

Supplementary Information

Facilitating charge transfer of ZnMoS₄/CuS p-n heterojunction through ZnO intercalation for efficient photocatalytic hydrogen generation

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Experimental section

Reagents and chemicals

Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), zinc chloride (ZnCl_2), sodium molybdate (Na_2MoO_4), methanol (CH_3OH), hexamethylenetetramine (HMTA or $(\text{CH}_2)_6\text{N}_4$), polyvinylpyrrolidone (average molecular weight 10000), sodium sulfide (Na_2S), sodium sulfite (Na_2SO_3), copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$) and ethylene glycol ($\text{CH}_2\text{OH})_2$ were analytical grade, and used as received without purification.

Synthesis of Zinc molybdate hexagonal plates

1 M $\text{Zn}(\text{CH}_3\text{COO})_2$ and 0.2 M Na_2MoO_4 aqueous precursor solution were prepared in separate containers. 1 ml of each Zn and Mo precursor solution were added into 18 ml deionized water and 10 ml methanol, forming a reacting solution with total H_2O /methanol ratio of 2:1. After the solution was stirred at 1000 rpm for 5 min, it was then transferred to a Teflon-lined stainless steel autoclave of 50 ml capacity and heated at 75°C for 12 h. Around 60 mg of $\text{Zn}_5\text{Mo}_2\text{O}_{11} \cdot 5\text{H}_2\text{O}$ white precipitate was obtained, washed with water and ethanol for three times successively under centrifugation in 4000 rpm, and dried for 3 h at 55°C.

Synthesis of Zinc thiomolybdate hexagonal plates and formation of Zinc oxide

The as-synthesized $\text{Zn}_5\text{Mo}_2\text{O}_{11} \cdot 5\text{H}_2\text{O}$ powder was dispersed in 25 ml of 0.2 M Na_2S aqueous solution. It is then transferred to a Teflon-lined stainless steel autoclave of 50 ml capacity and heated at 180°C for 12 h. Greyish precipitate was obtained, washed with water and ethanol for three times successively, and dried for 3 h at 55°C. The formation of ZnO layer involved an annealing process by heating ZnMoS_4 powder at 500°C for 2 h with a ramp rate of 5°C/min. The powder turned yellowish after being annealed.

Synthesis of controlled sample: Zinc sulfide hexagonal plates

1 M ZnCl_2 and 1 M hexamethylenetetramine (HMTA) were prepared in separate containers. 1 ml of ZnCl_2 solution and 1 ml of HMTA solution were added into 28 ml deionized water, followed by an addition of 250 mg polyvinylpyrrolidone (PVP). The solution is then heated at 90°C for 3 h. The precipitate was obtained, washed with water and ethanol for three times successively, and dried for 3 h at 55°C, resulting in ZnO hexagonal plates powder. Subsequently, sulfidation was carried out by dispersing the powder with 1 mmol Na_2S in 25 ml deionized water, and heated at 90°C for 12 h. The ZnS hexagonal plates precipitate was obtained, wash with water and ethanol for three times successively under centrifugation in 4000 rpm, and dried for 3 h at 55°C.

Characterization

Field-Emission scanning electron microscopy (FESEM, JEOL FEG JSM 7001F) operated at 15 kV was used to characterize the morphology of synthesized products. Their crystallographic structures were analysed using X-ray diffraction (XRD, Philips X-ray diffractometer equipped with graphite-monochromated Cu-K α radiation at $\lambda=1.541\text{\AA}$). Brunauer-Emmett-Teller (BET) measurements were conducted using Quantachrome Nova 2200e with N_2 as the adsorbate at liquid nitrogen temperature. The specific surface area (S_{BET}) was calculated according to the multiple-point BET method at relative pressure $P/P_0 = 0.01\text{--}0.1$. Porosity distributions were calculated using Barrett-Joyner-Halenda (BJH) method. The total pore volume was obtained from the volume of N_2 adsorbed at a relative pressure of $P/P_0 \approx 0.99$. X-ray photoelectron spectroscopy (XPS) spectra were obtained on a VG Thermo Escalab 220I-XL system, and all binding energies were referred to C1s peak of 284.8 eV. Transmission electron microscopy (TEM, Phillips FED

