

Electronic Supplementary Information

**Photoelectrochemical Reduction of CO₂ to Formate over a Hybrid
System of CuInS₂ Photocathode and Formate Dehydrogenase under
Visible Light Irradiation**

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a) Fabrication of CuInS₂ photocathode

The CuInS₂ photocathode was fabricated by sequential electrodeposition of Cu and In on a Mo substrate (Nilaco, 99.95 %) and subsequent sulfurization treatment, according to a report on the preparation of CuInS₂ films. An electrochemical cell consisting of a Mo substrate working electrode, a Pt counter electrode, and an Ag/AgCl (3.0 M NaCl, 0.209 V vs. SHE) reference electrode. The applied potential of the working electrode was controlled by using a potentiostat (VersaSTAT 4, Princeton Applied Research Co., Ltd.). For Cu deposition, an aqueous solution (50 mL) containing both 10 mM of CuSO₄·5H₂O (99.5%, Wako Pure Chemical Co., Ltd.) and 10 mM of citric acid (98.0%, Wako Pure Chemical Co., Ltd.) was used (pH = ~2.4). Cu deposition on the Mo working electrode was then conducted with a constant applied potential of -0.4 V vs. Ag/AgCl until the charge density that passed through the outer circuit exceeded 1042 mC cm⁻². (for about 25 min). For In deposition, an aqueous solution (50 mL) containing 30 mM of InCl₃·4H₂O (97.0%, Wako Pure Chemical Co., Ltd.), 36 mM of trisodium citrate dihydrate (99.0%, Wako Pure Chemical Co., Ltd.) and 10 mM of citric acid was used (pH = ~2.8). The applied potential was fixed to -0.78 V vs. Ag/AgCl until the charge density that passed through the outer circuit exceeded 1200 mC cm⁻² (for about 15 min).

The deposited In/Cu/Mo samples were sulfurized by heating in a stream of H₂S according to the procedure shown in Fig.S1. The sample was placed on the inside of a quartz tube (i.d.: 26 mm), and then the gas inside was thoroughly purged with a stream of N₂ gas (99.999%, 100 mL min⁻¹) at room temperature. The temperature of the sample was increased to 110 °C at 20 °C

min⁻¹ and then maintained for 60 min. The temperature was then increased to 520 °C at 40 °C min⁻¹. The N₂ gas stream was replaced with diluted H₂S (5 vol% in Ar, 10 mL min⁻¹) immediately upon reaching 520 °C to avoid the unfavorable formation of a solid solution of In and Cu at high temperatures. After maintaining this sample temperature for 30 min, the stream of H₂S/Ar was changed to 99.999% N₂ gas (100 mL min⁻¹). Finally, the sample was cooled naturally. The obtained sample was rinsed in water, immersed in 10% aqueous KCN for 2 min (to remove the surface Cu_xS layers that were generated during sulfurization), thoroughly washed with water, and finally dried at room temperature.

b) Surface modification of CuInS₂ photocathode

The CuInS₂/Mo samples were modified with CdS, by which charge separation in CuInS₂ is generally enhanced, by a chemical bath deposition (CBD) method according to a report. CuInS₂/Mo sample was immersed in 100 mL of an aqueous solution containing both 2.51 mmol of Cd(CH₃COO)₂ (98.0%, Wako Pure Chemical Co., Ltd.) and 0.67 mol of NH₄OH (98.0%, Wako Pure Chemical Co., Ltd.) at 75 °C for 1 min in order to adsorb Cd²⁺ onto the CuInS₂. Then, 38.09 mmol of SC(NH₂)₂ (98.0%, Wako Pure Chemical Co., Ltd.) was added to the solution, and the CuInS₂/Mo sample was immersed for 180 s. After the CdS deposition, the sample was rinsed in water.

Pt particles as reduction sites were loaded onto CdS/CuInS₂/Mo samples by a PEC deposition method. The CdS/CuInS₂/Mo sample was immersed in 0.1 M Na₂SO₄ (75 mL) containing 15.25 μmol of H₂PtCl₆•6H₂O (pH adjusted to 9.5 with NaOH), and then irradiated with a Xe lamp (300 W, Cermax, LX-300F) at a potential of -0.66 V vs Ag/AgCl.

