Electronic Supplementary Information

Cs,Rh-codoped WO_3 with a core–shell structure responsive up to 600 nm as an O_2-evolving photocatalyst for Z-schematic water splitting

Kenta Watanabe, Yugo Miseki* and Kazuhiro Sayama*

Artificial Photosynthesis Research team, Global Zero Emission Research Center (GZR), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba West, 16-1 Onogawa, Tsukuba, Ibaraki, 305-8569, Japan

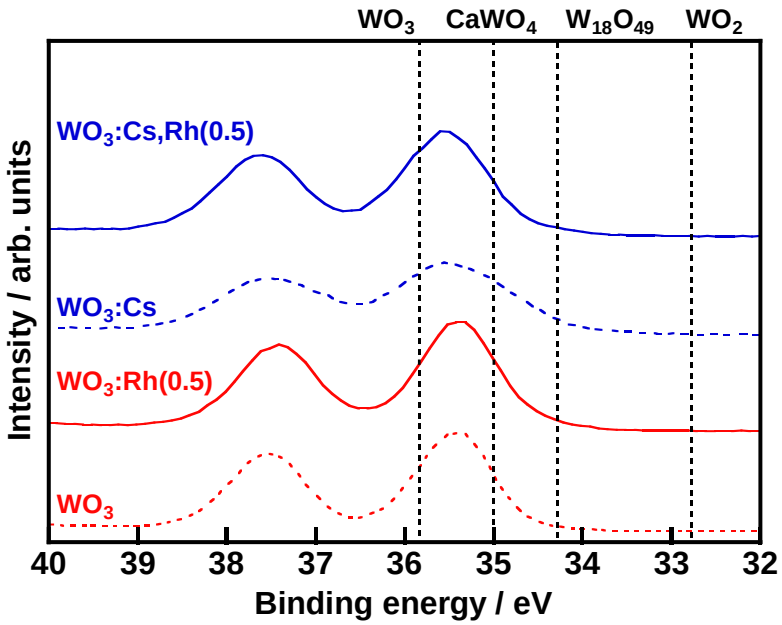

Fig. S1 W4f XPS spectra of WO_3, WO_3:Rh(0.5), WO_3:Cs, and WO_3:Cs,Rh(0.5) synthesized by a solid-state reaction at 1273 K for 5 h. The binding energy of the peaks was calibrated with C 1s (284.2 eV).

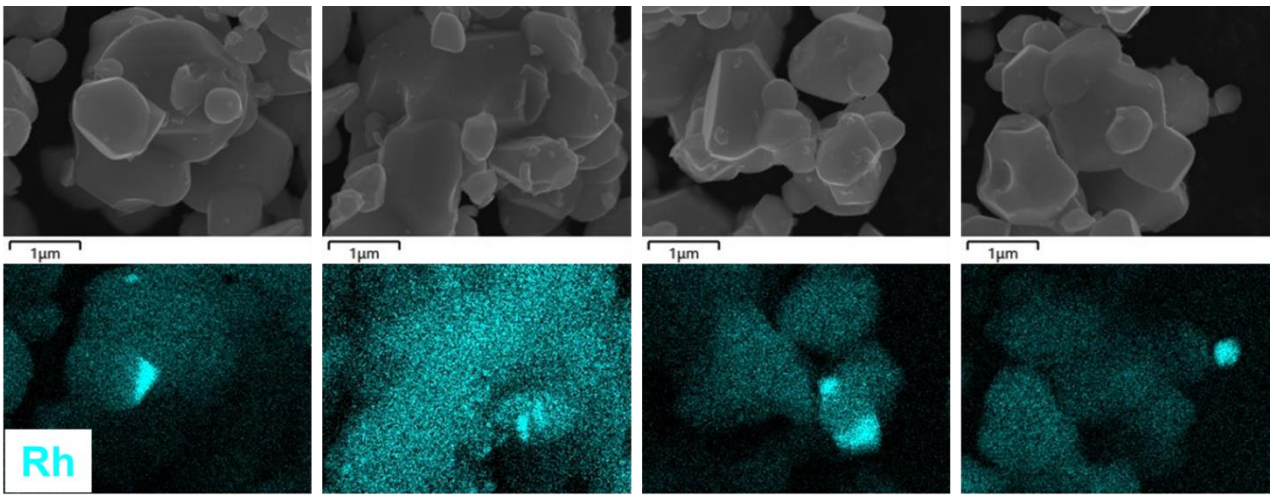

Fig. S2 SEM and Rh-EDS mapping images of WO_3:Rh(0.5) synthesized by a solid-state reaction at 1273 K for 5 h.

