Supporting Information for

Carbon-metal versus Metal-metal Synergistic Mechanism of Ethylene Electro-oxidation via Electrolysis Water on TM_2N_6 sites in Graphene

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Table S1. Free energy difference (ΔG, eV) of O atom adsorbed at difference sites for 19 TM_2N_6@graphenes, the "0 eV" represents the most stable O adsorption site, and "-" represents no corresponding configurations obtained during their optimization.

metal	site-1	site-2	site-3	site-4
TiTi	0	—	3.42	—
VV	0.17	0	4.21	—
CrCr	0.77	0	3.28	3.23
MnMn	0.43	0	1.74	1.61
FeFe	0	0.03	0.63	0.61
CoCo	0.17	0.17	0.17	0
NiNi	0.90	0.77	0.13	0
CuCu	0.93	0.88	0.09	0
ZnZn	0	—	0.43	0.39
MoMo	0.76	0	3.87	—
RuRu	0.44	0	1.23	1.20
RhRh	1.11	0.50	0.23	0
PdPd	1.20	0.84	0.09	0
TaTa	0	0.18	4.39	—
WW	0.73	0	4.11	—
ReRe	0.92	0	2.65	2.61
OsOs	1.56	0	1.48	1.43
IrIr	—	0.27	0.30	0
PtPt	1.44	0.62	0.20	0

Table S2. Total Gibbs free energy changes of ethylene oxidation reaction initiated by stable *O intermediates to AA and EO on various TM_2N_6@graphenes.

metal type	Ti	V	Cr	Mn	Fe
ΔG_{AA} (eV)	0.88	2.25	0.78	-0.98	-2.18
ΔG_{EO} (eV)	2.09	3.46	1.99	0.23	-0.97
metal type	Co	Ni	Cu	Zn	Mo
ΔG_{AA} (eV)	-2.80	-2.95	-2.65	-2.01	1.67
ΔG_{EO} (eV)	-1.60	-1.74	-1.44	-0.80	2.88
metal type	Ru	Rh	Pd	Ta	W
ΔG_{AA} (eV)	-1.44	-1.49	-2.58	2.12	1.68
ΔG_{EO} (eV)	-0.23	-2.70	-1.37	3.33	2.83
metal type	Re	Os	Ir	Pt	
ΔG_{AA} (eV)	0.32	-1.08	-2.51	-2.32	
ΔG_{EO} (eV)	1.53	0.13	-1.31	-1.11	

Table S3. Gibbs free energy difference (ΔG, eV) of OH adsorbed at difference sites on 12 TM_2N_6@graphenes, the "0 eV" represents the most stable OH adsorption site, and "-" represents no corresponding configurations obtained during their optimization.

metal	site-1	site-2	site-3	site-4
MnMn	—	0	—	1.30
FeFe	0.09	0	—	0.66
CoCo	—	0	—	0.48
NiNi	—	0	—	0.19
CuCu	0.02	0.02	—	0
ZnZn	0.09	0	—	1.25
RuRu	1.12	0	—	1.21
RhRh	—	0	—	0.18
PdPd	—	0.06	—	0
OsOs	1.54	0	—	1.29
IrIr	—	0	—	0.07
PtPt	—	0.16	—	0

