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Polarizability and Catalytic Activity Determine Good Titanium Oxide Crystals but Not Homogeneity in Solar Cells Using Photocatalysts on Both Electrodes

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Supporting Information

ABSTRACT: TiO_2 is advantageous when used on the anode of a solar cell (SC) and achieves an electromotive force of 2 V when using another photocatalyst on the cathode (dual-photoelectrode fuel cell). However, both sufficient photocatalytic activity and electronic conductivity are required for the film, and these two requirements compete with each other. Herein, uniformly sized and shaped spheroidal, cubic, and "rhombic" TiO₂ nanoparticles were synthesized, forming films using casting, slide, ball milling-slide (BS), and ball milling-



mechanical (BD) methods. The ac/dc impedances of the films followed the order "rhombic"-ball milling-slide > "rhombic"-slide > cubic-slide > spheroidal-ball milling-mechanical > P25-casting \approx P25-slide \approx spheroidal-BS \approx spheroidal-slide \approx P25-ball milling-mechanical, demonstrating that "rhombic" and cubic TiO₂ films were unsuitable for use on the SC photoanode. The reverse reaction rates of cathode reaction (water photooxidation), that is, the ¹⁸O₂ exchange reaction, were evaluated, which followed the order Cubic-TiO₂ > Spher-TiO₂ > Rhomb-TiO₂ \approx P25-TiO₂, demonstrating that the synthesized TiO₂ films were unsuitable for water oxidation. Polarizability and catalytic activity of TiO₂ crystals were critical to maximize the SC performance, and fluorescence peak intensity at 372–366 nm was well correlated with SC performance. P25-slide on a photoanode at pH 1.78 and BiOCI-Cast on a photocathode at pH 2.00 enabled a maximum power of 85.2 μ W cm⁻² and an open-circuit voltage of 1.94 V.

KEYWORDS: solar cell, dual-photoelectrode fuel cell, photocatalyst, water oxidation, TiO₂, polarizability, impedance, isotope tracing

INTRODUCTION

Photoanodes have been investigated for various applications, for example, perovskite solar cells (SCs),¹ dye-sensitized SCs,^{2,3} photofuel cells,^{4,5} solar water splitting,^{5,6} and sensors.^{7,8} Optimization of photoelectrodes is complex because their performance depends on the balance between the electronic conductivity^{9,10} and chemical performance; for example, for a photoanode, the electron injection efficiency from the highest occupied molecular orbital of the dye to the conduction band (CB) of the semiconductor and then to the anode¹¹ must be balanced against the catalytic reaction efficiency of photocatalytic oxidation on the anode. Dense and porous films, respectively, are required to achieve these attributes.¹²

The development of SCs with dual-photocatalyst systems on both the anode and cathode, called dual-photoelectrode fuel cells elsewhere,^{13–15} is highly desirable to enable a high opencircuit voltage ($V_{\rm OC}$) exceeding 2 V.^{12,16–19} Specifically, our power system utilizes the following reactions at the anode and cathode, respectively.

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+$$
 (1)

$$O_2 + 4H^+ + 4e^- \to 2H_2O$$
 (2)

As light energy is the power source in this system, it acts as a SC and water acts as the redox mediator. Based on the reaction

kinetics on the cathode (eq 2), an acidic electrolyte is advantageous rather than the neutral one, for example, KCl.^{17,19} Furthermore, TiO_2 is advantageous as a photocatalyst on the anode, and various commercially available TiO_2 particles were employed for preparing photoelectrode thin films. However, their size and shape were nonuniform, hindering the determination of the characteristics and effects on the photoelectrode performance of individual particles.

In this study, we synthesized TiO₂ particles with a uniform size and shape. Three types of model particles, spheroidal, cubic, and "rhombic" TiO₂, were synthesized to evaluate the effects of uniform size and shape. Spheroidal and cubic particles were prepared by hydrothermal treatment of a precursor gel with an added structure-directing agent.^{20–22} Uniformly sized "rhombic" particles were synthesized by a solvothermal method²³ and are called "rhombic" because one of the facets appeared rhombic based on the anatase unit cell of the tetragonal crystal system.

The performance of a SC with photocatalyst layers on both the anode and cathode $^{12,16-19}$ was improved by optimizing the film application method, that is, casting, slide, mechanical, and

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entry	type	mean primary particle size $(nm)^a$	specific SA $(m^2 g^{-1})^b$	crystal phase	preferred face	ref.
а	P25	21 ± 5	60	anatase/rutile = 8:2		12
b	JRC-TIO-6	15 ± 5	96.4	rutile		12
с	spheroidal	$(31 \pm 11) \times (13 \pm 2)$	115	anatase	except for (0 0 1)	
d	cubic	28 ± 5	161	anatase	$\{1 \ 0 \ 0\}, (0 \ 0 \ 1)$	
e	"rhombic"	$(22 \pm 2) \times (11 \pm 4)$	211	anatase	$\{1 \ 0 \ 1\}, (0 \ 1 \ 0)$	
^a Based or	n TEM. ^b Brunau	er-Emmett-Teller SA based on Na	adsorption at 77.3 K.			

Table 1. Basic Properties of TiO₂ Samples Used in This Study

Scheme 1. Synthetic Steps for Spher-TiO₂, Cubic-TiO₂, and Rhomb-TiO₂



ball milling, for TiO₂ and BiOCl films on the anode and cathode, respectively, and the pH of the HCl electrolyte. A SC utilizing photocatalysts on both electrodes achieved an electromotive force of 0.90-2.11 V using TiO₂ and polyterthiophene, ^{13,24} W-doped BiVO₄/Bi₄V₂O₁₁ and undoped BiVO₄/Bi₄V₂O₁₁,²⁵ and TiO₂/anthocyanidin and BiOCl.¹² Dual photoelectrodes were also simultaneously utilized to remove waste materials.^{14,15,26,27} In this study, the key parameters to improve the SC performance were investigated by scanning electron microscopy (SEM), fluorescence spectroscopy, film impedance measurements, exchange reactions in ¹⁸O₂ gas, and Bi L₃-edge extended X-ray absorption fine structure (EXAFS).

EXPERIMENTAL SECTION

Synthesis of TiO₂ and BiOCI. TiO₂ (Aeroxide P25; purity > 99.5%) was supplied by Japan Aerosil Co. TiO₂ (JRC-TiO-6, purity > 99%) was supplied by Sakai Chemical Industry Co., Japan (Table 1 a and b).

