A Z-scheme type photoelectrochemical cell consisting of porphyrin-containing polymer and dye-sensitized TiO₂ electrodes

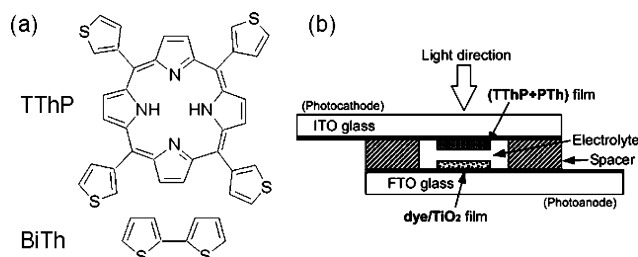Kensuke Takechi,*[a,b] Tohru Shiga,[a] Tsuyoshi Akiyama[c] and Sunao Yamada[c]

A Z-scheme type photoelectrochemical cell consisting of an electrochemically polymerized photoactive electrode and a dye-sensitized TiO₂ electrode is demonstrated. Nearly 1 V of open circuit voltage (V_{OC}) was achieved by the cooperation of a couple of photoactive electrodes toward uphill electron pumping.

In photosynthesis, two photosystems are exquisitely located for uphill electron transport with redox species to bridge these photosystems and this is called Z-scheme type structure. This smart photoenergy conversion system must be modeled in highly-efficient artificial photoenergy conversion.

Our strategy here is to cooperate a couple of photoactive electrodes for mimicking a Z-scheme type structure using two different photoelectrodes and bridging redox couple. An early study implied the possibility of a tandem-type photoelectric conversion system, though the cell performance had been considerably low.[1] Later, Bach's group also proposed a similar structure consisting of n- and p-type dye-sensitized solar cell (DSC) electrodes and achieved high conversion efficiency.[2]

Photoelectric conversion systems using organic molecules have been extensively studied, for example DSC and organic solar cells including polymer solar cells. Although polymer solar cells containing a photoactive polymer electrode have been easily fabricated by spin coating,[3] solution casting[4] and electropolymerization,[5] their operation has been limited to one side of the two electrodes.

Recently, we reported a simple fabrication method of photoactive polymer electrode consisting of 5,10,15,20-tetra(3-thienyl)-21H,23H-porphyrin (TThP) and 2,2′-bithiophene (BiTh) by electropolymerization (Scheme 1a).[6–9] As the photoactive electrode for a solar cell, it could generate 32% of photon-to-electron conversion efficiency under the monochromatic light. Since this polymer electrode functions as a photocathode and has a good affinity with the I⁻/I₃⁻ redox couple, it is very fascinating to use in a Z-scheme type photoelectrochemical cell with a smart choice of a good compatible photoanode. In this paper, we found that the combination of the above-described polymer electrode and the electrode for DSC successfully acted as a Z-scheme type photoelectrochemical cell with higher photovoltage (Fig. 1). We have prepared a couple of photoactive electrodes functioning as Z-scheme type photoelectrochemical cells as follows.

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Scheme 1 Structures of (a) TThP and monomeric BiTh, and (b) schematic illustration of Z-scheme type photoelectrochemical cell.
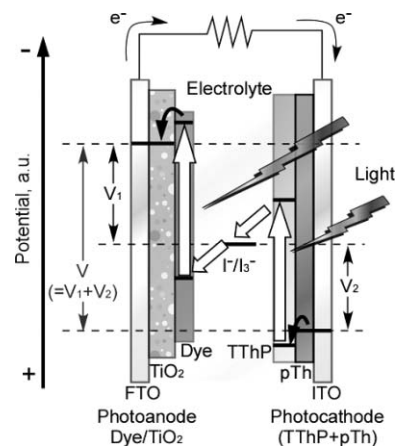
Fig. 1 Photocurrent generation diagram of (TThP+pTh)-dye/TiO₂ Z-scheme cell. In the photocathode, incident light excites electrons from HOMO to LUMO of TThP, followed by electron supply from pTh, and the excited TThP gives electrons to the redox couple (I⁻/I₃⁻) in the electrolyte, generating photovoltage V_2. Meanwhile, in the photoanode, photovoltage V_1 can be obtained by well-established dye-sensitizing mechanism. As a result, overall V_{OC} of the Z-scheme cell will be the sum of V_{OC} of each electrode unit ($V_1 + V_2$).