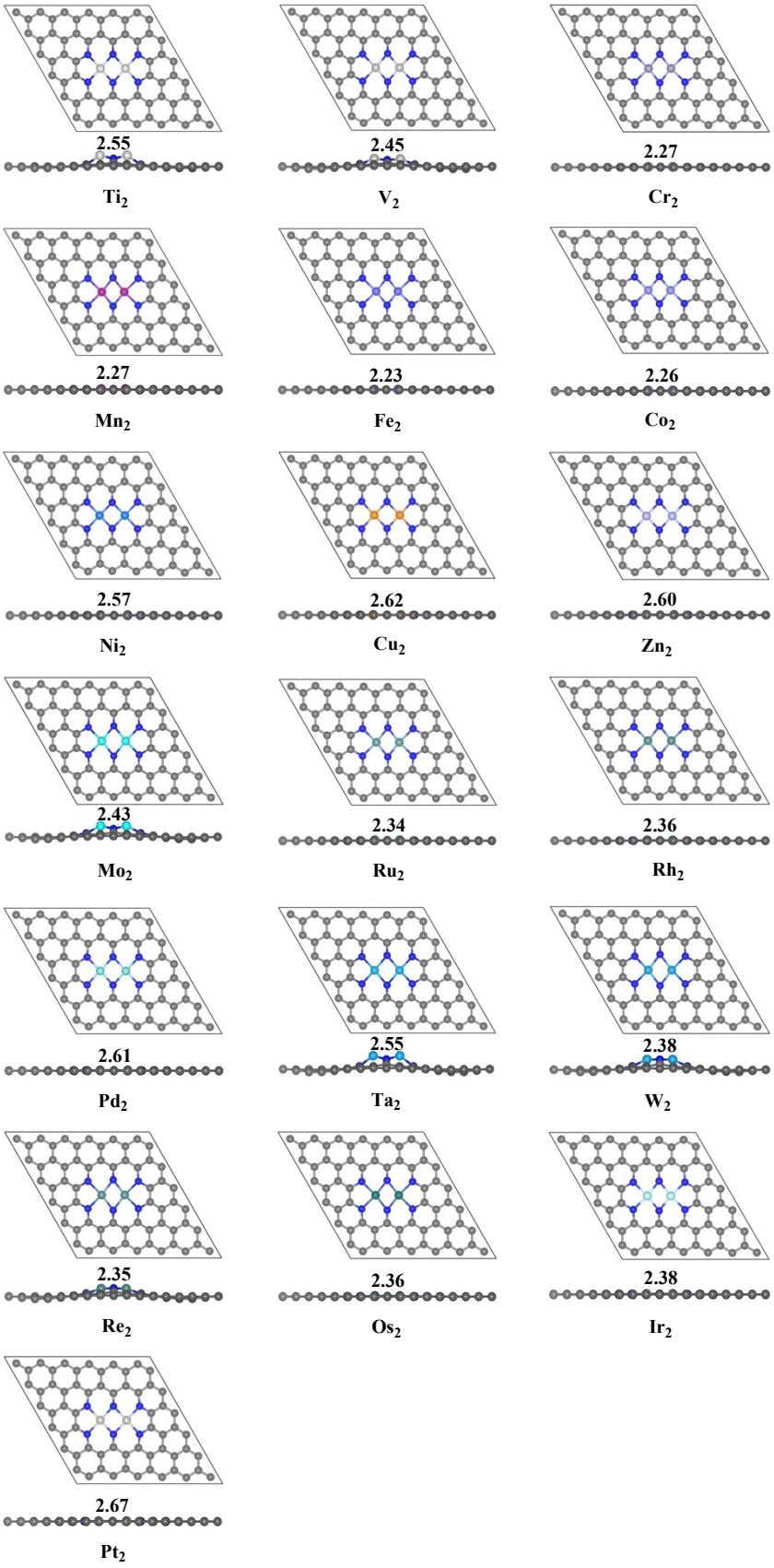

Fig. S1 Top and side views of various homonuclear TM_2N_6@graphene DMACs with distances between two metal atoms in angstroms (Å).

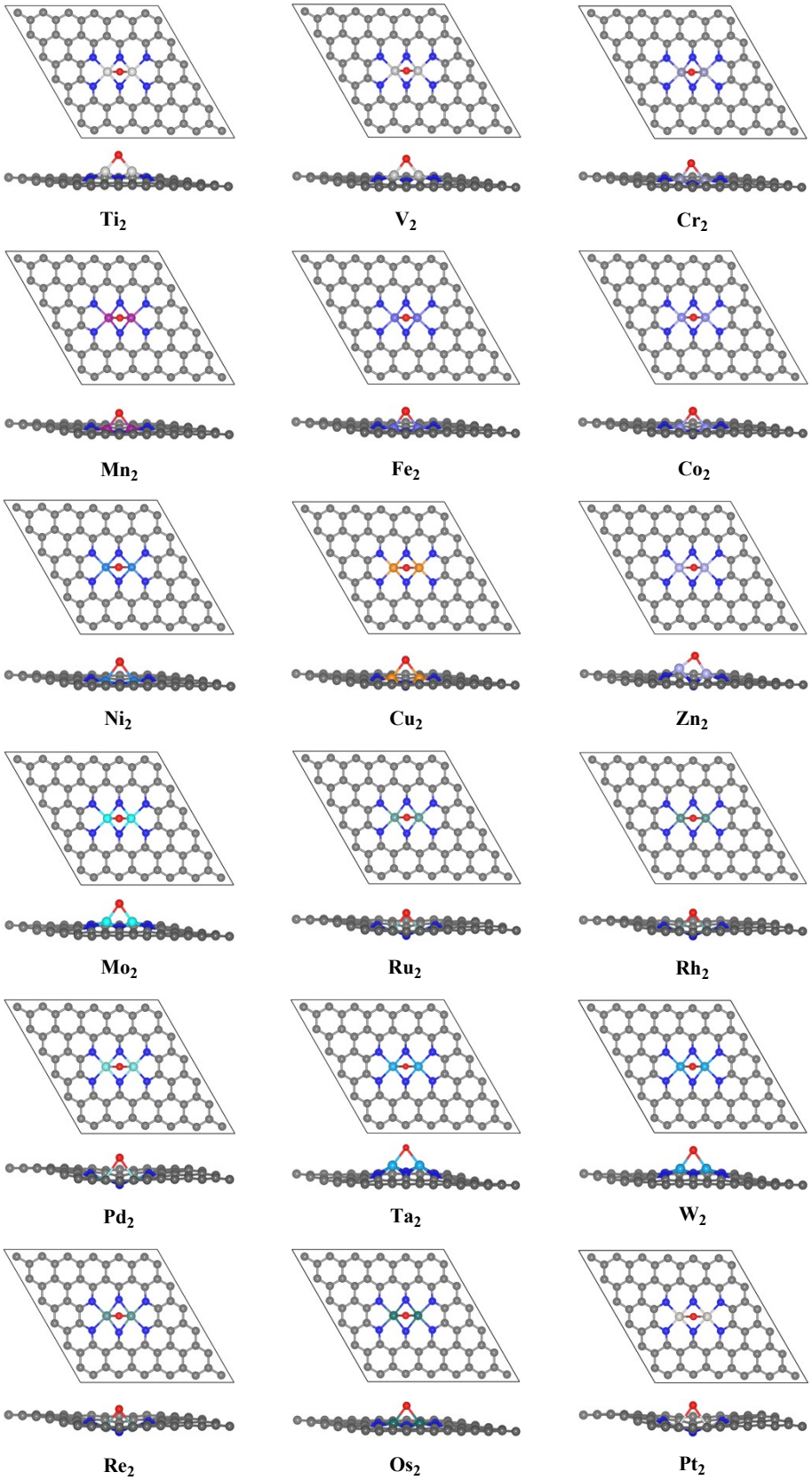

Fig. S2 Top and side views of O atom absorbed at **site-1** on various TM_2N_6@graphenes.

