Supplementary Information for

Interfacial Atomic Ni Tetragon Intercalation in NiO_2-to-Pd hetero-structure triggers an Outperform HER activity than Pt Catalyst

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Note S1. The energetically favorable adsorption sites of the H*, O*, H_2O, H_2, O_2 and OH on (111) facet of a transition metal.

With regard to the HER or ORR, it is generally believed that the energetically stable adsorption configuration on (111) surface of a transition-metal M catalyst (where "M" denotes Pd, Pt or Ni in this study) is the three-fold hollow site for atomic H* or O* (i.e. M-h / f site, where h and f stand respectively for the hcp hollow site and fcc hollow site), one-fold top site for H_2O molecule and H_2 molecule (i.e. M-t site), two-fold bridge site for O_2 molecule (i.e. M-b site), and top / bridge site for OH radicals (i.e. M-t / M-b site).

Table S1. The adsorption energies (E_{ads}, unit in eV) of H*, OH, H_2O and H_2 at different adsorption sites corresponding to the octahedral NiO_2, Pd (111) and Pt (111) catalyst configurations.

	NiO_2	Pd(111)	Pt(111)
H*-site E_{ads}	O-top −0.81	Pd-hcp −0.57 Pd-fcc −0.61	Pt-hcp −0.48 Pt-fcc −0.53
OH-site E_{ads}	O-top −0.82	Pd-top −2.39 Pd-bridge −2.67	Pt-top −2.42 Pt-bridge −2.50
H_2O-site E_{ads}	O-top −0.07 Ni-top −0.07	Pd-top −0.27	Pt-top −0.24
H_2-site E_{ads}	O-top 0.02 Ni-top 0.01	Pd-top −0.29	Pt-top 0.01

Table S2. The adsorption energies (E_{ads}, given in eV) of H*, OH, H_2O and H_2 at different adsorption sites corresponding to the Ni-doped NiO_2-Pd core-shell catalyst (i.e., NiO_2–Ni_1–Pd, NiO_2–Ni_2–Pd, NiO_2–Ni_3–Pd and NiO_2–Ni_4–Pd).

	NiO_2–Ni_1–Pd		NiO_2–Ni_2–Pd		NiO_2–Ni_3–Pd		NiO_2–Ni_4–Pd	
H*-site E_{ads}	Pd-hcp1	−0.56	Pd-hcp1	−0.55	Ni-hcp	−0.52	Ni-hcp	−0.51
	Pd-hcp2	−0.57	Pd-hcp2	−0.56	Pd-hcp1	−0.55	Pd-hcp1	−0.55
	Ni-fcc	−0.61	Ni-fcc	−0.61	Pd-hcp2	−0.58	Pd-hcp2	−0.58
	Pd-fcc	−0.61	Pd-fcc	−0.60	Ni-fcc	−0.59	Ni-fcc	−0.58
					Pd-fcc	−0.59	Pd-fcc1	−0.59
							Pd-fcc2	−0.61
							Pd-fcc3	−0.61
OH-site E_{ads}	Pd-top1	−2.45	Pd-top1	−2.45	Pd-top1	−2.46	Pd-top1	−2.46
	Pd-bridge1	−2.73	Pd-bridge1	−2.76	Pd-bridge1	−2.75	Pd-top2	−2.44
							Pd-top3	−2.45
							Pd-bridge1	−2.75
							Pd-bridge2	−2.75
							Pd-bridge3	−2.64
H_2O-site E_{ads}	Pd-top1	−0.36	Pd-top1	−0.35	Pd-top1	−0.32	Pd-top1	−0.31
							Pd-top2	−0.36
							Pd-top3	−0.37
H_2-site E_{ads}	Pd-top1	−0.36	Pd-top1	−0.36	Pd-top1	−0.33	Pd-top1	−0.31
							Pd-top2	−0.37

Table S3. The adsorption energies (E_{ads}, given in eV) of H*, OH, H_2O and H_2 at different adsorption sites corresponding to the Ni-doped NiO_2-Pd core-shell catalyst (i.e., NiO_2–Ni_7–Pd, NiO_2–Ni_{10}–Pd and NiO_2–Ni_{32}–Pd).

	NiO_2–Ni_7–Pd		NiO_2–Ni_{10}–Pd		NiO_2–Ni_{32}–Pd	
H*-site E_{ads}	Ni-hcp	−0.49	Ni-hcp	−0.47	Pd-hcp	−0.44
	Pd-hcp1	−0.54	Pd-hcp1	−0.54	Pd-fcc	−0.48
	Pd-hcp2	−0.58	Pd-hcp2	−0.58		
	Ni-fcc1	−0.56	Ni-fcc1	−0.51		
	Ni-fcc2	−0.58	Ni-fcc2	−0.56		
	Pd-fcc1	−0.62	Pd-fcc1	−0.59		
	Pd-fcc2	−0.63	Pd-fcc2	−0.59		
OH-site E_{ads}	Pd-top1	−2.44	Pd-top1	−2.39	Pd-top	−2.37
	Pd-top2	−2.46	Pd-top2	−2.38	Pd-bridge	−2.65
	Pd-top3	−2.47	Pd-top3	−2.42		
	Pd-bridge1	−2.70	Pd-bridge1	−2.72		
	Pd-bridge2	−2.74	Pd-bridge2	−2.66		
	Pd-bridge3	−2.75	Pd-bridge3	−2.61		
H_2O-site E_{ads}	Pd-top1	−0.29	Pd-top1	−0.26	Pd-top	−0.31
	Pd-top2	−0.35	Pd-top2	−0.34		
	Pd-top3	−0.38	Pd-top3	−0.35		
H_2-site E_{ads}	Pd-top1	−0.31	Pd-top1	−0.31	Pd-top	−0.27
	Pd-top2	−0.37	Pd-top2	−0.37		

Table S4. The calculated zero-point energy (ΔE_{ZPE}, unit in eV) for different model catalysts, including the seven NiO_2–Ni_d–Pd, Pd(111), NiO_2 and Pt(111).

