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Photocatalytic overall water splitting on Pt nanocluster-intercalated, restacked $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ nanosheets: the promotional effect of co-existing ions†

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Promotional effects of co-existing ions on overall water splitting into H_2 and O_2 have been studied in bulk-type semiconductor photocatalysts (e.g., TiO_2), but such an effect remains unexplored in two-dimensional nanosheet photocatalysts. Here we examined the effect of co-existing ions on the photocatalytic water splitting activity of Pt nanocluster-intercalated $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ nanosheets. Interestingly, not only anions, as usually observed in bulk-type photocatalysts, but also cations had a significant influence on the photocatalytic performance. The rates of H_2 and O_2 evolution over $\text{Pt/KCa}_2\text{Nb}_3\text{O}_{10}$ as well as the product stoichiometry were improved in the presence of NaI . I^- ions were found to effectively suppress undesirable backward reactions, consistent with the previous work by Abe *et al.* (*Chem. Phys. Lett.*, 2003, 371, 360–364). On the other hand, Na^+ ions in the reaction solution were exchanged for K^+ in the interlayer space of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ during the water splitting reaction, which promoted interlayer hydration and consequently improved photocatalytic performance.

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Introduction

Clean production of hydrogen by water splitting over a semiconductor photocatalyst has attracted considerable interest in order to meet the social demand for replacing CO_2 -emitting fossil fuels with clean energy sources.^{1–3} The efficiency of photocatalytic water splitting, however, still remains unsatisfactory. Therefore, not only enhancing the performance of known photocatalysts but also fundamental investigation, for example understanding the reaction mechanism and exploring new materials, is important in this research field.

Certain layered materials undergo exfoliation, producing colloidal suspensions of unilamellar sheets.^{4–27} The planar size of the exfoliated sheets typically ranges from several hundreds of nanometers to a few micrometers, with a thickness of 1–2 nm. Because of the sheet-like two-dimensional (2D) structure, it is

called a nanosheet. The nanosheets containing certain transition metal cations such as Ti^{4+} , Nb^{5+} , Ta^{5+} , and W^{6+} are known to exhibit photocatalytic activity. They are expected to have several advantages in heterogeneous photocatalysis, compared with conventional bulk-type 3D photocatalysts (e.g., TiO_2).

It is known that high crystallinity of a semiconductor has a positive impact on photocatalytic performance for overall water splitting, because of the prolonged lifetime of photo-generated electrons and holes.²⁸ To obtain a highly crystalline material, high calcination temperature is generally required in the synthesis process; however, such harsh calcination conditions facilitate grain growth of photocatalyst particles, resulting in smaller surface area and lower density of reaction sites, and *vice versa*.²⁹ Moreover, larger size of semiconductor particles can have a negative effect in terms of carrier diffusion to the surface, resulting in recombination between electrons and holes and lowering photocatalytic activity. On the other hand, a nanosheet has both high crystallinity and high surface area owing to its single-crystalline character and anisotropic structure.³⁰ Furthermore, the small thickness of the nanosheet is expected to shorten the migration distance of photogenerated carriers to the surface, thereby reducing the recombination probability.^{9,12} Despite these fascinating features, there are a limited number of examples of overall water splitting using a nanosheet photocatalyst.

Other than such structural factors, there are some key factors to achieve high photocatalytic performance. One of them is

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Results and discussion

Photocatalytic performance of Pt/KCa₂Nb₃O₁₀ for overall water splitting in the presence of various salts

Fig. 1 shows the TEM images of KCa₂Nb₃O₁₀ restacked nanosheets with deposited Pt. Very small Pt nanoparticles with homogeneous dispersion were observed on the restacked nanosheets as dark spots due to a difference in electron density between Pt and KCa₂Nb₃O₁₀. Our previous study revealed that the deposited Pt was intercalated in the KCa₂-Nb₃O₁₀ restacked nanosheets with an average size of smaller than 1 nm.^{23,24} The details of the structural characterization of the Pt-intercalated KCa₂Nb₃O₁₀ nanosheets can be found elsewhere.²³

Photocatalytic reactions were performed using the Pt/KCa₂-Nb₃O₁₀ restacked nanosheets in the presence of various salts. Table 1 summarizes the amounts of H₂ and O₂ evolved in the reaction after 10 h irradiation. When the reaction was carried out in the absence of salts (*i.e.* pure water), a certain amount of H₂ was evolved, with a low level of O₂ that was far below the stoichiometric value (H₂/O₂ < 2). On the other hand, addition of NaI to pure water dramatically improved the photocatalytic performance in terms of both gas evolution amount and H₂/O₂ stoichiometry. The experimental error in gas evolution rate was approximately 15%. Neither deactivation nor decomposition of Pt/KCa₂Nb₃O₁₀ has been confirmed by XRD and TEM after 30 h irradiation.²³