The spheroidal TiO₂ nanoparticles were prepared as follows.^{20,21} First, a suspension of seed particles was prepared to control the size of the spheroidal TiO₂ particles (Scheme 1, left). Titanium isopropoxide (TIPO, 7.3 mL, Ti(OCH(CH₃)₂)₄, >95.0%, Wako Pure Chemical, Japan) and perchloric acid (HClO₄, 1.1 mL, 60%, Wako Pure Chemical) were mixed and diluted to 99 mL with pure water (conductivity < 0.2 μ S cm⁻¹) to concentrations of 0.25 mol TIPO L⁻¹ and 0.1 mol HClO₄ L⁻¹. The solution was heated at 373 K for 24 h, resulting in a suspension comprising nanocrystal TiO₂. Then, 1.1 mL of HClO₄ was added, resulting in a stable suspension. This was named Suspension 1, and the final concentrations were 0.25 mol TIPO L⁻¹ and 0.2 mol HClO₄ L⁻¹.

Separately, Stock solution **2** was prepared by mixing TIPO and triethanolamine $(N(CH_2CH_2OH)_3, >99.0\%)$, Wako Pure Chemical) to a concentration of 0.50 mol L⁻¹ Ti and a molar ratio of 1:2 in pure water (Scheme 1, middle). Ethylenediamine $(H_2N(CH_2)_2NH_2, 0.34 \text{ mL}, >99.0\%)$, Wako Pure Chemical) as a structure-directing agent and

2.0 mL of Suspension 1 were added to 9.0 mL of Stock solution 2. The mixed solution was diluted with an aqueous solution of NaOH from 1.0 to 0.1 mol L^{-1} and then with pure water (total 20 mL). The final concentrations were 0.25 mol L^{-1} Ti and 0.25 mol L^{-1} ethylenediamine, and the solution pH was adjusted to 11.5 by adding NaOH aqueous solution. The solution was heated at 373 K for 24 h. The resulting gel was transferred to a polytetrafluoroethylene (PTFE)-lined autoclave and hydrothermally treated at 413 K for 72 h to form white crystals. This sample was denoted as Spher-TiO₂ (Scheme 1, middle and Figure 1a).



Figure 1. TEM images of as-prepared Spher- (a), Cubic- (b), and Rhomb-TiO₂ nanoparticles (c).

The cubic TiO₂ particles were prepared as follows (Scheme 1, middle).²² Sodium oleate ($C_{17}H_{33}CO_2Na$, >99%, Wako Pure Chemical) as a structure-directing agent was added to 10 mL of Stock solution **2**. The concentrations of Ti⁴⁺ and sodium oleate and the solution pH were then adjusted to 0.25 mol L⁻¹, 0.05 mol L⁻¹, and 10.5, respectively, by adding progressively diluted NaOH aqueous solution followed by pure water. The prepared solution was heated at 373 K for 24 h. The resulting gel was transferred to a PTFE-lined autoclave and hydrothermally treated at 413 K for a week to form white crystals. The obtained sample was denoted as Cubic-TiO₂ (Figure 1b).

The "rhombic" TiO_2 particles were prepared via a method developed by Wu et al. (Scheme 1, right).²³ TIPO (0.25 mL), benzyl alcohol ($C_6H_5CH_2OH$, 5.0 mL, >99.0%, Wako Pure

		n^{-2}	6					
		surfa (nn	.6					
		O atom ratio in ¹⁸ O ₂ introduced vs surface O	$1:1.47 \pm 0.02$					
	rate in	(h^{-1})	0.10					
TiO_2	¹⁸ O ¹⁶ O formation ¹⁸ O ₂	$(\mu \text{mol } h^{-1} g_{\text{cat}}^{-1})$	106^{b}					
	mce (MΩ)	500 mV ac, 2 V dc	0.76	0.65				0.47
	impeda	500 mV ac	135	69				127
		bulk density $(g \text{ cm}^{-3})$	0.8 ± 0.1	0.9 ± 0.1				2.0 ± 0.1
		$(\mu \mathrm{W}^{\mathrm{max}}_{\mathrm{cm}^{-2}})$	47.4 ^b	61.1 ± 4.0	85.2	33.0	23.7	43.7
		V _{oc} (V)	1.87^{b}	1.96 ± 0.05	1.94	1.85	1.80	1.91
	-	Hq	2.00		1.78	2.00		
	(cathode)	wt (mg)	0.64	0.51	0.43	0.46	0.55	0.65
	catalyst	type	BiOCl-Cast			BiOCI-Slide	BiOCI-BS	BiOCl-Cast
	le) at	wt (mg)	0.49	0.38	0.33	0.50	0.45	0.39
	catalyst (anoc pH 2.00	type	P25-Cast	P25-Slide				P25-BD
		ent	в	a,				a″

e Rhomb-Slide 0.40 0.70 1.92 \pm 0.21 32.9 \pm 15.0 2.2 \pm 0.4 172 2.3 106 0.23 1:0.61 \pm 0.03 e' Rhomb-BS 0.35 0.45 1.71 11.6 1.6 \pm 0.1 150 61 "HCl aqueous solution at pH 2.0 was used in both the anode and cathode unless otherwise noted. ^b In reference 12. ^c ac 100 mV applied. ^d Unable to obtain quantitative value	ď	Cubic-BS	0.38	0.55	1.62	21.4	2.0 ± 0.1	d	đ			
e^{i} Rhomb-BS 0.35 0.45 1.71 11.6 1.6 ± 0.1 1.50 61 ^a HCl aqueous solution at pH 2.0 was used in both the anode and cathode unless otherwise noted. ^b In reference 12. ^e ac 100 mV applied. ^d Unable to obtain quantitative value	e	Rhomb-Slide	0.40	0.70	1.92 ± 0.21	32.9 ± 15.0	2.2 ± 0.4	172	23	106	0.23	$1:0.61 \pm 0.03$
a HCl aqueous solution at pH 2.0 was used in both the anode and cathode unless otherwise noted. b In reference 12. c ac 100 mV applied. d Unable to obtain quantitative value	,	Rhomb-BS	0.35	0.45	1.71	11.6	1.6 ± 0.1	150	61			
	^a HCl	aqueous solutic	in at pH 2.0 was use	ed in both the ar	node and catho	de unless other	rwise noted.	^b In reference	12. ^c ac 100 mV	applied. ^d U	Inable to obtain qu	antitative value.
		-	4								•	

Table 2. Physicochemical Parameters for TiO₂ Photocatalyst on the Anode and the SC Power Using the TiO₂ Photocatalyst on the Anode and BiOCI-Cast of the SC^a

