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A water splitting system using an organo-photocathode and titanium dioxide photoanode capable of bias-free H₂ and O₂ evolution†

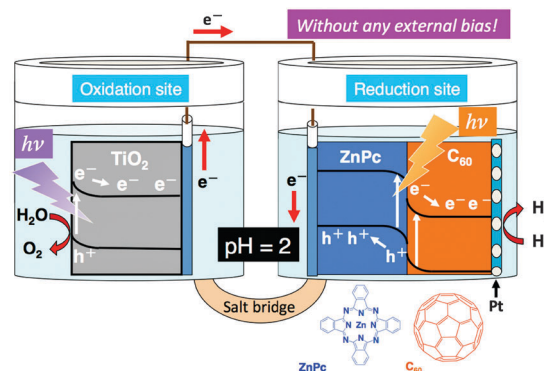Toshiyuki Abe,*[a] Katsuma Fukui,[a] Yuto Kawai,[a] Keiji Nagai[b] and Hideki Kato[c]

This study examined a water-splitting system comprising a TiO_2 photoanode and an organo-photocathode consisting of a p–n bilayer. Stoichiometric decomposition of water into H_2 and O_2 successfully occurred at bias voltages lower than the theoretical value (*i.e.* 1.23 V). Compared to the conventional TiO_2 and Pt systems, the proposed water-splitting system demonstrated water splitting without any externally applied bias.

For establishing a sustainable society, solar hydrogen has been considered to be a potentially clean energy substitute for fossil fuels. For acquiring solar hydrogen, water splitting has been actively investigated using both photoelectrochemical and photocatalytic approaches.[1–11] Since the discovery of photoelectrochemical water splitting by Honda and Fujishima,[12] TiO_2 has been recognised as one of the most efficient photoanodes for the evolution of O_2 from water. Various types of structures with TiO_2 have been fabricated based on novel approaches.[13–15] However, when TiO_2 is used as a photoanode along with a Pt counter electrode (*cf.* the corresponding system is abbreviated as TiO_2–Pt), the overall splitting of water into O_2 and H_2 occurs only upon the application of an external chemical or electrochemical bias.[13–17] This is because of the close potential of the conduction band (corresponding to the magnitude of reducing power) to the reduction potential of H^+ into H_2.

Photoelectrochemical and photocatalytic systems featuring organic semiconductors and a p–n bilayer have been investigated in our previous studies.[18–23] In some instances, photocatalytic reactions *via* organic p–n bilayers respond to the entire visible-light energy for the oxidative decomposition of organoamine,[19,20] alcohol,[21] aldehyde[21] and hydrazine.[22,23] In addition, when an organobilayer of phthalocyanine (H_2Pc, p type) and fullerene (C_{60}, n type) was employed as a photocathode in a three-electrode system,[24] the C_{60} surface modified by Pt induced the reduction of H^+ into H_2 at applied potentials that were more positive than the formal potential of H^+/H_2. The detailed characteristics of C_{60} for producing H_2 were clarified based on two types of *in situ* spectro-electrochemistry (*i.e.* VIS–NIR and Raman).[24] Recently, more efficient H_2 production was found to occur by the replacement of H_2Pc by zinc phthalocyanine (ZnPc, p type).[25]

In the present study, a photoelectrochemical water-splitting system was studied, where TiO_2 (photoanode) and a $ZnPc/C_{60}$ bilayer modified by Pt (photocathode, *vide supra*) were simultaneously employed for water oxidation and H^+ reduction, respectively (Scheme 1). The stoichiometric decomposition of water into H_2 and O_2 was found to occur upon application of bias voltages <1.23 V. Moreover, this study demonstrated that photocatalytic water decomposition (*i.e.* bias-free water splitting) occurs successfully in a system featuring an organo-photocathode, making it distinct from a conventional TiO_2–Pt system (*vide supra*).

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† Electronic supplementary information (ESI) available: Experimental details including calculation procedure for some types of efficiencies, both cyclic voltammograms and action spectra for photocurrents measured at photoelectrodes employed, and data for the reference system of a TiO_2 photoanode and a Pt wire. See DOI: 10.1039/c6cc01225f

Scheme 1 An illustration of the system employed for water splitting.

The ZnPc/C_{60} bilayer was prepared by vapour deposition (pressure, $< 1.0 \times 10^{-3}$ Pa; deposition speed, *ca.* 0.03 nm s^{-1}) using an indium-tin-oxide (ITO)-coated glass plate as the base material.[25] The organic p–n bilayer was composed of ZnPc coated on ITO and C_{60} coated on top of the ZnPc layer; moreover, a Pt co-catalyst was photocathodically deposited onto the C_{60} surface of the bilayer (the resulting device is abbreviated as ITO/ZnPc/C_{60}–Pt). A disk-like form of TiO_2 (rutile) was utilised as the photoanode, which was reductively treated under a hydrogen flow at 773 K for 2 h prior to use. In order to achieve an ohmic contact, Ga–In was applied to the back side of the TiO_2. As represented in Scheme 1, a cell made up of twin compartments separated by a salt bridge was utilised for the water-splitting studies. All studies were performed under an Ar atmosphere in an aqueous H_3PO_4 solution (pH = 2). Other experimental details are provided in the ESI.†