In order to investigate in detail the roles of Na⁺ and I⁻ in promoting the overall water splitting, KI, Na₂SO₄ or K₂SO₄ was dissolved in the reaction solution, and photocatalytic activity was examined. The addition of KI to the reaction solution improved the H₂/O₂ evolution rates and the stoichiometry, compared to the pure water case, but not as much as that with the addition of NaI. The photocatalytic activity in the presence of K₂SO₄ was almost the same as that in pure water, suggesting that both K⁺ and SO₄²⁻ had little impact on photocatalytic performance. On the other hand, the co-existence of Na₂SO₄ in the reaction solution enhanced the performance, although the extent was lower than that observed in the presence of NaI. These results indicate that both Na⁺ and I⁻ have a positive influence on the photocatalytic performance of Pt/KCa₂Nb₃O₁₀.

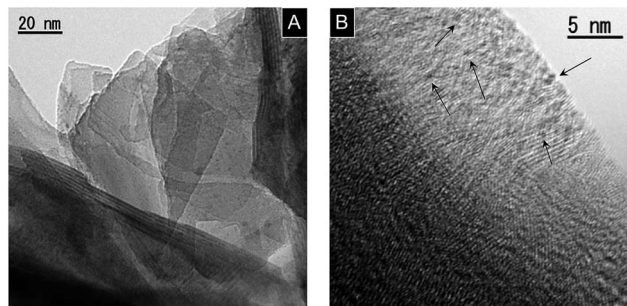


Fig. 1 TEM images of 1.0 wt% Pt/KCa₂Nb₃O₁₀ restacked nanosheets. (A) Lower and (B) higher magnification images. Arrows in (B) indicate some deposited Pt nanoclusters.

Table 1 Evolved amounts of H₂ and O₂ over Pt/KCa₂Nb₃O₁₀ restacked nanosheets in various reaction solutions^a

Dissolved salt	Amount of evolved gases/ μmol		H ₂ /O ₂ ratio
	H ₂	O ₂	
Pure water	21.6	3.6	6.0
NaI, 10 mM	85.5	37.4	2.3
KI, 10 mM	33.3	12.0	2.8
K ₂ SO ₄ , 5 mM	20.5	2.2	9.3
Na ₂ SO ₄ , 5 mM	56.4	20.0	2.8

^a Reaction conditions: catalyst, 50 mg; reaction solution, 100 mL; light source, a 300 W Xe lamp ($\lambda \geq 300$ nm). Reaction time: 10 h.

Effect of I⁻

A clear difference was also observed in the time course of overall water splitting in the presence of I⁻ anions. Fig. 2 shows the time courses of H₂ and O₂ evolution in an aqueous Na₂SO₄ or NaI solution. In the case of Na₂SO₄, rates of H₂ and O₂ evolution gradually decelerated over reaction time, although the initial evolution rates were almost the same as those recorded in the case of NaI, suggesting that backward reaction proceeded as the evolved H₂ and O₂ were accumulated in the reaction system. On the other hand, the gas evolution rates remained unchanged in the presence of NaI. Moreover, the stoichiometry of evolved H₂ and O₂ was also improved by NaI addition (H₂/O₂ \approx 2.3 for NaI, and 2.8 for Na₂SO₄). We observed a similar trend when photocatalytic reactions were performed in aqueous K₂SO₄ and KI solution (Fig. S1[†]). These results suggest that the undesirable reaction (*e.g.*, H₂/O₂ recombination and O₂ photoreduction) was suppressed in the presence of I⁻.

Abe *et al.* reported that Pt-loaded TiO₂ exhibited much higher water splitting performance in the presence of I⁻, because the iodine layer formed on Pt nanoparticles could suppress the backward reaction.³² We also confirmed the effect of I⁻ on backward reaction in this study. A certain amount of H₂

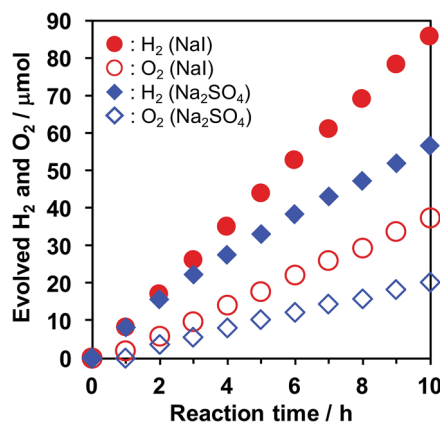


Fig. 2 Time courses of H₂ and O₂ evolution over Pt/KCa₂Nb₃O₁₀ in aqueous solution containing NaI (10 mM, red marks) or Na₂SO₄ (5 mM, blue marks). Closed marks: H₂; open marks: O₂. Reaction conditions: catalyst, 50 mg; reaction solution, 100 mL; light source, a 300 W Xe lamp ($\lambda \geq 300$ nm).



