Efficient hydrogen production by a photoredox cascade catalyst comprising dual photosensitizers and a transparent electron mediator

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Supporting Information Placeholder

ABSTRACT: One-directional electron transport between a photocatalyst and redox mediator is crucial for achieving highly active Z-scheme water-splitting photocatalysis. Herein, a photoredox cascade catalyst that artificially mimics the electron transport chain in natural photosynthesis was synthesized from a Pt-TiO2 nanoparticle catalyst, two photosensitizers (**RuCP6** and **RuP6**), and a visible-light-transparent electron mediator (**HCRu**). During photocatalytic hydrogen evolution in the presence of a redox-reversible electron donor, [Co(bpy)3]2+ (bpy = 2,2′-bipyridine), the **HCRu**-Zr-**RuCP6**-Zr-**RuP6**@Pt-TiO2 (**PRCC-1**) photocatalyst exhibited the highest reported initial (1 h) apparent quantum yield (*i*AQY = 2.23%) of dye-sensitized TiO2 photocatalysts to date. Furthermore, **PRCC-1** successfully produced hydrogen when using hydroquinone monosulfonate (H2QS−) as the hydrogen source.

Photocatalytic water splitting has attracted considerable attention for its potential to mitigate global environmental and energy crises.1–6 Z-scheme water-splitting photocatalysis, which utilizes a two-step photoexcitation process with a water oxidation catalyst (WOC), water reduction catalyst (WRC), and redox mediator (RM), is a powerful strategy for converting a wide spectrum of solar energy to chemical energy and storing it as H2 and O2; it also ensures the water-splitting and electron-transfer potentials are sufficient.7–13 Domen and coworkers recently reported a visible-light-driven Z-scheme photocatalytic system consisting of ZrO2/TaON, BiVO4, and [Fe(CN)6]3−/4− as the WRC, WOC, and RM, respectively, which exhibited a remarkably high solar-to-hydrogen energy conversion efficiency (0.6%) and apparent quantum efficiency (AQY = 12.3%) under light irradiation at 420 nm.14 However, thermodynamically favorable back reactions at the WOC–RM and RM–WRC interfaces remain a bottleneck issue. Thus, a new strategy of regulating the electron transfer direction (from WOC to WRC via RM) is strongly required.15–17

In natural photosynthesis, such back reactions are efficiently suppressed by the multistep photoredox cascade structure of the electron transport chain, in which precise arrays of chlorophyl- and quinone-type RMs surround the chlorophyl dimer reaction centers (P680 and P700).18 In contrast, multistep redox cascade structures with multiple RMs have hardly been

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Figure 1. Surface structure and energy diagram of **PRCC-*n*** (***n*** = 1, 2; **HCM** = **HCRu**, **HCFe**) for photocatalytic H2 production. The BQSK/H2QSK redox potential was estimated by cyclic voltammetry (Figure S6) and the other redox potentials were inferred from the literature.20, 21, 25

employed in water-splitting Z-scheme particulate photocatalysts.19 Thus, in this work, with the aim of suppressing back reactions at the WRC–RM interface, we constructed a three-step photoredox cascade catalyst, **HCRu**-Zr-**RuCP6**-Zr-**RuP6**@Pt-TiO2 (**PRCC-1**; **HCRu** = [Ru(CN)6]4−, **RuCP6** = [Ru(mpbpy)3]10−, **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)), by assembling two Ru(II)-based molecular photosensitizers (PSs), **RuP6** and **RuCP6**,20 and a visible-light-transparent RM, **HCRu**,21 on the surface of a Pt-TiO2 nanoparticle catalyst via water-stable Zr4+–PO3 coordination bonds (Figure 1). Among reported dye-sensitized TiO2 photocatalysts, **PRCC-1** exhibits the highest initial apparent quantum yield (*i*AQY) for H2 production in the first 1 h of irradiation (*i*AQY = 2.23%) in a redox-reversible electron donor (RrED) aqueous solution,22-24 which was ascribed to the superior charge separation behavior of the dual-dye layer and the electron-mediating effect of the surface-immobilized **HCRu**. Furthermore, the **PRCC-1** catalyst achieved photocatalytic H2 production with a sufficiently high *i*AQY (1.10%) in the presence of a hydrogen atom mediator, hydroquinone sulfonate.

**PRCC-1** was synthesized by immersing a dual-dye-sensitized photocatalyst,Zr-**RuCP6**-Zr-**RuP6**@Pt-TiO2(**DDSP**),25 in an aqueous **HCRu** solution (see Supporting Information for details). The Ru Kα X-ray fluorescence (XRF) peak of **PRCC-1** was stronger than that of **DDSP**, suggesting the successful immobilization of electron-mediating **HCRu** to the Zr4+ surface sites of **DDSP** (Figure S2 and Table S2). During photocatalytic H2 evolution experiments in aqueous [Co(bpy)3]SO4 (16.4 mM), which is a widely used RM in Z-scheme water-splitting photocatalysis,26 the H2 production and turnover number per PS molecule (PS TON) of **PRCC-1** (28.9 µmol and 116, respectively) were approximately 1.9-times greater than those of **DDSP** (15.2 µmol and 60.7, respectively) after 6 h of irradiation (Figure 2 and Table 1). The total amount of Ru(II) dye in the solution was constant (100 µM), and no H2 evolution was observed in the absence of Ru(II) dye or light (Table S3). The estimated *i*AQY for **PRCC-1** reached 2.23%, which was twice as high as that for **DDSP**; moreover, this value is the highest *i*AQY recorded for a dye-sensitized TiO2 photocatalyst with an aqueous RrED so far. After 6 h of reaction, the solution pH had increased to 3.0, suggesting that the proton source for H2 production was water.