c) Photoelectrochemical measurement

The electrochemical cell used for the photocurrent measurements consisted of prepared electrode, a counter electrode (Pt wire), a Ag/AgCl reference electrode, and a sodium phosphate buffer solution (pH = 7) containing 1,1'-dimethyl-4,4'-bipyridinium dichloride (MV, 10 mM, Tokyo Chemical Industry Co., Ltd.). The phosphate buffer solution was prepared by mixing 0.1 M Na₂HPO₄ aq. and 0.1 M NaH₂PO₄ aq. The potential of the working electrode was controlled using the potentiostat. The solution was purged with Ar for over 20 min prior to the measurement. The electrodes were irradiated by a 300 W Xe lamp (LX-300F, Cermax) fitted with a cut-off filter (L-42, Hoya) to block light in the UV region. The irradiated area was 2.25 cm² (1.5 × 1.5 cm²).

For the CO₂ reduction reaction, a two-compartment cell divided by Nafion membrane was used (each solution volume = 15 mL, each dead volume = 12 mL). In the ion chromatograph (Dionex ICS-1100, detector; electrical conductivity, column; Thermo ICE-AS1 9 × 150 mm),

the peak of PO_4^{3-} ions slightly overlaps that of HCOO^- ions; hence, an N-2-hydroxyethylpiperazine-N-2-ethane sulfonic acid (HEPES) buffer solution (pH= 7) was used as the electrolyte instead of a phosphate buffer solution. MV (10 mM) and FDH from *Candida boidinii* (20 units corresponding to 38.5 nmol, Sigma-Aldrich Co. LLC.) were added to the cathode side. The applied potential was set to 0.21 V vs. RHE. CO_2 gas was bubbled into the solution at a flow rate of approximately 30 mL min^{-1} . The produced formate was detected by an ion chromatograph.

d) IPCE measurement

The IPCE was calculated using the following equation:

$$\text{IPCE [\%]} = 1240 \times \text{photocurrent density [\text{mA cm}^{-2}]} \times 100 / (\text{wavelength [\text{nm}]} \times \text{photon flux [\text{mW cm}^{-2}]})$$

IPCE measurements were performed under monochromatic irradiation, emitted from a Xe lamp (MAX-303, Asahi Spectra Co. Ltd., Japan) equipped with bandpass filters (central wavelength: 500, 600, and 700 nm; full width at half maximum: 10 nm) and a variable neutral density filter. Monochromatic photon fluxes at each wavelength were measured using a Si photodiode power meter (9742, Hioki E. E. Co.) and were adjusted to around 1.5 mW cm^{-2} using the neutral density filter. The masked-off irradiated area was 0.48 cm^2 .

e) Turnover number and faradaic efficiency

Turnover number and faradaic efficiency were calculated using the following equations, respectively.

$$\text{Turnover number} = [\text{Number of produced formate}] / [\text{Number of used FDH}]$$

$$\text{Faradic efficiency [\%]} = [\text{Number of reacted electrons}] / [\text{Number of electrons passing through the outer circuit}] \times 100$$

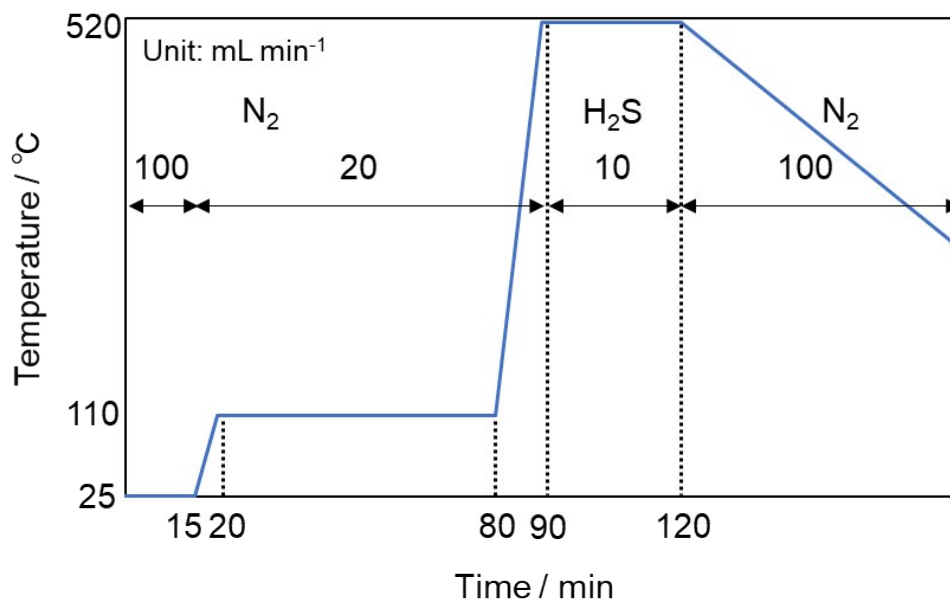


Figure S1. Time profile of heat treatment for sulfurization of In/Cu/Mo sample.

