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Photofuel cell comprising titanium oxide and bismuth oxychloride ($\text{BiO}_{1-x}\text{Cl}_{1-y}$) photocatalysts that uses acidic water as a fuel†

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Solar cells and fuel cells have been extensively investigated. However, the need for sustainability, durability, and an electromotive force greater than 1.5 V per cell has not yet been fully realized. Herein, a photofuel cell (PFC) comprising two photocatalysts TiO_2 and BiOCl that uses acidic water as a fuel is described. The PFC is designed such that water can be regenerated from the photogenerated O_2 in the cell, and the electromotive force is as high as the difference between the conduction band minimum of TiO_2 and the valence band maximum of BiOCl (theoretical: 2.75 V, experimental: 1.76 V). The photocurrents were in accordance with a kinetic model based on the combination of the excited electron concentration at TiO_2 and the hole concentration at BiOCl . The reaction between the surface sites of O and/or Cl-deficient $\text{BiO}_{1-x}\text{Cl}_{1-y}$ species formed by ultraviolet-visible light irradiation with O_2 was *in situ* monitored using Bi L₃-edge extended X-ray absorption fine structure and X-ray photoelectron spectroscopy supported by Raman and UV-visible spectroscopy and could be involved in the cathodic O_2 photoreduction in the PFC. Furthermore, amorphous-like $\text{BiO}_{1-x}\text{Cl}$ species were observed on the surface of the BiOCl crystallites in high-resolution transmission electron microscopy. Importantly, this PFC that comprises TiO_2 and BiOCl is sustainable, recyclable, and has a series resistance that can be controlled by adjusting the BiOCl particle size, and exhibits a more efficient charge flow because of band bending than that of a previously reported PFC based on the rectification of the Schottky barrier.

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1 Introduction

Fossil fuels have been utilized as the essential energy source for industrialization. However, industrial CO_2 emissions have led to an increase in the atmospheric CO_2 concentration (400 ppm), and thus the effects of this increase in terms of global warming cannot be underestimated. The development of renewable energy as a replacement for fossil fuels has been slow.^{1,2} Among these renewable energies, solar energy has the greatest potential; the solar energy that reaches the earth in 1 h is equivalent to the energy consumed on the earth in 1 year.^{1,2} Although

silicon solar cells (Si SCs) have been commercialized, achieving the widespread adoption of technologies that convert solar energy into electricity often requires government subsidies.³ Other types of SCs, including compound semiconductors and dye-sensitized SCs,⁴ and fuel cells (FCs) that use hydrogen as a fuel,⁵ which potentially can be generated using solar energy,⁶ have also been extensively investigated. However, all of the requisites (sustainability, durability, and an electromotive force greater than 1.5 V per cell) have not yet been fully realized.

Recently, a new device, a photofuel cell (PFC) consisting of the two photocatalysts TiO_2 and silver-doped TiO_2 on an electrode film both immersed in acidic water and separated by a proton-conducting polymer (PCP), was demonstrated.⁷ The Schottky barrier between TiO_2 and Ag nanoparticles at the cathode rectified the cell currents. In the present study, n- TiO_2 and p- BiOCl ⁸ were used as the anode and cathode, respectively, to enhance the photocurrent generation in the PFC by facilitating charge transfer at the interface between the photocatalyst film and the substrate in the acidic solution. The energy diagram and electron flow in the PFC comprising TiO_2 and BiOCl photocatalysts at pH 2 (typical conditions for PFC tests) are shown in Scheme 1. The energy of the bottom of the conduction band (CB) is -0.41 V @ pH 7 for TiO_2 (ref. 9) and -1.1 V @ pH 6.8 for BiOCl ,¹⁰ whereas the band gap values for

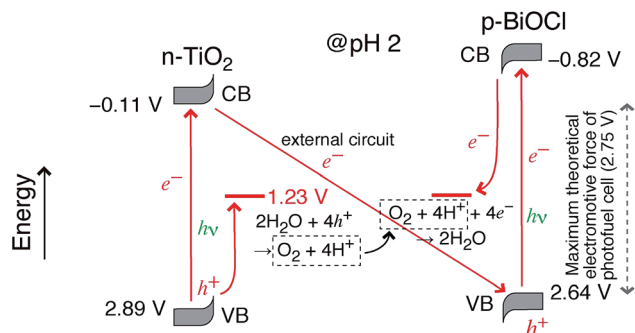
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† Electronic supplementary information (ESI) available: The derivation of eqn (6) for PFC photocurrents. An HR-TEM video observation of BiOCl in Ar atmosphere and irradiated under UV-visible light for 1 h is available, an HR-TEM video observation of BiOCl in Ar atmosphere and irradiated under UV-visible light for 1 h is available. See DOI: 10.1039/c4ta06824f

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Scheme 1 Energy diagram and electron flow for a PFC comprising TiO_2 and BiOCl .

anatase-type TiO_2 , rutile-type TiO_2 and BiOCl are 3.2, 3.0,^{11,12} and 3.46 eV (ref. 13) (Fig. 1A-a), respectively.

The charges in the semiconductors are separated because of ultraviolet (UV) and a small amount of visible light irradiation. The holes in $n\text{-TiO}_2$ are likely to diffuse to the surface of photooxidize water, whereas the electrons in $p\text{-BiOCl}$ are likely to diffuse to the surface to photoreduce O_2 molecules because of band bending at the interface (Scheme 1).^{14,15} Consequently, electron flow from the CB of TiO_2 to the holes in the valence band (VB) of BiOCl should become predominant with an external circuit. The theoretical electromotive force for the system is 2.75 V (Scheme 1) when any overvoltage due to the

carrier level of the electrodes, charge recombination in the photocatalysts, and reverse electron flow from the cathode to anode are not considered. In addition, the use of acidic water as “a fuel” is inexpensive and sustainable. It should be mentioned that acidic water was not exactly a “fuel” consumed in FCs, but rather a regenerative medium to transfer the charge.⁷

The PFC in this study was also compared to *photoelectrochemical electrolysis* (or *photoelectrocatalytic*) cells (PECs) already known in the literature (Scheme 2).^{16–33} Type 1 PECs consist of a photoanode, e.g., TiO_2 and WO_3 , a [photo]cathode, and a redox mediator, e.g., $\text{S}^{2-}/\text{S}_n^{2-}$ (ref. 16) and $\text{Fe}^{2+/3+}$,¹⁷ to diffuse the electrons from the cathode to the anode. Type 2 PECs are FCs that consist of a photoanode for fuel oxidation and a conventional cathode, e.g., Pt-carbon, for O_2 reduction.^{18–23} The photoanode and cathode are separated by a PCP film. Type 3 PECs (or *tandem photolysis cells*) consist of a photoanode and a [photo]cathode to form O_2 and H_2 , respectively, from water.^{23–27} In the cells, a redox mediator is used to diffuse electrons;^{28,29} alternatively, protons diffuse from the anode to the cathode if a redox mediator is not employed.^{30,31} Type 4 PECs consist of a photoanode to oxidize a fuel (not water) and a photocathode to reduce protons.^{32,33}

In summary, PFCs photooxidize water over a photoanode similar to Type 3 PECs and reduce O_2 over a photocathode similar to Type 2 PECs and other FCs. Thus, the specific advantage of a PFC is the photocatalytic reduction of O_2 at the cathode, which is in contrast to PEC Types 1 to 4 (Scheme 2).

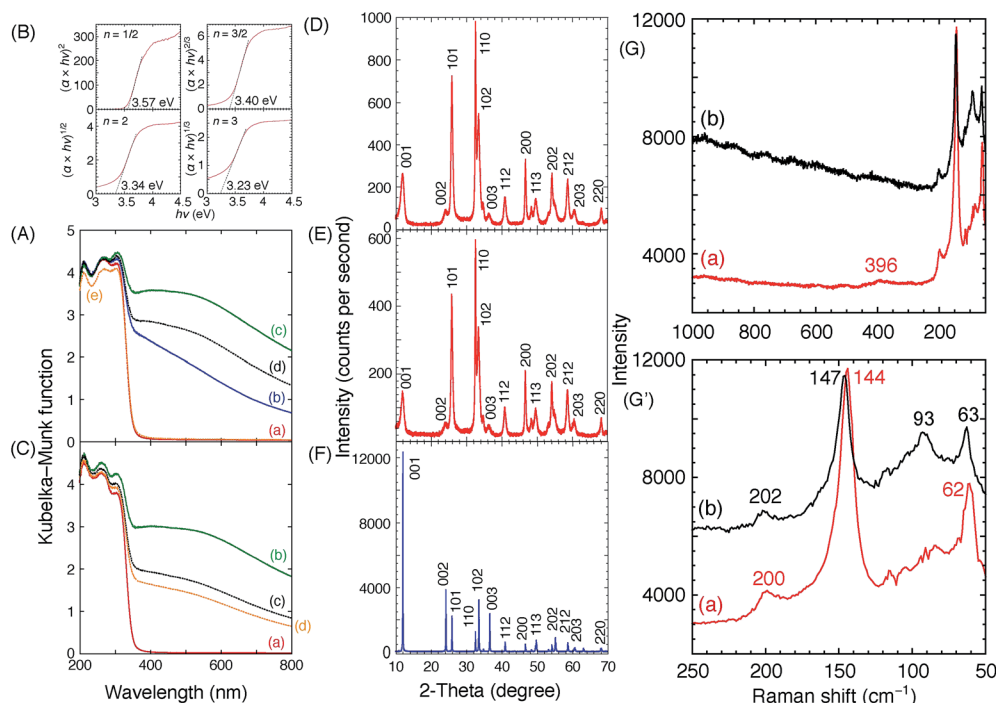
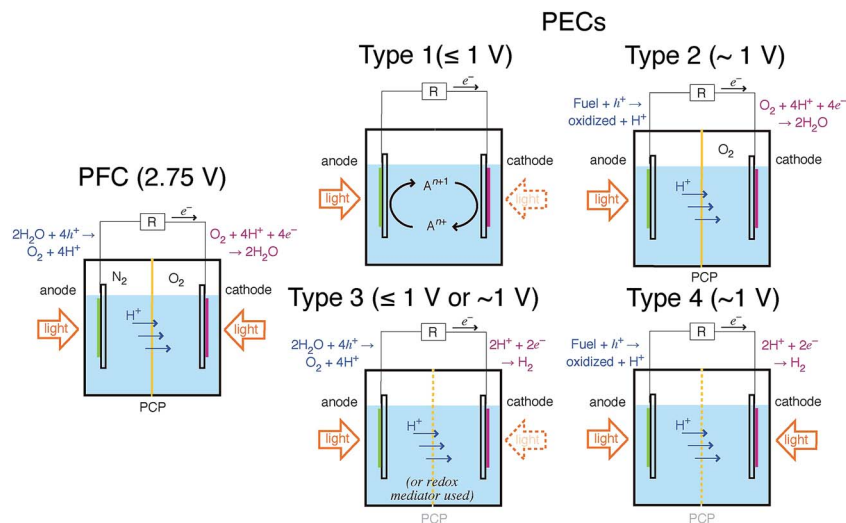


Fig. 1 (A) UV-visible absorption spectra for solvo- BiOCl (a) as-synthesized, irradiated under UV-visible light in Ar for (b) 1 min and (c) 1.0 h, (d) sample c in the dark for 24 h, and (e) sample d exposed to air for 5 h. (B) Fitting to the Davis–Mott equation for the data in (A-a). The values for $(\alpha \times h\nu)^2$, $(\alpha \times h\nu)^{1/2}$, or $(\alpha \times h\nu)^{1/3}$ versus $h\nu$ were plotted, and the intercept with the x-axis estimated the E_g value. (C) UV-visible absorption spectra for solvo- BiOCl (a) as-synthesized, (b) irradiated under UV-visible light in air for 1.0 h, and sample b in the dark (c) for 24 h and (d) 92 h. XRD patterns for solvo- BiOCl (D) as-synthesized, (E) irradiated with UV-visible light under Ar for 9 h, and aqua- BiOCl (F) as-synthesized. (G and G') Raman spectra for BiOCl (a) as-synthesized and (b) irradiated using UV-visible light for 12 h under vacuum.



Scheme 2 Components and chemical reactions in a PFC and Type 1–4 PECs. The dotted arrow indicates the possible use of a photoelectrode or a general electrode, and the dotted line at the middle of the cell indicates the possible use of a PCP for separation.

