Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

CdS/MnS p-n heterojunctions with directional carriers diffusion path for efficient photocatalytic H_2 production

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Characterization

The TD-3500 X-ray diffractometer operates at 40 kV and 30 mA using Cu Kα radiation is used to research the XRD patterns of the samples. FEI Apreo-S SEM system is employed to study the microstructure of samples. FEI Tecnai G2F20S-TWIN is employed to take transmission electron microscopy (TEM) images. Axis Ultra XPS instrument with an Mg Kα source is used to test the X-ray photoelectron spectroscopy (XPS). Varian Cary 5000 Scan UV−vis−NIR spectrometer is selected to test the UV-vis diffuse reflection. CHI 660E electrochemical workstation is selected to conduct the electrochemistry test in common three electrode system including the transient photocurrent response, electrochemical impedance spectroscopy (EIS), which uses Pt wire as reference electrode and Ag/AgCl electrode as counter electrode. Surface photovoltage (SPV) test is performed on a self-made device, including a lock-in amplifier and an optical chopper. Transient photovoltage (TPV) text is performed on a self-made device, including a oscilloscope (Tektronix MSO54) and a laser (Q-smart 450).

Research of photocatalytic hydrogen production activities

A Pyrex glass cell with upside window is employed to evaluation the photocatalytic H_2 production activity of the samples. The lighting area is 38 cm^2. A 300 W Xenon lamp with 420 bandpass filter is used as the light source. 0.05 g photocatalyst is suspended in 100 ml deionized water with 0.35 M Na_2S and 0.25 M Na_2SO_3 as sacrificial agent. The test interval period is 4 h. The H_2 production recycling test is similarly with the foregoing experimental process. The H_2-evolution quantumefficiency (AQE) is measured according to the equation:

$$\text{AQE}(100\%) = \frac{2 \times N(H_2) \times N_0}{IS\lambda/(hc)} \times 100\%$$

where $n(H_2)$ is the molar amount of unit time H_2 production, N_0 is Avogadro's constant (6.022×10^{23} mol^{-1}), I is the average irradiation intensity per unit area, S is the irradiation area, λ is the selected incident wavelength, h is Planck's constant (6.626×10^{-34} J s^{-1}), c is the speed of light (3.0×10^8 m s^{-1}).

Calculation details

The Perdew−Burke−Ernzerh of (PBE) exchange-correlation functional is selected within the generalized gradient approximation (GGA). A cutoff energy is 400 eV. The convergence tolerance is 1.0×10^{-5} eV/atom and 0.05 eV/ Å. The work function of CdS (001) and MnS (111) can be obtained by geometry optimization. The calculation models show in Figure S1. The work function (Φ) is defined as $\Phi = E_{vac} - E_f$, where the E_{vac} is vacuum energy and E_f is Fermi energy.

