

Supporting Information

Plasmonic Cu-Ni bimetal nanoparticles coupled with ultrathin CdS nanosheet for remarkably improved photocatalytic H₂ generation under visible-light irradiation

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Chemicals

Oleylamine, nickel acetylacetonate, copper acetylacetonate, thiourea were purchased from J&K Scientific Ltd. Benzyl alcohol was obtained from Tianjin Kermel Ltd. Dibenzyl ether and 1-hexadecanol were purchased from Sigma-Aldrich. Trioctylphosphine oxide was obtained from Strem chemicals. Ethylenediamine was purchased from Sinopharm Chemical Reagent Co., Ltd. Cadmium acetate dihydrate was obtained from Thermo Fisher Scientific Inc. All chemicals and reagents were used without further purification. Deionized (DI) water was used throughout the whole experiment.

Characterization

The crystallinity and structure were performed on a Rigaku D/MAX 2500V X-ray diffraction (XRD) diffractometer (Rigaku Ltd., Japan). Morphologies and microstructures were acquired by a scanning electron microscopy (SEM, ZEISS Sigma 360) and a field emission transmission electron microscope (TEM, Thermo Talos F200X G2). Ultraviolet-visible (UV-Vis) spectra were carried out using a UV-Vis spectrometer (UV-3600Plus). XPS analysis were performed by a Thermo Escalab 250 X-ray photoelectron spectroscopy with a monochromatic Al K α X-ray source. Photoluminescence (PL) spectra were acquired using an OmniFluo990LSP fluorescence spectrometer. Time-resolved photoluminescence (TRPL) spectra were measured on the FL3C-111 TCSPC fluorescence spectrometer. The Brunauer-Emmett-Teller (BET) surface area and pore structures were analyzed using N₂ adsorption-desorption experiments on a Micro-meritics instrument TriStar. The surface photovoltage (SPV) of the samples was investigated using a surface photovoltage system (CEL-SPS1000). The concentration of Cu, Ni, and Cd was

measured on an inductively coupled plasma-optical emission spectrometer (ICP-OES, ULTIMA Expert LT).

Photocatalytic measurements

Photocatalytic H₂ production reactions were performed in a sealed Pyrex flask reaction of photocatalytic activity evolution system. In a typical procedure, 30 mg of as-prepared sample powders were evenly dispersed into 60 ml Na₂S (0.35 M) and Na₂SO₃ (0.25 M) aqueous solution. The temperature of the system was maintained at 6 °C by circulating water system. The mixed aqueous solution of Na₂S and Na₂SO₃ serves as a sacrificial agent to consume photoinduced holes. The whole suspension was evacuated to remove the dissolved air prior to light irradiation. Visible Light was generated by a 300 W Xenon lamp (Aulight) coupled with a 420 nm UV cut-off filter . Photons at a particular wavelength was generated by filtering the output with different band pass filter (λ =400, 420, 435, 450, 475, 500, 520, 550, 600, 650, 700 nm). The apparent quantum yield (AQY) was calculated using the following equation:

$$\text{AQY(\%)} = \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\%$$

Photoelectrochemical measurements

All photoelectrochemical (PEC) measurements were tested in a three-electrode configuration on a VSP-300 (Biologic) electrochemical workstation. The working electrodes were fabricated by following method: firstly, 5 mg of photocatalyst was ultrasonically dispersed in the solution containing 0.5 mL of ethanol and 10 μ L Nafion. After 3 h ultrasonication, the mixture was dropped and spread on a half of indium tin oxide (ITO) glass (20 $\times$ 10 mm). Subsequently, the as-prepared working electrodes were dried at 150 °C for 6 h. The counter and reference electrode were served by platinum sheet and Ag/AgCl, respectively. 0.1 M Na₂SO₄ aqueous solution was used as electrolyte. A 300 W Xenon lamp (Aulight) coupled with a UV cutoff filter (λ > 420 nm) was applied as the light source. Electrochemical impedance

spectroscopy (EIS) spectra were obtained in the frequency range of 10^{-1} - 10^5 Hz. MottSchottky plots were recorded on 500, 1000, and 1500 Hz frequencies.

Density functional theory calculations

All Spin-polarization density functional theory (DFT) calculations was employed through the first-principles^{1, 2} using the Perdew-Burke-Ernzerhof (PBE)³ formulation within the generalized gradient approximation (GGA). The projected augmented wave (PAW) potentials^{4, 5} are chosen to describe the ionic cores, and a plane wave basis set with a kinetic energy cutoff of 450 eV was used to account for the valence electrons. Van der Waals interactions have been considered using the DFT-D3 method of Grimme.^{6, 7} The electronic energy and geometry optimization were considered self-consistent and convergent when the energy change was smaller than 10^{-5} eV and $0.02 \text{ eV } \text{\AA}^{-1}$, respectively. The Brillouin zone with a $2 \times 2 \times 1$ Gamma-centered grid was used during the relaxation. The $13 \text{ \AA}$ vacuum layer was normally added to the surface to eliminate the artificial interactions between periodic images. Spin-polarized calculations were executed for this calculation.

For each elementary step, the Gibbs reaction free energy ΔG is defined as the difference between free energies of the initial and final states and is given by the following expression:

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S$$

where ΔE is the reaction energy of reactant and product molecules adsorbed on the catalyst surface, obtained from DFT calculations; ΔZPE and ΔS are the change in zero-point energies and entropy because of the reaction.

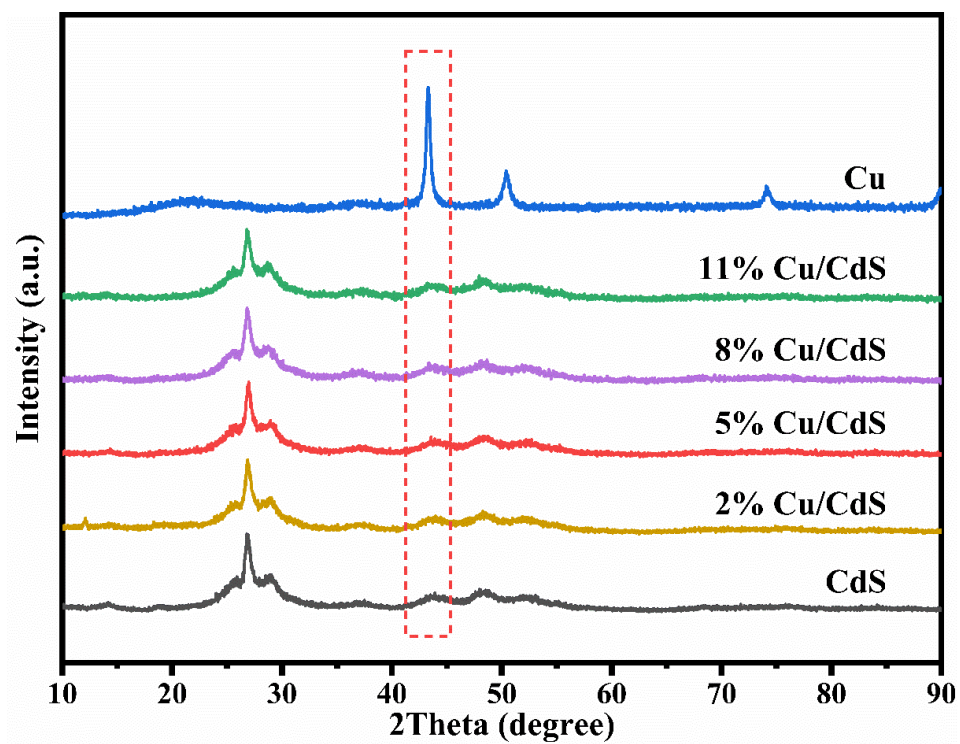


Fig. S1 XRD patterns of Cu/CdS.

