Electronic supplementary information (ESI)

Efficient spatial charge separation in unique 2D tandem heterojunction $Cd_xZn_{1-x}In_2S_4$-CdS-MoS_2 rendering highly-promoted visible-light-induced H_2 generation

Jiakun Wu,†[a] Bowen Sun,†[a] Hui Wang,[c] Yanyan Li,[a] Ying Zuo,[d] Wenjing Wang,[a] Haifeng Lin,*[a] Shaoxiang Li[b] and Lei Wang*[ab]

[a] Key Laboratory of Eco-chemical Engineering, Key Laboratory of Optic-electric Sensing and Analytical Chemistry of Life Science, Taishan Scholar Advantage and Characteristic Discipline Team of Eco-Chemical Process and Technology, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China. E-mail: hflin20088@126.com

[b] Shandong Engineering Research Center for Marine Environment Corrosion and Safety Protection, College of Environment and Safety Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China. E-mail: inorchemwl@126.com

[c] Key Laboratory of Rubber-Plastics of Ministry of Education, School of Polymer Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China.

[d] Scientific Instrument Center, Shanxi University, Taiyuan 030006, P. R. China.

† Equal contribution to this work.

Characterization Results

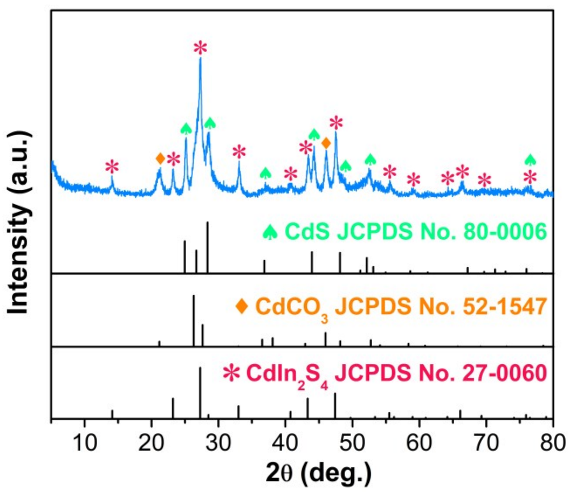

Fig. S1 XRD pattern of $CdIn_2S_4$ nanosheets.

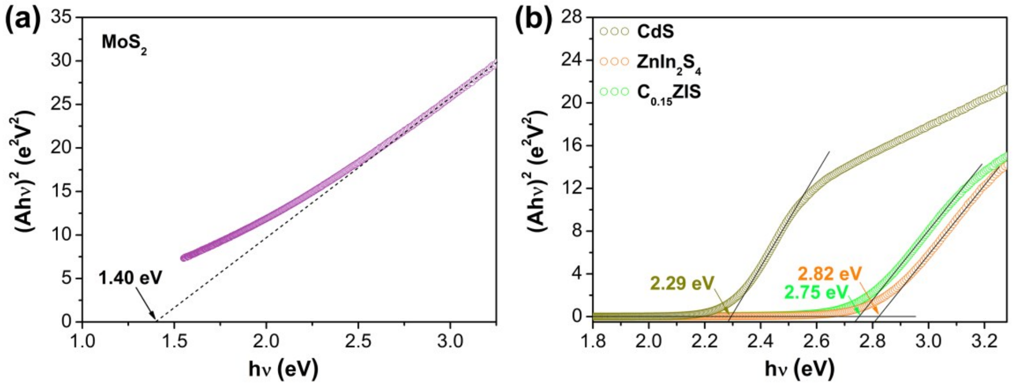

Fig. S2 Determined bandgaps of (a) MoS_2 and (b) CdS, $ZnIn_2S_4$, and $C_{0.15}$ZIS.

