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Supplementary Information

Universal descriptor for two-dimensional carbon nitrides based single-atom electrocatalysts towards nitrogen reduction reaction

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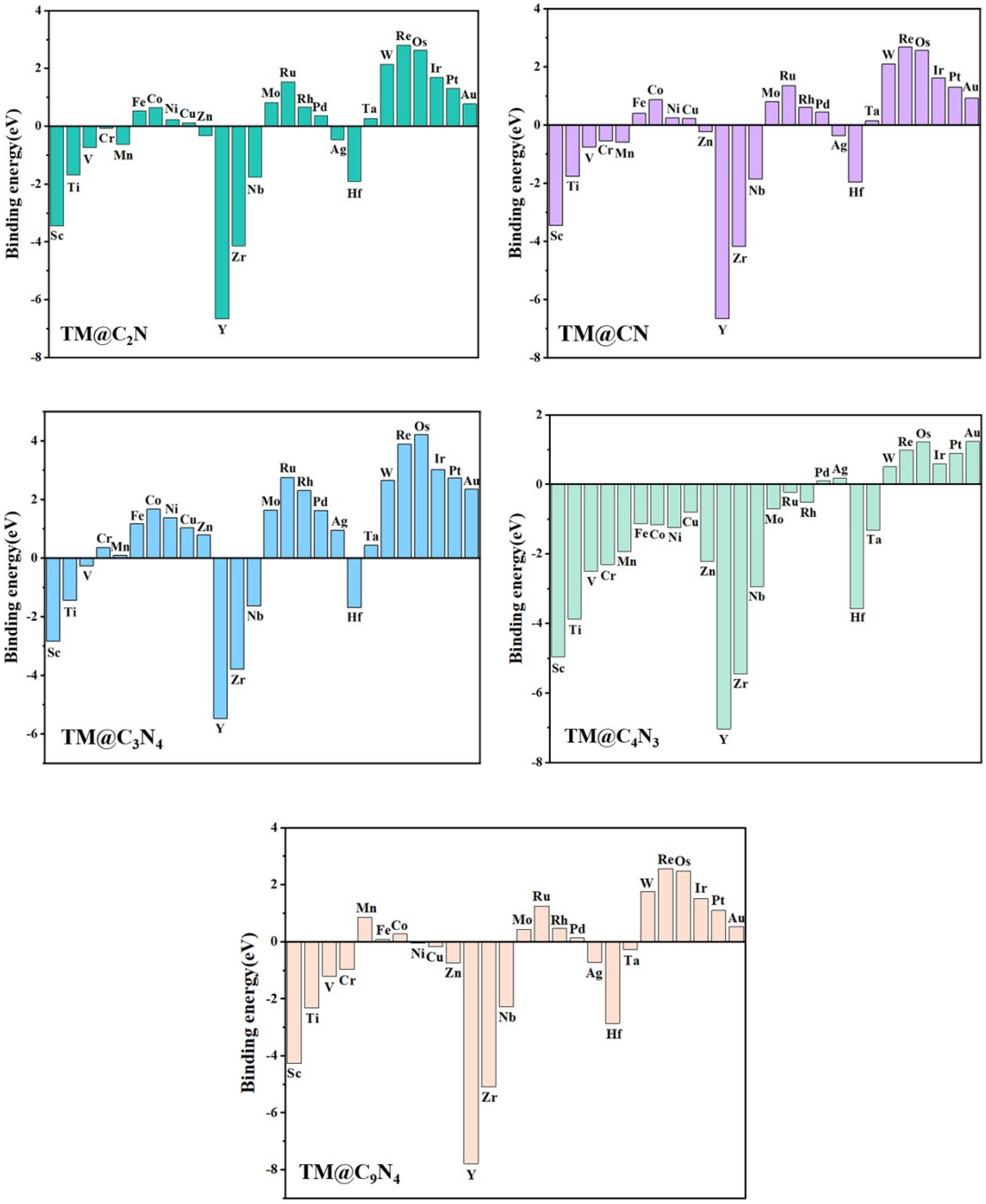

Figure S1. The binding energy (E_{bind}) diagrams of TM@C_2N, TM@CN, TM@C_3N_4, TM@C_4N_3, and TM@C_9N_4.