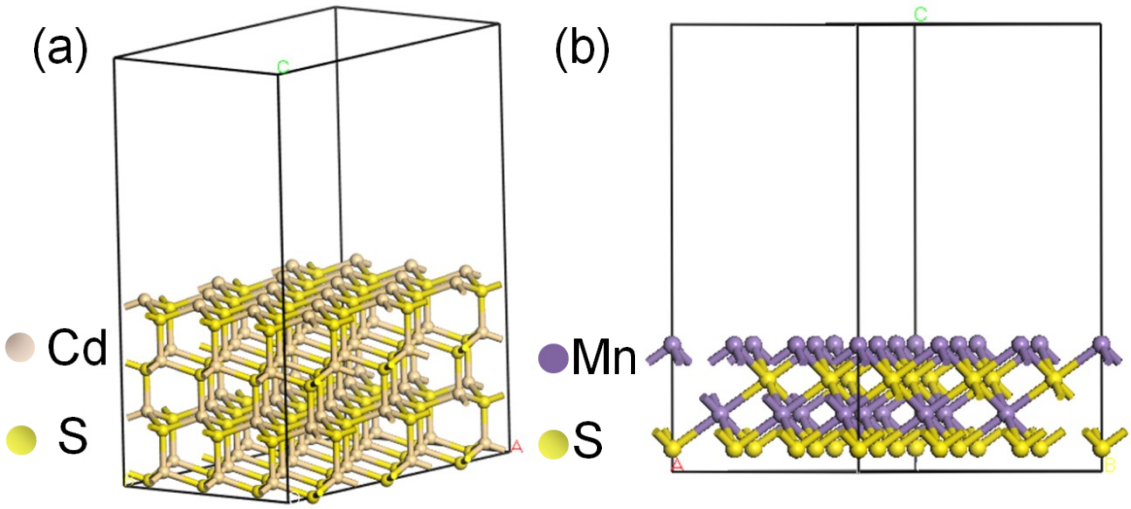

Figure S1 The calculation modes of (a) CdS(001) and (b) MnS (111) faces.

Table S1 The EDX elements content of samples

Samples	**Cd wt%**	**S wt%**	**Mn wt%**
CMS-5	66.67	23.86	6.62
CMS-10	43.62	28.38	28.00
CMS-15	25.89	26.85	47.26
CMS-20	13.68	29.38	59.94

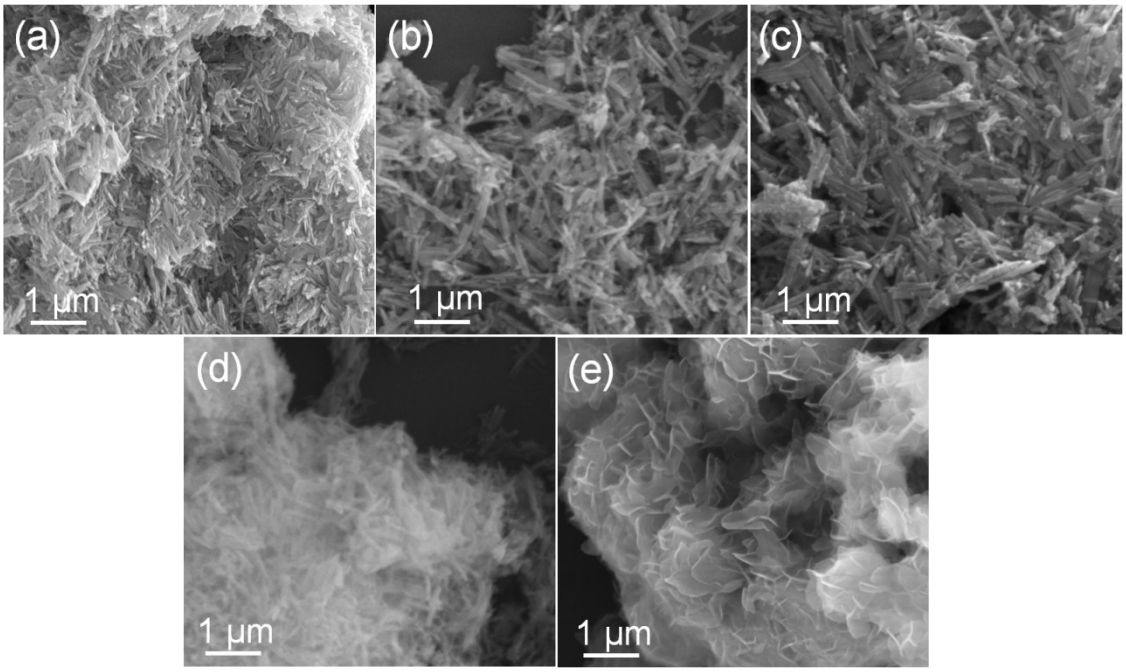

Figure S2 The SEM images of samples (a) CdS, (b) CMS-5, (c) CMS-10, (d) CMS-20, (e) MnS.