>1.5 3.6

 $1:>0.34 \pm 0.02$

<0.027

6.4^b 214

14.4 *d*

97 d

 $\begin{array}{c} 1.1 \pm 0.6 \\ 2.0 \pm 0.1 \\ 2.2 \pm 0.4 \end{array}$

0.23

 $1:1.39 \pm 0.02$

1.4

10.1

 $1:2.8 \pm 0.2$

0.078

162

0.47 0.48 0.63

127 83

 2.0 ± 0.1 1.0 ± 0.2

> 55.0 55.0 42.1

1.90 1.78 1.86

0.40

Spher-Slide Spher-BS Spher-BD JRC6-Cast

b b a

4.8

 2.48 ± 0.05 1.32 ± 0.05

91 ^{b,c} 112 126

 1.3 ± 0.2^{b}

56.1^b

1.93^b

0.65 0.75 0.70 0.60 0.68 0.68 0.55 0.70

0.48 0.28 0.31 0.39

Cubic-Slide

υP τ

43.1 21.4

1.92 l.62

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Chemical), and oleylamine $(CH_3(CH_2)_7CHCH(CH_2)_8NH_2, 2.0 \text{ mL}, >50\%$, Tokyo Chemical Industry, Tokyo, Japan) as a structuredirecting agent were mixed and stirred at 293 K for 30 min. Then, 0.1 mL of pure water was added. Solvothermal treatment was conducted in a PTFE-lined autoclave at 453 K for 24 h, resulting in white crystals. All the TiO₂ synthesized in this study was in anatase phase, which has a tetragonal crystal system. In comparison to Spher-TiO₂, which grew in the *c*-direction (*c* = 0.95143 nm) and cubic-TiO₂ which exposed fundamental {1 0 0} and (0 0 1) facets, this TiO₂ exposed a rhombic (0 1 0) facet neighboring relatively unstable rectangular (1 0 1) and (1 0 1) facets protected by oleylamine during the synthesis. Therefore, the crystals appeared to have a monoclinic crystal system, but based on their preferential exposure of the rhombic (0 1 0) facet (Figure 1c), we denoted them as "rhombic TiO₂", ²³ abbreviated as Rhomb-TiO₂.

BiOCl was synthesized from an aqueous solution using bismuth trichloride (>97%, Wako Pure Chemical). 28

Preparation of Photoelectrodes. The TiO₂ powder (0.10 g) was well mixed with 1.0 mL of *t*-butanol, and 50 μ L of ethylene glycol was added as a thickener. The suspension was ultrasonicated (430 W, 38 kHz) for 10 min. The paste (36 μ L) was cast on 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 × 2.5 cm, thickness 0.11 cm; Sigma-Aldrich, St. Louis, MO, USA).^{12,16} The prepared film was denoted as "TiO₂ type"-Cast.

A slide method was also employed for the preparation of TiO₂ film; that is, a 10 g flat Pyrex glass dish (bottom area 10 cm²) under the force of gravity was laterally slid on the pasted suspension (36 μ L) on an ITO/Pyrex plate at 3 cm s⁻¹ to achieve a homogeneous film thickness. The TiO₂/ITO/Pyrex plate was dried in air at 373 K for 18 h. The temperature was then increased to 573 K at 4 K min⁻¹ and maintained at 573 K for 30 min. The amount of TiO₂ deposited on the plate was 0.39 mg (±0.11 mg) throughout this study (Table 2), covering an ITO area of 1.0 × 1.3 cm. The prepared film was denoted as "TiO₂-type" slide.

For comparison, ball milling was also employed to prepare TiO₂ films. TiO₂ powder (0.10 g) was dispersed with *t*-butanol (1.0 mL) and ethylene glycol (36 μ L). Zirconia balls comprising 5% Y₂O₃ (25 g, φ = 5 mm; Nikkato Co., Japan, Type YTZ-5) were added to the suspension, and this was rotated at 50 rotations per minute (rpm) for 24 h. Thereafter, the mixture was agitated using dual-frequency ultrasound (23 and 43 kHz, 130 W). TiO₂ paste (1.3 g) was separated from the YTZ-5 balls. The paste (36 μ L) was dropped on an ITO/ Pyrex glass plate, and a flat Pyrex glass dish (10 g) under the force of gravity was laterally slid on the pasted suspension on the ITO/Pyrex plate at 3 cm s⁻¹. The TiO₂/ITO/Pyrex plate was dried in air at 373 K for 18 h, and then the temperature was increased to 573 K at 4 K min⁻¹ and maintained at 573 K for 30 min. The prepared film was denoted as "TiO₂-type" BS.

As with the TiO₂-BS film, the mixed TiO₂ paste (36 μ L) was rotated at 50 rpm for 24 h while dropping the YTZ-5 balls, pasted on an ITO/Pyrex glass plate, and the mixture was flattened using a film applicator (Paul N. Gardner Company Inc., Pompano Beach, FL, USA, Digital Microm II), maintaining an interval of 10 μ m between the blade and the substrate and laterally moving at 0.6 cm s⁻¹. Thereafter, the TiO₂/ITO/Pyrex plate was dried in air at 373 K for 18 h, and then the temperature was increased to 573 K at 4 K min⁻¹ and maintained at 573 K for 30 min. The prepared film was denoted as "TiO₂-type" BD.

The obtained BiOCl powder (6.0 mg) was suspended in deionized water (60 μ L, <0.055 μ S cm⁻¹) and ultrasonicated (430 W, 38 kHz) for 10 min. An aliquot of the suspension was pasted on the ITO-coated Pyrex glass plate. The amount of BiOCl deposited on each ITO-coated glass plate was 0.60 mg (±0.17 mg), covering an area of 1.0 × 1.3 cm. The prepared film was denoted as BiOCl-Cast (Table 2).

A slide method was also employed for BiOCl, that is, a 10 g flat Pyrex glass dish (flat area 10 cm²) under the force of gravity was laterally slid on a pasted suspension (36 μ L) prepared by mixing BiOCl (0.10 g), *t*-butanol (1.0 mL), and ethylene glycol (0.05 mL) on

an ITO/Pyrex plate at 3 cm s⁻¹. The BiOCl/ITO/Pyrex plate was dried in air at 373 K for 18 h. The temperature was then increased to 573 K at 4 K min⁻¹ and maintained at 573 K for 30 min. The prepared film was denoted as BiOCl-slide.

