Supporting Information

In-situ photo-assisted deposition of MoS_2 electrocatalyst onto Zinc-Cadmium-Sulphide nanoparticle surface to construct efficient photocatalyst for hydrogen generation

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1. General

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

2. Preparation of ternary alloyed $Zn_xCd_{1-x}S$ nanoparticles

Typically, 0.43 mmol cadmium acetate ($CdAc_2$. $2H_2O$), 0.54 mmol zinc acetate ($ZnAc_2$. $2H_2O$) and 1.33 mmol thioacetamide (CH_3CSNH_2) were dissolved in 50 mL ethanol to obtain the solution 2% for each sample. The $Zn_xCd_{1-x}S$ nanoparticles with a specified x value, x = 0.2, 0.4, 0.6 and 0.8) were synthetized by mixing the precursors in ethanol at 50^oC for 4 hours. The powders were collected and washed with ethanol twice then annealed in air at 150^o for 5 minute.

3. Preparation of $Zn_xCd_{1-x}S$ nanoparticles electrodes

The $Zn_xCd_{1-x}S$ (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^oC 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 CuKα radiation with the scanning range from 20^o to 80^oin 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 $Zn_xCd_{1-x}S$/FTO films

Electrochemical analysis was done using a CHI, model 852 potentiostat. Three electrodes configuration was employed. The working electrode was $Zn_xCd_{1-x}S$/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 $Zn_xCd_{1-x}S$/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 $2mV.s^{-1}$. During measurement, light illumination was manually chopped employing a metal mask placed between the light source and the $Zn_xCd_{1-x}S$/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 $Zn_xCd_{1-x}S$ nanopowder and a pre-determined $(NH_4)_2[MoS_4]$ 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