Importantly, the combination of a photoanode and a photocathode in a PFC enables a theoretical electromotive force as high as 2.75 V (Scheme 1). In Type 1 PECs, the difference (~ 1 V) between the CB minimum of the photoanode and the potential of the redox mediator is the electromotive force.^{30,32} In Type 2 PECs, the difference (~ 1 V) between the CB minimum of the photoanode and the electric potential of O_2 reduction is the electromotive force. In Type 3 PECs, the difference between the CB minimum of the photoanode and the VB maximum of the photocathode is the electromotive force if a redox mediator (IO_3^-/I^- , $Fe^{3+}/2e^+$, Br_2/Br^-)^{28,29} is not used.³⁰ Finally, in Type 4 PECs, the difference between the CB minimum of the photoanode and the VB maximum of the photocathode is the electromotive force. However, the electromotive force is less than 1 V when deep (positive) potential anodic WO_3 and high (negative) potential cathodic Cu_2O are used as photocatalysts for the selective oxidation of the fuel and selective reduction of protons, respectively.³³

A PFC is also different from a dye-sensitized SC, which consists of a dye on a semiconductor and a conventional cathode.⁴ The difference (~ 1 V) between the CB minimum of the photoanode and the potential of the redox mediator is the electromotive force in these systems.

Therefore, the electromotive force between the CB minimum of the photoanode and the VB maximum of the photocathode is advantageous for PFCs and Type 3 and 4 PECs (Scheme 2), but the potential for the reaction $2H^+ + 2e^- \rightarrow H_2$ (0 V @ 298 K and pH 0) in PECs requires a more negative voltage for the CB of the photocathode compared to the voltage (1.229 V @ 298 K and pH 0) required for the reaction $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ in a PFC. Consequently, for Type 3 and 4 PECs, the voltage of the VB maximum of the photocathode is more negative, and the difference (electromotive force) with respect to the CB minimum for the photoanode decreases (Scheme 2). Moreover, the reactions in a PFC are completely reversible, allowing the regeneration of water; thus, PFCs are recyclable (Scheme 1).

2 Experimental

2.1 Sample syntheses and preparation of the photoelectrodes

TiO_2 powder [1.00 g; P25, Degussa; anatase/rutile phases = 7/3; Brunauer–Emmett–Teller (BET) surface area (S_{BET}) = $60 \text{ m}^2 \text{ g}^{-1}$] was suspended in 3.0 mL of deionized water ($<0.06 \mu\text{S cm}^{-1}$) and then stirred well. The obtained suspension was dried at 373 K for 24 h and heated in air at 673 K for 2 h. The resultant powder was suspended in 75 μL of deionized water and placed on an indium tin oxide (ITO, thickness 1.2 to 1.6 μm)-coated Pyrex glass plate. The TiO_2 /ITO/Pyrex was dried at 373 K for 18 h and heated in air at 573 K for 30 min. The amount of TiO_2 deposited on the ITO-coated glass plate was 5.0 mg and covered an area of 1.3 cm^2 .

$BiOCl$ was synthesized using a solvothermal procedure.³⁴ Bismuth nitrate pentahydrate (2.00 g; $>99.5\%$, Wako Pure Chemical) was dissolved in 80 mL of ethylene glycol ($>99.5\%$, Wako Pure Chemical), and then cetyltrimethylammonium chloride (1.30 g; $>95\%$, Wako Pure Chemical) was added to the mixture. The solution was magnetically stirred at a rate of 900 rotations per minute (rpm) at 290 K for 1 h. Next, ethylene glycol solution (4.5 mL) of potassium hydroxide (1.0 mol L^{-1} ; 85%, Wako Pure Chemical) was added. The solution was then introduced into a Teflon-lined autoclave (Model TVS-N2-100, Taiatsu Techno) and maintained at 433 K for 12 h. This solution was filtered using a polytetrafluoroethylene membrane filter (Model Omnipore JGWP04700, Millipore) with a pore size of 0.2 μm , and the collected white powder was subsequently washed with deionized water (total 450 mL) and ethanol (total 450 mL) and dried at 323 K for 12 h. The obtained white $BiOCl$ powder is denoted as solvo- $BiOCl$ (or simply $BiOCl$).

For comparison, some of the experiments using $BiOCl$ synthesized from an aqueous solution were also performed.³⁵ For this process, 3.15 g of Bi trichloride ($>97\%$; Wako Pure Chemical) was dissolved in 100 mL of deionized water. The

solution was agitated by ultrasonication (430 W, 38 kHz) for 10 min, and then magnetically stirred at 290 K in the dark for 2 h. The precipitate was filtered using a JGWP04700 filter, washed with ethanol (total 200 mL), and dried at 353 K for 12 h. The obtained BiOCl is denoted as aqua-BiOCl.

The obtained BiOCl powders (solvo-BiOCl and aqua-BiOCl) were each suspended in 38 μL of deionized water and placed onto ITO-coated glass plates in a manner similar to that used for the $\text{TiO}_2/\text{ITO}/\text{Pyrex}$. The amount of BiOCl placed on each ITO-coated glass plate was 2.5 mg and covered an area of 1.3 cm^2 .

2.2 Characterization

Optical spectroscopic measurements were performed using a UV-visible spectrophotometer (Model V-650, JASCO) with D_2 and halogen lamps for wavelengths below and above 340 nm, respectively. An integrating sphere (Model ISV-469, JASCO) was used for the diffuse reflectance (DR) measurements. The samples were placed in contact with the quartz window glass in a gas-tight DR cell (photographs in Scheme 3), and the interior atmosphere was either argon or air. Measurements were performed at 290 K within the wavelength range of 200–800 nm using 200 mg of the sample. The DR spectra were converted to absorption spectra using the Kubelka–Munk equation.^{36,37} The band gap value was estimated *via* simple extrapolation of the absorption edge or by fitting to the Davis–Mott equation:

$$\alpha \times h\nu \propto (h\nu - E_g)^n, \quad (1)$$

where α , h , and ν are the absorption coefficient, Planck's constant, and frequency of light, respectively, and n is 1/2, 3/2, 2, and 3 for the allowed direct, forbidden direct, allowed indirect, and forbidden indirect electronic transitions, respectively.³⁸

High-resolution transmission electron microscopy (HR-TEM) images were obtained using a Titan G2 60-300 (FEI) field emission-type transmission electron microscope operating at 300 kV. HR-TEM videos were observed using a JEM-2100F (JEOL) field emission-type transmission electron microscope operating at 200 kV. The samples were mounted on a conductive carbon-with-Cu grid mesh (100 mesh per inch). The electron currents at the sample position were estimated to be between 500 and 100 pA cm^{-2} on the basis of the counts on a fluorescence plate that was placed at a distance of 76 cm from the sample on the opposite side of the electron source. We observed BiOCl samples after sufficient astigmatism correction

using an amorphous carbon film in the HR-TEM observation. The intervals of the lattice planes were calculated for tetragonal BiOCl with $a = 0.3891 \text{ nm}$ and $c = 0.7369 \text{ nm}$,^{39,40} and these were compared to the observed lattice intervals.

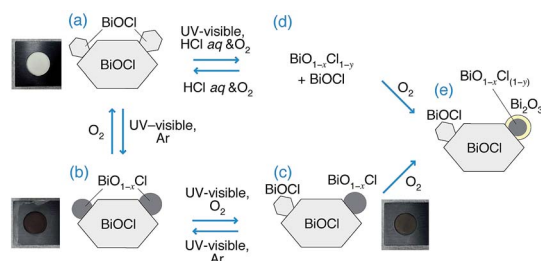
X-ray diffraction (XRD) patterns were observed at a Bragg angle of $2\theta_B = 10^\circ$ to 70° with a scan step of 0.01° and a scan rate of 4 s per step using a D8 ADVANCE diffractometer (Bruker) at the Center for Analytical Instrumentation, Chiba University. The measurements were performed at 40 kV and 40 mA using Cu $K\alpha$ radiation and a nickel filter. The sample irradiated with UV-visible light for 9 h under Ar atmosphere was also analyzed using a gas-tight XRD holder with a semispherical cap (Model A100-B37, Bruker). The mean particle size (t) of the BiOCl was determined using the Scherrer equation

$$t = \frac{0.9\lambda}{\text{Full width at half maximum} \times \cos \theta_B}. \quad (2)$$

Raman spectra were obtained at 290 K using a model NRS-5100 (JASCO) with the excitation wavelength of 532 nm for the solvo-BiOCl samples as-synthesized and irradiated by UV-visible light for 12 h under vacuum. The intensity of the laser was $\sim 1 \text{ mW}$ and a CCD detector was used at 203 K.

X-ray photoelectron spectra (XPS) were obtained using a Model AXIS-NOVA, Shimadzu/Kratos equipped with an X-ray source Al $K\alpha$ (1486.6 eV). O 1s, Bi 4f_{5/2}, and Bi 4f_{7/2} regions were narrowly scanned. The C 1s (284.8 eV) was used as a reference for energy calibration for adventitious hydrocarbon on the specimen surface.⁴¹ BiOCl sample irradiated by UV-visible light for 2.5 h under Ar, and another BiOCl sample immersed in HCl aqueous solution (pH 2.0) irradiated by UV-visible light for 2.5 h under O₂ were mounted on a sample holder and the sample holder was introduced to a transfer vessel under Ar atmosphere. The transfer vessel was connected to AXIS-NOVA, the gate valve was opened, and then the sample was transferred inside AXIS-NOVA without any contact with air.

Bismuth L₃-edge extended X-ray absorption fine structure (EXAFS) spectra were obtained at 290 K in the transmission mode in the Photon Factory Advanced Ring and Photon Factory at the High Energy Accelerator Research Organization (Tsukuba) on beam lines NW10A and 9C.^{42–45} The storage ring energy was 6.5 and 2.5 GeV, and the ring current was 33.0–55.8 and 450 mA. A Si (311) and (111) double-crystal monochromator and a platinum and rhodium-coated focusing cylindrical mirror were inserted into the X-ray beam path. X-ray intensity was maintained at 65% of the maximum flux using a piezo translator attached to the crystal. The slit opening size was 1 mm (vertical) \times 2 mm (horizontal) in front of the ionization chamber. The samples were thoroughly mixed with boron nitride and pressed to form disks. Some samples were in Pyrex glass cells equipped with polyethene naphthalate film (PEN; Q51-25, Teijin-Dupont; 25 μm thick) windows on both sides, purged with Ar or filled with HCl aqueous solution (pH 2.0) with O₂ gas. The PEN film was transparent for X-rays, visible light, and a portion of the UV light region ($>370 \text{ nm}$) and enabled *in situ* monitoring of the photocatalysts.^{36,46–49} The Bi L₃-edge absorption energy was calibrated to 13 426 eV for the spectrum of Bi metal.⁵⁰



Scheme 3 Proposed structural transformation for BiOCl.

The EXAFS data were analyzed using an XDAP package.⁵¹ The procedure has been described previously.^{36,47,52,53} Multiple-shell curve-fit analyses were performed for the Fourier-filtered k^3 -weighted EXAFS data in both k - and R -spaces using empirical amplitude and phase-shift parameters theoretically generated using FEFF version 8.4 (ref. 54) for the crystal structure of Bi metal powder or extracted from the EXAFS data for Bi₂O₃ (>98%, Wako Pure Chemical) and BiCl₃ powders. The interatomic distances (R) and associated coordination numbers (N) for Bi–Bi, Bi–O, and Bi–Cl pairs were set to 0.3071 nm with an N value of 3, 0.3529 nm with an N value of 3,⁵⁵ 0.2330 nm with an N value of 5,⁵⁶ and 0.2500 nm with an N value of 3 (Table 1d, e and g).⁵⁷

Cyclic voltammetry (CV) measurements were performed for BiOCl as the working electrode (WE) (BiOCl/ITO/Pyrex and a Au/Ni-coated stainless 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 (Model RE-1B, BAS Incorporation), immersed in a hydrochloric acid solution of pH 4.0. The voltage of the WE was swept between -1.22 and 1.50 V *versus* Ag/AgCl at a rate of 50 mV s^{-1} using a potentio/galvanostat (Model

VersaSTAT 3-100, Princeton Applied Research) in either O₂ or N₂ atmosphere at a flow rate of 100 mL min^{-1} irradiated using UV-visible light (8 mW cm^{-2} at the WE sample position) or in the dark.

2.3 PFC tests

TiO₂/ITO/Pyrex and BiOCl/ITO/Pyrex electrodes were immersed in HCl solutions (40 mL in each compartment; initial pH was between 2.0 and 4.0). The two compartments were separated by a 50 μm -thick PCP film (Nafion, DuPont; acid capacity $>9.2 \times 10^{-4}$ equivalent g⁻¹). N₂ and O₂ gases were bubbled 30 mm away from each photoelectrode at a flow rate of 100 mL min^{-1} (Fig. S1†).⁷ The PFC was equipped with quartz windows ($\phi = 80 \text{ mm}$) 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 a 500 W xenon arc lamp (Model SX-UID502XAM, Ushio). The distance between the light exit ($\phi = 5 \text{ mm}$) and the TiO₂ or BiOCl film was 46 mm. The light intensity was 8 mW cm^{-2} at the center of the photocatalyst film on each electrode.

