Electronic Supplementary Information (ESI)

Understanding the role of axial O in CO_2 electroreduction on NiN_4 single-atom catalysts via simulations in realistic electrochemical environment

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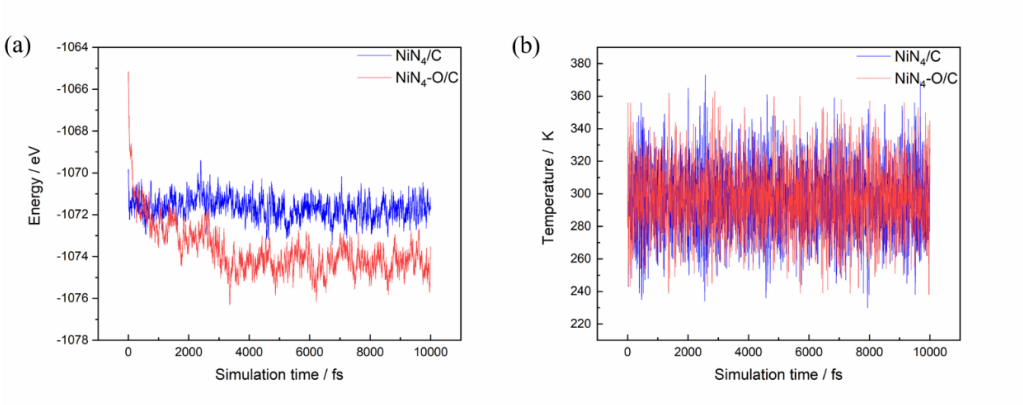

Figure S1. MD energy (a) and temperature (b) profiles for NiN_4-O/C and NiN_4/C during 10 ps AIMD simulations.

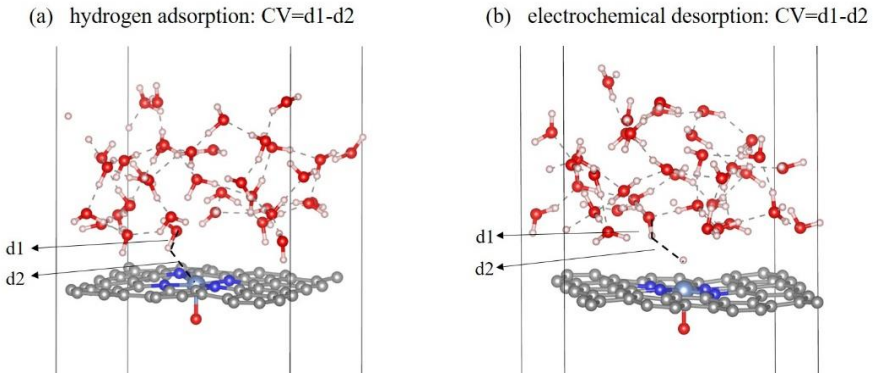

Figure S2. Illustrations of CV setting in the "slow-growth" method for the reaction of (a) hydrogen adsorption and (b) electrochemical desorption in HER.

