Supporting Information

Efficient oxidative hydrogen peroxide production and accumulation in photoelectrochemical water splitting using a tungsten trioxide/bismuth vanadate photoanode

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Experimental Section

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

Preparation of the $WO_3/BiVO_4$ photoelectrodes

The $WO_3/BiVO_4$ photoelectrode was prepared on F-doped SnO_2 conductive glass (FTO) substrate (Nippon Sheet Glass Co., Ltd.) by spin coating. Typically, *N,N*-dimethylformamide (DMF) solutions of tungsten hexachloride (WCl_6) adjusted to 504 mM was coated on FTO by spin coating (1000 rpm, 15 s), and then, the film was calcined at 500°C for 30 min. The coating of WO_3 layers was again performed using WCl_6 adjusted to 252 mM, resulting in the formation of a WO_3 underlayer possessing a rough porous surface.

The mixed solution (Bi:V=1:1) of bismuth oxide and vanadium oxide of EMOD (enhanced metal organic decomposition) materials (Symetrix Co., USA) solved in butyl acetate containing ethylcellulose as a thickener and aggregation inhibition agent was coated on the WO_3 underlayer by spin coating (500 rpm, 15 s). Then, the film was calcined at 550°C for 30 min to form $WO_3/BiVO_4$ photoelectrodes.

Characterization

The $WO_3/BiVO_4$ photoanodes were characterized using X-ray photoelectron spectrometer (XPS, Ulvac-Phi, XPS-1800), X-ray fluorescence spectroscopy (XRF, Rigaku, ZSXmini), scanning electron microscopy (SEM, Hitachi, Ltd., S-4800) and scanning transmission electron microscopy (STEM, Hitachi High-Technologies Co., Ltd., HD-2700).

Photoelectrochemical production of H_2O_2 and H_2

1. Photoelectrochemical properties

The photoelectrochemical performance of the $WO_3/BiVO_4$ photoelectrodes was measured using an electrochemical analyzer (BAS. Inc., ALS660B) and a solar simulator (SAN-EI ELECTRIC Co., XES-151S), calibrated to AM-1.5 (1 SUN, 100 mW cm^{-2}) using a spectroradiometer (SOMA Optics, Ltd.). The irradiation area (0.28 cm^2) was limited using a black mask. The simulated solar light was irradiated from the semiconductor side.

The current-voltage (*I-V*) characteristics were studied using a one-compartment cell consisting of a $WO_3/BiVO_4$ photoelectrode equipped with a back reflection plate as the working electrode, a Ag/AgCl electrode as the reference electrode, and a Pt mesh as the counter electrode at a low scan rate (50 mV s^{-1}). Aqueous solution of 0.5 M $KHCO_3$ adjusted to pH 7.3 by CO_2 gas bubbling, 0.5 M K_2SO_4 (pH 6.2), 0.5 M H_3BO_3 adjusted to pH 7.1 by the addition of KOH, and 0.5 M phosphate buffer (pH 6.9) were utilized as electrolytes.

2. Production and/or accumulation of H_2O_2 and H_2 using a two-compartment cell

The production and accumulation of H_2O_2 and H_2 were performed with CO_2 or Ar gas bubbling using a two-compartment cell equipped with a Nafion membrane (thickness 0.0035 in.) as an ion-exchange membrane between the anode and cathode. Aqueous solution (anode: 35 mL, cathode: 35 mL) of 0.1–2.0 M $KHCO_3$ (pH 6.9–7.7), 0.5 M K_2SO_4 (pH 6.2), 0.5 M H_3BO_3+KOH (pH 7.1), and 0.5 M phosphate buffer (pH 6.9) were utilized as electrolytes. In the photoelectrochemical production and accumulation of H_2O_2 and H_2 using a two-compartment cell, anode electrodes possessing size of 1.2 cm×5.5 cm were used without a black mask.

