

Supplementary Data

A novel p–n $\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}/\text{NiWO}_4$ heterojunction for highly efficient photocatalytic H_2 production

Table S1. The added amount of samples and reagents

Sample	$\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}$ (mg)	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (mg)	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (mg)
$\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}/\text{NiWO}_4$ -10 wt%	200	15	21
$\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}/\text{NiWO}_4$ -30 wt%	200	47	65
$\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}/\text{NiWO}_4$ -50 wt%	200	77	107
$\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}/\text{NiWO}_4$ -70 wt%	200	109	151
$\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}/\text{NiWO}_4$ -90 wt%	200	140	194
$\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}$	200	0	0
NiWO_4	0	140	194

Table S2. S_{BET} , pore volume and pore diameter of $\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}$, NiWO_4 and $\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}/\text{NiWO}_4$ -30 wt% composite

Sample	$S_{\text{BET}}^{\text{a}}$ ($\text{m}^2 \text{g}^{-1}$)	Pore Volume ^b ($\text{cm}^3 \text{g}^{-1}$)	Pore Diameter ^b (nm)
$\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}$	29.63	0.054	1.18
NiWO_4	172.16	0.112	1.50
$\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}/\text{NiWO}_4$ -30 wt%	40.48	0.074	2.52

^aGained by BET test.

^b Relative pressure (P/P_0) of 0.99.

Table S3. H₂ production activities of some related metal tungstates-based heterojunction

Photocatalyst	Light source	Sacrificial reagent	H ₂ production rate (mmol h ⁻¹ g ⁻¹)	Ref.
Mn _{0.2} Cd _{0.8} S/NiWO ₄	300 W Xe lamp (λ ≥ 420 nm)	Na ₂ S/Na ₂ SO ₃	17.76	This work

Zn _{0.7} Cd _{0.3} S/NiWO ₄	5W LED (λ ≥ 420 nm)	Na ₂ S/Na ₂ SO ₃	15.95	[S1]
CdS/NiWO ₄	300 W Xe lamp (λ ≥ 420 nm)	lactic acid	5.07	[S2]
NiWO ₄ /CdS/Pt	550W Xe lamp (λ ≥ 420 nm)	lactic acid	0.88	[S3]
CdS/NiWO ₄ /CoP	5 W LED (λ ≥ 420nm)	lactic acid	47.7	[S4]
CdS/InWO ₄	5W LED (λ ≥ 420 nm)	lactic acid	6.15	[S5]
CdS/CdWO ₄	500W Xe lamp	Na ₂ S/Na ₂ SO ₃	1.805	[S6]
CdS/CdWO ₄	300 W Xe lamp (λ ≥ 420 nm)	lactic acid	9.17	[S7]
CdS/CoWO ₄	300 W Xe lamp (λ ≥ 420 nm)	Na ₂ S/Na ₂ SO ₃	15.91	[S8]

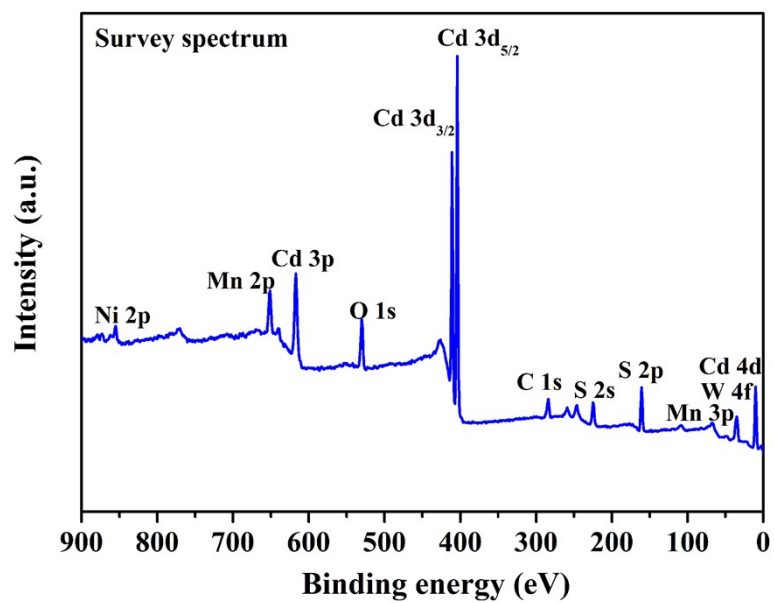


Fig. S1. XPS survey spectrum of $\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}/\text{NiWO}_4$ -30 wt% composite

