

## Supporting Information

### Efficient Photocatalytic Production of Hydrogen Peroxide from Water and Dioxygen with Bismuth Vanadate and a Cobalt(II) Chlorin Complex

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**General Procedures.** Chemicals were purchased from commercial sources and used without further purification, unless otherwise noted. Benzonitrile (PhCN) used for spectroscopic and electrochemical measurements was distilled over phosphorus pentoxide prior to use.<sup>S1</sup> Bismuth(III) nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\geq 99.9\%$ ), iron(II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), potassium hexacyanoferrate(III) ( $\text{K}_3[\text{Fe}(\text{CN})_6]$ ), and acetylacetone ( $\geq 99\%$ ) were purchased from Wako Pure Chemical Industries Ltd. Potassium hexacyanocobaltate ( $\text{K}_3[\text{Co}^{\text{III}}(\text{CN})_6]$ ,  $\geq 99.9\%$ ) was supplied by Stream Chemicals. Bis(2,4-pentanedionate)vanadium(IV) oxide ( $\text{VO}(\text{acac})_2$ ,  $\geq 95\%$ ), Oxo[5,10,15,20-tetra(4-pyridyl)porphinato]titanium(IV) ( $[\text{TiO}(\text{tpyp})]$ ) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). Red sea salt was supplied by Red Sea. Triton® X-100, Nafion® perfluorinated ion exchange resin solution and Nafion perfluorinated membrane (Nafion 117) were received from Sigma Aldrich. Carbon paper electrode (EC-TP1-060T produced by Toray Industry Inc.) was obtained from Toyo Co. 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. Tetra-*n*-butylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) purchased from Wako Pure Chemical Industries, Ltd. was twice recrystallized from ethanol and dried *in vacuo* prior to use. Purified water was provided by a Millipore Milli-Q water purification system (Millipore, Direct-Q 3 UV) with an electronic conductance of 18.2 MΩ cm. Cobalt chlorin complex  $[\text{Co}^{\text{II}}(\text{Ch})]$ ,<sup>S2</sup>  $\text{FeO}(\text{OH})/\text{BiVO}_4/\text{FTO}$  electrode,<sup>S3</sup> polynuclear cyanide complex ( $\text{Fe}^{\text{II}}_3[\text{Co}^{\text{III}}(\text{CN})_6]_2$ )<sup>S4</sup> were prepared by the published methods.

**Synthesis of Free Base Chlorin ( $\text{H}_2(\text{Ch})$ ).**  $\text{H}_2(\text{Ch})$  was synthesized by two-step reaction: extraction of pheophytin *a* from *Spirulina* algae and subsequent decarboxylation of the methoxycarbonyl group (position C-13<sup>2</sup>) according to published procedures.<sup>S5</sup> *Spirulina* algae was purchased from Japan Alge Corp. MeOH (500 mL) was poured to *Spirulina* powder (300 g) several times to extract organic compounds. After removal of insoluble residues by filtration, acetic acid (15 mL) was added to the filtrate to remove magnesium ion. The resulting solution was evaporated to reduce the volume to 100 mL and neutralized with an aqueous solution of saturated  $\text{NaHCO}_3$ . pheophytin *a* was extracted by adding  $\text{CH}_2\text{Cl}_2$  to the mixture and the  $\text{CH}_2\text{Cl}_2$  phase was washed with distilled water several times. After the solvent was evaporated, the concentrated solution was purified by silica gel column chromatography. The first yellow and red bands corresponding to carotenoids were eluted with  $\text{CH}_2\text{Cl}_2$ , and then a black band corresponding to the product (pheophytin *a*) was eluted with 20% ethyl acetate in  $\text{CH}_2\text{Cl}_2$ . The product was recrystallized from  $\text{CH}_2\text{Cl}_2$ /hexane to give pheophytin *a* as a dark blue solid (2.5g). Both 13<sup>2</sup> *R*-epimer and a small amount of 13<sup>2</sup> *S*-epimer were formed. <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 300 MHz, pheophytin *a*) =  $5.0 \times 10^{-3}$  M):  $\delta$  -1.63 (1H, br, s, -NH), 0.53 (1H, br, s, -NH), 1.53 (s,  $\text{H}_2\text{O}$ ), 1.68 (3H, t,  $J = 7.5$  Hz, 8<sup>2</sup>-CH<sub>3</sub>), 1.79 (3H, d,  $J = 8.1$  Hz, 18<sup>1</sup>-CH<sub>3</sub>), 2.17-2.32 (2H, m, 17<sup>2</sup>-CH<sub>2</sub>-), 2.55-2.65

(2H, m, 17<sup>1</sup>-CH<sub>2</sub>-), 3.22 (3H, s, 7<sup>1</sup>-CH<sub>3</sub>), 3.38 (3H, s, 2<sup>1</sup>-CH<sub>3</sub>), 3.55 (3H, s, 17<sup>4</sup>-CO<sub>2</sub>CH<sub>3</sub>), 3.69 (3H, s, 12<sup>1</sup>-CH<sub>3</sub>), 3.70 (2H, q,  $J = 7.8$  Hz, 8<sup>1</sup>-CH<sub>2</sub>-), 3.85 (3H, s, 13<sup>4</sup>-CO<sub>2</sub>CH<sub>3</sub>), 4.16-4.20 (1H, m, 17-H), 4.42-4.45 (1H, m, 18-H), 6.17 (1H, dd,  $J = 10.2, 1.5$  Hz, 3<sup>2</sup>=CH<sub>2</sub> *cis*), 6.24 (1H, s, 13<sup>2</sup>-CH-), 6.26 (1H, dd,  $J = 17.2, 1.5$  Hz, 3<sup>2</sup>=CH<sub>2</sub> *trans*), 7.24 (s, solvent), 7.97 (1H, dd,  $J = 18.4, 11.7$  Hz, 3<sup>1</sup>-CH=), 8.54 (1H, s, 20-H), 9.37 (1H, s, 5-H), 9.51 (1H, s, 10-H).

