

1 **Electronic Supplementary Information**

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3 **Hydrogenation of oxalic acid using light-assisted water electrolysis**
4 **for the production of an alcoholic compound**

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1 Experimental section

2 Materials

3 The WO_3 and Ga_2O_3 powder were commercially supplied (Kanto Chemical Co., Japan), and
4 JRC-TIO-7 and 8 (Japan Reference Catalyst of TiO_2 , anatase-type TiO_2 nanoparticles) were
5 used as TiO_2 samples. The BiVO_4 sample was synthesized via a homogenous precipitation
6 method.¹ Aqueous equivalent molar $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 solutions (0.8 mol/l)
7 containing HNO_3 (1.84 mol/l) were prepared separately, then two 100 cm^3 solutions were
8 mixed and 15 g of urea was added. The mixed solution was stirred at 363 K for 8 h. The
9 BiVO_4 precipitation formed by the hydrolysis was washed using water, filtered, and dried *in*
10 *vacuo* at 25°C.

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12 Preparation of electrodes

13 The photoanodes were prepared by using a squeegee method. A slurry of Ga_2O_3 , BiVO_4 and
14 WO_3 (sample: 0.1 g, water: 0.5 ml, acetylacetone: 0.03 ml, Toriton-X: 0.03 ml) was coated
15 onto a conductive glass (F-doped SnO_2 , 10 Ω/cm^2 , 2×2 cm), and the electrodes were calcined
16 at 450 °C for 4 h under air. For the TiO_2 cathodes, Ti foils (2×2 cm) were used after
17 calcination at 450 °C for 0.5 h under air flow. A suspension of TiO_2 samples (10 mg) in
18 methanol (0.2 ml) was applied to Ti foil, and then, the sample-modified Ti foils were calcined
19 at 500°C for 5 h or 450°C for 0.5 h under flowing air.

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21 Characterization

22 XRD measurements were conducted using SmartLab (Rigaku) with $\text{Cu-K}\alpha$ radiation ($\lambda =$
23 1.54059 Å) at 45 kV and 200 mA. UV-visible spectra were recorded on a V-670 spectrometer
24 (JASCO). The diffuse reflection spectra were converted into reflectance spectra using the
25 Kubelka-Munk function.

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1 Electrochemical measurement

2 All of the chemicals used for electrochemical experiments were purchased from Wako
3 Pure Chemical Industries, Ltd. The electrochemical experiments were conducted by
4 employing a two or three-electrode system connected to a VersaSTAT4 potentiostat
5 (AMETEC, Princeton Applied Research). In the two-electrode system, the prepared TiO₂
6 cathode (JRC-TIO-7 or JRC-TIO-8) and oxide photoanodes, as well as a two-compartment
7 electrochemical cell (75 ml volume for each), were used. Electrolyte aqueous solutions
8 (cathode: 40 ml of 0.16 or 0.03 M **OX** and 0.16 or 0.2 M Na₂SO₄, anode: 0.16 or 0.2 M
9 Na₂SO₄) were introduced into the cells. A piece of proton conducting membrane (Nafion®,
10 NRE-212, Sigma-Aldrich) was used as a separator, and each electrode was placed inside the
11 cathode and anode cell. After the Teflon caps were tightly closed, Ar gas was bubbled both in
12 cathode and anode cells for 30 min to purge the air from the cells. A 300 W Xe lamp with a
13 cut filter was applied as a light source. Bias between the working electrode and counter
14 electrode was applied from 0 V to 2.5 V at 25°C or 50°C in the dark or under light irradiation
15 ($\lambda > 200, 300$ and 400 nm) to photoanodes in the anode cell with light shielding of the
16 cathode cell. Chronoamperometric electro-reduction of **OX** to GO and **GC** was conducted by
17 employing the TiO₂ cathode (JRC-TIO-7) and a Ag/AgCl reference electrode (RE-1B, BAS)
18 in **OX** solution (pH 1.0, 40 ml, 0.03 M **OX**, 0.2 M Na₂SO₄) and the WO₃ photoanode in
19 Na₂SO₄ solution (pH 5.6, 40 ml, 0.2 M) while applying an external bias of 1.0 or 1.5 V
20 between the cathode and anode at 50°C for 2 h under irradiation of UV-visible light with $\lambda >$
21 300 nm or visible light with $\lambda > 400$ nm, or in the dark. The potential difference between the
22 TiO₂ cathode and reference electrode was measured using a multimeter (CDM-2000D,
23 CUSTOM Co.) to determine the cathode potential during the reaction as described in Fig. S6.
24 The reaction solution (50 μ l) was collected from the cathode cell and analyzed by using the
25 HPLC. The gas products were measured using gas chromatograph (GC-8A, Shimadzu).
26 In the three-electrode system, the prepared TiO₂ cathode (JRC-TIO-7), a coiled Pt wire