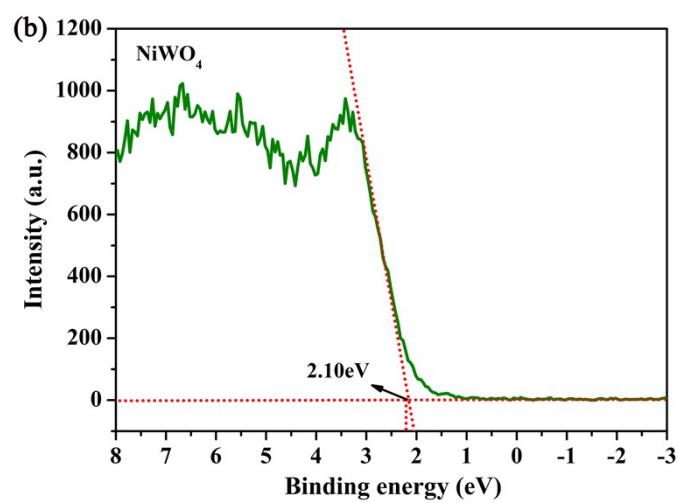
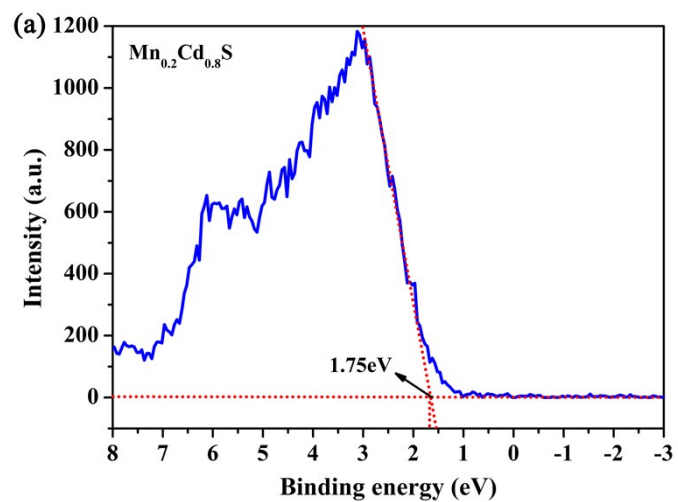


Fig. S2. XPS-VB of (a) $\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}$ and (b) NiWO_4

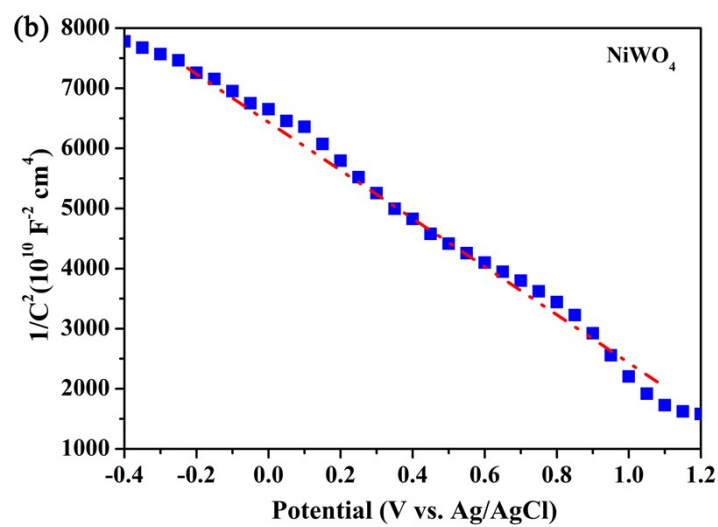
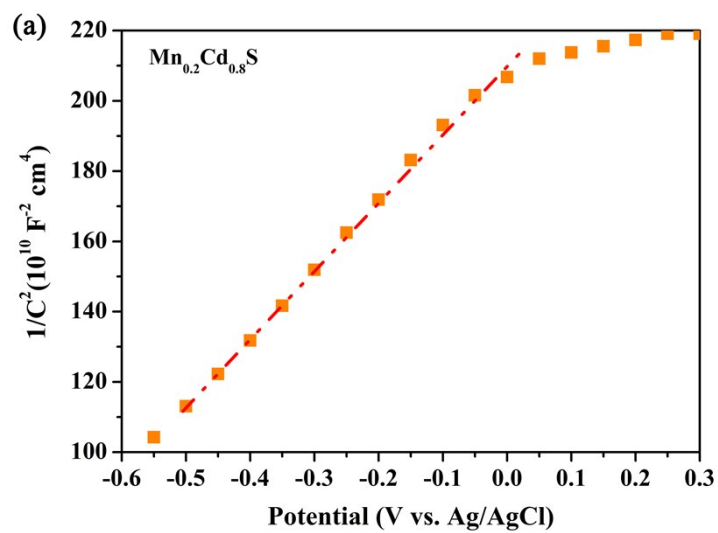


Fig. S3. Mott-Schottky polts of (a) $\text{Mn}_{0.2}\text{Cd}_{0.8}\text{S}$ and (b) NiWO_4 .

REFERENCES

- S1 Y. Liu, G. N. Wang, Y. B. Li and Z. L. Jin, *J. Colloid Interf. Sci.*, 2019, **554**, 113–124.
- S2 Y. K. Zhang and Z. L. Jin, *Catal. Sci. Technol.*, 2019, **9**, 1944–1960.
- S3 M. J. Li, S. Yokoyama, H. Takahashi and K. Tohji, *Appl. Catal. B*, 2019, **241**, 284–291.
- S4 H. Liu, T. Yan, Z.L. Jin and Q.X. Ma, *New J. Chem.*, 2020, **44**, 1426–1438.
- S5 Q. Jian, X.Q. Hao and Z. L. Jin, *New J. Chem.*, 2019, **43**, 12668–12677.
- S6 L. Wang and W. Z. Wang, *CrystEngComm.*, 2012, **14**, 3315–3320.
- S7 X. Jia, M. Tahir, L. Pan, Z.F. Huang, X. W. Zhang and L. Wang, *Appl. Catal. B*, 2016, **198**, 154–161.
- S8 H. J. Cui, B. B. Li, Y. Z. Zhang, X. D. Zheng, X. H. Li and Z. Y. Li, *Int. J. Hydrogen Energy*, 2018, **43**, 18242–18252.