Electronic Supplementary Information

for

Production of hydrogen peroxide by combination of semiconductor-photocatalysed oxidation of water and photocatalytic two-electron reduction of dioxygen

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Experimental section

Materials

All chemicals commercially available were used without further purification unless otherwise noted. $RuCl_3$ (38.220 wt% Ru) was purchased from Tanaka Kikinzoku Kogyo K.K. 4,7-dimethyl-1,10-phenanthroline (Me_2phen, 98%), 4,4'-dimethoxy-2,2'-bipyridine ($(MeO)_2$bpy, 97%), Ag_2SO_4 (99.9%), and $(NH_4)_2SO_4$ (99.99%) Pluronic® P-123, Triton® X-100, Nafion® perfluorinated membrane (Nafion® 117) were supplied from Aldrich Chemicals. Oxo[5,10,15,20-tetra(4-pyridyl)porphinato]titanium(IV) ($[TiO(tpypH_4)]^{4+}$) and Bis(2,4-pentanedionate)vanadium(IV) oxide ($VO(acac)_2$ ≧ 95%) were supplied from Tokyo Chemical Industry Co., Ltd. (TCI). $Sc(NO_3)_3•4H_2O$ (99.9%) was supplied from Mitsuwa Chemicals Co., Ltd. Tungsten hexachloride (WCl_6, ≧ 95%) was purchased from Nacalai Tesque. Bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3•5H_2O$, ≧ 99.9%) was purchased from Wako Pure Chemical Industries Ltd. Purification of water (18.2 MΩ cm) was performed with a Milli-Q system (Millipore, Direct-Q 3 UV). Glass slides coated with fluorine-doped tin oxide (FTO) (transmittance, 83.6%) were supplied by Aldrich Chemicals Co. and cut by Asahi Glass Co., Ltd.

Spectroscopic measurements in solution

^{1}H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer in D_2O solutions. The chemical shifts and relative integration signals were referenced by an external standard solution of 5.0 mM 3-(trimethylsilyl)propanoate-2,2,3,3-d_4 acid sodium salt (TSP) in D_2O sealed in a glass capillary. The UV-visible absorption spectra were recorded using a Hewlett Packard 8453 diode array spectrophotometer with a quartz cuvette (light-path length = 1.0 cm) at 298 K.

Synthesis of $[Ru^{II}(Me_2phen)_3]SO_4$ and $[Ru^{II}((MeO)_2bpy)_3]SO_4$

Tris(4,7-dimethyl-1,10-phenanthroline)ruthenium(II) sulfate ($[Ru^{II}(Me_2phen)_3]SO_4$) complex and Tris(4,4'-dimethoxy-2,2'-bipyridine)ruthenium(II) sulfate ($[Ru^{II}((MeO)_2bpy)_3]SO_4$) complex were synthesised according to the literature.[S1] $RuCl_3$ (40 mg) was refluxed under N_2 overnight in ethanol/water (v/v 80/20) with 6 equiv. of ligand, Me_2phen or $(MeO)_2$bpy, to form the red-orange $[Ru^{II}(Me_2phen)_3]Cl_2$ complex or $[Ru^{II}((MeO)_2bpy)_3]Cl_2$ complex, respectively. After evaporation of the solvent, the product was readily precipitated from acetone with ether. The precipitate, $[Ru^{II}(Me_2phen)_3]Cl_2$ or $[Ru^{II}((MeO)_2bpy)_3]Cl_2$, was added to water to be completely dissolved and Ag_2SO_4 (61 mg) solubilised in water was added to the solution. After stirring for 12 h, AgCl as precipitate was filtered off. An aqueous solution of $(NH_4)_2SO_4$ was added to the reaction solution to obtain crystalline product. ^{1}H-NMR (300 MHz, D_2O): δ (ppm) 2.88 (s, 6H), 7.41 (d, J = 5.12 Hz, 2H), 7.90 (d, J = 5.12 Hz, 2H), 8.39 (s, 2H) for $[Ru^{II}(Me_2phen)_3]SO_4$. ^{1}H-NMR (300 MHz, D_2O): δ (ppm) 4.00 (s, 6H), 6.97 (d, J = 6.58 Hz, 2H), 7.65 (d, J = 6.22 Hz, 2H), 7.94 (s, 2H) for $[Ru^{II}((OMe)_2bpy)_3]SO_4$. UV-Vis spectra of the synthesized Ru complexes are given in Fig. S2.

