† Electronic supplementary information

Photofuel cell comprising titanium oxide and bismuth oxychloride (BiO_{1-x}Cl_{1-y}) photocatalysts for use of acidic water as a fuel[†]

Yukiko Fujishima,^{a,b,#} Seiji Okamoto,^{a,#} Mao Yoshiba,^{a,#} Takaomi Itoi,^c Shogo Kawamura,^a Yusuke Yoshida,^a Yuta Ogura,^a and Yasuo Izumi^{a,*}

^a Department of Chemistry, Graduate School of Science, Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan.

^b Department of Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 163-8601, Japan.

^c Department of Mechanical Engineering, Graduate School of Engineering, Chiba University, Yayoi 1-33, Inage-ku, Chiba 263-8522, Japan.

* *E-mail address*: yizumi@faculty.chiba-u.jp, *FAX*: +81-43-290-2783, *Phone*: +81-43-290-3696.

These authors contributed equally to this paper.

Derivation of Equation 7

The kinetic model for the photocurrents in the PFCs was formulated on the basis of the principle shown in Scheme 1. The equilibrium constants K_a and K_c were defined in the main

text for the separation of electrons and holes in anodic TiO_2 and cathodic BiOCl, respectively, which are irradiated by light. The concentrations of O_2 , H⁺, and H₂O in the electrolyte solution and those of Ti^{4+} , Ti^{3+} , O^{2-} , O^- , Bi^{3+} , Bi^0 , Cl^- , and Cl^0 in the photocatalysts, with the subscript "a" (anode) or "c" (cathode), are represented by $[O_2]$, $[H^+]$, $[H_2O]$, $[Ti^{4+}]$, $[Ti^{3+}]$, $[O^{2-}]$, $[O^-]$, $[Bi^{3+}]$, $[Bi^0]$, $[Cl^-]$, and $[Cl^0]$, respectively. The hole concentrations at the VBs of TiO₂ and BiOCl are denoted by $[O^-]$ and $[Cl^-]$, and the electron concentrations at the CBs of TiO₂ and BiOCl are denoted by $[Ti^{3+}]_a$ and $[Bi^0]_c$, respectively. On the basis of the reported band population diagram versus energy, the predominant charge separation due to the electron transition from Cl 3p (and O 2p) to Bi 6p was assumed to occur following irradiation with UV–visible light.

$$K_{a} = \frac{\left[\operatorname{Ti}^{3+}\right]_{a}\left[\operatorname{O}^{-}\right]_{a}}{\left[\operatorname{Ti}^{4+}\right]_{a}\left[\operatorname{O}^{2-}\right]_{a}} \qquad (S1)$$
$$K_{c} = \frac{\left[\operatorname{Bi}^{0}\right]_{c}\left[\operatorname{Cl}^{0}\right]_{c}^{3}}{\left[\operatorname{Bi}^{3+}\right]_{c}\left[\operatorname{Cl}^{-}\right]_{c}^{3}} \qquad (S2)$$

Nitrogen gas was bubbled through the acidic TiO_2 solution to purge O_2 . The reaction rate at the anode is formally proportional to the fourth power of $[O^-]_a$ because it is a four-electron oxidation (Scheme 1):

$$r_{\rm ox} = k_{\rm ox} \left(\left[\mathrm{H}_2 \mathrm{O} \right]_{\mathrm{a}} \right)^2 \left(\mathrm{O}^{-} \right]_{\mathrm{a}} \right)^4.$$
 (S3)

For the O_2 photoreduction equilibrium, the forward and reverse reaction rates were formally proportional to the four-thirds powers of $[Bi^0]_c$ and the fourth power of $[O^-]_c$, respectively, because they are also four-electron reactions (Scheme 1):

$$K_{\rm red} = \frac{\left(\left[{\rm H}_2 {\rm O} \right]_{\rm c} \right)^2 \left(\left[{\rm Cl}^0 \right]_{\rm c} \right)^4}{\left[{\rm O}_2 \right]_{\rm c} \left({\rm H}^+ \right]_{\rm c} \right)^4 \left(\left[{\rm Bi}^0 \right]_{\rm c} \right)^{\frac{4}{7}}}.$$
 (S4)

The net electron flow rate (photocurrent) is the difference in the forward electron flow from TiO_2 to BiOCl via the external circuit and the reverse electron flow from BiOCl to TiO_2 via the external circuit.

Photocurrent
$$i = k \Big[\operatorname{Ti}^{3+} \Big]_{a} \Big[\operatorname{Cl}^{0} \Big]_{c}^{-} - k' \Big[\operatorname{Bi}^{0} \Big]_{c}^{\frac{1}{3}} \Big[\operatorname{O}^{-} \Big]_{a}^{-} = k \frac{K_{a}'(k_{ox}')^{\frac{1}{4}}(K_{c}')^{\frac{1}{6}}(K_{red}')^{\frac{1}{8}}}{(r_{ox})^{\frac{1}{4}}} ([\operatorname{O}_{2}]_{c})^{\frac{1}{9}} ([\operatorname{H}^{+}]_{c})^{\frac{1}{9}} - k' \frac{(r_{ox})^{\frac{1}{4}}(K_{c}')^{\frac{1}{6}}}{(k_{ox}')^{\frac{1}{4}}(K_{red}')^{\frac{1}{8}}} \frac{1}{([\operatorname{O}_{2}]_{c})^{\frac{1}{8}}} ([\operatorname{H}^{+}]_{c})^{\frac{1}{9}} .$$
(S5)

Thus, eq. 7 was obtained. Here, the equilibrium constants with the prime symbol are as follows: $K_a' = K_a \left[\text{Ti}^{4+} \right]_a \left[\text{O}^{2-} \right]_a$, $K_c' = K_c \left[\text{Bi}^{3+} \right]_c \left[\text{Cl}^{-} \right]_c^3$, $K_{\text{red}}' = K_{\text{red}} / \left([\text{H}_2 \text{O}]_c \right)^2$, and $k_{\text{ox}}' = k_{\text{ox}} \left([\text{H}_2 \text{O}]_a \right)^2$.

The solubility of O_2 in water is insensitive to the pH value: 4.063 and 4.060 mg per 100 mL of water (1.27 mmol L⁻¹) at pH values of 2.0 and 4.0, respectively. The H⁺ concentrations (10 mmol L⁻¹) were greater than that of the dissolved O_2 at pH 2.0 for the reaction $O_2 + 4H^+ + 4e^-$, whereas the H⁺ concentrations (0.1–1.0 mmol L⁻¹) were lower than that of dissolved O_2 at pH 3.0–4.0 for the reaction. The experimental dependence of the photocurrents on pH (Fig. 5B) was consistent with the kinetic model (eq. 6) in the pH range from 2 and 4.



Fig. S1 Components of the PFC comprising TiO_2 and BiOCl photocatalysts.