<center>**Supporting Information (SI)**</center>

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

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Calculation procedures

The **faradaic efficiency (*F.E.*)** was calculated as follows:

i) During the electrolysis reaction, the amount of charge passed was measured using a coulomb meter. The theoretical amount of formed N_2 (or H_2) was calculated from the obtained charge amount.

ii) After conducting the electrolysis reaction, both N_2 and H_2 were quantified by gas chromatography.

Concretely, the *F.E.* value for the formation of N_2 (or H_2) was estimated according to the following equation:

$$F.E. \ (\%) = [\text{amount of } N_2 \text{ (or } H_2\text{) evolved}]/[\text{theoretical amount of } N_2 \text{ (or } H_2\text{)}] \times 100$$
$$= [\text{amount of } N_2 \text{ (or } H_2\text{) evolved}]/[(\text{amount of charge passed})/(nF)] \times 100$$

where n is the number of electrons participating in the evolution of the products ($n = 4$ and 2 for the formation of N_2 and H_2, respectively) and F represents the Faraday's constant (9.65×10^4 C mol^{-1}).

The **incident photon-to-current conversion efficiency (*IPCE*)** was estimated according to the following equation:

$$IPCE \ (\%) = ([I/e]/[W/\varepsilon]) \times 100$$

where I (A cm^{-2}) is the photocurrent density, e (C) denotes the elementary electric charge, W (W cm^{-2}) is the light intensity, and ε is the photon energy of monochromatic light.
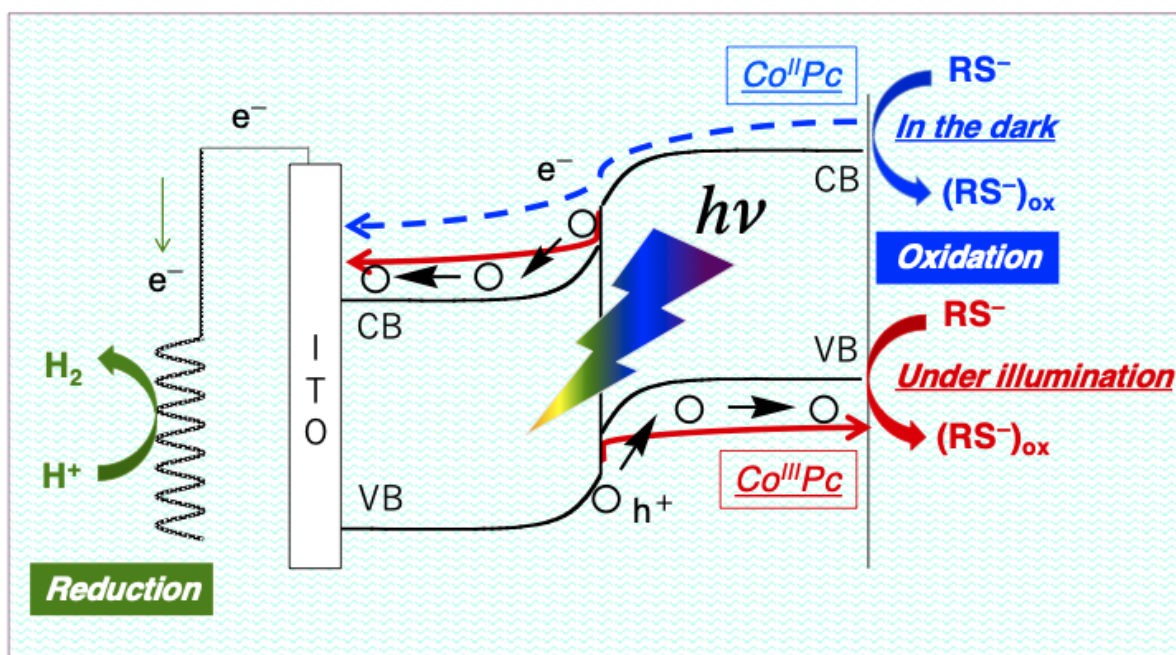
