

O-MoS₂/Mn_{0.5}Cd_{0.5}S composites with enhanced activity for visible-light-driven photocatalytic hydrogen evolution

Xuanxuan Yang, Yu Guo, Yongbing Lou*, Jinxi Chen*

School of Chemistry and Chemical Engineering, Jiangsu Engineering Laboratory of Smart Carbon-Rich Materials and Device, Southeast University, Nanjing 211189, PR China

**Corresponding author.*

**E-mail address: chenjinxi@seu.edu.cn (J. Chen); lou@seu.edu.cn (Y. Lou);*

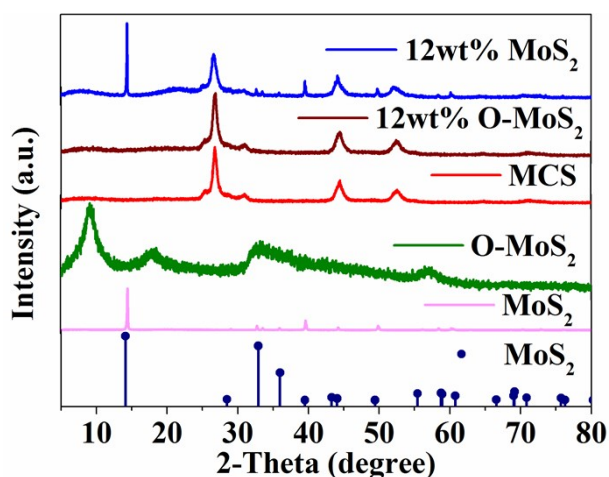


Fig. S1. XRD patterns of MoS₂, O-MoS₂ and their composites.

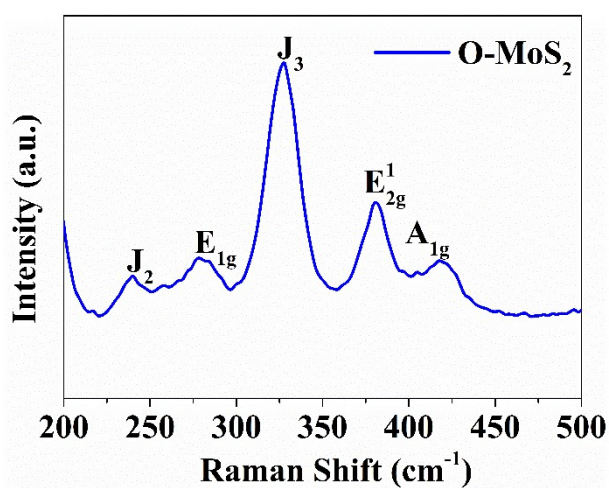


Fig. S2. Raman spectrum of O-MoS₂.

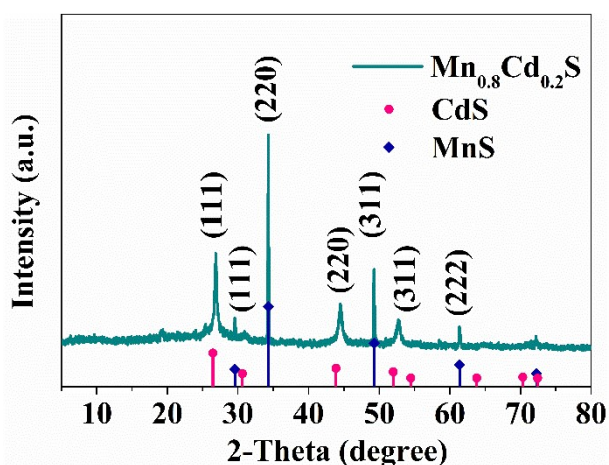


Fig. S3. XRD pattern of Mn_{0.8}Cd_{0.2}S nanoparticles.