TThP was synthesized by condensation of pyrrole (Aldrich) and 3-thiophenecarboxyaldehyde (Aldrich) according to the previous procedures.[6] TThP was identified by ¹H-NMR, absorption spectroscopy, matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) and elemental analysis; impurities in the TThP were found to be negligible. (TThP+polythiophene (pTh)) thin films were fabricated on the surface of an indium-tin-oxide (ITO) glass by electrochemical polymerization of TThP and BiTh (Wako pure chemicals) in a similar manner as before.[6] The ITO glass (Sanyo Vacuum Industries, $2 \times 2 \times 0.3$ cm), cleaned ultrasonically in 2-propanol and then dichloromethane, was used as a working electrode. A platinum wire and a silver wire were used as the counter and reference electrodes, respectively. A dichloromethane solution

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containing TThP (0.25 mmol L^{-1}), BiTh (1.50 mmol L^{-1}) and tetrabutylammonium hexafluorophosphate (0.1 mol L^{-1}) was used as the electrolyte for polymerization. The electrolyte solution was degassed by passing nitrogen gas through it for at least 15 min prior to use. Polymerization was carried out using a potentiostat (Hokuto Denko, HA-3001), and the potential applied to the working electrode was scanned between 0 and +2 V at a rate of 20 mV s^{-1} for one cycle. During polymerization, the solution was stirred at a speed of 500 rpm. The resultant polymer-modified electrode was then removed from the solution, followed by washing with dichloromethane and acetone, then dried in the air to give a (TThP+pTh) film on the ITO glass.

A TiO$_2$ paste including TiO$_2$ nanocrystals with 20 nm diameter (PST-18NR, JGC Catalysts and Chemicals) was spread over an F-doped tin oxide (FTO) coated glass electrode (Nippon Sheet Glass, 2 × 2 × 0.3 cm) by a doctor blade method. After air-drying, the electrode was annealed in an oven at 673 K for 1 h, and the needless part of the TiO$_2$ film was peeled away. The thickness of the TiO$_2$ film was about 12 μm. Then, the TiO$_2$ electrode was dipped in the solution of 0.3 mmol L^{-1} N749 dye (triisothiocyanato (2,2′:6′,6″-terpyridyl-4,4′,4″-tricarboxylato) ruthenium(II) tris(tetrabutylammonium), Solaronix) in the mixture of acetonitrile and t-butanol (1 : 1 v/v) for 24 h, and washed with 2-propanol followed by air-drying, to give dye/TiO$_2$ electrode.

In order to evaluate the performance of each single electrode, a sandwich-type photoelectrochemical cell was fabricated, which consisted of the photoactive ((TThP+pTh) or dye/TiO$_2$) electrode as the working electrode and a Pt-deposited semi-transparent ITO glass electrode as a counter electrode. All photoelectrochemical measurements were carried out with 3-methoxypropionitrile (MPN) containing 0.5 mol L^{-1} propylmethylimidazolium iodide (PMII), 0.05 mol L^{-1} I$_2$ and 0.5 mol L^{-1} N-methylbenzimidazole (NMBI) as an electrolyte.

The Z-scheme type photoelectrochemical cell has been fabricated as shown in Scheme 1b. A polyolefin-based sealant film as a spacer (25 μm thickness) was sandwiched between a couple of (TThP+pTh) and dye/TiO$_2$ electrodes. A small amount of the electrolyte solution dropped between the electrodes, and the whole cell parts were fixed tightly with clamps. Light irradiated from the side of the (TThP+pTh) electrode and passed through the electrolyte layer and then further irradiated the dye/TiO$_2$ electrode.

