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Author(s)	Yoshimura, Nobutaka; Yoshida, Masaki; Kato, Masako; Kobayashi, Atsushi
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Photocatalyst–mediator interface modification by surface-metal cations of a dye-sensitized H₂ evolution photocatalyst

Nobutaka Yoshimura,^a Masaki Yoshida,^a Masako Kato,^{a,b} Atsushi Kobayashi^{*a}

^aDepartment of Chemistry, Faculty of Science, Hokkaido University, North-10 West-8, Kita-ku, Sapporo 060-0810, Japan

^bDepartment of Applied Chemistry for Environment, School of Biological and Environmental Sciences, Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan. ABSTRACT: To develop a highly active H₂ evolving dye-sensitized photocatalysts (DSPs) applicable for Z-scheme water splitting, we synthesized a series of Ru(II)-dye-double-layered DSPs, M'-RuCP⁶-Zr-RuP⁶@Pt-TiO₂ (M'-DSP) with different surface-bound metal cations (M' = Fe²⁺, Y³⁺, Zr⁴⁺, Hf⁴⁺, and Bi³⁺). In 0.5 M KI aqueous solution, the photocatalytic H₂ evolution activity under blue light irradiation ($\lambda = 460\pm15$ nm) increased in the following order: non-metal-modified DSP, H⁺-DSP (turn over number for 6 h irradiation = 35.2) < Fe²⁺-DSP (54.9) \cong Bi³⁺-DSP (55.2) < Hf⁴⁺-DSP (65.5) \cong Zr⁴⁺-DSP (68.3) \cong Y³⁺-DSP (71.5), suggesting that the redox-inactive and highly-charged metal cations tend to improve the electron donation from the iodide electron mediator. On the other hand, DSPs having heavy metal cations, Hf⁴⁺-DSP (18.4) and Bi³⁺-DSP (16.6) exhibited better activity under green light irradiation ($\lambda = 530\pm15$ nm) than Zr⁴⁺-DSP (15.7) and H⁺-DSP (7.80), implying the contribution of heavy atom effect of the surface-bound metal cation to partially allow the spin-forbidden metal-to-ligand charge-transfer excitation.

Introduction

Photocatalytic solar water splitting is a desirable reaction for solving global energy and environmental issues.¹⁻⁵ Since the discovery of the Honda-Fujishima effect,⁶ many semiconductor photocatalysts have been developed. In particular, the construction of a Z-scheme system by combining H₂ and O₂ evolving photocatalysts (OEP and HEP) has attracted considerable attention as a useful strategy to utilize visible light and ensure a sufficiently large driving force for water splitting and electron transfer reactions.⁷⁻¹⁰ For example, in 2016, Domen *et al.* reported a Z-scheme photocatalyst composed of La- and Rh-codoped SrTiO₃ and Modoped BiVO₄—as the H₂ and O₂ evolving photocatalysts, respectively—on a gold layer, which exhibited 1.1% solar-to-hydrogen (STH) energy conversion efficiency and over 30% apparent quantum efficiency (AQY) at 419 nm.¹¹ However, further improvement of both the STH and AQY is still necessary for practical application. To achieve this, two targets must be reached: The first is to utilize the longer wavelength range to improve the STH energy conversion efficiency^{4,12-13} and the second is to achieve one-way electron transfer from the OEP to HEP *via* an electron mediator.¹⁴⁻¹⁶

Dye-sensitization is a well-known and extensively studied technique to overcome the weak visible light absorption of a semiconductor substrates.¹⁷⁻²⁹ Abe *et al.* reported on a Z-scheme water-splitting photocatalyst composed of coumarin-dye-sensitized Pt/H₄Nb₆O₁₇ as the HEP and IrO₂-Pt/WO₃ as the OEP.³⁰ A remarkably high AQY (2.4% at 420 nm) was achieved by a recently developed Z-scheme system consisting of a Ru(II)-dye-sensitized Al₂O₃ cluster-deposited/Pt/HCa₂Nb₃O₁₀ as the HEP.³¹ Although the AQY and STH values of dye-sensitized photocatalysts (DSPs) are still lower than those of their metal-oxide-based counterparts, the dye-sensitization technique offers a unique advantage. Indeed, further modification at the dye-

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semiconductor interface is possible by co-absorption and/or multilayering of functional molecules, as evidenced by recent studies in dye-sensitized solar (DSSCs) and electrochemical (DSPEC) cells.³²⁻³⁵ Meyer *et al.* demonstrated one-directional energy transfer in a bilayer film composed of two different Ru(II) dyes.³⁶⁻⁴⁰ Hanson *et al.* reported that the lifetime of the charge-separated state can be controlled by introducing an organic spacer molecule into the dye–semiconductor interface with various metal cation linkages.⁴¹⁻⁴⁴ Further, several research groups have reported that the host–guest interaction is useful for softly immobilizing dyes and catalyst molecules on the semiconductor surface.⁴⁵⁻⁴⁹ However, literature on the further modification of the dye–semiconductor interface in the field of DSP for water splitting remains limited.