Scheme S1 Mechanism of the dual-functional catalysis for thiol (RS⁻) oxidation occurring at PTCBI/CoPc-Nf in the dark and under illumination.
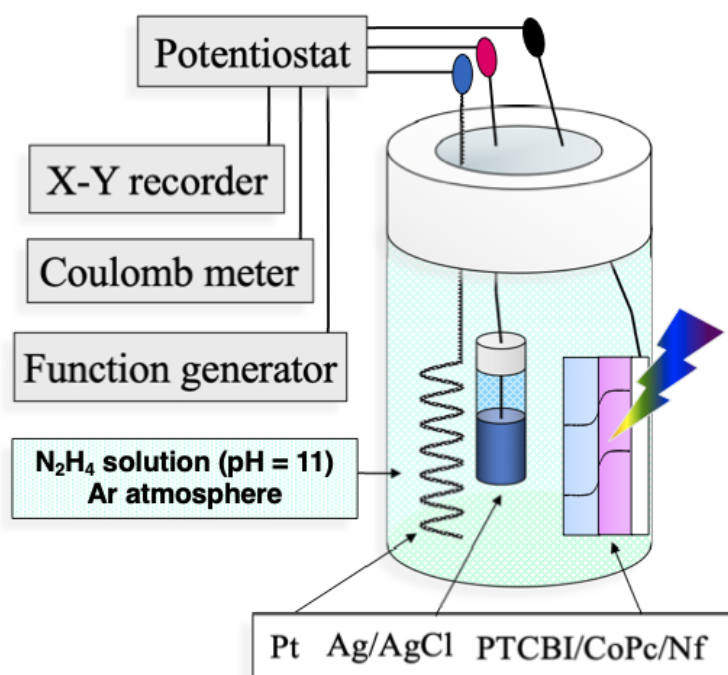
Scheme S2 Illustration of the photoelectrochemical cell employed for measuring both voltammograms and photocurrents under potentiostatic conditions.
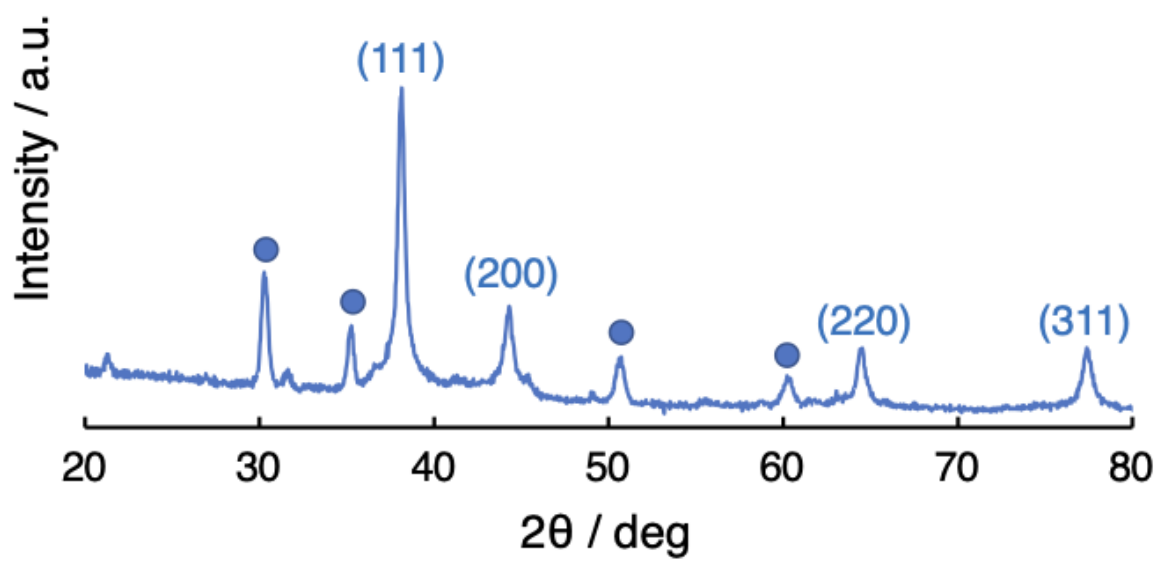
Fig. S1 XRD pattern of PTCBI/CoPc-Nf[Ag$_2$O] measured after Ar purge of the N$_2$H$_4$ solution for 30 min. As for the closed circles, those are consistent with Fig. 2(a).
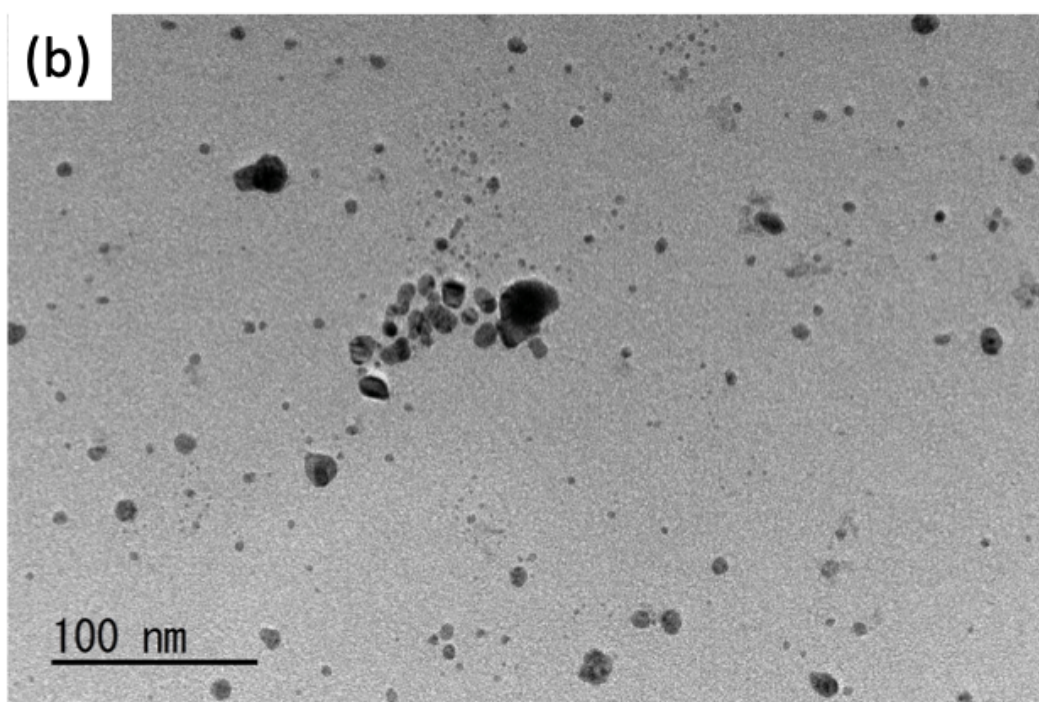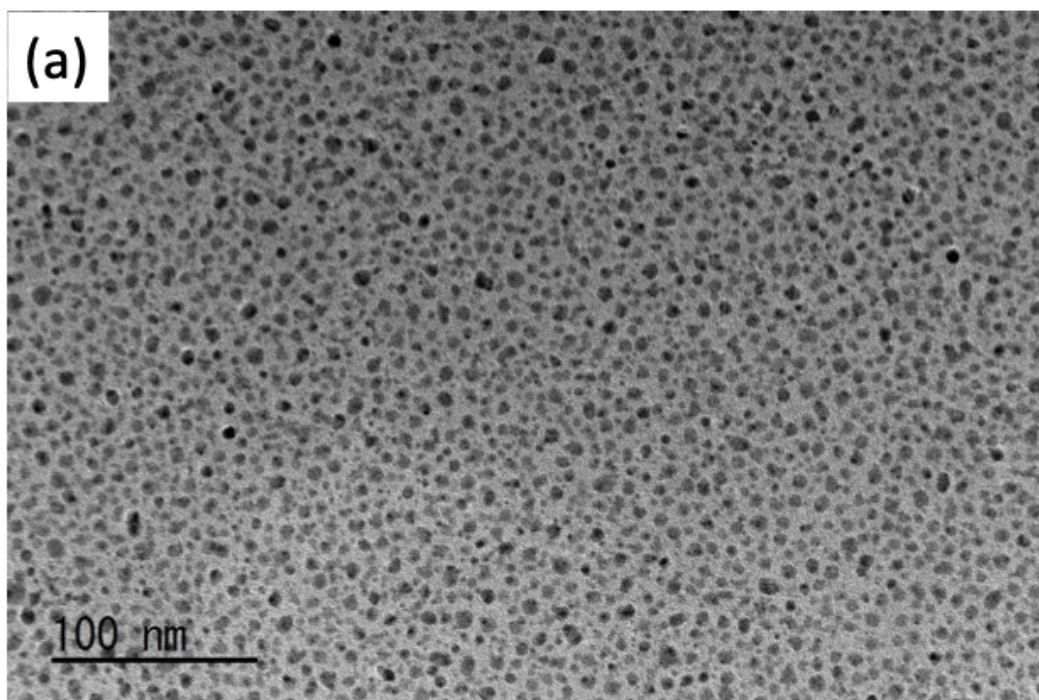
Fig. S2 TEM images of Ag$_2$O dispersed in a Nf membrane. A 4×10^{-5} dm^3 portion of the suspension, composed of Nf and Ag$_2$O (see main text), was cast onto a collodion membrane supported on a copper grid mesh and dried at room temperature.

