

# Positioning hydrogen reaction sites by constructing CdS/CoNiMoS<sub>4</sub> heterojunctions for efficient photocatalytic hydrogen evolution

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## 1. Experimental Methods

### 1.1. Synthesis of $\text{CoMoS}_4$ nanostructures

1.5 mmol of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 1.5 mmol  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  were respectively dissolved in DI (60 mL) water under vigorous stirring for 1 h to obtain a translucent solution. The solution mixture is then transferred into 100 mL Teflon-lined stainless-steel autoclave and heated to 180 °C for 12 h. After reaction a pink colour precipitate is obtained, which is washed with ethanol and distilled water three times and dried at 80 °C for 10 hours.

### 1.2. Synthesis of $\text{NiMoS}_4$ nanostructures

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.5 mmol) and  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (1.5 mmol) were diluted in deionized water (60 mL) and continuously stirred for 1 hour until complete dissolution of the mixture. The mixture was poured into a 100 mL Teflon-lined stainless-steel autoclave and held it at 120°C for 12 hours. The mixture was collected after the reaction and cooled to room temperature. Further, the light green precipitate formed was cleaned with ethanol and DI water to get it in pure form, and dried for 8 hours at 60 °C.

### 1.3. Synthesis of $\text{CoNiMoS}_4$ nanostructures

Different proportions of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (total mole number of  $\text{CoNi} = 1$  mmol), 1 mmol  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , and 10 mmol thiourea were dissolved in 60mL of deionized water and stirred for 1 h. Then, the solution was transferred to a Teflon-lined stainless-steel autoclave and heated to 120°C for 10 h. After the reaction completion, it was naturally cooled to room temperature. The final product obtained is a brownish-purple powder which is rinsed with ethanol and DI water and dried at 60 °C for 4h.



**The obtained (a) CoMoS<sub>4</sub>, (b) NiMoS<sub>4</sub>, and (c) CoNiMoS<sub>4</sub> particles via hydrothermal technique**

#### *1.4. Synthesis of CdS nanorods*

CdS nanorods were synthesized by a general and facile solvothermal method. The precursors include 4.62 g each of Cd (CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O and CH<sub>4</sub>N<sub>2</sub>S. Both were dissolved in 60 mL ethylenediamine and subjected to magnetic stirring for 1 hour. The mixture was then poured into a 100 mL Teflon-lined stainless-steel autoclave and heated to 160°C for 48 hours. After the reaction, a yellow precipitate is obtained, which is then washed several times with ethanol and DI to remove extra impurities. Finally, the product was dried at 60 °C for 12h.

#### *1.5. Synthesis of CdS/CoMoS<sub>4</sub>, CdS/NiMoS<sub>4</sub>, and CdS/CoNiMoS<sub>4</sub> nanostructures*

CdS/CoMoS<sub>4</sub>, CdS/NiMoS<sub>4</sub>, and CdS/CoNiMoS<sub>4</sub> nanostructures were fabricated using the solvent assisted exfoliation technique via ultrasonication. Different Wt. % of CoMoS<sub>4</sub>, NiMoS<sub>4</sub>, CoNiMoS<sub>4</sub> (0.5, 1, 1.5, 2, 2.5, and 3) nanostructures were separately dissolved in 10 mL of Dimethylformamide (DMF) solution and ultrasonicated for 2 h to obtain a few layered nanostructures. Then, desired quantity of CdS nanorods were added to it and resume the ultrasonication for 1 h. The final solution was kept for stirring overnight to obtain CdS/CoMoS<sub>4</sub>, CdS/NiMoS<sub>4</sub>, and CdS/CoNiMoS<sub>4</sub> nanostructures. The as-synthesized products were washed with ethanol and DI water and the final product was then heated to 100°C for 8 h. The synthesis details of CdS/CoNiMoS<sub>4</sub> nanostructures are illustrated in the Scheme 1.

## 2. Characterization Techniques

Bruker D8 ADVANCE diffractometer (Cu K radiation) has been utilised to evaluate the XRD of the synthesized nanostructures. The Al K radiation (1486.6 eV) with an energy of 15 kV/150 W was used for X-ray photoelectron spectroscopy (XPS). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were employed on the JEOL JEM-2100F, operated at 200 kV acceleration voltage, to obtain the microstructural parameters. A UV-1800 SHIMADZU and a Hitachi F-7000 fluorescence spectrometer, respectively, were used to record the diffuse reflectance spectrum and the photoluminescence (PL) spectrum.

### 2.1. Photocatalytic measurements

The photocatalytic H<sub>2</sub> evolution investigations were carried out in a quartz reactor with a 150 mL capacity, into which 12 mL DI water, 3 mL lactic acid, and 3 mg of as-prepared photocatalysts were poured. Also, the reactor was sealed tightly using an airtight rubber septum to keep the mixture away from the external environment. The light source used is a solar simulator occupied with AM 1.5 G filter and a Si reference cell was used to calibrate the brightness of the light to that of one sun (100 mW/cm<sup>2</sup>). The reactor was entirely evacuated for 30 minutes prior to the light exposure, and it was subsequently filled with argon for an additional 30 minutes. A thermal conductivity detector (TCD)-equipped offline gas chromatograph (GC) was used to measure the amount of H<sub>2</sub> produced. In addition, the following equation was used to calculate the apparent quantum efficiency (AQE) of the created nanostructures:

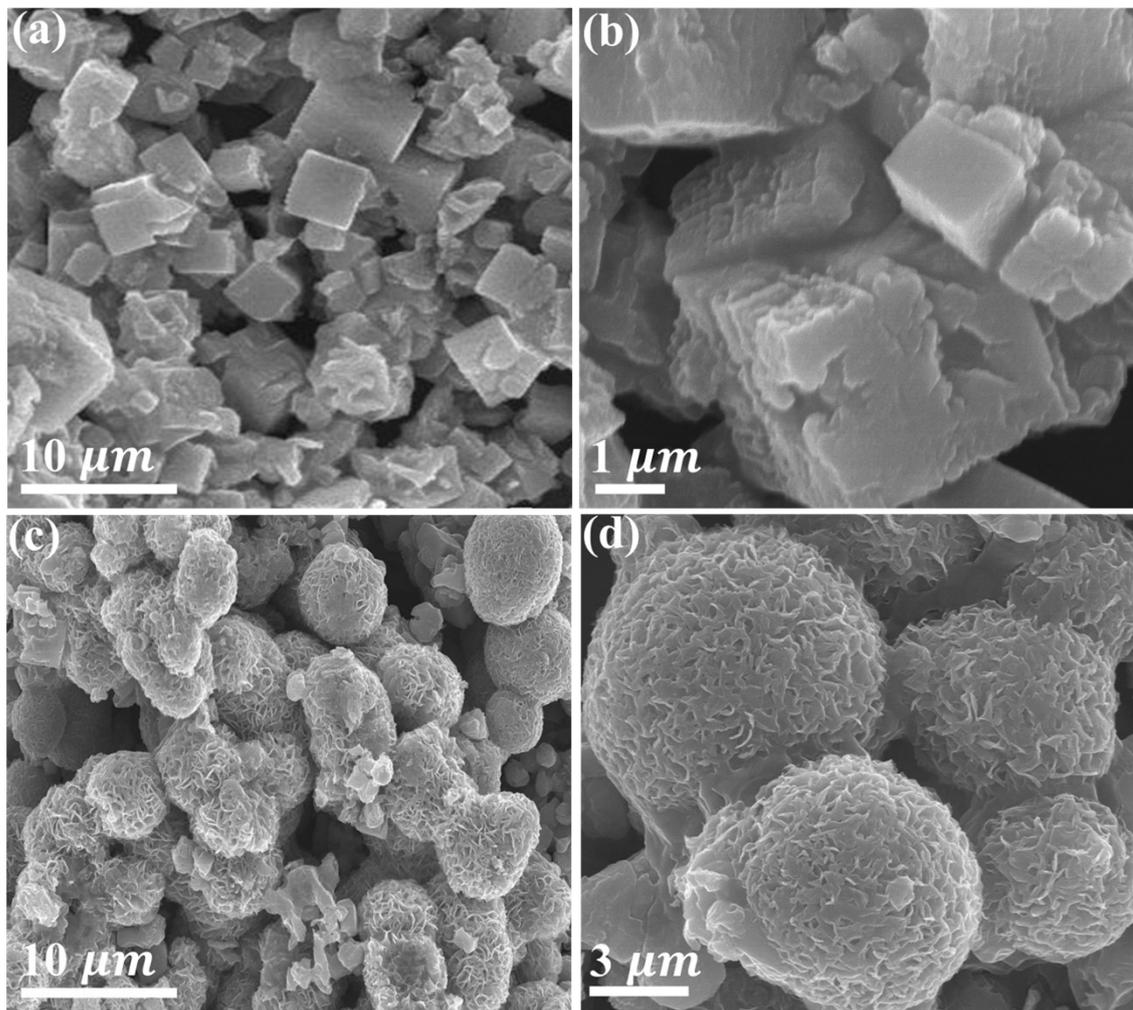
$$\text{Quantum yield} = \frac{\text{number of electrons reacted}}{\text{number of photons irradiated}} \times 100\%$$