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Figure 2. Photocatalytic H2 production driven by **PRCC-1** (blue closed circles), **PRCC-2** (black closed circles),and **DDSP** (red open squares) in the presence of (a) 16.4 mM [Co(bpy)3]SO4 and (b) 0.5 M H2QSK as the electron donor in HCl aqueous solution (initial pH = 2.0) under blue light irradiation (*λ* = 460 ± 15 nm; 70 mW). The Ru(II) dye concentration was 100 μM for all reactions.

Table 1. Results of photocatalytic H2 production experiments in HCl aqueous solution (pH = 2).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Photo-  catalyst | Donor,  concentration | H2 (μmol)  (0–6 h) | AQY*a* (%)  (0–6 h) | *i*AQY*a* (%)  (0–1 h) |
| **DDSP** | [Co(bpy)3]SO4, 16.4 mM | 15.2  ± 1.6 | 0.523 | 0.963 |
| **PRCC-1** | [Co(bpy)3]SO4, 16.4 mM | 28.9  ± 2.4 | 0.994 | 2.23 |
| **PRCC-2** | [Co(bpy)3]SO4, 16.4 mM | 11.9  ± 0.4 | 0.409 | 0.613 |
| **DDSP** | H2QSK,  0.5 M | 8.33  ± 0.95 | 0.280 | 0.519 |
| **PRCC-1** | H2QSK,  0.5 M | 12.6  ± 1.6 | 0.433 | 1.10 |
| **PRCC-1** | H2QSK,  16.4 mM | 7.47  ± 0.48 | 0.257 | 0.346 |

*a* Measurement conditions: [PS] = 100 µM, volume of aqueous solution = 5 mL; irradiation: *λ*ex = 460 ± 15 nm, 70 mW. The reaction solution was purged by Ar bubbling for 1 h prior to light irradiation. Values presented as mean ± standard deviation (*n* ≥ 3). Definitions: AQY = apparent quantum yield, *i*AQY = AQY in the initial 1 h, H2QSK = potassium hydroquinone monosulfonate.

Considering that **HCRu** has a more negative redox potential (Ru(III)/Ru(II) at +0.89 V vs. normal hydrogen electrode (NHE))21 than **RuCP6** (+1.12 V vs. NHE),20 the improved *i*AQY of **PRCC-1** compared to that of **DDSP** was ascribed to the enhanced charge-separation between the dual PS layers25 and RrED owing to electron mediationfrom one-electron-oxidized **RuCP6**(h+) to the [Co(bpy)3]2+ RrED via **HCRu** (Figure 1). In line with this theory, the photocatalytic H2 evolution activity of **PRCC-1** gradually decreased upon lowering the loading amount of **HCRu** (Figures S7 and S8 and Table S4). Furthermore, the H2 evolution activity of a **PRCC-1** analog with [Fe(CN)6]4− (**HCFe**) instead of **HCRu**, denoted as **PRCC-2**, was 36.3% lower than that of **DDSP** (Figure 2 and Table 1), probably because of the negligible difference in redox potential between **HCFe** and [Co(bpy)3]2+ (Figure 1, Fe(III)/Fe(II) at +0.36 V 27 and Co(III)/Co(II) at +0.32 V 26 vs. NHE, respectively). These results suggest that the three-step photoredox cascade structure with appropriate differences in redox potential (**RuP6**–**RuCP6**–**HCRu**) plays a key role in enhancing electron donation from the [Co(bpy)3]2+ RrED. Notably, **PRCC-1** produced a slight but detectable amount of H2 (0.08 µmol) without [Co(bpy)3]2+, whereas **DDSP** did not (Entries 4 and 5 in Table S3 and Figure S5). This suggests that, in the absence of an electron donor, approximately 20–30% of the surface-immobilized **HCRu** on **PRCC-1** acts as an electron source for H2 evolution.