CM300) were used to further examine the morphology, porosity and crystallographic structures associated with atomic d-spacing. Absorbance spectra of photocatalysts were acquired using Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Absorption spectra was acquired using UV-VIS-NIR spectrophotometer (Shimadzu UV-3600) while emission spectra was obtained using Spectrofluorophotometer (Shimadzu RG-5301PC) with an excitation wavelength of 325 nm. Electrochemical impedance spectroscopy (EIS) was measured using a CHI660E electrochemical workstation in a three-electrode electrochemical cell at room temperature with platinum foil as counter electrode. The working electrodes consist of 1.5 mg of photocatalysts drip-coated onto fluorine-doped tin oxide (FTO) glass substrates with an active area of 1.5 cm² using ethylene glycol (EG) as binder. EIS measurements were performed at respective open circuit potentials from 100k to 0.01 Hz with an AC potential amplitude of 5 mV in a 0.5 M Na₂SO₄ aqueous electrolyte.

In-situ photo-deposition of CuS and photocatalysis performance measurement

2 mg of photocatalyst powders were dispersed ultrasonically for 1 min in 10ml Na₂S/Na₂SO₃ (0.35 M/0.25 M) sacrificial agent aqueous solution in a cylindrical quartz vial. A desired amount of Cu(CH₃COO)₂ was added into each photocatalytic suspension system before it was sealed and purged with Ar gas for 10 min. Photocatalytic hydrogen generation was performed along with CuS photo-deposition concurrently under the illumination with a UV light source (365 nm). After a given illuminated time interval, photocatalytic hydrogen evolution amount was obtained from gas composition, typically through syringe drawing a 100μl gas sample from the headspace in the cylindrical quartz vial and injecting into gas chromatographer (Shimadzu, GC-2014AT). CuS-photodeposited photocatalysts were collected and washed with water for three times under centrifugation in 4000 rpm. The stability of the photocatalysts were assessed through identical settings with their gas composition determined at 15 min intervals of illumination, and subsequent purging with Ar gas for 10 min after every 60 min of illumination, repeatedly over a total illumination duration of 8 h. Photoelectrochemical (PEC) measurements, were conducted through similar electrochemical set-up in section 2.5, at zero bias with a 60 s span held between each light and dark modes containing Na₂S/Na₂SO₃ (0.35 M/0.25 M) aqueous electrolyte. Pure water photocatalytic hydrogen evolution measurements were evaluated using similar set up and process except only 10 ml of deionized water was used as dispersing solution in replace with Na₂S/Na₂SO₃ solution.

