Electronic supplementary information

Design of high-performance MoS_2 edge supported single-metal atom bifunctional catalyst for overall water splitting via simple equation

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1. The definition of chemical bond energy, H and S coverage:

(1) The chemical bond energy (ΔE_B) between H and the catalysts are defined as

$$\Delta E_B = E_{H^*} - E_{H^{*-H}} - \frac{1}{2} E_{H_2} \quad (1)$$

where E_{H^*} is the total energy of the stripe models with the adsorption of H on the active site. $E_{H^*\text{-}H}$ is the single point energy of H adsorption model with H removed. And E_{H_2} is the total energy of H_2 molecules in free gas phase.

(2) The coverage of H atoms is defined as

$$\theta_H(ML) = nH / (edge\ length) \quad (2)$$

So, the H coverage in the present work is 25% (0.25) ML.

(3) The coverage of S atoms is defined as

$$\theta_S(ML) = nS / (2 \times edge\ length) \quad (3)$$

So, the S coverage in T2 termination is 50% (4/(2x4)) ML.

2. Figure Captions

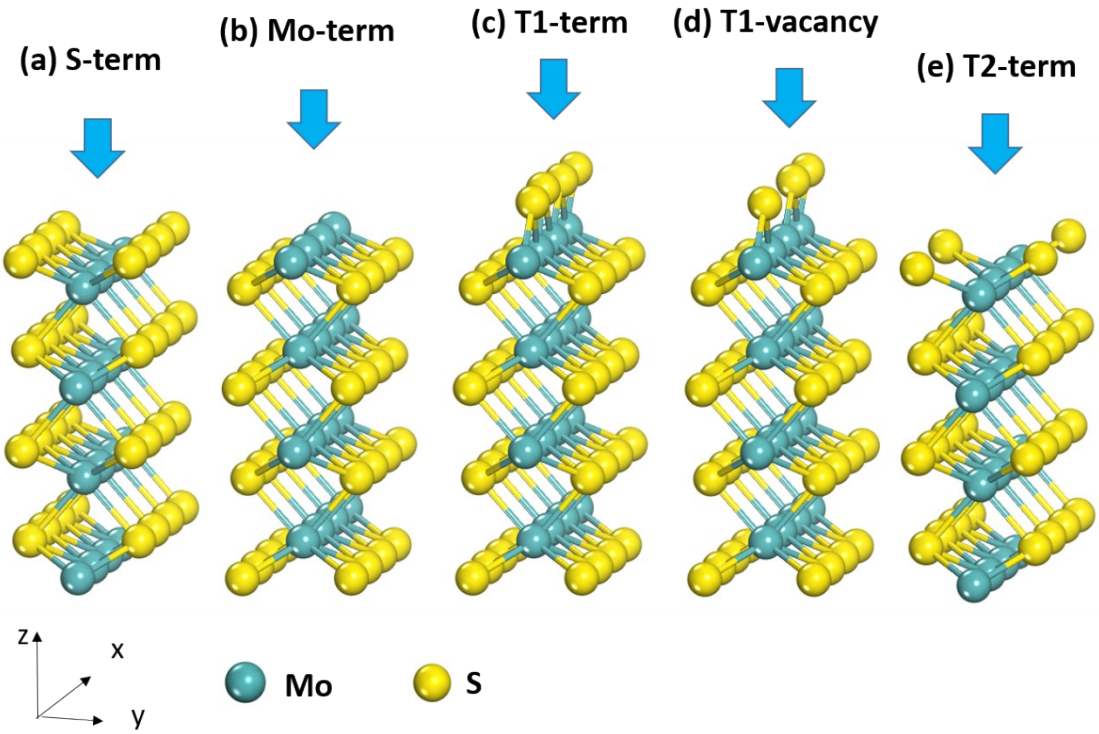

Figure S1 The crystal structure of hexagonal MoS_2 edges with (a) S termination, (b) Mo termination, (c) T1 termination: 50% sulfur addition at the initial Mo termination, (d) T1 vacancy termination: 37.5% surface sulfur coverage and (e) T2 termination: 50% sulfur removal at the S termination.

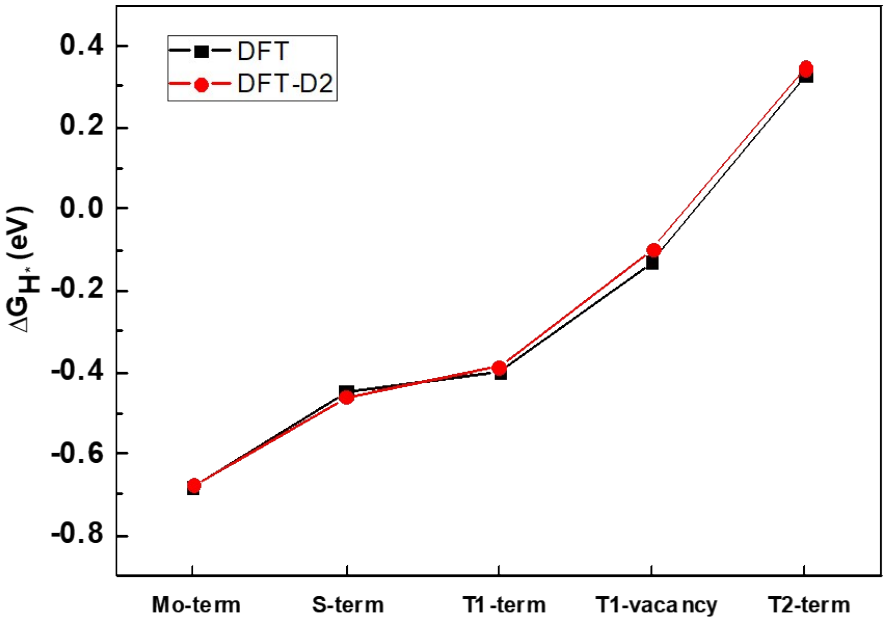

Figure S2 The comparison of calculated ΔG_{H^*} of different MoS_2 edges by using DFT method with and without D2 correction.

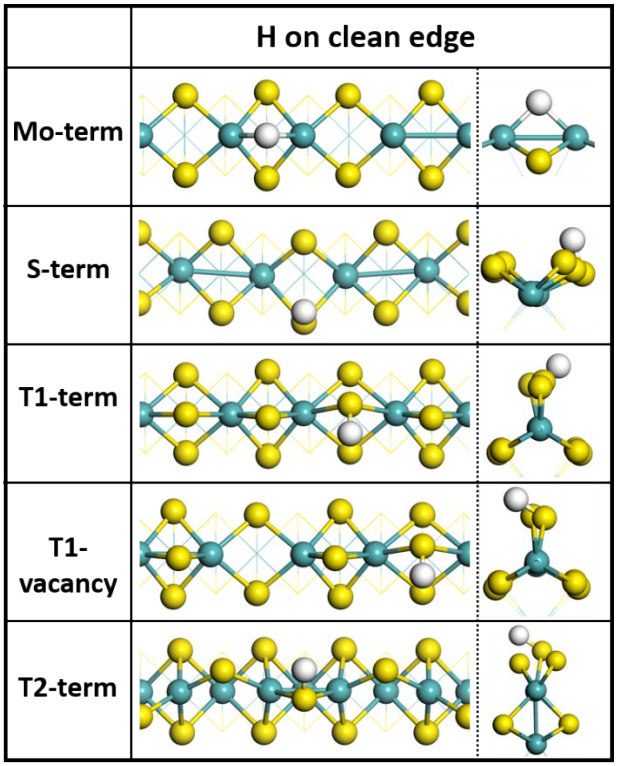

Figure S3 The favorable H* adsorption configurations on clean MoS_2 edges. The figure on the left side of the dashed line is top view, and the figure on the right side of the dashed line is side view.

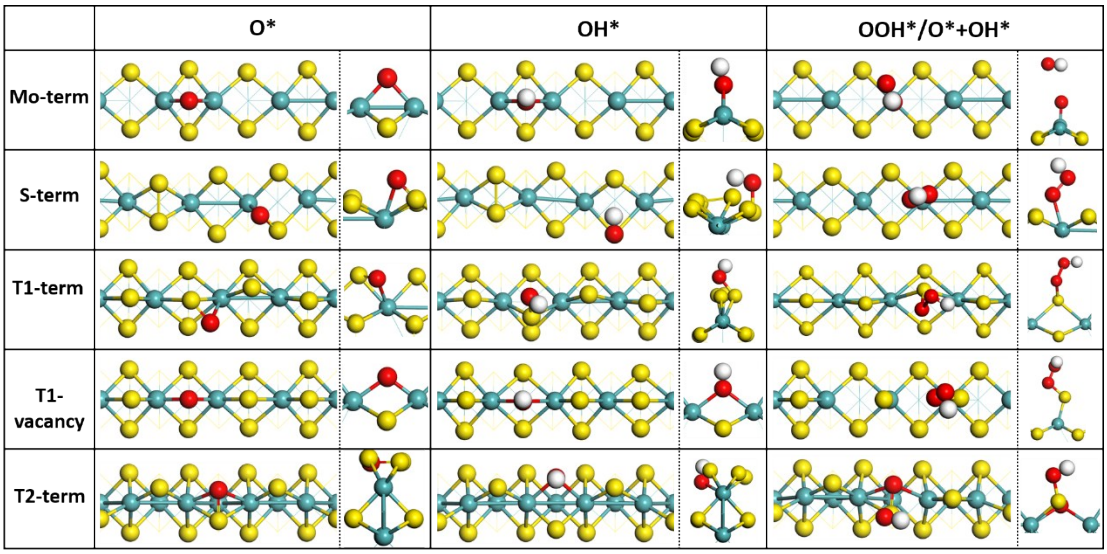

Figure S4 The O*, OH* and OOH* adsorption configurations on different MoS_2 edges. The figure on the left side of the dashed line is top view, and the figure on the right side of the dashed line is side view.