The amount of H_2O_2 in the liquid phase of the anode was measured by colorimetry of the color changes from Fe^{2+} to Fe^{3+}, as shown in Equation (S1)[1], using a microplate reader (Tecan Japan Co., Ltd., infinite M200PRO).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + 2OH^- \qquad \text{(S1)}$$

In aqueous solution of 0.1–0.5 M $KHCO_3$, 0.5 M K_2SO_4, 0.5 M H_3BO_3+KOH, and 0.5 M phosphate buffer, 0.1 mL of 0.1 M $FeCl_2$ 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_2O_2 concentration was measured by Fe^{3+} colorimetry (330 nm). In 1.0–2.0 M $KHCO_3$ aqueous solution, 0.1 mL of 0.1 M $FeCl_2$ 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_2O_2 concentration was measured by Fe^{3+} colorimetry (330 nm). The amounts of O_2 in the gas phase of the anode and H_2 in the cathode were measured using a Shimadzu GC-8A gas chromatograph equipped with a MS-5A column.

The Faraday efficiencies of H_2 and H_2O_2 ($\eta(H_2)$ and $\eta(H_2O_2)$) can be calculated as shown in Equation (S2), which takes into consideration the reaction shown in Equation (2-3).

$$\begin{aligned}\eta(\mathrm{H_2})\ \text{or}\ \eta(\mathrm{H_2O_2}) &= [\text{amount of generated } \mathrm{H_2} \text{ or } \mathrm{H_2O_2}]\times 100 \\ &\qquad / \, [\text{theoretical amount of } \mathrm{H_2} \text{ or } \mathrm{H_2O_2}] \\ &= [\text{amount of generated } \mathrm{H_2} \text{ or } \mathrm{H_2O_2}]\times 100 \\ &\qquad / \, [\text{amount of generated electrons} / 2] \qquad \text{(S2)}\end{aligned}$$