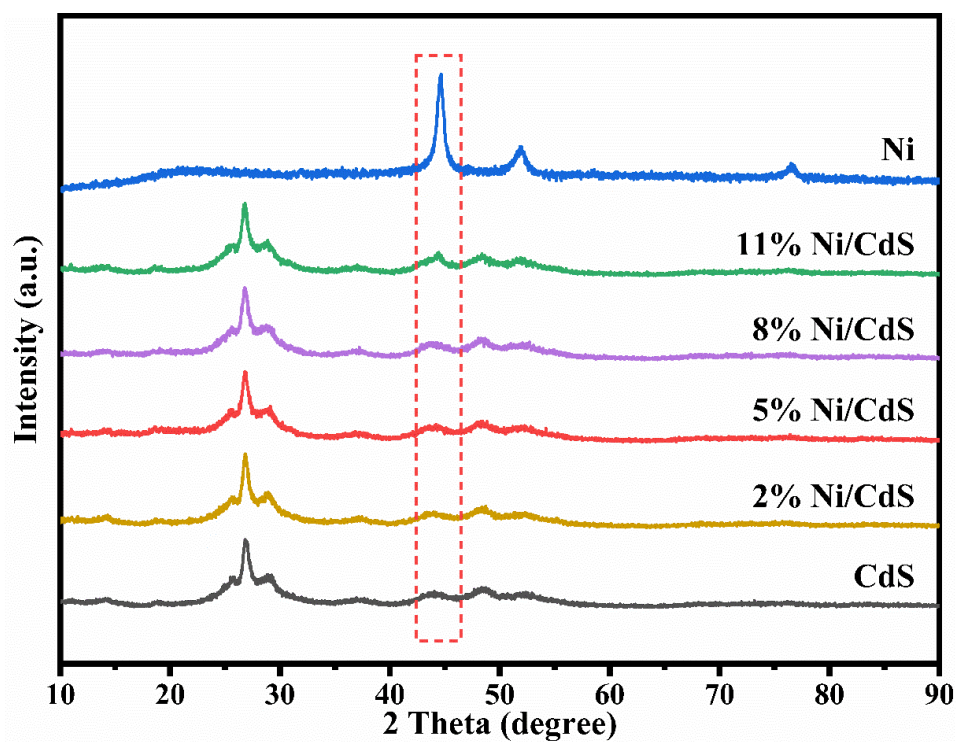


Fig. S2 XRD patterns of Ni/CdS.

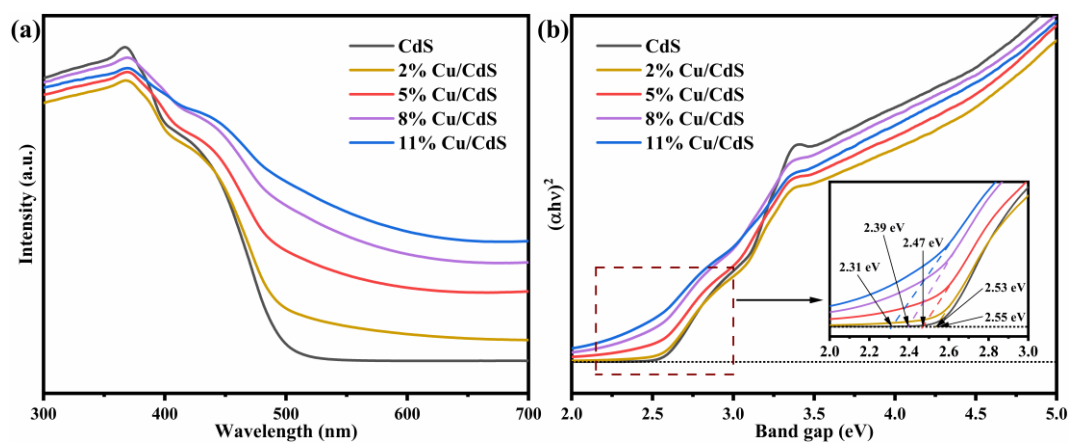


Fig. S3 (a) UV-vis spectra and (b) Tauc plot of Cu/CdS.

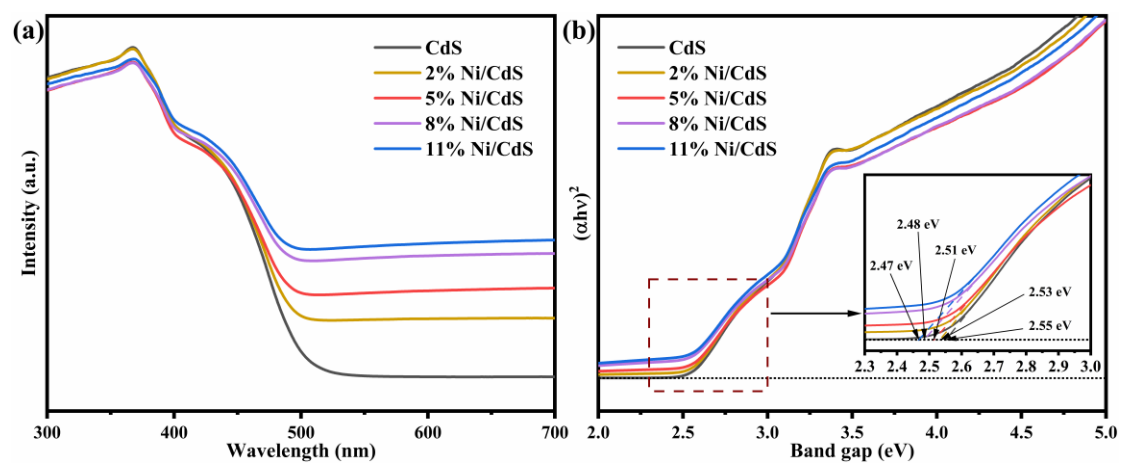


Fig. S4 (a) UV-vis spectra and (b) Tauc plot of Ni/CdS.

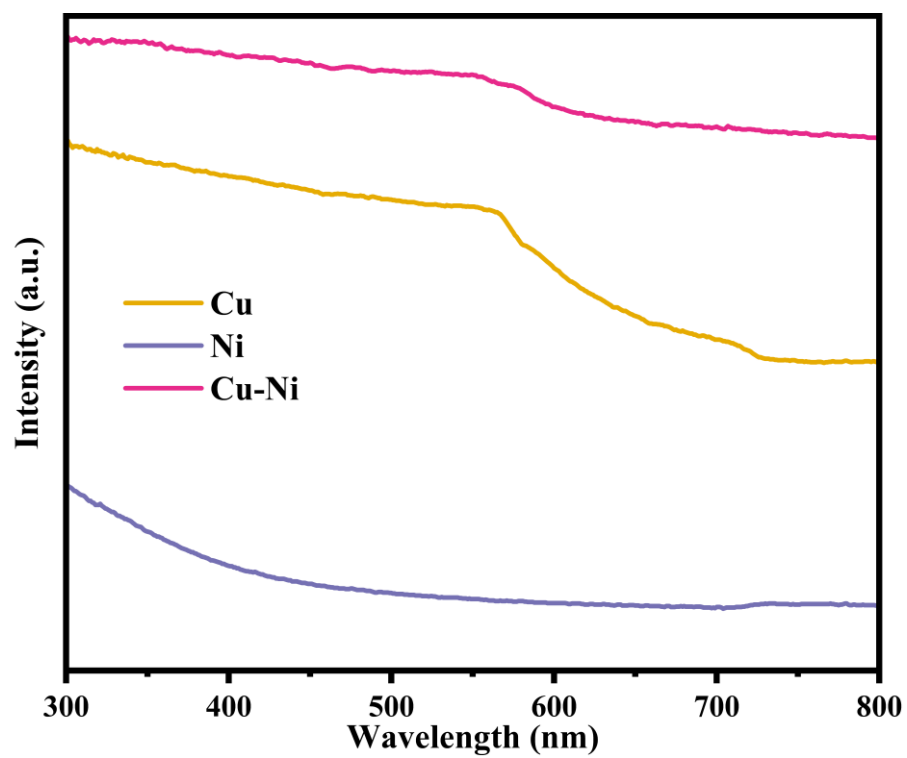


Fig. S5 UV-vis spectra of Cu, Ni, and Cu-Ni samples.

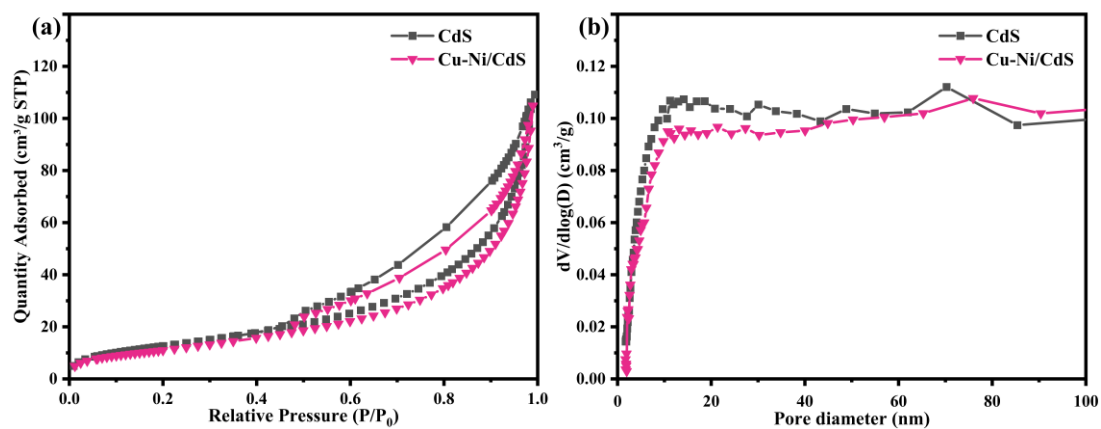


Fig. S6 (a) N₂ adsorption-desorption isotherms and (b) pore-size distribution curves of CdS and Cu-Ni/CdS samples.