In this context, we previously reported on a DSP nanoparticle consisting of a Pt-cocatalystloaded TiO₂ nanoparticle covered by a bilayer film formed from two Ru(II) dyes with Zr^{4+} cations—Zr-**RuCP6**-Zr-**RuP6**@Pt-TiO₂ (Zr^{4+} -**DSP**, **RuCP6** = [Ru(mpbpy)₃]¹⁰⁻, where **RuP6** = [Ru(pbpy)₃]¹⁰⁻, H₄mpbpy = 2,2'-bipyridine-4,4'-bis(methane-phosphonic acid), and H₄pbpy = 2,2'-bipyridine-4,4'-bis(phosphonic acid)}. The Zr^{4+} cations bound by the outer-surface phosphonate groups of the **RuCP6** dye played a key role in the dye regeneration by the iodide redox-reversible electron donor as in the case of DSSCs,⁴³ leading to superior photocatalytic H₂ evolution activity compared to that observed in the absence of the surface Zr^{4+} cations to other metal cations. Such an approach should be valuable not only to enhance the photocatalytic activity, but also to clarify the versatility of this surface-metal cation modification method for one-directional electron transfer at the photocatalyst–mediator interface. Several DSSC studies revealed that metal ion coordination to the functional groups of dye molecule certainly effects on the charge-separation/recombination processes at the photoelectrodemediator interface, leading to the improved DSSC performance.^{38-40,55} Herein, we report the preparation, characterization, and photocatalytic H₂ evolution reactions of surface-metal-replaced DSP nanoparticles—X'-RuCP⁶-Zr-RuP⁶@Pt-TiO₂ (X'-DSP; Scheme 1 and Scheme S1; X' = H^+ , Sr^{2+} , Fe^{2+} , Y^{3+} , Zr^{4+} , Hf^{4+} , and Bi^{3+}). The replacing surface-metal cation from Zr^{4+} to Sr^{2+} or Y³⁺ having the same closed [Kr] electronic configuration should reveal the importance of ionic radius and formal charge. Hf⁴⁺ exhibiting similar chemical bonding nature to Zr⁴⁺ was selected to reveal the effect of heavy atom effect on the charge-separation process at the TiO²⁺-dye-mediator interfaces. Further, the redox active metal cations Fe²⁺ and Bi³⁺ were also introduced to evaluate the importance of redox behavior of the surface metal cations that may promote the chargeseparation. We demonstrate that five of the as-synthesized DSPs ($X' = Fe^{2+}$, Y^{3+} , Hf^{4+} , Bi^{3+} , and the previously synthesized Zr^{4+}) showed 1.6- to 2-fold higher photocatalytic activity than that of H⁺-DSP without surface metal ions. Furthermore, the X'-DSPs comprising heavy metal cations $(X' = Zr^{4+}, Hf^{4+}, and Bi^{3+})$ maintained relatively high activities under green light irradiation ($\lambda =$ 530±15 nm, 0.2~0.3% AQY), which only excited the lower band edge of the metal-to-ligand charge-transfer (¹MLCT) transition of the Ru dyes. These results suggest that dye multilayering and surface modification by metal cations are useful approaches for improving the reactivity with anionic electron donors and enhancing the photocatalytic activity under light irradiation at the absorption band edge region.



Scheme 1. Schematic surface structure of the X'-RuCP⁶-Zr-RuP⁶@Pt-TiO₂ nanoparticle (X'-DSP, X' = H⁺, Sr²⁺, Fe²⁺, Y³⁺, Zr⁴⁺ Hf⁴⁺, and Bi³⁺).

