist of 2-dimenstional 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-dimenstional anion layers of metal oxides. Indeed, some cation-exchangeable layered metal oxides such as KₓNbₓOᵧ, 23-25 KₓLaₓTiₓOᵧ, 26, 27 RbₓTaₓOᵧ, 28 RhNdTaOᵧ, 29, 30 AₓZrTaOᵧ (A = H or K, A = La or Sr), 31, 32 NaCaₓTaOᵧ 33 have been reported as active photocatalyst for efficient water splitting into H₂ and O₂ 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-dimenstional 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, KₓCaₓNbₓOᵧ, has been reported to show significantly high activity for photocatalytic H₂ evolution from an aqueous methanol solution under UV light after the K⁺ cations in the interlayer by protons (H⁺), whereas it showed negligibly low activity for O₂ evolution in the presence of Ag⁺ ion as sacrificial electron acceptor. 37 Ebina et al. have reported simultaneous evolution of H₂ and O₂ on derivatives of KₓCaₓNbₓOᵧ that were prepared via exfoliation of 2-dimenstional layers with a soft-chemical method and following restack process, in which nanoparticles of RuO₂ cocatalysts were simultaneously incorporated between the 2-dimenstional niobate layers. 38 This finding implies that the niobate layers of KₓCaₓNbₓOᵧ are potentially capable of oxidation of water efficiently. In the present study, we thus focused on the utilization of KₓCaₓNbₓOᵧ and its derivatives as O₂-evolving photocatalysts in the Z-scheme water-splitting systems with redox mediator such as IO₃⁻/I⁻ or Fe³⁺/Fe²⁺. 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 KₓCaₓNbₓOᵧ were prepared by calcining a mixture of K₂CO₃, CaCO₃ and Nb₂O₅ (K:Ca:Nb = 1:1:2:3) at 1473 K for 12 h. The obtained KₓCaₓNbₓOᵧ powder was stirred with 5 M HNO₃ 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⁺/KₓCaₓNbₓOᵧ. The H⁺/KₓCaₓNbₓOᵧ particles (0.4 g) were suspended in 100 mL of aqueous solution, in which equimolar of tetrabutylammonium hydroxide (TBAOH) molecules to that of H⁺/KₓCaₓNbₓOᵧ (ca. 0.73 mmol, calculated as HCaₓNbₓOᵧ ⋅ 1.5H₂O) was added as an initiator of exfoliation. The suspension was continuously shaken at room temperature for 7 days until the H⁺/KₓCaₓNbₓOᵧ 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-CAₓCaₓNbₓOᵧ/K⁺ hereafter. The TEM images of the exfoliated nano sheets and the ex-CAₓCaₓNbₓOᵧ/K⁺ are shown in Fig. S1 in supporting information (SI). Modification of ex-CAₓCaₓNbₓOᵧ/K⁺ with cocatalysts was carried out by impregnation of an aqueous solution containing one of ammine complexes of metals such as [Pt(NH₃)₄]OH₂, [[NH₃]Ru-O-Ru(NH₃)₄-O-Ru(NH₃)₄]Cl₄, [Ir(NH₃)₄]Cl₄, [Rh(NH₃)₄]Cl₄ and [Co(NH₃)₆]Cl₄, 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 Pt⁴⁺, Ru⁴⁺, Ir⁴⁺, and Rh³⁺ by X-ray photoabsorption spectroscopy (XPS, ULVAC Phai MT-5500), the samples loaded with the cocatalysts will be denoted as PtO₂, IrO₂, RuO₂, RhO₂ and Rb₂O₂-loaded one, respectively. On the other hand, the samples loaded with Co species were confirmed to contain both Co²⁺ and Co³⁺ states, therefore will be denoted as CoO₂-loaded one for simplification. The products will be denoted as MOₓ/ex-CAₓCaₓNbₓOᵧ/K⁺ (MOₓ = PtO₂, RuO₂, IrO₂, Rh₂O₃ and CoO₂). When the protonated forms of these samples are required, the K⁺ cations exist in MOₓ/ex-CAₓCaₓNbₓOᵧ/K⁺ samples were replaced with H⁺ by stirring in an aqueous HNO₃ solution (1 M) at room temperature for 24 h (referred to as MOₓ/ex-CAₓCaₓNbₓOᵧ/K⁺H⁺).