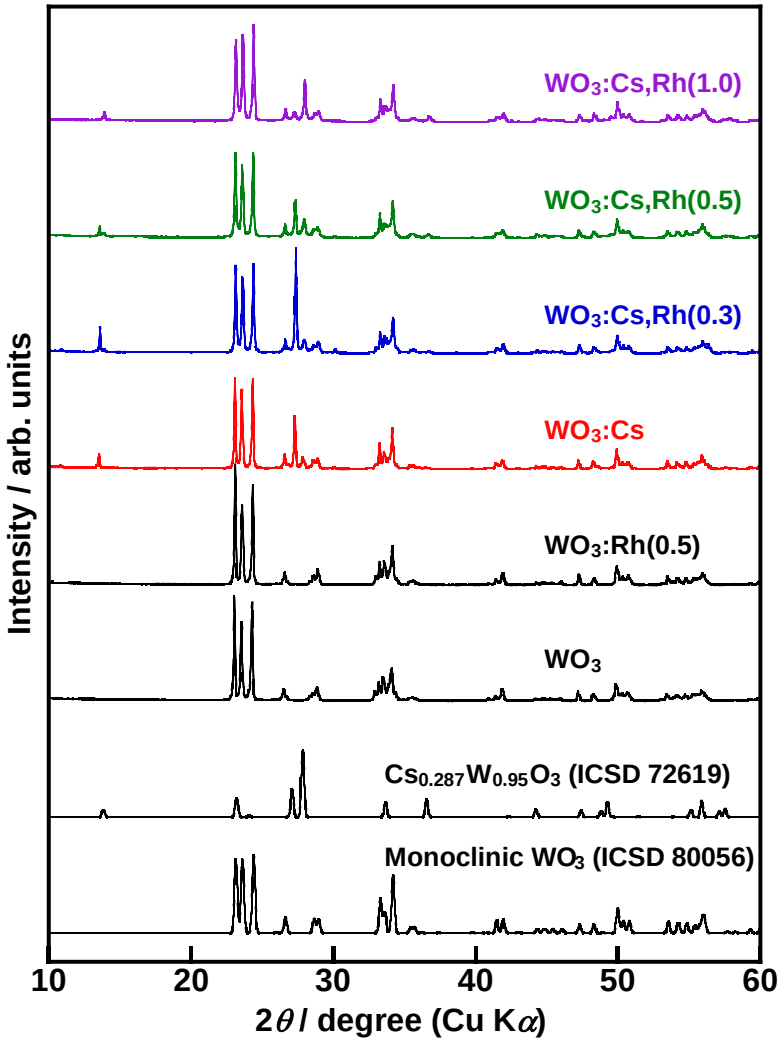

Fig. S3 XRD patterns of WO_3, WO_3:Rh(0.5), and WO_3:Cs,Rh(x%) (x = 0, 0.3, 0.5, 1.0) synthesized by a solid-state reaction at 1273 K for 5 h.