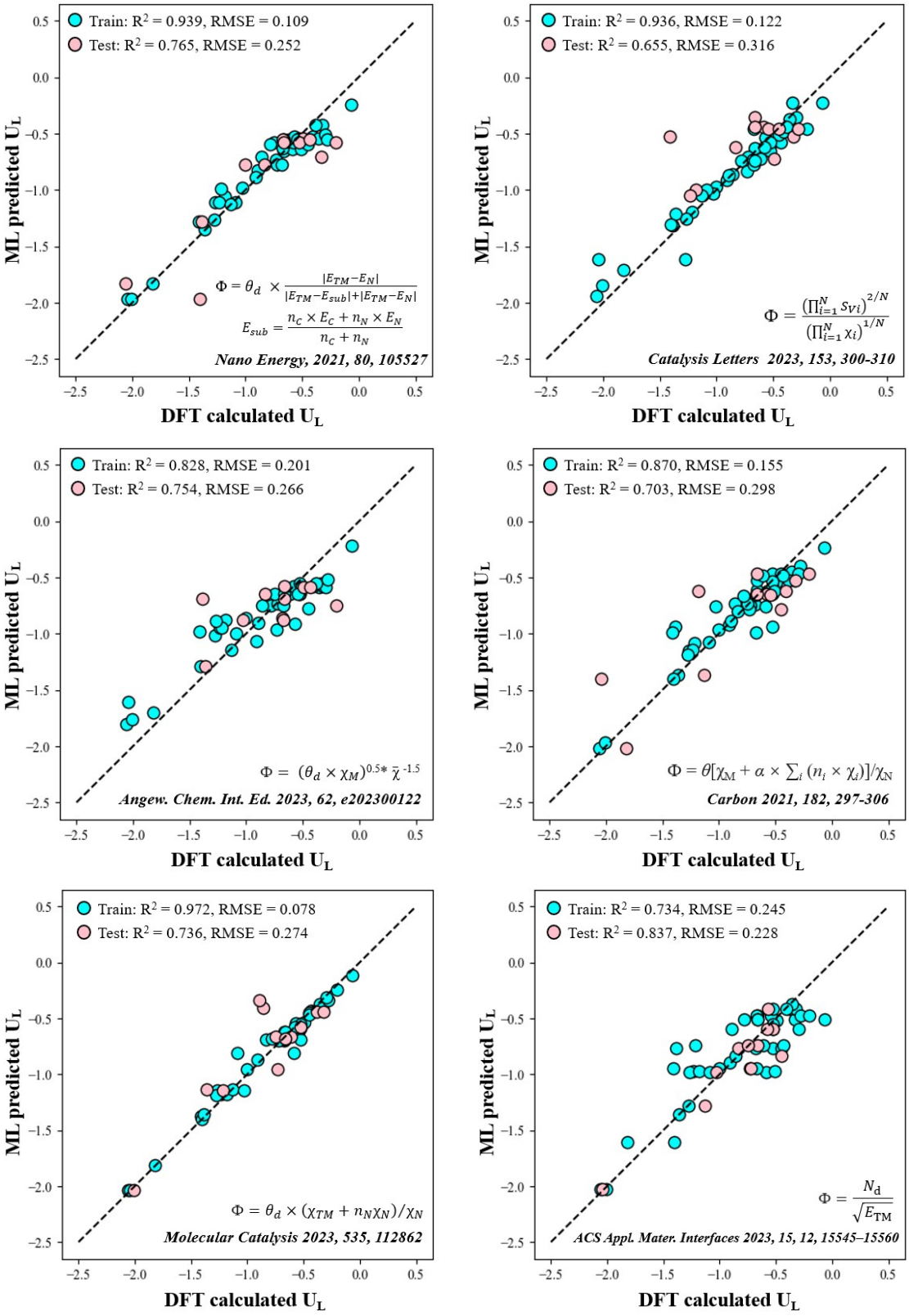

Figure S2. The fitting results between predicted U_L and DFT calculated U_L using the previously reported NRR descriptors for the TM@CN_x system.

