

Supporting Information

***In-situ* photo-assisted deposition of MoS₂ electrocatalyst onto Zinc-Cadmium-Sulphide nanoparticle surface to construct efficient photocatalyst for hydrogen generation**

Mai Nguyen,^a Phong D. Tran,^{*a} Stevin S. Pramana,^{b,c} Rui Lin Lee,^a Sudip K. Batabyal,^a Nripan Mathews,^b Lydia H. Wong,^{*a,b} Michael Graetzel^{d,e}

^a*Energy Research Institute @ Nanyang Technological University (ERI@N), Singapore; Email: dptran@ntu.edu.sg*

^b*School of Materials Science and Engineering, Nanyang Technological University, Singapore; Email: lydiawong@ntu.edu.sg*

^c*Facility of Analysis, Characterization, Testing and Simulation (FACTS), Nanyang Technological University, Singapore*

^d*Laboratory for Photonics and Interfaces, Ecole Polytechnique Federale de Lausanne, CH-1015 Lausanne, Switzerland*

^e*Center for Nanostructured Photosystems (CNPS), Nanyang Technological University, Research Techno Plaza, Singapore 637553*

1. General

The reagents were all analytical-grade from Sigma Aldrich and used without any further purification.

2. Preparation of ternary alloyed $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanoparticles

Typically, 0.43 mmol cadmium acetate ($\text{CdAc}_2 \cdot 2\text{H}_2\text{O}$), 0.54 mmol zinc acetate ($\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$) and 1.33 mmol thioacetamide (CH_3CSNH_2) were dissolved in 50 mL ethanol to obtain the solution 2% for each sample. The $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanoparticles with a specified x value, $x = 0.2, 0.4, 0.6$ and 0.8) were synthesized by mixing the precursors in ethanol at 50°C for 4 hours. The powders were collected and washed with ethanol twice then annealed in air at 150° for 5 minute.

3. Preparation of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanoparticles electrodes

The $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ (with a specified x value, $x = 0.2, 0.4, 0.6$ and 0.8) photoanode on conducting transparent fluorine-doped tin oxide (FTO) had been done by employing a precursor decomposition approach. The precursor was synthesized in ethanol by mixing Zinc acetate, Cadmium acetate and Thioacetamide. This precursor solution was spin-coated onto FTO followed by thermal decomposition at 150°C for 5 minute.

4. Material characterization

4.1 Morphology, Chemical Composition, and Structure Characterization

X-Ray powder diffraction (XRD) patterns were obtained using Bruker D8 Advance utilizing $\text{CuK}\alpha$ radiation with the scanning range from 20° to 80° in 2θ . The morphologies of

catalysts were investigated by field emission scanning electron microscopy (FESEM, JEOL JSM-7600F) at 5 kV. High resolution transmission electron micrograph and selected area electron diffraction were recorded using JEOL2100F operating at 200keV.

4.2 Electrochemical characterization of $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{FTO}$ films

Electrochemical analysis was done using a CHI, model 852 potentiostat. Three electrodes configuration was employed. The working electrode was $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{FTO}$ electrode, the reference electrode was Ag/AgCl, 3M KCl and the counter electrode was a Pt mesh. pH7 phosphate buffer (0.1M) solution was used as electrolyte. 0.01M Na_2S was added when sacrificial electron donor is required. Prior to measurement, electrolyte solution was carefully saturated with research-grade nitrogen gas to eliminate dissolved oxygen. Visible light illumination was provided by employing a 150W Xe lamp and a 420 nm cut-off filter. Light density on $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{FTO}$ working electrode was adjusted to 100 mW.cm^{-2} . I-V curves were recorded by employing linear sweep voltammetry with slow scan rate of 2 mV.s^{-1} . During measurement, light illumination was manually chopped employing a metal mask placed between the light source and the $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{FTO}$ electrode.

4.3 Photocatalytic H_2 production

Photocatalytic assays were carried out at room temperature in a closed system with outer irradiation. Briefly, 20 mL aqueous solution of Na_2S 0.35M/ Na_2SO_3 0.25M in a 50 mL gas-tight closed schlenk was well degassed by research-grade nitrogen gas for 1h to remove dissolved oxygen. 20 mg of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanopowder and a pre-determined $(\text{NH}_4)_2[\text{MoS}_4]$ precursor were added. Before illumination, the reaction mixture was vigorously stirred and further degassed by nitrogen gas for 15 min. The reaction mixture was then irradiated by a

300W Xe lamp (Asahi Spectra, MAX-302) equipped with a 420 nm cut-off filter. Gas in the head-cap of the reactor was manually sampled and analyzed by gas chromatography.

