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Supporting Information

Platinum and Indium Sulfide-Modified CuInS₂ as Efficient Photocathodes for Photoelectrochemical Water Splitting

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Experimental Methods

1. Synthesis of the CuInS₂ thin film

The CuInS₂ thin film was synthesized by electrodeposition of Cu and In layers followed by sulfurization. Electrodeposition was carried out potentiostatically using a Hokuto Denko HSV-100 potentiostat-galvanostat under N₂ atmosphere without stirring. A vertical three-electrode setup consisting of an Ag/AgCl reference electrode, a Pt wire counter electrode, and an Mo-coated glass substrate (Mo/glass) as a working electrode (area of the working electrode being 0.7 cm²) was employed. The electrolyte solution for Cu deposition consisted of 50 mM CuSO₄, 150 mM trisodium citrate, and 242 mM citric acid. The solution was adjusted to pH 2.4 using H₂SO₄. For In deposition, the electrolyte solution consisted of 30 mM InCl₃, 242 mM citric acid, and 36 mM trisodium citrate. Potentials used for Cu and In deposition were -0.2 V and -0.76 V (vs. Ag/AgCl), respectively. Electric charges of Cu and In deposition were fixed at 0.73 C and 0.84 C, respectively: this resulted in the composition ratio of Cu and In (Cu/In) in a Cu and In stacked layer of 1.3. The Cu/In stack as-deposited was then heated at 160 °C for 30 min under Ar flow (200 mL min⁻¹), followed by sulfurization at 560 °C under H₂S flow (5% H₂S in Ar, 200 mL min⁻¹) for 10 min in a glass tube furnace. Thus-obtained CuInS₂ films were then etched by immersion in an aqueous KCN solution (10%) for 2 min to remove excess Cu_xS components.

2. Surface modifications of the CuInS₂ thin film

A CuInS₂ thin film was added to an aqueous solution containing 12.5 mM CdSO₄, 0.22 M thiourea, and 11 M of ammonia; deposition of CdS was performed at 60 °C for 7 min. For In₂S₃ deposition, the CuInS₂ thin film was immersed in an aqueous solution containing 25 mM In₂(SO₄)₃, 0.1 M thioacetamide and 0.1 M acetic acid at 65 °C for 15 min. CdS and In₂S₃ layers were also deposited on an FTO glass substrate for transmittance measurements. Loading of platinum deposits on bare CuInS₂ and these modified-CuInS₂ thin films was conducted by photoirradiation of the films in an N₂-saturated 0.1 M

Na₂SO₄ solution containing 1 mM H₂PtCl₆ (with pH adjusted to 4.0) at -0.1 V (vs. Ag/AgCl) for 10 min. An Asahi Spectra HAL320 solar simulator was used as a light source.

3. PEC measurements

PEC water splitting was also performed using the three-electrode setup in an aqueous solution of 0.1 M Na₂SO₄ with pH adjusted to pH 9.0 under N₂ or Ar. Transient photocurrents were obtained by scanning applied potentials with a scan rate of 10 mV s⁻¹ under chopped illumination of simulated AM 1.5 solar irradiation from the above solar simulator. Applied bias photon-to-current efficiency (ABPE) for photocathode¹ was calculated from the data according to the following equation:

$$\text{ABPE} [\%] = J \times V_b \times 100 / P_{\text{AM1.5}}$$

where J (mA cm⁻²) is the measured photocurrent density, V_b (V) is the bias voltage measured by the reversible hydrogen electrode (RHE) scale (E_{RHE} , see below), and $P_{\text{AM1.5}}$ is the photon flux of the AM 1.5 simulated sunlight (100 mW cm⁻²). Incident photon-to-current conversion efficiency (IPCE) spectra of Pt-In₂S₃/CuInS₂ and Pt-CdS/CuInS₂ were also calculated using the following equation:

$$\text{IPCE} [\%] = 1240 \times J \times 100 / (\lambda \times P_i)$$

where J (mA cm⁻²) is the measured photocurrent density, λ is the wavelength of incident photons and P_i is the incident light intensity (mW cm⁻²). The measurement was performed at -0.73 V (vs. Ag/AgCl) by the lock-in technique using an NF LI5630 digital lock-in amplifier. For the measurement, photoirradiation was performed by chopping at 10 Hz of monochromatic light, which was obtained by passing light from the solar simulator through a monochromator. The number of incident photons was determined by an OPHIR Orion Laser power meter equipped with a photodiode. A PEC cell connected to an online gas chromatography system (INFICON 3000 Micro GC Gas Analyzer equipped with an MS-5 A column and a thermal conductivity detector) was used to detect H₂ and O₂ during the PEC water splitting. The PEC cell was immersed in a water bath to maintain the reaction temperature at 288 K, and photoirradiation was performed at -0.73 V (vs. Ag/AgCl) by using a Cermax LX-300F 300 W xenon lamp. The potentials in each measurement measured versus Ag/AgCl electrode ($E_{\text{Ag/AgCl}}$) were converted into E_{RHE} using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.199.$$

4. Characterizations

Crystal structures were measured by X-ray diffraction (XRD) using a Rigaku MiniFlex X-ray diffractometer (Cu K α , Ni filter). Surface morphologies were examined using a Hitachi S-5000 FEG field emission scanning electron microscope (FE-SEM). Elemental compositions of thus-obtained films were determined using a Hitachi TM3000 scanning electron microscope equipped with a Swift ED3000 energy dispersive X-ray spectrometer (EDX). Transmittance spectra of CdS and In₂S₃ layers deposited on an FTO glass substrate were measured by a Hitachi U-4100 UV/vis/NIR spectrometer.

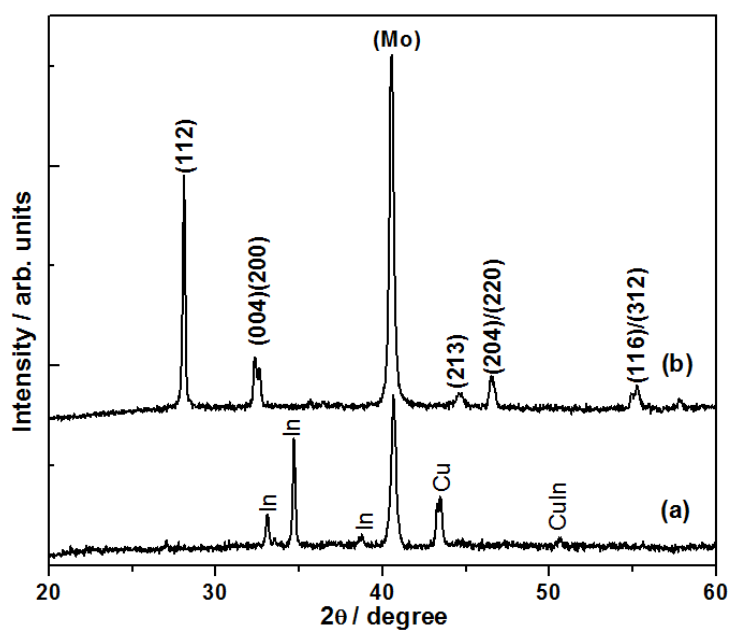


Fig. S1 XRD patterns of (a) as-deposited and (b) sulfurized samples.

