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

Supporting Information

for

Exploring the catalytic activity of graphene-based TM-N_xC_{4-x} single atom catalysts for oxygen reduction reaction via density functional theory calculation

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Table S1. The binding energy (E_b) of transition metals. The theoretical overpotential (η), Gibbs free energy change of the oxygenated intermediates (ΔG_{*OOH}, ΔG_{*O}, ΔG_{*OH}), and limiting potential (U_L) on TM-N_xC_y.

	E_b (eV)	η (V)	ΔG_{*OOH} (eV)	ΔG_{*O} (eV)	ΔG_{*OH} (eV)	U_L (V)
VN_4	-3.28	1.62	2.85	0.64	-0.39	-0.39 (U_{L4})
VN_3C	-3.02	2.92	1.54	-1.31	-1.69	-1.69 (U_{L4})
VN_2C_2	-2.14	3.09	1.43	-1.24	-1.86	-1.86 (U_{L4})
VNC_3	-2.22	3.03	1.75	-1.43	-1.80	-1.8 (U_{L4})
VC_4	-2.15	3.44	1.16	-1.44	-2.22	-2.22 (U_{L4})
CrN_4	-4.39	0.45	3.98	2.03	0.78	0.78 (U_{L4})
CrN_3C	-2.41	2.4	2.61	-0.66	-1.17	-1.17 (U_{L4})
CrN_2C_2	-3.12	1.61	3.42	-0.14	-0.38	-0.38 (U_{L4})
$CrNC_3$	-4.75	1.28	3.17	0.52	-0.05	-0.05 (U_{L4})
CrC_4	-1.22	2.39	2.24	-0.62	-1.16	-1.16 (U_{L4})
MnN_4	-5.34	1.06	4.75	2.44	1.39	0.17 (U_{L1})
MnN_3C	-5.91	1.01	3.45	2.15	0.22	0.22 (U_{L4})
MnN_2C_2	-5.39	0.86	3.55	1.87	1.50	<u>0.37</u> (U_{L3})
$MnNC_3$	-5.48	0.7	3.58	1.73	1.20	<u>0.53</u> (U_{L3})
MnC_4	-3.64	1.35	3.19	0.73	-0.12	-0.12 (U_{L4})
FeN_4	-2.66	0.47	4.16	1.97	1.06	0.76 (U_{L1})
FeN_3C	-2.88	0.86	3.65	1.84	0.37	0.37 (U_{L4})
FeN_2C_2	-2.47	0.75	3.83	1.98	0.48	0.48 (U_{L4})
$FeNC_3$	-2.63	0.68	4.08	1.68	0.55	0.55 (U_{L4})
FeC_4	-0.84	1.35	3.18	1.39	-0.12	-0.12 (U_{L4})
CoN_4	-2.92	0.57	4.25	3.59	0.85	<u>0.66</u> (U_{L2})
CoN_3C	-3.30	0.4	4.09	2.37	1.02	0.83 (U_{L1})
CoN_2C_2	-2.63	0.48	3.85	2.04	0.75	0.75 (U_{L4})
$CoNC_3$	-2.80	0.43	4.12	2.02	0.86	0.80 (U_{L1})
CoC_4	-1.03	0.87	3.51	1.56	0.36	0.36 (U_{L4})
NiN_4	-2.93	1.63	5.32	4.95	2.46	-0.40 (U_{L1})
NiN_3C	-3.51	0.98	4.67	3.81	1.64	0.25 (U_{L1})
NiN_2C_2	-3.03	1.81	5.50	4.11	2.46	-0.58 (U_{L1})
$NiNC_3$	-2.87	0.81	4.50	3.15	1.48	0.42 (U_{L1})
NiC_4	-1.19	0.41	4.10	2.60	1.06	0.82 (U_{L1})
CuN_4	-1.62	1.6	5.29	4.64	2.48	-0.37 (U_{L1})
CuN_3C	-2.04	1.79	4.66	1.15	1.71	<u>-0.56</u> (U_{L3})
CuN_2C_2	-2.21	1.08	4.77	4.10	1.77	0.15 (U_{L1})
$CuNC_3$	-2.61	2.23	4.98	1.23	2.23	<u>-1.00</u> (U_{L3})
CuC_4	-1.12	1.31	5.00	4.2	2.12	-0.08 (U_{L1})
ZnN_4	-2.65	0.98	4.67	3.90	1.40	0.25 (U_{L1})
ZnN_3C	-2.55	0.46	4.09	3.22	0.77	0.77 (U_{L4})
ZnN_2C_2	-1.72	0.5	3.97	3.24	0.78	<u>0.73</u> (U_{L2})
$ZnNC_3$	-2.07	0.49	4.18	3.39	0.95	0.74 (U_{L1})
ZnC_4	-1.36	0.95	4.64	3.98	1.67	0.28 (U_{L1})

