

## ***Supporting Information***

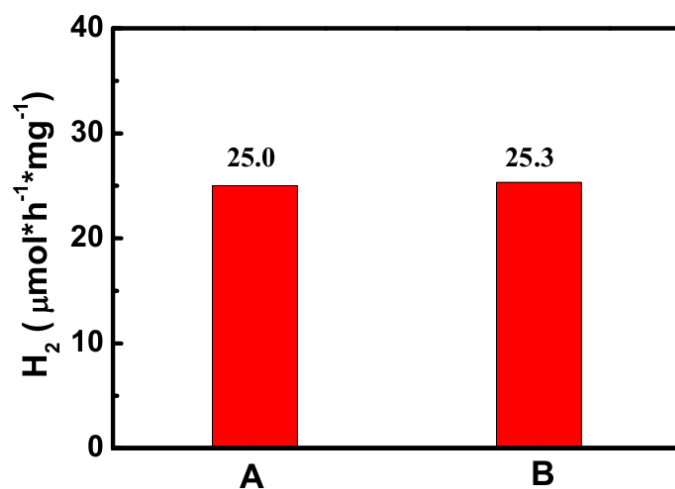
# **Extraordinarily Efficient Photocatalytic Hydrogen Evolution in Water Using Semiconductor Nanorods Integrated With Crystalline Nickel Phosphide Cocatalyst**

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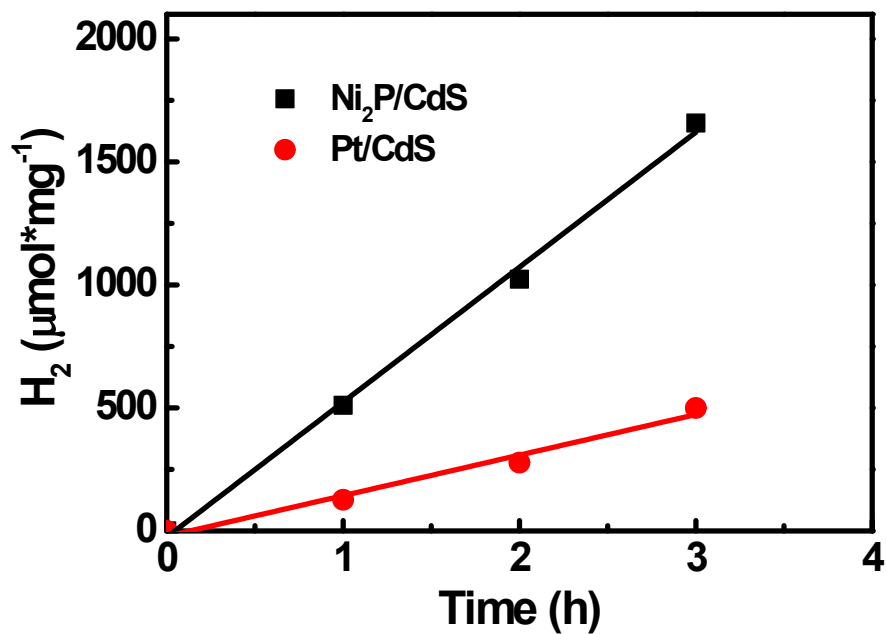
Key Laboratory of Materials for Energy Conversion, Chinese Academy of Sciences, Department of Materials Science and Engineering, and the Collaborative Innovation Center of Chemistry for Energy Materials (*iChEM*), University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui Province, 230026, P. R. China