To further elucidate the phase structure of Mn_{0.5}Cd_{0.5}S, Mn_{0.8}Cd_{0.2}S nanoparticles with a similar crystal phase are synthesized in the same condition (just increase the ratio

of Mn and Cd elements) and the crystallinity of them are investigated with XRD. As demonstrated, three sharp and noticeable diffraction peaks of all samples at 26.9° , 31.0° , 44.5° and 52.7° are assigned respectively to the (111), (200), (220) and (311) planes of cubic phase CdS (JCPDS No. 89-440), which is similar to that of $\text{Mn}_{0.5}\text{Cd}_{0.5}\text{S}$. Apart from that, the sample of $\text{Mn}_{0.8}\text{Cd}_{0.2}\text{S}$ displays four new features at about 29.6° , 34.3° , 49.3° and 61.3° (Fig.S3), which are separately matched with the (111), (220), (311) and (222) reflections of cubic α -MnS (JCPDS No. 89-4952). The result indicates that as-prepared $\text{Mn}_{0.5}\text{Cd}_{0.5}\text{S}$ solid solution is cubic phase.

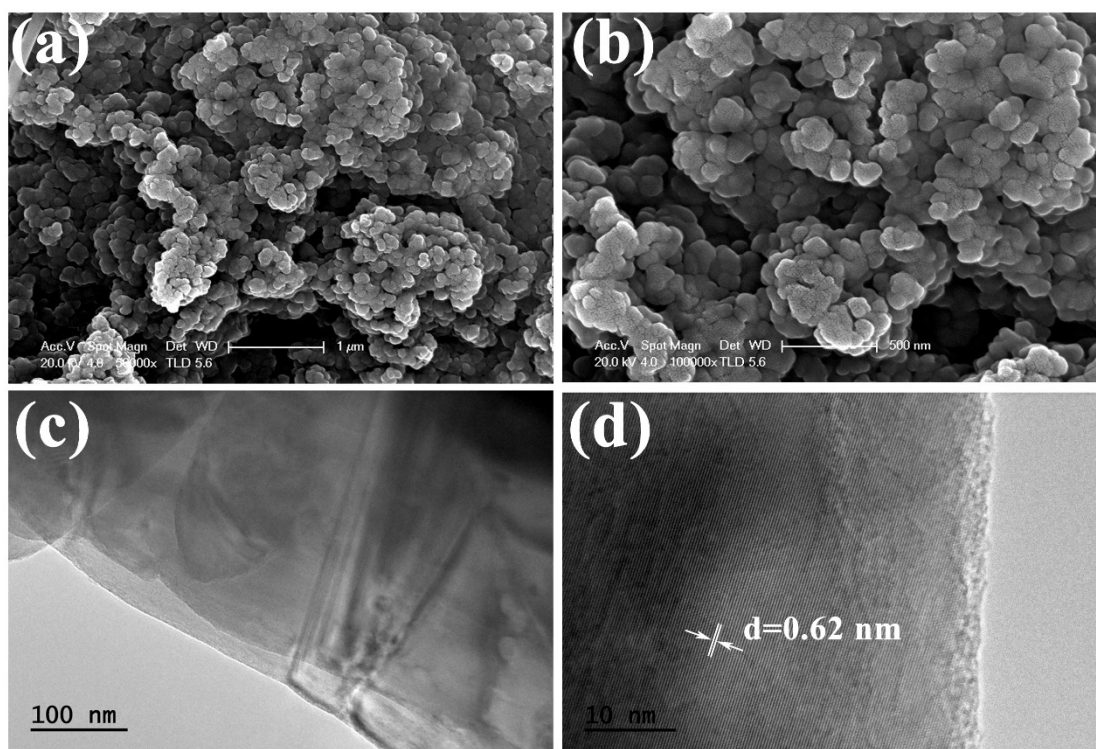


Fig. S4. SEM (a)(b) and TEM (c)(d) of MoS₂.

