Supporting Information

Nickel phosphonate-derived Ni_2P@N-doped carbon co-catalyst with built-in electron-bridge for boosting the photocatalytic hydrogen evolution

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1. Experimental section

1.1 Materials

All the chemical reagents of analytical grade were used as received. Cadmium acetate ($Cd(Ac)_2·2H_2O$, ≥99.5%) and Zinc acetate ($Zn(Ac)_2·2H_2O$, ≥99.5%) were purchased from Shengfeier Biotechnology Service Center, Tianjin. 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP, ≥99.5%) was purchased from Tianjin Hongfengweili Technology Development Co., Ltd. Nickel nitrate ($Ni(NO_3)_2$, ≥98.0%), sodium sulfide nonahydrate ($Na_2S·9H_2O$, 98.0%) and melamine ($C_3H_6N_6$, ≥99.0%) were purchased from Tianjin Damao Chemical Reagent Works (China). Sodium hypophosphite (NaH_2PO_2, ≥99.0%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Nonionic triblock copolymer F127 ($EO_{106}PO_{70}EO_{106}$) were purchased from Beijing Fenglijingqiu Pharmaceutical Co., Ltd. Sodium sulfite anhydrous (Na_2SO_3, 97.0%) was from Tianjin Jiangtian Chemical Technology Co., Ltd.

1.2 Apparent quantum efficiency (AQE) calculation

The power of light after the bandpass filter (420 nm) and the irradiation area were measured to be 25.22 $mW·cm^{-2}$ and 63.62 cm^2. The apparent quantum efficiency (AQE) was defined by the following equation:

$$\mathrm{AQE}(\%) = \frac{\text{the number of hydrogen molecules} \times 2}{\text{the number of incident photons}} \times 100\%$$

2. Supplementary Figures

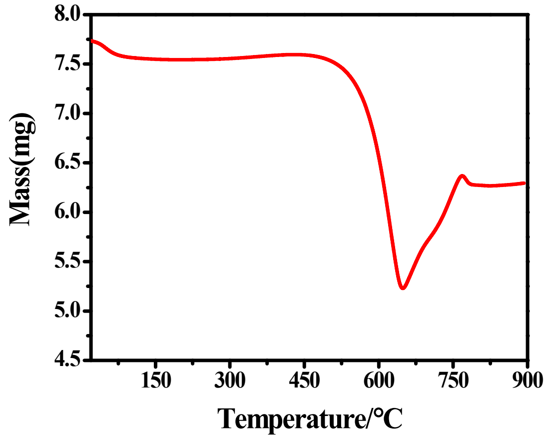

Figure S1. The TG curve of Ni_2P@CN.

The mass ration of Ni_2P to CN was calculated according to the equations:

$$m_{Ni_2P} = \frac{3m_{Ni_3(PO_4)_2}}{2M_{Ni_3(PO_4)_2}} M_{Ni_2P} \tag{1}$$

$$\frac{m_{Ni_2P}}{m_{CN}} = \frac{m_{Ni_2P}}{m_0 - m_{Ni_2P}} \tag{2}$$

In the two equations, $m_{Ni_3(PO_4)_2}$ is the remaining mass at the end of thermogravimetric curve (**Figure S1**), 6.294 mg. m_0 is the initial mass of Ni_2P@CN, 7.742 mg. The $M_{Ni_3(PO_4)_2}$ and M_{Ni_2P} refer to the molar mass of $Ni_3(PO_4)_2$ and Ni_2P, 366.02 g/mol and 148.35 g/mol, respectively. The m_{Ni_2P} and m_{CN} represent the mass of Ni_2P and CN in Ni_2P@CN, respectively.