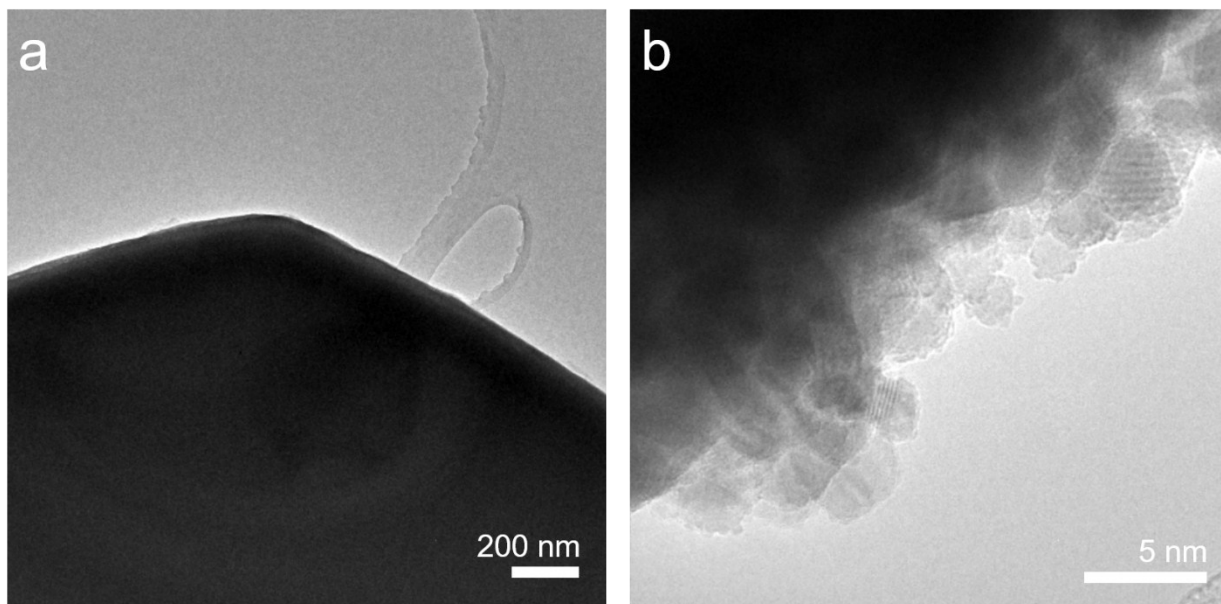


Figure S1. TEM images of (a) $\text{Zn}_5\text{Mo}_2\text{O}_{11}$ hexagonal plate (b) $\text{ZnMoS}_4/\text{ZnO}$.