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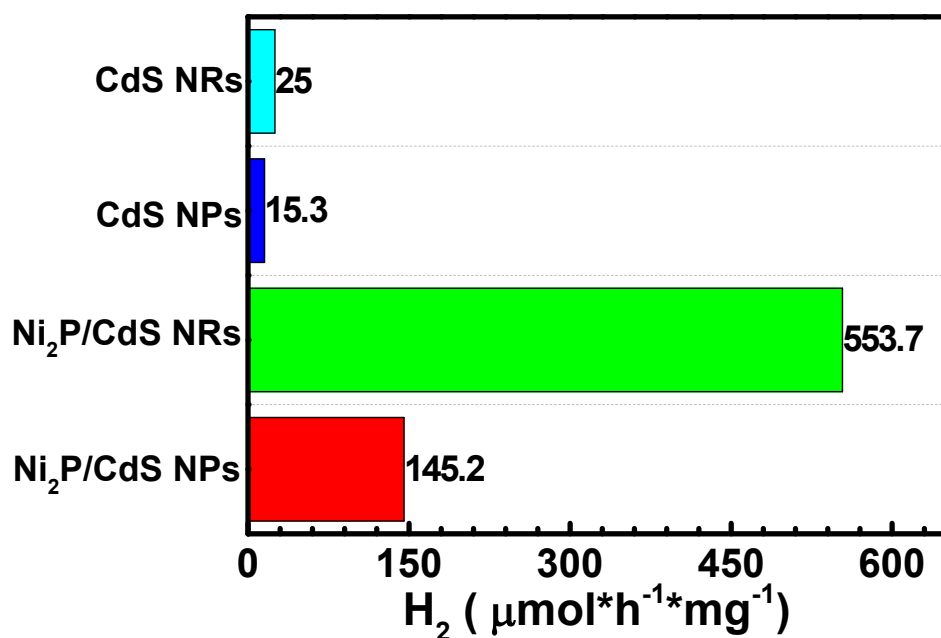
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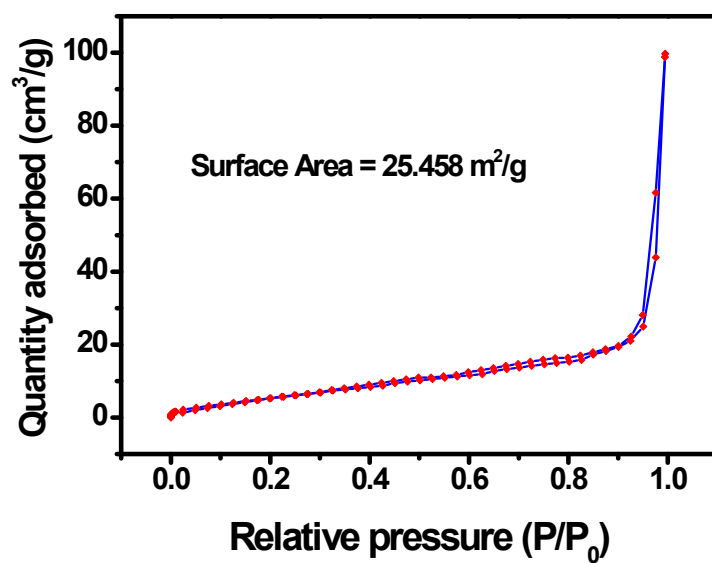
**Figure S1.** Comparison of photocatalytic activity of CdS NRs (**A**) with and without solvothermal treatment (**B**) under visible light ( $\lambda > 420$  nm). The conditions for solvothermal treatment were the same as that for synthesis of  $\text{Ni}_2\text{P}/\text{CdS}$  photocatalyst. The system contains 1.0 mg photocatalyst, 0.75 M  $\text{Na}_2\text{S}$ , and 1.05 M  $\text{Na}_2\text{SO}_3$  in 20 mL aqueous solution.