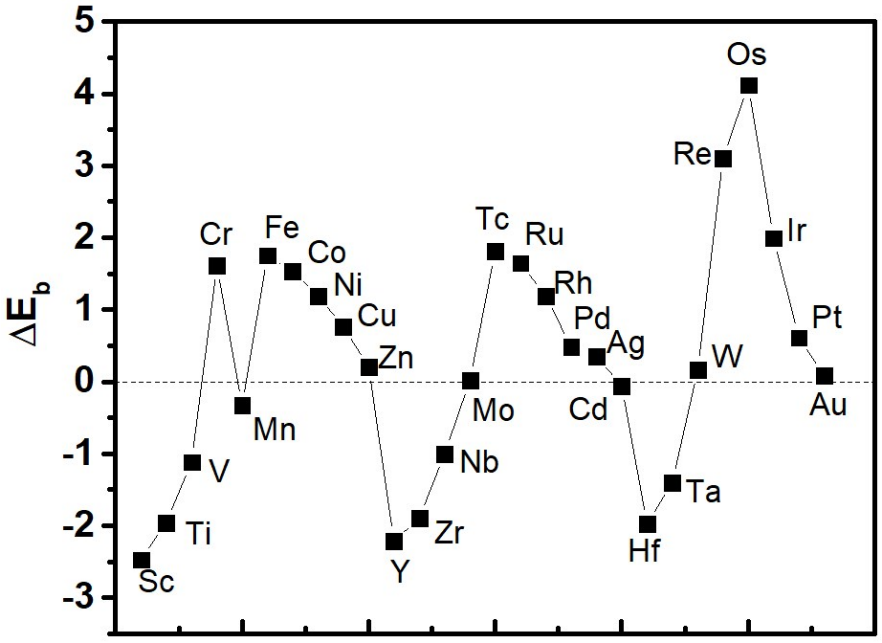

Figure S5 the energy difference between them $\Delta E_b = E_b - E_{coh}$.

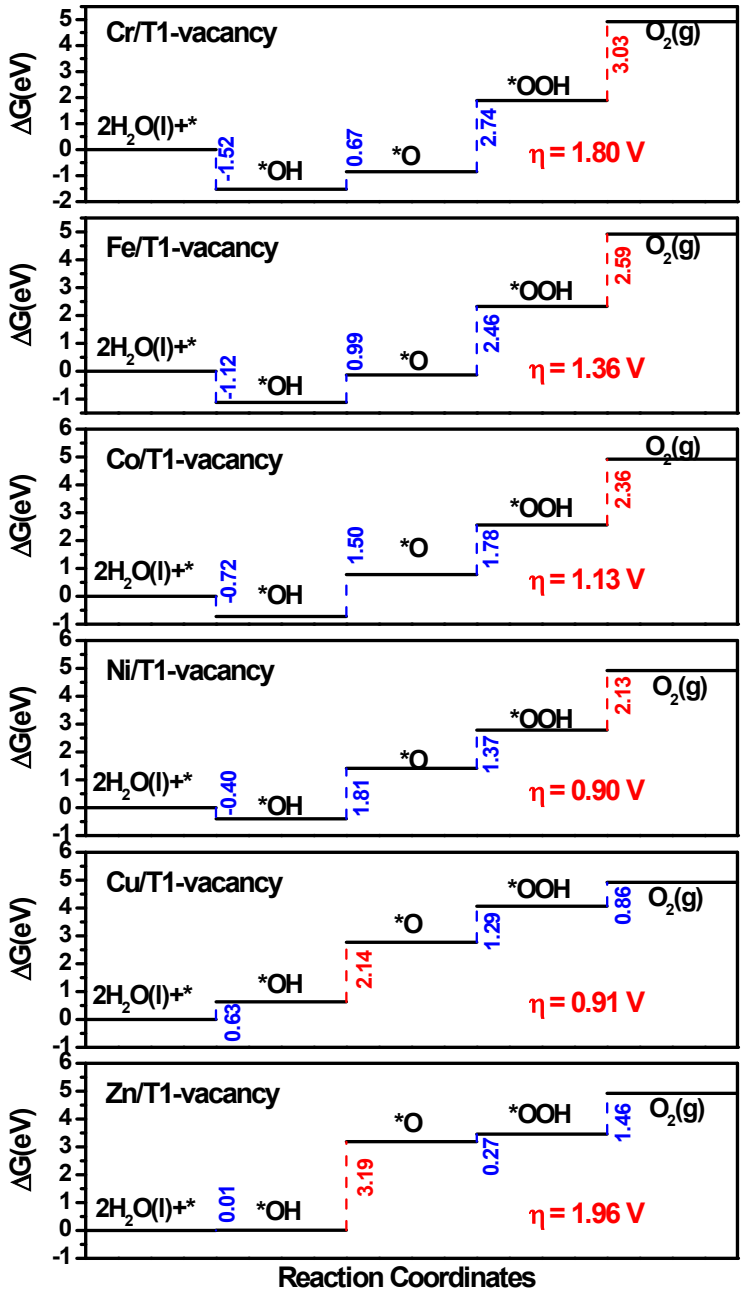

Figure S6 Free energy diagram for 3d single TM atom doped T1-vacancy term for OER, where the elementary reaction with ΔG in red shows the potential-determining step.

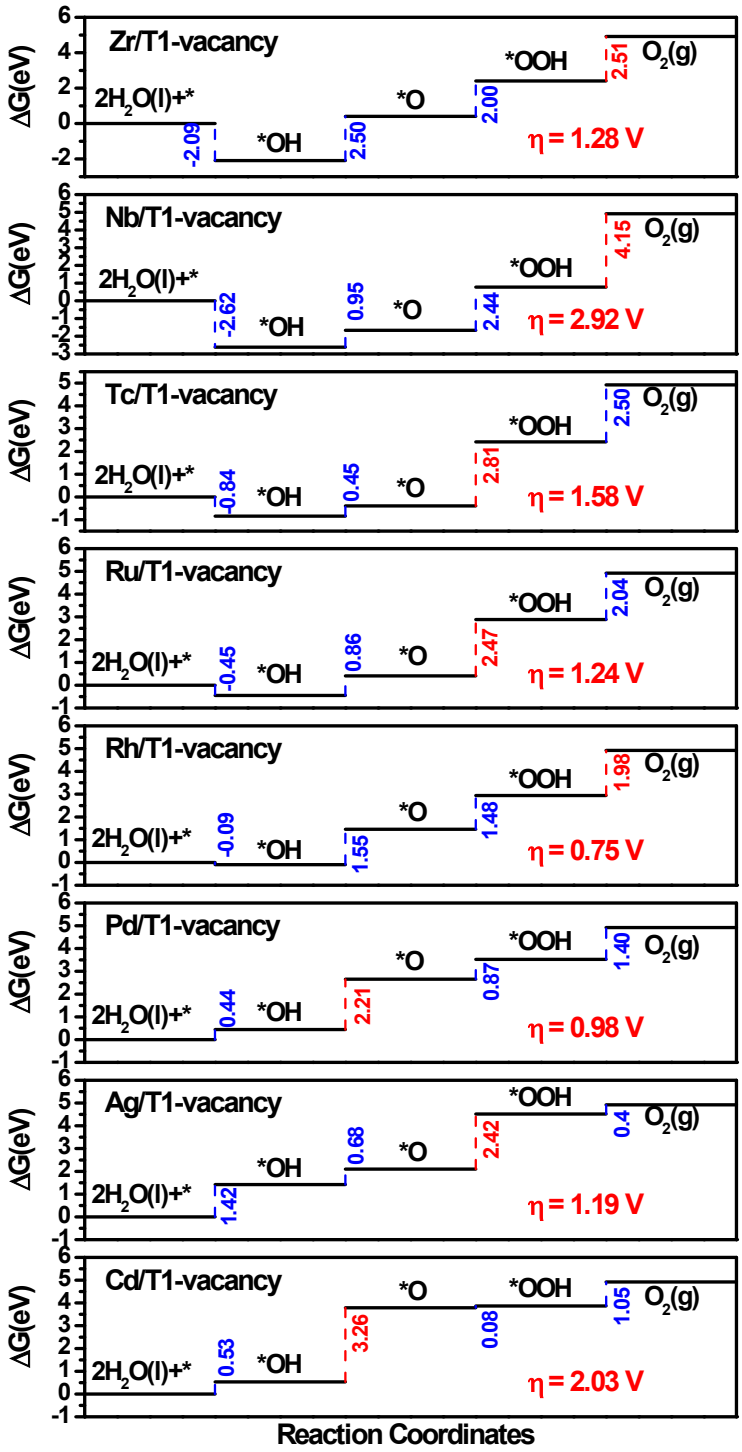

Figure S7 Free energy diagram for 4d single TM atom doped T1-vacancy term for OER, where the elementary reaction with ΔG in red shows the potential-determining step.