The obtained pheophytin *a* (1.0 g) was dissolved in 2,4,6-collidine, and the reaction mixture was refluxed for 3 h under dark and nitrogen. After the solvent was evaporated at reduced pressure, the resulting solution was dissolved in 10% sulfuric acid in CH<sub>3</sub>OH, and the reaction mixture was stirred for 12 h under dark and nitrogen at room temperature. The resulting solution was neutralized with the aqueous solution of saturated NaHCO<sub>3</sub>. H<sub>2</sub>(Ch) was extracted by adding CH<sub>2</sub>Cl<sub>2</sub> to the mixture and the CH<sub>2</sub>Cl<sub>2</sub> phase was washed with distilled water several times. After the solvent was evaporated, the crude solid was purified by silica gel column chromatography. A black band corresponding to the product (H<sub>2</sub>(Ch)) was eluted with the mixed solution (CH<sub>3</sub>OH/hexane/CHCl<sub>3</sub> [1/8/20 (v/v/v)]). The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to give H<sub>2</sub>(Ch) as a dark blue solid (660 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, H<sub>2</sub>(Ch) = 5.0 × 10<sup>-3</sup> M): δ -1.68 (1H, br, s, -NH), 0.47 (1H, br, s, -NH), 1.51 (s, H<sub>2</sub>O), 1.70 (3H, t,  $J = 7.7$  Hz, 8<sup>2</sup>-CH<sub>3</sub>), 1.80 (3H, d,  $J = 6.9$  Hz, 18-CH<sub>3</sub>), 2.24-2.35 (2H, m, 17<sup>2</sup>-CH<sub>2</sub>-), 2.51-2.70 (2H, m, 17<sup>1</sup>-CH<sub>2</sub>-), 3.25 (3H, s, 7<sup>1</sup>-CH<sub>3</sub>), 3.41 (3H, s, 2<sup>1</sup>-CH<sub>3</sub>), 3.61 (3H, s, 17<sup>4</sup>-CO<sub>2</sub>CH<sub>3</sub>), 3.68 (3H, s, 12<sup>1</sup>-CH<sub>3</sub>), 3.70 (2H, q,  $J = 7.7$  Hz, 8<sup>1</sup>-CH<sub>2</sub>-), 4.30 (1H, m, 17-H), 4.49 (1H, m, 18-H), 5.18 (2H, q,  $J = 20.1$  Hz, 13<sup>2</sup>-CH<sub>2</sub>-), 6.17 (1H, dd,  $J = 10.2, 1.5$  Hz, 3<sup>2</sup>=CH<sub>2</sub> *cis*), 6.29 (1H, dd,  $J = 17.5, 1.5$  Hz, 3<sup>2</sup>=CH<sub>2</sub> *trans*), 7.26 (s, solvent), 8.01 (1H, dd,  $J = 17.5, 11.3$  Hz, 3<sup>1</sup>-CH=), 8.56 (1H, s, 20-H), 9.40 (1H, s, 5-H), 9.51 (1H, s, 10-H).

**Synthesis of Cobalt Chlorin (Co(Ch)).** Cobalt chlorin was synthesized by following the published method.<sup>S2</sup> A mixture of Free base chlorin H<sub>2</sub>(Ch) (100 mg), Co(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>•4H<sub>2</sub>O (200 mg) and CH<sub>3</sub>COONa (500 mg) in 150 mL of CHCl<sub>3</sub>/CH<sub>3</sub>OH [2/1 (v/v)] was refluxed under dark and nitrogen for 6 h. The reaction mixture was poured into distilled water, extracted with CHCl<sub>3</sub>, washed several times with distilled water and dried over Na<sub>2</sub>SO<sub>4</sub>. The product was purified by silica gel column chromatography using a solution (acetone/CHCl<sub>3</sub> [1/10 (v/v)]) as an eluent and recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to give Co<sup>II</sup>(Ch) as a green solid.

**Synthesis of Fe<sup>II</sup><sub>3</sub>[Co<sup>III</sup>(CN)<sub>6</sub>]<sub>2</sub>.** Fe<sup>II</sup><sub>3</sub>[Co<sup>III</sup>(CN)<sub>6</sub>]<sub>2</sub> was synthesized by following the published method.<sup>S4</sup> An aqueous solution of FeSO<sub>4</sub>•7H<sub>2</sub>O (0.18 M, 10 mL) was slowly added to an aqueous solution of K<sub>3</sub>[Co<sup>III</sup>(CN)<sub>6</sub>] (0.12 M, 10 mL) with vigorous stirring. The formed precipitate was collected by filtration and washed with pure water several times. The resulting precipitate was dried at 60°C for 12 hours.

**Preparation of Co<sup>II</sup>(Ch)/CP Electrode.** Co<sup>II</sup>(Ch)/CP electrode was prepared by an MeCN solution (1 mL) of Co<sup>II</sup>(Ch) (0.3 mM), MWCNT (0.63 mg) and 5% Nafion (12  $\mu$ L). For each experiment, the mixture was sonicated for 20 min and then a 50  $\mu$ L of the mixture was applied on the both side of surface of a carbon paper (CP) with a 3.0 cm<sup>2</sup> area by drop-casting and allowed to evaporate to afford a film containing a MWCNT loading of 50  $\mu$ g cm<sup>-2</sup> and a catalyst loading of 30 nmol.

**Preparation of BiVO<sub>4</sub>/FTO Electrode.** BiVO<sub>4</sub>/FTO Electrode was prepared according to the literature procedures.<sup>S3</sup> At first, FTO glasses were cleaned prior to use by immersing in MeOH/HCl [1/1 (v/v)] solution for 30 min and washed by purified water. The resulting FTO glasses were hydroxylated in H<sub>2</sub>SO<sub>4</sub> for 2h and then boiled in purified water for 30 min with subsequent drying under N<sub>2</sub>.<sup>S6</sup> A 0.04 M of Bi(NO<sub>3</sub>)<sub>3</sub> solution prepared by dissolving Bi(NO<sub>3</sub>)<sub>3</sub>•5H<sub>2</sub>O (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<sub>3</sub>, 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 was soaked into as prepared solution with a 2.5 × 1.0 cm<sup>2</sup> area and cathodic deposition was performed with applied potential at -0.14 V (vs SCE) until total passing charge of 0.13 C cm<sup>-2</sup> at 298 K. The resulting orange-colored precipitate on electrode is corresponding to crystalline bismuth oxyiodide (BiOI). The SEM image of the BiOI/FTO electrode was shown in Figure S1a. The powder X-ray diffraction patterns of BiOI/FTO electrode was shown in Figure S8b.<sup>S3</sup> After washing with water, 0.1 mL of a DMSO solution containing 0.2 M vanadyl acetylacetonate (VO(acac)<sub>2</sub>) was dropcast on the BiOI/FTO electrode. The resulting electrode was annealed to form crystalline BiVO<sub>4</sub> at 450 °C with ramping rate of 2 °C/ min for 2 h. Excess V<sub>2</sub>O<sub>5</sub> existing in the BiVO<sub>4</sub>/FTO electrodes was removed by soaking them in 1 M of NaOH for 1 h and resulting BiVO<sub>4</sub>/FTO electrodes were washed with water. The SEM image of the BiVO<sub>4</sub>/FTO electrode was shown in Figure S1b. The Powder X-ray diffraction patterns of BiVO<sub>4</sub>/FTO electrode was shown in Figure S8c.<sup>S3</sup>

**Preparation of FeO(OH)/BiVO<sub>4</sub>/FTO Electrode.** FeO(OH)/BiVO<sub>4</sub>/FTO Electrode was prepared by photodeposition of FeO(OH) on the BiVO<sub>4</sub>/FTO Electrode according to the literature procedures.<sup>S4</sup> Photodeposition was performed in a N<sub>2</sub>-saturated aqueous solution containing 0.1 M of FeSO<sub>4</sub>•7H<sub>2</sub>O. A conventional three-electrode cell was used with a BiVO<sub>4</sub>/FTO working electrode, a platinum coil counter electrode, and SCE reference electrode. BiVO<sub>4</sub>/FTO working electrode was illuminated from back side of FTO electrode with a solar simulator (HAL-320, Asahi Spectra Co., Ltd.), where the light intensity was adjusted at 10 mW cm<sup>-2</sup> at the sample position by 1SUN checker (CS-20, Asahi Spectra Co., Ltd.) at 298 K. An external bias of 0.21 V (vs SCE) was applied to facilitate photodeposition until

total passing charge of  $45 \text{ mC cm}^{-2}$  at 298 K. To ensure the deposition of FeO(OH) on any bare BiVO<sub>4</sub> surface, electrodeposition of FeO(OH) was performed with applied potential at 1.16 V (vs SCE) for 90 s at 298 K. The SEM image of the FeO(OH)/BiVO<sub>4</sub>/FTO electrode was shown in Figure S1c.<sup>S3</sup> The Powder X-ray diffraction patterns of FeO(OH)/BiVO<sub>4</sub>/FTO electrode was shown in Figure S8d.<sup>S3</sup> The deposition of FeO(OH) on BiVO<sub>4</sub>/FTO electrode was confirmed by X-ray photoelectron spectra (XPS) measurements for the energy regions of Bi 4f, V 2P, O 1s, and Fe 2P, as shown in Figure S2.<sup>S7</sup> The binding energy of each element was corrected by C 1s peak (284.6 eV) from residual carbon.