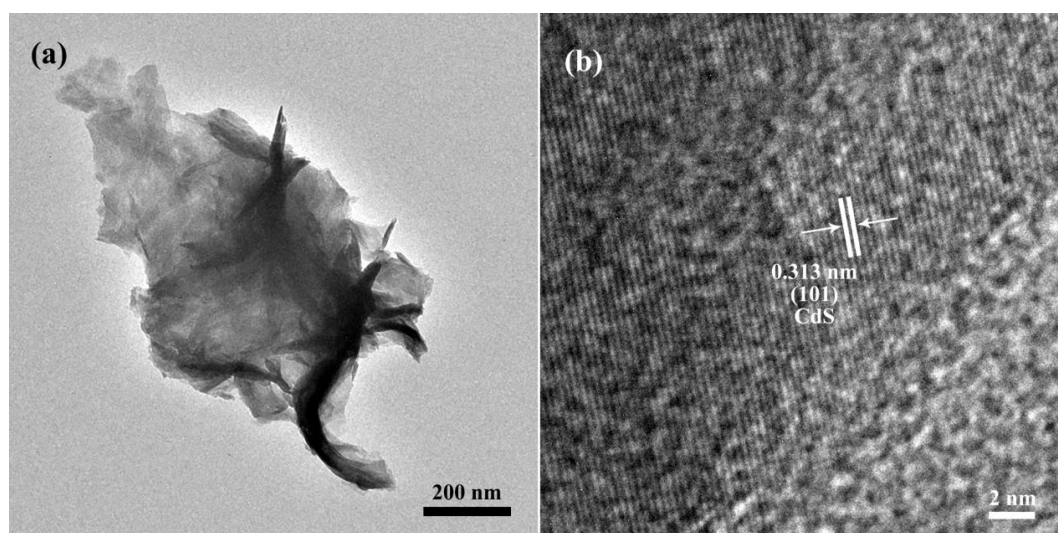


Fig. S7(a) TEM image and (b) HRTEM of pure CdS.

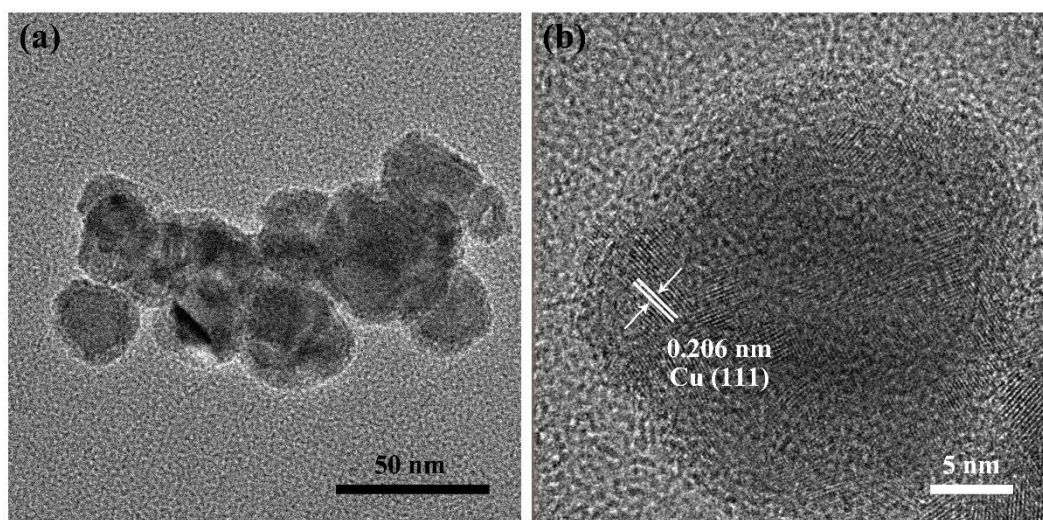


Fig. S8 (a) TEM image and (b) HRTEM of pure Cu nanoparticles.

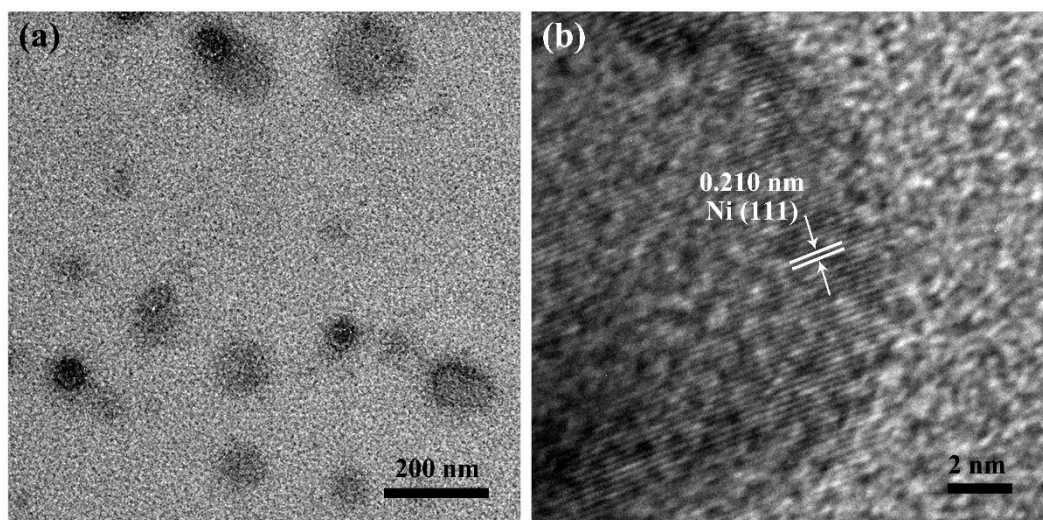


Fig. S9 (a) TEM image and (b) HRTEM of pure Ni nanoparticles.

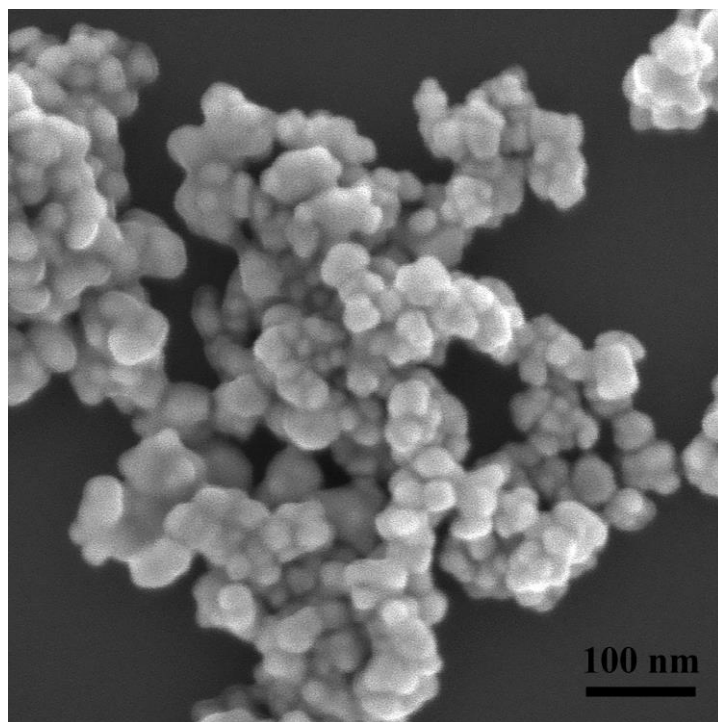


Fig. S10 SEM image of Cu-Ni nanoparticles.

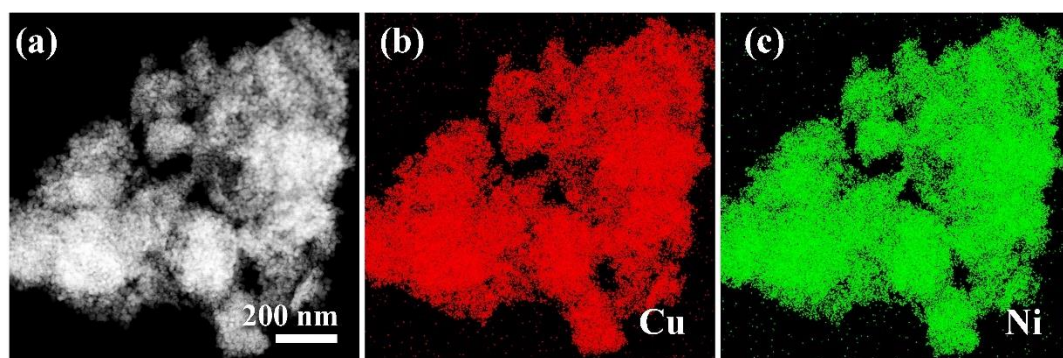


Fig. S11 EDS elemental mapping images of Cu-Ni nanoparticles.

