Surface-modified, dye-sensitized niobate nanosheets enabling an efficient solar-driven Z-scheme for overall water splitting

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While dye-sensitized metal oxides are good candidates as H2 evolution photocatalysts for solar-driven Z-scheme water splitting, their solar-to-hydrogen (STH) energy conversion efficiencies remain low because of uncontrolled charge recombination reactions. Here, we show that modification of Ru dye–sensitized, Pt-intercalated HCa2Nb3O10 nanosheets (Ru/Pt/HCa2Nb3O10) with both amorphous Al2O3 and poly(styrenesulfonate) (PSS) improves the STH efficiency of Z-scheme overall water splitting by a factor of ~100, when the nanosheets are used in combination with a WO3-based O2 evolution photocatalyst and an I3−/I− redox mediator, relative to an analogous system that uses unmodified Ru/Pt/HCa2Nb3O10. By using the optimized photocatalyst, PSS/Ru/Al2O3/Pt/HCa2Nb3O10, a maximum STH of 0.12% and an apparent quantum yield of 4.1% at 420 nm were obtained, by far the highest among dye-sensitized water splitting systems and comparable to conventional semiconductor-based suspended particulate photocatalyst systems.

INTRODUCTION

The development of artificial photosynthetic assemblies that can use the broad wavelength range of visible light and are operable under weak-intensity conditions (e.g., sunlight irradiation) is a long-standing challenge in energy research. Semiconductor photocatalysis is one of the most promising options for realizing clean H2 production from renewable resources on a large scale (1, 2). For any artificial photosynthetic scheme in which the standard Gibbs free energy change is positive, it is particularly important to suppress the rate of backward reactions including back electron transfer (1, 3–6). In Z-scheme overall water splitting using two different photocatalysts in the presence of a shuttle redox mediator, for example, photogenerated electrons in the H2-evolving photocatalyst must be consumed by reduction of H2O (or protons) to H2 while minimizing the reduction of more reducible electron-accepting species, which must be reduced by the O2-evolving photocatalyst (4).

Dye-sensitized wide-bandgap semiconductors with proper modifications are capable of catalyzing water reduction to H2 under visible light even in the presence of reversible electron donors such as I− (7, 8). Hence, they are potential candidates as H2 evolution photocatalysts for Z-scheme overall water splitting (9–12). Modification of a Ru dye–loaded layered niobate with poly(styrenesulfonate) (PSS) has previously been shown to improve the efficiency of dye-sensitized H2 evolution from aqueous KI solutions, while the use of undecyl-phosphonic acid or methylphosphonic acid, which do not form good surface monolayers, did not (8). In that case, the PSS layer on the niobate could selectively exclude I3−, the oxidation product of I−, from the semiconductor/solution interface, thereby suppressing the back electron transfer reaction between electrons in the conduction band of the niobate and I3−. Recently, it has been shown that restacked niobate nanosheets sensitized by a Ru(II) tri-dimine complex also act as good building blocks for the construction of Z-scheme overall water splitting systems, which outperform the parent layered analogs (10). An attractive feature of the oxide nanosheet is its high specific surface area, which enables it to accommodate more dye molecules on its surface, as compared to the parent lamellar solids (10, 13, 14). However, the high surface area of oxide nanosheets may act negatively by providing more exposed surface for the back electron transfer reaction, thereby lowering the overall efficiency.

In this work, we show that Ru dye–sensitized niobate nanosheets, further modified with Al2O3 and PSS layers, work as an efficient H2 evolution photocatalyst in Z-scheme overall water splitting in combination with a PtO2/H2O2/WO3 oxygen-evolving photocatalyst and an I3−/I− redox shuttle even under the weak intensity of simulated sunlight. As expected, our experiments showed that the undesirable back electron transfer reactions occur very efficiently on the Ru dye–sensitized nanosheets, thereby contributing to low solar-to-hydrogen (STH) energy conversion efficiency for overall water splitting. On the other hand, dual modification by Al2O3 and PSS enables nearly two orders of magnitude improvement in STH efficiency under optimized conditions.

