

Supplementary Material

Predicted Optimal Bifunctional Electrocatalysts for the Hydrogen Evolution Reaction and the Oxygen Evolution Reaction Using Chalcogenide Heterostructures Based on Machine Learning Analysis of in Silico Quantum Mechanics Based High Throughput Screening

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Calculation method of HER and OER activity

ΔG for Hydrogen Evolution Reaction: the ΔG for each step under $U=0$ ($\text{pH}=0$ and $T=298.15$ K).



$$\Delta E_{*H} = \frac{1}{n}(E(*+nH) - E_* - \frac{n}{2}E_{H_2}) \quad (\text{S2})$$

$$\begin{aligned} \Delta G_{*H} &= \Delta G(H^+ + e^- + * \leftrightarrow *H) = \mu_{*H} - \mu_{H^+} - \mu_{e^-} - \mu_* = \mu_{H^+} - \frac{1}{2}\mu_{H_2} - \mu_* \\ &= \left(E_{*H} - \frac{1}{2}E_{H_2} - E_*\right) + \left(E_{\text{ZPE}(*H)} - \frac{1}{2}E_{\text{ZPE}(H_2)} - E_{\text{ZPE}(*)}\right) - T \times \left(S_{*H} - \frac{1}{2}S_{H_2} - S_*\right) \quad (\text{S3})^1 \end{aligned}$$

ΔG for Oxygen Evolution Reaction: the ΔG for each step under $U=0$ ($\text{pH}=0$ and $T=298.15$ K).

$$\Delta E_{*OH} = E_{*OH} - E_* - \left(E_{H_2O} - \frac{1}{2}E_{H_2}\right) \quad (\text{S4})$$

$$\Delta E_{*OOH} = E_{*OOH} - E_* - \left(2 \times E_{H_2O} - \frac{3}{2}E_{H_2}\right) \quad (\text{S5})$$

$$\Delta E_{*O} = E_{*O} - E_* - \left(E_{H_2O} - E_{H_2}\right) \quad (\text{S6})^2$$

$$\begin{aligned} \Delta G_{*O} &= \Delta G(H_2O(g) + * \rightarrow *O + H_2(g)) = \mu_{*O} + \mu_{H_2} - \mu_{H_2O} - \mu_* \\ &= \left(E_{*O} + E_{H_2} - E_{H_2O} - E_*\right) + \left(E_{\text{ZPE}(*O)} + E_{\text{ZPE}(H_2)} - E_{\text{ZPE}(H_2O)} - E_{\text{ZPE}(*)}\right) - \\ &\quad T \times (S_{*O} + S_{H_2} - S_{H_2O} - S_*) \quad (\text{S7})^3 \end{aligned}$$

$$\begin{aligned} \Delta G_{*OH} &= \Delta G\left(H_2O(g) + * \rightarrow *OH + \frac{1}{2}H_2(g)\right) = \mu_{*OH} + \frac{1}{2}\mu_{H_2} - \mu_{H_2O} - \mu_* \\ &= \left(E_{*OH} + \frac{1}{2}E_{H_2} - E_{H_2O} - E_*\right) + \left(E_{\text{ZPE}(*OH)} + \frac{1}{2}E_{\text{ZPE}(H_2)} - E_{\text{ZPE}(H_2O)} - E_{\text{ZPE}(*)}\right) - \\ &\quad T \times \left(S_{*OH} + \frac{1}{2}S_{H_2} - S_{H_2O} - S_*\right) \quad (\text{S8})^4 \end{aligned}$$

$$\begin{aligned} \Delta G_{*OOH} &= \Delta G\left(2H_2O(g) + * \rightarrow *OOH + \frac{3}{2}H_2(g)\right) = \mu_{*OOH} + \frac{3}{2}\mu_{H_2} - 2\mu_{H_2O} - \mu_* \\ &= \left(E_{*OOH} + \frac{3}{2}E_{H_2} - 2E_{H_2O} - E_*\right) + \left(E_{\text{ZPE}(*OOH)} + \frac{3}{2}E_{\text{ZPE}(H_2)} - 2E_{\text{ZPE}(H_2O)} - \right. \\ &\quad \left. E_{\text{ZPE}(*)}\right) - T \times \left(S_{*OOH} + \frac{3}{2}S_{H_2} - 2S_{H_2O} - S_*\right) \quad (\text{S9})^5 \end{aligned}$$

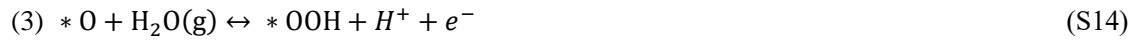
The ΔG for each step can be calculated by:



$$\Delta G_1 = \mu_{* \text{OH}} + \mu_{\text{H}^+} + \mu_{\text{e}^-} - \mu_{\text{H}_2\text{O}} - \mu_* = \mu_{* \text{OH}} + \frac{1}{2} \mu_{\text{H}_2} - \mu_{\text{H}_2\text{O}} - \mu_* = \Delta G_{* \text{OH}} \quad (\text{S11})$$



$$\Delta G_2 = \mu_{* \text{O}} + \mu_{\text{H}^+} + \mu_{\text{e}^-} - \mu_{* \text{OH}} = \mu_{* \text{O}} + \frac{1}{2} \mu_{\text{H}_2} - \mu_{* \text{OH}} = \Delta G_{* \text{O}} - \Delta G_{* \text{OH}} \quad (\text{S13})$$



$$\Delta G_3 = \mu_{* \text{OOH}} + \mu_{\text{H}^+} + \mu_{\text{e}^-} - \mu_{* \text{O}} - \mu_{\text{H}_2\text{O}} = \mu_{* \text{OOH}} + \frac{1}{2} \mu_{\text{H}_2} - \mu_{* \text{O}} - \mu_{\text{H}_2\text{O}} = \Delta G_{* \text{OOH}} - \Delta G_{* \text{O}} \quad (\text{S15})$$



$$\Delta G_4 = \mu_* + \mu_{\text{O}_2} + \mu_{\text{H}^+} + \mu_{\text{e}^-} - \mu_{* \text{OOH}} = \mu_* + \mu_{\text{O}_2} + \frac{1}{2} \mu_{\text{H}_2} - \mu_{* \text{OOH}} = 4.92 - \Delta G_{* \text{OOH}} \quad (\text{S17})$$

Calculation of OER Overpotential: The theoretical overpotential η , which is determined by the potential limiting step:

$$\eta = \max [\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4] / e - 1.23[\text{V}] \quad (\text{S18})^6$$

Supplementary Figures

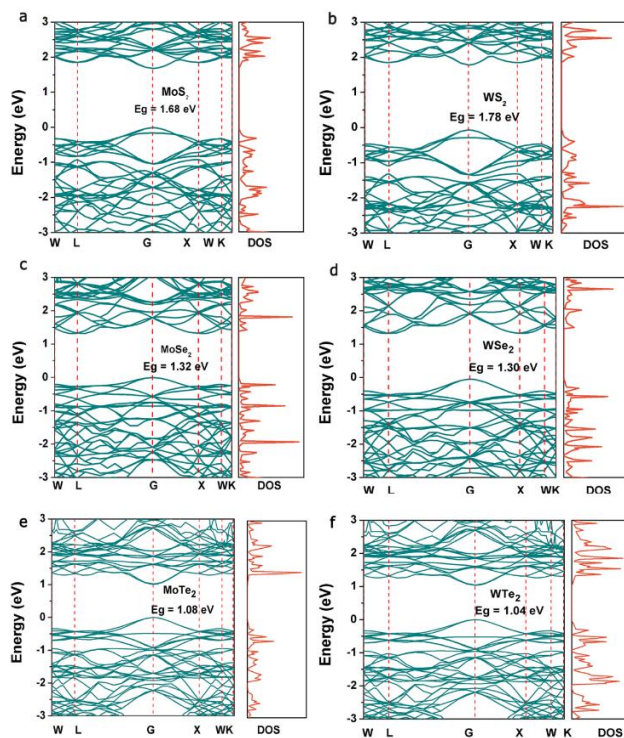


Figure S1. Band structures and density of states of the single-layer MoS_2 , WS_2 , WSe_2 , MoSe_2 , MoTe_2 and WTe_2 (a, b, c, d, e, f), computed at the level of PBE+U respectively.

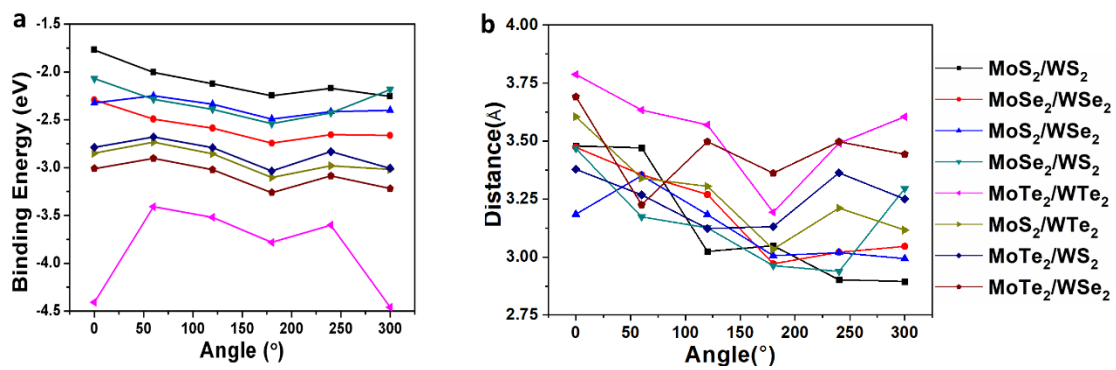


Figure S2. The trend of binding energy and distance for various heterojunctions with various angles.