Experimental Section

Materials and Syntheses

Caution! *Although we did not encounter any difficulties, most of the chemicals used in this study are potentially harmful and should be used in small quantities and handled with care in a fume hood.* All the commercially available starting materials were used as received without further purification. TiO₂ nanoparticles (SSP-M, ~15 nm in diameter) were purchased from Sakai Chemical Industry Co., Ltd. (Sakai, Osaka, Japan) Pt-TiO₂ (1 wt%) was prepared using a previously reported photodeposition method.⁵⁶ The Ru(II) molecular photosensitizers (PSs; **RuCP⁶** and **RuP⁶**)^{50,57} were synthesized using previously reported methods. FeCl₂·4H₂O, SrCl₂·6H₂O, YCl₃·6H₂O, ZrCl₂O·8H₂O, HfCl₂O·8H₂O, and BiCl₃ were used as the starting materials for the immobilization of the outer metal ions.

Preparation of Ru(II)-dye-immobilized Pt-TiO₂ nanoparticles (X'-DSPs)

RuCP⁶-Zr-RuP⁶@Pt-TiO₂ (**H⁺-DSP**) nanoparticles were synthesized with reference to our previous reports.^{50,53} Immobilization of the outer metal ions was conducted by the same synthetic method as that of Zr⁴⁺-**RuCP⁶-**Zr-**RuP⁶**@Pt-TiO₂ (**Zr⁴⁺-DSP**), except for the use of other metal salts instead of ZrCl₂O-8H₂O as follows. 30 mg of **H⁺-DSP** was added to 25 mM of FeCl₂·4H₂O, SrCl₂·6H₂O, YCl₃·6H₂O, ZrCl₂O-8H₂O, HfCl₂O-8H₂O, or BiCl₃ MeOH solution (6 mL, about 50 eq. to the surface immobilized Ru(II) dye) and this suspension was stirred for 1 h at 298 K under dark. Then, the orange suspension was ultra-centrifugated (50,000 rpm, 20 min) and washed twice with small portions of MeOH. The precipitation was dried for a few days at 298~328 K to afford **X'-DSP**. The amount of Ru(II) dye immobilized on the Pt-TiO₂ nanoparticle surface was estimated using X-ray fluorescence (XRF) spectroscopy of the solid samples and UV-vis absorption spectroscopy of the supernatant solution (see Figure S1, Table S1, and the "Calculation of the amount of Ru(II) complex immobilized on the Pt-TiO₂ nanoparticles" section of the ESI). The loaded amounts of Pt cocatalyst on the Pt-TiO₂ nanoparticles were estimated from the XRF spectra to be 0.99 wt%.

Measurements

UV–vis absorption spectra were recorded on a Shimadzu UV-2400PC spectrophotometer and Hitachi U-3000 UV-vis spectrometer. Luminescence spectra were recorded on JASCO FP-6600 and FP-8600 spectrofluorometers at 298 K. Each sample solution was deoxygenated by N₂ bubbling for 30 min at 298 K. Energy-dispersive XRF spectra were recorded using a Bruker S2 PUMA analyzer at 298 K. Scanning electron microscope and energy dispersive X-ray spectroscopy (SEM-EDS) analysis was performed using Phenom World Phenom ProX scanning electron microscope (15 kV).

Photocatalytic water reduction reaction

Under dark conditions, an aqueous solution of KI (0.5 M) in hydrochloride (pH 2) containing Ru(II)-dye-immobilized nanoparticles (100 µM Ru(II) dye) was placed into an in-lab Schlenk flask-equipped quartz cell (volume, 265 mL) with a small magnetic stirring bar. Each sample flask was doubly sealed with rubber septum. This mixed solution was deoxygenated by bubbling with Ar for 1 h. The flask was then irradiated from the bottom using a blue { $\lambda = 460 \pm 15$ nm; 70 mW; Opto Device Lab. Ltd., (Kumagaya, Saitama, Japan) OP6-4710HP2} or green ($\lambda = 530 \pm$ 15 nm; 40 mW; Opto Device Lab. Ltd., OP6-5310HP2) LED lamp (Figure S2 and Table S2) as peak top and edge of ¹MLCT absorption band of Ru(II) dye (Table S3). The temperature was maintained at 293 K using an in-lab aluminum water-cooling jacket with a water-circulating temperature controller {Eyela (Bunkyo-ku, Tokyo, Japan) CCA-1111}. The gas samples (0.6 mL) for each analysis were collected from the headspace using a gastight syringe {1 mL, Valco Instruments Co. Inc. (Houston, Texas, USA)}. The amount of evolved H₂ was determined using gas chromatography {Agilent (Santa Clara, California, USA) 490 Micro}. The turnover number and turnover frequency per Ru dye (PS TON and TOF, respectively) were estimated from the amount of evolved H₂, wherein two photoredox cycles of the Ru(II) PS are required to produce one H₂ molecule. Each photocatalytic H₂ evolution reaction was conducted thrice under the same conditions, and the average value with the standard deviation was reported. The detection limit of the gas chromatography analysis for H₂ gas in this study was 0.005 µmol. The AQY was calculated using the following equation I:

$$AQY = N_e/N_p = 2N_{H2}/N_p$$
(I)

where N_e represents the number of reacted electrons, N_{H2} is the number of evolved H_2 molecules, and N_p is the number of incident photons.