Ni_1	Ni_2	Ni_3	Ni_4	Ni_7	Ni_{10}	Ni_{32}	Pd(111)	NiO_2	Pt(111)
0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.30	0.14

Table S5. Reaction energy barrier (ΔE) (given in eV) of the three HER steps "Volmer" (ΔE_{Volmer}), "Heyrovsky" ($\Delta E_{Heyrovsky}$) and "Tafel" (ΔE_{Tafel}) on the different surface models.

	I. Volmer (eV)	II. Heyrovsky (eV)	III. Tafel (eV)
NiO_2–Ni_1–Pd	1.109	0.781	-1.432
NiO_2–Ni_2–Pd	1.162	0.963	-1.629
NiO_2–Ni_3–Pd	1.104	0.765	-1.646
NiO_2–Ni_4–Pd	1.100	0.763	-1.533
NiO_2–Ni_7–Pd	1.155	0.754	-1.418
NiO_2–Ni_{10}–Pd	1.165	0.935	-1.606
NiO_2–Ni_{32}–Pd	1.173	0.907	-1.442
NiO_2	1.660	4.177	2.600
Pd(111)	1.120	0.850	1.463
Pt(111)	0.740	0.417	1.466

Table S6. The calculated lattice mismatch (in %) between Pd and NiO_2 (denoted as Pd–NiO_2), Ni and NiO_2 (denoted as Ni–NiO_2), Ni and Pd (denoted as Ni–Pd) for different heterostructural NiO_2–Ni_d–Pd model (d = 1 to 4, 7, 10 and 32).

	Ni_1	Ni_2	Ni_3	Ni_4	Ni_7	Ni_{10}	Ni_{32}
Pd–NiO_2	0.1%	0.5%	0.5%	0.5%	1.0%	1.6%	0.3%
Ni–NiO_2	2.0%	2.3%	2.4%	3.2%	1.8%	1.7%	0.1%
Ni–Pd	2.0%	2.3%	2.5%	3.7%	2.8%	3.2%	0.4%

Table S7. Bader charge population of the triatomic adsorption site on surfaces of the different model catalysts. Excess charge (ne^-, relative to the d electrons of its bulk atoms) of the triatomic site of the proposed NiO_2–Ni_d–Pd model catalyst and three transition metal reference models (Pd(111), Pt(111) and Ni(111)). The triatomic site selected for charge analysis is the hcp-site with the weakest E_{ads}-H* on each surface model, the corresponding data is listed in Table S1 to S3.

	Excess charge (e^-)
NiO_2–Ni_1–Pd	0.079
NiO_2–Ni_2–Pd	0.058
NiO_2–Ni_3–Pd	0.137
NiO_2–Ni_4–Pd	0.132
NiO_2–Ni_7–Pd	0.145
NiO_2–Ni_{10}–Pd	0.191
NiO_2–Ni_{32}–Pd	0.355
Pd(111)	0.109
Pt(111)	0.128
Ni(111)	0.063

Table S8. The calculated d-band center (ε_d ,given in eV) of the selected triatomic M-hcp sites on the Pd(111), Ni(111), NiO_2–Ni_4–Pd and Pt(111) models corresponding to Figure 4(d).

