Coordination Environment Engineering on Nickel Single-Atom Catalysts for CO_2 Electroreduction

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Table S1. Computed formation energy (E_f) and dissolution potential (U_{diss}) of Ni-$B_XC_YN_Z$ (X+Y+Z=4), the number of electrons (n_e) involved in the dissolution for the Ni metals and the experimental standard dissolution potential ($U^o_{diss(metal)}$) of metal atoms are listed. Some of them refers to the publication of Li et al.[1]

Species	n_e	$U^0_{diss(metal)}$ (V)	E_f (eV)	U_{diss} (V)
Ni-$B_0C_3N_1$	2	-0.26	-1.58	0.53
Ni-$B_0C_2N_{2\text{-N-oppo}}$	2	-0.26	-2.91	1.19
Ni-$B_0C_2N_{2\text{-N-pen}}$	2	-0.26	-3.01	1.24
Ni-$B_0C_2N_{2\text{-N-hex}}$	2	-0.26	-3.41	1.44
Ni-$B_0C_1N_3$	2	-0.26	-4.40	1.94
Ni-$B_0C_0N_4$	2	-0.26	-5.44	2.46
Ni-$B_1C_0N_3$	2	-0.26	-4.04	1.76

Ni-$B_2C_0N_{2\text{-B-oppo}}$	2	-0.26	-3.18	1.33
Ni-$B_2C_0N_{2\text{-B-pen}}$	2	-0.26	-2.79	1.13
Ni-$B_2C_0N_{2\text{-B-hex}}$	2	-0.26	-3.17	1.32
Ni-$B_3C_0N_1$	2	-0.26	-2.58	1.03
Ni-$B_4C_0N_0$	2	-0.26	-2.16	0.82
Ni-$B_3C_1N_0$	2	-0.26	-1.60	0.54
Ni-$B_2C_2N_{0\text{-C-oppo}}$	2	-0.26	-0.98	0.23
Ni-$B_2C_2N_{0\text{-C-pen}}$	2	-0.26	-0.94	0.21
Ni-$B_2C_2N_{0\text{-C-hex}}$	2	-0.26	-1.18	0.33
Ni-$B_1C_3N_0$	2	-0.26	-0.44	-0.04
Ni-$B_0C_4N_0$	2	-0.26	0.18	-0.35
Ni-$B_1C_2N_{1\text{-C-oppo}}$	2	-0.26	-1.57	0.52
Ni-$B_1C_2N_{1\text{-C-pen}}$	2	-0.26	-1.67	0.57
Ni-$B_1C_2N_{1\text{-C-hex}}$	2	-0.26	-1.45	0.46
Ni-$B_1C_1N_{2\text{-N-oppo}}$	2	-0.26	-2.65	1.06
Ni-$B_1C_1N_{2\text{-N-pen}}$	2	-0.26	-2.85	1.17
Ni-$B_1C_1N_{2\text{-N-hex}}$	2	-0.26	-3.18	1.33
Ni-$B_2C_1N_{1\text{-B-oppo}}$	2	-0.26	-2.06	0.77
Ni-$B_2C_1N_{1\text{-B-pen}}$	2	-0.26	-1.58	0.53
Ni-$B_2C_1N_{1\text{-B-hex}}$	2	-0.26	-2.03	0.76

Table S2. Adsorption free energy (ΔG, in eV) of CO_2 and the charge transfer, with the positive

value standing for the loss of electrons (q, in $|e|$) of CO_2.

Species	q (e)	ΔG (eV)	Species	q (e)	ΔG (eV)
Ni-$B_0C_3N_1$	0.0057	-0.01	Ni-$B_2C_2N_{0\text{-C-oppo}}$	-0.012	0.20
Ni-$B_0C_2N_{2\text{-N-oppo}}$	0.0042	0.10	Ni-$B_2C_2N_{0\text{-C-pen}}$	-0.010	0.01
Ni-$B_0C_2N_{2\text{-N-pen}}$	0.0087	0.08	Ni-$B_2C_2N_{0\text{-C-hex}}$	-0.0083	0.11
Ni-$B_0C_2N_{2\text{-N-hex}}$	0.011	0.09	Ni-$B_1C_2N_{1\text{-C-oppo}}$	0.0076	0.11
Ni-$B_0C_1N_3$	0.012	0.17	Ni-$B_1C_2N_{1\text{-C-pen}}$	0.0051	0.13
Ni-$B_0C_0N_4$	0.012	0.12	Ni-$B_1C_2N_{1\text{-C-hex}}$	0.0084	0.13
Ni-$B_1C_0N_3$	0.009	-0.09	Ni-$B_1C_1N_{2\text{-N-oppo}}$	0.76	-0.25
Ni-$B_2C_0N_{2\text{-B-oppo}}$	-0.014	0.16	Ni-$B_1C_1N_{2\text{-N-pen}}$	0.96	-0.39
Ni-$B_2C_0N_{2\text{-B-pen}}$	0.019	0.09	Ni-$B_1C_1N_{2\text{-N-hex}}$	0.0080	0.06
Ni-$B_2C_0N_{2\text{-B-hex}}$	-0.0088	0.11	Ni-$B_2C_1N_{1\text{-B-oppo}}$	-0.012	0.02
Ni-$B_3C_0N_1$	-0.014	0.07	Ni-$B_2C_1N_{1\text{-B-pen}}$	0.36	-0.18
Ni-$B_4C_0N_0$	-0.011	-0.05	Ni-$B_2C_1N_{1\text{-B-hex}}$	-0.0067	0.09
Ni-$B_3C_1N_0$	-0.013	0.06			