1 (230×0.5 mm, BAS) and an Ag/AgCl electrode were used as a working, counter and reference
2 electrode, respectively. The electrochemical reduction of **OX** at a constant potential, i.e.,
3 chronoamperometry (CA), was performed in the same cell as that in the two-electrode system.
4 Electrolyte aqueous solutions (cathode: 40 ml of 0.16 or 0.03 M **OX** and 0.16 or 0.2 M
5 Na₂SO₄, anode: 0.16 or 0.2 M Na₂SO₄) were introduced into the cells. The working/reference
6 and counter electrodes were placed inside the cathode and anode cell, respectively. The pH
7 value of the electrolyte solution in the cells was adjusted by adding H₂SO₄ or NaOH solution.
8 After the Teflon caps were tightly closed, Ar gas was bubbled both in cathode and anode cells
9 for 30 min to purge the air from the cells. **OX** electrochemical reductions were conducted by
10 controlling the working electrode potential at 50°C. Potentials impressed on the working
11 electrode were measured against a reference electrode and converted to the RHE reference
12 scale using the following equation: E (versus RHE) = E (versus Ag/AgCl) + 0.199 V + 0.059
13 V × pH. The reaction solution was analyzed using the same procedure as for the two-electrode
14 system. Chemical activators were not used in this study because the TiO₂ cathode stably
15 worked during the reactions. We demonstrated **OX** reduction experiments both under light
16 irradiation and in the dark to elucidate effects of light irradiation on the applied bias using the
17 identical TiO₂ catalyst, TIO-7, except for the experimental results shown in Fig. 2.

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20 **Definitions of Faradaic efficiency**

21 Faradaic efficiencies in electro-reduction experiments were defined using the following
22 equation:

$$23 \text{ Faradaic efficiency (\%)} = \frac{m_{\text{products}} \times n \times F}{Q} \times 100,$$

24 where m_{products} is the moles of the reduction products; n represents the number of electrons
25 required for the formation of GO and **GC** from **OX** ($n = 2$ and 4 for the formation of GO and
26 **GC**, respectively); F is the Faradaic constant (96485 C/mol of electrons); Q is the total charge

1 in Coulombs passed across the electrode during the electrolysis.

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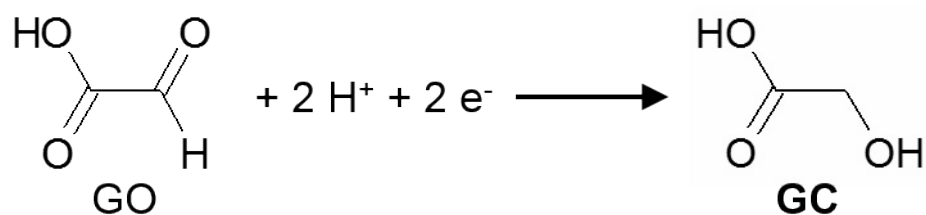
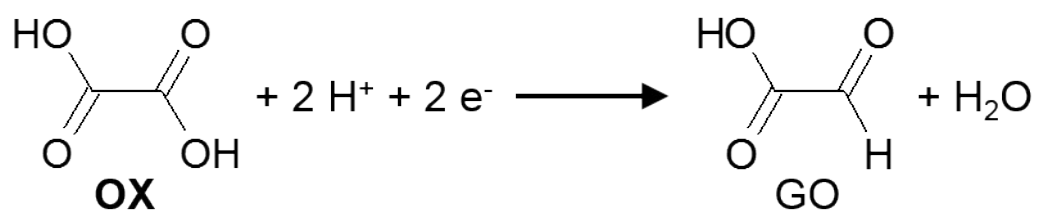
3 **References**