**Preparation of NiO(OH)/BiVO<sub>4</sub>/FTO Electrode.** NiO(OH)/BiVO<sub>4</sub>/FTO Electrode was prepared by photodeposition of NiO(OH) on the BiVO<sub>4</sub>/FTO Electrode according to the literature procedures.<sup>S4</sup> Photodeposition was performed in a N<sub>2</sub>-saturated aqueous solution containing 0.1 M of NiSO<sub>4</sub>•6H<sub>2</sub>O. A conventional three-electrode cell was used with a BiVO<sub>4</sub>/FTO working electrode, a platinum coil counter electrode, and SCE reference electrode. BiVO<sub>4</sub>/FTO working electrode was illuminated from back side of FTO electrode with a solar simulator (HAL-320, Asahi Spectra Co., Ltd.), where the light intensity was adjusted at  $10 \text{ mW cm}^{-2}$  at the sample position by 1SUN checker (CS-20, Asahi Spectra Co., Ltd.) at 298 K. An external bias of 0.07 V (vs SCE) was applied to facilitate photodeposition until total passing charge of  $22 \text{ mC cm}^{-2}$  at 298 K. To ensure the deposition of NiO(OH) on any bare BiVO<sub>4</sub> surface, electrodeposition of NiO(OH) was performed with applied potential at 1.16 V (vs SCE) for 90 s at 298 K. The SEM image of the NiO(OH)/BiVO<sub>4</sub>/FTO electrode was shown in Figure S1d.

**Preparation of Seawater.** The seawater was prepared by dissolving 33.4 g of red sea salt in 1 L of water to form a solution containing *ca.* 550 mM of NaCl.

**Spectroscopic Measurements.** UV-vis spectroscopy was carried out on a Hewlett Packard 8453 diode array spectrophotometer at room temperature using a quartz cell (light path length = 1 cm).

**Characterization of MO(OH)/BiVO<sub>4</sub>/FTO Electrodes (M = Fe and Ni).** X-ray photoelectron spectra (XPS) were measured by a Kratos Axis 165x with a 165 mm hemispherical electron energy analyzer. An incident radiation was Al K $\alpha$  X-ray (1486.6 eV) at 200 W and a charge neutralizer was turned on for acquisition. FeO(OH)/BiVO<sub>4</sub>/FTO electrode was attached on a stainless stage with a double-sided carbon scotch tape. The binding energy of each element was corrected by C 1s peak (284.6 eV) from residual carbon. Powder X-ray diffraction patterns were recorded on a Rigaku MiniFlex 600. Incident X-ray radiation was produced by a Cu X-ray tube, operating at 40 kV and 15 mA with Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The scan rate was  $1^\circ \text{ min}^{-1}$  from  $2\theta = 10\text{--}70^\circ$ . Scanning electron microscope images of particles on FTO electrode were observed by a FE-SEM (JSM-6320F or JSM-6701F) operating at 10 kV.

**Electrochemical Measurements.** Cyclic voltammetry (CV) measurements were performed on an ALS 630B electrochemical analyzer. Electrochemical performance of Co<sup>II</sup>(Ch) deposited on a carbon

paper electrode for the catalytic O<sub>2</sub> reduction was evaluated in a N<sub>2</sub>- or O<sub>2</sub>-saturated aqueous HClO<sub>4</sub> (pH 1.3) solution containing NaClO<sub>4</sub> (0.1 M) as a supporting electrolyte and in N<sub>2</sub>- or O<sub>2</sub>-saturated seawater containing HClO<sub>4</sub> (pH 1.3) and NaClO<sub>4</sub> (0.1 M) at 298 K using a conventional three-electrode cell consisting of Co<sup>II</sup>(Ch)/CP as a working electrode and a platinum coil as the counter electrode. The potentials in aqueous solutions were measured with respect to the saturated calomel electrode (SCE) reference electrode and all results in this work are presented against the RHE. The conversion of potentials vs SCE to vs RHE was performed according to the following equation (eq 1).

$$E \text{ (vs RHE)} = E \text{ (vs SCE at measured pH)} + 0.0591 \times \text{pH} + 0.241 \text{ V} \quad (1)$$

The rotating ring-disk electrode (RRDE) measurements were carried out using a BAS RRDE-3A rotator linked to an ALS 730D electrochemical analyzer. A three-electrode cell (100 mL) was employed with the RRDE consisting of a platinum ring (Pt) electrode and a glassy carbon (GC) disk electrode, platinum coil (Pt) as a counter electrode, and SCE as a reference electrode. The voltammograms were measured in an O<sub>2</sub>-saturated aqueous HClO<sub>4</sub> solution (pH 1.3) containing NaClO<sub>4</sub> (0.1 M) at 5 mV s<sup>-1</sup> with various rotating rates (100, 300, 600, 900, 1200, 1500, 2000, 2500, 3000, 3500, 4000, and 4500 rpm). A RRDE for the investigation of transferred electrons during O<sub>2</sub> reduction with Co<sup>II</sup>(Ch)/CP was performed by the modification of GC disk electrode with a thin film of Co<sup>II</sup>(Ch). The thin film was prepared by a solution consisting of MeCN (1 mL) containing Co<sup>II</sup>(Ch) (0.3 mM), MWCNT (1.26 mg), and 5% Nafion (12 μL). For each experiment, the mixture was sonicated for 20 min and then a 10 μL drop was applied on the surface of a polished GC disk electrode and allowed to evaporate to afford a thin film containing a MWCNT loading of 100 μg cm<sup>-2</sup> and a catalyst loading of 3 nmol.

The number of transferred electrons (*n*) is determined by following equation  $n = 4I_D/(I_D + I_R/N)$ , where *I<sub>D</sub>* is the faradic current at the disk electrode, *I<sub>R</sub>* is the faradic current at the ring electrode, and *N* is the collection efficiency of the RRDE. The *N* value is measured using an aqueous solution of K<sub>3</sub>[Fe<sup>III</sup>(CN)<sub>6</sub>] (2 mM) as a standard one-electron redox couple ([Fe<sup>III</sup>(CN)<sub>6</sub>]<sup>3-</sup>/[Fe<sup>II</sup>(CN)<sub>6</sub>]<sup>4-</sup>) in the presence of KNO<sub>3</sub> (0.5 M) and is determined to be *N* = 0.37 when the GC disk electrode of RRDE is loaded with the same amount of MWCNT (100 μg cm<sup>-2</sup>) as used above.<sup>S8</sup>