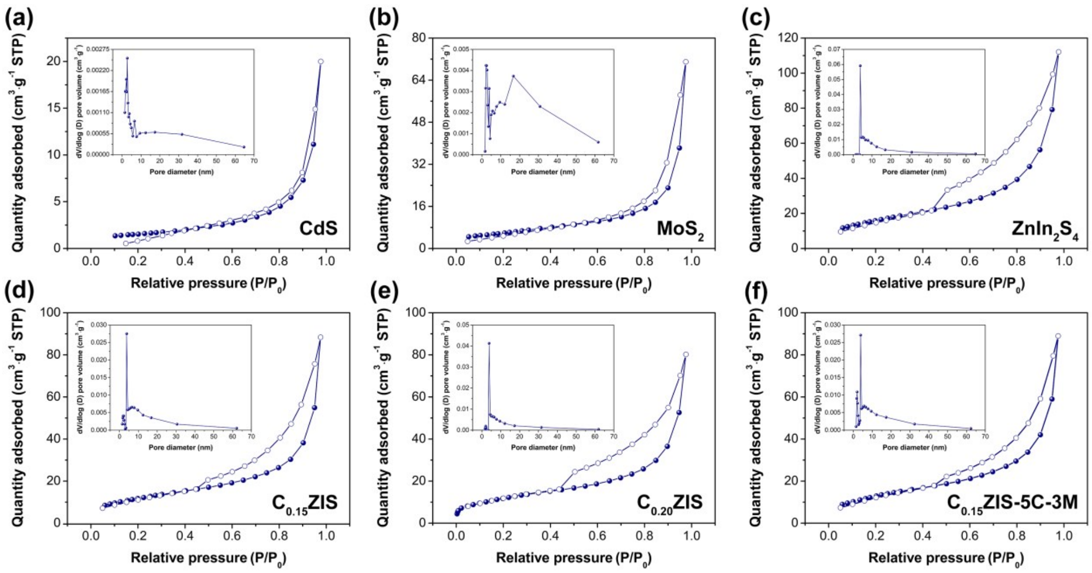

Fig. S3 N_2 adsorption-desorption isotherms and corresponding pore-size distributions of (a) CdS, (b) MoS_2, (c) $ZnIn_2S_4$, (d) $C_{0.15}$ZIS, (e) $C_{0.20}$ZIS, and (f) $C_{0.15}$ZIS-5C-3M.

Table S1. BET surface areas of different samples.

Photocatalyst	CdS	MoS_2	$ZnIn_2S_4$	$C_{0.15}$ZIS	$C_{0.20}$ZIS	$C_{0.15}$ZIS-5C-3M
S_{BET} ($m^2 \cdot g^{-1}$)	5.39	23.78	60.94	46.85	42.32	54.64

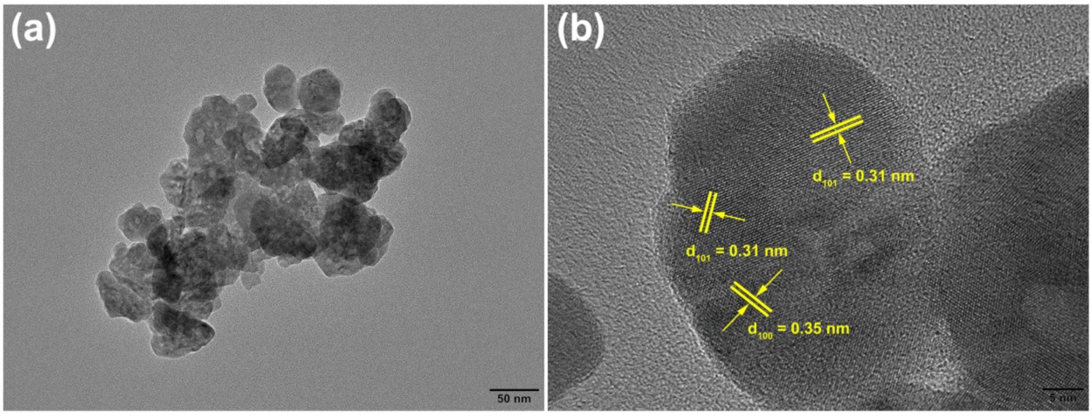

Fig. S4 (a) TEM and (b) HRTEM images of the CdS nanocrystals prepared without the presence of $C_{0.15}ZIS$ substrate.

