2D ultrathin CoP modified $Mn_xCd_{1-x}S$ with controllable band structure and robust photocatalytic performance for hydrogen generation

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Characterization

X-ray diffraction (XRD) characterization was employed to analyze catalyst structure by a Shimadzu/XD-3A diffractometer system. Copper Kα radiation (λ = 1.5418 Å) was used. Morphologies of the catalysts were employed through transmission electron microscopy (TEM) by using an JEOL 2100 system **and SEM by using Hitachi S-4800.** UV-vis diffuse reflectance spectra (DRS) was used by a Shimadzu/UV-3600 equipment. Photoluminescence (PL) analysis was adopted to explore the electrons transfer via a Hitachi/F-7000 apparatus. X-ray photoelectron spectra (XPS) was carried out by using PHI 5000 Versaprobe with Al-Kα radiation.

Photoelectrochemical (PEC) measurements

The synthesized catalysts was tested in 0.5M H_2SO_4 using a typical three electrode setup on an electrochemical station (Chenhua Instruments, CHI660D) with a Ag/AgCl reference electrode, a graphite rod or Pt foil as counter electrode and CdS composites as working electrode to study the electrochemical property. All potential data are

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given versus reversible hydrogen electrode (RHE) according to the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 \times pH$ (V). The electrochemical impedance spectroscopy (EIS) and photocurrent were conducted under the irradiation of visible light by a 300 W xenon lamp.

Photocatalytic H_2 generation measurements

Photocatalytic performance of the prepared catalysts were explored in a 150 ml quartz reactor. Typically, 5 mg samples were added in 50 ml solution. 0.25 M Na_2S and 0.35 M Na_2SO_3 were also used as sacrificial reagents. Next, evacuated the whole system for half an hour to keep the system vacuum. After that, turn on the xenon lamp with a 420 nm cut-off filter (CELHXF300, Beijing China Education Au-light Co., Ltd) to start the reaction. At last, the produced H_2 was determined by an online gas chromatogram (GC 7900) equipped with a TCD.

The apparent quantum efficiency (AQE) of hydrogen generation was calculated as follows:

$$\mathbf{AQE} = \frac{\mathbf{Number\ of\ reacted\ electrons}}{\mathbf{Number\ of\ incident\ photons}} \times \mathbf{100\%}$$

$$= \frac{\mathbf{2 \times Number\ of\ evolved\ H_2\ molecules}}{\mathbf{Number\ of\ incident\ photons}} \times \mathbf{100\%}$$