**Photoelectrochemical Measurements.** Photoelectrochemical measurements were performed in a quartz cell (light path length = 1 cm) using a conventional three-electrode cell consist of as prepared FTO working electrode modified with photocatalysts, a platinum coil counter electrode, and a SCE reference electrode in an air-saturated aqueous solution (8 mL) containing HClO<sub>4</sub> (pH 1.3) and NaClO<sub>4</sub> (0.1 M) at 298 K (Figure S3a). Photoanodes were illuminated from the back side of the FTO electrodes

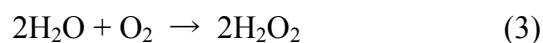
(FTO/electrolyte interface) with a solar simulator (HAL-320, Asahi Spectra Co., Ltd.), where the light intensity was adjusted at  $100 \text{ mW cm}^{-2}$  (AM1.5G) at the sample position by a 1SUN checker (CS-20, Asahi Spectra Co., Ltd.). The faradaic efficiency for  $\text{O}_2$  evolution was determined by following equation (eq 2), where  $F$  denotes faradaic constant ( $9.65 \times 10^4 \text{ C mol}^{-1}$ ).

$$\text{The faradaic efficiency for } \text{O}_2 \text{ evolution (\%)} = \frac{[\text{Amount of evolved } \text{O}_2, \text{ mol}]}{\text{Total charge passed} / 4 \times F, \text{ mol}} \times 100 \quad (2)$$

**Photocatalytic Production of  $\text{H}_2\text{O}_2$ .** Photocatalytic reaction was performed in a quartz anode cell (light path length = 1 cm) connected with a pyrex cathode cell through a Nafion membrane (Figure S3b). The anode cell is composed of as prepared photoanode ( $\text{MO(OH)/BiVO}_4/\text{FTO}$  ( $\text{M} = \text{Fe, Ni}$ )) for the water oxidation in an air-saturated aqueous solution (8 mL) containing  $\text{HClO}_4$  (pH 1.3) and  $\text{NaClO}_4$  (0.1 M). The cathode cell is composed of as prepared cathode ( $\text{Co}^{\text{II}}(\text{Ch})/\text{CP}$ ) for  $\text{O}_2$  reduction in an  $\text{O}_2$ -saturated aqueous solution (10 mL) containing  $\text{HClO}_4$  (pH 1.3) and  $\text{NaClO}_4$  (0.1 M) at 298 K. These two electrodes were connected with alligator clips and copper wire. Photoanodes were illuminated from the back side of the FTO electrode with the solar simulator (HAL-320, Asahi Spectra Co., Ltd.), where the light intensity was adjusted at  $100 \text{ mW cm}^{-2}$  (AM1.5G) at the sample position by the 1SUN checker (CS-20, Asahi Spectra Co., Ltd.). The anode and cathode solution was saturated by continuous bubbling with argon and oxygen gas for 30 min, respectively, before the photocatalytic reaction. The  $\text{O}_2$  bubbling was continued during the photocatalytic reaction. The cathode cell was kept in dark to prevent the decomposition of produced  $\text{H}_2\text{O}_2$  by UV-light irradiation during photocatalytic reaction. The amount of produced hydrogen peroxide was determined by spectroscopic titration with an acidic solution of  $[\text{TiO}(\text{tpypH}_4)]^{4+}$  complex (Ti-TPyP reagent).<sup>S9</sup> The Ti-TPyP reagent was prepared by dissolving 3.40 mg of the  $[\text{TiO}(\text{tpyp})]$  complex in 100 mL of 50 mM hydrochloric acid. A small portion of the reaction solution was sampled and diluted with water depending on the concentration of produced  $\text{H}_2\text{O}_2$ . To 0.25 mL of 4.8 M  $\text{HClO}_4$  and 0.25 mL of the Ti-TPyP reagent, a diluted sample was added. The mixed solution was then allowed to stand for 5 min at room temperature. This sample solution was diluted to 2.5 mL with water and used for the spectroscopic measurement. The absorbance at  $\lambda = 434 \text{ nm}$  was measured by using a Hewlett Packard 8453 diode array spectrophotometer. A blank solution was prepared in a similar manner by adding distilled water instead of the sample solution to Ti-TPyP reagent in the same volume with its absorbance designated as  $A_B$ . The difference in absorbance was determined as follows:  $\Delta A_{434} = A_B - A_S$ . Based on  $\Delta A_{434}$  and the volume of the solution, the amount of hydrogen peroxide was determined.<sup>S8</sup>

**Detection of O<sub>2</sub>.** The concentration of O<sub>2</sub> in the anolyte was monitored during both photocatalytic production of H<sub>2</sub>O<sub>2</sub> and photoelectrochemical measurements (*vide supra*) by using a fluorescence-based oxygen sensor (FOXY Fiber Optic Oxygen Sensor, Ocean Optics). The O<sub>2</sub>-sensing needle probe was installed in a gas-tight quartz anode cell filled with 8 mL of a solution, which left 7 mL of a headspace, through a rubber septum on the end of the cell. The solution and headspace were purged with argon gas for 30 min prior to measurements. Two-point calibration of the O<sub>2</sub> sensor was performed against solutions (air, 20.9% O<sub>2</sub>, and Ar, 0% O<sub>2</sub>) used in each measurement. The amount of O<sub>2</sub> leaked in the anode cell during measurements was determined under dark and subtracted from the data obtained under illumination. The amount of dissolved O<sub>2</sub> in solutions was recorded as mole %. The total amount O<sub>2</sub> evolved in the anode cell was determined using Henry's Law and converted, using the ideal gas law, into  $\mu\text{mol}$ .

**Measurements of Solar-to-H<sub>2</sub>O<sub>2</sub> Energy Conversion Efficiency.** Measurement of solar energy conversion efficiency of the photocatalytic production of H<sub>2</sub>O<sub>2</sub> was carried out in a quartz anode cell (light path length = 1 cm) connected with a pyrex cathode cell through a Nafion membrane as used in photocatalytic production of H<sub>2</sub>O<sub>2</sub> (*vide supra*). The photoanodes were illuminated from the back side of the FTO electrode with the solar simulator (HAL-320, Asahi Spectra Co., Ltd.), where the light intensity was adjusted at 10 ~ 100 mW cm<sup>-2</sup> (AM1.5G) at the sample position by the 1SUN checker (CS-20, Asahi Spectra Co., Ltd.). The amount of produced H<sub>2</sub>O<sub>2</sub> was determined by the titration with the Ti-TPyP reagent (*vide supra*). The solar energy conversion efficiency was determined by equations (3,4), where output energy as H<sub>2</sub>O<sub>2</sub> was calculated by the multiplication of enthalpy change in eq 4( $\Delta H$



Solar Energy Conversion Efficiency (%)

$$= \frac{[\text{Output energy as H}_2\text{O}_2]}{[\text{Energy density of incident solar light}] \times [\text{Irradiation area}]} \times 100$$

$$= \frac{[\text{Enthalpy change of equation (eq 3) } (\Delta H)] \times [\text{Produced amount of H}_2\text{O}_2]}{[\text{Energy density of incident solar light}] \times [\text{Irradiation area}]} \times 100 \quad (4)$$

= 98.3 kJ mol<sup>-1</sup>), and energy density of incident solar light was adjusted at 5 ~ 100 mW cm<sup>-2</sup> s<sup>-1</sup> (Air Mass 1.5 (AM1.5 G)) at the sample position for whole irradiation area (2.5 cm<sup>2</sup>) by the 1 SUN checker (CS-20, Asahi Spectra Co., Ltd.) at room temperature.



