Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

The preparation of phosphorus doped $Mn_xCd_{1-x}S$ with boosted photocatalytic hydrogen evolution from pure water

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Characterizations

X-ray diffraction (XRD) patterns of all resultant photocatalysts were characterized on a Bruker D8 Advance X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) was measured on Thermo Fisher Scientific Escalab 250. The features of photocatalysts were observed by scanning electron microscope (SEM, HITACHI SU8010). JEM-2100F transmission electron microscope (TEM) was used to characterize the microtopographies of photocatalysts. The light response property of as-obtained photocatalysts was characterized on An Agilent Cary 5000 UV-vis spectrometer. The photoluminescence spectra (PL) were recorded on an Agilent Cary Eclipse spectrometer. Time resolved PL decay profiles were recorded on an Edinburg Instruments FLS1000 spectrofluorometer. N_2 adsorption/desorption isotherms and pore size distribution curves were measured by Quantachrome Autosorb-IQ2-MP analyzer

Photocatalytic evaluation and Characterizations

A series of prepared samples were evaluated for hydrogen evolution under the visible light irradiation to investigate the photocatalytic activity. The experiments were performed in a Pyrex top-irradiation reaction vessel connected to a sealed glass gas-circulation system. 30 mg photocatalyst and 50 mL water were added into the vessel and Pt as co-catalyst (2 wt%) was in situ photo-deposited on the catalyst by using H_2PtCl_6 as a precursor to enhance the effect of photocatalytic hydrogen evolution. The temperature of the whole system was maintained at 6 ^oC with

circulated cooling water, and the system was deoxygenated with Ar several times to remove the air prior to the visible light irradiation and then irradiated by a 300 W Xe lamp with a UV-cutoff filter (λ>400 nm) and 15 A working current. The amounts of H_2 production were measured by a TCD at a regular time. In order to explore the detailed description of photocatalytic H_2 production performance, the e AQY of the 30 mg samples at 420 nm, 450 nm and 550 nm band-pass filters respectively, the AQY was estimated by the following equation:

$$\text{AQY [\%]} = \frac{2 \times \text{amount of } H_2 \text{ molecules evolved}}{\text{number of incident photons}} \times 100$$

Photoelectrochemical measurements

The photocurrent and electrochemical impedance spectra measurements were performed at the electrochemical workstation CHI660E (Chenhua Instrument, Shanghai, China). Working with simple three electrodes, the working electrode (50 mg samples into 10 mg of PEG and 10 μL adhesive Nafion stir into a paste evenly dispersed an amount of ethanol was prepared on FTO glass of 2 cm ×1.2 cm), reference electrode (Ag/AgCl) and Pt plate as the counter electrode was in the process of measuring the linear sweep voltammetry and transient photocurrent property. The whole test was carried out in a 2 M Na_2SO_4 solution with a 300 W xenon lamp as the light source with a UV cut filter (λ > 400 nm) and the current intensity was fixed at 15A.

Measurements of H_2O_2

After hydrogen production, the liquid supernatant was centrifuged several times. 2 ml of the solution was added by 0.01 g KI, 0.02 g of starch, 0.04 g NaCl, 2 ml DI water and finally added 1mL HCl (1M). After 10-20 minutes of reaction, the solution was characterized on An Agilent Cary 5000 UV-vis spectrometer. The results are shown in Fig. S8.