Incident photon-to-electron conversion efficiency (IPCE) and the current–voltage (I–V) curve of the fabricated photoelectrochemical cell were measured using a spectral sensitivity analysis system (Bunkoh-Keiki, CEP-2000) which has a 300 W xenon lamp for monochromatic light and a 150 W xenon lamp with an air mass (AM) 1.5 filter for simulated sunlight. The light intensity of the monochromatic light was 1.0×10^{16} photon s^{-1} cm^{-2}. The IPCE values at various excitation wavelengths were determined from eqn (1)

$$\text{IPCE (\%)} = [(1240 \times i_{sc})/(\lambda \times I_{inc})] \times 100 \quad (1)$$

where i_{sc} is the short-circuit photocurrent (A cm^{-2}), I_{inc} is the incident light intensity (W cm^{-2}), and λ is the excitation wavelength.

The photoactive (TThP+pTh) electrode was fabricated by electropolymerization procedure under a stirring condition.[9] As shown in Fig. 2a, the transmission absorption spectrum proves
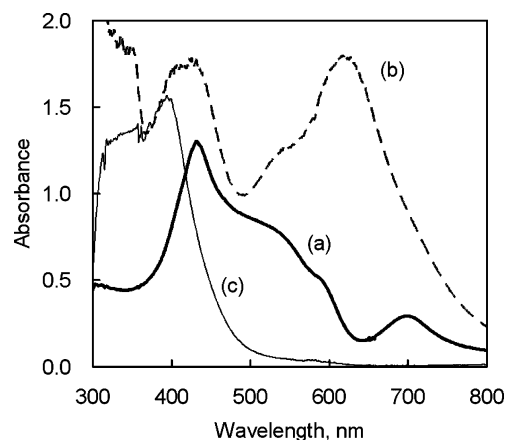
Fig. 2 Transmission absorption spectra of (a) (TThP+pTh) electrode, (b) 0.2 mmol L^{-1} N749 dye solution in the mixture of acetonitrile and t-butanol (1 : 1 v/v) and (c) an electrolyte layer (25 μm thickness of 0.5 mol L^{-1} PMII, 0.05 mol L^{-1} I$_2$ and 0.5 mol L^{-1} NMBI in MPN).

that TThP molecules were successfully incorporated in the polythiophene film because of the appearance of a clear peak around 420 nm corresponding to the Soret band of the porphyrin moiety. Detailed characterization of the electrode has been made in previous papers.[6,9] Photon-to-electron conversion properties of the (TThP+pTh) electrode are shown in Fig. 3a. Short circuit current (J_{sc}), V_{OC}, and total photon-to-electron conversion efficiency (η) were 0.45 mA cm^{-2}, 0.29 V, and 0.05%, respectively. The most important point is that the electrode generates cathodic photocurrents, giving electrons to the I$^-$/I$_3^-$ redox couple in the electrolyte under illumination.
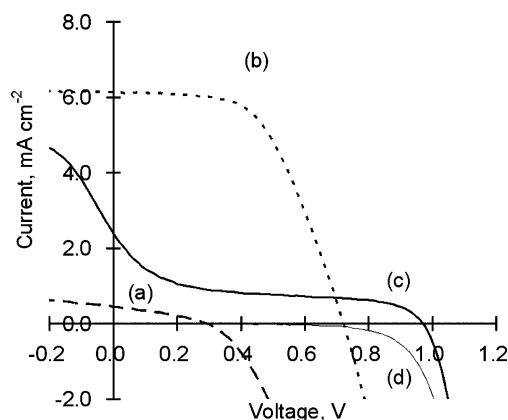
Fig. 3 I–V characteristics of photoelectrochemical cells: (a) (TThP+pTh) electrode, (b) dye/TiO$_2$ electrode, (c) (TThP+pTh) dye/TiO$_2$ Z-scheme cell under illumination and (d) in dark condition.

