

Solar Cell with Photocatalyst Layers on Both the Anode and Cathode Providing an Electromotive Force of Two Volts per Cell

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Supporting Information

ABSTRACT: Solar cells and fuel cells are essential devices that convert sustainable energy into electricity. However, the electromotive forces they provide are in principle limited to less than 1 V, and consequently, they need to be connected in series for practical use. In this study, photocatalyst layers with thicknesses of 0.8–2.1 μ m were applied to both electrodes. The primary particle size of TiO_2 was optimized (15–21 nm), and its performance was further improved by doping with organic dyes, e.g., anthocyanins. The electron conductivity of TiO₂ was found to be a primary factor in the performance of the cells, but the film flatness also reduced resistance and improved cell performance. Interestingly, the efficiency of TiO₂ could be evaluated based on the exchangeable surface O atoms via its ¹⁸O₂ exchange



tests to suppress the reverse reaction step in water photo-oxidation, which occurs on the anode. UV and visible light were absorbed by TiO_2 and the organic dyes, respectively, creating an electron flow path from the valence band to the conduction band of TiO₂, then, the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the organic dyes, then the anode, and finally the cathode via the external circuit. The flow of electrons and holes (separated from electrons in BiOCl on the cathode by UV–visible light) enabled a V_{OC} value of 2.11 V and maximum power of 73.1 μ W cm⁻². KEYWORDS: Solar cell, Photocatalyst, Open-circuit voltage, Organic dye, Anthocyanidin, Titanium oxide, Bismuth oxychloride,

Isotope tracing

INTRODUCTION

The process of replacing fossil fuel energy sources with renewable energy sources such as wind, waves, hydro, geothermal, solar, and biomass is proceeding and cannot be halted or reversed if a sustainable global environment is to be realized.¹ Solar cells (SCs) are a key technology for the effective conversion of renewable energy into electricity. Accordingly, silicon (crystal-type and amorphous-type), dye-sensitized, and perovskite SCs have been developed.² In principle, the electromotive force of a solar cell is determined by the conduction band minimum (CBM), valence band maximum (VBM), and/or reaction potential of the constituents, e.g., the redox mediator.^{2,3} Accordingly, the values are mostly less than 1 V and do not vary significantly for different cell designs, and thus, multiple cells must be connected in series for practical use.

Several researchers have reported the possibility of photoanodes⁴⁻¹³ or photocathodes¹⁴ incorporated into fuel cells (FCs). The photoanodes consume fuels such as methanol,^{4,5} ethanol,^{5,6} hydrogen peroxide,⁷ urea,⁸ phenol,⁹ glucose,¹⁰⁻¹² glycerol,⁵ or starch¹³ and constitute "photofuel" cells when they are combined with conventional cathodes, e.g., platinumcarbon. The electromotive force they provide is determined by the difference between the CBM and the reduction potential of O₂ in the cathode and, thus, is typically less than 1 V.^{2,3,15} If photocatalysts are used on both electrodes and excited by light,

the electromotive force is primarily determined by the CBM and VBM of the two photocatalysts. Zhang et al.¹⁰ rationalized the superiority of cells that use photocatalysts on both electrodes^{3,15,16} in terms of the higher open-circuit voltages ($V_{\rm OC}$, 1.59-1.69 V) they provide compared to those provided by FCs that comprise only a photoanode or a photocathode. SCs do not require fuel, and acidic water in the cell behaves as a redox mediator (eqs 1 and 2).

$$2H_2O \xrightarrow{n\nu} 4H^+ + 4e^- + O_2 \qquad (anode) \qquad (1)$$

$$4\mathrm{H}^{+} + 4\mathrm{e}^{-} + \mathrm{O}_{2} \xrightarrow{h\nu} 2\mathrm{H}_{2}\mathrm{O} \qquad \text{(cathode)} \tag{2}$$

The energy levels in such SCs are tunable by the choice of the two photocatalysts, with the only prerequisite for the choice is that the common reaction potential for eqs 1 and 2 should be positioned between the VBM and CBM on both the anode and cathode.^{3,15,16} However, Zhang et al. reported FCs with maximum power densities (W_{max}) of 36–82 μ W cm⁻² prepared using glucose or phenol as the fuel, far superior to the W_{max} of $11-16 \,\mu\text{W} \,\text{cm}^{-2}$ achieved using acidic water as the fuel.¹⁰ This

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paper limits the comparison to SCs comprising two photocatalysts on both electrodes. If platinum is used at the cathode, a $V_{\rm OC}$ of 0.80–1.73 V and $W_{\rm max}$ of 75–750 μ W cm⁻² are reported using FCs with a TiO₂-based¹⁷ or BiVO₄-based photoanode.¹⁸ Furthermore, based on photosynthesis, FCs using a tylakoid-C nanotube anode and Pt cathode generated a $V_{\rm OC}$ of 0.4 V and $W_{\rm max}$ of 5.3 μ W cm^{-2.19}

In this study, to exceed a $V_{\rm OC}$ of 2.0 V and achieve a $W_{\rm max}$ higher than 70 μ W cm⁻², higher-voltage-type SCs with photocatalysts on both electrodes were investigated using various nanocrystalline forms of TiO₂. Thus far, a $V_{\rm OC}$ of 1.91 V and $W_{\rm max}$ of 42.2 μ W cm⁻² were the best values reported for this type of SCs.³ A breakthrough is needed to fill the gap as compared to the theoretical $V_{\rm OC}$ value of 2.75 V.^{3,15} To overcome the breakthrough, very thin (0.8–2.1 μ m) TiO₂ and BiOCl nanocrystalline photocatalyst films were formed on the anode and cathode to minimize the diffusion overvoltage. Furthermore, to achieve the target performance values ($V_{\rm OC} > 2.0$ V and $W_{\rm max} > 70 \ \mu$ W cm⁻²), the new method employed organic dyes in the SC as a novel highlight of this study. The TiO₂ layers on the anodes were sensitized using anthocyanidintype organic dyes (Scheme 1a), such as pelargonidin,

Scheme 1. Structural Formula of Anthocyanidin: (a) General Formula and Three Typical Types of Anthocyanidin (b) Pelargonidin, (c) Delphinidin, and (d) Cyanidin⁴



 a The pH dependence of the structure of pelargonidin is also illustrated.

delphinidin, and cyanidin (Scheme 1b–d).^{20,21} These dyes present colors between purple and orange and absorption peaks of the complementary color range between 532 and 553 nm (Scheme 1b–d and Figure 1). These absorptions are due to HOMO–LUMO electronic transitions.²² As a result, organic dyes work as an enhancer, increasing the electron flow from the



Figure 1. UV–visible absorption spectra of (a) a 0.10 mM ethanolic pelargonidin chloride solution, (b) a 0.030 mM ethanolic PEC-TOM-P04 solution, and an ethanol extract (120 mg L^{-1}) of (c) rosehip/hibiscus flowers (1/10 diluted), (d) rosehip flowers (1/25 diluted), and (e) hibiscus flowers (1/25 diluted).

anode and simultaneously suppressing the diffusion overvoltage within the photocatalyst layer. Consequently, the $V_{\rm OC}$ and $W_{\rm max}$ values were increased to 2.11 V and 73.1 μ W cm⁻² (per cell), respectively.