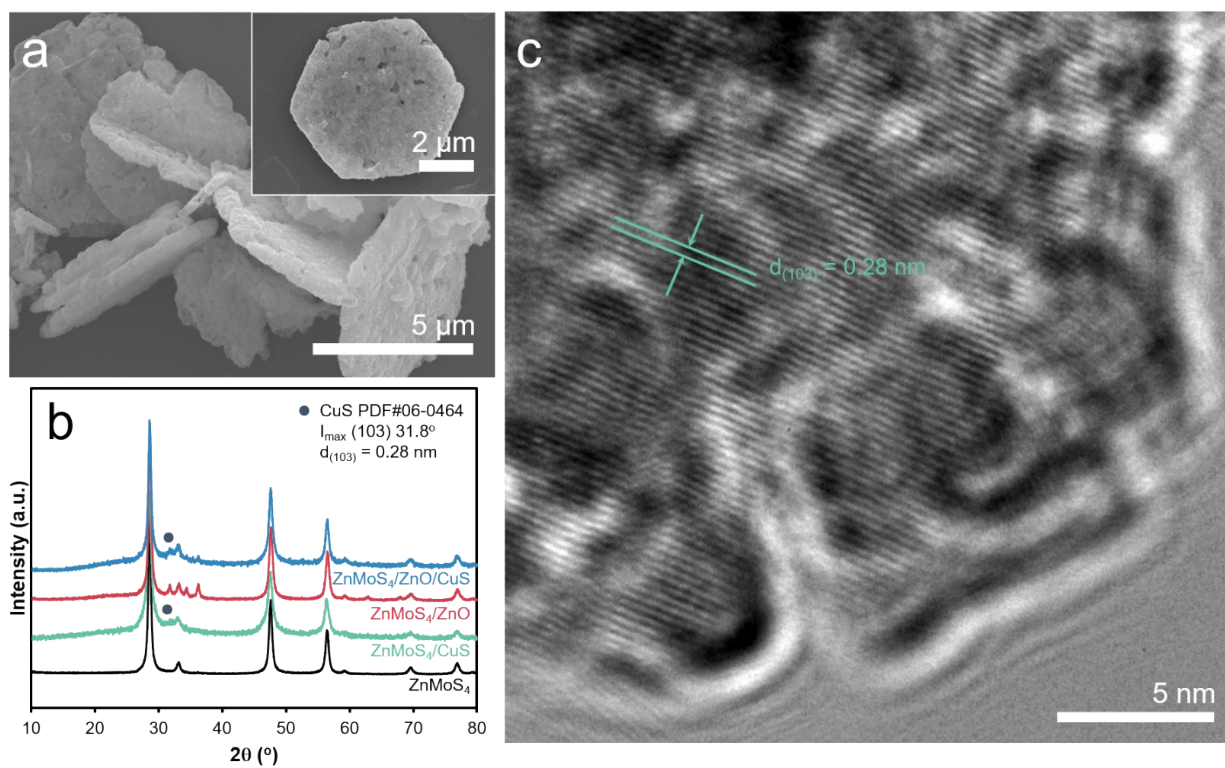


Figure S2. (a) low magnification SEM image of ZnMoS₄/ZnO/CuS with high magnification SEM image inset. (b) XRD of ZnMoS₄ and ZnMoS₄/ZnO before and after CuS loading. (c) HRTEM of CuS fine nanoparticles at the edge, with d-spacing corresponds to CuS (103) plane.

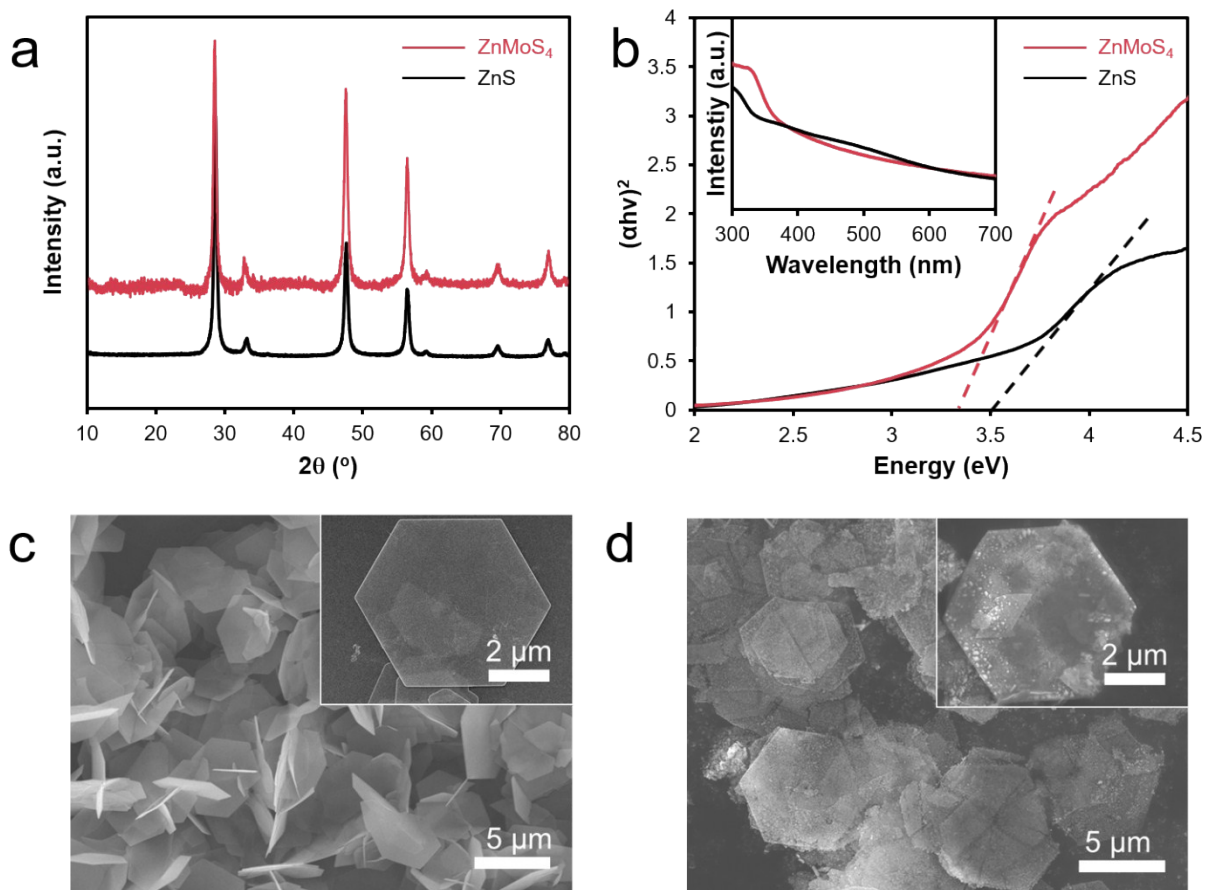


Figure S3. (a) XRD spectra and (b) Tauc plots, derived from UV-visible spectra inset using direct transition band gap model, of ZnS and ZnMoS₄. SEM images of (c) ZnO and (d) ZnS.