$$= \frac{\text{Number of H}_2\text{ molecules generated}}{2 \times \text{Number of photons incident on the substrate}} \times 100\%$$

## 2.2. Photo-electrochemical (PEC) analysis

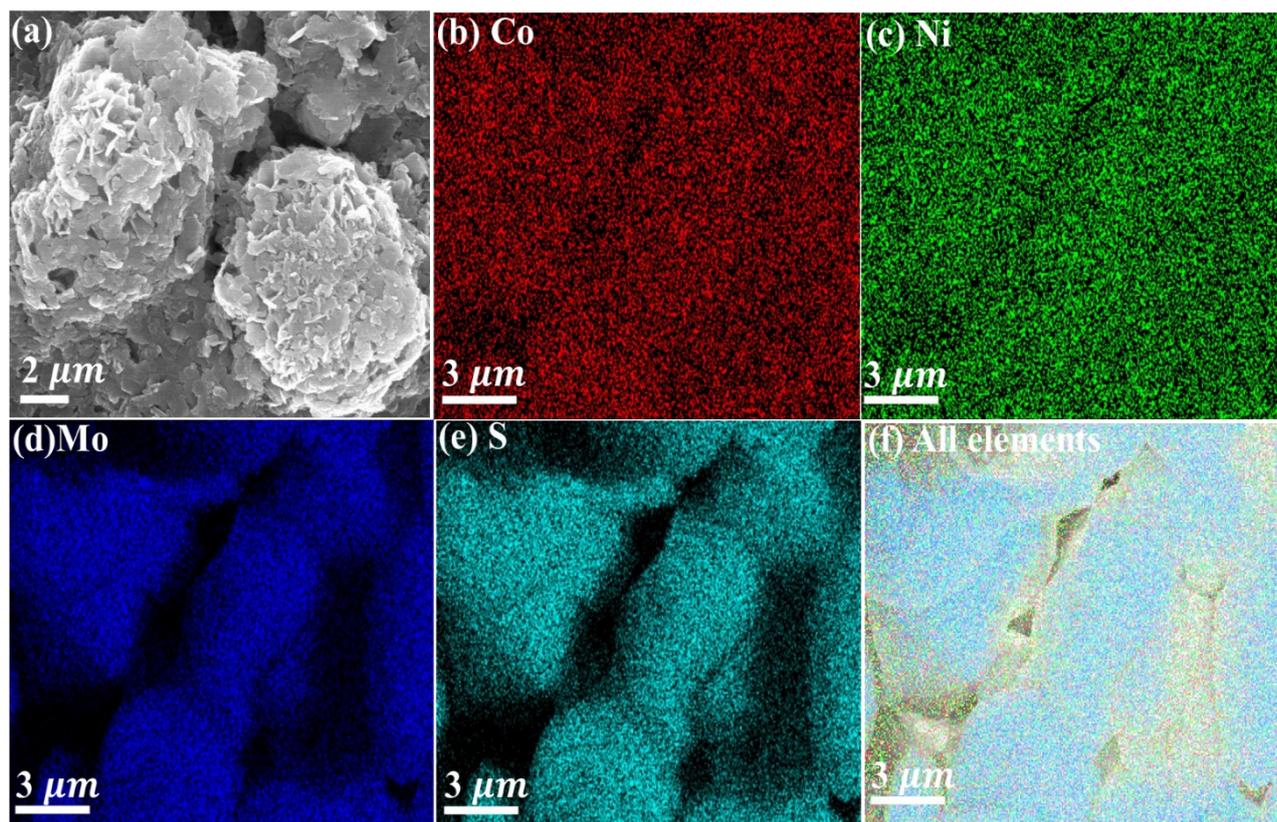
The Photoelectrochemical (PEC) tests were performed in a system employed with three electrodes (reference (Ag/AgCl), counter (Pt), and working (photocatalyst coated on the indium-tin oxide (ITO) electrodes). Na<sub>2</sub>SO<sub>4</sub> (0.5 M, pH=6.72) was used as the electrolyte. Biologic (SP 150e) electrochemical workstation is used for implementing PEC techniques. A solar simulator with an AM 1.5G filter served as the light source, and a calibrated Si reference cell was used to set the light intensity to equal one sun (100 mW/cm<sup>2</sup>). To guarantee appropriate light irradiation, the sample-light source distance was adjusted to be 3 cm. CdS, CdS/CoMoS<sub>4</sub>, CdS/NiMoS<sub>4</sub>, and CdS/CoNiMoS<sub>4</sub> nanocomposites (10 mg each) were first mixed into the solution mixture of ethanol (450 l) and Nafion (50 l) through ultrasonication for the fabrication of the working electrode. Additionally, 30 l of the catalyst solution were poured onto the conductive side of the ITO substrate and allowed to dry for three hours in an oven set to 80 °C. 0.0 V was estimated as the photoresponses for each on-off cycle of the solar simulator. Using an AC voltage of 5 mV and an open-circuit potential with a frequency between 105 and 101 Hz, electrochemical impedance spectroscopy (EIS) was conducted. Additionally, the Mott-Schottky analysis was used to estimate the flat-band potential ( $V_{fb}$ ) of the CdS, CoMoS<sub>4</sub>, NiMoS<sub>4</sub>, and CoNiMoS<sub>4</sub> at a frequency of 1 kHz (in the dark). Using the equation  $E_{NHE} = E_{Ag/AgCl} + 0.197$  at pH=7, the measured  $V_{fb}$  vs Ag/AgCl reference electrode was converted to the NHE scale.