and O_2 was introduced in a closed reaction system and the amount was monitored under dark conditions, as shown in Fig. 3. Although the backward reaction over bare $KCa_2Nb_3O_{10}$ was negligible in pure water, a decrease of H_2 and O_2 was observed over $Pt/KCa_2Nb_3O_{10}$, indicating that the backward reaction took place on Pt. The water formation rate over $Pt/KCa_2Nb_3O_{10}$ became slower in the presence of NaI than in pure H_2O . On the other hand, the backward reaction rate in aqueous Na_2SO_4 solution was almost the same as that in pure water. These results suggest that the I^- , not Na^+ , interacted with Pt and suppressed the backward reactions, which are most likely to occur on the externally deposited Pt, contributing to higher photocatalytic activity. Note here that SO_4^{2-} is in principle unreactive during the photocatalytic reaction.³⁵

We attempted to detect the iodine species adsorbed on $Pt/KCa_2Nb_3O_{10}$ after the water splitting reaction. However, no iodine signal was observed in this sample (Fig. S2†), most likely because I^- cannot interact with the intercalated Pt due to electrostatic repulsion between negatively charged nanosheets and I^- . On the other hand, a small, but distinct photoelectron signal attributable to I 3d was detected in the restacked $KCa_2Nb_3O_{10}$ nanosheets that consisted of externally deposited Pt nanoparticles. It in turn indicates that the number of externally deposited Pt nanoparticles in the present $Pt/KCa_2Nb_3O_{10}$ was not large enough to produce an observable quantity of iodine layers by XPS. Nevertheless, backward reactions that occurred on such lower density Pt islands are significant, and the suppression of the backward reactions is essential. In the photocatalytic reaction, I^- also improved the H_2/O_2 stoichiometry. It is known that photo-reduction of O_2 proceeds very efficiently on Pt nanoparticles, reducing the O_2 evolution performance.³⁸ Therefore, the improved stoichiometry would originate from the suppression of O_2 photo-reduction on Pt as well.

I^- is often used as an electron mediator between H_2 and O_2 evolution photocatalysts in Z-scheme water splitting.^{33,38–41} One may suspect that I^- has a negative impact on photocatalytic

performance because the oxidation of I^- on the semiconductor surface hinders water oxidation, which has been observed in Pt/TiO_2 at high concentration of NaI.³² Thus, we investigated the dependence of water splitting performance of $Pt/KCa_2Nb_3O_{10}$ on the NaI concentration. Fig. 4 displays a relationship between H_2/O_2 evolution rates in the water splitting reaction and NaI concentration. H_2 and O_2 evolution rates monotonically increased up to 10 mM NaI and reached a plateau at higher concentration of NaI. UV-visible absorption spectroscopy indicated that before and after the photocatalytic reaction in 10 mM NaI solution, the concentration of I^- remained almost unchanged. These facts indicate that the oxidation of H_2O , not I^- , dominated on $KCa_2Nb_3O_{10}$. Adsorption isotherm measurement of NaI revealed that no adsorption of I^- took place on the surface of bare $KCa_2Nb_3O_{10}$. The surface properties inhibited the oxidation of I^- on $KCa_2Nb_3O_{10}$, leading to O_2 evolution even in the presence of higher concentration of NaI.

Effect of Na^+

As demonstrated above, the photocatalytic activity of $Pt/KCa_2Nb_3O_{10}$ restacked nanosheets for overall water splitting was promoted in the presence of Na^+ as well. In order to elucidate the reason, the reacted $Pt/KCa_2Nb_3O_{10}$ samples in the presence of various salts were characterized by XRD. Fig. 5 displays the X-ray diffraction peaks of $Pt/KCa_2Nb_3O_{10}$ attributed to the (002) plane, which is the stacking direction of restacked nanosheets. The diffraction peaks were shifted to lower two-theta directions after photocatalytic reactions in all cases, indicating that the (002) plane distance, namely the interlayer distance of restacked nanosheets, was expanded most likely due to an intercalation of water in the interlayer space, as reported previously.⁶ It should be noted that the peak positions were altered depending on the cations in the reaction solution. $Pt/KCa_2Nb_3O_{10}$ after photocatalytic reaction in the presence of Na^+ exhibited 002 diffraction peaks at lower two-theta positions compared to the peaks

