Supporting Information

Understanding Activity Origin for Oxygen Reduction Reaction on Bi-Atom Catalysts by DFT Study and Machine-Learning

Chaofang Deng[a, b], Yang Su[b], Fuhua Li[b], Weifeng Shen[b], Zhongfang Chen*, [c]and Qing Tang*,[b]

[a] Cooperative Innovation Center of Lipid Resources and Children's Daily Chemicals, Chongqing University of Education, Chongqing 400067, China

[b] School of Chemistry and Chemical Engineering, Chongqing Key Laboratory of Theoretical and Computational Chemistry, Chongqing University, Chongqing 401331, China

[c]Department of Chemistry, University of Puerto Rico, Rio Piedras, San Juan, PR 00931, USA

* To whom correspondence should be addressed. E-mail: zhongfangchen@gmail.com; qingtang@cqu.edu.cn.

Computational details

The detailed pathway for associative mechanism in ORR was adopted in our work as the following four steps:

$$O_2 + H^+ + e^- \leftrightarrow *OOH \quad \text{(SR1)}$$

$$*OOH + H^+ + e^- \leftrightarrow *O + H_2O \quad \text{(SR2)}$$

$$*O + H^+ + e^- \leftrightarrow *OH \quad \text{(SR3)}$$

$$*OH + H^+ + e^- \leftrightarrow * + H_2O \quad \text{(SR4)}$$

Accordingly, considering the effect of electrode potential (U), the reaction free energy of SR1-SR4 can be calculated by:

$$\Delta G_1 = G_{*OOH} - G_{*O_2} - 0.5G_{H_2} + eU \quad \text{(S1a)}$$

$$\Delta G_2 = G_{*O} + G_{H_2O} - G_{*OOH} - 0.5G_{H_2} + eU \quad \text{(S1b)}$$

$$\Delta G_3 = G_{*OH} - G_{*O} - 0.5G_{H_2} + eU \quad \text{(S1c)}$$

$$\Delta G_4 = G_{H_2O} + G_{*} - G_{*OH} - 0.5G_{H_2} + eU \quad \text{(S1d)}$$

Owing to the high-spin ground state of the O_2 molecule, it is poorly described in DFT computations. To avoid calculating energy of O_2, we first calculated reaction free energy of equations of S2a-S2c.

$$*+2H_2O \leftrightarrow *OOH+3/2H_2 \quad \text{(S2a)}$$

$$*+H_2O \leftrightarrow *O+H_2 \quad \text{(S2b)}$$

$$*+H_2O \leftrightarrow *OH+1/2H_2 \quad \text{(S2c)}$$

Then, the reaction free energy of equations of S2a-S2c can be defined as：

$$\Delta G_{*OOH} = 1.5G_{*H_2} + G_{*OOH} - 2G_{H_2O} - G_{*} \quad \text{(S3a)}$$

$$\Delta G_{*\mathrm{O}} = G_{*\mathrm{H_2}} + G_{*\mathrm{O}} - G_{\mathrm{H_2O}} - G_{*} \quad \text{(S3b)}$$

$$\Delta G_{*\mathrm{OH}} = 0.5G_{*\mathrm{H_2}} + G_{*\mathrm{OH}} - G_{\mathrm{H_2O}} - G_{*} \quad \text{(S3c)}$$

At the equilibrium potential of 1.23 V, the reaction free energy of $\mathrm{O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O}$ is 4.92 eV. Therefore, ΔG_1 can be determined by $\Delta G_1 = 4.92 - (\Delta G_2 + \Delta G_3 + \Delta G_4)$. Combining with equations S3a-S3c, the reaction free energy of SR1-SR4 can be represented by:

$$\Delta G_1 = \Delta G_{*\mathrm{OOH}} - 4.92 + \mathrm{e}U \quad \text{(S4a)}$$

$$\Delta G_2 = \Delta G_{*\mathrm{O}} - \Delta G_{*\mathrm{OOH}} + \mathrm{e}U \quad \text{(S4b)}$$

$$\Delta G_3 = \Delta G_{*\mathrm{OH}} - \Delta G_{*\mathrm{O}} + \mathrm{e}U \quad \text{(S4c)}$$

$$\Delta G_4 = -\Delta G_{*\mathrm{OH}} + \mathrm{e}U \quad \text{(S4d)}$$

Based on above analysis, the elementary reaction of SR1-SR4 can be expressed by the adsorption free energies of OOH ($\Delta G_{*\mathrm{OOH}}$), O ($\Delta G_{*\mathrm{O}}$) and OH ($\Delta G_{*\mathrm{OH}}$).

