

Electronic Supplementary Information (ESI) for

Ultrathin Ni (II)-based Coordination Polymer Nanosheets for Co-catalyst Promoting Photocatalytic H₂-production

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Part I: Experimental Section

1.1 Materials synthesis

Ni-CPs Crystals

Typically, a mixture of 4,4'-Bipyridine (0.11g), $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.586g) and H_2O (5ml) was mixed in a 23 ml Teflon, which was heated at 130 °C for 2 days and then cooled to room temperature. The blue crystals (**Ni-CPs**) were obtained.

few-layer Ni-CPs nanosheets (Ni-CPNS)

The fresh bulk Ni- CPNS were fabricated by a liquid-phase exfoliation using an ultrasonic probe in absolute ethanol. In detail, the fresh bulk Ni- CPs crystals (50 mg) was added in ethanol, and ultra-sonicated for 8 hours. Subsequently, the dispersion was centrifuged to collect the supernatant.

CdS nanoparticle (Cd NP)

CdS nanoparticle was synthesized by a precipitation-hydrothermal strategy. For example, 1.09 g $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was added into 23.5 ml deionized water followed by stirring for 2 hour. Then 6.5 ml 0.92 M Na_2S aqueous solution was added dropwise into the above solution, followed by stirring for 3 hours. Finally, the mixed solution was transferred to a 60 ml Teflon-lined autoclave and heated at 180 °C for 12 hours. Then it cooled to room temperature, the obtained yellow samples (Cd NP) were washed by deionized water and ethanol for three times, respectively.

Ni-CPNS coupled CdS nanoparticle (Ni-CPNS@CdS)

Ni-CPNS@CdS was obtained by mechanically mixing the Ni-CPNS ethanol solution with the CdS NP in a mortar inside a glovebox under the Argon gas conditions. Typically, 20 mg of as-synthesized CdS NP mixed Ni-CPNS (e.g., 3mg), which were added into the mortar and followed by addition ethanol solution. Then the sample a was mechanically ground for 20 min inside the glovebox. Finally, the nominal weight Ni-CPNS loaded on to CdS were 13 wt.% for the final product. The procedure for fabrication of different content Ni-CPNS loaded on to CdS (1.5, 5.7, 13, 18 and 22.0 wt.%) was the same as that for 13 wt.%.

1.2 Main Physicochemical Characterization

All powder X-ray diffraction (PXRD) analyses were studied by a Rigaku Dmax2500

diffractometer with Cu K α radiation. UV-Visible diffuse reflectance spectra were acquired on a UV-Vis spectrophotometer. Steady-state photoluminescence spectra and time-resolved PL decay curves were measured at room temperature. XPS was tested on a VG ESCALAB 210 XPS spectrometer system with Mg Ksource. The XANES measurements were carried out at the Australian Synchrotron.

1.3 Photocatalytic H₂ production test

The photocatalytic H₂ production were evaluated in a 100 ml Pyrexflask, followed the 300 W Xenon arc lamp, which equipped with a UV-cutoff filter ($\lambda \geq 420$ nm) was used as the light source to drive the photocatalytic reaction.

Part II: Supplementary Results

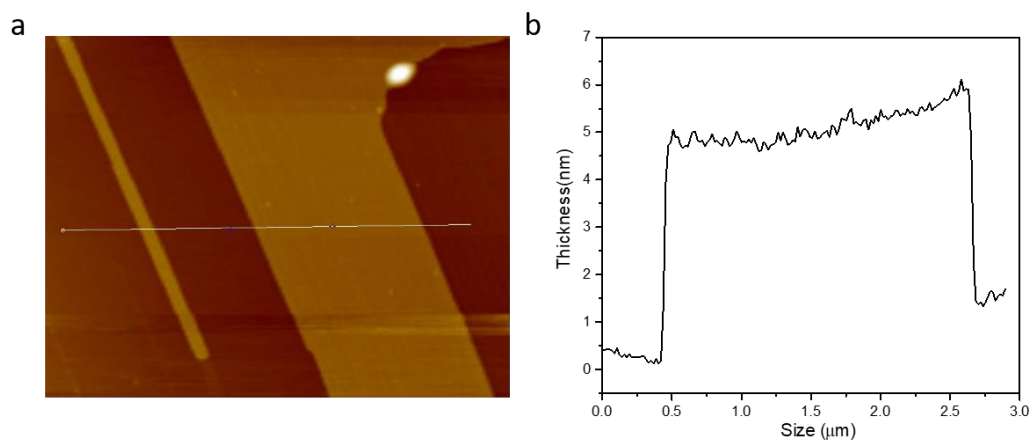


Fig. S1. AFM image of ultra-thin Ni-CPNS (a) and the corresponding height profiles (b).