Table S1. Band gap (eV) for all systems (130 SACs, including TM@C_2N, TM@CN, TM@C_3N_4, TM@C_4N_3, and TM@C_9N_4).

SACs	Band gap (eV)	SACs	Band gap (eV)
Sc@C_2N	0.0141	Sc@CN	0.0012
Ti@C_2N	0.0549	Ti@CN	0.1491
V@C_2N	0.0856	V@CN	0.1278
Cr@C_2N	0.0062	Cr@CN	0.0032
Mn@C_2N	0.0026	Mn@CN	0.0007
Fe@C_2N	0.0015	Fe@CN	0.0552
Co@C_2N	0.0017	Co@CN	0.0044
Ni@C_2N	0.0051	Ni@CN	0.0226
Cu@C_2N	0.0008	Cu@CN	0.0031
Zn@C_2N	0.1547	Zn@CN	0.2499
Y@C_2N	0.0013	Y@CN	0.004
Zr@C_2N	0.0005	Zr@CN	0.063
Nb@C_2N	0.0213	Nb@CN	0.0007
Mo@C_2N	0.0606	Mo@CN	0.0641
Ru@C_2N	0.0791	Ru@CN	0.0379
Rh@C_2N	0.0023	Rh@CN	0.0049
Pd@C_2N	0.0025	Pd@CN	0.0037
Ag@C_2N	0.0012	Ag@CN	0.0049
Hf@C_2N	0.0802	Hf@CN	0.0371
Ta@C_2N	0.0685	Ta@CN	0.0425
W@C_2N	0.1024	W@CN	0.1409
Re@C_2N	0.0718	Re@CN	0.0068
Os@C_2N	0.3719	Os@CN	0.1928
Ir@C_2N	0.0003	Ir@CN	0.0004
Pt@C_2N	0.1359	Pt@CN	0.181
Au@C_2N	0.0048	Au@CN	0.0051

$Sc@C_3N_4$	0.0041	$Sc@C_4N_3$	0.0025
$Ti@C_3N_4$	0.0031	$Ti@C_4N_3$	0.0312
$V@C_3N_4$	0.0059	$V@C_4N_3$	0.0018
$Cr@C_3N_4$	0.0072	$Cr@C_4N_3$	0.0042
$Mn@C_3N_4$	0.0151	$Mn@C_4N_3$	0.0009
$Fe@C_3N_4$	0.0006	$Fe@C_4N_3$	0.003
$Co@C_3N_4$	0.0008	$Co@C_4N_3$	0.0038
$Ni@C_3N_4$	0.0022	$Ni@C_4N_3$	0.0008
$Cu@C_3N_4$	0.0036	$Cu@C_4N_3$	0.0026
$Zn@C_3N_4$	0.0031	$Zn@C_4N_3$	0.0281
$Y@C_3N_4$	0.0045	$Y@C_4N_3$	0.0031
$Zr@C_3N_4$	0.0098	$Zr@C_4N_3$	0.0208
$Nb@C_3N_4$	0.0087	$Nb@C_4N_3$	0.0009
$Mo@C_3N_4$	0.0025	$Mo@C_4N_3$	0.0006
$Ru@C_3N_4$	0.0004	$Ru@C_4N_3$	0.0041
$Rh@C_3N_4$	0.0025	$Rh@C_4N_3$	0.0038
$Pd@C_3N_4$	0.0018	$Pd@C_4N_3$	0.0088
$Ag@C_3N_4$	0.0015	$Ag@C_4N_3$	0.0032
$Hf@C_3N_4$	0.0021	$Hf@C_4N_3$	0.0211
$Ta@C_3N_4$	0.0163	$Ta@C_4N_3$	0.0023
$W@C_3N_4$	0.0006	$W@C_4N_3$	0.0015
$Re@C_3N_4$	0.0123	$Re@C_4N_3$	0.0005
$Os@C_3N_4$	0.0229	$Os@C_4N_3$	0.0023
$Ir@C_3N_4$	0.0027	$Ir@C_4N_3$	0.0027
$Pt@C_3N_4$	0.0051	$Pt@C_4N_3$	0.0109
$Au@C_3N_4$	0.0038	$Au@C_4N_3$	0.0042
$Sc@C_9N_4$	0.0022	$Cr@C_9N_4$	0.0045
$Ti@C_9N_4$	0.0031	$Mn@C_9N_4$	0.0031
$V@C_9N_4$	0.0049	$Fe@C_9N_4$	0.0012