The detailed pathway for dissociative mechanisms in ORR was adopted in our work as the following five steps:

$$\mathrm{O_2 \leftrightarrow {*O_A}{*O_B}} \quad \text{(SR5)}$$

$$\mathrm{{*O_A}{*O_B} + H^+ + e^- \leftrightarrow {*O_B}\ {*OH}} \quad \text{(SR6)}$$

$$\mathrm{{*O_B}{*OH} + H^+ + e^- \leftrightarrow {*O_B} + H_2O} \quad \text{(SR7)}$$

$$\mathrm{{*O_B} + H^+ + e^- \leftrightarrow *OH} \quad \text{(SR8)}$$

$$\mathrm{*OH + H^+ + e^- \leftrightarrow * + H_2O} \quad \text{(SR9)}$$

Similarly, the reaction free energy of SR5-SR8 can be represented by:

$$\Delta G_1^{'} = \Delta G_{*\mathrm{O_A}*\mathrm{O_B}} - 4.92 \quad \text{(S5a)}$$

$$\Delta G_{2}^{'} = \Delta G_{*\mathrm{O_B}*\mathrm{OH}} - \Delta G_{*\mathrm{O_A}*\mathrm{O_B}} + \mathrm{e}U \quad \text{(S5b)}$$

$$\Delta G_{3}^{'} = \Delta G_{*\mathrm{O_B}} - \Delta G_{*\mathrm{O_B}*\mathrm{OH}} + \mathrm{e}U \quad \text{(S5c)}$$

$$\Delta G_{4}^{'} = \Delta G_{*\mathrm{OH}} - \Delta G_{*\mathrm{O_B}} + \mathrm{e}U \quad \text{(S5d)}$$