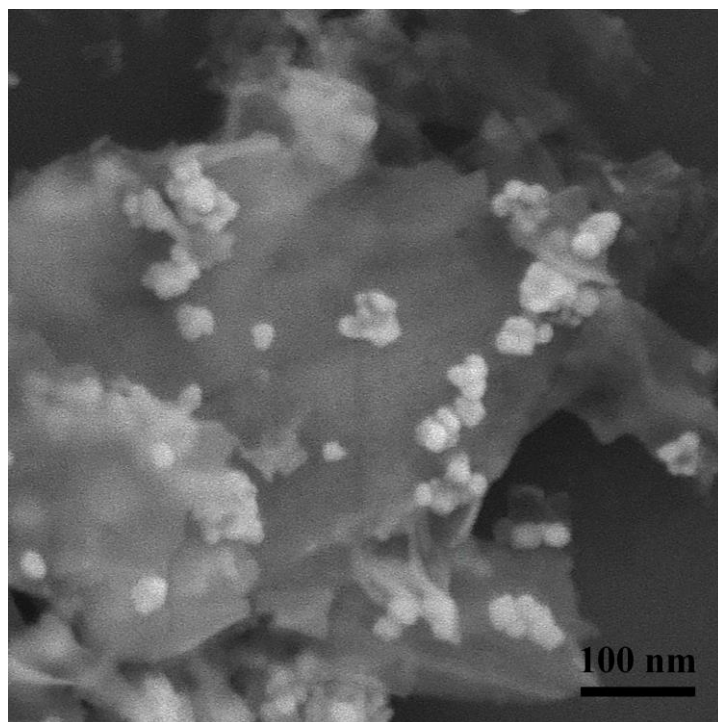


Fig. S12 SEM image of 8% Cu-Ni/CdS nanocomposite.

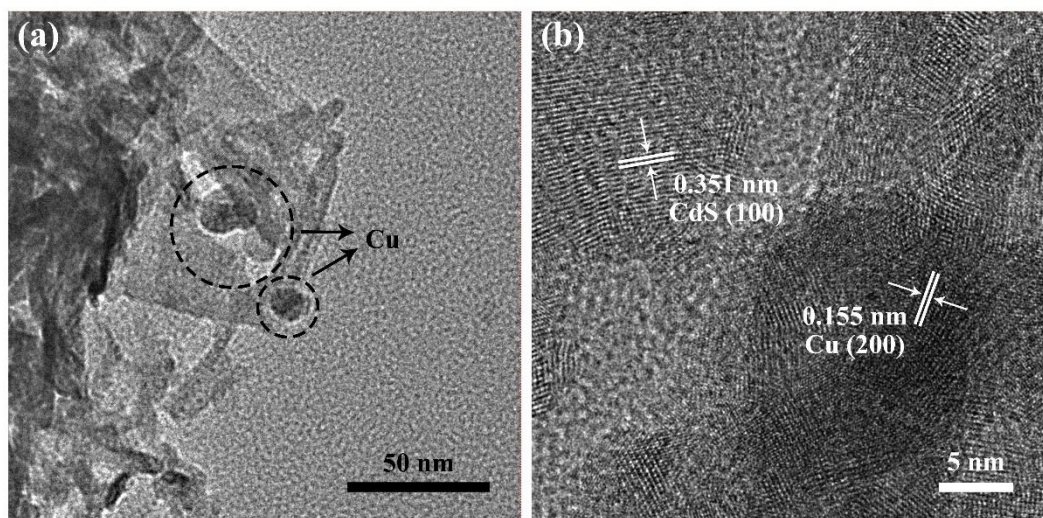


Fig. S13 (a) TEM image and (b) HRTEM of Cu/CdS nanocomposite.

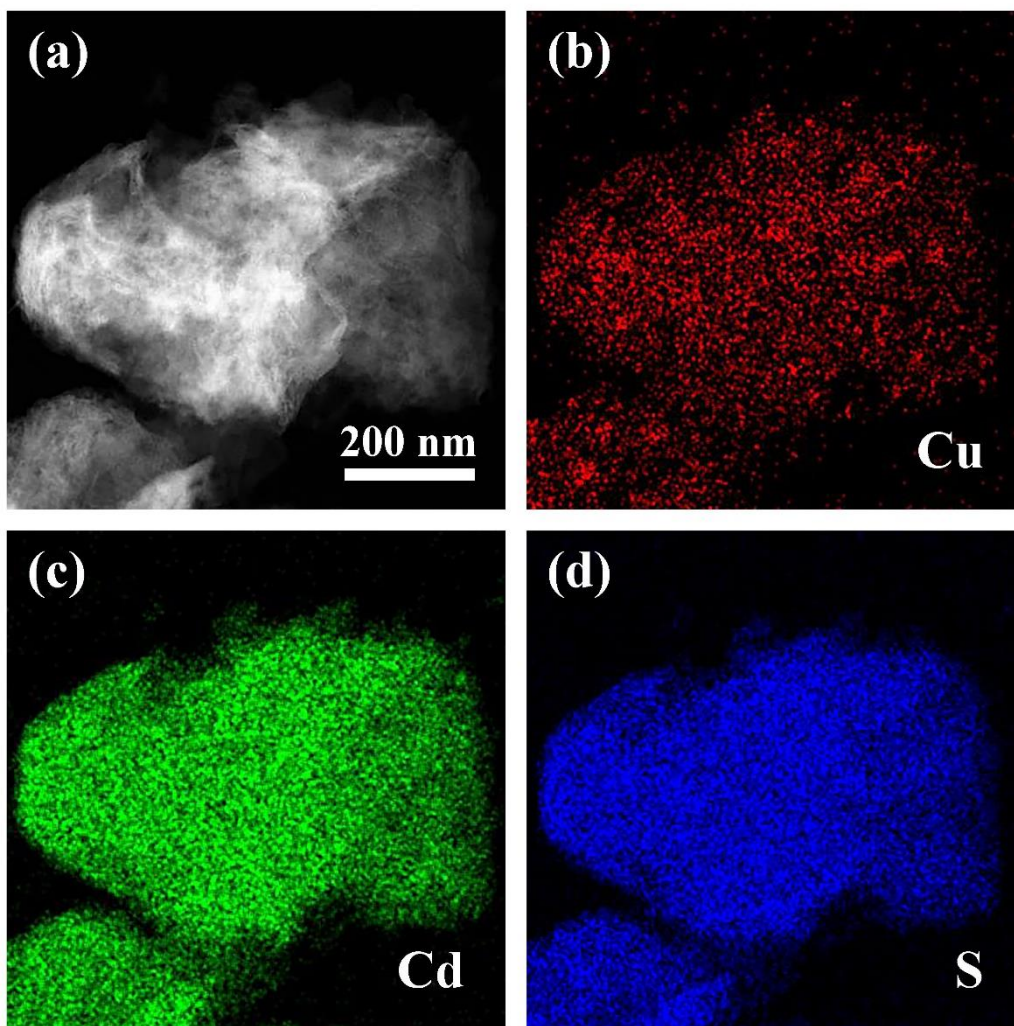


Fig. S14 EDS elemental mapping images of Cu/CdS nanocomposite.

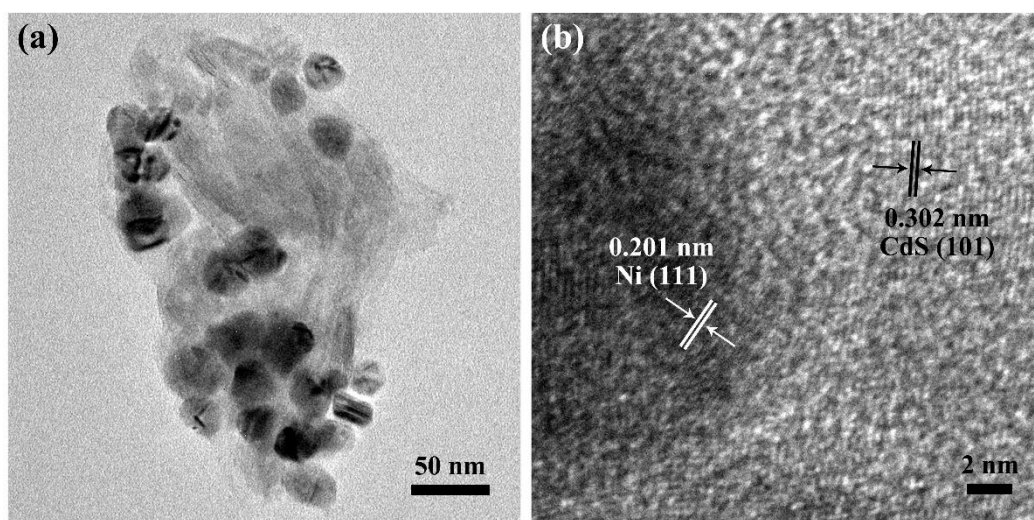


Fig. S15 (a) TEM image and (b) HRTEM of Ni/CdS nanocomposite.

