## **Supporting Information**

CoP/CdS/WS<sub>2</sub> p-n-n Tandem Heterostructure: A Novel Photocatalyst for Hydrogen Evolution without Using Sacrificial Agents

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Fig. S1 XRD pattern of Co<sub>3</sub>O<sub>4</sub>.



Fig. S2 XRD pattern of CoP./CoO



Fig. S3 EDS of CCW-5% nanocomposites.



Fig. S4 (a) Nitrogen sorption isotherms, and (b) Corresponding pore size distribution curves of CdS, CC-5%, and CCW-5%, respectively.



**S5** Mott-Schottky plots of (a) CoO and (b) CW at an AC frequency of 1 KHz in the dark.

CC-5%, and CCW-5% excited by 360 nm light ( $\lambda_{em}$ =535 nm).		
	$\tau_1$ /ns	$\tau_2$ /ns
CdS	0.7182 (27.18%)	3.0384 (53.45%)
CC-5%	0.8651 (42.17%)	3.6817 (43.99%)
CCW-5%	1.0977 (51.58%)	5.4191 (48.42 %)

**Table S1.** Fit results of the time-resolved photoluminescence (TRPL) spectra of CW, CC-5%, and CCW-5% excited by 360 nm light ( $\lambda_{em}$ =535 nm).



Fig. S6 Nyquist plots for electrochemical impedance spectroscopy (EIS) obtained from 0.01 Hz to 100 KHz in dark.



Fig. S7 The PHE rates under 420 nm light irradiation and the corresponding AQE of CCW-5% in pure water and RhB solution, respectively.

The AQE of  $H_2$  evolution are measure using typical experimental setup in pure water and RhB solution, respectively. The solution containing CCW-5% is irradiated with 300 W Xe lamps by applying a band-pass filter (420 nm) for 5 h. The average intensity of irradiation is determined to be 31.79 mW cm<sup>-2</sup> by a PL-MW2000 optical power metre and the irradiation area is 18.85 cm<sup>2</sup>. Hence, AQE can be estimated as follows:



Fig. S8 Cycling tests of photocatalytic degradation of RhB soluiton by CCW-5% under visible light irradiation.



Fig.S9 SEM image and EDS of CCW-5% nanocomposites after 20 h irradiation.



Fig. S10 XRD patterns of CCW-5% before and after 20 h irradiation.



Fig. S11 The absorption intensity of  $H_2O_2$  over the CCW-5% suspension before and after 5 h visible light irradiation.

The content of  $H_2O_2$  was measured by UV–vis spectrophotometry. In acidic condition (pH=1~2), Fe<sup>2+</sup> can be oxidized into Fe<sup>3+</sup> by  $H_2O_2$ , and Fe<sup>3+</sup> can be combined with KSCN to form [Fe(SCN)]<sup>2+</sup>. [Fe(SCN)]<sup>2+</sup> has the maximum absorption peak at

475 nm.1

The details are as follows: 20 mL of CCW-5% solution before and after 5 h visible light irradiation was taken, respectively, and then centrifuged to remove solid substances. The pH was adjusted to 1~2 by HCl. 0.05g FeSO<sub>4</sub> was added and mixed evenly. Finally, 0.05g KSCN was added and mixed evenly before the UV–vis absorption measurement.

## References

 R. Shi, H. F. Ye, F. Liang, Z. Wang, K. Li, Y. Weng, Z. Lin, W. F. Fu; C. M. Che, Y. Chen, *Adv. Mater.*, 2018, **30**, 1705941.