

# Electronic Supplementary

## Information

**In *situ* addition of Ni salt on skeletal Cu<sub>7</sub>S<sub>4</sub> integrated CdS nanorods photocatalyst for efficient production of H<sub>2</sub> under solar light irradiation**

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# Experiments

## *Materials*

Cadmium acetate dihydrate ( $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ), copper nitrate ( $\text{Cu}(\text{NO}_2)_3 \cdot 3\text{H}_2\text{O}$ ), polyvinylpyrrolidone (PVP), sodium hydroxide (NaOH), and ethanol were purchased from Daejung Chemicals & Metals Co., Ltd.. Ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ) was obtained from Junsei Chemical Co., Inc. Thiourea ( $\text{NH}_2\text{CSNH}_2$ ) was purchased from Kanto Chemical Co., Ltd. Ethylene diamine was obtained from Alfa Aesar. All chemicals were used without further purification.

## *Synthesis of CdS nanorods*

CdS nanorods were synthesized following the previous study of the hydrothermal method.<sup>S1</sup> The 1:1 molar ratio of  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{NH}_2\text{CSNH}_2$  was dissolved in 60 mL of ethylene diamine with vigorous stirring for 30 min to obtain homogeneous solution. The resultant yellowish-precipitated solution was transferred to 100 mL Teflon-lined autoclave and heated in furnace at 160 °C for 48 h. The autoclave was cooled down to room temperature and the yellow-colored solid product was collected, which was washed with distilled water and ethanol three times to remove impurities and then dried at 60 °C for 12 h.

## *Synthesis of skeletal $\text{Cu}_7\text{S}_4$ nanocages*

The skeletal  $\text{Cu}_7\text{S}_4$  nanocages were synthesized following the templating method with some modifications,<sup>S2</sup> as shown in Scheme 1. Initially, 0.20 g of PVP was dissolved in 100 mL of aqueous solution with  $\text{Cu}(\text{NO}_2)_3$  (0.01 M) under vigorous stirring. Upon addition of NaOH, blue precipitates were immediately formed, which was kept under stirring for more than one minute. Then, 25.0 mL of ascorbic acid (0.10 M) was added in the mixture and stirred for another 15 min.

During this process, a gradual change of color from blue to orange and to red was observed. Then, 5.0 mL of thiourea (0.20 M) was added. The resultant transparent red solution was transferred to 100 mL Teflon-lined autoclave. It was placed inside furnace and maintained at 180 °C for 10 h. After natural cooling of system to room temperature, the collected black residue was washed many times with distilled water to remove impurities. Finally, the obtained Cu<sub>7</sub>S<sub>4</sub> powder was dried at 80 °C overnight.

### ***Synthesis of Cu<sub>7</sub>S<sub>4</sub>/CdS composites***

The Cu<sub>7</sub>S<sub>4</sub>/CdS composites were prepared by mixing different weight percentages (2–8 wt%) of the as-prepared Cu<sub>7</sub>S<sub>4</sub> with CdS, under stirring for 30 min, which was followed by drying at 60 °C for 12 h.

## **Characterizations**

The structural information of materials was determined by X-ray diffraction (XRD) using Cu K $\alpha$  radiation (D8 Advanced X-ray diffractometer, Bruker). Diffuse reflectance spectra (DRS) were measured using ultraviolet (UV)-visible spectrometer (UV-1800, Shimadzu). The morphology and elemental analysis were acquired using field emission scanning electron microscope (FESEM, S-4800, HITACHI) equipped with the energy dispersive spectrometer (EDS, Inca 400, Oxford Instruments). The morphology and elemental analysis were also obtained using transmission electron microscope (TEM, JEM-2100F, JEOL) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out using monochromatic Al K $\alpha$  X-ray source (1486.6 eV) at 15 kV/150 W. Photoluminescence (PL) spectra of the as-synthesized photocatalysts were recorded using fluorescence spectrometer (F-7000, Hitachi).

