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# Efficient organo-photocatalysis system of an n-type perylene derivative/p-type cobalt phthalocyanine bilayer for the production of molecular hydrogen from hydrazine

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**The stoichiometric decomposition of hydrazine (N<sub>2</sub>H<sub>4</sub>) into N<sub>2</sub> and H<sub>2</sub> was observed to occur efficiently in a photocatalysis system of an organic p–n bilayer. The primary feature of the present system is that the entire visible-light energy spectrum is available for N<sub>2</sub>H<sub>4</sub> decomposition. Furthermore, this paper presents the first demonstration of H<sub>2</sub> formation by reducing power photogenerated at n-type perylene derivative in an organic bilayer.**

## Introduction

Solar hydrogen has attracted attention as a potential clean energy technology for establishing a sustainable society and is actively investigated by photoelectrochemistry and photocatalysis.<sup>1,2</sup> Ever since Honda and Fujishima reported a photoelectrochemical water-splitting system with UV-responsive TiO<sub>2</sub>,<sup>3</sup> photocatalysis researchers have aimed to extend the visible-light response of catalyst in longer-wavelength regions, particularly to enhance its photocatalytic activity towards the water-splitting reaction. However, the literature contains few examples of photocatalysts capable of H<sub>2</sub>/O<sub>2</sub> evolution, even in the near-infrared region;<sup>4–7</sup> i.e. the conventional photocatalysts of band-engineered semiconductors usually exhibit diminished activity because of band-gap reduction, which is a serious issue that needs to be addressed.

We studied and reported photocatalysis systems featuring an organic p–n bilayer in terms of H<sub>2</sub> evolution from H<sup>+</sup><sup>8,9</sup> as well as the decomposition of trimethylamine, alcohol and thiol into CO<sub>2</sub>,<sup>10,11</sup> thereby demonstrating novel approaches to

photocatalysis. These organo-photocatalysis systems can utilise the entire visible-light energy spectrum, where a series of photophysical events (i.e. exciton formation, charge separation at a heterojunction and subsequent hole and electron conduction within p-type and n-type layers, respectively) can be induced in a manner similar to that in corresponding photovoltaic systems.<sup>12,13</sup> Thus, a photocatalytic reaction can be achieved by oxidising and reducing power generated at the surface of p-type and n-type conductors, respectively.

In this study, a photocatalysis system of a 3,4,9,10-perylenetetracarboxylic-bis-benzimidazole (PTCBI, n-type)/cobalt(II) phthalocyanine (CoPc, p-type) bilayer was applied to the decomposition of a carbon-free hydrogen storage material, i.e. hydrazine (N<sub>2</sub>H<sub>4</sub>). The literature contains only a few examples of UV-responsive TiO<sub>2</sub> photocatalysts capable of photocatalysing the decomposition of N<sub>2</sub>H<sub>4</sub> into N<sub>2</sub> and H<sub>2</sub> through a four-electron transfer (*vide infra*).<sup>14</sup> We recently reported a novel instance of a bilayer of n-type C<sub>60</sub> and p-type Zn phthalocyanine (ZnPc) photocatalytically inducing the stoichiometric decomposition of N<sub>2</sub>H<sub>4</sub>, particularly under visible-light irradiation;<sup>8</sup> however, the photocatalytic activity of the present system is twice that of our previous system (based on a comparison of the optimised photocatalysis systems). Here, we present and discuss the details of the photocatalytic decomposition of N<sub>2</sub>H<sub>4</sub> by a PTCBI/CoPc bilayer.

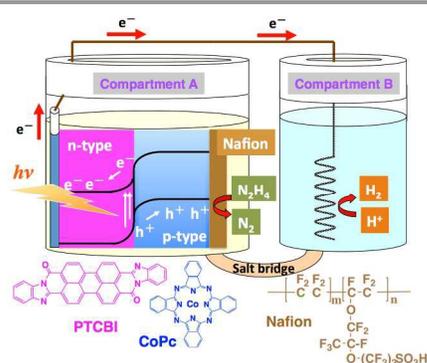
## Experimental

The PTCBI/CoPc bilayer was prepared by vapour deposition (pressure, <1.0 × 10<sup>−3</sup> Pa; deposition speed, ca. 0.03 nm·s<sup>−1</sup>), and an indium-tin oxide (ITO)-coated glass plate was used as the base material. The organic bilayer comprised PTCBI coated on ITO, and CoPc coated on top of the PTCBI layer (denoted as ITO/PTCBI/CoPc). Furthermore, a Nafion membrane (denoted as Nf) was used in combination with the bilayer, where (i) an alcoholic solution of Nf was cast onto the CoPc surface, followed by solvent evaporation under air, resulting in (ii) the loading of a 1-μm-thick Nf film onto that surface (the resulting photocatalytic device is abbreviated as ITO/PTCBI/CoPc/Nf). A cell of twin compartments separated by a salt bridge was