$Co@C_9N_4$	0.0027	$Pd@C_9N_4$	0.0021
$Ni@C_9N_4$	0.0018	$Ag@C_9N_4$	0.0039
$Cu@C_9N_4$	0.0007	$Hf@C_9N_4$	0.0022
$Zn@C_9N_4$	0.0015	$Ta@C_9N_4$	0.0016
$Y@C_9N_4$	0.0053	$W@C_9N_4$	0.0026
$Zr@C_9N_4$	0.0015	$Re@C_9N_4$	0.0056
$Nb@C_9N_4$	0.0013	$Os@C_9N_4$	0.001
$Mo@C_9N_4$	0.0058	$Ir@C_9N_4$	0.0032
$Ru@C_9N_4$	0.0045	$Pt@C_9N_4$	0.008
$Rh@C_9N_4$	0.0023	$Au@C_9N_4$	0.0043

Table S2. The N≡N bond lengths d_{N-N} (Å) of N_2 molecule on the initially screened TM@CNx catalysts, along with corresponding adsorption configuration (AC) and adsorption energy E_{ads} (eV).

SACs	d_{N-N} (Å)	AC	E_{ads} (eV)
Sc@C_2N	1.1534	side-on	-0.06
Ti@C_2N	1.1723	side-on	-0.26
V@C_2N	1.1498	side-on	0.07
Cr@C_2N	1.1243	end-on	-0.40
Mn@C_2N	1.1245	end-on	0
Zn@C_2N	1.1161	end-on	0.05
Y@C_2N	1.1519	side-on	-0.10
Zr@C_2N	1.1416	end-on	-0.82
Nb@C_2N	1.1460	end-on	-0.76
Ag@C_2N	1.1147	end-on	0.44
Hf@C_2N	1.1917	side-on	-0.49
Sc@CN	1.1536	side-on	-0.05
Ti@CN	1.1376	end-on	-0.55
V@CN	1.1737	side-on	0.18
Cr@CN	1.1261	end-on	0.09
Mn@CN	1.1503	side-on	0.26
Zn@CN	1.1157	end-on	0.04
Y@CN	1.1520	side-on	-0.08
Zr@CN	1.1418	end-on	-0.78
Nb@CN	1.1457	end-on	-0.80
Ag@CN	1.1150	end-on	0.36
Hf@CN	1.1915	side-on	-0.50
Sc@C_3N_4	1.1367	end-on	-0.41
Ti@C_3N_4	1.1445	end-on	-0.55
V@C_3N_4	1.1496	end-on	0.03

$Y@C_3N_4$	1.1534	side-on	-1.53
$Zr@C_3N_4$	1.1506	end-on	-0.49
$Nb@C_3N_4$	1.1553	end-on	-0.50
$Hf@C_3N_4$	1.1559	end-on	-0.59
$Sc@C_4N_3$	1.1214	end-on	-0.05
$Ti@C_4N_3$	1.1623	side-on	-0.08
$V@C_4N_3$	1.1750	side-on	-0.57
$Cr@C_4N_3$	1.1832	side-on	0.11
$Mn@C_4N_3$	1.1436	side-on	-0.04
$Fe@C_4N_3$	1.1684	side-on	-0.15
$Co@C_4N_3$	1.1536	side-on	0.06
$Ni@C_4N_3$	1.1269	end-on	-0.25
$Cu@C_4N_3$	1.1454	side-on	-0.02
$Zn@C_4N_3$	1.1162	end-on	0.10
$Y@C_4N_3$	1.1211	end-on	0.02
$Zr@C_4N_3$	1.1680	side-on	-0.11
$Nb@C_4N_3$	1.1874	side-on	-0.72
$Mo@C_4N_3$	1.2055	side-on	-0.76
$Ru@C_4N_3$	1.1356	side-on	-0.97
$Rh@C_4N_3$	1.1269	end-on	-0.68
$Hf@C_4N_3$	1.1605	side-on	-0.23
$Ta@C_4N_3$	1.1916	side-on	-0.95
$Sc@C_9N_4$	1.1455	side-on	0.11
$Ti@C_9N_4$	1.1772	side-on	-0.03
$V@C_9N_4$	1.1508	side-on	0.15
$Cr@C_9N_4$	1.1242	side-on	0.13
$Ni@C_9N_4$	1.1287	side-on	-0.13
$Cu@C_9N_4$	1.1256	end-on	-0.29
$Zn@C_9N_4$	1.1161	side-on	0.40