$$\Delta G_{5}^{'} = -\Delta G_{*\mathrm{OH}} + \mathrm{e}U \quad \text{(S5e)}$$

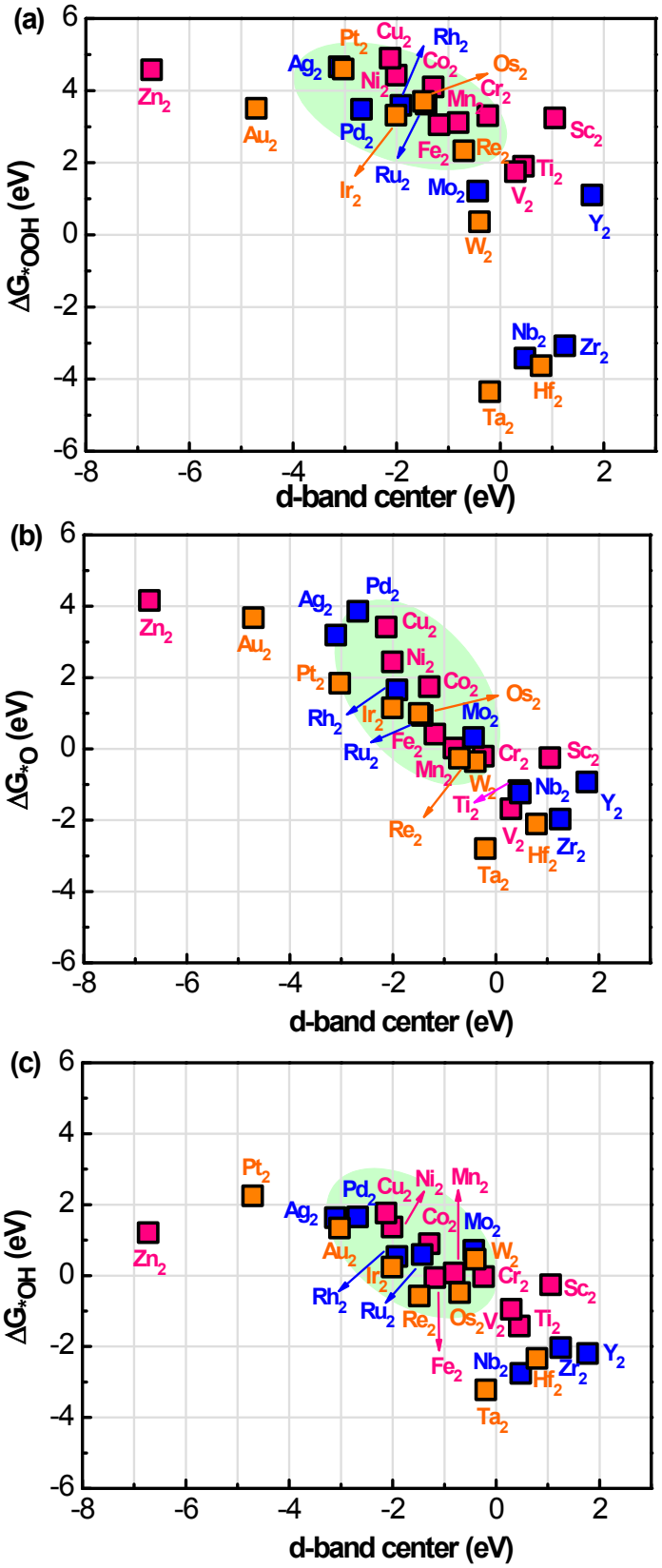


Figure S1. Correlations between adsorption free energy of oxygenated intermediates (*OOH, *O and *OH) and the d-band center of metal dimer in BACs.

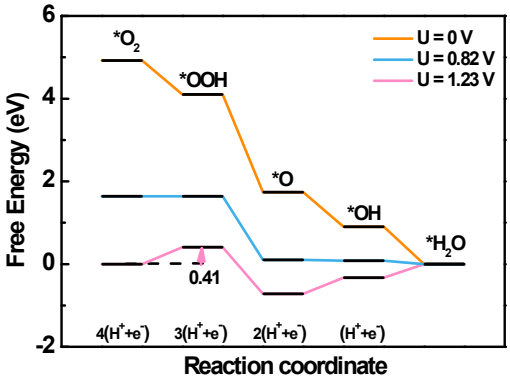


Figure S2. The reaction free energy diagrams at three different potentials for homonuclear Co_2/NC BACs.