Supplementary data

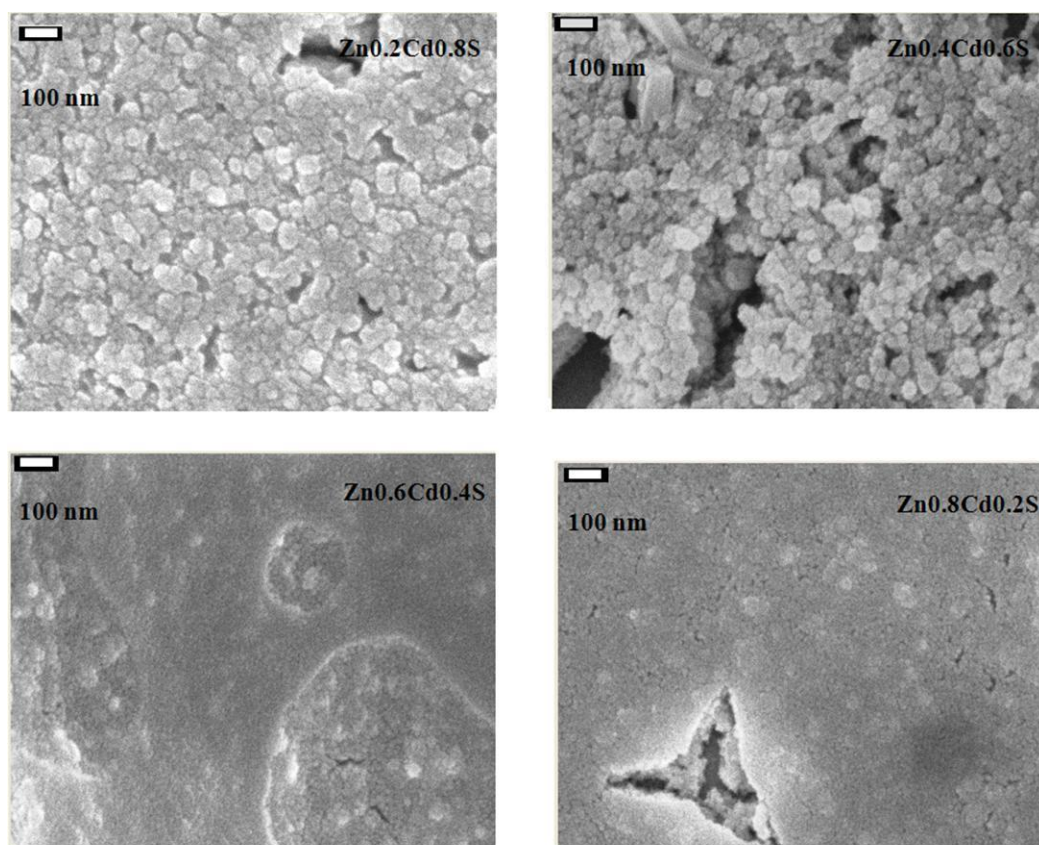


Figure S1: *Morphology of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanoparticles*