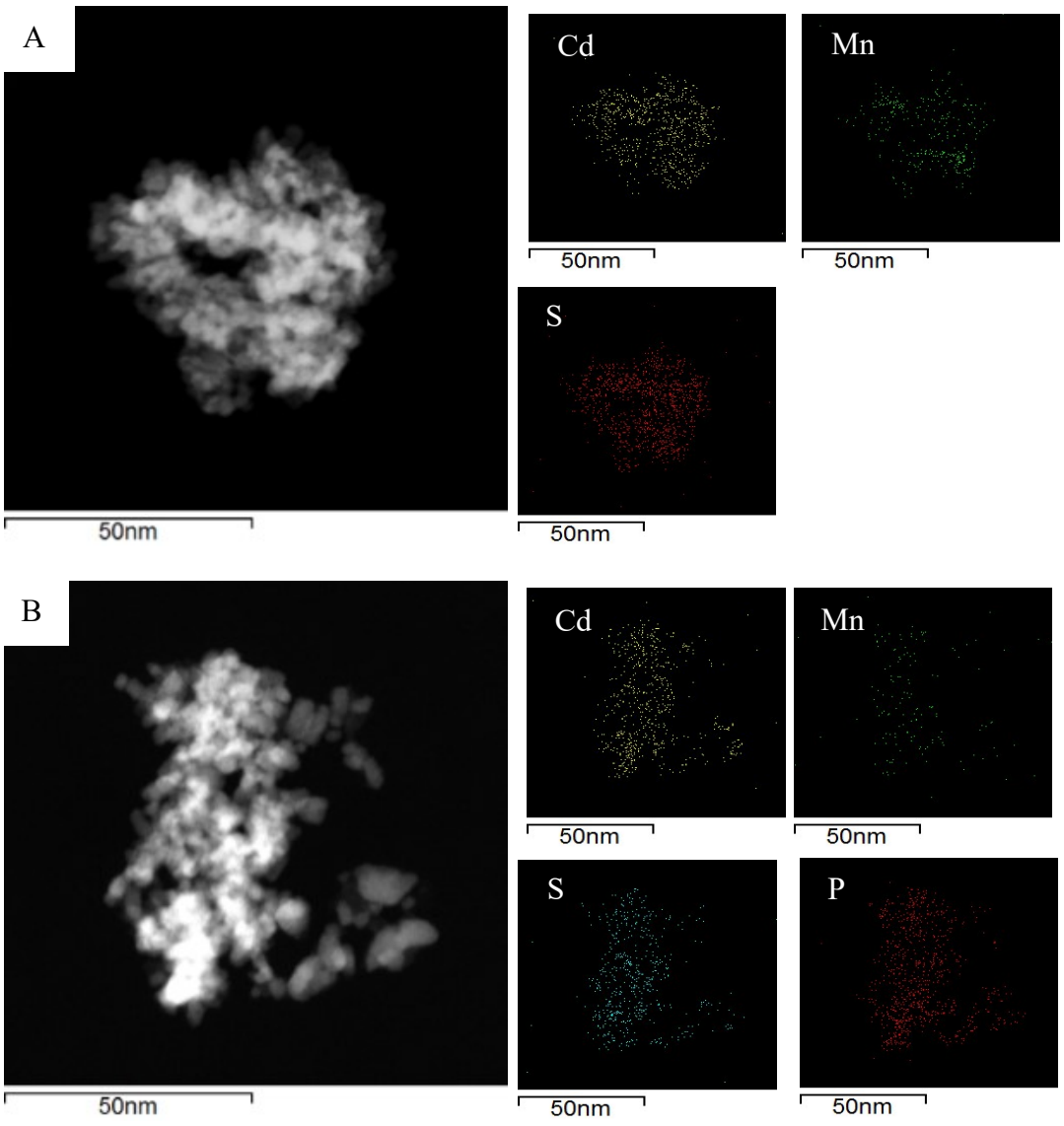

Fig. S1 Element mapping of (A) Cd, Mn and S of $Mn_{0.25}Cd_{0.75}S$ and (B) Cd, Mn, S and P of 0.1-P/$Mn_{0.25}Cd_{0.75}S$.

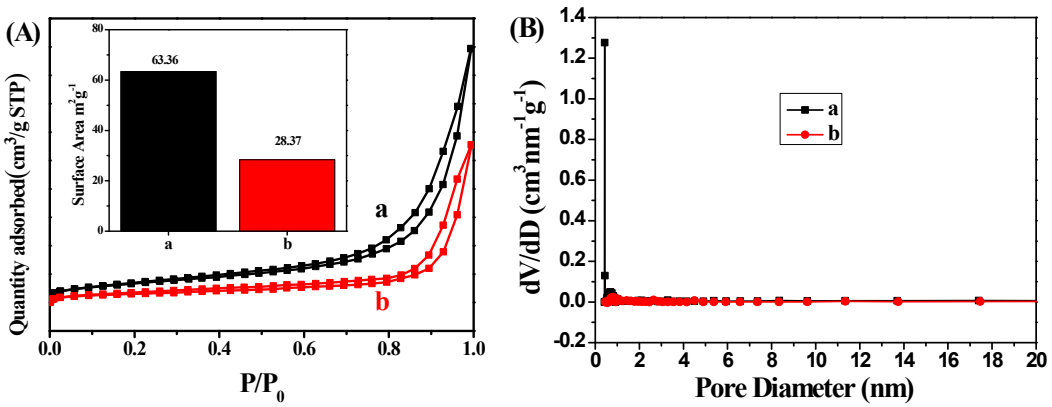

Fig. S2 (A) N_2 adsorption-desorption isotherms and (B) pore size distribution curves of (a) $Mn_{0.25}Cd_{0.75}S$, (b) 0.1-P/$Mn_{0.25}Cd_{0.75}S$.

