

## Supporting Information

### Experimental Section

All reagents were commercially available, of reagent grade and used without further purification.

#### Preparation of the WO<sub>3</sub>/BiVO<sub>4</sub>/MeO<sub>x</sub> photoanodes

The WO<sub>3</sub>/BiVO<sub>4</sub> photoelectrode was prepared on an F-doped SnO<sub>2</sub> conductive glass (FTO) substrate (Nippon Sheet Glass Co., Ltd.) via spin coating. Typically, *N,N*-dimethylformamide (DMF) solutions of tungsten hexachloride (WCl<sub>6</sub>), adjusted to 504 mM, was coated onto the FTO via spin coating (1000 rpm, 15 s) and the film then calcined at 500°C for 30 min. Then, the WO<sub>3</sub> layers were coated using WCl<sub>6</sub>, adjusted to 252 mM, resulting in the formation of a WO<sub>3</sub> underlayer.

A mixed solution of 0.5 M bismuth oxide solution (0.4 mL) and 0.4 M vanadium oxide solution (0.5 mL) of enhanced metal–organic decomposition (EMOD) materials (Symetrix Co., USA), butyl acetate (2.1 mL) and 10 wt% ethylcellulose (2.0 mL) as a thickener and aggregation inhibition agent was coated on the WO<sub>3</sub> underlayer via spin coating (500 rpm, 15 s). Then, the film was calcined at 550°C for 30 min to form the WO<sub>3</sub>/BiVO<sub>4</sub> photoelectrodes. The thickness of WO<sub>3</sub> and BiVO<sub>4</sub> were *ca.* 150–200 nm and 100–200 nm, respectively.<sup>28</sup>

The introduction of MeO<sub>x</sub> onto the WO<sub>3</sub>/BiVO<sub>4</sub> was performed via the same spin coating method (1000 rpm, 15 s) using EMOD materials (60 mM) of various metal precursors solved in butyl acetate containing ethylcellulose. After spin coating, the film was calcined at 550°C for 30 min to form WO<sub>3</sub>/BiVO<sub>4</sub>/MeO<sub>x</sub>.

The Al<sub>2</sub>O<sub>3</sub> particle for N<sub>2</sub> adsorption–desorption measurement was prepared by evaporating and calcining Al<sub>2</sub>O<sub>3</sub> of EMOD solved in butyl acetate containing ethylcellulose in the same condition.

#### Characterisation

The photoanodes were characterised using scanning electron microscopy (SEM, Hitachi, Ltd., S-4800), X-ray diffraction (XRD, PANalytical, EMPYREAN) and X-ray fluorescence spectroscopy (XRF, Rigaku, ZSXmini). The pore size of Al<sub>2</sub>O<sub>3</sub> was calculated by N<sub>2</sub> adsorption-desorption measurement using a BELSORP-mini II (MicrotracBEL Corp) at 77 K. The light harvesting efficiency (LHE) was calculated from Equation (S1) using UV-vis spectroscopy (JASCO, V-570, ISN-470).

$$LHE = 1 - \%R - \%T \quad (S1)$$

where %*R* and %*T* represent the reflectance and transmittance, respectively; these values were obtained from the UV-vis measurements.

#### Photoelectrochemical production of H<sub>2</sub>O<sub>2</sub>

##### 1. Photoelectrochemical properties

The photoelectrochemical performance of the photoanodes was measured using an electrochemical analyser (BAS. Inc., ALS660B) and a solar simulator (SAN-EI ELECTRIC Co., XES-151S) calibrated to AM-1.5 (1 sun, 100 mW cm<sup>-2</sup>) with a spectroradiometer (SOMA Optics, Ltd.). The irradiation area (0.28 cm<sup>2</sup>) was limited using a black mask. The simulated solar light was applied from the semiconductor side.

The current–voltage (*I*–*V*) characteristics were studied using a one-compartment cell comprising a photoanode equipped with a back reflection plate as the working electrode; an Ag/AgCl electrode as the reference electrode; and a Pt mesh as the counter electrode at a low scan rate (50 mV s<sup>-1</sup>). Aqueous solution of 0.5 M KHCO<sub>3</sub>, adjusted to pH 7.3 by CO<sub>2</sub> bubbling, were utilised as electrolytes.