4 1. J. Q. Yu and A. Kudo, *Adv. Funct. Mater.*, 2006, **16**, 2163-2169.

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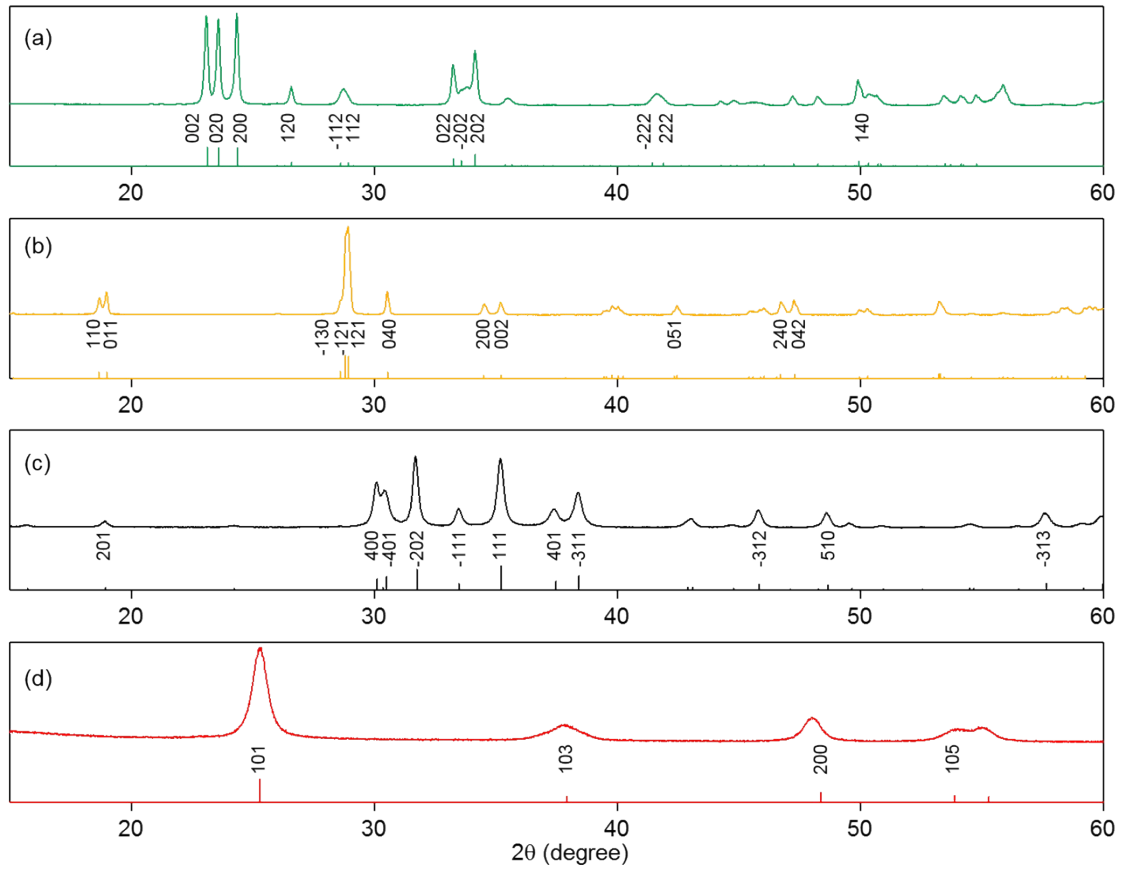
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Scheme S1 Consecutive electroreduction of **OX** to **GC**.