Table 1 Curve-fitting analysis of the Bi L₃-edge EXAFS results for BiOCl^a

	Bi–O	Bi–Cl	Bi–Cl	Bi–Bi	Bi–Bi
	R (nm)				
	N				
Sample	$\Delta\sigma^2$ (10^{-5} nm ²)	Goodness of fit			
(a) As-synthesized	0.244(±0.002) 4.0(±0.7) 2.7(±5.5)	0.307(±0.011) 4.0(±1.7) 1.2(±3.7)			3.5×10^4
(b) In Ar & UV-visible, 19 h	0.241(±0.015) 1.9(±0.9) 3.3(±2.5)	0.276(±0.021) 3.7(±0.2) 5.5(±1.6)			1.6×10^5
(c) In HCl (pH 2.0), O ₂ gas, & UV-visible, 35 min	0.250(±0.001) 2.2(±0.2) 1.4(±0.5)	0.329(±0.012) 3.1(±0.7) 2.2(±1.7)			1.4×10^5
(d) Sample c, 12 min after UV-visible was off	0.247(±0.001) 4.2(±0.6) 6.0(±1.4)	0.331(±0.012) 4.6(±1.9) 5.7(±1.8)			3.2×10^5
(e) Sample c, directly exposed to air	0.247(±0.012) 5.1(±1.6) 3.6(±1.9)	0.301(±0.009) 3.1(±1.7) 2.2(±3.6)			
(f) Bi ₂ O ₃ (model) ⁵⁶	0.2330 5 —				
(g) BiCl ₃ (model) ⁵⁷		0.2500 3 —			
(h) BiOCl ³⁹	0.2314 4 —	0.3071 4 —	0.3500 1 —		
(i) Bi metal (model) ⁵⁵				0.3071 3	0.3529 3

^a The values in parentheses are evaluated fit errors.

Static photocurrent generation tests were performed by connecting an external parallel circuit for one route *via* a voltmeter and another route *via* an ammeter with a resistance of 0.5 Ω (Fig. S1†). Both the catalysts were exposed for 30 min to UV-visible light and then placed in the dark for 30 min, and this process was typically repeated five times. As a reference, a static photocurrent test was performed using $\text{TiO}_2/\text{ITO}/\text{Pyrex}$ and $\text{BiOCl}/\text{ITO}/\text{Pyrex}$ electrodes immersed in H_2SO_4 and HCl solutions, respectively, both at pH 2.0. A static photocurrent test comprising continuous UV-visible light exposure for 3 h was also performed. The current (i) and voltage (V) between the two electrodes were monitored. The i - V characteristics were also obtained using a similar parallel circuit; however, the resistance was gradually varied from 500 k Ω to 0.3 Ω over 20 min.

In comparison, the BiOCl (solvo- BiOCl , aqua- BiOCl) fine powder (0.135 g) was irradiated using UV-visible light for 12 h in a quartz glass reactor^{2,36,48,53} under vacuum connected to rotary and diffusion pumps (10^{-6} Pa), and then the reaction with 2.91 kPa of O_2 was monitored by the pressure change using a capacitance manometer (Models CCMT-100A and GM-2001, ULVAC). The rate constant k was determined by fitting to the equation for the first order reaction rate

$$\ln \frac{P_{\text{O}_2} - P_{\text{O}_2,\text{final}}}{P_{\text{O}_2,\text{initial}} - P_{\text{O}_2,\text{final}}} = -kt \quad (3)$$

where $P_{\text{O}_2,\text{initial}}$ and $P_{\text{O}_2,\text{final}}$ are the initial and final pressures of O_2 , respectively.⁴⁷

3 Results

3.1 Characterization of BiOCl

3.1.1 As-synthesized BiOCl

Solvo- BiOCl . The UV absorption edge for the as-synthesized BiOCl was simply extrapolated to 358 nm (Fig. 1A-a). The E_g value was evaluated on the basis of the fit to eqn (1). As shown in the fittings for $(\alpha \times h\nu)^{1/n}$ versus $h\nu$ ($n = 1/2, 3/2, 2$, and 3 ; Fig. 1B), the E_g values (3.57–3.40 eV) when n was $1/2$ or $3/2$ were consistent with that given by simple extrapolation of the absorption edge (3.46 eV) and results reported in the literature (3.46 eV).¹³ In fact, when the $\ln(\alpha \times h\nu)$ value was plotted versus $\ln(h\nu - 3.46)$, the n value was determined to be 1.030 from the slope. Thus, a direct transition from Cl 3p (and/or O 2p) to Bi 6p was suggested.⁵⁸

The XRD peak position and intensity ratio for the as-synthesized BiOCl (Fig. 1D) were in accordance with those reported in literature.^{13,59} The mean particle size of the BiOCl was determined to be $24(\pm 12)$ nm using eqn (2). The mean particle size in the (001) direction was smaller ($13(\pm 2)$ nm) compared to the mean particle size $40(\pm 13)$ nm in the perpendicular plane to the [001] direction, indicating a disk-like crystalline growth.

Raman spectrum for as-synthesized BiOCl was obtained (Fig. 1G-a and G'-a). For the tetragonal symmetry of BiOCl ,¹³ A_{1g} , B_{1g} , and E_g Raman vibrational modes were possible and if we assume the ionic crystal of BiOCl as a “molecular” crystal, internal and external vibration modes were considered within and beyond the “molecule”, respectively. The peaks at 200, 144,

and 62 cm^{-1} were assigned to internal E_g , internal A_{1g} (and minor external E_g), and external A_{1g} for Bi-Cl stretching modes, respectively.¹⁰ The weak peak at 396 cm^{-1} was assigned to E_g and/or B_{1g} modes for the motion of oxygen.

The XP spectrum in the Bi $4f_{5/2}$ and Bi $4f_{7/2}$ regions was obtained for as-synthesized BiOCl (Fig. 2A-a). The peaks centered at 164.7 and 159.4 eV, correspond to the Bi^{3+} state of BiOCl .⁴¹ These values are consistent with the reported values at 164.4–164.5 and 159.1–159.9 eV,^{58,60} respectively, if the C 1s peak energy is assumed to be 284.8 eV.⁴¹

The Bi $L_{3\text{-edge}}$ EXAFS curve-fitting analysis for the as-synthesized BiOCl indicated Bi-O and Bi-Cl coordination at 0.244 and 0.307 nm, respectively (Table 1a and Fig. 3a), confirming the synthesis of BiO^+ layers and intercalated Cl^- anions.¹³

From the HR-TEM images of the as-synthesized BiOCl (Fig. 4a), the particle size was ranged between 10 and 20 nm, which is nearly in accordance with the mean particle size (24 nm) estimated on the basis of the XRD analysis. Lattice patterns with intervals of 0.33–0.34 nm were assigned to the 011 planes (calculated interval 0.34 nm based on the crystal structure).³⁹ Lattice patterns with intervals of 0.40 nm were also observed and assigned to the 002 planes (calculated interval 0.37 nm).

Aqua- BiOCl . UV-visible spectrum and XRD peak position obtained for the aqua- BiOCl were similar to those of the BiOCl (Fig. 1D and F); however, the mean particle size was significantly larger at $115(\pm 49)$ nm, as determined from the XRD peak width. This trend was in accordance with the literature in which water was the hydrolyzing agent in contrast to ethylene glycol, which was the crystal growth inhibitor during the synthesis of BiOCl .⁶¹ The mean particle size in the [001] direction was larger ($168(\pm 28)$ nm) compared to mean particle size ($121(\pm 72)$ nm) in the perpendicular plane to the (001) direction, indicating preferable crystalline growth in the c -axis.

3.1.2 BiOCl irradiated under Ar/vacuum. When the BiOCl powder under Ar atmosphere was irradiated with UV-visible light, the white color changed to brown and the light absorption increased over the entire visible light range in 1 min (Fig. 1A-b). When the irradiation was continued, the color further changed to black (Scheme 3b, photograph) and light absorption

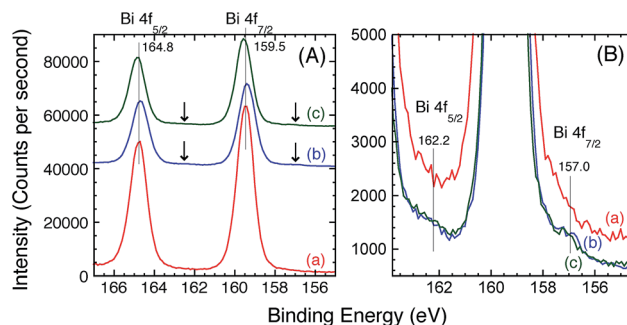


Fig. 2 XPS spectra in the Bi $4f_{5/2}$ and Bi $4f_{7/2}$ regions for as-synthesized BiOCl (a), BiOCl in Ar irradiated by UV-visible light for 2.5 h (b), and BiOCl in HCl aqueous solution with O_2 irradiated by UV-visible light for 2.5 h (c).

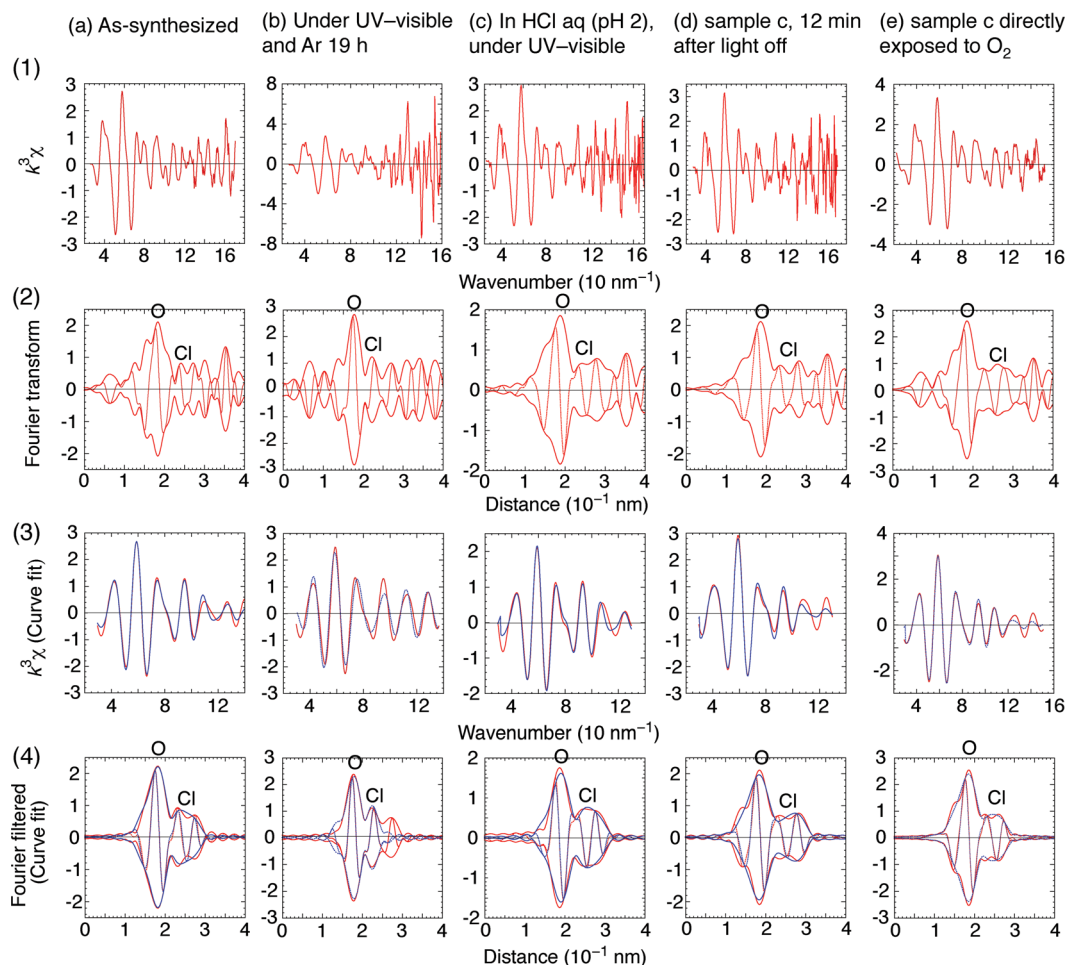


Fig. 3 (a) Bi L_3 -edge EXAFS spectra for as-synthesized BiOCl, (b) sample "a" under Ar and UV-visible light for 19 h, and (c) sample "a" immersed in a pH 2.0 HCl solution under O_2 and UV-visible light for 35 min, (d) 12 min after UV-visible light was off for sample "c", and (e) sample "c" was directly exposed to ambient air. (1) k^3 -weighted EXAFS χ -function, (2) its associated Fourier transform, and best-fit results in (3) k -space and (4) R -space to the Fourier-filtered transformed data. The red and blue lines represent the experimental and calculated values, respectively. The solid line represents the magnitude, and the dotted line indicates the imaginary part in panels 2 and 4.