##### 3. Simultaneous production and/or accumulation of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub> from H<sub>2</sub>O as the raw material

The simultaneous production and accumulation of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub> was performed under CO<sub>2</sub> bubbling with a Pt mesh as a cathode and a two-compartment cell, equipped with a Nafion membrane (thickness: 0.0035 in) as an ion-exchange membrane, between the anode and

cathode. Aqueous solutions (anode: 35 mL; cathode: 35 mL) of 0.1–2.0 M KHCO<sub>3</sub> (pH 6.9–7.7) were utilised as electrolytes. In the photoelectrochemical production of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>, using a two-compartment cell, photoanodes of sizes 1.2 cm × 5.5 cm were used without a black mask.

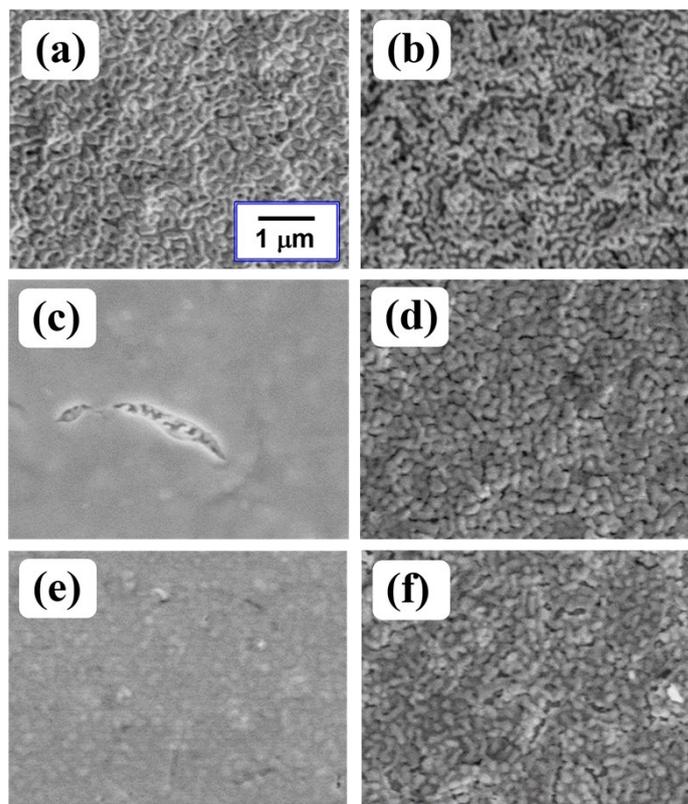
The quantification of H<sub>2</sub>O<sub>2</sub> in the liquid phase was performed using two different colorimetry methods by a reductive reaction from Ce<sup>4+</sup> to Ce<sup>3+</sup> and by an oxidative reaction from Fe<sup>2+</sup> to Fe<sup>3+</sup> using a microplate reader (Tecan Japan Co., Ltd., infinite M200PRO). The H<sub>2</sub>O<sub>2</sub> amount measured in the colorimetry using Fe<sup>2+</sup> were in close agreement with that in the colorimetry using Ce<sup>4+</sup>. The colorimetry using Fe<sup>2+</sup>, which can be easily measured, was used as the main quantification method, as shown in Equation (S2).<sup>28-30</sup>