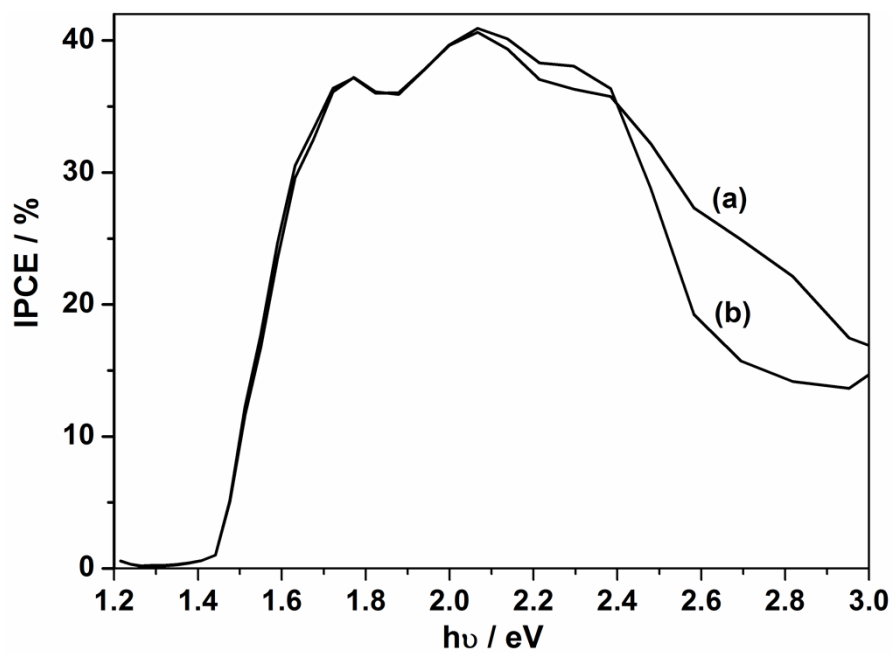


Fig. S2 IPCE curves of (a) Pt-In₂S₃/CuInS₂ and (b) Pt-CdS/CuInS₂ measured in 0.1 M Na₂SO₄ (pH 9) at 0 V (vs. RHE).

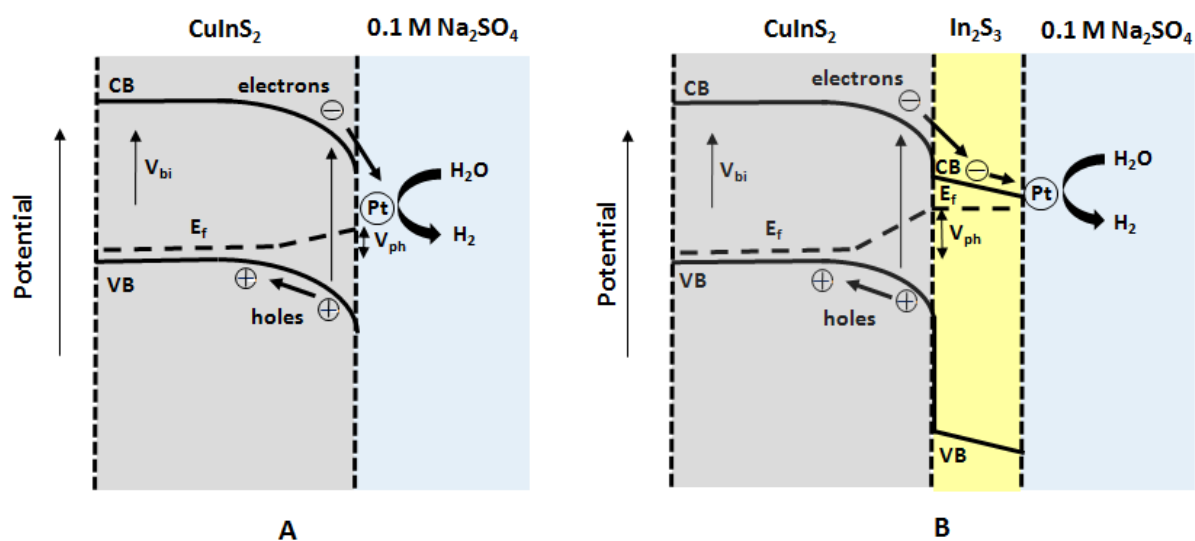


Fig. S3 Qualitative band diagrams for Pt-CuInS₂ (A) and Pt-In₂S₃/CuInS₂ (B) photocathodes under illumination in a 0.1 M Na₂SO₄ solution. CB, VB, E_f, V_{bi} and V_{ph} represent conduction band, valence band, fermi level, built-in potential and photovoltage, respectively. For the system (A), electrons are excited to the CB of p-CuInS₂, leaving holes at VB, the photogenerated electrons, then are driven to the surface by V_{bi} where they may reduce protons to molecular hydrogen at Pt particles, whereas the photogenerated holes will be transferred through back contact to counter electrode to perform oxygen evolution. In the system (B), the photogenerated electrons in p-CuInS₂ drift to the n-type In₂S₃ part in the gradient of the V_{bi}, contributing electrons to the surface where they may reduce protons to molecular hydrogen at Pt particles. A higher V_{ph} is generated on the Pt-In₂S₃/CuInS₂ photocathode due to the presence of the higher V_{bi} at the p-n interface.