### ***Photocatalytic H<sub>2</sub> production***

The photocatalytic H<sub>2</sub> production reactions were evaluated in 150 mL quartz reactor at ambient conditions. Typically, 1.0 mg of photocatalyst was dispersed in 15 mL of aqueous solution containing 20% lactic acid (LA), which acted as a sacrificial reagent. Then, the reactor was closed with a gas-tight rubber septum. Prior to irradiation, the suspension was evacuated and outgassed with Ar for 30 min to remove air. A solar simulator equipped with AM 1.5 G filter and 150 W Xe lamp (Abet Technologies) was used as the irradiation source. The output light intensity was adjusted to 1 sun (100 W/m<sup>2</sup>) using 15151 calibrated Si reference cell (Abet Technologies). The experiments were repeated for three times to check reproducibility. Every test was carried for 3 h under irradiation. H<sub>2</sub> production was analyzed using off-line gas chromatograph (GC, Autochro-3000, model 4900, Young Lin) equipped with thermal conductivity detector (TCD) and 5 Å molecular sieve column. The generated H<sub>2</sub> was collected at the headspace of quartz reactor, purged into GC, and evaluated by the calibration plot. The apparent quantum efficiency (QE) was calculated by the following equation,

$$\begin{aligned}\text{QE}(\%) &= \frac{(\text{Numbers of reacted electrons})}{(\text{Numbers of incident photons})} \times 100 \\ &= \frac{2 \times (\text{Numbers of evolved H}_2 \text{ molecules})}{(\text{Numbers of incident photons})} \times 100.\end{aligned}$$

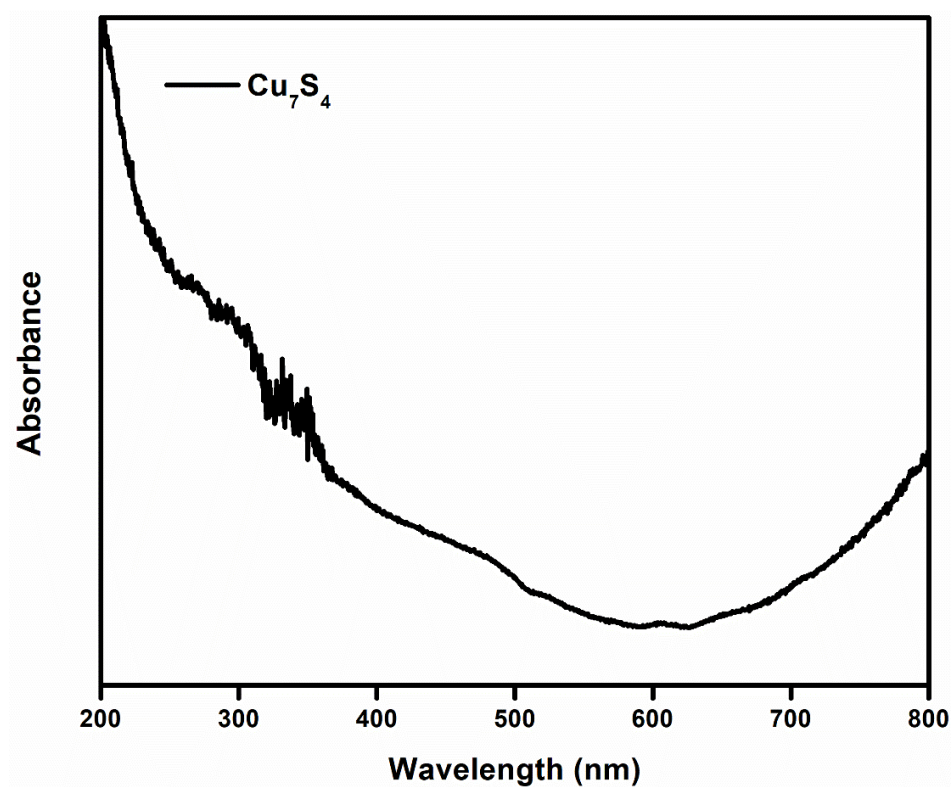
QE was measured under the identical experimental condition except the irradiation source, where 150 W Xe lamp with different wavelength filters were used as the light source, instead of the solar simulator. The output light intensity was measured using 15151 calibrated Si reference cell.

