Solar-Driven One-Compartment Hydrogen Peroxide-Photofuel Cell Using Bismuth Vanadate Photoanode

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Supporting Information

ABSTRACT: One-compartment H₂O₂-photofuel cells using monoclinic scheelite BiVO₄ film deposited on fluorine-doped tin oxide (ms-BiVO₄/ FTO) as the photoanode, Prussian blue film-coated FTO cathode, and deaerated aqueous electrolyte solution of 0.1 M NaClO₄ and 0.1 M H₂O₂ were constructed. Mesoporous TiO₂ photoanode cells with the same cathode and electrolyte solution were also prepared for comparison. The ms-BiVO₄/FTO photoanode was prepared by a two-step route consisting of spin coating of a precursor solution on FTO and subsequent heating at 500 °C in the air. The thickness of the ms-BiVO₄ film was controlled in the range from 50 to 500 nm by the number of the spin-coating times. There is an optimum thickness of the ms-BiVO₄ film in the cell performances under illumination of simulated sunlight (AM 1.5, 100 mW cm⁻², 1 sun). Under the optimum conditions, the ms-BiVO₄/FTO photoanode cell provides a short-circuit current (Jₛ𝑐) = 0.81 mA cm⁻² and an open-circuit voltage (Vₒ𝑐) = 0.61 V, far surpassing the values of Jₛ𝑐 = 0.01 mA cm⁻² and Vₒ𝑐 = 0.31 V for the conventional mesoporous TiO₂ photoanode cell. The striking cell performance is ascribable to the high visible-light activity of ms-BiVO₄ for H₂O₂ oxidation and its low thermocatalytic activity for the decomposition.

INTRODUCTION

A sustainable “solar oxygen cycle” can be completed by combining the technology for synthesizing H₂O₂ from H₂O and/or O₂ and H₂O₂-fuel cell (FC) (Scheme 1). At present, most H₂O₂ is industrially produced by the anthraquinone method with the consumption of a large amount of energy. As an alternative method, photocatalytic synthesis of H₂O₂ via O₂ reduction and H₂O oxidation are currently in rapid progress. On the other hand, photofuel cells (PFCs) using TiO₂ photoanode have recently been developed as a chemical-to-electric energy conversion device. The PFCs have attracted considerable interest because of the availability of biomass derivatives as the fuel, but the operation emits CO₂. Meanwhile, clean one-compartment FCs can be constructed without the expensive separator by only using H₂O₂ as the fuel and oxidant. We have recently reported a prototype of one-compartment H₂O₂-PFC consisting of mesoporous TiO₂ film coated on fluorine-doped tin oxide (mp-TiO₂/FTO, photoanode), glassy carbon (cathode), and an aqueous electrolyte solution of H₂O₂ (pH 3). In this cell, H₂O₂ is oxidized to O₂ on the mp-TiO₂/FTO photoanode (eq 1), whereas H₂O is reduced to H₂O at the cathode (eq 2).

Scheme 1. Solar Oxygen Cycle with H₂O₂ as the Key Component

H₂O₂ → O₂ + 2H⁺ + 2e⁻ Eₒ = +0.518 V at pH 3
H₂O₂ + 2H⁺ + 2e⁻ → 2H₂O Eₒ = +1.586 V at pH 3

where the electrode potentials are values with respect to the standard hydrogen electrode (SHE).

The H₂O₂-FC and H₂O₂-PFC afford a thermodynamic electromotive force (ΔE = Eₒ) of 1.07 V comparable with the value for the H₂/O₂-FC (1.23 V). In addition, the H₂O₂-PFC has various advantages over the H₂/O₂-FC, i.e., it can be easily handled at ambient temperature and pressure and does not need separator and electrocatalysts such as Pt. The most serious drawback common with these PFCs is that TiO₂ only responds to UV-light occupying a few percent of the solar spectrum. The photoanode material for the H₂O₂-PFC.
should possess the following properties: (1) high visible-light activity for H$_2$O$_2$ oxidation, (2) low thermocatalytic activity for H$_2$O$_2$ decomposition, (3) high stability, and (4) nontoxicity. In the biomass-PFC, the cell performances have been improved by using a visible-light-responsive TiO$_2$ photoanode.\textsuperscript{16,17} The simultaneous fulfillment of conditions (1) and (2) is a difficult subject because H$_2$O$_2$ undergoes catalytic decomposition by various materials. Among the visible-light-responsive semiconductor photocatalysts, bismuth vanadate (BiVO$_4$) is a promising material because it is known to have a high level of activity for H$_2$O oxidation\textsuperscript{18} as well as high stability (condition 3) and nontoxicity (condition 4),\textsuperscript{19} whereas Prussian blue (PB) can be used as the cathode material effectively improving the cell performances of H$_2$O$_2$-FC\textsuperscript{20} and H$_2$O$_2$-PFC.\textsuperscript{21} Here, we report a visible-light-driven one-compartment H$_2$O$_2$-PFC using BiVO$_4$/FTO photoanode and PB/FTO cathode and the performances under simulated sunlight.