## Supporting Figures



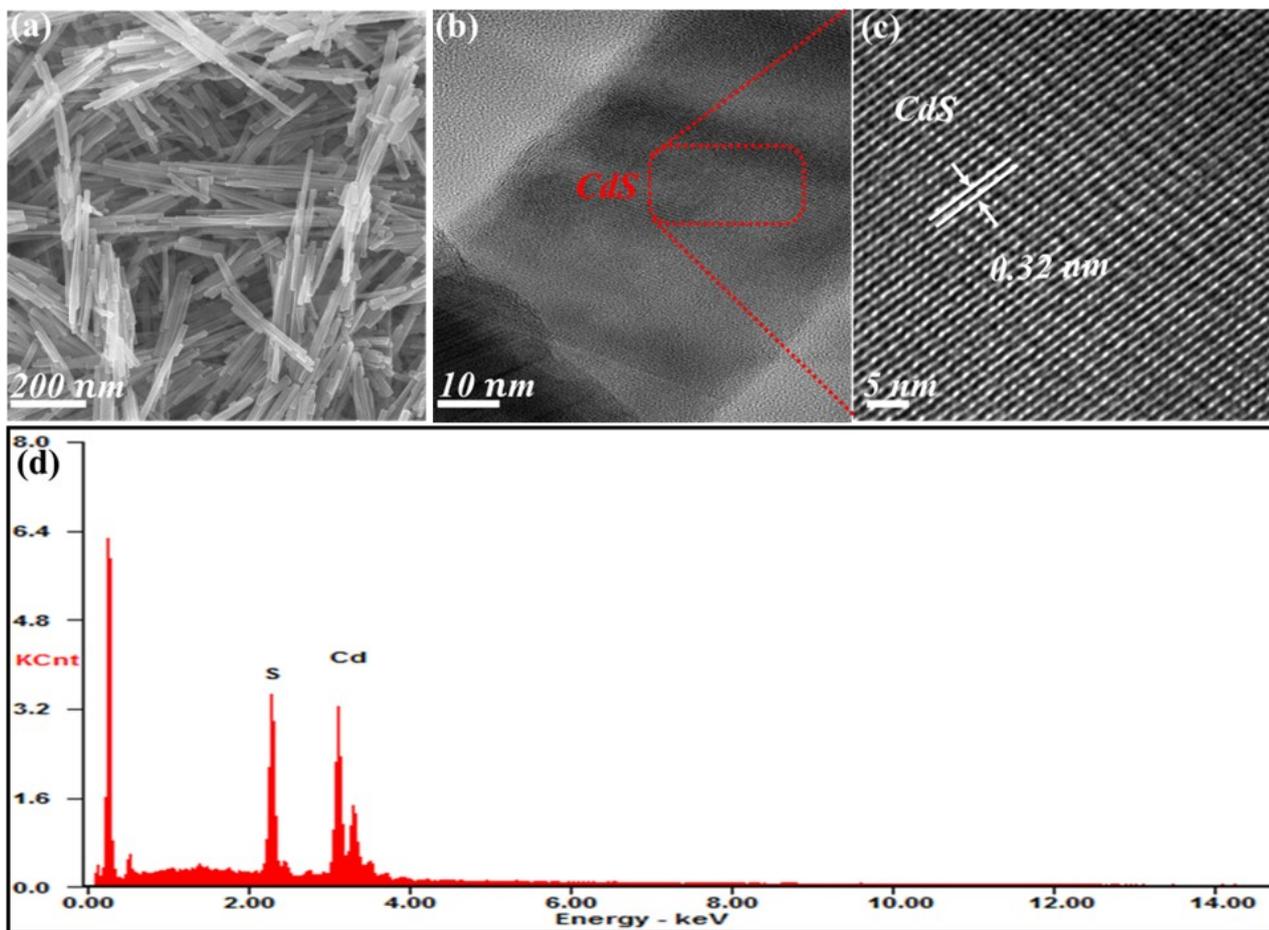
**Figure S1:** Low and high resolution FESEM micrographs of (a, b) CoMoS<sub>4</sub>, and (c, d) NiMoS<sub>4</sub> nanostructures.

As shown in Fig. S1(a, b), pure CoMoS<sub>4</sub> is obviously aggregated and appeared to be a multi-folded sheet like building block which favours more surface area to enhance the hydrogen production. Moreover, the hydrothermally grown NiMoS<sub>4</sub> nanostructures provided in Fig. S1(c, d) appears to be a uniform wrinkle-like nanosheet structure aggregated together to facilitate the charge carrier transfer by providing a greater number of active sites.

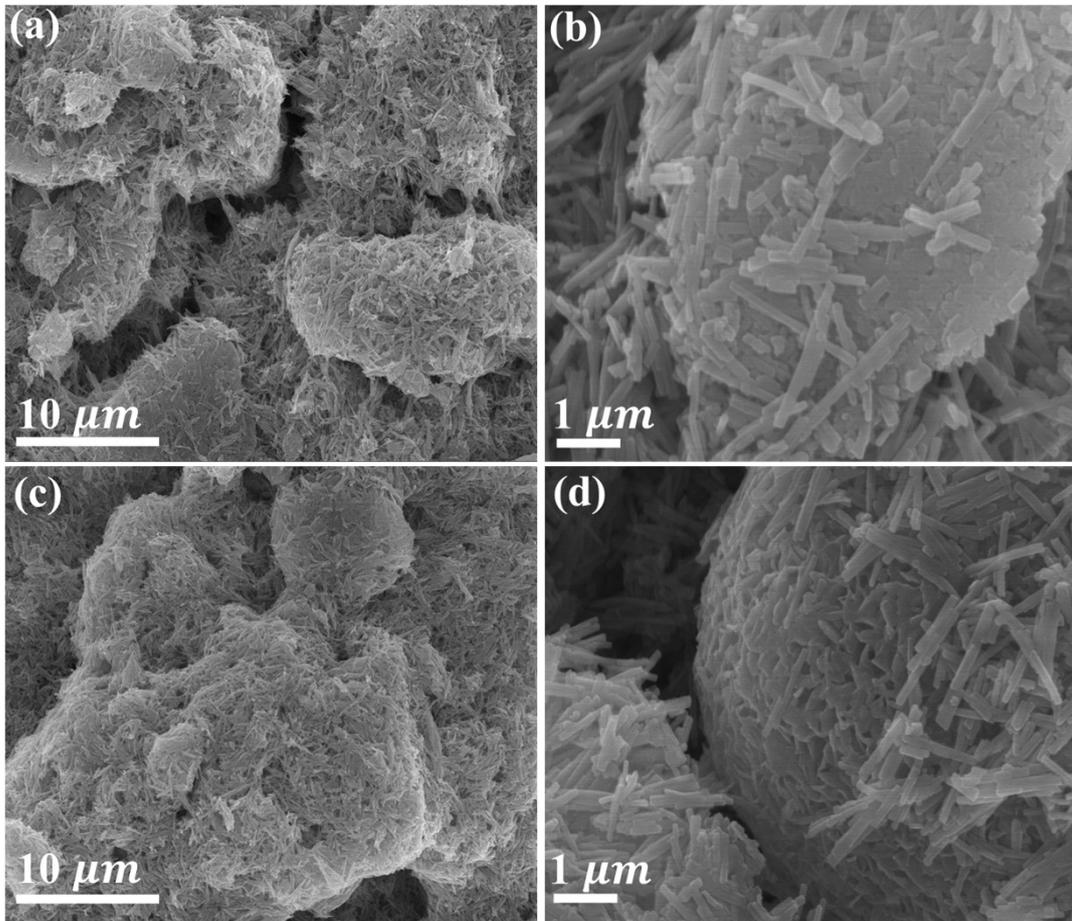


**Figure S2:** (a) FESEM micrograph of  $\text{CoNiMoS}_4$  nanostructures, (b-e) corresponding EDS image of Co, Ni, Mo, S elements individually, and (f) all elements