Strontium titanate doped with rhodium species (SrTiO₃:Rh) 36 was prepared by solid state reaction. A mixture of SrCO₃, TiO₂ and Rh₂O₃ (Sr : Ti : Rh = 1 : 0.99 : 0.01 to form ideal formula of SrTi₀.₉₈Rh₀.₀₂O₃.₈) was calcined in air at 873 K for 2 h and subsequently at 1273 K for 10 h. Pt cocatalyst was loaded onto SrTiO₃:Rh by impregnation using H₂PtCl₄•6H₂O and subsequent heating under a H₂ flow at 573 K for 2 h. In the case of Ru cocatalyst, Ru species were loaded on SrTiO₃:Rh by means of photodeposition method using RuCl₃•nH₂O 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 (O₂ evolution) in the presence of an electron accepter (i.e., half reaction of water splitting) catalyst powder (50 or 100 mg) was suspended in 70 mL of an aqueous NaIO₃ or Fe(NO₃)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 HNO₃ solution, when needed. Since it was demonstrated that the O₂
evolution in the presence of IO	extsubscript{3}\textsuperscript{-} generally proceeded more efficiently in basic conditions (above pH 9), the original KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} and its derivatives (100 mg) were suspended to NaIO\textsubscript{3}aq. without proton-exchange. The addition of these K\textsuperscript{+}-contain samples spontaneously change the pH of NaIO\textsubscript{3}aq. (originally ca. 6.8) to higher values up to ca. 9.6 due to the exchange of K\textsuperscript{+} with H\textsuperscript{+} in the solutions. As for the O\textsubscript{2} evolution in the presence of Fe\textsuperscript{3+} electron acceptor, the reaction must be carried out in acidic condition with pH below ca. 3, because Fe\textsuperscript{3+} cations easily precipitate as Fe(OH)\textsubscript{3} with higher pH values. In order to maintain the pH values below 3 stably through the reactions, the KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}−derivatives were treated by HNO\textsubscript{3}aq. before the use as described above, and furthermore a small amount of HNO\textsubscript{3}aq. was added into Fe(NO\textsubscript{3})\textsubscript{3}aq. to adjust the pH to 2.5 before reaction.

For the two-step water-splitting reaction with IO\textsubscript{3}/I\textsuperscript{−} redox couple, the Pt-loaded SrTiO\textsubscript{3}:Rh (50 mg) and one of the KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}−derivatives (100 mg) were suspended in an aqueous KI solution (5 mM, 70 mL) as H\textsubscript{2}-evolving and O\textsubscript{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 Fe\textsuperscript{3+}/Fe\textsuperscript{2+} redox couple, the Ru-loaded SrTiO\textsubscript{3}:Rh (50 mg) and one of the proton-exchanged KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}−derivative (500 mg) were suspended in 250 mL of an aqueous Fe(ClO\textsubscript{4})\textsubscript{2} solution (5 mM), whose pH values were adjusted to ca. 2.5 by adding a small amount of aqueous HClO\textsubscript{4} solution. The suspension was irradiated using 300 W Xe lamp (Cermax LF-300F, λ > 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\textsubscript{2}, IrO\textsubscript{2}, RhO\textsubscript{2}, and CoO\textsubscript{2}) used as cocatalysts, these particles were prepared on conductive glass substrate (FTO) via basically same procedure to that on KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}−derivatives as follows. Small amount (50 μL) of [Pt(NH\textsubscript{3})\textsubscript{4}]Cl\textsubscript{2}, [NH\textsubscript{3}RhO-Ru(NH\textsubscript{3})\textsubscript{6}-O-Ru(NH\textsubscript{3})\textsubscript{6}]Cl\textsubscript{6}, [Ir(NH\textsubscript{3})\textsubscript{6}]Cl\textsubscript{6}, [Rh(NH\textsubscript{3})\textsubscript{6}]Cl\textsubscript{6} or [Co(NH\textsubscript{3})\textsubscript{6}]Cl\textsubscript{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 KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}−derivatives. The electrochemical cell used for the experiments consisted of a prepared MO/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\textsubscript{3}− and Fe\textsuperscript{3+} reduction over the MO/FTO electrodes were estimated by means of cyclic voltammetry (CV) in a 0.5 M Na\textsubscript{2}SO\textsubscript{4} aqueous solution (40 mL) in the absence and presence of NaIO\textsubscript{3} or Fe(NO\textsubscript{3})\textsubscript{3} with different concentrations. The overpotentials for water oxidation were estimated based on the CV profiles of the MO/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 KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} and its proton-exchanged form (H\textsuperscript{+}/H\textsubscript{2}Ca\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}) exhibited strong and sharp diffraction peaks corresponding to (00n) facets as reported\textsuperscript{39,40}, indicating well-regulated stacking of niobate layers along with c-axis. The (00n) diffraction peaks shifted to lower angles after the proton-exchange due to the spontaneous hydration of interlayer space, forming average formula of HCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}·1.5H\textsubscript{2}O.\textsuperscript{40} As seen in the SEM images (see Fig. 2-a and b), both the original KCa\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} and H\textsuperscript{+}/H\textsubscript{2}Ca\textsubscript{2}Nb\textsubscript{3}O\textsubscript{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\textsuperscript{2}/g) as described in the SEM images. Because the probe N\textsubscript{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 (00n) was significantly decreased along with obvious broadening in the peak width after the exfoliation-restack process (see Fig. 1-c for ex-Ca\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}/K\textsuperscript{+} sample). The change in the (00n) 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\textsuperscript{+} cations added into the solution, forming loosely
3-2. Photocatalytic water oxidation on KCa$_2$Nb$_3$O$_{10}$-based samples using IO$_3^-$ as electron acceptor