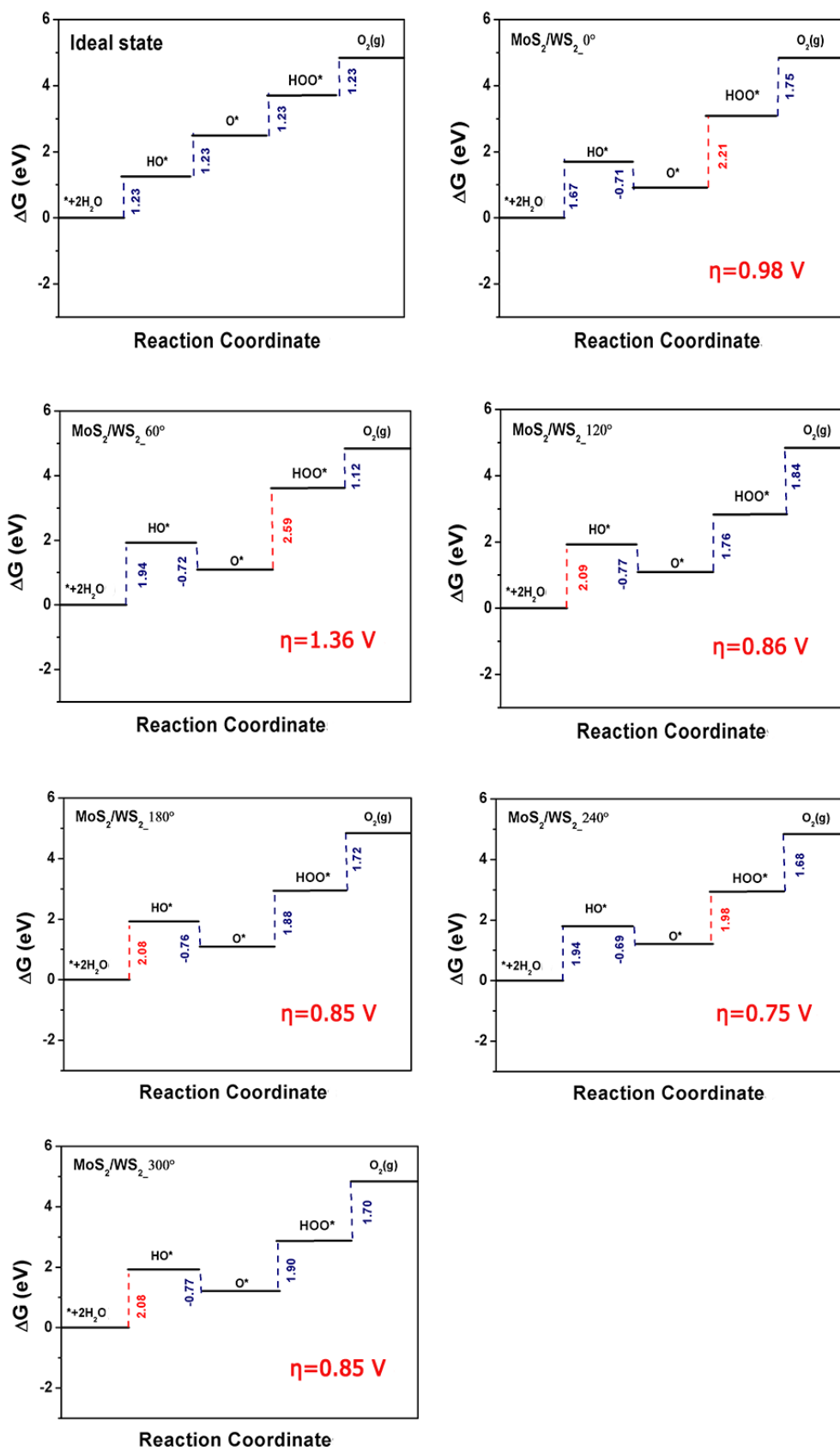


Figure S3. Free-energy diagram for OER of MoS₂/WS₂ at zero electrode potential.

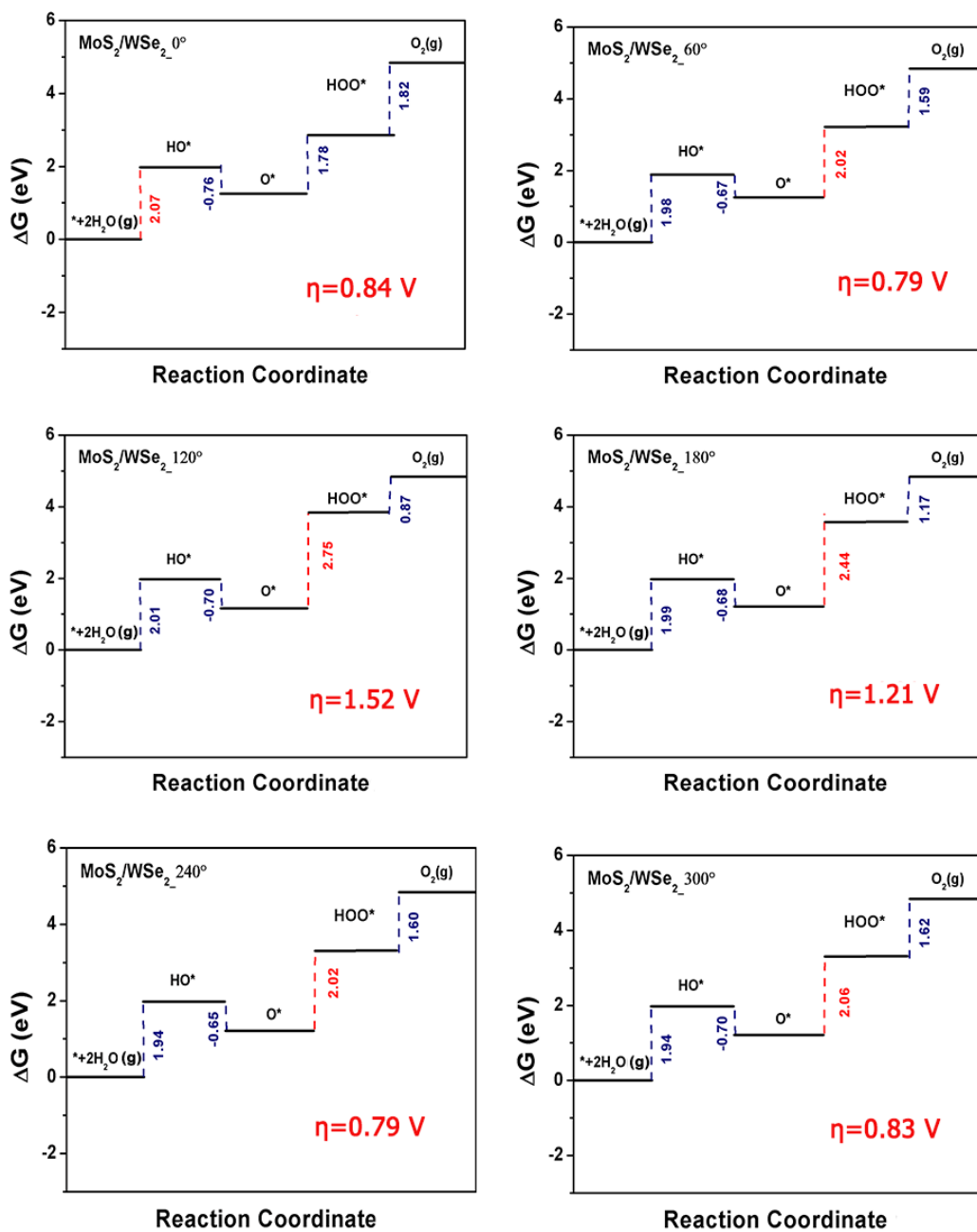


Figure S4. Free-energy diagram for OER of MoS₂ supported on WSe₂ at zero electrode potential.