BiOCl was also treated by ball milling. BiOCl powder (1.5 g) was mixed and dispersed with deionized water (15.0 mL). YTZ-5 balls (40 g) were added to the suspension, and the mixture was rotated at 100 rpm for 24 h. The suspension was slid to form a BiOCl thin film on an ITO/Pyrex plate as described in the previous paragraph. The temperature was then increased to 573 K at 4 K min⁻¹ and maintained at 573 K for 30 min. The prepared film was denoted as BiOCl-BS.

Characterization. The specific surface area (SA) of the samples was measured using an automatic specific SA/pore size distribution analyzer (BELSORP-max, Microtrac BEL, Japan). Transmission electron microscopy (TEM) images were obtained using a H-7650A transmission electron microscope (Hitachi, Japan) at an accelerating voltage of 100 kV. Cross-sectional SEM images were obtained using a JSM-6510 scanning electron microscope (JEOL, Tokyo, Japan) 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. 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.

Absorption-fluorescence spectra were recorded on model FP-8600 (JASCO; Chiba Iodine Resource Innovation Center, Chiba University) using a 150 W Xe arc lamp equipped with a photomultiplier tube within the excitation range from 250 to 300 nm and fluorescence range from 300 (or 340) to 800 nm. TiO₂ powder (2.0 mg) was mixed with water (4.0 mL) and ultrasonicated (430 W, 38 kHz) for 2 h. All spectra were recorded for the suspensions in a quartz cell at 295 K. Bismuth L₃-edge EXAFS spectra were obtained at 290 K in transmission mode using a Si (3 1 1) double-crystal monochromator^{29–34} calibrated to 13 426 eV³⁵ and were analyzed using the Athena and Artemis package³⁶ using refs 37–42. The details are given in the Supporting Information.

Impedance Measurements. Impedance measurements were performed for film samples of TiO_2 (0.4 mg) and BiOCl (0.6 mg) on ITO/Pyrex plates using a potentio/galvanostat (VersaSTAT 3-100, Princeton Applied Research, Oak Ridge, TN, USA) equipped with a low current option (VersaSTAT-LC). An iron nail (front curvature radius 0.5 mm) was perpendicularly in contact with the $TiO_2/BiOCl$ film surface utilizing a micrometer, and the ITO/Pyrex plate was electrically in contact via a Au/Ni-coated stainless steel clip (Toyo Corporation, Japan).¹² The applied alternating voltage was 500 mV, and the frequency was scanned between 10^2 and 10^6 Hz. Another series of impedance measurements were performed by applying both an alternating voltage of 500 mV and a direct voltage of 2 V.

¹⁸O₂ Exchange Photoreaction Tests. Isotope-labeled photoreaction tests were performed using gas chromatography-mass spectrometry (GC-MS, JMS-Q1050GC, JEOL).^{12,29} Helium (purity > 99.9999%) was used as the carrier gas. The sampling loop comprised a Pyrex glass system placed under vacuum using rotary and diffusion pumps (10⁻⁶ Pa) and connected to the gas chromatographmass spectrometer using a 1.5 m deactivated fused silica tube (no. 160-2845-10, Agilent, Santa Clara, CA, USA; internal diameter 250 μ m) maintained at 393 K.

A photocatalyst sample (0.135 g) was placed in a quartz photoreactor and evacuated at 295 K for 2 h at 10^{-6} Pa. Then, ${}^{18}O_2$ photoexchange (0.55 kPa; ${}^{18}O$ 97.8%, chemical purity >99.9%, Cambridge Isotope Laboratories, Inc., Tewksbury, MA, USA) with the photocatalyst was monitored in a Pyrex closed circulation system (265.0 mL) at 295 K under irradiation with UV–visible light from a 500 W xenon arc lamp (SX-UID502XAM, Ushio, Japan). The distance between the exit of the lamp window and the photocatalyst was 160 mm. The exchange with ${}^{16}O$ atoms (natural ${}^{16}O$ abundance 99.76%) at the photocatalyst surface was monitored using a column packed with 13X-S molecular sieves (GL Sciences, Inc., Japan) set in the GC-MS.

SC Tests. The TiO₂/ITO/Pyrex and BiOCl/ITO/Pyrex electrodes were immersed in hydrochloric acid solution (40 mL in each compartment, initial pH 2.00). The two compartments were separated by a 50 μ m-thick H⁺-conducting polymer film (Nafion, Dupont, Wilmington, DE, USA; acid capacity >9.2 × 10⁻⁴ equiv. g⁻¹).^{12,16-19} N₂ (purity > 99.999%) and O₂ (purity > 99.6%) (50 mm) were bubbled from each photoelectrode to the anode and cathode compartments, respectively, at a flow rate of 100 mL min⁻¹. The SC was equipped with quartz windows ($\varphi = 80$ mm) on both sides. Both the TiO₂ and BiOCl photocatalysts were irradiated with UV–visible light from a 500 W xenon arc lamp (SX-UID502XAM) through quartz windows using a two-way branched quartz fiber light guide (5 φ -2B-1000L, San-ei Electric Co., Japan). The distance between the light exit ($\varphi = 5$ 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 anode and cathode configurations was assessed in front-rear configuration^{12,16} by varying the resistance between 500 k Ω and 0.3 Ω over 20 min. The front and rear configurations allowed perpendicular UV-visible light irradiation from the photocatalyst and Pyrex/ITO glass plate, respectively.

Furthermore, the pH dependence of the i-V characteristics was investigated by varying the pH of the HCl electrolyte in the cathode compartment between 2.00 and 1.78. The pH of the HCl electrolyte in the anode was fixed at 2.00, and TiO₂-Slide and BiOCl-Cast were used on the photoanode and photocathode, respectively.

RESULTS AND DISCUSSION

TEM Observation of Synthesized TiO₂ **Nanoparticles.** Figure 1 shows the TiO₂ particles synthesized in this study. Regarding the homogeneity of these crystals, on progressively increasing the Ti molar ratio in seed particles (Suspension 1) to Stock solution 2, the length of the major *c*-axis of needlelike TiO₂⁻²⁰ became shorter and the crystals became spheroidal in shape (Spher-TiO₂), and the particle size distribution became wider: (31 ± 11 nm, major) × (13 ± 2 nm, minor) when the Ti molar ratio was 1:9 for Suspension 1 with Stock solution 2 (Figure 1a and Table 1c). The mean oblateness ((major axis – minor axis)/major axis) of Spher-TiO₂ was 0.6.