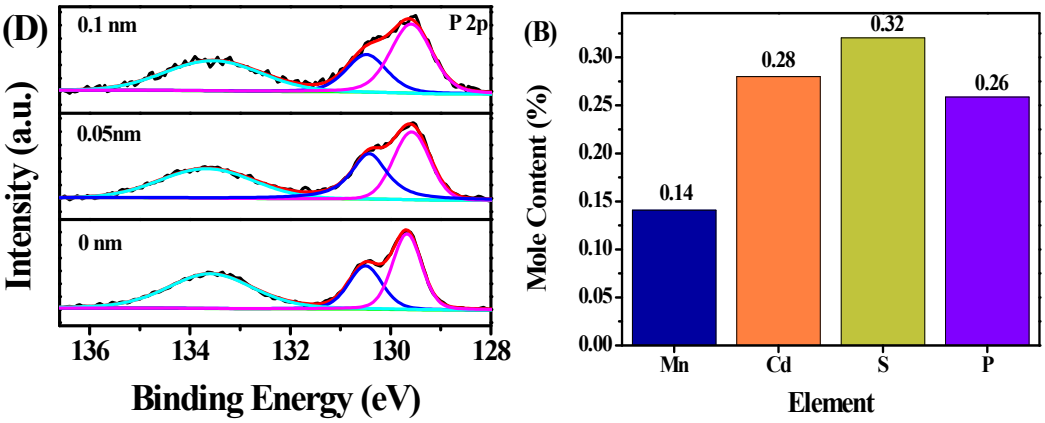

Fig. S3 (A) XPS spectra of P 2p for 0.1-P/$Mn_{0.25}Cd_{0.75}S$ by Ar+ beam etching for 0, 0.05, 0.1 nm. (B)The content spectrum of each element in 0.1-P/$Mn_{0.25}Cd_{0.75}S$ measured by XPS.

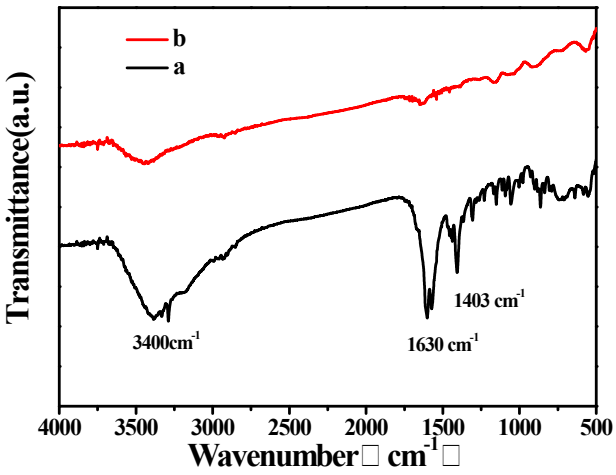

Fig. S4 FT-IR spectra of (a) $Mn_{0.25}Cd_{0.75}S$ and (b) 0.1-P/$Mn_{0.25}Cd_{0.75}S$

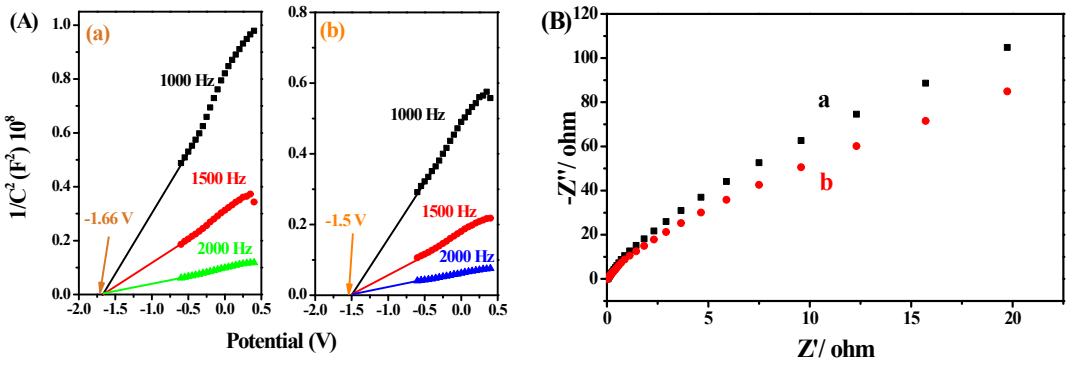

Fig. S5 (A) The Mott-Schottky plots and (B) EIS of (a) $Mn_{0.25}Cd_{0.75}S$ and (b) 0.1-P/$Mn_{0.25}Cd_{0.75}S$.

