Electronic Supplementary Information

Decomposition of hydrazine by an organic fullerene/phthalocyanine p–n bilayer photocatalysis system over the entire visible-light region

Toshiyuki Abe,*^a Naohiro Taira,^a Yoshinori Tanno^a, Yuko Kikuchi^a and Keiji Nagai^b

a: Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki 036-8561, Japan

b: Chemical Resources Laboratory, Tokyo Institute of Technology, Suzukake-dai, Midori-ku, Yokohama 226-8503, Japan

* Correspondence to be addressed

Experimental details

Chemicals: Pure C₆₀ (>99.5%, Tokyo Kasei) was used as received. Commercially available ZnPc (Kanto Chemical Co., Inc.) was purified by sublimation prior to use. During sublimation, the vessel exterior was thermally controlled (temperature, 530°C; pressure within the vessel, $<1.0 \times 10^{-2}$ Pa). N₂H₄ and a 5 wt% Nafion alcoholic solution were purchased from Kanto Chemical Co., Inc. and Aldrich Chemical Co., Ltd, respectively. The ITO-coated glass plate (sheet resistance, 8 $\Omega \cdot cm^{-2}$; transmittance, >85%; ITO thickness, 174 nm) was obtained from Asahi Glass Co., Ltd.

Procedure for coating Nafion onto the surface of a photocatalyst device: A 1 wt% Nafion solution was prepared by diluting commercial Nafion with methanol (density of Nafion in the resulting solution: 8.74×10^{-3} g·cm⁻³). Typically, twenty-three microlitres of this solution were cast onto the ZnPc surface (effective area: 1 cm²), followed by solvent evaporation under air. The resulting thickness of Nf (the abbreviation was represented in the main text) was estimated as ca.1 µm by considering the Nafion membrane density of 2 g·cm⁻³ [1].

Measurements: Absorption spectral measurements were taken using a Hitachi U-2010 spectrophotometer. The resulting absorption spectra of C_{60} [2] and ZnPc (α -phase) [3-5] were identical to those reported previously, and their absorption coefficients were used to determine the thickness of the obtained film [6].

The photoelectrochemical and photocatalytic studies were usually carried out under Ar atmosphere. A halogen lamp was typically used as the light source, and irradiation was carried out from the back side of the ITO-coated face. In particular, for irradiation with monochromatic light, the lamp was used with a monochromator (Soma Optics, Ltd., S-10). Light intensity was measured using a power metre (type 3A from Ophir Japan, Ltd.).

As depicted in Scheme S1 and Scheme 1, a twin-compartment cell was utilized in the photoelectrolysis and photocatalysis experiments, respectively. The use of such a cell was helpful for the clear analysis of the reaction products. For salt bridge preparation (in Scheme S1 and Scheme 1), agar (1.3 g) and KNO₃ (4.74 g) were first dissolved in hot water $(1.0 \times 10^{-2} \text{ dm}^3)$, and then, the mixture was allowed to flow into the bridging part of the cell and to solidify at room temperature. For measuring cyclic voltammograms, a single-compartment electrochemical glass cell was used and equipped with a modified ITO working electrode (effective area, 1 cm²), spiral Pt

counter electrode and Ag/AgCl (in saturated KCl electrolyte solution) reference electrode (see Fig. S2).

Voltammetric measurement and potentiostatic electrolysis were performed using a potentiostat (Hokuto Denko, HA-301) with a function generator (Hokuto Denko, HB-104), coulomb metre (Hokuto Denko, HF-201) and X–Y recorder (GRAPHTEC, WX-4000) under illumination.

Gaseous products were analysed using a gas chromatograph equipped with a thermal conductivity detector (Shimadzu, GC-8A), which contains a 5 Å molecular sieve column and Ar carrier gas. Quantification of gaseous products was performed using a chromatogram analyzer (Shimadzu, C-R8A) equipped with the chromatograph.

Calculation methods:

The <u>Faradaic efficiency (F.E.)</u> of N_2 evolution was calculated according to the following procedure:

i) During the photoelectrochemical decomposition of N_2H_4 , the amount of charge passed was measured by a coulomb metre. Based on the charge amount, the theoretical amount of N_2 evolved was estimated.

ii) After the photoelectrochemical reaction, the amount of N_2 evolved was quantified by a gas chromatograph.

Therefore, the F.E. value can be estimated using the following equation:

F.E. (%) = [amount of N₂ evolved]/[theoretical amount of N₂] × 100 = [amount of N₂ evolved]/[(amount of charge passed)/(nF)] × 100,

where n is the number of electrons that participated in the evolution of N₂ (n = 4 for the oxidation of N₂H₄ into N₂), and F is the Faraday constant (i.e. $9.65 \times 10^4 \text{ C} \cdot \text{mol}^{-1}$).