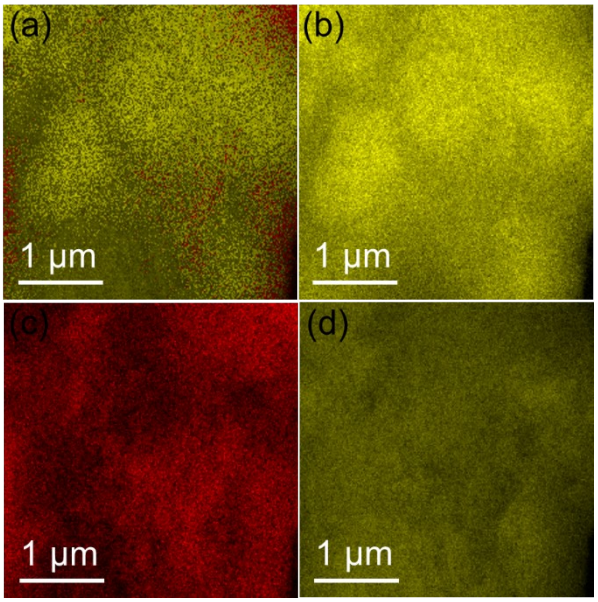

Figure S3 The EDX mapping of CMS-15. (a) Element distribution, (b) S , (c) Cd, (d) Mn.

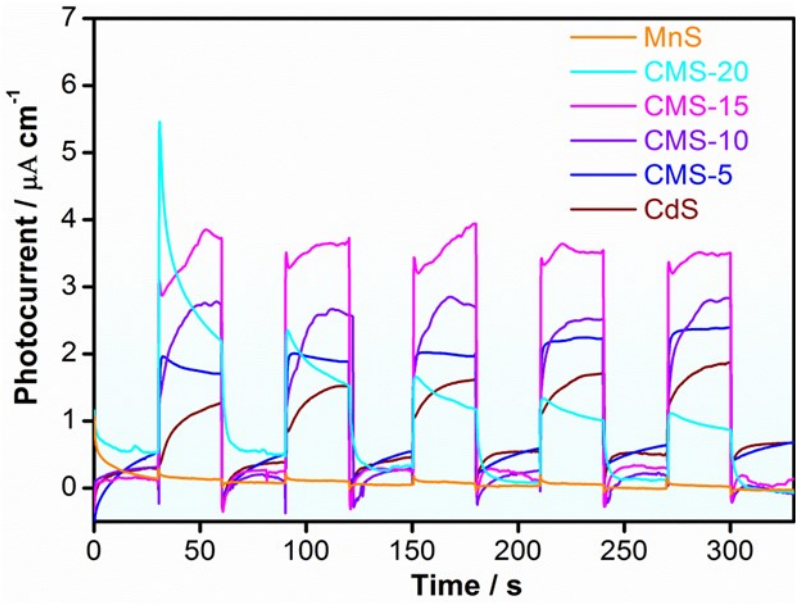

Figure S4 The transient photocurrent of samples.