Transient absorption measurement $[Ru^{II}((MeO)_2bpy)_3]^{2+}$

For nanosecond transient absorption measurements, the 3rd harmonic of Nd:YAG laser (Continuum, SLI-10, 4-6 ns fwhm, 355 nm), a continuous Xe lamp (75 W) and a photomultiplier (Hamamatsu R2949; 350–800 nm) were used as the excitation source, probe light, detector, respectively. The output from the photomultiplier was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz).

Synthesis of WO_3

WO_3 was synthesised according to the published method.[S2] Pluronic P-123 (1.0 g) and WCl_6 (4.0 g, 0.01 mol) were dissolved in 10 mL of EtOH with vigorous stirring in ice bath. The resulting dark blue solution was gelled in an open Petri dish for aging at 40ºC in air for 3 days. The resulting dark blue solid was calcined at 400ºC with ramping rate of 0.5 ºC/min for 5 h under air to remove surfactant species. The obtained yellow solid was ground with mortar.

Preparation of FTO glasses

FTO glasses were cleaned prior to use by immersing in a MeOH/HCl [1/1 (v/v)] solution for 30 min and washed by purified water. The resulting FTO glasses were hydroxylated in H_2SO_4 for 2 h and then boiled in purified water for 30 min with subsequent drying under N_2.[S3]

Preparation of WO_3/FTO Electrode

WO_3/FTO electrode was prepared by a solution consisting of 1.0 mL of water containing 50 mg of WO_3 and acetyl acetone (30 mL) and 1 drop of Triton X-100. The mixture was sonicated for 5 min and then a 50 μL drop was applied on the surface of FTO electrode with a 2.5 cm^2 area and allowed to evaporate to afford a thin film. The resulting electrode was annealed to form crystalline WO_3 at 400ºC with ramping rate of 2 ºC/min (held at 400ºC for 2h) under air to remove surfactant species. The combustion of residual surfactant was confirmed by TG/DTA analysis of WO_3 dispersion prepared above. The exothermic current peak along with weight loss observed at around 180ºC was disappeared after the annealing at 400ºC. The Brunauer−Emmett−Teller (BET) surface area of WO_3 was 21 m^2 g^{-1}. Diffused reflectance UV-Vis spectrum of the prepared electrode is given in Fig. S2.

Preparation of $BiVO_4$/FTO Electrode

$BiVO_4$/FTO Electrode was prepared according to the literature procedures.[S4] A 0.04 M of $Bi(NO_3)_3$ solution prepared by dissolving $Bi(NO_3)_3•5H_2O$ (291 mg) and KI (996 mg) in 15 mL of water. After the pH of the resulting solution was adjusted to 1.7 by adding HNO_3, 20 mL of EtOH containing 0.23 M of *p*-benzoquinone (149 mg) was added and vigorously stirred for 10 min. After removal of insoluble residues by filtration, a three-electrode cell composed of a fluorine-doped tin oxide (FTO) working electrode, a platinum coil counter electrode, a SCE reference electrode was employed for electrodeposition. A FTO working electrode with a 2.5 × 1.0 cm^2 area was soaked into the solution just after filtration and the cathodic deposition was performed with an applied potential at –0.14 V (*vs.* SCE) until total passing charge of 0.13 C cm^{-2} at 298 K. The resulting orange-coloured precipitate on electrode corresponded to crystalline bismuth oxyiodide (BiOI). After washing with water, 0.1 mL of a DMSO solution containing 0.2 M vanadyl acetylacetonate ($VO(acac)_2$) was dropcast on the BiOI/FTO electrode. The resulting electrode was annealed to form crystalline BiVO4 at 450 ºC with ramping rate of 2 ºC/ min for 2 h. Excess V_2O_5 existing in the $BiVO_4$/FTO electrodes was removed by soaking them in 1.0 M of NaOH for 1 h and resulting $BiVO_4$/FTO electrodes were washed with water. The synthesised electrode was characterised using powder X-ray diffraction patterns to be $BiVO_4$.[S4] Diffused reflectance UV-Vis spectrum of the prepared electrode is given in Fig. S2.

