

Supporting Information (SI)

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**Solid Solution  $\text{ZnW}_{1-x}\text{Mo}_x\text{O}_4$  for the Enhanced Photocatalytic  $\text{H}_2$   
Evolution**

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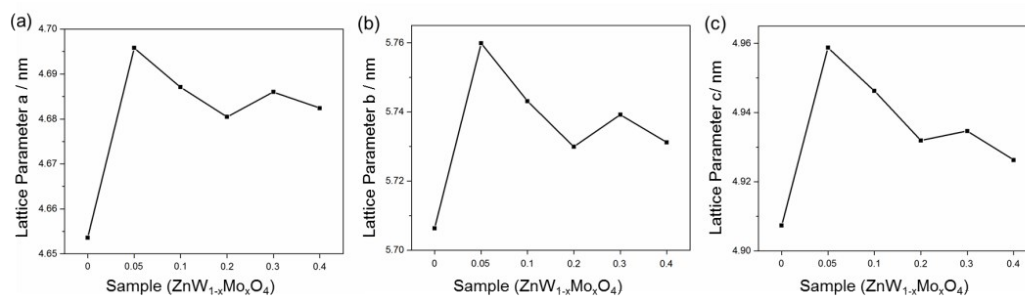
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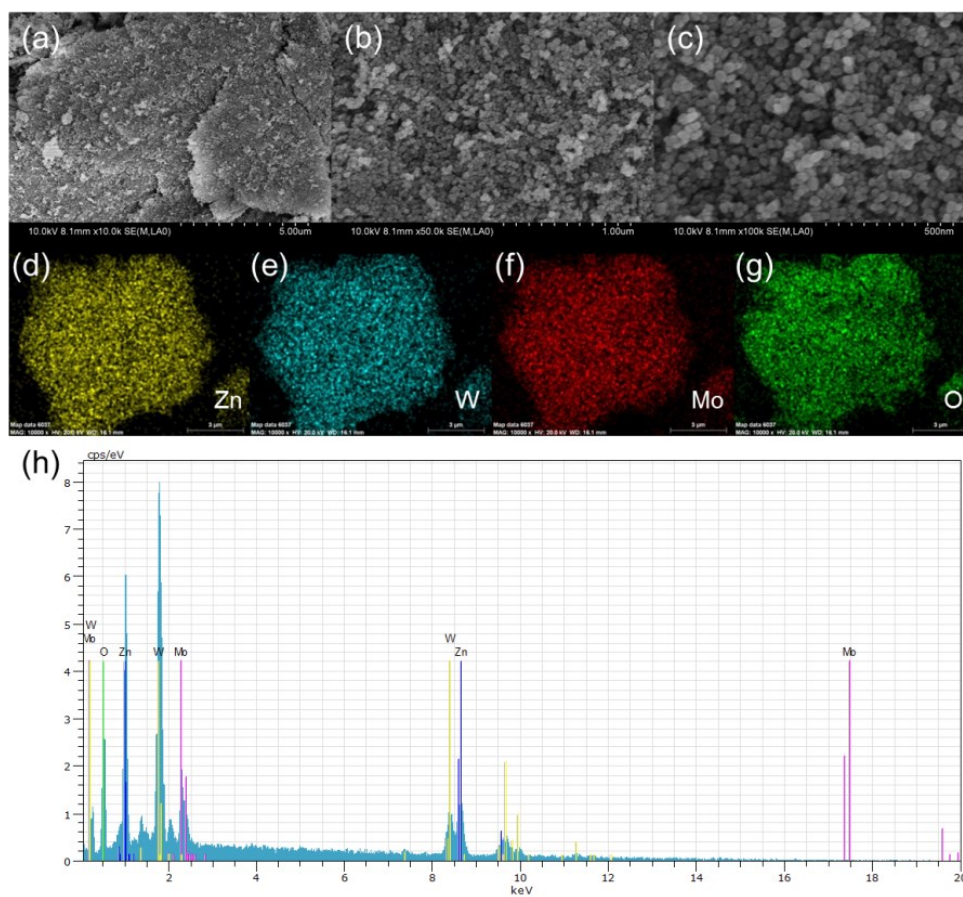
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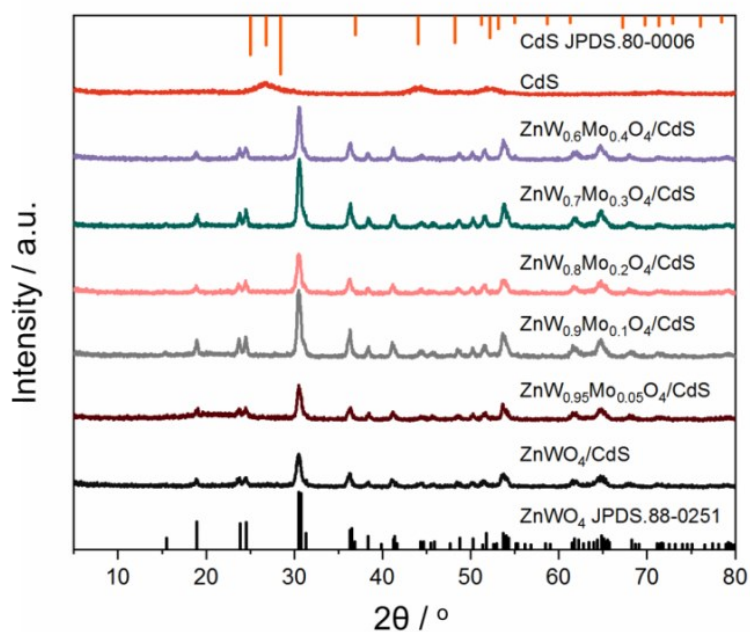
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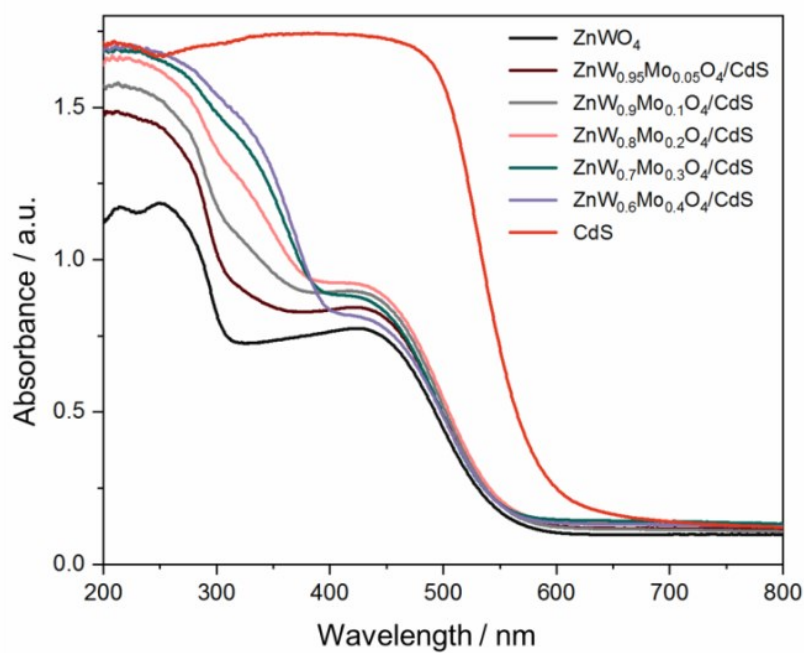
**Fig. S1** Lattice parameter of different  $\text{ZnW}_{1-x}\text{Mo}_x\text{O}_4$  solid solutions.