Table S2. The binding energy (E_b/eV) of transition metals on three different structures of the TMN_2C_2.

	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
N_2C_2 (1)	**-2.15**	**-3.12**	**-5.39**	**-2.47**	**-2.63**	**-3.03**	**-2.21**	**-1.72**
N_2C_2 (2)	-2.11	-2.95	-5.23	-2.24	-2.32	-2.67	-1.88	-1.47
N_2C_2 (3)	-2.04	-2.88	-5.10	-2.07	-2.19	-2.49	-1.60	-1.46

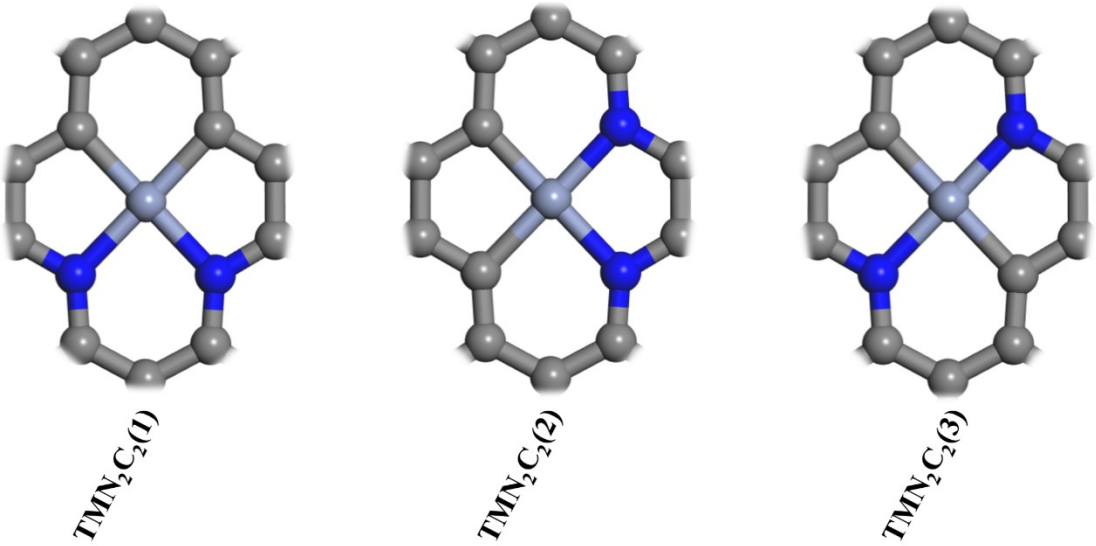

Figure S1. Three different structures of TMN_2C_2

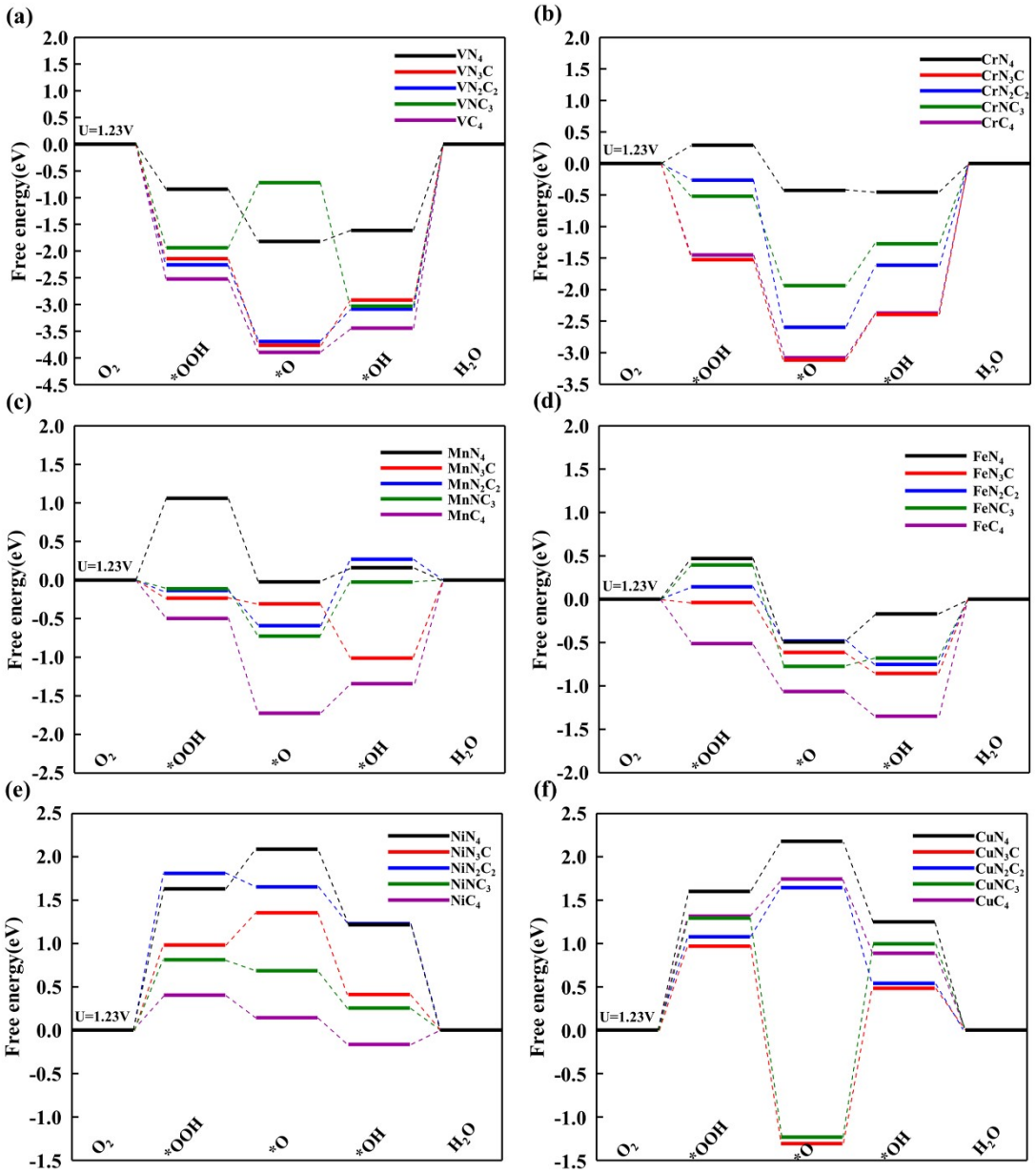

Figure S2. ORR reaction profiles of (a) V-N_xC_y, (b) Cr-N_xC_y, (c) Mn-N_xC_y, (d) Fe-N_xC_y, (e) Ni-N_xC_y, and (f) Cu-N_xC_y.