Transient absorption spectral measurements of $BiVO_4$/FTO electrodes

The $BiVO_4$/FTO electrode for the measurement of transient absorption spectra of the photoexcited $BiVO_4$ film was prepared by cathodic deposition of BiOI on an FTO electrode for total passing charge of 0.033 C cm^{-2} followed by the treatment by DMSO solution of $VO(acac)_2$ and annealing (vide supra). The electrode was placed in a quartz cell (1.0 cm i.d.) together with an aqueous solution of Sc^{3+} (100 mM, 3.4 mL) for the transient absorption measurements. Subnanosecond to microsecond transient absorption spectra were collected using recently developed RIPT method.[S5] The pump source is a passively Q-switched microchip laser, (PowerChip PNV-M02510, Teem Photonics, 1 kHz, 350 ps, 355 nm, 25 μJ), and the probe source is a supercontinuum radiation source (SC-450, Fianium, 20 MHz, 50–100 ps, 450–2000 nm). The monochromatized probe pulses with a pre-dispersive monochromator (MD200, Unisoku) which is asynchronous with a pump pulse were irradiated on the sample and the beams transmitted through the sample and its reference beam were detected by InGaAs-photodiodes (G10899-01K, 400-1600 nm, Hamamatsu). A post-dispersive monochromator (CM110, Spectral Products) were positioned before the detector to minimize fluorescence signals from the sample. Si PIN photodiodes (S5972, Hamamatsu) were used to pick up the pump pulse and the probe pulses and to evaluate delay-times between them in a shot-by-shot manner. All photodiodes' outputs are recorded with a digitizing oscilloscope (HDO8038, Teledyne Lecroy) then transferred to a PC to construct the TA temporal profile. Time resolution of the system was estimated at 400 ps from the 10-90% rise time.

Photocurrent measurements

For Ru complexes, photocurrent was observed under photoirradiation of Ru complexes (160 μM) at 0.25 V vs. SCE in an aqueous solution (8.0 mL) of $Sc(NO_3)_3$ (100 mM) in a quartz anode cell (light path length = 1 cm) at 298 K using a conventional three-electrode cell consisting of carbon cloth electrode as working electrode, a platinum coil as the counter electrode and saturated calomel electrode (SCE) as the reference electrode.

For $BiVO_4$ and WO_3, photocurrent at 0.25 V vs. SCE was observed under photoirradiation of $BiVO_4$/FTO or WO_3/FTO electrode in an aqueous solution (8.0 mL) of $Sc(NO_3)_3$ (100 mM) in a quartz anode cell (light path length = 1 cm) at 298 K using a conventional three-electrode cell consisting of semiconductor electrode as working electrode, a platinum coil as the counter electrode and saturated calomel electrode (SCE) as the reference electrode.

Photocurrent was measured on an ALS 630B electrochemical analyser under photoirradiation of the photocatalysts with a Xe lamp (MAX-302 Xenon Light Source 300W, Asahi Spectra Co., Ltd.) equipped with a cut-off filter (Asahi Techno Glass L42) transmitting $\lambda > 420$ nm at room temperature.

