Efficient hydrogen production by photo-redox-cascade catalyst composing dual photosensitizers and transparent hole acceptor

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Keywords: Photosensitization; Hydrogen production; Electron mediator; Charge separation

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 H_2 and O_2; it also ensures the water-splitting and electron-transfer potentials are sufficient. 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. 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-**RuCP^6**-Zr-**RuP^6**@Pt-TiO_2 (**PRCC-1**), by assembling two Ru(II)-based molecular photosensitizers (PSs), **RuP^6** and **RuCP^6**,[1] and a visible-light-transparent RM, **HCRu**,[2] on the surface of a Pt-TiO_2 nanoparticle catalyst via water-stable Zr^{4+}–PO_3 bonds (Fig. 1a). During photocatalytic H_2 evolution in aqueous $[Co(bpy)_3]SO_4$ (16.4 mM), the H_2 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 without **HCRu** (15.2 μmol and 60.7, respectively) after 6 h of irradiation (Fig. 1b). Considering that **HCRu** has a more negative redox potential than **RuCP^6**, the improved activity of **PRCC-1** was ascribed to the enhanced charge-separation between the dual PS layers and $[Co(bpy)_3]^{2+}$ RM owing to electron mediation via **HCRu**.

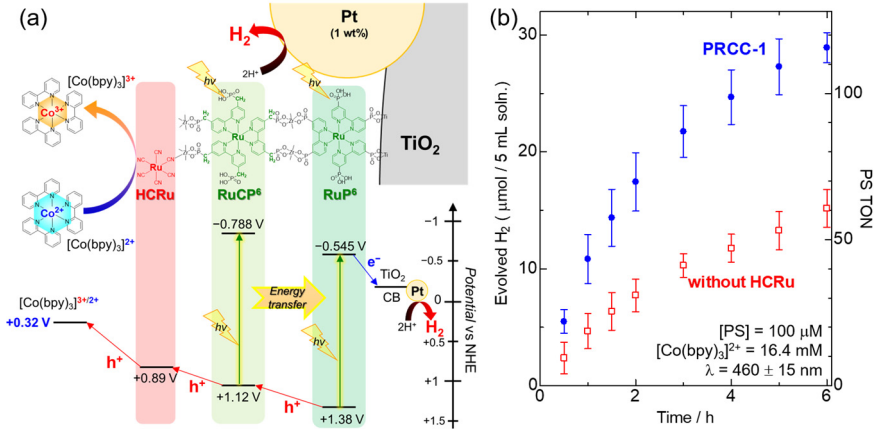

Fig. 1. (a) Schematic energy diagram and (b) photocatalytic H_2 production of **PRCC-1**.

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