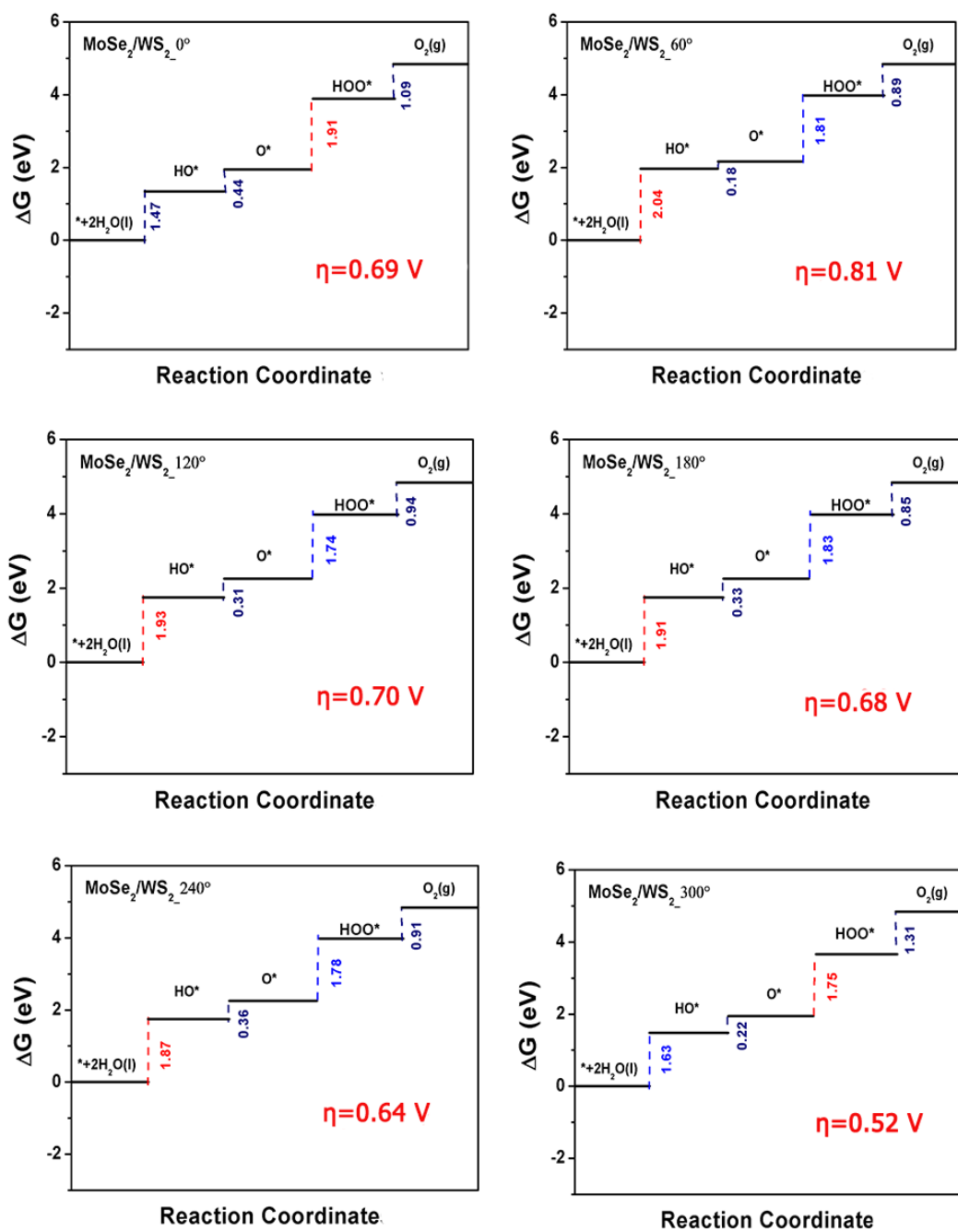


Figure S5. Free-energy diagram for OER of MoSe₂/WS₂ at zero electrode potential.

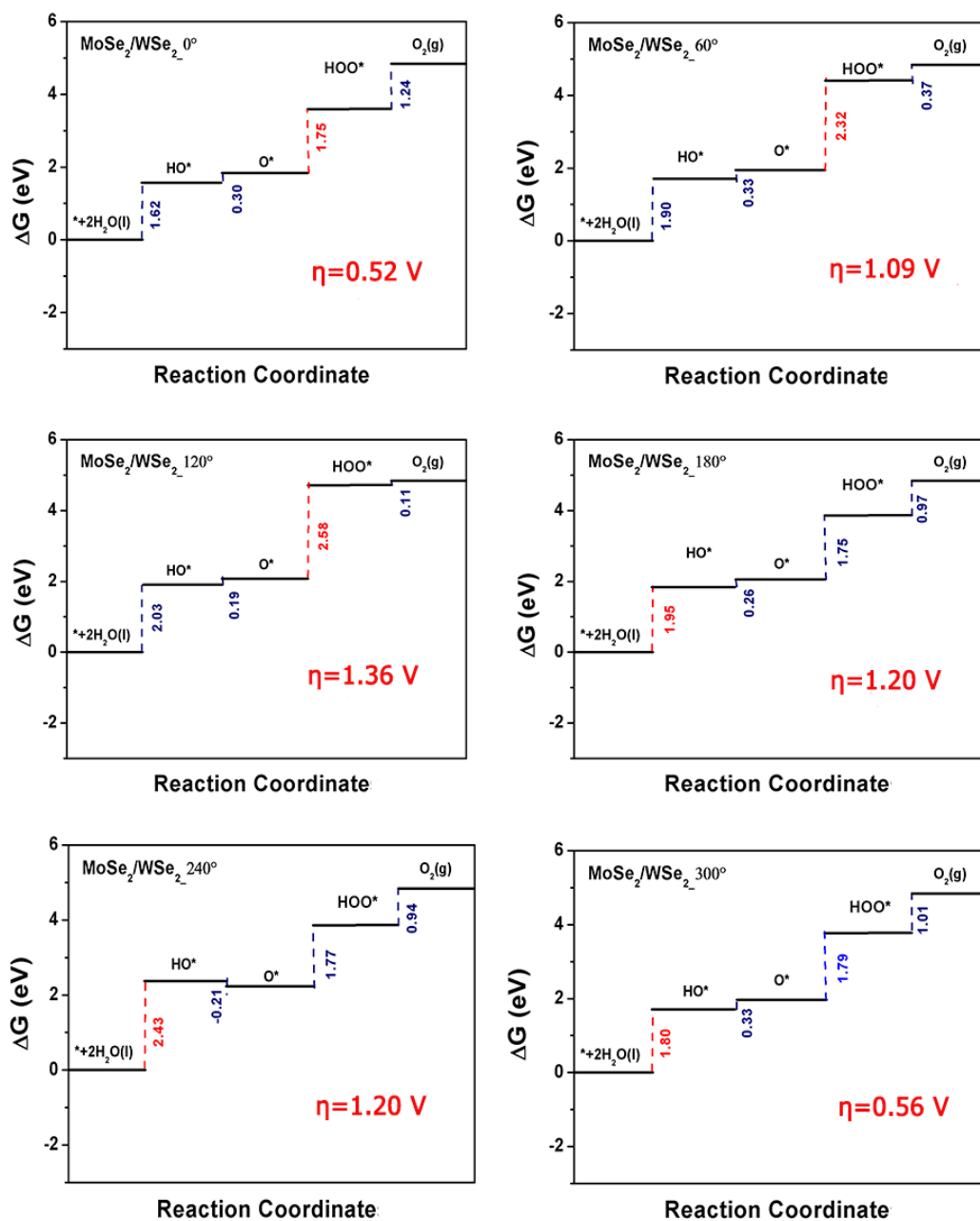


Figure S6. Free-energy diagram for OER of MoSe₂/WSe₂ at zero electrode potential.

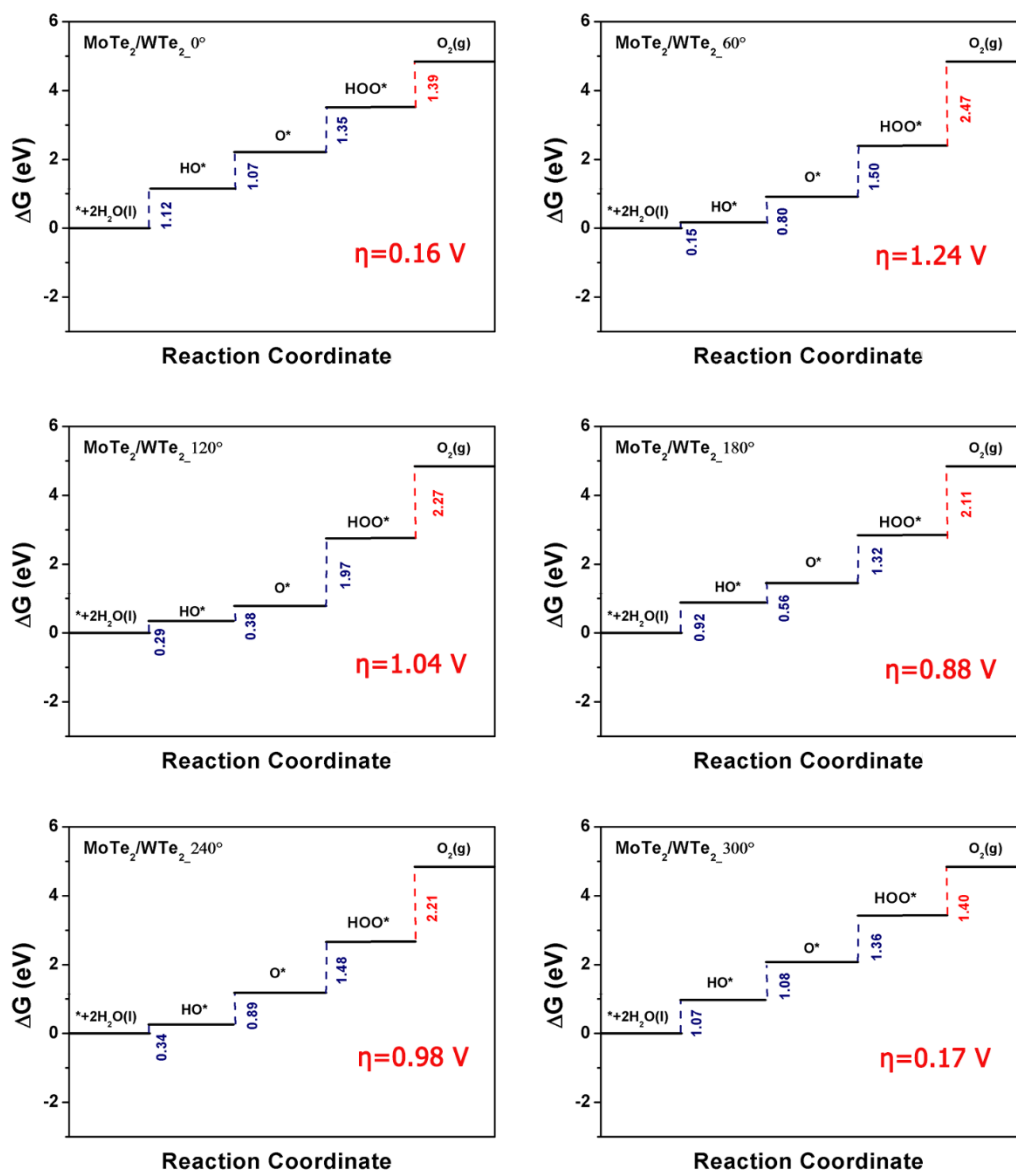


Figure S7. Free-energy diagram for OER of MoTe₂/WTe₂ at zero electrode potential.