**H<sub>2</sub>O<sub>2</sub> Fuel Cell.** Fe<sup>II</sup><sub>3</sub>[Co<sup>III</sup>(CN)<sub>6</sub>]<sub>2</sub> was mounted onto a carbon cloth by drop-casting or by spraying a dispersion of Fe<sup>II</sup><sub>3</sub>[Co<sup>III</sup>(CN)<sub>6</sub>]<sub>2</sub> in isopropanol with an airbrush (TAMIYA Spray-work HG). An aqueous solution of Nafion (0.2 wt.%) was used to protect the film of Fe<sup>II</sup><sub>3</sub>[Co<sup>III</sup>(CN)<sub>6</sub>]<sub>2</sub> on a carbon cloth. A Ni mesh (150 mesh) and Fe<sup>II</sup><sub>3</sub>[Co<sup>III</sup>(CN)<sub>6</sub>]<sub>2</sub> that was mounted onto a carbon cloth were immersed in the solution of H<sub>2</sub>O<sub>2</sub>. The performance tests of H<sub>2</sub>O<sub>2</sub> fuel cell were conducted in a one-compartment cell with the reaction solution containing H<sub>2</sub>O<sub>2</sub> produced by the photocatalytic reaction transferred from the cathode cell of the two-compartment cell system. The current and power values normalized by the geometric surface area of an electrode were recorded on an ALS 630B electrochemical analyzer and KFM 2005 FC impedance meter at 25°C. The performance tests in solutions containing various concentrations of standard H<sub>2</sub>O<sub>2</sub>, HClO<sub>4</sub> (pH 1), and NaCl (1.0 M) were performed for the control experiment (Figure S4).

**Energy Conversion Efficiency of an H<sub>2</sub>O<sub>2</sub> Fuel Cell.** Fe<sup>II</sup><sub>3</sub>[Co<sup>III</sup>(CN)<sub>6</sub>]<sub>2</sub>/carbon cloth and Ni mesh electrodes were prepared as noted above. Each electrode was connected with Pt wire and protected by PP (polypropylene) sheet to avoid electrical short circuit. The performance tests were conducted in a well-sealed one-compartment cell with a rubber septum. The reaction solution containing H<sub>2</sub>O<sub>2</sub> (0.3 M), NaCl (1.0 M) and Sc(NO<sub>3</sub>)<sub>3</sub>•4H<sub>2</sub>O (0.1 M)<sup>S10</sup> and the headspace (6.5 mL) of the one-compartment cell were purged separately with argon gas for 30 min prior to measurements. After the argon-saturated reaction solution was transferred to the one-compartment cell using gas-tight syringe, cell voltage, applying constant current of 3.3 mA, was recorded on a KFM 2005 FC impedance meter at 25°C. The amount of evolved O<sub>2</sub> gas in the headspace of one-compartment cell was quantified by a Shimadzu GC-17A gas chromatograph (GC) [Ar carrier, a capillary column with molecular sieves (Agilent Technologies, 19095PMS0, 30 m × 0.53 mm) at 313 K] equipped with a thermal conductivity detector (TCD). The energy conversion efficiency of H<sub>2</sub>O<sub>2</sub> fuel cell was determined to be 50 ~ 30% by following equations (5 and 6), where consumed chemical energy as H<sub>2</sub>O<sub>2</sub> was calculated by the multiplication of enthalpy change ( $\Delta H = -98.3 \text{ kJ mol}^{-1}$ ) and twice of the produced amount of O<sub>2</sub>.<sup>S8</sup>



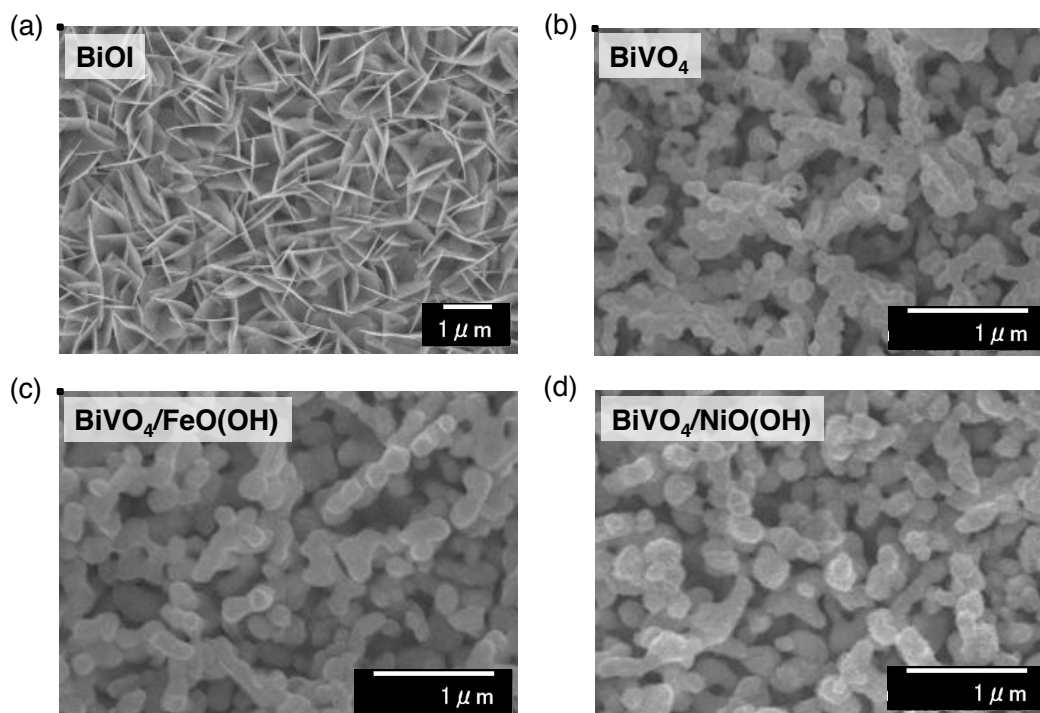
Energy Conversion Efficiency of H<sub>2</sub>O<sub>2</sub> Fuel Cell (%)

$$= \frac{[\text{Output energy as electrical energy}]}{[\text{Consumed chemical energy as H}_2\text{O}_2]} \times 100$$