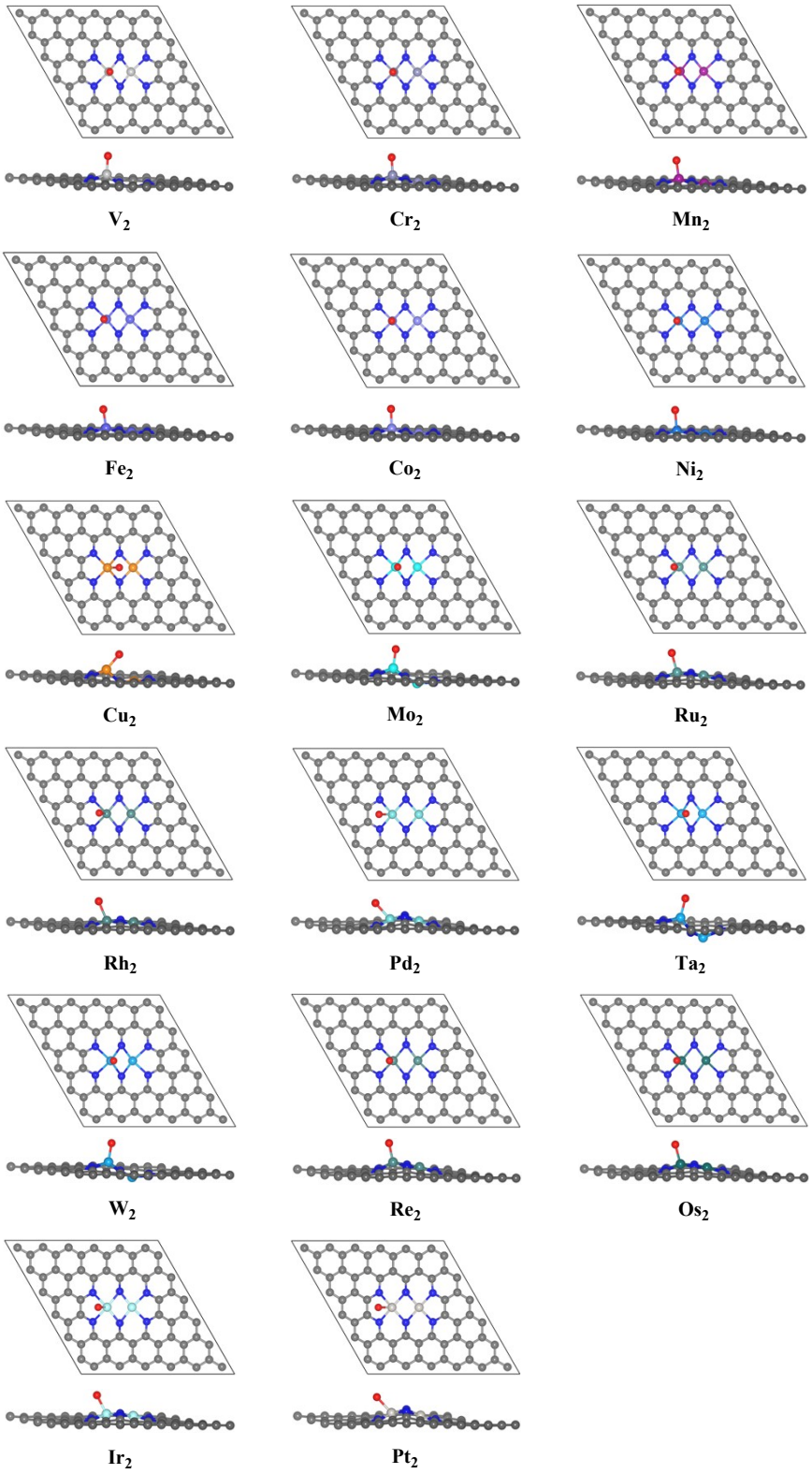

Fig. S3 Top and side views of O atom absorbed at **site-2** on various TM_2N_6@graphenes.