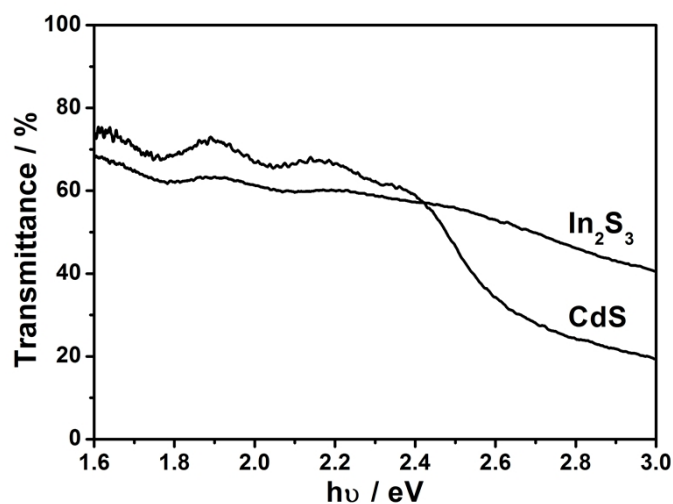


Fig. S4 Transmission spectra of In₂S₃ and CdS film on an FTO substrate prepared by chemical bath deposition.

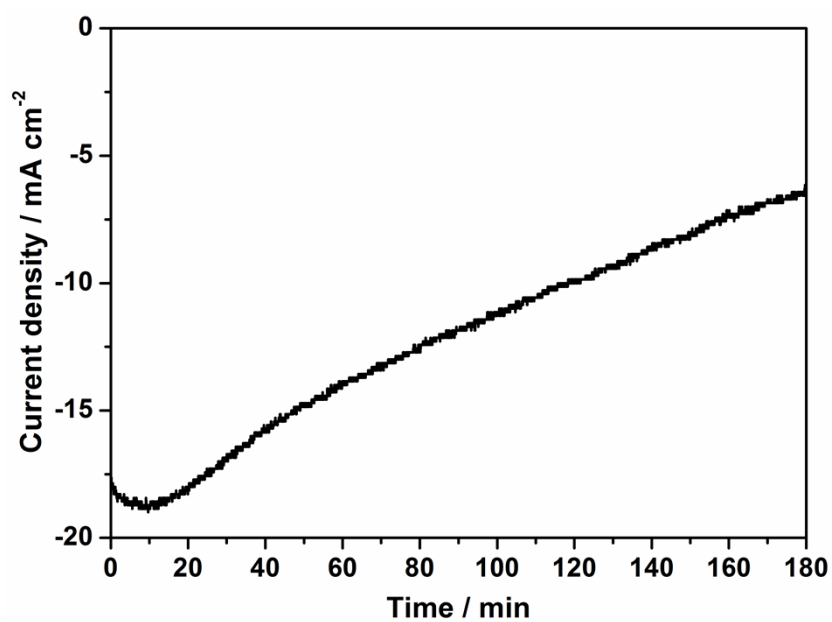


Fig. S5 Current-time curve for Pt-In₂S₃/CuInS₂ electrode in 0.1 M Na₂SO₄, pH 9 at 0 V vs RHE under irradiation from a 300 W xenon lamp.

Table S1 Atomic ratio of CuInS₂ and In₂S₃/CuInS₂ deposited on Mo-substrates.

Semiconductor	Cu	In	S	O	Cu/In
CuInS ₂	25.77	23.62	46.71	3.91	1.09
In ₂ S ₃ /CuInS ₂	19.47	26.78	46.73	7.02	0.73

References

1. Z. Li, W. Luo, M. Zang, J. Feng and Z. Zou, *Energy Environ. Sci.*, 2013, **6**, 347-370.