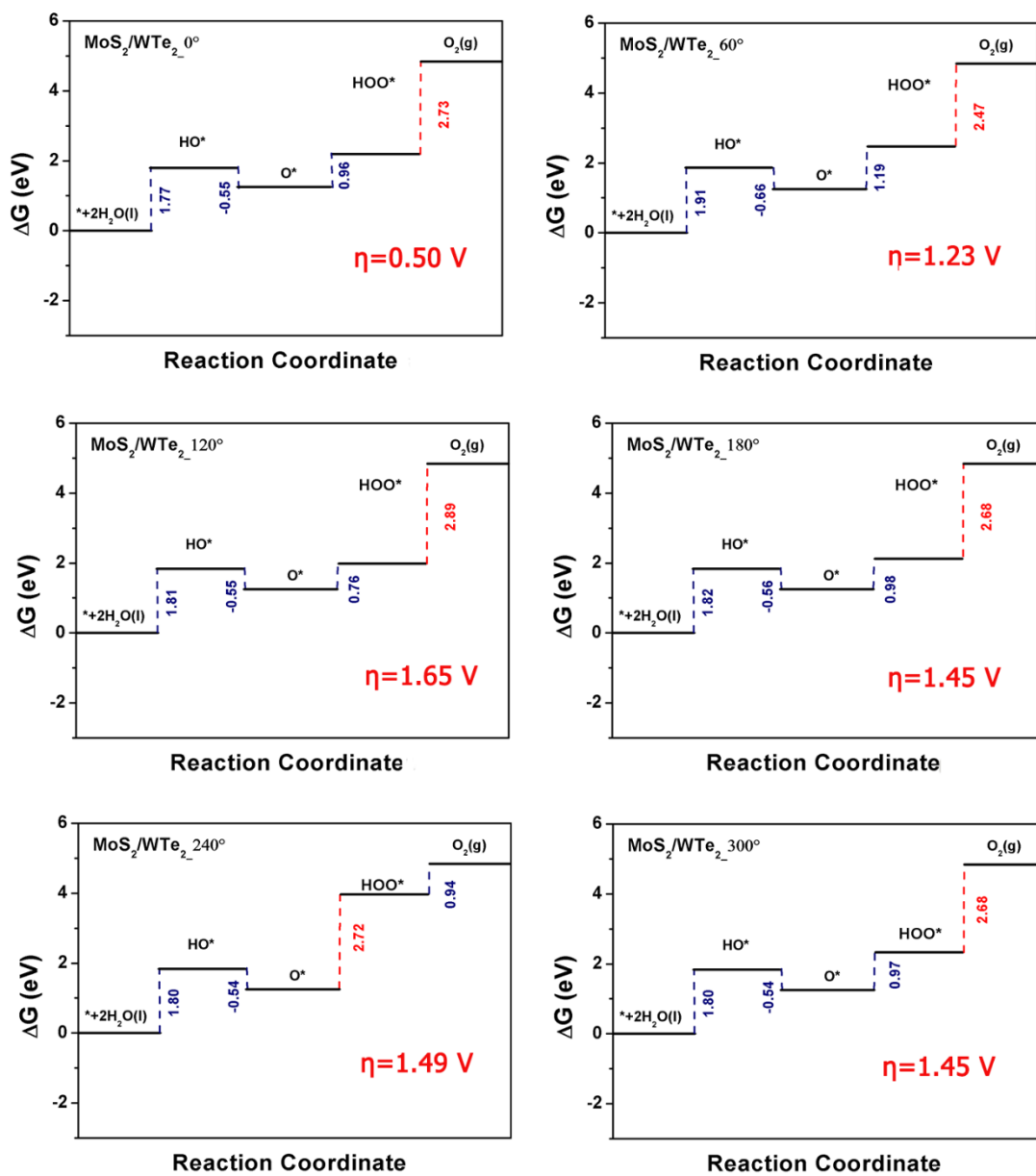


Figure S8. Free-energy diagram for OER of MoS₂/WTe₂ at zero electrode potential.

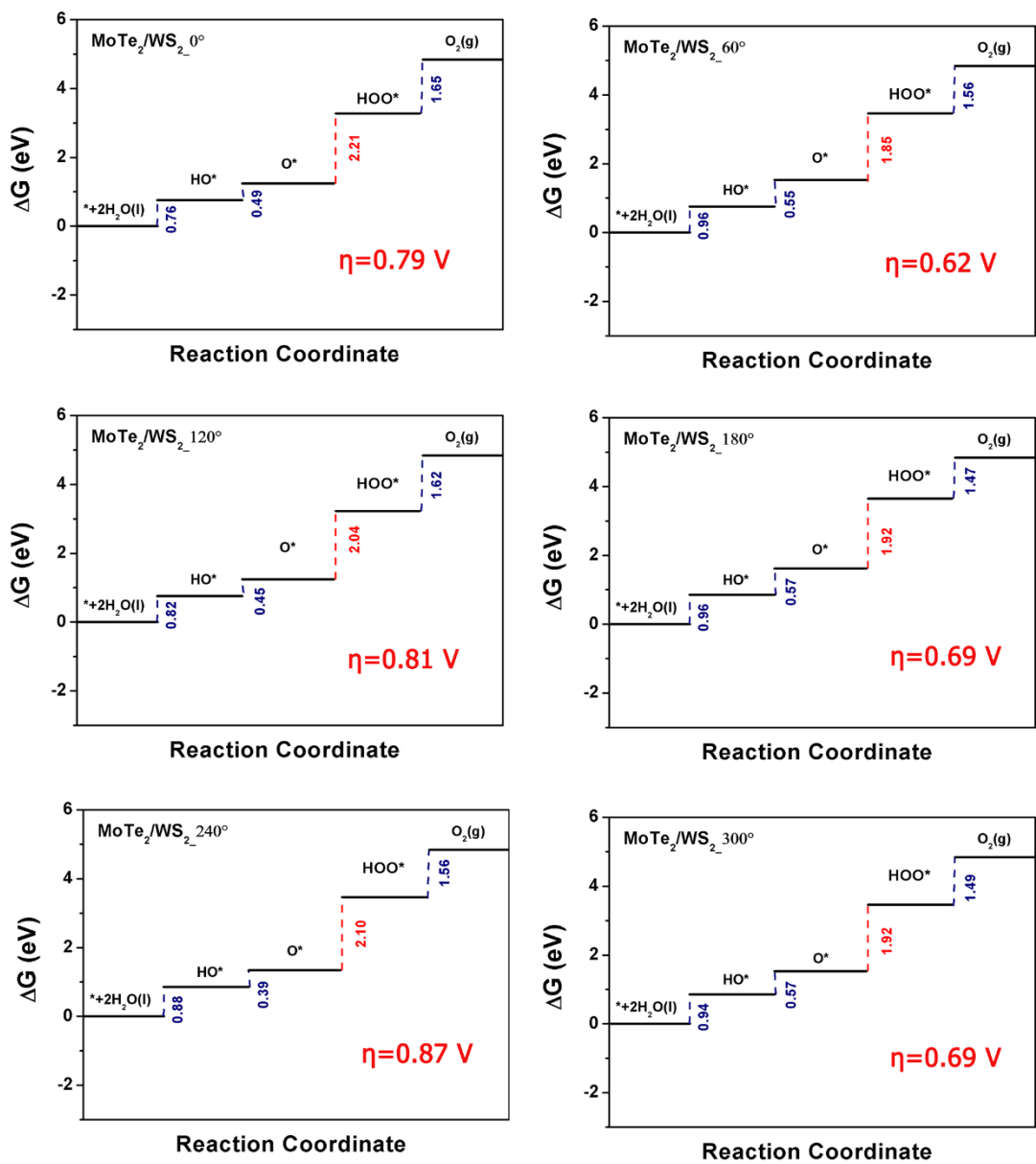


Figure S9. Free-energy diagram for OER of MoTe₂/WS₂ at zero electrode potential.