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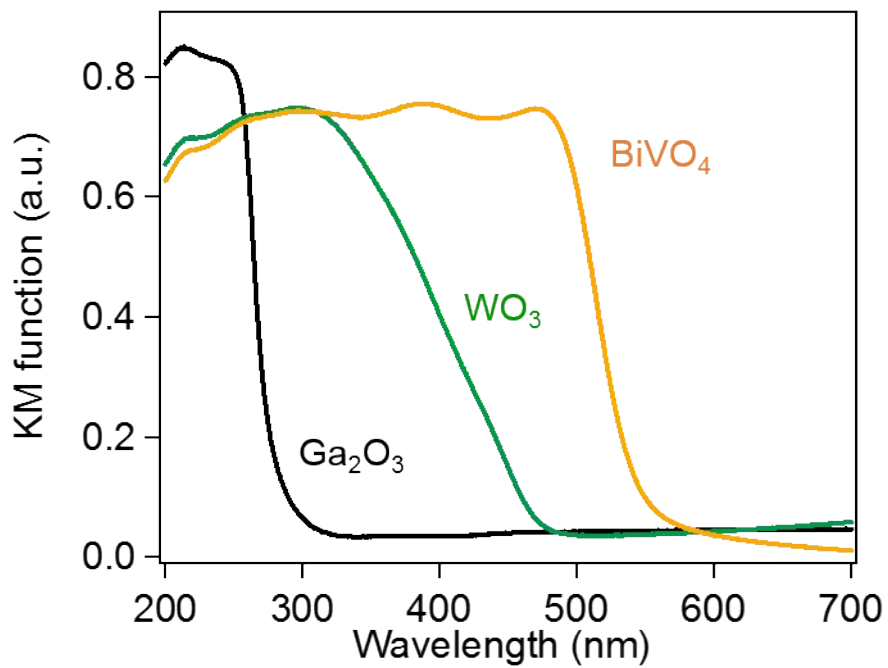


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4 **Fig. S1** XRD patterns of (a) WO₃, (b) BiVO₄, (c) Ga₂O₃, and (d) TiO₂ (TIO-8), which are
5 used as catalysts for **OX** reduction and water oxidation. Solid vertical lines indicate
6 diffraction angles from (a) an anatase-type TiO₂ (JCPDF card file 01-0562), (b) a monoclinic
7 WO₃ (JCPDF card file 43-1035), (c) a monoclinic BiVO₄ (JCPDF card file 14-0688), (d) a
8 monoclinic β-Ga₂O₃ (JCPDF card file 87-1901).

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2 **Fig. S2** Photoabsorption spectra of Ga₂O₃ (black), WO₃ (green) and BiVO₄ (orange).

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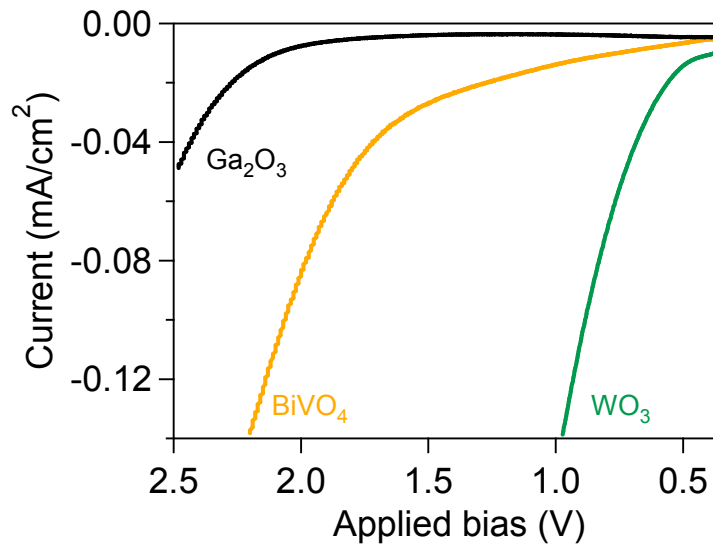
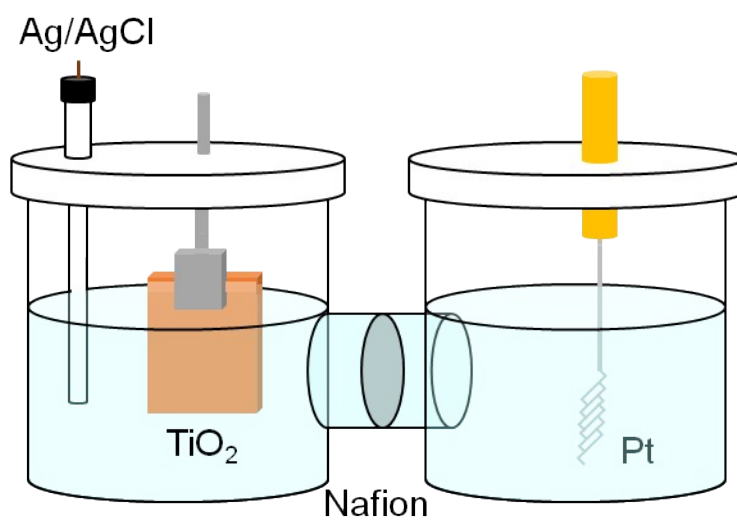