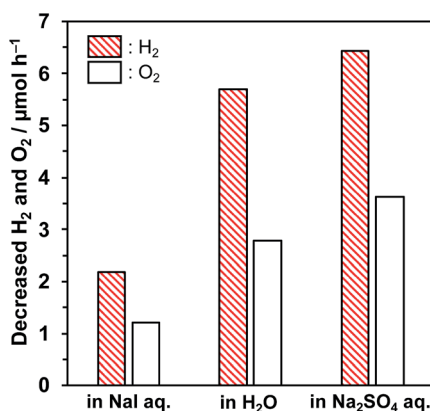


Fig. 3 Decreasing rates of H_2 and O_2 evolution over $Pt/KCa_2Nb_3O_{10}$ in aqueous NaI solution (10 mM), pure water, and Na_2SO_4 solution (5 mM) under dark conditions. Reaction conditions: photocatalyst, 50 mg; reactant volume, 100 mL; introduced amount of H_2 , ca. 200 μmol and O_2 , ca. 100 μmol .

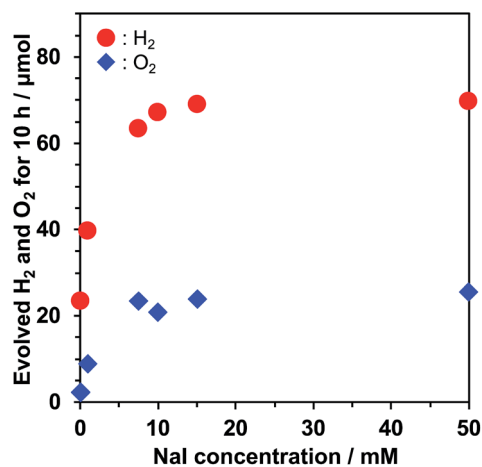


Fig. 4 Dependence of the photocatalytic water splitting activity of $Pt/KCa_2Nb_3O_{10}$ on the NaI concentration. Reaction conditions: catalyst, 50 mg; reaction solution, 100 mL; light source, a 300 W Xe lamp ($\lambda \geq 300$ nm).



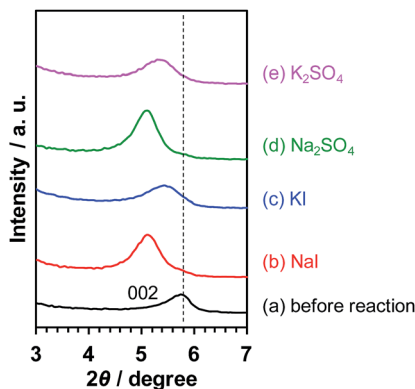


Fig. 5 002 diffraction peaks of Pt/KCa₂Nb₃O₁₀ in XRD (a) before reaction and after reaction in aqueous (b) NaI (10 mM), (c) KI (10 mM), (d) Na₂SO₄ (5 mM), and (e) K₂SO₄ (5 mM) solution.

in the presence of K⁺, suggesting that a structural change occurred during the water splitting reaction.

It is known that interlayer cations of certain layered materials can be exchanged for H⁺ and/or other kinds of alkali cations.⁴² Therefore, one possibility is that the K⁺ in the interlayer space of Pt/KCa₂Nb₃O₁₀ was exchanged for Na⁺, which was present in the reaction solution. As shown in Fig. 6, XPS analysis revealed that photoelectron signals attributable to the K 2p orbital almost disappeared, while new peaks corresponding to the Na 1s orbital were clearly detected after reactions in aqueous NaI and Na₂SO₄ solution. In contrast, photoelectron singles of not Na 1s, but K 2p were observed before and after reaction in aqueous KI and K₂SO₄ solution. The results indicate that the ion-exchange of K⁺ in the interlayer for Na⁺ occurred, and that the structure of Pt/KCa₂Nb₃O₁₀ restacked nanosheets after reaction turned into Pt/NaCa₂Nb₃O₁₀.