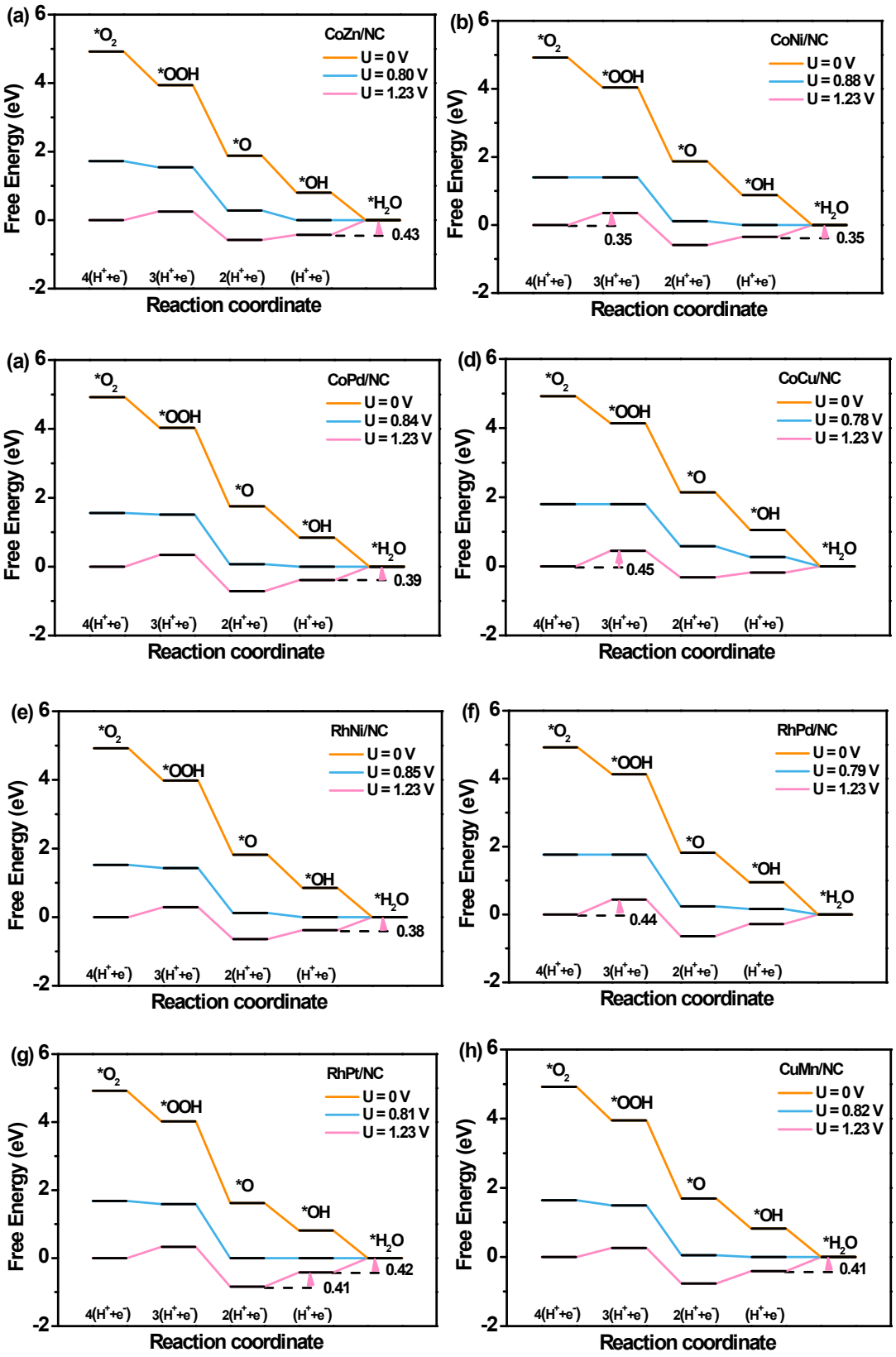


Figure S3. The reaction free energy diagrams at three different potentials for the 8 screened out promising heteronuclear BACs.

Table S1. Adsorption free energy (in eV) of oxygenated intermediates (associative mechanism) on different homonuclear BACs and the corresponding limiting potential (in V).

Catalysts	**ΔG_{*OOH}**	**ΔG_{*O}**	**ΔG_{*OH}**	**U_L**
Sc_2/NC	3.24	-0.25	-0.26	-0.26
Ti_2/NC	1.90	-1.17	-1.42	-1.42
V_2/NC	1.75	-1.68	-0.95	-0.95
Cr_2/NC	3.30	-0.21	-0.03	-0.17
Mn_2/NC	3.11	0.02	0.07	-0.05
Fe_2/NC	3.05	0.41	-0.06	-0.06
Co_2/NC	4.10	1.74	0.90	**0.82**
Ni_2/NC	4.43	2.44	1.37	0.49
Cu_2/NC	4.90	3.42	1.76	0.02
Zn_2/NC	4.58	4.16	1.21	0.34
Y_2/NC	1.10	-0.93	-2.20	-2.20
Zr_2/NC	-3.08	-1.97	-2.03	-2.03
Nb_2/NC	-3.42	-1.24	-2.76	-2.76
Mo_2/NC	1.21	0.32	0.71	-0.39
Ru_2/NC	3.62	0.94	0.59	0.35
Rh_2/NC	3.59	1.65	0.54	0.54
Pd_2/NC	4.66	3.19	1.63	0.26
Ag_2/NC	3.48	3.86	1.65	-0.38
Hf_2/NC	-3.63	-2.11	-2.34	-2.34
Ta_2/NC	-4.35	-2.80	-3.22	-3.22
W_2/NC	0.36	-0.36	0.46	-0.82
Re_2/NC	2.33	-0.26	-0.48	-0.48
Os_2/NC	3.70	0.99	-0.58	-0.58
Ir_2/NC	3.32	1.15	0.24	0.24
Pt_2/NC	4.60	1.84	1.34	0.32
Au_2/NC	3.51	3.68	2.25	-0.17

Table S2. Adsorption free energy (in eV) of oxygenated intermediates (dissociative mechanism) on different homonuclear BACs and the corresponding limiting potential (in V).

Catalysts	**ΔG_{*O*O}**	**ΔG_{*O*OH}**	**ΔG_{*O}**	**ΔG_{*OH}**	**U_L**
Sc_2/NC	0.89	-1.81	-0.25	-0.26	-1.56
Ti_2/NC	-2.36	-2.48	-1.17	-1.42	-1.42
V_2/NC	-2.46	-2.10	-1.68	-0.95	-0.95
Cr_2/NC	-1.91	-2.03	-0.21	-0.03	-1.82
Y_2/NC	1.13	-1.53	-0.93	-2.20	-2.20
Zr_2/NC	-3.56	-3.23	-1.97	-2.03	-2.03
Nb_2/NC	-3.73	-3.57	-1.24	-2.76	-2.76
Mo_2/NC	-0.52	0.00	0.32	0.71	-0.52
Ru_2/NC	1.97	0.93	0.94	0.59	-0.01
Hf_2/NC	-4.06	-3.78	-2.11	-2.34	-2.34
Ta_2/NC	-4.75	-4.50	-2.80	-3.22	-3.22
W_2/NC	-2.18	-1.53	-0.36	0.46	-1.17
Re_2/NC	-0.10	-0.39	-0.26	-0.48	-0.48

Table S3. The adsorption geometry of ORR intermediates on the 8 optimal catalysts.