Cubic-TiO₂ (Figure 1b) and Rhomb-TiO₂ (Figure 1c) nanoparticles with narrow particle size distributions and unique shapes were successfully synthesized; the size distributions were 28 \pm 5 nm and (22 \pm 2 nm, major) \times $(11 \pm 4 \text{ nm}, \text{minor})$, respectively (Table 1d,e). Using the route involving stock solution and sodium oleate (Scheme 1, middle), most of the particles had a cubic shape that exposed the {1 0 0} and (0 0 1) facets (Figure 1b) because of the control by the strong adsorption of oleate.²² The crystal shape of the Rhomb-TiO₂ particles was similar to that reported in ref 23, exposing the $\{1 \ 0 \ 1\}$ and $(0 \ 1 \ 0)$ facets with a dihedral angle of 43.4° between the $(1\ 0\ 1)$ and $(1\ 0\ 1)$ facets (Figure 1c). Furthermore, the particles tended to be tightly packed and connected at the $\{1 \ 0 \ 1\}$ facets because they had a uniform particle size and shape because of capillary forces during drying on the TEM grid.

SEM Observation of TiO₂ **Films on Electrode.** The SEM images confirmed the film quality of Spher-TiO₂, Cubic-TiO₂, Rhomb-TiO₂, and various other types of TiO₂ films formed on ITO/Pyrex plates (Table 2). The film preparation methods, cast, sliding, BS, and BD, were also compared. Based on the side view as shown in Figure 2, upper rows, the mean film thickness ($t \ \mu$ m) was evaluated. The bulk density (ρ g cm⁻³) of the TiO₂ film was then calculated based on eq 3 (Table 2).

Research Article



Figure 2. Side and top view SEM images of (a) P25-Cast, (a') P25-Slide, (a") P25-BD, (b) Spher-Slide, (b') Spher-BD, (b") Spher-BD, (c) Cubic-Slide, (c') Cubic-BS, (d) Rhomb-Slide, and (d') Rhomb-BS films.

$$\rho = \frac{(0.39 \pm 0.11) \times 10^{-3}}{(1.0 \times 1.3)t \times 10^{-4}} = \frac{3.00 \pm 0.85}{t}$$
(3)

Using conventional P25-TiO₂, the film thickness decreased from 4.8 μ m (Cast, Figure 2a) to 3.1 μ m (Slide, Figure 2a') and then to 1.5 μ m (BD, Figure 2a"), corresponding to progressive increases in the bulk density of 0.8, 0.9, and 2.0 g cm⁻³, respectively (Table 2a,a',a"). The film flatness was satisfactory for these films, and the side views demonstrate that the porous films became more stacked in the above order because of the effect of the applicator (weight of the glass dish or mechanical applicator).

Similarly, using Spher-TiO₂, the film thickness decreased from 3.1 μ m (Slide, Figure 2b) to 2.8 μ m (BS, Figure 2b') and then to 0.86 μ m (BD, Figure 2b"), corresponding to progressive increases in the bulk density of 1.0, 1.32, and 2.48 g cm⁻³, respectively (Table 2b,b',b"), compared to P25-TiO₂. Several coagulated parts on the micrometer scale were seen for the Spher-Slide films (Figure 2b, top view) that were sufficiently flattened by ball milling to form Spher-BS and Spher-BD (Figure 2b',b"). These changes were due to a progressive decrease in the pores in the TiO₂ film and/or liberation of coagulated crystals because of the differences in the TiO₂ film formation method.

In a previous study,¹² JRC6-Cast was the thinnest photocatalyst film ($t = 1.8 \ \mu$ m, Figure 2c). The mean primary particle size and crystalline phase were 15 nm and rutile in contrast to those for P25 (21 nm and an anatase and rutile mixture with a ratio of 8:2) (Table 1a,b). Because of the smaller primary particle size, the JRC6-Cast film was thinner and thus stacked more effectively than P25-Cast with a thickness of 4.8 μ m (Figure 2a). However, as opposed to the TiO₂ type (Table 1), the film preparation method was more critical, and a much denser film was formed via the BD method (2.48–2.0 g cm⁻³ for Spher-BD and P25-BD) in comparison

to JRC6-Cast $(1.3 \text{ g cm}^{-3})^{12}$ (Table 2b",a",c and Figure 2b",a").

The TiO₂ types were then compared for films formed by the slide method. As the mean film thicknesses were 3.1, 3.1, 2.8, and 1.2 μ m for P25-Slide, Spher-Slide, Cubic-Slide, and Rhomb-Slide, respectively (Figure 2a',b,c,d), the TiO₂ bulk density followed the order (Table 2a',b,d,e)

Rhomb-Slide > Cubic-Slide \approx Spher-Slide \approx P25-Slide

The density was more than doubled by using Rhomb-Slide (2.2 g cm^{-3}) with a homogeneous size and shape, and this could be explained based on the smaller mean primary particle size $(22 \times 11 \text{ nm})$ in comparison to Cubic-TiO₂ (28 nm) or Spher-TiO₂ (31 × 13 nm; Table 1c-e and Figure 1) and the close packing of the "rhombic" crystals with a homogeneous size and shape (Figure 1c). Coagulated parts were observed for Cubic-Slide and Spher-Slide films in contrast to flat Rhomb-Slide or P25-Slide films (Figure 2a',b,c,d). As for Spher-BS, Cubic-BS, and Rhomb-BS, the ball milling and slide method ultimately flattened the films (Figure 2b',c',d').

Fluorescence Spectra of TiO₂ **Suspensions.** The fluorescence spectra were compared among the TiO₂ samples with excitation at 250 and 300 nm (Figure 3a,b). Because of



Figure 3. Fluorescence spectra of aqueous TiO_2 suspensions with excitation at (a) 250 and (b) 300 nm. TiO_2 sample powder (2.0 mg) (Spher-, Cubic-, Rhomb-, and P25- TiO_2) was suspended in 4.0 mL of water.

the excitation both at 250 and 300 nm, a predominant fluorescence peak appeared at 372-366 nm, for all the TiO₂ samples. This occurred because of the band edge emission of TiO₂.⁴³ Therefore, an increase in the excitation wavelength for fluorescence at 372-366 nm leads to a corresponding monotonous decrease in the excitation spectra for all the TiO₂ samples. Therefore, we compared the peak intensity with the excitation at 250 nm (Figure 3a)

Rhomb-TiO₂ > Cubic-TiO₂ > Spher-TiO₂ > P25-TiO₂

The blue shift of the band edge emission peak from 372 nm (Spher, Cubic, Rhomb) to 408 nm (P25) which appeared in Figure 3a should be the de-excitation at the band gap (BG) for anatase phase (Spher, Cubic, Rhomb). Also, the shift of excited electrons from the CB of anatase phase (80% of P25, Table 1a) to the CB of rutile phase (20% of P25) followed by band edge emission at BG of rutile phase.⁴³ For the same reason, we have a band edge emission shift from 366 to 420 nm shown in Figure 3b. The order above is contrary to the W_{max} values derived by the TiO₂ photocatalyst film prepared slide method on the anode of SC (see the section on SC Tests). This is because the electronic excitation at BG contributes to the photooxidation as charge separation at the anode (eq 1). In fact, fluorescence at 372–420 nm is an alternative process as a result of electronic excitation at BG.