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

Fig. 3 shows the time courses of O$_2$ evolution from water on KCa$_2$Nb$_3$O$_{10}$-based samples using iodate (IO$_3^-$) as an electron acceptor under UV light irradiation. Although O$_2$ evolution on the original KCa$_2$Nb$_3$O$_{10}$ sample was negligible, the ex-Ca$_2$Nb$_3$O$_{10}/K^+$ was found to generate appreciable amount of O$_2$ with steady rate. The proton-exchanged form (H$^+$/KCa$_2$Nb$_3$O$_{10}$) also showed negligibly low activity for O$_2$ evolution, while the ex-Ca$_2$Nb$_3$O$_{10}/K^+$ sample treated with acid (ex-Ca$_2$Nb$_3$O$_{10}/K^+$/H$^+$) generated appreciable amount of O$_2$ (see Fig. S3). Since the IO$_3^-$ anion cannot penetrate into the interlayer spaces of KCa$_2$Nb$_3$O$_{10}$ (or H$^+$/KCa$_2$Nb$_3$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., (Ca$_2$Nb$_3$O$_{10})^3^-$, the reduction of IO$_3^-$ by the photoexcited electrons must occur at the outermost layer or at the edge of niobate layers of KCa$_2$Nb$_3$O$_{10}$ (or H$^+$/KCa$_2$Nb$_3$O$_{10}$). Therefore the rate of IO$_3^-$ reduction on KCa$_2$Nb$_3$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 ex-Ca$_2$Nb$_3$O$_{10}/K^+$ 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 ex-Ca$_2$Nb$_3$O$_{10}/K^+$. The loading of RuO$_2$ cocatalyst on the surface of KCa$_2$Nb$_3$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.\[^{31}\]

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\text{IO}_3^- + 3H_2O + 6e^- \rightarrow I^- + 6OH^- \tag{1}
\]

Combination of the exfoliation-restack process and the loading of RuO$_2$ cocatalyst drastically increased the rate of O$_2$ evolution.
(see Fig. 3-d). This significant increase in $O_2$ evolution rate is undoubtedly due to the much further enhanced $IO_3^{-}$ reduction at large number of active sites, i.e., the RuO$_2$ cocatalysts loaded on the surface of niobate sheets, to which $IO_3^{-}$ anion can readily access.