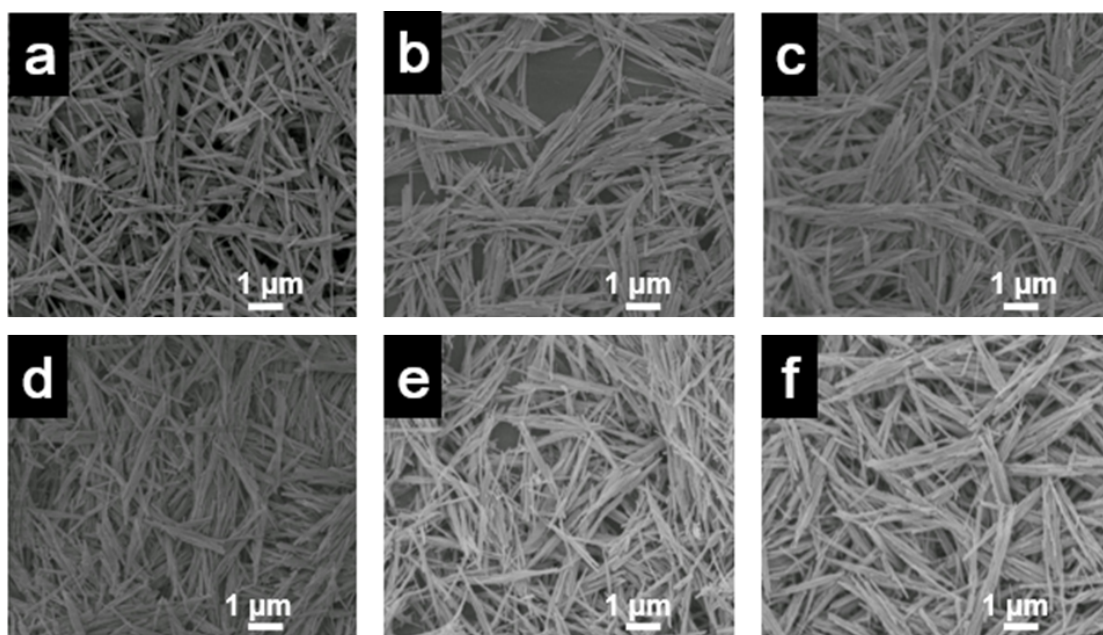
**Figure S2.** Comparison of photocatalytic activity of  $\text{Ni}_2\text{P}/\text{CdS}$  NRs and  $\text{Pt}/\text{CdS}$  NRs. Photocatalytic  $H_2$  evolution over 0.5 wt %  $\text{Ni}_2\text{P}/\text{CdS}$  NRs (black line) and 0.5 wt %  $\text{Pt}/\text{CdS}$  NRs (red line) at room temperature under visible light ( $\lambda > 420$  nm). The system contains 1.0 mg photocatalyst, 0.75 M  $\text{Na}_2\text{S}$  and 1.05 M  $\text{Na}_2\text{SO}_3$  in 20 mL aqueous solution.



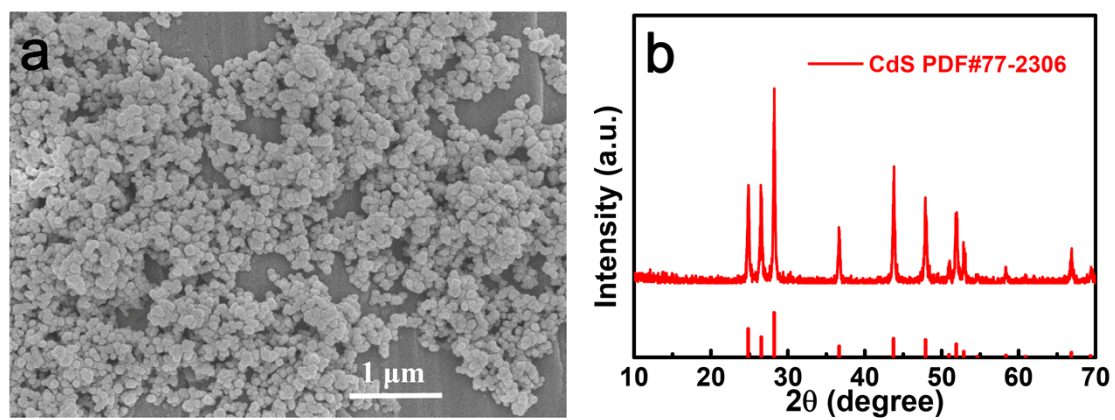
**Figure S3.** Comparison of photocatalytic activity of CdS NRs, CdS NPs, 0.5 wt % Ni<sub>2</sub>P/CdS NRs, and 0.5 wt % Ni<sub>2</sub>P/CdS NPs at room temperature under visible light ( $\lambda > 420$  nm). The system contains 1.0 mg photocatalyst, 0.75 M Na<sub>2</sub>S and 1.05 M Na<sub>2</sub>SO<sub>3</sub> in 20 mL aqueous solution.