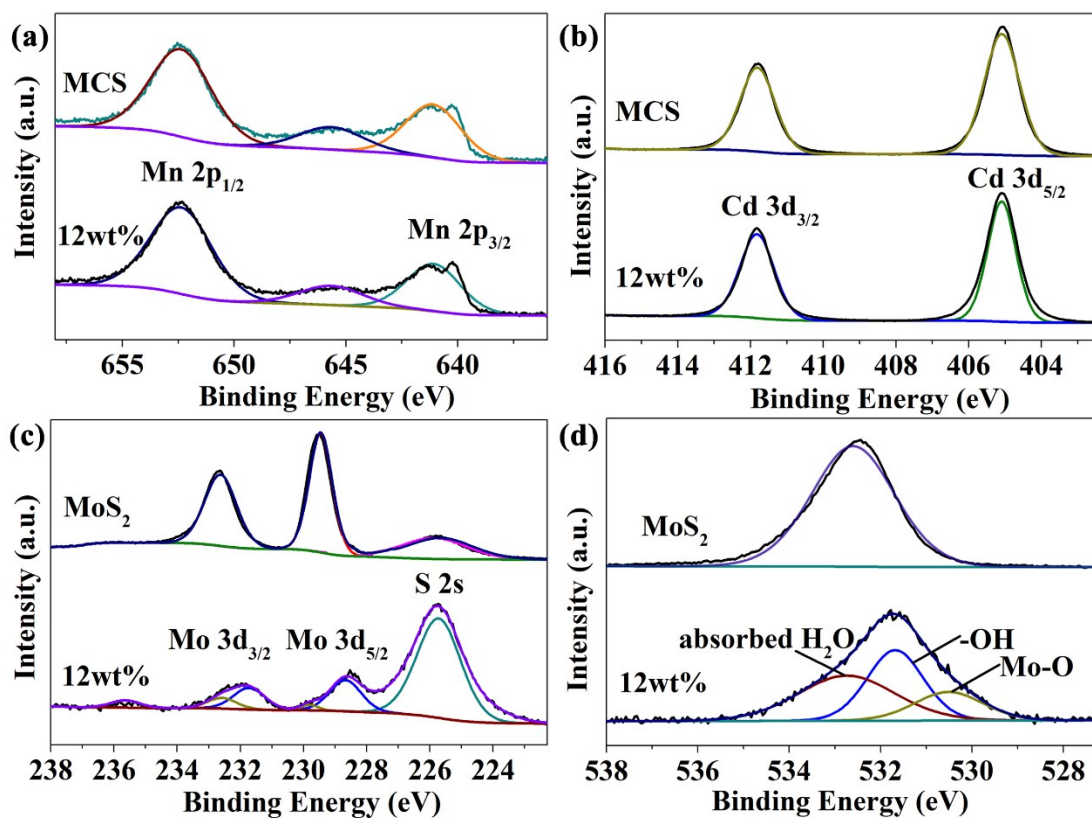


Fig. S5. XPS comparisons of Mn_{0.5}Cd_{0.5}S, MoS₂ and 12wt% O-MoS₂/Mn_{0.5}Cd_{0.5}S.

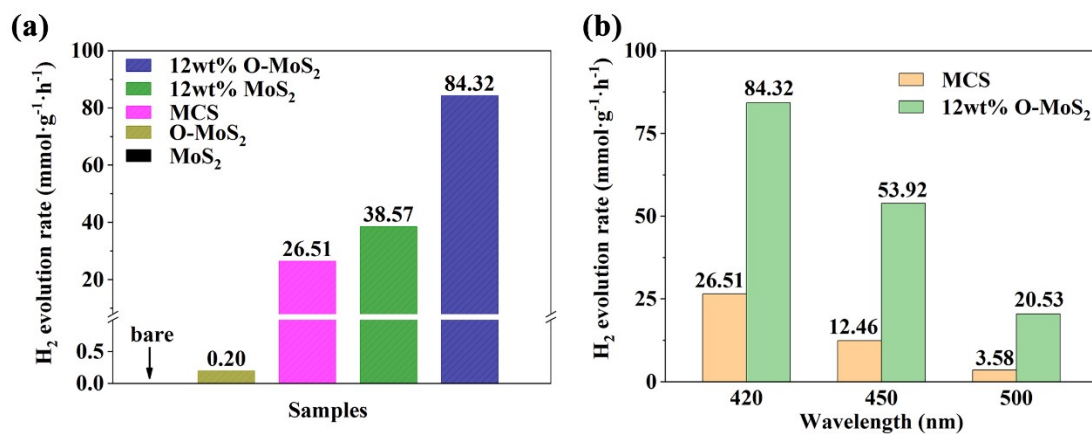


Fig. S6. Photocatalytic hydrogen evolution rates of composites (a) at 420 nm and (b) at different wavelengths.