EXPERIMENTAL SECTION

Synthesis of TiO₂ and BiOCl and Preparation of Photoelectrodes. TiO₂ (JRC-TIO-14; purity >93.4%)²³ was supplied by Ishihara Sangyo Co. TiO₂ (JRC-TIO-15; purity >99.5%)²³ and TiO₂ (Aeroxide P25; purity >99.5%)²⁴ were supplied by the Japan Aerosil Co. TiO₂ (PEC-TOM-P03) was purchased from Peccell Technologies as an organic/aqueous suspension. TiO₂ (JRC-TIO-6; purity >99%) was supplied by the Sakai Chemical Industry Co.²³ TiO₂ (particle size < 5 μ m, purity 99.9%) was purchased from Wako Pure Chemical and denoted as "rutile-W". These samples were used without further purification. The mean primary particle sizes and specific surface areas (SAs) for these TiO₂ samples are summarized in Table 1. The Brunauer–Emmett–Teller SAs were measured based on N₂ adsorption at several pressure points between $P/P_0 = 0.05$ and 0.35 at 77.4 K (P_0 101.3 kPa).

The TiO₂ powder (0.10 g) was well mixed with 1.0 mL of *t*-butanol, and 0.05 mL of ethylene glycol was added as a thickener. The suspension was agitated using ultrasonification (430 W, 38 kHz) for 10 min, and pasted onto an indium tin oxide (ITO) coated (thickness 0.12–0.16 μ m, sheet resistivity 8–12 Ω /square) Pyrex glass substrate (area 2.5 cm × 2.5 cm, thickness 0.11 cm; Aldrich). In the film preparation of JRC-TIO-6 and P25, a slide method was also employed, i.e., 10 g of flat Pyrex glass plate (area 10 cm²) was slowly slid on the pasted suspension. Each TiO₂/ITO/Pyrex plate was dried in air at 373 K for 18 h and then the temperature was elevated to 573 K at 4 K min⁻¹ where it was maintained for 30 min. The amount of TiO₂ deposited on the plate was 0.4 mg, and it covered an area of 1.0 cm × 1.3 cm. The organic/aqueous suspension of PEC-TOM-PO3 was directly pasted onto an ITO-coated glass and treated following a similar procedure to that used for the other TiO₂ samples.

Pelargonidin chloride (compound 1; molecular weight 306.70; ChromaDex, Inc., USA) ethanol solution (0.10 mM) was prepared as a standard for the anthocyanidins. The solution was red. The organic dye/ethanol solutions were used as received (1.0 mM; PEC-TOM-P04, Peccell Technologies). The molar absorption coefficient was similar to that for compound 1 within a variation of 13%. The color was orange. Three drops (0.036 mL, 36 nmol) were cast onto TiO₂/ITO/Pyrex plates. The dye-adsorbed TiO₂ film was yellow. Anthocyanins were extracted from 1.0 g of rosehip and hibiscus flower herbal tea (Pompadour, Germany, No. 1519-88) using ethanol (10 mL) at 298 K for 24 h. The hydroxy groups of the anthocyanin, e.g., at the 3- and/or 5position of the benzopyrylium ring (Scheme 1a), are dehydrated with sugar. Rosehip and hibiscus flowers contain delphinidin and cyanidin, respectively. The extract solution was transparent red, and the

ent		sample	mean primary particle size (nm)	specific surface area $(m^2 g^{-1})$	mean film thickness (µm) ^f	crystalline phase	photocurrent @ 1.0 V, SHE $(\mu A)^h$	impedance (MΩ)	ref
a	TiO ₂	JRC-TIO-14	7.4 ^{<i>a,c</i>}	308		anatase	60	247	23
b	(0.4 mg)	JRC-TIO-15	$21^{a}, 26^{b,c}$	50		anatase:rutile = 8:2	79	137	23
с		P25	21 ^{<i>a</i>,<i>c</i>}	60	2.0	anatase:rutile = 8:2	79	137	24
d		PEC-TOM-P03	16 ^{<i>a</i>,<i>c</i>}	82.7 ^g	2.1	anatase dominant, rutile and brookite minor	68	85	
e		JRC-TIO-6	15 ^a	96.4 ^g	1.8	rutile	101	91	23
f		rutile-W ^e	61 ^{<i>a</i>,<i>d</i>}	8.0 ^g		rutile	77	120	
g	BiOCl (0.6	mg)		10.5 ^g	0.83			108	

^{*a*}Fresh sample. ^{*b*}Heated at 523 K. ^{*c*}Based on XRD peak width (101 diffraction of anatase, ^{*d*}110 diffraction of rutile). ^{*e*}The particle size was less than 5 μ m. ^{*f*}Based on cross-sectional SEM. ^{*g*}Based on N₂ adsorption at 77.4 K. ^{*h*}Standard hydrogen electrode (SHE).

concentration was 120 mg L⁻¹. If the molar absorption coefficient of visible light absorption for these anthocyanidins (Figure 1) is equivalent to that for compound 1, the concentration was 0.13 mM and the average molecular weight was 920. Ten drops (0.12 mL, 16 nmol of the anthocyanidin) were cast onto a TiO₂/ITO/Pyrex plate. The dye-adsorbed TiO₂ film was light red (Figure S1b and the Supporting Information). For comparison purposes, anthocyanins were also extracted from rosehip herbal tea (Tree of Life Co., Ltd., Japan, No. 02-520-7340) and hibiscus herbal tea (Tree of Life Co., Ltd., Japan, No. 02-620-6650) using ethanol (10 mL) at 298 K for 24 h. The extracts were cast onto a TiO₂/ITO/Pyrex plate in a manner similar to that used for the Pompadour herbal tea.

BiOCl was synthesized from an aqueous solution using bismuth trichloride.²⁵ The obtained BiOCl powder (6.0 mg) was suspended in deionized water (60 μ L; < 0.055 μ S cm⁻¹) supplied by a RFU424TA system (Advantec) and agitated using ultrasonification (430 W, 38 kHz) for 10 min. An aliquot of the suspension was pasted onto the ITO-coated Pyrex glass plate in a manner similar to that used to prepare the TiO₂/ITO/Pyrex anodes. The amount of BiOCl deposited on each ITO-coated glass plate was 0.6 mg, and it covered an area of 1.0 cm × 1.3 cm.

Characterization. Cross-sectional scanning electron microscopy (SEM) images were obtained using a JSM-6510 scanning electron microscope (JEOL) at an accelerating voltage of 15 kV. A tungsten filament was used in the electron gun. The photocatalyst film on the ITO/Pyrex plate was cut and mounted on an aluminum sample holder using an adhesive.^{26,27} The incident angle of electrons with reference to the sample surface was between 5° and 15° . The magnification was between $\times 500$ and $\times 20$ 000.

