

## Supporting Information

### The highly improved hydrogen evolution performance of 0D/0D MoP-modified P-doped Mn<sub>0.5</sub>Cd<sub>0.5</sub>S photocatalyst

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#### Characterization methods

The microscopic morphology of the catalysts was photographed by transmission electron microscopy (TEM, JEM-2010) and scanning electron microscopy (SEM, SU8010); the crystal type was determined by X-ray polycrystalline powder diffraction (XRD, D8 Advance); the chemical composition was determined by X-ray photoelectron spectroscopy (XPS, ESCALAB Xi+); Photoluminescence spectroscopy (PL) by fluorescence spectrophotometer (Cary Eclipse) with 375 nm as excitation wavelength; UV-vis diffuse reflectance spectroscopy (UV-vis DRS) by UV-vis spectrophotometer (Agilent Cary 5000). Time resolved PL decay profiles of the as-synthesized MCS and PMOMCS-P were recorded on an Edinburg Instruments spectrofluorometer (FLS1000).

#### Electrochemical analysis

Instantaneous photocurrents (i-t curves), electrochemical impedance spectroscopy (EIS), linear sweep voltammetry curves (LSV) and Mott-Schottky (MS) of the samples were tested by an electrochemical workstation (CHI-660E, CH Instruments Ins.). The working, reference and counter electrodes used in the measurement were the sample, standard Ag/AgCl (saturated KCl solution) and Pt wire, respectively. The LSV tests were performed at a sweep rate of 0.1 V/s. The EIS measurements were performed without light irradiation and at open circuit voltage with a frequency range of 0.1-10<sup>5</sup> Hz and an AC amplitude of 5 mV, and sample, calomel electrode and Pt wire were working, reference and counter electrodes, respectively. 0.2 mol/L Na<sub>2</sub>SO<sub>4</sub> was used as the electrolyte.

### Photocatalytic test

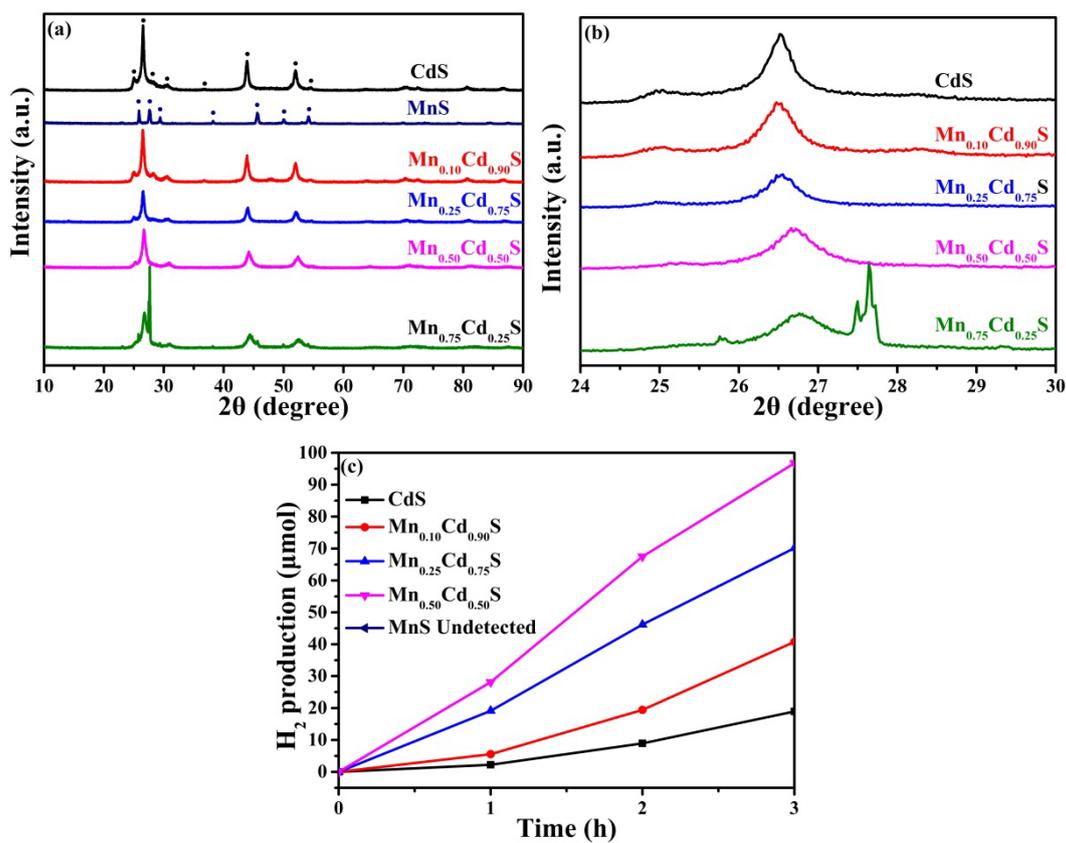
The samples were tested for photocatalytic hydrogen evolution by dispersing 30 mg of sample in 40 ml of trap solution or pure water. The reaction was carried out in a closed vacuum system and the reactor was irradiated with a 300 W xenon lamp ( $\lambda \geq 400$  nm). The cyclic experiment procedure is to disperse 30 mg of catalyst in 40 mL of trap solution, and continue to react under light. The gases produced by the photocatalytic reaction were all detected by gas chromatography, which was detected every hour. The trapping agent solutions were 0.1 mol/L Na<sub>2</sub>S and 0.3 mol/L Na<sub>2</sub>SO<sub>3</sub>. The apparent quantum yields (AQY) of the synthesized catalysts were measured under equivalent conditions, with monochromatic light (400, 420, 450, 500 and 550 nm) irradiation. The equations were calculated as follows:

$$AQY(\%) = \frac{2 \times \text{amount of H}_2 \text{ molecules evolved}}{\text{number of incident photons}} \times 100\%$$

### Synthesis Mn<sub>x</sub>Cd<sub>1-x</sub>S.

9x mmol Mn(CH<sub>3</sub>COO)<sub>2</sub>•4H<sub>2</sub>O and 9(1-x) mmol Cd(CH<sub>3</sub>COO)<sub>2</sub>•2H<sub>2</sub>O were dissolved in 20 mL of deionized water; then 13.5 mmol of C<sub>2</sub>H<sub>5</sub>NS were dissolved in 20 mL of deionized water. The solution containing Cd<sup>2+</sup> and Mn<sup>2+</sup> was dropped into the sulfur source solution, then the mixed solution was placed at 130 °C for 10 h. The sample was washed and collected by centrifugation and dried at 60 °C for 12 h. The samples were labelled as CdS (x=0), Mn<sub>x</sub>Cd<sub>1-x</sub>S (x=0.10, 0.25, 0.5, 0.75), and MnS (x=1).

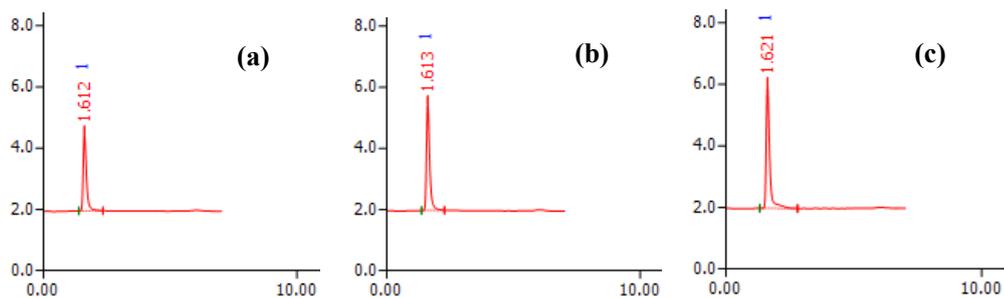
## Selection of Cd/Mn feed ratio



**Fig. S1** (a) XRD of  $Mn_xCd_{1-x}S$ , (b) Magnified plot of  $Mn_xCd_{1-x}S$  at  $2\theta = 26.7^\circ$ , (c) Hydrogen evolution of  $Mn_xCd_{1-x}S$  with the addition of trapping agents ( $Na_2S$  (0.1 M) and  $Na_2SO_3$  (0.3 M)) and loading of 1.5 wt% Pt.