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† Electronic Supplementary Information (ESI) available: Experimental details, function and role of Nf as absorbent, illustration of twin-compartment cell used for photoelectrolysis experiments, cyclic voltammograms, action spectrum for photocurrents, absorption spectra of PTCBI/CoPc bilayer and single-layered CoPc, photocatalysis data for N<sub>2</sub>H<sub>4</sub> decomposition with respect to film thickness of photocatalyst device of PTCBI/CoPc, light intensity, hydrazine concentration and pHs employed in compartment B. See DOI: 10.1039/x0xx00000x



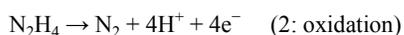
**Scheme 1** Twin-compartment cell employed for photocatalysis experiments and the structures of the chemicals used in this study.

utilised for photocatalytic experiments (see Scheme 1). Other experimental details are provided in the ESI†.

## Results and discussion

ITO/PTCBI/CoPc and ITO/PTCBI/CoPc/Nf were applied to photoanodes in an aqueous phase containing  $N_2H_4$ ; this setup was used for the initial evaluation of these devices (see Figure S1 in the ESI†). The resulting voltammograms exhibited photoanodic characteristics due to  $N_2H_4$  oxidation (in each case, almost no electrochemical response was recorded in the absence of light). These results are consistent with those reported in our previous work, where the p-type material/water interface in an organic p–n bilayer induced oxidation under irradiation.<sup>15</sup> The aforementioned voltammetric characteristics also revealed that ITO/PTCBI/CoPc/Nf is superior to ITO/PTCBI/CoPc. This result indicates that Nf functions as an absorbent material for  $N_2H_4$ , thus producing in a high surface concentration of the reactant, ensuring its efficient oxidation. Details of the function and role of Nf in the oxidation of  $N_2H_4$  are provided in the ESI†.<sup>8</sup>

Photoelectrochemical decomposition of  $N_2H_4$  at the organo-photoelectrodes was conducted under a potentiostatic condition of +0.3 V (vs. Ag/AgCl); a twin-compartment cell was used in this study (see Scheme S1 in the ESI†). Photoelectrolysis data related to the decomposition of  $N_2H_4$  are presented in Table 1. In the cases of both ITO/PTCBI/CoPc/Nf (Entry 1) and ITO/PTCBI/CoPc (Entry 2), the stoichiometric decomposition of  $N_2H_4$  into  $N_2$  (oxidation product) and  $H_2$  (reduction product) was confirmed to occur according to the following equations (eqs. 1, 2 and 3):



When the faradaic efficiency (F.E.) of  $N_2$  formation from  $N_2H_4$  was estimated under the assumption of a four-electron transfer oxidation (i.e. eq. 2), the F.E. values for Entries 1 and 2 were calculated to be >90% (see the ESI† for the F.E. calculation procedure). The  $N_2H_2$  intermediate may be formed through a two-electron transfer oxidation of  $N_2H_4$  (i.e.  $N_2H_4 \rightarrow N_2H_2 + 2H^+ + 2e^-$ ), followed by the further spontaneous decomposition of  $N_2H_2$  (i.e.  $N_2H_2 \rightarrow N_2 + H_2$ ).<sup>16</sup> However, such processes can be neglected, i.e. in the case of  $N_2$  formation via  $N_2H_2$ , the F.E.