Ultraviolet (UV)-visible absorption spectra were obtained in transmission mode using a spectrophotometer (Model V-650, JASCO) in the wavelength range 200–800 nm with D_2 and halogen lamps for wavelengths below and above 340 nm, respectively. The ethanol solutions of pelargonidin chloride, organic dye (PEC-TOM-P04), and herbal tea extract were set in quartz glass cells with 1.0 cm sample thickness.

X-ray diffraction (XRD) patterns were obtained for the photocatalyst films. The XRD patterns were measured at a Bragg angle of $2\theta_{\rm B} = 20^{\circ} - 80^{\circ}$ with a scan step of 0.02° and scan rate of 4 s per step using a D8 ADVANCE (Bruker) operated at 40 kV and 40 mA with Cu K α emission (wavelength $\lambda = 0.15419$ nm) and a nickel filter. The mean particle size (*t*) was determined using the Scherrer equation

$$t = \frac{0.9\lambda}{\text{full width at half maximum } \times \cos \theta_{\text{p}}}$$
(3)

Photoelectrochemical Measurements. Cyclic voltammetry (CV) measurements were performed for several samples of TiO₂ (Table 1) as the working electrode (WE; TiO₂/ITO/Pyrex and an Au/Ni-coated stainless steel clip; Toyo Corporation), glassy carbon as the counter electrode (CE; Model 002012, $\Phi_{\text{polyetheretherketone}}$ 6.0 mm, Φ_{C} 3.0 mm; BAS Incorporation), and Ag/AgCl as the reference electrode (RE; Model RE-1B, BAS Incorporation), immersed in a hydrochloric acid solution (80 mL, pH 4.0). A quartz glass window was

used to allow UV–visible light irradiation. The voltage of the WE was swept between -1.00 and 1.50 V versus Ag/AgCl at a rate of 50 mV s⁻¹ using a potentio/galvanostat (VersaSTAT 3-100, Princeton Applied Research) in a N₂ atmosphere at a flow rate of 30 mL min⁻¹, either under irradiation with UV–visible light or in the dark.

Impedance measurements were performed for several film-form samples of TiO₂ (0.4 mg) and BiOCl (0.6 mg, mean thickness 0.8 μ m) on ITO/Pyrex plates using a potentio/galvanostat (VSP, Bio-Logic). A square Cu plate (6 mm × 6 mm × 30 μ m) was attached to these photocatalyst films, and the impedance between the Cu plate and ITO film was monitored using Au-coated Cu probes (KPRO-RY, Toyo Corporation) in low-current mode. The applied alternative voltage was 100 mV, and the frequency was scanned between 10⁻¹ Hz and 10⁶ Hz.

¹⁸O₂ Exchange Photoreaction Tests. Isotope-labeled photoreaction tests were monitored using gas chromatography–mass spectrometer (Model JMS-Q1050GC, JEOL).²⁸ Helium (purity >99.9999%) was used as the carrier gas. The sampling loop comprised a Pyrex glass system vacuumed using rotary and diffusion pumps (10^{-6} Pa) and connected to the JMS-Q1050GC using 1.5 m of deactivated fused silica tube (No. 160-2845-10, Agilent; internal diameter 250 μ m) maintained at 393 K.

A photocatalyst sample (0.135 g, Table 1a–f) was placed in a quartz photoreactor and evaluated at 295 K for 2 h at 10^{-6} Pa.^{1,28–32} Then, ¹⁸O₂ photoexchange (0.55 kPa; ¹⁸O 97.8%, chemical purity > 99.9%, Cambridge Isotope Laboratories, Inc.) with the photocatalyst was monitored at 295 K under irradiation by UV–visible light from a 500 W xenon arc lamp (Model SX-UID502XAM, Ushio). The distance between the exit of the lamp window and the photocatalyst was 160 mm. The exchange with ¹⁶O atoms at the surface was monitored using a packed column of 13X-S molecular sieves (GL Sciences, Inc.) set in the JSM-Q1050GC.

Photodecomposition of $H_2^{18}O(0.25-1.8 \text{ kPa}; {}^{18}O 97\%$, chemical purity > 99.9%, Cambridge Isotope Laboratories, Inc.) with TiO₂ samples (0.135 g) and those impregnated with silver nitrate (Wako, purity 99.9%) was also monitored at 295 K using the JSM-Q1050GC under irradiation from a Model SX-UID502XAM similar to the ${}^{18}O_2$ photoexchange experiments.

SC Tests. The TiO₂/ITO/Pyrex and BiOCl/ITO/Pyrex electrodes were immersed in HCl solutions (40 mL in each compartment, initial pH 2.0). The two compartments were separated by a 50 μ m-thick H⁺-conducting polymer film (Nafion, DuPont; acid capacity > 9.2 × 10⁻⁴ equiv g⁻¹).^{16,33,34} N₂ (purity >99.999%) and O₂ (purity >99.6%) were bubbled 30 mm from each photoelectrode at a flow rate of 100 mL min⁻¹. The SC was equipped with quartz windows ($\Phi = 80$ mm) on both sides. Both the TiO₂ and BiOCl photocatalysts were irradiated with UV–visible light through the quartz windows using a two-way branched quartz fiber light guide (Model 5 Φ -2B-1000L, San-ei Electric Co.) from the model SX-UID502XAM. The distance between the light exit ($\Phi = 5$ mm) and the surface of the TiO₂ and BiOCl film was 46 mm. The light intensity was 91.3 mW cm⁻² at the center of the photocatalyst film on each electrode.

The dependence of the current (i)-voltage (V) curves on the configuration of the anode and cathode was assessed in front-rear



Figure 2. Cross-sectional SEM images of TiO_2 films prepared from (a) PEC-TOM-P03, (b, b') JRC-TIO-6, and (c) a BiOCl film. The film for b' was prepared via the slide method (*see the Experimental Section*).

configuration with N₂ and O₂ flows, respectively, by varying the resistance between 500 k Ω and 0.3 Ω .^{3,15,16} The front and rear configurations allow perpendicular UV–visible light irradiation from the photocatalyst and Pyrex/ITO glass sides, respectively.³ For comparison, a Xe arc lamp (300–500 W) and LED lights (BR-244HK, SO-2123, Gentos Co.) at 3 W were also used for irradiation from both sides. Some of the *i*–V tests were conducted by irradiating the anode with visible light filtered with a L39 sharp cut filter (thickness 2.5 mm, Kenko) and the cathode being irradiated with UV–visible light as above.

RESULTS AND DISCUSSION

UV–Visible Spectra of Organic Dyes. UV–visible absorption spectra were obtained for ethanol solutions of the organic dyes to evaluate absorption wavelength for PEC-TOM-P04 and the herbal tea extracts (Figure 1). Standard pelargonidin chloride solution shows a major peak at 532 nm and a shoulder peak at 430 nm in the visible-light range. The color of the solution was complementary red and the molecule is protonated at the 4'-position of the phenyl ring (Scheme 1b).