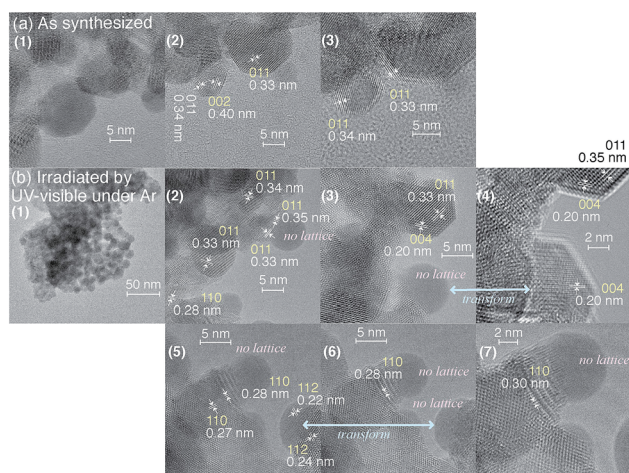


Fig. 4 HR-TEM images observed for the (a) as-synthesized BiOCl and (b) a BiOCl irradiated with UV-visible light for 9 h in Ar atmosphere.

progressively enhanced over the entire visible light region for 1 h (Fig. 1A-c).

The black color slowly diminished to gray after 24 h under Ar in the dark (Fig. 1A-d), and the gray color changed negligibly after 5 days under Ar and in the dark, but returned to white within 5 h when the sample was exposed to air. In addition, the UV-visible spectrum of the recovered white sample was essentially identical to that for the as-synthesized BiOCl (Fig. 1A-e). Thus, the species/phase responsible for the black color under Ar and light exposure was reversibly transformed into the original BiOCl crystallite in air.

Raman spectrum for BiOCl irradiated using UV-visible light for 12 h under vacuum was obtained (Fig. 1G-b and G'-b). The peaks at 200 (internal E_g), 144 [internal A_{1g} (and minor external E_g)], and 62 cm^{-1} (external A_{1g}) for Bi-Cl stretching modes of the as-synthesized BiOCl remained almost constant at 202, 147, and 63 cm^{-1} , respectively.¹⁰ Furthermore, a new peak appeared at 93 cm^{-1} (Fig. 1G'-b). A pair of peaks at 95 and 69 cm^{-1} was reported for metallic Bi;¹⁰ however, no peak at 69 cm^{-1}

appeared in Fig. 1G-b. Therefore, we assume the new peak at 93 cm^{-1} was due to the Bi–Cl stretching mode enabled for the black, O-deficient BiOCl.

XP spectrum in the Bi $4f_{5/2}$ and Bi $4f_{7/2}$ regions was obtained for BiOCl irradiated by UV-visible light for 2.5 h in Ar atmosphere (Fig. 2A-b). The peaks remained at the same position (164.7 and 159.4 eV) as that for the as-synthesized sample (Fig. 2A-a). In addition to the peaks due to the Bi^{3+} state, weaker peaks appeared centered at 162.2 and 157.0 eV (arrows in Fig. 2A-b and B-b). The two peaks shifted by -2.5 and -2.4 eV compared to the corresponding $4f_{5/2}$ and $4f_{7/2}$ peaks due to Bi^{3+} , respectively. Compared to chemical shift for the Bi $4f_{7/2}$ peak on going from $\text{Bi}^{\text{III}}\text{OCl}$ to Bi^0 (3.1 eV),⁴¹ the weaker peaks at 162.2 and 157.0 eV could be obtained from reduced Bi sites at the valence between 3 and 0.

Based on the EXAFS analyses, the N values for the interatomic Bi–O pair decreased from 4.0 to 1.9 when the as-synthesized BiOCl powder was irradiated under Ar using UV-visible light for 19 h (Table 1a and b and Fig. 3a and b). Conversely, after irradiation, the $N(\text{Bi–Cl})$ value only changed slightly from 4.0 to 3.7. Bi atoms that lost neighboring lattice O atoms may have formed shorter bonds with Cl: 0.276 nm compared to 0.307 nm for the original crystalline BiOCl (Table 1a and b). Thus, these results suggest that the generation of O deficiencies in the crystalline BiOCl due to UV-visible irradiation in Ar atmosphere occurred. The curve fitting to the model function for a metallic Bi–Bi pair was unsuccessful (Fig. 3b).

Even after UV-visible light irradiation in Ar atmosphere for 9 h, the entire XRD pattern negligibly changed compared to that for the as-synthesized BiOCl (Fig. 1D and E). The mean particle size did not change at $24(\pm 12)$ nm for the as-synthesized BiOCl and one irradiated with UV-visible light under Ar. Thus, following UV-visible light irradiation under Ar atmosphere, the major phase was crystalline BiOCl, and a minor O-deficient amorphous-like phase resulted in the black color.

HR-TEM image for BiOCl irradiated with UV-visible light in Ar atmosphere was obtained (Fig. 4b). Similar to the image for the as-synthesized BiOCl (Fig. 4a), particles with sizes ranging from 10 to 20 nm were observed, and lattice patterns with intervals of 0.33–0.35, 0.20, 0.22–0.24, and 0.27–0.30 nm were assigned to the 011, 004, 112, and 110 planes (calculated lattice intervals of 0.34, 0.19, 0.22, and 0.28 nm), respectively.

During the HR-TEM observation, a portion of the external nanocrystals of BiOCl transformed into spherical nanoparticles without lattices (Fig. 4b3, right, bottom and 4b6, center, right, and bottom; Fig. 4b7 is a zoomed image of 4b6). When observation was continued, the amorphous-like spherical nanoparticles transformed back to nanocrystals of BiOCl with a clear lattice pattern (Fig. 4b4, right, bottom and 4b5, right and bottom). This phase transformation was reversible (a video is available as an ESI material†). Thus, the amorphous-like spherical nanoparticles were oxygen-deficient $\text{BiO}_{1-x}\text{Cl}$ that formed under the electron flux of the HR-TEM. The 110 and 112 lattice patterns in Fig. 4b5 (left and right) in the reversibly transformed BiOCl crystals were continuous with 110 and 112 lattice patterns, respectively, present in the lower, unchanging BiOCl particles. This fact suggests that O atoms were supplied

from the lower BiOCl particles to the amorphous-like, oxygen-deficient $\text{BiO}_{1-x}\text{Cl}$ species to enable crystallization as BiOCl from the boundary toward the $\text{BiO}_{1-x}\text{Cl}$ nanoparticles.

The observed reversible phase transformation should not be an artifact because the amorphous-like spherical nanoparticles (Fig. 4b3, right, bottom and 4b6, center, right, and bottom, and Fig. 4b7) were rarely observed for the as-synthesized BiOCl (Fig. 4a1–3). The adjustment of astigmatism was sufficient as is shown in the video (ESI material†).

3.1.3 BiOCl irradiated under O_2 /air and/or HCl aqueous solution. Corresponding to the conditions of PFC tests, the on/off exposure of BiOCl to UV-visible light in air was performed, and the UV-visible absorption spectra were monitored (Fig. 1C). When fresh BiOCl was irradiated with UV-visible light for 1 h, the color changed to black, and its light absorption increased over the entire visible light region (Fig. 1C-b). The maximum absorbance at ~ 540 nm was $\sim 80\%$ of that following irradiation with light for 1 h under Ar (Fig. 1A-c). When the black sample was stored in air in the dark for 24 h, the color faded to gray, and the absorbance was $\sim 65\%$ of that of the corresponding sample stored under Ar in the dark for 24 h (Fig. 1C-c and A-d).

In addition, the BiOCl irradiated in air remained gray in the dark, even after 92 h (Fig. 1C-d), which is in clear contrast to the behavior of the BiOCl irradiated under Ar, which completely turned white within 5 h upon exposure to air (Fig. 1A-e). Thus, it can be concluded that the $\text{BiO}_{1-x}\text{Cl}$ formed when the BiOCl was irradiated in air (or O_2) with UV-visible light was stabilized by the outer oxidized layers (Scheme 3e).

XP spectrum in Bi $4f_{5/2}$ and Bi $4f_{7/2}$ regions was also obtained for BiOCl irradiated by UV-visible light for 2.5 h immersed in an HCl aqueous solution (pH 2.0) saturated with O_2 (Fig. 2A-c). Although the Bi^{3+} peaks were again predominant at 164.8 and 159.5 eV, weaker peaks appeared centered at 162.2 and 157.0 eV (arrows in Fig. 2A-c and B-c) similar to reduced Bi sites at the valence between 3 and 0 for irradiated BiOCl in Ar atmosphere (Fig. 2B-b). The peak intensity of $4f_{5/2}$ and $4f_{7/2}$ peaks for reduced Bi sites was difficult to compare between Fig. 2B-b and B-c because the intensities of these peaks were quite weak.

The BiOCl film immersed in HCl aqueous solution (pH 2.0) irradiated by UV-visible light at beamline was analyzed using Bi $L_{3\text{-edge}}$ EXAFS (Fig. 3c). The color of the film was light gray. The coordination number of both Bi–O and Bi–Cl decreased (from 4.0 to 2.2 and from 4.0 to 3.1, respectively; Table 1c and Fig. 3c). The oxygen vacancy could be formed similar to the conditions of under Ar and with UV-visible irradiation.

Then, UV-visible light was turned off after 60 min of irradiation. A Bi $L_{3\text{-edge}}$ EXAFS spectrum was obtained at 12 min in the dark (Fig. 3d). The shape of EXAFS oscillation was similar to that for the sample irradiated by UV-visible light (Fig. 3c1), but the reduced amplitude in the whole spectrum region irradiated by light (Fig. 3c1) seemed to recover to the level for the as-synthesized sample (Fig. 3a1). In fact, the $N(\text{Bi–O})$ and $N(\text{Bi–Cl})$ values recovered to 4.2 and 4.6 (Table 1d), respectively, similar to that for as-synthesized BiOCl (4.0; Table 1a). Thus, the O and Cl vacancy formed in HCl aqueous solution irradiated by UV-visible light is suggested to be transformed to the original BiOCl crystalline state soon after the light was turned off.

Furthermore, a few percent of chlorine loss/recovery was reported for BiOCl immersed in water in response to irradiation/stop of UV light and the transformation was reversible based on the analysis using ion chromatography.³⁴ The chlorine vacancy based on the decrease of $N(\text{Bi-Cl})$ in EXAFS (Table 1c) was qualitatively in accordance with the report.

Finally, the BiOCl film that was subjected to five 1 hour cycles of the PFC test (2.5 h of irradiation) and directly exposed to air was analyzed using Bi $L_{3\text{-edge}}$ EXAFS (Fig. 3e). The $N(\text{Bi-O})$ values for the as-synthesized BiOCl (4.0) increased to 5.1, whereas the $N(\text{Bi-Cl})$ values decreased from 4.0 to 3.1 (Table 1a and e). The R values, on the other hand, were essentially constant at 0.244–0.247 and 0.301–0.307 nm. Notably, the $N(\text{Bi-O})$ value (5.1) was similar to that for Bi_2O_3 (5; Table 1f); however, the interatomic distance was longer by 0.014 nm. In contrast to reversible transformation between $\text{BiO}_{1-x}\text{Cl}_{1-y}$ and BiOCl by on/off exposure to UV-visible light in HCl solution saturated with O_2 , the $\text{BiO}_{1-x}\text{Cl}_{1-y}$ species was not totally transformed back to the original BiOCl by direct exposure to air.

3.2 Photocurrent changes and the i - V dependence of the PFC

3.2.1 Static PFC tests. In static PFC cycle tests at pH 3.0, following UV-visible irradiation, the photocurrents of the PFC increased and stabilized within 0.84–3.4 min (Fig. 5A). In five light on/off cycles, the photocurrents converged to 32.7–34.0 μA . Similarly, the photocurrents increased and converged to 4.29–4.40 μA within 1.7–4.1 min at pH 4.0. In contrast, at pH 2.0, the current gradually increased and stabilized within 20 min in the

first cycle, but did not fully stabilize in the following cycles. The current nearly converged from 102 to 118 μA in five cycles. Separately, photocurrents converged to 106 μA within 60 min at pH 2.0 when the irradiation was continued for 3 h (Fig. 5A'), suggesting reversible structure/state changes for BiOCl photocatalyst when the light was off. Throughout this study, the pH values of the electrolyte changed negligibly (within a variation of 0.02) over 5 h.