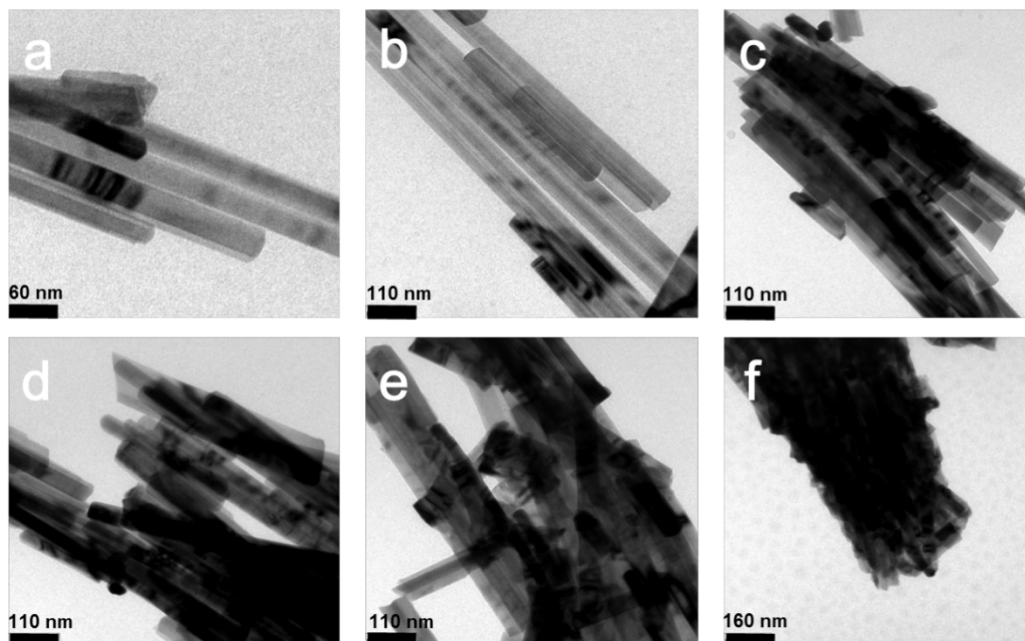
**Figure S4.** Nitrogen adsorption-desorption isotherms of the 0.5 wt % Ni<sub>2</sub>P/CdS NRs.



**Figure S5.** SEM images of pure CdS NRs and Ni<sub>2</sub>P/CdS NRs. SEM images of **(a)** pure CdS NRs, **(b)** 0.25 wt % Ni<sub>2</sub>P/CdS NRs, **(c)** 0.5 wt % Ni<sub>2</sub>P/CdS NRs, **(d)** 1.0 wt % Ni<sub>2</sub>P/CdS NRs, **(e)** 2.0 wt % Ni<sub>2</sub>P/CdS NRs, **(f)** 10.0 wt % Ni<sub>2</sub>P/CdS NRs.