Results and Discussion

Characterization of the Ru(II)-dye-immobilized Pt-TiO2 nanoparticles

Figure 1 shows the XRF spectra of the Ru(II)-dye-immobilized Pt-TiO₂ nanoparticles in the solid state at 298 K. As we previously reported,⁵⁰ Zr Ka and Ru Ka radiation originating from the bridging Zr⁴⁺ cations and Ru(II) dyes (RuCP⁶ and RuP⁶) was clearly observed at the 15.7 and 19.2 keV regions, respectively, in addition to the Pt L and Ti K radiation originating from the Pt-TiO₂ nanoparticles. The Zr/Ru molecular ratio for Zr^{4+} -DSP was estimated from the radiation intensity ratio to be 2.2(1), which is approximately twice the estimated value for H^+ -DSP (1.3(1), see Table S4). This result suggests that the Zr^{4+} -DSP nanoparticle was formed by binding of the Zr^{4+} ion with the phosphonate groups on the outer surface of H⁺-DSP. For the X'-DSPs comprising the other metal cations ($X' = Sr^{2+}$, Fe^{2+} , Y^{3+} , Hf^{4+} , and Bi^{3+}) at the outer surface of H^+ -DSP, the characteristic X-ray radiation assignable to the metal ions (Fe K α ; Sr K α ; Y K α ; Hf L α and L β ; and Bi L α , L β , and L γ) was observed. The peak intensities of the Zr K α and Ru K α radiation for all five X'-DSPs were almost comparable to those of H⁺-DSP. Thus, we supposed that the metal ions were immobilized on the outer phosphonate groups of RuCP⁶ without substitution of the inner Zr^{4+} ions or desorption of the **RuCP**⁶ dye. In fact, the characteristic ¹MLCT absorption of **RuCP**⁶ dye was hardly observed in the UV-vis absorption spectrum of the 2nd Zr⁴⁺ loading solution (see Figure S3). The X'/Ru molecular ratio was estimated based on the intensity of the K α or L α radiation of the outer metal cation (Table S4) and decreased in the

order Zr^{4+} -DSP (X'/Ru = 0.9(1)) = Hf^{4+}-DSP (X'/Ru = 0.9(1)) \geq Bi³⁺-DSP (X'/Ru = 0.7(1)) \geq Fe²⁺-DSP (X'/Ru = 0.5(1)) > Y³⁺-DSP (X'/Ru = 0.1(1)) > Sr²⁺-DSP (X'/Ru < 0.1). The estimated X'/Ru ratio tends to decrease with decreasing formal charge ($V_{X'}$) and absolute value of the hydration enthalpy (ΔH_{hvd}) of the outer metal cation (see Table S4, Table S5). Although additional experiments are necessary to make the conclusion about this trend, it may occur because the smaller $V_{X'}$ weakens the ionic bond between X' and the phosphonate, and the smaller ΔH_{hyd} causes rapid ligand exchange reaction of the X' cation. In fact, the Sr²⁺ ions with the smallest $V_{X^{\prime}}$ and ΔH_{hyd} values examined in this work were easily desorbed from the nanoparticle surface of Sr^{2+} -DSP by immersion into a 0.5 M KCl aqueous solution for 1 h at 298 K (Figure S4). Specifically, metal ions with larger $V_{X'}$ and ΔH_{hvd} values, such as Hf^{4+} , can be tightly bound by the surface phosphonates even in highly polar aqueous solutions, and are suitable for the surface functionalization of nanoparticle photocatalysts. In addition, we also found that the loading amount of Zr^{4+} cation of Zr^{4+} -DSP hardly increased by twice repeating the immobilization reaction of Zr^{4+} in MeOH solution (Figure S5), suggesting that most of the surface phosphonate groups were bound to Zr^{4+} .



Figure 1. X-ray fluorescence (XRF) spectra of **X'-DSPs** in the solid state. All spectra were normalized using the Ti K α peak. The peak marked as *1 is the background of the Cu sample holder.

