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$_2$O$_2$ 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$_2$SO$_4$ (pH 6.2), 0.5 M H$_3$BO$_3$ 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$_2$O$_2$ and H$_2$ using a two-compartment cell

The production and accumulation of H$_2$O$_2$ 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$_2$SO$_4$ (pH 6.2), 0.5 M H$_3$BO$_3$+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$_2$O$_2$ 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$_2$O$_2$ 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 (Tecn Japan Co., Ltd., infinite M200PRO).

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + 2\text{OH}^- \quad (\text{S1})$$

In aqueous solution of 0.1–0.5 M KHCO$_3$, 0.5 M K$_2$SO$_4$, 0.5 M H$_3$BO$_3$+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$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ ($\eta$(H$_2$) and $\eta$(H$_2$O$_2$)) can be calculated as shown in Equation (S2), which takes into consideration the reaction shown in Equation (2-3).
\( \eta(H_2) \) or \( \eta(H_2O_2) \)

\[
= \left[ \text{amount of generated } H_2 \text{ or } H_2O_2 \right] \times 100 \\
/ \left[ \text{theoretical amount of } H_2 \text{ or } H_2O_2 \right] \\
= \left[ \text{amount of generated } H_2 \text{ or } H_2O_2 \right] \times 100 \\
/ \left[ \text{amount of generated electrons } / 2 \right] \quad (S2)
\]
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$_2$O$_2$ and O$_2$ generated, (B) the Faraday efficiencies of H$_2$O$_2$ 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$_2$O$_2$ (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$_2$O$_2$ at ambient temperature.
**Fig. S7** Effect of the applied voltage on oxidative H$_2$O$_2$ 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$_2$O$_2$ 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$^2$).

<table>
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<th></th>
<th>Bi</th>
<th>V</th>
<th>W</th>
<th>Sn</th>
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<td>0.087</td>
<td>0.30</td>
<td>2.7</td>
<td>1.08</td>
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<tr>
<td>After</td>
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<td>0.087</td>
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Reference