Table 1 Results of photoelectrolysis in the presence of hydrazine.<sup>a</sup>

System	$N_2$ evolved / $\mu$ l (compartment A)	$H_2$ evolved / $\mu$ l (compartment B)	Note
Entry 1 <sup>b</sup>	53.1	115.8	Full conditions
Entry 2 <sup>c</sup>	38.7	80.2	Without Nf
Entry 3 <sup>c</sup>	1.72	0	Without applied potential <sup>d</sup>
Entry 4 <sup>c</sup>	0	0	Without irradiation
Entry 5 <sup>c</sup>	0	0	In the absence of $N_2H_4$

<sup>a</sup> ITO/PTCBI/CoPc/Nf was used as the photoanode, except in the case of Entry 2. <sup>b</sup> Film thickness: PTCBI = 200 nm, CoPc = 150 nm, Nf = 1  $\mu$ m; effective area (i.e. geometrical area) of the photoelectrode: 1  $cm^2$ ; electrolyte solution in compartment A, 5 mM  $N_2H_4$  (pH = 11); electrolyte solution in compartment B,  $H_3PO_4$  (pH = 2); applied potential, +0.3 V vs. Ag/AgCl (satd.); light intensity,  $\sim 70 \text{ mW}\cdot\text{cm}^{-2}$ ; irradiation direction, back side of the ITO-coated face; electrolysis time, 1 h. <sup>c</sup> Each potentiostatic electrolysis experiment was performed under conditions similar to those used for ITO/PTCBI/CoPc/Nf (i.e. Entry 1). <sup>d</sup> Irradiation of ITO/PTCBI/CoPc/Nf in compartment A was conducted in an open circuit.

value should be only ca. 50%; in addition, particularly in compartment A (see Scheme S1), no detection of  $H_2$  from  $N_2H_4$  was confirmed in the present study. As supported by the aforementioned voltammograms (see Fig. S1), the results in Table 1 also indicate that ITO/PTCBI/CoPc/Nf is the more efficient photoanode for  $N_2H_4$  decomposition than ITO/PTCBI/CoPc. Furthermore, the results of control experiments (i.e. Entries 3, 4 and 5) indicate that the efficient decomposition of  $N_2H_4$  can occur, particularly when employing the complete components of Entry 1.

Photocatalytic decomposition of  $N_2H_4$  was conducted in a system of ITO/PTCBI/CoPc/Nf (oxidation site) and Pt wire (reduction site) (see Scheme 1). The results are listed in Table 2, including the results for the control experiments. The stoichiometric  $N_2H_4$  decomposition was observed to occur in the constructed photocatalysis system (i.e. Entry 1). In a control experiment, the photocatalytic decomposition of  $N_2H_4$  was conducted in the presence of  $O_2$  (electron acceptor), where only compartment B was left under aerobic conditions (i.e. Entry 2). A comparison of the results for Entry 2 with those for Entry 1 revealed that the amount of  $N_2$  evolved is almost invariable. The similarity of these results indicates that the rate-limiting oxidation of  $N_2H_4$  can proceed at ITO/PTCBI/CoPc/Nf. The Nf absorbent resulted in an increase in the surface concentration of  $N_2H_4$  (*vide supra*); thus, its use can lead to an enhancement of the rate-determining reaction. Furthermore, a lack of components in Entry 1 in Table 2 for the experimental results of negative control experiments (i.e. Entries 3, 4 and 5) indicates inactivity towards  $N_2H_4$  decomposition.

Factors affecting the photocatalysis of  $N_2H_4$  decomposition—specifically, the thickness of film employed (Figure S2 in the ESI†), the light intensity (Figure S3 in the ESI†) and the  $N_2H_4$  concentration in compartment A (Figure S4 in the ESI†)—were examined. These results demonstrated that the conditions listed in Entry 1 in Table 2 were the most appropriate conditions for operating the present photocatalysis system.

ITO/PTCBI/CoPc/Nf was also used in a prolonged photocatalysis study. This study was conducted under the aforementioned optimum conditions, except that the concentration of  $N_2H_4$  was 10 mM. The amounts of  $N_2$  and  $H_2$  evolved after 12 h of irradiation ( $N_2$  amount, 265.7  $\mu$ l;  $H_2$  amount, 548.4  $\mu$ l) were almost proportional to those after 1 h of

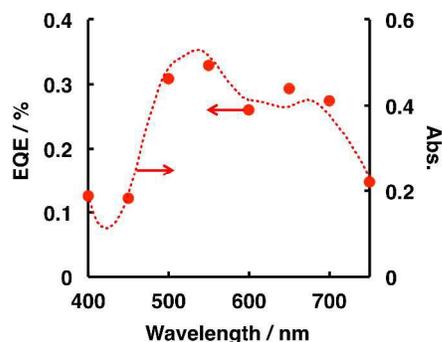
Table 2 Results of photocatalytic  $N_2H_4$  decomposition in the photocatalysis system of ITO/PTCBI/CoPc/Nf and a Pt wire (see Scheme 1).<sup>a</sup>