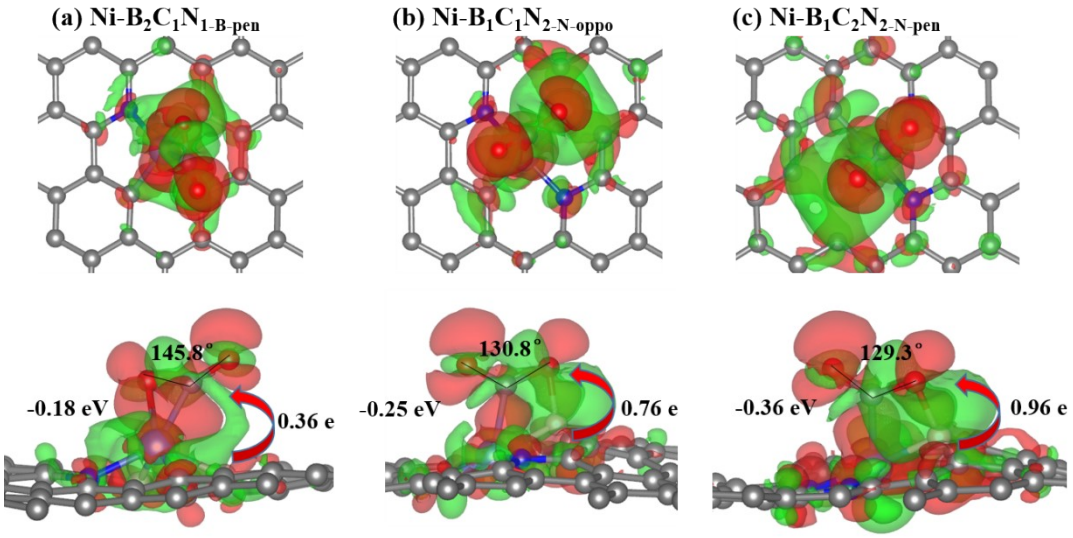


Figure S1. The charge density difference of CO_2 adsorption over Ni-$B_2C_1N_{1\text{-}B\text{-}pen}$ (a), Ni-$B_1C_1N_{2\text{-}N\text{-}oppo}$ (b), and Ni-$B_1C_1N_{2\text{-}N\text{-}pen}$ (c), with isosurface level of 0.001 e $Å^{-3}$. The green and red region represents electron depletion and accumulation, respectively.

Table S3. The adsorption energies of *COOH and *CO on Ni-$B_XC_YN_Z$ systems.

Species	E_{ads}(*COOH)	E_{ads}(*CO)	Species	E_{ads}(*COOH)	E_{ads}(*CO)
Ni-$B_0C_3N_1$	-0.45	-1.31	Ni-$B_2C_2N_{0\text{-}C\text{-}oppo}$	-0.13	-1.38
Ni-$B_0C_2N_{2\text{-}N\text{-}oppo}$	-0.11	-1.37	Ni-$B_2C_2N_{0\text{-}C\text{-}pen}$	-0.36	-1.77
Ni-$B_0C_2N_{2\text{-}N\text{-}pen}$	-0.19	-1.21	Ni-$B_2C_2N_{0\text{-}C\text{-}hex}$	0.06	-1.30
Ni-$B_0C_2N_{2\text{-}N\text{-}hex}$	-0.03	-1.25	Ni-$B_1C_2N_{1\text{-}C\text{-}oppo}$	-0.91	-2.35
Ni-$B_0C_1N_3$	0.07	-0.60	Ni-$B_1C_2N_{1\text{-}C\text{-}pen}$	-1.16	-2.30
Ni-$B_0C_0N_4$	0.88	-0.32	Ni-$B_1C_2N_{1\text{-}C\text{-}hex}$	-1.50	-2.70
Ni-$B_1C_0N_3$	-1.02	-1.79	Ni-$B_1C_1N_{2\text{-}N\text{-}oppo}$	-1.48	-1.61
Ni-$B_2C_0N_{2\text{-}B\text{-}oppo}$	-1.14	-2.02	Ni-$B_1C_1N_{2\text{-}N\text{-}pen}$	-1.13	-2.04
Ni-$B_2C_0N_{2\text{-}B\text{-}oppo}$	-1.27	-2.35	Ni-$B_1C_1N_{2\text{-}N\text{-}hex}$	-1.01	-1.90

Ni-$B_2C_0N_{2\text{-B-hex}}$	-0.91	-1.89	Ni-$B_2C_1N_{1\text{-B-oppo}}$	-0.99	-2.12
Ni-$B_3C_0N_1$	-0.43	-1.90	Ni-$B_2C_1N_{1\text{-B-pen}}$	-1.64	-2.51
Ni-$B_4C_0N_0$	-0.56	-1.91	Ni-$B_2C_1N_{1\text{-B-hex}}$	-0.62	-1.70
Ni-$B_3C_1N_0$	-0.26	-1.71			

Table S4. The detailed electronic energy (E_*), zero-point energy (E_{ZPE}), entropy corrections (TS), free energy (G), and Gibbs free energy change (ΔG) of critical intermediate in Ni-$B_XC_YN_Z$ systems during electrochemical CO_2RR.

Species	E_*	E_{*CO_2}	E_{ZPE}	TS	G	ΔG
Ni-$B_0C_3N_1$	-61653.05	-66780.15	0.31	0.07	-66779.91	-0.01
Ni-$B_0C_2N_{2\text{-N-oppo}}$	-62106.96	-67233.95	0.31	0.07	-67233.71	0.10
Ni-$B_0C_2N_{2\text{-N-pen}}$	-62107.06	-67234.08	0.31	0.07	-67233.84	0.08
Ni-$B_0C_2N_{2\text{-N-hex}}$	-62107.46	-67234.41	0.31	0.13	-67234.23	0.09
Ni-$B_0C_1N_3$	-62561.03	-67687.95	0.30	0.07	-67687.72	0.17
Ni-$B_0C_0N_4$	-63014.66	-68141.59	0.31	0.13	-68141.40	0.12
Ni-$B_1C_0N_3$	-62199.82	-67326.93	0.31	0.14	-67326.76	-0.09
Ni-$B_2C_0N_{2\text{-B-oppo}}$	-61385.51	-66512.46	0.31	0.06	-66512.21	0.16
Ni-$B_2C_0N_{2\text{-B-pen}}$	-61385.12	-66512.08	0.31	0.12	-66511.89	0.09
Ni-$B_2C_0N_{2\text{-B-hex}}$	-61385.50	-66512.45	0.31	0.12	-66512.25	0.11
Ni-$B_3C_0N_1$	-60571.48	-65698.43	0.32	0.15	-65698.26	0.07
Ni-$B_4C_0N_0$	-59757.62	-64884.67	0.32	0.16	-64884.52	-0.05
Ni-$B_3C_1N_0$	-60117.92	-65244.90	0.31	0.12	-65244.71	0.06
Ni-$B_2C_2N_{0\text{-C-oppo}}$	-60478.15	-65604.97	0.31	0.14	-65604.80	0.20
Ni-$B_2C_2N_{0\text{-C-pen}}$	-60478.11	-65605.08	0.31	0.18	-65604.95	0.01
Ni-$B_2C_2N_{0\text{-C-hex}}$	-60478.35	-65605.28	0.31	0.13	-65605.09	0.11
Ni-$B_1C_2N_{1\text{-C-oppo}}$	-61292.18	-66419.10	0.31	0.13	-66418.93	0.11
Ni-$B_1C_2N_{1\text{-C-pen}}$	-61292.28	-66419.19	0.31	0.12	-66419.00	0.13
Ni-$B_1C_2N_{1\text{-C-hex}}$	-61292.06	-66418.96	0.31	0.13	-66418.79	0.13
Ni-$B_1C_1N_{2\text{-N-oppo}}$	-61745.84	-66873.13	0.31	0.13	-66872.95	-0.25
Ni-$B_1C_1N_{2\text{-N-pen}}$	-61746.05	-66873.47	0.33	0.16	-66873.30	-0.39
Ni-$B_1C_1N_{2\text{-N-hex}}$	-61746.37	-66873.37	0.31	0.11	-66873.16	0.06
Ni-$B_2C_1N_{1\text{-B-oppo}}$	-60931.81	-66058.80	0.32	0.17	-66058.65	0.02
Ni-$B_2C_1N_{1\text{-B-pen}}$	-60931.34	-66058.55	0.30	0.12	-66058.37	-0.18
Ni-$B_2C_1N_{1\text{-B-hex}}$	-60931.78	-66058.74	0.31	0.12	-66058.55	0.09