Weak peaks at 451, 468–469, and 482 nm were also observed with the excitation at 250–300 nm, associated with the surface trap sites, for example, Ti or O defect to VB.⁴³ The correlation between the trap site peak intensity and the W_{max} values is not clear at the moment.

Impedance of TiO₂ Films. The impedance of various TiO_2 films formed in this study was evaluated while applying 500 mV ac. The Cole–Cole plot showed part of a semicircle beginning at the origin in the first quadrant for each TiO_2 film sample (Supporting Information, Figure S1a). The diameter correlated with the film impedance. Based on the fit with a circular function, the order of impedances (Table 2) was

Rhomb-Slide > Rhomb-BS > P25-Cast \approx P25

 $-BD \approx Spher-BD \approx Spher-BS > Cubic-Slide > Spher$

-Slide > P25-Slide

When 2 V dc was also applied to the TiO_2 film simultaneously with 500 mV ac (Figure S1b), the order of impedance changed to

Rhomb-BS > Rhomb-Slide > Cubic-Slide > Spher

-BD > P25-Cast
$$\approx$$
 P25-Slide \approx Spher-BS \approx Spher

-Slide \approx P25-BD

Overall, the impedance of the films prepared via the slide method, especially Rhomb-Slide and Cubic-Slide, relatively increased, suggesting that they were less polarizable by application of dc, while films comprising anisotropic nanoparticles were effectively polarized by 2 V dc (Scheme 2, top).

Scheme 2. Reasons for the Dependence of the Impedance with Applied ac/dc, ¹⁸O₂ Photoexchange Rates, and W_{max} on the Particle Size and Shape of TiO₂ Used on the Anode and the Energetics of O₂ Exchange and Water Oxidation Reactions



Yun et al. reported that the capacitance of TiO_2 nanoparticles followed the order

Spherical (mean 25 nm)

< ellipsoidal (39 \times 132 nm)

< ellipsoidal (27 \times 156 nm)

which matched well the aspect ratios of the films formed on ITO/Pyrex.⁴⁴ As the capacitance is defined for two flat plates as eq 4,

$$\times \frac{\text{plate area}}{\text{distance between plates}}$$
(4)

the dielectric constant increased with the aspect ratio of nanoparticles. In this context, in comparison to Rhomb-TiO₂ and Cubic-TiO₂ crystals, P25-TiO₂ and Spher-TiO₂ crystals were anisotropic, had greater dielectric constants, tended to become more polarized, and were expected to show smaller impedance during application of both ac and dc.

¹⁸O₂ Exchange Photoreaction with TiO₂ Films. The photoexchange reaction was conducted using Spher-TiO₂, Cubic-TiO₂, and Rhomb-TiO₂ powders. Gas-phase ¹⁸O₂ reacted with surface ¹⁶O to form ¹⁸O¹⁶O, and the formed ¹⁸O¹⁶O reacted with surface ¹⁶O to form secondary ¹⁶O₂ (Figure 4). When using Cubic-TiO₂, the amount of ¹⁸O₂ gas



Figure 4. Time course of ${}^{18}O_2$ (0.55 kPa) photoexchange reaction using (a) Spher-TiO₂, (b) Cubic-TiO₂, and (c) Rhomb-TiO₂ photocatalysts (each 0.135 g).

decreased rapidly within 0.5–1 h of the reaction and reached isotope-exchange equilibrium after 8 h of reaction (Figure 4b). Corresponding to the ¹⁸O₂ decrease, ¹⁸O¹⁶O was formed at an initial rate of 214 μ mol h⁻¹ g_{cat}⁻¹ (Table 2d), followed by the secondary formation of ¹⁶O₂. Among TiO₂ samples, the order of the rate of ¹⁸O₂ decrease was

 $Cubic-TiO_2 > Spher-TiO_2 > Rhomb-TiO_2$

which was consistent with the initial formation rate of ${}^{18}O^{16}O$ (Table 2b-e)

$$Cubic-TiO_2 > Spher-TiO_2 > Rhomb-TiO_2 \approx P25$$

$$-\text{TiO}_2 \gg \text{JRC6-TiO}_2$$

Clearly, the exchange reaction in $^{18}O_2$ was faster with TiO₂ crystals having a uniform size and shape than with conventional P25-TiO₂ and JRC6-TiO₂.¹² If we assume complete Cubic-TiO₂ (anatase phase), 67% of {1 0 0} and 33% of (0 0 1) faces were exposed.²² For Rhomb-TiO₂ (anatase phase), ~two-thirds of thermodynamically unstable {1 0 1} facets and ~one-third of stable (0 1 0) facets were exposed.²³ Meanwhile, the major axis of Spher-TiO₂ coincided with the *c*-axis of anatase, and all facets other than (0 0 1) appeared to be exposed.^{20,22}

Based on the ¹⁸O₂ exchange tests, the surface (exchangeable) O atom populations were evaluated as 3.6, 10.1, 1.4, 9.9, and >1.5 nm⁻² (Table 2) for film samples in the order of ¹⁸O¹⁶O formation above (Cubic-TiO₂, Spher-TiO₂, Rhomb-TiO₂, P25-TiO₂, and JRC6-TiO₂); however, no correlation with the ¹⁸O₂ exchange rate was found. The specific SAs of these TiO₂ samples were 161, 115, 211, 60, and 96.4 m² g⁻¹ (Table 1) in the order, and again, no correlation with the ¹⁸O₂ exchange rate was found. Conversely, JRC6-TiO₂ is only one pure rutilephase sample in this study and the ¹⁸O¹⁶O formation rate was the lowest: 6.4 μ mol h⁻¹ g_{cat}⁻¹. A different type of rutile TiO₂ with a surface O population of 8.7 nm⁻² and a specific SA of 8.0 m² g⁻¹ was tested in another study,¹² and the ¹⁸O¹⁶O formation rate was also sufficiently slow (34 μ mol h⁻¹ g_{cat}⁻¹) compared to the rates for samples in this study. Thus, anatase TiO₂ was favorable in the ¹⁸O₂ exchange reaction with surface O. Furthermore, nonpolar {1 0 0} facets of anatase comprising 50% of surface Ti and 50% of surface O (e.g., on Cubic-TiO₂) would be advantageous as oxo Lewis base sites rather than hydroxy sites at, for example, polar (0 0 1) or {1 0 1} (e.g., on Rhomb-TiO₂) facets. A weaker interaction between O₂ and the anatase TiO₂ (1 0 1) face was also reported.⁴⁵