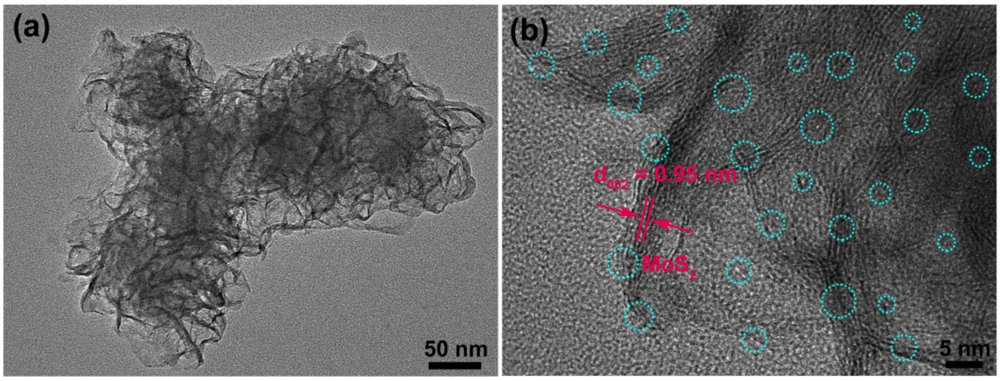

Fig. S5 (a) TEM and (b) HRTEM images of MoS_2 nanosheets.

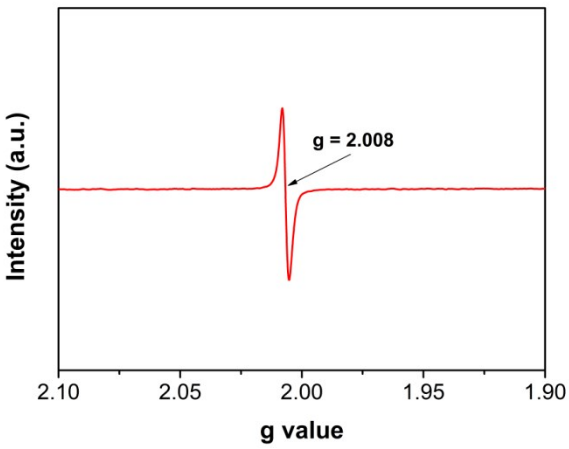

Fig. S6 EPR spectrum of MoS_2 nanosheets.

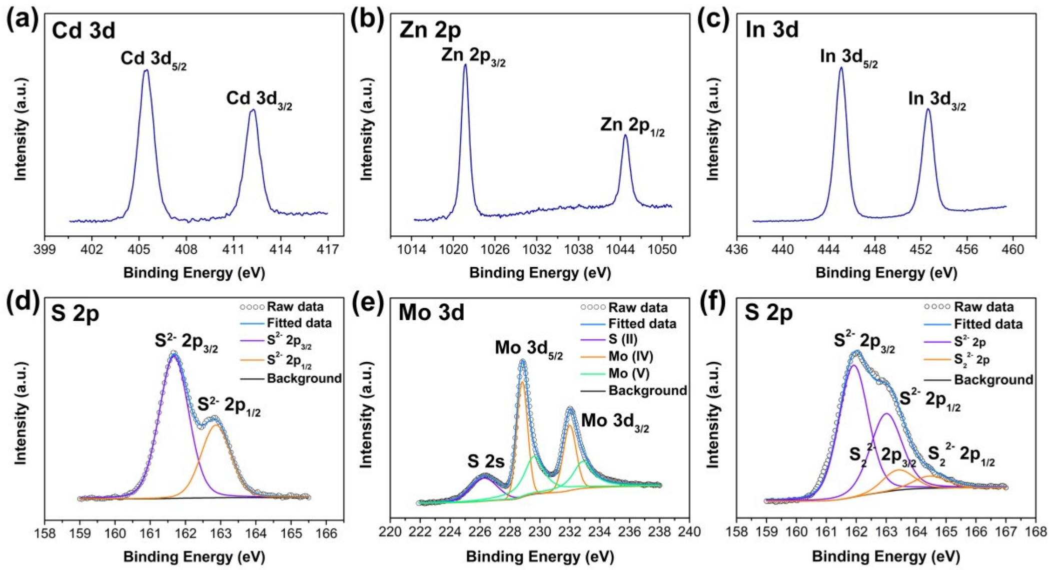

Fig. S7 (a) Cd 3d, (b) Zn 2p, (c) In 3d, and (d) S 2p XPS spectra of $C_{0.15}$ZIS nanosheets. (e) Mo 3d and (f) S 2p XPS spectra of MoS_2 nanosheets.