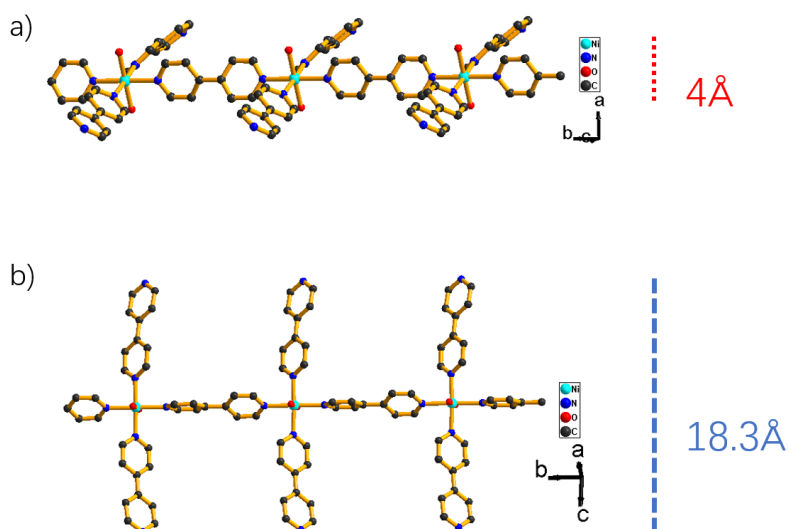


Fig. S2. The thickness of Ni-CPs single chain with $\sim 4\text{\AA}$ (a) or $\sim 18\text{\AA}$ corresponding to metal coordination layer and 4, 4'-bipyridine ligands, respectively.

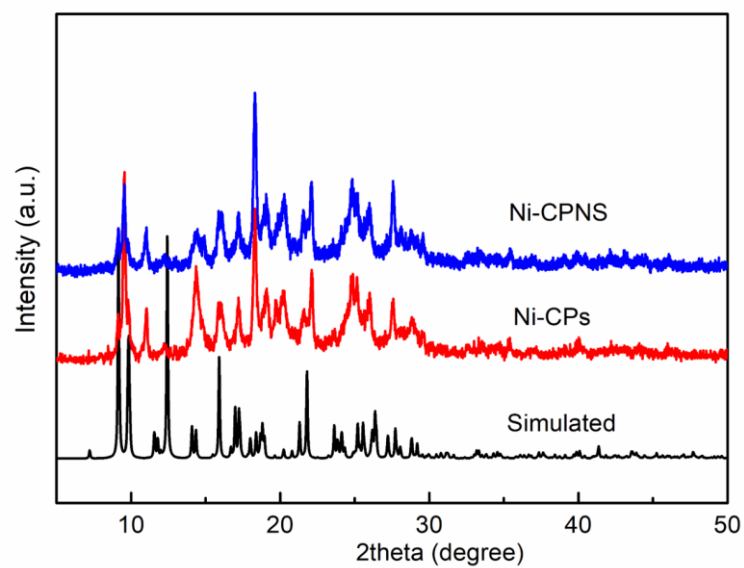


Fig. S3. The PXRD patterns of Ni-CPs and Ni-CPNS.

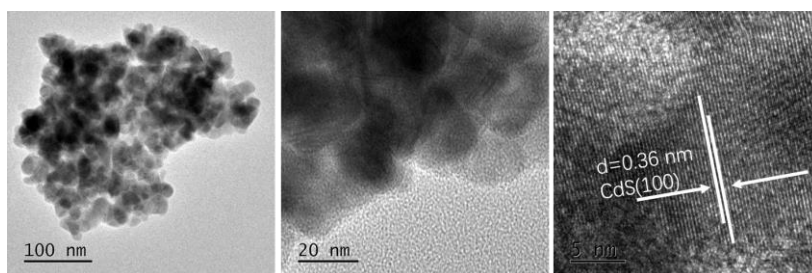


Fig. S4. The typical TEM images of CdS nanoparticles.