The $O_2$ evolution on ex-Ca$_2$Nb$_2$O$_6$/K$^+$ samples loaded with other metal oxides (MO$_y$) was also evaluated in the presence of $IO_3^{-}$ as an electron accepter. The rates of $O_2$ 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 $O_2$ evolution, all the other cocatalysts were found to increase the rate of $O_2$ evolution on the ex-Ca$_2$Nb$_2$O$_6$/K$^+$ samples. The $O_2$ evolution rate increased in the following order: Rh$_2$O$_3$ < IrO$_2$ < RuO$_2$ < 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 $IO_3^{-}$ 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-Ca$_2$Nb$_2$O$_6$/K$^+$ samples. Fig. 5 shows CV profiles of FTO substrates loaded with various MO$_y$, along with unmodified one, in the presence of $IO_3^{-}$ (10 mM). Although the loading of CoO$_x$ on FTO had almost no effect, the loading of other MO$_y$, specifically PtO and RuO$_2$, drastically increased the cathodic current, suggesting the catalytic activity of these MO$_y$ for $IO_3^{-}$ 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 $IO_3^{-}$ reduction. To estimate the overpotentials for $IO_3^{-}$ reduction on each catalyst, CV profiles were examined in the absence and in the presence of different concentrations of $IO_3^{-}$. As shown in Fig. 6 for example, the onset of cathodic current for $IO_3^{-}$ reduction on RuO$_2$/FTO was observed at around 0.79 V vs. RHE. The apparent overpotential on RuO$_2$/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 ($E(IO_3^{-}/I)$ = 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$_x$ > Rh$_2$O$_3$ > IrO$_2$ > RuO$_2$ > PtO. Clearly, the rate of $O_2$ evolution on ex-Ca$_2$Nb$_2$O$_6$/K$^+$ samples loaded with these MO$_y$ cocatalysts increased with the decreased overpotentials for $IO_3^{-}$ reduction on the MO$_y$. On the other hand, clear relationship could not be observed between the $O_2$ 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 $IO_3^{-}$ and thus the activation of this step is key to
achieve efficient O₂ evolution on the ex-Ca₂Nb₃O₁₀/K⁺ photocatalysts similar to the case of WO₃ photocatalysts, while one cannot exclude the possibility that these MO₃ 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⁺, RuO₂/H⁺/KCa₂Nb₃O₁₀, RuO₂/ex-Ca₂Nb₃O₁₀/K⁺/H⁺ in Fe(NO₃)₃ aqueous solution (5 mM, pH 2.3) under UV light irradiation (λ > 300 nm, Xe lamp).

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, pH 2.3) under UV light irradiation (λ > 300 nm, Xe lamp).

The enhancement was not so significant compared to that in the case of IO₃⁻ acceptor (see Fig. 3). The effect of MO₃ 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 MO₃ 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 CoO₃ (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)
was used as the \( \text{H}_2 \)-evolution photocatalyst, which had been first reported by Kudo et al. to show reasonable activity for \( \text{H}_2 \)-evolution in the presence of \( \text{Fe}^{2+} \) electron donor under visible light.\(^9\) We also confirmed that the \( \text{SrTiO}_3 \)-Rh loaded with Pt cocatalysts can generate \( \text{H}_2 \) from aqueous solution containing \( \Gamma^- \) as an electron donor both under UV and visible light irradiation (see Fig. S7); no \( \text{O}_2 \) generation was observed even under UV light irradiation. Before constructing \( Z \)-scheme systems for simultaneous evolution of \( \text{H}_2 \) and \( \text{O}_2 \), 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., \( \text{IO}_3^- \) or \( \text{Fe}^{3+} \)) and an electron donor (i.e., \( \Gamma^- \) or \( \text{Fe}^{2+} \)). Although high concentration of electron donor is generally required for achieving efficient \( \text{H}_2 \) generation on \( \text{H}_2 \)-evolving photocatalyst, it adversely decrease the rate of \( \text{O}_2 \) evolution on \( \text{O}_2 \)-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 \( \text{O}_2 \) evolution even in the presence of considerable concentration of electron donor (\( \Gamma^- \) or \( \text{Fe}^{2+} \)), is required for the \( \text{O}_2 \)-evolving photocatalysts that are employed in \( Z \)-scheme water splitting systems.