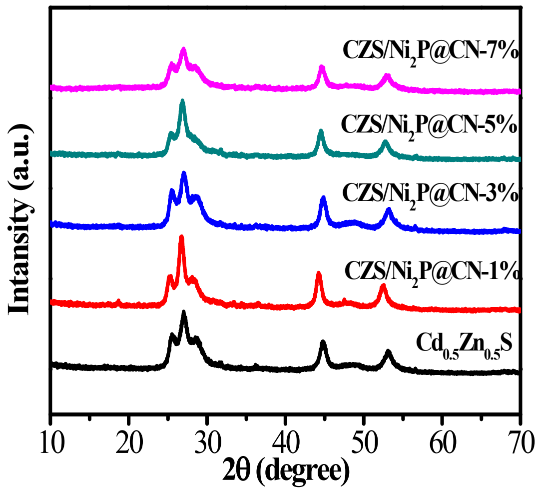

Figure S2. XRD patterns of CZS/Ni_2P@CN-*x*% composites with various cocatalyst contents.

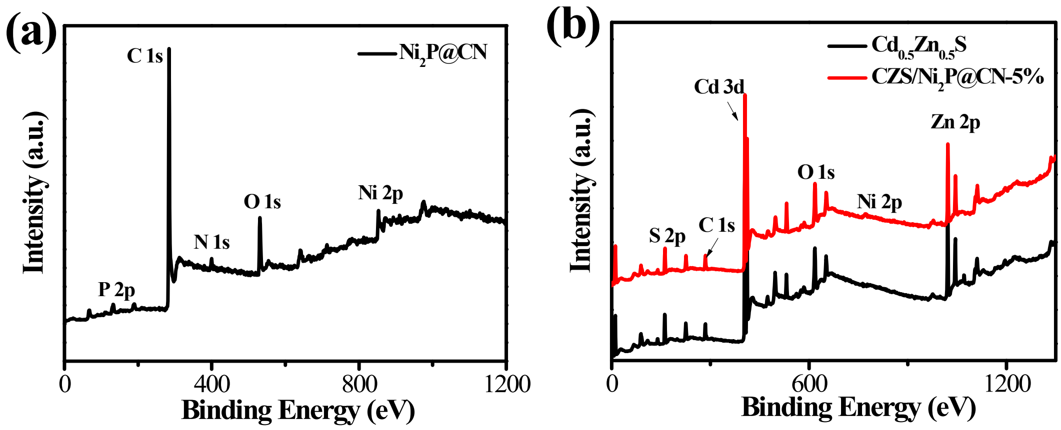

Figure S3. Survey XPS spectra of (a)Ni_2P@CN, (b) CZS/Ni_2P@CN-5% and $Cd_{0.5}Zn_{0.5}S$.

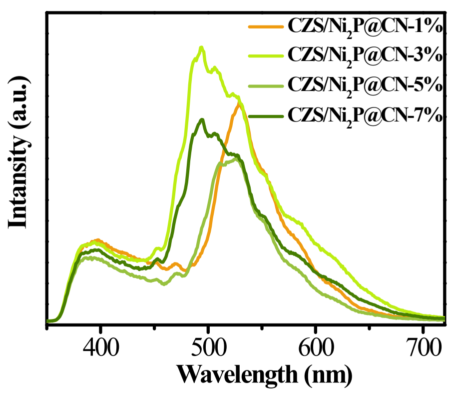

Figure S4. PL spectra of CZS/Ni_2P@CN-*x* (*x* represents 1%, 3%, 5% and 7%)

3. Supplementary Table

Table S1. Surfaces area and pore structures of the prepared samples.

Sample	S_{BET}/m^2 g^{-1}	Pore volume/cm^3 g^{-1}
$Cd_{0.5}Zn_{0.5}S$	52	0.22
CZS/Ni_2P@CN-5%	75	0.21
CZS/Ni_2P	70	0.38
CZS/Ni_2P/CN	51	0.26

Table S2. The molar ratio of Cd(Zn)/Ni and H_2 production of the samples.

Samples	Molar ratio of Cd(Zn)/Ni	H_2 production (mmol h^{-1}g^{-1})
CZS	—	12.35
CZS/Ni_2P@CN-1%	1:0.016	12.57
CZS/Ni_2P@CN-3%	1:0.048	21.42
CZS/Ni_2P@CN-5%	1:0.080	28.52
CZS/Ni_2P@CN-7%	1:0.112	22.06