Electrochemical water oxidation reaction

Electrochemical water oxidation reaction using semiconductor electrodes as catalysts was performed in an aqueous solution of $Sc(NO_3)_3$ (100 mM) at 298 K using a conventional three-electrode cell consisting of semiconductor electrode as working electrode, a platinum coil as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The amount of evolved oxygen gas in the headspace was analysed by an oxygen sensor (FOXY Fiber Optic Oxygen Sensor, Ocean Optics). The total amount of evolved O_2 was calculated based on the equation shown in page S12.

Photocatalytic Production of H_2O_2.

Photocatalytic reaction was performed in a quartz anode cell (light path length = 1 cm) connected with a pyrex cathode cell through a Nafion membrane. Cathode cell is composed of as prepared semiconductor photoanode (WO_3 or $BiVO_4$ deposited on a FTO electrode) for the water oxidation in an air-saturated aqueous solution (8.0 mL) containing $Sc(NO_3)_3$ (100 mM). Anode cell is composed of a carbon mesh anode in O_2-saturated aqueous solution (8.0 mL) containing $[Ru^{II}((MeO)_2bpy)_3](SO_4)$ or $[Ru^{II}(Me_2phen)_3](SO_4)$ (160 μM) and $Sc(NO_3)_3$ (100 mM). These two electrodes were connected with alligator clips and copper wire. Photoanode was illuminated from the back side of the FTO electrode with the solar simulator (HAL-320, Asahi Spectra Co., Ltd.), while cathodic chamber was irradiated with a Xe lamp (MAX-302 Xenon Light Source 300W, Asahi Spectra Co., Ltd.,) equipped with a cut-off filter (Asahi Techno Glass L42) transmitting $\lambda > 420$ nm at room temperature. The amount of produced hydrogen peroxide in anodic chamber was determined by spectroscopic titration with an acidic solution of $[TiO(tpypH_4)]^{4+}$ complex (Ti-TPyP reagent, *vide infra*).[S6]

Quantification of produced H_2O_2

From spectroscopic titration with an acidic solution of $[TiO(tpypH_4)]^{4+}$ complex (Ti-TPyP reagent), the amount of produced H_2O_2 was determined.[S6] The [TiO(tpyp)] complex (34 mg) was dissolved in 1.0 L of 50 mM hydrochloric acid and the solution was used as a Ti-TPyP reagent. An aliquot (e.g., 10 🕴 L) of the reaction solution was diluted with water and 0.25 mL of the sample solution was mixed with 0.25 mL of 4.8 M perchloric acid and 0.25 mL of the Ti-TPyP reagent. After 5 min at room temperature, the mixture was diluted to 2.5 mL with water and used for the spectroscopic measurement. The absorbance at $\lambda = 434$ nm was measured by using a Hewlett Packard 8453 diode array spectrometer (A_S). In the similar manner, a blank solution was prepared by adding distilled water in place of the sample solution in the same volume with its absorbance designated as A_B. The difference in absorbance was determined by following the equation: $\Delta A_{434} = A_B - A_S$. Based on ΔA_{434} and the volume of the solution, the amount of hydrogen peroxide was determined according to the literature.[S6]

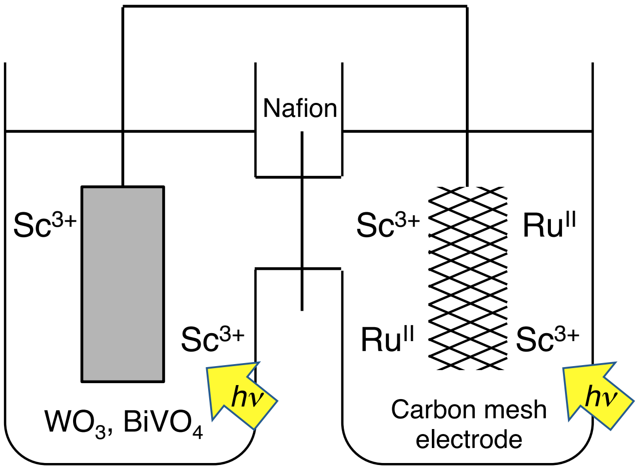

Fig. S1 Schematic representation of a two-compartment cell employed in this study for photocatalytic production of H_2O_2 from H_2O and O_2 under visible light irradiation.