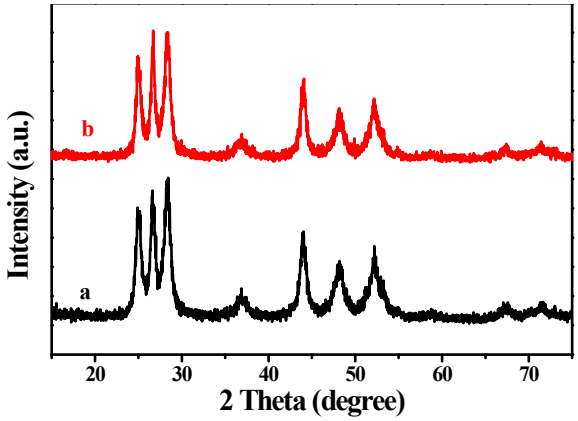

Fig. S6 The XRD patterns of (a) fresh 0.1-P/$Mn_{0.25}Cd_{0.75}S$ and (b) used 0.1-P/$Mn_{0.25}Cd_{0.75}S$

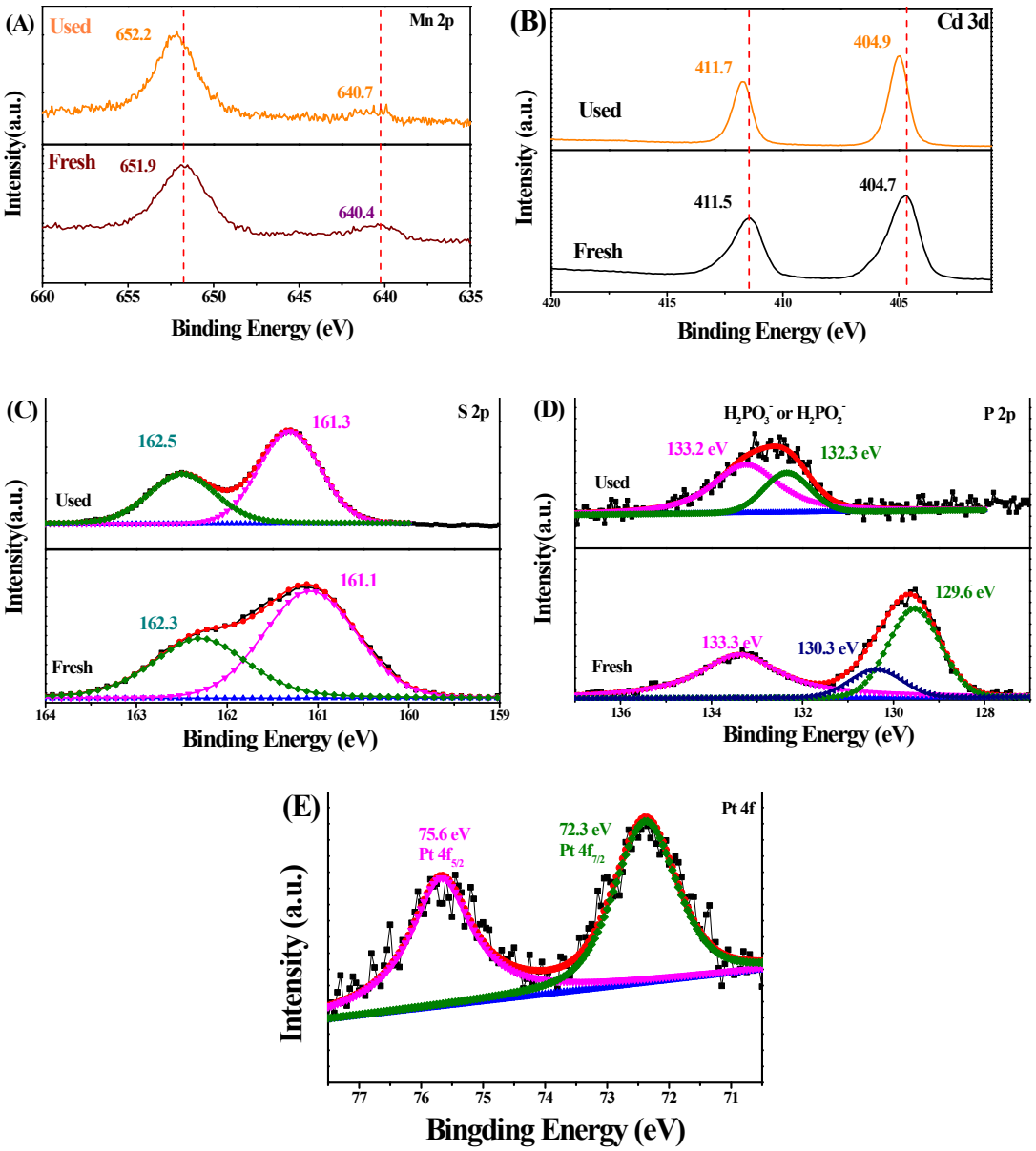

Fig. S7 The XPS (A) Mn 2p, (B) Cd 3d, (C) S 2p, (D) P 2p patterns of fresh0.1-P/$Mn_{0.25}Cd_{0.75}S$ and used 0.1-P/$Mn_{0.25}Cd_{0.75}S$, (E) XPS Pt 4f of used 0.1-P/$Mn_{0.25}Cd_{0.75}S$