The voltammetric characteristics of photoelectrodes employed were examined in a three-electrode system (see Scheme S1 and Fig. S1 (ESI†)). When using TiO_2 as a photoanode, a photocurrent due to the oxidation of H_2O was observed at potentials more positive than 0 V (*vs.* Ag/AgCl (sat.)). The voltammogram measured for ITO/ZnPc/C_{60}–Pt is shown in Fig. S1 (ESI†).[25] The CV data revealed that both the photoanodic and photocathodic currents are generated in the same potential window. In other words, the water-splitting system of TiO_2 and ITO/ZnPc/C_{60}–Pt may produce H_2 and O_2 without any bias voltage.

A water-splitting study was conducted with and without applied bias voltages (Scheme 1). The stoichiometric decomposition of water into H_2 and O_2 was found to occur at bias voltages less than 1.23 V (the theoretical voltage for water splitting). Fig. 1(a) shows the relationship between the amounts of H_2 and O_2 evolved and the respective applied voltages. The H_2 and O_2 amounts increased when a large bias was applied to the system; however, the evolved amounts gently increased, particularly at voltages larger than 0.25 V. The bias-free H_2 and O_2 evolution occurred stoichiometrically (*cf.* detailed data are also shown in the following figures). Based on the results shown in Fig. 1(a), the light to hydrogen conversion efficiency (η, ESI†) was estimated with respect to the applied voltages.
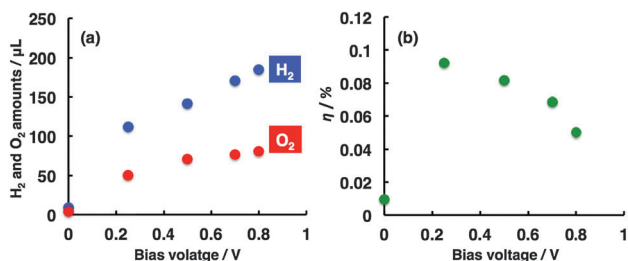
As shown in Fig. 1(b), efficient water splitting occurred at a small bias voltage of 0.25 V with *ca.* 0.1%. The results of Fig. 1(a) and (b) can be interpreted as follows. When a bias voltage is applied to the system, efficient charge separation can occur along with an efficient charge transfer between the photoanode and the photocathode, which can involve the suppression of carrier recombination. In such an occasion, the amounts of H_2 and O_2 may essentially increase. However, it appeared that a large bias of > 0.25 V cannot cause the proportional formation of H_2 and O_2 due to the presence of carriers sufficient to induce water splitting at those voltages. For example, the band bending for water oxidation at TiO_2 can sufficiently occur to be almost independent of carrier formation with respect to applied voltages. Therefore, the application of a large bias voltage to a water splitting system can only lead to a gentle enhancement of kinetics for H_2 and O_2 formation, thus resulting in decreasing efficiency (η). Such a phenomenon was also exhibited in other systems of water splitting.[3,26–28]

A prolonged study was conducted to test the durability of the present system. The linear relationships between the amounts of H_2 and O_2 evolved and the irradiation time, demonstrating the stable and durable performance for water splitting with and without bias voltages, are shown in Fig. 2.

Control experiments conducted in the presence of methanol (electron donor) or Ag^+ (electron acceptor) were compared with a typical result from the present system, as shown in Table 1. Irrespective of the presence of methanol, the amount of H_2 evolved was relatively constant (Table 1, entries 1 and 2); however, in the presence of an Ag^+ acceptor, the amount of
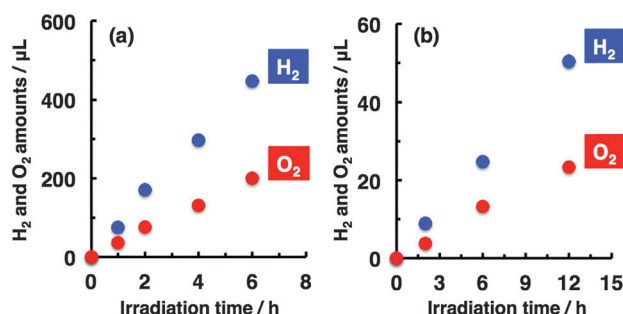

Fig. 2 Relationships between the H_2 and O_2 amounts and irradiation time ((a) 0.7 V; (b) 0 V, *i.e.* no-biased condition). Experimental conditions were the same as those used in Fig. 1, except that the irradiation time was changed.