RESULTS

Half-cell H2 evolution reactions

Following the method described in our previous report (10, 15), calcium niobate nanosheets intercalated with Pt nanoclusters were synthesized, and modification of the as-prepared Pt/HCa2Nb3O10 with an amorphous Al2O3 overlayer and [Ru(dmb)2(4,4′-(PO3H2)2bpy)]2+ (dmb = 4,4′-dimethyl-2,2′-bipyridine, bpy = 2,2′-bipyridine), abbreviated as Ru, was conducted. Loading PSS onto the nanosheet...
materials was performed at room temperature by dispersing the dye-adsorbed niobate nanosheets in a sodium polystyrene sulfonate aqueous solution at pH 2 for 1 hour (8). No significant change in the morphology of the Pt/HCa$_2$Nb$_3$O$_{10}$ nanosheets was seen before and after the PSS modification step (fig. S1). Energy-dispersive x-ray spectroscopy was also carried out to visualize the distribution of PSS on the nanosheets, but did not give meaningful results. This was because of the low concentration of the loaded PSS, as confirmed by x-ray photoelectron spectroscopy (XPS) measurements. As shown in fig. S2, a clear S 2p photoelectron signal at 168.0 eV, assignable to PSS (16), was observed, but with very low concentration of PSS; the surface atomic ratio of S/Nb in the PSS/Pt/HCa$_2$Nb$_3$O$_{10}$ was about 0.04. It should be noted that the 1 MLCT absorption band of the adsorbed Ru at around 460 nm was maintained even after PSS modification (fig. S3).

First, half-cell H$_2$ evolution reactions were conducted using Ru/Pt/HCa$_2$Nb$_3$O$_{10}$ with and without postmodification under two different light intensity conditions using a 300-W xenon lamp. A schematic illustration of the energy diagram of the Ru-sensitized Pt/HCa$_2$Nb$_3$O$_{10}$ nanosheets for H$_2$ evolution is shown in Fig. 1. The reaction consists of reduction of H$^+$ into H$_2$ on the intercalated Pt in the nanosheet photocatalyst and oxidation of I$^-$ into I$_3^-$ by one-electron oxidized Ru as follows

$$2H^+ + 2e^- \rightarrow H_2 (\text{reduction of } H^+ \text{ into } H_2) \quad (1)$$

$$3I^- + 2h^+ \rightarrow I_3^- (\text{oxidation of } I^- \text{ into } I_3^-) \quad (2)$$

As shown in Fig. 2A, the Ru/Pt/HCa$_2$Nb$_3$O$_{10}$ produced H$_2$ from aqueous NaI solution under high-intensity visible light (80 mW cm$^{-2}$, $\lambda > 400$ nm), but the H$_2$ evolution rate was slowed down after only 1 hour of irradiation. This can be explained by the increasing predominance of the back reaction involving the oxidized donor (I$_3^-$) and the injected electrons in the Pt/HCa$_2$Nb$_3$O$_{10}$ nanosheets (Eq. 3), which is thermodynamically more favorable than the forward reaction of proton reduction (Eq. 1) (7, 8)

$$I_3^- + 2e^- \rightarrow 3I^- (\text{reduction of } I_3^- \text{ into } I^-) \quad (3)$$

Effect of dual modification with Al$_2$O$_3$ and PSS

On the basis of these results, we can expect that the promotional effect of chemical modifiers on H$_2$ evolution by the Ru/Pt/HCa$_2$Nb$_3$O$_{10}$ photocatalyst will be maximized if the concentration of I$_3^-$ in the reaction solution is minimized. This situation can be realized in the presence of an O$_2$ evolution photocatalyst, which can efficiently recombine I$_3^-$ and oxidize water into O$_2$. With this idea in mind, Z-scheme overall water splitting systems were constructed using Ru/Pt/HCa$_2$Nb$_3$O$_{10}$ with different modifications in the presence of Al$_2$O$_3$ modification has been reported to suppress back electron transfer reaction from the conduction band of a metal oxide to the oxidized form of the Ru dye in Ru dye–sensitized metal oxide systems (11, 17). In the present Ru/Pt/HCa$_2$Nb$_3$O$_{10}$ system, Al$_2$O$_3$ modification did not measurably improve the H$_2$ evolution activity. Modification of the Ru/Pt/HCa$_2$Nb$_3$O$_{10}$ with PSS also had no measurable impact on the H$_2$ evolution activity under these conditions. These results imply that the negative impact of the backward reaction on the Ru/Pt/HCa$_2$Nb$_3$O$_{10}$ (Eq. 3) is significant under high-intensity irradiation conditions.