The 0.030 mM ethanol solution of PEC-TOM-P04 shows a resolved peak at 415 nm in the visible-light region (Figure 1). The ethanolic rosehip/hibiscus herbal tea extract shows a broad peak at 553 nm accompanied by a shoulder feature at 452 nm in the visible-light range.

The absorption peak position depends primarily on the structure of the aglycone (Scheme 1b-d) and the pH of the solution (b and b'). To check absorption peak position for each anthocyanidin, absorption spectra of the ethanol extract of the rosehip flower and that of the hibiscus flower were measured independently (Figure 1d and e). A peak at 456 nm appeared for the cyanidin in rosehip flowers corresponding to a shoulder feature at 452 nm in rosehip/hibiscus tea (Figure 1c). A peak at 547 nm appeared for the delphinidin in hibiscus flowers corresponded to the peak at 553 nm in rosehip/hibiscus flowers (Figure 1c).

The structural differences between pelargonidin, cyanidin, and delphinidin is the number of hydroxy groups on the phenyl ring, i.e., one, two, and three, respectively, and these lead to differences in absorption peak position, i.e., 500 nm for pelargonidin 3-*O*-glucoside, 510 nm for cyanidin 3-*O*-glucoside, and 516 nm for delphinidin 3-*O*-glucoside.³⁵ Thus, the absorption peak shift of ~100 nm in ethanol shown in Figure 1 could be attributed to the effects of organic acid contained in

samples. It should be noted that the dyes were used in SC in acidic pH solutions (2.0). Under the same pH conditions, the absorption peak for the cyanidin in rosehip should be between 532 nm (pelargonidin) and 553 nm (delphinidin) based on the number of hydroxy groups (Scheme 1b-d).

The major peak at 532 nm for pelargonidin chloride corresponds to the HOMO–LUMO gap of 2.33 eV. This value is consistent with the previously reported energy levels of the HOMO (+0.13 V) and LUMO (–2.11 V) relative to standard hydrogen electrode (SHE) for pelargonidin extracted from Ixara Flora.³⁶ The absorptions for cyanidin (\approx 543 nm) and delphinidin (553 nm) correspond to the very similar HOMO–LUMO gap values of 2.28 and 2.24 eV, respectively. Conversely, the major peak at 415 nm for the organic dye in PEC-TOM-P04 corresponds to the relatively larger HOMO–LUMO gap of 2.99 eV.

Cross-Sectional SEM Measurements for the Electrode with TiO₂. In a previous study,³ the bulk density for the flat TiO₂ film (2.0 mg) prepared from a PEC-TOM-P03 suspension was calculated to be 3.3 ± 0.3 g cm⁻³ based on cross-sectional SEM images (mean thickness $4.7 \pm 0.5 \,\mu$ m). This value is 84% of the density of anatase-type TiO₂ crystals (3.89 g cm⁻³),³⁷ demonstrating the formation of a dense, closely packed TiO₂ film on the ITO glass. In contrast, the mean thickness of the TiO₂ film (0.4 mg) prepared from PEC-TOM-PO3 in this study is $2.1 \pm 0.1 \,\mu$ m (Figure 2a and Table 1d), and the bulk density is calculated as 1.47 ± 0.07 g cm⁻³ (Figure S2). This value is $38 \pm$ 2% of the density of anatase-type TiO₂ crystals,³⁷ indicating the formation of a relatively porous but sufficiently flat TiO₂ film on the ITO glass.

The TiO₂ film (0.4 mg) prepared from JRC-TIO-06 is inhomogeneous and comprises dispersed nanoparticles with diameters of 2–20 μ m (Figure 2b1), unlike the flat film prepared from PEC-TOM-PO3 (Figure 2a). The mean thickness is 1.8 ± 0.5 μ m taking the uncovered ITO part of the film area into account (Figure 2b1–3 and Table 1e). Therefore, the bulk density of these films is 1.7 ± 0.5 g cm⁻³ (Figure S2). This value is 40 ± 12% of the density of rutile-type TiO₂ crystals (4.25 g cm⁻³),³⁷ indicating an extensively loose packing arrangement. In comparison, a film formed via the slide method starting from JRC-TIO-6 became more flat (mean thickness 2.4 ± 0.3 μ m, Figure 2b') and the bulk density of the film is 1.3 ± 0.2 g cm⁻³ (Figure S2). The slide method successfully controlled the film so as to be more flat and effectively removed powders greater than 10 μ m (Figure 2b and b').

The bulk density of TiO₂ could be controlled to ~3.5 g cm⁻³ for the TiO₂ films of mean thickness greater than 4 μ m, i.e. the weight greater than 1.8 mg (Figure S2). However, if the TiO₂ weight is less than 1.8 mg (Figure 2a and b), the bulk density of TiO₂ varied between 1.3 and 3.5 g cm⁻³ depending on the degree of coagulation of primary and/or secondary nanoparticles and mixed polyethylene glycol (Scheme 2).

Scheme 2. Conceptual Explanations for the Effects of Primary Particle Size of TiO_2 and Mixed PEG in the Photocatalyst Film Used on the Anode of SC on the Photocurrent



In a previous study,³ the bulk density of a relatively porous BiOCl film (2.5 mg) was 3.6 g cm⁻³ based on the cross-sectional SEM images (mean thickness 5.4 μ m). This value is 46% that of tetragonal BiOCl crystals (7.784 g cm⁻³),³⁸ demonstrating the formation of a loose BiOCl film on the ITO glass. In contrast, the thinner BiOCl film in this study (0.6 mg) is relatively dense and flat with a mean thickness of 0.83 ± 0.24 μ m (Figure 2c and Table 1g). The bulk density is thus 5.6 ± 1.8 g cm⁻³, which is 72 ± 23% that of tetragonal BiOCl crystals,³⁸ and 1.57-times that reported from the previous study (2.5 mg).³

CV Measurements of Several Types of TiO₂ Film. CV measurements using several types of TiO₂ film under N₂ atmosphere in the presence or absence of UV-visible light irradiation were performed (Table 1a-f). In this study, in the SC comprising photocatalysts on both the anode and cathode, the electrons photoexcited to the CB in TiO₂ at the anode flow into the VB in BiOCl at the cathode via the external circuit. Based on the difference of the two levels, the electromotive force is always greater than 1 V.^{3,15,16} Therefore, the difference in currents recorded in the presence and absence of UV-visible light for the CV region >1 V generally indicates the efficiency of charge separation and the conductivity of photogenerated charges from TiO₂ to the cathode. An increment in current due to electrochemical/photocatalytic oxidation of water is also observed in the oxidation wave in the region above 1.6 V (Figure 3).

The difference in currents recorded in the presence and absence of UV-visible light at 1 V versus SHE is in the order:



Figure 3. CV results for several different WEs in aqueous solutions of pH 4.0 under N_2 flow with either irradiation by UV–visible light (red/thin) or in the dark (blue/thick). The source of TiO₂ in the photocatalyst was (a) JRC-TIO-14, (b) JRC-TIO-15, (c) P25, (d) PEC-TOM-P03, (e) JRC-TIO-6, and (f) rutile-W. The light was applied perpendicularly from the photocatalyst side.