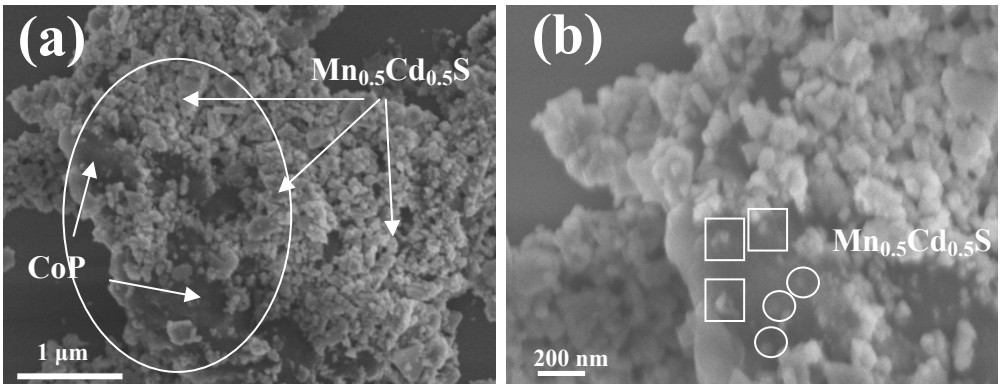

Figure S1. Low and high magnification of SEM images of MCSCP-4% sample

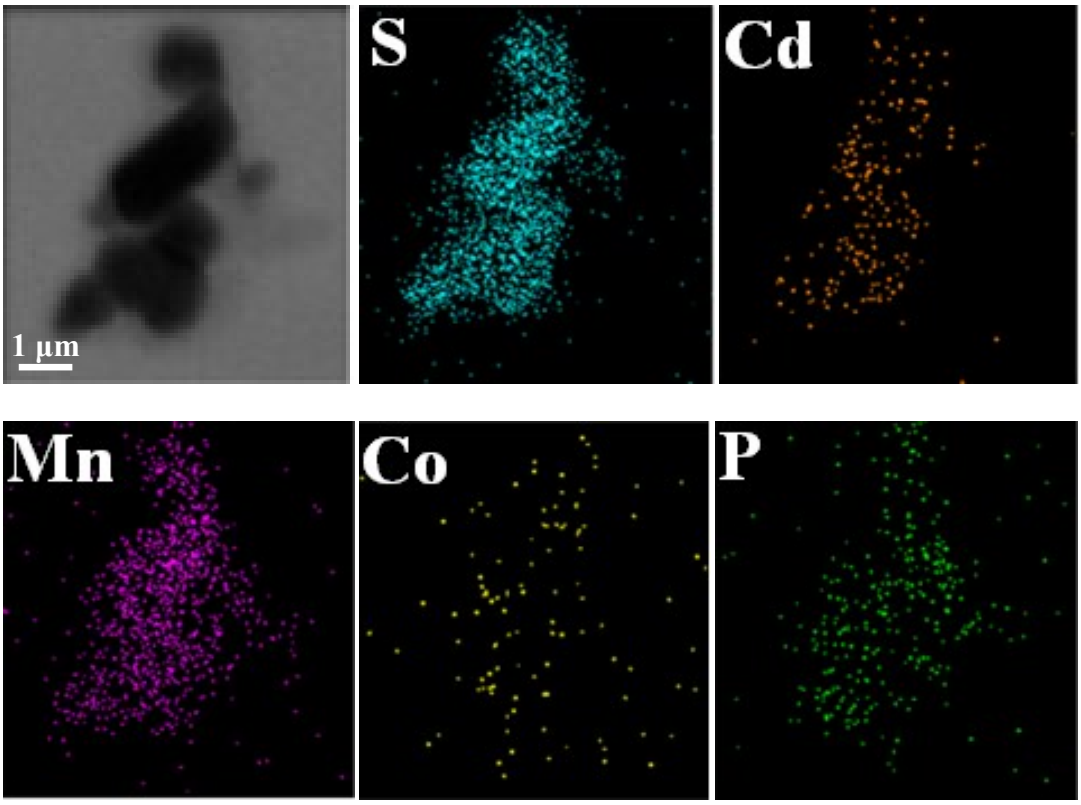

Figure S2. TEM image and EDX analysis of select area in MCSCP-4% sample

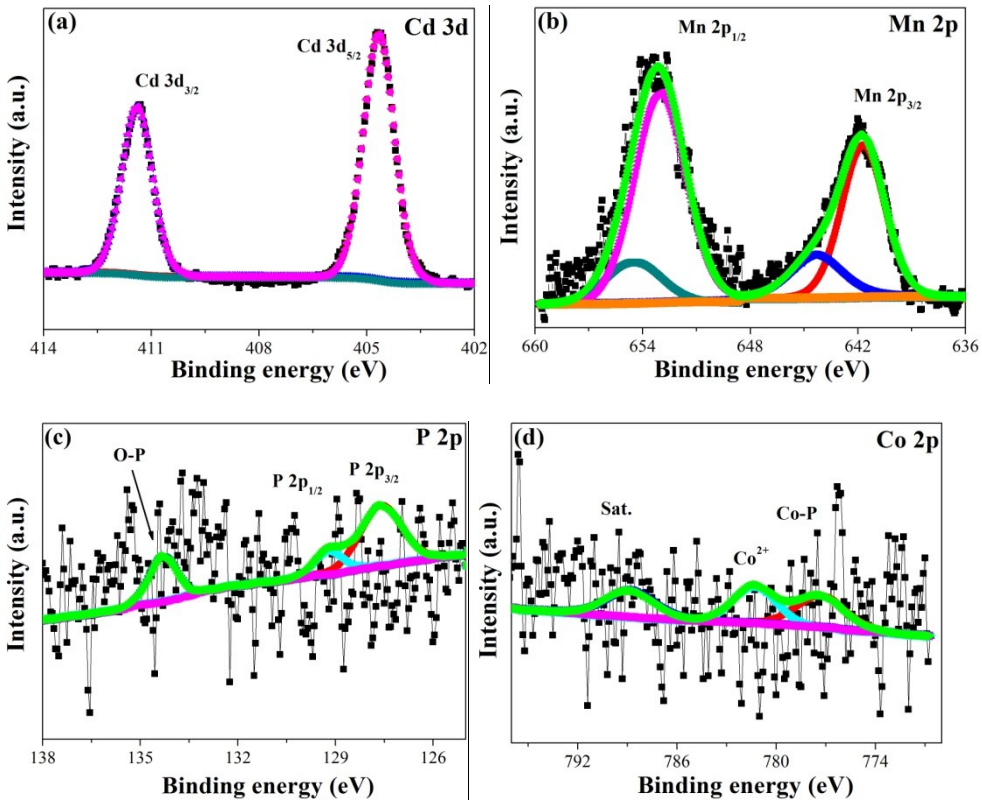

Figure S3. X-ray photoelectron spectra (XPS) of MCSCP-4% photocatalysts after reaction, high-resolution signals of Cd 3d(a); Mn 2p(b); P 2p(c); Co 2p(d)