	E_{*COOH}	E_{ZPE}	TS	G	ΔG
Ni-$B_0C_3N_1$	-66795.88	0.63	0.15	-66795.40	0.36
Ni-B0$C_2N_{2\text{-N-oppo}}$	-67249.45	0.62	0.22	-67249.05	0.51
Ni-$B_0C_2N_{2\text{-N-pen}}$	-67249.64	0.63	0.16	-67249.18	0.51
Ni-$B_0C_2N_{2\text{-N-hex}}$	-67249.88	0.61	0.12	-67249.38	0.69
Ni-B_0C1N_3	-67703.35	0.61	0.17	-67702.91	0.66
Ni-$B_0C_0N_4$	-68156.17	0.57	0.16	-68155.76	1.49
Ni-$B_1C_0N_3$	-67343.23	0.63	0.15	-67342.74	-0.13
Ni-$B_2C_0N_{2\text{-B-oppo}}$	-66529.05	0.65	0.20	-66528.60	-0.54
Ni-$B_2C_0N_{2\text{-B-pen}}$	-66528.78	0.64	0.17	-66528.31	-0.57
Ni-$B_2C_0N_{2\text{-B-hex}}$	-66528.80	0.62	0.17	-66528.35	-0.25
Ni-$B_3C_0N_1$	-65714.30	0.63	0.15	-65713.82	0.28
Ni-$B_4C_0N_0$	-64900.57	0.62	0.18	-64900.12	0.25
Ni-$B_3C_1N_0$	-65260.57	0.63	0.17	-65260.11	0.45
Ni-$B_2C_2N_{0\text{-C-oppo}}$	-65620.67	0.62	0.12	-65620.16	0.48
Ni-$B_2C_2N_{0\text{-C-pen}}$	-65620.85	0.62	0.11	-65620.34	0.46
Ni-$B_2C_2N_{0\text{-C-hex}}$	-65620.68	0.62	0.23	-65620.29	0.65
Ni-$B_1C_2N_{1\text{-C-oppo}}$	-66435.48	0.64	0.15	-66434.98	-0.21
Ni-$B_1C_2N_{1\text{-C-pen}}$	-66435.83	0.64	0.14	-66435.33	-0.48
Ni-$B_1C_2N_{1\text{-C-hex}}$	-66435.95	0.64	0.14	-66435.44	-0.81
Ni-$B_1C_1N_{2\text{-N-oppo}}$	-66889.71	0.65	0.16	-66889.21	-0.42
Ni-$B_1C_1N_{2\text{-N-pen}}$	-66889.57	0.64	0.15	-66889.08	0.06
Ni-$B_1C_1N_{2\text{-N-hex}}$	-66889.77	0.64	0.16	-66889.28	-0.27
Ni-$B_2C_1N_{1\text{-B-oppo}}$	-66075.19	0.65	0.13	-66074.68	-0.18
Ni-$B_2C_1N_{1\text{-B-pen}}$	-66075.37	0.66	0.15	-66074.85	-0.64
Ni-$B_2C_1N_{1\text{-B-hex}}$	-66074.80	0.64	0.13	-66074.29	0.11
	E_{*CO}	E_{ZPE}	TS	G	ΔG
Ni-$B_0C_3N_1$	-64734.22	0.19	0.12	-64734.14	-0.42
Ni-$B_0C_2N_{2\text{-N-oppo}}$	-65188.20	0.19	0.04	-65188.05	-0.68
Ni-$B_0C_2N_{2\text{-N-pen}}$	-65188.13	0.19	0.05	-65187.99	-0.49
Ni-$B_0C_2N_{2\text{-N-hex}}$	-65188.57	0.19	0.11	-65188.49	-0.78
Ni-$B_0C_1N_3$	-65641.50	0.17	0.12	-65641.45	-0.21
Ni-$B_0C_0N_4$	-66094.84	0.15	0.15	-66094.84	-0.76
Ni-$B_1C_0N_3$	-65281.48	0.21	0.06	-65281.33	-0.26
Ni-$B_2C_0N_{2\text{-B-oppo}}$	-64467.39	0.22	0.12	-64467.30	-0.38
Ni-$B_2C_0N_{2\text{-B-pen}}$	-64467.34	0.22	0.11	-64467.23	-0.60
Ni-$B_2C_0N_{2\text{-B-hex}}$	-64467.26	0.20	0.10	-64467.16	-0.49
Ni-$B_3C_0N_1$	-63653.24	0.21	0.15	-63653.18	-1.03
Ni-$B_4C_0N_0$	-62839.39	0.20	0.10	-62839.30	-0.86
Ni-$B_3C_1N_0$	-63199.48	0.20	0.10	-63199.39	-0.96
Ni-$B_2C_2N_{0\text{-C-oppo}}$	-63559.39	0.20	0.04	-63559.23	-0.75
Ni-$B_2C_2N_{0\text{-C-pen}}$	-63559.74	0.21	0.09	-63559.62	-0.96