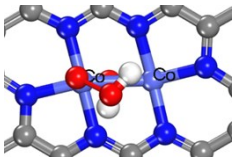
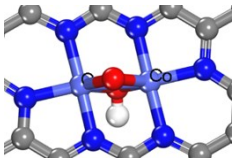
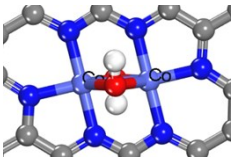
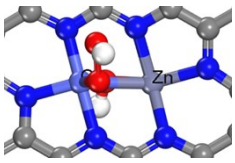
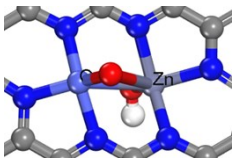
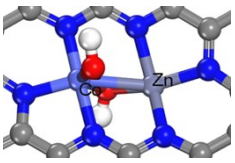
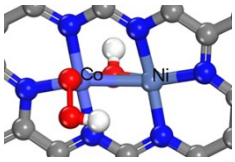
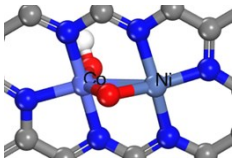
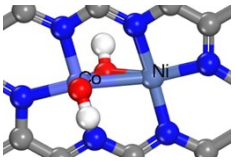
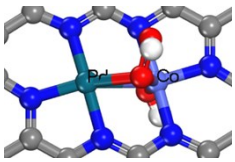
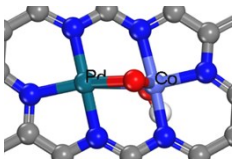
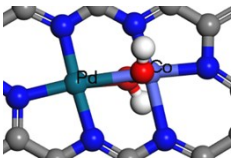
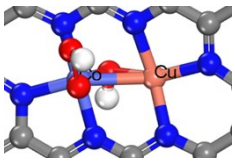
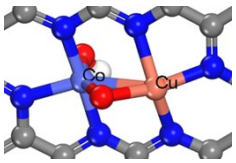
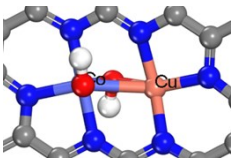
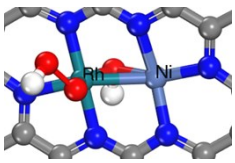
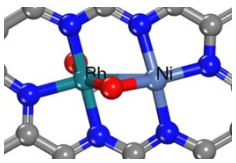
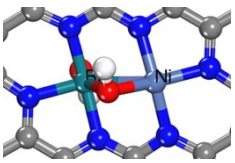
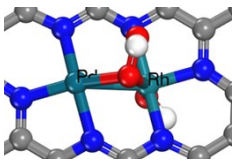
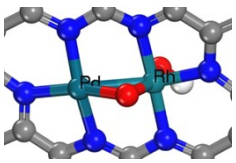
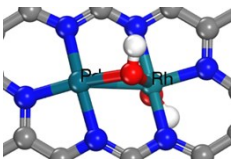
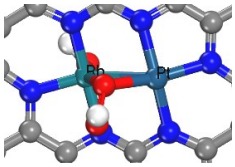
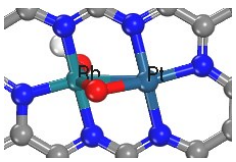
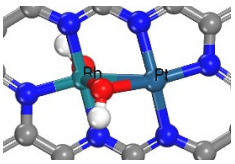
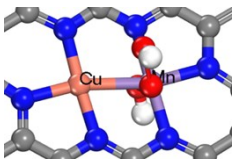
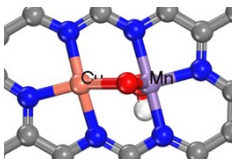
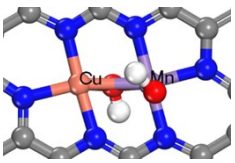
Catalysts	*OOH	*O	*OH
Co_2/NC			
CoZn/NC			
CoNi/NC			
CoPd/NC			
CoCu/NC			
RhNi/NC			
RhPd/NC			
RhPt/NC			
CuMn/NC			

Table S4. Adsorption free energy (in eV) of oxygenated intermediates on different heteronuclear BACs and the corresponding limiting potential (in V).