(a), Ag$_2$O sample after drying; (b), the sample exposed to a N$_2$H$_4$ solution under Ar purge (i.e., Ag).
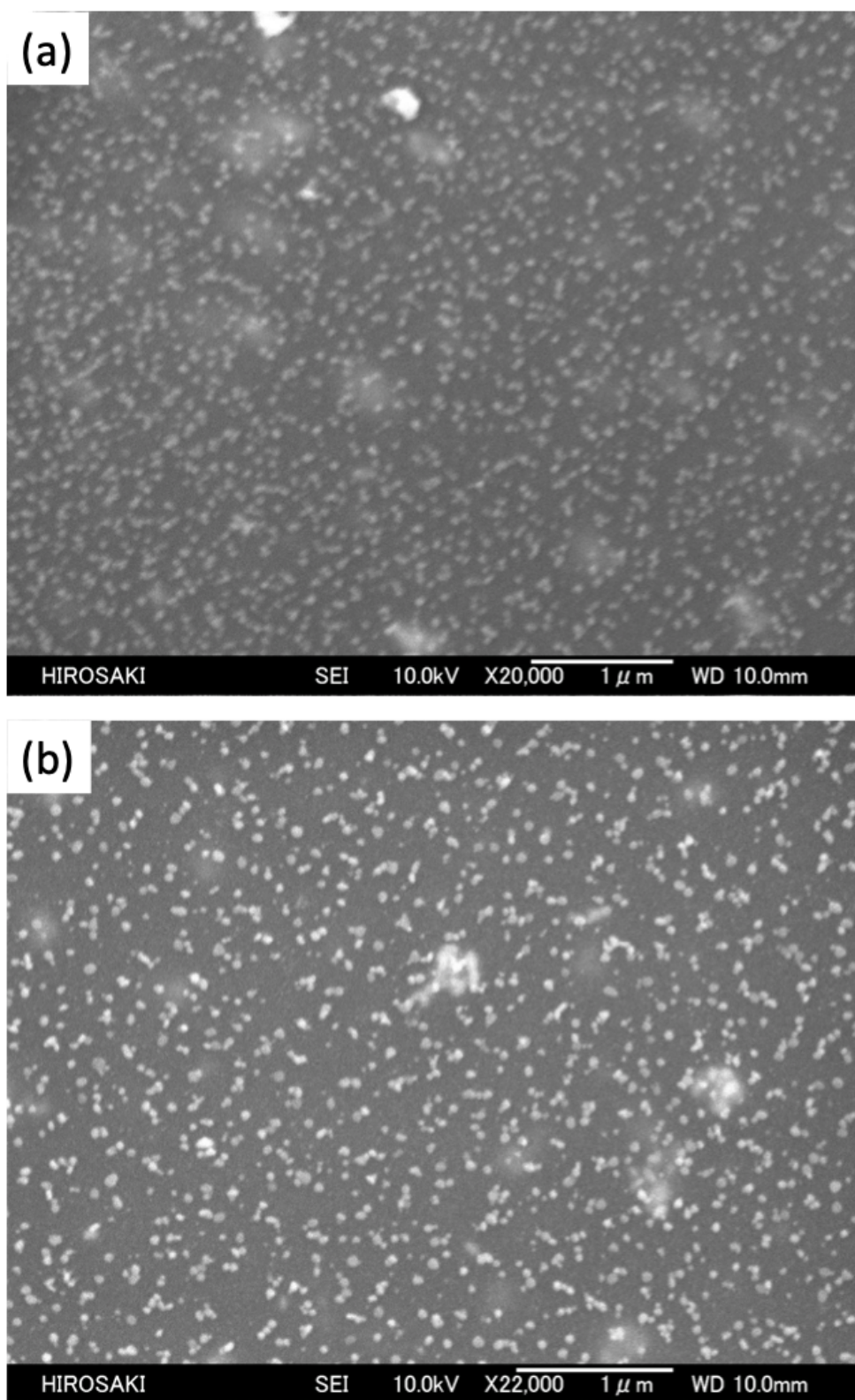
Fig. S3 SEM images of PTCBI/CoPc-Nf[Ag_2O].

(a), the sample exposed to a N_2H_4 solution under Ar purge (i.e., Ag); (b), the sample after the photoelectrolysis.