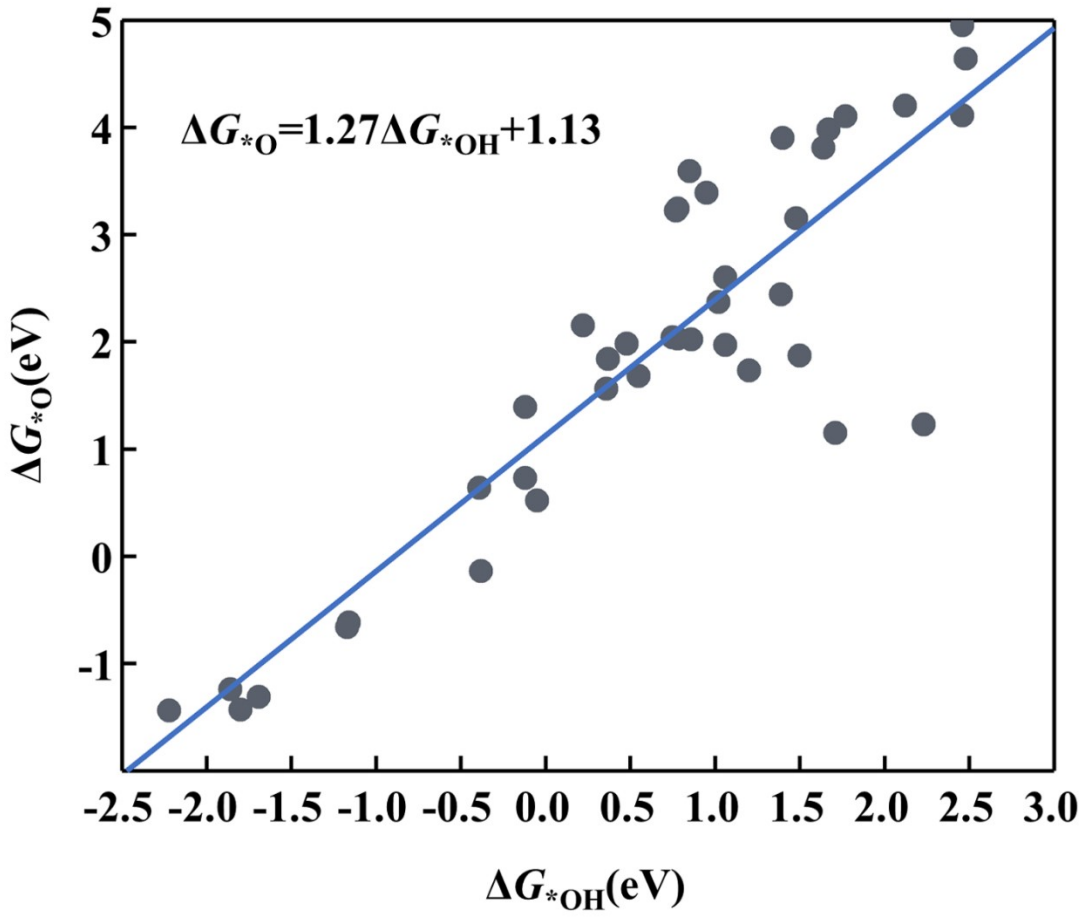

Figure S3. Scaling relationships for adsorption free energy of *OH vs *O.