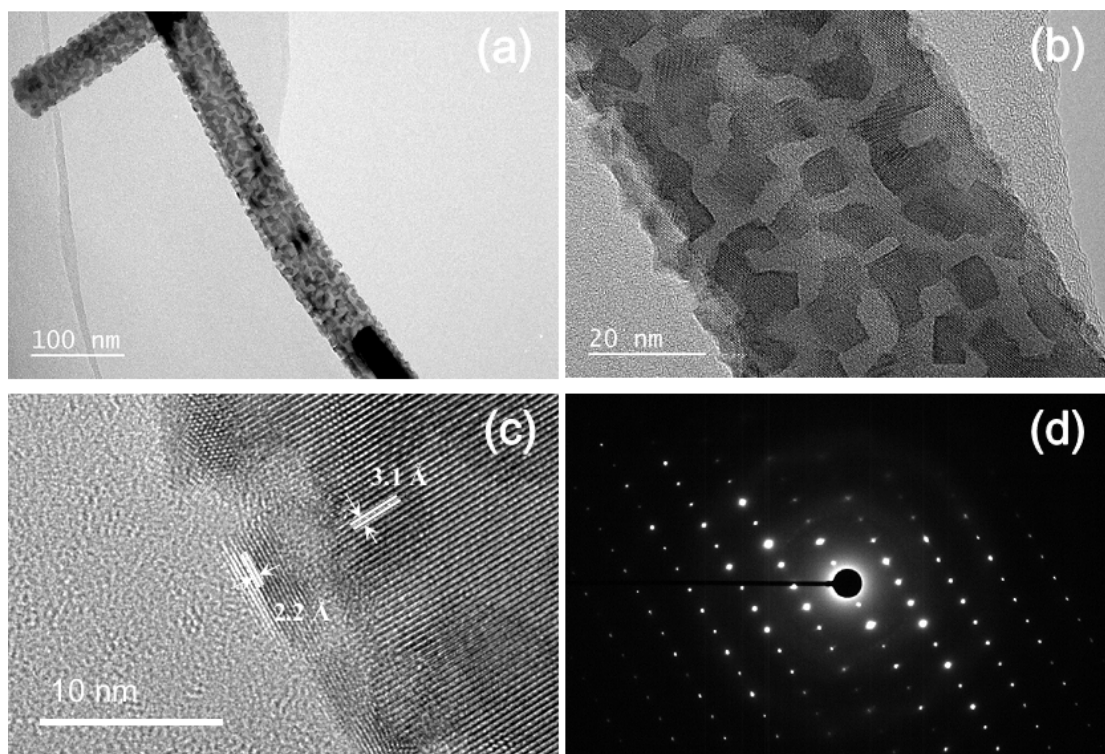


**Figure S6.** (a) SEM image and (b) XRD diffraction pattern of pure CdS nanoparticles.

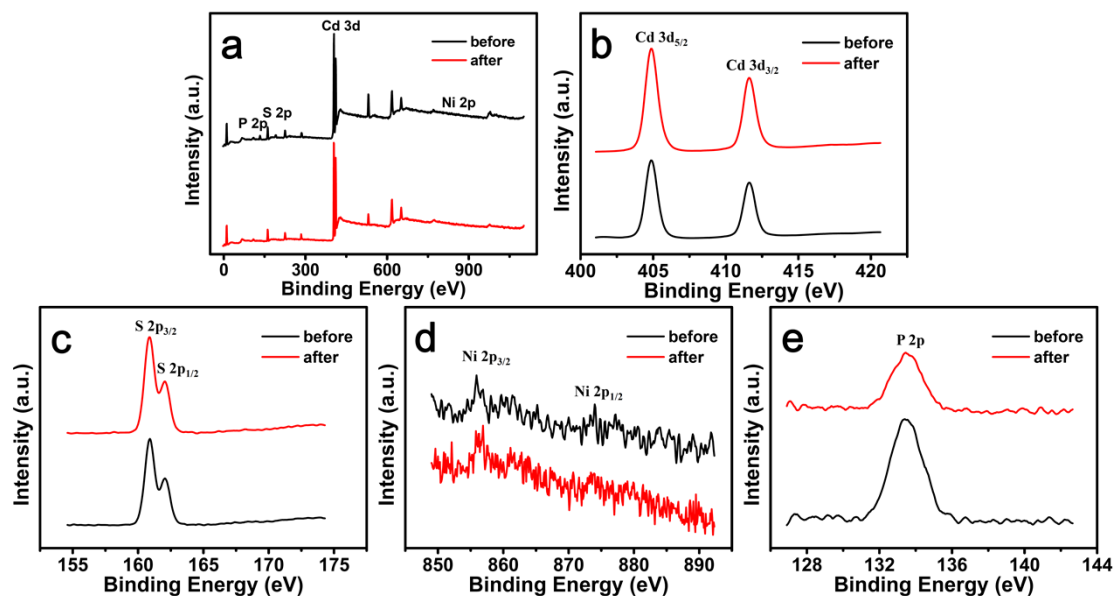


**Figure S7.** TEM images of pure CdS NRs and Ni<sub>2</sub>P/CdS NRs. TEM images of (a) pure CdS NRs, (b) 0.25 wt % Ni<sub>2</sub>P/CdS NRs, (c) 0.5 wt % Ni<sub>2</sub>P/CdS NRs, (d) 1.0 wt % Ni<sub>2</sub>P/CdS NRs, (e) 2.0 wt % Ni<sub>2</sub>P/CdS NRs, (f) 10.0 wt % Ni<sub>2</sub>P/CdS NRs.

