Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Design of high performance nitrogen reduction electrocatalysts by doping defective polyoxometalate with a single atom promoter

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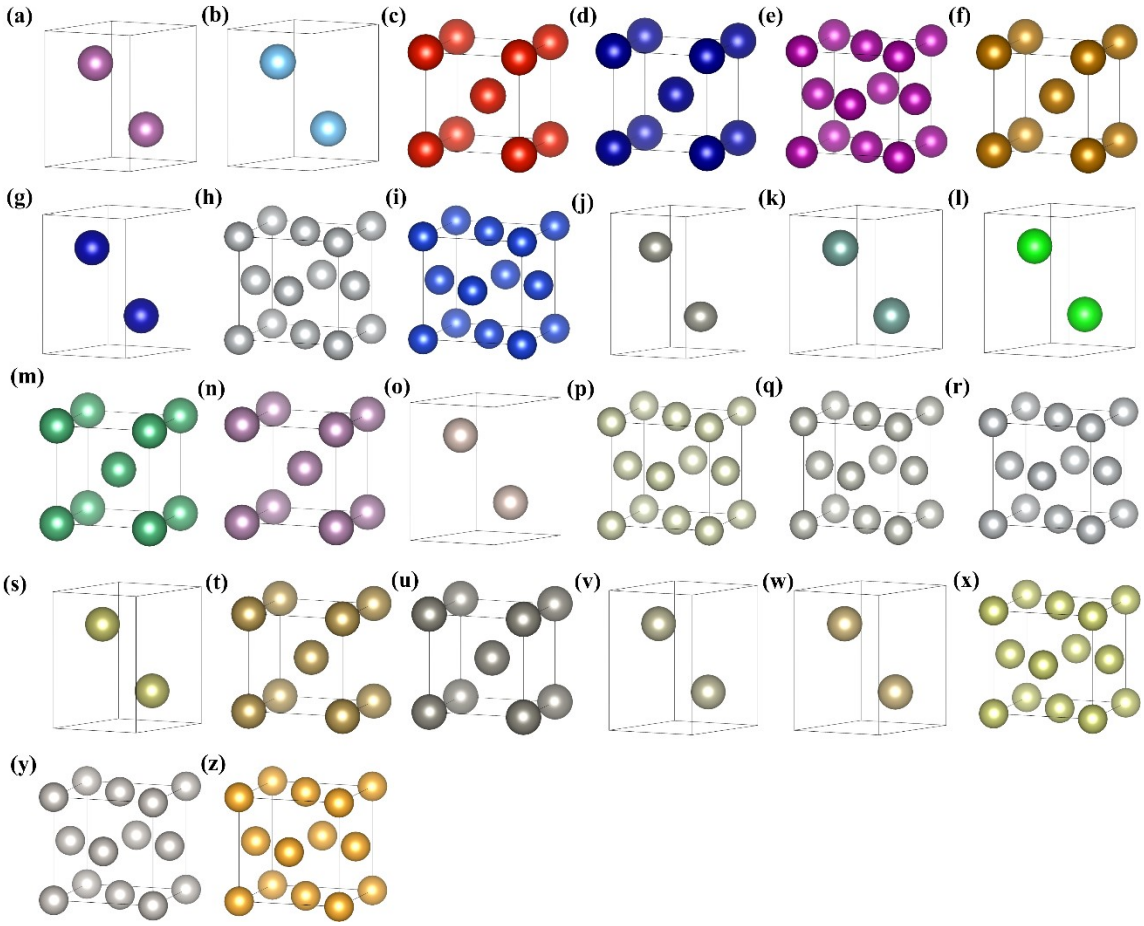

Figure R1. The corresponding structures of the bulk crystal unit cell are shown. Figures (a) to (z) represent Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt and Au, respectively.

Table S1. The energies of the bulk crystal unit cell ($E_{(bulk)}$) and the free single metal atom ($E_{(M)}$), and the number of atoms in the bulk (N) are shown.

Metal	$E_{(bulk)}$	N	$E_{(M)}$
Sc	-13.22	2	-2.11
Ti	-16.47	2	-2.32
V	-15.49	2	-2.31
Cr	-19.87	2	-5.48
Mn	-37.09	4	-5.16
Fe	-17.25	2	-3.40
Co	-14.91	2	-1.21
Ni	-23.89	4	-0.73
Cu	-16.92	4	-0.24
Zn	-32.43	2	-0.16
Y	-13.46	2	-2.13
Zr	-17.82	2	-1.96
Nb	-21.58	2	-3.20
Mo	-22.98	2	-4.30
Ru	-19.53	2	-2.10
Rh	-31.35	4	-1.28
Pd	-23.02	4	-1.48
Ag	-13.25	4	-0.40
Hf	-20.71	2	-3.47
Ta	-24.89	2	-3.49
W	-27.25	2	-4.54
Re	-26.00	2	-1.94
Os	-23.69	2	-2.91
Ir	-38.27	4	-1.24
Pt	-27.26	4	-0.53
Au	-15.66	4	-0.29

Table S2. The zero point energies and TS of different adsorbed species.

Species	ZPE	TS
H	0.14	0.2
N_2	0.15	0.59
$*N_2$	0.200	0.176
$*N_2H$	0.455	0.199
$*N_2H_2$	0.812	0.204
*N	0.087	0.06
*NH	0.346	0.099
$*NH_2$	0.660	0.140
$*NH_3$	1.024	0.127
$*HN_2H$	0.796	0.147
$*HN_2H_2$	1.120	0.168
$*H_2N_2H_2$	1.492	0.169

Table S3. *N_2 adsorption energy of five possible configurations.

promoter \ ΔE_{ads}(eV)	end-on(Mo)	side-on(Mo)	bridge-on	end-on(M)	side-on(M)
None	−0.63	***	***	***	***
Sc	−0.70	−0.21	***	−0.51	***
Ti	−0.89	−0.47	***	−0.71	−0.28
V	−0.84	−0.29	***	−0.65	−0.28
Cr	−0.73	−0.15	***	−0.51	0.35
Mn	−0.72	−0.13	***	−0.35	***
Fe	−0.96	−0.20	***	−0.44	***
Zn	−0.78	−0.23	***	−0.50	***
Y	−0.70	−0.27	***	−0.41	***
Zr	−0.92	−0.54	***	−0.68	−0.26
Nb	−0.90	−0.47	−0.12	−0.68	−0.47
Mo	−0.89	−0.45	−0.18	−0.65	−0.79
Hf	−0.92	−0.54	***	−0.81	−0.36
Ta	−0.91	−0.47	0.01	−0.75	−0.58
W	−0.79	−0.35	***	−0.45	−0.61

Table S4. Bond length of * N_2 adsorbed via the end-on (Mo) configuration.

Promoter	Bond length (Å)	Promoter	Bond length (Å)
Free N_2	1.117	Zn	1.122
None	1.115	Y	1.130
Sc	1.128	Zr	1.133
Ti	1.131	Nb	1.131
V	1.128	Mo	1.130
Cr	1.123	Hf	1.133
Mn	1.124	Ta	1.130
Fe	1.125	W	1.129