Surface metal ion dependence

Figure 2 shows the results of the photocatalytic H₂ evolution reactions using **X'-DSPs** (X' = H⁺, Fe²⁺, Y³⁺, Zr⁴⁺ Hf⁴⁺, Bi³⁺) nanoparticles in 0.5 M KI aqueous solution as the photocatalyst. The PS TON, PS TOF, and AQY are listed in Table 1. Note that the total amount of Ru(II) dye in each solution was constant (100 μ M) and no hydrogen evolution was observed in the absence of Ru(II) dye, light, or electron donor (Table S6). The characteristic absorption bands of triiodide anion (I₃⁻⁻) was clearly observed in the UV-vis absorption spectra of the reaction solution after 6

h irradiation (Figure S6). The amount of I₃⁻ was estimated based on the molar absorption coefficient at 350 nm (about 14 µmol) to be comparable to that of H₂, indicating that the electron source of H_2 evolution is the iodide anions in the reaction solution. In addition, observed pH change from 2.0 to 2.4 in the reaction driven by Zr⁴⁺-DSP suggest that the protons in the reaction solution were reduced photocatalytically to H₂. All metal-cation-immobilized X'-DSPs evolved at least 1.5 times more H_2 than did the H⁺-DSP, suggesting a positive effect of metal ion coordination to the surface of the phosphonate groups on the photocatalytic H₂ evolution reaction. This result qualitatively agrees with the Hanson's works on the Ru(II)-dve-sensitized solar cells in which the open circuit voltage was improved by the surface-metal cation modification.³⁹ Although all metal-cation-immobilized X'-DSPs nanoparticles evolved comparable amounts of H₂, notable trends were observed, whereby the amounts of evolved H₂ with **Bi³⁺-DSP** and **Fe²⁺-DSP** were 20% less than those with **X'-DSPs** ($X' = Zr^{4+}$, Hf⁴⁺, and Y³⁺). The plausible reason may be the redox-active nature of these metal cations, wherein Bi^{3+} and Fe^{2+} have more positive reduction potentials than the oxidation potential of the photoexcited Ru(II)* dyes (E(Bi³⁺/Bi⁺) = +0.20 V vs. NHE, E(Fe³⁺/Fe²⁺) = +0.77 V vs. NHE, see Table S7) in addition to the energy transfer quenching by paramagnetic Fe^{2+} cation as reported in the literature.³⁹ These may induce the opposite electron/energy transfers from the outer **RuCP^{6*}** dve to the surface X' cation, leading to the lower photocatalytic activity. It is interesting to note that Y^{3+} -DSP, which has the largest X' ionic radius (Y^{3+} : 116 pm, Zr^{4+} : 98 pm, Hf^{4+} : 97 pm) with 10times diluted X' cations on the surface than Zr^{4+} -DSP, exhibited near-identical activity as that of Zr⁴⁺-DSP.



Figure 2. Photocatalytic H₂ evolution reactions driven by **X'-DSPs** in the presence of 100 μ M Ru(II) dye and 0.5 M KI as the electron donor (initial pH = 2.0, λ = 460 ± 15 nm, 70 mW in total). Dashed line in each panel indicates AQY = 1%.

To clarify the interaction between **X'-DSP** and iodide mediator, the zeta (ζ) potentials in HCl aqueous solution (pH 2) with/without KI were evaluated (Table S8). In the HCl aqueous solution without iodide, all metal-cation-immobilized **X'-DSPs** showed an almost neutral ζ potential (– 3.5 to +3.8 mV). On the other hand, in the presence of KI, the ζ potential of each metal-cation-immobilized **X'-DSPs** was negatively shifted (–7.6 to –13 mV). Considering that the comparable

zeta potential shift was also observed for the Pt-TiO₂ nanoparticle without Ru(II) dyes (+27 to +12 mV) and the **RuP**⁶-sensitized Pt-TiO₂ nanoparticle (**RuP**⁶@Pt-TiO₂, from -4.6 to -14 mV), the positively charged TiO₂ surface in the acidic pH condition may attract iodide anions electrostatically even after the loading of negatively charged Ru(II) dyes. This zeta potential shift by adding KI was negligible only for Zr-RuP⁶@Pt-TiO₂, implying that not only the bare TiO₂ surface but also the 2nd-outer **RuCP**⁶ dye layer with the surface X' cations may act as the interaction sites for iodide attraction. The photocatalytic activity of all the samples gradually decreased; for example, the AQY at the initial 1 h of reaction (iAQY) of Hf⁴⁺-DSP was 1.09%, whereas the average AQY after 6 h was approximately reduced by half (0.562%). The SEM image of Hf⁴⁺-DSP was hardly changed after 6 h reaction, and the L and M radiations of Ru and Hf elements were clearly observed at 2.6 and 1.6 keV, respectively in the EDS spectra (Figure S7), suggesting that Hf⁴⁺-DSP hardly decomposed during the reaction. Thus, the origin of gradual decrease of photocatalytic activity is because triiodide, generated as the oxidation product of H₂ evolution, exhibited moderate light absorptivity (1110 M⁻¹ cm⁻¹ at 460 nm) and disturbed the light absorption of the Ru(II) PSs (Figure S8).