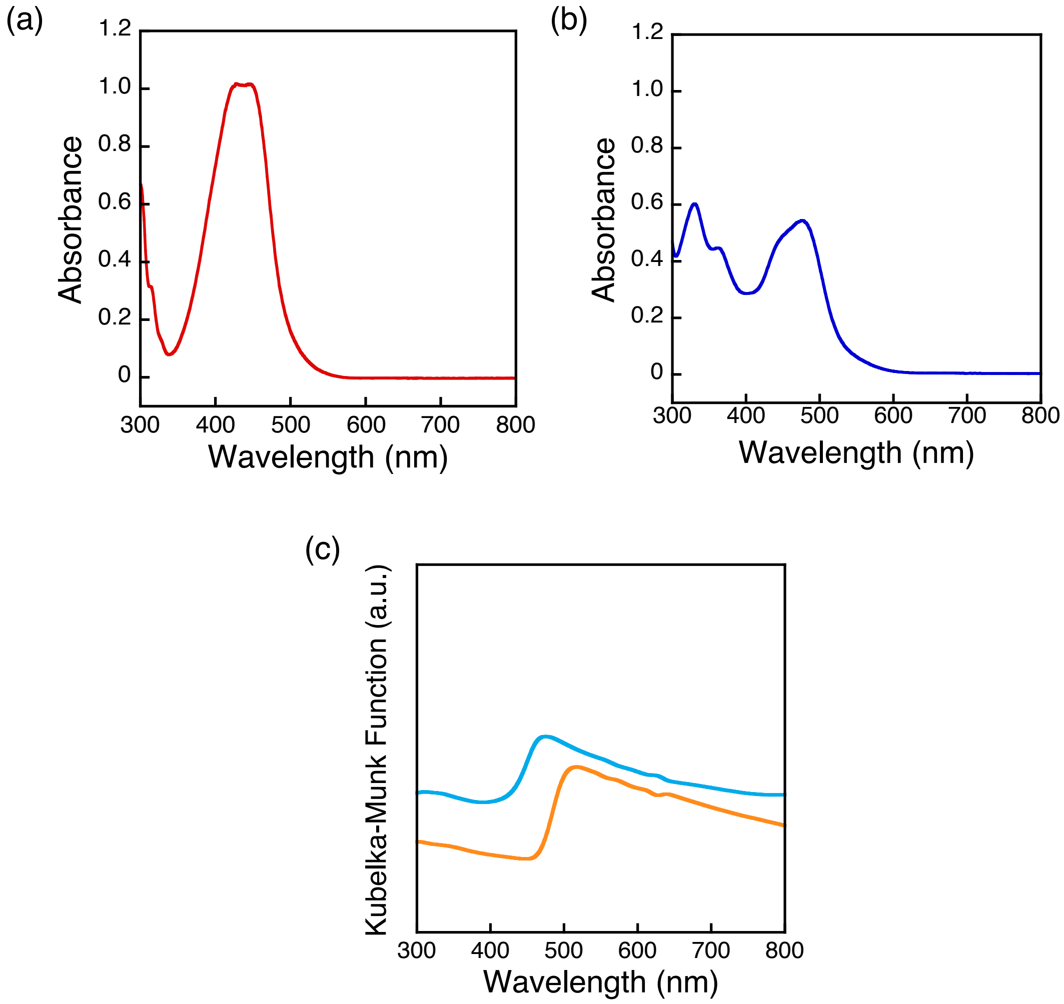

Fig. S2 (a) UV-Vis absorption spectrum of an aqueous solution of $[\mathrm{Ru^{II}(Me_2phen)_3}]^{2+}$ (40 μM). (b) UV-Vis absorption spectrum of an aqueous solution of $[\mathrm{Ru^{II}((MeO)_2bpy)_3}]^{2+}$ (40 μM). (c) Diffused reflectance UV-Vis spectra of WO_3/FTO electrode (blue) and $BiVO_4$/FTO electrode (orange).