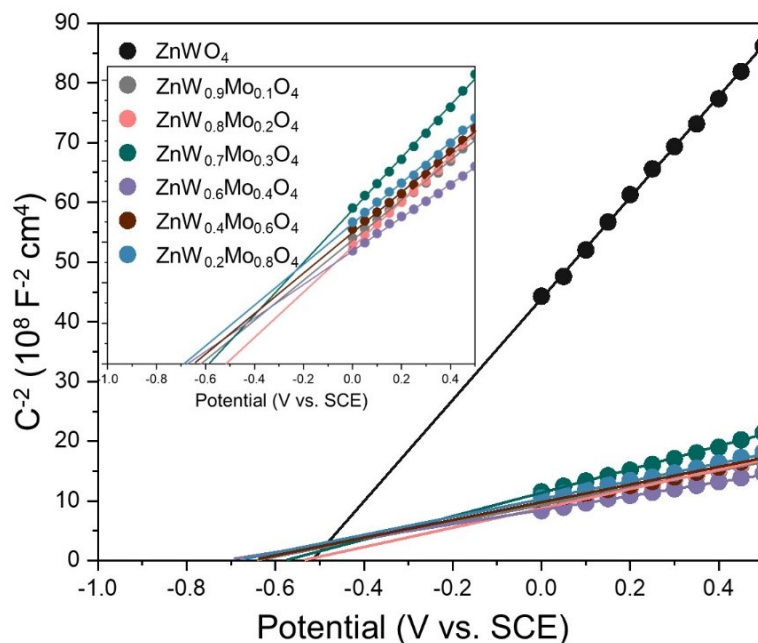
**Fig. S2** SEM images (a, b, c), SEM mapping (d, e, f, g) and SEM-EDS (h) of  $\text{ZnW}_{0.6}\text{Mo}_{0.4}\text{O}_4$ .