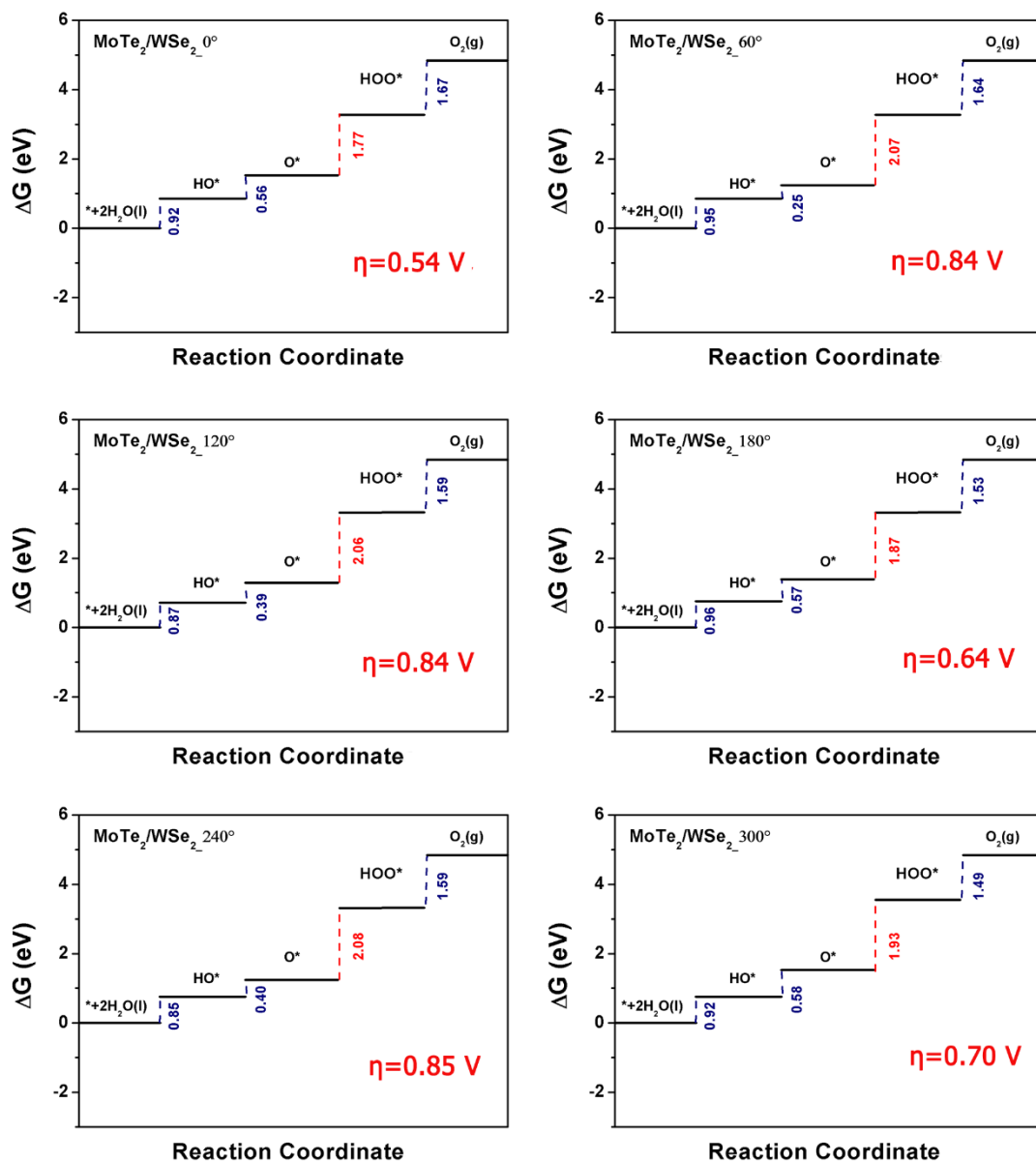


Figure S10. Free-energy diagram for OER of MoTe₂/WSe₂ at zero electrode potential.

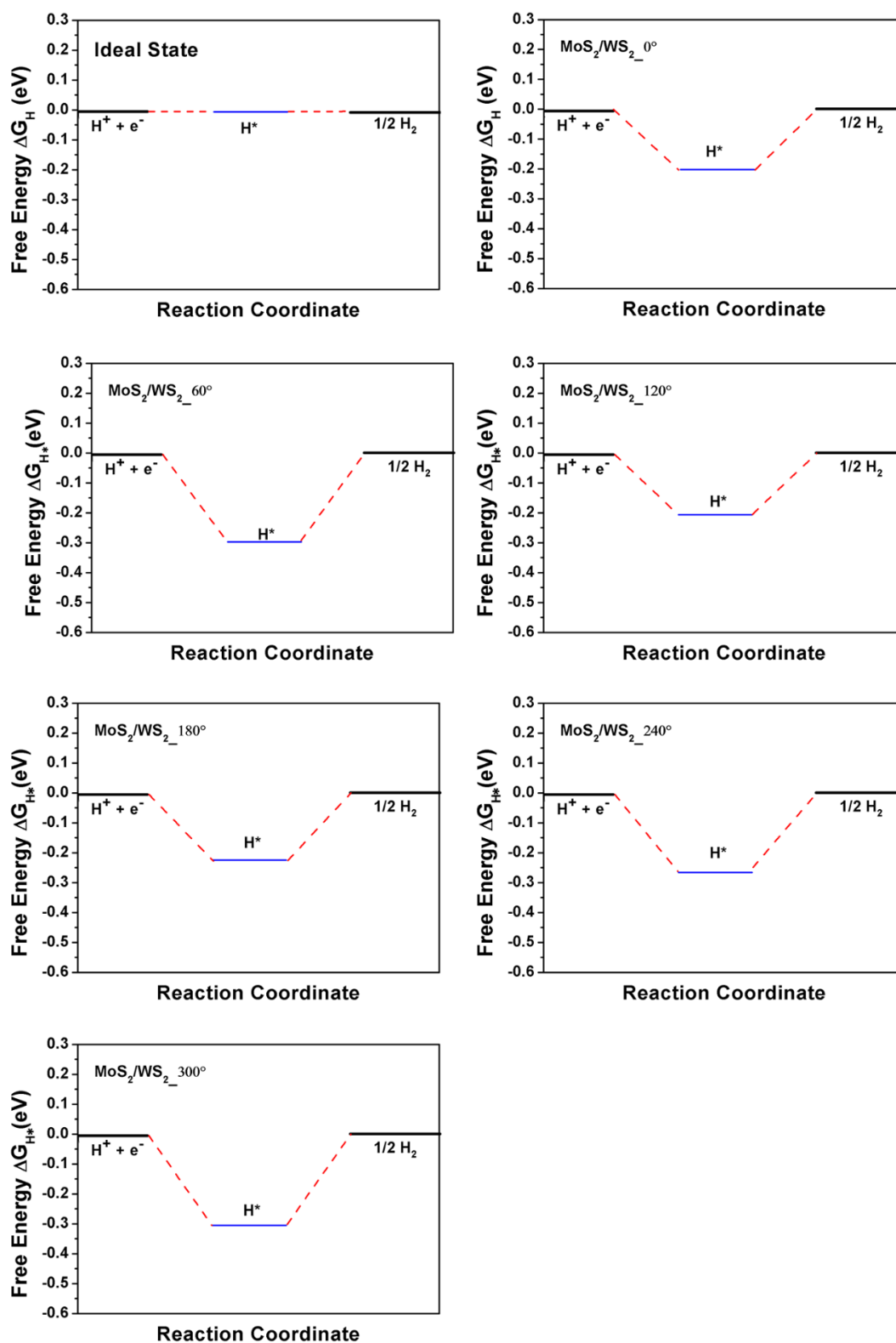


Figure S11. Free-energy diagram for HER of MoS₂/WS₂ at zero electrode potential.

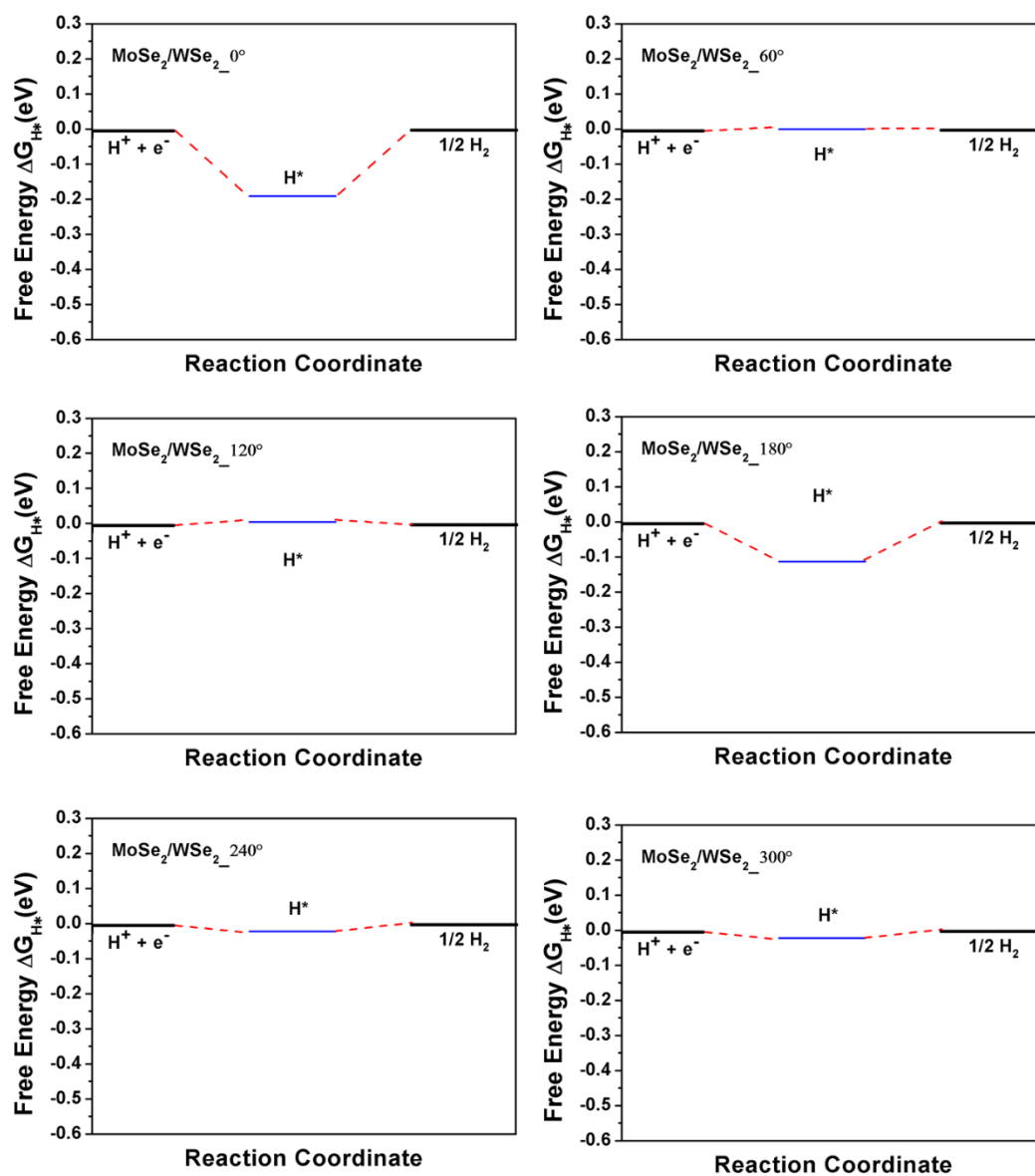


Figure S12. Free-energy diagram for HER of MoSe₂/WSe₂ at zero electrode potential.

