

Electronic Supplementary Information

A visible-light-induced photoelectrochemical water splitting system featuring organo-photocathode along with tungsten oxide photoanode

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Experimental details

Chemicals

Commercially available C₆₀ of sublimated grade (>99.5%, Tokyo Chemical Industry (TCI)) was used as received. ZnPc (TCI) was purified by sublimation prior to use, as described elsewhere [1,2]. Other reagents were of extra-pure grade. ITO-coated glass plates (sheet resistance, 8 $\Omega\cdot\text{cm}^{-2}$; transmittance, >85%; ITO thickness, 174 nm) and FTO-coated glass plates (sheet resistance, 11 $\Omega\cdot\text{cm}^{-2}$; FTO thickness, 300 nm) were purchased from Asahi Glass Co., Ltd and Peccell Technologies, Inc., respectively.

Measurements

The absorption spectrum was measured using a PerkinElmer Lambda-25 spectrophotometer. The resulting absorption spectra of ZnPc (α -phase) [3-5] and C₆₀ [6] were identical to those reported previously, and their absorption coefficients were used to determine the thicknesses of the prepared film. Typically, the thicknesses of ZnPc and C₆₀ in the bilayer employed were estimated as 75 nm and 125 nm, respectively.

Gaseous products were analyzed using a gas chromatograph (GL Sciences, GC-3200) equipped with a thermal conductivity detector and a 5-Å molecular sieve column. Argon was used as the carrier gas.

The surface of WO₃ was observed through a scanning electron microscope (FE-SEM: JEOL, JSM-7000F).

Photoelectrochemical experiments

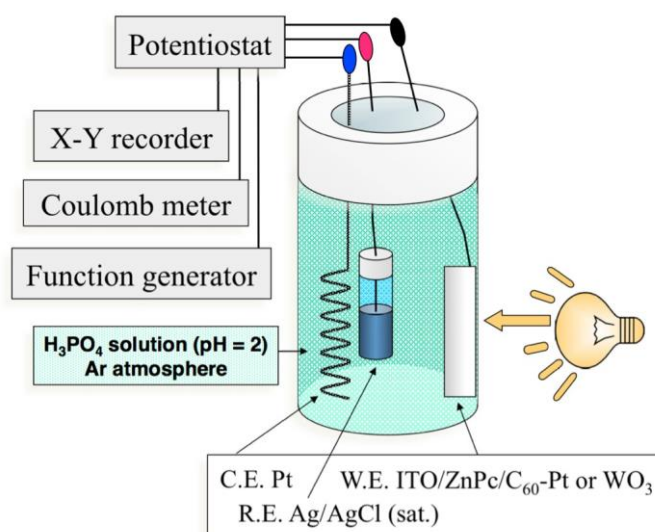
Photoelectrochemical operation was conducted using a potentiostat (Hokuto Denko, HA-301) equipped with a function generator (Hokuto Denko, HB-104), a coulomb meter (Hokuto Denko, HF-201) and a X-Y recorder (GRAPHTEC, WX-4000). A halogen lamp (light intensity: ca. 90 $\text{mW}\cdot\text{cm}^{-2}$) was used as the light source for photocathode; irradiation was performed from the back side of the ITO-coated face. A xenon lamp (light intensity: ca. 50 $\text{mW}\cdot\text{cm}^{-2}$) was also used for irradiating the photoanode. Monochromatic light, generated by the combination of a monochromator (Soma Optics, Ltd., S-10) with a light source, was used to irradiate the sample for measuring action spectra for photocurrents. Light intensity was measured using a power meter (type 3A from Ophir Japan, Ltd., or CS-40 from ASAHI SPECTRA). All photoelectrochemical studies were performed under an Ar atmosphere in an aqueous H₃PO₄ solution (pH = 2).