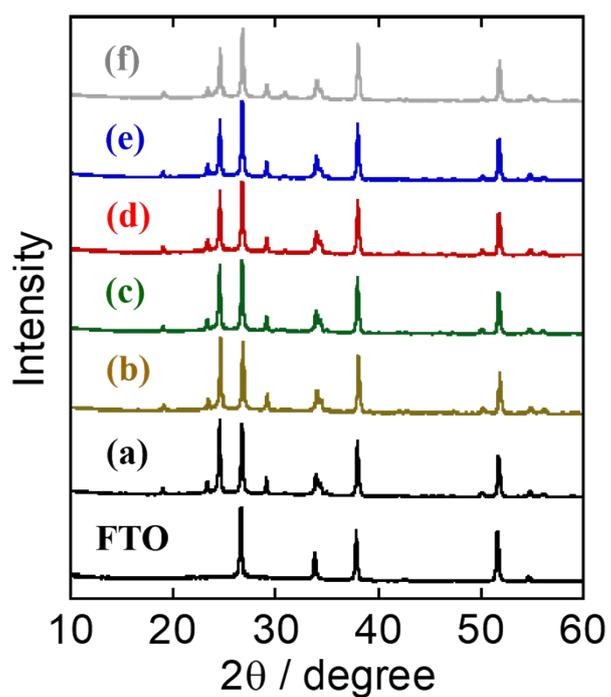
In aqueous solutions of 0.1–0.5 M KHCO<sub>3</sub>, 0.1 mL of 0.1 M FeCl<sub>2</sub> in 1.0 M HCl aqueous solution was added to a mixed solution containing 1.0 mL of sample and 0.9 mL of 1.0 M HCl aqueous solution. Then, the H<sub>2</sub>O<sub>2</sub> concentration was measured by Fe<sup>3+</sup> colorimetry (330 nm). In 1.0–2.0 M KHCO<sub>3</sub> aqueous solutions, 0.1 mL of 0.1 M FeCl<sub>2</sub> in 1.0 M HCl was added to a mixed solution containing 1.0 mL of sample and 0.9 mL of 3.0 M HCl aqueous solution. Then, the H<sub>2</sub>O<sub>2</sub> concentration was measured by Fe<sup>3+</sup> colorimetry (330 nm).

The faradaic efficiencies of H<sub>2</sub>O<sub>2</sub> ( $\eta(\text{H}_2\text{O}_2)$ ) can be calculated as shown in Equation (S3), which takes into consideration the reaction shown in Equation (1).

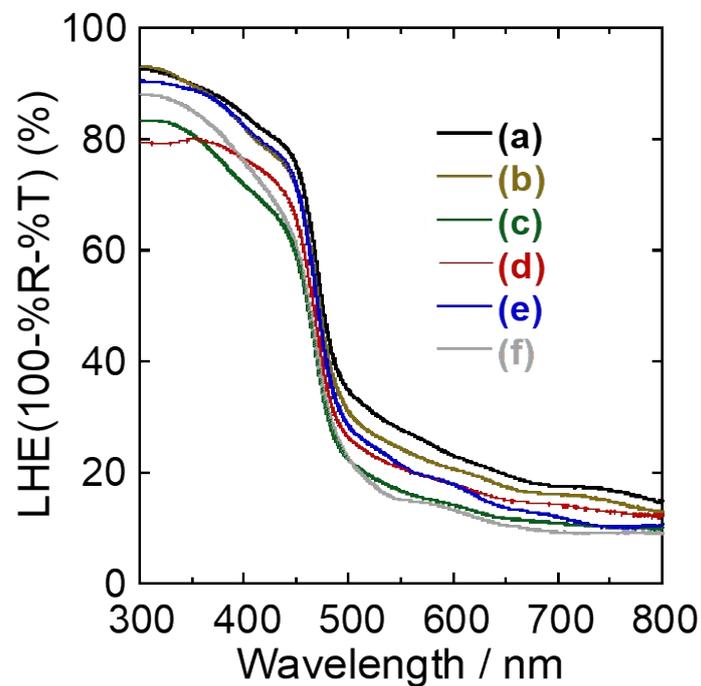
$$\begin{aligned} \eta(\text{H}_2\text{O}_2) &= (\text{amount of generated H}_2\text{O}_2) \times 100 / (\text{theoretical amount of H}_2\text{O}_2) \\ &= (\text{amount of generated H}_2\text{O}_2) \times 100 / (\text{amount of generated electrons} / 2) \end{aligned} \quad (\text{S3})$$



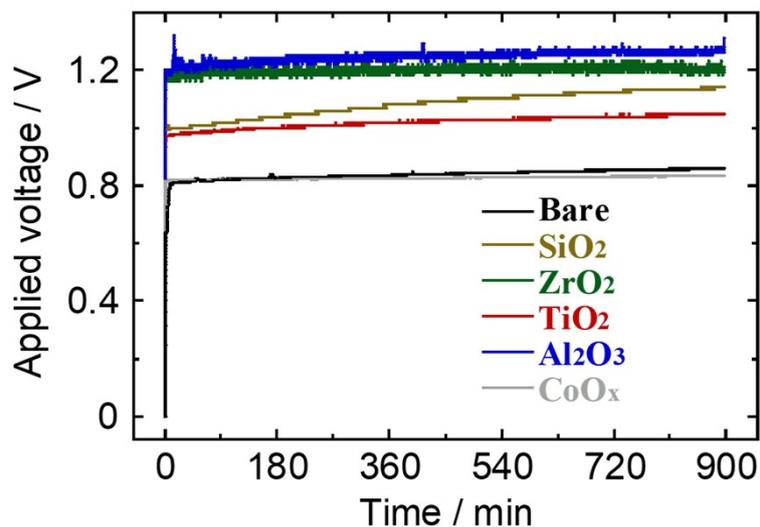
**Fig. S1** SEM images of (a) bare, (b) SiO<sub>2</sub>, (c) ZrO<sub>2</sub>, (d) TiO<sub>2</sub>, (e) Al<sub>2</sub>O<sub>3</sub> and (f) CoOx modified WO<sub>3</sub>/BiVO<sub>4</sub> photoanodes.