On the other hand, when the reactions were conducted under lower-intensity visible light (8.0 mW cm$^{-2}$, $\lambda > 400$ nm), a clear enhancement effect by PSS modification appeared (Fig. 2B). In contrast to the high–light intensity condition, the concentration of I$_3^-$ produced should be lower under low-intensity irradiation. Under these conditions, the injected electrons in the conduction band of the nanosheets have a higher probability of escaping from recombination with I$_3^-$ and reacting with protons at the intercalated Pt. Thus, the positive effect of PSS modification on H$_2$ evolution activity becomes apparent only when the concentration of I$_3^-$ in the reaction system is sufficiently low. It is also noted that the Al$_2$O$_3$ modification slightly improved the H$_2$ evolution activity under low–light intensity conditions, suggesting that the primary role of the Al$_2$O$_3$ modifier is to suppress the back electron transfer reaction from the oxide to the adsorbed dye, as noted above. In other words, when I$_3^-$ is present at low concentration, back electron transfer to I$_3^-$ will occur more readily than reverse electron transfer to the oxidized Ru dye.

Fig. 1. Electron transfer mechanism. Schematic electron transfer mechanism and energy level diagram of the Ru/Pt/HCa$_2$Nb$_3$O$_{10}$ nanosheets for H$_2$ evolution and PtO$_x$/H-Cs-WO$_3$ for O$_2$ evolution. C.B., conduction band; V.B., valence band.
When electron transfer to I$_3^-$ > 400 nm). Irradiation area, 44 cm$^2$. (pH 3.8 to 4.0); light source, xenon lamp (300 W) fitted with CM-1 cold mirror and L42 cutoff filter (λ > 400 nm). Reaction conditions: catalyst, 20 mg; solution, aqueous NaI (10 mM, 100 ml, pH 3.8 to 4.0); light source, xenon lamp (300 W) fitted with CM-1 cold mirror and L42 cutoff filter (λ > 400 nm). Irradiation area, 44 cm$^2$. (A and B) Data taken under higher-intensity (80 mW cm$^{-2}$) and lower-intensity (8.0 mW cm$^{-2}$) irradiation, respectively. Experimental error in the H$_2$ amount was ~20%.

A PtO$_x$/H-Cs-WO$_3$ photocatalyst, which has been reported to work efficiently even at low concentration of I$_3^-$ and to produce O$_2$ (18).

Table 1 lists the results of Z-scheme overall water splitting reactions, which were conducted under high-intensity visible light (80 mW cm$^{-2}$, λ > 400 nm). Full time course data are shown in fig. S4. When Ru/Pt/HCa$_2$Nb$_3$O$_{10}$ was used, a larger amount of H$_2$ (57.7 μmol) as well as nearly stoichiometric O$_2$ was produced in the Z-scheme reaction (entry 1), as compared to that in the half-cell H$_2$ evolution (21.9 μmol; Fig. 2A). This confirms that back electron transfer to I$_3^-$ can be suppressed in the H$_2$ evolution photocatalyst, owing to the fact that the O$_2$ evolution photocatalyst efficiently consumes I$_3^-$ ions. As expected from the results of half reaction at low light intensity (Fig. 2B), PSS modification enhanced the overall water splitting activity (entry 2). While the Al$_2$O$_3$ modification had little impact on the half-cell H$_2$ evolution rate even under low light intensity (Fig. 2B), it increased the Z-scheme activity by a factor of 3 (entry 3). These results can also be explained in terms of the I$_3^-$ concentration. When the local concentration of I$_3^-$ around the H$_2$ evolution photocatalyst is high (e.g., in the half reaction), electron transfer from HCa$_2$Nb$_3$O$_{10}$ to I$_3^-$ is efficient. Under this condition, the Al$_2$O$_3$ modification only slightly influences the yield of hydrogen, even if it has a positive effect on suppressing back electron transfer to the oxidized Ru dye. At low concentration of I$_3^-$, on the other hand, the back electron transfer to I$_3^-$ is less efficient, and so back electron transfer to the oxidized Ru dye becomes more kinetically competitive with hydrogen evolution. This qualitatively implies the positive effect of Al$_2$O$_3$ modification.

Thus, the two modifiers were shown to behave differently, depending on the local concentration of I$_3^-$ around, or adsorption of I$_3^-$ onto, the surface of the H$_2$ evolution photocatalyst. Both modifiers provide a positive kinetic effect on the activity under Z-scheme water splitting conditions; Al$_2$O$_3$ should primarily suppress back electron transfer to the surface-adsorbed oxidized Ru complex, whereas PSS should inhibit reduction of I$_3^-$. Here, we combined both of the modifiers and found that the doubly modified sample was more active than the individually modified analogs (entry 4). In this system, it is reasonable that both back electron transfer reactions are suppressed more effectively, and thus, the injected electrons in HCa$_2$Nb$_3$O$_{10}$ can more efficiently react at the intercalated Pt to evolve H$_2$.