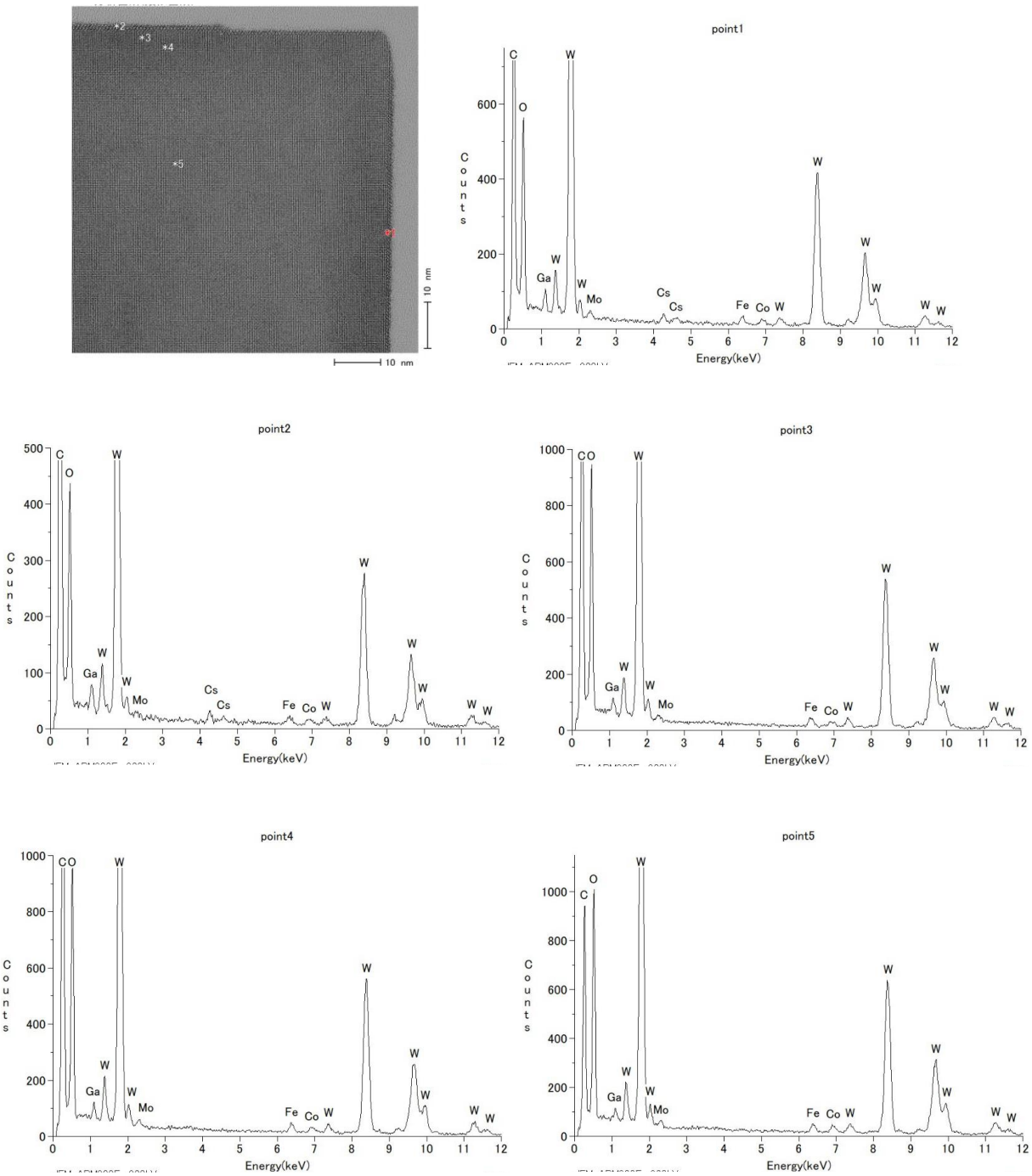

Fig. S4 TEM-EDS analysis of WO_3:Cs,Rh(1.0) synthesized by a solid-state reaction at 1273 K for 5 h.