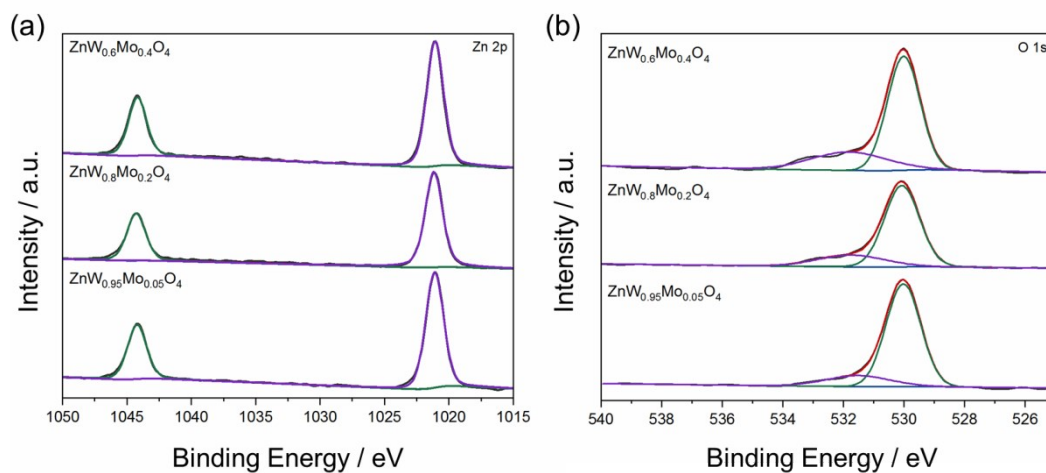
**Fig. S3** XRD patterns of ZnW<sub>1-x</sub>Mo<sub>x</sub>O<sub>4</sub>/CdS heterojunctions with 10 mol% CdS and pure CdS.