Fig. 9 shows the rates of \( \text{O}_2 \) evolution over \( \text{PtO/ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+ \) and \( \text{PtO/KCa}_2\text{Nb}_3\text{O}_{10} \) samples from the solution containing different concentration of \( \Gamma^- \) (0 – 50 mM) and a fixed concentration of \( \text{IO}_3^- \) (5 mM). On the both samples, the \( \text{O}_2 \) evolution rates significantly decrease with increasing concentration of \( \Gamma^- \) in the solution, undoubtedly due to the occurrence of backward reaction (the oxidation of \( \Gamma^- \)) instead of oxidation of water to \( \text{O}_2 \). The \( \text{O}_2 \) evolution rate on \( \text{PtO/ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+ \) sample was reduced to about one-half by the addition of 10 mM of \( \Gamma^- \) to the solution, while that on \( \text{PtO/KCa}_2\text{Nb}_3\text{O}_{10} \) was reduced to almost one-fifth of that in the absence of \( \Gamma^- \). These findings indicated that \( \text{PtO/ex-Ca}_2\text{Nb}_3\text{O}_{10}/\text{K}^+ \) sample possess relatively high selectivity for water oxidation, and therefore can be used as \( \text{O}_2 \)-evolving photocatalyst with an appropriate concentration of \( \Gamma^- \) electron donor lower than 10 mM, while the original \( \text{PtO/KCa}_2\text{Nb}_3\text{O}_{10} \) sample should be used with much lower concentration of \( \Gamma^- \) below 1 mM.

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

\[
\text{H}_2 + \text{KCa}_2\text{Nb}_3\text{O}_{10} + \text{PtO} \rightarrow \text{H}_2 + \text{KCa}_2\text{Nb}_3\text{O}_{10} + \text{PtO} + \text{K}^+ + \text{H}^+ + \text{K}^+ + \text{H}_2O + \text{H}^+
\]
5 mM and almost saturated at higher concentrations. As shown in Fig. 10a, the combination of PtO/ex-Ca$_2$Nb$_3$O$_{10}$/K$^+$ and Pt/SrTiO$_3$:Rh resulted in simultaneous and stable evolution of H$_2$ and O$_2$ 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$. These findings indicated that the water splitting into H$_2$ and O$_2$ proceeded through two-step photoexciatation between these two different photocatalysts. Although the use of PtO/KCa$_2$Nb$_3$O$_{10}$ with Pt/SrTiO$_3$:Rh resulted in simultaneous evolution of H$_2$ and O$_2$ as seen in Fig. 10b, the amount of O$_2$ was obviously lower than the stoichiometric value expected by the amount of H$_2$ generated. This deviation is certainly due to both the low activity and selectivity for water oxidation of PtO/KCa$_2$Nb$_3$O$_{10}$ sample, as indicated by the result shown in Fig. 9.

The construction of Z-scheme water splitting system with Fe$^{3+}$/Fe$^{2+}$ redox was also attempted using the KCa$_2$Nb$_3$O$_{10}$ derivatives as O$_2$-evolving photocatalysts. To suppress the precipitation of Fe$^{3+}$ into Fe(OH)$_3$ under higher pH condition than ca. 3, the KCa$_2$Nb$_3$O$_{10}$ derivatives were used after exchanging the K$^+$ cations by H$^+$ as described in a previous section. Fig. 11 shows the rates of O$_2$ evolution over H$^+$/KCa$_2$Nb$_3$O$_{10}$ and ex-Ca$_2$Nb$_3$O$_{10}$/K$^+$/H$^+$ samples from the solution containing different concentration of Fe$^{2+}$ (0 – 100 mM) and a fixed concentration of Fe$^{3+}$ (5 mM). Because the aqueous solutions containing high concentration of Fe(ClO$_4$)$_2$ 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 HClO$_4$aq., to minimize the influence of pH difference on the O$_2$ evolution. Interestingly, the rate of O$_2$ evolution on H$^+$/KCa$_2$Nb$_3$O$_{10}$ was rarely affected by the increasing concentration of Fe$^{2+}$ electron donor in the solution, indicating the high selectivity for water oxidation on this sample. On the other hand, the rate of O$_2$ evolution on ex-Ca$_2$Nb$_3$O$_{10}$/K$^+$/H$^+$ sample appreciably decreased with increasing concentration of Fe$^{2+}$, strongly suggesting the occurrence of backward reaction (oxidation of Fe$^{2+}$) on this catalyst. One of the most likely reasons for the selective oxidation of water on the original H$^+$/KCa$_2$Nb$_3$O$_{10}$ sample even in the presence of considerable amount of Fe$^{2+}$ will be the preferential intercalation of Fe$^{3+}$ cations instead of Fe$^{2+}$ into the active interlayer spaces. Considering the size of Fe$^{3+}$ and Fe$^{2+}$ cations, the larger size of Fe$^{2+}$ certainly makes it difficult for the Fe$^{2+}$ cations to stay in the narrow interlayer spaces, resulting in the elimination of them from the interlayers, whereas smaller Fe$^{3+}$ can be there. In that case, the photoexcited electrons generated on 2-dimensional niobate sheet can efficiently reduce Fe$^{3+}$ cations that are intercalated into the interlayer space, whereas the photogenerated holes can selectively oxidize water in the interlayer space where the Fe$^{2+}$ cations are excluded. Although the clear clues for preferential intercalation of Fe$^{2+}$ rather than Fe$^{3+}$ 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 O$_2$ evolution in the two-step water splitting systems with Fe$^{3+}$/Fe$^{2+}$ redox couple.