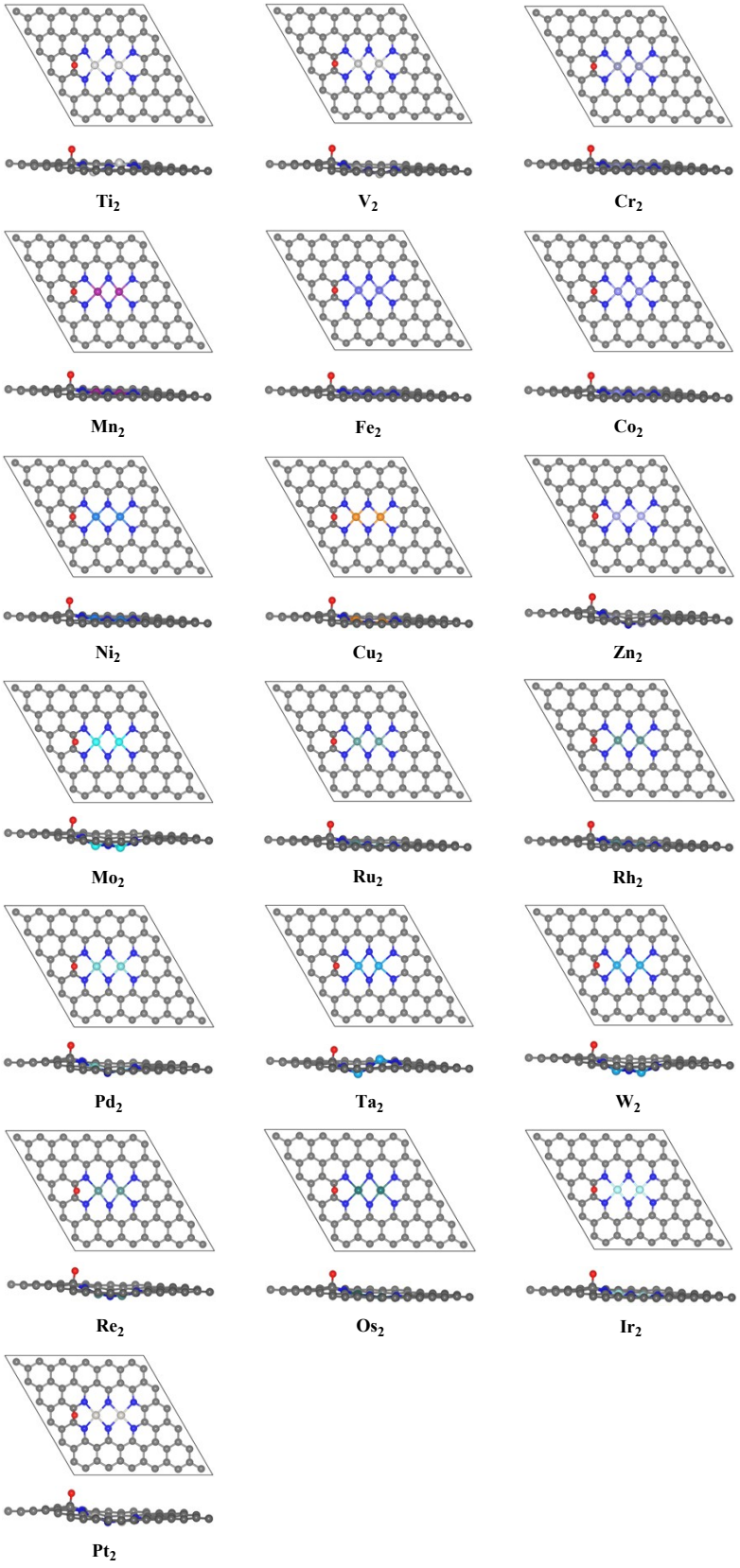

Fig. S4 Top and side views of O atom absorbed at **site-3** on various TM_2N_6@graphenes.

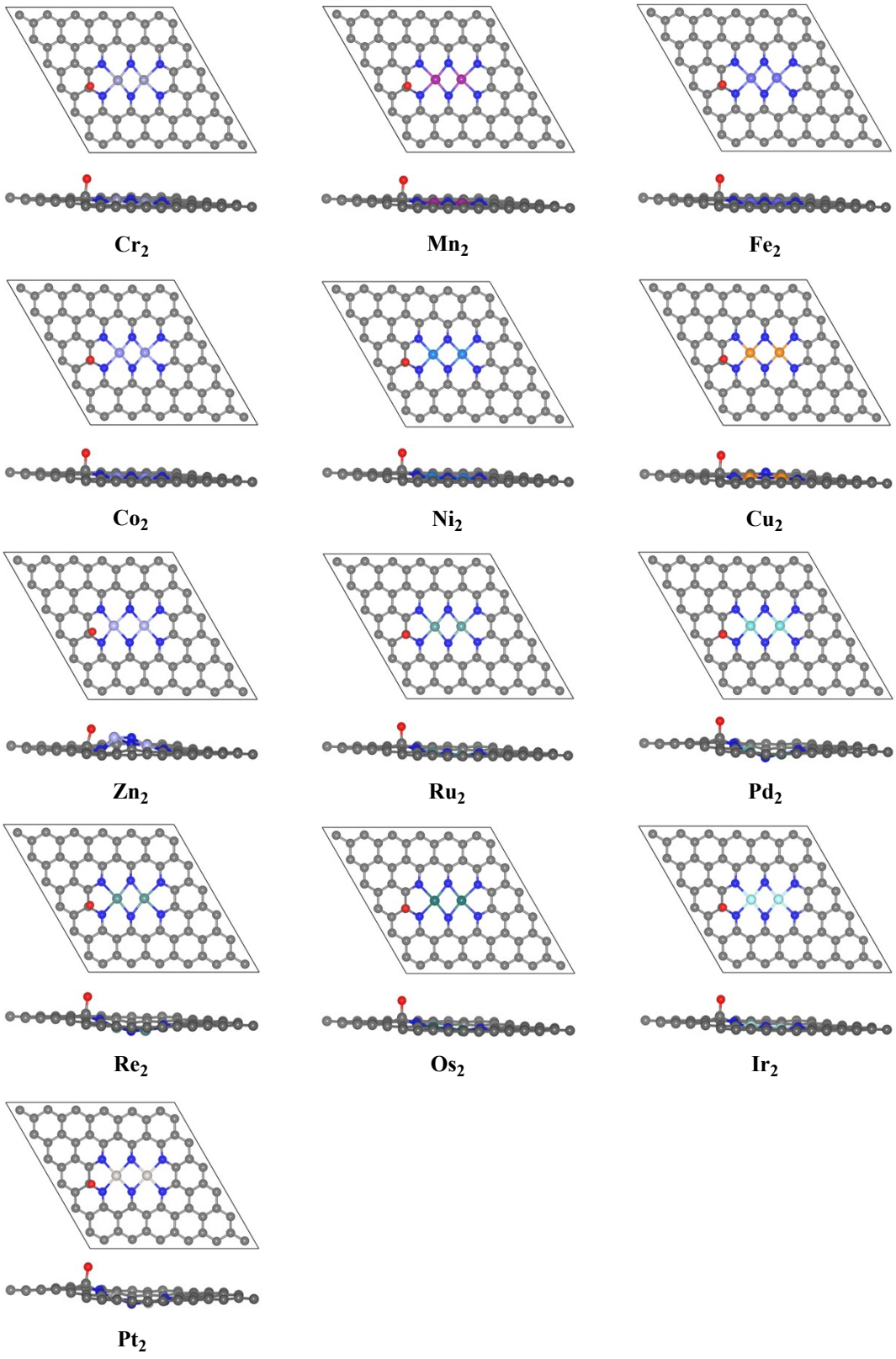

Fig. S5 Top and side views of O atom absorbed at **site-4** on various TM_2N_6@graphenes.