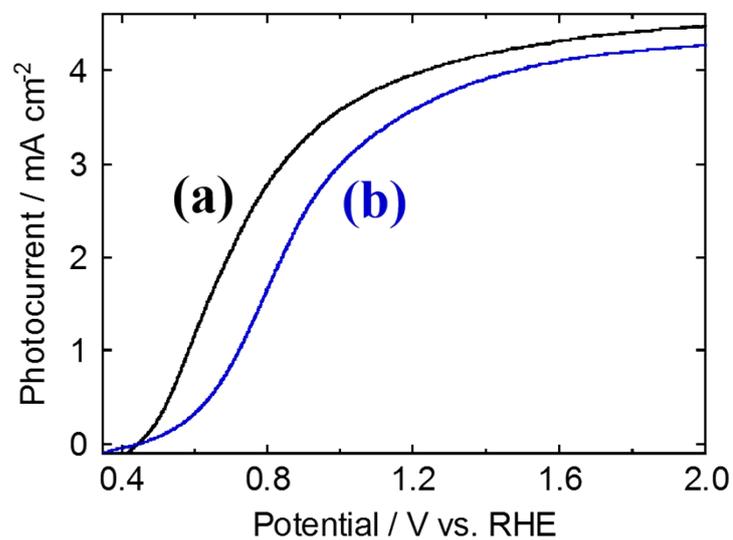
**Fig. S2** XRD spectra of (a) bare, (b) SiO<sub>2</sub>, (c) ZrO<sub>2</sub>, (d) TiO<sub>2</sub>, (e) Al<sub>2</sub>O<sub>3</sub> and (f) CoOx modified WO<sub>3</sub>/BiVO<sub>4</sub> photoanodes.



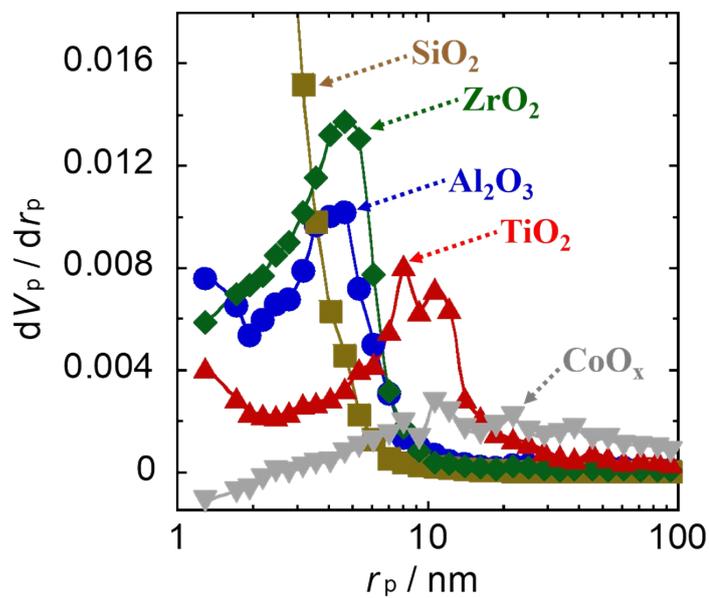
**Fig. S3** LHE spectra of (a) bare, (b) SiO<sub>2</sub>, (c) ZrO<sub>2</sub>, (d) TiO<sub>2</sub>, (e) Al<sub>2</sub>O<sub>3</sub> and (f) CoO<sub>x</sub> modified WO<sub>3</sub>/BiVO<sub>4</sub> photoanodes.