	Pd(111)	Ni(111)	NiO_2-Ni_4-Pd	Pt(111)
ε_d (eV)	–1.73	–1.26	–2.31	–2.25

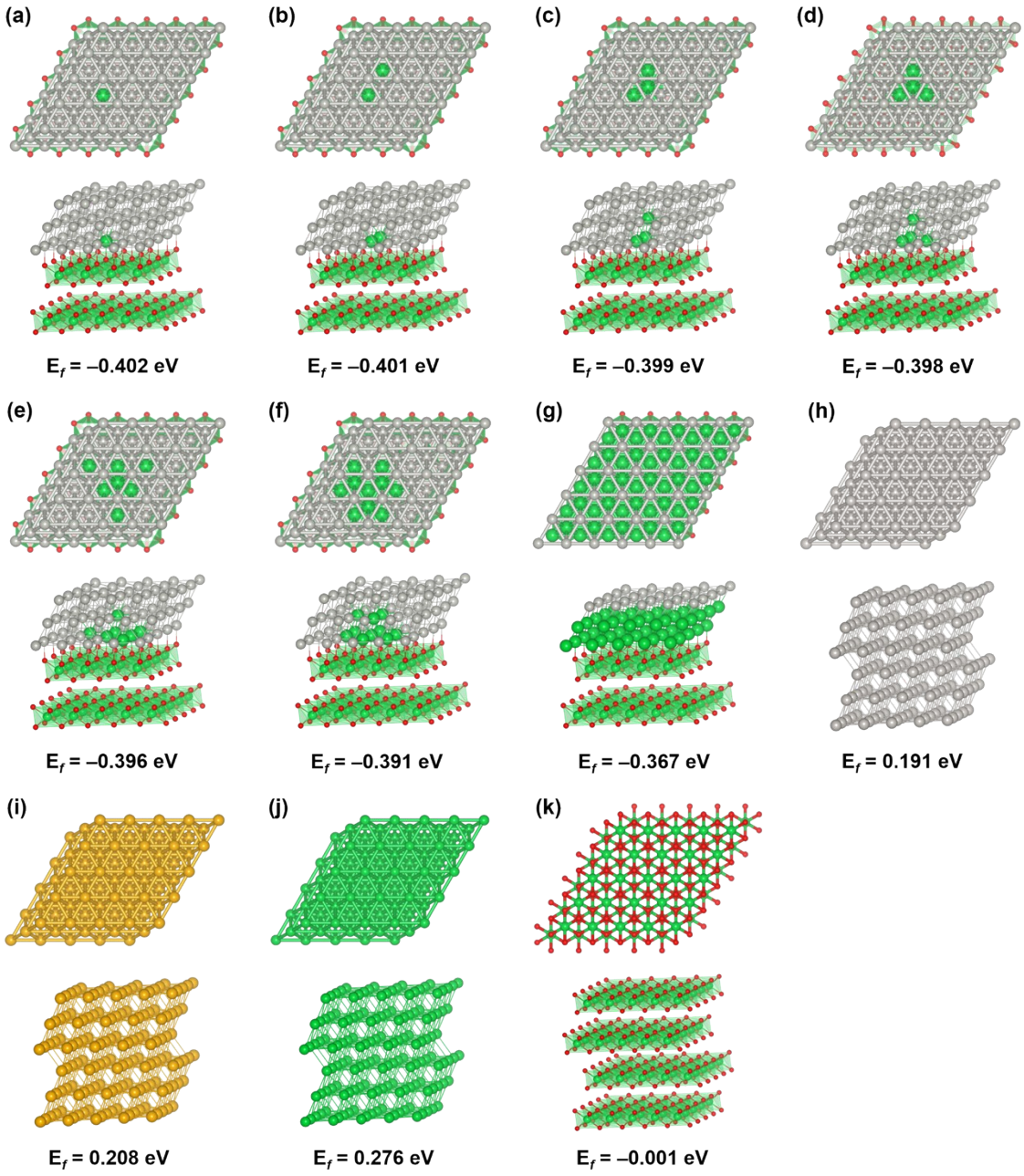

Figure S1. Top and oblique views of the different surface models, together with the calculated E_f of each configuration below. (a) NiO_2–Ni_1–Pd, (b) NiO_2–Ni_2–Pd, (c) NiO_2–Ni_3–Pd, (d) NiO_2–Ni_4–Pd, (e) NiO_2–Ni_7–Pd, (f) NiO_2–Ni_{10}–Pd, (g) NiO_2–Ni_{32}–Pd, (h) Pd(111), (i) Pt(111), (j) Ni(111), (k) layered-octahedral NiO_2. The grey, green, gold and red spheres represent Pd, Ni, Pt and O atoms, respectively.