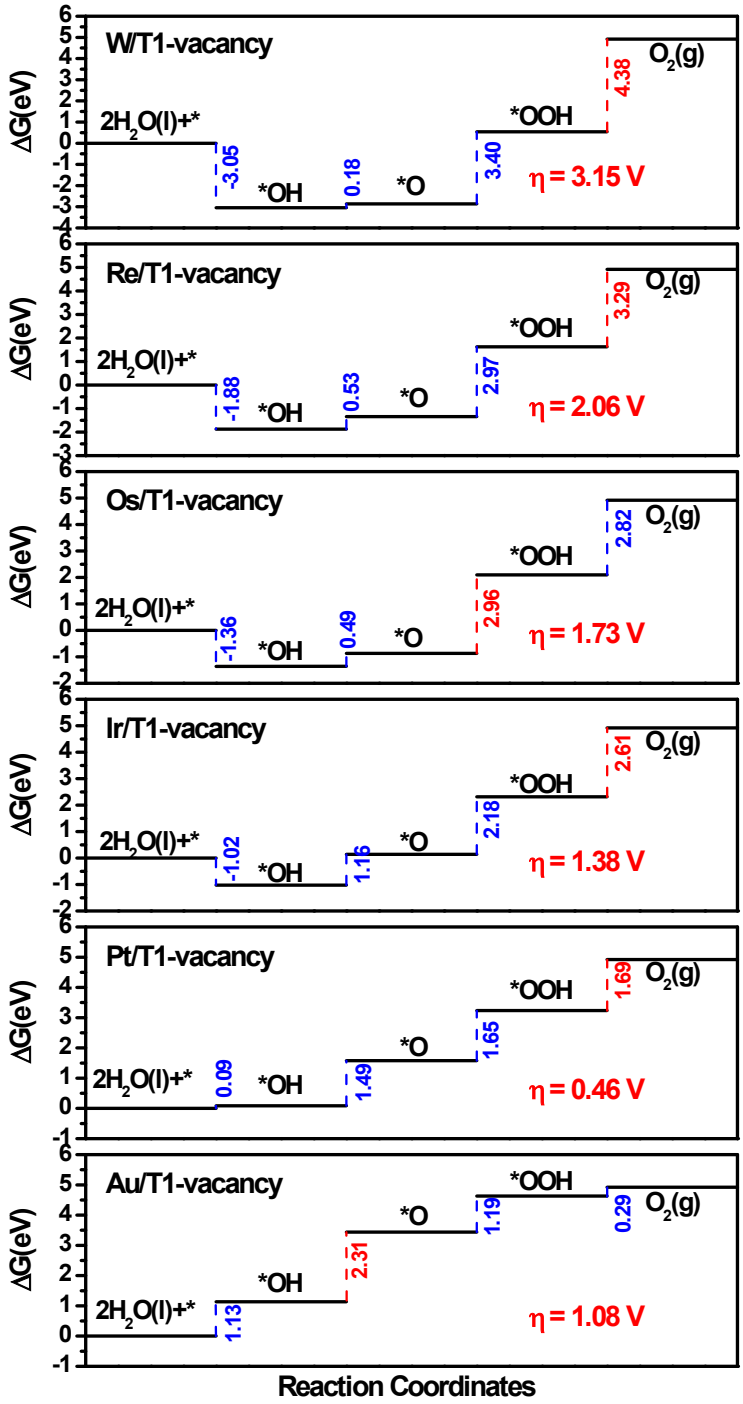

Figure S8 Free energy diagram for 5d single TM atom doped T1-vacancy term for OER, where the elementary reaction with ΔG in red shows the potential-determining step.

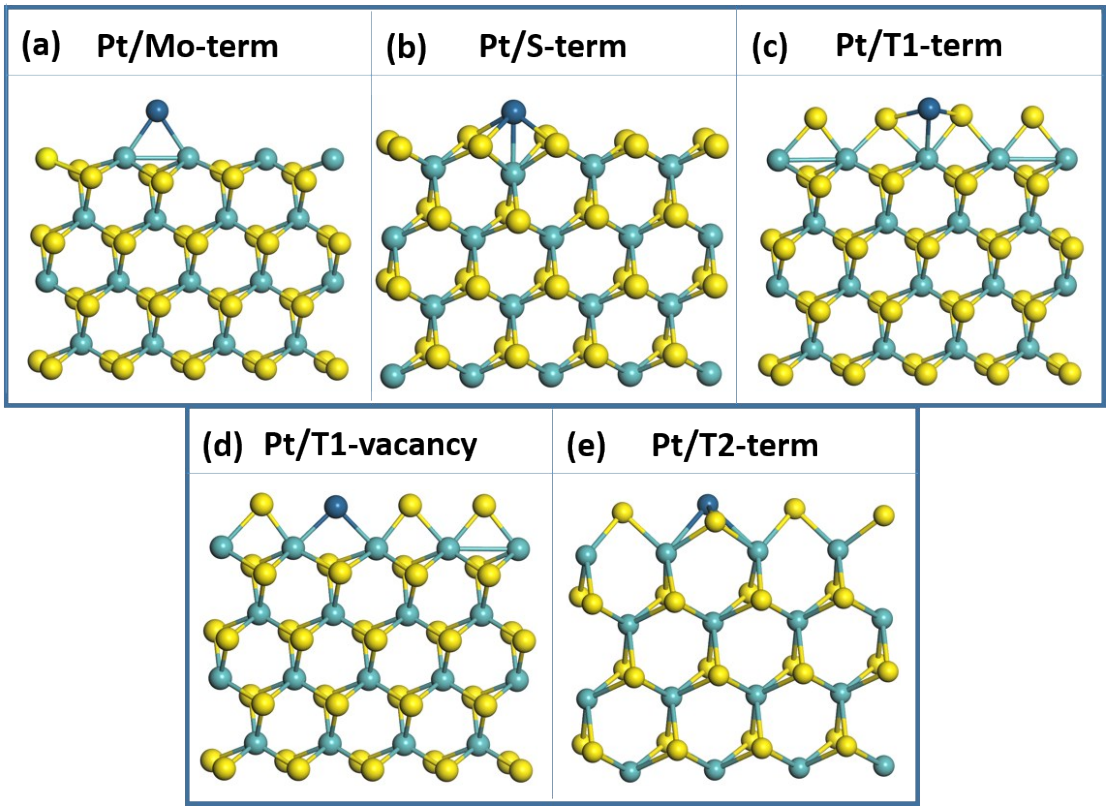

Figure S9 The crystal structure of (a) Pt/Mo-term, (b) Pt/S-term, (c)Pt/T1-term, (d)Pt/T1-vacancy and (e)Pt/T2-term.

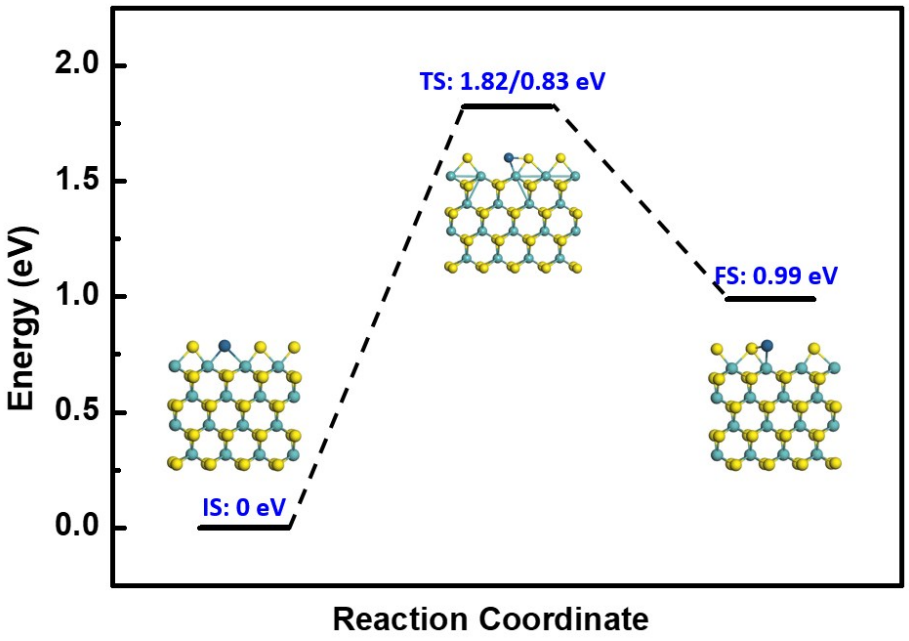

Figure S10 diffusion barrier of Pt on T1-vacancy.