To further investigate the effects of Al$_2$O$_3$ and PSS modification on the excited charge carrier dynamics, laser flash photolysis/transient absorption measurements were carried out. By observing transient bleaching recovery of the dye without any added reducing agent, one can measure the rate of back electron transfer from the semiconductor to the oxidized Ru complex. Following a laser flash at 532 nm to selectively photoexcite Ru, bleaching of the 1 MLCT absorption of ground-state Ru was observed at 475 nm (fig. S5). As reported previously (10), Al$_2$O$_3$ modification clearly decelerated the bleaching recovery, indicating that the back electron transfer reaction is suppressed. Although a similar effect was observed with PSS-modified samples, the decrease in the bleaching recovery rate was not as great as with Al$_2$O$_3$.

By monitoring the transient absorbance in an aqueous NaI solution, the reactivity of the photocatalyst with iodide ions can be measured. In this case, the bleaching recovery of the 1 MLCT absorption provides information about the rate of electron transfer from I$^-$ to the oxidized dye. Figure 3A shows time-dependent change in the 1 MLCT absorption of Ru for Al$_2$O$_3$ and PSS-modified samples in aqueous NaI solutions. The Al$_2$O$_3$ modifier markedly accelerates the bleaching recovery in the presence of I$^-$, indicating that Al$_2$O$_3$ promotes the reaction between the oxidized Ru complex and iodide ions. As noted previously (11), because Al$_2$O$_3$ modification makes the surface ζ-potential positive, anions in the solution can access the surface of the photocatalyst more readily. This implies that triiodide ions are also attracted to the surface of the Al$_2$O$_3$-modified photocatalyst. On the contrary, the PSS modifier clearly decelerates the 1 MLCT bleaching recovery. The reverse effect of PSS, as compared with Al$_2$O$_3$, is understandable because PSS is an anionic polymer. Retardation of the 1 MLCT bleaching recovery was observed even with dual modification by Al$_2$O$_3$ and PSS. It is, therefore, expected that the PSS modifier inhibits the access of not only I$^-$ but also I$_3^-$ to the photocatalyst surface.

The reactivity of conduction band electrons in the semiconductor with triiodide ion can be followed by measuring the transient absorbance change at 380 nm, where I$_3^-$ absorbs strongly (8). To obtain a high signal intensity of I$_3^-$, this measurement was conducted.
in 100 mM aqueous NaI solution where recovery of the ground state of Ru is very fast. The time-dependent absorbance changes at 380 nm are shown in Fig. 2B, and the measured lifetimes are tabulated in Table 2. All the profiles could be fitted by double- or triple-exponential functions (Eqs. 4 and 5)

\[
f(x) = y_0 + A_1 \exp\left(-\frac{x-x_0}{t_1}\right) - A_2 \exp\left(-\frac{x-x_0}{t_2}\right)
\]

\[
f(x) = y_0 + A_1 \exp\left(-\frac{x-x_0}{t_1}\right) - A_2 \exp\left(-\frac{x-x_0}{t_2}\right) - A_3 \exp\left(-\frac{x-x_0}{t_3}\right)
\]

In each case, there was an abrupt increase in the ΔO.D. and a subsequent decay, which correspond to an increase and decrease in the triiodide concentration, respectively. Unmodified and Al₂O₃-modified samples had a positive component (τ₁), corresponding to generation of I₃⁻, which was one order of magnitude faster than that of the PSS-modified samples, confirming again that the PSS modifier suppresses the reaction of I⁻ with the surface-bound oxidized Ru complex. While the acceleration of this reaction by Al₂O₃ modification was clear in the 475-nm transient (the ¹MLCT bleaching recovery; Fig. 3A), the trend was obscured at 380 nm. This is probably because the time window for monitoring the absorption changes of I₃⁻ was 16 ms, far longer than the τ₁ values (<1 µs). On the other hand, an obvious increase in the ΔO.D. was seen with the Al₂O₃-modified sample, which is consistent with acceleration of the reaction of I⁻ with the oxidized Ru complex by Al₂O₃ modifier.

