Electronic Supplementary Information

A visible-light-induced photoelectrochemical water splitting system featuring organo-photocathode along with tungsten oxide photoanode
Yuto Kawai, Keiji Nagai and Toshiyuki Abe*

Contents:
1. Experimental details
2. An illustration of a three-electrode system employed in the present work [Scheme S1]
3. Action spectrum for photocurrents generated at WO₃, and its absorption spectrum and SEM image [Fig. S1]
4. CVs measured at both WO₃ (photoanode) and ITO/ZnPc/C₆₀–Pt (photocathode), and SEM images of C₆₀ surface and Pt-loaded C₆₀ surface in the organo-photoanode [Fig. S2]
5. 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]
6. Data of control experiments in the reference WO₃–Pt system in the presence of methanol or Fe³⁺ ion [Table S1].
Experimental details

Chemicals

Commercially available \( \text{C}_6\text{O} \) 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 (\( \alpha \)-phase) [3-5] and \( \text{C}_6\text{O} \) [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 \( \text{C}_6\text{O} \) 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 WO\(_3\) 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 mW·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 mW·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 H\(_3\)PO\(_4\) 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 $5.0 \times 10^{-4}$ mol·dm$^{-3}$ H₂PtCl₆·6H₂O under anaerobic conditions. The amount of Pt deposited was controlled by the amount of charge passed (typically, $4.0 \times 10^{-2}$ C).

2) Two-electrode system

Photoelectrochemical water splitting was conducted in a system of WO₃ (photoanode, 1 cm$^2$) and ITO/ZnPc/C₆₀–Pt (photocathode, 1 cm$^2$). In order to avoid the spontaneous recombination of H$_2$ and O$_2$, 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 KNO$_3$ (4.74 g) were first dissolved in hot water ($1.0 \times 10^{-2}$ 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 H$_2$ and O$_2$ 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:

$$\text{F.E. (\%)} = \left[ \frac{\text{amount of H}_2 \ (\text{or O}_2 \ \text{evolved})}{\text{theoretical amount of H}_2 \ (\text{or O}_2)} \right] \times 100$$

$$= \left[ \frac{\text{amount of H}_2 \ (\text{or O}_2 \ \text{evolved})}{\text{(amount of charge passed)}/(nF)} \right] \times 100,$$

where $n$ is the number of electrons that participated in the evolution of a gaseous product ($n = 2$ for the reduction of $\text{H}^+$ into $\text{H}_2$; $n = 4$ for $\text{O}_2$ 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 ($\eta$)

The $\eta$ value was estimated using the following equation:

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

where $\Delta G^\circ(\text{H}_2 \text{O}) [237.13 \text{kJ} \cdot \text{mol}^{-1}]$ is Gibbs free energy for the decomposition of $\text{H}_2 \text{O}$ into $\text{H}_2$ (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:

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

where $I$ (A·cm⁻²) is the photocurrent density, $e$ (C) is the elementary electric charge, $W$ (W·cm⁻²) is the light intensity, and $\varepsilon$ is the photon energy.

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$_3$PO$_4$ solution (pH = 2)

Light intensity: ca. 90 mW·cm$^{-2}$ for photoanode, and ca. 50 mW·cm$^{-2}$ for photocathode

Scan rate: 20 mV·s$^{-1}$

Dependencies of both the amounts of $H_2$ and $O_2$ evolved during photoelectrochemical water splitting and light-to-hydrogen conversion efficiency on applied bias voltages in the reference WO$_3$–Pt system

![Graph showing relationships of both the amounts of $H_2$ and $O_2$ evolved and $\eta$ values with applied bias voltages.](image)

**Fig. S3** Relationships of both the amounts of $H_2$ and $O_2$ evolved and $\eta$ values with applied bias voltages. This study was conducted in a two-electrode system depicted in Scheme 1

- **Photoanode (geometrical area):** WO$_3$ (1 cm$^2$)
- **Counter electrode:** Pt wire
- **Electrolyte:** H$_3$PO$_4$ solution (pH = 2)
- **Light intensity:** ca. 50 mW·cm$^{-2}$

Data of photoelectrochemical water splitting at 0.4 V

$H_2$ amount = 0.39 µL·h$^{-1}$, $O_2$ amount = 0.18 µL·h$^{-1}$, and $\eta$ value = 5.2 × 10$^{-4}$%
<table>
<thead>
<tr>
<th>System</th>
<th>$\text{H}_2$ evolved/µL·h$^{-1}$</th>
<th>$\text{O}_2$ evolved/ µL·h$^{-1}$</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entry 1$^b$</td>
<td>55.6</td>
<td>26.6</td>
<td>No control system.</td>
</tr>
<tr>
<td>Entry 2$^c$</td>
<td>106</td>
<td>-----</td>
<td>In the presence of methanol.</td>
</tr>
<tr>
<td>Entry 3$^d$</td>
<td>-----</td>
<td>25.3</td>
<td>In the presence of Fe$^{3+}$.</td>
</tr>
</tbody>
</table>

$^a$ 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(NO$_3$)$_3$ (5 mM, pH = 2) was employed.