### RESULTS AND DISCUSSION

BiVO$_4$ is an n-type semiconductor with three crystal polymorphs, i.e., monoclinic scheelite (ms), tetragonal scheelite (ts), and tetragonal zircon (tz) structures. Among them, ms-BiVO$_4$ was reported to show the highest photocatalytic activity due to its narrower band gap energy ($E_g$) of 2.4 eV against tz-BiVO$_4$ with $E_g = 2.9$ eV\textsuperscript{22} and the more significant distortion of the metal polyhedra than ts-BiVO$_4$.\textsuperscript{23} The crystal form of the present BiVO$_4$ film was determined by X-ray diffraction (XRD) measurements. Figure 1A shows the XRD patterns for the samples prepared at various spin-coating cycles (N). In the XRD patterns, sharp diffraction peaks are present at 2θ = 18.9, 28.9, and 30.6°. The first peak is derived from the overlapping of the diffraction peaks assignable to the (110) and (011) crystal planes of ms-BiVO$_4$, the second peak to the (130), (121), and (121) planes, and the third peak to the (040) plane (ICDD 00-014-0688). Also, the diffraction peaks observed at 26.6, 33.9, 37.9, and 51.8° are assignable to the diffraction from the (110), (101), (200), and (211) crystal planes of SnO$_2$ (ICDD 01-070-6995), respectively. Clearly, films consisting of single-phase ms-BiVO$_4$ are formed on FTO by the spin-coating technique. As shown in the inset in Figure 1B, the scanning electron microscopy (SEM) image confirms the formation of uniform ms-BiVO$_4$ layer on the FTO surface.

Figure 2A shows the relation between the thickness of ms-BiVO$_4$ film (l) and N. The l increases linearly with respect to N according to the following equation of l (nm) = 25.5N − 57.0 at N ≥ 5. In Figure 1A, the intensity of the diffraction peaks of SnO$_2$ monotonically decreases with an increase in N or l.

Raman spectra were recorded to gain information about the bulk and local structures of the ms-BiVO$_4$ film. Figure 2A shows the Raman spectra for ms-BiVO$_4$/FTO with varying N. Every spectrum has several signals that increase in intensity with an increase in N. In the spectrum of the sample (N = 15), the signals at 375 and 335 cm$^{-1}$ are due to the symmetric and antisymmetric bending modes of VO$_4^{3-}$ anion ($\delta_s$(VO$_4^{3-}$) and $\delta_a$(VO$_4^{3-}$)), respectively. Also, the intense signal at 822 cm$^{-1}$ and the weak signal around 710 cm$^{-1}$ are assignable to the...
symmetric and antisymmetric stretching vibrations of the VO$_4^{3-}$ anion ($\nu_s(V-O)$ and $\nu_{as}(V-O)$), respectively.\textsuperscript{24} The emergence of the forbidden $\nu_{as}(V-O)$ band can be induced by the distortion of the local symmetry of VO$_4^{3-}$ tetrahedron in ms-BiVO$_4$. Yu and Kudo reported that the local structure as well as crystallinity affect the photocatalytic activity of the O$_2$ evolution from an AgNO$_3$ aqueous solution.\textsuperscript{25} The absence of the $\nu_{as}(V-O)$ signal in the spectrum of the sample ($N=5$) is probably due to the small film thickness of $\sim 70$ nm.\textsuperscript{26} Figure 2B shows the UV−vis absorption spectra of ms-BiVO$_4$/FTO with varying $N$. Every sample has a strong absorption due to the interband transition at $\lambda < 500$ nm, whose intensity increases with increase in $N$. Density functional theory calculations for the ms-BiVO$_4$ crystal indicated that the valence band (VB) maximum and conduction band (CB) minimum mainly consist of the nonbonding O 2p and nonbonding V 3d states, and the interband transition is allowed along the polarization direction of $E//a$ and $E//c$.\textsuperscript{27} The direct band gap ($E_g$) was determined from the $[F(R_{sh}) \ h\nu]^2$ vs $(h\nu - E_g)$ plot, where $h\nu$ is the photon energy.\textsuperscript{28} The $E_g$ lies in the range from 2.6 to 2.7 eV, and there is a trend that it increases with decreasing $N$ or $l$. The $E_g$ values are somewhat larger than the value of 2.45 ± 0.05 eV reported for ms-BiVO$_4$ particles at room temperature (Figure S1).\textsuperscript{29}