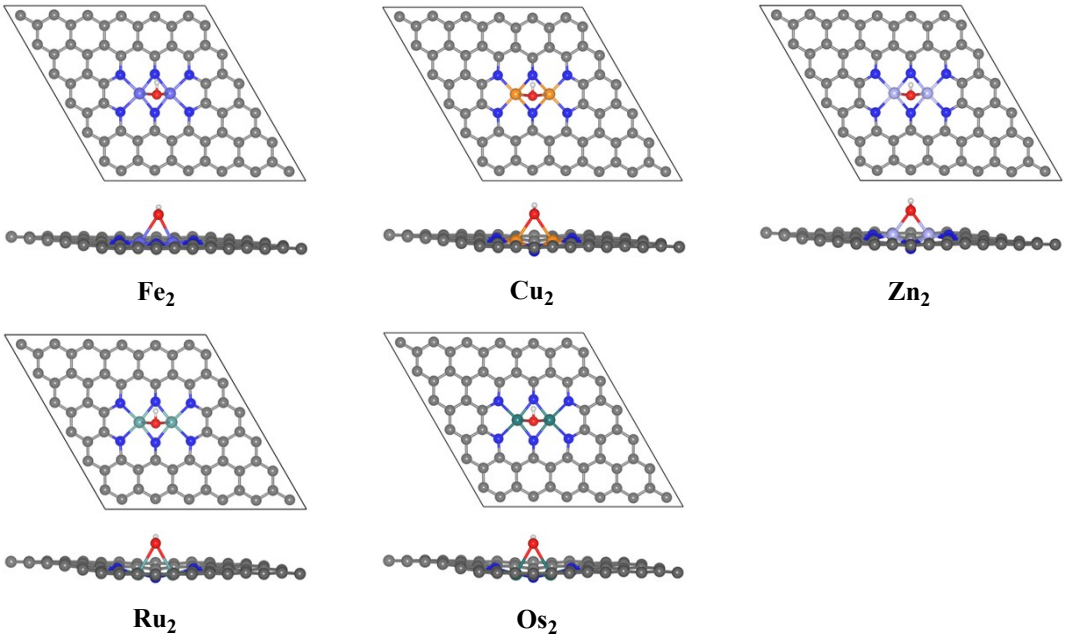

Fig. S6 Top and side views of OH absorbed at **site-1** on various TM_2N_6@graphenes.