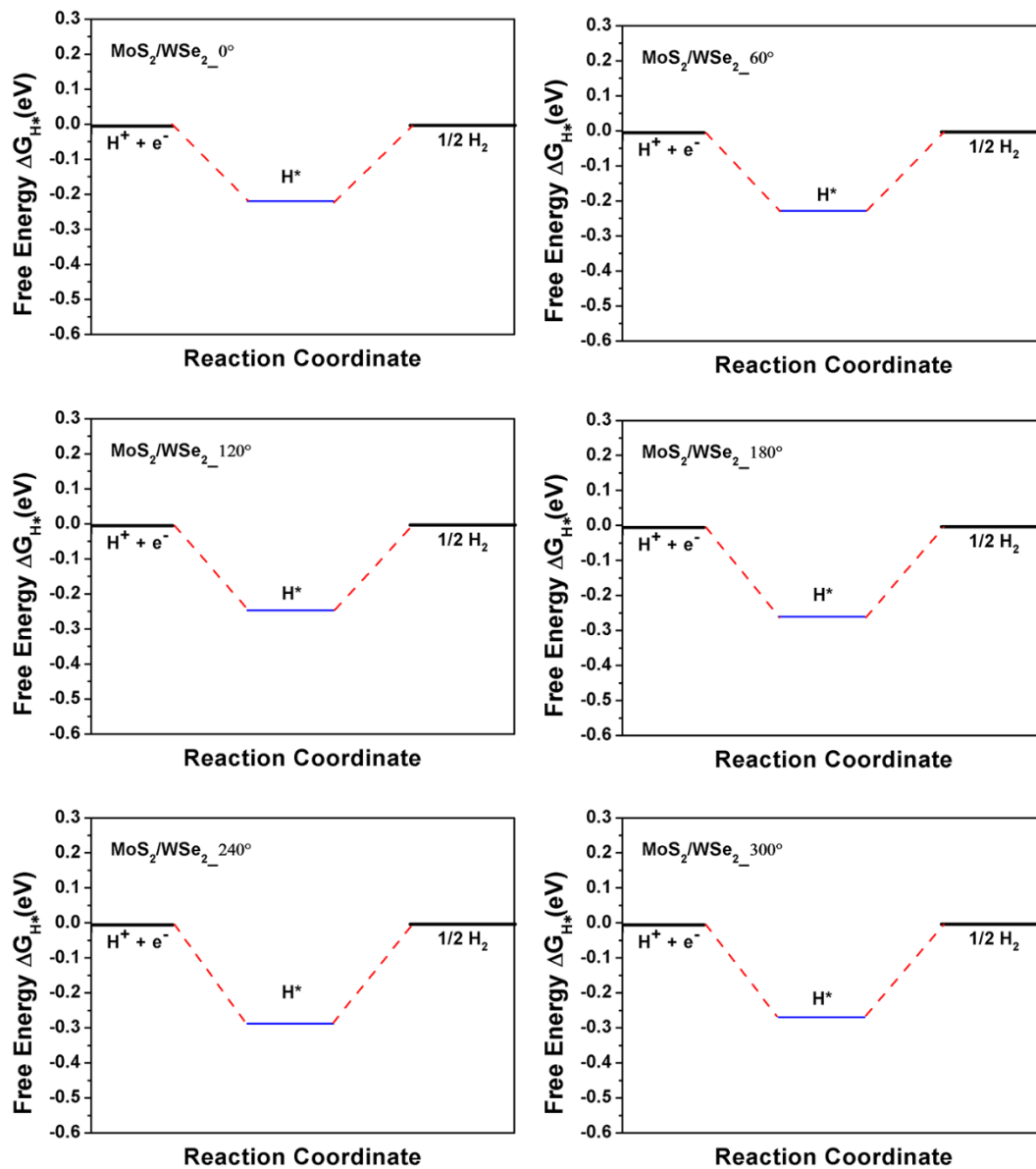


Figure S13. Free-energy diagram for HER of MoS₂/WSe₂ at zero electrode potential.

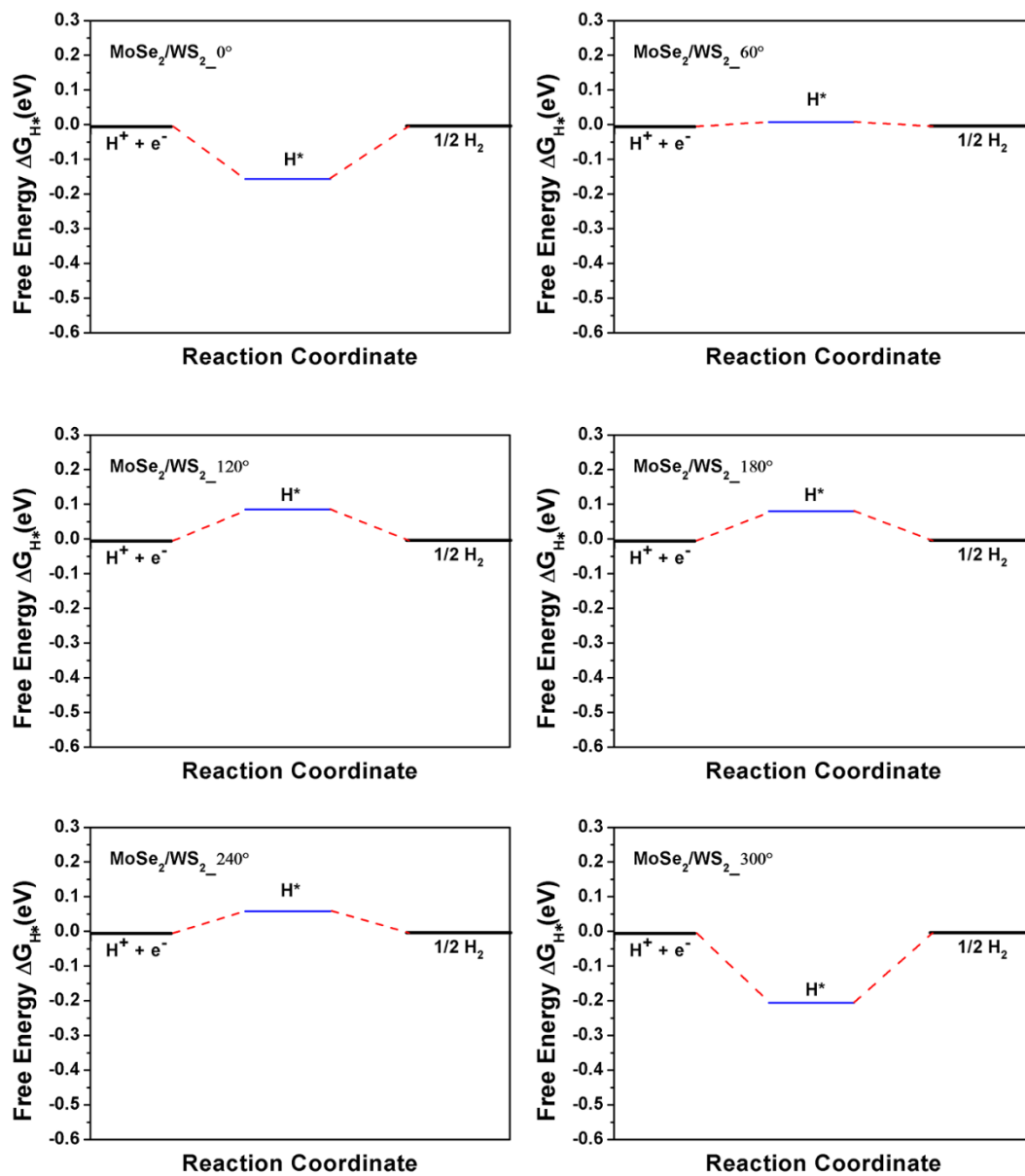


Figure S14. Free-energy diagram for HER of MoSe₂/WS₂ at zero electrode potential.