The external quantum efficiency (EQE) of H₂ evolution was estimated as follows:

EQE (%) =
$$(N_A \times M)/(I \times A) \times 100$$
,

where N_A is Avogadro's number (particles·mol⁻¹), M is the amount of reacted electrons in H₂ evolution (mol), I is the number of incident photons at a given wavelength (particles·cm⁻²) and A is the effective area of the photocatalyst film employed (in the present system: 1 cm²).

Function of Nf as absorbent

As for the Nf absorbent employed in this study, it can increase the surface concentration of N_2H_4 , effectively acting on the rate-limiting oxidation (see the main text). Considering the acid dissociation constant (pK_a) of the terminal sulfonic acid in Nf (pKa = -6) [7] and that of the hydrazinium ions [pK_{a1} (H₃N⁺–NH₃⁺/H₃N⁺–NH₂) = -0.9, pK_{a2} (H₃N⁺–NH₂/H₂N–NH₂) = 7.9],[8] N₂H₄ dissolved in the electrolyte solution (pH = 11) is once incorporated within Nf, following which N₂H₄ is most probably protonated to H₃N⁺–NH₃⁺ in the hydrophilic environment surrounded by sulfonic ions. Through such a procedure, N₂H₄ can be considered to be concentrated in Nf; however, the hydrazinium ions (i.e. the protonated species of N₂H₄) cannot undergo oxidation into one molecule of N₂, because the oxidation point on the hydrazinium ion(s) is blocked.

As the concentration of the hydrazinium ions in Nf increases, some ions are pushed out into the interfacial region (between the hydrophilic and hydrophobic regions)[9] where the deprotonated species, N_2H_4 , can be oxidized successfully to N_2 .

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Photoelectrolysis cell



Scheme S1 Schematic illustration of a twin-compartment cell employed for photoelectrolysis study.

Structural characterization



Fig. S1 (a) Absorption spectrum of $C_{60}/ZnPc$ (blue line, the bilayer employed in the present study; red line, the sum of the single components, i.e. C_{60} and ZnPc). Film thickness: C_{60} -200 nm, ZnPc-150 nm. (b) A typical SEM image of the photocatalyst device employed, i.e. ITO/ $C_{60}/ZnPc/Nf$.

The absorption spectrum of the present $C_{60}(200 \text{ nm})/\text{ZnPc}(150 \text{ nm})$ bilayer was compared with the sum of the absorption spectra of C_{60} (200 nm) and ZnPc (150 nm). As a result, both were coincident with each other, indicating no formation of a new band (such as a CT absorption band).

The resulting SEM image exhibited a layered structure of the photocatalyst device, which also showed that Nafion membrane is loaded on top of the $C_{60}/ZnPc$ bilayer (cf. for the observation of the microscopic image, the typical thicknesses of the components were not employed).

Cyclic voltammograms



Fig. S2 Cyclic voltammograms measured at ITO/C₆₀/ZnPc/Nf and ITO/C₆₀/ZnPc. Film thickness C₆₀, 200 nm; ZnPc, 150 nm; Nf, 1 μ m; hydrazine solution, 5 mM (pH = 11); light intensity, ca. 70 mW·cm⁻²; scan rate, 20 mV·s⁻¹. A schematic illustration of a single-compartment cell employed for voltammogram measurements is also depicted.

Those results are supported by previous evidence (see references in the main text) that the p-type surface in the p-n bilayer can induce oxidation along with photophysical events in the p-n interior.

Dependence of the amounts of H_2 and N_2 evolved on applied potentials in the photoelectrochemical decomposition of N_2H_4



Fig. S3 The relationship between the amounts of H_2 and N_2 evolved in photoelectrolysis in the presence of N_2H_4 and applied potentials. The photoelectrolysis was conducted by employing the experimental system shown in Scheme S1. The conditions employed were similar to Entry 1 in Table 1 except that applied potentials changed.

Working electrode, ITO/C₆₀/ZnPc/Nf (photoanode). Film thickness: C₆₀-200 nm, ZnPc-150 nm, Nf-1 μ m; effective area (i.e. geometrical area) of the photoelectrode: 1 cm²; electrolyte solution in Compartment A, 5 mM N₂H₄ (pH = 11); electrolyte solution in Compartment B, H₃PO₄ (pH = 2); light intensity, ca. 70 mW·cm⁻²; irradiation direction, back side of the ITO-coated face; electrolysis time, 1 h.

The photoelectrochemical hydrazine decomposition into N_2 and H_2 was studied with respect to applied potentials. The amounts of N_2 and H_2 decreased by applying less positive potentials to the photoanode, and consequently, no decomposition of hydrazine occurred at around -0.3 V (vs. Ag/AgCl). It probably means that the onset potential for hydrazine decomposition is approximately close to the position of the conduction band of n-type C_{60} ; in other words, when the applied potential is less positive than the conduction band of n-type C_{60} , little exchange of electrons between C_{60} and a base electrode (i.e. ITO) can occur.