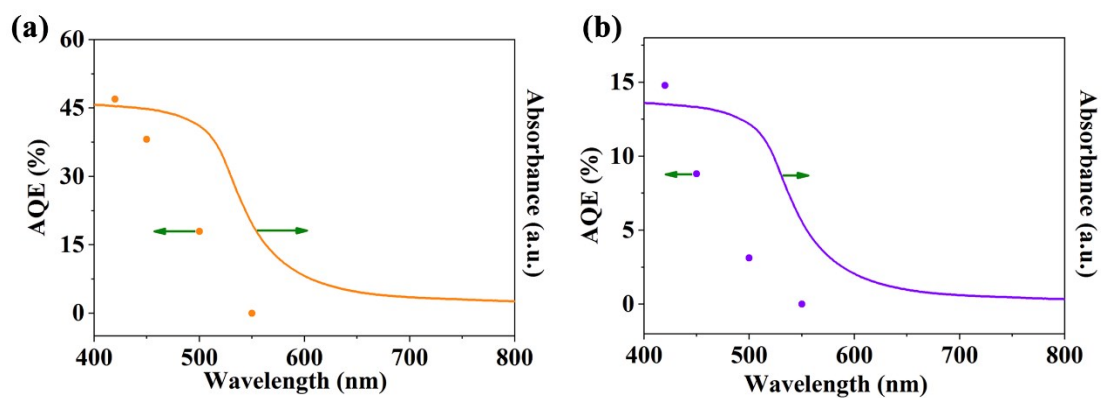


Fig. S7. The wavelength-dependent AQE of 12wt% O-MoS₂/Mn_{0.5}Cd_{0.5}S and pristine Mn_{0.5}Cd_{0.5}S for hydrogen evolution.

Table S1. The AQE values of Mn_{0.5}Cd_{0.5}S and 12wt% O-MoS₂/Mn_{0.5}Cd_{0.5}S at different wavelengths.

Sample	Wavelength (nm)	420	450	500	550
12wt%	Evolved H ₂ (mmol g ⁻¹ h ⁻¹)	84.32	53.92	20.53	0
	AQE (%)	46.92	38.14	17.94	0
Mn _{0.5} Cd _{0.5} S	Evolved H ₂ (mmol g ⁻¹ h ⁻¹)	26.51	12.46	3.58	0
	AQE (%)	14.79	8.81	3.13	0

