Supplementary Materials for

Fabrication of Ni_2P Cocatalyzed CdS Nanorods with a Well-Defined Heterointerface for Enhanced Photocatalytic H_2 Evolution

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1. Experimental

CdS-H nanoparticles were prepared by the hydrothermal method. Typically, 12.5 mmol of $Cd(NO_3)_2·4H_2O$ and 37.5 mmol of thiourea (NH_2CSNH_2) were dissolved in 60 mL of distilled water. The mixture solution was stirred for 2h and then transferred to a 100 mL Teflon-lined autoclave. The hydrothermal reaction temperature was kept at 160 °C for 24 h. Afterward, the yellow precipitate was collected by centrifugation and then washed with distilled water and ethanol six times. Finally, the product was dried in a vacuum oven (60 °C) for 24 h.

A Ni_2P/CdS-H composite was prepared using the in situ phosphorization method. A total of 200 mg of as-synthesized CdS NRs were added into a mixture of $NiCl_2·6H_2O$ and red phosphorous (1:4 M ratio) in 20 ml ethanolamine. After 30 min stirring, the mixed solution was transferred into 100 ml Teflon-lined stainless-steel autoclaves and kept at 180 °C for 10 h. The resulting Ni_2P/CdS-H were collected, washed with distilled

water and absolute ethanol several times, and the dried in a vacuum at 60 °C. A 2% Ni_2P/CdS NRs + M sample was prepared by the physical mixing method with 2% of Ni_2P and CdS NRs. The pristine Ni_2P nanoparticle was synthesized by using the same approach to that of Ni_2P/CdS NRs except for no addition of CdS NRs. As a control, the synthesis of 1.0 wt.% Pt/CdS NRs was carried out by using a traditional photodeposition method. In brief, 100 mg of CdS NRs was ultrasonically dispersed in the 100 mL aqueous solution, containing Na_2S and Na_2SO_3 as sacrificial agents, and the appropriate amount of 0.01 g/mL $H_2PtCl_6 \cdot 6H_2O$ solution calculated with the content of Pt in the Pt/CdS NRs was 1.0 wt.%.

Electrochemical tests

The transient photocurrent was performed on an electrochemical workstation of CHI 760 E (Shanghai, China) using Pt as a counter electrode and Ag/AgCl as reference. For the preparation of the working electrode, 5 mg of the photocatalyst and 20 μL of Nafion (0.25%) solution were added to 2 mL of ethanol solution, followed by ultrasonication for 2 h. A portion (500 μL) of the suspension was transferred to a fluorine-doped tin oxide (FTO, 2 cm × 3.5 cm) glass substrate in 10 drops, and each dispersion was dried under an infrared lamp. The last step involved maintaining the FTO at 150 °C for 1 h under Ar protection. Transient photocurrent experiments were performed using electrochemical workstations and standard three-electrode batteries. Ag/AgCl, the prepared working electrode, Pt electrode, and 0.1 mol/L Na_2SO_4 were used as the reference electrode, working electrode, counter electrode, and electrolyte, respectively. The irradiation light source was a 300 W Xe lamp. LSV test was carried out in a 0.5 M H_2SO_4 solution in the dark with a 50 mV/s scan rate.