Dependence of the amount of H_2 evolved in the photocatalytic decomposition of N_2H_4 by light intensity



Fig. S4 Relationship between the irradiated light intensity and evolved amount of H_2 in Compartment B. Film thickness C_{60} , 200 nm; ZnPc, 150 nm; Nf, 1 µm; geometrical area of photocatalyst device (ITO/ C_{60} /ZnPc/Nf), 1 cm²; hydrazine solution in Compartment A, 5 mM (pH = 11); electrolyte solution in Compartment B, H_3PO_4 (pH = 0); irradiation time, 1 h. The dashed line indicates the condition employed in Entry 1 in Table 2.

For intensities greater than 30 mW·cm⁻², the amount of H₂ evolved was not proportional to light intensity, indicating that the generation of carriers is not the rate-limiting step under those conditions.

Dependence of the amount of H_2 evolved on film thickness in the photocatalytic decomposition of N_2H_4



Fig. S5 Relationship between the film thickness of $C_{60}/ZnPc/Nf$ and the amount of H_2 evolved through the photocatalytic decomposition of N_2H_4 . The conditions for Entry 1 in Table 2 were applied to this study, except that the thickness varied. In (a) and (b), the photocatalytic study was conducted by changing the thickness of only one layer (i.e. C_{60} (a) or ZnPc (b)) in the bilayer. In the part of (c), the $C_{60}/ZnPc$ bilayer of a constant thickness was employed for the photocatalytic study, where only the Nf thickness changed.

Film thickness of Nf (for a and b), 1 μ m; Film thickness of the bilayer (for c): C₆₀-200 nm, ZnPc-150 nm; N₂H₄ solution in Compartment A, 5 mM (pH = 11); electrolyte solution in Compartment B, H₃PO₄ (pH = 0); light intensity, ca. 70 mW·cm⁻²; irradiation time, 1 h. The dashed line indicates the condition employed in Entry 1 of Table 2. Irradiation was carried out from the back side of the ITO-coated face.

The optimum thickness of the C_{60} layer was investigated by maintaining the thickness of ZnPc (150 nm) constant and varying the C_{60} thickness (Fig. S5a). This experiment indicated that a thickness of 200 nm for the C_{60} layer was the most effective. A thickness of greater than 200 nm for the C_{60} layer may induce an optical filter effect, disturbing the light absorption of C_{60} as well as ZnPc next to the p–n interface, leading to lower H₂ evolution.

When the thickness of C_{60} was maintained constant (200 nm), the optimum ZnPc thickness was found to be 150 nm (Fig. S5b), indicating that a thick layer of ZnPc was effective for carrier generation. However, a thickness of greater than 150 nm for the ZnPc layer led to a decreasing amount of H₂. In ZnPc farther away from the p–n interface, week absorption can occur, resulting in inefficient carrier generation.

Fig. S5c shows the relationship between the amount of H_2 evolved and the thickness of Nf combined with the optimal C_{60} /ZnPc bilayer. The H_2 amount was approximately constant with more than 1 µm of the Nf thickness. Although a photocatalytic reaction may be kinetically dominated by the surface concentration of reactant as well as carrier, this result indicated that 1-µm-thick Nf, which was typically employed in the present study, is an optimum; in other words, the amount of N_2H_4 in 1-µm-thick Nf is sufficiently high for the photocatalytic decomposition of hydrazine.

The results of Figs. S4 and S5 reveal that the experimental conditions for Entry 1 in Table 2 are appropriate for the present photocatalysis system.

Schematic energy diagram



Fig. S6 A schematic diagram for the decomposition of N_2H_4 in the photocatalysis system of $ITO/C_{60}/ZnPc/Nf$ and Pt wire.

As stated in introduction in the main text, carrier generation takes place through a series of photophysical events within the C₆₀/ZnPc bilayer. The stoichiometric decomposition of N₂H₄ into N₂ and H₂ corresponds to a down-hill reaction ($\Delta G^{\circ} = -378.3 \text{ kJ} \cdot \text{mol}^{-1} < 0$), as realized from the diagram. N₂H₄ concentrated in Nf can be oxidized by hole attained at ZnPc surface. Considering the energy level of valence band representative of oxidizing power under illumination, ZnPc (5.2 eV [1]) is equal to the previously studied H₂Pc (5.2 eV [2, 3]); however, in separate experiment, we confirmed that the organic p-n bilayer of C₆₀/H₂Pc cannot induce the photocatalytic decomposition of hydrazine. A Zn ion coordinated with phthalocyanine may play a roll of the activation point for hydrazine oxidation although we would like to leave the clarification of the further details as a future subject.

While, reducing power generated at C_{60} can transferred to the site of Pt, where the formation of H_2 from H^+ can occur. The detailed mechanism of H_2 evolution at C_{60} in an organic p/n bilayer has been clarified previously by the authors [3].

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