Χ'	λ_{ex} (nm)	H2 ^{<i>a</i>} (µmol)	PS TON ^a	PS TON ^a	PS initial	AQY ^a (%)	iAQY ^a (%)
		(0–6 h)	(0–3 h)	(0–6 h)	TOF ^a	(0–6 h)	(0–1 h)
H^+	460 ± 15	8.80±0.7	23.2	35.2	8.47	0.302	0.436
Y ³⁺	460 ± 15	17.9±1.3	49.6	71.5	21.5	0.614	1.11
Zr^{4+}	460 ± 15	17.1±1.5	45.9	68.3	18.5	0.587	0.952
Hf^{4+}	460 ± 15	16.4±1.0	45.2	65.5	21.1	0.562	1.09
Bi ³⁺	460 ± 15	13.8±2.5	37.4	55.2	15.6	0.474	0.803
Fe ²⁺	460 ± 15	13.7±1.9	37.4	54.9	15.5	0.470	0.798
H^{+}	530 ± 15	1.95±0.47	5.06	7.80	2.01	0.102	0.157
Zr ⁴⁺	530 ± 15	3.93±0.27	9.95	15.7	4.30	0.205	0.337
Hf^{4+}	530 ± 15	4.61±0.08	11.8	18.4	4.41	0.241	0.345
Bi ³⁺	530 ± 15	4.14±0.07	9.79	16.6	2.81	0.216	0.220

Table 1. Results of the photocatalytic H₂ evolution experiments of **X'-DSPs** in 0.5 KI aqueous solution.

^{*a*}Reaction conditions: [Ru-PS] = 100 μ M in total, [KI] = 0.5 M, HCl aqueous solution (pH 2), λ_{ex} = 460 ± 15 nm (70 mW in total) or 530 ± 15 nm (40 mW in total). The reaction solution was purged with bubbling Ar for 1 h before light irradiation. The numerical values represent the averages of more than three experiments. Definitions: PS, photosensitizer; TON, turnover number; TOF, turnover frequency; AQY, apparent quantum yield for total 6 h reaction; *i*AQY, AQY at the initial 1h of reaction.

Excitation wavelength dependence

From the viewpoint of the effective utilization of solar light, the utilization of longer-wavelength

light for photocatalytic H₂ evolution is crucial. The photocatalytic activities of Zr⁴⁺-DSP, Hf⁴⁺-

DSP, and **Bi³⁺-DSP** under green light excitation ($\lambda = 530 \pm 15$ nm) were next investigated.

Although [Ru(bpy)₃]-type dyes are well-known PSs for blue light excitation because of their

strong ¹MLCT absorption character at approximately 460 nm, both **RuCP**⁶ and **RuP**⁶ exhibit weak MLCT absorption shoulders up to approximately 590 nm (molar absorption coefficient, ε is 1540 and 1910 M⁻¹ cm⁻¹ at 530 nm, respectively. See Figure S2 and Table S3). We thus expected that heavier surface X' cations, such as Hf⁴⁺ and Bi³⁺, might partially allow spinforbidden ³MLCT excitation by the strong heavy-atom effect *via* the coordination bonds with the phosphonate group. In addition, light shielding by triiodide should be suppressed under green light irradiation because of its smaller ε at 530 nm (152 M⁻¹ cm⁻¹) than at 460 nm (1110 M⁻¹ cm⁻¹; see Figure S8 and Table S9).