System	$N_2$ evolved / $\mu$ l (compartment A)	$H_2$ evolved / $\mu$ l (compartment B)	Note
Entry 1 <sup>b</sup>	20.5	41.1	Full conditions
Entry 2 <sup>c</sup>	18.6	---	Aerobic atmosphere in compartment B
Entry 3 <sup>c</sup>	1.72	0	No connection between ITO/PTCBI/CoPc/Nf and Pt wire
Entry 4 <sup>c</sup>	0	0	Without irradiation
Entry 5 <sup>c</sup>	0	0	In the absence of $N_2H_4$
Entry 6 <sup>d</sup>	10.7	20.4	Data for $N_2H_4$ decomposition in $C_{60}/ZnPc$ photocatalysis system (ref. 8)

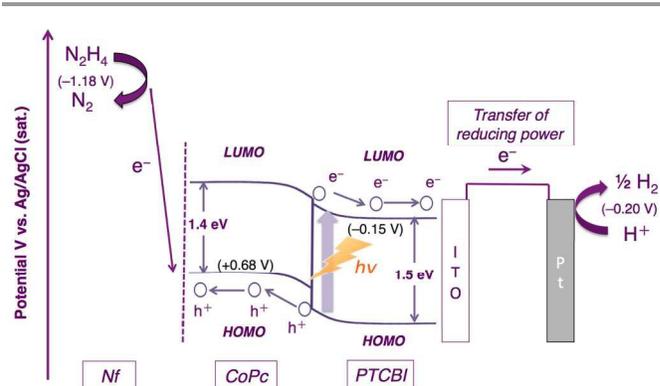
<sup>a</sup> These experiments were conducted under a greater chemical bias between the compartments compared to those listed in Table 1. <sup>b</sup> Film thickness: PTCBI = 200 nm, CoPc = 150 nm, Nf = 1  $\mu$ m; effective area (i.e. geometrical area) of the photocatalytic device, 1  $cm^2$ ; electrolyte solution in compartment A, 5 mM  $N_2H_4$  (pH = 11); electrolyte solution in compartment B,  $H_3PO_4$  (pH = 0); light intensity,  $\sim 70$   $mW \cdot cm^{-2}$ ; irradiation direction, back side of the ITO-coated face; irradiation time, 1 h. <sup>c</sup> Controlled experiments were performed under conditions similar to those for Entry 1. <sup>d</sup> The experimental conditions were the same as those listed for Entry 1 in this table, except that a photocatalyst device of 200-nm  $C_{60}$ , 150-nm  $ZnPc$  and 1- $\mu$ m Nf was used.

irradiation ( $N_2$  amount, 22.3  $\mu$ l;  $H_2$  amount, 45.8  $\mu$ l), indicating stable performance of the present photocatalysis system.

The external quantum efficiency (EQE) was estimated on the basis of the amount of  $H_2$  evolved (see the ESI<sup>†</sup> for the EQE calculation procedure), where the decomposition of  $N_2H_4$  photocatalysed by ITO/PTCBI/CoPc/Nf under irradiation by monochromatic light was studied. Figure 1 shows the relation between EQE values and radiation wavelength; the resulting EQE values are consistent with the absorption spectrum of the PTCBI monolayer (Fig. 1) rather than with the spectrum of the PTCBI/CoPc bilayer (Figure S5 in the ESI<sup>†</sup>). Moreover, the  $N_2H_4$  decomposition was induced over the entire visible-light wavelength region of  $\lambda < 750$  nm. Such action spectral characteristics originating from the sole absorption of PTCBI in an organic p-n bilayer have been reported by the authors.<sup>15,17,18</sup> The details are discussed in the following paragraph, along with the mechanism of  $N_2H_4$  decomposition.



**Figure 1** Dependence of the EQE value (closed circles) on the incident wavelength in the ITO/PTCBI/CoPc/Nf and Pt wire photocatalysis system and the absorption spectrum (dashed line) of PTCBI single layer. The conditions for Entry 1 in Table 2 were used for the EQE measurements, except that monochromatic light was used. The irradiated intensity for the photocatalytic device was  $0.83$   $mW \cdot cm^{-2}$ .