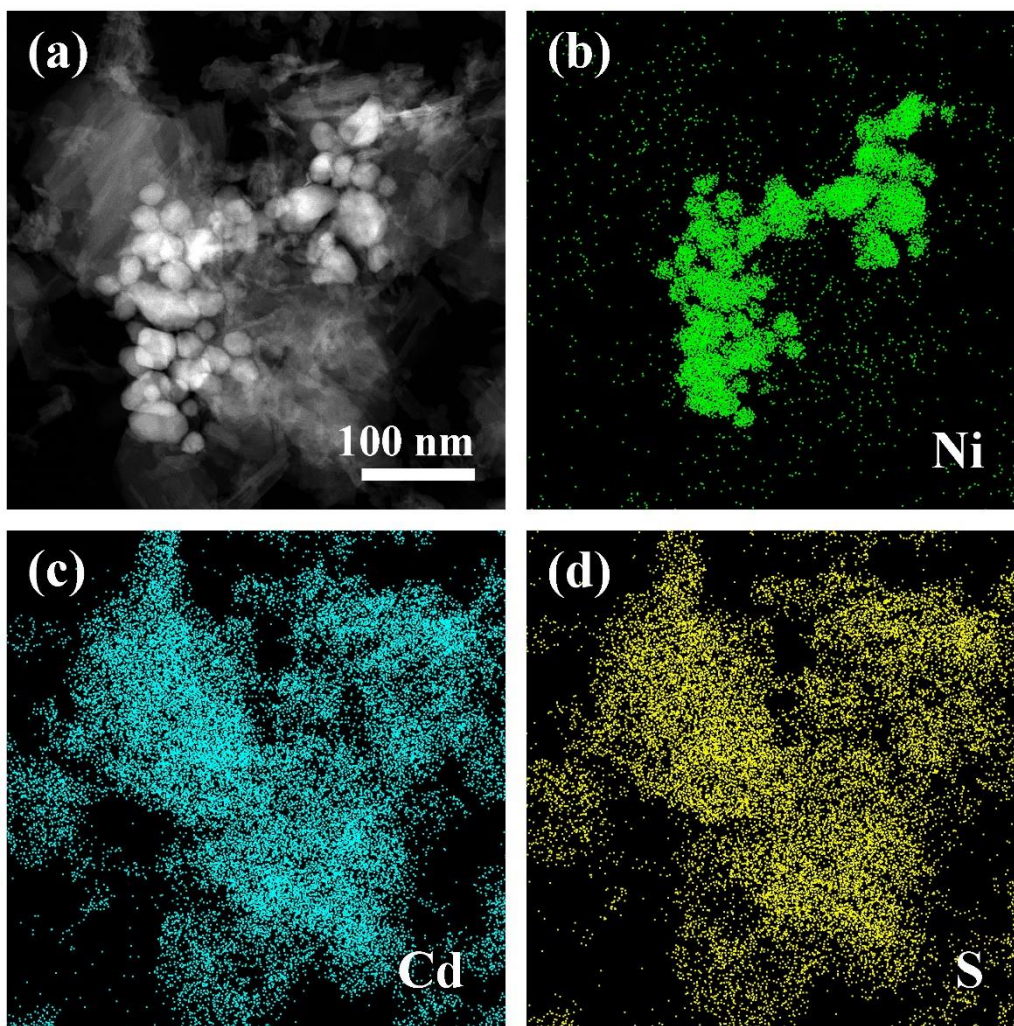


Fig. S16 EDS elemental mapping images of Ni/CdS nanocomposite.

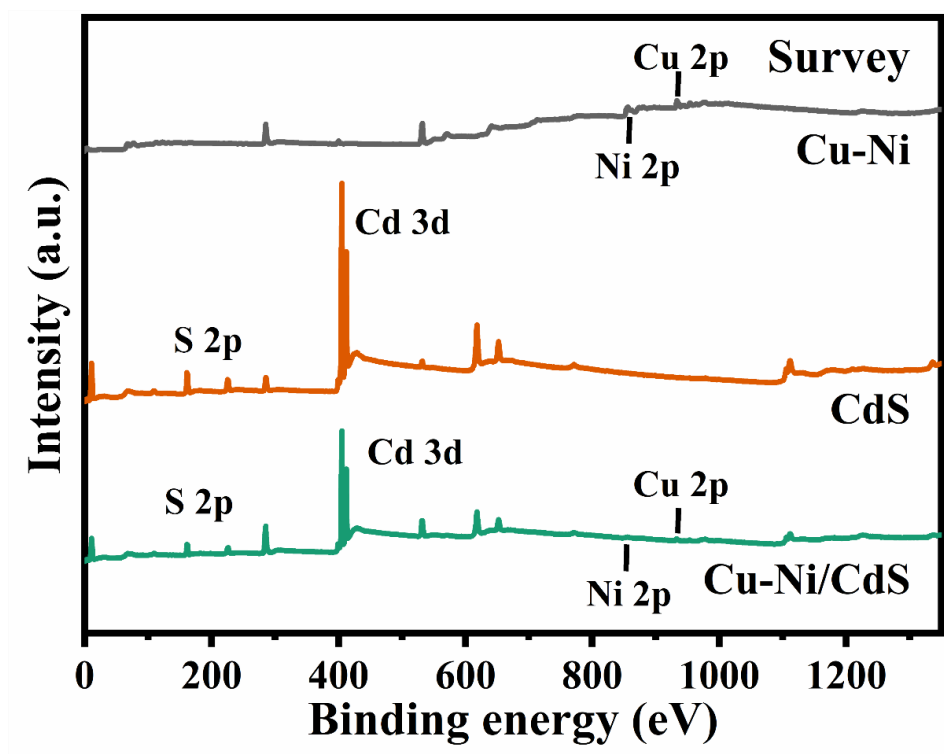


Fig. S17 (a) XPS survey spectra of CdS, Cu-Ni and 8% Cu-Ni/CdS.

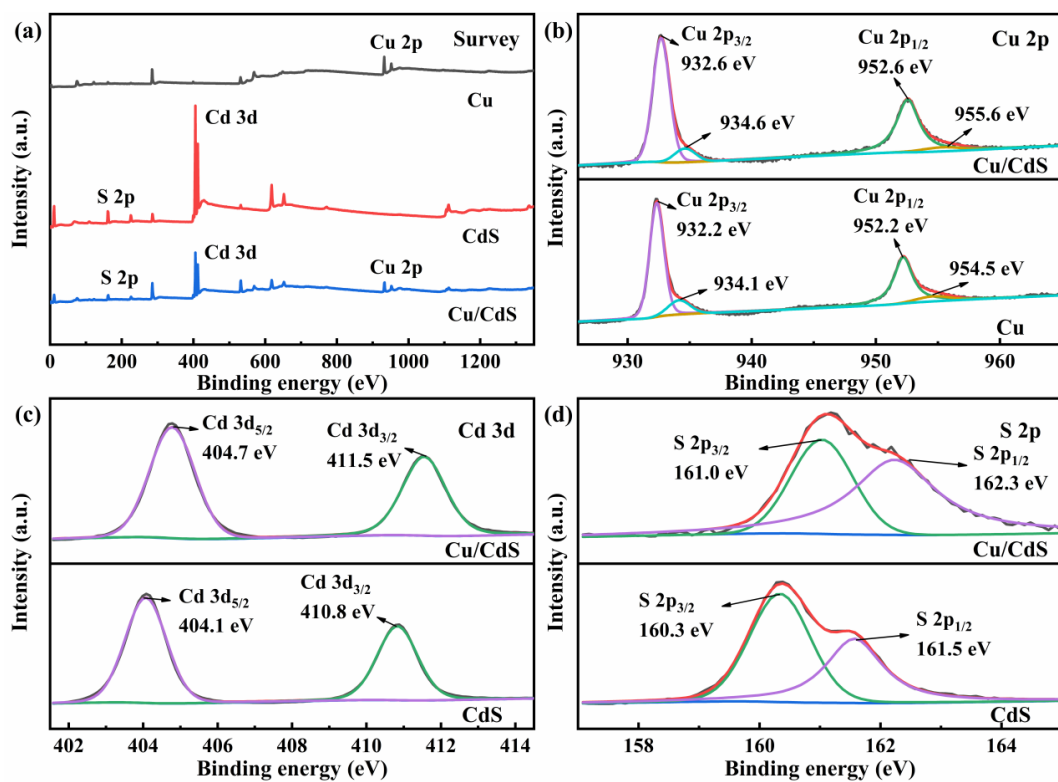


Fig. S18 (a) XPS survey spectra of CdS, Cu and 5% Cu/CdS. High-resolution XPS spectra of (b) Cu 2p, (c) Cd 3d and (d) S 2p of CdS, Cu and 5% Cu/CdS.