Water splitting into H$_2$ and O$_2$ was attempted by combining these O$_2$-evolving photocatalyst with SrTiO$_3$:Rh loaded with Ru cocatalyst$^{11}$ in an aqueous Fe(ClO$_4$)$_2$ solution (5 mM, pH 2.5) under UV and visible light irradiation ($\lambda > 300$ nm). As shown in Fig. 12a, the combination of H$^+$/KCa$_2$Nb$_3$O$_{10}$ and Ru/SrTiO$_3$:Rh generated H$_2$ and O$_2$ with the stoichiometric rate quite stably for long time. On the other hand, the use of ex-Ca$_2$Nb$_3$O$_{10}$/K$^+$/H$^+$ sample resulted in the smaller amount of O$_2$ than stoichiometric amount as seen in Fig. 12b, undoubtedly due to the occurrence of backward reaction (oxidation of Fe$^{2+}$) on ex-Ca$_2$Nb$_3$O$_{10}$/K$^+$/H$^+$ as demonstrated in the half reactions (Fig. 11). These findings indicate the potential availability of cation-exchangeable layered materials as efficient O$_2$-evolving photocatalysts for achieving efficient water splitting in the Fe$^{3+}$/Fe$^{2+}$ redox mediator.

4. Conclusions

In the present study, we attempted to apply a cation-exchangeable layered semiconductor KCa$_2$Nb$_3$O$_{10}$ and its derivatives as O$_2$-evolving photocatalyst in Z-scheme type water splitting systems with redox mediators, IO$_3$/$I^-$ and Fe$^{3+}$/Fe$^{2+}$. The optimum form of the photocatalyst materials was found to strongly depend on the redox couples combined. When IO$_3$ was used as an electron acceptor for O$_2$ evolution, combination of the exfoliation-restacking process and the loading of appropriate cocatalysts such as PtO were quite effective to increase the rate of O$_2$ evolution. The former one can effectively increase the numbers of the opened active sites where the large and anionic IO$_3$ can access, and the later one significantly catalyzes the reduction of IO$_3^-$, which proceed via 6-electrons process. On the other hand, the original layered structure of H$^+$/KCa$_2$Nb$_3$O$_{10}$ sample, which was obtained via simple proton exchange of KCa$_2$Nb$_3$O$_{10}$, was effective for achieving efficient and selective water oxidation to O$_2$ in the presence of Fe$^{3+}$ 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 Fe$^{3+}$. Simultaneous and stoichiometric evolutions of H$_2$ and O$_2$ with were indeed demonstrated under UV light irradiation by employing the optimum KCa$_2$Nb$_3$O$_{10}$-based material as an O$_2$-evolving photocatalyst combined with a H$_2$-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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Notes and references

Supporting Information

Two-step photocatalytic water splitting into H₂ and O₂ using layered metal oxide KCa₂Nb₂O₁₀ and its derivatives as O₂-evolving photocatalysts with IO₃⁻/I⁻ or Fe³⁺/Fe²⁺ redox mediator

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Fig. S1 Time courses of O\textsubscript{2} evolution over H\textsubscript{2}WO\textsubscript{4}-W and H\textsubscript{2}WO\textsubscript{4}-K in Fe(ClO\textsubscript{4})\textsubscript{3} aqueous solution (5 mM, pH2.3) under visible light irradiation (\lambda > 400 nm, Xe lamp).

Fig. S2 Raman spectra of (a)WO\textsubscript{3} and (b,c) H\textsubscript{2}WO\textsubscript{4} before and after O\textsubscript{2} evolution from Fe(ClO\textsubscript{4})\textsubscript{3} aqueous solution.
Fig. S3 SEM image of H$_2$WO$_4$ (a) before and (b) after O$_2$ evolution from Fe(ClO$_4$)$_3$ aqueous solution.