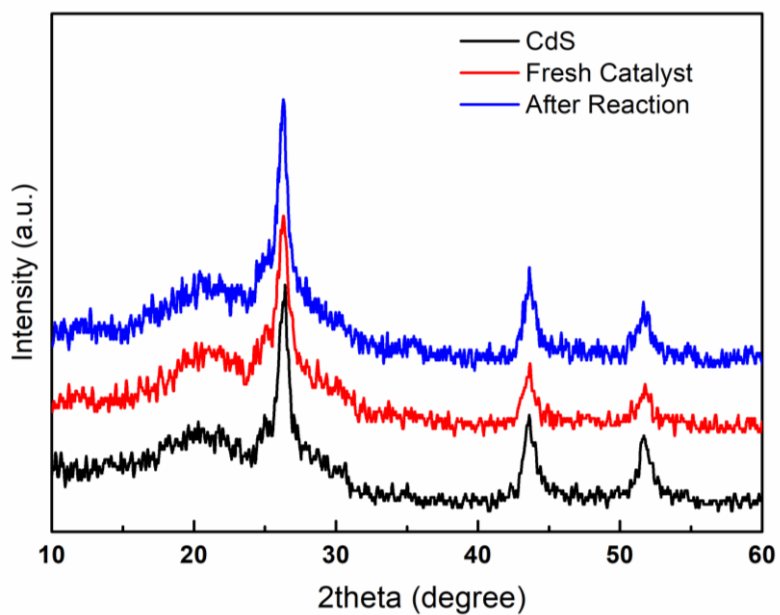


Fig. S5. The XRD patterns of CdS and Ni-CPNS@CdS before and after reaction.

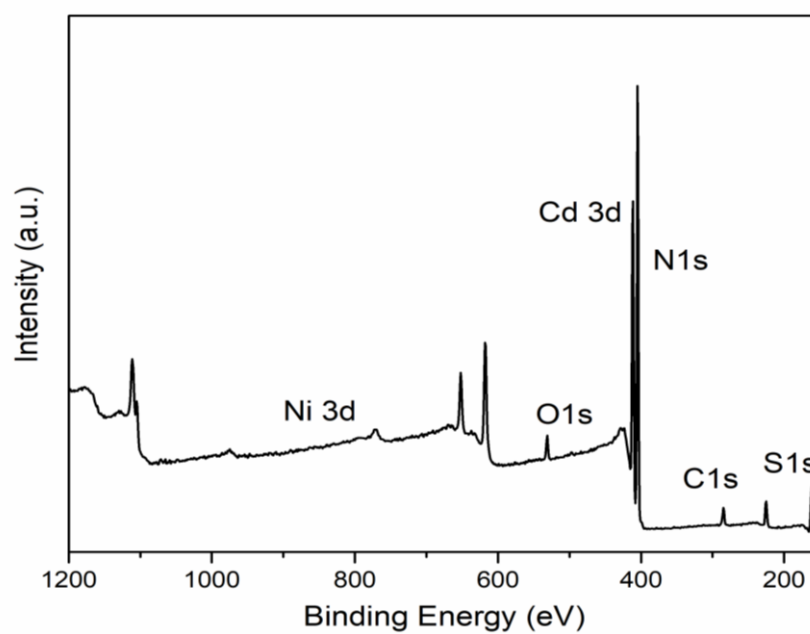


Fig. S6. XPS survey of Ni-CPNS@CdS.

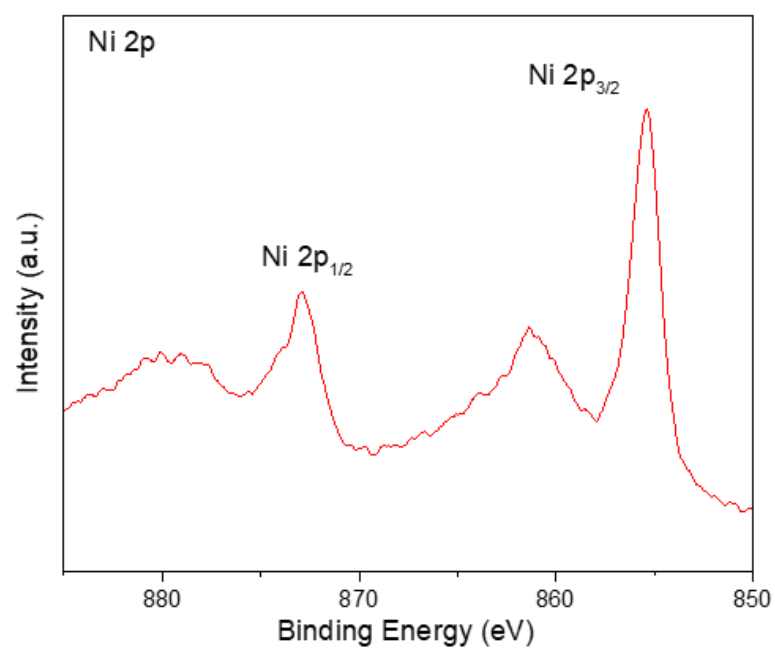


Fig. S7. XPS spectra of the Ni 2p in the Ni-CPNS@CdS.