Catalysts	ΔG_{*OOH}	ΔG_{*O}	ΔG_{*OH}	U_L
CoRh/NC	3.79	1.60	0.69	0.69
CoRu/NC	3.44	0.68	0.58	0.11
CoIr/NC	3.78	1.48	0.69	0.69
CoFe/NC	3.50	0.75	0.23	0.23
CoMn/NC	3.70	0.75	0.43	0.32
CoZn/NC	3.94	1.88	0.80	**0.80**
CoNi/NC	4.04	1.87	0.88	**0.88**
CoPd/NC	4.03	1.75	0.84	**0.84**
CoPt/NC	3.81	2.21	0.70	0.70
CoCu/NC	4.14	2.14	1.05	**0.78**
ZnRh/NC	4.78	2.30	1.20	0.14
ZnRu/NC	3.12	0.85	0.16	0.16
ZnIr/NC	4.41	1.84	0.85	0.51
ZnFe/NC	3.85	1.58	0.66	0.66
ZnMn/NC	3.74	1.29	0.47	0.47
ZnNi/NC	4.20	2.60	1.14	0.72
ZnPd/NC	4.52	3.57	1.11	0.40
ZnPt/NC	4.37	3.45	0.96	0.55
ZnCu/NC	4.67	3.63	1.58	0.25
NiRh/NC	3.98	1.82	0.85	**0.85**
NiRu/NC	3.61	0.99	0.40	0.40
NiIr/NC	3.98	1.47	0.74	0.73
NiFe/NC	3.56	1.01	0.45	0.45
NiMn/NC	3.82	1.13	0.57	0.56
NiPd/NC	4.36	3.00	1.25	0.56
NiPt/NC	4.30	2.96	1.22	0.62
NiCu/NC	4.48	2.76	1.34	0.44
PdRh/NC	4.13	1.82	0.95	**0.79**
PdRu/NC	3.81	1.13	0.62	0.51
PdIr/NC	4.19	1.60	0.95	0.65
PdFe/NC	3.90	1.24	0.74	0.50
PdMn/NC	4.13	1.32	0.85	0.46
PdPt/NC	4.64	2.23	1.69	0.28
PdCu/NC	4.79	3.63	1.66	0.13
PtRh/NC	4.02	1.62	0.81	**0.81**
PtRu/NC	3.79	1.14	0.60	0.54
PtIr/NC	4.12	1.47	0.86	0.60
PtFe/NC	3.96	1.15	0.79	0.36
PtMn/NC	3.84	1.09	0.82	0.27

PtCu/NC	4.74	3.59	1.61	0.18
CuRh/NC	3.68	2.13	0.55	0.55
CuRu/NC	3.23	1.05	0.15	0.15
CuIr/NC	3.48	1.66	0.33	0.33
CuFe/NC	3.71	1.64	0.60	0.60
CuMn/NC	3.95	1.69	0.82	**0.82**
RhRu/NC	2.95	0.72	-0.09	-0.09
RhIr/NC	3.62	1.20	0.52	0.52
RhFe/NC	3.40	1.40	0.30	0.30
RhMn/NC	3.54	1.08	0.28	0.28
RuIr/NC	2.85	0.44	-0.20	-0.20
RuFe/NC	2.13	0.75	0.55	0.20
RuMn/NC	1.87	0.51	0.47	0.04
IrFe/NC	3.37	1.49	0.26	0.26
IrMn/NC	3.50	1.40	0.25	0.25
FeMn/NC	3.30	0.33	0.03	0.03

Table S5. The formation energy (in eV) for two N-doped graphene geometry (reference to graphene and nitrogen).

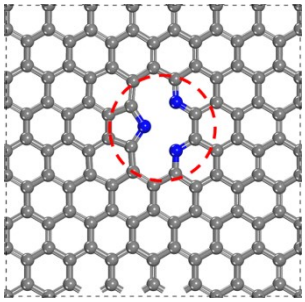
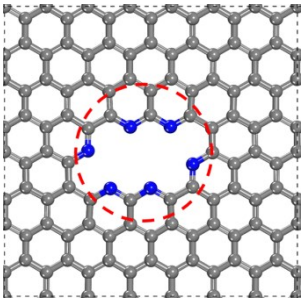
	pyrroN3	**pyriN6**
geometry		
$E_f^{'}$	4.42	3.99

Table S6. The formation energy (in eV) for the nine promising BACs (reference to graphene and nitrogen).