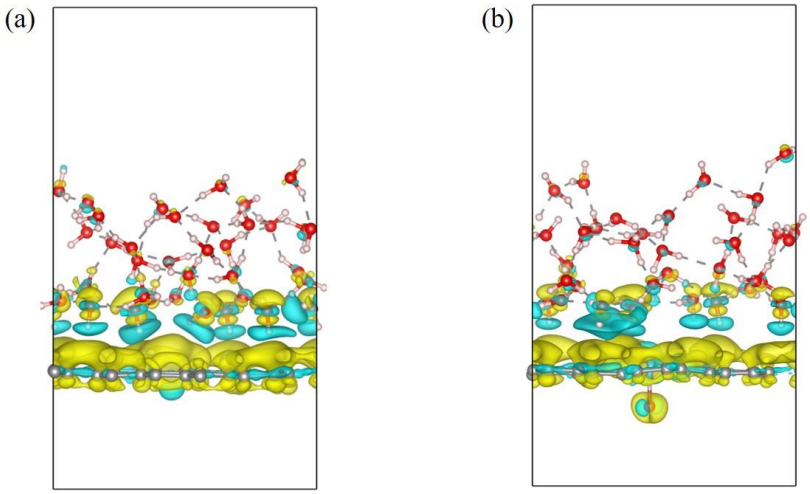

Figure S3. Charge density difference (0.0005 e $Å^{-3}$) for NiN_4/C (a) and NiN_4-O/C (b). The yellow and cyan areas indicate electron accumulation and depletion, respectively. The calculated charge density difference figures are given by subtracting the charge density of the whole explicit model from that of the corresponding isolated NiN_4/C and pure water bulk. $\Delta\rho = \rho_{NiN4/C-water\ bulk} - (\rho_{NiN4/C} + \rho_{water\ bulk})$ where $\rho_{(NiN4/C\text{-water bulk})}$ is the charge density of the whole system, $\rho_{(NiN4/C)}$ is the charge density of NiN_4/C catalyst slab without water molecules, and $\rho_{(water\ bulk)}$ is the charge density of the pure water bulk. The NiN_4-O/C system is also calculated as the above.

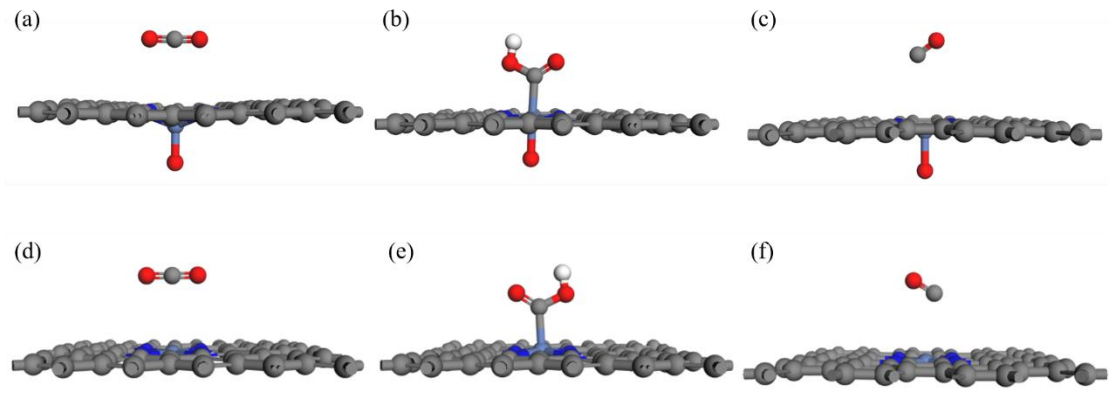

Figure S4. Optimized reaction intermediates during CO_2RR catalyzed by NiN_4-O/C (a, b, c) and NiN_4/C (d, e, f). C, grey; N, blue; Ni, light blue; O, red; H, white.

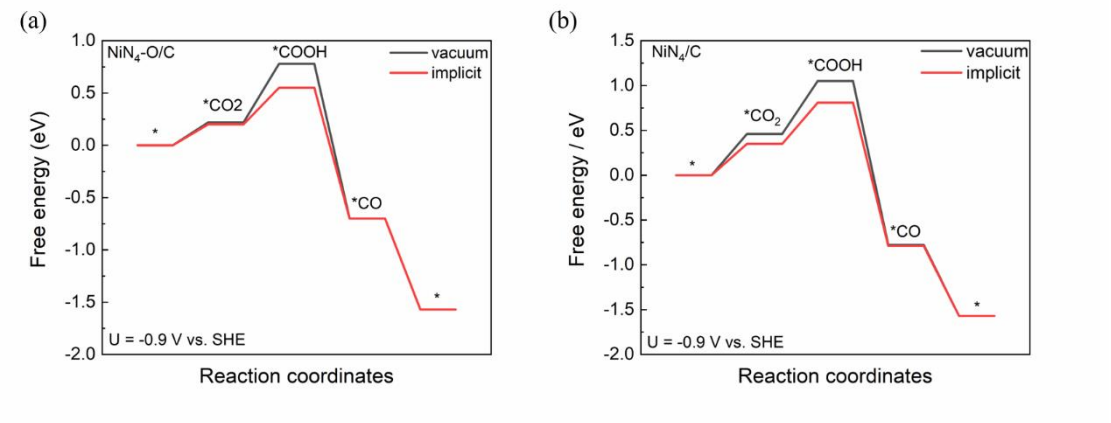

Figure S5. DFT-based free energies profiles for the NiN_4-O/C (a) and NiN_4/C (b) with vacuum and implicit models during CO_2RR (pH = 0). The implicit solvent model in this study is modelled as a continuum dielectric as implemented by the Hennig group in the VASPsol code.[1,2]