**Scheme 2** Decomposition of  $N_2H_4$  in the photocatalysis system of ITO/PTCBI/CoPc/Nf and a Pt wire.

The photocatalysis system of ITO/PTCBI/CoPc/Nf is discussed with respect to the  $N_2H_4$  decomposition mechanism. A schematic for the present  $N_2H_4$  decomposition is presented in Scheme 2. The photocatalytic function of the PTCBI/CoPc bilayer originates in the absorption of visible light by PTCBI (see Figs. 1 and S1), thus resulting in the generation of oxidising power at the CoPc surface via a series of photophysical events within the p-n bilayer (see Introduction). An exciton, photogenerated within the PTCBI layer, can consequently undergo charge separation into electrons and holes at the heterojunction, followed by carrier conduction through the PTCBI and CoPc layers, respectively. In other words, the CoPc layer needs to transport hole carriers towards  $N_2H_4$  oxidation occurring at the phthalocyanine surface when the visible-light absorption of CoPc cannot participate in carrier generation (refer to a supporting result in Figure S6 in the ESI<sup>†</sup>). The formal potential of  $CoPc^+/CoPc$  (estimated to be  $+0.68$  V vs. Ag/AgCl from refs. 19 and 20) is more positive than that of  $N_2/N_2H_4$  ( $-1.18$  V (at pH = 11) vs. Ag/AgCl)<sup>21</sup>; thus, in compartment A, the photocatalytic oxidation of  $N_2H_4$  into  $N_2$  is reasonably assumed to occur at the CoPc surface. Reducing power photogenerated at PTCBI is transferred to the Pt wire (i.e. co-catalyst for  $H_2$  evolution) in compartment B where the reduction of  $H^+$  into  $H_2$  can occur; notably, however, the formal potential of PTCBI/PTCBI<sup>-</sup> (i.e.  $-0.15$  V vs. Ag/AgCl, as estimated on the basis of data from refs. 22-24) is very similar to that of  $H^+/H_2$  (i.e.  $-0.20$  V (at pH = 0) vs. Ag/AgCl). To gain insight into the process of  $H_2$  formation induced by PTCBI<sup>-</sup>, we conducted a separate experiment to examine the relation between the amount of  $H_2$  evolved and pH in compartment B. As shown in Figure S7 in the ESI<sup>†</sup>, decreasing amounts of  $H_2$  were formed with increasing pH. This result may indicate that the PTCBI/PTCBI<sup>-</sup> potential is independent of pH, thus leading to a shortage of reducing power for  $H_2$  evolution at a high pH (i.e. the difference between the PTCBI/PTCBI<sup>-</sup> and  $H^+/H_2$  potentials is enhanced by an increase in pH level). The magnitude of steady concentration of electrons at the Pt wire is associated with the magnitude of reducing power for  $H_2$  formation; i.e. efficient  $H_2$  evolution at pH = 0 is attributed to an effective gain of reducing power based on the locally concentrated electrons.

## Conclusions

In the present study, we demonstrated a novel photocatalysis system featuring a PTCBI/CoPc bilayer, which led to the

stoichiometric decomposition of  $N_2H_4$  into  $N_2$  and  $H_2$  over the complete visible-light wavelength range ( $\lambda < 750$  nm). Furthermore, this paper included the first instance of  $H_2$  evolution originating from the reducing power of PTCBI (i.e. PTCBI<sup>-</sup>). We recently reported an optimised photocatalysis system of an n-type  $C_{60}$ /p-type ZnPc bilayer for  $N_2H_4$  decomposition,<sup>8</sup> however, the photocatalytic activity of the present system is double that of the  $C_{60}$ /ZnPc system (see Entry 6 in Table 2). A large built-in potential at the heterojunction can lead to a high carrier concentration, which is critical to the rate-limiting step in the photocatalytic reaction. However, the built-in potentials in both systems were constant (according to a previous procedure,<sup>18</sup> the potential in each system was estimated to be ca. 400 mV). Although the details are currently unclear, the more efficient activity in the PTCBI/CoPc system is speculated to originate from the higher steady concentration of holes for the rate-limiting  $N_2H_4$  oxidation. We first realised and clarified the instance of  $C_{60}$  (n-type) participating in  $H_2$  formation,<sup>25</sup> and, in the current paper, revealed that PTCBI is also an n-type organic material capable of  $H_2$  generation. Organophotocatalysts have an advanced characteristic in that the entire visible-light spectrum is available to photocatalyse reactions. The development of such organophotocatalysts is expected to open a path to the large-scale production of solar hydrogen. Towards this end, materials and active structures with p–n bilayers based on the abundant varieties of organic semiconductors must be developed to realise efficient photocatalysis.

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