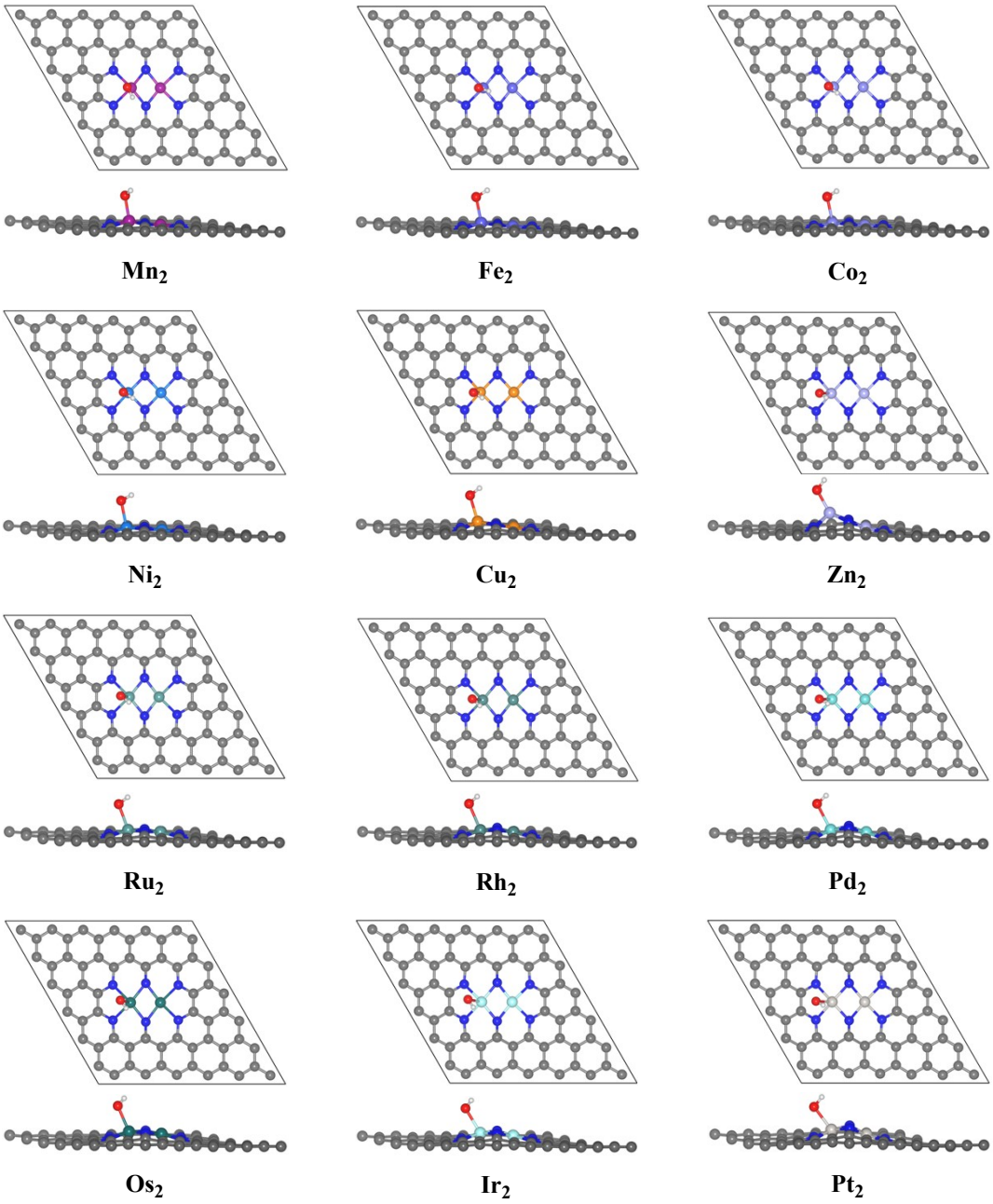

Fig. S7 Top and side views of OH absorbed at **site-2** on various TM_2N_6@graphenes.

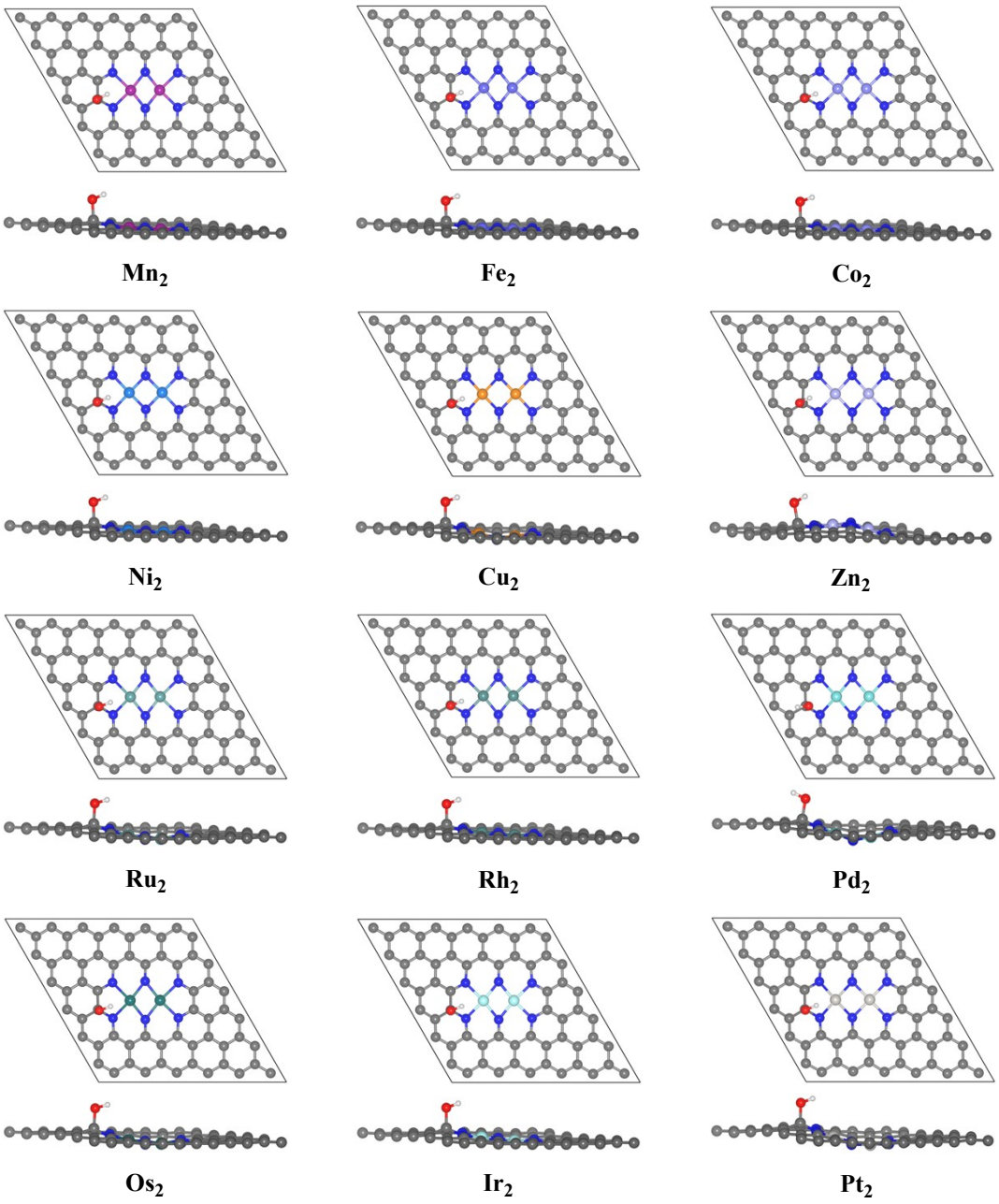

Fig. S8 Top and side views of OH absorbed at **site-4** on various TM_2N_6@graphenes.