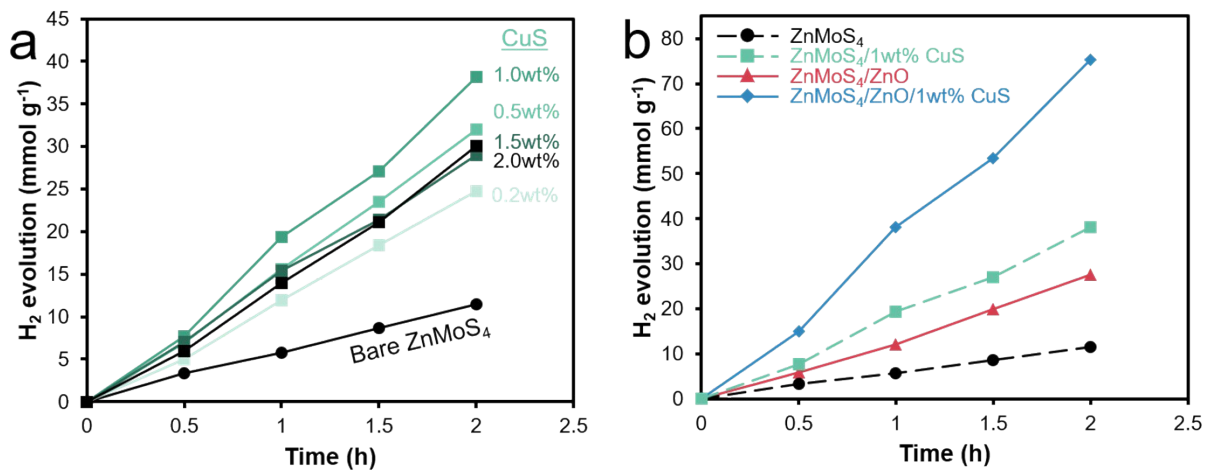


Figure S4. Photocatalytic hydrogen evolution versus time of (a) ZnMoS₄ with various CuS loading in Na₂S/Na₂SO₃ aqueous solution, (b) ZnMoS₄/ZnO with and without 1wt% CuS loading in Na₂S/Na₂SO₃ aqueous solution under UV LED illumination.

