Development of dual-functional catalysis for hydrazine oxidation by an organic p–n bilayer through in situ formation of a silver co-catalyst†

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Dual-functional catalysis indicates that an organic p–n bilayer induces the catalytic oxidation involved in downhill reactions, not only under illumination but also in the dark. When the organo-bilayer is composed of a perylene derivative (3,4,9,10-perylenetetracarboxylic-bis-benzimidazole (PTCBI), n-type) and cobalt phthalocyanine (CoPc, p-type), only the photocatalytic oxidation of hydrazine (N₂H₄) occurs. However, the loading of Ag co-catalyst onto the CoPc surface in the PTCBI/CoPc bilayer successfully led to dual catalysis in terms of the oxidation of N₂H₄ to N₂. To develop the present dual catalysis Ag loading was essential to achieve the catalysis performance particularly without irradiation.

Experimental

PTCBI was synthesized according to a reported procedure and purified by sublimation prior to use. CoPc was purchased from...
Tokyo Chemical Industry and used as received. Indium tin oxide (ITO)-coated glass plate (sheet resistance = 8 Ω cm\(^{-2}\); transmittance ≥ 85%; and ITO thickness = 174 nm) was acquired from AGC Inc. \(\text{N}_2\text{H}_4\) and Nafion (Nf) alcoholic solution were purchased from Kanto Chemical and Sigma-Aldrich, respectively. All other chemicals employed were of extra pure grade.

The PTCBI/CoPc bilayer was fabricated by vapor deposition (pressure ≤ 1.0 × 10\(^{-3}\) Pa; deposition speed = 0.03 nm s\(^{-1}\)),\(^{28}\) in which PTCBI was first coated on an ITO, followed by coating CoPc on top of the PTCBI layer. The thickness of the organo-bilayer was determined by measuring a UV-VIS absorption spectrum. Determination procedure of the thickness with each layer has so far been described elsewhere.\(^{28}\) Silver(i) oxide was synthesized according to a reported procedure.\(^{28}\) Silver(i) nitrate (0.58 g) was dissolved in water (50 mL), and the pH value of the aforementioned AgNO\(_3\) solution was adjusted to pH 11 using 1 M NaOH solution. The resulting solution was maintained by stirring overnight, following which Ag\(_2\)O was collected by filtration and dried at 70 °C. The resulting particles of Ag\(_2\)O (13 mg) were suspended in 1 wt% Nafion (Nf) alcoholic solution (1 mL). The mixture solution (23 μL) was dropped on the CoPc surface in the PTCBI/CoPc bilayer and dried at 70 °C. The fabricated electrode is denoted as PTCBI/CoPc-Nf[Ag\(_2\)O] (i.e., effective area = 1 cm\(^2\); thickness of Nf = 1 μm; loaded amount of Ag\(_2\)O = ca. 1.3 μmol cm\(^{-2}\)). Nf membrane was employed as the absorbent for \(\text{N}_2\text{H}_4\) and support for Ag\(_2\)O. In the present study, the controlled electrode free of Ag\(_2\)O was also prepared and used (denoted as PTCBI/CoPc-Nf).

The structural analyses of Ag\(_2\)O and Ag were performed using an X-ray diffractometer (XRD: Rigaku, SmartLab 9 kW), a tunneling electron microscope (TEM: JEOL, JEM-2100) and a scanning electron microscope (SEM: JEOL, JSM-7000F).

When measuring voltammograms and photocurrents for acquiring an action spectrum, a single-compartment cell was operated using a potentiostat (Hokuto Denko, HA-301) equipped with a function generator (Hokuto Denko, HB-104), a coulomb meter (Hokuto Denko, HF-201), and an X-Y recorder (see Scheme S2†). Particularly for the action spectral measurements, the light source was used in the combination with a monochromator (Soma Optics, Ltd, S-10) for irradiating monochromatic light.

The electrolysisis study was performed in a twin-compartment cell separated by a salt bridge (Scheme 1). PTCBI/CoPc-Nf[Ag\(_2\)O] and Pt were placed as oxidation site in a \(\text{N}_2\text{H}_4\) solution (5 mM, pH = 11) and as reduction site in a phosphoric acid solution (pH = 0), respectively. Ag/AgCl reference was set along with the Pt counter. For preparing the salt bridge, both agar (1.3 g) and KNO\(_3\) (4.7 g) were dissolved in hot water (10 mL). Subsequently, the mixture was allowed to flow into the bridging part of the cell, followed by its solidification at room temperature. The twin-compartment cell for electrolysis reaction was operated using the aforementioned electrochemical apparatus.