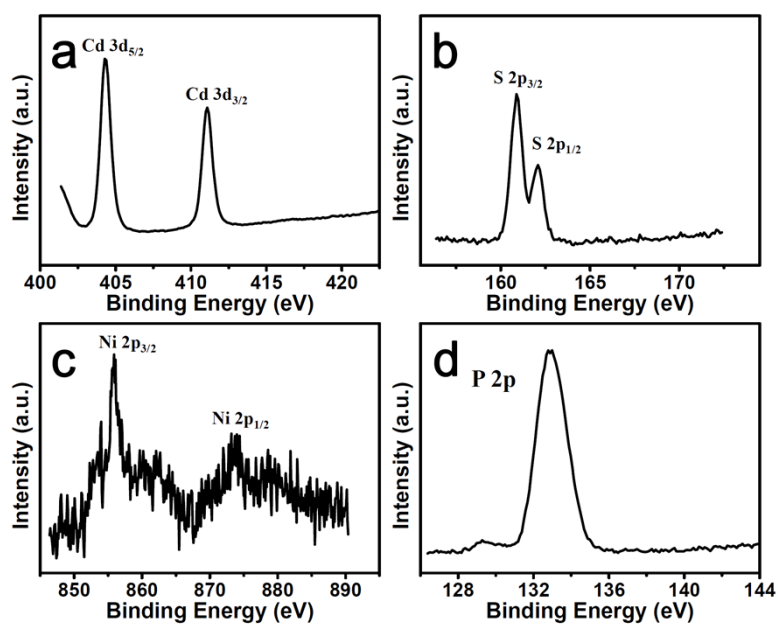




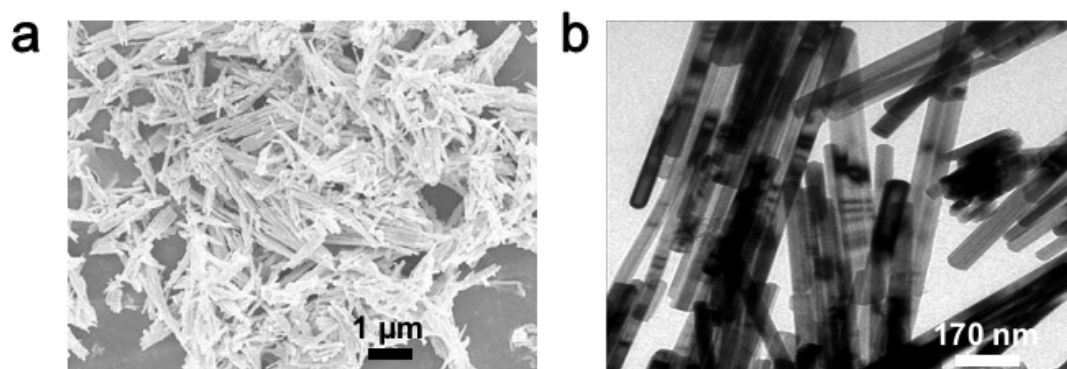
**Figure S8.** HRTEM images of  $\text{Ni}_2\text{P}/\text{CdS}$  NRs and SAED patterns. (a) HRTEM image, and (b) and (c) high-magnification HRTEM images of 0.5 wt %  $\text{Ni}_2\text{P}/\text{CdS}$  NRs; (d) selected-area electron diffraction (SAED) patterns.