For $C_{0.15}$ZIS nanosheets, the doublet signals of Cd 3d, Zn 2p, and In 3d spectra locating at 405.5-412.2 eV (Fig. S7a), 1021.7-1044.7 eV (Fig. S7b), and 445.1-452.6 eV (Fig. S7c) are associated with the Cd^{2+},[1] Zn^{2+},[2] In^{3+}[3] valence states, respectively. In the S 2p spectrum (Fig. S7d), the peaks at 161.7 and 162.9 eV could be assigned to the S^{2-} ions.[4] Regarding to MoS_2 nanosheets, the Mo 3d spectrum consists of two sets of doublet peaks at 228.8-232.0 eV and 229.6-232.9 eV (Fig. S7e), which match well with that of Mo^{4+} and Mo^{5+} species,[5,6] respectively. Moreover, the S 2p spectrum exhibits two sets of doublet signals at 161.9-163.0 eV and 163.4-164.5 eV (Fig. S7f), corresponding to the S^{2-} and S_2^{2-} ions,[7,8] respectively.

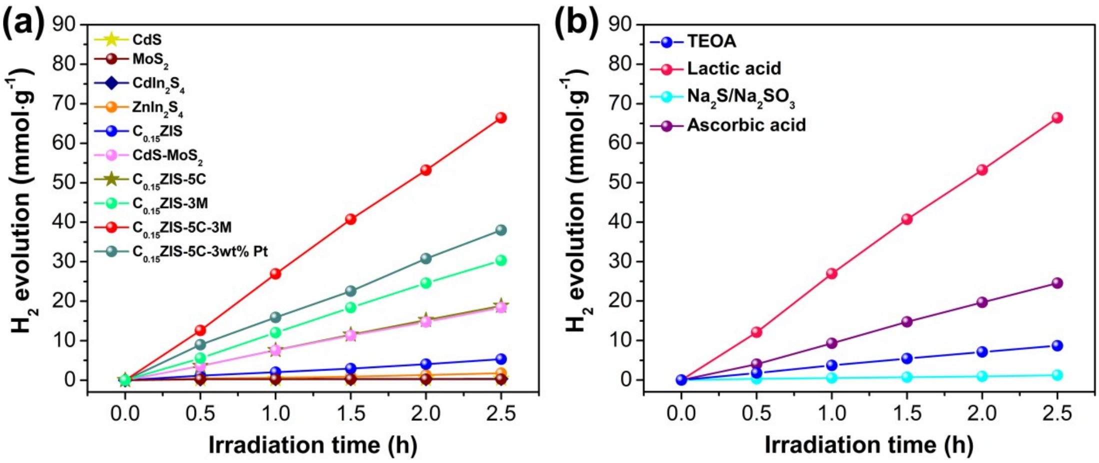

Fig. S8 (a) Visible-light-induced H_2 formation activities of different samples. (b) The influence of sacrificial agent on the HER activity of $C_{0.15}$ZIS-5C-3M.