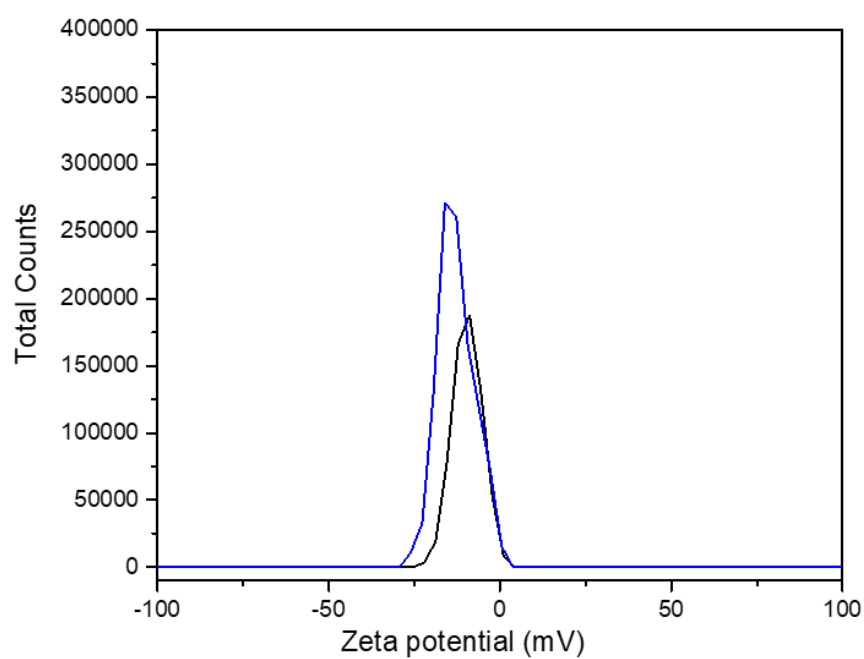


Fig. S8. The Zeta potential of the CdS (black line) and Ni-CPNS@CdS (blue line).

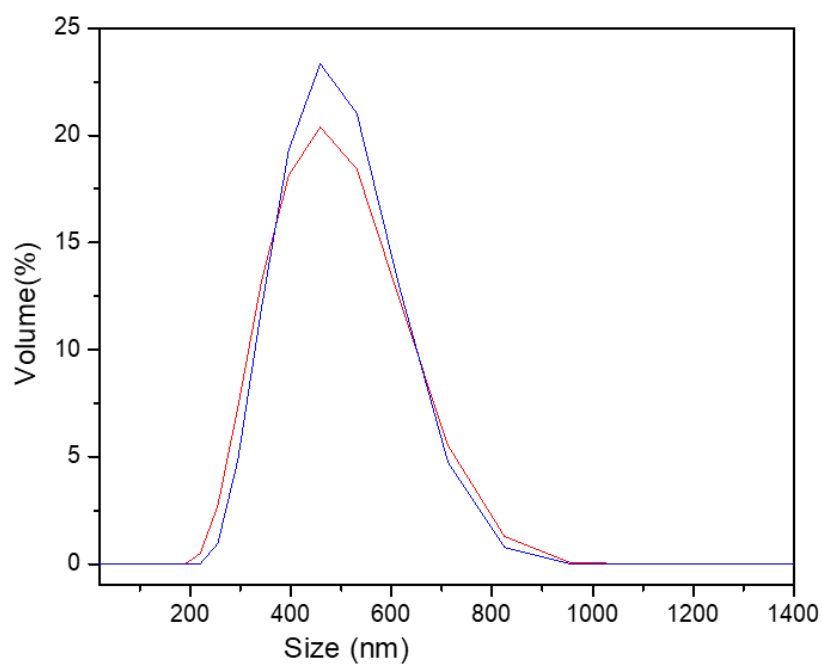


Fig. S9. The particle size distribution of the CdS (red line) and Ni-CPNS@CdS (blue line).