$Y@C_9N_4$	1.1388	side-on	0.04
$Zr@C_9N_4$	1.1793	side-on	-0.20
$Nb@C_9N_4$	1.1487	end-on	-0.08
$Ag@C_9N_4$	1.1158	side-on	0.38
$Hf@C_9N_4$	1.1923	side-on	-0.15
$Ta@C_9N_4$	1.2122	side-on	-0.17

Table S3. Gibbs free energy values ($*N_2 \rightarrow *N_2H$(PCET1) and $*NH_2 \rightarrow *NH_3$(PCET6)) and limiting potential (U_L) for 60 SACs.

SACs	$\Delta G(*N_2 \rightarrow *N_2H)$ (eV)	$\Delta G(*NH_2 \rightarrow *NH_3)$ (eV)	U_L (V)
$Sc@C_2N$	0.83	-0.02	-0.83
$Ti@C_2N$	0.67	0.04	-0.67
$V@C_2N$	0.78	-0.26	-0.78
$Cr@C_2N$	1.09	-0.56	-1.09
$Mn@C_2N$	1.23	-0.89	-1.23
$Zn@C_2N$	1.45	-1.12	-1.45
$Y@C_2N$	0.72	0.09	-0.72
$Zr@C_2N$	0.58	0.42	-0.58
$Nb@C_2N$	0.38	0.25	-0.38
$Ag@C_2N$	2.01	-1.71	-2.01
$Hf@C_2N$	0.44	0.66	-0.66
Sc@CN	0.53	0.08	-0.53
Ti@CN	0.66	0.01	-0.66
V@CN	0.66	-0.23	-0.66
Cr@CN	1.03	-0.78	-1.03
Mn@CN	1.18	-0.89	-1.18
Zn@CN	1.49	-1.13	-1.49
Y@CN	0.67	0.13	-0.67
Zr@CN	0.53	0.40	-0.53
Nb@CN	0.41	0.28	-0.41
Ag@CN	2.04	-1.72	-2.04
Hf@CN	0.46	0.61	-0.61
$Sc@C_3N_4$	-0.04	0.45	-0.45
$Ti@C_3N_4$	-0.31	0.28	-0.28
$V@C_3N_4$	-0.44	0.07	-0.07
$Y@C_3N_4$	0.73	0.26	-0.73

$Zr@C_3N_4$	-0.55	0.89	-0.89
$Nb@C_3N_4$	-0.69	0.53	-0.53
$Hf@C_3N_4$	-0.49	1.22	-1.22
$Sc@C_4N_3$	1.39	-0.51	-1.39
$Ti@C_4N_3$	0.20	0.06	-0.20
$V@C_4N_3$	0.33	0.14	-0.33
$Cr@C_4N_3$	0.59	-0.21	-0.59
$Mn@C_4N_3$	0.51	-0.17	-0.51
$Fe@C_4N_3$	0.49	-0.36	-0.49
$Co@C_4N_3$	0.53	-0.59	-0.53
$Ni@C_4N_3$	1.13	-0.81	-1.13
$Cu@C_4N_3$	1.40	-1.16	-1.40
$Zn@C_4N_3$	1.64	-1.39	-1.64
$Y@C_4N_3$	1.41	-0.47	-1.41
$Zr@C_4N_3$	0.26	0.30	-0.30
$Nb@C_4N_3$	-0.06	0.57	-0.57
$Mo@C_4N_3$	0.15	0.36	-0.36
$Ru@C_4N_3$	0.91	-0.20	-0.91
$Rh@C_4N_3$	1.36	-0.81	-1.36
$Hf@C_4N_3$	0.18	0.43	-0.43
$Ta@C_4N_3$	0.11	0.86	-0.86
$Sc@C_9N_4$	0.68	-0.04	-0.68
$Ti@C_9N_4$	0.54	-0.02	-0.54
$V@C_9N_4$	0.66	-0.34	-0.66
$Cr@C_9N_4$	1.27	-0.93	-1.27
$Ni@C_9N_4$	1.28	-1.34	-1.28
$Cu@C_9N_4$	1.82	-1.64	-1.82
$Zn@C_9N_4$	1.21	-1.22	-1.21
$Y@C_9N_4$	1.00	-0.12	-1.00