### ***Photoelectrochemical measurements***

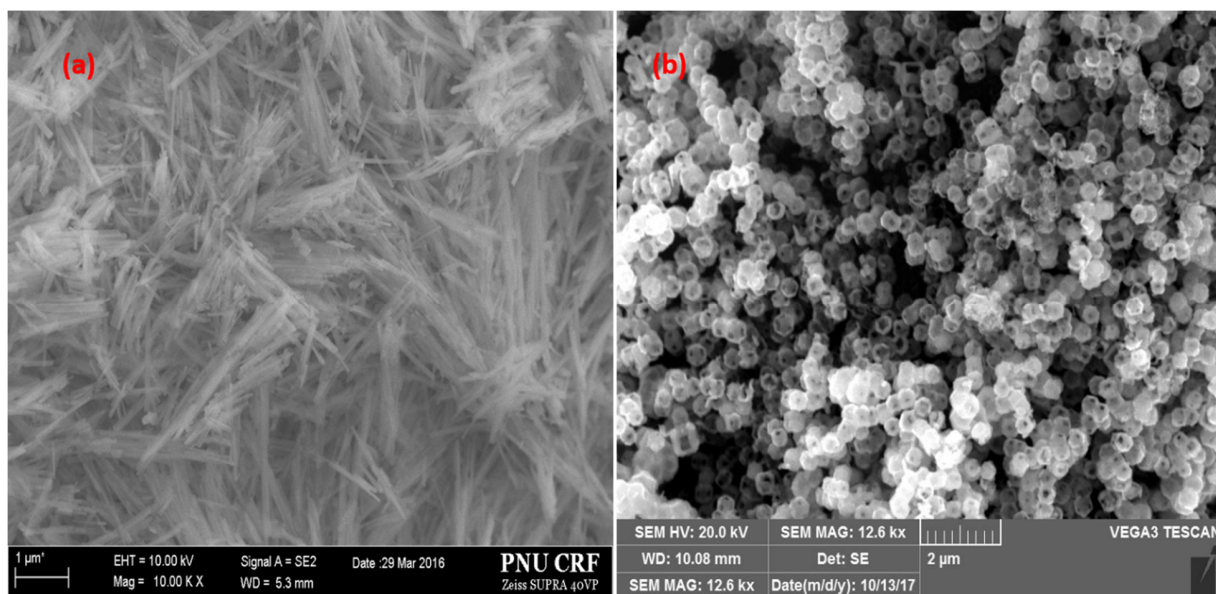
Photoelectrochemical studies were carried out using a three-electrode system by CHI 617B electrochemical workstation. A solar simulator equipped with an AM 1.5G filter and 150 W Xe

lamp was used as the irradiation source. The output light intensity was adjusted to 1 sun ( $100 \text{ W/m}^2$ ) using 15151 calibrated Si reference. The reference and counter electrodes were Ag/AgCl and platinum wire, respectively, and aqueous solution of  $\text{Na}_2\text{SO}_4$  (0.5 M) was served as the electrolyte. The measured pH value was 6.72. To prepare the working electrode, 10 mg of as-synthesized CdS and  $\text{Cu}_7\text{S}_4/\text{CdS}$  was first dispersed into mixtures of ethanol (450  $\mu\text{L}$ ) and Nafion (50  $\mu\text{L}$ ) by soft ultrasonic stirring to obtain uniform suspension. The solution containing the catalyst (30  $\mu\text{L}$ ) was dropped onto the pretreated indium tin oxide (ITO) conductor glass substrate, which was then dried in an oven at  $80^\circ\text{C}$  for 3 h. Photoresponses were measured at 0.0 V during on-off cycling of the solar simulator. To evaluate the band potentials of CdS,  $\text{Cu}_7\text{S}_4$ , and  $\text{Cu}_7\text{S}_4/\text{CdS}$ , Mott–Schottky plots were measured at a frequency of 1 kHz using a standard potentiostat equipped with an impedance spectra analyzer in the identical electrochemical configuration and electrolyte under the dark condition. The measured potentials versus Ag/AgCl were converted to the scale of normal hydrogen electrode (NHE) by  $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197$ . The cyclic voltammogram (CV) was measured at the scanning rate of 10 mV/s in the aqueous electrolyte solution consisting of  $\text{Na}_2\text{SO}_4$  (0.1 M) and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (1 mM).<sup>S3</sup>