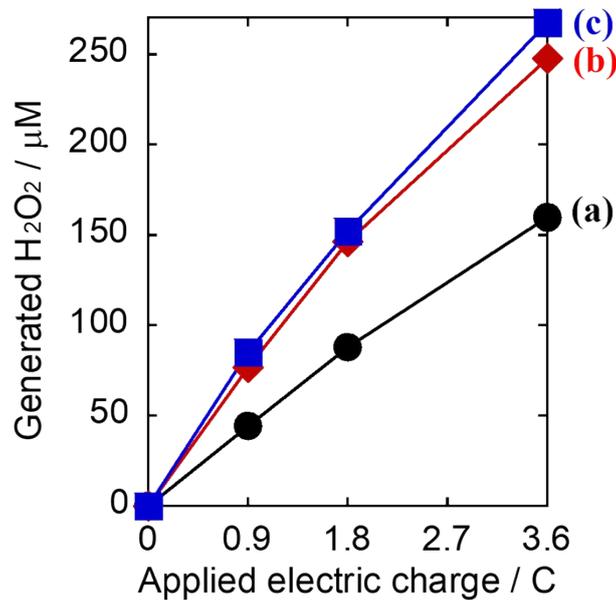
**Fig. S4** Time courses of voltages applied between photoanode and a counter electrode of Pt mesh at steady photocurrent of 1 mA in oxidative H<sub>2</sub>O<sub>2</sub> generation reaction shown in Fig. 2 in a 0.5 M KHCO<sub>3</sub> aqueous electrolyte in an ice bath (below 5°C) on WO<sub>3</sub>/BiVO<sub>4</sub>/MeO<sub>x</sub> photoanodes under simulated solar light irradiation.



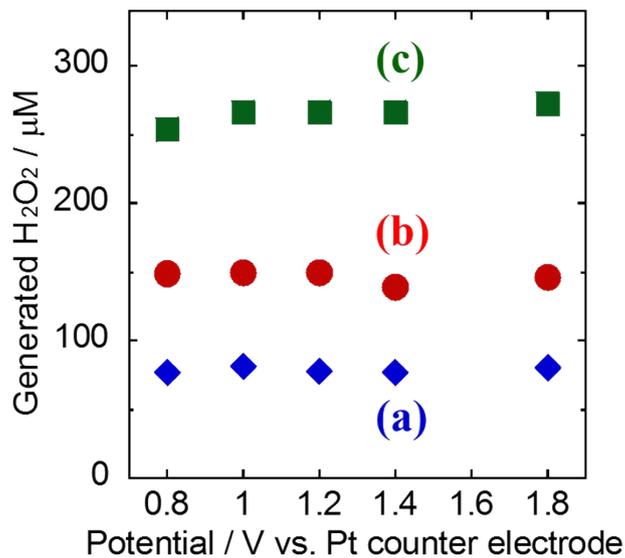
**Fig. S5**  $I$ - $V$  curves in an aqueous electrolyte of 0.5 M KHCO<sub>3</sub> on a (a) bare WO<sub>3</sub>/BiVO<sub>4</sub> and (b) WO<sub>3</sub>/BiVO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> photoanodes under simulated solar light irradiation.



**Fig. S6** Pore size distributions of the MeOx particles calculated by the BJH method from N<sub>2</sub> absorption and desorption measurements.



**Fig. S7** Oxidative H<sub>2</sub>O<sub>2</sub> generation in a 0.5 M KHCO<sub>3</sub> aqueous electrolyte in an ice bath (below 5°C) under simulated solar light irradiation at steady photocurrent of 1 mA on (a) WO<sub>3</sub>/BiVO<sub>4</sub> photoanode and WO<sub>3</sub>/BiVO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> photoanodes prepared at spin coating number of (b) 500 rpm and (c) 1000 rpm.



**Fig. S8** Effect of the voltages applied between a WO<sub>3</sub>/BiVO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> photoanode as the working electrode and a Pt mesh as counter electrode using 0.5 M KHCO<sub>3</sub> aqueous solution (35 mL) under CO<sub>2</sub> gas bubbling and simulated solar light irradiation in an ice bath (below 5°C) on oxidative H<sub>2</sub>O<sub>2</sub> generation. Applied electric charge (C): (a) 0.9, (b) 1.8 and (c) 3.6.