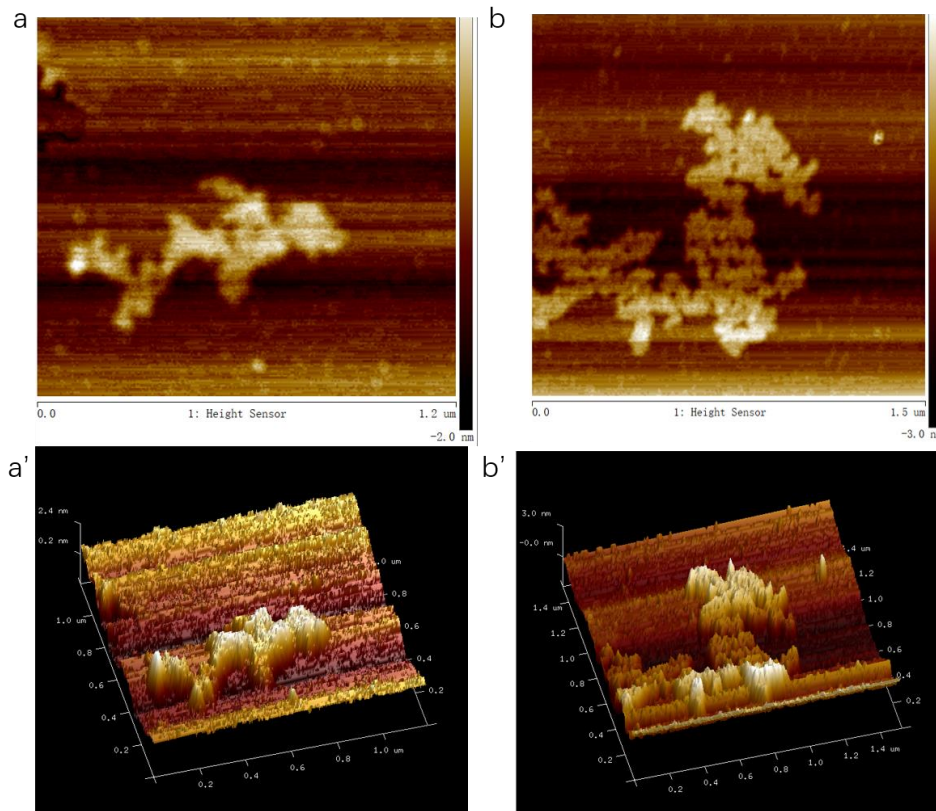


Fig. S10. AFM images of Ni-CPNS@CdS.

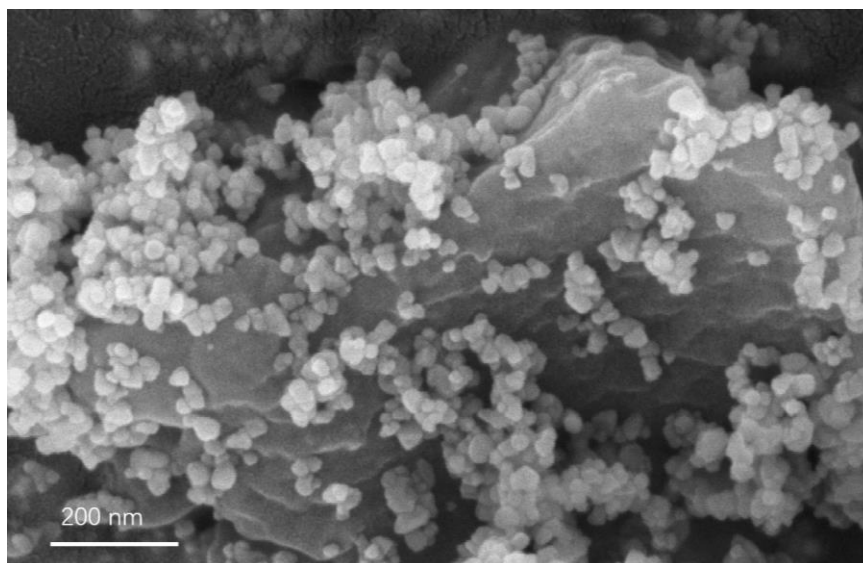


Fig. S11. SEM image of bulk Ni-CPs with CdS NPs after grinding.