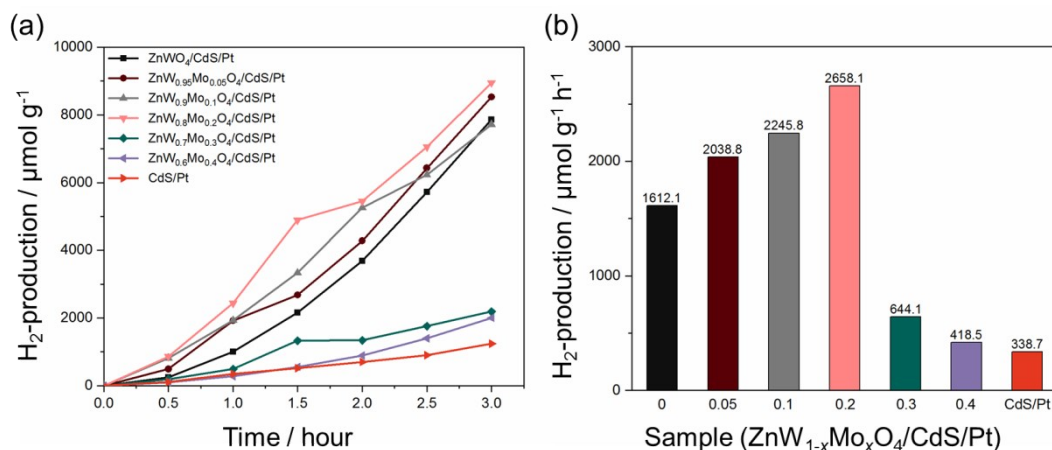
**Fig. S4** UV-vis spectra of ZnW<sub>1-x</sub>Mo<sub>x</sub>O<sub>4</sub>/CdS.



**Fig. S5** Mott-Schottky plots of ZnW<sub>1-x</sub>Mo<sub>x</sub>O<sub>4</sub> with 1000 Hz frequencies in a 0.5M Na<sub>2</sub>SO<sub>4</sub> solution.



**Fig. S6** XPS of ZnW<sub>1-x</sub>Mo<sub>x</sub>O<sub>4</sub> (x = 5, 20, 40%) of Zn (a) and O (b).



**Fig. S7** (a) Hydrogen evolution in 3 hours of ZnW<sub>1-x</sub>Mo<sub>x</sub>O<sub>4</sub>/CdS/Pt. (b) HER activity of ZnW<sub>1-x</sub>Mo<sub>x</sub>O<sub>4</sub>/CdS/Pt.

**Table S1.** Refined structural parameters and reliability factors for lab XRD data for ZnW<sub>1-x</sub>Mo<sub>x</sub>O<sub>4</sub> ( $x = 0.4$ ) measured at 297 K.

Atom	Coordinates			Occupancy	Uiso / Å <sup>2</sup>	site
	$x$	$y$	$z$			
Zn	0.50000	0.68330	0.25000	1.000	0.028	2f
W	0.00000	0.18230	0.25000	0.595	0.011 <sup>[a]</sup>	2e
Mo	0.00000	0.18230	0.25000	0.405	0.011 <sup>[a]</sup>	2e
O1	0.25470	0.37720	0.40050	1.000	0.054	4g
O2	0.21710	0.89550	0.43600	1.000	0.031	4g

<sup>[a]</sup> Atomic displacement parameters for cations were assumed to be the same.

**Table S2.** Carrier density calculated from Mott-Schottky plots in Figure S5.

Samples	E <sub>FB</sub> (V)	Slope (cm <sup>4</sup> F <sup>-2</sup> V <sup>-1</sup> 10 <sup>-8</sup> )	Straight Line fit (R <sup>2</sup> )	N <sub>D</sub> (cm <sup>-3</sup> )
ZnWO <sub>4</sub>	-0.520	84.31	0.99924	1.0075*10 <sup>19</sup>
ZnW <sub>0.9</sub> Mo <sub>0.1</sub> O <sub>4</sub>	-0.622	14.73	0.99526	5.7664*10 <sup>19</sup>
ZnW <sub>0.8</sub> Mo <sub>0.2</sub> O <sub>4</sub>	-0.526	16.61	0.99778	5.1138*10 <sup>19</sup>
ZnW <sub>0.7</sub> Mo <sub>0.3</sub> O <sub>4</sub>	-0.587	19.45	0.99714	4.3671*10 <sup>19</sup>
ZnW <sub>0.6</sub> Mo <sub>0.4</sub> O <sub>4</sub>	-0.680	12.23	0.99868	6.9452*10 <sup>19</sup>
ZnW <sub>0.4</sub> Mo <sub>0.6</sub> O <sub>4</sub>	-0.651	14.90	0.99526	5.7007*10 <sup>19</sup>
ZnW <sub>0.2</sub> Mo <sub>0.8</sub> O <sub>4</sub>	-0.683	15.06	0.99569	5.6401*10 <sup>19</sup>

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**Table S3.** Binding Energies for Mo3d and W4d Core Lines of the Products.