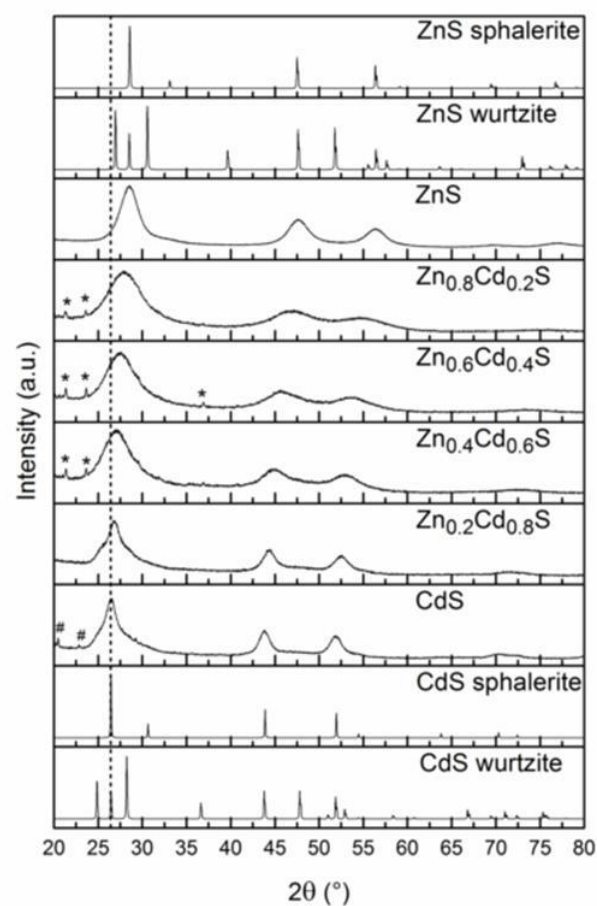


Figure S2 : X-ray diffraction patterns of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ together with the reported ZnS and CdS sphalerite and wurtzite [1-4]

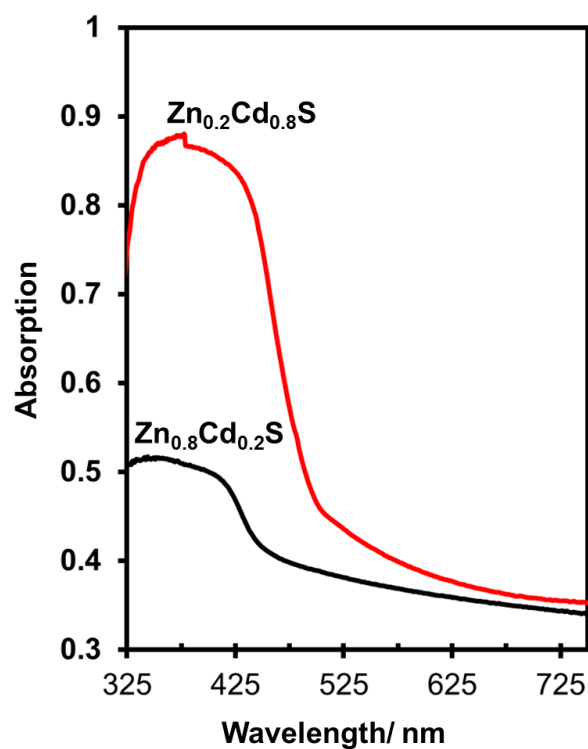


Figure S3: Optical properties of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanoparticles

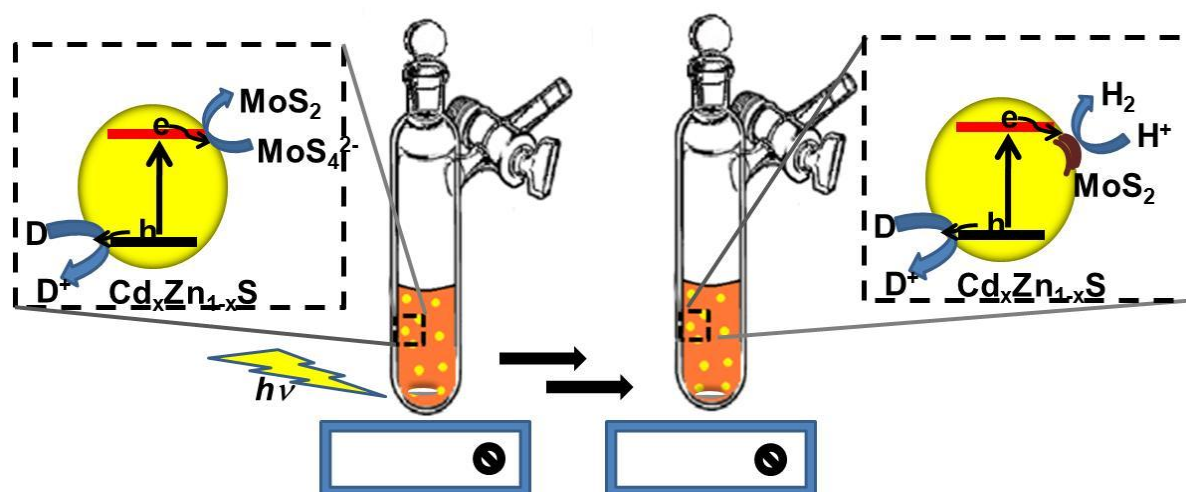


Figure S4: Schematic presentation of in-situ photo-assisted deposition of MoS_2 co-catalyst on $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ semiconductor and H_2 photo-evolution from an aqueous solution catalyzed by $\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{MoS}_2$ photocatalyst