SC Tests: Dependence on TiO₂. The *i*–*V* dependence was tested using BiOCl-Cast on the photocathode and various types of TiO₂ films prepared via various methods on the photoanode. First, the effects of the film preparation method were compared for P25-TiO₂ (Figure S2a and Table 2a,a',a") and Spher-TiO₂ samples (Figure S2b and Table 2b,b',b"). In both series, TiO₂ films prepared by the slide method enabled higher V_{OC} values and generation of the maximum cell power (W_{max})

P25-Slide (1.96 V)
> P25-BD (1.91 V)
> P25-Cast (1.87 V)
P25-Slide (61.1
$$\mu$$
W cm⁻²)
> P25-Cast (47.4 μ W cm⁻²)¹²
 \approx P25-BD (43.7 μ W cm⁻²)
Spher-Slide (1.90 V)
> Spher-BD (1.86 V)
> Spher-BS (1.78 V)
Spher-Slide (55.0 μ W cm⁻²)
 \approx Spher-BS (55.0 μ W cm⁻²)
> Spher-BD (42.1 μ W cm⁻²)

The SC test results (V_{OC} , W_{max}) were well reproduced using different P25-Slide films on the anode with a deviation of 2.6–6.5% (Table 2a'), owing to the flatness of the film (Figure 2a'). The film preparation method was then fixed via slide, and the performances of various TiO₂ types were systematically compared (Figure S2c). The orders of V_{OC} and W_{max} values were

P25-Slide (1.96 V) > Cubic-Slide (1.92 V) ≈ Rhomb -Slide (1.92 V) > Spher-Slide (1.90 V)

P25-Slide (61.1 μ W cm⁻²) > Spher-Slide (55.0 μ W cm⁻²)

> Cubic-Slide (43.1 μ W cm⁻²) > Rhomb

-Slide $(32.9 \,\mu W \, \text{cm}^{-2})$

These orders clearly demonstrated that TiO_2 crystals with a uniform size and shape were unfavorable with respect to both the electromotive force and cell power when used on the photoanode in the SC. The test results (V_{OC} and W_{max}) varied greatly using different Rhomb-Slide films on the anode with a deviation of 11–63% (Table 2e), mostly because of the less flat film compared to P25-Slide (Figure 2a',d). Cubic-BS and Rhomb-BS were also tested; however, their performance was the poorest (Table 2d',e').

SC Tests: Dependence on pH. The P25-Slide film was the best for the SC performance on the photoanode (Table 2a', Figure S2a,c). The V_{OC} of 1.96 V was based on the energylevel difference between the CB minimum (CBM) of TiO₂ and the valence band maximum (VBM) of BiOCl,¹² which exceeded the electromotive force reported for similar SCs: TiO₂ and polyterthiophene (0.90 V),^{13,24} and W-doped BiVO₄/Bi₄V₂O₁₁ and undoped BiVO₄/Bi₄V₂O₁₁ (1.54 V).²⁵

Furthermore, the effects of the electrolyte pH on the SC performance were assessed using the optimized combination of photocatalysts: P25-Slide and BiOCl-Cast (Table 2a'). By changing the pH of the HCl electrolyte in the cathode from 2.00 to 1.78 while maintaining the pH at 2.00 in the anode, i_{SC} was increased by 66% from 61.7 to 102.4 μ A cm⁻², and W_{max} was also increased by 39% from 61.1 to 85.2 μ W cm⁻² (Figure 5 and Table 2a'). Conversely, when we set the pH of the cathode to 1.78 from the beginning, i_{SC} and W_{max} decreased to 55.9 and 38.9 μ W cm⁻² (data not shown).



Figure 5. Dependence of the i-V test results on the pH of the HCl solution for the SC using P25-Slide on the photoanode and BiOCl-Cast on the photocathode. Anode compartment: initial pH 2.00 (fixed) and cathode compartment: initial pH 1.78 (\bigcirc) and 2.00 (\square).

The proton concentration in the cathode increased by 1.66 times at pH 1.78 compared to that at pH 2.00. The increase in the current density in the voltage range 0-1.4 V (Figure 5) was due to the increase in the kinetic rate of the cathode reaction (eq 2) consistent with the difference in proton concentration if we assume a first-order reaction of [H⁺]. Conversely, the voltage range 1.4–2.0 V was controlled not by kinetics but by the equilibrium based on the applied external resistance because the electron energy difference in both electrodes on light excitation $^{12,16-19}$ and/or sufficient electrons for the reduction reaction of O2 were not supplied through the resistance of external circuit. The local site structure of Bi³⁺ did not change between pH 1.78 and 2.00 based on Bi L3-edge EXAFS; the interatomic distance and its associated coordination number for Bi-O and Bi-Cl interatomic pairs changed negligibly at pH values between 2.00 and 1.78 (Table S1a,b), excluding the possibility of pH-dependent changes in the ${\rm Bi}^{3+}$ site structure and reactivity (Figure S3).

Critical Factors in Controlling the W_{max} Value of the SC. To determine the critical factors in determining the SC performance, the correlations between six parameters, V_{OC} , W_{max} for the SC (Table 2 and Figures S2 and 4), bulk density, ac impedance (Figure S1a), ac/dc impedance (Figure S1b), and the ¹⁸O¹⁶O formation rate in ¹⁸O₂ (Figure 4) for 11 TiO₂ films used on the anode (Table 2), were examined. If we assumed a linear relationship and accepted a correlation only for cases with a correlation coefficient exceeding 0.5 (eq 5), four correlations with W_{max} were verified (Figure 6), whereas no correlations were found with V_{OC} .