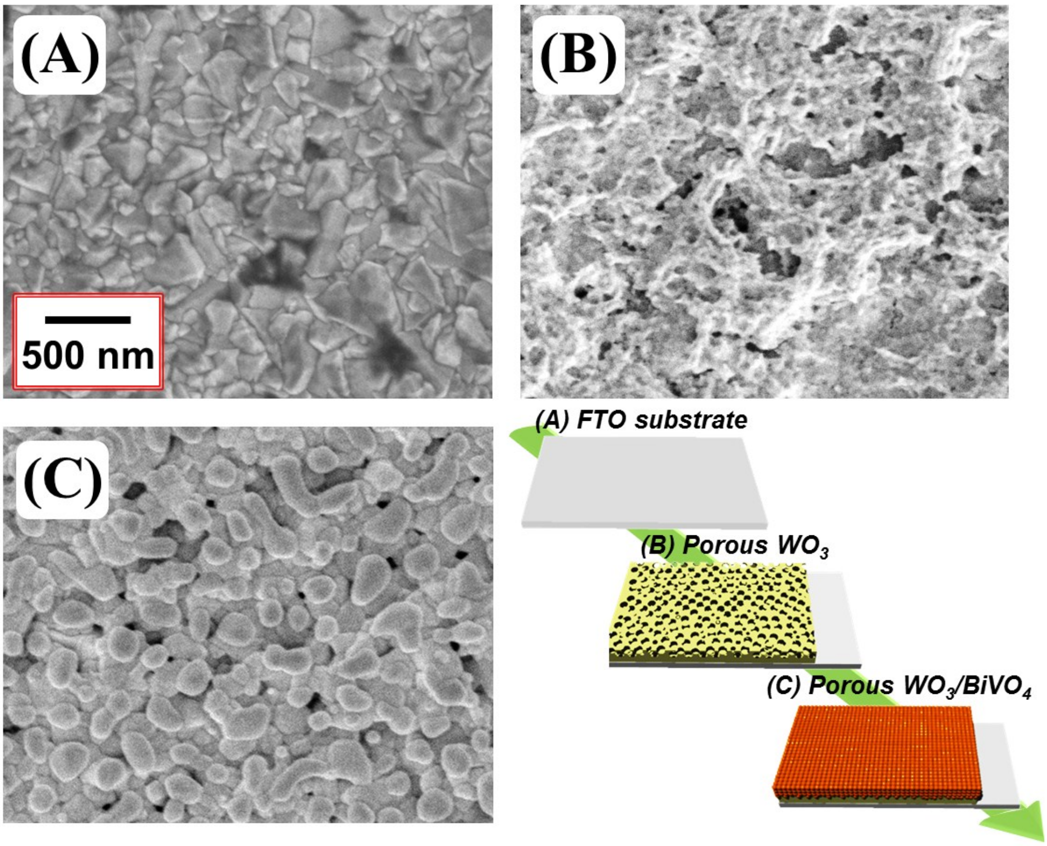

Fig. S1 SEM images of (A) FTO substrate, (B) WO$_3$ underlayer, and (C) WO$_3$/BiVO$_4$ photoelectrode.

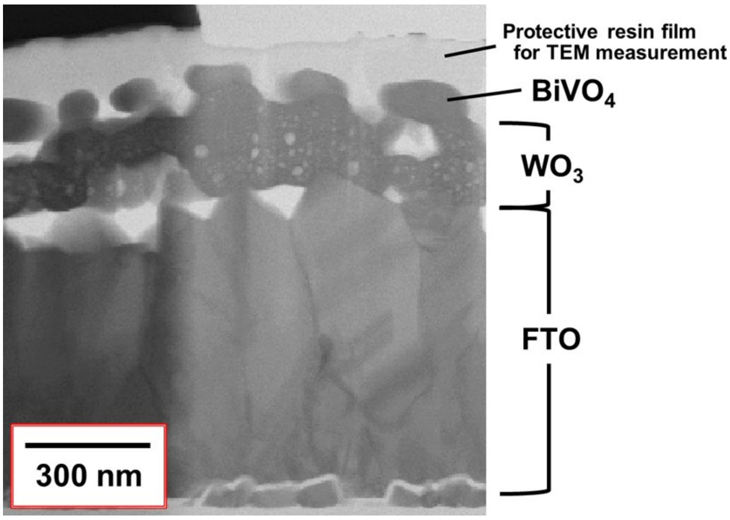

Fig. S2 Section STEM image of WO$_3$/BiVO$_4$ photoelectrode.

