Electronic Supplementary Information

Efficient photoelectrochemical hydrogen production over $CuInS_2$ photocathodes modified with amorphous Ni-MoS_x operating in a neutral electrolyte

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Experimental section

Preparation of $CuInS_2$ thin films by electrodeposition and sulfurization

Metallic Cu and In layers were deposited successively onto Mo-coated soda-lime glass substrates under potentiostatic control using a potentiostat (HSV-100, Hokuto Denko). Cu deposition was performed at -0.4 V vs. an Ag/AgCl reference electrode in 75 mL of an aqueous solution containing 10 mM $CuSO_4 \cdot 5H_2O$ (Wako, 99.5%) and 10 mM citric acid (Wako, 98%). In deposition onto the Cu layer was performed at -0.8 V vs. an Ag/AgCl reference electrode in 75 mL of an aqueous solution containing 30 mM $InCl_3 \cdot 4H_2O$ (Wako, 99.9%), 36 mM trisodium citrate (Wako, 99%) and 10 mM citric acid with the pH adjusted to 2.2-2.3. The amounts of Cu and In deposited were controlled by adjusting the total electric charge to 522 and 600 mC/cm^2, respectively, using a coulomb/ampere-hour meter (HF-301, Hokuto Denko). The Cu:In ratio was thus fixed at 1.3:1. Sulfurization of the as-prepared Cu/In film was performed using a two-step process. The film was initially heated to 110 °C under N_2 and maintained at this temperature for 1 h. After this pre-treatment, the film was heated to 500 °C for 10 min and then sulfurized for 20 min under a H_2S flow at a rate of 5 mL/min. Finally, the film was cooled to room temperature under N_2. The excess Cu_xS phase was selectively etched by immersing the as-sulfurized $CuInS_2$ film in an aqueous KCN solution (10%) for 2 min and then in an NH_4OH solution (10%) for 10 min.

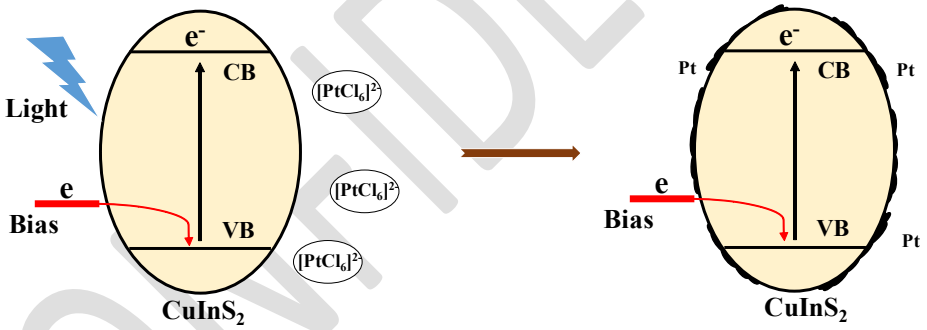
(Photo-)electrodeposition of Ni-MoS_x

Ni-MoS_x was applied via a (photo-)electrochemical deposition technique originally developed by Hu's research group. The deposition of Ni-MoS_x onto the $CuInS_2$ electrode was performed under AM 1.5G simulated sunlight at 100 mW/cm^2 (SAN-EI Electric, XES-301 S) in a freshly prepared solution containing 0.2 mM $(NH_4)_2MoS_4$ (Aldrich, 99.97%), 0.04 mM $NiCl_2$ (Aldrich, 98%) and 0.1 M $NaClO_4 \cdot H_2O$ (Wako, 98.0%). The electrolyte was stirred and purged with Ar gas for 30 min before the deposition, and stirring and Ar purging were continued throughout the deposition process. Consecutive cyclic voltammograms were acquired with potentiostatic control using a potentiostat (HSV-100, Hokuto Denko) in conjunction with a

three-electrode configuration. This apparatus included a $CuInS_2$ electrode, a Ti wire and an Ag/AgCl (KCl sat.) electrode as the working, counter and reference electrodes, respectively. Cyclic voltammograms (based on 99 scans) were acquired at voltages between 0.4 and -0.7 V versus an Ag/AgCl reference electrode at a scan rate of 50 mV/s starting at 0 $V_{Ag/AgCl}$. Ni-MoS_x was deposited onto the fluorine-doped tin oxide surface by electrochemical deposition using the same conditions as employed for the $CuInS_2$ surface, except that the potential range was between 0.1 and -1.0 V versus an Ag/AgCl reference electrode, starting at -0.3 $V_{Ag/AgCl}$.