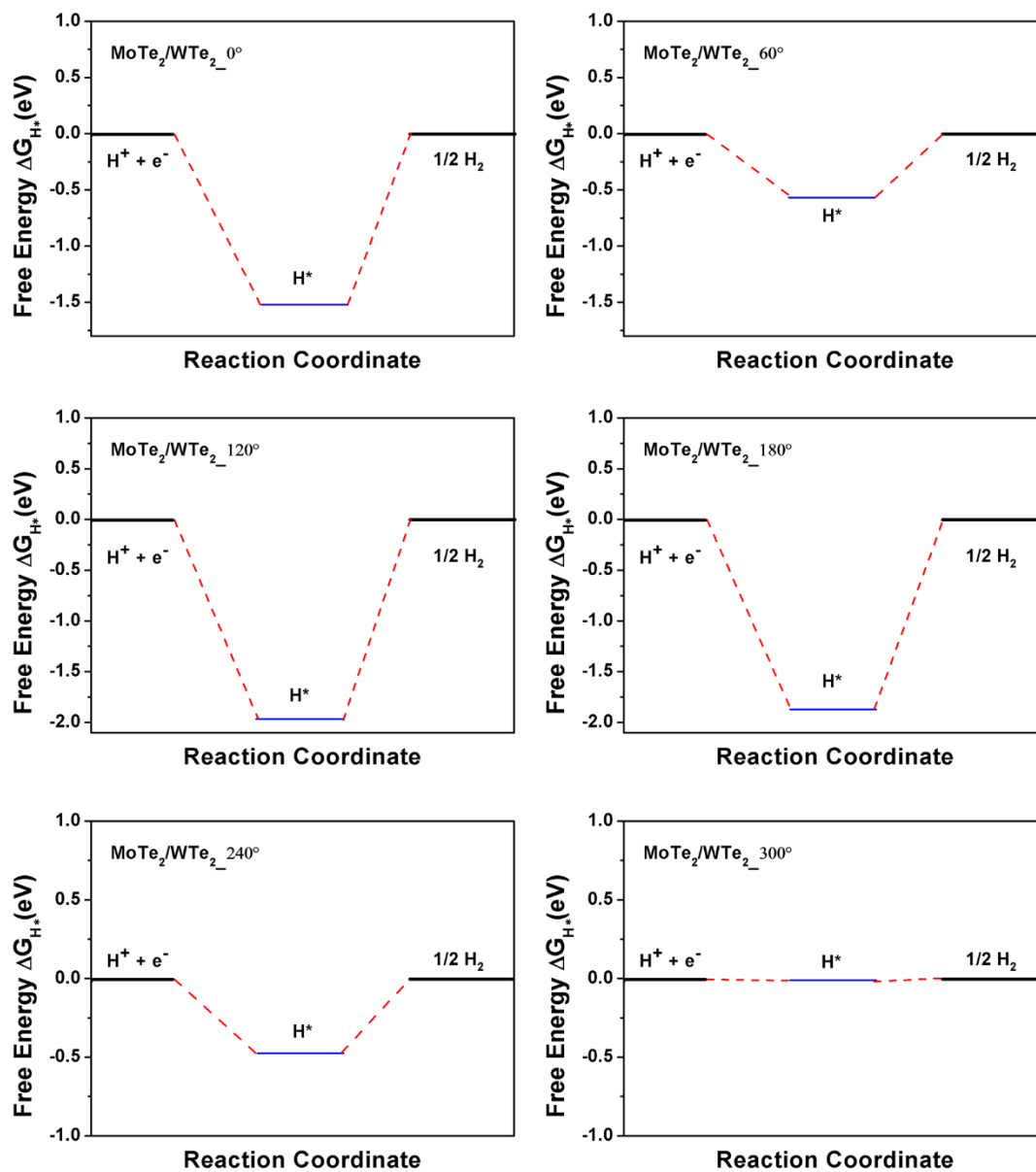


Figure S15. Free-energy diagram for HER of MoTe₂/WTe₂ at zero electrode potential.

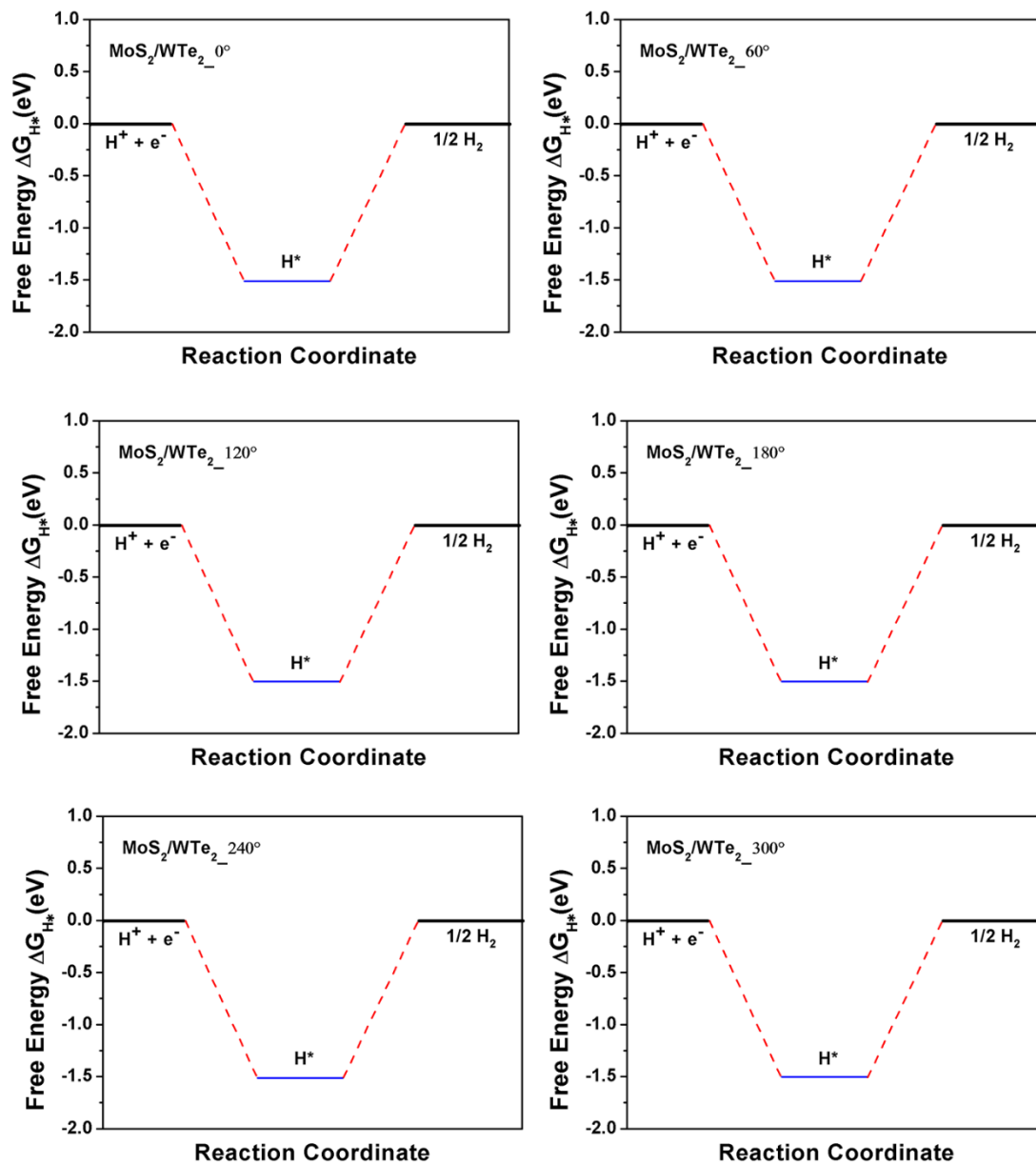


Figure S16. Free-energy diagram for HER of MoS₂/WTe₂ at zero electrode potential.

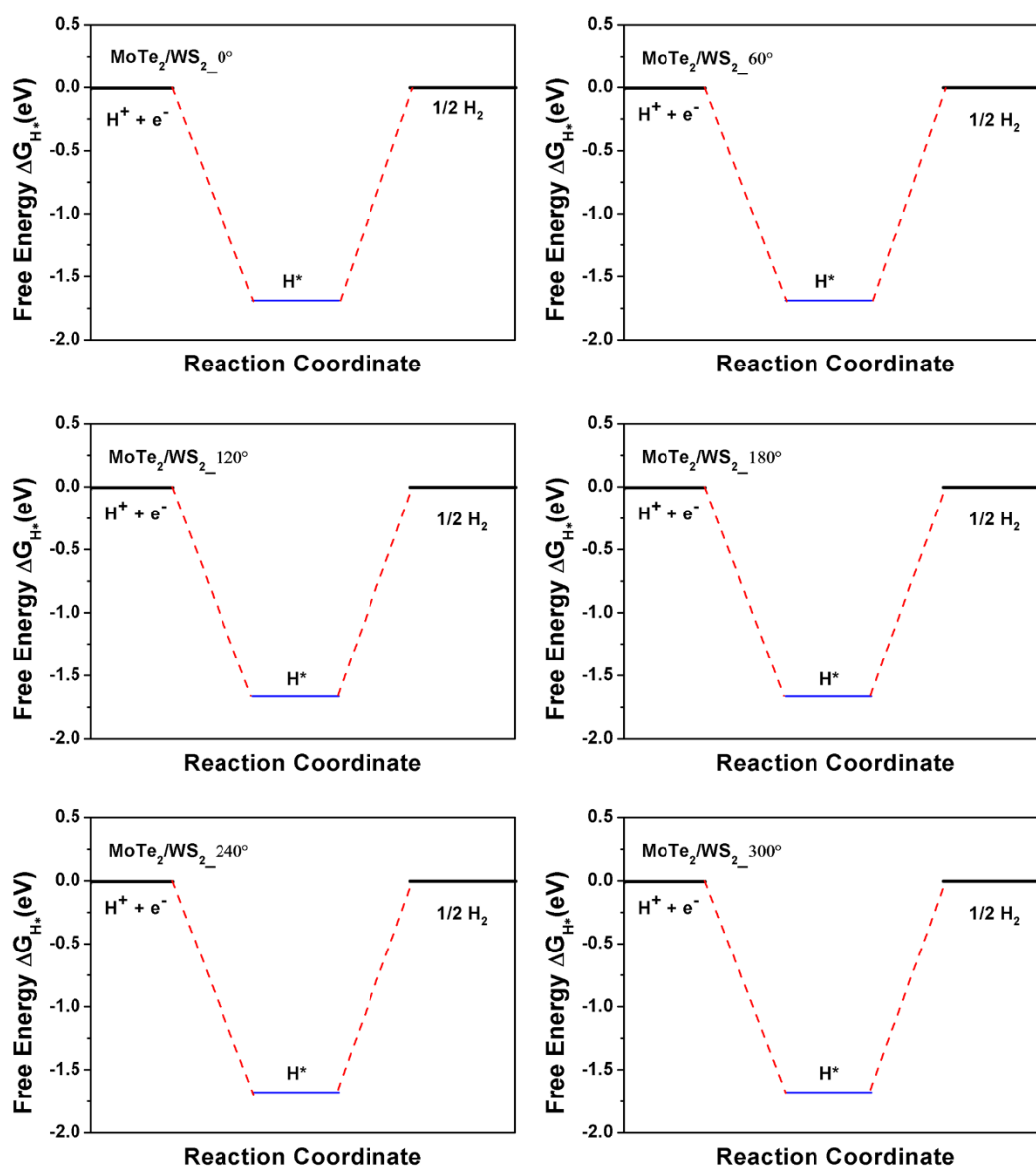


Figure S17. Free-energy diagram for HER of MoTe₂/WS₂ at zero electrode potential.