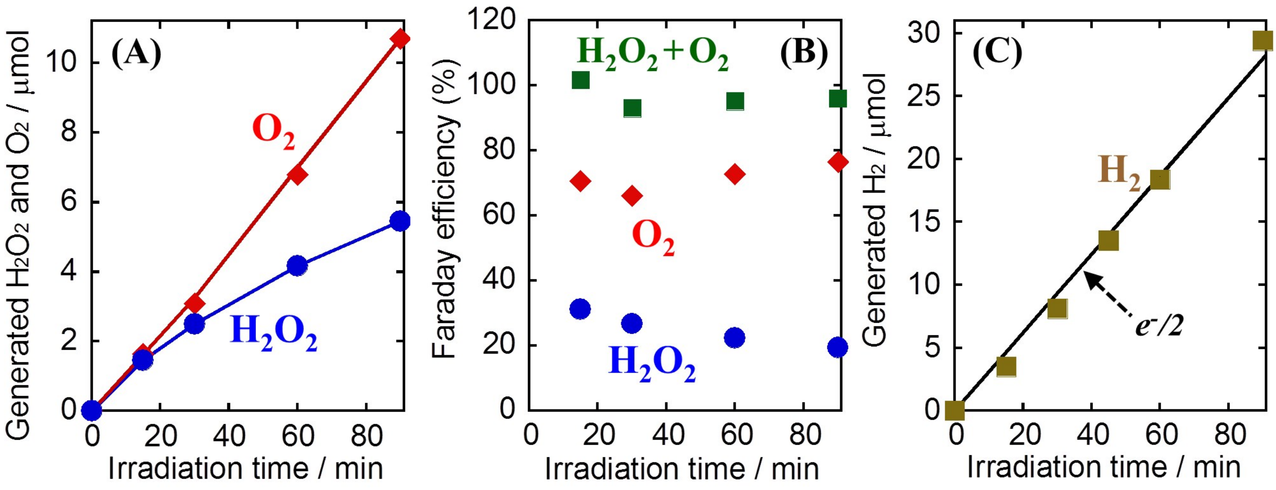

Fig. S3 Time courses of (A) the amount of H_2O_2 and O_2 generated, (B) the Faraday efficiencies of H_2O_2 and O_2 generated in the anode (oxidative) reaction, and (C) the amount of H_2 generated in the cathode (reductive) reaction in 0.5 M $KHCO_3$ aqueous solution (anode: 35 mL, cathode: 35 mL) using a $WO_3/BiVO_4$ photoanode under CO_2 gas (anoxic) atmosphere and simulated solar light irradiation at ambient temperature (approximately 25°C); (steady photocurrent of 1 mA at 0.4–1.2 V, photoanode size: 1.2 × 5.5 cm).

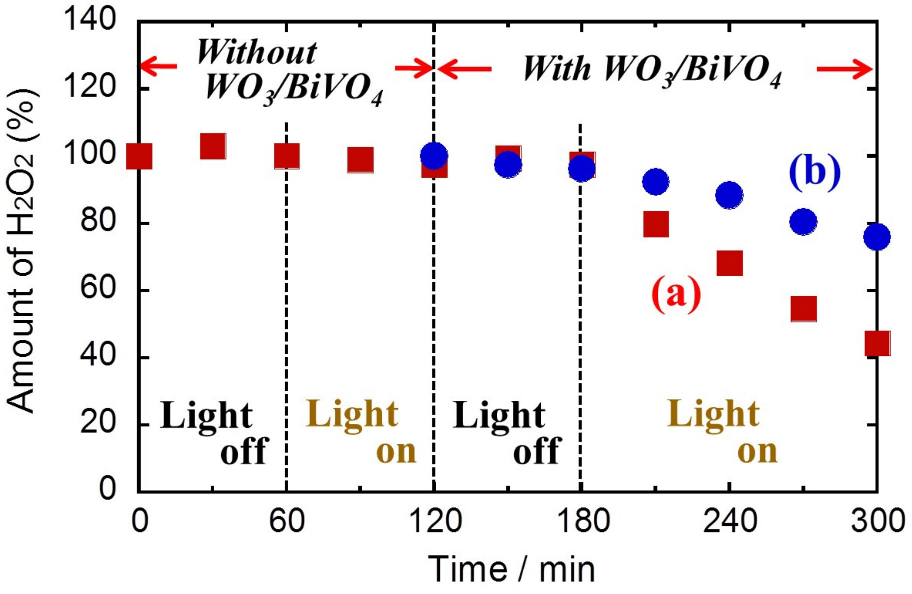

Fig. S4 Stability of H_2O_2 (550 μM) in 0.5 M $KHCO_3$ aqueous solution under CO_2 gas bubbling in the presence or absence of simulated solar light and a $WO_3/BiVO_4$ photoelectrode in (a) water bath (approximately 25°C) and (b) ice bath (below 5°C).