Photoelectrochemical deposition of Pt

Pt deposition was performed at a potential of -0.66 V vs. an Ag/AgCl reference electrode in a 0.1 M aqueous Na_2SO_4 (Wako, 99%) solution (pH 9.5) containing 15 μmol H_2PtCl_6 (Kanto, 98.5%). The electrode was irradiated under simulated sunlight (AM 1.5G) until the photocurrent plateaued. The photo-assisted electrodeposition procedure was presented in Scheme S1.



Scheme S1 The schematic presentation of the photo-assisted electrodeposition procedure.

PEC assessments

The PEC performance of each specimen was investigated in conjunction with a three-electrode PEC configuration, using the modified $CuInS_2$ as a photocathode, a Pt wire as a counter electrode and an Ag/AgCl electrode as a reference electrode. The measured potentials vs. the Ag/AgCl reference electrode were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059\ pH + 0.197.$$

The electrolyte was a 0.5 M aqueous KPi solution (a mixture of 0.25 M K_2HPO_4 and 0.25 M KH_2PO_4 adjusted to pH 7 with 8 M aqueous KOH). This solution was stirred and purged with Ar gas for 15 min prior to the PEC trial and the stirring and Ar purge were continued throughout each trial. AM 1.5G simulated solar radiation at 100 mW cm^{-2} (SAN-EI Electronic, XES40S1) was used as the light source while acquiring current-potential curves and gas evolution data. Half-cell solar-to-hydrogen (HC-STH) conversion efficiency values were calculated using the equation:

$$\eta_{\text{HC-STH}} = [\,|J_{\text{ph}}| \times (E_{\text{RHE}} - E_{H^+/H_2}) / P_{\text{sun}}] \times 100\%,$$

where J_{ph} is the photocurrent density obtained with an applied bias of E_{RHE} and E_{H^+/H_2} is the equilibrium potential for hydrogen evolution (0 V_{RHE}).

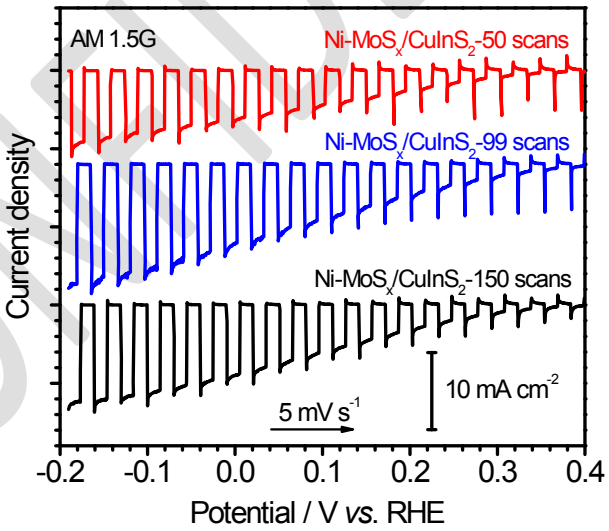


Fig. S1 Photocurrent density-potential curves for Ni-MoS_x/$CuInS_2$ electrodes with different loading amount of Ni-MoS_x which was controlled by scan numbers of 50, 99 and 150. These data were acquired under chopped AM 1.5G illumination in an aqueous 0.5 M KPi electrolyte at pH 7.

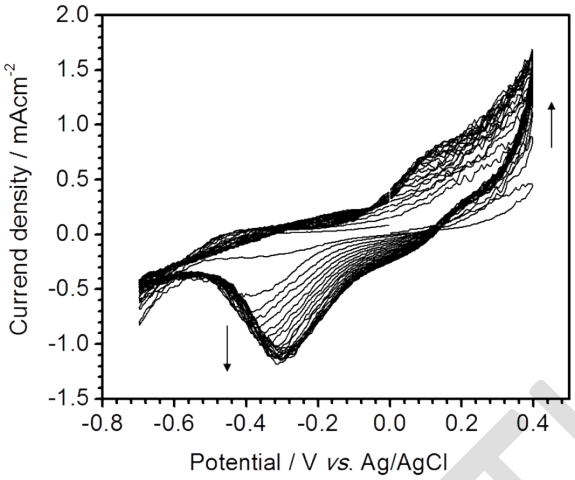


Fig. S2 Cyclic voltammetry scans during the photoelectrodeposition of Ni-MoS_x onto a $CuInS_2$ electrode. Scan numbers from 1 to 90 at intervals of 5 as well as scan number 99 are shown.