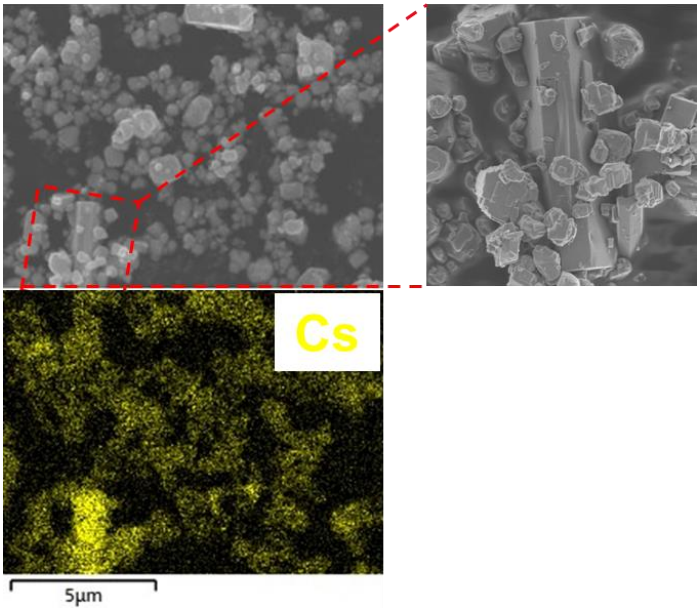

Fig. S5 SEM and Cs-EDS mapping images of WO_3:Cs,Rh(1.0) synthesized by a solid-state reaction at 1273 K for 5 h.

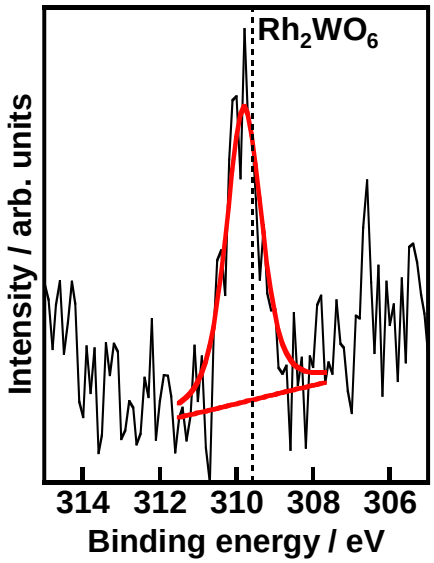

Fig. S6 Rh $3d_{5/2}$ XPS spectrum of WO_3:Cs,Rh(1.0) synthesized by a solid-state reaction at 1273 K for 5 h. The binding energy of the peak was calibrated with C 1s (284.2 eV).

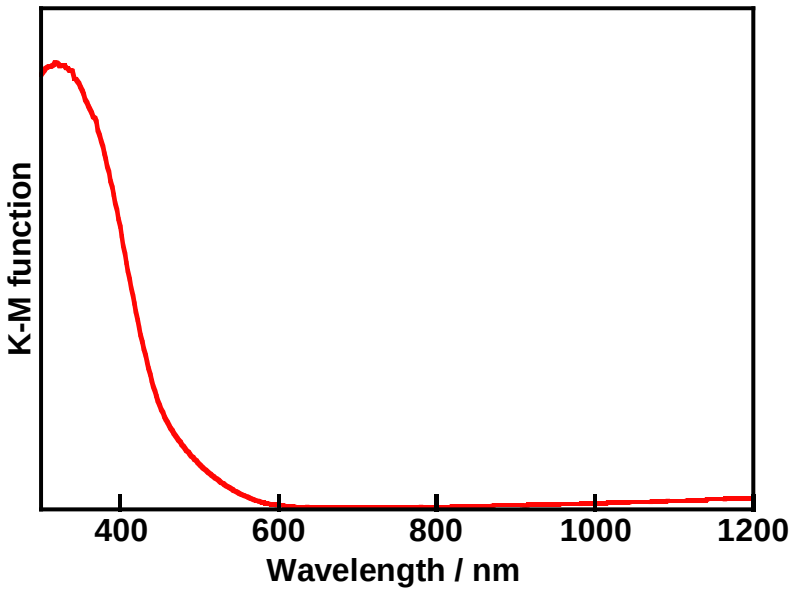

Fig. S7 Diffuse reflectance spectrum of WO_3:Cs,Rh(0.5) synthesized by a solid-state reaction at 1273 K for 5 h.