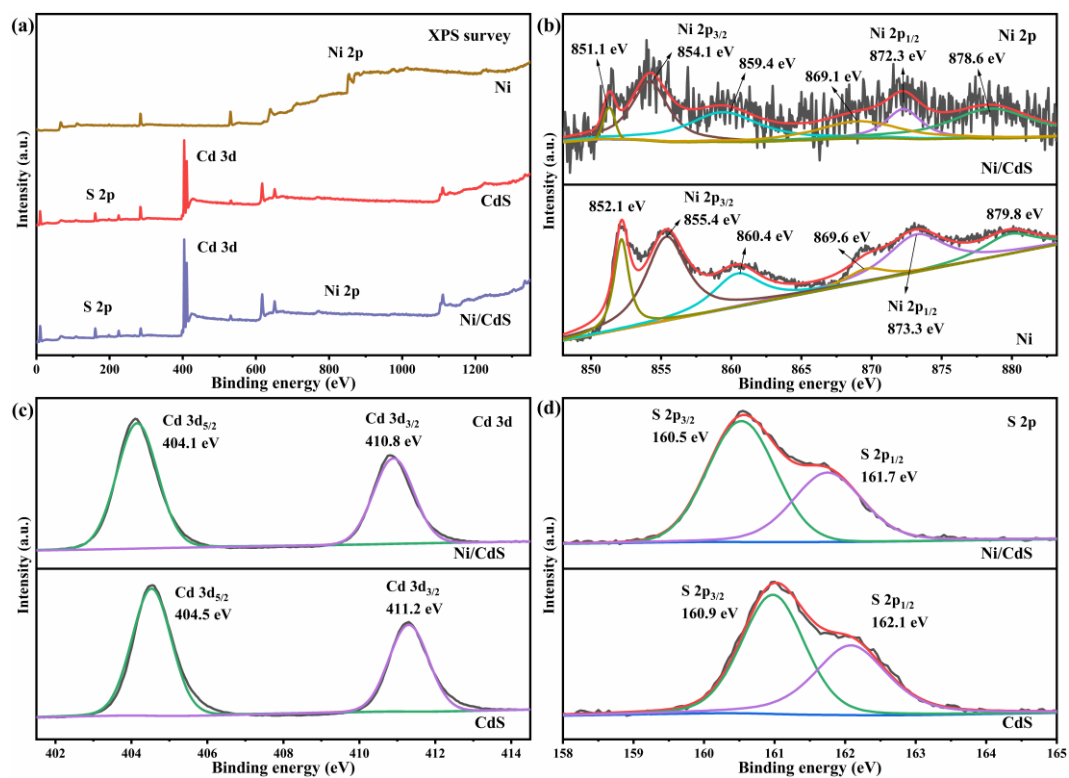


Fig. S19 (a) XPS survey spectra of CdS, Ni and 5% Ni/CdS. High-resolution XPS spectra of (b) Ni 2p, (c) Cd 3d and (d) S 2p of CdS, Ni and 5% Ni/CdS.

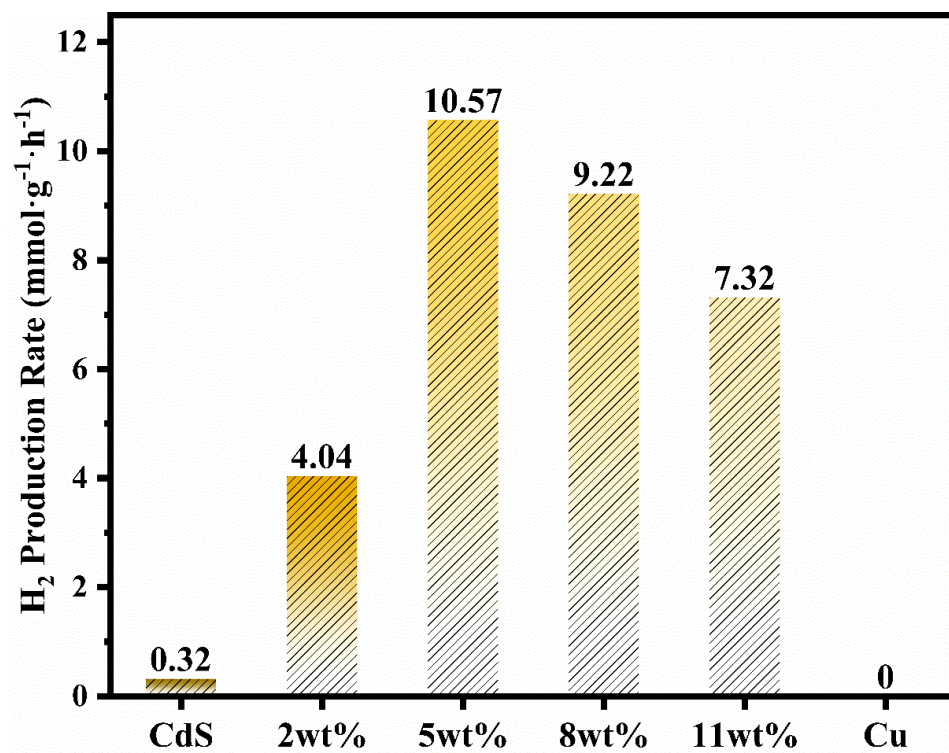


Fig. S20 Photocatalytic H₂ generation rate of different Cu loading in Cu/CdS.

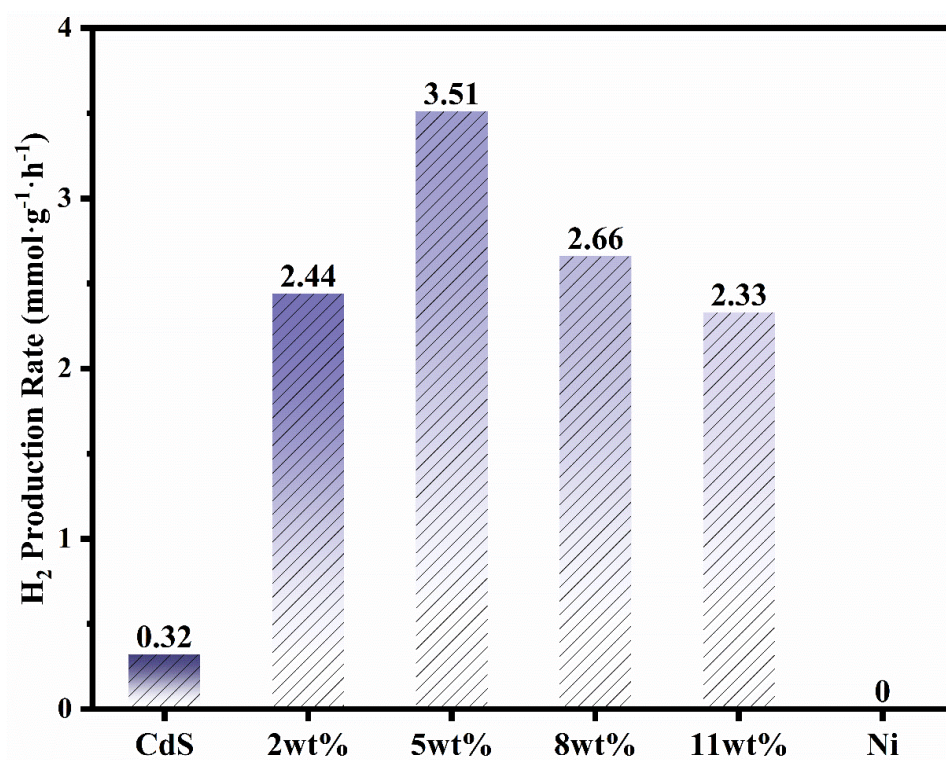


Fig. S21 Photocatalytic H₂ generation rate of different Ni loading in Ni/CdS.