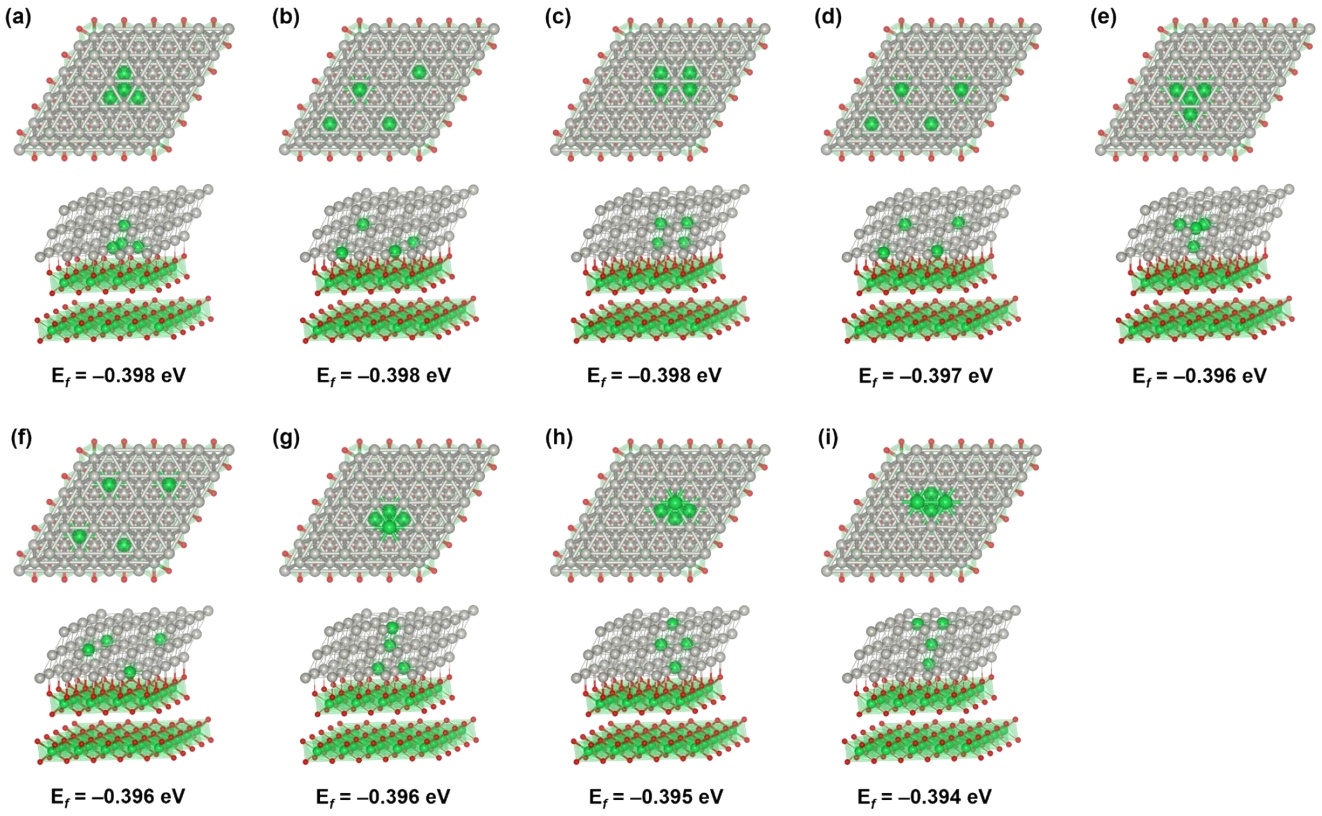

Figure S2. Top and oblique views of the different NiO_2–Ni_4–Pd models, together with the calculated E_f of each configuration below. (a) 3-1-compact (pyramid), (b) 3-1-far, (c) 2-2-compact, (d) 2-2-far, (e) 1-3-compact, (f) 1-3-far, (g) 2-1-1-compact, (h) 1-2-1-compact, (i) 1-1-2-compact. For clarity, the different NiO_2–Ni_4–Pd systems are denoted by the 4-Ni doping sequence in the Pd shell from bottom to top. The grey, green and red spheres represent Pd, Ni and O atoms, respectively.

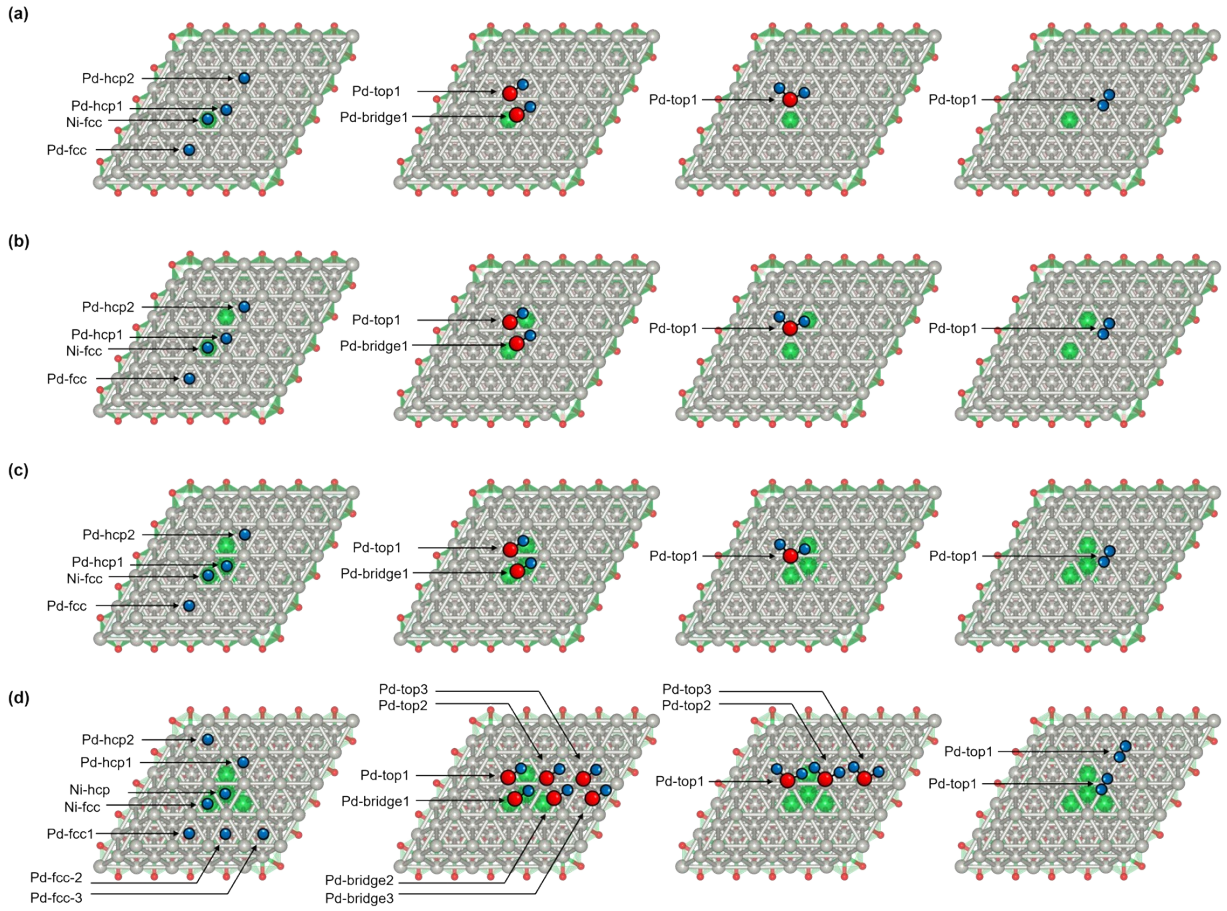

Figure S3. Top view atomic adsorption structures of H*, OH, H_2O and H_2 (panels from left to right) at different adsorption sites on the (a) NiO_2–Ni_1–Pd, (b) NiO_2–Ni_2–Pd, (c) NiO_2–Ni_3–Pd and (d) NiO_2–Ni_4–Pd surface models. For clarity, the grey, green, red and blue spheres stand for Pd, Ni, O and H atoms, respectively.