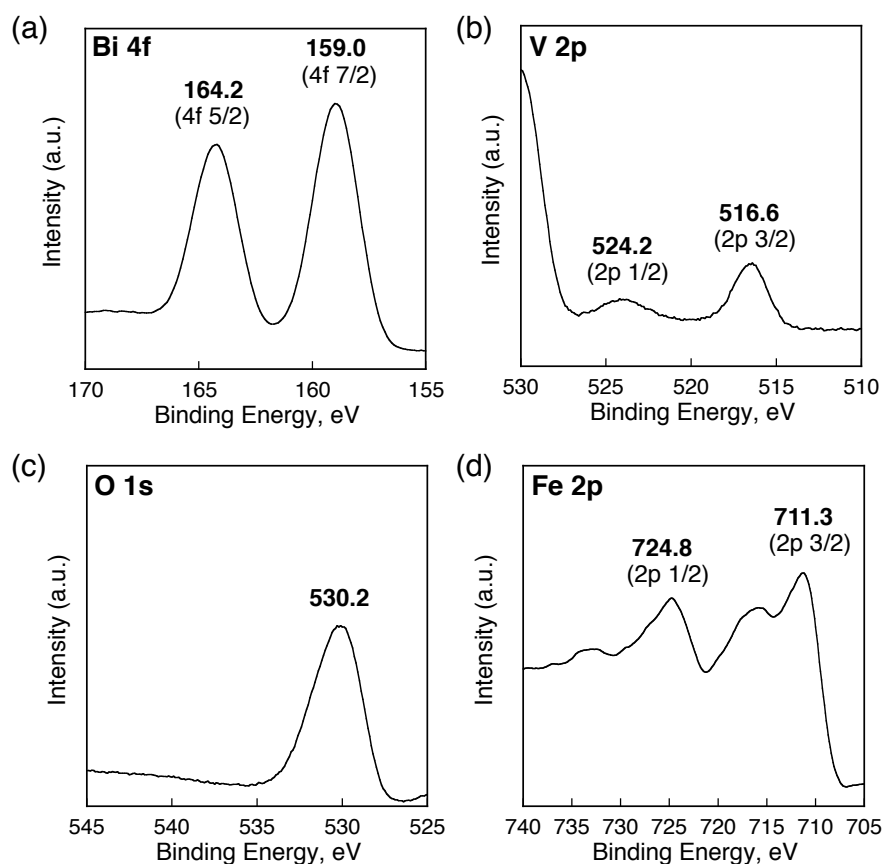
$$= \frac{[\text{Cell voltage}] \times [\text{Current}] \times [\text{Reaction time}]}{[\text{Enthalpy change of equation (eq 5) } (\Delta H)] \times [\text{Produced amount of O}_2] \times 2} \times 100 \quad (6)$$

## References for SI

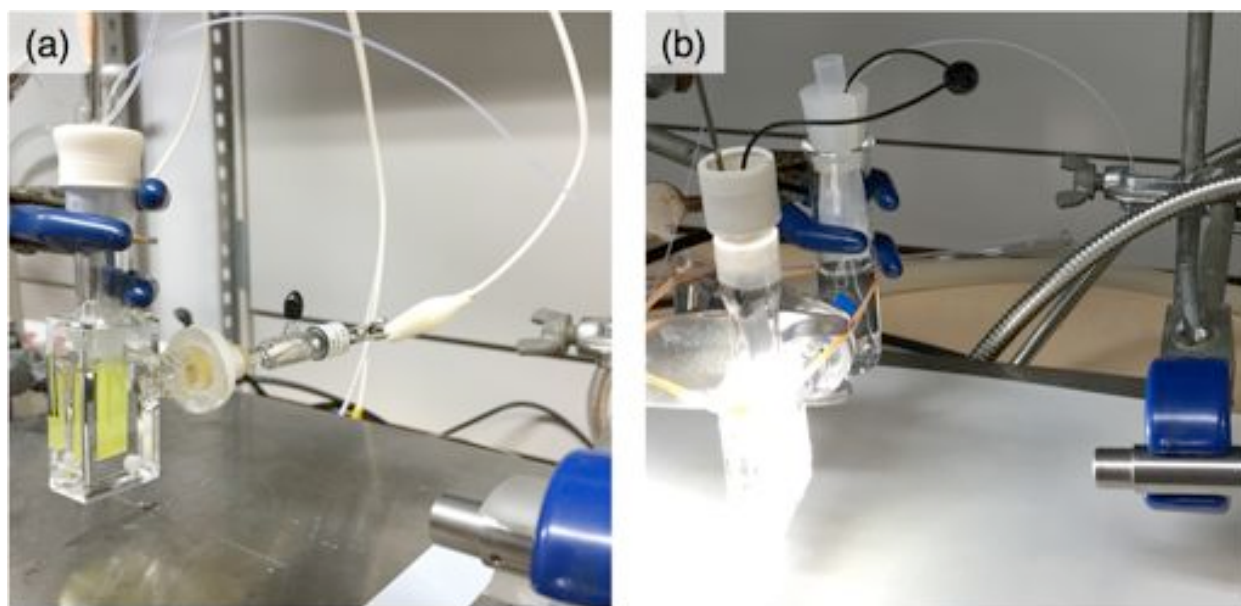
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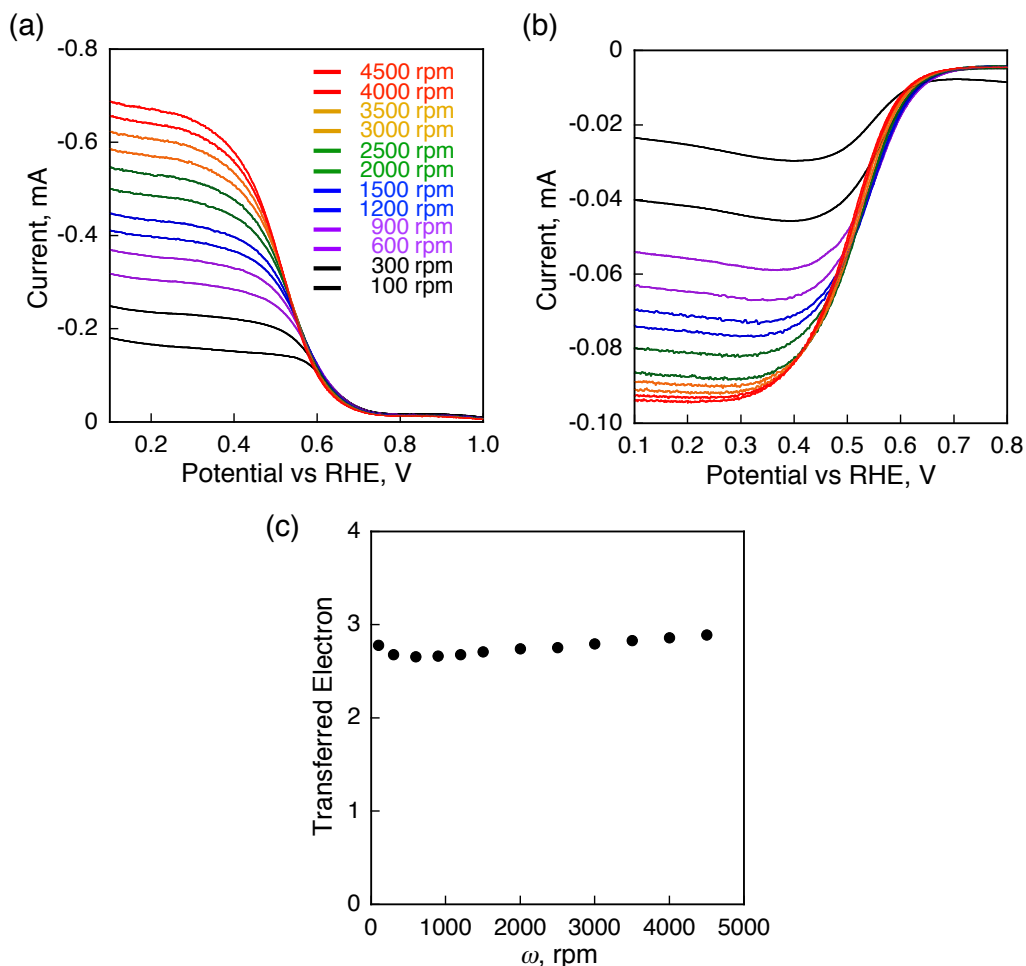
**Figure S1.** SEM images of (a) as-deposited BiOI/FTO electrode, (b) as-prepared BiVO<sub>4</sub>/FTO electrode, and (c) as-prepared FeO(OH)/BiVO<sub>4</sub>/FTO electrode. (d) as-prepared NiO(OH)/BiVO<sub>4</sub>/FTO electrode.