The thermocatalytic and photocatalytic activities of TiO$_2$ and ms-BiVO$_4$ particles for H$_2$O$_2$ decomposition were examined in a deaerated 0.1 M H$_2$O$_2$ aqueous solution (pH 3). The rates of H$_2$O$_2$ decomposition in the dark and under irradiation are denoted as $v_{dark}$ and $v_{ph}$, respectively.\textsuperscript{30} Figure 3A compares the time courses of O$_2$ evolution from 0.1 M H$_2$O$_2$ aqueous solution in the TiO$_2$ and ms-BiVO$_4$ systems in the dark. In the TiO$_2$ system, the amount of O$_2$ increases with a $v_{dark}$ of 0.36 $\mu$mol h$^{-1}$, whereas the decomposition is very sluggish in the ms-BiVO$_4$ system ($v_{dark} < 0.03$ $\mu$mol h$^{-1}$). Clearly, ms-BiVO$_4$ is almost inert for H$_2$O$_2$ decomposition in the dark, whereas TiO$_2$ has a significant thermocatalytic activity.\textsuperscript{30} Figure 3B shows time courses for O$_2$ evolution from 0.1 M H$_2$O$_2$ aqueous solution in the TiO$_2$ and ms-BiVO$_4$ systems under simulated sunlight (AM 1.5, 19 mW cm$^{-2}$). Irradiation of ms-BiVO$_4$ causes H$_2$O$_2$ decomposition with a $v_{ph}$ of 0.45 $\mu$mol h$^{-1}$. In the TiO$_2$ system, O$_2$ is produced with a $v_{ph}$ of 0.42 $\mu$mol h$^{-1}$. The $v_{ph}/v_{dark}$ ratio for ms-BiVO$_4$ reaches 16.7, which is larger than the value for TiO$_2$ by a factor of 14. The high level of visible-light activity (condition 1) and low thermocatalytic activity (condition 2) of ms-BiVO$_4$ for the H$_2$O$_2$ decomposition lead us to expect its application as the photoanode material for the H$_2$O$_2$-PFC. In the absence of H$_2$O$_2$, O$_2$ is hardly generated in the ms-BiVO$_4$ system (Figure S2). Previously, the flatband potential of ms-BiVO$_4$ or the
approximate conduction band (CB) minimum potential \( E_{\text{CB}} \) was determined to be \(-0.064 \text{ V at pH 3 (SHE)} \) by the slurry method.\(^{31}\) By using this value and the \( E^0 \) of \( 2.60 \text{ eV} \), the valence band (VB) maximum potential \( E_{\text{VB}} \) can be estimated to be \( +2.54 \text{ V at pH 3 (SHE)} \). Thus, the potential of the solutions with (red) and without \( 0.1 \text{ M H}_2\text{O}_2 \) (black). In the SHE at pH 3, \(^{32}\) whereas the VB-holes can oxidize \( \text{H}_2\text{O} \) oxidation \( (E_{\text{O}_2/\text{H}_2\text{O}} = +1.05 \text{ V vs SHE}) \).32

To study the \( \text{H}_2\text{O}_2 \) additive effect on the photoelectrochemical (PEC) properties of ms-BiVO\(_4\)/FTO, three-electrode PEC cells with a structure of ms-BiVO\(_4\)/FTO (\( N = 5 \), working electrode)\(/\)deaerated aqueous electrolyte solution containing \( 0.1 \text{ M NaClO}_4 \) (pH 3)\(/\)Ag/AgCl (reference electrode)\(/\)glassy carbon (counter electrode) were fabricated, and the photocurrent \( J \)–electrode potential \( E \) curves were measured for the cells under the illumination of simulated solar light (AM 1.5, 100 \text{ mW cm}^{-2}, 1 \text{ sun}) . Figure 4A compares the \( J=E \) curves of the ms-BiVO\(_4\)/FTO electrode in the electrolyte solutions with (red) and without \( 0.1 \text{ M H}_2\text{O}_2 \) (black). In the \( \text{H}_2\text{O}_2\)-free cell, the photocurrent starts to flow around \( +0.4 \text{ V vs SHE} \). In the \( \text{H}_2\text{O}_2\)-cell, the photocurrent sharply increases at the onset potential of \( +0.2 \text{ V vs SHE} \). Figure 4B shows the photochronoamperometry curves for the PEC cells. In the \( \text{H}_2\text{O}_2\)-free cell, a sharp decay in the photocurrent is observed immediately after photoirradiation. This feature indicates that significant surface recombination occurs via surface peroxy species generated during the \( \text{H}_2\text{O} \) oxidation by the VB-holes. On the other hand, the initial anodic photocurrent spike and its subsequent decay disappear in the \( \text{H}_2\text{O}_2\)-cell, providing a very stable photocurrent. Thus, \( \text{H}_2\text{O}_2 \) works as an excellent scavenger for the VB-holes in ms-BiVO\(_4\) effectively suppressing the surface recombination.\(^{33}\)