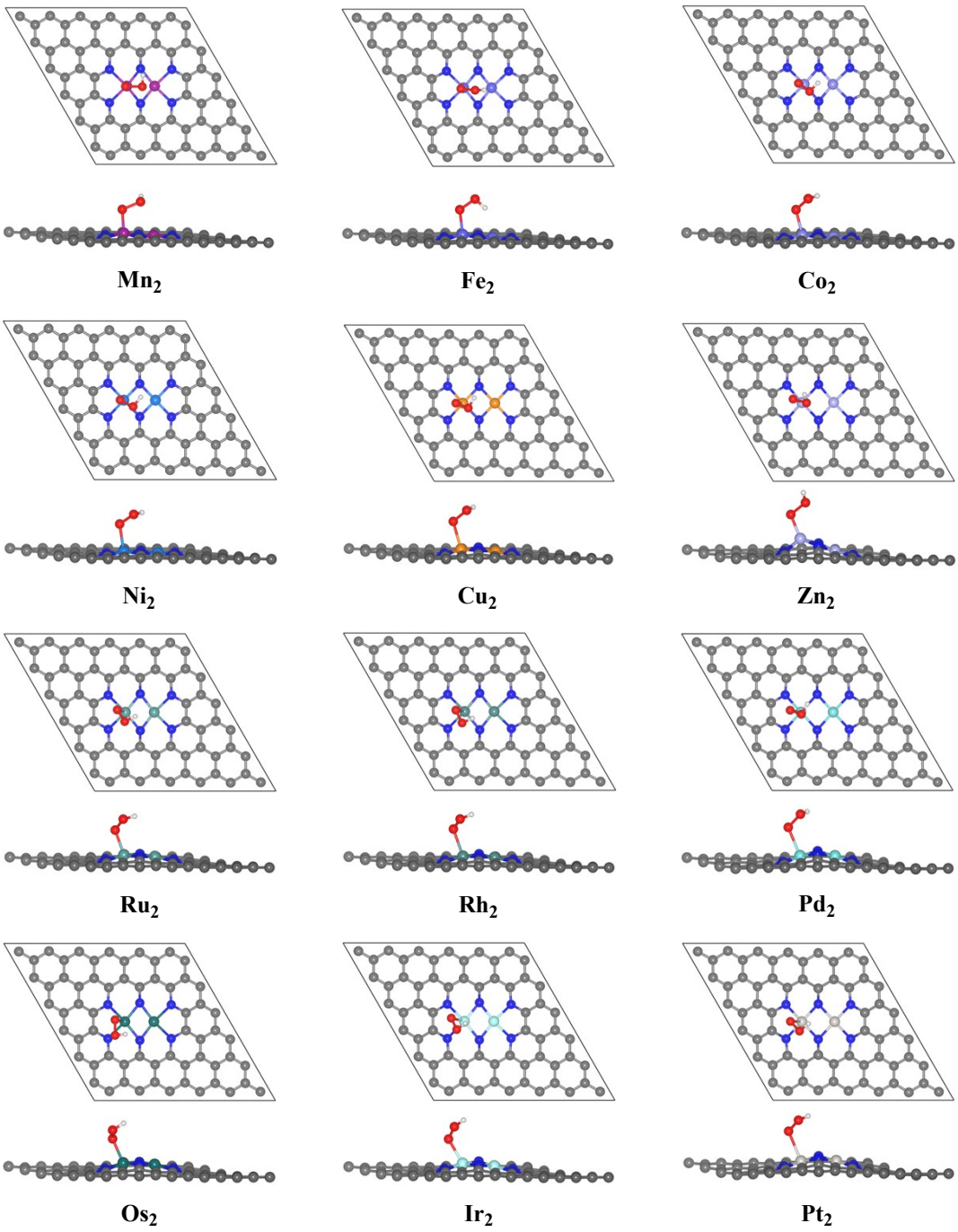

Fig. S9 Top and side views of OOH absorbed on various TM_2N_6@graphenes.