JRC-TIO-6 (101
$$\mu$$
A) > P25 (79 μ A)
~ JRC-TIO-15 (79 μ A) ~ rutile-W (77 μ A)
> PEC-TOM-P03 (68 μ A) > JRC-TIO-14 (60 μ A)
(4)

The photocurrents shown above are not simply correlated to the specific SA, mean primary particle size, or crystalline phase (Table 1). The optimum mean particle size in terms of current is 15-21 nm due to the balance of two competing factors for the electron conductivity in TiO₂ film, i.e., (a) fast electron conductance in the primary particles of TiO₂, for which larger particles are favorable (Scheme 2a) and (b) effective packing of primary particles as a film to minimize the resistance at their interfaces, for which smaller particles are favorable (Scheme 2b). Nonconducting polyethylene glycol (PEG) was added to the PEC-TOM-PO3 (Table 1d) and would be disadvantageous in terms of electron conductivity (Scheme 2c) compared to the polymer-free sources JRC-TIO-6, P25, JRC-TIO-15, and rutile-W (Table 1b, c, e, and f).

An electrochemical increment in the oxidative wave in the range >1.6 V for water oxidation is clearly observed using P25 (Figure 3c) and JRC-TIO-6 (Figure 3e) in the dark. However, the peaks recorded in light become weaker and less clear than those recorded in the dark because water oxidation proceeds both electrochemically and photocatalytically in the range lower than 1.6 V.

Impedance Measurements of Photocatalyst Films. The impedance of the TiO_2 films was evaluated based on the Cole–Cole plots (Figure 4a). The resistance values were evaluated based on eq 5:

$$(\text{impedance}_{\text{real}} - a)^2 + (\text{impedance}_{\text{imaginary}} - b)^2$$
$$= \left(\frac{\text{resistance}}{2}\right)^2 \tag{5}$$

If the sample behaves as an ideal equivalent circuit comprising a parallel resistor and condenser, a perfect semicircle is drawn in the first quadrant. However, the impedance of TiO_2 films in this study is affected by the particle size distribution of TiO_2 (Table 1) and the effectiveness of the electric contact between TiO_2



Figure 4. Cole–Cole plots for TiO_2 (a) and BiOCl films (b) and the theoretical data fitted to eq 5.

nanocrystals. Thus, the value b needs to be included in eq 5, and we tried to fit the plot data to a complete circle. The resulting order of resistance was

PEC-TOM-P03 (85 MΩ) ~ JRC-TIO-6 (91 MΩ) < rutile-W (120 MΩ) ~ P25 (137 MΩ) ~ JRC-TIO-15 (137 MΩ) < JRC-TIO-14 (247 MΩ) (6)

This order generally corresponds to that of the CV measurements divided into three groups, (i) JRC-TIO-6, (ii) rutile-W, P25, and JRC-TIO-15, and (iii) JRC-TIO-14 (see order 4). A similar charge transfer resistance value (7.1 M Ω) has been

reported for a TiO₂ layer with no bias potential, as in this study.³⁹ The only exception is PEC-TOM-P03. In the previous section on CV, the addition of PEG negatively reduced the electron conductivity by more than 33 μ A (order 4, Figure 3d, and Scheme 2c). The flatness of the photocatalyst film would be the other factor to reduce the resistance because the impedance measurements were performed by attaching a flat Cu plate to photocatalyst film. As is evident from the cross-sectional SEM images, the PEC-TOM-P03 film is significantly more flat and smooth in comparison to the JRC-TIO-6 film (Figure 2a and b).

Thus, while the CV performance of the TiO_2 film was determined by the primary particle size (15–21 nm) in the previous section (Scheme 2a and b), the effects of the added PEG and potential effects of the flatness of the TiO_2 film should be essential for the impedance values for PEC-TOM-P03 (Scheme 2c and d).

Similarly, the resistances of the BiOCl films were also evaluated (Figure 4b). The value of 206 M Ω for the 2.5 mg film in a previous study³ was decreased to 108 M Ω for the more flat 0.6-mg film prepared in this study (Table 1g).

¹⁸O₂ Exchange Reaction Rates. The time courses for the exchange of ¹⁸O₂ with O (oxo, hydroxy) and/or O of water on different TiO₂ surfaces are summarized in Figure 5a–f. The decrease in ¹⁸O₂ balances with the sum of the increases in ¹⁸O¹⁶O, and ¹⁶O₂, except in the case of PEC-TOM-PO3, for which the decrease in ¹⁸O₂ is significantly faster, suggesting



Figure 5. Results of ¹⁸O₂ exchange experiments using several TiO₂ and BiOCl photocatalysts (0.135 g) under irradiation by UV-visible light. Initial ¹⁸O₂ pressure: 0.55 kPa. (a) JRC-TIO-14, (b) JRC-TIO-15, (c) P25, (d) PEC-TOM-P03, (e) JRC-TIO-6, (f) rutile-W, and (g) BiOCl.

Table 2. Results of ¹⁸O₂ Exchange Experiments

			Initial decrement/formation rate $(\mu \text{mol } \text{h}^{-1} \text{g}_{\text{cat}}^{-1})$				surface O		
entry		sample	¹⁸ O ₂	¹⁸ O ¹⁶ O	¹⁶ O ₂	calculated O atom ratio in ${\rm ^{18}O_2}$ introduced vs surface O	nm ⁻²	μ mol 0.135 g ⁻¹	
a	TiO ₂	JRC-TIO-14	-445	315	154	$1: 6.0 \pm 0.2$	8.3	560	
b		JRC-TIO-15	-135	103	20	$1: 1.34 \pm 0.02$	11.4	130	
с		P25	-156	106	39	$1: 1.47 \pm 0.02$	9.9	140	
d		PEC-TOM-P03	-78	17	3.0	$1: 1.26 \pm 0.05$	6.5	120	
e		JRC-TIO-6	-6.0	6.4	0.98	$1: > 0.34 \pm 0.02$	>1.5	>32	
f		rutile-W	-32	34	1.4	$1: 0.17 \pm 0.01$	8.7	16	
g	BiOCl		-3.2	1.9	0.13	$1:>0.12\pm0.01$	>4.7	>11	

excessive adsorption of ${}^{18}O_2$ rather than a balanced exchange. The formation rates of ${}^{18}O^{16}O$ are in the following order:

$$[\text{RC-TIO-14} (315 \,\mu\text{mol}\,\text{h}^{-1}\,\text{g}_{\text{cat}}^{-1}) > \text{P25} (106 \,\mu\text{mol}\,\text{h}^{-1}\,\text{g}_{\text{cat}}^{-1})$$

~ JRC-TIO-15 (103
$$\mu$$
mol h⁻¹ g_{cat}⁻¹)

- > rutile-W (34 μ mol h⁻¹ g_{cat}⁻¹)
- > PEC-TOM-P03 (17 μ mol h⁻¹ g_{cat}⁻¹)

> JRC-TIO-6 (6.4 μ mol h⁻¹ g_{cat}⁻¹) (7)

This order is not directly correlated to that of specific SA. However, O_2 exchange is faster in general on anatase-type TiO₂ than that on rutile-type TiO₂ (Table 1).