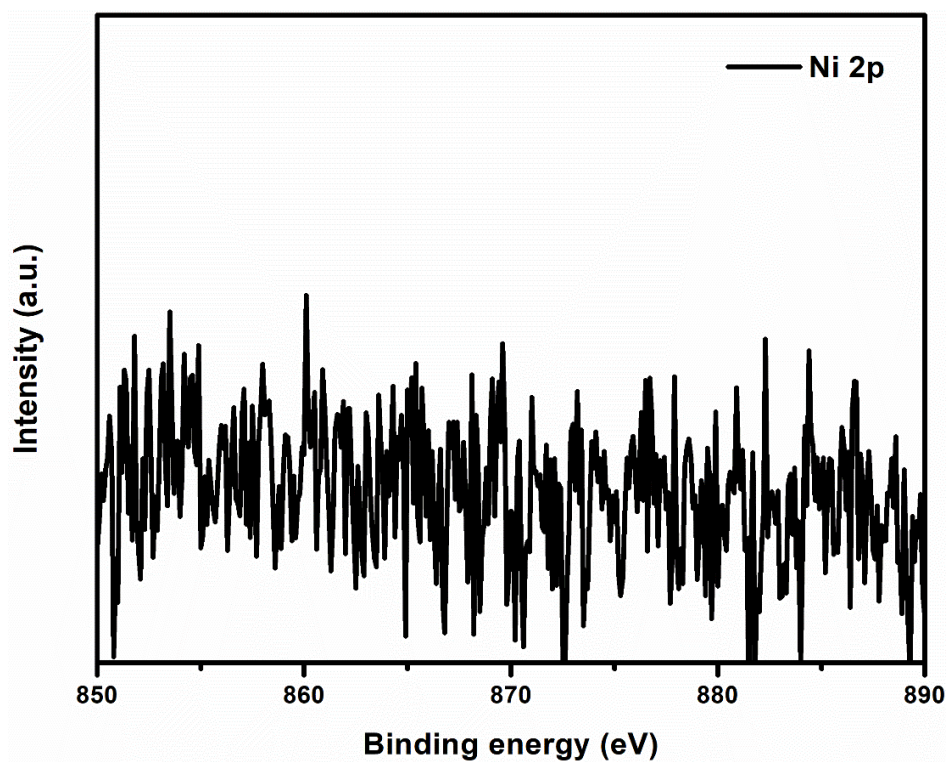
## Supporting Figures and Table



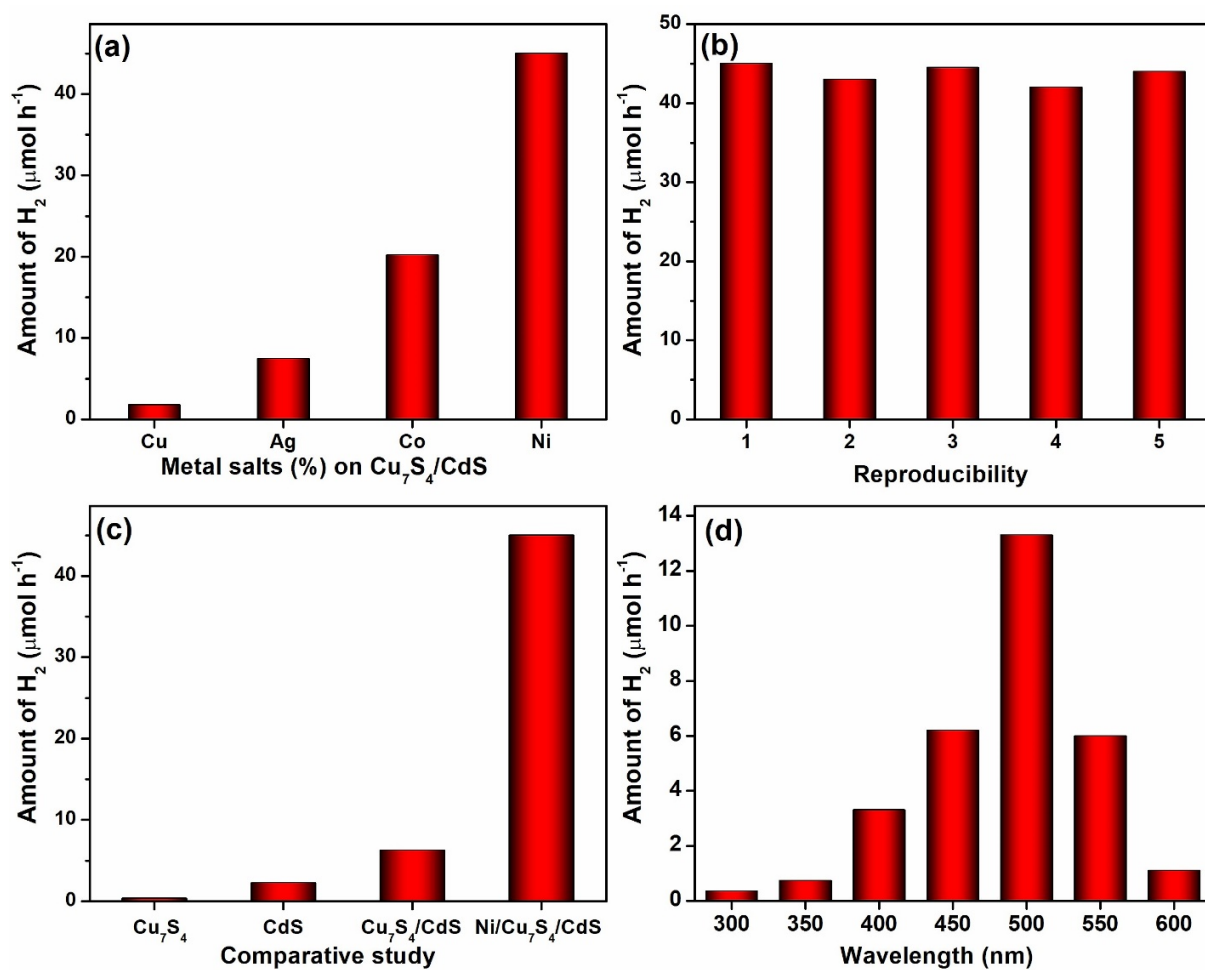
**Fig. S1.** DRS UV-visible spectrum of skeletal  $\text{Cu}_7\text{S}_4$  nanostructures.