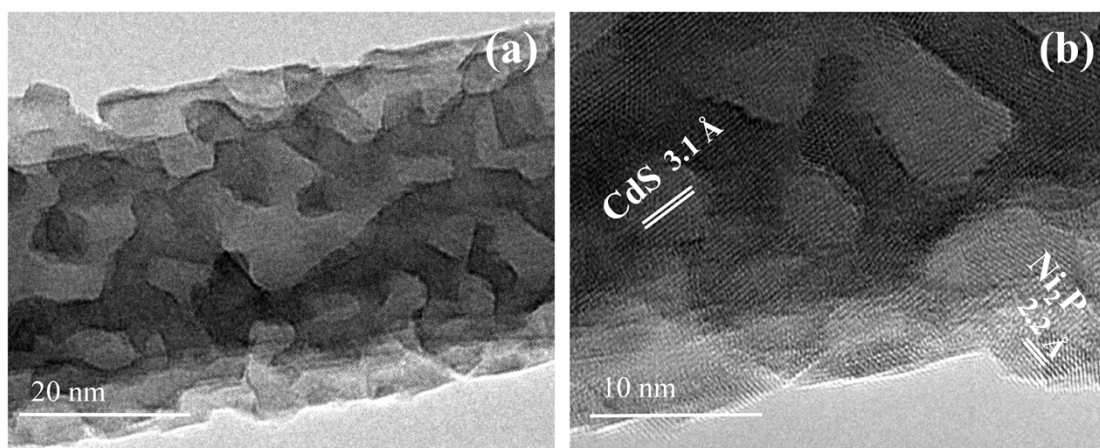
**Figure S9.** XPS data of 0.5 wt% Ni<sub>2</sub>P/CdS NRs before and after photocatalysis. **(a)** XPS survey spectra and High-resolution XPS spectra of **(b)** Cd 3d, **(c)** S 2p, **(d)** Ni 2p, and **(e)** P 2p of the 0.5 wt % Ni<sub>2</sub>P/CdS NRs sample before and after photocatalytic H<sub>2</sub> production for 6 hours under visible light irradiation ( $\lambda > 420$  nm). The system contains 1.0 mg photocatalyst, 0.75 M Na<sub>2</sub>S, and 1.05 M Na<sub>2</sub>SO<sub>3</sub> in 20 mL aqueous solution.



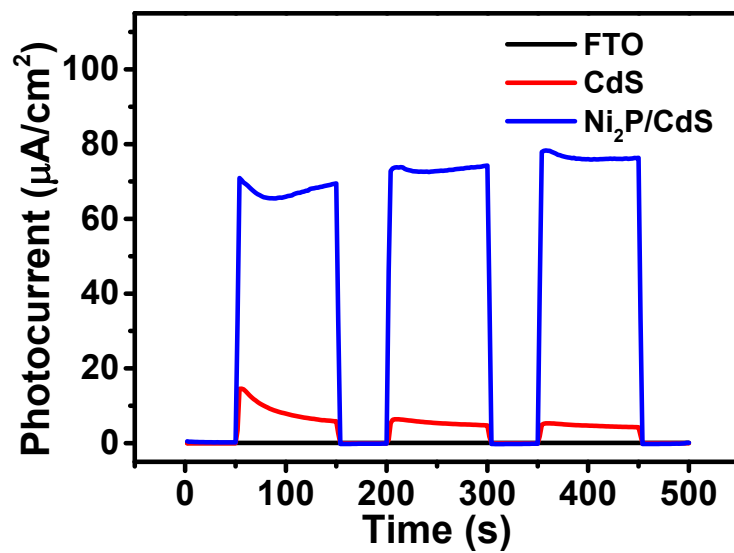
**Figure S10.** XPS data of 10 wt% Ni<sub>2</sub>P/CdS. High-resolution XPS spectra of (a) Cd 3d, (b) S 2p, (c) Ni 2p, and (d) P 2p.



**Figure S11.** SEM and TEM images of Ni<sub>2</sub>P/CdS NRs after photocatalysis. **(a)** SEM and **(b)** TEM images of 0.5 wt% Ni<sub>2</sub>P/CdS NRs sample after photocatalytic H<sub>2</sub> production for 6 hours under visible light irradiation ( $\lambda > 420$  nm). The system contains 1.0 mg photocatalyst, 0.75 M Na<sub>2</sub>S, and 1.05 M Na<sub>2</sub>SO<sub>3</sub> in 20 mL aqueous solution.



**Figure S12.** HRTEM images of 0.5 wt% Ni<sub>2</sub>P/CdS NRs after photocatalytic H<sub>2</sub> production for 6 hours under visible light irradiation ( $\lambda > 420$  nm). The system contains 1.0 mg photocatalyst, 0.75 M Na<sub>2</sub>S, and 1.05 M Na<sub>2</sub>SO<sub>3</sub> in 20 mL aqueous solution.



**Figure S13.** The transient photocurrent responses of blank FTO, CdS NRs, and 0.5 wt% Ni<sub>2</sub>P/CdS NRs.