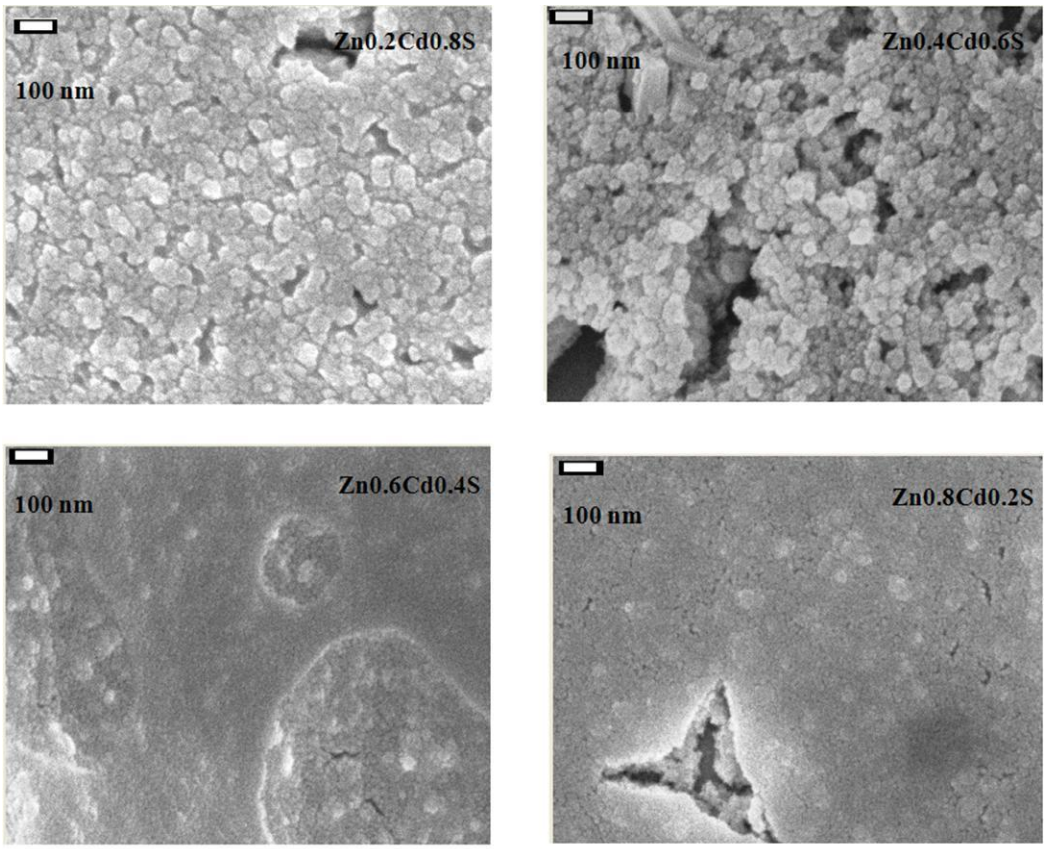

Figure S1: *Morphology of $Zn_xCd_{1-x}S$ nanoparticles*

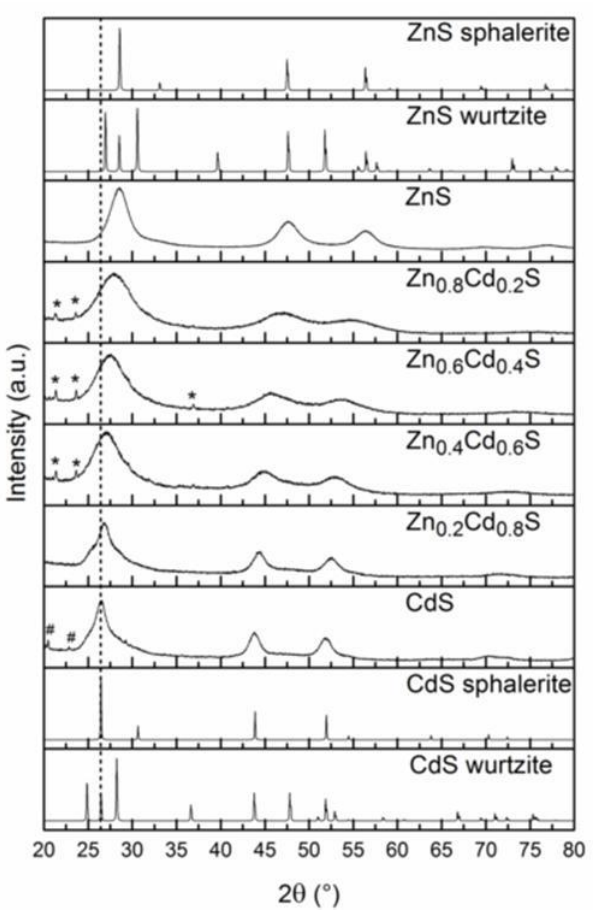

Figure S2 : *X-ray diffraction patterns of $Zn_xCd_{1-x}S$ together with the reported ZnS and CdS sphalerite and wurtzite [1-4]*

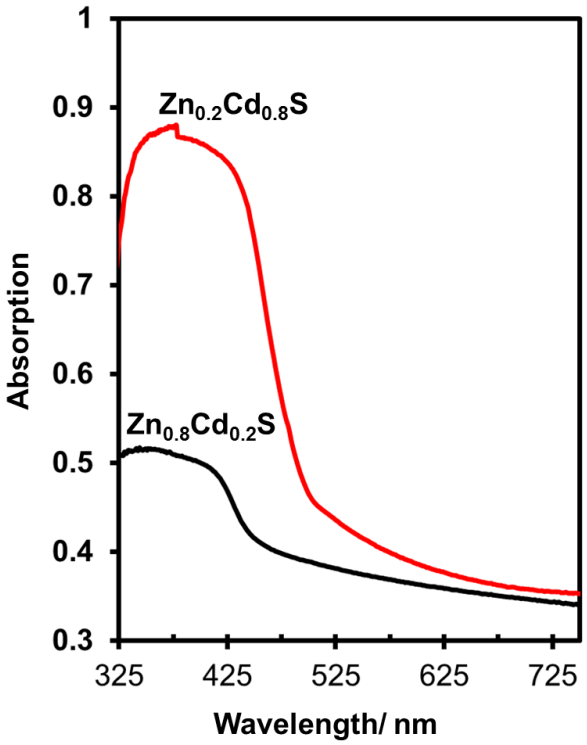

Figure S3: *Optical properties of $Zn_xCd_{1-x}S$ nanoparticles*

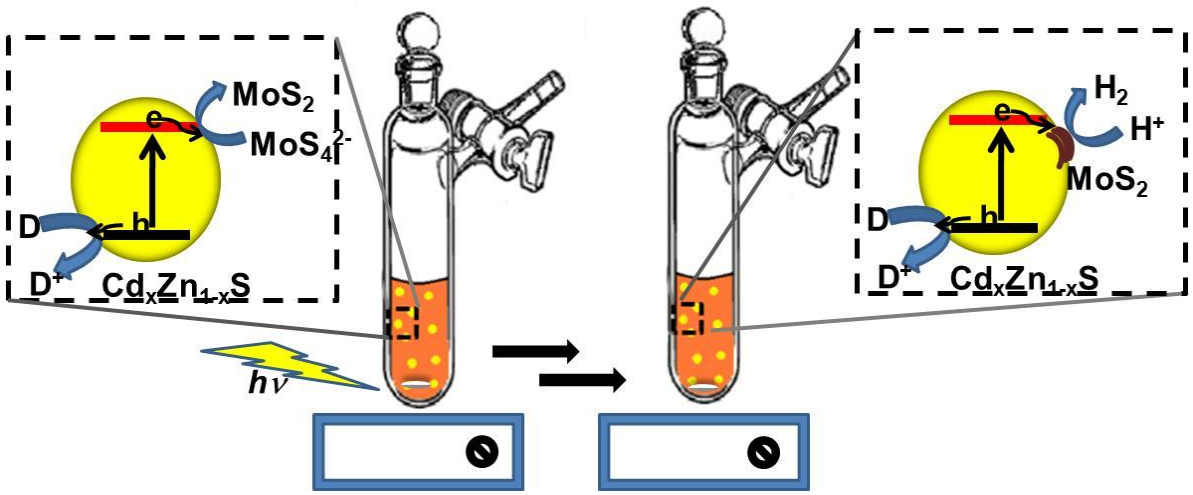

Figure S4: *Schematic presentation of in-situ photo-assisted deposition of MoS_2 co-catalyst on $Zn_xCd_{1-x}S$ semiconductor and H_2 photo-evolution from an aqueous solution catalyzed by $Zn_xCd_{1-x}S/MoS_2$ photocatalyst*