The results of the photocatalytic H_2 evolution reactions under green light irradiation are shown in Figure 3, while the estimated PS TON, TOF, and AQY values are listed in Table 1. Even under green light irradiation, the estimated TON for all cases exceeded one, indicating that H_2 evolution from iodide occurred photocatalytically. The amount of H₂ produced after 6 h of green light irradiation was smaller than that under blue light irradiation in all cases, because of the lower ε of the Ru PSs for green light. The comparable TON value of Hf⁴⁺-DSP to that under blue light irradiation (TON = 45.2 for 3 h) was achieved by long-term photocatalytic reaction for 20 h (TON \sim 40, see Figure S9). A notable difference between the metal-cation-immobilized X'-DSPs and H⁺-DSP was observed. Under blue light irradiation, the PS TON of metal-cationimmobilized **X'-DSPs** after 6 h irradiation was 1.6–1.94 times higher than that of **H⁺-DSP**, while the difference under green light illumination was more pronounced (e.g., 1.9–2.4 times larger PS TON for metal-cation-immobilized **X'-DSPs**). The electron transfer from the redox-reversible iodide donor to the one-electron oxidized Ru(III) dye should be the important step in these photocatalytic H₂ evolutions, because the back electron transfer to the iodide radical (I^{\bullet} , $E(I^{\bullet}/I^{-})$) = 1.33 V vs NHE) from the regenerated Ru(II) dye ($E(Ru^{III}/Ru^{II}) = 1.12$ V for RuCP⁶) possibly

occurs just after the dye regeneration.⁵⁸⁻⁵⁹ The photoexcitation frequency of Ru dyes under green light irradiation ($\lambda = 530$ nm, 40 mW) must be lower than that under blue light ($\lambda = 460$ nm, 70 mW) because of the lower ε of the Ru dye and lower light intensity of the LED light source. Hence, the direct coupling between two iodine radicals to form a stable and weaker oxidant iodine molecule (I₂, $E(I_2/I^-) = 0.54$ V) should be negligible. The possible reaction in this case would be bond formation between the iodine radical I• and iodide anion I⁻ to form a diiodide radical anion (I₂•⁻, $E(I_2•^-/I^-) = 1.03$ V), which should be favorable at high I⁻ concentrations. Thus, the superior activity of metal-cation-immobilized X'-DSPs compared to that of H⁺-DSP was attributed to the more effective interaction between the iodide and surface of metal-cationimmobilized X'-DSPs than that with H⁺-DSP. This leads to more efficient dye regeneration by iodide, even at the lower photoexcitation frequency from green light irradiation.



Figure 3. (a) Photocatalytic H₂ evolution reactions driven by **X'-DSPs** under blue light (460 \pm 15 nm, 70 mW) or (b) green light (530 \pm 15 nm, 40 mW in total) irradiation in the presence of 100 μ M Ru(II) dye and 0.5 M KI as the electron donor (initial pH = 2.0).

The molar absorption coefficients of **RuCP**⁶ and **RuP**⁶ at 530 nm were estimated to be 1540 and 1950 M⁻¹ cm⁻¹, respectively, by UV-vis absorption spectroscopy in dilute HCl aqueous solution (pH 2, Figure S2 and Figure S10). The total amount of Ru(II) dye used in each photocatalytic H₂ evolution was 100 μ M, so that the absorbance at 530 nm was estimated to be 0.17, based on the Lambert-Beer law in which the effects of dye immobilization on Pt-TiO₂, the crosslinking Zr ions, and surface metal ions were ignored. This value indicates that only 33% of irradiated green light was absorbed by the Ru(II) dyes. The absorbance of the reaction solution at 460 nm was similarly estimated to be approximately 1.6, suggesting that most of the irradiated blue light (~97%) was absorbed by the Ru(II) dyes. Thus, the decrease in AQY of **Zr⁴⁺-DSP** at 530 nm

irradiation to a third of that at 460 nm irradiation was primarily due to the smaller absorptivity. This implies that the irradiation wavelength dependence of the charge separation efficiency at the semiconductor-dye and dye-mediator interfaces of \mathbf{Zr}^{4+} -DSP should be negligible.

Interestingly, the amounts of evolved H₂ for Bi³⁺-DSP and Hf⁴⁺-DSP after 6 h of green light irradiation were slightly larger than that of Zr^{4+} -DSP. The reverse trend was observed for blue light irradiation, wherein Bi³⁺-DSP and Hf⁴⁺-DSP respectively evolved slightly lower and comparable amounts of H_2 compared to that evolved by Zr^{4+} -DSP. The electrostatic interaction between the photocatalyst nanoparticle and iodide electron donor should be independent of the light source and was roughly estimated to be comparable among the three photocatalysts, as suggested by their zeta potentials (Table S8). One possible origin of the slightly higher activity of Bi^{3+} -DSP and Hf^{4+} -DSP than that of Zr^{4+} -DSP under green light illumination may be due to the different contributions of the spin-forbidden ³MLCT transition—this could be partially allowed by the stronger heavy atom effect of the surface-immobilized Hf⁴⁺ and Bi³⁺ cations compared to that of Zr^{4+} . Unfortunately, a negligible difference was observed in the UV-vis diffuse reflectance spectra in the solid state (Figure S10), probably because of the light scattering of the TiO₂ nanoparticles. Further investigations to clarify the role of the heavy-atom effect are now in progress, wherein not only the outer surface Zr^{4+} but also the inner bridging Zr^{4+} cations are replaced with heavier metal ions.