2. Results

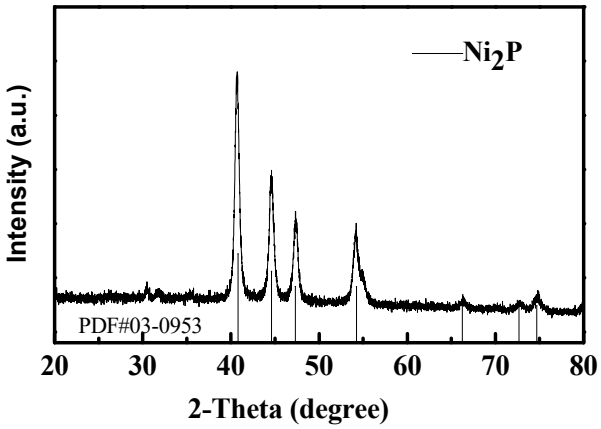

Figure S1. XRD pattern of the Ni_2P

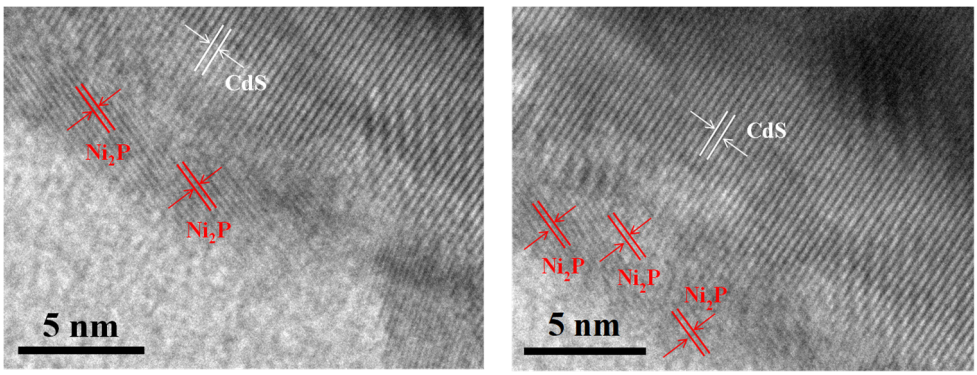

Figure S2. The HRTEM images of 2%Ni_2P/CdS NRs

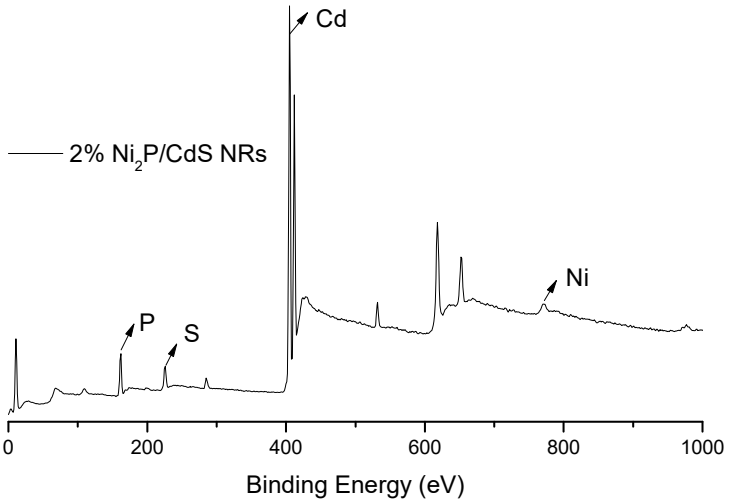

Figure S3. The XPS survey spectra of 2%Ni_2P/CdS NRs

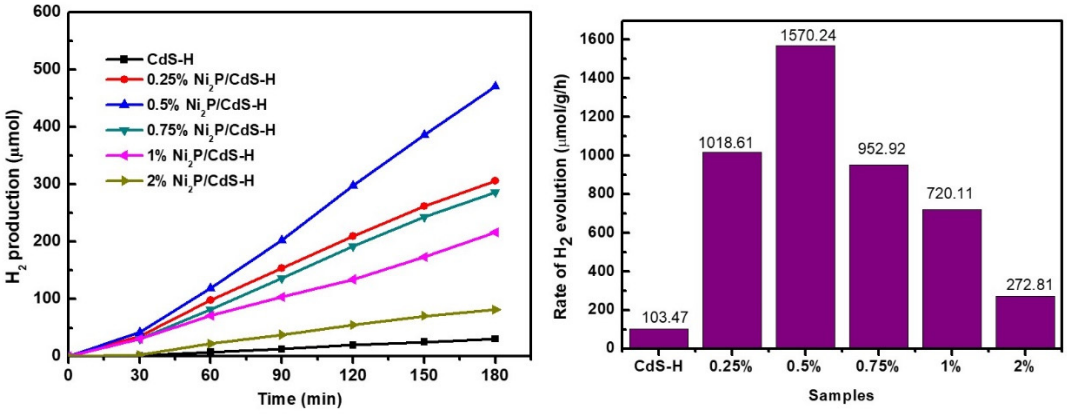

Figure S4. The photocatalytic H_2 evolution activity of as-prepared m%Ni_2P/CdS-H samples

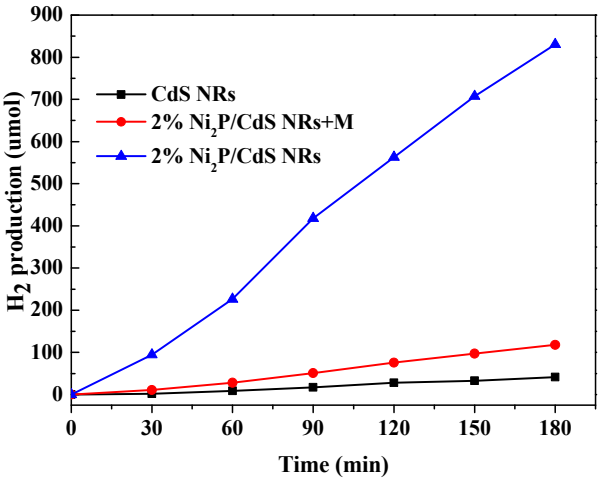

Figure S5. The photocatalytic H_2 evolution activity of CdS NRs, 2%Ni_2P/CdS NRs + M and 2%Ni_2P/CdS NRs

Table S1. Comparison on the H_2 evolution performance of various CdS based photocatalysts

Catalyst	Reactant solution	Light source	Activity	Ref
Ni_2P-$Cd_{0.9}Zn_{0.1}S$	100 mL sacrificial reagents (0.7 M Na_2S and 0.5 M Na_2SO_3	300 W xenon lamp ($\lambda \geq$ 400 nm)	1.31 mmol·h^{-1}	[1]
Ru/CdS /Halloysite	100 ml of an aqueous 0.1 M Na_2S / 0.1 M Na_2SO_3	monochromatic LED (30 W), with the maximum emission at a wavelength of 450 nm	1.3 ± 0.1 mmol·h^{-1}·g^{-1}	[2]
Co_9S_8/Cd/CdS	10 ml aqueous solution containing 0.35 M Na_2S and 0.25 M Na_2SO_3	300 W Xenon lamp ($\lambda \geq 400$ nm)	10.42 μmol·h^{-1}	[3]
1%Pt/$Cd_{0.6}Zn_{0.4}S$/$Cd_{0.1}Zn_{0.9}S$	100 mL of xylose aqueous solution with 5 M NaOH	450-nm LED with light intensity equal to 48 mW cm^{-2}	3.4 mmol·h^{-1}·g^{-1}	[4]
PCN-CdS-5% Ni_2P	100 mL of 10 vol.% triethanolamine aqueous solution	300W Xe lamp ($\lambda \geq 400$ nm)	2905.86 μmol·h^{-1}·g^{-1}	[5]
2% Ni_2P/ CdS NRs	100 ml aqueous solution containing 0.35 M Na_2S and 0.25 M Na_2SO_3	300W Xe lamp ($\lambda \geq 420$ nm)	260.2 μmol·h^{-1} or 2.6 mmol·h^{-1}·g^{-1}	This work

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