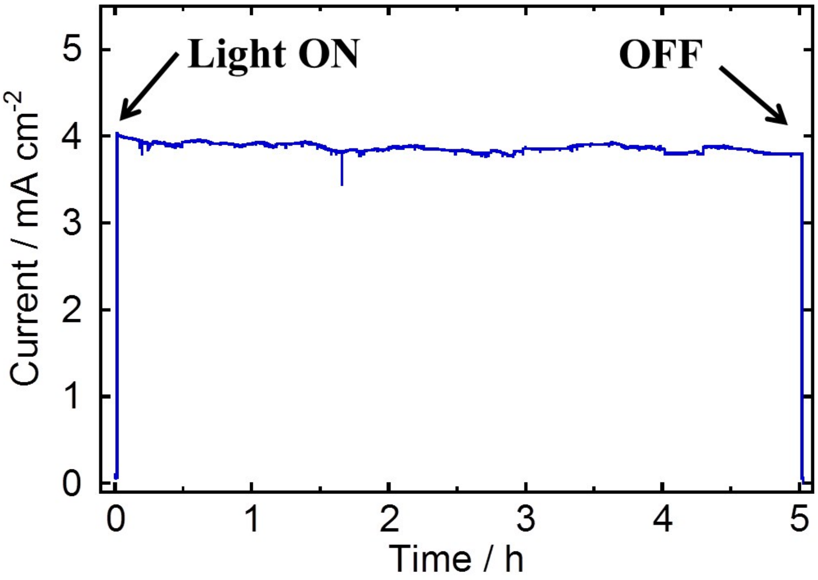

Fig. S5 *I-T* characteristic using a $WO_3/BiVO_4$ photoanode under CO_2 gas bubbling and simulated solar light irradiation in an ice bath in a 0.5 M $KHCO_3$ aqueous solution (1.2 V vs. RHE) using a two-compartment cell (irradiation area: 0.28 cm^2).

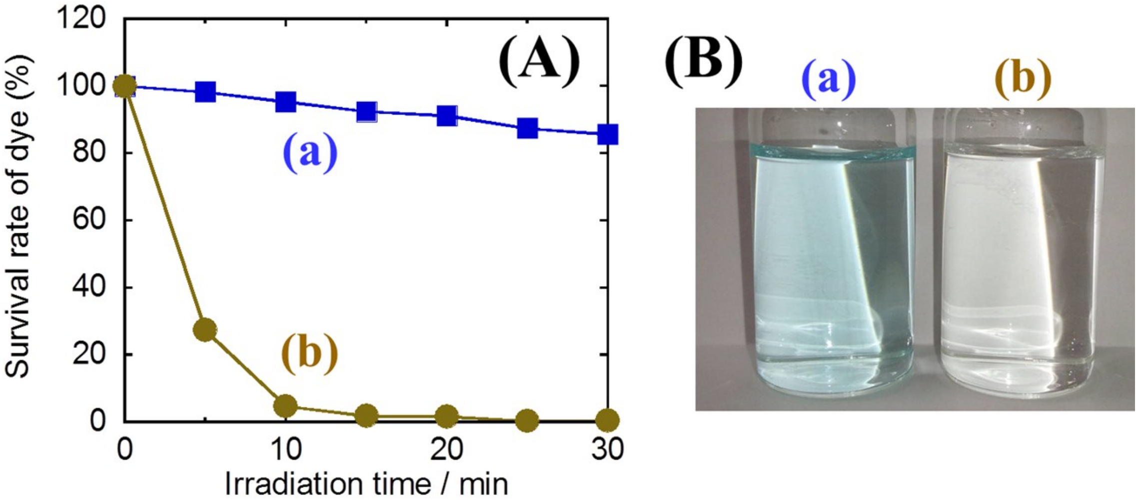

Fig. S6 (A) Time courses and (B) photographs after 30 min reaction of decolorization test of an organic methine dye (NK-3350, Hayashibara Co., Ltd.) in a 2.0 M $KHCO_3$ aqueous solution (a) non-containing and (b) containing *ca.* 2 mM H_2O_2 at ambient temperature.