The τ₂ component mainly reflects the recombination reaction, in which conduction band electrons are scavenged by I₃⁻ (Eq. 3). The millisecond-order absorption decay lifetime of τ₂ is consistent with earlier observations (8). Unmodified and Al₂O₃-modified samples had τ₂ values that were similar to each other, indicating that Al₂O₃ does not effectively suppress this recombination reaction. On the contrary, PSS modification resulted in a nearly twofold longer τ₂, indicating clear inhibition of the reduction of I₃⁻. It is most likely that suppression of the reactions of both I⁻ and I₃⁻ by PSS results from electrostatic repulsion between the anionic polymer and the anions. This effect is also evident with the PSS/Al₂O₃ comodified sample. Another important observation is that there is an additional lifetime component (τ₃) that is needed to fit the decay curve of the Al₂O₃-modified sample. τ₃ is one of the decay components of the I₃⁻ absorption and is significantly shorter than τ₂. The appearance of a very short lifetime component obviously suggests that there is a very fast decay process involving I₃⁻ in the Al₂O₃-modified photocatalyst.

From the results of transient absorption spectroscopy, it is apparent that the PSS modifier alone can suppress the reduction of I₃⁻ (the recombination reaction) in Z-scheme water splitting, but the reaction with I⁻ (the forward reaction) is also decelerated. PSS modification alone does not suppress back electron transfer from the semiconductor to the oxidized Ru complex, a rapid reaction that can compete kinetically with the reduction of I₃⁻. Therefore, the full potential of the nanosheet photocatalyst for Z-scheme water splitting is reached only by dual modification with Al₂O₃ and PSS. We note that the retardation of the reaction with I⁻ by PSS does not significantly affect the photocatalytic activity of the Z-scheme. This is because the reaction of I⁻ with the oxidized Ru complex is always much faster than the photocatalytic reactions, as demonstrated in our previous studies (11). A schematic reaction mechanism that we propose is shown in fig. S6.

**Solar-driven Z-scheme overall water splitting**

The difference in Z-scheme activity among the differently modified nanosheet photocatalysts was found to be much clearer when the Z-scheme reactions were conducted under simulated sunlight. Figure 4 shows STH energy conversion efficiencies recorded under different light intensity conditions using Ru/Pt/HCa₂Nb₃O₁₀

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**Table 2. Absorption decay lifetimes.** Absorption decay lifetimes of Ru adsorbed on HCa₂Nb₃O₁₀ nanosheets with different surface modifications.

| Entry | H₂ evolution photocatalyst       | τ₁ (µs)     | τ₂ (µs)     | τ₃ (µs) |
|-------|---------------------------------|-------------|-------------|--------|
|       |                                 | %           | %           |
| 1     | Ru/Pt/HCa₂Nb₃O₁₀                | 0.22 ± 0.07 | 3200 ± 300  |        |
|       |                                 | 62          | 38          | 1      |
| 2     | PSS/Ru/Pt/HCa₂Nb₃O₁₀            | 2.6 ± 0.7   | 7000 ± 3000 |        |
|       |                                 | 60          | 40          | 1      |
| 3     | Ru/Al₂O₃/Pt/HCa₂Nb₃O₁₀          | 0.26 ± 0.03 | 3400 ± 100  | 5 ± 1  |
|       |                                 | 59          | 30          | 11     |
| 4     | PSS/Ru/Al₂O₃/Pt/HCa₂Nb₃O₁₀      | 3 ± 1       | 7000 ± 2000 |        |
|       |                                 | 48          | 52          | 1      |

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Z-scheme systems [e.g., Ru/SrTiO$_3$:Rh–BiVO$_4$ with Fe$^{3+}$/2$^+$ redox] is comparable to those reported in typical powder-suspension–type/Pt/HCa$_2$Nb$_3$O$_{10}$. This value of Ru nanosheet photocatalyst, relative to H$_2$ moderately with little O$_2$ evolution, and the STH could not be achieved in conventional semiconductor-based photocatalysts and a component of Z-scheme overall water splitting.

The apparent quantum yield (AQY), another important metric in heterogeneous photocatalysis, was also determined. The optimized system gave a maximum AQY of 4.1% at 420 nm (see table S1), again with stoichiometric H$_2$ and O$_2$ evolution (fig. S7). This value is the highest among Z-scheme overall water splitting systems that incorporate a dye-sensitized H$_2$ evolution photocatalyst. Although an approach by “photocatalyst sheet” has recently been shown to substantially improve the Z-scheme activity (23, 24), AQY’s recorded in powder suspension systems under visible light still remain several percentages (19, 23, 25–27), and ~10% at the highest (28). Considering these, the AQY obtained in this work is comparable to those achieved in conventional semiconductor-based photocatalysts and demonstrates the great potential of a dye-sensitized photocatalyst as a component of Z-scheme overall water splitting.