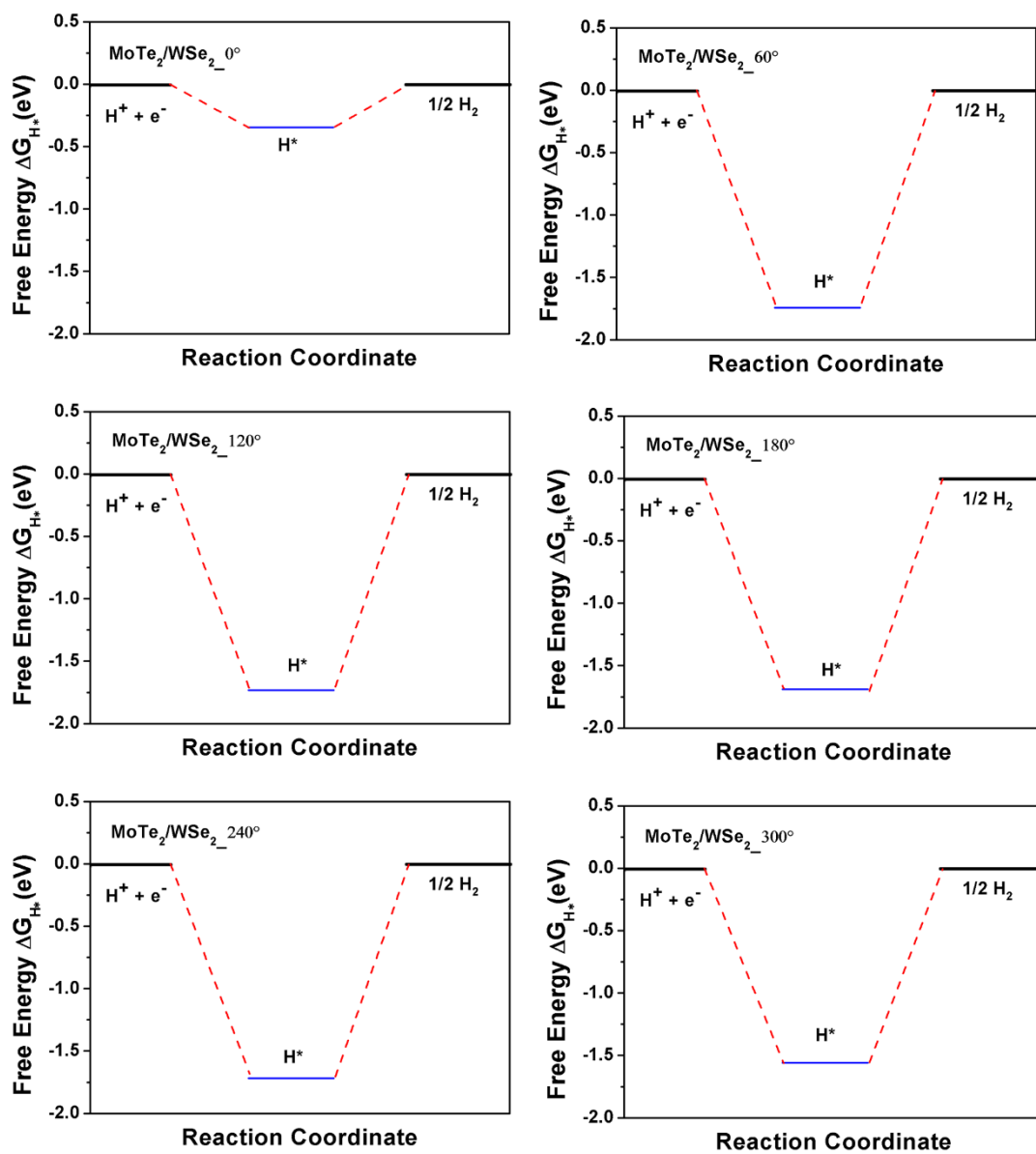


Figure S18. Free-energy diagram for HER of MoTe₂/WSe₂ at zero electrode potential.

Supplementary Tables

Table S1. The correction for free energy of the gas phase material and adsorbates, including corrections for entropy and enthalpy.

Species	E	TS	E _{ZPE}
	(eV)	(eV) (298 K)	(eV)
H ₂	-6.86	/	/
H ₂ O	-13.71	/	/
H*	/	/	0.205
O*	/	/	0.08
OH*	/	/	0.338
OOH*	/	/	0.398

Table S2. The binding energy (eV) of different structures with different rotating angles.

Structure Angle (°)	MoS₂ /WS₂ (eV)	MoSe₂ /WSe₂ (eV)	MoS₂ /WSe₂ (eV)	MoSe₂ /WS₂ (eV)	MoTe₂ /WT₂ (eV)	MoS₂ /WTe₂ (eV)	MoTe₂ /WS₂ (eV)	MoTe₂ /WSe₂ (eV)
0	-1.77	-2.29	-2.32	-2.07	-4.41	-2.85	-2.79	-3.01
60	-2.00	-2.49	-2.25	-2.29	-3.41	-2.73	-2.68	-2.90
120	-2.12	-2.59	-2.34	-2.39	-3.52	-2.86	-2.79	-3.02
180	-2.25	-2.74	-2.49	-2.54	-3.78	-3.10	-3.03	-3.26
240	-2.17	-2.66	-2.42	-2.43	-3.60	-2.98	-2.83	-3.09
300	-2.25	-2.66	-2.40	-2.18	-4.46	-3.02	-3.01	-3.22

Table S3. Adsorption free energies of *OH, *O, *OOH and *H (eV) of MoS₂/ WS₂.

Angle/°	ΔG_{*OH} (eV)	ΔG_{*O} (eV)	ΔG_{*OOH} (eV)	ΔG_{*H} (eV)
0	1.67	0.96	3.17	-0.20
60	1.94	1.22	3.80	-0.29
120	2.09	1.32	3.08	-0.22
180	2.08	1.32	3.20	-0.22
240	1.94	1.25	3.23	-0.25
300	2.08	1.31	3.22	-0.30

Table S4. Adsorption free energies of *OH, *O, *OOH and *H (eV) of MoSe₂/WSe₂.

Angle/ ^o	ΔG_{*OH} (eV)	ΔG_{*O} (eV)	ΔG_{*OOH} (eV)	ΔG_{*H} (eV)
0	2.07	1.31	3.09	-0.22
60	1.98	1.31	3.33	-0.23
120	2.00	1.31	4.06	-0.22
180	1.99	1.31	3.75	-0.25
240	1.94	1.30	3.32	-0.26
300	1.94	1.24	3.30	-0.25

Table S5. Adsorption free energies of *OH, *O, *OOH and *H (eV) of MoS₂/WSe₂.

Angle/ ^o	ΔG_{*OH} (eV)	ΔG_{*O} (eV)	ΔG_{*OOH} (eV)	ΔG_{*H} (eV)
0	1.47	1.91	3.83	-0.15
60	2.04	2.23	4.03	0.09
120	1.93	2.24	3.98	0.10
180	1.91	2.24	4.07	0.09
240	1.87	2.23	4.01	0.07
300	1.63	1.86	3.61	-0.19

Table S6. Adsorption free energies of *OH, *O, *OOH and *H (eV) of MoSe₂/WS₂.

Angle/ ^o	ΔG_{*OH} (eV)	ΔG_{*O} (eV)	ΔG_{*OOH} (eV)	ΔG_{*H} (eV)
0	1.62	1.93	3.68	-0.17
60	1.90	2.23	4.55	0.10
120	2.03	2.23	4.81	0.10
180	1.95	2.21	3.95	-0.11
240	2.43	2.22	3.98	-0.01
300	1.80	2.12	3.91	-0.03

Table S7. Adsorption free energies of *OH, *O, *OOH and *H (eV) of MoTe₂/WTe₂.

Angle/°	ΔG_{*OH} (eV)	ΔG_{*O} (eV)	ΔG_{*OOH} (eV)	ΔG_{*H} (eV)
0	1.12	2.18	3.53	-1.54
60	0.15	0.95	2.45	0.58
120	0.29	0.68	2.65	-1.97
180	0.92	1.48	2.81	-1.89
240	0.34	1.22	2.70	-0.48
300	1.08	2.15	3.51	-0.03

Table S8. Adsorption free energies of *OH, *O, *OOH and *H (eV) of MoS₂/WTe₂.

Angle/ ^o	ΔG_{*OH} (eV)	ΔG_{*O} (eV)	ΔG_{*OOH} (eV)	ΔG_{*H} (eV)
0	1.77	1.22	2.19	-1.52
60	1.92	1.26	2.45	-1.52
120	1.54	1.26	2.02	-1.51
180	1.82	1.26	2.24	-1.51
240	1.80	1.25	3.98	-1.52
300	1.80	1.26	2.24	-1.51

Table S9. Adsorption free energies of *OH, *O, *OOH and *H (eV) of MoTe₂/WS₂.

Angle/ ^o	ΔG_{*OH} (eV)	ΔG_{*O} (eV)	ΔG_{*OOH} (eV)	ΔG_{*H} (eV)
0	0.76	1.25	3.27	-1.71
60	0.96	1.51	3.36	-1.71
120	0.82	1.27	3.30	-1.70
180	0.96	1.53	3.45	-1.66
240	0.88	1.26	3.36	-1.70
300	0.94	1.51	3.43	-1.67

Table S10. Adsorption free energies of *OH, *O, *OOH and *H (eV) of MoTe₂/WSe₂.

Angle/ ^o	ΔG_{OH^*} (eV)	ΔG_{O^*} (eV)	ΔG_{OOH^*} (eV)	ΔG_{H^*} (eV)
0	0.92	1.48	3.25	-0.34
60	0.95	1.20	3.28	-1.72
120	0.87	1.26	3.33	-1.71
180	0.96	1.52	3.39	-1.68
240	0.85	1.25	3.33	-1.71
300	0.92	1.50	3.43	-1.54

Supplementary References

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