When the UV-visible light was off, the photocurrent values quickly decreased to zero within 0.84–4.1 min at pH 2.0, but decreased more slowly (14–20 min) at pH 3.0, and most slowly (25–26 min) at pH 4.0. This trend suggests limited diffusion at lower proton concentrations. Thus, the nearly converged PFC photocurrent values were plotted as a function of the electrolyte solution proton concentrations (Fig. 5B), and it was found that the values increased proportionally to the square root of the proton concentration.

When sulfuric acid solution (pH 2.0) was used as the electrolyte for the photoanode (TiO_2) instead of HCl solution, the converged photocurrent was 76 μA in the first cycle, but gradually decreased to 77, 63, 64, and 64 μA with five cycles (Fig. 5A''). When the UV-visible light was off, the photocurrents decreased to zero within 3.0–6.5 min under this condition. This response was significantly slower than the relaxation of currents in HCl solution for the photoanode (0.84–4.1 min; Fig. 5A, pH 2.0).

3.2.2 Reactivity of BiOCl with O_2 gas. For comparison, as-synthesized solvo-BiOCl fine powder was irradiated with UV-visible light for 12 h in vacuum and then placed into contact with O_2 . The quantity of O_2 (2.91 kPa) in a closed glass system

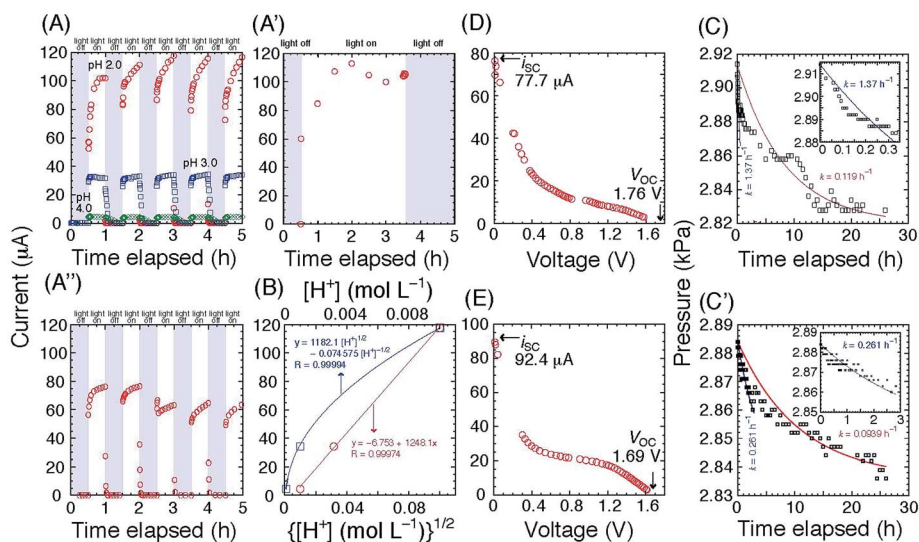


Fig. 5 (A) Time course of the photocurrents in the PFC comprised of the TiO_2 and solvo-BiOCl photocatalyst electrodes, which were immersed in HCl solutions at a pH of 2.0 (circle, \circ), 3.0 (square, \square), and 4.0 (diamond, \diamond). (A') Continuous test at a pH of 2.0 (circle, \circ) was also plotted. (A'') Time course of the photocurrents in the PFC comprised of the TiO_2 and solvo-BiOCl photocatalyst electrodes, which were immersed in H_2SO_4 and HCl solutions, respectively, both at a pH of 2.0 (circle, \circ). (B) correlation between the converged photocurrents within 5 h and the H^+ concentrations of the acidic water in the PFC or the square root of the H^+ concentrations. The fittings were to the linear function (lower x-axis) or to the kinetic model equation $i = A[\text{H}^+]_c^{1/2} - B[\text{H}^+]_c^{-1/2}$ (eqn (7), see text; upper x-axis). (C and C') Time course of the O_2 pressure in contact with solvo-BiOCl (C) and aqua-BiOCl (C') previously irradiated with UV-visible light for 12 h. (D) i - V dependence of the PFC comprising TiO_2 and solvo-BiOCl immersed in a pH 2.0 HCl solution. (E) i - V dependence of the PFC comprising TiO_2 and aqua-BiOCl immersed in a pH 2.0 HCl solution.

corresponded to the dissolved amount of O₂ in acidic water (40 mL) at 290 K. The time course of the reaction for 26 h is shown in Fig. 5C. The rate constant k was 0.119 h⁻¹ by fitting to eqn (3). Because the initial reaction rate was significantly faster than the rate at 26 h, an alternative fitting of the data only for the initial 20 min gave a k' value of 1.37 h⁻¹ (Fig. 5C, inset).

In the corresponding reactivity test for aqua-BiOCl, the rate constant k was 0.0939 h⁻¹ by fitting to eqn (3) (Fig. 5C'), which was 21% smaller compared to that for solvo-BiOCl (Fig. 5C). An alternative fitting of the data for the initial 20 min was difficult for aqua-BiOCl, and the fit of the data for the initial 170 min gave a k' value of 0.261 h⁻¹ (Fig. 5C', inset).

Furthermore, based on the total O₂ reacted with solvo-BiOCl and aqua-BiOCl irradiated with UV-visible light for 12 h in vacuum (6.1 and 3.6 μmol; Fig. 5C and C'), the stoichiometry of the BiOCl subjected to the kinetic tests of Fig. 5C and C' was estimated to be BiO_{1-0.023}Cl and BiO_{1-0.014}Cl, respectively.

3.2.3 *i*-V characteristics. The *i*-V characteristics were then studied for a PFC comprising TiO₂ and BiOCl at pH 2.0 (Fig. 5D). The *i* value gradually increased as the cell voltage decreased beginning at the open circuit voltage (V_{OC} , 1.76 V), which is similar to the *i*-V dependence for SCs.⁶² When the voltage was less than 0.39 V, the current increased linearly from 24.7 to 77.7 μA (short circuit current, i_{SC}), and the maximum electric power (P_{max}) was 10.5 μW (1.01 V × 10.5 μA) for a photocatalyst film area of 1.3 cm² (Table 2A).

For comparison, the *i*-V characteristics of a PFC comprising TiO₂ and aqua-BiOCl at pH 2.0 were also investigated (Fig. 5E). The major difference between the solvo-BiOCl and aqua-BiOCl is the mean particle size: 24 *versus* 115 nm, respectively, based on the XRD analysis (Fig. 1D and F). Although the V_{OC} value (1.69 V) for the PFC based on the aqua-BiOCl was 0.07 V less than that for the PFC containing the solvo-BiOCl, the former i_{SC} value increased to 92.4 μA, which is 14.7 μA greater than the latter. Consequently, the maximum electric power was 21.1 μW (1.15 V × 18.3 μA) for a photocatalyst film area of 1.3 cm² (Table 2B).

3.3 CV for BiOCl

3.3.1 Under N₂ atmosphere. The CV results for BiOCl in a pH 4.0 aqueous HCl solution under N₂ atmosphere are depicted in Fig. 6A. In the dark, a pair of oxidation and reduction peaks appeared centered at 0.57 and -0.39 V, respectively, *versus* a standard hydrogen electrode (SHE). The center of the two peaks

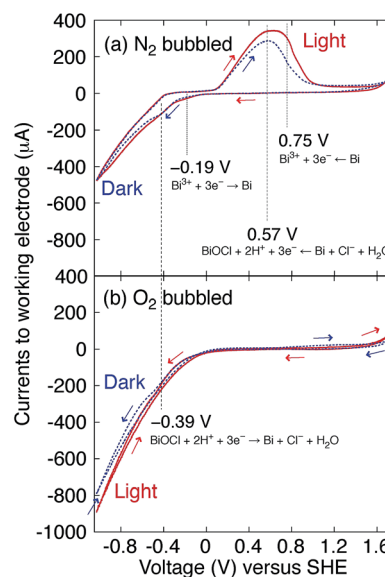
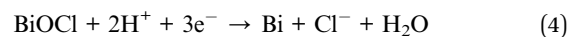


Fig. 6 CV for a BiOCl WE and glassy carbon CE in a pH 4.0 aqueous HCl solution under a (a) N₂ flow and (b) O₂ flow during UV-visible light irradiation (solid lines) or in the dark (dotted lines).

(0.09 V) coincides with the equilibrium voltage at the pH (Table 3B) for the reaction:



Under light irradiation, another pair of oxidation and reduction peaks appeared at 0.75 and -0.19 V, respectively, as shoulder peaks on the redox peaks due to eqn (4) (Fig. 6a). The peak at -0.19 V was very weak. The center of the new peaks (0.28 V) corresponds to the equilibrium voltage (0.32 V @ pH 0; Table 3A) for the reaction of the anodic dissolution of Bi and reduction back to Bi:



3.3.2 Under O₂ atmosphere. In the dark, only a weak reduction peak for reaction 4 (-0.39 V) appeared under O₂ atmosphere (Fig. 6b). Furthermore, no distinct peaks were observed with irradiation of UV-visible light. This contrast suggests a stabilized BiOCl-based phase under O₂ atmosphere.

Table 2 Electrochemical data for PFCs obtained from the *i*-V analysis^a

Entry	Photocatalyst		V_{OC} (V)	i_{SC} (μA)	P_{max} (μW)	Source
	Anode	Cathode				
A	TiO ₂ ^b (25 nm)	Solvo-BiOCl (24 nm)	1.76	77.7	10.5	This work
B	TiO ₂ ^b (25 nm)	Aqua-BiOCl (115 nm)	1.69	92.4	21.1	This work
C	TiO ₂ ^b (25 nm)	Ag (3.0 wt%)-TiO ₂ ^b (25 nm)	1.59	73.7	14.0	Ref. 7

^a The pH of each HCl solution was 2.0. The area of each photocatalyst was 1.3 cm². ^b Mean particle size estimated from the XRD pattern; anatase: 21 nm, rutile: 35 nm, anatase/rutile ratio = 7 : 3.

Table 3 Electrochemical data for BiOCl

Redox reaction conditions	CV peak (V) versus SHE			Equilibrium voltage @ 298 K
	Reduction wave	Oxidation wave	Center	
(A) $\text{Bi}^{3+} + 3\text{e}^- = \text{Bi}$				
O_2 , light	—	—	—	0.3172 @ pH 0
O_2 , dark	—	—	—	
N_2 , light	−0.19	0.75	0.28	
N_2 , dark	—	—	—	
(B) $\text{BiOCl} + 2\text{H}^+ + 3\text{e}^- = \text{Bi} + \text{Cl}^- + \text{H}_2\text{O}$				
O_2 , light	—	—	—	0.1697–0.0197 pH (0.0909 @ pH 4.0)
O_2 , dark	−0.39	—	—	
N_2 , light	−0.39	0.57	0.09	
N_2 , dark	−0.39	0.57	0.09	
(C) $\text{Bi}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- = 2\text{Bi} + 3\text{H}_2\text{O}$				0.376–0.0591 pH (0.1396 @ pH 4.0)
(D) $4\text{H}^+ + \text{O}_2 + 4\text{e}^- = 2\text{H}_2\text{O}$				1.229–0.0591 pH (0.993 @ pH 4.0)

4 Discussion

4.1 Phase transformation of BiOCl

The band gap for as-synthesized BiOCl powder was 3.46 eV (Fig. 1A-a), and the mean disk-like particle size was 24 nm (Fig. 1D). When the BiOCl powder was irradiated with UV-visible light under Ar atmosphere, the color changed to black in 1 h (Fig. 1A-c and Scheme 3b). The black color turned to gray after 24 h placed under Ar in the dark (Fig. 1A-d), and then back to white when the powder was exposed to air for 5 h (Fig. 1A-e). Thus, (a part of) the crystalline BiOCl changed to something else following UV-visible light irradiation under Ar, but reversibly converted back to BiOCl in air. Furthermore, a new Raman peak appeared at 93 cm^{-1} for BiOCl irradiated by UV-visible light under vacuum due to the Bi–Cl stretching vibration (Fig. 1G-b and G'-b). Because the peak was not detected for the as synthesized BiOCl, the new Bi–Cl stretching vibration mode was enabled by the modulation of symmetry for O-deficient BiOCl.