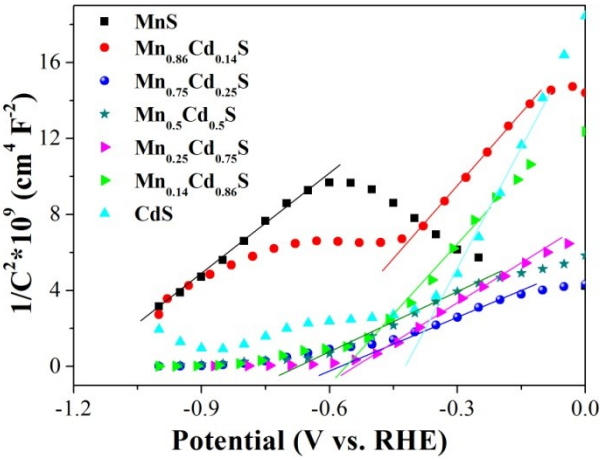

Figure S4. Mott-schottky characterization of CdS, MnS and a series of $Mn_xCd_{1-x}S$ photocatalysts.

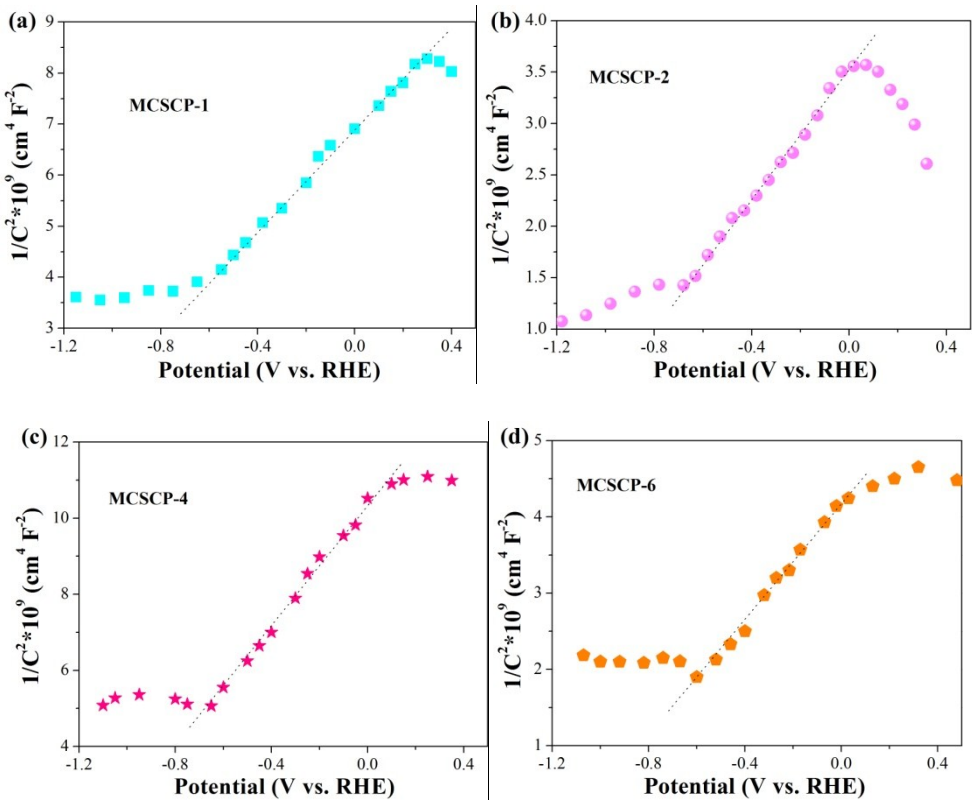

Figure S5. Mott-schottky characterization of $Mn_{0.5}Cd_{0.5}S$ with different CoP content modifying.

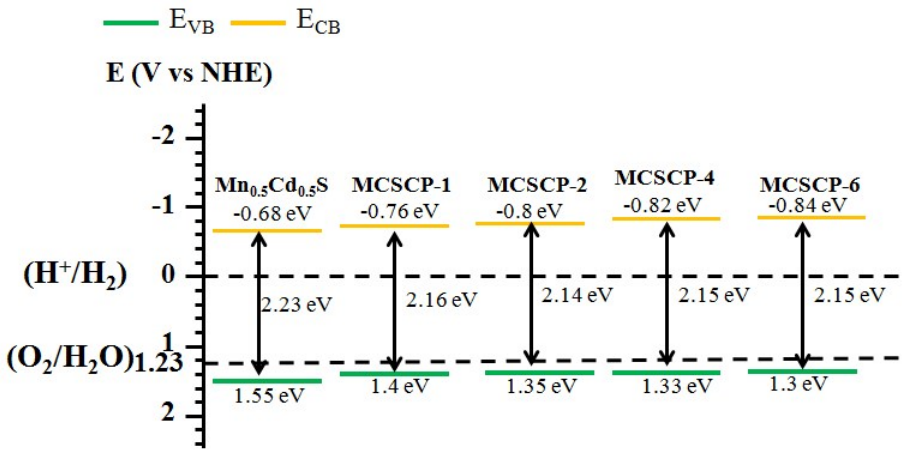

Figure S6. Energy band structure schematic of $Mn_{0.5}Cd_{0.5}S$ with different CoP content modifying.