When the ratio of the number of O atoms in the gas-phase ¹⁸O₂ (¹⁸O 97.8%) to the ¹⁶O species on TiO₂ (natural abundance ¹⁶O 99.8%) is 1:*n*, the molar ratio of ¹⁸O₂:¹⁸O¹⁶O:¹⁶O₂ reaches 1:2*n*:*n*² at the equilibrium of the exchange reaction. Thus, the *n* values were determined for six types of TiO₂ (Table 2). Furthermore, the number of O atoms in the unit area (nm²) on the TiO₂ samples was calculated to be 6.5–11.4 based on the *n* and specific SA values (Table 2a–d, f), but this number is quite small (1.5) for JRC-TIO-6 because the O₂ exchange reaction in this case is extremely slow and does not reach equilibrium within 28 h (Figure 5e). A simplified kinetic equation for the ¹⁸O₂ exchange rates is

$$r = kP(^{18}O_2)N\theta(^{16}O)$$
(8)

where *k* is the rate constant, $P({}^{18}O_2)$ is the pressure of ${}^{18}O_2$, *N* is the total number of surface sites, and $\theta({}^{16}O)$ is the ratio of ${}^{16}O$ surface sites to *N*. $P({}^{18}O_2)$ and catalyst amount are constant in the exchange tests in Figure 5, and the order of the formation rates of ${}^{18}O^{16}O$ needs to be reinterpreted by dividing the rates (μ mol h⁻¹ g_{cat}⁻¹) with the $N\theta({}^{16}O)$ value (mol) based on the *n* value given in Table 2.

rutile-W
$$(0.30 \text{ h}^{-1}) > \text{JRC-TIO-15} (0.11 \text{ h}^{-1}) \sim \text{P25} (0.10 \text{ h}^{-1})$$

> JRC-TIO-14 $(0.076 \text{ h}^{-1}) > \text{PEC-TOM-P03} (0.020 \text{ h}^{-1})$
~ JRC-TIO-6 $(< 0.027 \text{ h}^{-1})$ (9)

The exchange reaction was even slower using BiOCl compared to those with TiO_2 . The reaction did not reach the equilibrium within 38 h elapsed, suggesting that the number of O atoms per unit area (nm²) of BiOCl is more than 4.7 (Table 2g).

The photooxidation of $H_2^{18}O$ at 0.25–1.8 kPa using the TiO₂ samples listed in Table 1 was assessed. The conversion is below the detection limits for ¹⁸O₂ and ¹⁸O¹⁶O using JSM-Q1050GC (data not shown). Furthermore, when the TiO₂ is impregnated with 3.0 wt % Ag⁺, oxidation of $H_2^{18}O$ is still below the detection

limit. Thus, the reverse reaction of the O_2 formed on the TiO₂ with protons and electrons, reforming water molecules, is significant. In this study, the SC utilizing photocatalysts on both electrodes forms electrons as the result of water oxidation that quickly transfer to the cathode via the external circuit, thus effectively suppressing the reverse reaction on the anode (Scheme 3).

Scheme 3. Energy Diagram for a Solar Cell Comprising TiO₂ Enhanced with Pelargonidin on the Anode and BiOCl on the Cathode



i–V Dependence of SC Performance for Different TiO₂ Photocatalysts. First, *i–V* dependence was investigated for several kinds of TiO₂ photocatalysts (Table 1a–f). The photocatalyst on the cathode was always BiOCl. In ref 3, PEC-TOM-PO3 (2.0 mg) and BiOCl (2.5 mg) formed on ITO electrodes using water as the solvent (Figure 6a) provided a V_{OC} of 1.85 V. However, two problems remained in the previous study:³ (i) non-negligible current leakage in the region below 0.7 V owing to electron flow from the CB of TiO₂ directly to oxygen vacancy sites on/in BiOCl via the external circuit and (ii) linear *i–V* dependence in the region 1.0–1.85 V (W_{max} 42.2 μ W cm⁻², Table 3i) in comparison to the typical convex curve for Si SCs, increasing W_{max} as the product area of the *i* and *V* values.

These two problems are well resolved using thinner photocatalyst films in this study. For the thinner TiO_2 films, the electron diffusion overvoltage in the TiO_2 and the electrons flowing from the anode effectively coupled with holes remaining in the VB of BiOCl for the rear configuration of the cathode (Scheme 3, right). Using PEC-TOM-P03 (0.4 mg) and BiOCl (0.6 mg) formed on ITO electrodes, the current leakage is negligible in the lower voltage region and a convex i-V



Figure 6. Current—voltage dependence using (a) PEC-TOM-P03 (2.0 mg, 0.4 mg ■) and (b) JRC-TIO-14 (\diamondsuit), JRC-TIO-15 (\Box), P25 (\bigcirc), PEC-TOM-P03 (\blacksquare), JRC-TIO-6 (\triangle), and rutile-W (\blacktriangle) TiO₂ photocatalysts on the anode. BiOCl was used on the cathode.

dependence curve is formed, providing a $W_{\rm max}$ of 53.7 μ W cm⁻² while keeping the $V_{\rm OC}$ value the same, i.e., 1.85 V (Table 3d and Figure 6a). Furthermore, using the same amounts of photocatalyst on the anode and cathode, the i-V curves are convex and current leakage is negligible for all the types of TiO₂ employed (Table 1a–f and Figure 6b). Thus, in the current study, *t*-butanol as solvent and ethylene glycol as a thickener are effective for the formation of thin TiO₂ films. The $V_{\rm OC}$ values are divided into three groups: (i) JRC-TIO-6 (1.93 V), (ii) JRC-TIO-15, JRC-TIO-14, P25, and PEC-TOM-P03 (1.88–1.85 V), and (iii) rutile-W (1.76 V). However, the maximal difference between them is only 8.8%. Conversely, the $i_{\rm max}$ values are in the same order as that for $W_{\rm max}$ and the difference is as large as 30%. The order of $W_{\rm max}$ values is

JRC-TIO-6 (56.1
$$\mu$$
W cm⁻²) > PEC-TOM-P03 (53.7 μ W cm⁻²)
> rutile-W (49.5 μ W cm⁻²) ~ P25 (47.4 μ W cm⁻²)
~ JRC-TIO-15 (45.6 μ W cm⁻²)
> JRC-TIO-14 (39.9 μ W cm⁻²) (10)

Table 3.	Summary	of i-	-V De	pendence	Tests
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In other words, the V_{max} values do not vary much, all falling in the range 1.23–1.36 eV (Table 3a–f). The order of W_{max} values (order 8) is consistent with the order of photocurrents obtained from CV measurements (order 4) except for that of PEC-TOM-P03. The electron conductivity in the TiO₂ film, rather than the number of active sites on the TiO₂, is a critical factor for SC performance in this study (Scheme 2a and b). However, the homogeneity of TiO₂ films prepared from PEC-TOM-P03 (Figure 2A) is also critical (Scheme 2c and d) because it leads to lower resistance (order 6 and Figure 4).