The generation of O defects in the BiOCl irradiated with UV light was suggested on the basis of additional Bi $4f_{5/2}$ and $4f_{7/2}$ peaks at lower binding energy than the main peaks due to Bi^{3+} (Fig. 2b). The additional peaks were also reported in the literature.^{35,60,63} This interpretation was supported by the $N(\text{Bi-O})$ decrease (4.0 to 1.9) based on Bi L_3 -edge EXAFS analysis for BiOCl irradiated with UV-visible light under Ar (Table 1b and Fig. 3b).

The origin of the black color and O deficiency of the BiOCl irradiated with UV-visible light under Ar atmosphere (Scheme 3b, photograph) was clarified *via* HR-TEM analysis. A reversible phase transformation from crystalline BiOCl to amorphous-like spherical nanoparticles was observed during the HR-TEM analysis (Fig. 4b3–b6 and the video available in the ESI material†). In contrast, the amorphous-like spherical nanoparticles were rarely observed for the as-synthesized BiOCl (Fig. 4a1–3). Thus, it is concluded that the origin of the black color of the irradiated BiOCl is O-deficient $\text{BiO}_{1-x}\text{Cl}$. An amorphous-like $\text{BiO}_{1-x}\text{Cl}$ phase present as spherical nanoparticles in the electron flow of the HR-TEM was observed to reversibly transform to crystalline BiOCl with a clear lattice pattern once O atoms were

supplied from inside the crystalline BiOCl grains to achieve phase equilibrium (Fig. 4b3–6 and Scheme 3a and b).

In the HR-TEM images of BiOCl irradiated by UV light under Ar, an outer, $\sim 1\text{ nm}$ -thick layer of the crystalline BiOCl was disordered and considered to be amorphous-like $\text{BiO}_{1-x}\text{Cl}$.^{35,58} Density functional theory (DFT) calculations reported for O displacement in BiOCl from an original position in the lattice and generation of vacancies in the BiO^+ layers revealed the formation of an additional energy state slightly below the CB of BiOCl. Such vacancies would function as electron trapping sites; however, they could also recombine with the displaced O under equilibrium conditions.⁶⁴

The maximum electron current at the position of the sample in the JEM-2100F was 500 pA cm^{-2} . Thus, considering the elementary charge, 4×10^9 electrons per second reached the 1.3 cm^2 of sample. In comparison, the photon flux from the SX-UID502XAM *via* the fiber light guide was 2×10^{16} photons s^{-1} , and generated photocurrents for the PFC were 7×10^{14} electrons per s (118 μA at the most; Fig. 5A) to the photocatalyst film area of 1.3 cm^2 (Scheme 1). Although the physical situation for the electron flow to BiOCl in the HR-TEM *versus* the charge separation for TiO_2 and BiOCl following irradiation and the resulting PFC current is different, the effective electron flow during the PFC tests was approximately 10^5 times greater than that in the HR-TEM apparatus.

In XPS spectra in Bi $4f_{5/2}$ and Bi $4f_{7/2}$ regions, weaker peaks were detected at 162.2 and 157.0 eV on the lower energy side of major peaks at $164.8(\pm 0.1)$ and $159.5(\pm 0.1)$ eV, respectively, for BiOCl irradiated by UV-visible light in Ar or in HCl aqueous solution saturated with O_2 (Fig. 2b and c). The weaker peaks suggest a reduced Bi state at the valence between 3 and 0, shifted by 2.5–2.6 eV toward the lower energy side from major peaks due to the Bi^{3+} state. Furthermore, both an O and Cl-deficient structure was directly confirmed by the decrease in $N(\text{Bi-O})$ and $N(\text{Bi-Cl})$ values from 4 to 2.2 and 4 to 3.1, respectively (Fig. 3c and Table 1c), based on Bi L_3 -edge EXAFS in HCl aqueous solution (pH 2.0) saturated with O_2 irradiated by UV-visible light. Thus, $\text{BiO}_{1-x}\text{Cl}$ formed in Ar (Scheme 3b) further lost a small amount of chlorine ($\text{BiO}_{1-x}\text{Cl}_{1-y}$), but it

transformed back to BiOCl when the light was off (Fig. 3d, Table 1d, and Scheme 3a), which is in accordance with literature.³⁴ In relation to the EXAFS results, a reduction peak due to Cl loss *via* eqn (4) was observed at -0.39 V in HCl aqueous solution with N_2 or O_2 (Fig. 6a and b).

In summary, amorphous-like $BiO_{1-x}Cl$ spherical nanoparticles (Scheme 3b) would be present in the BiOCl samples irradiated with UV-visible light under Ar and for which the UV-visible spectra (Fig. 1A–b–d), XRD patterns (Fig. 1E), Bi $4f_{5/2}$ and $4f_{7/2}$ XPS peaks (Fig. 2b), and Bi L_{3} -edge EXAFS measurements (Fig. 3b) were obtained. Both O and Cl-deficient $BiO_{1-x}Cl_{1-y}$ species could be present for the BiOCl film on the photocathode irradiated by UV-visible light immersed in HCl solution under O_2 gas for XPS (Fig. 2c), Bi L_{3} -edge EXAFS (Fig. 3c), and during the PFC tests (Fig. 5A).

It is thought that the O and/or Cl-deficient $BiO_{1-x}Cl_{1-y}$ or $BiO_{1-x}Cl$ nanoparticles were covered with thin Bi_2O_3 layers (Scheme 3e) in samples subjected to UV-visible (Fig. 1C) and EXAFS (Fig. 3e) analyses and used in the PFC tests in HCl with light irradiation and direct exposure to air.

4.2 Factors for controlling PFC performance

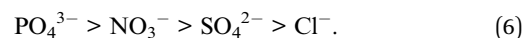
The V_{OC} , i_{SC} , and P_{max} values are based on i - V characteristics and are summarized in Table 2. Although the theoretical maximum electromotive force for the PFC comprising TiO_2 and BiOCl is 2.75 V in the energy diagram (Scheme 1), the best V_{OC} value obtained in this study was 1.69–1.76 V (Fig. 5D and E). It is also possible that the carrier level of the ITO [work function (WF) 4.6–4.8 eV] determined the voltage of the photoexcited electrons to the CB of TiO_2 (WF 4.13–4.3 eV)^{65,66} if the ITO film behaved similar to a semiconductor rather than a conductor. If this logic applies, the voltage loss due to the difference in the WF is 0.3–0.67 V, and the theoretical maximum voltage of 2.75 V would be reduced to 2.08–2.45 V.

Even though, the V_{OC} values (1.69–1.76 V) were still higher for the PFC comprising TiO_2 and solvo/aqua-BiOCl than the 1.59 V reported for the PFC comprised of TiO_2 and Ag- TiO_2 (Table 2).⁷ Depending on the energy diagram (Scheme 1), the maximum electromotive force is theoretically smaller for the PFC comprised of TiO_2 and BiOCl (2.75 V) than that for the PFC comprised of TiO_2 and Ag- TiO_2 (3.0 V).⁷ In this context, the combination of n- and p-semiconductors was advantageous for minimizing the overpotential compared to rectification by a Schottky barrier.

4.3 Kinetics of the PFC

4.3.1 Derivation of kinetics. The photocurrents in the present PFCs were generated by the balance between the photoexcitation and charge recombination both in the TiO_2 and BiOCl photocatalysts, and the reaction rates of water photooxidation and O_2 photoreduction (Scheme 1). The allowed indirect^{53,67} and direct⁵⁸ (Fig. 1B) band gap electronic transitions lead to the separation of electrons and holes in TiO_2 and BiOCl, respectively, and equilibrium constants for charge separation (K_a and K_c) are assumed in the anodic TiO_2 and cathodic BiOCl, respectively.

The photooxidation over TiO_2 was essentially irreversible under N_2 flow, which purged the generated O_2 . The superiority of an HCl aqueous solution (pH 2.0) to H_2SO_4 aqueous solution (pH 2.0) as an electrolyte for the photoanode was demonstrated (Fig. 5A and A'). One of the major reasons would be the difference in molar conductivity of the solutions (411.1 *versus* 336.4 S cm² mol⁻¹).⁶⁸ The converged photocurrents gradually increased in Fig. 5A when HCl solution was used, which is in contrast to the decreases in Fig. 5A' when H_2SO_4 solution was used. This difference suggests the inhibition of hole transfer from the surface to a water molecule due to the blocking of Ti sites by sulfate ions. Larger blocking effects of Ti sites by the anions of electrolyte were reported for the photodecomposition of 2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide and the order of the effects was in the order⁶⁹



The rate and rate constant for this reaction are denoted as r_{ox} and k_{ox} , respectively. The O_2 photoreduction at BiOCl was in equilibrium with the product (water), and the constant is denoted as K_{red} . Based on the principles of PFCs, the forward electron flow rate from TiO_2 to BiOCl *via* the external circuit could be proportional to both the excited electron concentration in TiO_2 and the hole concentration in BiOCl (Scheme 1). In addition, the reverse electron flow rate could be proportional to both the unreacted excited electron concentration at BiOCl and the unreacted hole concentration at TiO_2 . Thus, the effective electron flow rate (photocurrent i) is formulated in eqn (7). The derivation is shown in eqn (S1)–(S4) (ESI†).

$$i = k \frac{K'_a (k'_{ox})^{\frac{1}{4}} (K'_c)^{\frac{1}{6}} (K'_{red})^{\frac{1}{8}}}{(r_{ox})^{\frac{1}{4}}} ([O_2]_c)^{\frac{1}{8}} ([H^+]_c)^{\frac{1}{2}} - k' \frac{(r_{ox})^{\frac{1}{4}} (K'_c)^{\frac{1}{6}}}{(k'_{ox})^{\frac{1}{4}} (K'_{red})^{\frac{1}{8}}} \frac{1}{([O_2]_c)^{\frac{1}{8}} ([H^+]_c)^{\frac{1}{2}}} \quad (7)$$

where $[O_2]$ and $[H^+]$ with a subscript "c" denote the concentrations of O_2 and H^+ in the acidic solution around the cathode, and the rate and equilibrium constants with the prime symbol denote the constants multiplied with essentially constant concentrations for the predominant species in the acidic solution/photocatalysts (see ESI† for a detailed definition).

4.3.2 Comparison of kinetics to experimental data. Fitting of the experimental data for the pH dependence in eqn (7) is presented in the upper x-axis of Fig. 5B. The second term was negligible in the fitting to eqn (7) ($i = 1182[H^+]^{1/2} - 0.07458[H^+]^{-1/2}$), demonstrating that the reverse electron flow from the CB of BiOCl to the VB of anodic TiO_2 via the external circuit was minimal. Moreover, the net photocurrents were in fact proportional to $[H^+]^{1/2}$ (Fig. 5B, lower x-axis), which is in accordance with eqn (7).

A kinetic equation similar to eqn (6) was reported for the PFC comprising TiO_2 and Ag- TiO_2 .⁷ The fitted equation for the pH dependence was $i = 626.7[H^+]^{1/2} - 0.009977[H^+]^{-1/2}$. The coefficient of the second term was even smaller than that for the p-n type PFC of the present study because of the rectification by the

Schottky barrier between the TiO₂ and Ag nanoparticles. Notably, the combination of TiO₂ and BiOCl was nearly a factor less efficient with respect to rectification.

Conversely, the coefficient of the first term was greater for the p–n type PFC compared to that for the Schottky-type PFC (1182 *versus* 626.7, respectively). Faster charge transfer rates (holes to H₂O at the anode and electrons to O₂ at the cathode) at the interfaces between the photocatalysts and the acidic solution due to band bending^{14,15} could enhance the first term: the *i*_{SC} values of 77.7–92.4 μA (Table 2A and B) *versus* 73.7 μA for the Schottky-type PFC⁷ (Table 2C).

Another reason for this difference is the layered structure of BiOCl. If a Cl 3p electron is excited to Bi 6p (Fig. 1A and C) upon irradiation with UV-visible light, the holes and electrons could preferably diffuse in the Cl[−] and BiO⁺ layers, respectively, both of which are in the 001 plane.¹³ The crystallites of solvo-BiOCl tended to grow in the perpendicular direction to [001], whereas the crystallites of aqua-BiOCl tended to grow in the direction of [001] (Fig. 1D and F). Therefore, the charges separated in bulk would effectively diffuse in the 001 plane and favorably reach the photocatalyst surface, *e.g.* {100} and {110}, for aqua-BiOCl,¹³ which is in accordance with the PFC performances (Table 1A and B). Alternatively, aqua-BiOCl was advantageous to solvo-BiOCl because the larger number of crystallites led to a smaller serial resistance⁷⁰ of the cathode photocatalyst film.