Table S1. DFT energies (denoted as E(DFT)) and free energy correction values (ΔG) of H_2(g), CO_2(g), and CO(g) are calculated at 1 bar, while the free energy of H_2O(l) is calculated at 0.035 bar. Besides, a correction of -0.41 eV to the DFT energy of CO molecule has been employed since there is an error in describing the energy of CO molecule by using PBE functional.[3] The free energy correction is done by the VASPKIT code.[4]

	pressure/bar	temperature/K	E(DFT)/eV	ΔG/eV	G/eV
CO(g)	1	298.15	-14.8	-0.39	-15.576
CO_2(g)	1	298.15	-23.0	-0.26	-23.212
H_2(g)	1	298.15	-6.8	-0.04	-6.814
H_2O(l)	0.035	298.15	-14.2	0	-14.221

Table S2. Calculated DFT energies (denoted as E(DFT)) and free energy correction values (ΔG) of the pure slab, slab with *CO_2 (*CO_2), slab with *COOH (*COOH), and slab with *CO (*CO) in the vacuum and implicit model of NiN_4-O/C and NiN_4/C.

NiN_4-O/C							
Vacuum model	E(DFT)/eV	Δ G/eV	G/eV		G(total)/eV	U=0 V vs. SHE	U=-0.9 V vs. SHE
slab	-539.24	0.00	-539.24	+CO_2+H_2	-569.27	0.00	0.00
*CO_2	-562.40	0.16	-562.23	+H_2	-569.05	0.22	0.22
*COOH	-564.70	0.51	-564.19	+1/2H_2	-567.59	1.68	0.78
*CO	-553.99	0.05	-553.95	+H_2O	-568.17	1.10	-0.70
slab	-539.24	0.00	-539.24	+CO+H_2O	-569.04	0.23	-1.57
Implicit model	E(DFT)/eV	Δ G/eV	G/eV		G(total)/eV	U=0 V vs. SHE	U=-0.9 V vs. SHE
slab	-539.46	0.00	-539.46	+CO_2+H_2	-569.49	0.00	0.00
*CO_2	-562.64	0.16	-562.48	+H_2	-569.29	0.20	0.20
*COOH	-565.13	0.50	-564.63	+1/2H_2	-568.04	1.45	0.55
*CO	-554.23	0.07	-554.17	+H_2O	-568.39	1.10	-0.70
slab	-539.46	0.00	-539.46	+CO+H_2O	-569.26	0.23	-1.57
NiN_4/C							
Vacuum model	E(DFT)/eV	Δ G/eV	G/eV		G(total)/eV	U=0 V vs. SHE	U=-0.9 V vs. SHE
slab	-535.98	0.00	-535.98	+CO_2+H_2	-566.01	0.00	0.00
*CO_2	-558.97	0.24	-558.73	+H_2	-565.55	0.46	0.46
*COOH	-561.16	0.50	-560.66	+1/2H_2	-564.06	1.95	1.05
*CO	-550.78	0.01	-550.76	+H_2O	-564.99	1.02	-0.78
slab	-535.98	0.00	-535.98	+CO+H_2O	-565.78	0.23	-1.57
Implicit model	E(DFT)/eV	Δ G/eV	G/eV		G(total)/eV	U=0 V vs. SHE	U=-0.9 V vs. SHE
slab	-535.87	0.00	-535.87	+CO_2+H_2	-565.90	0.00	0.00
*CO_2	-558.95	0.21	-558.74	+H_2	-565.55	0.35	0.35
*COOH	-561.29	0.50	-560.79	+1/2H_2	-564.19	1.71	0.81
*CO	-550.68	0.01	-550.67	+H_2O	-564.89	1.01	-0.79
slab	-535.87	0.00	-535.87	+CO+H_2O	-565.67	0.23	-1.57

Table S3. Calculated work functions and Bader charge for the initial, transition, and final states for each elementary step during CO_2RR and HER. All E and Φ are listed in eV, q in the atomic unit, |e|. Is, ts and fs are the initial, transition, and final states.