**DISCUSSION**

We have successfully improved the efficiency of a Z-scheme overall water splitting system by using a surface-modified dye-sensitized nanosheet photocatalyst. The optimal systems gave an STH conversion efficiency of 0.12% and an AQY of 4.1% at 420 nm, which are new benchmarks for Z-scheme water splitting using dye-sensitized photocatalysts.

The present study highlights that surface modification of dye-sensitized oxide photocatalysts is critically important in terms of suppressing the two principal pathways of back electron transfer reactions, the negative impact of which is most pronounced under irradiation at low intensity. This idea has not been fully appreciated in earlier studies, most of which have been carried out in sacrificial systems (29, 30), in which the negative impact of back electron transfer reactions can be minimized. Understanding the mechanisms of back electron transfer reactions in the hydrogen-evolving component of a Z-scheme enables it to be used more effectively. For example, the STH may be further improved by revisiting dye molecules and H$_2$-evolving cocatalysts. These findings may also provide a useful guide for the construction of other dye-sensitized systems, such as those that carry out CO$_2$ reduction (31–33), because the control of back electron transfer reactions is essential to achieving high efficiency in any nonsacrificial artificial photosynthetic schemes.

**MATERIALS AND METHODS**

**Synthesis of Ca$_2$Nb$_3$O$_{10}^-$ nanosheets**

First, layered KCa$_2$Nb$_3$O$_{10}$ was synthesized by a flux method (34). K$_2$SO$_4$ ($\geq$99.0%; Kanto Chemical Co.), CaCO$_3$ ($\geq$99.99%; Kanto Chemical Co.), and Nb$_2$O$_5$ ($\geq$99.95%; Kanto Chemical Co.) were mixed in a molar ratio of K/Ca/Nb = 5/2/3 using an agate mortar and a pestle. The mixture was put into a Pt crucible and heated at a ramp rate of 300 K hour$^{-1}$ to 1173 K, then at 100 K hour$^{-1}$ to 1573 K, and kept at that temperature for 24 hours. It was cooled down to 1073 K at 25 K hour$^{-1}$ and then naturally cooled. The nanosheets with different modifications. Under 1-Sun conditions (100 mW cm$^{-2}$), the Ru/Pt/HCa$_2$Nb$_3$O$_{10}$-based system produced H$_2$ moderately with little O$_2$ evolution, and the STH could not be calculated on the basis of the O$_2$ evolution rate. Both H$_2$ and O$_2$ evolution were observable under 2-Sun conditions, giving STHs of 0.0020 and 0.00088% based on each gas evolution rate. Thus, higher light intensity was necessary for the Ru/Pt/HCa$_2$Nb$_3$O$_{10}$ nanosheets without modification to operate as a Z-scheme overall water splitting system.

On the other hand, the PSS/Ru/Pt/HCa$_2$Nb$_3$O$_{10}$ nanosheets gave a nearly 10-fold enhancement in STH, as compared to an analogous system without PSS. The system worked even under 0.5-Sun conditions, with almost the same STH value of ~0.02% as that recorded under 1-Sun conditions. The Al$_2$O$_3$ modification also provided an enhancement effect similar to PSS, but the effect was less pronounced. This is opposite to the trend observed in Z-scheme experiments under high-intensity visible light, where Al$_2$O$_3$ was better pronounced. This is opposite to the trend observed in Z-scheme experiments (21, 22) has shown a similar phenomenon; a Ru/SrTiO$_3$:Rh–BiVO$_4$ composite photocatalyst designed for Z-scheme overall water splitting does not work efficiently under low-intensity visible light because of recombination of minority carriers at the Ru/SrTiO$_3$:Rh–BiVO$_4$ interface. In our system, because the Ru/Pt/HCa$_2$Nb$_3$O$_{10}$ nanosheets have undesirable back electron transfer pathways that favor charge carrier recombination, high light intensity is needed to drive water splitting. In other words, appropriate surface modifications that suppress these back electron transfer reactions are necessary for light-driven water splitting with a dye-sensitized nanosheet photocatalyst.
obtained sample was centrifuged and washed with water and dried at 343 K overnight. The as-synthesized KCa$_2$ Nb$_3$ O$_{10}$ was stirred in an aqueous 1 M HNO$_3$ solution for 3 days. The acid solution was refreshed once on the second day. The product was centrifuged and washed with H$_2$O thoroughly until the pH of the supernatant became six to seven, followed by drying at 343 K overnight. The prepared HCa$_2$ Nb$_3$ O$_{10}$ was stirred in an aqueous TBA$^+$OH solution [40 weight % (wt %) in H$_2$O; Sigma Aldrich] for 1 week to obtain TBA$^+$/ Ca$_2$ Nb$_3$ O$_{10}^{-}$ nanosheets (35). The molar ratio of TBA$^+$ to the exchangeable cations in the protonated solids was 1. The unreacted lamellar solid was removed by decantation. The concentration of the as-prepared Ca$_2$ Nb$_3$ O$_{10}$ nanosheet suspension was typically $\sim$5 g liter$^{-1}$. 