Binding Energy(eV)	W 5p <sub>3/2</sub>	W 4f <sub>5/2</sub>	W 4f <sub>7/2</sub>	Mo <sup>6+</sup> 3d <sub>3/2</sub>	Mo <sup>5+</sup> 3d <sub>3/2</sub>	Mo <sup>6+</sup> 3d <sub>5/2</sub>	Mo <sup>5+</sup> 3d <sub>5/2</sub>
ZnW <sub>0.95</sub> Mo <sub>0.05</sub> O <sub>4</sub>	40.87	37.27	35.12	235.44	234.14	232.29	230.99
ZnW <sub>0.8</sub> Mo <sub>0.2</sub> O <sub>4</sub>	41.01	37.39	35.24	235.49	234.19	232.34	231.04
ZnW <sub>0.6</sub> Mo <sub>0.4</sub> O <sub>4</sub>	40.82	37.35	35.20	235.43	234.13	232.28	230.98

**Table S4.** Calculated surface area from BET test.

Samples	BET surface area (m <sup>2</sup> /g)	Mean pore width (nm)	Pore volume (cm <sup>3</sup> /g)
ZnWO <sub>4</sub>	22.4325	17.9857	0.0964
ZnW <sub>0.9</sub> Mo <sub>0.1</sub> O <sub>4</sub>	24.0332	17.7196	0.1521
ZnW <sub>0.8</sub> Mo <sub>0.2</sub> O <sub>4</sub>	27.7555	16.0345	0.1897
ZnW <sub>0.6</sub> Mo <sub>0.4</sub> O <sub>4</sub>	28.0925	14.0462	0.1070
ZnW <sub>0.4</sub> Mo <sub>0.6</sub> O <sub>4</sub>	27.0959	15.8311	0.1496
ZnWO <sub>4</sub> /CdS	27.8417	13.5459	0.1031
ZnW <sub>0.8</sub> Mo <sub>0.2</sub> O <sub>4</sub> /CdS	31.3771	17.8342	0.2085
ZnW <sub>0.6</sub> Mo <sub>0.4</sub> O <sub>4</sub> /CdS	33.7774	13.9542	0.1424

**Table S5.** Parameters (elements) of the EIS fitting using Rs-Rct | CPE equivalent circuit.

Samples	R <sub>s</sub> (Ω)	R <sub>ct</sub> (kΩ)
ZnWO <sub>4</sub>	19.78	4.73*10 <sup>4</sup>
ZnW <sub>0.95</sub> Mo <sub>0.05</sub> O <sub>4</sub>	17.35	412.64
ZnW <sub>0.9</sub> Mo <sub>0.1</sub> O <sub>4</sub>	16.10	159.41
ZnW <sub>0.8</sub> Mo <sub>0.2</sub> O <sub>4</sub>	20.3	2.02*10 <sup>3</sup>
ZnW <sub>0.7</sub> Mo <sub>0.3</sub> O <sub>4</sub>	16.86	276.07
ZnW <sub>0.6</sub> Mo <sub>0.4</sub> O <sub>4</sub>	13.18	67.015
ZnWO <sub>4</sub> /CdS	27.97	42.25
ZnW <sub>0.9</sub> Mo <sub>0.1</sub> O <sub>4</sub> /CdS	14.51	43.328
ZnW <sub>0.8</sub> Mo <sub>0.2</sub> O <sub>4</sub> /CdS	32.62	41.201
ZnW <sub>0.6</sub> Mo <sub>0.4</sub> O <sub>4</sub> /CdS	17.78	42.547