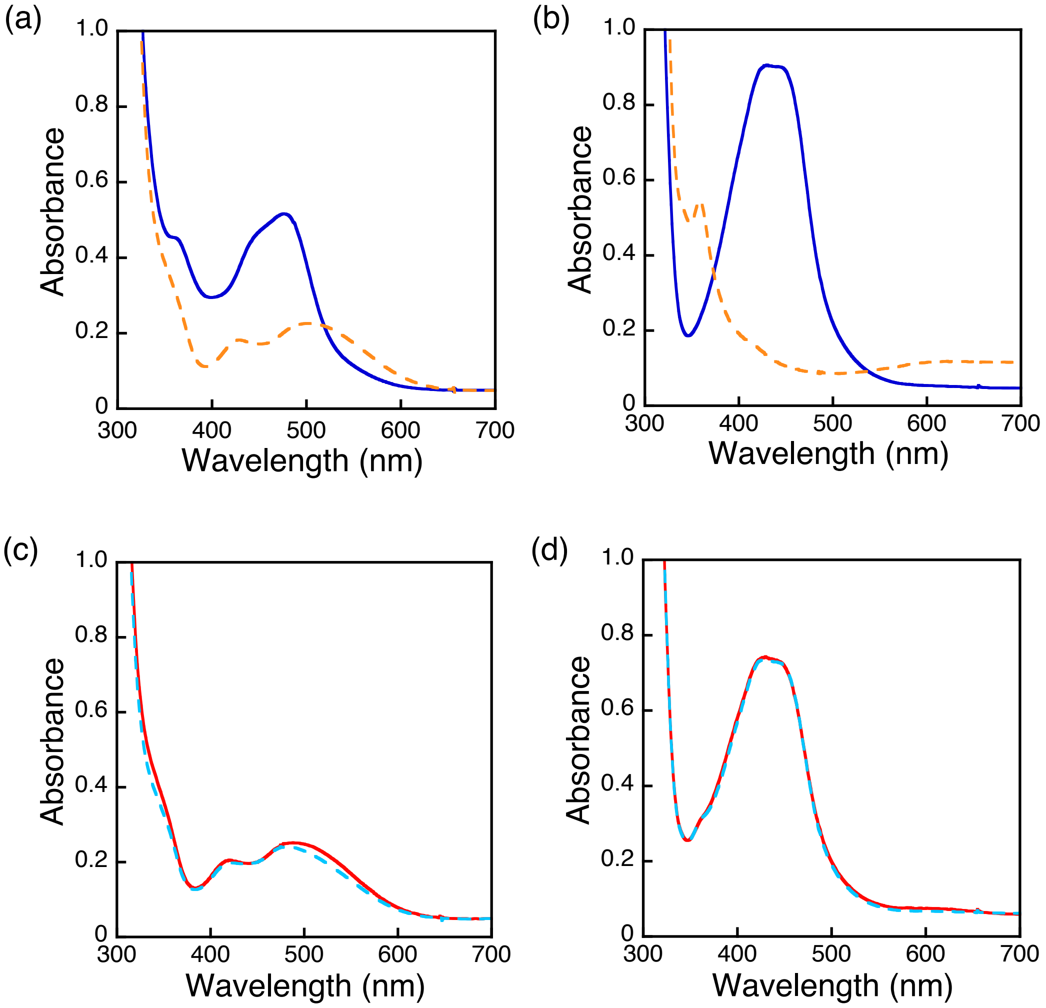

Fig. S3 (a) UV-Vis absorption spectrum of an aqueous solution of $[Ru^{II}((MeO)_2bpy)_3]^{2+}$ (40 μM, blue line) and $[Ru^{III}((MeO)_2bpy)_3]^{3+}$ (40 μM, orange dotted line) containing Sc^{3+} (100 mM). (b) UV-Vis absorption spectrum of an aqueous solution of $[Ru^{II}(Me_2phen)_3]^{2+}$ (40 μM, blue line) and $[Ru^{III}(Me_2phen)_3]^{3+}$ (40 μM, orange dotted line) containing Sc^{3+} (100 mM). (c) UV-Vis absorption spectrum of an aqueous solution of $[Ru^{II}((MeO)_2bpy)_3]^{2+}$ (40 μM) after photoirradiation by monochromic light (λ = 450 nm) for 3500 s (red line) and simulated spectrum of an aqueous solution containing $[Ru^{II}((MeO)_2bpy)_3]^{2+}$ (3.2 μM, 8% of Ru complex *in situ*), $[Ru^{III}((MeO)_2bpy)_3]^{3+}$ (37 μM, 92% of Ru complex *in situ*) and Sc^{3+} (100 mM) (blue dotted line). (d) UV-Vis absorption spectrum of an aqueous solution of $[Ru^{II}(Me_2phen)_3]^{2+}$ (40 μM) after photoirradiation by monochromic light (λ = 450 nm) for 3500 s (red line) and simulated spectrum of an aqueous solution containing $[Ru^{II}(Me_2phen)_3]^{2+}$ (31 μM, 78% of Ru complex *in situ*), $[Ru^{III}(Me_2phen)_3]^{3+}$ (8.8 μM, 22% of Ru complex *in situ*) and Sc^{3+} (100 mM) (blue dotted line). Simulated spectrum shown in (c) and (d) are calculated based on spectrum given in (a) and (b), respectively. The details of calculations are explained in page S15.

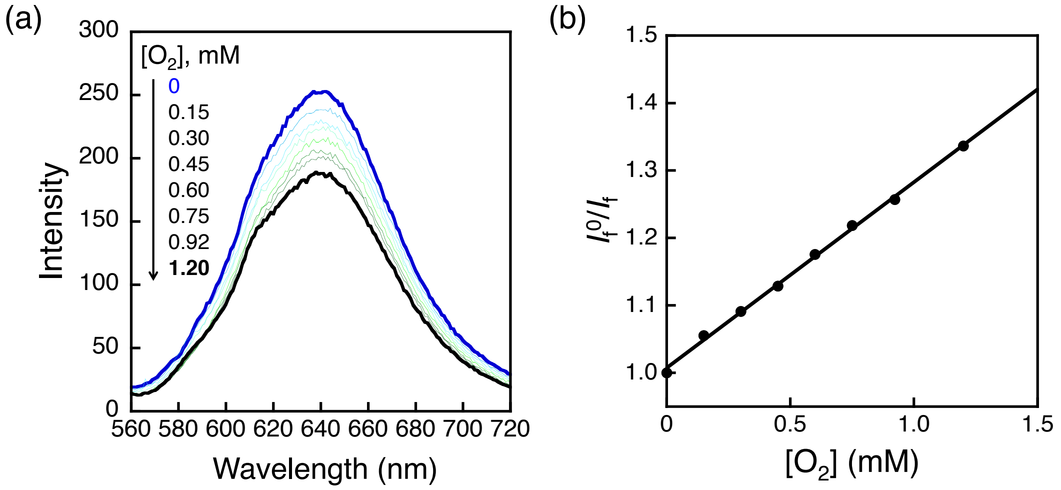

Fig. S4 (a) Phosphorescence spectrum of $[Ru((MeO)_2bpy)_3]^{2+*}$ with various concentrations of O_2 in water. (b) Stern-Volmer plot.