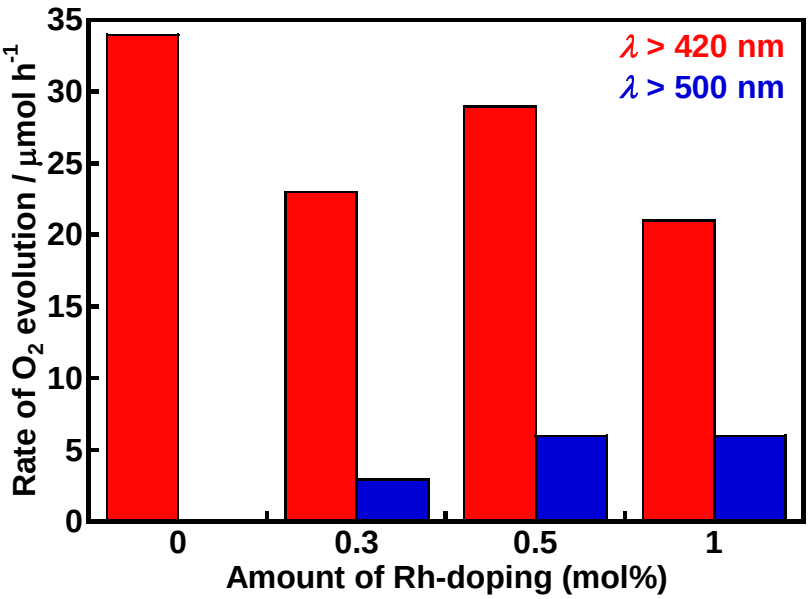

Fig. S8 Photocatalytic O_2 evolution over WO_3:Rh(x) and WO_3:Cs,Rh(x) (x = 0~1.0) synthesized by a solid-state reaction at 1273 K for 5 h from an aqueous $Fe(ClO_4)_3$ solution under irradiation of light with wavelength longer than 420 and 500 nm. Photocatalyst: 0.4 g, reactant solution: 4 mmol L^{-1} $Fe(ClO_4)_{3\ aq.}$ (pH2.1 adjusted with $HClO_{4\ aq.}$, 300 mL), cell: side-irradiation cell made of Pyrex, light source: 300 W Xe-arc lamp with a long-pass filter (HOYA; L42 or Y50).

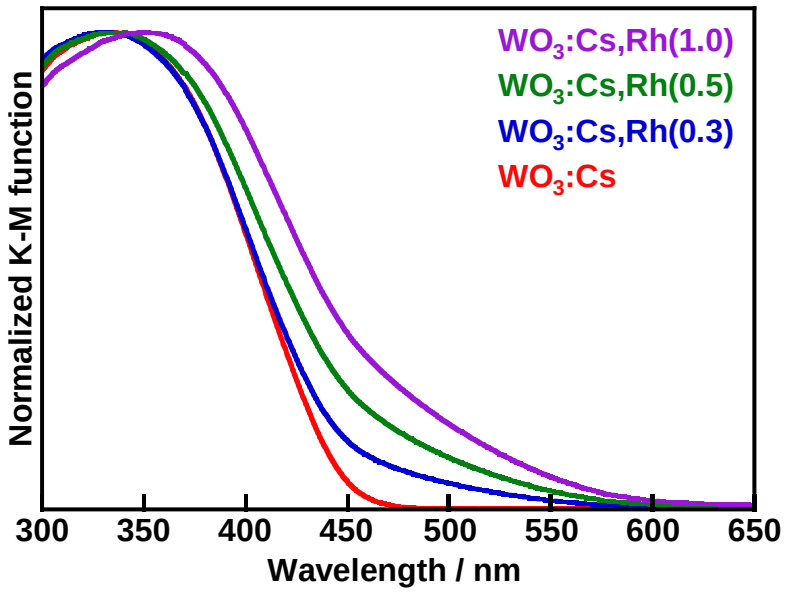

Fig. S9 Diffuse reflectance spectra of WO_3:Cs,Rh(x%) (x = 0, 0.3, 0.5, 1.0) synthesized by a solid-state reaction at 1273 K for 5 h.