Conclusion

To promote the dye regeneration by the redox-reversible electron donor, we investigated the outer metal ion dependence of the photocatalytic H₂ evolution activity of DSP nanoparticles, X'-**RuCP⁶-Zr-RuP⁶** (\mathbb{A}) Pt-TiO₂ (**X'-DSPs**). We found that not only the previously reported Zr⁴⁺ but also the other metal cations (Fe²⁺, Y³⁺, Hf⁴⁺, and Bi³⁺) were successfully immobilized onto the outer surface of the RuCP⁶-Zr-RuP⁶@Pt-TiO₂nanoparticle (H⁺-DSP), whereas the labile cation Sr^{2+} was easily desorbed from the nanoparticle surface in the aqueous solution. These results suggest that metal cations with small hydration enthalpies are not suitable for the surface functionalization of the H⁺-DSP nanoparticle photocatalyst. The AQY values of metal-cationimmobilized X'-DSPs at 460 nm in the presence of 0.5 M KI aqueous solution were in the range 0.47–0.61%, which are higher than that of H^+ -DSP (AQY = 0.302%). This suggests that the surface metal cations act as the attracting site to promote the electron donation from iodide mediator. Although not only I⁻ but also the oxidative byproduct I₃⁻ could be also attracted by the surface metal cations, the charge recombination between the surface attracted I₃⁻ and electron injected TiO₂(e⁻) could be suppressed by the thick doubly-layered Ru(II) dyes.^{52,53} On the other hand, **Bi**³⁺-**DSP** and **Fe**²⁺-**DSP**, which comprise redox-active outer metal ions, showed slightly lower photocatalytic activity than the photocatalysts with redox-inactive outer metal cations (X'-**DSPs**, $X' = Zr^{4+}$, Hf^{4+} , and Y^{3+}), possibly because of the reverse electron transfer from the photoexcited Ru dye to the outer metal cations. We also observed that Zr⁴⁺-DSP, Hf⁴⁺-DSP, and **Bi³⁺-DSP** can drive the photocatalytic H₂ evolution reaction with 0.2-0.3% AQY under green light illumination at 530 nm, which is located in the absorption band edge of Ru PSs. Further studies to reveal the role of crosslinked Zr cations in interlayer energy/electron transfer processes by substituting the Zr cations with other metal cations are now in progress.

ASSOCIATED CONTENT

Supporting Information. Experimental details of the Ru(II) dye immobilized on the Pt-TiO₂ nanoparticles; UV-vis absorption spectra of all supernatant solutions obtained from the syntheses of Ru(II)-dye-immobilized Pt-TiO₂; XRF spectra of Sr^{2+} -DSP after immersion in 0.5 M KCl aq.; molar ratios of Zr/Ru and X'/Ru estimated by XRF analysis; UV-vis absorption spectra of the reaction solution of Zr⁴⁺- and Hf⁴⁺-DSPs after 6 h irradiation; SEM-EDS analysis for Hf⁴⁺-DSP before and after 6 h irradiation; photocatalytic H₂ evolution by Hf⁴⁺-DSP under green light irradiation for 20 h; and zeta potentials and UV-vis diffuse reflectance spectra of X'-DSPs (PDF). This material is available free of charge on the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: akoba@sci.hokudai.ac.jp (A.K.).

Author Contributions

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To improve the reactivity between photosensitizer and electron mediator in photo water splitting reaction, we synthesized an X'-RuCP⁶–Zr-RuP⁶@Pt-TiO₂ (X'-DSPs) series composed of Pt-cocatalyst-loaded TiO₂ nanoparticles, sensitized by a double layer of Ru(II) dyes with different surface-bound metal cations. We found that metal-cation-immobilized X'-DSPs exhibited 1.5–2-fold higher apparent quantum yields in 0.5 KI aqueous solution under green light than H⁺-DSP.