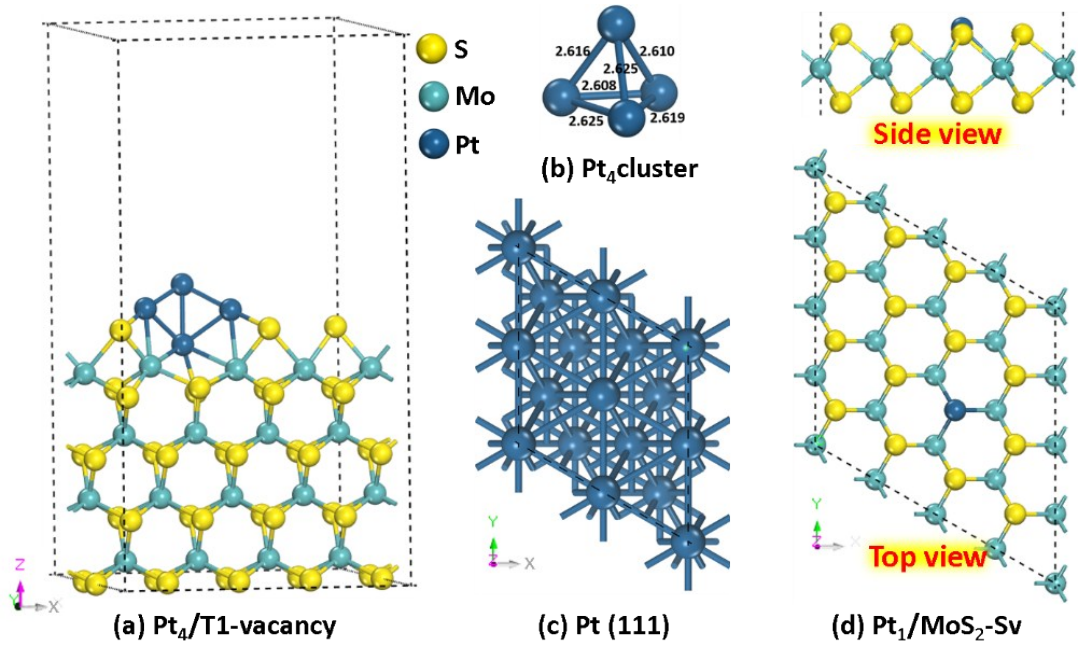

Figure S11 (a) The most stable crystal structure of Pt_4/1T-vacancy with Pt_4 cluster doped on 1T-vacancy. (b) The energetically favorable Pt_4 cluster. The numbers show the bond length of Pt_4 cluster. (c) the top view of Pt (111) slab. (d) the side and top view of Pt_1/MoS_2-Sv.

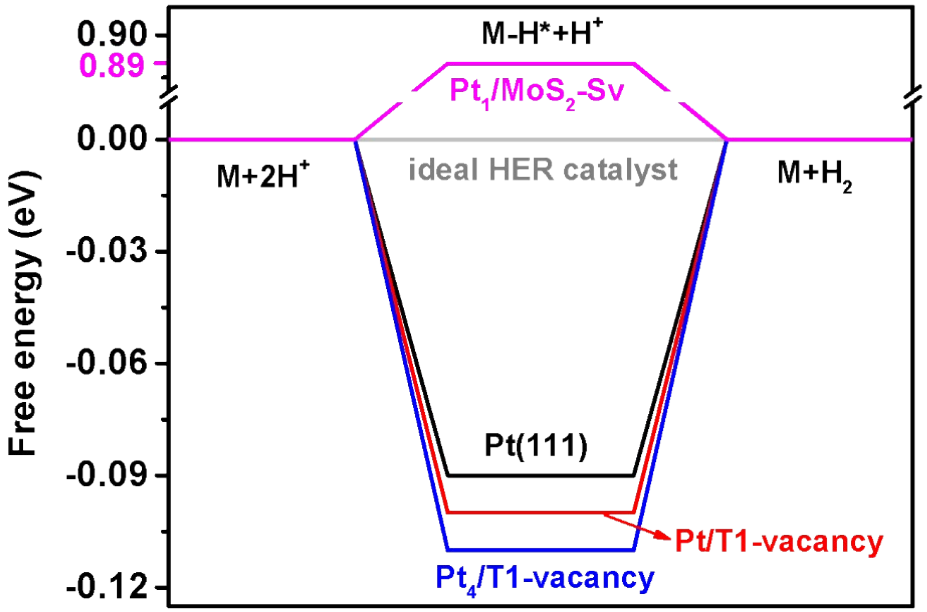

Figure S12 Free energy diagram for HER on ideal electrocatalyst, Pt(111), Pt/T1-vacancy, Pt4/T1-vacancy and Pt_1/MoS_2-Sv at zero electrode.

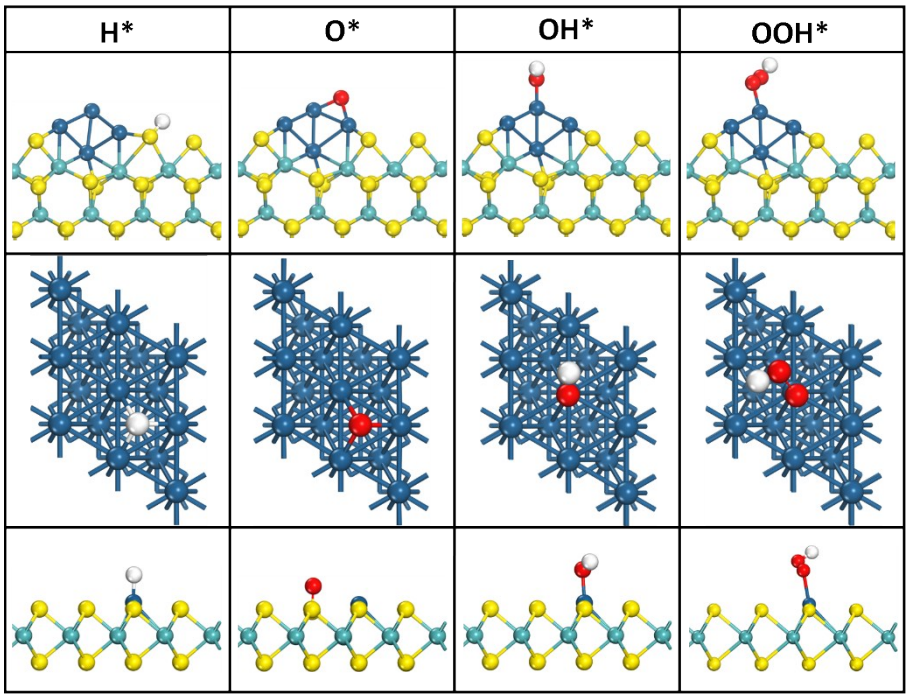

Figure S13 The favorable H*, O*, OH* and OOH* adsorption configurations on Pt_4/1T-vacancy term, Pt (111) surface and Pt_1/MoS_2-Sv surface.