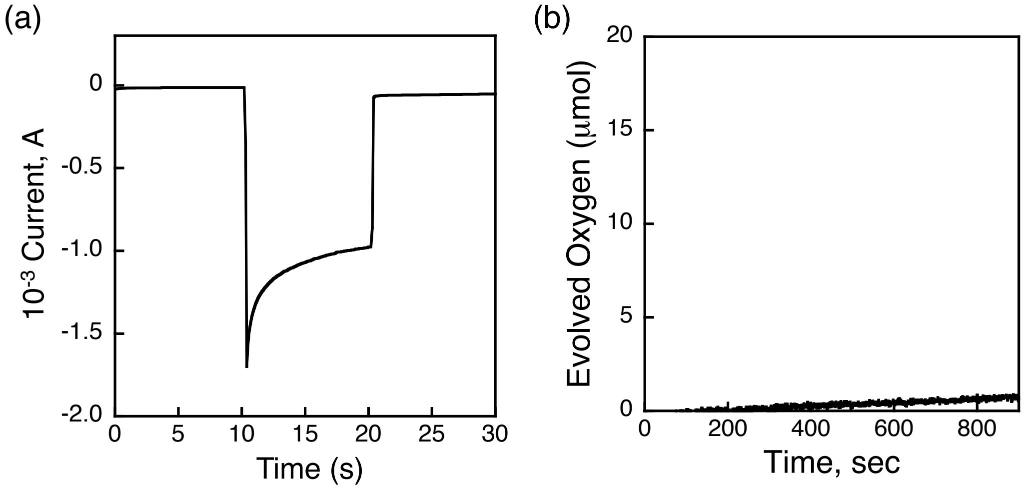

Fig. S5 (a) Photocurrent (at 0.25 V vs. SCE) under photoirradiation of the WO_3 anode in an aqueous solution of Sc^{3+} (100 mM) with a Xe lamp (λ > 420 nm). (b) O_2 evolution during photocurrent generation at an applied potential of 0.52 V vs SCE.

Estimation of the total amount of evolved O_2 by measuring the O_2 amount in the headspace in equilibrium with that dissolved in solution

The total amount of evolved O_2 (T [μmol]) was calculated based on the following equations where G [μmol] is the O_2 amount in the headspace in equilibrium with O_2 dissolved in solution (amount: L [μmol]) as expressed in eqn (S1). The G value can be expressed by eqn (S2) using volume of the headspace (x [mL]) and O_2 molar fraction (z %) in the headspace where the volume of O_2 gas is 2.5 ×10 [L] at 298 K under atmospheric pressure, 1.0×10^4 [Pa]. The L value can be expressed by eqn (S3) using the volume of the reaction solution (y [mL]) and z where the concentration O_2 in an O_2-saturated water is 1.2 [mM].[S7]

$$T\,[\mu\text{mol}] = G[\mu\text{mol}] + L[\mu\text{mol}] \qquad \text{(S1)}$$

$$G\,[\mu\text{mol}] = \frac{x\,[\text{mL}]}{2.5 \times 10\,[\text{L mol}^{-1}]} \times \frac{z[\%]}{100} \times 1000 \qquad \text{(S2)}$$

$$L\,[\mu\text{mol}] = 1.2\,[\text{mM}] \times y\,[\text{mL}] \times \frac{z[\%]}{100} \qquad \text{(S3)}$$

Calculation of the simulated spectrum

The simulated spectrum is drawn by performing following calculation, eqn (S4), for every 1 nm of the wavelength in the range of 300 nm to 700 nm where Abs_{Ru2}, Abs_{Ru3} and Abs_{sim} each corresponding to absorbance of Ru^{II} complex, absorbance of Ru^{III} complex and simulated absorbance at the given wavelength; and r ($0 \leq r \leq 100$) referring to percentage of Ru^{II} species present *in situ*.

$$Abs_{Ru2} \times \frac{\mathrm{r}}{100} + Abs_{Ru3} \times (1 - \frac{\mathrm{r}}{100}) = Abs_{sim} \qquad \text{(S4)}$$

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