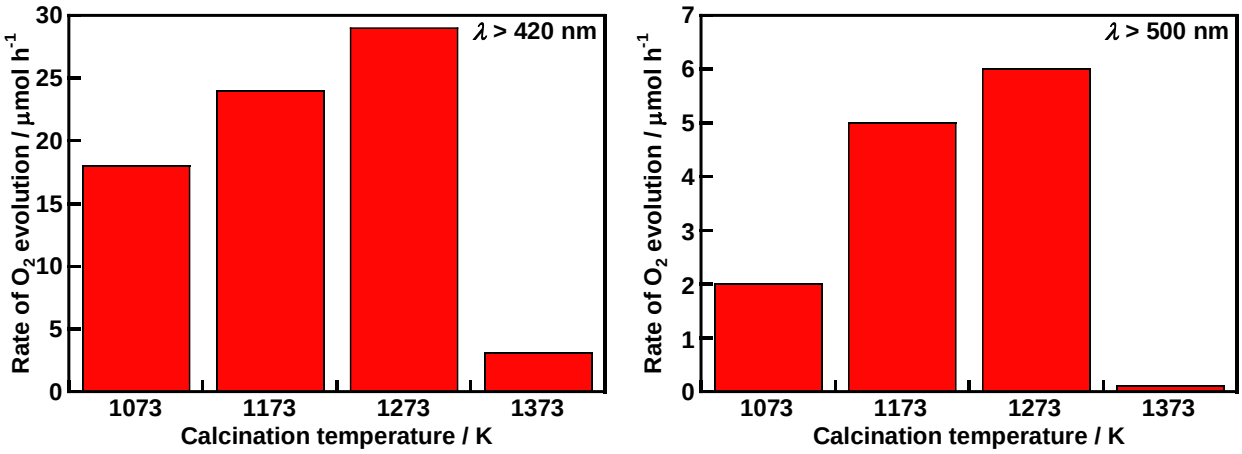

Fig. S10 Photocatalytic O_2 evolution over WO_3:Cs,Rh(0.5) synthesized by a solid-state reaction at 1073~1373 K for 5 h from an aqueous $Fe(ClO_4)_3$ solution under irradiation of light with a wavelength longer than 420 and 500 nm. Photocatalyst: 0.4 g, reactant solution: 4 mmol L^{-1} $Fe(ClO_4)_{3\ aq.}$ (pH2.1 adjusted with $HClO_{4\ aq.}$, 300 mL), cell: side-irradiation cell made of Pyrex, light source: 300 W Xe-arc lamp with a long-pass filter (HOYA; L42 or Y50).

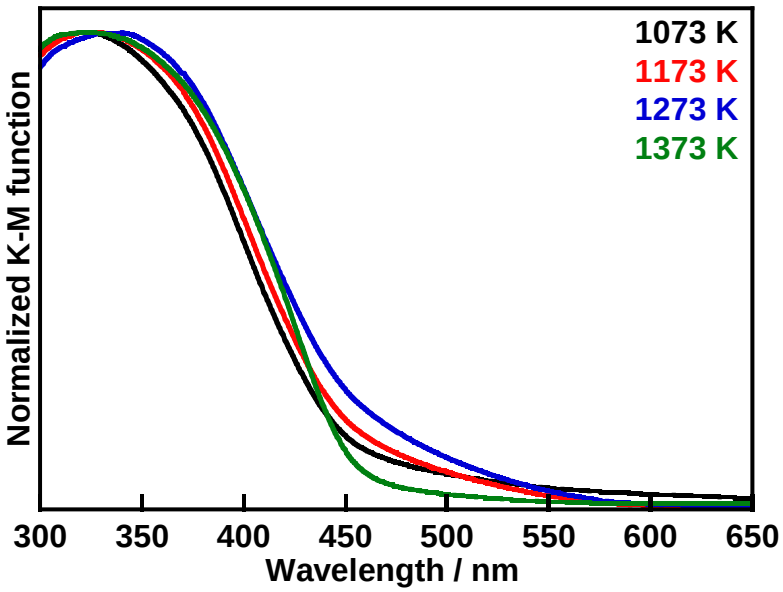

Fig. S11 Diffuse reflectance spectra of WO_3:Cs,Rh(0.5) synthesized by a solid-state reaction at 1073~1373 K for 5 h.