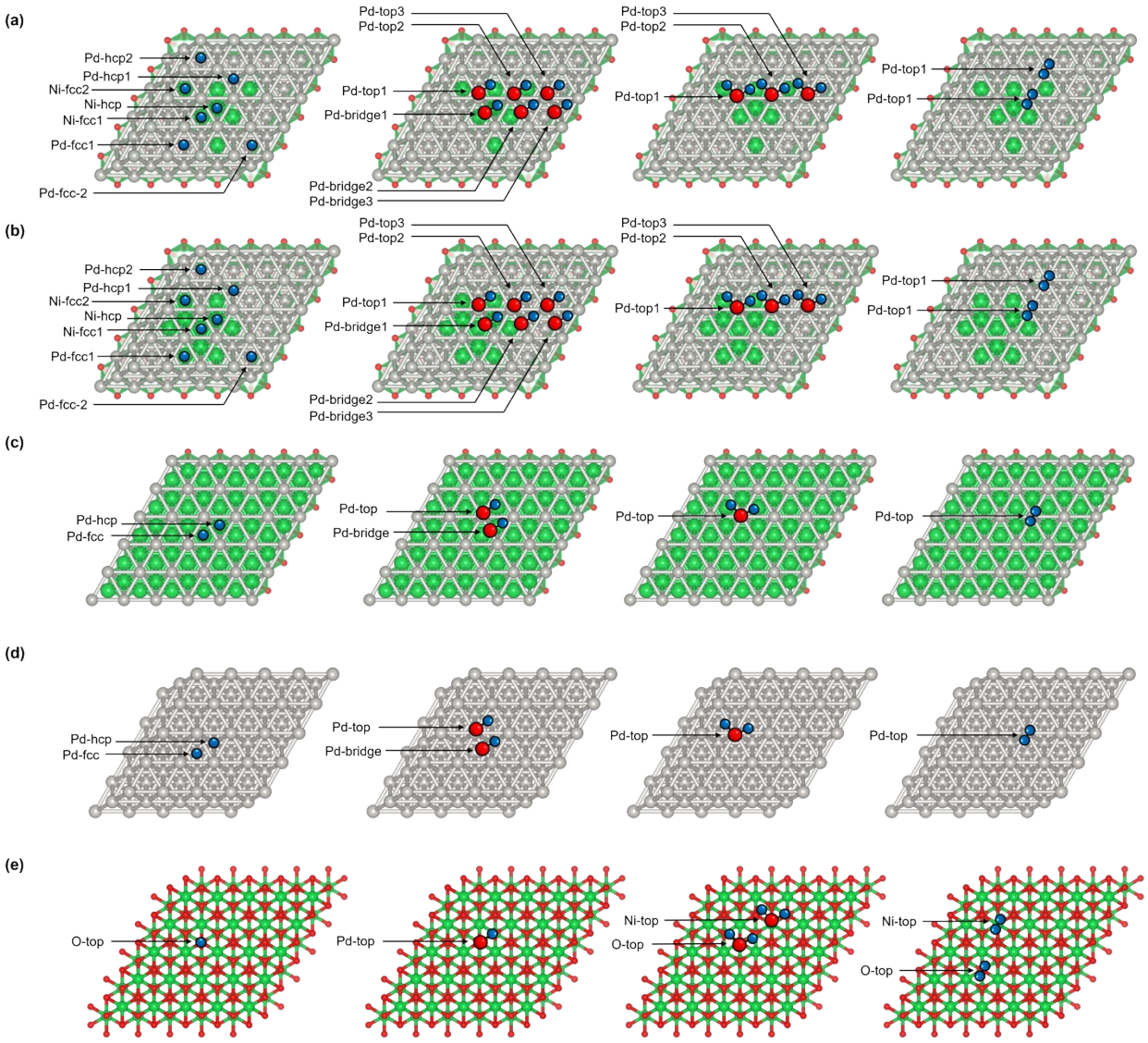

Figure S4. Top view atomic adsorption structures of H*, OH, H_2O and H_2 (panels from left to right) at different adsorption sites on the (a) NiO_2–Ni_7–Pd, (b) NiO_2–Ni_{10}–Pd, (c) NiO_2–Ni_{32}–Pd, (d) Pd(111) / Pt(111) and (e) NiO_2 surface models. For clarity, the grey, green, red and blue spheres stand for Pd, Ni, O and H atoms, respectively.