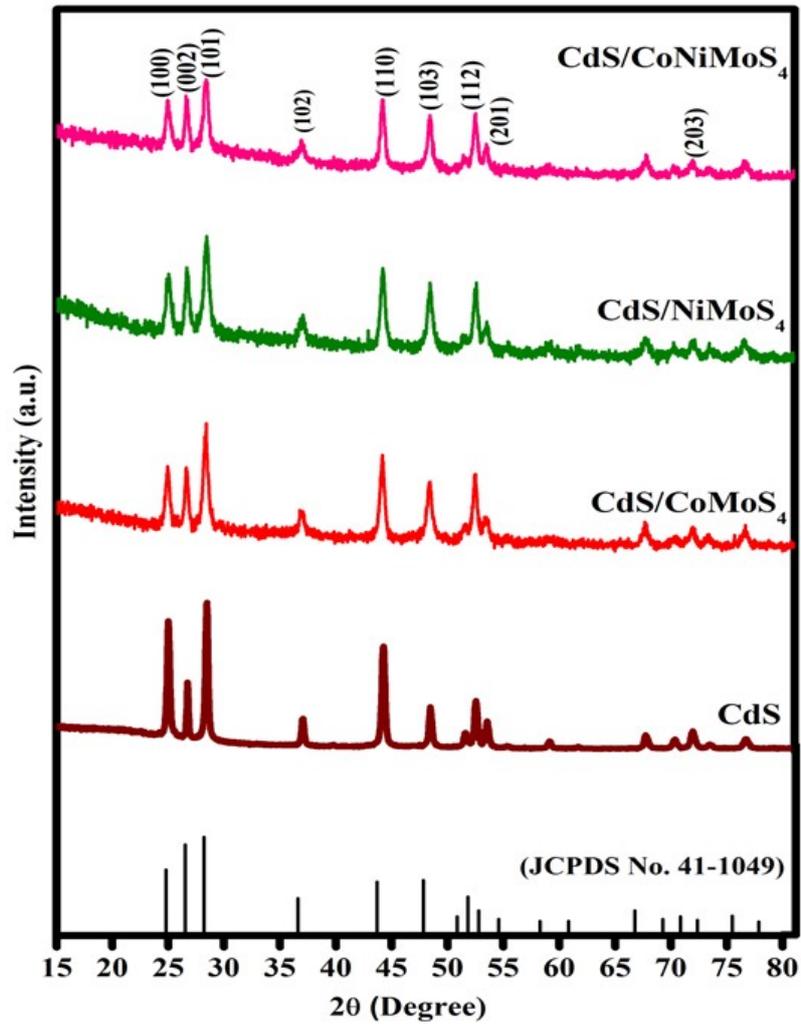
Fig. S2(a) represents closely connected  $\text{CoNiMoS}_4$  nanosheets which are appeared to be a cross-linked three-dimensional network that may serves as an excellent channel for charge transport. The elemental mapping in Fig. S2 (b-f) aids the visualization of homogenous distribution of elements such as Co, Ni, Mo, and S in  $\text{CoNiMoS}_4$  nanostructures.



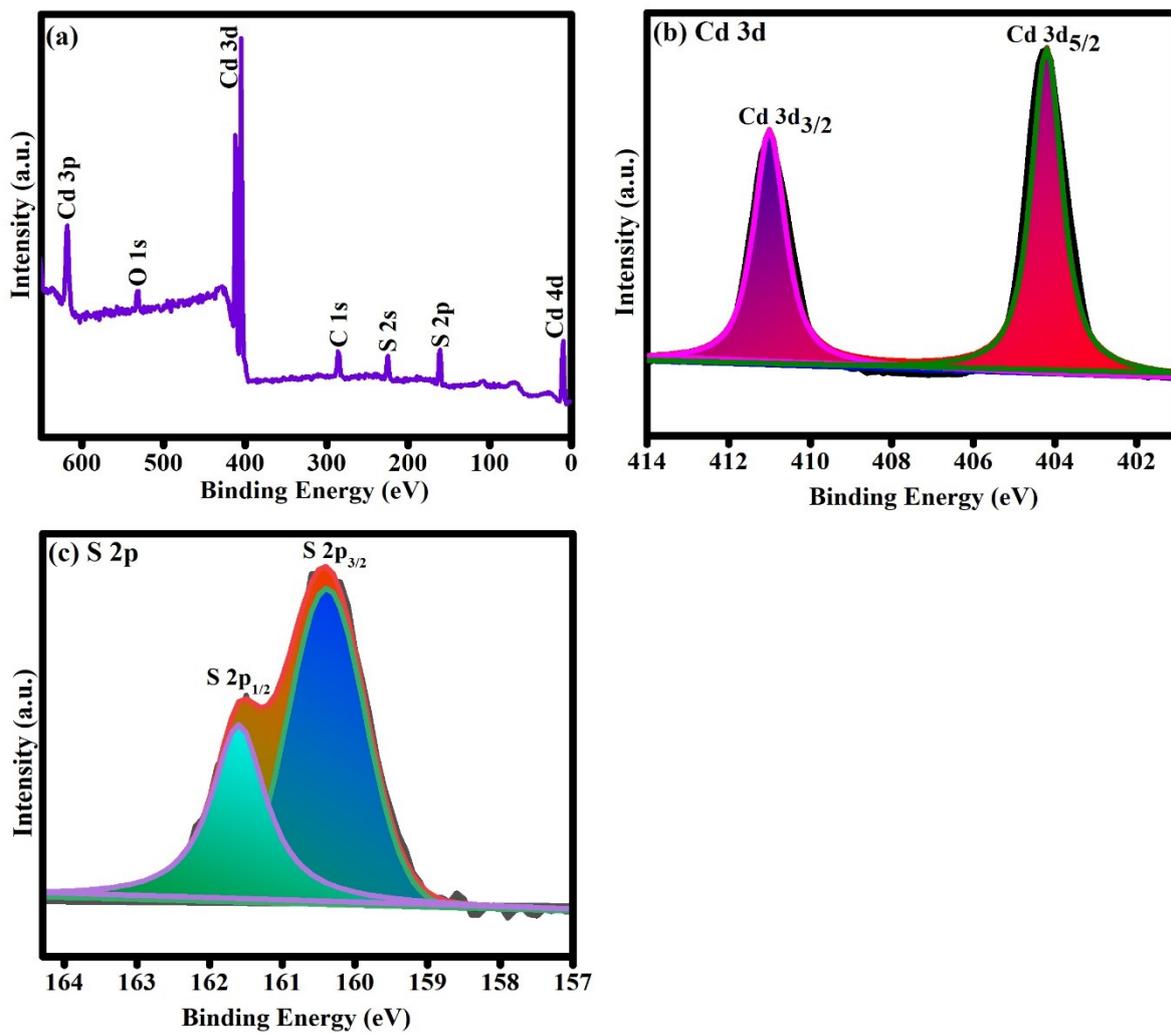
**Figure S3:** (a) FESEM micrograph of CdS nanorods, (b, c) corresponding HRTEM micrographs, and (d) EDS line spectra of CdS nanorods.