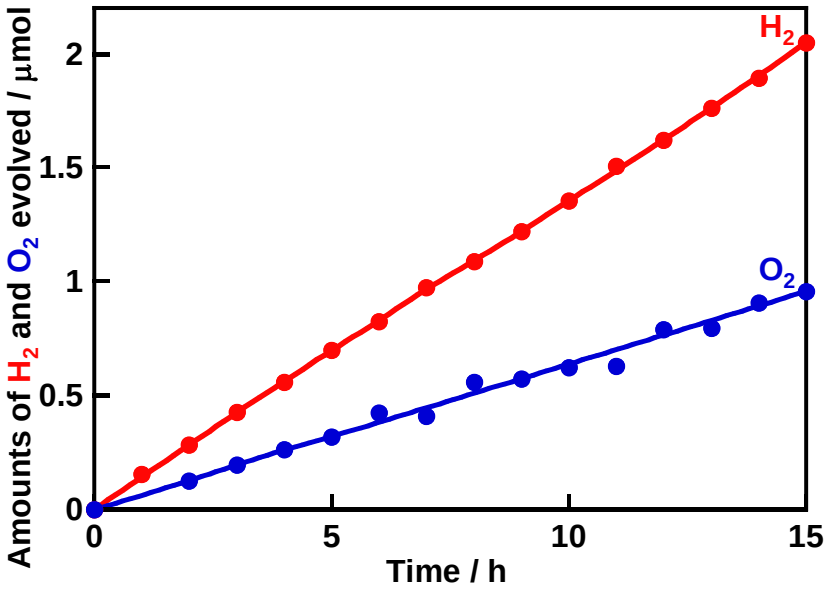

Fig. S12 Z-schematic water splitting via interparticle electron transfer using Ru/$SrTiO_3$:Rh for a H_2-evolvng photocatalyst and WO_3:Cs,Rh(0.5) synthesized at 1273 K for an O_2-evolving photocatalyst. Photocatalyst: 50 mg each, reactant solution: $HClO_4$ aq. (pH2.3, 200 mL), cell: top-irradiation cell made of Pyrex, light source: 300 W Xe-arc lamp with a long-pass filter (HOYA; Y50).

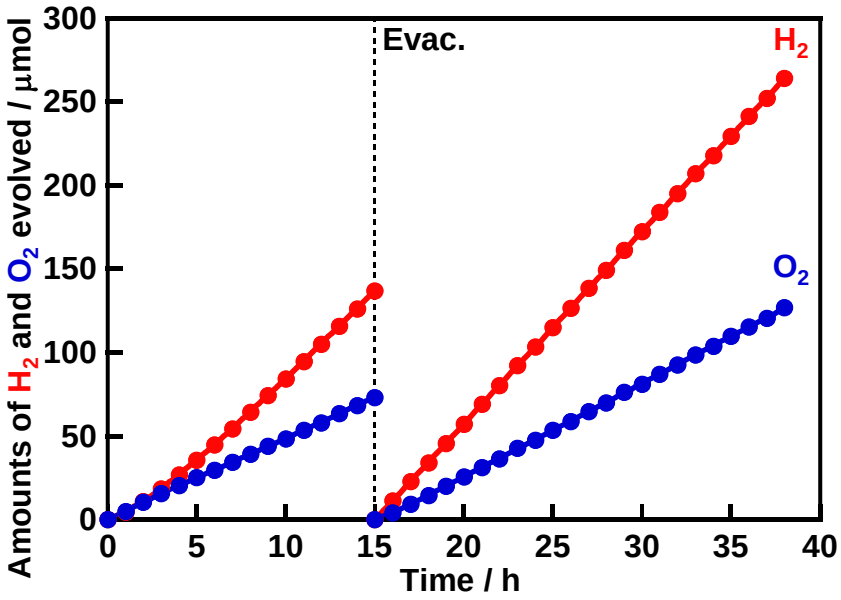

Fig. S13 Z-schematic solar water splitting using Ru/$SrTiO_3$:Rh for a H_2-evolvng photocatalyst, WO_3:Cs,Rh(0.5) synthesized at 1273 K for an O_2-evolving photocatalyst, and $Fe^{3+/2+}$ ion for an electron mediator. Photocatalyst: 50 mg each, reactant solution: 1mmol L^{-1} $Fe(ClO_4)_3$ aq. (pH2.3 adjusted with $HClO_4$ aq., 200 mL), cell: top-irradiation cell made of Pyrex, light source: solar simulator (SAN-EI ELECTRIC; XES-40S3-TT, AM-1.5 G), irradiation area: 25 cm^2.