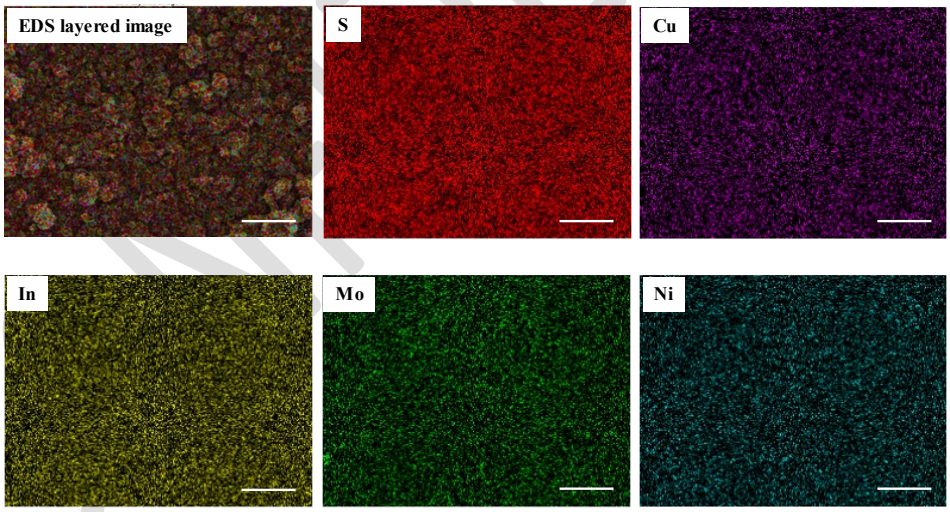


Fig. S3 The elemental mapping images of the Ni-MoS_x/$CuInS_2$ film; scale bars are 10 μm.

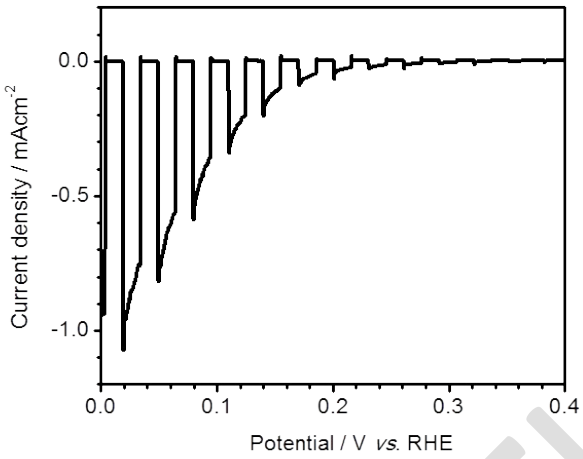


Fig. S4 The photocurrent density-potential curve generated by a $CuInS_2$ electrode in response to chopped AM 1.5G illumination in an aqueous 0.5 M KPi electrolyte at pH 7.

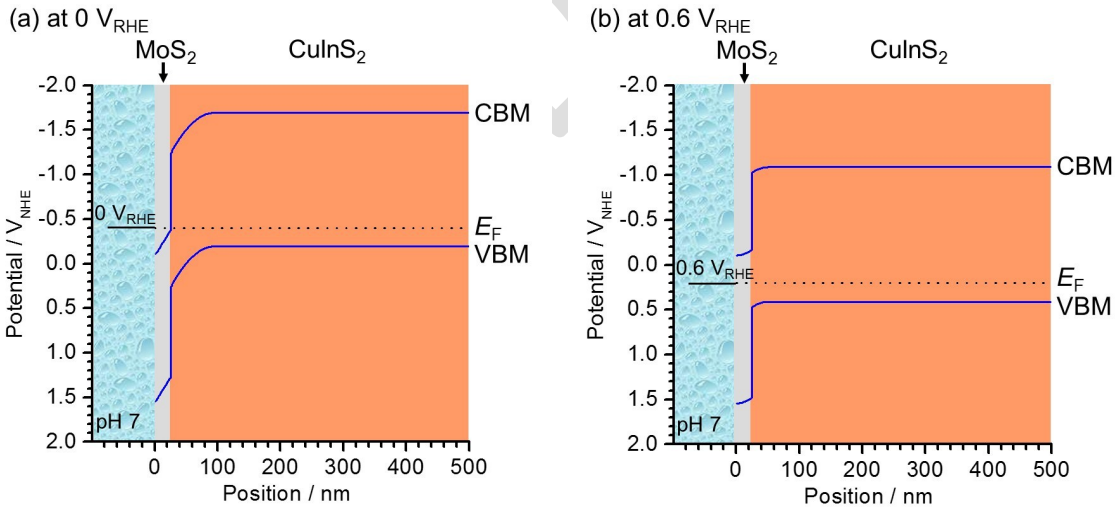


Fig. S5 Calculated band diagrams for the Ni-MoS_x/$CuInS_2$ solid-liquid interface at (a) 0 and (b) 0.6 V_{RHE}.