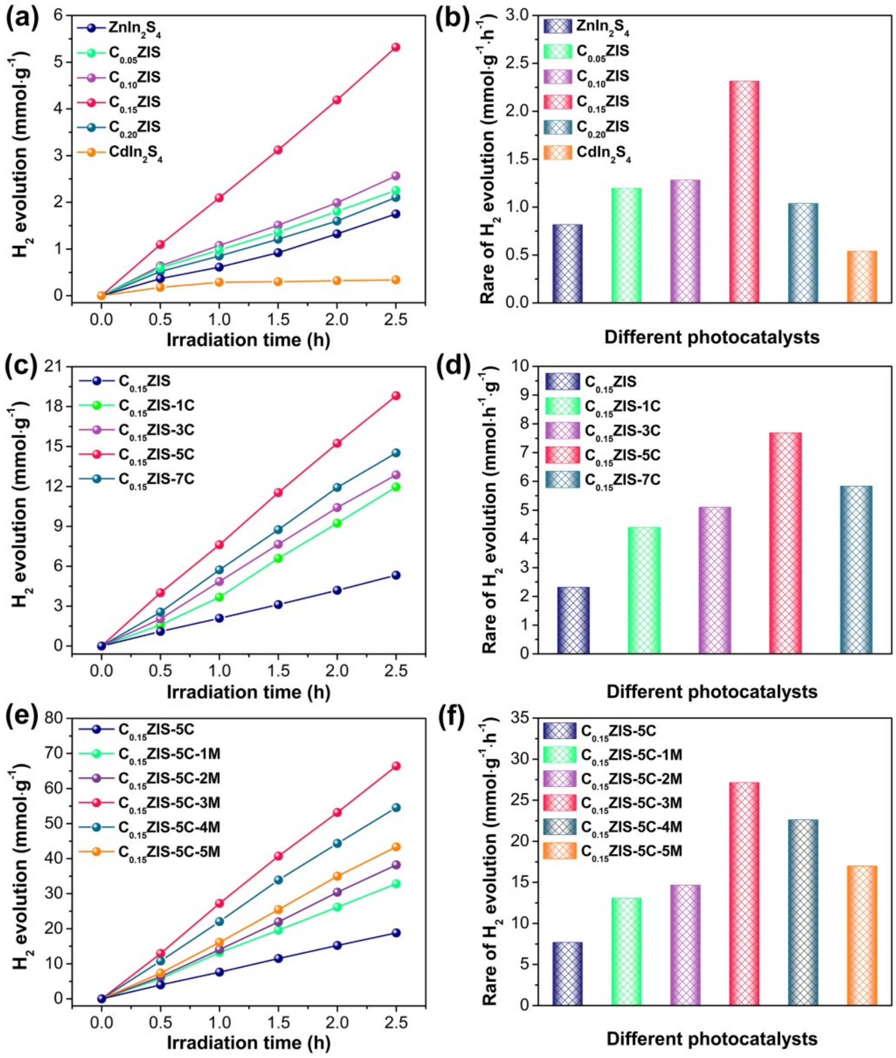

Fig. S9 Photocatalytic HER activities and corresponding rates different photocatalysts. (a, b) C_xZIS (x = 0.05, 0.10, 0.15, and 0.20), x equals to 0 and 1 for $ZnIn_2S_4$ and $CdIn_2S_4$, respectively. (c, d) $C_{0.15}ZIS$-yC (y = 0, 1, 3, 5, and 7). (e, f) $C_{0.15}ZIS$-5C-zM (z = 0, 1, 2, 3, 4, and 5).

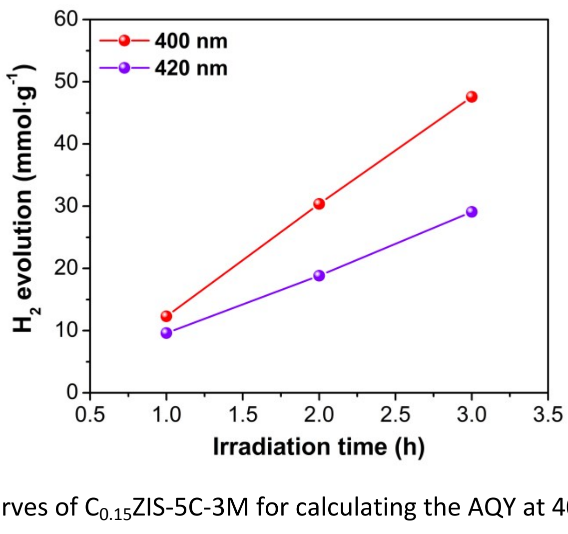

Fig. S10 H_2 evolution curves of $C_{0.15}ZIS$-5C-3M for calculating the AQY at 400 and 420 nm.

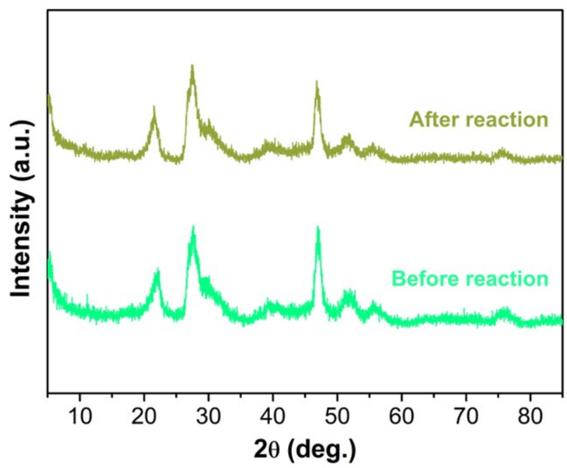

Fig. S11 XRD patterns of the $C_{0.15}$ZIS-5C-3M hybrid before and after HER test.