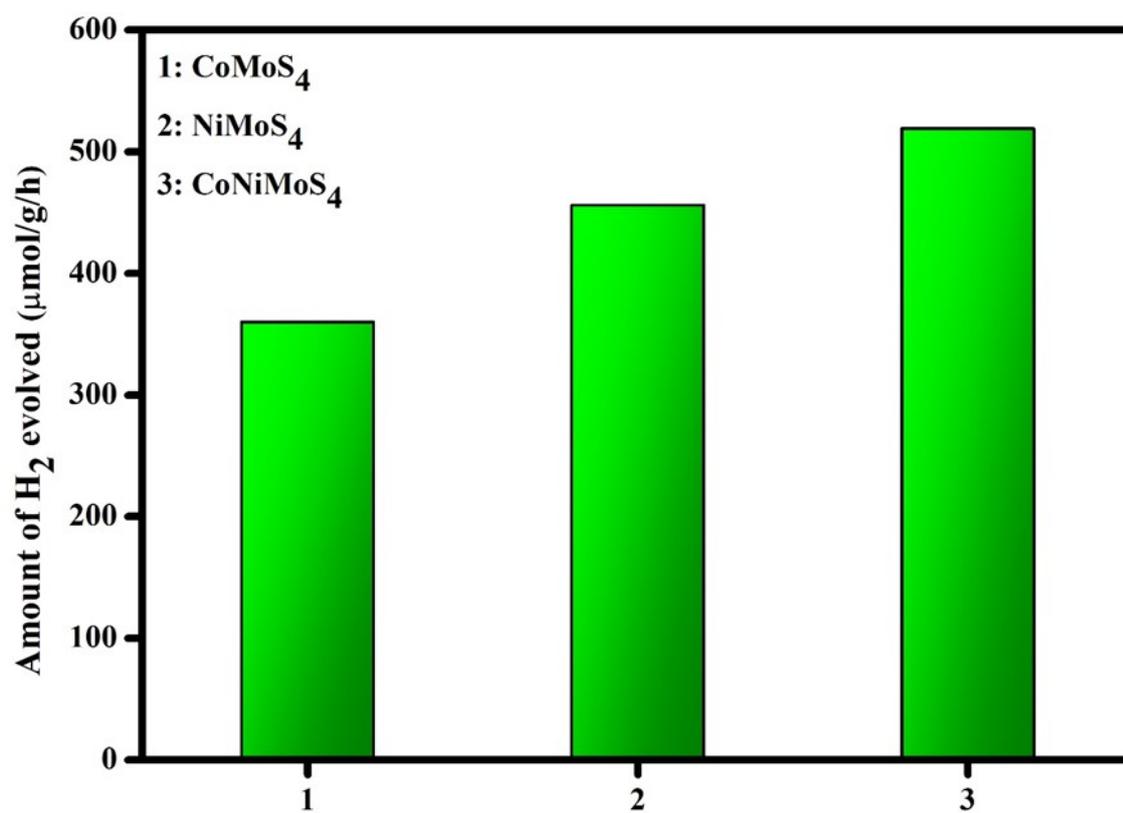
**Figure S4:** Low and high resolution FESEM micrographs of (a, b) CdS/CoMoS<sub>4</sub>, and (c, d) CdS/NiMoS<sub>4</sub> nanostructures



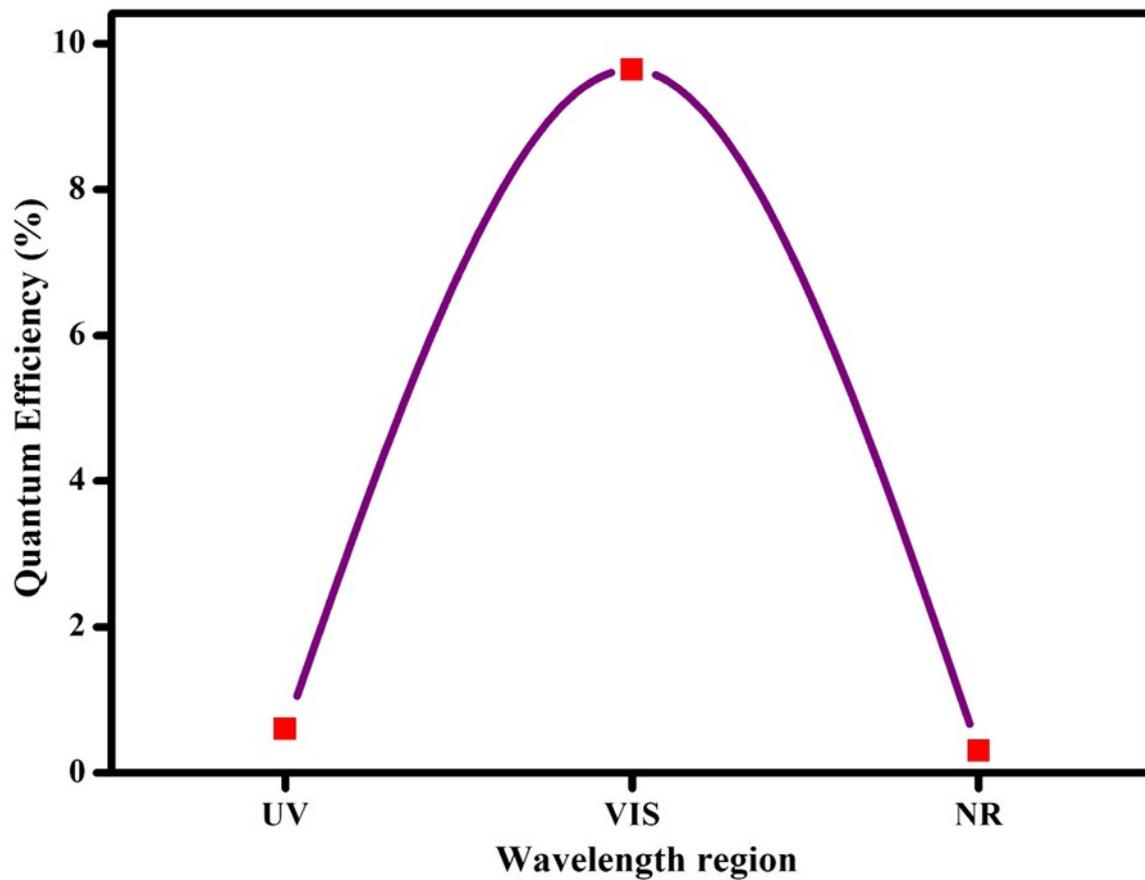
**Figure S5:** XRD patterns pristine CdS, CdS/CoMoS<sub>4</sub>, CdS/NiMoS<sub>4</sub> and CdS/CoNiMoS<sub>4</sub> nanocomposite respectively



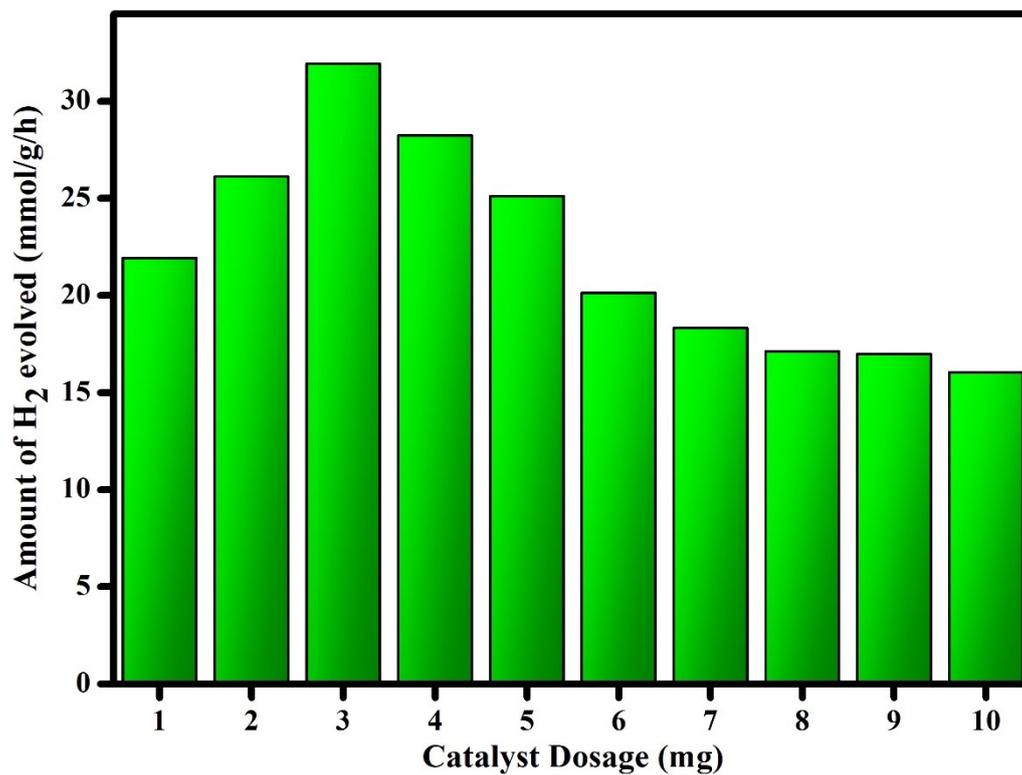
**Figure S6:** (a) XPS survey spectrum illustrating elemental distribution of pure CdS, and (b, c) respective core level spectra of Cd 3d and S 2p.