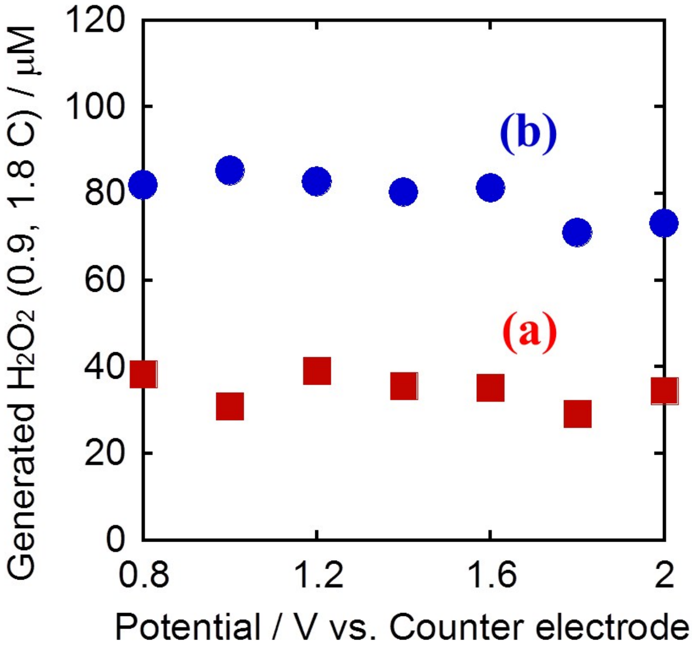

Fig. S7 Effect of the applied voltage on oxidative H_2O_2 generation in 0.5 M $KHCO_3$ aqueous solution (35 mL) under CO_2 gas bubbling and simulated solar light irradiation in an ice bath (below 5°C) using a $WO_3/BiVO_4$ photoanode; (applied electric charge: (a) 0.9 and (b) 1.8 C).

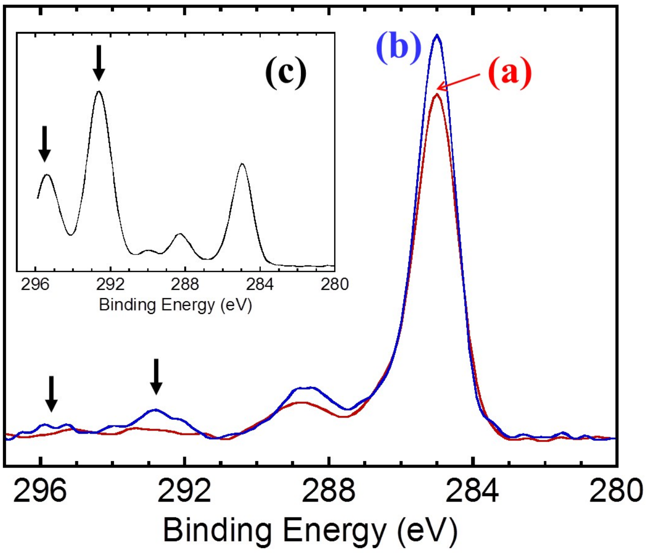

Fig. S8 XPS (C 1s) spectra of $WO_3/BiVO_4$ photoanode washed with deionized water (a) before and (b) after photoreaction at an applied electric charge of 7.2 C (1 mA for 120 min at 0.4–1.8 V, photoanode size: 1.2 × 5.5 cm) in a 0.5 M $KHCO_3$ aqueous solution, and (c) reference sample prepared by drying after a 0.5 M $KHCO_3$ aqueous solution was coated on the $WO_3/BiVO_4$ photoanode by spin coating (1000 rpm, 15 s). The binding energy was set with reference to contamination peak derived from aliphatic carbon (285.0 eV). The arrows exhibit spectra of hydrated bicarbonate derived from $KHCO_3$.[8]