**Fig. S2.** SEM images of (a) CdS nanorods and (b) skeletal Cu<sub>7</sub>S<sub>4</sub> nanostructures.

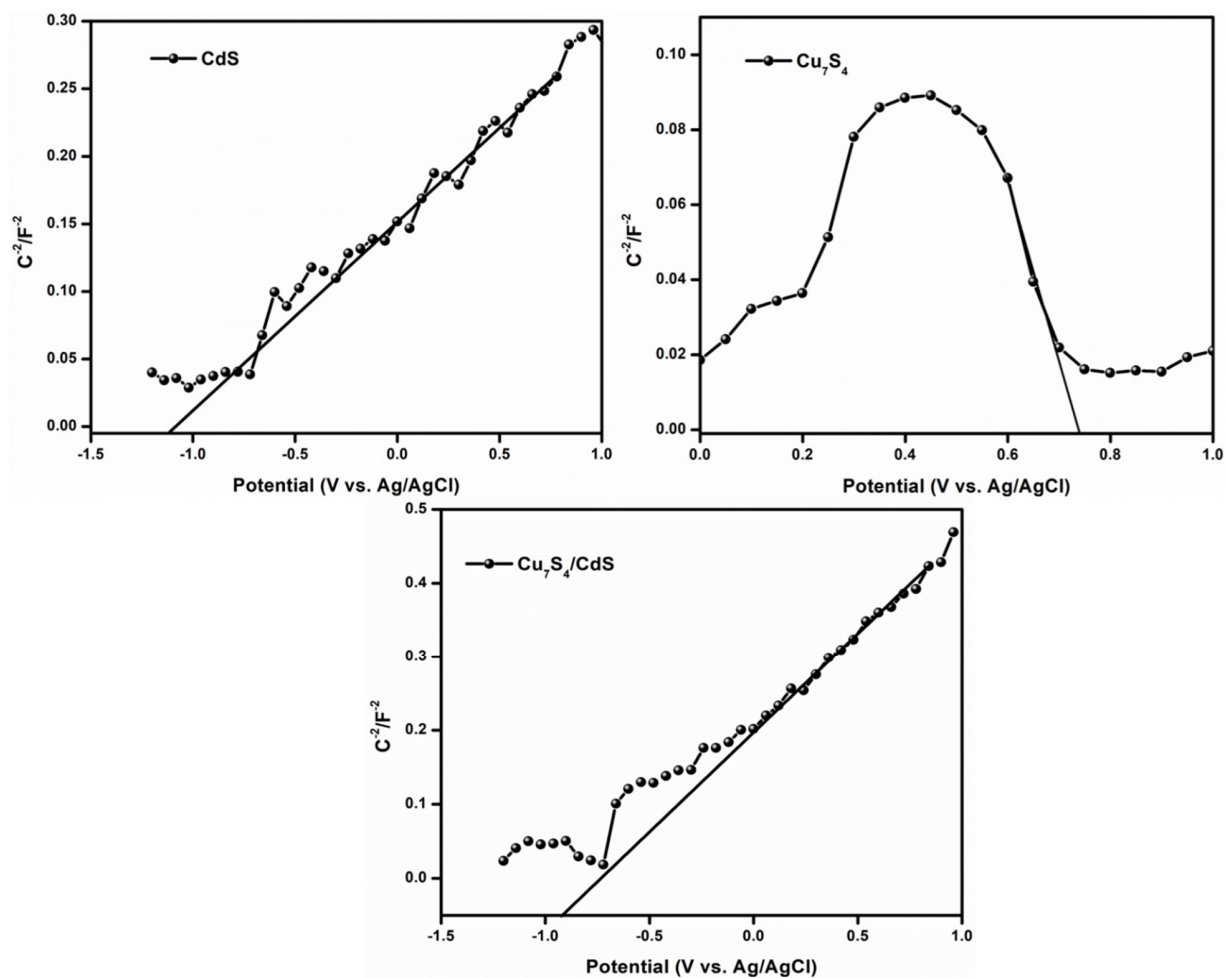


**Fig. S3.** XPS spectrum in Ni 2p region of Ni-Cu<sub>7</sub>S<sub>4</sub>/CdS nanocomposites.

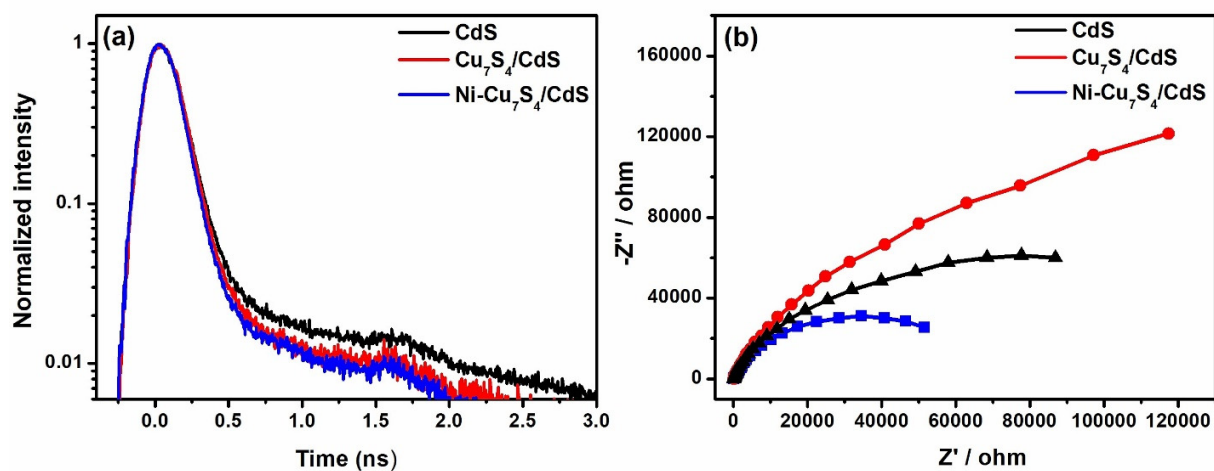


**Fig. S4.** Photocatalytic assessments of Ni-Cu<sub>7</sub>S<sub>4</sub>/CdS nanocomposites. (a) Effects of metal salts on the photocatalytic production rate and (b) reproducibility of H<sub>2</sub> production rate of Ni-Cu<sub>7</sub>S<sub>4</sub>/CdS. (c) Photocatalytic H<sub>2</sub> production rates of Cu<sub>7</sub>S<sub>4</sub>, CdS, Cu<sub>7</sub>S<sub>4</sub>/CdS and Ni-Cu<sub>7</sub>S<sub>4</sub>/CdS nanostructures. (d) Wavelength dependent H<sub>2</sub> production rate of Ni-Cu<sub>7</sub>S<sub>4</sub>/CdS nanocomposite.