Ni-$B_2C_2N_{0\text{-C-hex}}$	-63559.51	0.19	0.11	-63559.43	-0.82
Ni-$B_1C_2N_{1\text{-C-oppo}}$	-64374.39	0.22	0.12	-64374.29	-0.98
Ni-$B_1C_2N_{1\text{-C-pen}}$	-64374.44	0.22	0.11	-64374.33	-0.68
Ni-$B_1C_2N_{1\text{-C-hex}}$	-64374.62	0.22	0.11	-64374.51	-0.74
Ni-$B_1C_1N_{2\text{-N-oppo}}$	-64827.31	0.20	0.10	-64827.22	0.32
Ni-$B_1C_1N_{2\text{-N-pen}}$	-64827.95	0.22	0.12	-64827.85	-0.45
Ni-$B_1C_1N_{2\text{-N-hex}}$	-64828.13	0.22	0.12	-64828.04	-0.43
Ni-$B_2C_1N_{1\text{-B-oppo}}$	-64013.79	0.22	0.11	-64013.68	-0.68
Ni-$B_2C_1N_{1\text{-B-oppo}}$	-64013.71	0.22	0.11	-64013.60	-0.43
Ni-$B_2C_1N_{1\text{-B-oppo}}$	-64013.35	0.21	0.12	-64013.25	-0.65
	$E_{*\mathrm{H}}$	E_{ZPE}	TS	G	ΔG
Ni-$B_0C_3N_1$	-61669.55	0.28	0.00	-61669.27	-0.38
Ni-$B_0C_2N_{2\text{-N-oppo}}$	-62123.37	0.28	0.00	-62123.09	-0.28
Ni-$B_0C2N_{2\text{-N-pen}}$	-62123.36	0.27	0.00	-62123.09	-0.19
Ni-$B_0C_2N_{2\text{-N-hex}}$	-62122.93	0.16	0.03	-62122.80	0.50
Ni-$B_0C_1N_3$	-62577.05	0.28	0.00	-62576.77	0.11
Ni-$B_0C_0N_4$	-63029.05	0.11	0.01	-63028.95	1.55
Ni-$B_1C_0N_3$	-62216.55	0.25	0.00	-62216.30	-0.63
Ni-$B2C_0N_{2\text{-B-oppo}}$	-61402.28	0.26	0.00	-61402.02	-0.66
Ni-$B_2C0N_{2\text{-B-pen}}$	-61402.10	0.25	0.00	-61401.86	-0.89
Ni-$B_2C_0N_{2\text{-B-hex}}$	-61402.42	0.25	0.00	-61402.17	-0.82
Ni-$B_3C_0N_1$	-60587.75	0.24	0.00	-60587.51	-0.19
Ni-$B_4C_0N_0$	-59773.80	0.23	0.00	-59773.57	-0.11
Ni-$B_3C_1N_0$	-60133.96	0.23	0.00	-60133.74	0.03
Ni-$B_2C_2N_{0\text{-C-oppo}}$	-60494.08	0.28	0.00	-60493.80	0.19
Ni-$B_2C_2N_{0\text{-C-pen}}$	-60494.44	0.25	0.00	-60494.19	-0.24
Ni-$B_2C_2N_{0\text{-C-hex}}$	-60494.44	0.24	0.00	-60494.20	-0.01
Ni-$B_1C_2N_{1\text{-C-oppo}}$	-61309.09	0.25	0.00	-61308.84	-0.82
Ni-$B_1C_2N_{1\text{-C-pen}}$	-61309.29	0.26	0.00	-61309.03	-0.90
Ni-$B_1C_2N_{1\text{-C-hex}}$	-61309.40	0.26	0.00	-61309.14	-1.24
Ni-$B_1C_1N_{2\text{-N-oppo}}$	-61763.05	0.25	0.00	-61762.80	-1.11
Ni-$B_1C_1N_{2\text{-N-pen}}$	-61762.90	0.25	0.00	-61762.65	-0.75
Ni-$B_1C_1N_{2\text{-N-hex}}$	-61763.18	0.26	0.00	-61762.93	-0.71
Ni-$B_2C_1N_{1\text{-B-oppo}}$	-60948.52	0.25	0.00	-60948.27	-0.61
Ni-$B_2C_1N_{1\text{-B-oppo}}$	-60948.73	0.25	0.00	-60948.48	-1.30
Ni-$B_2C_1N_{1\text{-B-oppo}}$	-60948.26	0.25	0.00	-60948.02	-0.39

Table S5. The detailed electronic energy (E_*), zero-point energy (E_{ZPE}), entropy corrections (TS), and free energy (G) of isolated molecule during electrochemical CO_2RR.

Species	E_*	E_{ZPE}	TS	G

CO_2	-5126.61	0.31	0.66	-5126.86
H_2	-31.56	0.27	0.40	-31.69
CO	-3079.86	0.13	0.61	-3080.34
H_2O	-2077.44	0.59	0.58	-2077.52

Table S6. The reaction free energy change of the elementary reaction step of CO_2RR and the competitive HER on the Ni-$B_XC_YN_Z$ systems with the unit in eV.

	ΔG_i	ΔG_{ii}	ΔG_{iii}	ΔG_{iv}	ΔG_{HER}
Ni-$B_0C_3N_1$	-0.01	0.36	-0.42	0.07	0.38
Ni-$B_0C_2N_{2\text{-N-oppo}}$	0.10	0.51	-0.68	0.06	0.28
Ni-$B_0C_2N_{2\text{-N-pen}}$	0.08	0.51	-0.49	-0.10	0.19
Ni-$B_0C_2N_{2\text{-N-hex}}$	0.09	0.69	-0.78	0.00	0.50
Ni-$B_0C_1N_3$	0.17	0.66	-0.21	-0.62	0.11
Ni-$B_0C_0N_4$	0.12	1.49	-0.76	-0.84	1.55
Ni-$B_1C_0N_3$	-0.09	-0.13	-0.26	0.48	0.63
Ni-$B_2C_0N_{2\text{-B-oppo}}$	0.16	-0.54	-0.38	0.76	0.66
Ni-$B_2C_0N_{2\text{-B-pen}}$	0.09	-0.57	-0.60	1.08	0.89
Ni-$B_2C_0N_{2\text{-B-hex}}$	0.11	-0.25	-0.49	0.63	0.82
Ni-$B_3C_0N_1$	0.07	0.28	-1.03	0.67	0.19
Ni-$B_4C_0N_0$	-0.05	0.25	-0.86	0.66	0.11
Ni-$B_3C_1N_0$	0.06	0.45	-0.96	0.45	0.03
Ni-$B_2C_2N_{0\text{-C-oppo}}$	0.20	0.48	-0.75	0.06	0.19
Ni-$B_2C_2N_{0\text{-C-pen}}$	0.01	0.46	-0.96	0.49	0.24
Ni-$B_2C_2N_{0\text{-C-hex}}$	0.11	0.65	-0.82	0.05	0.01
Ni-$B_1C_2N_{1\text{-C-oppo}}$	0.11	-0.21	-0.98	1.08	0.82
Ni-$B_1C_2N_{1\text{-C-pen}}$	0.13	-0.48	-0.68	1.02	0.90
Ni-$B_1C_2N_{1\text{-C-hex}}$	0.13	-0.81	-0.74	1.42	1.24
Ni-$B_1C_1N_{2\text{-N-oppo}}$	-0.25	-0.42	0.32	0.35	1.11
Ni-$B_1C_1N_{2\text{-N-pen}}$	-0.39	0.06	-0.45	0.78	0.75
Ni-$B_1C_1N_{2\text{-N-hex}}$	0.06	-0.27	-0.43	0.64	0.71
Ni-$B_2C_1N_{1\text{-B-oppo}}$	0.02	-0.18	-0.68	0.84	0.61
Ni-$B_2C_1N_{1\text{-B-oppo}}$	-0.18	-0.64	-0.43	1.24	1.30
Ni-$B_2C_1N_{1\text{-B-oppo}}$	0.09	0.11	-0.65	0.44	0.39