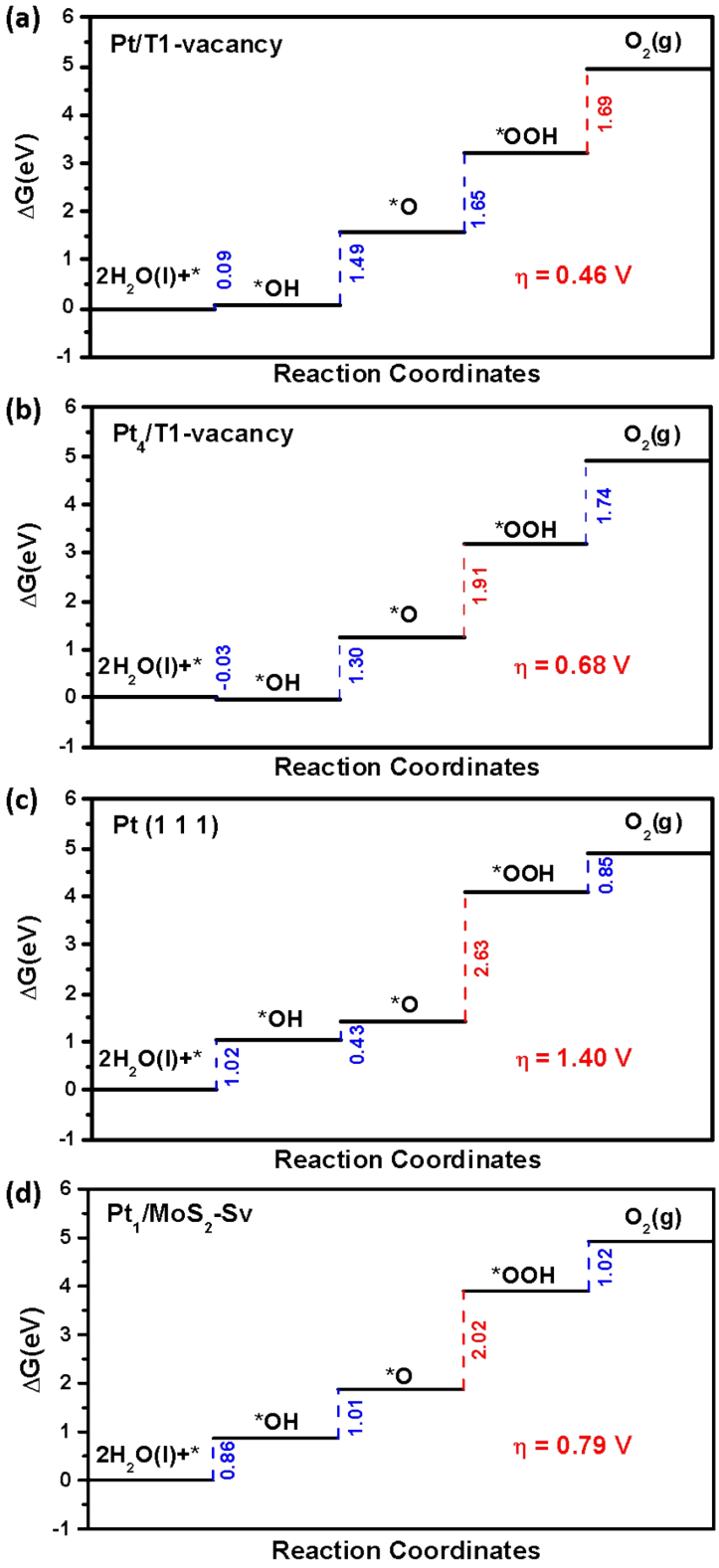

Figure S14 Free energy diagram for OER on (a) Pt/T1-vacancy, (b) Pt_4/T1-vacancy, (c) Pt (111) surface and (d) Pt_1/MoS_2-Sv, where the elementary reaction with ΔG in red shows the potential-determining step.

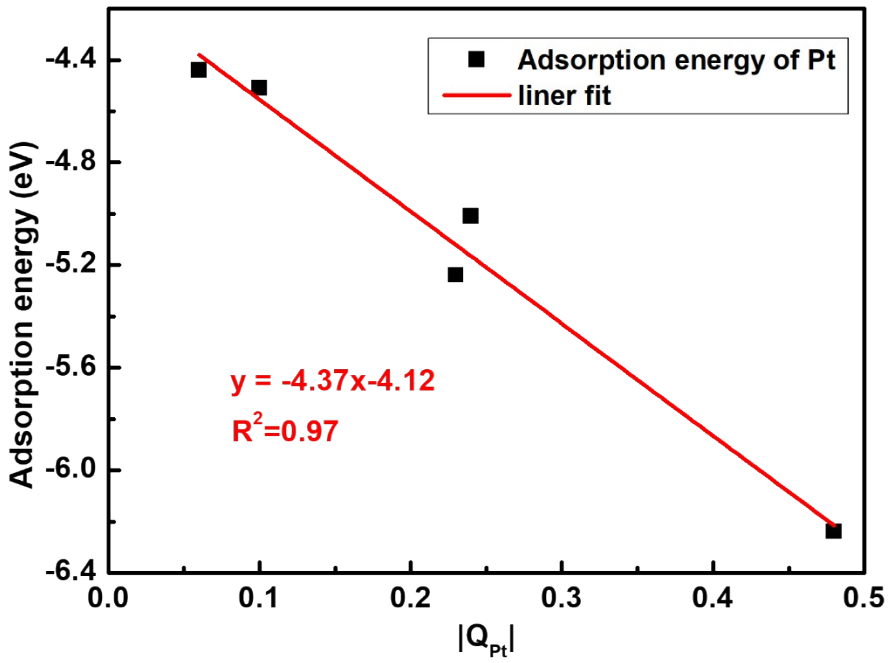

Figure S15 The adsorption energy as a function of the $|Q_{Pt}|$ (the electron accumulation and depletion of Pt atom). The red line is achieved by linear fitting.

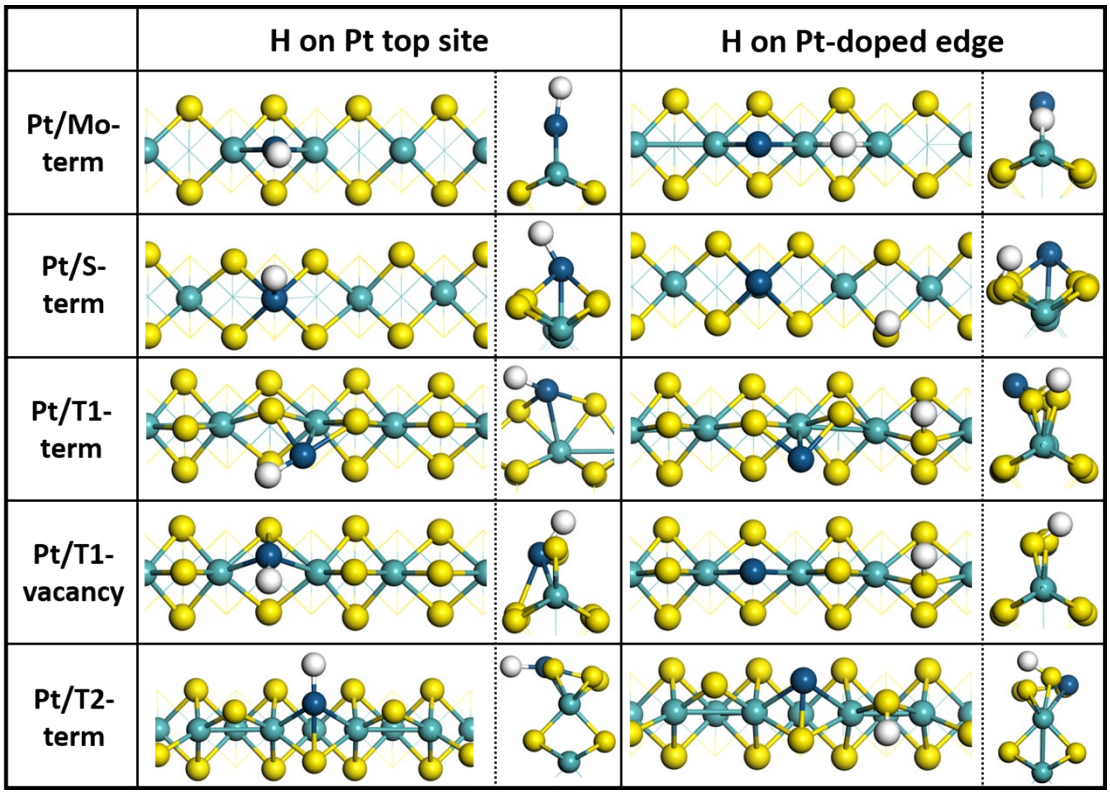

Figure S16 The favorable H* adsorption configurations on Pt/MoS_2 edges with H adsorbed on Pt and edge. The figure on the left side of the dashed line is top view, and the figure on the right side of the dashed line is side view.