So called "black dye" (N749 dye) was used as the dye for the electrode of DSC because of its absorption property in the wide wavelength region. In our Z-scheme type photoelectrochemical cell, the dye/TiO$_2$ electrode has to be located on the rear side of the cell as to the light irradiation direction in order to maximize the performance of the (TThP+pTh) electrode placed on the front side (Scheme 1b). Actually, the light around 400 nm cannot reach to the dye/TiO$_2$ electrode because the I$^-$/I$_3^-$ redox mostly absorbs the light of around 400 nm (Fig. 2c). Therefore, the dye/TiO$_2$ electrode was prepared non-transparent to absorb weak light

after penetration through those absorptive layers and only the absorption spectrum of the original dye solution can be shown in Fig. 2b. Similarly, the power characteristics of the dye/TiO$_2$ electrode is shown in Fig. 3b but is not comparable to the (TThP+pTh) electrode because the light intensity and spectrum are totally different in the actual cell. Anodic photocurrents were clearly obtained and the V_{OC} of 0.73 V has been observed.

In the case of our Z-scheme type photoelectrochemical cell (Fig. 3c), we have observed the maximum V_{OC} of 0.97 V and the J_{SC} of 2.30 mA cm^{-2} under visible-IR light illumination (100 mW cm^{-2}). The high V_{OC} was almost the sum of V_{OC} of each single electrode unit (0.29 V for (TThP+pTh), 0.73 V for dye/TiO$_2$), and it confirms the operation by Z-scheme type electron flow, even though the overall power conversion efficiency is rather small (0.51%).
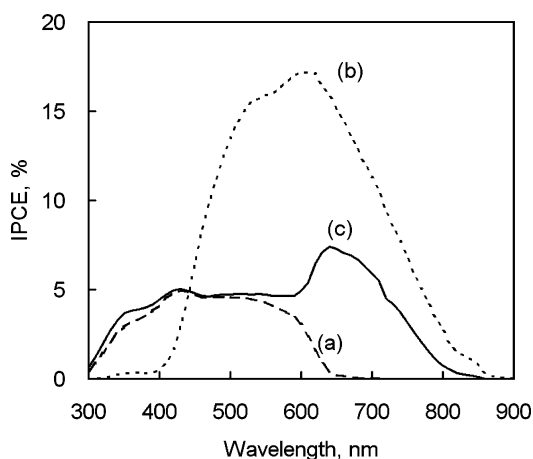
IPCE measurements (Fig. 4) also show that the photoelectrochemical cell could harvest a wide range of irradiating light, reflecting the independent performance of the each electrode. On the other hand, one of the major problems of the present cell is relatively low J_{SC}. The Z-scheme type electron pumping strategy (Fig. 1) only works at 450–650 nm in which both cathodic and anodic electrodes work at the same time, and the IPCE measurements (Fig. 4) obviously show that the (TThP+pTh) electrode caused the limitation of the photocurrent. In our previous research, J_{SC} and V_{OC} could be influenced by the composition of electrolyte and the structure of electrode.[6] In this case, we chose the optimum condition to maximize the V_{OC} value even though the sacrifice of the J_{SC} value. In order to improve J_{SC} as a next step, some appropriate conducting polymer layers should be added between the photoactive layer and the electron collecting ITO surface, in order to reduce electrical resistance and recombination of excited electrons. Also, careful tuning of the LUMO level of photoactive species in the polymer electrode may be important to further improve the V_{OC} performance, because it determines the ground state level of the electrode (Fig. 1). Such approaches need to be exploited in the construction of more highly efficient photoelectrochemical cells.

In conclusion, a Z-scheme type photoelectrochemical cell has been proposed. It consisted of an electrochemically polymerized photoactive electrode and a dye-sensitized TiO$_2$ electrode. The cell stably afforded nearly 1 V of open circuit voltage. The results strongly suggest that one can easily obtain photoelectrochemical cells showing higher V_{OC} only by a smart choice of the counter electrode of the dye-sensitized solar cells from a Pt or a carbon electrode to the polymer electrode. At the same time, significant effort for improving J_{SC} by putting support layer or alternative photoactive species in the polymer electrode should be made to improve the cell performance more and more.

Fig. 4 IPCE performances of photoelectrochemical cells: (a) (TThP+pTh) electrode, (b) dye/TiO$_2$ electrode and (c) (TThP+pTh)-dye/TiO$_2$ Z-scheme cell. In the case of (b), photocurrent around 400 nm was suppressed because of the light absorption of the electrolyte (see Fig. 2b, c).

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