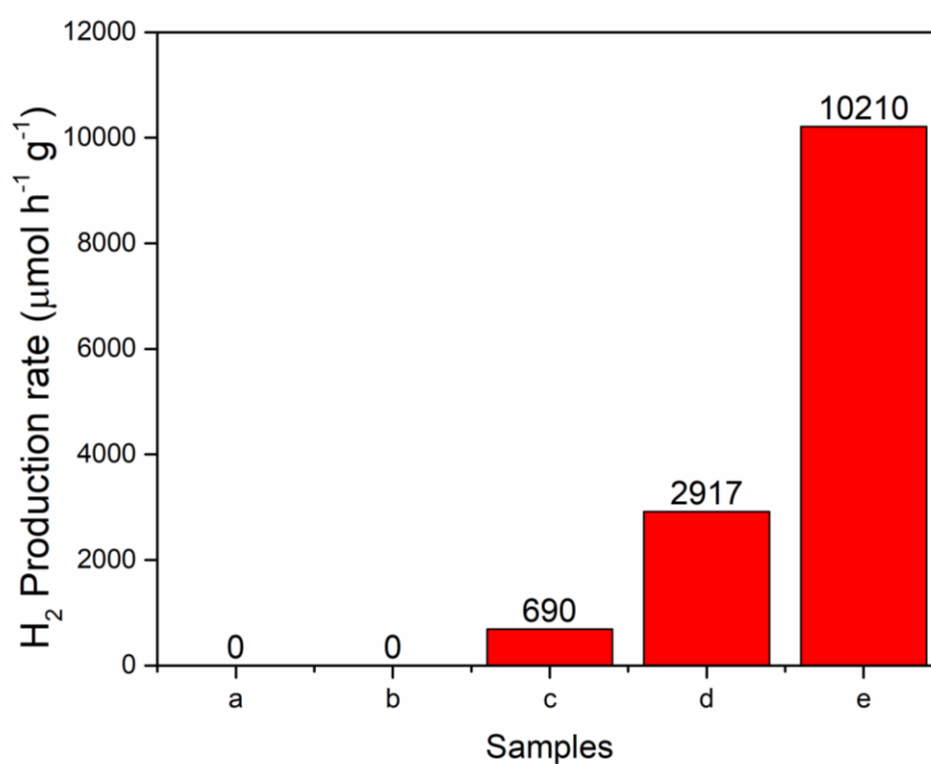


Fig. S12. A comparison of the photocatalytic H₂-production activities of Ni-CPs (a: Ni-CPs), Ni-CPNS (b: Ni-CPNS), CdS (c) and co-catalysts (d: Ni-CPs@CdS; e: Ni-CPNS@CdS).

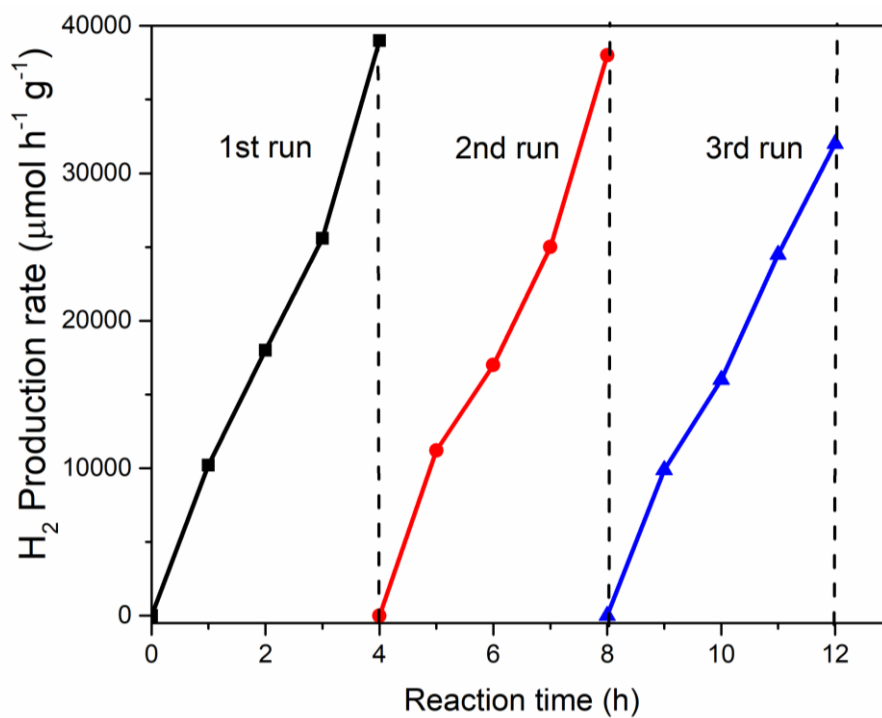


Fig. S13. Time course of H₂ production over Ni-CPNS@CdS under visible-light.

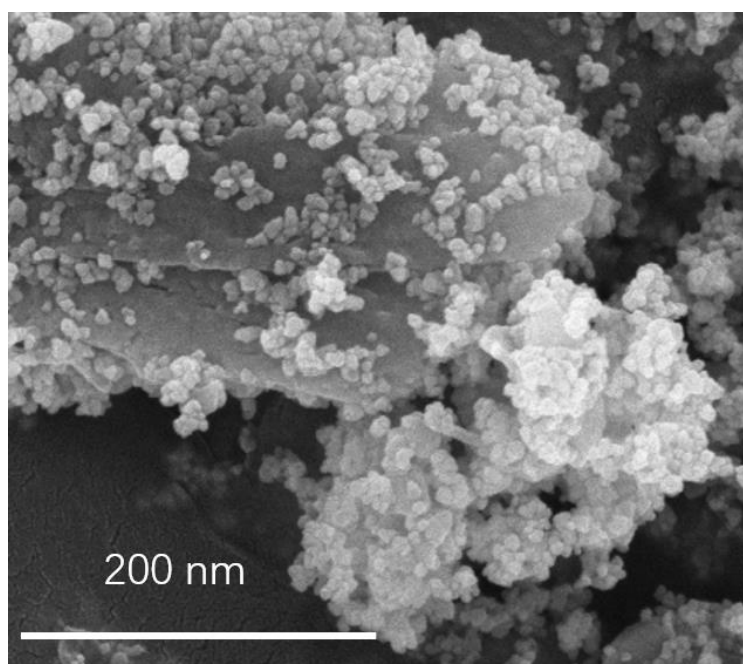


Fig. S14. SEM image of Ni-CPNS@CdS after photocatalyze H₂ evolution under visible-light.