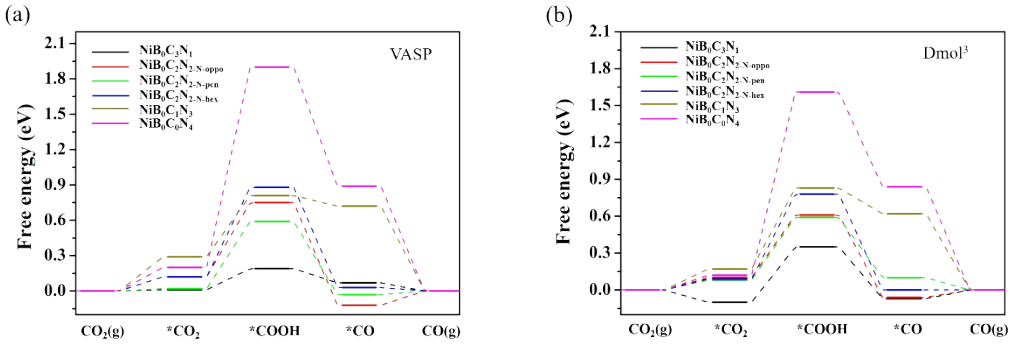


Figure S2. Free energy diagrams of CO_2RR on B-free Ni-$B_XC_YN_Z$ (X = 0) systems based on VASP (a) and DMol³ (b) calculations.

Table S7. Comparison of the reaction free energy change of the potential-determining step of CO_2RR on B-free Ni-$B_XC_YN_Z$ (X = 0) based on DMol³ and VASP results.

	DMol³	VASP
	ΔG(*COOH)/eV	ΔG(*COOH)/eV
Ni-$B_0C_3N_1$	0.36	0.18
Ni-$B_0C_2N_{2\text{-N-oppo}}$	0.51	0.62
Ni-$B_0C_2N_{2\text{-N-pen}}$	0.51	0.57
Ni-$B_0C_2N_{2\text{-N-hex}}$	0.69	0.75
Ni-$B_0C_1N_3$	0.66	0.52
Ni-$B_0C_0N_4$	1.49	1.70