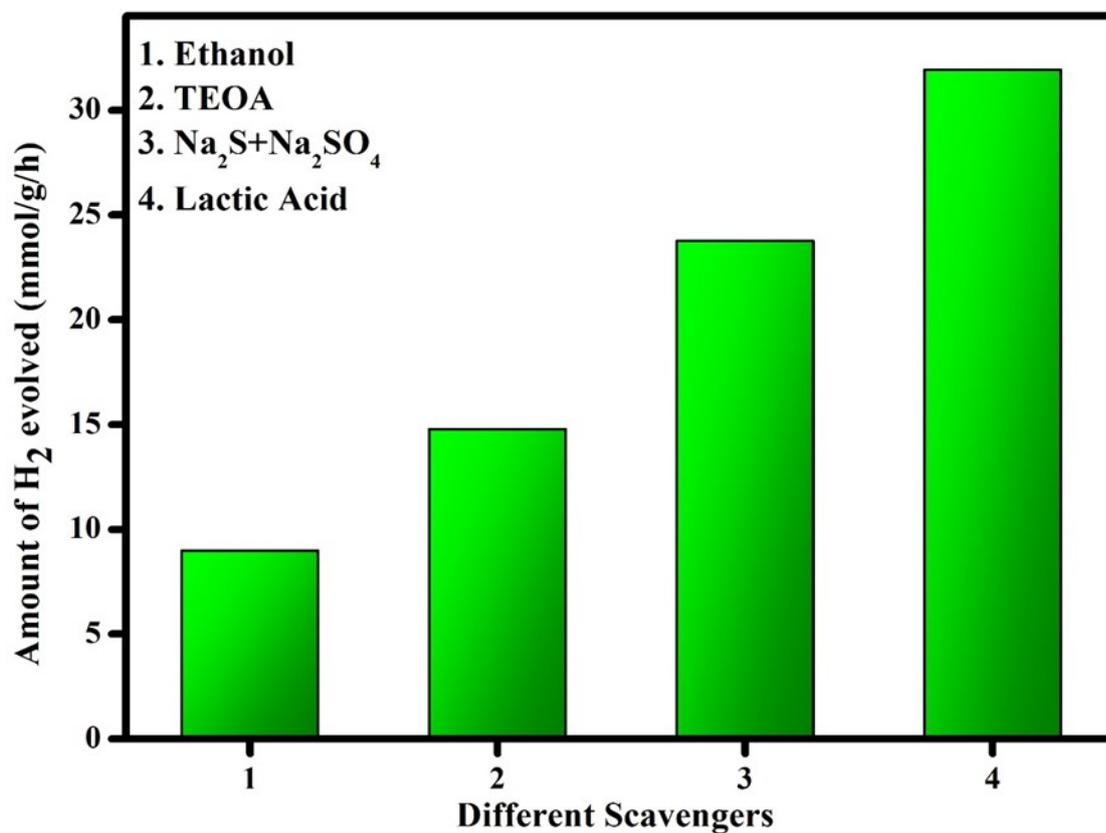
**Figure S7:** Hydrogen evolution rate of optimized CoMoS<sub>4</sub>, NiMoS<sub>4</sub>, and CoNiMoS<sub>4</sub> nanostructures (2 wt.%)



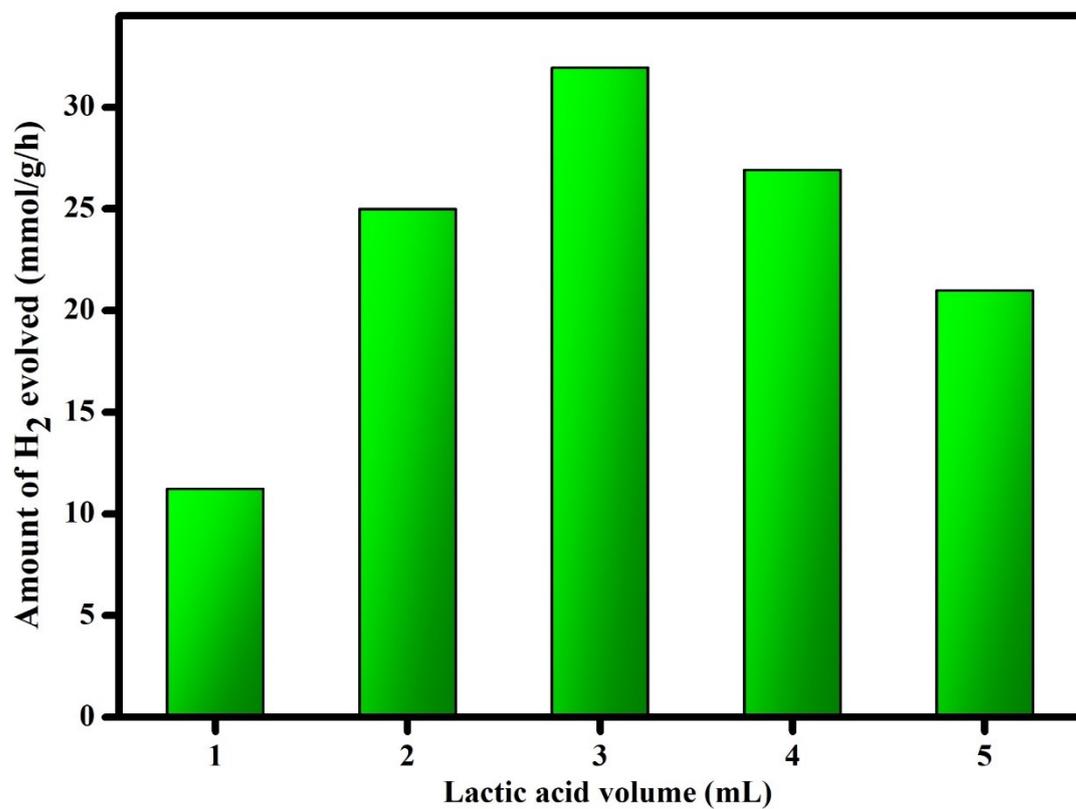
**Figure S8:** Wavelength dependent QE (%) (UV-Vis-NIR) of the optimized CdS/CoNiMoS<sub>4</sub> (2 wt. %) nanostructures.