Table 1 Control experiment data for the TiO_2 (photoanode) and ITO/ZnPc/C_{60}–Pt (photocathode) system[a]

System	H_2 evolved/µL	O_2 evolved/µL	Note
Entry 1[b]	171	76.2	No control system
Entry 2[c]	176	—	In the presence of methanol
Entry 3[d]	—	101	In the presence of Ag^+

[a] Bias voltage of 0.7 V was applied to the system under experimental conditions similar to those in Fig. 1. [b] Data obtained from Fig. 1. [c] A methanol solution (methanol/aqueous H_3PO_4 solution (v/v) = 1:1, pH = 2) was used. [d] An aqueous solution of AgNO$_3$ (5 mM, pH = 2) was employed.

Fig. 1 Relationships of (a) the evolved H_2 and O_2 amounts and (b) η values with applied voltages. This study was conducted in the two-electrode system depicted in Scheme 1. The amounts of H_2 and O_2 evolved with a 2h-irradiation time are represented. Faradaic efficiencies for H_2 and O_2 evolution were >90% and >80%, respectively (ESI†). Photoanode, TiO_2 (geometrical area, 0.5 cm^2); photocathode, ITO/ZnPc(75 nm)/C_{60}(125 nm)–Pt (geometrical area, 1 cm^2); electrolyte, H_3PO_4 solution (pH = 2); light intensity (for photoanode), *ca.* 70 mW cm^{-2}; light intensity (for photocathode), *ca.* 90 mW cm^{-2}.

Table 2 Comparison of water splitting data in the present system to the TiO$_2$–Pt system[a]

System	Photoanode	Cathode	H$_2$ evolved/µL	O$_2$ evolved/µL
Entry 1[b]	TiO$_2$	ITO/ZnPc/C$_{60}$–Pt	171	76.2
Entry 2[c]	TiO$_2$	Pt wire	86.7	44.0

[a] Bias voltage of 0.7 V was applied to the system, and other experimental conditions were similar to those of Fig. 1. [b] Data obtained from Fig. 1. [c] Instead of ITO/ZnPc/C$_{60}$–Pt, a Pt wire was employed as the cathode. Data listed in this table can also be seen in Fig. S2 (ESI).

evolved O$_2$ increased (Table 1, entries 1 and 3). Therefore, these results may suggest that the kinetics of the present system (Table 1, entry 1) is dominated by H$_2$ formation.

The evolution of H$_2$ and O$_2$ in the conventional TiO$_2$–Pt system was examined for use as a reference system. Similar to previous results (*vide supra*), Fig. S2 (ESI†) demonstrates that the TiO$_2$–Pt system needs an applied bias voltage for achieving water splitting. A comparison between the present and conventional systems is represented in Table 2. The amounts of H$_2$ and O$_2$ originating from water splitting are greater in the TiO$_2$–ITO/ZnPc/C$_{60}$–Pt system compared to the TiO$_2$–Pt system. These results indicate that rate-limiting H$_2$ evolution becomes more efficient when employing ITO/ZnPc/C$_{60}$–Pt instead of a Pt counter as the cathode.

The individual reactivity of the photoelectrodes employed in TiO$_2$–ITO/ZnPc/C$_{60}$–Pt has been previously clarified: O$_2$ and H$_2$ evolution can occur by the oxidising and reducing power produced at the TiO$_2$ photoanode[13–17] and the ITO/ZnPc/C$_{60}$–Pt photocathode,[24,25] respectively. Distinct from the conventional TiO$_2$–Pt system, the electrons photogenerated at TiO$_2$ cannot directly participate in the reduction of H$^+$ into H$_2$; however, they can contribute to the regeneration of the pristine ZnPc through electron transfer *via* an external circuit (Scheme 1). Action spectra for photocurrents generated at TiO$_2$ and ITO/ZnPc/C$_{60}$–Pt are shown in Fig. S3 (ESI†), confirming that TiO$_2$ (rutile) can induce O$_2$ evolution based on bandgap excitation (3.06 eV in rutile TiO$_2$).[29,30] In addition, we have previously reported that the entire visible-light energy range is available for H$_2$ evolution occurring at an ITO/ZnPc/C$_{60}$–Pt electrode.[25]

In summary, the photoelectrochemical splitting of water was demonstrated in a TiO$_2$–ITO/ZnPc/C$_{60}$–Pt system featuring an organo-photocathode with a TiO$_2$ photoanode, and bias-free decomposition of water into H$_2$ and O$_2$ was also found to occur. Based on the resulting action spectral characteristics (ESI†), the full region of visible light energy (*i.e.* <750 nm in wavelength) was available for H$_2$ evolution at the organo-photocathode. This implies that efficient water splitting can occur when simultaneously utilising a photoanode, responsive to visible light, for O$_2$ evolution. Thus, this work exhibited the effectiveness of using an organic p–n bilayer for a water-splitting system. The application of two types of materials for water splitting has merits in terms of the harvesting of solar energy and individual generation of oxidising and reducing power for O$_2$ and H$_2$ evolution, respectively. This is similar to the Z-scheme type photocatalytic water splitting.[31–34] Novel and efficient photoelectrodes for H$_2$ and O$_2$ evolution need to be developed for both organic and inorganic semiconductors so that a breakthrough in establishing a practical system for water splitting can be found.

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