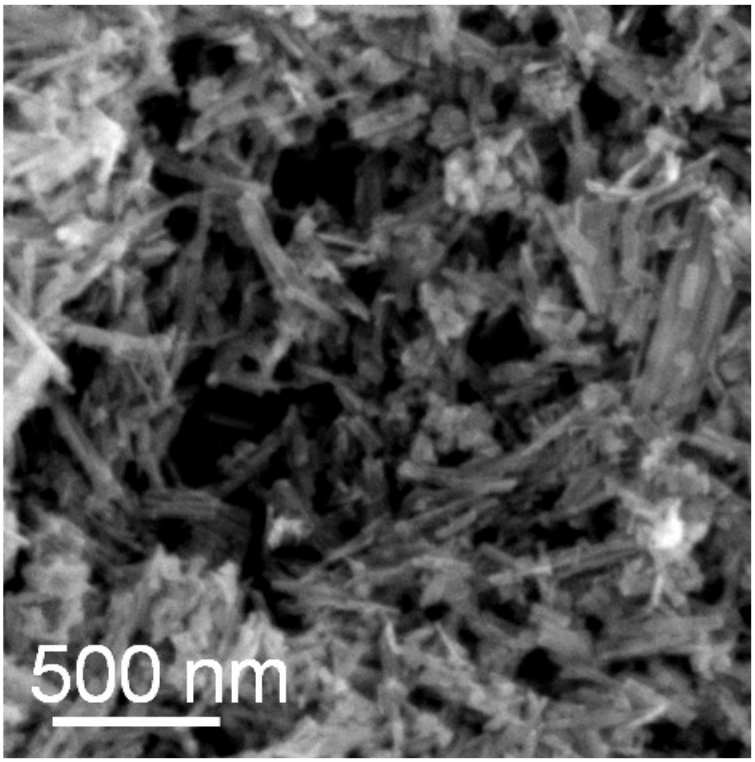

Figure S5 The SEM image of CMS-15.

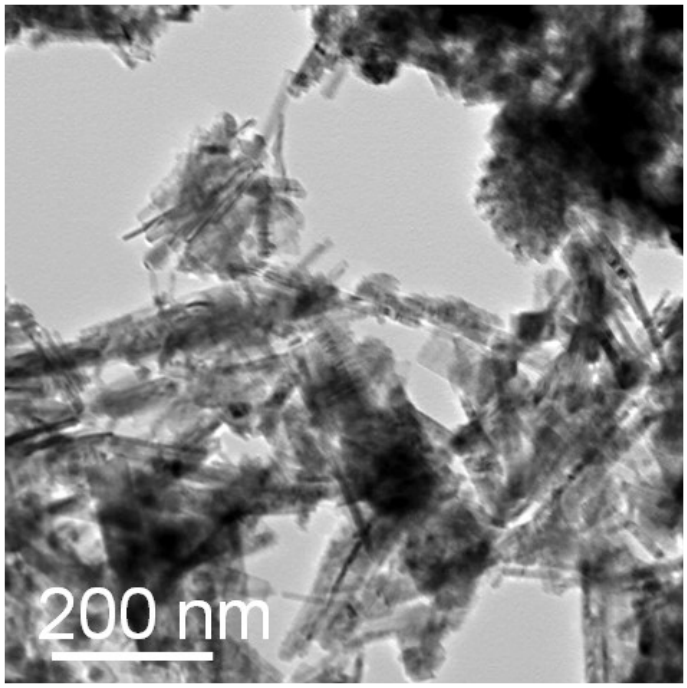

Figure S6 The TEM image of CMS-15 after 20 h recycling.