$Zr@C_9N_4$	0.52	0.53	-0.53
$Nb@C_9N_4$	0.30	0.32	-0.32
$Ag@C_9N_4$	2.06	-1.73	-2.06
$Hf@C_9N_4$	0.34	0.75	-0.75
$Ta@C_9N_4$	0.11	0.45	-0.45

Table S4. The number of d electrons in TM atoms (θ_d), d-band canter in TM atoms (ε_d), the average electronegativity of the substrate (χ_{sub}), the electronegativity of TM (χ_{TM}) and the corresponding descriptor (Φ).

SACs	θ_d	ε_d	χ_{sub}	χ_{TM}	Φ
Sc@C_2N	1	1.22	2.71	1.36	1.57
Ti@C_2N	2	0.88	2.71	1.54	0.55
V@C_2N	3	1.38	2.71	1.63	0.57
Cr@C_2N	5	-0.02	2.71	1.66	0.00
Mn@C_2N	5	-1.15	2.71	1.55	-0.29
Zn@C_2N	10	-7.49	2.71	1.65	-0.93
Y@C_2N	1	1.99	2.71	1.22	2.27
Zr@C_2N	2	1.65	2.71	1.33	1.07
Nb@C_2N	4	0.29	2.71	1.59	0.09
Ag@C_2N	10	-2.70	2.71	1.92	-0.32
Hf@C_2N	2	1.80	2.71	1.32	1.16
Sc@CN	1	1.17	2.80	1.36	1.53
Ti@CN	2	1.18	2.80	1.54	0.75
V@CN	3	1.92	2.80	1.63	0.81
Cr@CN	5	-0.25	2.80	1.66	-0.06
Mn@CN	5	-1.18	2.80	1.55	-0.30
Zn@CN	10	-7.64	2.80	1.65	-0.96
Y@CN	1	1.59	2.80	1.22	1.81
Zr@CN	2	1.43	2.80	1.33	0.94
Nb@CN	4	0.48	2.80	1.59	0.15
Ag@CN	10	-2.73	2.80	1.92	-0.33
Hf@CN	2	1.63	2.80	1.32	1.07
Sc@C_3N_4	1	1.18	2.83	1.36	1.28
Ti@C_3N_4	2	1.09	2.83	1.54	0.59