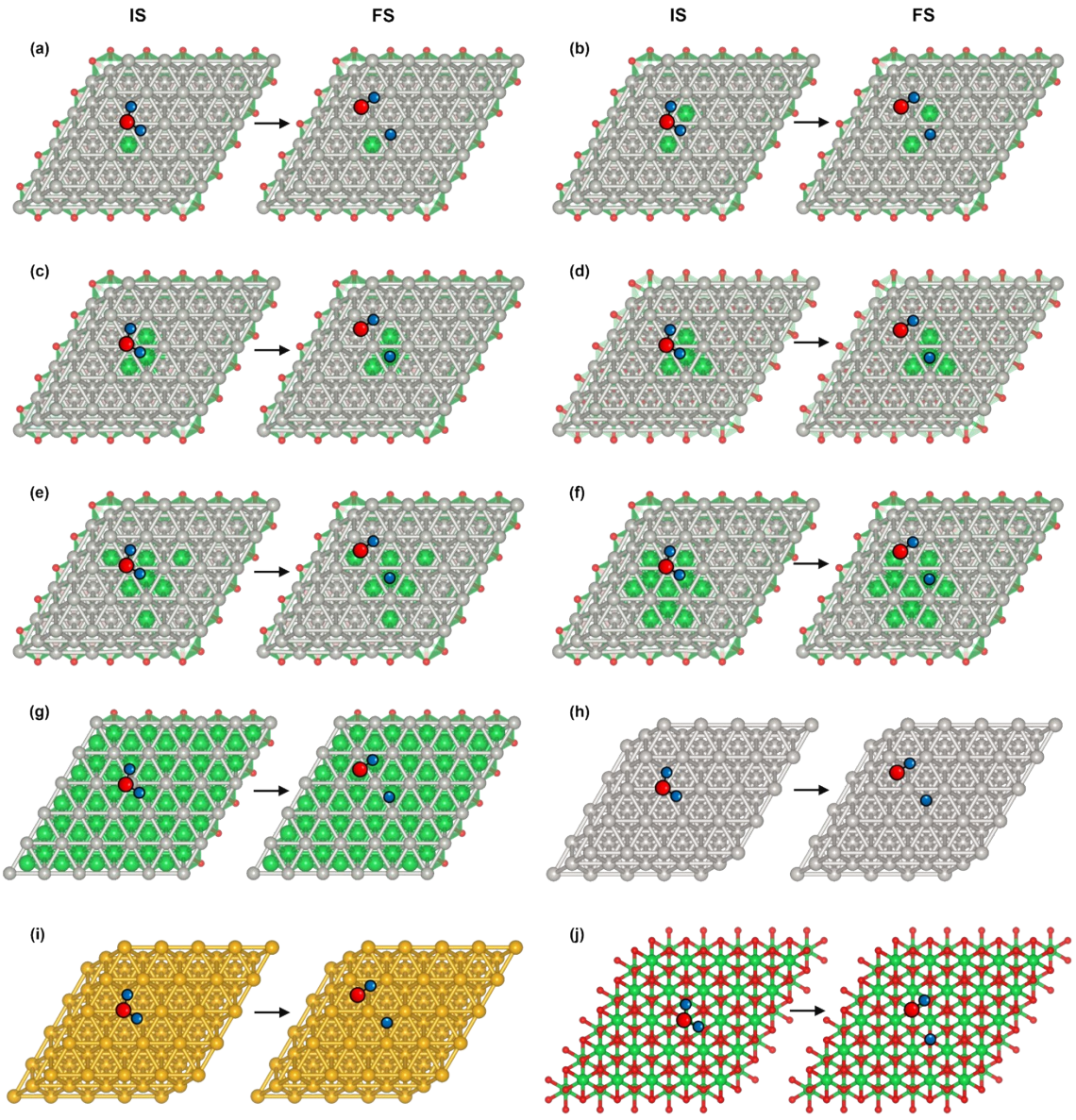

Figure S5. Top view structures of the "Volmer" step (H_2O dissociation) in HER on the different surface models, including (a) NiO_2–Ni_1–Pd, (b) NiO_2–Ni_2–Pd, (c) NiO_2–Ni_3–Pd, (d) NiO_2–Ni_4–Pd, (e) NiO_2–Ni_7–Pd, (f) NiO_2–Ni_{10}–Pd, (g) NiO_2–Ni_{32}–Pd (h) Pd(111), (i) Pt(111), (j) layered-octahedral NiO_2. The IS and FS respectively stands for the initial state and final state. The grey, green, yellow, red and blue spheres stand for Pd, Ni, Pt, O and H atoms, respectively.