The ion-exchange, however, does not seem to explain the shift of the diffraction peak position (Fig. 5). The ionic radius of Na⁺ (1.02 Å) in a 6-coordination environment is smaller than that of K⁺ (1.38 Å). Thus, one can suppose that the 002 diffraction peak after ion-exchange of K⁺ for Na⁺ appears at a higher two-theta position because of the smaller size of Na⁺ and the resulting shorter (002) plane distance. A plausible

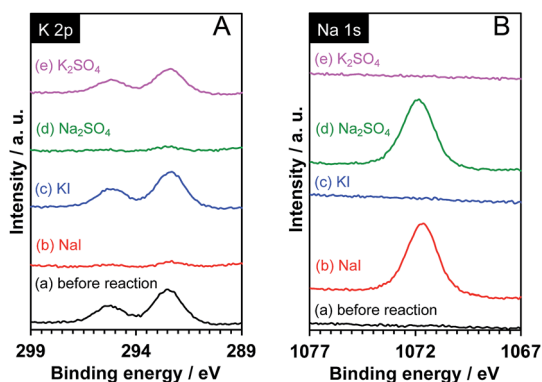


Fig. 6 XPS spectra for (A) K 2p and (B) Na 1s of Pt/KCa₂Nb₃O₁₀ (a) before and after reaction in aqueous (b) NaI (10 mM), (c) KI (10 mM), (d) Na₂SO₄ (5 mM), and (e) K₂SO₄ (5 mM) solution.

Table 2 Specific surface area of KCa₂Nb₃O₁₀ and NaCa₂Nb₃O₁₀ restacked nanosheets estimated from N₂ and H₂O adsorption

Material	$S_{N_2}/\text{m}^2 \text{ g}^{-1}$	$S_{H_2O}/\text{m}^2 \text{ g}^{-1}$	S_{H_2O}/S_{N_2}
KCa ₂ Nb ₃ O ₁₀	10.7	30.2	2.8
NaCa ₂ Nb ₃ O ₁₀	10.0	48.3	4.8

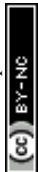
explanation for the phenomena opposite to our expectation is more hydration of the interlayer of Pt/NaCa₂Nb₃O₁₀, concealing the effect of K⁺/Na⁺ exchange.

In order to evaluate the correlation between interlayer cations and the affinity for water, we measured H₂O and N₂ adsorption isotherms of KCa₂Nb₃O₁₀ and NaCa₂Nb₃O₁₀ (Fig. S3[†]). The surface areas estimated from the H₂O and N₂ isotherms (represented as S_{H_2O} and S_{N_2} , respectively) are listed in Table 2. In both cases of KCa₂Nb₃O₁₀ and NaCa₂Nb₃O₁₀, the specific surface areas estimated from H₂O adsorption (S_{H_2O}) were larger than those from N₂ adsorption (S_{N_2}), indicating that H₂O molecules could penetrate into the interlayer space of these materials. Although S_{N_2} was not affected by interlayer cations, NaCa₂Nb₃O₁₀ exhibited obviously larger S_{H_2O} than KCa₂Nb₃O₁₀. It is thus likely that the stronger affinity for H₂O promoted the photo-redox reaction in the interlayer space of Na⁺-exchanged Pt/KCa₂Nb₃O₁₀, leading to higher photocatalytic performance for overall water splitting.

Ebina *et al.* suggested that Na⁺ ions in the interlayer of restacked nanosheets have stronger affinity toward water than K⁺.⁶ Very recently, we also reported that a layered metal oxide photocatalyst, K₂CaNaNb₃O₁₀, provided better access for reactant(s) in the interlayer space, which led to higher photocatalytic performance.⁴³ Therefore, the enhanced photocatalytic activity in the presence of Na⁺ is ascribed to better affinity for water in the interlayer of restacked nanosheets, which resulted from the ion-exchange reaction of K⁺ to Na⁺. Because interlayer modification is very important for enhancing the activity of nanosheet photocatalysts, we believe that the finding of this work would be an “indirect” means of decorating the interlayer nanospace of ion-exchangeable metal oxide nanosheets that improves photocatalytic activity for overall water splitting.

Conclusions

Effects of co-existing ions on the photocatalytic water splitting activity of Pt nanocluster-intercalated KCa₂Nb₃O₁₀ restacked nanosheets were investigated. The performance was much improved in aqueous NaI solution, compared to the pure water case, in terms of gas evolution rate, stability and H₂/O₂ stoichiometry. The results strongly suggest that during the water splitting reaction, I⁻ ions suppressed H₂/O₂ recombination and photo-reduction of O₂. Furthermore, K⁺ ions in the interlayer of Pt/KCa₂Nb₃O₁₀ underwent ion-exchange for Na⁺ in the Na⁺-containing reaction solution, producing Pt/NaCa₂Nb₃O₁₀. H₂O and N₂ adsorption measurements demonstrated that NaCa₂Nb₃O₁₀ had better affinity for H₂O in the interlayer space than KCa₂Nb₃O₁₀. It appears that this character of NaCa₂Nb₃O₁₀ is the key to improving the accessibility of H₂O and the photocatalytic redox reaction in the interlayer space.



Conflicts of interest

There are no conflicts to declare.

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