The $V_{\rm OC}$ and $W_{\rm max}$ values obtained using JRC-TIO-6 on the photoanode and BiOCl on the photocathode (1.93 V and 56.1 μ W cm⁻²) were moderately improved in comparison to reported values of $V_{\rm OC}$ of 1.91 V and $W_{\rm max}$ of 42.2 μ W cm⁻².³ The $W_{\rm max}$ value by the SC free from fuel (56.1 μ W cm⁻²) is comparable to that previously reported for a phenol-FC using CdS on the photoanode and Cu₂O on the photocathode (60 μ W cm⁻²) and slightly smaller than those reported for a phenol/glucose-FCs using TiO₂ on the photoanode and C/Cu₂O/Cu on the photocathode (73 μ W cm⁻²) or W:BiVO₄ on the photoanode and polyterthiophene on the photocathode (82 μ W cm⁻²).¹⁰

The exchange of ¹⁸O₂ with ¹⁶O₂ or surface O species has been correlated with catalytic activity in the total oxidation of methane,⁴⁰ N₂O decomposition,⁴¹ NO_x reduction with alkanes,⁴² and the CO–NO reaction.⁴³ Furthermore, fundamental studies of this exchange in terms of basic sites⁴⁴ or Raman shifts⁴⁵ have also been reported. Interestingly, in the current study, the $W_{\rm max}$ values (order 8 and Table 3) are negatively correlated to ¹⁸O¹⁶O formation rates in the ¹⁸O₂ exchange tests (order 7 and Figure 7a). However, the $W_{\rm max}$ values did not correlate to the formation rates if the numbers of surface O atom in photocatalyst (Table 2) are considered (eq 9) in the kinetics (eq 8). Instead, the numbers of surface O atom was plotted versus $W_{\rm max}$ values and negative correlation was clearly demonstrated (Figure 7b). Thus, water photooxidation

	photocatalyst				W _{max}			
entry	anode	cathode	light source power (W)	$(\mu \mathrm{A~cm^{-2}})$	$V_{ m OC}$ (V)	$W_{ m max} \ (\mu { m W~cm^{-2}})$	$(\mu A cm^{-2})$	V _{max} (V)
a	JRC-TIO-14 (0.4 mg)	BiOCl (0.6 mg)	Xe arc (500)	41.5	1.88	39.9	31.9	1.25
b	JRC-TIO-15 (0.4 mg)			65.7	1.88	45.6	34.5	1.32
с	P25 (0.4 mg)			54.0	1.87	47.4	34.9	1.36
c'	P25 (0.4 mg) + PEC-TOM-P04			78.0	2.00	73.1	53.5	1.37
c"	P25 (0.4 mg) + rosehip-hibiscus flowers			69.2	2.04	64.7	45.5	1.42
c"'	P25 (0.4 mg) + rosehip flowers ^b			82.7	2.04	64.5	50.5	1.28
c""	P25 (0.4 mg) + hibiscus flowers ^{b}			85.2	2.11	72.9	53.5	1.36
d	PEC-TOM-P03 (0.4 mg)			49.9	1.85	53.7	41.2	1.30
e	JRC-TIO-6 (0.4 mg)			57.9	1.93	56.1	45.6	1.23
f	rutile-W (0.4 mg)			55.5	1.76	49.5	40.2	1.23
g	JRC-TIO-15 (0.4 mg)		(450)	47.3	1.86	36.8	29.0	1.27
g'			(400)	43.3	1.86	33.2	24.6	1.35
g"			(300)	26.5	1.82	18.6	11.3	1.65
g""			LED (3)	< 0.01	0.23	< 0.002	< 0.01	0.20
h	P25 (0.4 mg)		Xe arc (500), L39 filter	21.0	1.77	10.6	8.65	1.23
h'	P25 (0.4 mg) + PEC-TOM-P04			21.6	1.82	16.5	12.7	1.31
h"	P25 (0.4 mg) + rosehip-hibiscus flowers			24.4	2.05	29.4	20.1	1.47
i	PEC-TOM-P03 (2.0 mg)	BiOCl (2.5 mg)	Xe arc (500)	65.4 ^a	1.85 ^a	42.2 ^{<i>a</i>}	41.9 ^a	1.01 ^{<i>a</i>}

^aReported in ref 3. ^bA slide method was employed for pasted TiO₂ suspension on ITO.



Figure 7. Negative correlation between (a) ¹⁸O¹⁶O formation rate and (b) surface O amount in photocatalyst in the ¹⁸O₂ exchange reaction and W_{max} values generated using TiO₂ on the anode.

proceeded faster and/or the reverse reaction from O_2 to water was effectively suppressed over TiO₂ comprising less exchangeable surface O atoms.

i–V Dependence of SC Output as a Function of Incident-Light Power. The origin of cell power and the dependence of cell power on incident-light power were reconfirmed. Using JRC-TIO-15 and BiOCl photocatalysts, *i–V* dependence tests were performed by changing the power (x) of the incident Xe arc lamp (300–500 W) and also using LED light (3 W) (Figure 8a). Based on the dependence observed, it is



Figure 8. (a) i-V dependence as a function of the power of UV-visible light source using JRC-TIO-15 and BiOCl as the photocatalysts on anode and cathode, respectively. (b) Current at 0.50 V as a function of the power of UV-visible light source. Xe arc lamp with a branched fiber light guide was operated between 500 and 300 W and LED lights were operated at 3 W.

apparent that light energy is transformed into electricity, and the current at 0.5 V was plotted because of a sudden current rise below 0.3–0.4 V owing to current leakage and the fact that the current at 0.5 V is a good representation of current due to electron flow from the CB of TiO₂ on the anode to the VB of BiOCl on the cathode (Scheme 3). The dependence was fit to *i* = 0.000883 $x^{1.751}$ (Figure 8b). The power is nearly 2, suggesting that the product of the concentration of electrons in the CB of TiO₂ and that of holes in the VB of BiOCl determines the current based on formulation by reaction kinetics.¹⁶

Enhanced *i*–*V* Dependence of SC Performance by the Addition of Organic Dyes. The effect of the addition of organic dyes to TiO_2 (P25) upon cell voltage and current was assessed. The *i*–*V* dependence for the SC using a P25 film supplemented with 36 nmol of organic dye (PEC-TOM-P04) on the anode was compared to that for the SC using dye-free P25 film on the anode under irradiation by UV–visible light (Figure 9a1). The V_{OC} and i_{SC} values increase from 1.87 to 2.00 V and 54.0 to 78.0 μ A cm⁻², respectively, upon the addition of the organic dye (Table 3c and 3c'). Accordingly, the cell power also

increases from 47.4 to 73.1 μ W cm⁻², i.e., by a factor of 1.54, mainly due to the increase in i_{max} (53.5 μ A cm⁻²).