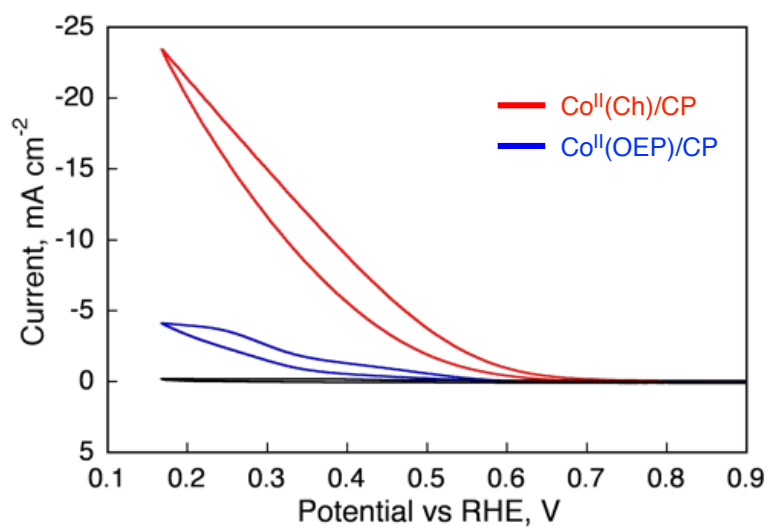
**Figure S2.** X-ray photoelectron spectra in the binding energy regions of (a) Bi 4f, (b) V 2p, (c) O 1s, and (d) Fe 2p for as prepared FeO(OH)/BiVO<sub>4</sub>/FTO electrode.



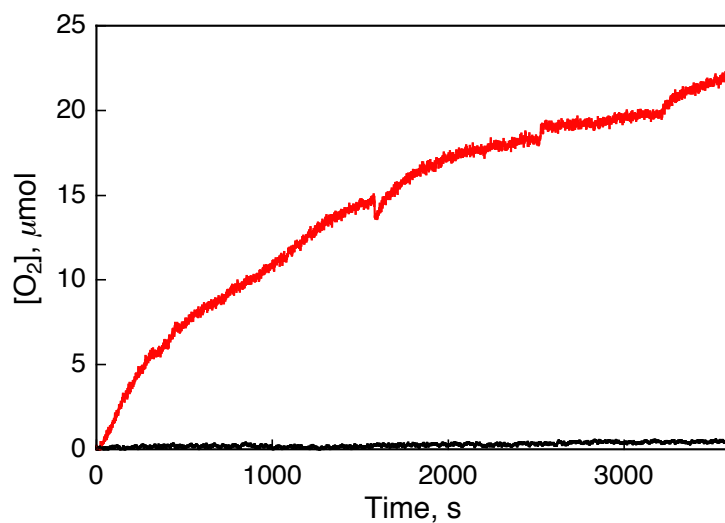
**Figure S3.** (a) A photoelectrochemical cell composed of the as prepared m-WO<sub>3</sub>/FTO electrode, a platinum coil counter electrode, and a SCE reference electrode. (b) A photoelectrochemical cell connected with a pyrex cathode cell through a Nafion membrane.



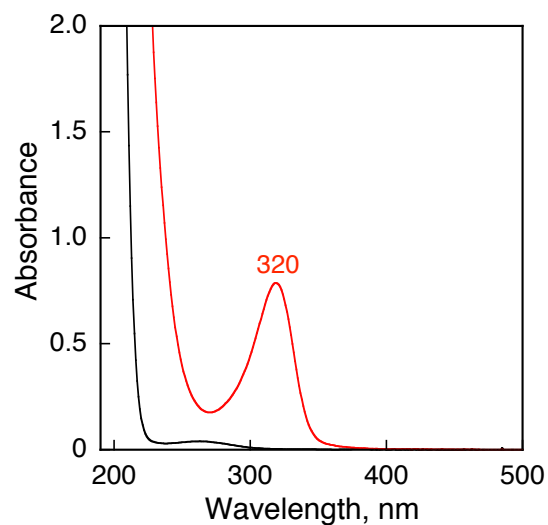
**Figure S4.** Linear sweep voltammograms (polarization curves) of an  $O_2$ -saturated aqueous solution in the presence of  $HClO_4$  (1.0 M) recorded at a rotating-ring (Pt)-disk (GC with physisorbed MWCNT/Co(Ch) electrode). (a) Currents at disk electrode for the reduction of  $O_2$ . (b) Currents at ring electrode for the re-oxidation of  $H_2O_2$  with applied potential at 1.44 V vs RHE. Sweep rate:  $5 \text{ mV s}^{-1}$ . (c) Plot of the number of transferred electrons at 0.24 V as a function of rotation rates.



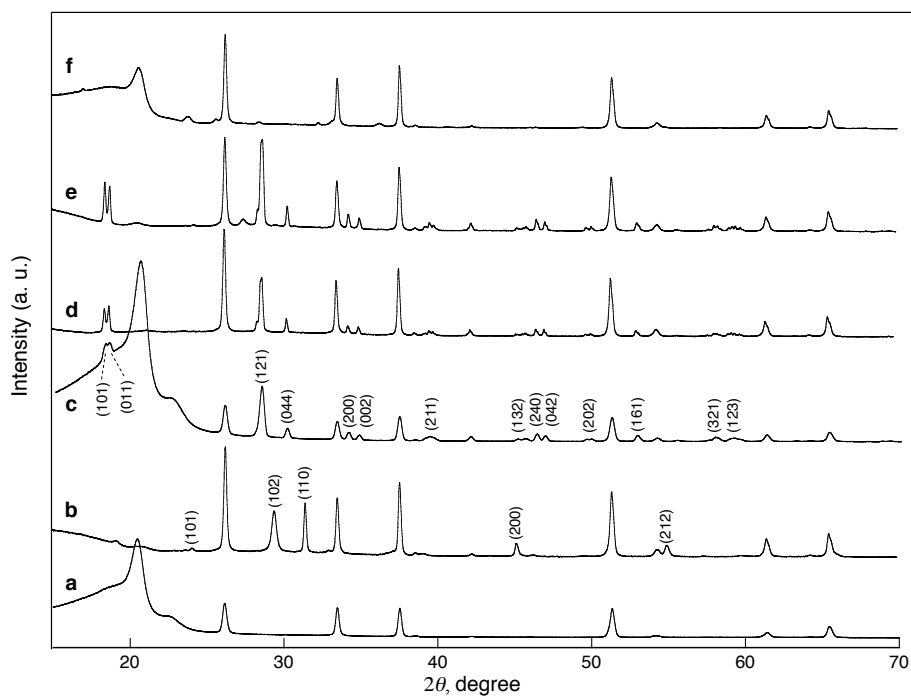
**Figure S5.** Cyclic voltammograms of an  $\text{O}_2$ -saturated aqueous  $\text{HClO}_4$  (pH 1.3) solution containing 0.1 M  $\text{NaClO}_4$  recorded at  $\text{Co}^{\text{II}}(\text{Ch})/\text{CP}$  electrode (red) and  $\text{Co}^{\text{II}}(\text{OEP})/\text{CP}$  electrode (blue). The black line shows cyclic voltammogram of  $\text{N}_2$ -saturated aqueous solution recorded at  $\text{Co}^{\text{II}}(\text{Ch})/\text{CP}$  electrode.; Sweep rate:  $0.1 \text{ V s}^{-1}$ .