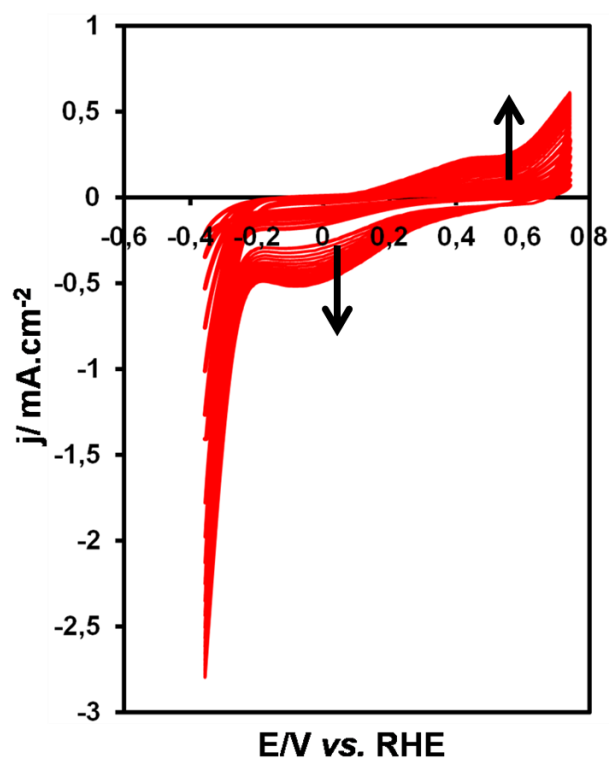


Figure S5: Typical consecutive cyclic voltammograms recorded on a carbon glassy electrode for a 0.5mM $(\text{NH}_4)_2[\text{MoS}_4]$ solution in pH7 phosphate buffer. Potential scan rate was 50mV.s^{-1} .

On a fluorine-doped tin oxide (FTO) electrode, deposition of MoS_2 amorphous thin film was visible after repeating 10 potential cycles or by holding this FTO electrode at 0V vs. RHE for 20 min.

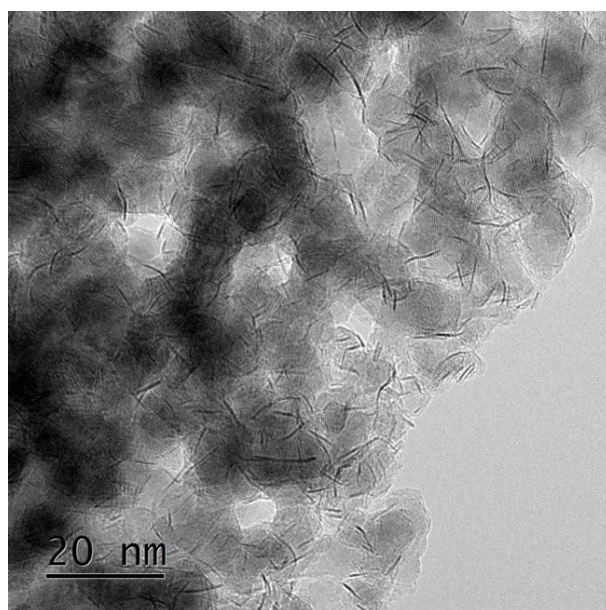


Figure S6: TEM image recorded on a $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}/\text{MoS}_2$ 3% photocatalyst

Table S1 : Surface area measured for different $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanoparticles

Catalysts	BET Surface Area ($\text{m}^2.\text{g}^{-1}$)	Langmuir Surface Area ($\text{m}^2.\text{g}^{-1}$)
$\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$	29.2546	40.6323
$\text{Zn}_{0.4}\text{Cd}_{0.6}\text{S}$	51.1519	72.8227
$\text{Zn}_{0.6}\text{Cd}_{0.4}\text{S}$	49.0176	68.3543
$\text{Zn}_{0.8}\text{Cd}_{0.2}\text{S}$	5.5090	7.64955

References

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