A halogen lamp was used for irradiating the organo-bilayer. The light intensity was measured using a power meter (type 3A from Ophir Japan, Ltd), and the intensity was determined at approximately 100 mW cm\(^{-2}\), except for the action spectral measurement. The gaseous products of \(\text{N}_2\) and \(\text{H}_2\) were analyzed using a gas chromatograph (GL Sciences, GC-3200) equipped with a thermal conductivity detector (column, 5 Å molecular sieve; carrier gas, Ar). Additional experimental details are described in the ESI†.

**Results and discussions**

First, the voltammograms of PTCBI/CoPc-Nf[Ag\(_2\)O] were measured in the dark and under irradiation (see Scheme S2†) and compared with those of PTCBI/CoPc-Nf. Similar to our previous study,\(^{28}\) PTCBI/CoPc-Nf induced the oxidation of \(\text{N}_2\text{H}_4\) only under irradiation (Fig. 1(a)). However, when loading Ag\(_2\)O on the PTCBI/CoPc bilayer, irrespective of irradiation, anodic currents occurred at PTCBI/CoPc-Nf[Ag\(_2\)O] because of the \(\text{N}_2\text{H}_4\) oxidation (Fig. 1(b)). Electrochemical oxidation of \(\text{N}_2\text{H}_4\) was examined under potentiostatic conditions (see Scheme 1), and the electrolysis data are summarized in Table 1. The oxidative formation of \(\text{N}_2\) from \(\text{N}_2\text{H}_4\) was confirmed in the dark along with the reduction of \(\text{H}^+\) to \(\text{H}_2\). Moreover, the \(\text{N}_2\) (oxidation product) and \(\text{H}_2\) (reduction product) amounts increased significantly under irradiation (note in each case the faradaic efficiency of the \(\text{N}_2\) and \(\text{H}_2\) formation was estimated to be >85% and >90%, respectively), which are consistent with the aforementioned voltammetric characteristics of Fig. 1(b). As a supplementary explanation, the oxidation of \(\text{N}_2\text{H}_4\) to \(\text{N}_2\text{H}_2\) and subsequent spontaneous decomposition of \(\text{N}_2\text{H}_2\) to \(\text{N}_2\) and \(\text{H}_2\) (ref. 37) are considered not to occur in the present system because no formation of \(\text{H}_2\) was confirmed in the oxidation site in Scheme 1.

It is important to verify how Ag\(_2\)O participated in the \(\text{N}_2\text{H}_4\) oxidation, particularly in the dark (vide supra). To clarify the catalytically active Ag species for the \(\text{N}_2\text{H}_4\) oxidation, X-ray diffractometer (XRD) patterns were measured (Fig. 2). For reference, the XRD pattern of PTCBI/CoPc-Nf is shown in Fig. 2(a). In the unused PTCBI/CoPc-Nf[Ag\(_2\)O] (Fig. 2(b)), the resulting XRD pattern was characterized by cubic Ag\(_2\)O.\(^{38}\) From
the XRD patterns after the electrolysis in the dark (Fig. 2(c)) and under irradiation (Fig. 2(d)), the formation of cubic Ag was confirmed, indicating a reductive transformation of Ag₂O in the presence of N₂H₄. The XRD pattern depicted in Fig. S1† indicates that the Ag formation is probably occurring during the Ar purge of the electrolyte solution (30 min) prior to the electrochemical measurements. Comparing the potentials of +0.70 V vs. SHE (pH = 11) for $E^\circ_\text{CoO/Co} = +0.93$ V vs. SHE, pH = 11) and $E^\circ_\text{Ag/AgCl} = +0.32$ V vs. SHE, pH = 11), the reduction of Ag₂O to Ag can occur reasonably using N₂H₄ as reductant (i.e., N₂H₄ + 2Ag₂O → N₂ + 4Ag + 2H₂O). Thus, the present dual catalysis for N₂H₄ oxidation originates from the in situ formation of Ag co-catalyst at the PTCBI/CoPc bilayer, revealing that Ag₂O does not collaboratively show photocatalytic activity for the N₂H₄ oxidation along with the organo-bilayer (vide supra). Some TEM and SEM images of Ag₂O (or Ag) dispersed in Nf membrane were observed. As for the samples prior to electrochemical study, those TEM images indicated the particle sizes were approximately <10 nm and 3–35 nm for Ag₂O and Ag, respectively (Fig. S2(a) and (b)†). The SEM images were observed for PTCBI/CoPc-Nf[Ag₂O] exposed to the N₂H₄ solution under Ar purge (Fig. S3(a)†) as well as that after photoelectrolysis (Fig. S3(b)†). Each image was almost the same as each other, indicating that Ag transformed from Ag₂O remains unchanged even after the photoelectrolysis. That is, the aggregation and growth of Ag particles was not be recognized after its use.