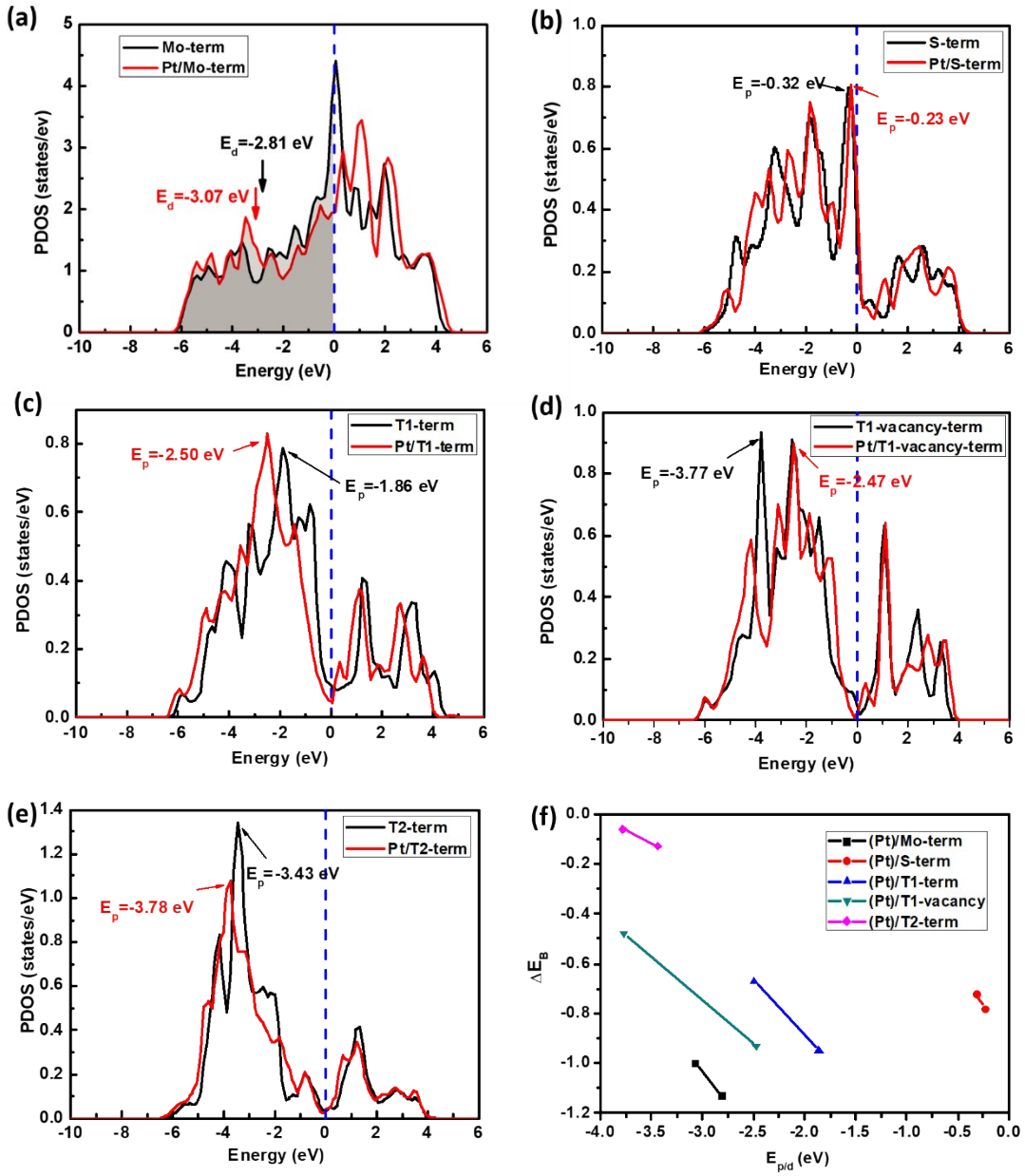

Figure S17 (a) The projected density of states plots of 4d orbitals for Mo atoms around the H atom on Mo-term and Pt/Mo-term. The shaded area corresponds to the filled states up to the Fermi level. (b), (c), (d) and (e) The p-projected DOS of S atom neighboring H atom on (b) S-term and Pt/S-term, (c) T1-term and Pt/T1-term, (d) T1-vacancy and Pt/T1-vacancy, and (e) T2-term and Pt/T2-term. The blue dash line represents the Fermi level. (f) The d-band center(Ed) or the position of 2p orbit peak (Ep) vs the chemical bond energy (ΔE_B) between H and S/Mo on MoS_2 and Pt/MoS_2 edge

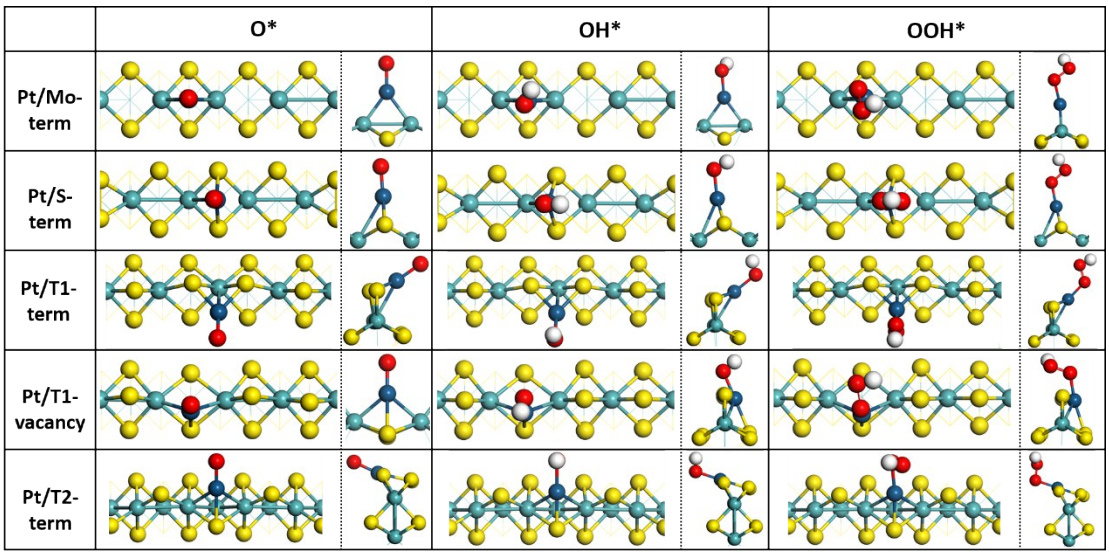

Figure S18 The favorable O*, OH* and OOH*/O*+OH* adsorption configurations on different Pt/MoS_2 edges. The figure on the left side of the dashed line is top view, and the figure on the right side of the dashed line is side view.

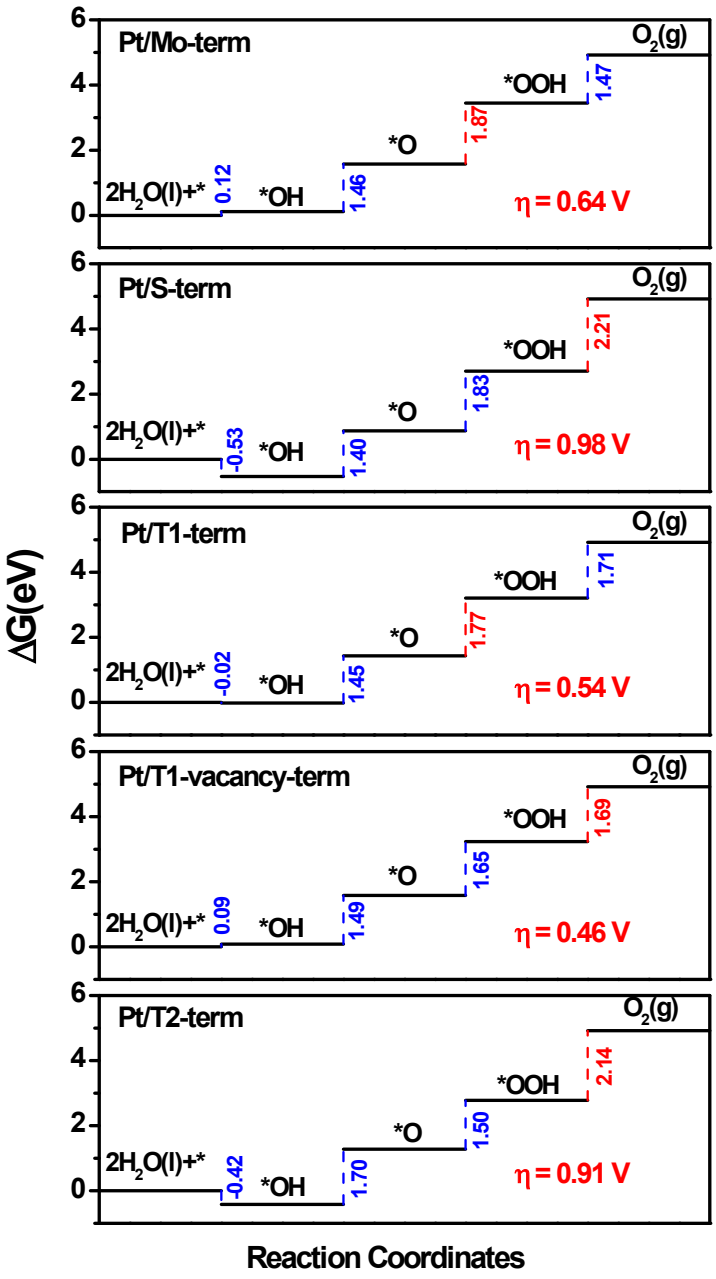

Figure S19 Free energy diagram for Pt doped MoS_2 terminations for OER, where the elementary reaction with ΔG in red shows the potential-determining step.