The addition of 16 nmol of anthocyanin (delphinidin and cyanidin) extracted from rosehip and hibiscus flowers to P25 was also evaluated in the same way (Figure 9a2). The V_{OC} value further increases to 2.04 V (Table 3c"). Accordingly, the cell power also increases from 47.4 to 64.7 μ W cm⁻², i.e., by a factor of 1.36, mainly due to the increase in i_{max} (45.5 μ A cm⁻²).

The effects of organic dye addition were also evaluated for an anode under irradiation by light with a wavelength greater than 390 nm (Figure 9b). Most of the UV light is eliminated under these conditions. The cell power falls to 22.4% that under full UV–visible light (Table 3c and 3h) for the SC containing the dye-free TiO₂ (P25) and BiOCl. When PEC-TOM-P04 is added to the TiO₂ film, the cell power falls to 22.6% that under full light (Figure 9b1 and Table 3c' and 3h'). Thus, the photoexcitation of TiO₂ is the major factor controlling the performance of the SCs, and the PEC-TOM-P04 dye clearly promotes electron flow from/to TiO₂.

In contrast, when the rosehip/hibiscus extract (16 nmol) is added to P25, the cell power under visible-only irradiation falls to 45.4% that under full light (29.4 μ W cm⁻², Figure 9b2 and Table 3c" and h"), which is significantly more than that observed for the dye-free test (22.4%) or that using PEC-TOM-P04 (22.6%). Furthermore, the V_{OC} value under UV–visible light is maintained at 2.05–2.04 V under full visible light (Figure 9a2 and b2, blue). Thus, the dyes from the tea extract not only promote electron flow from/to TiO₂, but enhance charge separation in TiO₂ and boost the W_{max} value.

On the anode, the electrons in the VB in TiO₂ are mostly excited by UV light, whereas organic dyes, e.g., pelargonidin, adsorbed on the TiO₂ nanoparticles are excited by visible light (Scheme 3). The theoretical electromotive force of the SC in this study is the difference (2.75 V) between the CBM of TiO₂ and the VBM of BiOCl.^{3,15,16,46} The theoretical electromotive force is decreased by the overvoltage (0.23 V) due to electron diffusion in the TiO₂ layer (Scheme 3, left).³ The organic dyes are well adsorbed in the TiO2 and should distribute homogeneously within a variation of 30% in the TiO_2 layers (Figure S1). If the excited electrons in the CB of TiO_2 flow into the unfilled HOMO of organic dye molecules in which an electron has already been excited to the LUMO and then the flow into the CB of TiO_2 again (Scheme 3, left), the effective diffusion path is shortened from water photooxidation sites on the TiO₂–ITO layer to the dye-ITO layer. Thus, the V_{OC} values increase from 1.87 V to 2.00-2.04 V (Figure 9) upon the addition of organic dyes.

If we compare the effects of PEC-TOM-P04, rosehip flowers (cyanidin), and hibiscus flowers (delphinidin), the W_{max} values were similar (73.1, 64.5, and 72.9 μ W cm⁻²); however, a progressive increase in V_{oc} values was observed (2.00, 2.04, and 2.11 V, respectively; Table 3c', c"', and c""). Thus, the structural differences between pelargonidin, cyanidin, and delphinidin in the number of hydroxy groups on the phenyl ring (one, two, and three, respectively; Scheme 1) appear to be related to the electromotive force of SC in this study, e.g., to elevate the potential of CBM due to the increase of hydroxy groups (Scheme 3, left).

The increase of cell current by organic dyes (Figure 9) is primarily due to the visible light, which is unutilized by TiO_2 film, contributing to HOMO–LUMO electron excitation in the organic dyes, resulting in an increase in total electron flow to the anode (Scheme 3, left). Such effects explain the increase in W_{max}



Figure 9. Current–voltage dependence obtained on the anode: (1) using P25 (\bigcirc) and P25 mixed with PEC-TOM-P04 (\diamondsuit), (2) using P25 (\bigcirc) and P25 mixed with ethanol rosehip/hibiscus extract (\Box), (3) using P25 (\bigcirc) and P25 mixed with ethanol rosehip extract (\Box), and (4) using P25 (\bigcirc) and P25 mixed with ethanol hibiscus extract (\Box). BiOCl was used on the cathode. Irradiated under (a) UV–visible light and (b) visible light only.

by the addition of PEC-TOM-P04 to TiO₂ irradiated by UV– visible light (by 1.54 times) and by visible light only ($\lambda > 390$ nm, by 1.56 times; Figure 9a1 and b1).

However, this interpretation does not totally explain the increase in W_{max} upon the addition of the rosehip—hibiscus tea extract to TiO₂ irradiated under UV—visible light (by 1.36 times) and under visible light only ($\lambda > 390$ nm, by 2.77 times; Figure 9a2 and b2). The improved charge separation in TiO₂ by electron flow from the CB of TiO₂ to the HOMO then LUMO of the organic dyes is one contributing factor.

CONCLUSIONS

Thin photoelectrodes were formed on ITO glass layers by deposition of TiO₂ to thicknesses of $1.8-2.1 \,\mu\text{m}$ for and BiOCl to a thickness of 0.8 μ m. The power efficiency of SCs containing these photoelectrodes critically depends on the electron conductivity of the TiO₂ layer on the anode. TiO₂ nanoparticles of 15-21 nm were found to be favorable based on the balance between the primary particle size, where larger is better, and the particle-particle interface area, where smaller particles are preferred. The electron conductance in commercial TiO₂ for dye-sensitized SCs was worse than those of TiO₂ types with comparable primary particle sizes, but its impedance is the best among all the TiO₂ types tested in this study because nonconducting polyethylene glycol is added and thus the resulting film layer is quite flat (thickness $2.1 \pm 0.1 \ \mu m$). The efficiency of the TiO₂ film layer in SCs can be critically evaluated based on the amounts of ¹⁸O₂ exchange with surface O species over the TiO₂ because the number of exchangeable O sites on TiO₂ negatively correlates with the rate of water photo-oxidation at the anode owing to the contribution to the reverse reaction from O₂ to water. Thinner TiO₂ film layers are favorable for SCs with higher W_{max} and V_{OC} values, and the addition of organic dyes, e.g., anthocyanins, on/in the TiO₂ layer significantly increases the $W_{\rm max}$ and $V_{\rm OC}$ values, i.e., 73.1 μ W cm⁻² and 2.11 V

per cell. As UV light excites electrons in the VB to the CB of TiO_2 while visible light excites electrons in the HOMO to the LUMO of organic dyes, new electron paths from VB to CB to HOMO to LUMO and then to electrode are created, improving the performance of the SC. With organic dyes, the charge separation in the TiO_2 is improved and the diffusion overvoltage in the TiO_2 layer is suppressed. Finally, electrons transfer via the external circuit to the cathode and effectively combine with holes gathered at the interface between the ITO electrode and the BiOCl film layer excited by UV–visible light.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b02166.

Color change of dropped organic dye extracted from rosehip/hibiscus flowers on TiO_2 (P25) for 1 h and the correlation between film thickness and the bulk density of TiO_2 films (PDF)

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Notes

The authors declare no competing financial interest.

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