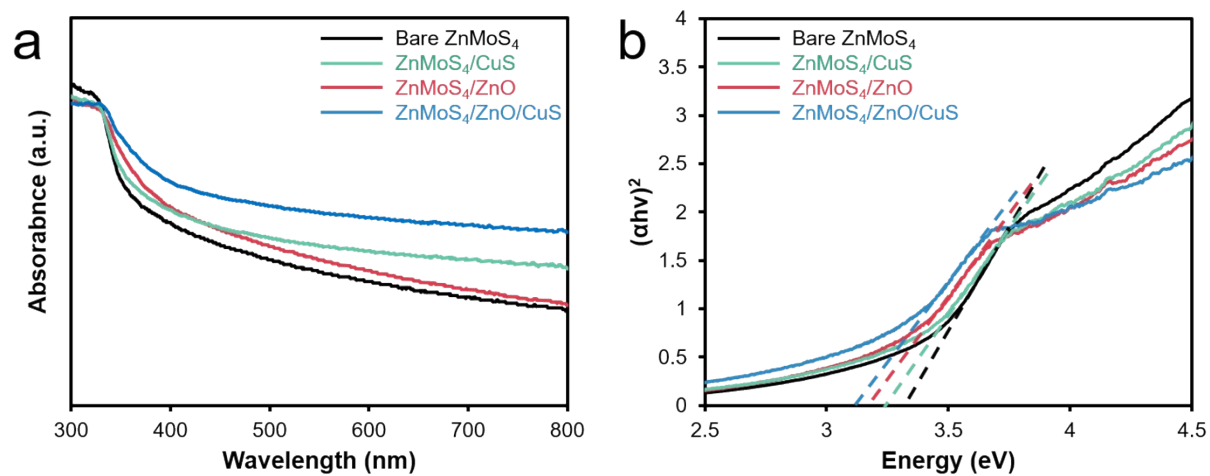


Figure S5. (a) UV-vis spectra and their derivatives Tauc plots using direct transition band gap model of ZnMoS₄, ZnMoS₄/CuS, ZnMoS₄/ZnO and ZnMoS₄/ZnO/CuS.

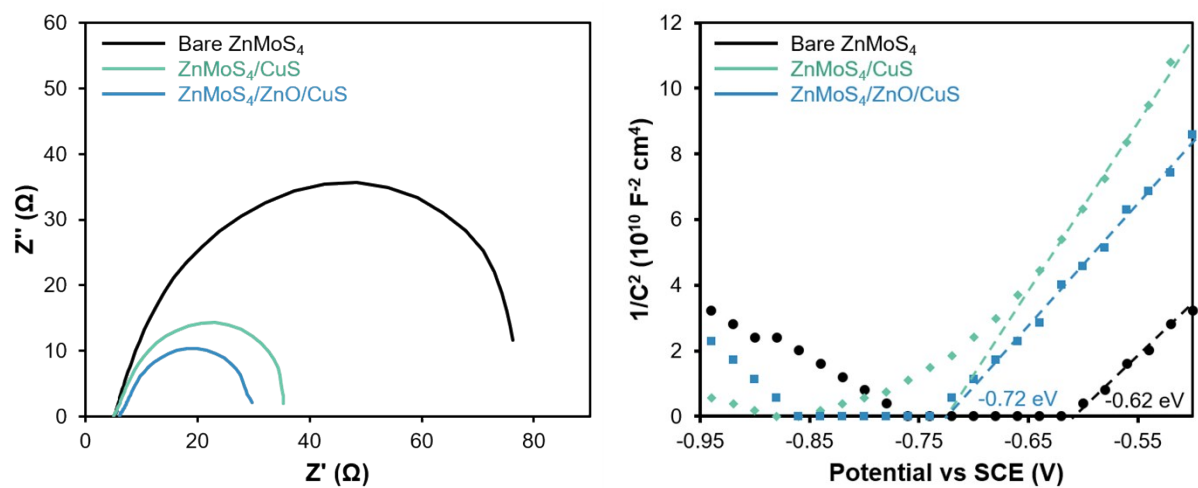


Figure S6. (a) Electrical impedance spectra and (b) Mott-Schottky plots of ZnMoS₄, ZnMoS₄/CuS and ZnMoS₄/ZnO/CuS.