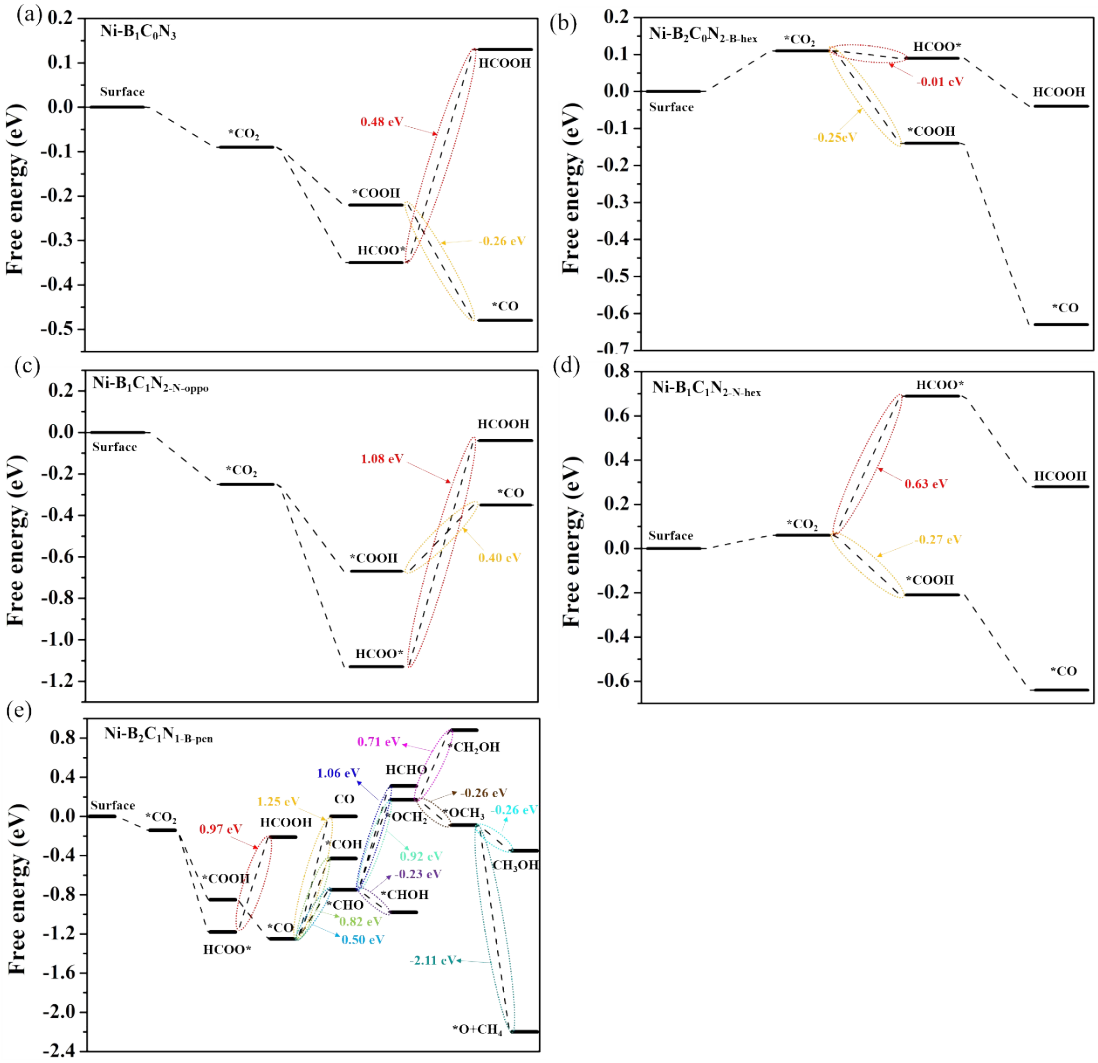
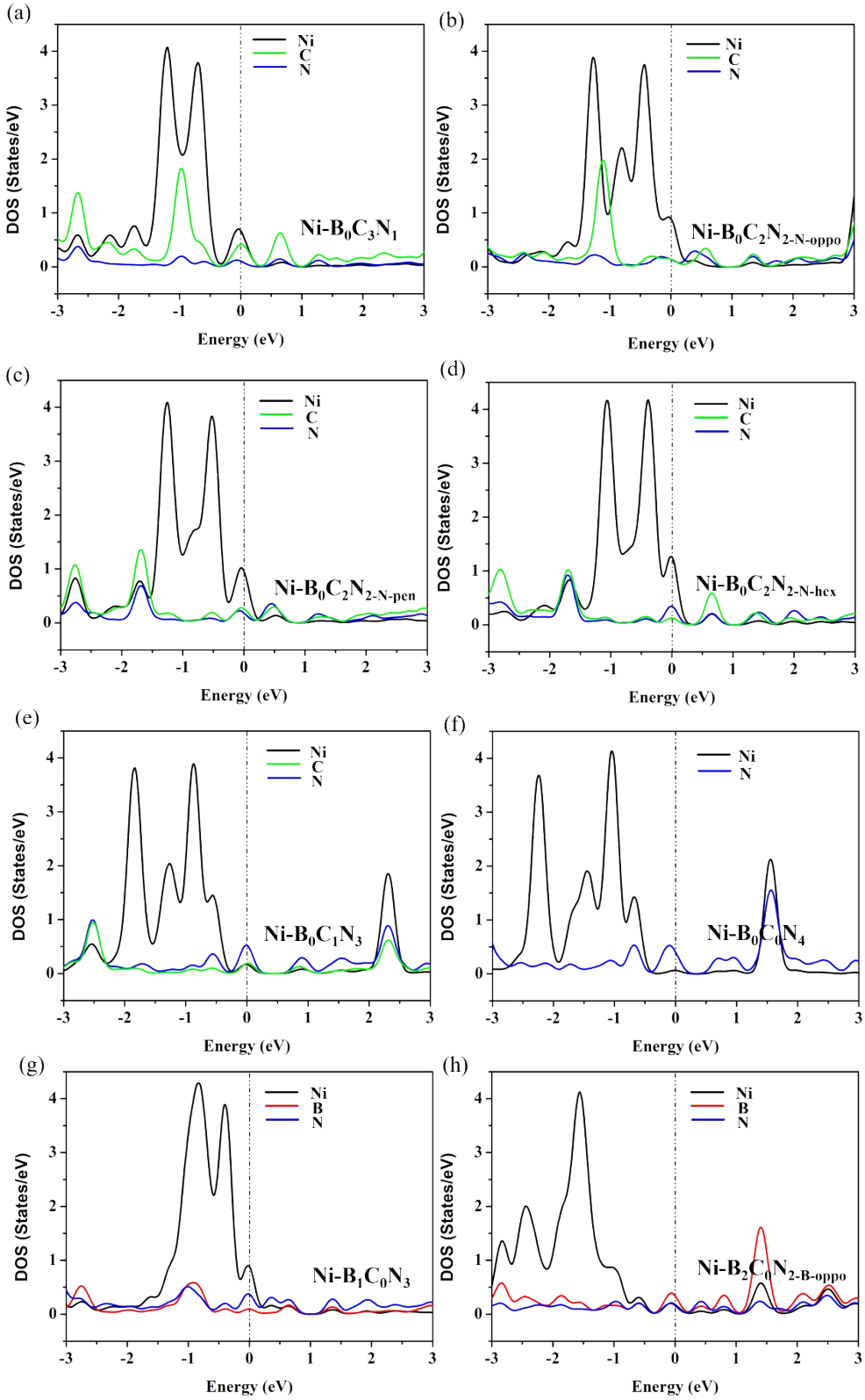
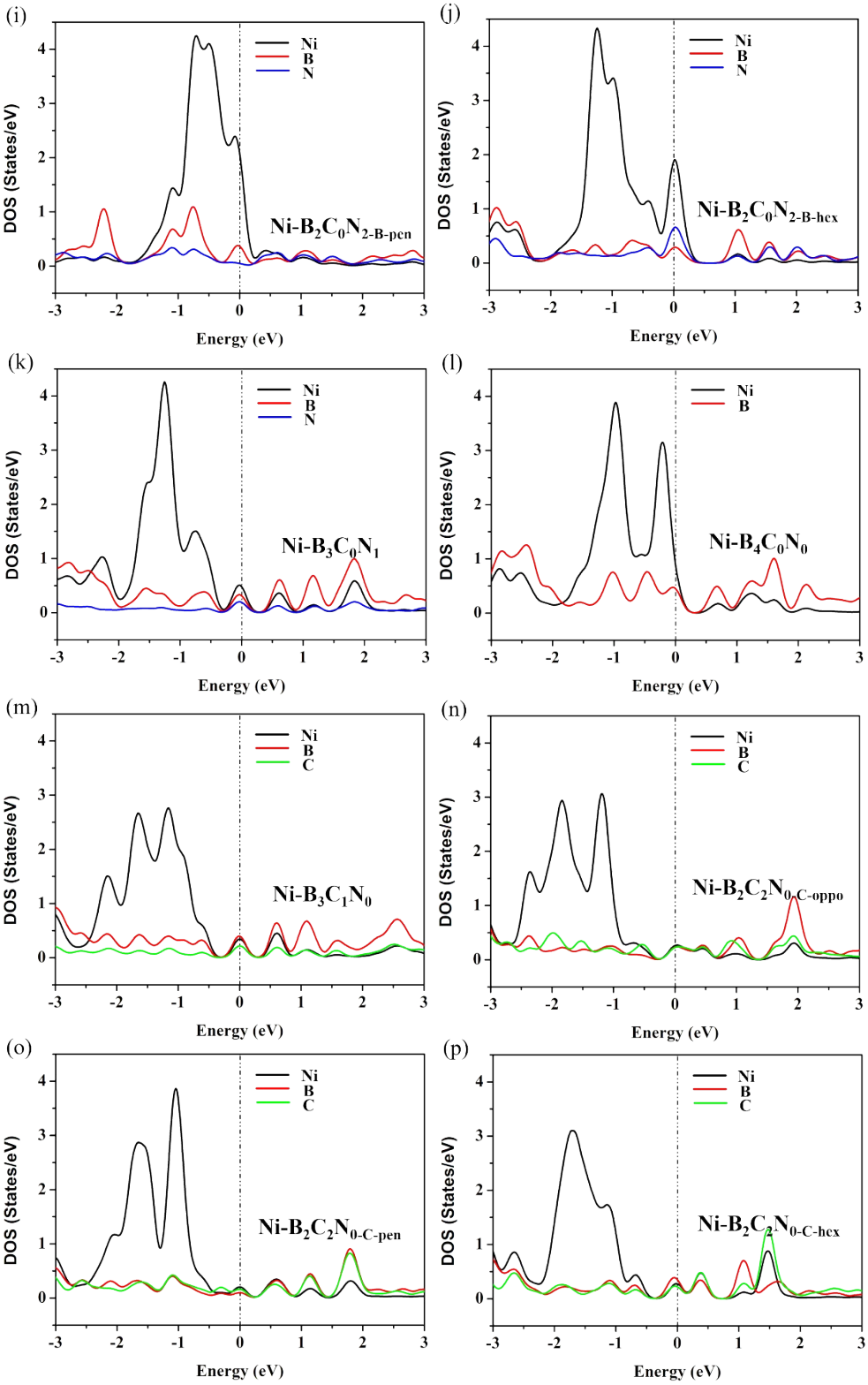
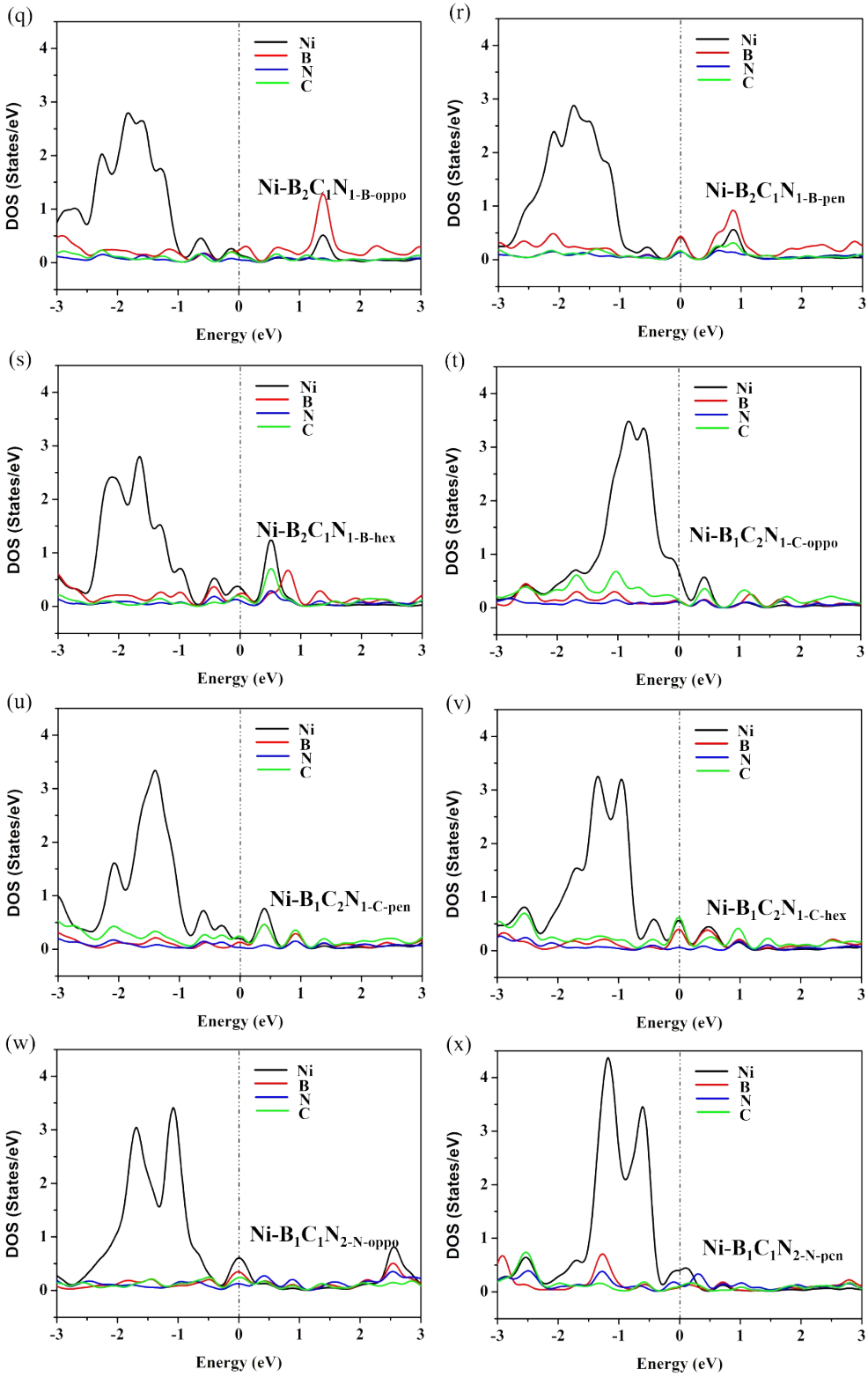