**Intercalation of Pt nanoparticles into HCa$_2$ Nb$_3$ O$_{10}$ nanosheets**

Pt was selectively deposited in the interlayer according to a previous report (15). A 1 mM aqueous solution of dissolved [Pt(NH$_3$)$_4$]Cl$_2$ (Wako Pure Chemicals) was dropped at a rate of 1 to 2 ml min$^{-1}$ into the as-prepared Ca$_2$ Nb$_3$ O$_{10}$ nanosheet suspension (1 wt % Pt), and the suspension was stirred for 1 day. Then, the colloidal nanosheets were restacked by adding an aqueous 2 M HCl solution. The precipitate was washed with H$_2$O and dried at 343 K. The sample was ground and heated at 473 K for 1 hour under H$_2$ flow of 20 ml min$^{-1}$. Last, the product was stirred in aqua regia at the boiling temperature for 15 min to dissolve Pt on the external surface of HCa$_2$ Nb$_3$ O$_{10}$. The bulk amount of Pt loaded was 0.3 to 0.4 wt %, corresponding to a near-surface Pt/Nb atomic ratio of 0.007 to 0.008 from previous XPS measurements (10). The restacked Pt/HCa$_2$ Nb$_3$ O$_{10}$ nanosheets had a Brunauer-Emmett-Teller (BET) surface area of 38 m$^2$ g$^{-1}$.

**Al$_2$O$_3$ modification**

Al$_2$O$_3$ was deposited by a sol-gel method on the as-prepared Pt/HCa$_2$ Nb$_3$ O$_{10}$ (10). Pt/HCa$_2$ Nb$_3$ O$_{10}$ (100 mg) was suspended in 20 ml of ethanol containing 100 μl of aqueous 0.1 M H$_2$SO$_4$ solution and aluminum isopropoxide (2 wt %, ≥98.0%, TCI). The suspension was subjected to sonication for 30 min, followed by stirring for 1 day. The resulting powder was washed with water and dried at room temperature under vacuum. The surface Al/Nb atomic ratio in the Al$_2$O$_3$-modified Pt/HCa$_2$ Nb$_3$ O$_{10}$ was measured to be 0.2 by XPS (fig. S2B).

**Synthesis and adsorption of a Ru(II) photosensitizer**

[Ru(4,4$'$-(CH$_3$)$_2$-bpy)$_2$(4,4$'$-(PO$_3$H$_2$)$_2$-bpy)]Cl$_2$, referred to as Ru, was synthesized by literature methods with some modifications (36). The successful synthesis of Ru was confirmed by $^1$H nuclear magnetic resonance spectroscopy, electrospray ionization–mass spectroscopy, and ultraviolet-visible (UV-vis) absorption spectroscopy. The spectroscopic and electrochemical properties of Ru can be found in our previous paper (11). Adsorption of Ru onto the nanosheet surface was performed as follows: 50 mg of nanosheet powder was suspended in an appropriate volume of the aqueous Ru(II) complex solution (50 μM). The pH was adjusted to 2 by addition of an aqueous HCl solution. The suspension was stirred for 15 hours at room temperature in the dark, followed by filtration, washing with H$_2$O, and drying at room temperature under vacuum. The amount of Ru(II) complex adsorbed was estimated from the difference in the $^1$MLCT absorbance in the UV-vis absorption spectrum before and after adsorption using molar extinction coefficients of Ru(II) complexes reported previously.