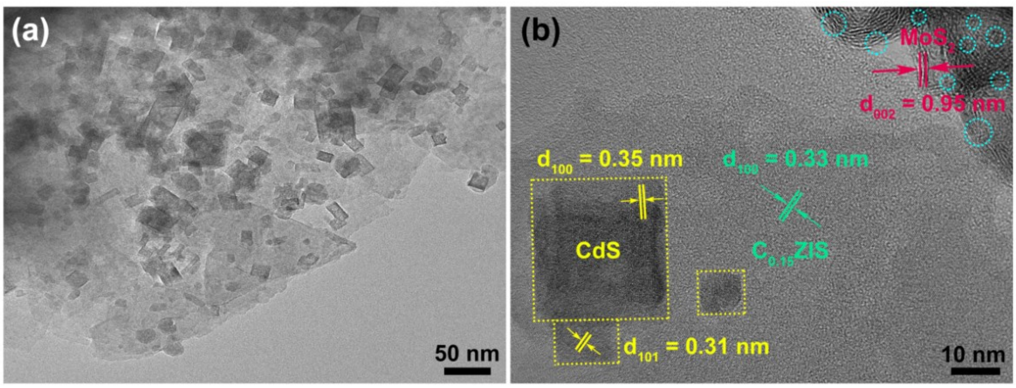

Fig. S12 (a) TEM and (b) HRTEM graphs of the $C_{0.15}$ZIS-5C-3M after HER measurement.

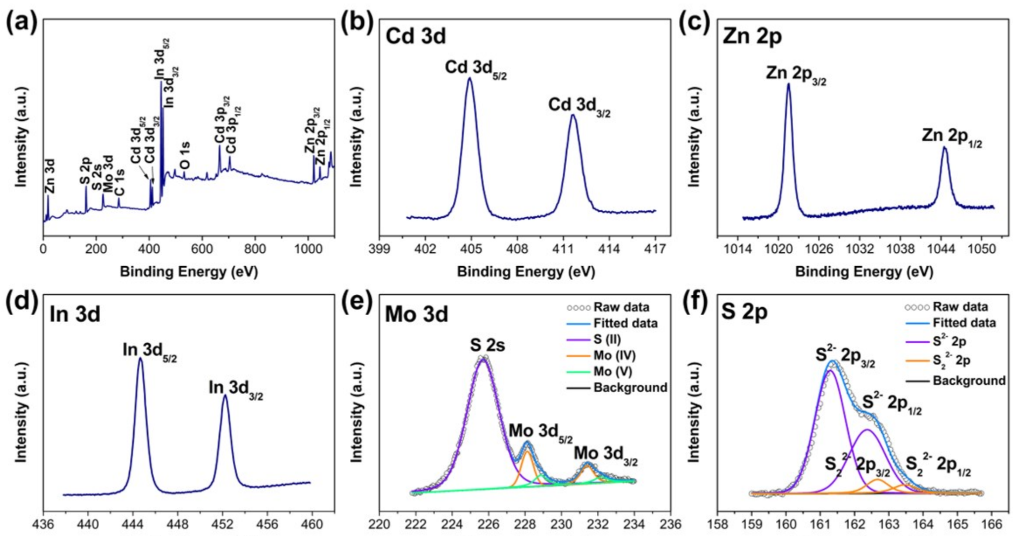

Fig. S13 (a) XPS survey, (b) Cd 3d, (c) Zn 2p, (d) In 3d, (e) Mo 3d, and (f) S 2P spectra of $C_{0.15}$ZIS-5C-10M after HER test.