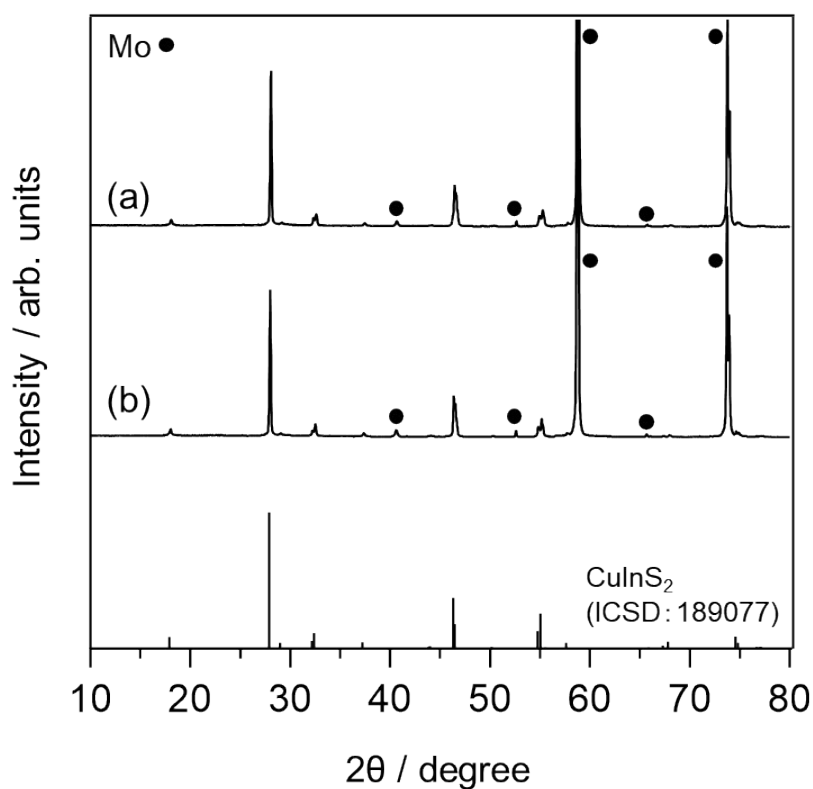


Figure S2. XRD pattern of CuInS_2 electrode (a) before and (b) after KCN etching.

Anode, Cathode sides: 0.1 M Phosphate buffer
Cathode side: 5mM MV

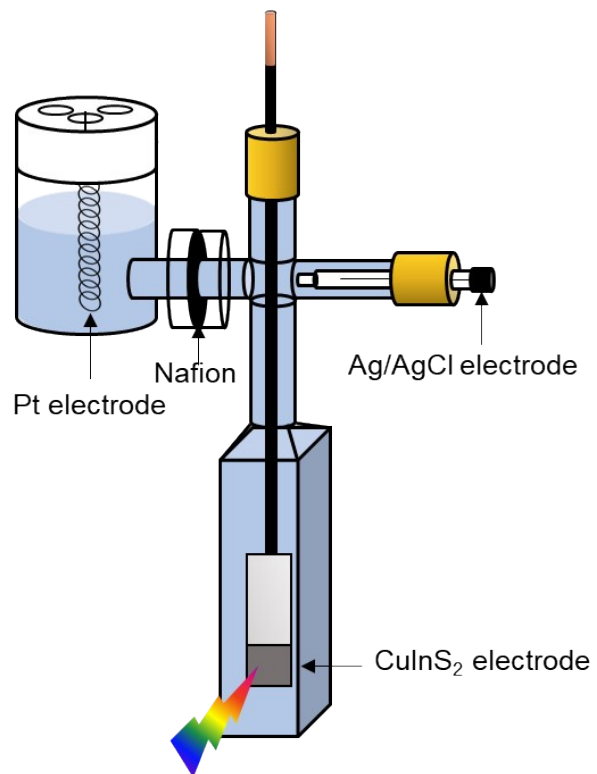


Figure S3. Electrochemical cell for measurement of UV-vis absorption.