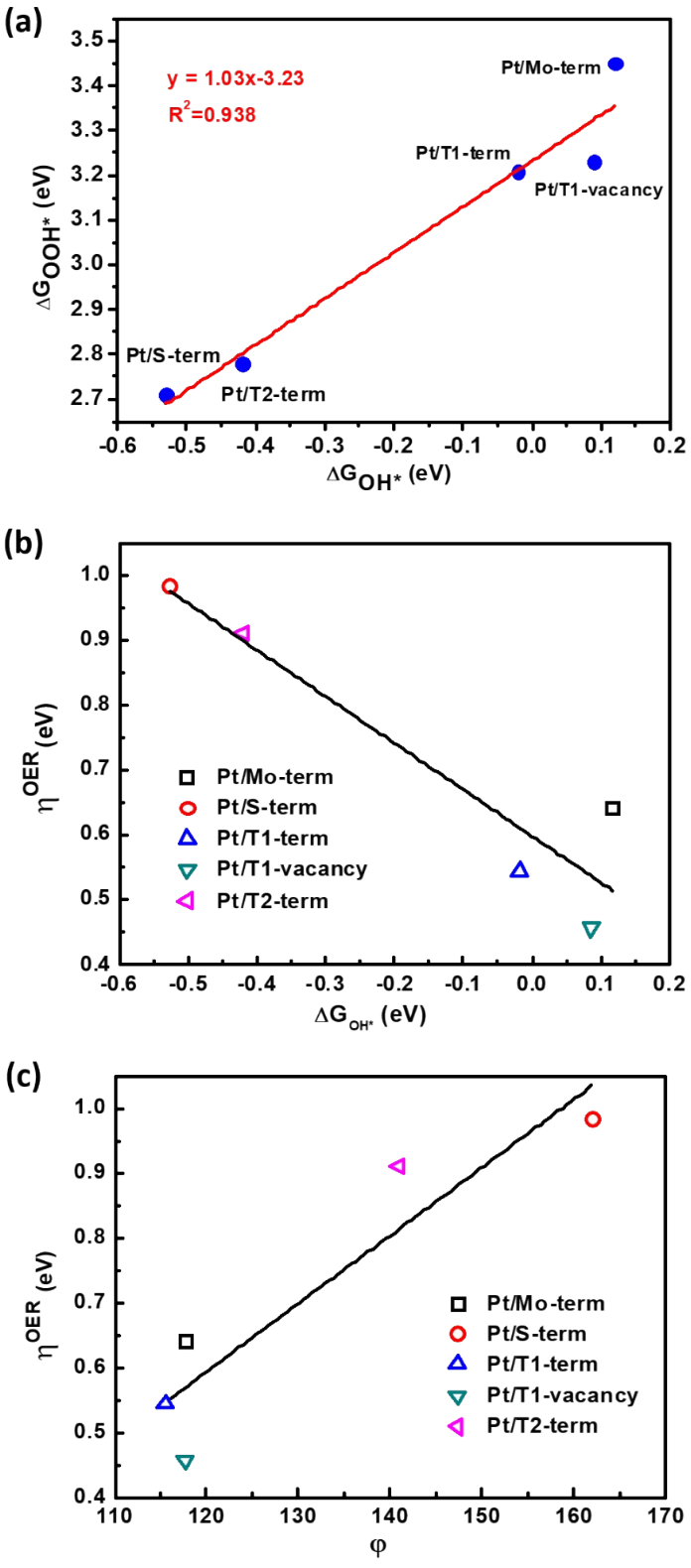

Figure S20 The linear relationship between(a) ΔG_{OH^*} and ΔG_{OOH^*}, (b) ΔG_{OH^*} and the Over potential (η^{OER}), and (c) η^{OER} and structure descriptor (φ) in different Pt/MoS_2 systems.

3. Table Captions

Table S1 The zero point energy (ZPE) of H adsorbed on the clean and Pt doped MoS_2 terminations with the H bonding with S, Mo, or Pt.

Structure	ZPE	structure	$ZPE_{H\text{-}edge}$	$ZPE_{H\text{-}Pt}$
Mo-term	0.174	Pt/Mo-term	0.176	0.159
S-term	0.232	Pt/S-term	0.238	0.171
T1-term	0.225	Pt/T1-term	0.228	0.204
T1-vacancy	0.223	Pt/T1-vacancy	0.227	0.212
T2-term	0.223	Pt/T2-term	0.227	0.199

Table S2 The *Z*PE values of H adsorption used in the previous literatures and our present work.

Species	ZPE[1]	ZPE[2]	ZPE[3]	ZPE[4-6]	ZPE[g]
H*	0.16	0.14~0.19	0.3	0.17	0.20

[g]The present work, the average value of ZPE of H adasorption listed in Table S1.

Table S3 The zero point energy (ZPE) of O*, OH* and OOH* adsorbed on the clean and Pt doped MoS_2 terminations.

Structure	O*	OH*	OOH*
Mo-term	0.07	0.34	-
S-term	0.08	0.37	0.44
T1-term	0.08	0.36	0.44
T1-vacancy	0.07	0.36	0.44
T2-term	0.07	0.38	-
Pt/Mo-term	0.06	0.33	0.44
Pt/S-term	0.06	0.35	0.45

Pt/T1-term	0.06	0.36	0.45
Pt/T1-vacancy	0.06	0.35	0.45
Pt/T2-term	0.06	0.35	0.44

Table S4 The *Z*PE values of the adsorbents used in the previous literatures and our present work.

Species	ZPE[7]	ZPE[8]	ZPE[9]	ZPE[10]	ZPE[11]	ZPE[12]	ZPE[g]
O*	0.07	0.05	0.084	0.05	0.07	0.07	0.07
OH*	0.36	0.36	0.386	0.35	0.36	0.33	0.36
OOH*	0.39	0.40	0.457	0.41	-	0.43	0.44
O_2	-	0.11	-	-	0.10	-	-
H_2	0.27	0.27	0.27	0.27	0.27	0.27	0.27
H_2O	0.56	0.56	0.56	0.56	0.56	0.57	0.56

[g]The present work, the average value of ZPE of various species listed in Table S3.

Table S5 The calculated binding energy (E_b) of various single metal atoms on 1T-vacancy. Cohesive energy (E_{coh}) of different metal as well as the energy difference between E_{ads} and E_{coh} (ΔE_b).

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
E_b	-6.61	-7.22	-6.44	-2.41	-4.28	-3.23	-3.63	-3.61	-2.73	-0.90
E_{coh}	-4.13	-5.27	-5.32	-4.03	-3.95	-4.99	-5.13	-4.80	-3.49	-1.10
ΔE_b	-2.47	-1.96	-1.12	1.61	-0.33	1.75	1.50	1.19	0.77	0.20
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
E_b	-6.36	-8.15	-7.92	-6.22	-5.19	-5.04	-4.50	-3.15	-2.13	-0.79
E_{coh}	-4.16	-6.25	-6.92	-6.24	-7.00	-6.69	-5.69	-3.63	-2.49	-0.73
ΔE_b	-2.21	-1.90	-1.00	0.02	1.81	1.65	1.19	0.48	0.36	-0.06
		Hf	Ta	W	Re	Os	Ir	Pt	Au	

E_b	-8.45	-9.73	-8.31	-4.71	-5.37	-5.24	-4.84	-2.90
E_{coh}	-6.48	-8.34	-8.48	-7.82	-9.49	-7.23	-5.45	-2.99
ΔE_b	-1.98	-1.40	0.16	3.10	4.12	1.99	0.61	0.09

E_b is binding energy of single atom on 1T-vacancy term, which is calculated by $E_b=E_{edge+M}-E_{edg}-E_M$, where the E_{edge+M}, E_{edge} and E_M are the energies of single atom doped on 1T-vacancy, pure 1T-vacancy and metal atoms;

E_{coh} is the cohesive energy of metals, which is calculated by, $E_{coh}= (E_{M(bulk)}-E_M)/n$, where the $E_{M(bulk)}$ is the energy of metal crystal and n is the number of metal atoms in the crystal;

ΔE_b is the energy difference between E_b and $E_{coh.}$

Table S6 Adsorption energies of H* (ΔE_{H*}, eV), bond length of sulfur-hydrogen (d(S-H), Å) on TM/T1-vacancy terminations.

Single TM atom	ΔE_{H*}	d(S-H)
Sc	0.44	1.357
Ti	0.49	1.361
V	0.39	1.367
Cr	-0.26	1.356
Mn	0.19	1.360
Fe	-0.43	1.404
Co	-0.38	1.356
Ni	-0.52	1.359
Cu	-0.48	1.359
Zn	-0.06	1.358
Y	0.13	1.356
Zr	-0.13	1.360
Nb	-0.41	1.359
Mo	0.48	1.357

Tc	-0.30	1.357
Ru	-0.38	1.358
Rh	-0.04	1.358
Pd	-0.42	1.357
Ag	-0.46	1.359
Cd	-0.04	1.357
Hf	0.55	1.360
Ta	0.36	1.361
W	-0.19	1.362
Re	-0.36	1.358
Os	-0.28	1.357
Ir	-0.52	1.357
Pt	-0.37	1.358
Au	-0.16	1.357

Table S7 Adsorption energies of O* (ΔE_{O*}, eV), bond length of metal-oxygen (d(M-O), Å) on TM/T1-vacancy terminations.

Single TM atom	ΔE_{O*}	d(M-O)
Sc	--	--
Ti	--	--
V	--	--
Cr	-0.89	1.592
Mn	--	--
Fe	-0.17	1.589
Co	0.74	1.606
Ni	1.37	1.622
Cu	2.73	1.678
Zn	3.15	1.771

Y	--	--
Zr	0.37	1.821
Nb	-1.71	1.752
Mo	--	--
Tc	-0.44	1.700
Ru	0.37	1.710
Rh	1.42	1.755
Pd	2.61	1.807
Ag	4.89	2.12
Cd	3.75	2.002
Hf	--	--
Ta	--	--
W	-2.90	1.738
Re	-1.38	1.727
Os	-0.91	1.724
Ir	0.10	1.737
Pt	1.54	1.781
Au	3.40	1.845

Table S8 Adsorption energies of OH* (ΔE_{OH*}, eV), bond length of metal-oxygen (d(M-O), Å) and oxygen -hydrogen (d(O-H), Å) on TM/T1-vacancy terminations.