$V@C_3N_4$	3	0.85	2.83	1.63	0.30
$Y@C_3N_4$	1	2.16	2.83	1.22	2.37
$Zr@C_3N_4$	2	2.58	2.83	1.33	1.40
$Nb@C_3N_4$	4	3.16	2.83	1.59	0.85
$Hf@C_3N_4$	2	1.94	2.83	1.32	1.06
$Sc@C_4N_3$	1	1.55	2.76	1.36	1.83
$Ti@C_4N_3$	2	-0.11	2.76	1.54	-0.06
$V\text{-}C_4N_3$	3	0.23	2.76	1.63	0.09
$Cr@C_4N_3$	5	-0.75	2.76	1.66	-0.17
$Mn@C_4N_3$	5	-0.17	2.76	1.55	-0.04
$Fe@C_4N_3$	6	-1.33	2.76	1.83	-0.25
$Co@C_4N_3$	7	-1.88	2.76	1.88	-0.30
$Ni@C_4N_3$	8	-1.78	2.76	1.92	-0.25
$Cu@C_4N_3$	10	-2.21	2.76	1.9	-0.25
$Zn@C_4N_3$	10	-6.34	2.76	1.65	-0.73
$Y@C_4N_3$	1	2.13	2.76	1.22	2.54
$Zr@C_4N_3$	2	0.52	2.76	1.33	0.31
$Nb@C_4N_3$	4	-0.22	2.76	1.59	-0.06
$Mo@C_4N_3$	5	-0.84	2.76	2.16	-0.18
$Ru@C_4N_3$	7	-1.48	2.76	2.2	-0.23
$Rh@C_4N_3$	8	-2.50	2.76	2.28	-0.33
$Hf@C_4N_3$	2	0.06	2.76	1.32	0.03
$Ta@C_4N_3$	3	-0.77	2.76	1.51	-0.30
$Sc@C_9N_4$	1	0.98	2.70	1.36	1.26
$Ti@C_9N_4$	2	0.64	2.70	1.54	0.40
$V@C_9N_4$	3	0.87	2.70	1.63	0.36
$Cr@C_9N_4$	5	-0.47	2.70	1.66	-0.11
$Ni@C_9N_4$	8	-1.20	2.70	1.92	-0.18
$Cu@C_9N_4$	10	-1.21	2.70	1.9	-0.14

$Zn@C_9N_4$	10	-7.77	2.70	1.65	-0.96
$Y@C_9N_4$	1	1.89	2.70	1.22	2.05
$Zr@C_9N_4$	2	1.31	2.70	1.33	0.85
$Nb@C_9N_4$	4	0.45	2.70	1.59	0.14
$Ag@C_9N_4$	10	-2.19	2.70	1.92	-0.26
$Hf@C_9N_4$	2	1.48	2.70	1.32	0.96
$Ta@C_9N_4$	3	0.43	2.70	1.51	0.18

Table S5. The d-band center (ε_d) and the electron transfer number on N_2 (Q) of Zn-anchored SACs.

SACs	ε_d	Q
Zn@C_2N	-7.49	0.0105
Zn@CN	-7.64	0.0050
Zn@C_4N_3	-6.34	-0.0052
Zn@C_9N_4	-7.77	0.0074

Table S6. The relevant feature data of TM@C_8N_8, along with the limiting potential values predicted (Pred_U_L) based on the descriptor Φ.

SACs	θ_d	ε_d	χ_{sub}	χ_{TM}	Φ	Pred_U_L
Sc@C_8N_8	1	1.35	2.80	1.36	1.53	-0.81
Ti@C_8N_8	2	1.22	2.80	1.54	0.68	-0.52
V@C_8N_8	3	1.16	2.80	1.63	0.43	-0.43
Cr@C_8N_8	5	0.41	2.80	1.66	0.09	-0.46
Mn@C_8N_8	5	-0.90	2.80	1.55	-0.20	-1.08
Fe@C_8N_8	6	-0.51	2.80	1.83	-0.09	-0.85
Co@C_8N_8	7	-0.42	2.80	1.88	-0.06	-0.79
Ni@C_8N_8	8	-1.17	2.80	1.92	-0.16	-0.99
Cu@C_8N_8	10	-2.17	2.80	1.9	-0.24	-1.16
Zn@C_8N_8	10	-6.80	2.80	1.65	-0.75	-2.26
Y@C_8N_8	1	2.20	2.80	1.22	2.51	-1.16
Zr@C_8N_8	2	2.92	2.80	1.33	1.66	-0.86
Nb@C_8N_8	4	1.30	2.80	1.59	0.36	-0.41
Mo@C_8N_8	5	0.59	2.80	2.16	0.13	-0.38
Ru@C_8N_8	7	-0.30	2.80	2.2	-0.04	-0.75
Rh@C_8N_8	8	-0.63	2.80	2.28	-0.08	-0.83
Pd@C_8N_8	10	-2.87	2.80	2.2	-0.30	-1.30
Ag@C_8N_8	10	-3.59	2.80	1.92	-0.39	-1.48
Cd@C_8N_8	10	-8.11	2.80	1.69	-0.90	-2.57