	q_{is}	q_{ts}	q_{fs}	Φ_{is}	Φ_{ts}	Φ_{fs}
NiN_4-O/C						
$CO_2 \rightarrow *CO_2$	0.78	0.56	-0.16	4.21	4.31	4.59
$*CO_2 \rightarrow *COOH$	-0.15	-0.34	-0.42	4.54	4.65	4.78
$*COOH \rightarrow CO(aq)$	-0.31	-0.90	-0.97	4.78	5.26	5.55
NiN_4/C						
$CO_2 \rightarrow *CO_2$	0.74	0.34	0.06	3.54	3.72	3.67
$*CO_2 \rightarrow *COOH$	0.39	-0.09	-0.18	3.57	3.75	3.87
$*COOH \rightarrow CO(aq)$	-0.30	-0.87	-1.00	4.04	5.04	5.53
NiN_4-O/C						
$*+H_2O+e^-+H^+ \rightarrow *H+H_2O$	0.79	0.25	-0.22	4.27	4.63	4.62
$*H+H_2O+H^+ \rightarrow H_2+H_2O+*$	-0.23	-0.86	-0.97	4.69	5.64	5.26

Table S4. Calculated work functions and Bader charge changes for the initial, transition, and final states during each elementary step. ΔE and ΔE^* are the free energy change under constant charge condition and constant electrode potential condition, respectively. ΔE_{corr} is the constant potential correction energy according to the method proposed by Chan and Nørskov.[5] All E and Φ are listed in eV, q in the atomic unit, |e|.

	Δq(is→ts)	$\Delta\Phi$(is→ts)	Δq(is→fs)	$\Delta\Phi$(is→fs)	ΔE_{corr}(is→ts)	ΔE_{corr}(is→fs)	ΔE(is→ts)	ΔE(is→fs)	ΔE^*(is→ts)	ΔE^*(is→fs)
NiN_4-O/C										
CO_2→*CO_2	-0.22	0.10	-0.94	0.38	-0.01	-0.18	0.30	0.03	0.29	-0.15
*CO_2→ *COOH	-0.19	0.11	-0.28	0.24	-0.01	-0.03	0.35	0.31	0.34	0.28
*COOH→ CO(aq)	-0.59	0.48	-0.67	0.77	-0.14	-0.26	1.26	1.05	1.12	0.80
NiN_4/C										
CO_2→*CO_2	-0.40	0.18	-0.68	0.13	-0.04	-0.04	0.25	0.21	0.21	0.17
*CO_2→ *COOH	-0.47	0.18	-0.56	0.30	-0.04	-0.09	0.27	0.24	0.23	0.16
*COOH→ CO(aq)	-0.58	1.00	-0.70	1.50	-0.29	-0.52	0.93	0.58	0.64	0.06
NiN_4-O/C										
*+H_2O+e^- +H^+→ *H+H_2O	-0.54	0.36	-1.01	0.35	-0.10	-0.17	1.36	1.13	1.26	0.96
H+H_2O+H^+ → H_2+H_2O+	-0.63	0.95	-0.74	0.57	-0.30	-0.21	0.95	0.72	0.65	0.51

Table S5. Extrapolated reaction energies and dynamic barriers for each elementary step within CO_2RR and HER under -0.9 V vs. SHE based on the method proposed by Chan and Nørskov.[6]

$CO_2 \rightarrow *CO_2$	$\Delta q(is \rightarrow ts)$	$\Delta q(is \rightarrow fs)$	$\Delta E^*(is \rightarrow ts)$	$\Delta E^*(is \rightarrow fs)$	U vs. SHE
NiN_4-O/C	-0.22	-0.94	0.14	-0.78	-0.9
NiN_4/C	-0.40	-0.68	0.21	0.17	-0.9
$*CO_2 \rightarrow *COOH$					
NiN_4-O/C	-0.15	-0.28	0.19	0.00	-0.9
NiN_4/C	-0.47	-0.56	0.22	0.14	-0.9
$*COOH \rightarrow CO(aq)$					
NiN_4-O/C	-0.59	-0.63	0.39	-0.03	-0.9
NiN_4/C	-0.58	-0.70	0.35	-0.29	-0.9
HER process					
Volmer step	-0.54	-1.01	0.86	0.22	-0.9
Heyrovsky step	-0.63	-0.74	-0.07	-0.34	-0.9

References:

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2. K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. A. Arias and R. G. Hennig, *J. Chem. Phys.*, 2014, **140**, 084106.
3. A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl and J. K. Nørskov, *Energy Environ. Sci.*, 2010, **3**, 1311-1315.
4. V. Wang, N. Xu, J.-C. Liu, G. Tang and W.-T. Geng, *Comput. Phys. Commun.* 2021, **267**, 108033.
5. K. Chan and J. K. Nørskov, *J. Phys. Chem. Lett.*, 2015, **6**, 2663-2668.
6. K. Chan and J. K. Nørskov, *J. Phys. Chem. Lett.*, 2016, **7**, 1686-1690.