1) Three-electrode system

Photoelectrochemical measurements (such as CV measurements and action spectral measurements) were conducted in a single-compartment glass cell with a working electrode, a Ag/AgCl (sat.) reference electrode and a Pt counter electrode (see **Scheme S1**). The deposition of Pt onto ITO/ZnPc/C₆₀ was performed under photocathodic conditions where the photoelectrode was polarized from +0.4 V (vs. Ag/AgCl (sat.)) to -0.2 V in an acidic solution (pH = 2) containing $5.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3} \text{ H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ under anaerobic conditions. The amount of Pt deposited was controlled by the amount of charge passed (typically, $4.0 \times 10^{-2} \text{ C}$).

2) Two-electrode system

Photoelectrochemical water splitting was conducted in a system of WO₃ (photoanode, 1 cm²) and ITO/ZnPc/C₆₀-Pt (photocathode, 1 cm²). In order to avoid the spontaneous recombination of H₂ and O₂, a cell with twin compartments separated by a salt bridge was employed for the water splitting (Scheme 1). For preparing the salt bridge, agar (1.3 g) and KNO₃ (4.74 g) were first dissolved in hot water ($1.0 \times 10^{-2} \text{ dm}^3$). Then the mixture was allowed to flow into the bridging part of the cell and solidify at room temperature. Water-splitting studies were also conducted using the aforementioned electrochemical apparatus.



Scheme S1 An illustration of a three-electrode system employed in the present work

Calculation methods

1) Faradic efficiency (F.E.)

The F.E. value was calculated according to the following procedure:

- i) During the photoelectrochemical splitting of water, the amount of charge passed was measured by a coulomb meter. Based on the resulting amount of charge, the theoretical amounts of H₂ and O₂ evolved were calculated.

ii) After the photoelectrochemical reaction, the amounts of H₂ and O₂ evolved were quantified by a gas chromatograph.

The F.E. value for H₂ (or O₂) evolution is then determined using the following equation:

$$\begin{aligned} \text{F.E. (\%)} &= [\text{amount of H}_2 \text{ (or O}_2\text{) evolved}]/[\text{theoretical amount of H}_2 \text{ (or O}_2\text{)}] \times 100 \\ &= [\text{amount of H}_2 \text{ (or O}_2\text{) evolved}]/[(\text{amount of charge passed})/(nF)] \times 100, \end{aligned}$$

where n is the number of electrons that participated in the evolution of a gaseous product ($n = 2$ for the reduction of H⁺ into H₂; $n = 4$ for O₂ evolution from water), and F is Faraday's constant (i.e. $9.65 \times 10^4 \text{ C}\cdot\text{mol}^{-1}$).

2) Light-to-hydrogen conversion efficiency (η)

The η value was estimated using the following equation:

$$\eta (\%) = (\Delta_r G^\circ(\text{H}_2\text{O}) [\text{kJ}\cdot\text{mol}^{-1}] \times \text{amount of H}_2 \text{ evolved} [\text{mol}] - \text{voltage applied between anode and cathode} [\text{V}] \times \text{charge passed during water splitting} [\text{C}]) / (\text{total of incident photoenergy irradiated for photoelectrodes} [\text{J}]) \times 100,$$

where $\Delta_r G^\circ(\text{H}_2\text{O})$ [$237.13 \text{ kJ}\cdot\text{mol}^{-1}$] is Gibbs free energy for the decomposition of H₂O into H₂ (1 mol). This calculation is in accordance with the previous procedure [7].

3) Incident photon-to-current efficiency (IPCE)

In order to obtain an action spectrum for photocurrent, the IPCE value was calculated using the following equation:

$$\text{IPCE (\%)} = [I/e]/[W/\varepsilon] \times 100,$$

where I ($\text{A}\cdot\text{cm}^{-2}$) is the photocurrent density, e (C) is the elementary electric charge, W ($\text{W}\cdot\text{cm}^{-2}$) is the light intensity, and ε is the photon energy.