The photocatalytic activities of both **PRCC-1** and **DDSP** decreased with time during the 6 h reaction, probably because of back electron transfer from the photoexcited Ru\*(II) PS to the oxidized [Co(bpy)3]3+. However, **PRCC-1** exhibited a remarkably higher PS TON (1–2 h, PS TON = 26.4) than **DDSP** (3–4 h, PS TON = 5.9) when approximately one-third of the initially added [Co(bpy)3]2+ was one-electron oxidized (~5 mM). This suggests that the immobilization of **HCRu** as a RM is also effective for suppressing back electron transfer from PS\* to oxidized [Co(bpy)3]3+. This is further supported by the fact that the emission of **RuCP6** was hardly quenched by **HCRu** (Figure S9). Therefore, the photosensitization cycle of Ru(II) PSs of **PRCC-1** is not triggered by the reductive quenching of **HCRu** but by the oxidative quenching of TiO2 nanoparticle (Figure 1). **PRCC-1** produced approximately 40 μmol of H2 after further irradiation for 1 d, suggesting that the [Co(bpy)3]2+ RrED (82 μmol) was completely one-electron oxidized (Figure S10). This was further supported by 1H NMR spectroscopy, in which the characteristic proton signals assignable to the diamagnetic one-electron-oxidized [Co(bpy)3]3+ species were clearly observed without any signals of Ru(II) PSs (Figure S11). The Ru/Zr molar ratio estimated by XRF spectroscopy hardly changed after 1 d of irradiation (Figure S12 and Table S6), indicating that negligible desorption of **HCRu** from the **PRCC-1** surface occurred under these reaction conditions (pH = 2).  Further, two-cycle photocatalytic H2 evolution experiment of **PRCC-1** revealed that H2 production was restarted by addition of [Co(bpy)3]2+ RrED (Figure S13), indicating that the gradual decrease of photocatalytic activity is not due to the decomposition of **PRCC-1** but due to some backward reactions with RrED.

To further clarify the electron-mediating effect of the surface-immobilized **HCRu**, the photocatalytic H2 production activity of **PRCC-1** was investigated in the presence of hydroquinone monosulfonate (H2QS−), which is an analog of the proton and electron mediator (that is, a hydrogen atom mediator, H2QS− → BQS− + 2e− + 2H+) used in the electron transport chain of natural photosynthesis (Figure 2b).28,29 Although dye-sensitized photocatalytic H2 production from hydrogen atom mediators has scarcely been reported, both **PRCC-1** and **DDSP** successfully produced H2 from H2QS− photocatalytically. The estimated *i*AQY for **PRCC-1** (1.10%) was approximately twice that for **DDSP** (*i*AQY = 0.519%), even though the driving force for electron donation from H2QS− to the **HCRu** of **PRCC-1** was smaller than that to the one-electron-oxidized **RuCP6**(h+) of **DDSP** (Figure 1), suggesting that **HCRu** has a superior electron-mediating effect.Although the *i*AQY of **PRCC-1** decreased by approximately two-thirds (*i*AQY = 0.345%) when the H2QS− concentration was reduced to 16.4 mM (Figure S14), the pH of the reaction solution after 6 h of irradiation was almost unchanged (~2.0). These results suggest that H2QSK acted not only as an electron source but also as a proton source for H2 production. Further characterization of the oxidation byproduct from H2QSK is necessary; however, it is noteworthy that **PRCC-1** exhibited a remarkably high *i*AQY of over 1% in the presence of a hydrogen atom mediator, H2QS−. Our preliminary experiments in the other RrED (K4[Fe(CN)6] and KI, Figure S15) solutions suggest that the number of donatable electron by RrED could be a key factor for the photocatalytic activity of **PRCC-1**. Considering that photocatalytic activity of the single dye sensitized analogues (**HCM**-Zr-**RuP6**@Pt-TiO2) was hardly improved by immobilization of **HCM** (Figure S16), therapid electron and energy transfers in the dual-dye layer structure30,31 should play the key role on the effective charge-separation process. These results emphasize the importance of the electron-mediating effect for multi-electron transfer at the photocatalyst–RM interface.

In summary, we synthesized a novel photoredox cascade catalyst, **PRCC-1**, that mimics the electron transport chain of natural photosynthesis by using two Ru(II) PSs and a visible-light-transparent electron mediator. Photocatalytic H2 production was successfully achieved from both a RrED [Co(bpy)3]2+ and hydrogen atom donor H2QSK, with the highest reported *i*AQY values (over 2 and 1%, respectively) among dye-sensitized TiO2 photocatalytic systems to date. Although these values are still one-order of magnitude lower than that in the sacrificial electron donor solution (*i*AQY = 12% for **PRCC-1** in *L*-ascorbic acid aqueous solution, Figure S17), these findings indicate that photoredox cascade structures formed by the molecular layering of PSs and RMs on a semiconductor catalyst surface are effective for achieving one-directional electron transfer at the photocatalyst–RM interface, as suggested by the electron transport chain in natural photosynthesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details; UV−vis absorption spectra of all supernatant solutions obtained in the syntheses; XRF spectra and estimated M/Zr molar ratios of **PRCC-1**, **PRCC-2**, and **DDSP**; Experimental power X-ray diffraction patterns of **PRCC-1**; Particle diameter distributions estimated by dynamic light scattering for **DDSP** and **PRCC-1**; Control experiments of photocatalytic H2 evolution of **PRCC-1** and **DDSP**; Cyclic voltammograms of H2QSK; Photocatalytic H2 evolution reactions and XRF spectra of **PRCC-1** after washing with water; 1H NMR spectra of the supernatant after H2 evolution reaction; H2QSK concentration dependence of H2 evolution reaction driven by **PRCC-1**. (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes  
The authors declare no competing financial interests.

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Table of Contents Graphic