Fig. S3 Current-voltage curves of electro-reduction of **OX** using a two-electrode system comprising a TiO₂ (JRC-TIO-8) cathode in solution containing **OX** (0.16 M) and a Na₂SO₄ solution (pH 1.2, 40 ml, 0.16 M) and Ga₂O₃, BiVO₄ and WO₃ photoanodes in a Na₂SO₄ solution (pH 5.8, 40 ml, 0.16 M) under irradiation of UV-visible light ($\lambda > 200$ nm) at 25 °C.

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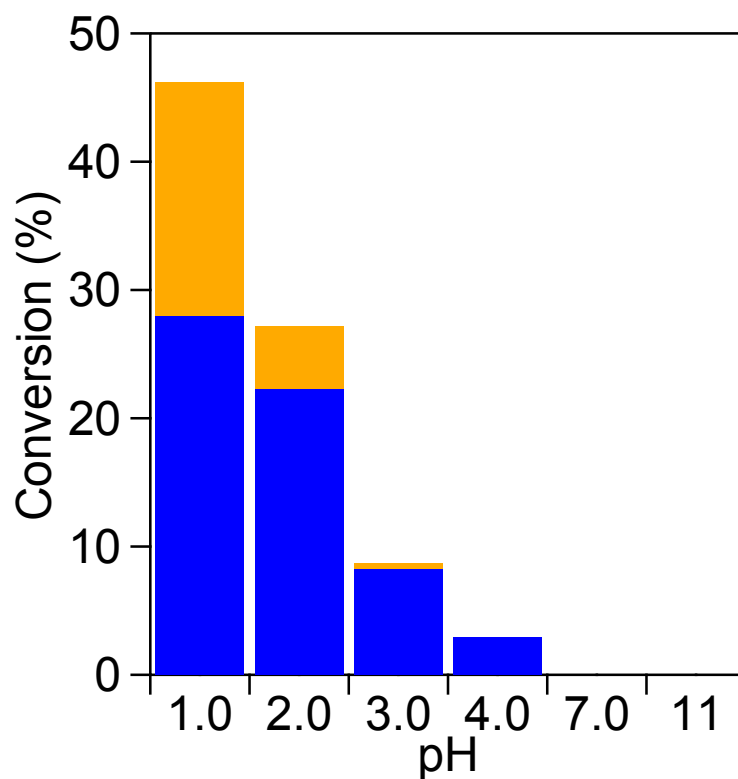


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4 **Fig. S4** The three-electrode electrochemical system comprising a TiO₂ cathode, Pt anode and
5 an Ag/AgCl reference electrode.