- [1] T. Abe, K. Nakamura, H. Ichinohe and K. Nagai, *J. Mater. Sci.*, **47**(2), 1071 (2012).
- [2] T. Abe, Y. Hiyama, K. Fukui, K. Sahashi, K. Nagai, *Int. J. Hydrogen Energy*, **40**, 9165 (2015).
- [3] T. Morikawa, C. Adachi, T. Tsutsui and S. Saito, *Nippon Kagaku Kaishi*, 962 (1990).
- [4] J. H. Sharp and M. Lardon, *J. Phys. Chem.*, **72**, 3230 (1968).
- [5] H. Yoshida, Y. Tokura and T. Koda, *Chem. Phys.* **109**, 375 (1986).
- [6] A. Capobianchi and M. Tucci, *Thin Solid Films*, **451-452**, 33 (2004).
- [7] M. Radecka, M. Rekas, A. Trenczek-Zajac and K. Zakrzewska, *J. Power Sources*, **181**, 46 (2008).

Action spectrum for photocurrents generated at WO₃, and its absorption spectrum and SEM image

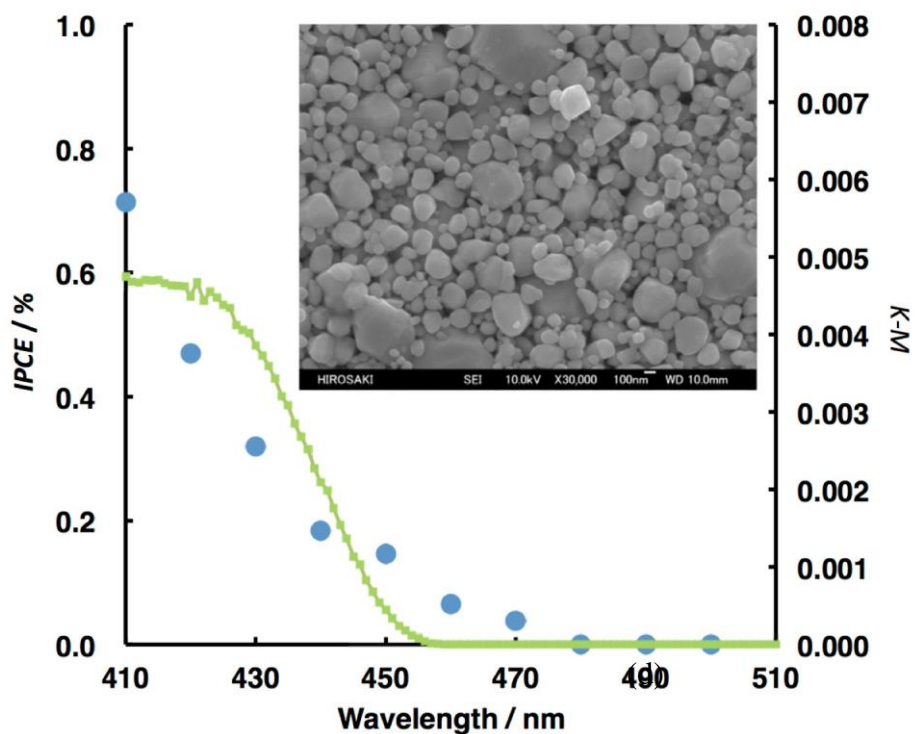


Fig. S1 Action spectrum of the photocurrents generated at WO₃ and its absorption spectrum. Inset shows SEM image of WO₃. In this study, photocurrents were measured in a three-electrode system depicted in Scheme S1 (*vide supra*)

Geometrical area of photoelectrode: WO₃, 1 cm²
Applied potential: +0.35 V (vs. Ag/AgCl (sat.))
Electrolyte: H₃PO₄ solution (pH = 2)

A detailed interpretation of action spectra acquired for ITO/MPC/C₆₀-Pt (M = H₂ and Zn) was stated in the previous reports (i.e. T. Abe *et al.*, (i) *J. Phys. Chem. C* 2011, **115**, 7701 and (ii) *Int. J. Hydrogen Energy* 2015, **40**, 9165).