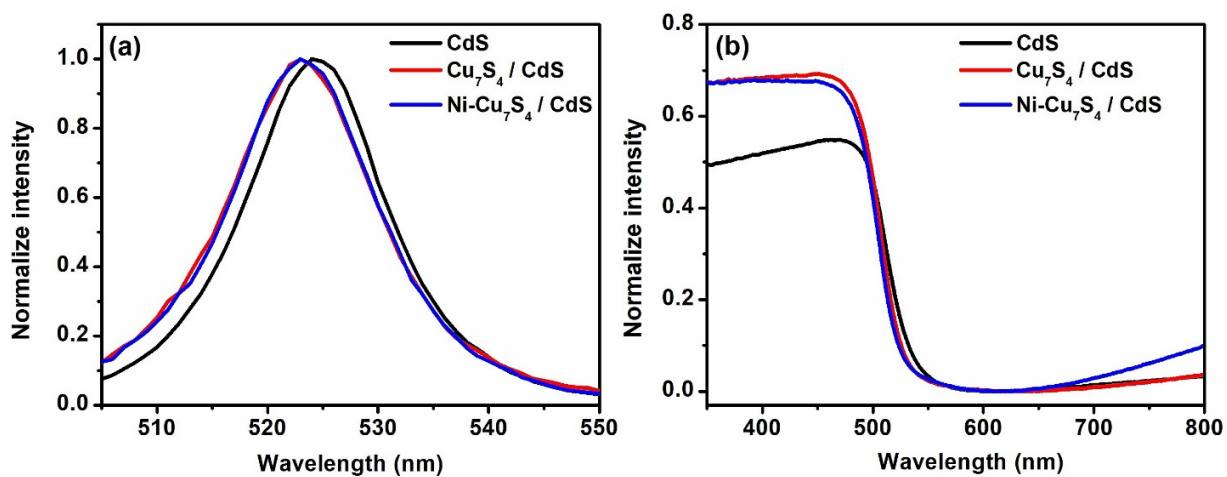




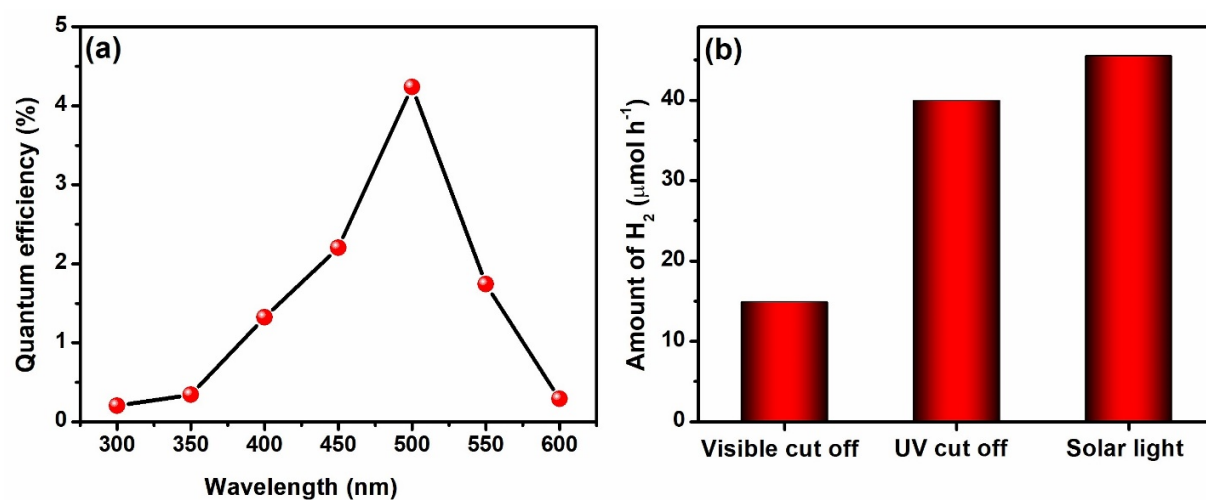
**Fig. S5.** Mott–Schottky measurements of (a) CdS, (b)  $Cu_7S_4$ , and (c)  $Cu_7S_4/CdS$  in  $Na_2SO_4$  electrolyte solutions.



**Fig. S6.** (a) Time-resolved PL spectra and (b) electrochemical impedance spectra of CdS, Cu<sub>7</sub>S<sub>4</sub>/CdS and Ni- Cu<sub>7</sub>S<sub>4</sub>/CdS nanostructures.



**Fig. S7.** (a) Normalized PL and (b) DRS UV-visible spectra of CdS, Cu<sub>7</sub>S<sub>4</sub>/CdS and Ni- Cu<sub>7</sub>S<sub>4</sub>/CdS nanostructures.



**Fig. S8.** (a) Wavelength dependent quantum efficiencies and (b) photocatalytic H<sub>2</sub> production rate (with and without UV and visible cut-off filters) of Ni- Cu<sub>7</sub>S<sub>4</sub>/CdS nanocomposites.

**Table. S1.** Comparison of photocatalytic H<sub>2</sub> production rates of *in situ* metal addition of various photocatalysts and Cu<sub>7</sub>S<sub>4</sub> based photocatalysts with this work.