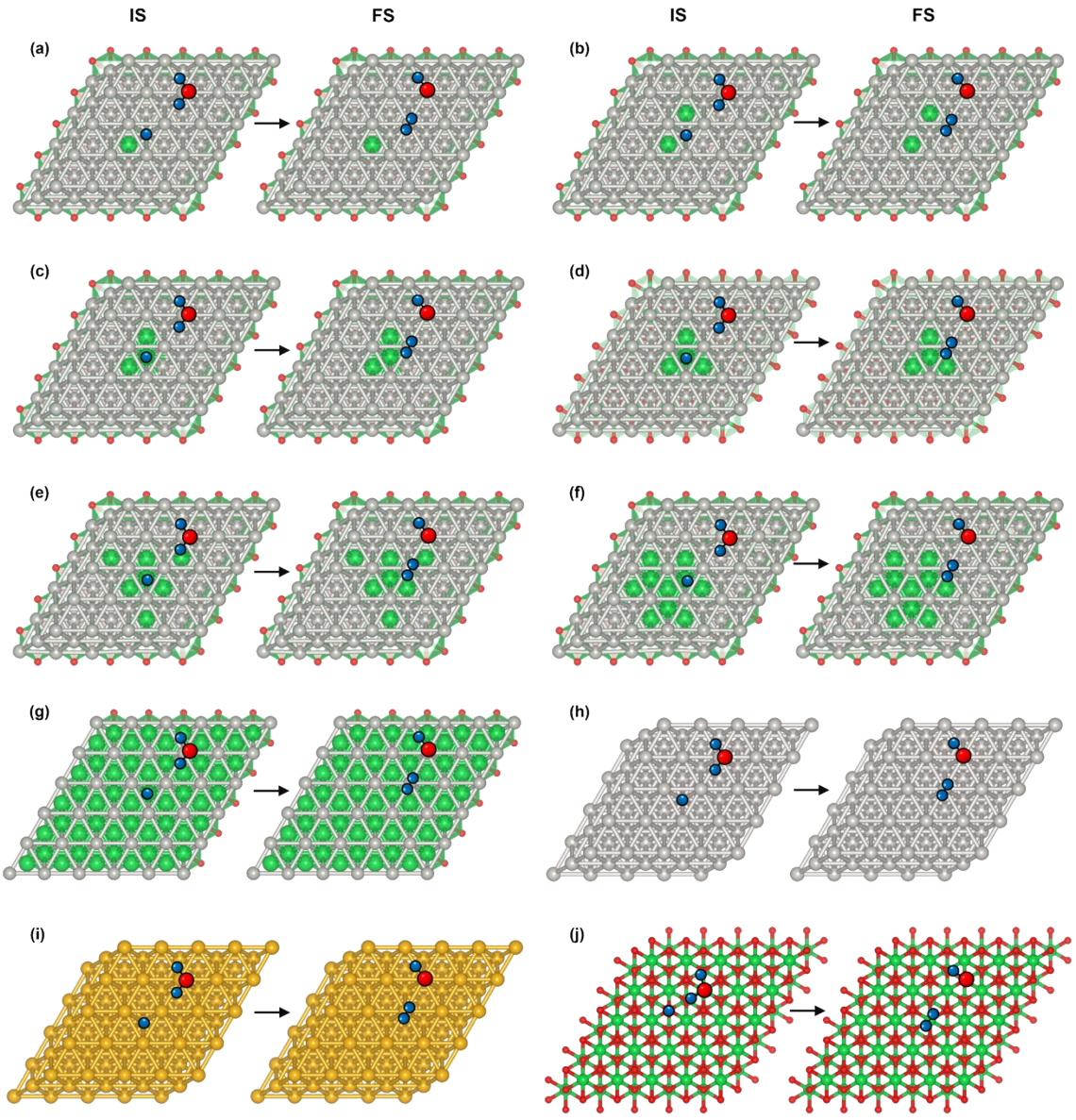

Figure S6. Top view structures of the "Heyrovsky" step (H* recombination) in HER on the different surface models, including (a) NiO_2–Ni_1–Pd, (b) NiO_2–Ni_2–Pd, (c) NiO_2–Ni_3–Pd, (d) NiO_2–Ni_4–Pd, (e) NiO_2–Ni_7–Pd, (f) NiO_2–Ni_{10}–Pd, (g) NiO_2–Ni_{32}–Pd (h) Pd(111), (i) Pt(111), (j) layered-octahedral NiO_2. The IS and FS respectively stands for the initial state and final state. The grey, green, yellow, red and blue spheres stand for Pd, Ni, Pt, O and H atoms, respectively.