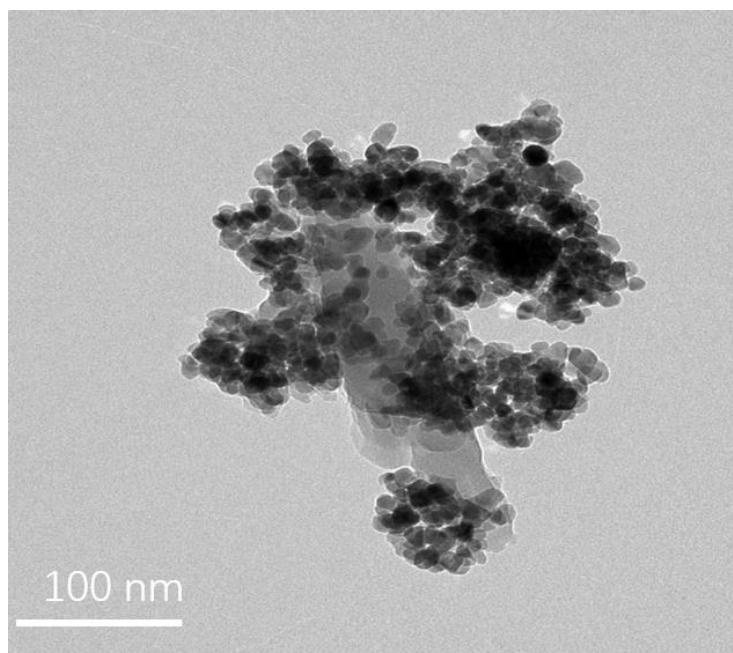


Fig. S15. TEM image of Ni-CPNS@CdS after photocatalytic H₂ evolution under visible-light.

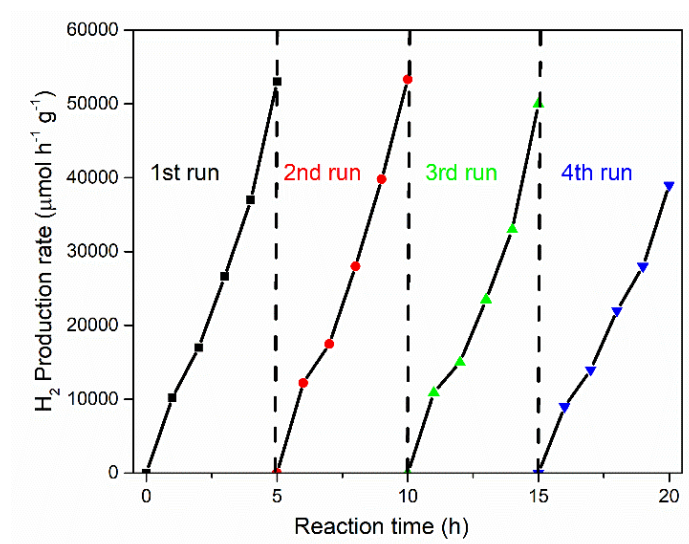


Fig. S16. Time course of H₂ production over Ni-CPNS@CdS over 20 hours test under visible light-driven catalytic processes

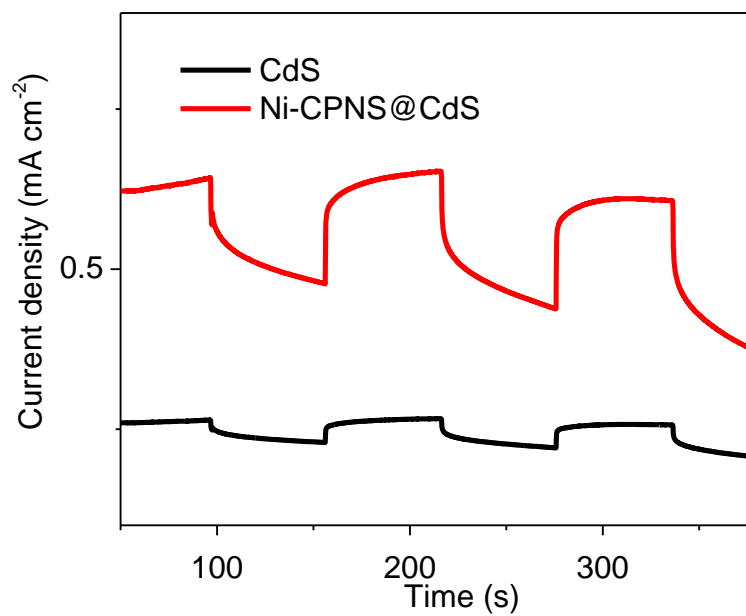


Fig. S17. Photocurrent tests of CdS nanoparticle and Ni-CPNS@CdS.