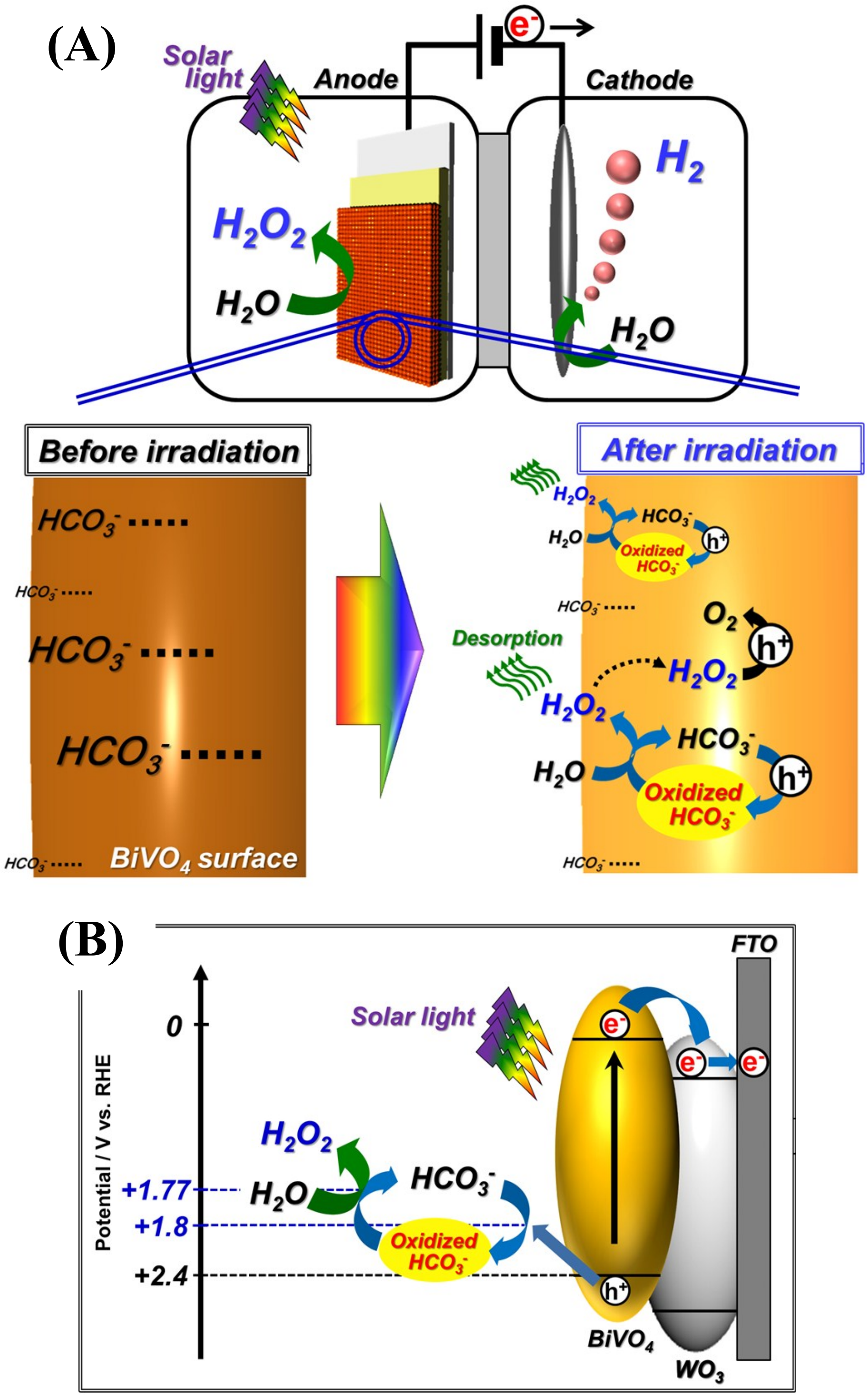

Fig. S9 Proposed (A) mechanism and (B) energy diagram on oxidative H_2O_2 generation on a $WO_3/BiVO_4$ photoanode under solar light irradiation using a $KHCO_3$ aqueous solution as the electrolyte.

Table S1. Comparison of XRF analysis on a $WO_3/BiVO_4$ photoanode before and after long-term reaction (5 h) under CO_2 gas bubbling and simulated solar light irradiation in an ice bath in a 0.5 M $KHCO_3$ aqueous solution (1.2 V vs. RHE) using a two-compartment cell (irradiation area: 0.28 cm^2).

	/ μmol cm^{-2}				Bi/V (mole ratio)
	Bi	V	W	Sn	
Before	0.094	0.087	0.30	2.7	1.08
After	0.091	0.087	0.27	2.5	1.04

Reference

(1) M. H. Mariano, *Anal. Chem.,* 1968, **40**, 1662.