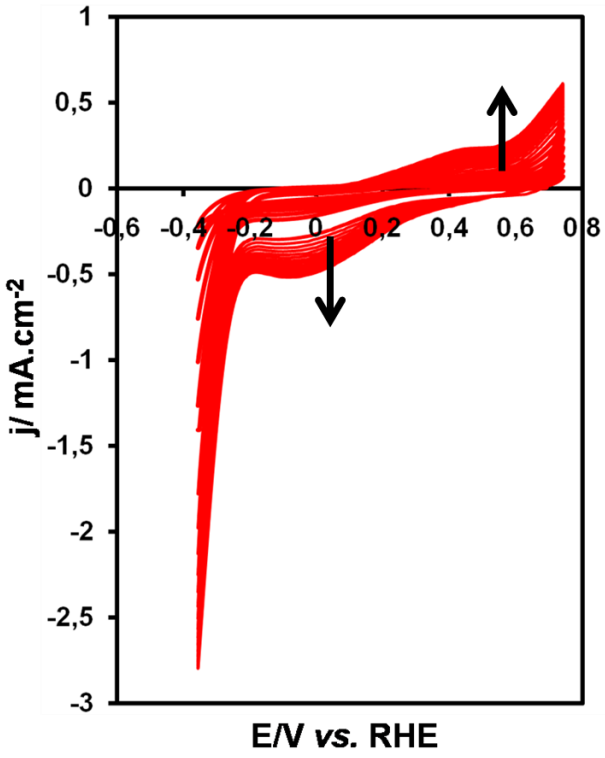

Figure S5: *Typical consecutive cyclic voltammograms recorded on a carbon glassy electrode for a 0.5mM $(NH_4)_2[MoS_4]$ solution in pH7 phosphate buffer. Potential scan rate was 50mV.s^{-1}.*

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.

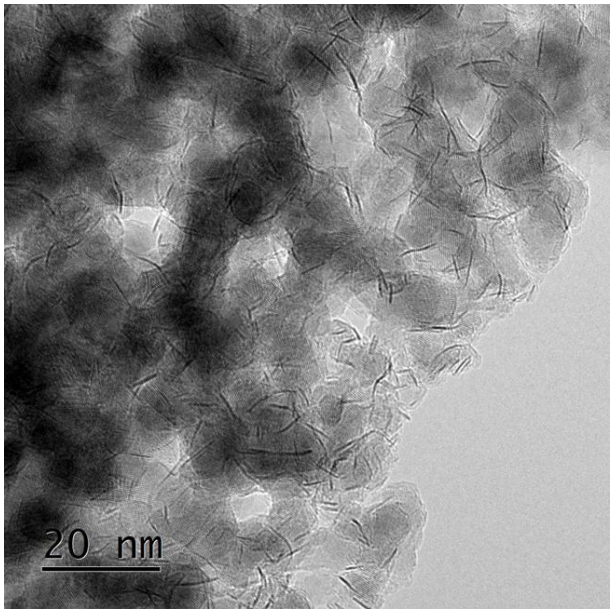

Figure S6: *TEM image recorded on a $Zn_{0.2}Cd_{0.8}S/MoS_2$ 3% photocatalyst*

Table S1 : Surface area measured for different $Zn_xCd_{1-x}S$ nanoparticles

Catalysts	**BET Surface Area ($m^2.g^{-1}$)**	**Langmuir Surface Area ($m^2.g^{-1}$)**
$Zn_{0.2}Cd_{0.8}S$	29.2546	40.6323
$Zn_{0.4}Cd_{0.6}S$	51.1519	72.8227
$Zn_{0.6}Cd_{0.4}S$	49.0176	68.3543
$Zn_{0.8}Cd_{0.2}S$	5.5090	7.64955

References

1. C. Hua, R. D. Pike, R. Kershaw, K. Dwight. A. Wold, *Journal of Solid State Chemistry* 1992, **101**, 115-118.

2. M. K. Rabadanov, *Kristallografiya* 1995**, 40**, 21-27.

3. M. Ikeda, H. Wada, T. Wada, T. Hirao, *Japanese Journal of Applied Physics*, Part 1 1994, **33**, 4540-4545.

4. D. Rodic, V. Spasojevic, A. Bajorek, P. Oennerud, *Journal of Magnestism and Magnetic Materials* 1996, **152**, 159-164