Figure S3. Free-energy profiles for the CO_2 reduction reaction to CO and HCOOH on (a) Ni-$B_1C_0N_3$, (b) Ni-$B_2C_0N_{2\text{-B-hex}}$, (c) Ni-$B_1C_1N_{2\text{-N-oppo}}$, (d) Ni-$B_1C_1N_{2\text{-N-hex}}$ and the more deep-reduced products on (e) Ni-$B_2C_1N_{1\text{-B-pen}}$ at zero applied potential.


(a)
Ni
C
N
Ni-B0C3N1
DOS (States/eV)
Energy (eV)
(b)
Ni
C
N
Ni-B0C2N2-N-oppo
DOS (States/eV)
Energy (eV)
(c)
Ni
C
N
Ni-B0C2N2-N-pen
DOS (States/eV)
Energy (eV)
(d)
Ni
C
N
Ni-B0C2N2-N-hex
DOS (States/eV)
Energy (eV)
(e)
Ni
C
N
Ni-B0C1N3
DOS (States/eV)
Energy (eV)
(f)
Ni
N
Ni-B0C0N4
DOS (States/eV)
Energy (eV)
(g)
Ni
B
N
Ni-B1C0N3
DOS (States/eV)
Energy (eV)
(h)
Ni
B
N
Ni-B2C0N2-B-oppo
DOS (States/eV)
Energy (eV)


(i)
Ni
B
N
Ni-B2C0N2-B-pen
DOS (States/eV)
Energy (eV)
(j)
Ni
B
N
Ni-B2C0N2-B-hex
DOS (States/eV)
Energy (eV)
(k)
Ni
B
N
Ni-B3C0N1
DOS (States/eV)
Energy (eV)
(l)
Ni
B
Ni-B4C0N0
DOS (States/eV)
Energy (eV)
(m)
Ni
B
C
Ni-B3C1N0
DOS (States/eV)
Energy (eV)
(n)
Ni
B
C
Ni-B2C2N0-C-oppo
DOS (States/eV)
Energy (eV)
(o)
Ni
B
C
Ni-B2C2N0-C-pen
DOS (States/eV)
Energy (eV)
(p)
Ni
B
C
Ni-B2C2N0-C-hex
DOS (States/eV)
Energy (eV)


(q)
Ni
B
N
C
Ni-B2C1N1-B-oppo
DOS (States/eV)
Energy (eV)
(r)
Ni-B2C1N1-B-pen
(s)
Ni-B2C1N1-B-hex
(t)
Ni-B1C2N1-C-oppo
(u)
Ni-B1C2N1-C-pen
(v)
Ni-B1C2N1-C-hex
(w)
Ni-B1C1N2-N-oppo
(x)
Ni-B1C1N2-N-pen

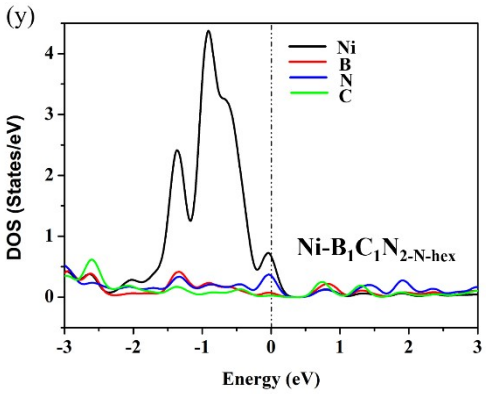


Figure S4. Projected density of states of Ni and coordination atoms (B, C and N) on B-free Ni-$B_XC_YN_Z$ (X = 0) (a-f) and B-coordinated Ni-$B_XC_YN_Z$ (X ≠ 0) (g-y). The Fermi level is set as 0 eV and denoted by a black vertical dotted line.