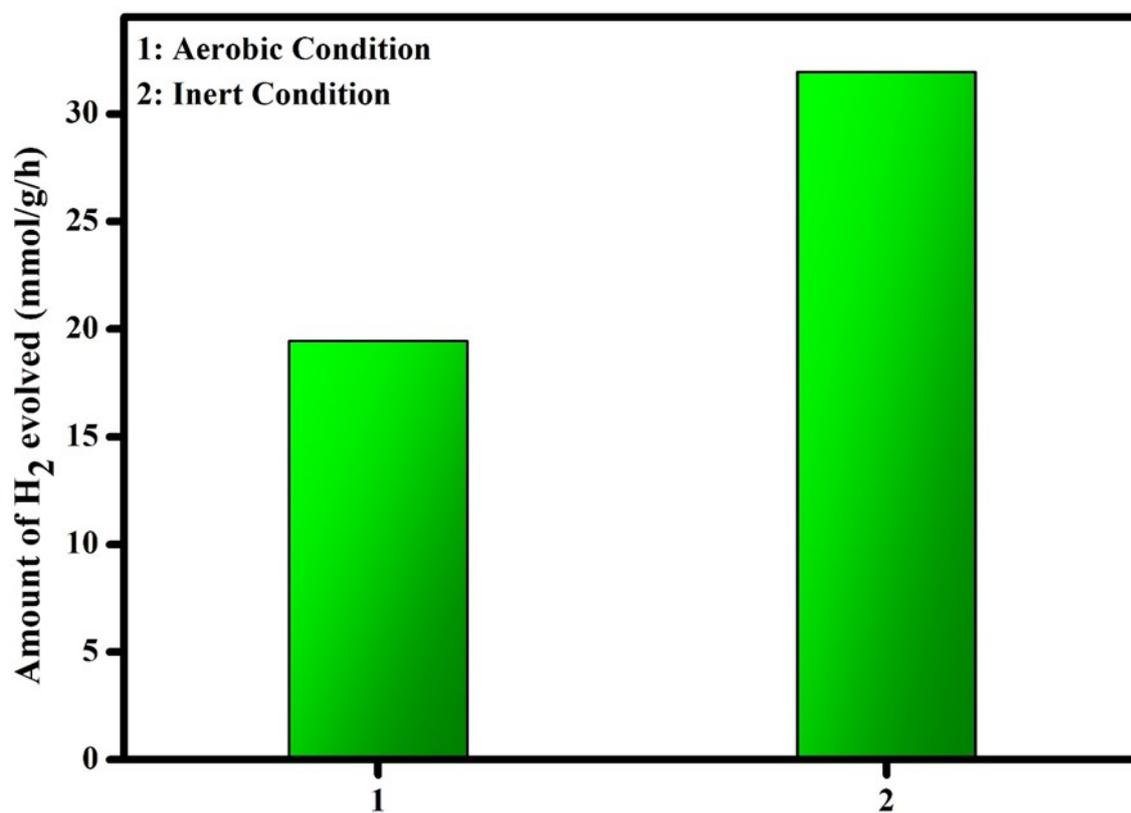
**Figure S9:** Hydrogen evolution rate of optimized CdS/ CoNiMoS<sub>4</sub> nanostructures with different catalyst dosage; varies from 1-10 mg.



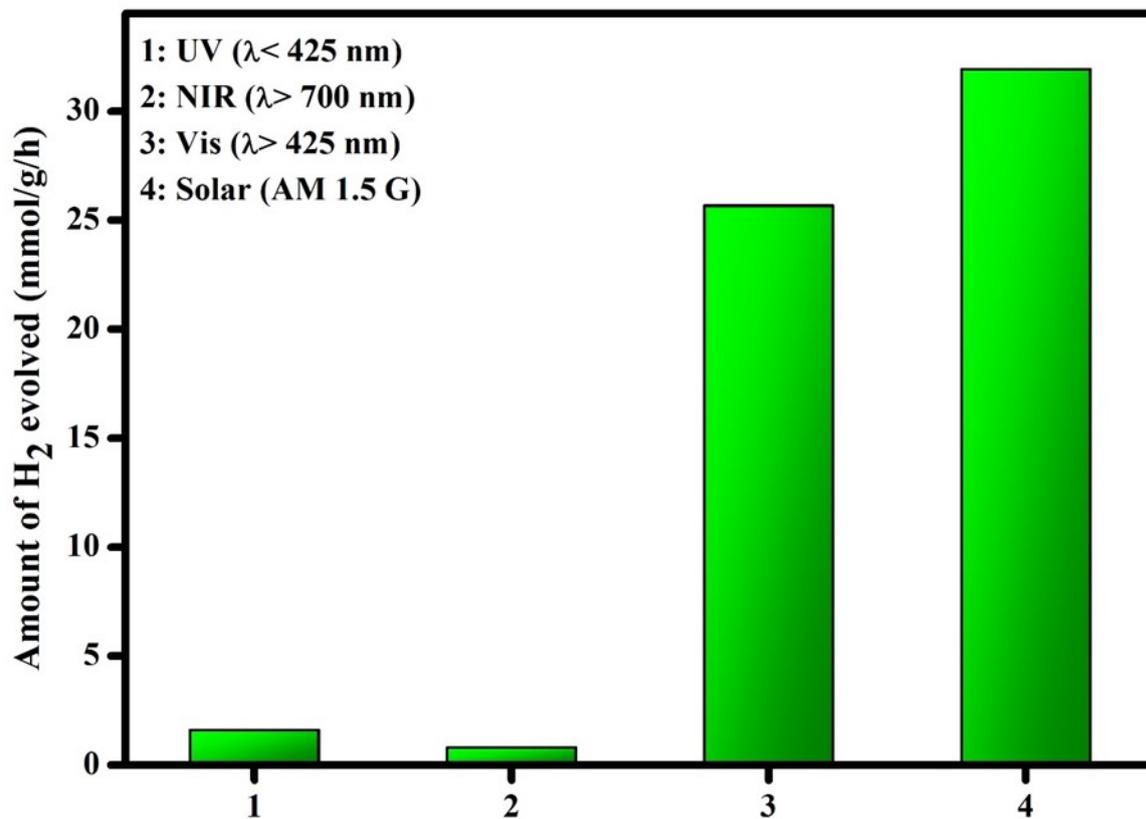
**Figure S10:** Amount of hydrogen evolved by optimized CdS/CoNiMoS<sub>4</sub> photocatalysts with various hole sacrificial agents.



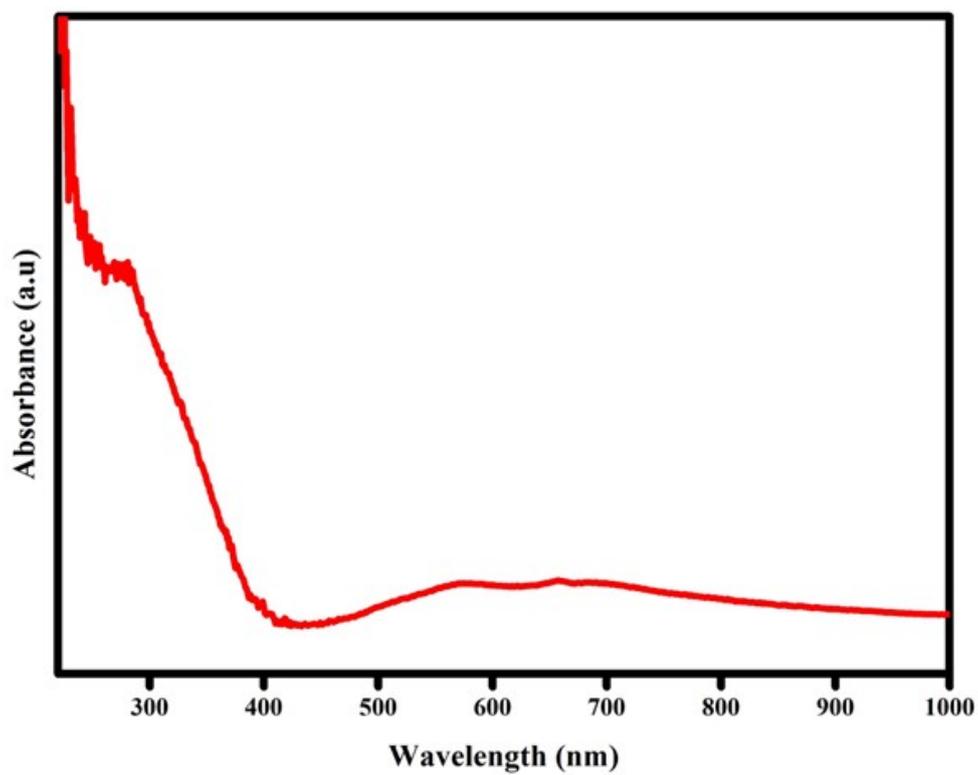
**Figure S11:** H<sub>2</sub> evolution rate of optimized CdS/CoNiMoS<sub>4</sub> nanostructures at various concentration of lactic acid.