CVs measured at both WO_3 (photoanode) and ITO/ZnPc/ C_{60} -Pt (photocathode)

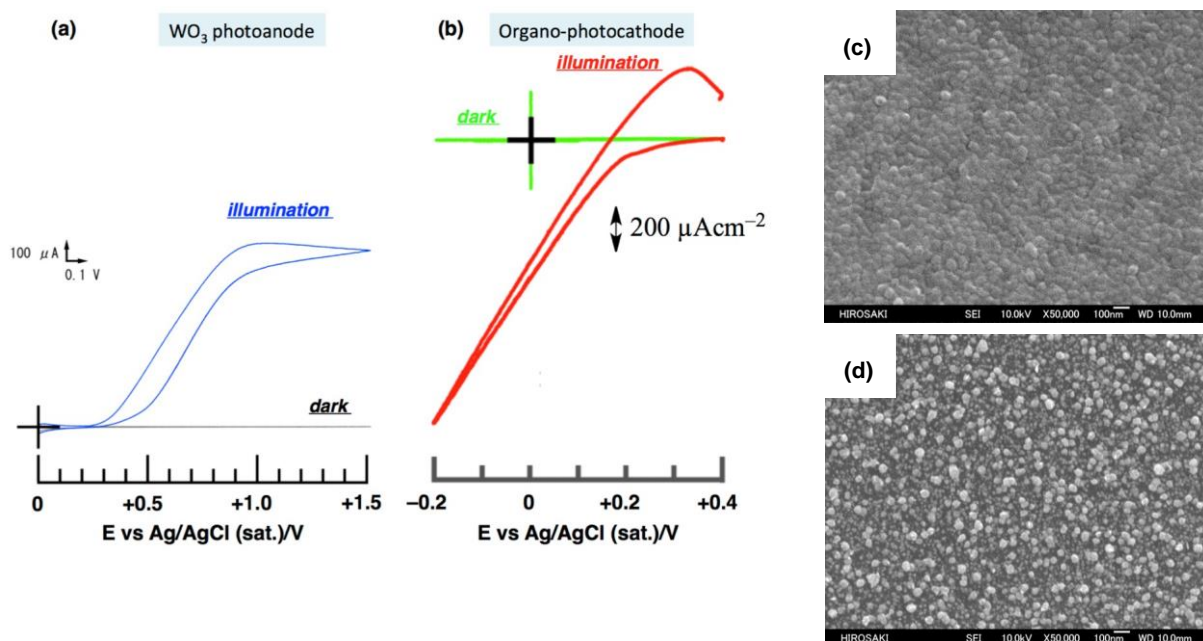


Fig. S2 Cyclic voltammograms measured at WO_3 (a, photoanode) and ITO/ZnPc/ C_{60} -Pt (b, photocathode [1]). CV measurements were conducted in the three-electrode system depicted in Scheme S1 (*vide supra*). SEM images of C_{60} surface (c) and Pt-loaded C_{60} surface (d) in the organo-photocathode are also depicted.

Geometrical area of photoelectrodes: WO_3 , 1 cm^2 ; ITO/ZnPc/ C_{60} -Pt, 1 cm^2
 Film thickness in organic p-n bilayer: ZnPc, 75 nm; C_{60} , 125 nm
 Electrolyte: H_3PO_4 solution (pH = 2)
 Light intensity: ca. $90 \text{ mW} \cdot \text{cm}^{-2}$ for photoanode, and ca. $50 \text{ mW} \cdot \text{cm}^{-2}$ for photocathode
 Scan rate: $20 \text{ mV} \cdot \text{s}^{-1}$

[1] T. Abe, Y. Hiyama, K. Fukui, K. Sahashi, K. Nagai, *Int. J. Hydrogen Energy*, **40**, 9165 (2015).