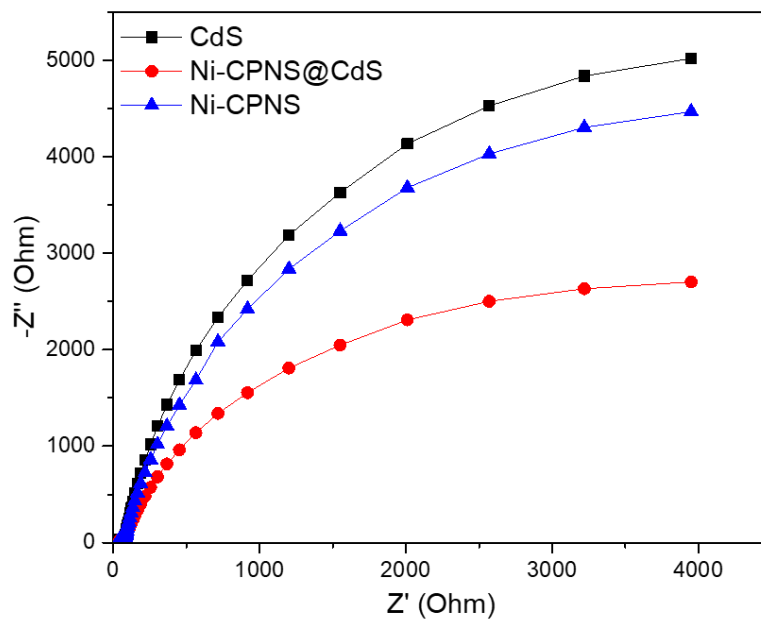


Fig. S18. EIS plots of CdS nanoparticle, Ni-CPNS and Ni-CPNS@CdS.

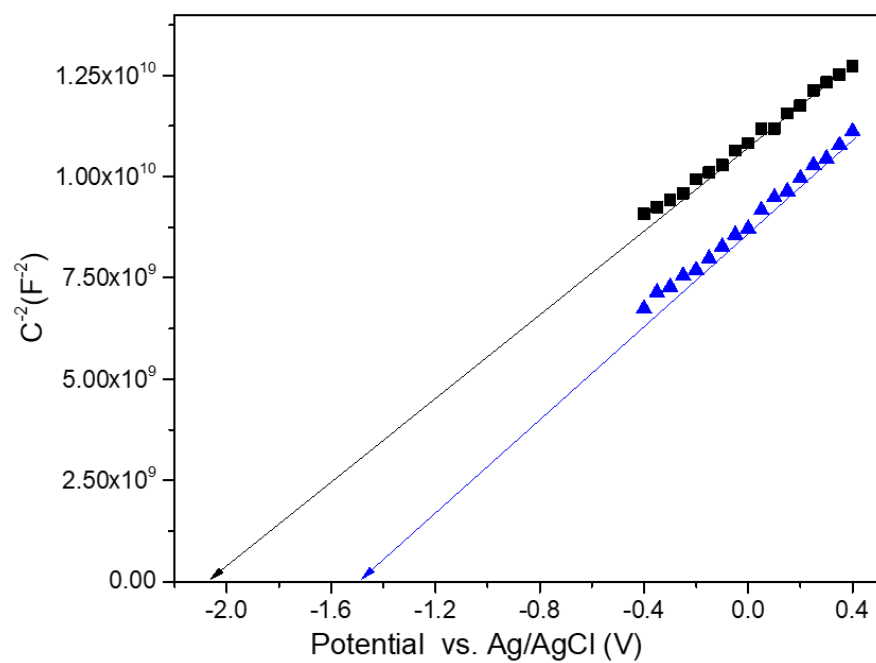


Fig. S19. Mott-Schottky plots of CdS (blue line) nanoparticle and Ni-CPNS@CdS (black line).

Table S1. The hydrogen production comparison of this work with other photocatalytic Co-catalyst.

Photocatalyst	Co-catalyst	H₂ production Rate ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	Ref.
CdS/NiS	NiS	1130	Phys. Chem. Chem. Phys. 2013, 15, 12088
CdS/N-Graphene	N-Graphene	1050	J. Phys. Chem. C 2011, 115, 11466
CdS/NiO	NiO	4460	Catal. Commun. 2013, 36, 104.
CdS/NiO _x	NiO _x	5910	Appl. Catal. B-Environ. 2014, 152, 68.
UiO-66/CdS/RGO	UiO-66	210	Chem. Commun. 2014, 50, 8533–8535
CdS/MoS ₂ -Graphene	MoS ₂ /Graphene	9000	ACS Nano 2014, 8, 7078
Ni-CPNS@CdS	Ni-CPNS	10210	This work