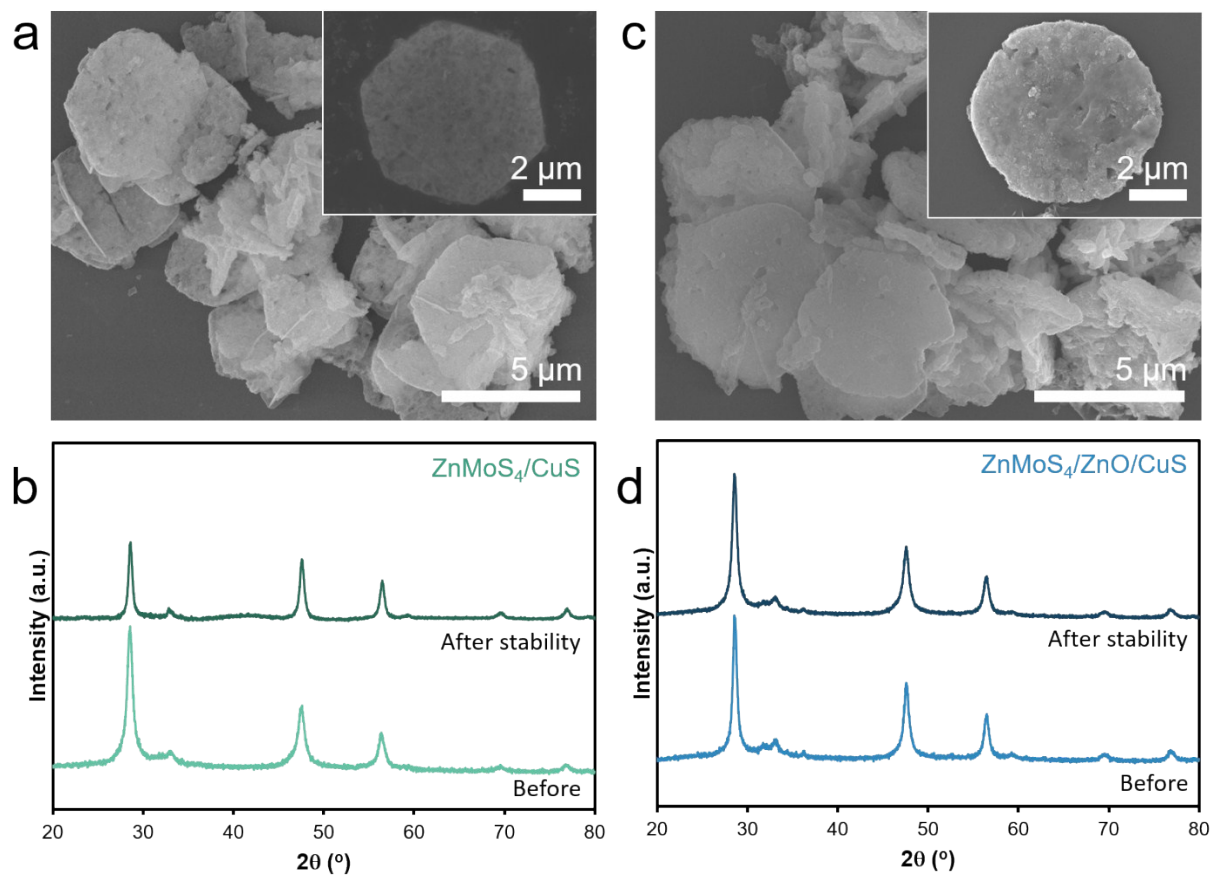


Figure S7. SEM images and XRD diffraction patterns of (a-b) $\text{ZnMoS}_4/\text{CuS}$ and (c-d) $\text{ZnMoS}_4/\text{ZnO}/\text{CuS}$ after photocatalysis stability test.

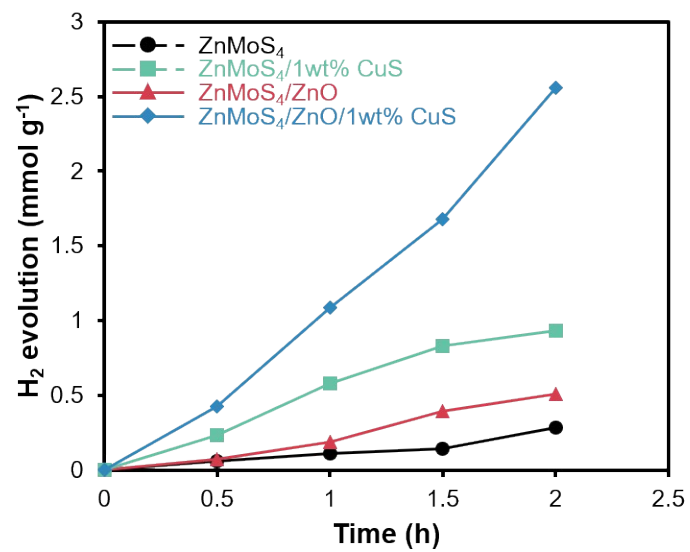


Figure S8. Photocatalytic hydrogen evolution versus time of ZnMoS₄/ZnO with and without 1wt% CuS loading in pure water under UV LED illumination.