BACs	**Co_2/NC**	**CoZn/NC**	**CoNi/NC**	**CoPd/NC**	**CoCu/NC**
$E_f^{'}$	2.68	2.40	2.34	2.54	2.39
BACs	**RhNi/NC**	**RhPd/NC**	**RhPt/NC**	**CuMn/NC**	
$E_f^{'}$	2.80	3.30	3.26	2.34	

Table S7. Summary of the distance of two metal atoms (M-M, Å), average distance between two metal atoms and the coordinated N atoms (M-N, Å), Radii of two metal atoms (R_1 and R_2, pm), the outer electron number of two metal atoms (N_{e1} and N_{e2}), the Pauling electronegativity of two atoms (P_1 and P_2), first ionization energy of two atoms (I_1 and I_2, aJ) and electron affinity of two atoms (A_1 and A_2, kJ/mol).

Catalysts	M-M	M-N	R_1	N_{e1}	P_1	I_1	A_1	R_2	N_{e2}	P_2	I_2	A_2
Fe_2/NC	2.397	1.925	126	8	1.8	759.3	44	126	8	1.8	759.3	44
Mn_2/NC	2.495	1.972	137	7	1.5	717.4	-94	137	7	1.5	717.4	-94
Ir_2/NC	2.628	1.986	136	9	2.2	880	190	136	9	2.2	880	190
Ru_2/NC	2.478	2.003	134	8	2.2	711	146	134	8	2.2	711	146
Rh_2/NC	2.590	1.983	134	9	2.2	720	162	134	9	2.2	720	162
Co_2/NC	2.532	1.883	125	9	1.9	760	102	125	9	1.9	760	102
Zn_2/NC	2.629	2.014	137	12	1.6	906.4	9	137	12	1.6	906.4	9
Ni_2/NC	2.685	1.887	125	10	1.9	736.7	156	125	10	1.9	736.7	156
Pt_2/NC	2.579	1.998	139	10	2.2	870	247	139	10	2.2	870	247
Pd_2/NC	2.599	1.997	137	10	2.2	805	98.4	137	10	2.2	805	98.4
Cu_2/NC	2.515	1.968	128	11	1.9	745.4	118.3	128	11	1.9	745.4	118.3
CoRh/NC	2.535	1.938	125	9	1.9	760	102	134	9	2.2	720	162
CoRu/NC	2.455	1.955	125	9	1.9	760	102	134	8	2.2	711	146
CoIr/NC	2.528	1.939	125	9	1.9	760	102	136	9	2.2	880	190
CoFe/NC	2.294	1.931	125	9	1.9	760	102	126	8	1.8	759.3	44
CoMn/NC	2.452	1.927	125	9	1.9	760	102	137	7	1.5	717.4	-94
CoZn/NC	2.595	1.941	125	9	1.9	760	102	137	12	1.6	906.4	9
CoNi/NC	2.518	1.894	125	9	1.9	760	102	125	10	1.9	736.7	156
CoPd/NC	2.512	1.942	125	9	1.9	760	102	137	10	2.2	805	98.4
CoPt/NC	2.602	1.938	125	9	1.9	760	102	139	10	2.2	870	247
CoCu/NC	2.445	1.915	125	9	1.9	760	102	128	11	1.9	745.4	118.3
ZnRh/NC	2.583	2.003	137	12	1.6	906.4	9	134	9	2.2	720	162
ZnRu/NC	2.593	2.005	137	12	1.6	906.4	9	134	8	2.2	711	146
ZnIr/NC	2.579	1.996	137	12	1.6	906.4	9	136	9	2.2	880	190
ZnFe/NC	2.610	1.960	137	12	1.6	906.4	9	126	8	1.8	759.3	44
ZnMn/NC	2.640	1.978	137	12	1.6	906.4	9	137	7	1.5	717.4	-94
ZnNi/NC	2.593	1.957	137	12	1.6	906.4	9	125	10	1.9	736.7	156
ZnPd/NC	2.647	2.005	137	12	1.6	906.4	9	137	10	2.2	805	98.4
ZnPt/NC	2.634	1.997	137	12	1.6	906.4	9	139	10	2.2	870	247
ZnCu/NC	2.536	2.015	137	12	1.6	906.4	9	128	11	1.9	745.4	118.3
NiRh/NC	2.502	1.952	125	10	1.9	736.7	156	134	9	2.2	720	162
NiRu/NC	2.464	1.953	125	10	1.9	736.7	156	134	8	2.2	711	146
NiIr/NC	2.505	1.951	125	10	1.9	736.7	156	136	9	2.2	880	190
NiFe/NC	2.477	1.912	125	10	1.9	736.7	156	126	8	1.8	759.3	44
NiMn/NC	2.434	1.942	125	10	1.9	736.7	156	137	7	1.5	717.4	-94