Photocatalyst	Scavenger	Light source	H <sub>2</sub> production rate (μmol·h <sup>-1</sup> ·g <sup>-1</sup> )	Wavelength (nm)/ Quantum efficiency (%)	Ref.
CdS/Cu <sub>7</sub> S <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	300 W Xe lamp (λ > 420 nm)	3,570	420/4.4	S4
Co-CdS	Lactic acid	300 W Xe lamp (λ > 420 nm)	15,590	420/12.4	S5
RGO–CdS–Ni	Ethanol	500 W Hg lamp (λ > 400 nm)	17,500	410/2.8	S6
Ni-Co/CdS Ni/CdS Co/CdS	NaHCO <sub>2</sub> / Formic acid	750 W Xe lamp (λ ≥ 420 nm)	32,600 22,800 14,200	420 nm cut-off/15.5 – –	S7
Cu-TiO <sub>2</sub>	Methanol	450 W Hg lamp UV light	8,500	365/7	S8
γ-MnS/Cu <sub>7</sub> S <sub>4</sub>	Na <sub>2</sub> S/ Na <sub>2</sub> SO <sub>3</sub>	Full spectrum	718	420/18.8	S9
Ni-Cu <sub>7</sub> S <sub>4</sub> /CdS	Lactic acid	Full spectrum λ = 500 nm 420 nm cut-off	45,050 13,300 39,000	– 500/4.2 420 nm cut-off/14.8	This work

## References

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