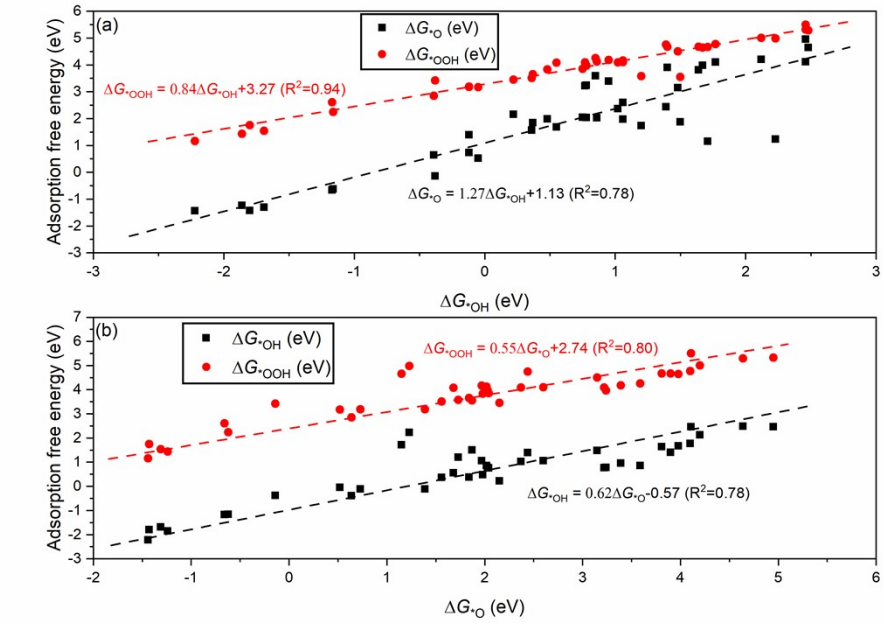

Figure S4. Linear scaling relation of (a) ΔG*O vs. ΔG*OH, ΔG*OOH vs. ΔG*OH; (b) ΔG*OH vs. ΔG*O, ΔG*OOH vs. ΔG*O.

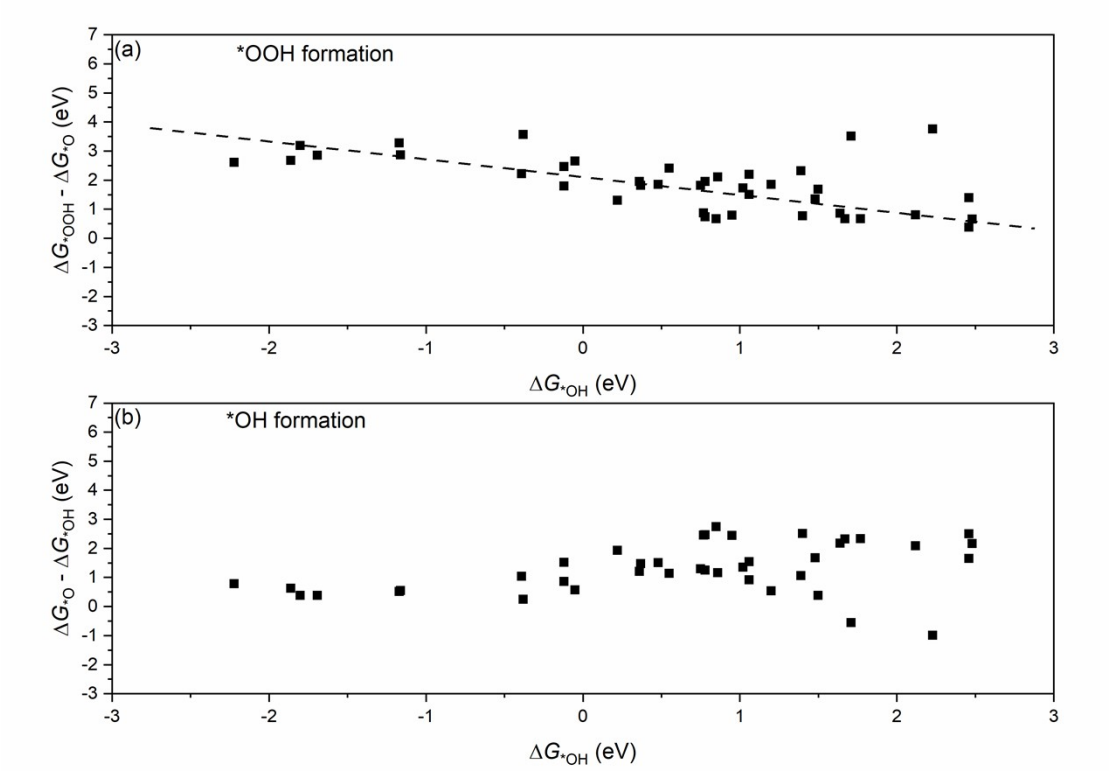

Figure S5. Linear scaling relation of (a) ΔG*OOH-ΔG*O vs. ΔG*OH; (b) ΔG*O-ΔG*OH vs. ΔG*OH