Single TM atom	ΔE_{OH*}	d(M-O)	d(O-H)
Sc	--	--	--
Ti	--	--	--
V	--	--	--
Cr	-1.62	1.745	0.967
Mn	--	--	--
Fe	-1.22	1.759	0.973

Co	-0.82	1.733	0.975
Ni	-0.50	1.735	0.975
Cu	0.53	1.795	0.975
Zn	-0.10	1.814	0.945
Y	--	--	--
Zr	-2.19	1.962	0.967
Nb	-2.72	1.923	0.969
Mo	--	--	--
Tc	-0.94	1.869	0.979
Ru	-0.55	1.895	0.976
Rh	-0.19	1.927	0.980
Pd	0.34	1.937	0.977
Ag	1.32	2.049	0.975
Cd	0.43	2.035	0.974
Hf	--	--	--
Ta	--	--	--
W	-3.15	1.890	0.957
Re	-1.98	1.895	0.976
Os	-1.46	1.879	0.978
Ir	-1.12	1.898	0.977
Pt	-0.01	1.935	0.980
Au	1.03	2.022	0.972

Table S9 Adsorption energies of OOH* (ΔE_{OOH*}, eV), bond length of metal-oxygen (d(M-O), Å), oxygen - oxygen (d(O-O) and oxygen -hydrogen (d(O-H), Å) on TM/T1-vacancy terminations.

Single TM atom	**ΔE_{OOH*}**	**d(M-O)**	**d(O-O)**	**d(O-H)**
Sc	--	--	--	--

Ti	--	--	--	--
V	--	--	--	--
Cr	1.79	1.754	1.431	0.967
Mn	--	--	--	--
Fe	2.23	1.669	1.459	0.984
Co	2.46	1.710	1.464	0.982
Ni	2.69	1.757	1.470	0.983
Cu	3.96	1.876	1.429	0.982
Zn	3.36	1.881	1.453	0.980
Y	--	--	--	--
Zr	2.31	2.008	1.352	0.979
Nb	0.67	2.020	1.493	0.983
Mo	--	--	--	--
Tc	2.32	1.868	1.455	0.983
Ru	2.78	1.834	1.466	0.984
Rh	2.84	1.923	1.472	0.982
Pd	3.42	1.970	1.436	0.986
Ag	4.42	2.218	1.402	0.984
Cd	3.77	2.116	1.356	0.981
Hf	--	--	--	--
Ta	--	--	--	--
W	0.44	1.901	1.476	0.981
Re	1.53	1.878	1.463	0.982
Os	2.00	1.876	1.454	0.973
Ir	2.21	1.881	1.482	0.982
Pt	3.13	1.920	1.452	0.982
Au	4.53	2.164	1.409	0.984

Table S10 The free energies of H, OH, O and OOH (eV) on single TM atom supported on TM/T1-vacancy terminations.

Single TM atom	ΔG_{H^*}	ΔG_{OH^*}	ΔG_{O^*}	ΔG_{OOH^*}
Sc	0.71	--	--	--
Ti	0.76	--	--	--
V	0.66	--	--	--
Cr	0.01	-1.52	-0.85	1.89
Mn	0.46	--	--	--
Fe	-0.16	-1.12	-0.13	2.33
Co	-0.11	-0.72	0.78	2.56
Ni	-0.25	-0.40	1.41	2.79
Cu	-0.21	0.63	2.77	4.06
Zn	0.21	0.00	3.19	3.46
Y	0.40	--	--	--
Zr	0.14	-2.09	0.41	2.41
Nb	-0.14	-2.62	-1.67	0.77
Mo	0.75	--	--	--
Tc	-0.03	-0.84	-0.40	2.42
Ru	-0.11	-0.45	0.41	2.88
Rh	0.23	-0.09	1.46	2.94
Pd	-0.15	0.44	2.65	3.52
Ag	-0.19	1.42	4.93	4.52
Cd	0.23	0.53	3.79	3.87
Hf	0.82	--	--	--
Ta	0.63	--	--	--
W	0.08	-3.05	-2.86	0.54
Re	-0.09	-1.88	-1.34	1.63
Os	-0.01	-1.36	-0.87	2.10
Ir	-0.25	-1.02	0.14	2.31

Pt	-0.10	0.09	1.58	3.23
Au	0.11	3.44	1.13	4.63

Table S11 Reaction free energies (eV) of elementary step for OER on single TM atom supported on TM/T1-vacancy terminations.

Single TM atom	ΔG_1	ΔG_2	ΔG_3	ΔG_{4*}
Sc	--	--	--	--
Ti	--	--	--	--
V	--	--	--	--
Cr	-1.52	0.67	2.74	3.03
Mn	--	--	--	--
Fe	-1.12	0.99	2.46	2.59
Co	-0.72	1.50	1.78	2.36
Ni	-0.40	1.81	1.37	2.13
Cu	0.63	2.14	1.29	0.86
Zn	0.00	3.19	0.27	1.46
Y	--	--	--	--
Zr	-2.09	2.50	2.00	2.51
Nb	-2.62	0.95	2.44	4.15
Mo	--	--	--	--
Tc	-0.84	0.45	2.81	2.50
Ru	-0.45	0.86	2.47	2.04
Rh	-0.09	1.55	1.48	1.98
Pd	0.44	2.21	0.87	1.40
Ag	1.42	3.51	-0.41	0.40
Cd	0.53	3.26	0.08	1.05
Hf	--	--	--	--
Ta	--	--	--	--

W	-3.05	0.18	3.40	4.38
Re	-1.88	0.53	2.97	3.29
Os	-1.36	0.49	2.96	2.82
Ir	-1.02	1.16	2.18	2.61
Pt	0.09	1.49	1.65	1.69
Au	3.44	2.31	1.19	0.29

Table S12 Valance electron in d-orbital (θ_d), electronegativity of single TM atom and structure descriptor (φ) of TM/T-vacancy termination..

Single TM atom	θ_d	E_{TM}	φ	**Single TM atom**	θ_d	E_{TM}	φ	**Single TM atom**	θ_d	E_{TM}	φ
Sc	1	1.36	12.16	**Y**	1	1.22	12.02				
Ti	2	1.54	24.68	**Zr**	2	1.33	24.26	**Hf**	2	1.32	24.24
V	3	1.63	37.29	**Nb**	4	1.59	49.56	**Ta**	3	1.51	36.93
Cr	5	1.66	62.3	**Mo**	5	2.16	64.8	**W**	4	2.36	52.64
Mn	5	1.55	61.75	**Tc**	6	1.91	76.26	**Re**	5	1.93	63.65
Fe	6	1.83	75.78	**Ru**	7	2.2	91	**Os**	6	2.2	78
Co	7	1.88	88.76	**Rh**	8	2.28	104.64	**Ir**	7	2.2	91
Ni	8	1.92	101.76	**Pd**	10	2.2	130	**Pt**	9	2.28	117.72
Cu	10	1.9	127	**Ag**	10	1.93	127.3	**Au**	10	2.54	133.4
Zn	10	1.65	124.5	**Cd**	10	1.69	124.9				

Table S13 The adsorption properties of Pt on different MoS_2 edge terminations. E_{ads} (in eV): the adsorption energy of Pt; E_d (in eV): the diffusion barrier of Pt atom; site: the most favorable adsorption site; $D_{Pt\text{-}Mo(S)}$ (in Å): the bond length of the S-Cu; Pt-Chg (in e): the net charge of the

adsorbed Pt.

	E_{ads}(eV)	E_d(eV)	site	D_{Pt-Mo}(Å)	D_{Pt-S}(Å)	Pt-Chg(e)
Mo-term	-5.82	1.08	Mo-bridge	2.51, 2.51		0.48
S-term	-4.81	1.06	S-hollow	2.50	2.46, 2.45, 2.44,2.45	-0.23
T1-term	-4.01	0.90	2S-Mo	2.69	2.29, 2.28	-0.06
T1-vacancy	-4.58	1.82	vacancy	2.52, 2.52		0.24
T2-term	-4.08	0.95	2Mo-S-hol	2.67, 2.67	2.26	0.10

Table S14 The hydrogen Gibbs free energy (ΔG_{H^*}) and the chemical bond energy (ΔE_B) between H and S/Mo on MoS_2 and Pt/MoS_2 edge.

Structure	ΔG_{H^*}	ΔE_B(eV)	$d_{H-Mo/S}$	structure	edge-ΔG_{H^*}	ΔE_B(eV)	$d_{H-Mo/S}$
Mo-term	-0.68	-1.13	1.925	Pt/Mo-term	-0.24	-1.00	1.931
S-term	-0.45	-0.72	1.352	Pt/S-term	-0.33	-0.78	1.352
T1-term	-0.40	-0.95	1.357	Pt/T1-term	-0.15	-0.67	1.359
T1-vacancy	-0.13	-0.48	1.358	Pt/T1-vacancy	-0.10	-0.93	1.358
T2-term	0.33	-0.13	1.362	Pt/T2-term	0.26	-0.06	1.362

Table S15 The number of Mo and S atoms in the nearest-neighbor Pt for Pt/MoS_2 edge

structure	Mo atom	S atom
Pt/Mo-term	2	0
Pt/S-term	1	4

Pt/T1-term	1	2
Pt/T1-vacancy	2	0
Pt/T2-term	2	1

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