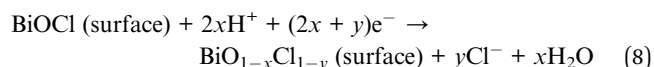
4.3.3 Redox of Bi sites. The peaks for the reduction of BiOCl to Bi⁰ and the reverse oxidation reaction (eqn (4)) were observed in a pH 4.0 acidic solution under N₂ (Fig. 6a and Table 3B). When the electrode was irradiated with UV-visible light, weaker peaks for the reduction of Bi³⁺ to Bi⁰ and the reverse oxidation reaction (eqn (5)) were also detected (Table 3A). In contrast, in a pH 4.0 acidic solution under O₂ in the dark, only a very weak peak for the reduction of BiOCl to Bi⁰ was observed, and during irradiation, no CV peaks appeared (Fig. 6b).

The Bi⁰ species formed at voltages lower than −0.19 V during the CV experiments was not detected *via* XRD, XPS, EXAFS, or HR-TEM analysis of BiOCl irradiated under Ar or O₂. The color change from white to black (under Ar) or gray (under air/O₂) was due to O-deficient BiO_{1−x}Cl species formed because of UV-visible light irradiation. Under vacuum and irradiation of UV-visible light for 12 h, the stoichiometry of the sample was estimated to be BiO_{1−0.023}Cl for solvo-BiOCl and BiO_{1−0.014}Cl for aqua-BiOCl based on a kinetic study with O₂ gas (Fig. 5C and C'). Amorphous-like BiO_{1−x}Cl particles (~5 nm) were observed in the HR-TEM image (Fig. 4b3, 5–7), and these particles reversibly transformed to crystalline BiOCl (Fig. 4b4 and 5) because of the balance of electron flows in the HR-TEM apparatus and the O supply from the supporting BiOCl grains.

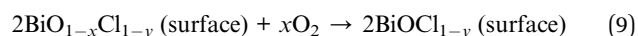
The presence of BiO_{1−x}Cl_{1−y} species in HCl aqueous solution (pH 2.0) and O₂ gas irradiated by UV-visible light was proposed by weaker intensity peaks at 162.2 and 157.0 eV at the lower binding energy side for 4f_{5/2} and 4f_{7/2} for Bi³⁺ states of BiOCl crystallites in XPS (Fig. 2c) and reduced *N*(Bi–O) and *N*(Bi–Cl) values (Table 1c) given by Bi L₃-edge EXAFS (Fig. 3c). No peaks corresponding to Bi⁰ and no metallic Bi–Bi bonds were detected in XPS and EXAFS, respectively.

4.3.4 Reaction steps. The converged photocurrent (118 μA, Fig. 5A) of the PFC at pH 2.0 corresponds to 1.8 mmol e[−] h^{−1} g_{BiOCl}^{−1}, which is ten times faster than the reaction rate of the black solvo-BiO_{1−x}Cl with O₂: *k* × 0.206 mmol (initial O₂ amount)/0.135 g_{BiOCl} = 0.18 mmol O₂ h^{−1} g_{BiOCl}^{−1} based on the fitting for 26 h, but is of the same order as the initial reaction rate *k'* during the first 20 min (2.1 mmol O₂ h^{−1} g_{BiOCl}^{−1}). The initial higher rate suggests that the reaction with O₂ first occurs at surface BiO_{1−x}Cl sites (or BiO_{1−x}Cl_{1−y} in HCl aqueous solution), rather than at bulk sites. The *k* value for 26 h was almost reproduced for solvo- and aqua-BiOCl (1.37 *versus* 0.0939 h^{−1}; Fig. 5C and C'), but the initial fast reaction at surface BiO_{1−x}Cl sites was difficult to follow for aqua-BiOCl due to the lower dispersion (larger mean particle size, see section 3.1.1, Fig. 1D and F).

On the basis of these results, a mechanism for photocatalysis by BiOCl has been proposed. In the PFC, a part of BiOCl on the photocathode immersed in HCl at a pH of 2.0–4.0 is thought to be photoreduced to BiO_{1−x}Cl_{1−y} (Scheme 3d) in a manner similar to that described in eqn (4):



Reaction (4) was observed as a CV peak at −0.39 V in an O₂ atmosphere, but only in the dark (Fig. 6b). The reaction with O₂ at the BiO_{1−x}Cl_{1−y} surface sites irradiated by UV-visible light (2.1 mmol O₂ h^{−1} g_{cat}^{−1}, Fig. 5C) follows eqn (9):



Summing up eqn (8) and (9), eqn (10) is obtained:



in which the partial dissolution of Cl was neglected because it was not related to the photoconversion of H₂O and O₂. The total current generated in Fig. 5A (pH 2.0) corresponds to 9.7 μmol e[−], whereas the quantity of the BiOCl mounted on the cathode was 9.6 μmol. Because the oxygen vacancy (*x*) in BiO_{1−x}Cl irradiated by UV-visible light was estimated to be 2.3% (Fig. 5C), the cathode reaction could be catalytic.

Suggested active species for the catalysis using BiOCl-based photocatalysts are summarized in Table 4. Due to the exposure to UV and/or visible light, black/gray BiO_{1−x}Cl was suggested to be the active species for dyes and 2-naphthol degradation.^{35,58,60} The Cl dissolution *via* the reaction of [•]Cl and electron was also reported to form BiOCl_{1−x}(OH)_{*x*}.³⁴ On the other hand, metallic Bi nanoparticles were suggested on the BiOCl or BiO_{1−x}Cl surface using a reducing agent, *e.g.* oxalate and ethanol effective for dyes, acetophenone, and *p*-chlorobenzaldehyde degradation.^{10,63} Furthermore, the reactivity of O-defects to form [•]O₂[−] and O₂^{2−} was proposed over (001) and (010) surfaces of BiO_{1−x}Cl, respectively, for the O₂ reduction based on DFT calculations.⁷¹

In this study, *in situ* spectroscopic monitoring of BiOCl during photocatalysis was performed for the first time by Bi L₃-

Table 4 Suggested active species using BiOCl and the derivatives as photocatalysts

Substrate	Medium	Type of light	Catalyst	Suggested active species	Ref.
Rhodamine B	Water & air	UV (254 nm)	(001)-preferred BiOCl	BiOCl	60
Rhodamine B	Water & air	Vis (>420 nm)	(001)-preferred BiOCl	BiOCl	60
Methyl orange	Dil. HCl aq & N ₂	High P Hg	BiOCl	BiOCl _{1-x} (OH) _x	34
Methyl orange	Dil. HCl aq & air	High P Hg	BiOCl	BiOCl _{1-x} (OH) _x	34
Phenol	Water & air	High P Hg	BiOCl	BiOCl _{1-x} (OH) _x	34
Rhodamine B	Water & air	High P Xe (>400 nm)	BiOCl under UV in Ar	BiO _{1-x} Cl	35
2-Naphthol degrad.	Water & air	Vis	(010)-preferred BiOCl	BiO _{1-x} Cl	60
Methylene blue	Water & air	W-halogen (>420 nm)	UV-reduced BiOCl	BiO _{1-x} Cl	58
Methyl orange	Water & air	Wideband	C ₂ O ₄ ²⁻ -reduced BiOCl	Bi ⁰ -BiOCl	10
Rhodamine B	Water & air	Vis	EtOH/HCl-reduced BiOCl	Bi ⁰ -BiO _{1-x} Cl	63
Methyl blue	Water & air	Vis	EtOH/HCl-reduced BiOCl	Bi ⁰ -BiO _{1-x} Cl	63
Eosin B	Water & air	Vis	EtOH/HCl-reduced BiOCl	Bi ⁰ -BiO _{1-x} Cl	63
Coomassie brilliant blue	Water & air	Vis	EtOH/HCl-reduced BiOCl	Bi ⁰ -BiO _{1-x} Cl	63
Acetophenone	Water & air	Vis	EtOH/HCl-reduced BiOCl	Bi ⁰ -BiO _{1-x} Cl	63
p-Chlorobenzaldehyde	Water & air	Vis	EtOH/HCl-reduced BiOCl	Bi ⁰ -BiO _{1-x} Cl	63
Rhodamine B	Water & air	UV (365 nm)	Ultrathin BiOCl	Bi-defect	72
Rhodamine B	Water & air	Xe (>420 nm)	Ultrathin BiOCl	Bi-defect	72
O ₂ reduction	—	(DFT)	(001) face	O-defect to form [•] O ₂ ⁻	71
O ₂ reduction	—	(DFT)	(010) face	O-defect to form O ₂ ²⁻	71

edge EXAFS (Fig. 3c). No special reducing agent^{10,63} was used in this study. Thus, active species BiO_{1-x}Cl_{1-y} (Scheme 3d) is proposed based on the XPS (Fig. 2c), EXAFS (Fig. 3c), and reactivity test with O₂ (Fig. 5C) being consistent with the suggested active structure in ref. 34, 35, 60, and 58 and the reaction route *via* eqn (9) is in accordance with ref. 71.

In addition to plausible incorporation as active sites in eqn (9), the O-deficient state of BiO_{1-x}Cl_(1-y) is slightly lower than that of the CB of BiOCl. Consequently, it can effectively trap photoexcited electrons^{59,73} and contribute to the photocatalysis *via* transfer of the trapped electrons to O₂ molecules in a similar manner to that observed for dye photodecomposition in the presence of O₂ (ref. 35, 58 and 73) and as predicted by DFT calculations for the (001) surface.⁷¹

4.4 Energetic efficiency of the PFC

The quantum efficiency of the PFC was evaluated on the basis of the absorption (6.9%) by the photocatalyst of the incident light (1.7×10^{17} photons per s) that the photocatalyst layers were exposed to and the short circuit current (92.4 μ A to 5.7×10^{14} electrons per s; Fig. 5E). The overall efficiency of the cell current per absorbed light was 0.024 and is considered as the product of the efficiencies of the anode (TiO₂) and the cathode (BiOCl). If a similar efficiency is assumed for electron generation at the CB of the anode and hole generation at the VB of the cathode, then the efficiencies of the anode and cathode were each approximately 0.16 ($0.16 \times 0.16 = \sim 0.024$). Practically, as the absorbance at the photocatalyst film was low (6.9%), the true overall efficiency was lower (0.0017), that may be divided into the contribution of anode and cathode: $0.041 \times 0.041 = 0.0017$.

Next, the contribution of the entropy of mixing (ΔS_{mix}) was considered for an equivalent amount of N₂ and O₂ supplied to the photoanode and photocathode, respectively, in comparison to the concentration cells.⁷⁴ When the maximum power was

produced by the PFCs comprised of TiO₂ and solvo-BiOCl (Fig. 5D) or aqua-BiOCl at pH 2.0 (Fig. 5E), the power generation efficiencies were 10.5 μ W (1.01 V \times 10.5 μ A) and 21.1 μ W (1.15 V \times 18.3 μ A), respectively, *versus* the energy generated because of mixing of N₂ and O₂ ($T\Delta S_{\text{mix}}$) per second:

$$T\Delta S_{\text{mix}} = -RT(n_{\text{N}_2} \ln x_{\text{N}_2} + n_{\text{O}_2} \ln x_{\text{O}_2}) \\ = -8.31 \times 290 \times 2 \times \frac{10.5 \times 10^{-6}}{4 \times 9.65 \times 10^4} \ln \frac{1}{2} = 0.091 \mu\text{W}, \quad (11)$$

and

$$T\Delta S_{\text{mix}} = -8.31 \times 290 \times 2 \times \frac{18.3 \times 10^{-6}}{4 \times 9.65 \times 10^4} \ln \frac{1}{2} = 0.16 \mu\text{W}, \quad (12)$$

respectively. Thus, the contribution of the entropy of mixing of the feed gases was negligible, and the light energy for band gap excitation at both the anode and cathode exclusively generated power up to 21.1 μ W (Table 2B). The electromotive force of the PFC can thus be explained on the basis of the energy diagram in Scheme 1, including the equilibrium charge separation at the anode and cathode following irradiation, rather than the simple difference in the concentrations of O₂ and the Gibbs free energies for the O₂ fractions at the anode and cathode for the concentration of the cells.⁷⁴

5 Conclusions

A PFC comprising two photocatalysts (TiO₂ and BiOCl) was demonstrated to achieve V_{OC} values of 1.69–1.76 V on the basis of the difference in the CB minimum of TiO₂ and the VB maximum of BiOCl, which are larger than those for PECs, dye-sensitized SCs, and a PFC comprising TiO₂ and Ag–TiO₂.⁷ The larger particle size (mean 115 nm) of aqua-BiOCl was advantageous by facilitating electron transfer from particle to particle,

whereas the smaller particle size (mean 24 nm) of solvo-BiOCl was advantageous for suppressing charge recombination within the nanoparticles. The maximum power was 21.1 μW for the PFC comprised of TiO_2 and aqua-BiOCl, and the energetic efficiency per absorbed light at the photocatalysts was estimated as the product (0.024) of electron generation at TiO_2 (0.16) and hole generation at BiOCl (0.16) for recombination *via* the external circuit.