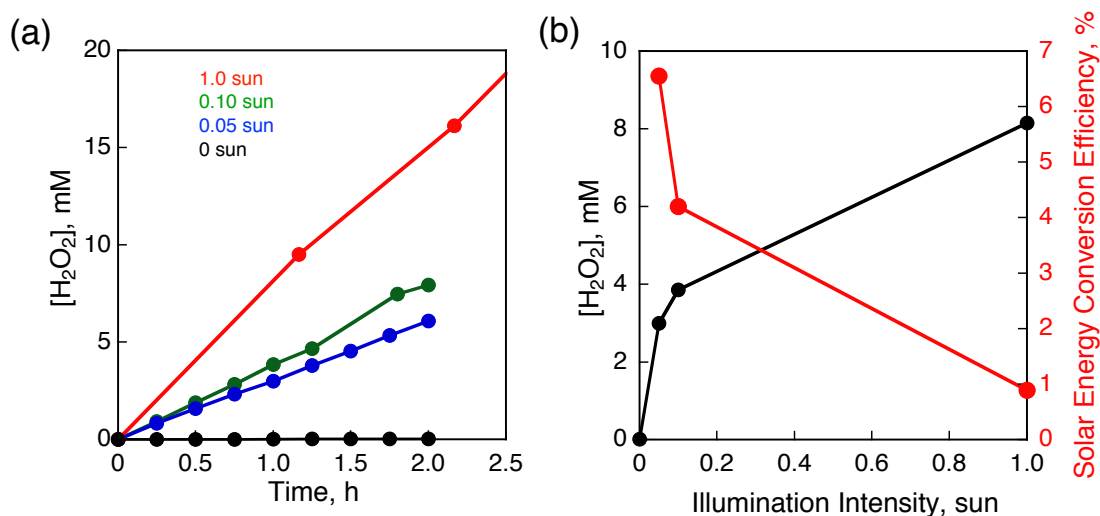
**Figure S6.** Time courses of  $\text{O}_2$  evolution for the water oxidation with the  $\text{FeO}(\text{OH})/\text{BiVO}_4/\text{FTO}$  electrode measured at 0.59 V (vs RHE) in an Ar-saturated pH 1.3 water containing 0.1 M  $\text{NaClO}_4$  under simulated 1 sun (AM 1.5G,  $100 \text{ mW cm}^{-2}$ ) illumination (red) and under dark (black).



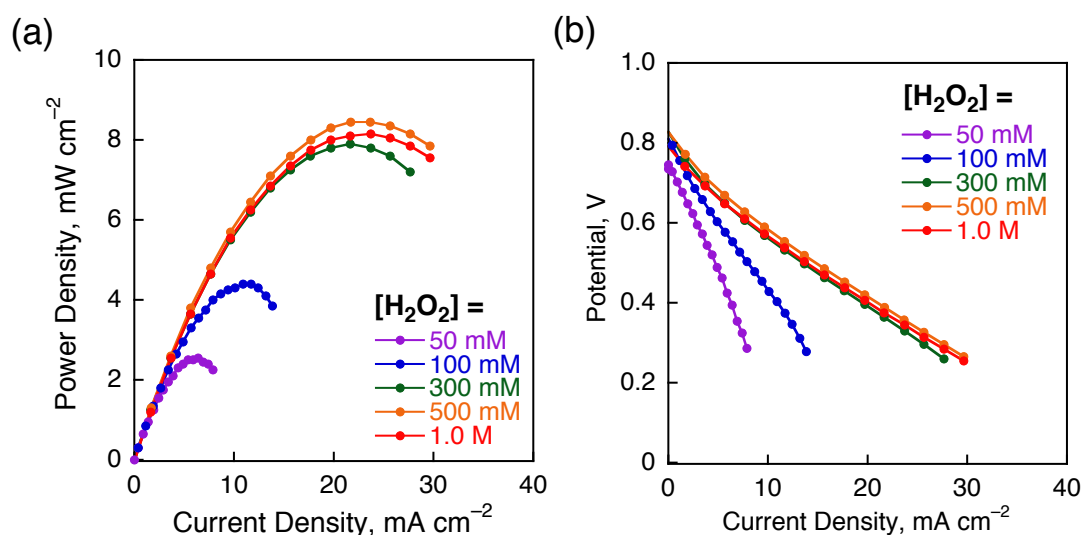
**Figure S7.** Absorption spectra of the reaction solution in the anode cell. The black and red lines show the spectra before and after 17 h of photocatalytic reaction in pH 1.3 seawater containing 0.1 M NaClO<sub>4</sub> under simulated 1 sun (AM 1.5G, 100 mW cm<sup>-2</sup>) illumination, respectively.



**Figure S8.** Powder X-ray diffraction pattern of (a) FTO electrode, (b) as-deposited BiOI/FTO electrode, (c) as-prepared BiVO<sub>4</sub>/FTO electrode, (d) as-prepared FeO(OH)/BiVO<sub>4</sub>/FTO electrode, (e) as-prepared FeO(OH)/BiVO<sub>4</sub>/FTO electrode after photocatalytic reaction in pH 1.3 water containing 0.1 M NaClO<sub>4</sub> for 24 h, and (f) as-prepared FeO(OH)/BiVO<sub>4</sub>/FTO electrode after photocatalytic reaction in pH 1.3 seawater containing 0.1 M NaClO<sub>4</sub> for 17 h. Blue circles indicate the peaks derived from FTO electrode.



**Figure S9.** (a) Time courses of the photocatalytic production of  $\text{H}_2\text{O}_2$  in the two-compartment cell composed of  $\text{FeO}(\text{OH})/\text{BiVO}_4/\text{FTO}$  photoanode and  $\text{Co}^{\text{II}}(\text{Ch})/\text{CP}$  cathode in pH 1.3 aqueous solutions containing 0.1 M  $\text{NaClO}_4$  under different intensity of simulated illumination (AM 1.5G,  $100 \text{ mW cm}^{-2}$  for 1 sun conditions); 0 sun (black), 0.05 sun (blue), 0.10 sun (green), and 1.0 sun (red). (b) Plots of the produced amount of  $\text{H}_2\text{O}_2$  and solar energy conversion efficiency vs illumination intensity determined after 1 h of photocatalytic reaction. The value of solar energy conversion efficiency was determined from the produced amount of  $\text{H}_2\text{O}_2$  during initial 1 h illumination.



**Figure S10.** (a)  $I$ - $P$  and (b)  $I$ - $V$  curves of the one-compartment  $\text{H}_2\text{O}_2$  fuel cell with a Ni mesh anode and  $\text{Fe}^{\text{II}}_3[\text{Co}^{\text{III}}(\text{CN})_6]_2/\text{carbon cloth}$  cathode in an aqueous  $\text{HClO}_4$  (pH 1.0) solution containing various concentration of authentic  $\text{H}_2\text{O}_2$  (50 mM ~ 1 M) and  $\text{NaCl}$  (1.0 M) as a supporting electrolyte.