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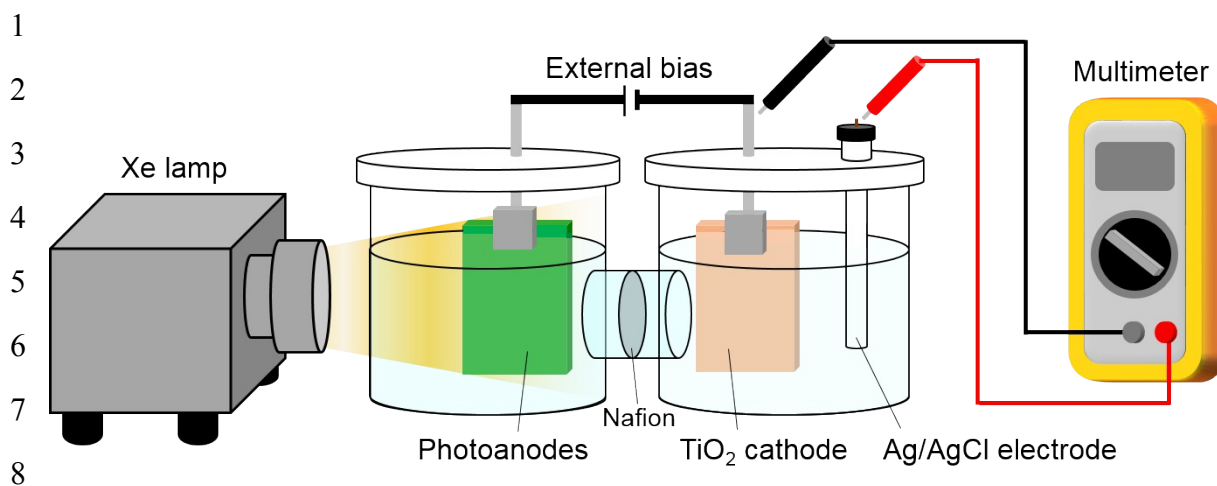


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3 **Fig. S5** Influence of pH value on distribution of GO (orange) and GC (blue) in electro-
4 reduction of **OX** using the three-electrode system comprising a TiO₂ cathode (JRC-TIO-7), a
5 Pt wire as the counter anode and Ag/AgCl as the reference electrode at 50°C for 2 h. The
6 cathode and anode solution contained 0.2 M Na₂SO₄ and the cathode solution contained 0.03
7 M **OX**, the pH of which was controlled by using an H₂SO₄ or NaOH solution.

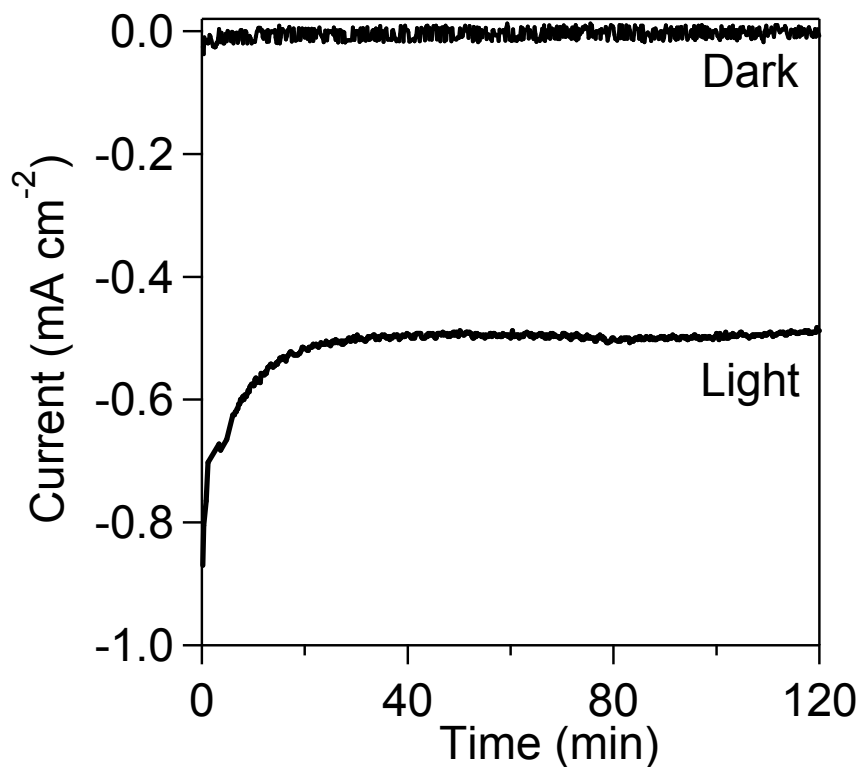
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9 **Fig. S6** Illustration of the two-electrode electrochemical system employing a TiO₂ cathode, a
10 photoanode and a Ag/AgCl reference electrode. External bias was applied between the TiO₂
11 cathode and photoanodes under light irradiation from a Xe lamp or in the dark. The Potential
12 of the TiO₂ cathode referred to that of the Ag/AgCl reference electrode during the reaction
13 was measured using a multimeter.