Table S8. The Bader charge analyses of Ni and B in pure Ni-$B_XC_YN_Z$ systems. The unit of Bader charge is in $|e|$.

	Pure catalysts	
	q(Ni)	q(B)
Ni-$B_0C_3N_1$	0.625	-
Ni-$B_0C_2N_{2\text{-N-oppo}}$	0.674	-
Ni-$B_0C_2N_{2\text{-N-pen}}$	0.626	-
Ni-$B_0C_2N_{2\text{-N-hex}}$	0.629	-
Ni-$B_0C_1N_3$	0.726	-
Ni-$B_0C_0N_4$	0.830	-
Ni-$B_1C_0N_3$	0.439	1.43
Ni-$B_2C_0N_{2\text{-B-oppo}}$	0.316	1.47, 1.47
Ni-$B_2C_0N_{2\text{-B-pen}}$	0.144	1.31, 1.23
Ni-$B_2C_0N_{2\text{-B-hex}}$	0.337	1.30, 1.24

Ni-$B_3C_0N_1$	0.0703	1.46, 1.25, 1.19
Ni-$B_4C_0N_0$	-0.0411	1.30, 1.29, 1.19, 1.19
Ni-$B_3C_1N_0$	0.0834	1.42, 1.25, 1.19
Ni-$B_2C_2N_{0\text{-C-oppo}}$	0.150	1.51, 1.50
Ni-$B_2C_2N_{0\text{-N-pen}}$	0.133	1.46, 1.39
Ni-$B_2C_2N_{0\text{-N-hex}}$	0.400	1.23, 1.15
Ni-$B_1C_2N_{1\text{-C-oppo}}$	0.389	1.38
Ni-$B_1C_2N_{1\text{-C-pen}}$	0.421	1.39
Ni-$B_1C_2N_{1\text{-C-hex}}$	0.421	1.31
Ni-$B_1C_1N_{2\text{-N-oppo}}$	0.491	1.30
Ni-$B_1C_1N_{2\text{-N-pen}}$	0.404	1.30
Ni-$B_1C_1N_{2\text{-N-hex}}$	0.410	1.33
Ni-$B_2C_1N_{1\text{-B-oppo}}$	0.154	1.47, 1.45
Ni-$B_2C_1N_{1\text{-B-pen}}$	0.199	1.44, 1.43
Ni-$B_2C_1N_{1\text{-B-hex}}$	0.473	1.22, 1.19

Table S9. Bader charge analysis of active sites (Ni or B atom) on *COOH and *CO adsorbed Ni-$B_XC_YN_Z$. The unit of Bader charge is in $|e|$.

	*COOH		*CO	
	q (Ni)	q (B)	q (Ni)	q (B)
Ni-$B_0C_3N_1$	0.653	-	0.655	-

Ni-$B_0C_2N_{2\text{-}N\text{-}oppo}$	0.759	-	0.748	-
Ni-$B_0C_2N_{2\text{-}N\text{-}pen}$	0.728	-	0.718	-
Ni-$B_0C_2N_{2\text{-}N\text{-}hex}$	0.719	-	0.702	-
Ni-$B_0C_1N_3$	0.811	-	0.804	-
Ni-$B_0C_0N_4$	0.908	-	0.848	-
Ni-$B_1C_0N_3$	0.665	1.57	0.653	1.64
Ni-$B_2C_0N_{2\text{-}B\text{-}oppo}$	0.384	1.66, 1.48	0.412	1.70, 1.47
Ni-$B_2C_0N_{2\text{-}B\text{-}pen}$	0.326	1.70, 1.44	0.345	1.67, 1.35
Ni-$B_2C_0N_{2\text{-}B\text{-}hex}$	0.293	1.46, 1.36	0.501	1.21, 1.13
Ni-$B_3C_0N_1$	0.211	1.43, 1.28, 1.22	0.249	1.50, 1.23, 1.13
Ni-$B_4C_0N_0$	0.0782	1.45, 1.38, 1.44, 1.18	0.107	1.28, 1.26, 1.18, 1.17
Ni-$B_3C_1N_0$	0.291	1.51, 1.22, 1.13	0.203	1.42, 1.26, 1.16
Ni-$B_2C_2N_{0\text{-}C\text{-}oppo}$	0.513	1.45, 1.40	0.536	1.39, 1.39
Ni-$B_2C_2N_{0\text{-}N\text{-}pen}$	0.380	1.48, 1.38	0.291	1.49, 1.43
Ni-$B_2C_2N_{0\text{-}N\text{-}hex}$	0.480	1.25, 1.19	0.449	1.20, 1.20
Ni-$B_1C_2N_{1\text{-}C\text{-}oppo}$	0.580	1.62	0.585	1.69
Ni-$B_1C_2N_{1\text{-}C\text{-}pen}$	0.562	1.67	0.588	1.70
Ni-$B_1C_2N_{1\text{-}C\text{-}hex}$	0.539	1.68	0.566	1.67
Ni-$B_1C_1N_{2\text{-}N\text{-}oppo}$	0.618	1.64	0.500	1.43
Ni-$B_1C_1N_{2\text{-}N\text{-}pen}$	0.602	1.60	0.613	1.65
Ni-$B_1C_1N_{2\text{-}N\text{-}hex}$	0.612	1.61	0.605	1.65
Ni-$B_2C_1N_{1\text{-}B\text{-}oppo}$	0.341	1.68, 1.40	0.317	1.70, 1.40

Ni-$B_2C_1N_{1\text{-}B\text{-}pen}$	0.235	1.75, 1.44	0.311	1.67, 1.43
Ni-$B_2C_1N_{1\text{-}B\text{-}hex}$	0.512	1.44, 1.18	0.382	1.67, 1.28

1. F. H. Li and Q. Tang, *J. Mater. Chem. A*, 2021, **9**, 8761-8771.