Dependencies of both the amounts of H₂ and O₂ evolved during photoelectrochemical water splitting and light-to-hydrogen conversion efficiency on applied bias voltages in the reference WO₃-Pt system

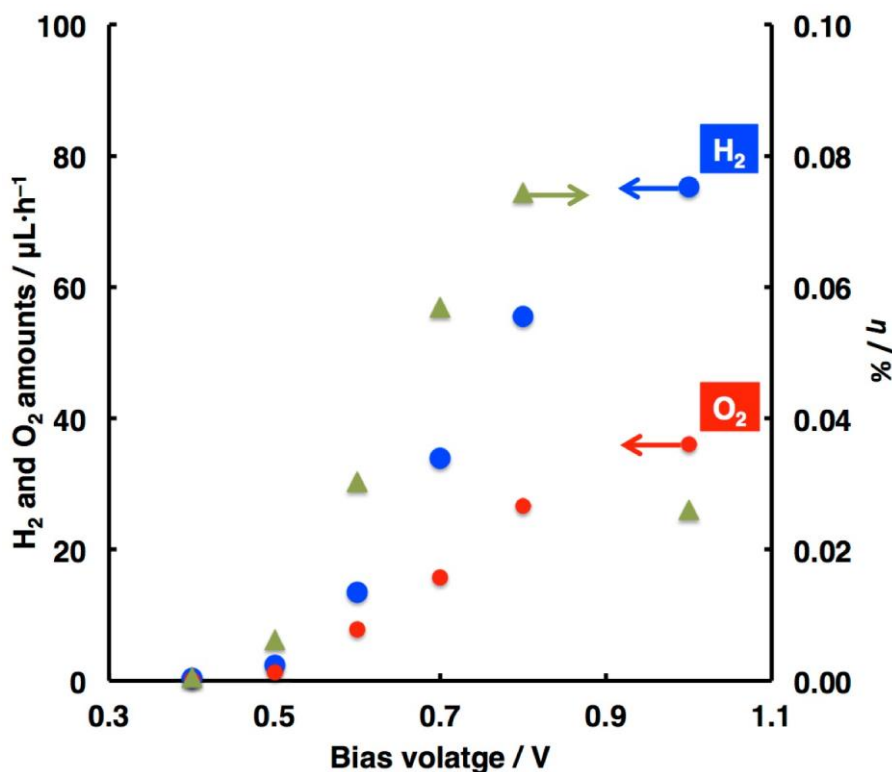


Fig. S3 Relationships of both the amounts of H₂ and O₂ evolved and η values with applied bias voltages. This study was conducted in a two-electrode system depicted in Scheme 1

Photoanode (geometrical area): WO₃ (1 cm²)
 Counter electrode: Pt wire
 Electrolyte: H₃PO₄ solution (pH = 2)
 Light intensity: ca. 50 mW·cm⁻²

Data of photoelectrochemical water splitting at 0.4 V
 H₂ amount = 0.39 μL·h⁻¹, O₂ amount = 0.18 μL·h⁻¹, and η value = 5.2 × 10⁻⁴%

Table S1 Data of control experiments in the WO₃ (photoanode) and Pt (cathode) system.^a

System	H ₂ evolved/ $\mu\text{L}\cdot\text{h}^{-1}$	O ₂ evolved/ $\mu\text{L}\cdot\text{h}^{-1}$	Note
Entry 1 ^b	55.6	26.6	No control system.
Entry 2 ^c	106	-----	In the presence of methanol.
Entry 3 ^d	-----	25.3	In the presence of Fe ³⁺ .

^a Bias voltage of 0.8 V was applied to the system with experimental conditions similar to those in Fig. 1. ^b Data from Fig. S3. ^c A methanol solution (methanol/water(v/v) = 1:1, pH = 2) was used. ^d An aqueous solution of Fe(NO₃)₃ (5 mM, pH = 2) was employed.