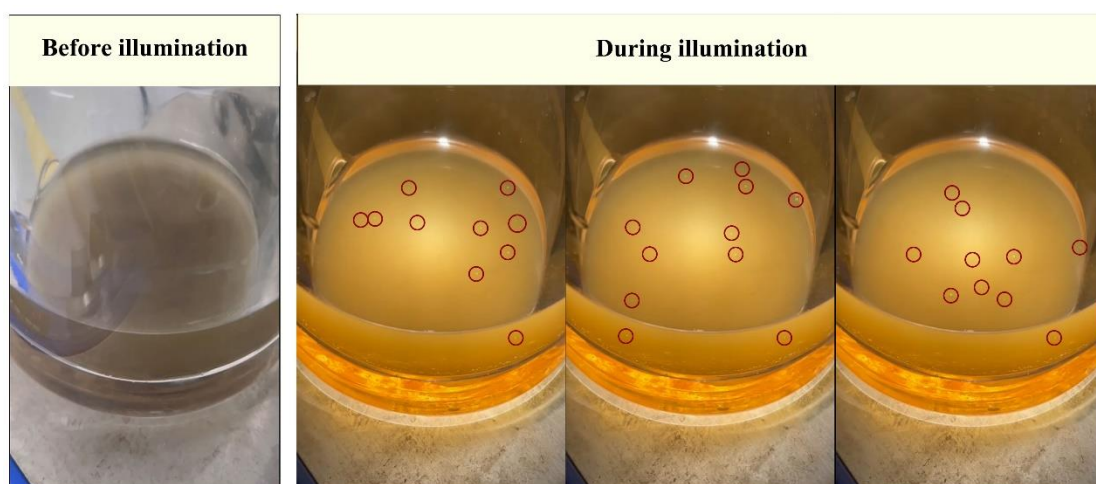


Fig. S22 Real-time photos of H_2 production (the red circles represent the position of H_2 bubbles).

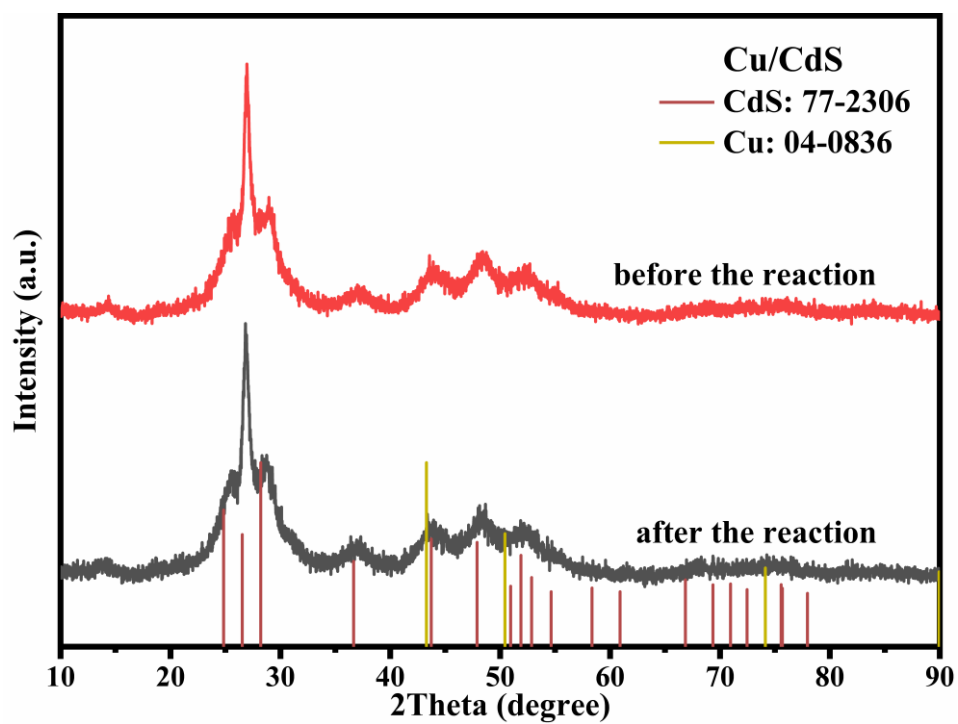


Fig. S23 XRD pattern of Cu/CdS before and after cycling run.

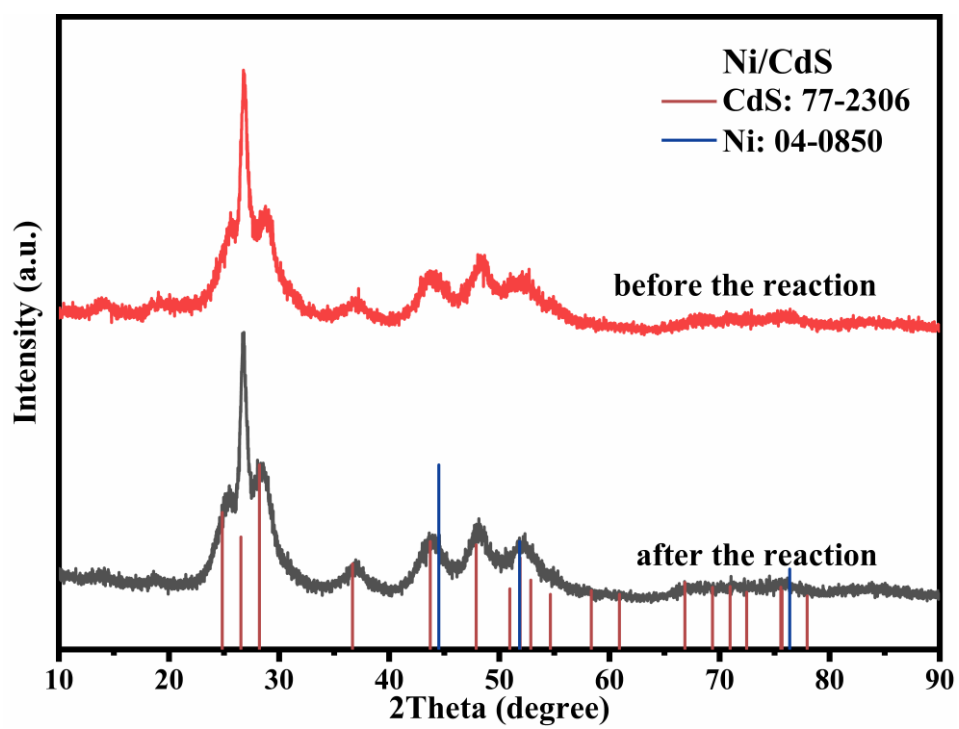


Fig. S24 XRD pattern of Ni/CdS before and after cycling run.

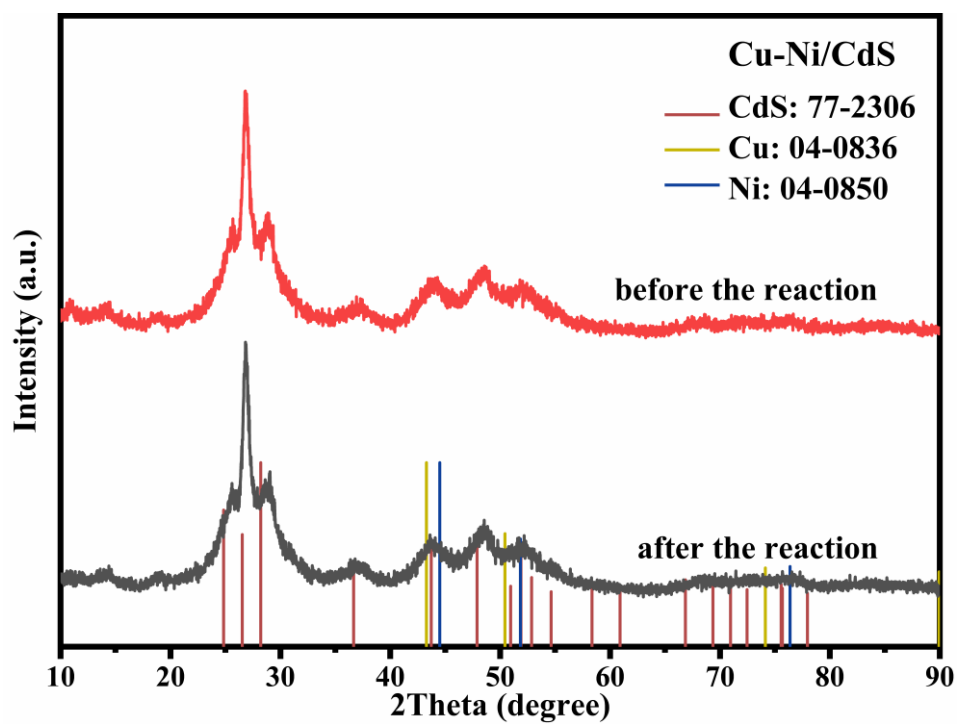


Fig. S25 XRD pattern of Cu-Ni/CdS before and after cycling run.