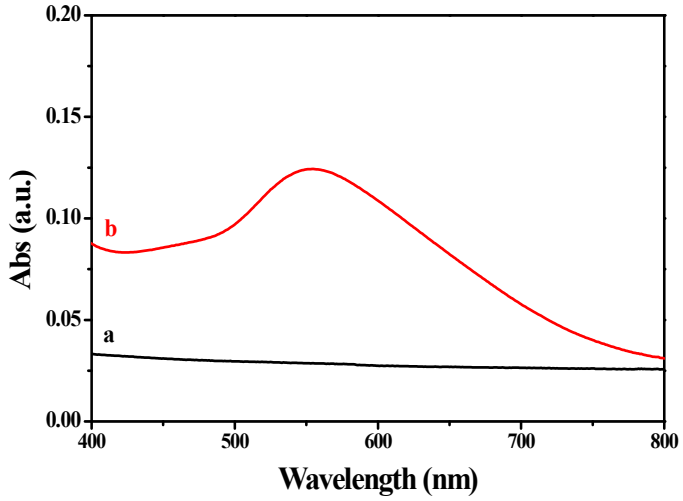

Fig. S8 The absorption intensity of H_2O_2 of (a) blank and (b) 0.1-P/$Mn_{0.25}Cd_{0.75}S$.

Table S1 The content of H_2 and H_2O_2

Product	**Content (μmol/h)**
H_2	25.89
H_2O_2	1.3

Table S2 Comparison of photocatalytic performance of 0.1-P/$Mn_{0.25}Cd_{0.75}S$ and other systems in recently reports

Samples	Light source	Cocatalyst loading	Performance ($\mu molg^{-1}h^{-1}$)	Reference
$CdS/WO_3/CdWO_4$	300W Xe Lamp ($\lambda > 420nm$)	1 wt% Pt	H_2 6.896 O_2 3.162	[1]
d-ZCS-P300	500 W Xe lamp ($\lambda \geq 400$ nm)	None	H_2 32.33 O_2 14	[2]
$BiVO_4$/CDs/CdS(Z-scheme)	300 W Xe lamp ($\lambda \geq 420$ nm)	3 wt% Pt	H_2 15.5 O_2 7.625	[3]
Ag-$ZnIn_2S_4$	300W Xe lamp (＞420 nm)	None	H_2 56.6 O_2 29.1	[4]
0.1-P/$Mn_{0.25}Cd_{0.75}S$	300W Xe Lamp ($\lambda > 400nm$)	2 wt% Pt	H_2 863 H_2O_2 43.3	This work

[1] Nagakawa, H.; Ochiai, T.; Konuma, S.; Nagata, M.; Visible-Light overall water splitting by $CdS/WO_3/CdWO_4$ tricomposite photocatalyst suppressing photocorrosion. ACS Applied Energy Materials, 12 (2018) 6730–6735.

[2] Ng, B. J.; Putri, L. K.; Kong, X. Y.; Pasbakhsh, P.; Chai, S.; Overall pure water splitting using one-dimensional P-doped twinned $Zn_{0.5}Cd_{0.5}S_{1-x}$ nanorods via synergetic combination of long-range ordered homojunctions and interstitial S vacancies with prolonged carrier lifetime. Applied Catalysis B: Environmental, 262 (2020) 118309.

[3] Wu, X.; Zhao, J.; Wang, L.; Han, M.; Zhang, M.; Wang, H.; Huang, H.; Liu, Y.; Kang, Z.; Carbon dots as solid-state electron mediator for $BiVO_4$/CDs/CdS Z-scheme photocatalyst working under visible light. Applied Catalysis B: Environmental, 206 (2017) 501-509.

[4] Pan, R.; Hu, M.; Liu, J.; Li, D.; Wan, X.; Wang, H.; Li, Y.; Zhang, X.; Wang, X.; Jiang, J.; Zhang J.; Two-Dimensional all-in-one sulfide monolayers driving photocatalytic overall water splitting. Nano Letters, 14 (2021) 6228–6236.