NiPd/NC	2.659	1.940	125	10	1.9	736.7	156	137	10	2.2	805	98.4
NiPt/NC	2.634	1.942	125	10	1.9	736.7	156	139	10	2.2	870	247
NiCu/NC	2.492	1.917	125	10	1.9	736.7	156	128	11	1.9	745.4	118.3
PdRh/NC	2.528	1.994	137	10	2.2	805	98.4	134	9	2.2	720	162
PdRu/NC	2.505	2.002	137	10	2.2	805	98.4	134	8	2.2	711	146
PdIr/NC	2.529	1.995	137	10	2.2	805	98.4	136	9	2.2	880	190
PdFe/NC	2.509	1.963	137	10	2.2	805	98.4	126	8	1.8	759.3	44
PdMn/NC	2.376	1.934	137	10	2.2	805	98.4	137	7	1.5	717.4	-94
PdPt/NC	2.582	1.996	137	10	2.2	805	98.4	139	10	2.2	870	247
PdCu/NC	2.557	1.973	137	10	2.2	805	98.4	128	11	1.9	745.4	118.3
PtRh/NC	2.531	1.999	139	10	2.2	870	247	134	9	2.2	720	162
PtRu/NC	2.482	2.001	139	10	2.2	870	247	134	8	2.2	711	146
PtIr/NC	2.529	2.335	139	10	2.2	870	247	136	9	2.2	880	190
PtFe/NC	2.428	2.003	139	10	2.2	870	247	126	8	1.8	759.3	44
PtMn/NC	2.437	1.998	139	10	2.2	870	247	137	7	1.5	717.4	-94
PtCu/NC	2.546	1.965	139	10	2.2	870	247	128	11	1.9	745.4	118.3
CuRh/NC	2.500	1.964	128	11	1.9	745.4	118.3	134	9	2.2	720	162
CuRu/NC	2.539	1.961	128	11	1.9	745.4	118.3	134	8	2.2	711	146
CuIr/NC	2.499	1.963	128	11	1.9	745.4	118.3	136	9	2.2	880	190
CuFe/NC	2.484	1.924	128	11	1.9	745.4	118.3	126	8	1.8	759.3	44
CuMn/NC	2.498	1.954	128	11	1.9	745.4	118.3	137	7	1.5	717.4	-94
RhRu/NC	2.570	1.986	134	9	2.2	720	162	134	8	2.2	711	146
RhIr/NC	2.601	1.984	134	9	2.2	720	162	136	9	2.2	880	190
RhFe/NC	2.506	1.952	134	9	2.2	720	162	126	8	1.8	759.3	44
RhMn/NC	2.448	1.983	134	9	2.2	720	162	137	7	1.5	717.4	-94
RuIr/NC	2.569	1.985	134	8	2.2	711	146	136	9	2.2	880	190
RuFe/NC	2.305	1.985	134	8	2.2	711	146	126	8	1.8	759.3	44
RuMn/NC	2.388	1.992	134	8	2.2	711	146	137	7	1.5	717.4	-94
IrFe/NC	2.496	1.953	136	9	2.2	880	190	126	8	1.8	759.3	44
IrMn/NC	2.443	1.984	136	9	2.2	880	190	137	7	1.5	717.4	-94
FeMn/NC	2.489	1.931	126	8	1.8	759.3	44	137	7	1.5	717.4	-94

Table S8. The M-M distance in homonuclear BACs and the corresponding values in bulk metals (in Å).

Metal	**Distance (bulk)**	**Distance (BACs)**	**Metal**	**Distance (bulk)**	**Distance (BACs)**
Mn	2.705/2.611	2.495	Ru	2.706/2.650	2.478
Fe	2.866/2.482	2.397	Rh	3.804/2.690	2.590
Co	2.507/2.497	2.532	Pd	3.891/2.751	2.599
Ni	3.524/2.492	2.685	Ir	3.839/2.715	2.628
Cu	3.615/2.556	2.515	Pt	3.924/2.775	2.579
Zn	2.913/2.665	2.629			

Note: The two values in bulk phase denote the longest and shortest adjacent M-M distance, respectively.