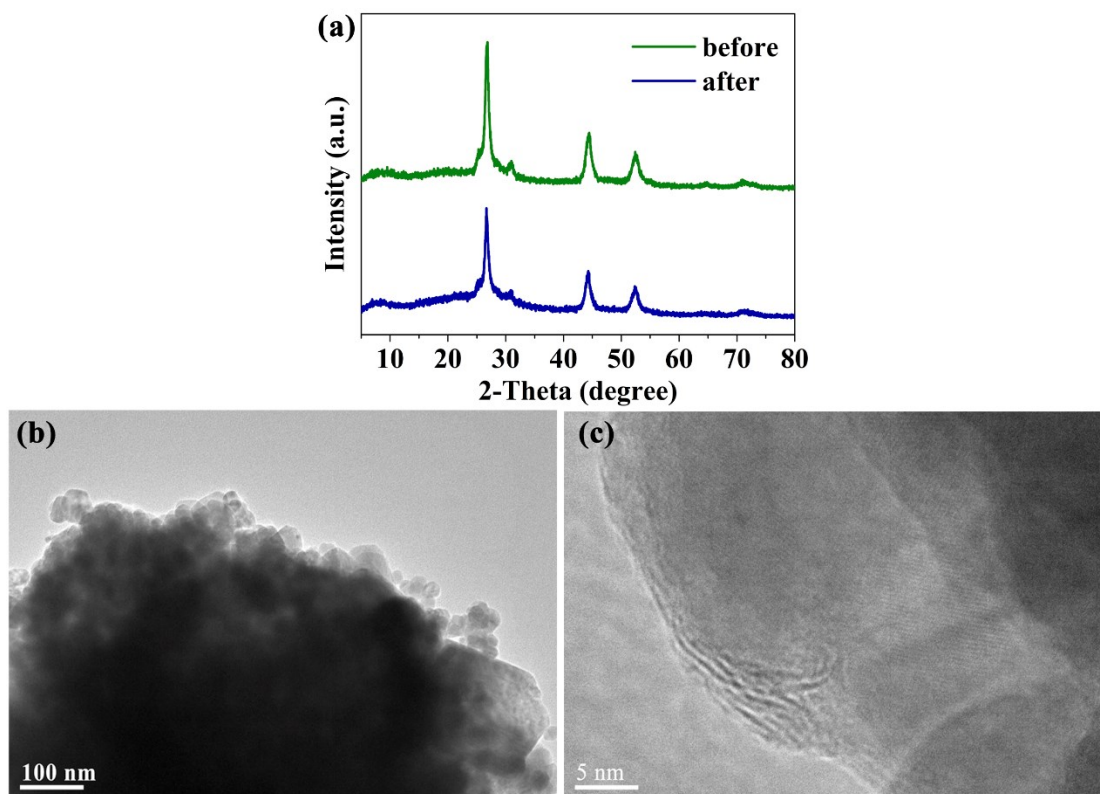


Fig. S8. (a) XRD patterns of 12wt% O-MoS₂/Mn_{0.5}Cd_{0.5}S after reaction for 16 h under visible light irradiation (b) TEM and (c) HRTEM image of 12wt% O-MoS₂/Mn_{0.5}Cd_{0.5}S after reaction for 16 h under visible light irradiation.

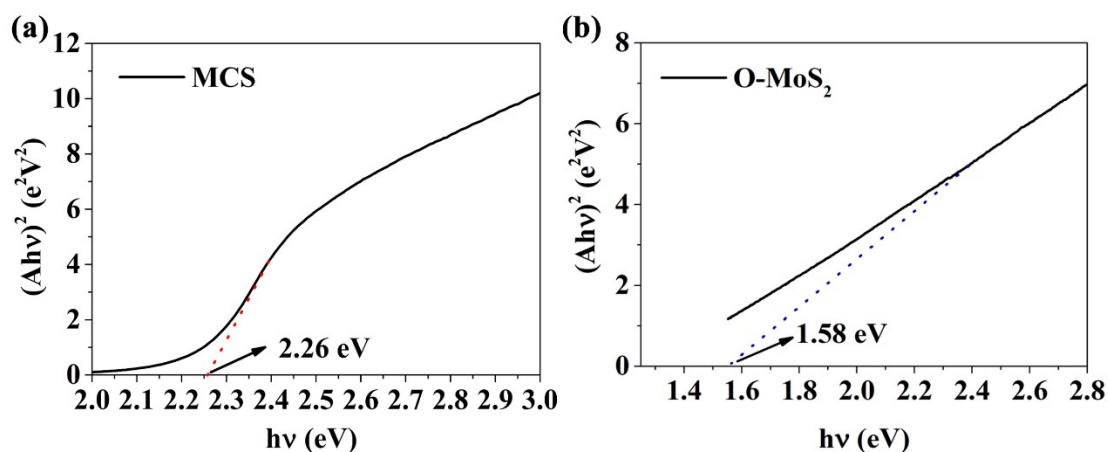


Fig. S9. (a) calculated bandgap of Mn_{0.5}Cd_{0.5}S and (b) O-MoS₂.

Table S2. The data obtained from of time-resolved PL decay spectra fitted curves of

Mn_{0.5}Cd_{0.5}S and 12wt% O-MoS₂/Mn_{0.5}Cd_{0.5}S.

Sample	T ₁ (ns)	T ₂ (ns)	T ₃ (ns)	A ₁ (%)	A ₂ (%)	A ₃ (%)	Avlifetime (ns)
Mn _{0.5} Cd _{0.5} S	0.93	3.48	17.59	29.16	53.11	17.73	5.24
12wt%	1.13	5.43	18.65	32.52	54.36	13.12	5.77

Table S3. Comparison on the hydrogen evolution rates of other Mn-Cd-S-based composites.