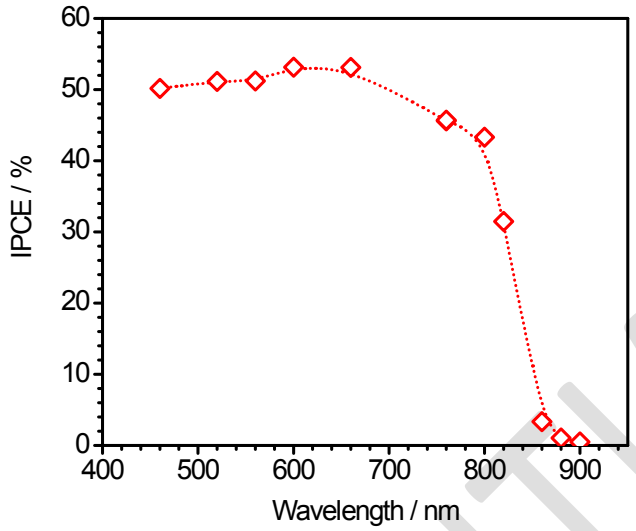


Fig. S6 Wavelength dependent IPCE curve of the Pt/Ni-MoS_x/$CuInS_2$ electrode measured at 0 V_{RHE} under monochromatic irradiation using a Xe lamp equipped with bandpass filters (FWHM of ~10 nm).

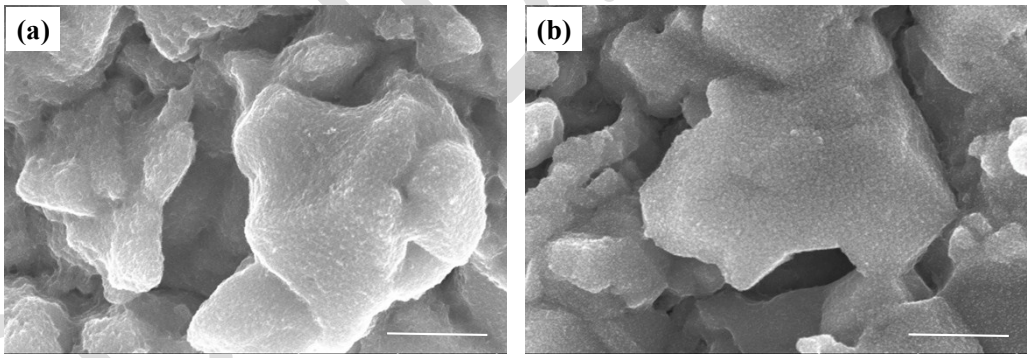


Fig. S7 SEM images of the Pt/Ni-MoS_x/$CuInS_2$ film (a) before and (b) after stability test; scale bars are 500 nm.

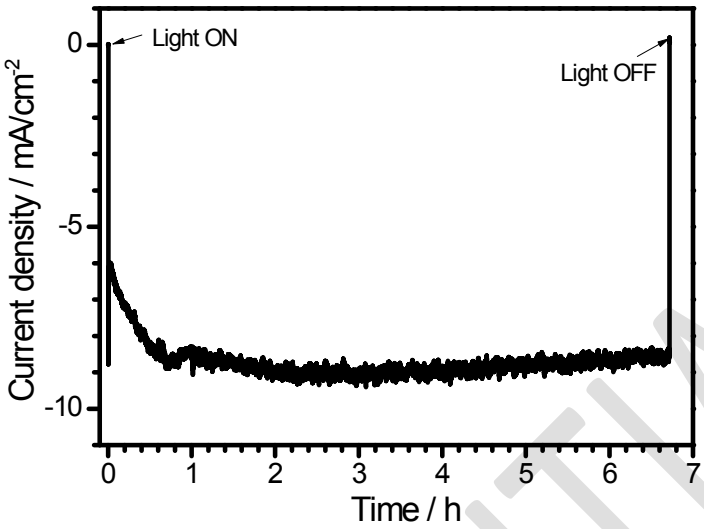


Fig. S8 Time course of the photocurrent generated by a Ni-MoS_x/$CuInS_2$ electrode at 0 V_{RHE} under AM 1.5G illumination in an aqueous 0.5 M KPi electrolyte at pH 7.