Impedance AC/DC (MΩ) Bulk density (g cm⁻³) **Figure 6.** Correlations between W_{max} and the impedance of TiO₂ films on applying 500 mV ac (a), between W_{max} and the impedance of TiO₂ films when both 500 mV ac and 2 V dc were applied (b), between W_{max} and the ¹⁸O¹⁶O formation rate in the ¹⁸O₂ exchange reaction (c), and between W_{max} and the bulk density of TiO₂ films (d).

30

0.5

1

2.5

1.5 2

30

20 40 60

A negative correlation was verified between the ac impedance and W_{max} (R = 0.769, Figure 6a), demonstrating that electronic conductivity both in the TiO₂ film and at the interface from the TiO₂ film to the ITO electrode was essential to maximize the SC power. The correlation coefficient between the ac/dc impedance and W_{max} increased (R = 0.924, Figure 6b), but the smaller impedances (0.47–0.76 M Ω) for five films $(P25-TiO_2 \text{ and } Spher-TiO_2)$ did not faithfully correlate with $W_{\rm max}$. Polarization caused by applying 2 V dc at the anode was plausible (Scheme 2, top) during the SC test because of the energy bias between the CBM of TiO2 and VBM of BiOCl due to irradiation with UV-visible light.^{12,16,18} The ac/dc impedance inversely correlated with the electronic conductivity in the TiO₂ film and also at the interface between the TiO₂ film and ITO. Cubic-TiO₂ and Rhomb-TiO₂ with a uniform size and shape were unsuitable based on the impedances (Figure 6b), probably because of packing problems in the film (Scheme 2, top, right). Conversely, W_{max} could be controlled through the cathode using the BiOCl photocatalyst when the ac/dc impedance was below 0.76 M Ω (Figure 6b).

 $W_{\rm max}$ was also negatively correlated with the ¹⁸O¹⁶O formation rates in ¹⁸O₂ with various TiO₂ samples (R = 0.793; Figures 4 and 6c). The ¹⁸O¹⁶O formation rates were divided by the number of surface (exchangeable) ¹⁶O atoms to evaluate the rate constant k of the ¹⁸O¹⁶O formation reaction (Table 2). The ¹⁸O¹⁶O formation proceeds through an ¹⁸O-¹⁸O bond dissociation step (Scheme 2, bottom, reverse reaction). This step is a reverse reaction of O–O formation, which is the key step in the water photooxidation to O₂ occurring on the anode (Scheme 2, bottom, forward reaction). The correlation between fluorescence peak intensity (Figure 3) and SC power (Table 2) existed among TiO₂ films, demonstrating the efficiency of O₂ photoreduction reaction over these films.

Assuming the Arrhenius-type rate dependence and (nearly) equivalent pre-exponential factors for the ¹⁸O₂ exchange reaction, the difference in the apparent activation energies, ΔE_1 for Rhomb-Slide (0.23 h⁻¹) and ΔE_2 for JRC6-Cast (<0.027 h⁻¹), is 5.2 kJ mol⁻¹. Conversely, water photo-oxidation is the forward reaction in Scheme 2, bottom, and proceeds faster for JRC6-Cast (lower activation barrier from left to right) than for Rhomb-Slide. In this context, Cubic-TiO₂ and Rhomb-TiO₂ with a uniform size and shape were the most unfavorable for the forward reaction in Scheme 2, bottom, and thus gave the lowest W_{max} (Figure 6c).

We have ensured that the ${}^{18}O_2$ exchange tests were carefully performed using TiO₂ powder, not film while W_{max} varied according to the film preparation method (Slide, Cast, BS, and BD) for P25 and Spher-TiO₂ (Table 2). Currently, it is uncertain whether the exchange rate is dependent on the film preparation method.

A linear correlation between the bulk density of the TiO_2 film and W_{max} existed, but this was weak (R = 0.517; Figure 6d) and only discussed in the Supporting Information.

In summary, the crystals of Cubic-TiO₂ and Rhomb-TiO₂ were homogeneous in size and shape. However, the homogeneity led to smaller polarizability, resulting in greater impedance on application of 2 V dc to the anode. A further disadvantage was confirmed by the ¹⁸O₂ exchange reaction on TiO₂, which showed that the reverse reaction of water oxidation was catalyzed. To solve this situation, anisotropic TiO₂ crystals proved favorable for polarizability, and a wider particle size distribution was favorable for forming films with a lower bulk density to maximize the surface exposure of photooxidation sites. Spher-Slide and P25-Slide were the most favorable, enabling 85.2 μ W cm⁻² when combined with BiOCl-Cast.

CONCLUSIONS

The crystal size, shape, homogeneity, and method of preparing a film of TiO₂ on the photoanode of a SC were critical for the SC performance. A SC using P25-Slide and BiOCl-Cast on its electrodes was optimized to achieve a $V_{\rm OC}$ of 1.94 V and a $W_{\rm max}$ of 85.2 μ W cm⁻². An appropriate particle size range (15– 30 nm) was obtained, and needlelike TiO₂ was controlled to form spheroids with a mean size of 31 × 13 nm. The performance of the SC ($W_{\rm max}$) critically depended on film impedance measurements using ac and both ac and dc and the ¹⁸O₂ exchange rate. The order of SC performance was supported by the major peak intensity of fluorescence spectra at 372–366 nm. Both film impedance and the ¹⁸O₂ exchange rate were high for Cubic-TiO₂ and Rhomb-TiO₂ with a uniform size and shape, demonstrating their poor performance on the photoanode, while nonuniform anisotropic Spher-TiO₂ and commercial P25 achieved satisfactory values of these parameters and proved advantageous as photocatalysts on the anode of the SC in this study. With regard to the method of preparing the films on each electrode, the slide method was advantageous in maximizing $V_{\rm OC}$ and $W_{\rm max}$ for TiO₂ (anode), while the casting method was superior to the slide method for forming a BiOCl film on the cathode with a perpendicular crystal orientation.

The polarizability and photocatalytic activity of TiO_2 crystals were the most effective control factors. The impedance of TiO_2 on application of both 500 mV ac and 2 V dc was closely correlated with the polarizability of TiO_2 ; anisotropic TiO_2 showed higher polarizability and lower ac/dc impedance, achieving the best SC performance.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.9b05576.

Cole–Cole plot for various TiO_2 films on ITO/Pyrex, *i*–*V* test graphs and the dependence on BiOCl, experimental results of Bi L₃-edge EXAFS, and correlation between bulk density of TiO₂ film and SC power (PDF)

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Notes

The authors declare no competing financial interest.

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