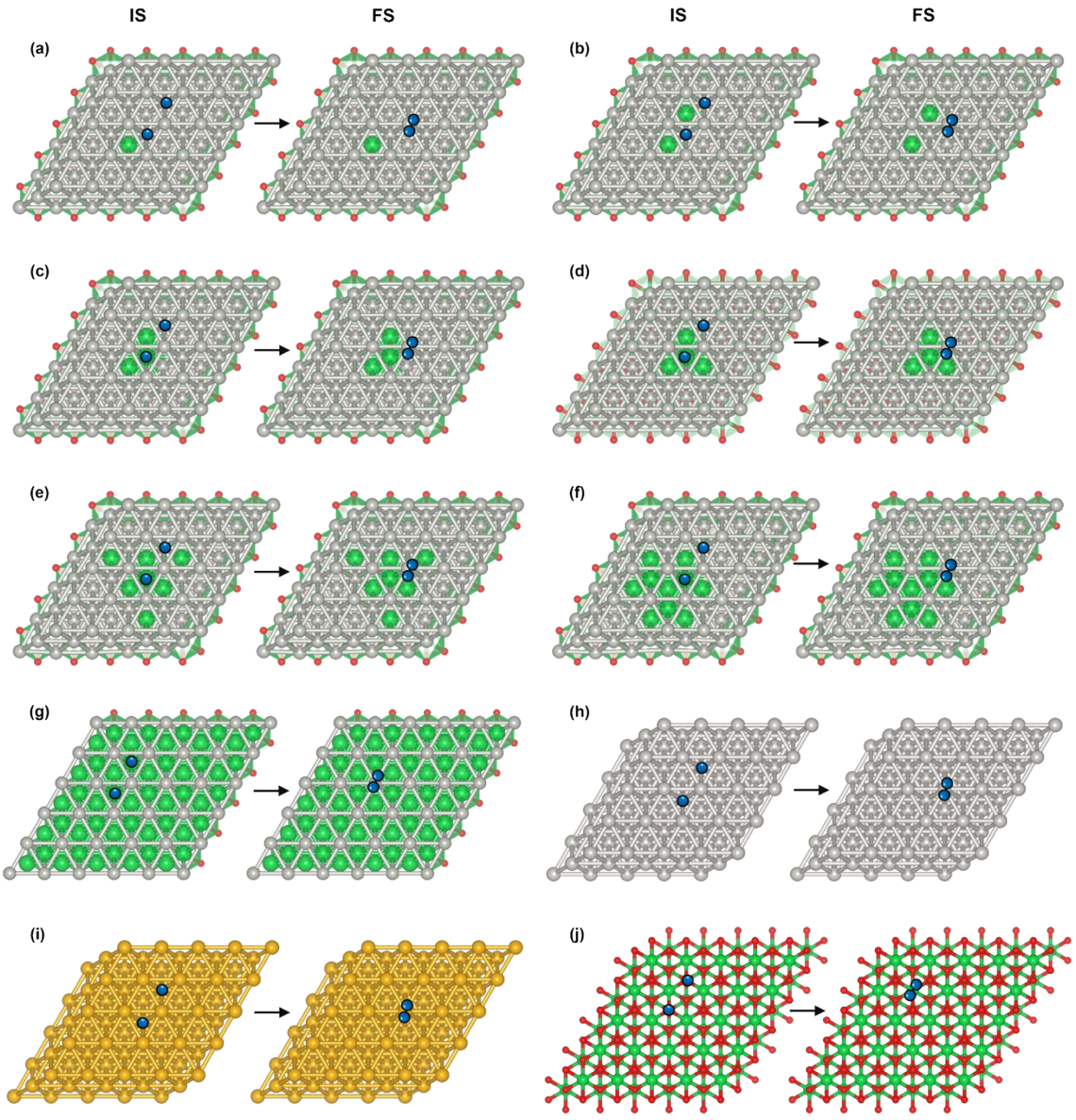

Figure S7. Top view structures of the "Tafel" step (H* recombination) in HER on the different surface models, including (a) NiO_2–Ni_1–Pd, (b) NiO_2–Ni_2–Pd, (c) NiO_2–Ni_3–Pd, (d) NiO_2–Ni_4–Pd, (e) NiO_2–Ni_7–Pd, (f) NiO_2–Ni_{10}–Pd, (g) NiO_2–Ni_{32}–Pd (h) Pd(111), (i) Pt(111), (j) layered-octahedral NiO_2. The IS and FS respectively stands for the initial state and final state. The grey, green, yellow, red and blue spheres stand for Pd, Ni, Pt, O and H atoms, respectively.

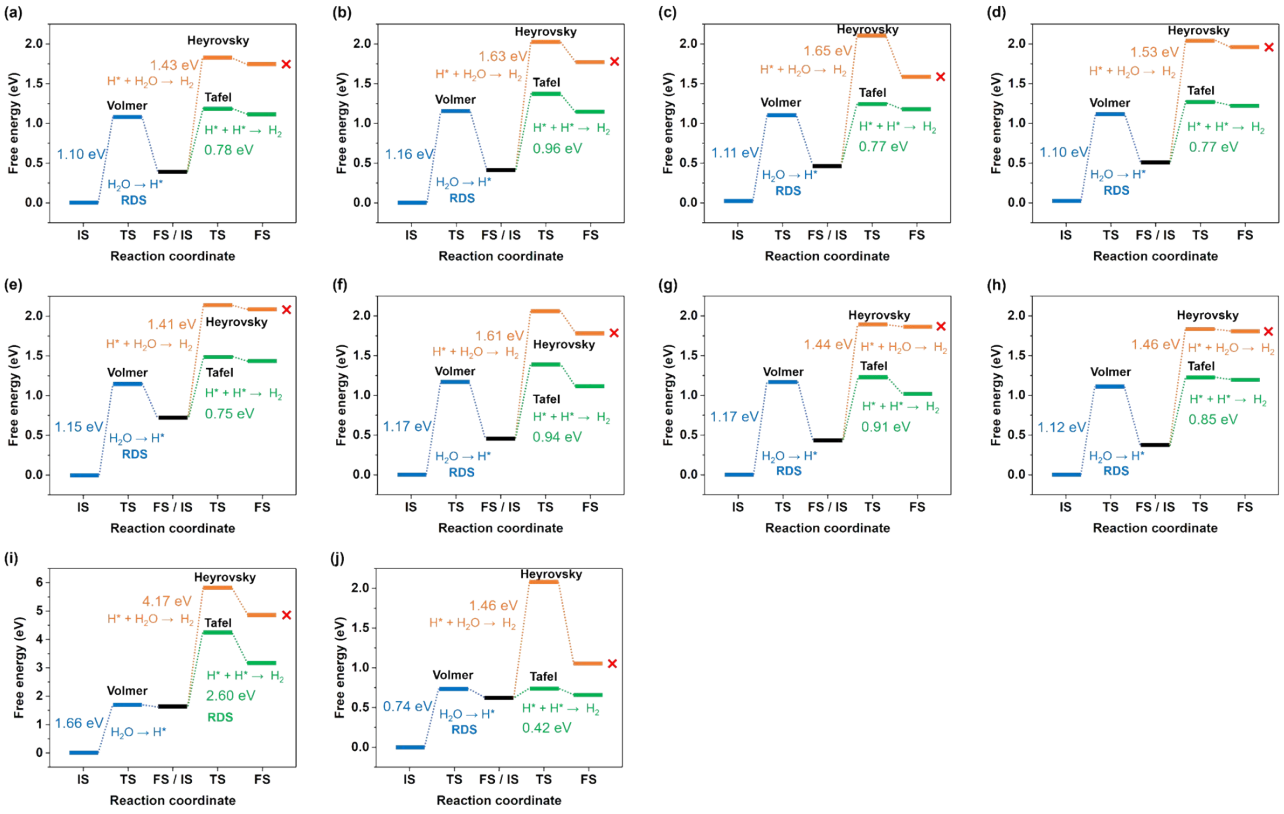

Figure S8. Free energy diagram of the HER including the energy reaction barriers of the three steps "Volmer" (ΔE_{Volmer}), "Heyrovsky" ($\Delta E_{Heyrovsky}$) and "Tafel" (ΔE_{Tafel}) for (a) NiO_2–Ni_1–Pd, (b) NiO_2–Ni_2–Pd, (c) NiO_2–Ni_3–Pd, (d) NiO_2–Ni_4–Pd, (e) NiO_2–Ni_7–Pd, (f) NiO_2–Ni_{10}–Pd, (g) NiO_2–Ni_{32}–Pd, (h) Pd(111), (i) layered-octahedral NiO_2 and (j) Pt(111) model catalysts. For clarity, the three reaction pathways of the "Volmer" , "Heyrovsky" and "Tafel" on different surface models are highlighted in blue, orange and green, respectively.