The performance of one-compartment \( \text{H}_2\text{O}_2\)-PFCs were examined for the cell with a structure of ms-BiVO\(_4\)/FTO photoanoddeaerated aqueous electrolyte solution containing \( 0.1 \text{ M NaClO}_4 \) and \( 0.1 \text{ M H}_2\text{O}_2 \) (pH 3)\(/\)PB/FTO cathode under irradiation of simulated solar light (AM 1.5, 100 \text{ mW cm}^{-2}, 1 \text{ sun}) . Figure 5A exhibits the \( J=E \) curves of the ms-BiVO\(_4\)/FTO electrode in the electrolyte solutions with and without \( 0.1 \text{ M H}_2\text{O}_2 \). In the \( \text{H}_2\text{O}_2\)-free cell, the photocurrent starts to flow around \( +0.4 \text{ V vs SHE} \). In the \( \text{H}_2\text{O}_2\)-cell, the photocurrent sharply increases at the onset potential of \( +0.2 \text{ V vs SHE} \). Figure 5B shows the photocurrent, \( I_{\text{ph}} \), and open-circuit voltage \( (V_{\text{oc}}) \) curves for the two-electrode cell with the structure of BiVO\(_4\)/FTO photoanode cell. In the \( \text{H}_2\text{O}_2\)-PFC, \( V_{\text{oc}} \) is almost independent of \( N \) at \( \geq 1 \). The ms-BiVO\(_4\)/FTO (\( N = 10 \)) photoanode cell provides \( I_{\text{ph}} = 0.81 \text{ mA cm}^{-2} \) and \( V_{\text{oc}} = 0.61 \text{ V much greater than the values for the mp-TiO\(_2\)/FTO photoanode cell (} I_{\text{ph}} = 0.01 \text{ mA cm}^{-2} \text{ and } V_{\text{oc}} = 0.31 \text{ V) under the same irradiation conditions. Clearly, there exists an optimal thickness of ms-BiVO\(_4\). These experiments were carried out in deaerated electrolyte solution to prove that \( \text{H}_2\text{O}_2 \) works both as a fuel and an oxidant in this cell. However, the presence of \( \text{O}_2 \) was confirmed to hardly affect the cell performances (Figure S3).

The photocurrent was measured under irradiation of monochromatic light whose wavelength \( (\lambda_{\text{ex}}) \) continuously varied. The incident photon-to-current efficiency (IPCE) was calculated by the equation \( \text{IPCE} = J_{\text{ph}} N_{\text{h}} h c / F I \), where \( J_{\text{ph}} \) is the photocurrent, \( N_{\text{h}} \) is Avogadro constant, \( h \) is Planck constant, \( c \) is the speed of light, \( I \) is the light intensity, \( F \) is Faraday constant, and \( \lambda \) is the wavelength of the light. Figure 6A shows the IPCE action spectrum of the ms-BiVO\(_4\)-PFC. The photocurrent rises at \( \lambda_{\text{ex}} = 500 \text{ nm} \), which is in agreement with the absorption edge of the ms-BiVO\(_4\)/FTO electrode. Also, the IPCE action spectrum well traces the absorption spectrum of the ms-BiVO\(_4\)/FTO electrode in Figure 2B (Figure S4). Further, the IPCE value at \( \lambda_{\text{ex}} = 400 \text{ nm} \) reaches 6% at \( \lambda_{\text{ex}} = 400 \text{ nm} \), which is as much as 60 times greater than the value of the prototype of H\(_2\text{O}_2\)-PFC using the mp-TiO\(_2\)/FTO photoanode.\(^{14}\) Finally, the effect of light intensity \( (I) \) on the cell performance was studied for the one-compartment \( \text{H}_2\text{O}_2\)-PFC. Figure 6B shows the maximum power density \( (P_{\text{max}}) \) as a function of \( I \). The \( P_{\text{max}} \) increases with an increase in \( I \) to reach a saturated value of 0.13 \text{ mW cm}^{-2} \text{ at } I > 1 \text{ sun} (100 \text{ mW cm}^{-2}) $.