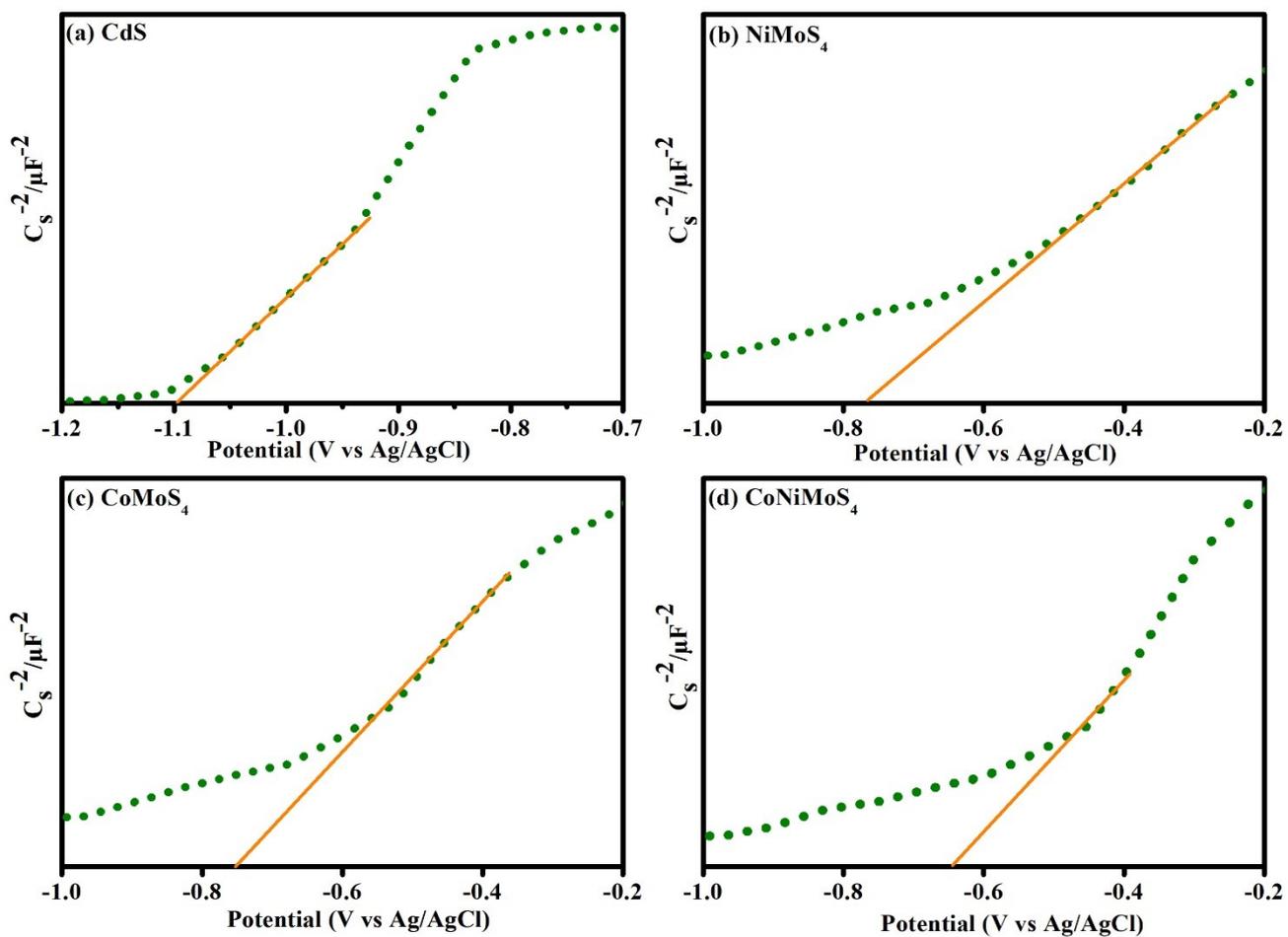
**Figure S12:** Rate of hydrogen evolution under aerobic and inert atmosphere using optimized CdS/CoNiMoS<sub>4</sub> photocatalyst.



**Figure S13:** Amount of hydrogen produced using the optimized CdS/CoNiMoS<sub>4</sub> nanocomposite at various wavelengths of light irradiation (UV, NIR, Vis, Solar)



**Figure S14:** UV-vis DRS spectra of CoNiMoS<sub>4</sub> nanostructure



**Figure S15:** Mott-Schottky plots of (a) CdS, (b) NiMoS<sub>4</sub>, (c) CoMoS<sub>4</sub>, and (d) CoNiMoS<sub>4</sub> nanostructures

**Table S1:** Comparison of the hydrogen evolution activity of previously reported semiconductor-based photocatalysts our experimental outcomes

Catalyst	Illumination Source	Sacrificial agent	H <sub>2</sub> evolution performance (mmol/g/h)	Ref.
CdS/CoNiMoS <sub>4</sub>	AM 1.5 G	Lactic acid	31.9	Present work
In <sub>2</sub> S <sub>3</sub> /In <sub>2</sub> O <sub>3</sub>	300 W Xe lamp	Triethanolamine (TEOA)	0.683	[1]
RuN <sub>3</sub> /ZIF-67	405 nm LED lamp (280 mW)	TEOA	4.85	[2]
Co <sub>9</sub> S <sub>8</sub> @ZnIn <sub>2</sub> S <sub>4</sub>	300 W Xe lamp	TEOA	6.2	[3]
Bi <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	UV-LEDs	Glycerol	0.92	[4]
SiPc/N-usRGO/Pt	UV-vis	TEOA	0.004	[5]
Nb <sub>2</sub> O <sub>5</sub> /g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp	TEOA	1.7	[6]
CdS/Nb <sub>2</sub> O <sub>5</sub> /N-doped graphene	150 W Xe lamp	Na <sub>2</sub> S + Na <sub>2</sub> SO <sub>3</sub>	0.1	[7]
CdS/MoS <sub>2</sub>	300 W Xe lamp	Lactic acid	1.36	[8]
C@Co-NCT/CdS	300 W Xe lamp	Lactic acid	3.8	[9]
CQDs/KNbO <sub>3</sub>	300 W Xe lamp		0.468	[10]
NiMoS <sub>4</sub> /CdS	300 W Xe lamp	Benzyl alcohol	7.27	[11]
CoMoS <sub>4</sub> /CdS	300 W Xe lamp	Benzyl alcohol	2.86	
CuMoS <sub>4</sub> /CdS	300 W Xe lamp	Benzyl alcohol	1.11	
3Au-3 P/30Fe-CN	UV-visible irradiation	-	3.172	[12]

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