A portion of the BiOCl nanoparticles was transformed into amorphous-like $\text{BiO}_{1-x}\text{Cl}$ nanoparticles because of irradiation with UV-visible light, and then reversibly transformed back in a vacuum (HR-TEM and Raman) or under Ar (UV-visible spectroscopy and XPS) when the light was turned off. These O-deficient nanoparticles were the origin of the black color appearance of the irradiated BiOCl. In addition, a BiOCl sample sufficiently irradiated with UV-visible light reacted with the quantity of O_2 gas corresponding to the dissolved amount in the HCl solution in the PFC at a rate ($2.1 \text{ mmol O}_2 \text{ h}^{-1} \text{ g}_{\text{BiOCl}}^{-1}$) during the initial 20 min that was on the same order as the photocurrent of the PFC ($1.8 \text{ mmol e}^{-} \text{ h}^{-1} \text{ g}_{\text{BiOCl}}^{-1}$), suggesting that surface O-deficient $\text{BiO}_{1-x}\text{Cl}$ sites may contribute to the photocatalytic O_2 reduction in the PFC. The reduced Bi sites observed for BiOCl in Ar irradiated by UV-visible light was also detected but further lost a part of Cl as $\text{BiO}_{1-x}\text{Cl}_{1-y}$ in HCl aqueous solution (pH 2.0) in O_2 irradiated by UV-visible light by Bi 4f XPS and Bi $L_{3\text{-edge}}$ EXAFS. Again, the reaction of O-deficient $\text{BiO}_{1-x}\text{Cl}_{1-y}$ sites with O_2 and subsequent reaction with protons and electrons suggested a catalytic cycle for O_2 reduction in the PFC.

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References

- N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729–15735.
- Y. Izumi, *Coord. Chem. Rev.*, 2013, **257**, 171–186.
- J. R. Bolton, *Sol. Energy*, 1996, **57**, 37–50.
- M. Grätzel, *Nature*, 2001, **414**, 338–344.
- H. A. Gasteiger and N. M. Marković, *Science*, 2009, **324**, 48–49.
- K. S. Joya, Y. F. Joya, K. Ocakoglu and R. van de Krol, *Angew. Chem., Int. Ed.*, 2013, **52**, 10426–10437.
- Y. Ogura, S. Okamoto, T. Itoi, Y. Fujishima, Y. Yoshida and Y. Izumi, *Chem. Commun.*, 2014, **50**, 3067–3070.
- H. Cheng, B. Huang and Y. Dai, *Nanoscale*, 2014, **6**, 2009–2026.
- Y. Bessekhoud, D. Robert and J. V. Weber, *Catal. Today*, 2005, **101**, 315–321.
- S. Weng, B. Chen, L. Xie, Z. Zheng and P. Liu, *J. Mater. Chem. A*, 2013, **1**, 3068–3075.
- X. Chen and S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891–2959.
- N. Serpone, *J. Phys. Chem. B*, 2006, **110**, 24287–24293.
- K. L. Zhang, C. M. Liu, F. Q. Huang, C. Zheng and W. D. Wang, *Appl. Catal., B*, 2006, **68**, 125–129.
- M. S. Wrighton, *Acc. Chem. Res.*, 1979, **9**, 303–310.
- M. S. Wrighton, A. B. Ellis, P. T. Wolczanski, D. L. Morse, H. B. Abramson and D. S. Ginley, *J. Am. Chem. Soc.*, 1976, **98**, 2774–2779.
- Z. Li, L. Yu, Y. Liu and S. Sun, *Electrochim. Acta*, 2014, **129**, 379–388.
- G. W. Ho, K. J. Chua and D. R. Siow, *Chem. Eng. J.*, 2012, **181/182**, 661–666.
- K. Li, Y. Xu, Y. He, C. Yang, Y. Wang and J. Jia, *Environ. Sci. Technol.*, 2013, **47**, 3490–3497.
- P. Lianos, *J. Hazard. Mater.*, 2011, **185**, 575–590.
- B. D. Alexander, P. J. Kulesza, I. Rutkowska, R. Solarska and J. Augustynski, *J. Mater. Chem.*, 2008, **18**, 2298–2303.
- K. Ren, K. Y. X. Gan, T. J. Young, Z. M. Moutassem and L. Zhang, *Composites, Part B*, 2013, **52**, 292–302.
- K. Ren, C. A. McConnell, Y. X. Gan, A. A. Afjeh and L. Zhang, *Electrochim. Acta*, 2013, **109**, 162–167.
- J. Yang, D. Wang and C. Li, *Acc. Chem. Res.*, 2013, **46**, 1900–1909.
- C. Leygraf, M. Hendewerk and G. A. Somorjai, *J. Phys. Chem.*, 1982, **86**, 4484–4485.
- A. Berger, R. A. Segalman and J. Newman, *Energy Environ. Sci.*, 2014, **7**, 1468–1476.
- Z. Wang, R. R. Roberts, G. F. Naterer and K. S. Gabriel, *Int. J. Hydrogen Energy*, 2012, **37**, 16287–16301.
- R. C. Kainthla, B. Zelenay and J. O'M Bockris, *J. Electrochem. Soc.*, 1987, **134**, 841–845.
- K. Sayama, K. Mukasa, R. Abe, Y. Abe and H. Arakawa, *Chem. Commun.*, 2001, **35**, 2416–2417.
- K. Fujihara, T. Ohno and M. Matsumura, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 3705–3709.
- M. C. Hanna and A. J. Nozik, *J. Appl. Phys.*, 2006, **100**, 074510.
- M. Morikawa, Y. Ogura, N. Ahmed, S. Kawamura, G. Mikami, S. Okamoto and Y. Izumi, *Catal. Sci. Technol.*, 2014, **4**, 1644–1651.
- A. Heller, *Acc. Chem. Res.*, 1981, **14**, 154–162.
- Q. Chen, J. Li, X. Li, K. Huang, B. Zhou, W. Cai and W. Shangguan, *Environ. Sci. Technol.*, 2012, **46**, 11451–11458.
- F. Chen, H. Liu, S. Bagwasi, X. Shen and J. Zhang, *J. Photochem. Photobiol., A*, 2010, **215**, 76–80.
- L. Ye, K. Deng, F. Xu, L. Tian, T. Peng and L. Zan, *Phys. Chem. Chem. Phys.*, 2012, **14**, 82–85.
- N. Ahmed, Y. Shibata, T. Taniguchi and Y. Izumi, *J. Catal.*, 2011, **279**, 123–135.
- N. Ahmed, M. Morikawa and Y. Izumi, *Catal. Today*, 2012, **185**, 263–269.

- 38 F. Wooten, *Optical Properties of Solids*, Academic Press, New York, U. S. A., 1972, p. 142.
- 39 W. L. Huang and Q. Zhu, *Comput. Mater. Sci.*, 2008, **43**, 1101–1108.
- 40 X. Zhang, C. Fan, Y. Wang, Y. Wang, Z. Liang and P. Han, *Comput. Mater. Sci.*, 2013, **71**, 135–145.
- 41 J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomden, *Handbook of X-ray Photoelectron Spectroscopy*, ed. J. Chastain, Perkin-Elmer Co., Minnesota, U. S. A., 1992.
- 42 K. Oka, Y. Ogura and Y. Izumi, *J. Power Sources*, 2014, **258C**, 83–88.
- 43 S. Wada, K. Oka, K. Watanabe and Y. Izumi, *Front. Chem.*, 2013, **1**, 8.
- 44 Y. Izumi, H. Nagamori, F. Kiyotaki, D. Masih, T. Minato, E. Roisin, J.-P. Candy, H. Tanida and T. Uruga, *Anal. Chem.*, 2005, **77**, 6969–6975.
- 45 Y. Izumi and H. Nagamori, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1581–1587.
- 46 M. Morikawa, N. Ahmed, Y. Yoshida and Y. Izumi, *Appl. Catal., B*, 2014, **144**, 561–569.
- 47 Y. Yoshida, Y. Mitani, T. Itoi and Y. Izumi, *J. Catal.*, 2012, **287**, 190–202.
- 48 Y. Izumi, K. Konishi and H. Yoshitake, *Bull. Chem. Soc. Jpn.*, 2008, **81**, 1241–1249.
- 49 Y. Izumi, K. Konishi, D. Obaid, T. Miyajima and H. Yoshitake, *Anal. Chem.*, 2007, **79**, 6933–6930.
- 50 J. A. Bearden, *Rev. Mod. Phys.*, 1967, **29**, 78–124.
- 51 M. Vaarkamp, H. Linders and D. Koningsberger, *XDAP version 2.2.7*, XAFS Services International, Woudenberg, The Netherlands, 2006.
- 52 K. Oka, Y. Shibata, T. Itoi and Y. Izumi, *J. Phys. Chem. C*, 2010, **114**, 1260–1267.
- 53 Y. Izumi, T. Itoi, S. Peng, K. Oka and Y. Shibata, *J. Phys. Chem. C*, 2009, **113**, 6706–6718.
- 54 L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, **58**, 7565–7576.
- 55 P. Cucka and C. S. Barrett, *Acta Crystallogr.*, 1962, **15**, 865–872.
- 56 N. Jiang and J. C. H. Spence, *J. Phys.: Condens. Matter*, 2006, **18**, 8029–8036.
- 57 S. C. Nyburg, G. A. Ozin and J. T. Szymański, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1971, **27**, 2298–2304.
- 58 B. Sarwan, B. Pare and A. D. Acharya, *Mater. Sci. Semicond. Process.*, 2014, **25**, 89–97.
- 59 X. Zhang, T. Guo, X. Wang, Y. Wang, C. Fan and H. Zhang, *Appl. Catal., B*, 2014, **150/151**, 486–495.
- 60 S. Weng, J. Hu, M. Lu, X. Ye, Z. Pei, M. Huang, L. Xie, S. Lin and P. Liu, *Appl. Catal., B*, 2015, **163**, 205–213.
- 61 X. Zhang, X. B. Wang, L. W. Wang, W. K. Wang, L. L. Long, W. W. Li and H. Q. Yu, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7766–7772.
- 62 A. Y. Anderson, P. R. Barnes, J. R. Durrant and B. C. O'Regan, *J. Phys. Chem. C*, 2011, **115**, 2439–2447.
- 63 Y. Yu, C. Cao, H. Liu, P. Li, F. Wei, Y. Jiang and W. Song, *J. Mater. Chem. A*, 2014, **2**, 1677–1681.
- 64 X. Zhang, L. Zhao, C. Fan, Z. Liang and P. Han, *Comput. Mater. Sci.*, 2012, **61**, 180–184.
- 65 A. Imanishi, E. Tsuji and Y. Nakato, *J. Phys. Chem. C*, 2007, **111**, 2128–2132.
- 66 D. O. Scanlon, C. W. Dunnill, J. Buckeridge, S. A. Shevlin, A. J. Lodsdaile, S. M. Woodley, R. A. Catlow, M. J. Powell, R. G. Palgrave, I. P. Parkin, G. W. Watson, T. W. Keal, P. Sherwood and A. A. Sokol, *Nat. Mater.*, 2013, **12**, 798–801.
- 67 Y. Izumi and Y. Shibata, *Chem. Lett.*, 2009, **38**, 912–913.
- 68 E. W. Washburn, C. J. West and C. Hull, International critical tables of numerical data, physics, chemistry and technology, Volume VI, National Academy of Sciences, U. S. A., International Council of Scientific Unions., National Research Council, U. S. A., 1929, p. 242.
- 69 C. C. Wong and W. Chu, *Chemosphere*, 2003, **50**, 981–987.
- 70 K. Bouzidi, M. Chegaar and A. Bouhemadou, *Sol. Energy Mater. Sol. Cells*, 2007, **91**, 1647–1651.
- 71 K. Zhao, L. Zhang, J. Wang, Q. Li, W. He and J. J. Yin, *J. Am. Chem. Soc.*, 2013, **135**, 15750–15753.
- 72 M. Guan, C. Xiao, J. Zhang, S. Fan, R. An, Q. Cheng, J. Xie, M. Zhou, B. Ye and Y. Xie, *J. Am. Chem. Soc.*, 2013, **135**, 10411–10417.
- 73 B. Pare, B. Sarwan and S. B. Jonnalagadda, *J. Mol. Struct.*, 2012, **1007**, 196–202.
- 74 M. Gellender, *J. Renewable Sustainable Energy*, 2010, **2**, 023101.