The photocatalytic hydrogen precipitation activity of solid-solution semiconductor materials is closely related to their composition. To determine the optimum Cd/Mn ratio for the synthesis of  $Mn_xCd_{1-x}S$  in the photocatalytic reaction, we prepared MnS, CdS and  $Mn_xCd_{1-x}S$ . The synthesized  $Mn_xCd_{1-x}S$  was demonstrated to consist of cubic CdS, hexagonal CdS and hexagonal MnS by comparing the XRD characterization results with the standard cards of the substances. As shown in Fig. S1(a), the characteristic peaks located at  $2\theta = 26.5^\circ$ ,  $30.5^\circ$ ,  $43.9^\circ$  and  $52.0^\circ$  are considered to be the (111), (200), (220), (311) lattice planes of cubic CdS (JCPDS 89-440)[1]. The characteristic peaks at  $2\theta = 25.2^\circ$ ,  $26.7^\circ$ ,  $28.3^\circ$ ,  $36.6^\circ$ ,  $43.9^\circ$ ,  $52.2^\circ$ ,  $54.1^\circ$ , (100), (002), (101), (102), (103), (112), (004) belong to the hexagonal phase of CdS (JCPDS 41-1049)[2]. MnS is hexagonal  $\gamma$ -MnS (JCPDS 40-1289) and the characteristic peaks at  $2\theta = 25.9^\circ$ ,  $27.6^\circ$ ,  $29.4^\circ$ ,  $38.2^\circ$ ,  $45.6^\circ$ ,  $50.0^\circ$  and  $54.2^\circ$  are

considered to be (100), (002), (101), (102), (110), (103) and (112) crystal planes[3]. In Fig. S1(b), the peaks of  $Mn_xCd_{1-x}S$  ( $x = 0.10, 0.25, 0.5$  and  $0.75$ ) are all significantly shifted in a more angular direction compared to CdS, which indicated that Mn is successfully doped into CdS, indicating that the  $Mn_xCd_{1-x}S$  solid solution compound was successfully prepared [4]. It shows that  $Mn_xCd_{1-x}S$  solid solution compound was successfully prepared. When  $x=0.75$ , the XRD pattern of  $Mn_{0.75}Cd_{0.25}S$  at  $2\theta=27.64^\circ$  appeared extremely strong peak. By comparing with the standard card, it is the (002) crystal plane of hexagonal MnS. It shows that MnS also exist in  $Mn_{0.75}Cd_{0.25}S$ , to form MnS/ $Mn_{0.75}Cd_{0.25}S$  composite materials, hence, in this system, to obtain the  $Mn_xCd_{1-x}S$  solid solution, the max value of  $x$  is 0.5. Then, Fig. S1(c) gives the photocatalytic hydrogen evolution curves of  $Mn_xCd_{1-x}S$  with different Mn/Cd feed ratios. By comparison, it is easy to draw a conclusion that as the amount of Mn increases, their photocatalytic hydrogen evolution activity gradually becomes stronger. Among these,  $Mn_{0.50}Cd_{0.50}S$  showed the best trend in photocatalytic hydrogen production and was therefore chosen as the base material for further modification



**Fig. S2** The detection results of PMOMCS-P5 in pure water by gas chromatography

## References

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- [3] Q. Z. Huang, Y. Xiong, Q. Zhang, H. C. Yao, Z. J. Li. Noble metal-free MoS<sub>2</sub> modified Mn<sub>0.25</sub>Cd<sub>0.75</sub>S for highly efficient visible-light driven photocatalytic H<sub>2</sub> evolution. *Applied Catalysis B: Environmental*, 2017, 209: 514-522.
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