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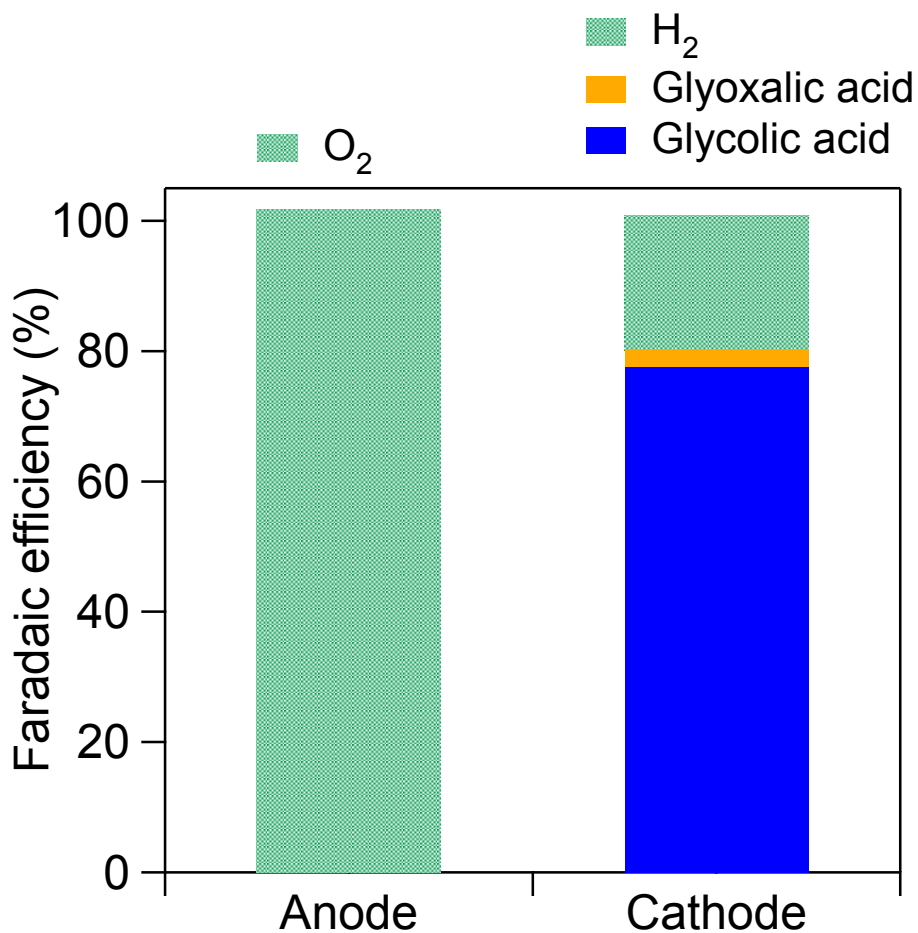
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2 **Fig. S7** Time courses of reductive current in electro-reduction of **OX** while applying an
3 external bias of 1.5 V under the irradiation of UV-visible light ($\lambda > 300$ nm) or in the dark.
4 The experiment was conducted using a two-electrode system comprising a TiO₂ cathode in
5 **OX** solution (pH 1.0, 40 ml, 0.03 M of **OX**, 0.2 M Na₂SO₄) and a WO₃ photoanode in
6 Na₂SO₄ solution (pH 5.6, 40 ml, 0.2 M) at 50°C.