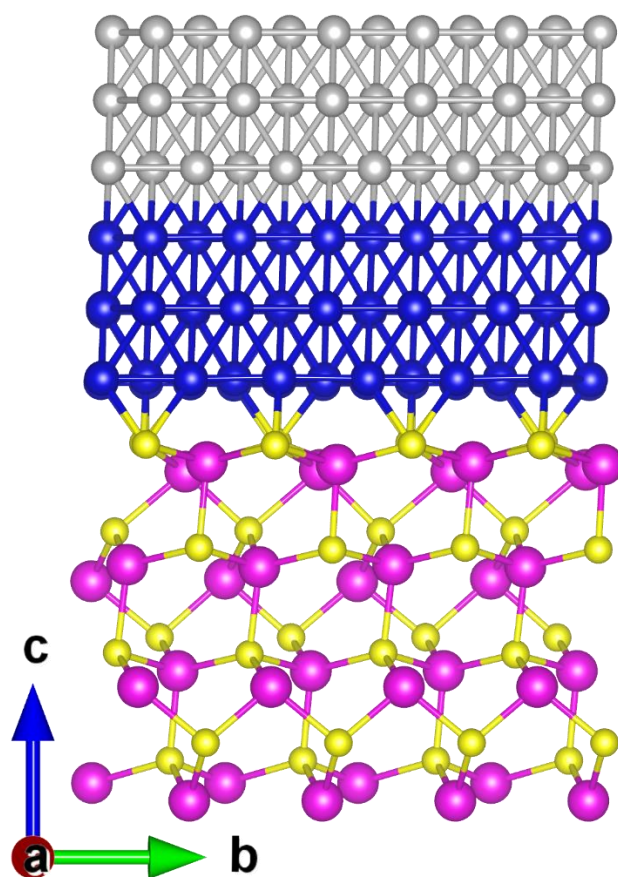


Fig. S26 The DFT optimization models of Cu-Ni/CdS. (Cd: pink spheres, S: yellow spheres, Cu: dark blue spheres, Ni: light gray spheres).

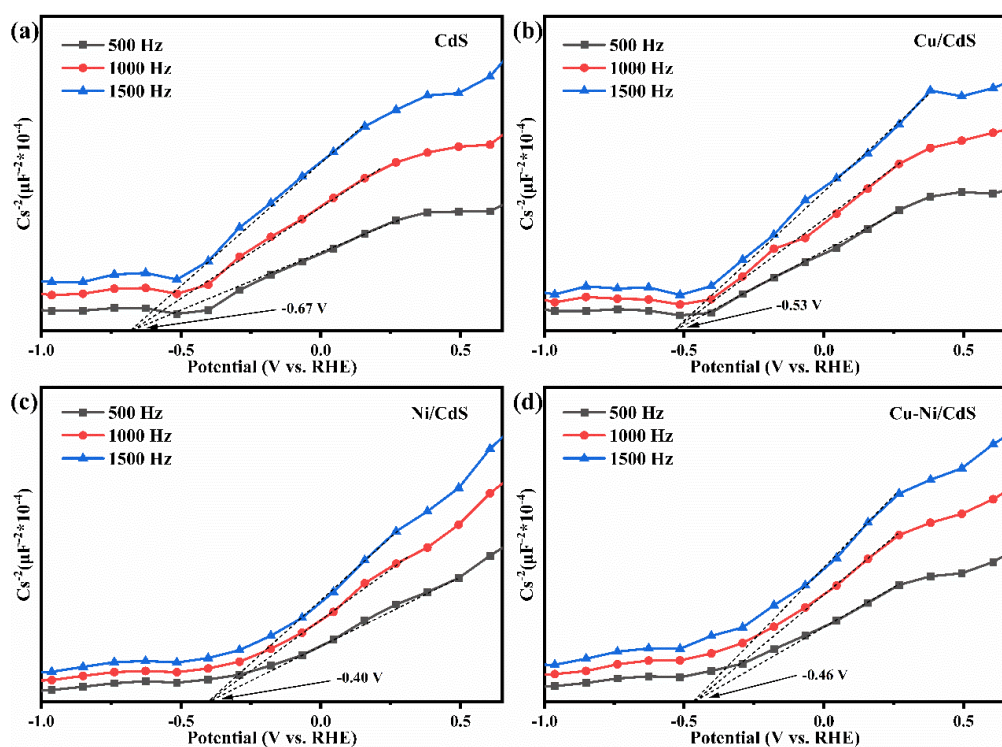


Fig. S27 Mott-Schottky plots of (a) CdS, (b) Cu/CdS, (c) Ni/CdS and (d) Cu-Ni/CdS.

Table S1. The concentration of Cu and Ni in Cu-Ni and 8% Cu-Ni/CdS samples.

photocatalyst	Measured concentration (mg·L ⁻¹)		Molecular weight (mol)		Mole ratio (Cu:Ni)
	Cu	Ni	Cu	Ni	
Cu-Ni	25.309	22.043	0.0398	0.0376	1.06
8% Cu-Ni/CdS	2.410	2.177	0.0038	0.0037	1.02

Table S2. BET surface area, mean pore diameter and pore volume of CdS and 8%

Cu-Ni/CdS samples.

photocatalyst	S_{BET}	Average pore	Pore volume
	($\text{m}^2\cdot\text{g}^{-1}$)	diameter (nm)	($\text{cm}^3\cdot\text{g}^{-1}$)
CdS	48.19	13.93	0.1678
8% Cu-Ni/CdS	41.96	15.47	0.1622

Table S3. Photocatalytic H₂ evolution activity of CdS-based photocatalysts.

Photocatalyst	Additives	Light source	Scavenger	Activity (mmol·h ⁻¹ ·g ⁻¹)	Refs
CdS	CoO _x	420 W Xe lamp (λ > 420 nm)	Na ₂ S/Na ₂ SO ₃	3.500	8
CdS	Co ₉ S ₈	300 W Xe lamp Simulated sunlight	Na ₂ S/Na ₂ SO ₃	1.061	9
CdS	MoO _x S _y	300 W Xe lamp (λ > 420 nm)	methanol	1.756	10
CdS	F/G	300 W Xe lamp (λ > 420 nm)	methanol	0.127	11
CdS	GNR	300 W Xe lamp (λ > 400 nm)	Lactic acid	1.890	12
CdS	g-C ₃ N ₄	300W Xe lamp Simulated sunlight	Lactic acid	3.370	13
CdS	Cu ₂ Ni ₁	100 W broad band lamp	ethanol	14.160	14
CdS	ZnO	350W Xe lamp	Na ₂ S/Na ₂ SO ₃	4.134	15
CdS	Ca@CoP _x	300 W Xe lamp (λ > 420 nm)	Na ₂ S/Na ₂ SO ₃	2.442	16
CdS	Mo ₂ C	Xe lamp (λ > 420 nm)	Lactic acid	7.700	17
CdS	Ru/WC	300 W Xe lamp (λ > 420 nm)	Lactic acid	16.800	18
CdS	Ti ₃ C ₂ /MoS ₂	300 W Xe lamp (λ > 420 nm)	Lactic acid	14.88	19
CdS	VC	300 W Xe lamp (λ > 420 nm)	Lactic acid	14.2	20
CdS	Ni ₂ P	300 W Xe lamp (λ > 420 nm)	Lactic acid	18.2	21
CdS	Ni ₃ C	300 W Xe lamp (λ > 420 nm)	Na ₂ S/Na ₂ SO ₃	14.28	22
CdS	Cu-Ni	300 W Xe lamp (λ > 420 nm)	Na ₂ S/Na ₂ SO ₃	28.19	This work

Table S4. AQY of 8% Cu-Ni/CdS under different wavelength light.

Light wavelength (nm)	Photocatalytic H₂ evolution rate (mmol·h⁻¹·g⁻¹)	AQY (%)
400	5.36	21.5
420	2.72	10.8
435	2.76	11.6
450	3.55	13.5
475	4.36	12.6
500	3.84	12.7
520	3.55	12.1
550	1.72	5.6
600	0.67	5.3
650	0.23	1.7
700	0.15	0.7

Table S5. E_g , CB and VB of CdS, 5% Cu/CdS, 5% Ni/CdS and 8% Cu-Ni/CdS.

photocatalyst	E_g (V)	CB (V)	VB (V)
CdS	2.55	-0.67	1.88
5% Cu/CdS	2.47	-0.53	1.94
5% Ni/CdS	2.51	-0.40	2.11
8% Cu-Ni/CdS	2.48	-0.46	2.02

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