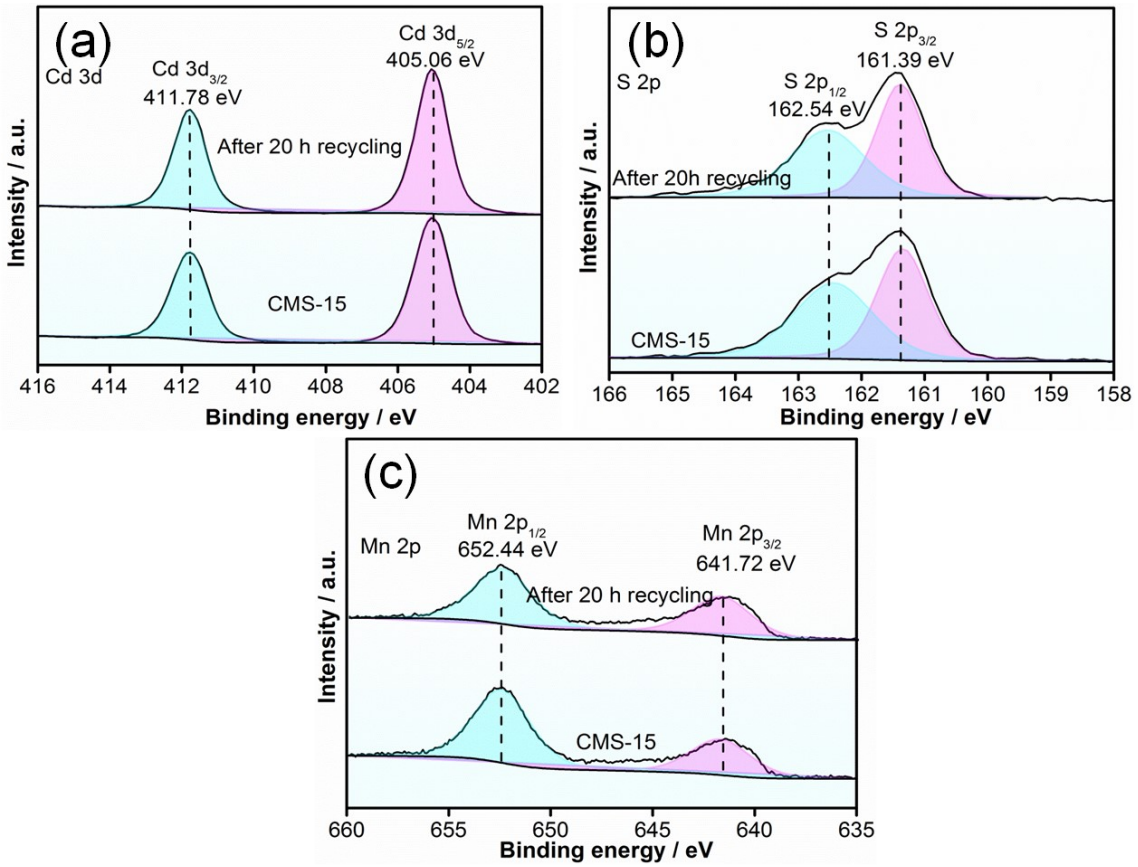

Figure S7 The high resolution XPS spectra of CMS-15 and after 20 h recycling. (a) Cd 3d, (b) S 2p, (c) Mn 2p.

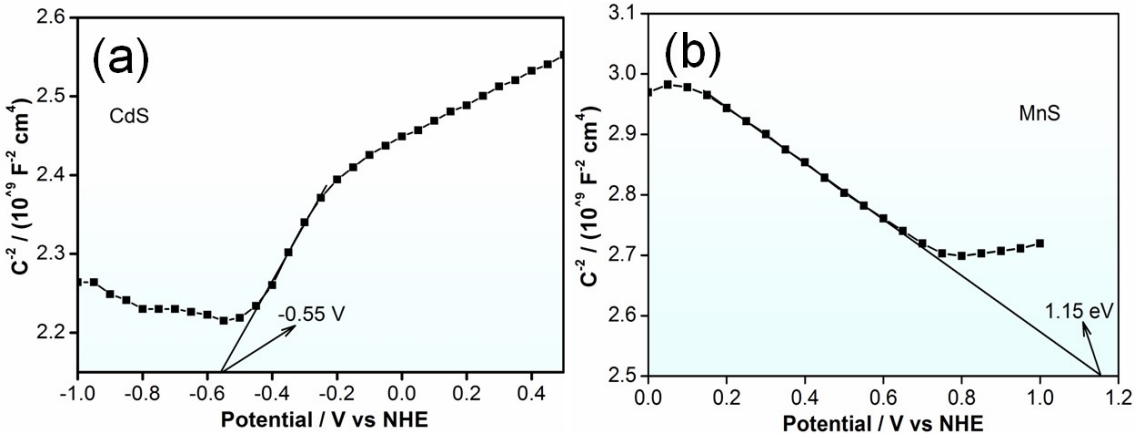

Figure S8 The Mott–Schottky plots of (a) CdS and (b) MnS.