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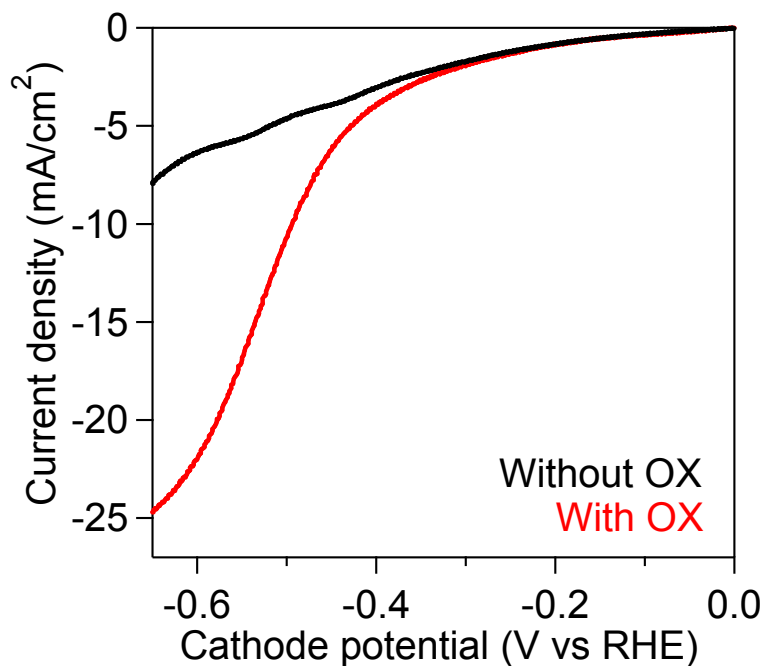


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2 **Fig. S8** Faradaic efficiencies based on the amount of GO, GC and H₂ formed in the cathode
 3 cell and O₂ formed by water oxidation in the anode cell when applying a bias of 1.5 V under
 4 the irradiation of UV-visible light ($\lambda > 300$ nm). The experiment was conducted using a two-
 5 electrode system comprising a TiO₂ cathode in **OX** solution (pH 1.0, 40 ml, 0.03 M of **OX**,
 6 0.2 M Na₂SO₄) and a WO₃ photoanode in Na₂SO₄ solution (pH 5.6, 40 ml, 0.2 M) at 50°C for
 7 2 h.

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Fig. S9 Cyclic voltammogram curves measured using a three-electrode system employing a TiO₂ cathode, Pt anode and Ag/AgCl reference electrode in the dark. Red and black curves present reduction currents recorded in electrolyte solutions with and without the **OX** substrate, respectively. The electrochemical experiments were conducted in **OX** solution (pH 1.0, 80 ml, 0.03 M of **OX**, 0.2 M Na₂SO₄) or blank Na₂SO₄ solution (pH 1.0, 80 ml, 0.2 M) at 50°C.

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Table S1 Yields and reaction rates for **OX** reduction reported in this work and others.

Report	Yields (%)	Reaction rate ($\mu\text{mol h}^{-1}$)
This work (Two-electrode system) ^a	2.2	16
Previous work ref. 32	31	230
(Three-electrode system) ^b		
Ref. 12	19	99-100
Ref. 13	5.0-76	18-2900
Ref. 14	41-95	8.5-20
Ref. 15	34-100	14-42

2 a: The experiment was demonstrated when applying a bias of 1.5 V under irradiation of UV-
3 vis light.

4 b: The experiment was demonstrated using the highly active porous TiO₂ catalyst as a cathode,
5 Pt anode and Ag/AgCl reference electrode in the dark. The applied potential at the cathode
6 was -0.7 V vs RHE.

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