Photocatalyst	Sacrificial agents	Light source	Maximum rate (mmol g ⁻¹ h ⁻¹)	Reference
O-MoS ₂ /Mn _{0.5} Cd _{0.5} S	Na ₂ S/Na ₂ SO ₃	λ ≥ 420nm	84.32	This work
Mn _{0.8} Cd _{0.2} S	Na ₂ S/Na ₂ SO ₃	λ > 420nm	3.56	1
Mn _{0.5} Cd _{0.5} S	Na ₂ S/Na ₂ SO ₃	λ > 400nm	26.00	2
Pt/Mn _{0.6} Cd _{0.4} S	Lactic acid	λ > 420nm	2.25	3
MoS ₂ /Mn _{0.25} Cd _{0.75} S	Na ₂ S/Na ₂ SO ₃	λ > 400nm	12.47	4
MoS ₂ /Mn _{0.5} Cd _{0.5} S	Na ₂ S/Na ₂ SO ₃	λ ≥ 420nm	9.82	5
MoS ₂ /Mn _{0.8} Cd _{0.2} S/MnS	Na ₂ S/Na ₂ SO ₃	λ ≥ 420nm	19.90	6
MoS ₂ /Mn _{0.5} Cd _{0.5} S/Cu _{2-x} S	Na ₂ S/Na ₂ SO ₃	λ ≥ 420nm	13.75	7
MoS ₂ /Mn _{0.5} Cd _{0.5} S/RGO	Na ₂ S/Na ₂ SO ₃	Solar light	12.84	8
CuS/Mn _{0.5} Cd _{0.5} S	Na ₂ S/Na ₂ SO ₃	λ ≥ 420nm	106.84	9
CoS _x /Mn _{0.5} Cd _{0.5} S	Na ₂ S/Na ₂ SO ₃	λ > 420nm	8.60	10
CoP ₃ /Mn _{0.8} Cd _{0.2} S	Na ₂ S/Na ₂ SO ₃	λ ≥ 420nm	29.53	11
CoP/Mn _{0.5} Cd _{0.5} S	Na ₂ S/Na ₂ SO ₃	λ ≥ 420nm	65.32	12
NiS/Mn _{0.5} Cd _{0.5} S	Na ₂ S/Na ₂ SO ₃	λ ≥ 420nm	8.39	13
g-C ₃ N ₄ /Mn _{0.8} Cd _{0.2} S	Na ₂ S/Na ₂ SO ₃	λ > 420nm	4.00	14

References

- 1 H. Liu, J. Meng and J. Zhang, *Catal. Sci. Technol.*, 2017, **7**, 3802-3811.
- 2 L. Li, G. Liu, S. Qi, X. Liu, L. Gu, Y. Lou, J. Chen and Y. Zhao, *J. Mater. Chem. A*, 2018, **6**, 23683-23689.
- 3 H. Li, Z. Wang, Y. He, S. Meng, Y. Xu, S. Chen and X. Fu, *J. Colloid Interface Sci.*, 2019, **535**, 469-480.
- 4 Q. Huang, Y. Xiong, Q. Zhang, H. Yao and Z. Li, *Appl. Catal., B*, 2017, **209**, 514-522.
- 5 P. Zeng, J. Luo, J. Wang and T. Peng, *Catal. Sci. Technol.*, 2019, **9**, 762-771.

- 6 J. Wang, J. Luo, D. Liu, S. Chen and T. Peng, *Appl. Catal., B*, 2019, **241**, 130-140.
- 7 X. Liu, Q. Liu, P. Wang, Y. Liu, B. Huang, E. A. Rozhkova, Q. Zhang, Z. Wang, Y. Dai and J. Lu, *Chem. Eng. J.*, 2018, **337**, 480-487.
- 8 Y. Liu, Z. Gong, Y. Xie, H. Lv and B. Zhang, *Appl. Surf. Sci.*, 2020, **505**, 144637.
- 9 Y. Han, X. Dong and Z. Liang, *Catal. Sci. Technol.*, 2019, **9**, 1427-1436.
- 10 M. Wang, Q. Liu, N. Xu, N. Su, X. Wang and W. Su, *Catal. Sci. Technol.*, 2018, **8**, 4122-4128.
- 11 Q. Huang, Z. Tao, L. Ye, H. Yao and Z. Li, *Appl. Catal., B*, 2018, **237**, 689-698.
- 12 R. Chen, Y. Ao, C. Wang and P. Wang, *Dalton Trans.*, 2019, **48**, 14783-14791.
- 13 X. Liu, X. Liang, P. Wang, B. Huang, X. Qin, X. Zhang and Y. Dai, *Appl. Catal., B*, 2017, **203**, 282-288.
- 14 H. Liu, Z. Xu, Z. Zhang and D. Ao, *Appl. Catal. A: Gen.*, 2016, **518**, 150-157.