The N₂H₄ oxidation occurring at PTCBI/CoPc-Nf[Ag₂O] is represented in Scheme 2. In the dark, the potential of CoIIIPc (corresponding to the lower edge of the conduction band: $E^\circ_\text{Co/Co} = 0.32$ V vs. SHE, pH = 11) is available for the N₂H₄ oxidation, and thus, N₂H₄ is catalytically oxidized at the Ag-loaded CoPc surface. When the photoinduced oxidation of N₂H₄ occurs, the oxidizing power is generated at the top edge of the valence band of CoPc (i.e., CoIII-Pc, +0.93 V vs. SHE, pH = 11) through a series of the photophysical events within the organo-bilayer (vide supra). According to the resulting action spectrum for photocurrents (Fig. 3), the photoinduced N₂H₄ oxidation occurred originating in the absorption of PTCBI over the entire visible light region. This is a specific characteristic usually observed

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Table 1. Typical photoelectrolysis data of the decomposition of N₂H₄ by PTCBI/CoPc/Nf[Ag₂O] under illumination and in the dark.

| Entry | H₂ evolved/μL | N₂ evolved/μL | Note |
|-------|---------------|----------------|------|
| 1     | 14.3          | 8.08           | In the dark |
| 2     | 94.8          | 48.4           | Under irradiation |

Film thickness: PTCBI = 205 nm and CoPc = 60 nm; electrolyte solution (oxidation site), an aqueous N₂H₄ solution (5 mM, pH = 11); electrolyte solution (reduction site), an aqueous H₃PO₄ solution (pH = 0); applied potential, +0.3 V (vs. Ag/AgCl); reaction time, 3 h. Irradiation was conducted from the backside of ITO-coated face (light intensity, 100 mW cm⁻²).

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The N₂H₄ oxidation occurring at PTCBI/CoPc-Nf[Ag₂O] is represented in Scheme 2. In the dark, the potential of CoIIIPc (corresponding to the lower edge of the conduction band: $E^\circ_\text{Co/Co} = 0.32$ V vs. SHE, pH = 11) is available for the N₂H₄ oxidation, and thus, N₂H₄ is catalytically oxidized at the Ag-loaded CoPc surface. When the photoinduced oxidation of N₂H₄ occurs, the oxidizing power is generated at the top edge of the valence band of CoPc (i.e., CoIII-Pc, +0.93 V vs. SHE, pH = 11) through a series of the photophysical events within the organo-bilayer (vide supra). According to the resulting action spectrum for photocurrents (Fig. 3), the photoinduced N₂H₄ oxidation occurred originating in the absorption of PTCBI over the entire visible light region. This is a specific characteristic usually observed.

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Scheme 2. Mechanism of the dual-functional catalysis for N₂H₄ oxidation occurring at PTCBI/CoPc-Nf[Ag₂O] under illumination and in the dark.
Such catalysis for N$_2$H$_4$ oxidation did not occur at the Ag-free in situ ment of the present dual-functional catalysis was attributed to Ag$_2$O in the presence of N$_2$H$_4$ as reductant, whereby the catalytic oxidation of N$_2$H$_4$ effectively occurred even in the dark. Such catalysis for N$_2$H$_4$ oxidation did not occur at the Ag-free PTehbi/CoPc bilayer. Therefore, the so-called dual-functional catalysis is a novel catalytic process for oxidation reactions, irrespective of irradiation. The loading of a co-catalyst on an organo-bilayer is expected to expand the application for several types of downhill reactions, opening new opportunities in the field of pollutant degradation.

**Conclusion**

In summary, the oxidation of N$_2$H$_4$ to N$_2$ occurred successfully at the PTehbi/CoPc bilayer under irradiation and in the dark, particularly by loading Ag on the CoPc surface. The development of the present dual-functional catalysis was attributed to the in situ formation of Ag through the reductive transformation of Ag$_2$O in the presence of N$_2$H$_4$ as reductant, whereby the catalytic oxidation of N$_2$H$_4$ effectively occurred even in the dark. Consequently, the photoinduced N$_2$H$_4$ oxidation is noticeably superior to the oxidation in the dark. In thermodynamic sense, the N$_2$H$_4$ oxidation can occur at the CoPc in the dark. However, to induce kinetically the forward oxidation of N$_2$H$_4$ to N$_2$ particularly in the dark, the Ag co-cocatalyst needs to be loaded.

**Conflicts of interest**

There are no conflicts to declare.

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