### Table 1. Cell Parameters of the H\(_2\text{O}_2\)-PFCs under Illumination of Simulated Sunlight (AM 1.5, 100 \text{ mW cm}^{-2}, 1 \text{ sun})

| Photoanode | \( V_{\text{oc}} \) (V) | \( J_{\text{ph}} \) (mA cm\(^{-2}\)) | \( J_{\text{max}} \) (mA cm\(^{-2}\)) | \( P_{\text{max}} \) (mW cm\(^{-2}\)) |
|------------|-----------------|-----------------|-----------------|-----------------|
| ms-BiVO\(_4\) | 1 | 0.59 | 0.068 | 0.034 | 0.0092 |
| ms-BiVO\(_4\) | 3 | 0.54 | 0.61 | 0.26 | 0.075 |
| ms-BiVO\(_4\) | 5 | 0.58 | 0.67 | 0.37 | 0.11 |
| ms-BiVO\(_4\) | 7 | 0.59 | 0.79 | 0.44 | 0.13 |
| ms-BiVO\(_4\) | 10 | 0.61 | 0.81 | 0.46 | 0.13 |
| ms-BiVO\(_4\) | 15 | 0.61 | 0.58 | 0.29 | 0.09 |
| mp-TiO\(_2\) | | | 0.31 | 0.007 | 0.0015 |

\(^{a}\)The thickness of mp-TiO\(_2\) film was \( \sim 4 \text{ \textmu m} \).

\( V_{\text{oc}} \) is the open-circuit voltage, \( J_{\text{ph}} \) is the photocurrent, \( J_{\text{max}} \) is the maximum photocurrent, and \( P_{\text{max}} \) is the maximum power density.
The present H2O2-PFC using ms-BiVO4/FTO photoanode is considered to operate via the mechanism explained as follows (Scheme 2). Under irradiation of simulated sunlight, the ms-BiVO4/FTO photoanode absorbs light at $\lambda < 500$ nm and the electrons in the VB are excited to the CB. The VB-holes ($E_{VB} = +2.44$ V vs SHE at pH 3) can oxidize H2O2 to produce O2 with $E(O_2/H_2O_2) = +0.518$ V vs SHE at pH 3 (eq 1).32 Importantly, the surface recombination of the unmodified BiVO4 photoanode can be effectively suppressed in the oxidation of H2O2, whereas it undergoes significant surface recombination in the H2O oxidation.33 Simultaneously, the CB-electrons ($E_{CB} = −0.064$ V at pH 3 vs SHE) are transported to the FTO electrode, and further to the PB/FTO cathode through the external circuit, taking part in the reduction of H2O2 to H2O with $E(H_2O_2/H_2O) = +1.586$ V (vs SHE at pH 3) (eq 2). According to this scheme, the theoretical $V_{oc,\text{theo}}$ can be determined to be 1.65 V from eq 3.34

$$V_{oc,\text{theo}} = E(H_2O_2/H_2O) - E_{CB}(\text{BiVO}_4)$$

The practical power-generating efficiency of FCs ($\varepsilon_{FC}$) is expressed by eq 4.14

$$\varepsilon_{FC} = \varepsilon_{\text{theo}} \times \varepsilon_{v} \times \varepsilon_{c}$$

where $\varepsilon_{\text{theo}}$ is the theoretical power-generating efficiency and $\varepsilon_{v}$ and $\varepsilon_{c}$ are the voltage efficiency and the current efficiency, respectively.

Because the $\varepsilon_{\text{theo}}$ is 119%14 and the voltage efficiency ($\varepsilon_{v}$) is given by 0.571 (=0.61/1.068 V) for the H2O2-PFC with N = 10, the maximum $\varepsilon_{FC}$ can be estimated to be 68% by assuming the current efficiency to be 100% in this H2O2-PFC. However, the $V_{oc}$ of the present cell (~0.6 V) is much smaller than the $V_{oc,\text{theo}}$ value (1.65 V) for which the overpotential for H2O2 reduction at the cathode is partly responsible. Also, van de Krol and co-workers have shown that the IPCE of the PEC cell for water splitting with BiVO4/FTO as the photoanode can be drastically boosted by doping $W^{6+}$ ions into BiVO4 and intervening a SnO2 layer between BiVO4 and FTO.35 Thus, there is still plenty of room for improvement in the present H2O2-PFC performances by exploring cathode materials and enhancing the electron transport in the ms-BiVO4 film and charge collection at the interface with the back-contact.