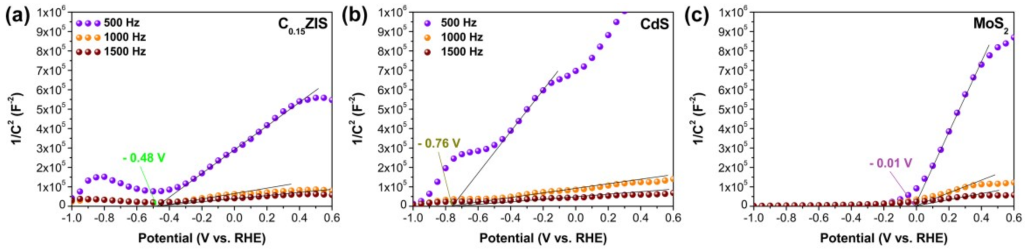

Fig. S14 Mott-Schottky curves of (a) $C_{0.15}$ZIS, (b) CdS, and (c) MoS_2.

Table S2. Comparison on the photocatalytic HER activities of $ZnIn_2S_4$-based composites.

Photocatalyst	Hole scavenger (aqueous solution)	Light source (Xe lamp)	Maximum rate (mmol·h^{-1}·g^{-1})	AQE (420 nm)	Reference
$Cd_xZn_{1-x}In_2S_4$-CdS-MoS_2	Lactic acid	λ > 400 nm	27.14	11.80% 19.97% (400 nm)	This work
MoS_2/$ZnIn_2S_4$	Na_2S/Na_2SO_3	λ > 420 nm	3.89	-	9
MoS_2/$ZnIn_2S_4$	Lactic acid	λ > 420 nm	8.04	-	10
MoS_2QDs@$ZnIn_2S_4$@RGO	Lactic acid	UV and vis	5.791	54.17%	11
MoS_2QDs@Vs-M$ZnIn_2S_4$	Na_2S/Na_2SO_3	λ > 420 nm	6.88	63.87%	12
RGO/$ZnIn_2S_4$	Lactic acid	λ > 420 nm	0.81	-	13
RGO/$ZnIn_2S_4$	TEOA	λ > 420 nm	2.64	4.4%	14
$ZnIn_2S_4$@NH_2-MIL-125(Ti)	Na_2S/Na_2SO_3	λ > 420 nm	2.20	4.3%	15
UiO-66@$ZnIn_2S_4$	TEOA	λ > 400 nm	3.06	9.84%	16
H-doped $ZnIn_2S_4$	Na_2S/Na_2SO_3	λ > 420 nm	2.15	13.2%	17
N-doped $ZnIn_2S_4$	TEOA	λ > 400 nm	11.08	13.8%	18
Oxygen-Doped $ZnIn_2S_4$	Na_2S/Na_2SO_3	λ > 420 nm	2.12	-	19
Cubic/Hexagonal $ZnIn_2S_4$	Na_2S/Na_2SO_3	λ > 420 nm	3.80	18.67%	20
Half-unit-cell $ZnIn_2S_4$	TEOA	λ > 400 nm	13.47	53.68% (365 nm)	21
Co_9S_8@$ZnIn_2S_4$	TEOA	λ > 400 nm	6.25	-	22
$AgIn_5S_8$/$ZnIn_2S_4$	Na_2S/Na_2SO_3	λ > 420 nm	0.94	-	23
Ti (IV)/$ZnIn_2S_4$	Na_2S/Na_2SO_3	λ > 420 nm	3.68	-	24
$Ti_3C_2T_X$ MXene@$ZnIn_2S_4$	TEOA	λ > 420 nm	3.47	11.14%	25
NiS/$ZnIn_2S_4$	Lactic acid	λ > 420 nm	3.33	32%	26
g-C_3N_4/$ZnIn_2S_4$	TEOA	λ > 420 nm	4.85	-	27
MoC-QDs/C/$ZnIn_2S_4$	lactic acid	λ > 400 nm	1.13	-	28
$ZnIn_2S_4$/pCN	TEOA	λ > 420 nm	0.81	-	29
MoS_2/Cu-$ZnIn_2S_4$	Ascorbic acid	λ > 420 nm	5.46	13.6%	30
$ZnIn_2S_4$/$In(OH)_3$-%Pt	TEOA	λ > 420 nm	1.47	38.3%	31
$ZnIn_2S_4$/$MoSe_2$	Na_2S/Na_2SO_3	λ > 420 nm	2.22	21.39%	32
Mo_2C/$ZnIn_2S_4$	TEOA	λ > 400 nm	22.11	71.6%	33

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