**PSS modification**

PSS modification onto Ru adsorbed nanosheets was performed as follows: 50 mg of the Ru-adsorbed nanosheet sample was suspended in 20 ml of 0.25 mM poly(sodium 4-styrenesulfonate) (PSS; Sigma-Aldrich, MW 70,000) aqueous solution at pH 2 for 1 hour in the dark, followed by filtration, washing with H$_2$O, and drying at room temperature under vacuum (8).

**Transient absorption measurements**

Transient absorption spectroscopy measurements were performed using an enVision transient absorption system (Magnitude Instruments, State College, PA) described previously (10, 11). Briefly, approximately 10 mg of the Ru-sensitized HCa$_2$ Nb$_3$ O$_{10}$ nanosheet sample was dispersed in an aqueous NaI (10 or 100 mM, 4 ml, ≥99.9%; Fisher Science Education) or pure water in a quartz cuvette, and spectra were recorded in diffuse reflectance mode. The pH of the solution was adjusted to about 4 with aqueous H$_2$SO$_4$ solution. The suspension was purged with Ar at least for 30 min before experiments.

**Characterization**

Scanning electron microscopy (SEM) images were taken using a Hitachi SU9000 field emission SEM. XPS measurements were conducted using an ESCA-3400 apparatus (Shimadzu). The binding energies were determined by referencing the C 1s peak (284.5 eV) for each sample. UV-vis diffuse reflectance spectra were obtained using a spectrophotometer (V-670, JASCO). The BET surface area was measured using a gas adsorption apparatus (MICROTAC MRB, BELSORP-mini) at liquid nitrogen temperature (77 K).

**Photocatalytic reactions**

The experimental detail of photocatalytic reactions was essentially the same as reported previously (10). Briefly, 20 mg of dye-adsorbed sample was suspended in an aqueous 100-ml solution containing an electron donor, NaI (≥99.5%), purchased from Kanto Chemical Co. was used as an electron donor without further purification. The pH of the reaction solution was adjusted to 4 with aqueous HCl solution. When Z-scheme overall water splitting was performed, 50 mg of PtO$_2$/H-Cs-WO$_3$ photocatalyst (18, 37) was used together with the dye-adsorbed H$_2$ evolution photocatalyst. The details of the preparation and characterization of the O$_2$ evolution photocatalyst can be found in a previous paper (18). Our previous study has shown that the optimal pH of the solution for nonsacrificial overall water splitting in the presence of NaI is ~4 (10). The light source was a 300-W xenon lamp (Cermax, PE300BF) fitted with a CM-1 cold mirror and an L42 cutoff filter to allow for visible light irradiation ($\lambda > 400$ nm). The irradiation area was 44 cm$^2$. The light intensity was measured using a calibrated silicon photodiode to be 80 mW cm$^{-2}$ in the wavelength range of 400 to 600 nm. For experiments with lower-intensity visible light (8.0 mW cm$^{-2}$), a neutral density filter was used. These photoreaction experiments were conducted at room temperature using a top irradiation–type cell connected to a closed gas circulation system made of glass. The evolved gases were analyzed by gas chromatography (Shimadzu, GC-8A with a TCD detector and an MS-5A column, argon carrier gas).

STH conversion efficiency was measured using a HAL-320 solar simulator as the light source and was estimated according to the following equation
where $R_{H2}$, $R_{O2}$, $AG^\circ$, P, and S are the rates of hydrogen/oxygen evolution (mol s$^{-1}$) in Z-scheme water splitting, the standard Gibbs free energy of liquid water (237$\times$10$^{-3}$ mol J$^{-1}$), the intensity of simulated sunlight (50, 100, or 200 mW cm$^{-2}$), and the irradiation area (9 cm$^2$).

The AQY for H$_2$ evolution was measured using a band-pass filter ($\lambda$ = 420 nm) and was estimated as

$$AQY(%) = \frac{A \times R}{I} \times 100$$

where A, R, and I represent the reaction coefficient (H$_2$ evolution, 4; O$_2$ evolution, 8), the H$_2$ or O$_2$ evolution rate, and the rate of incident photons, respectively (18, 25). The rate of incident photons (1.03 mW cm$^{-2}$) was measured using a calibrated silicon photodiode. The irradiation area was 44 cm$^2$. In the AQY measurements, the amounts of photocatalysts used were changed for optimization of the performance (25).

**SUPPLEMENTARY MATERIALS**

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View/request a protocol for this paper from Bio-protocol.

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