## CONCLUSIONS

This study has shown that monoclinic scheelite (ms)-BiVO4 possesses the basic properties required for the photoanode of H2O2-PFC. A solar-driven one-compartment H2O2-PFC using ms-BiVO4 as the photoanode and Prussian blue as the cathode provides $J_{sc} = 0.81$ mW cm$^{-2}$ and $V_{oc} = 0.61$ V under illumination of simulated solar light (AM 1.5, 1 sun), and the incident photon-to-current efficiency at the excitation wavelength of 400 nm exceeds 6%. We anticipate that the performance can be further improved by reducing the losses during the electron transport in the photoanode and at the interface between the back-contact.

## EXPERIMENTAL SECTION

Synthesis of ms-BiVO4 Particles. The BiVO4 particles were synthesized by the method reported in the literature.36 $\text{Bi(NO}_3)_3\cdot5\text{H}_2\text{O}$, 0.2 M, and 0.2 M NH4VO3 were completely dissolved in dilute nitric acid (500 mL, volume ratio: concn $\text{HNO}_3/\text{H}_2\text{O} = 1:4$) by gentle stirring at room temperature for 1 h. After the addition of 1.66 M urea to the solution, the...
mixed solution was heated at 80 °C for 8 h. Precursor particles thus prepared were harvested from the solution by centrifugal separation and then repetitively washed with purified water and vacuum dried at room temperature. The samples were then heated at 400 °C under an air atmosphere for 1 h to form the BiVO₄ particles.

**Preparation and Characterization of Electrodes.**

BiVO₄/FTO electrodes were prepared by the metal–organic decomposition method. ²⁵ Mixed solution of acetic acid (15 mL) containing 0.6 mol/L Bi(NO₃)₃·5H₂O and acetylacetone (75 mL) containing 0.04 M VO(acac)₂ was spin-coated on fluorine-doped tin oxide (FTO) film-coated glass substrate (20 × 20 mm², <10 Ω/sq) at a rotation speed of 500 rpm for 30 s at room temperature. After this process was repeatedly conducted for N cycles, the as-obtained films were heated in air at 673 K for 4 h to form BiVO₄/FTO. The film thickness of BiVO₄/FTO was determined by cross-sectional SEM observation of the photoanode with Hitachi S-4800 Type II. The X-ray diffraction (XRD) analysis was carried out with a Rigaku SmartLab X-ray diffractometer. Diffuse reflectance UV–vis spectra of the photoanodes were recorded on a UV-2600 spectrometer (Shimadzu) with integrating sphere unit (Shimadzu, ISR-2600Plus) at room temperature. The reflectance (Rₕ) of the photoanodes was measured with respect to a standard sample (BaSO₄), and the Kubelka–Munk function (F(Rₕ)) defined by the equation of \( F(Rₕ) = (1 - Rₕ)^2/2Rₕ \) was plotted against the wavelength. The Raman spectroscopy was carried out with a JASCO NRS-1000 laser Raman spectrometer at room temperature. Green laser with an optical power of 1.5, 19 mW cm⁻² was irradiated by simulated sunlight without (AM 1.5) and with an optical cutoff filter (λ > 430 nm, AM 1.5, 15 mW cm⁻²) at 25 °C. The amount of O₂ was determined by gas chromatography (Shimadzu, GC-8A). For comparison, the same experiments were carried out using anatase TiO₂ particles (10 mg, specific surface area = 309 m² g⁻¹, ST-01, Ishihara Sangyo). ²⁶

**Evaluation of Photofuel Cell Performances.**

The photoelectrochemical (PEC) response of the photoanodes incorporated in three-electrode PEC cells was evaluated by the measurements of current (I)–electrode potential (E) curves and decay curves of photocurrent at the rest potential under the irradiation of simulated solar light (AM 1.5, 100 mW cm⁻², 1 sun). Current (I)–cell voltage (Vₗₒ) and power density–I curves were measured to determine the cell performance of two-electrode H₂O₂ PFCs. The action spectra of the incident photon-to-current conversion efficiency (IPCE) were measured by the same method as recently reported. ²⁶

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