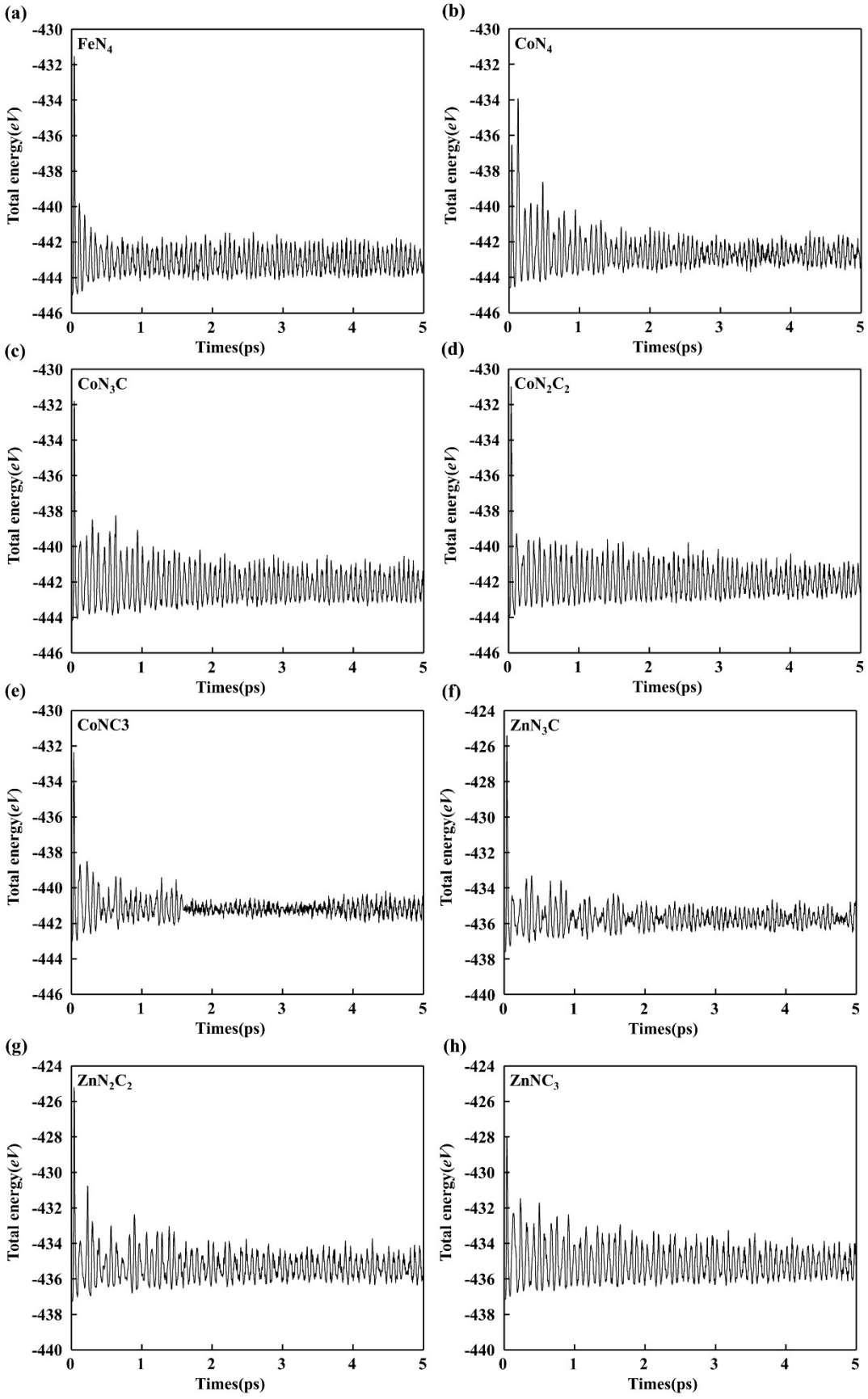

Figure S6. Variations of energy versus the AIMD simulation time for (a) FeN_4, (b) CoN_4, (c)

CoN_3C, (d) CoN_2C_2, (e) $CoNC_3$, (f) ZnN_3C, (g) ZnN_2C_2, and (h) $ZnNC_3$.