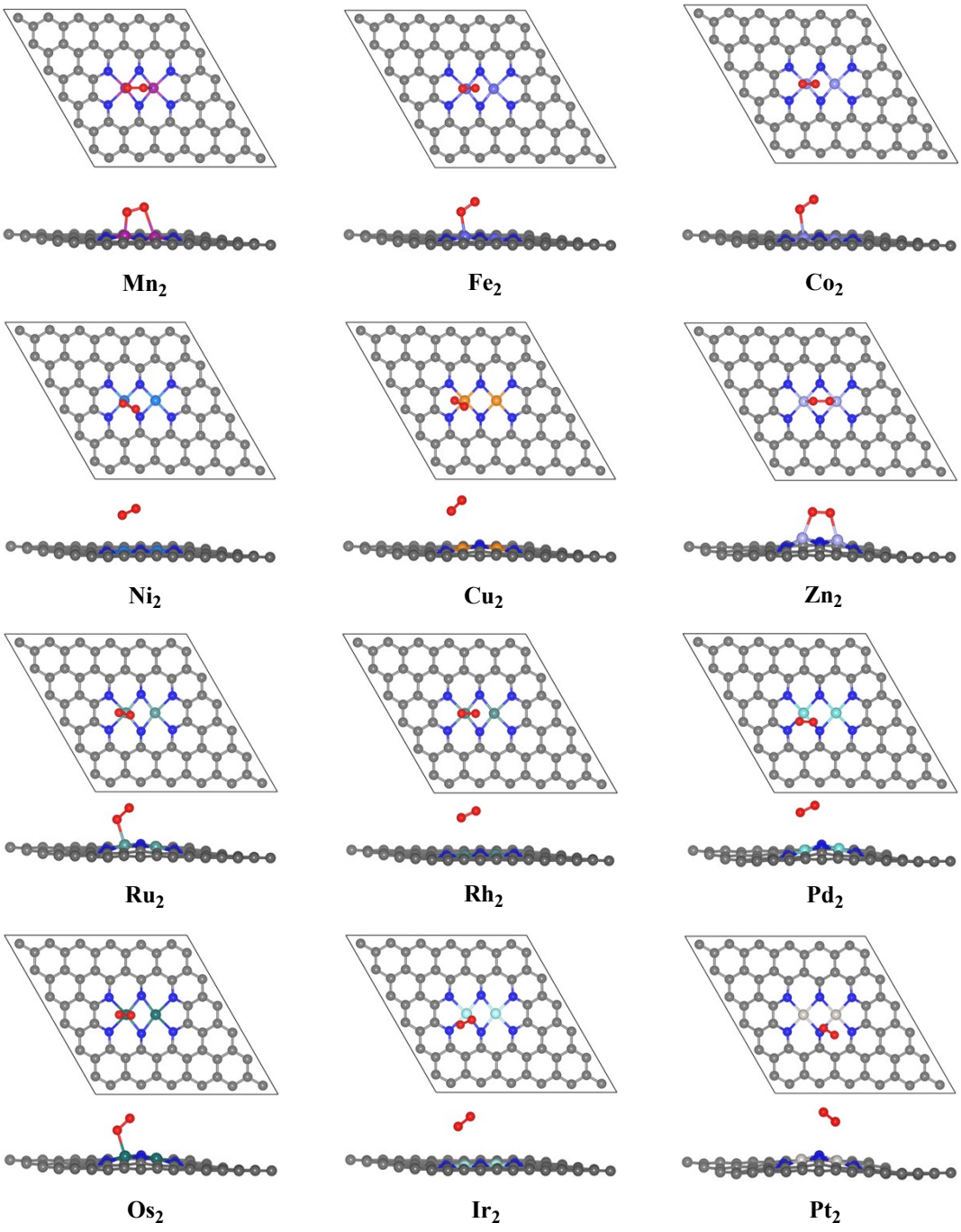

Fig. S10 Top and side views of OO absorbed on various TM_2N_6@graphenes.

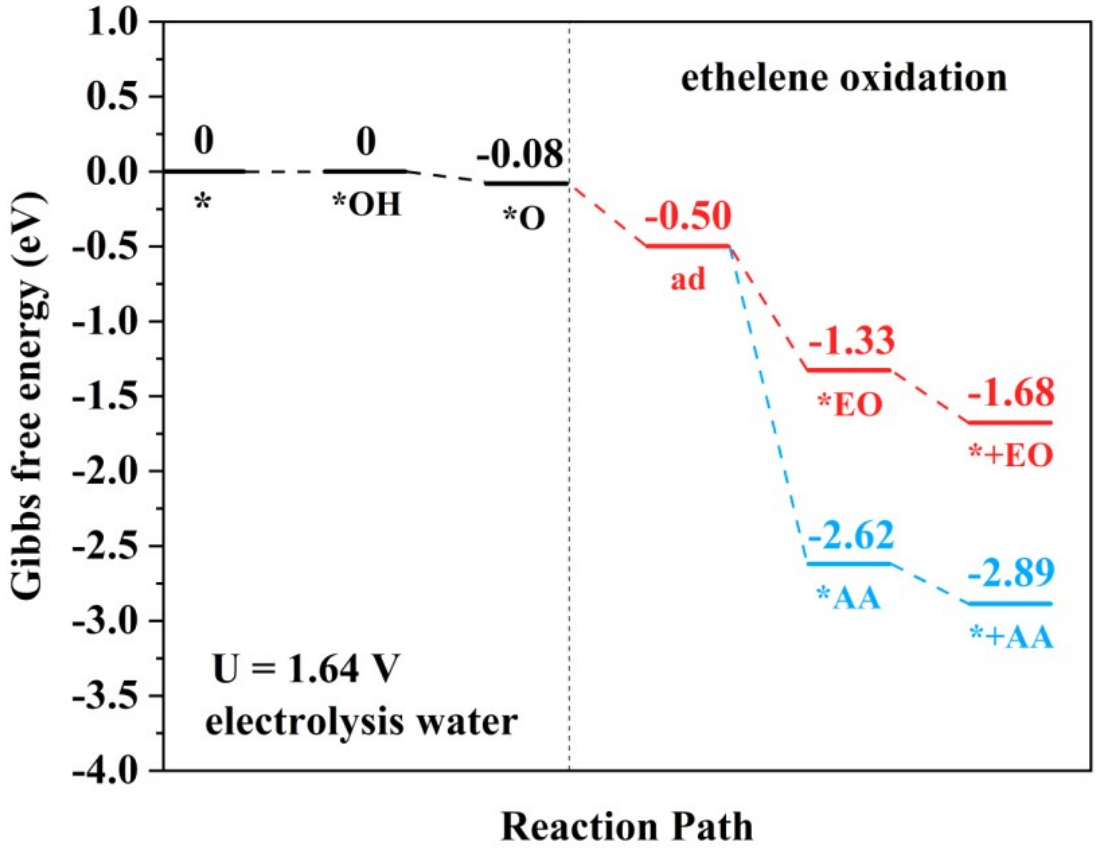

Fig. S11 Gibbs free energy change diagrams for ethylene electro-oxidation on Co_2N_6@graphenes at the lowest applied potential to generate *O intermediates at pH=0.

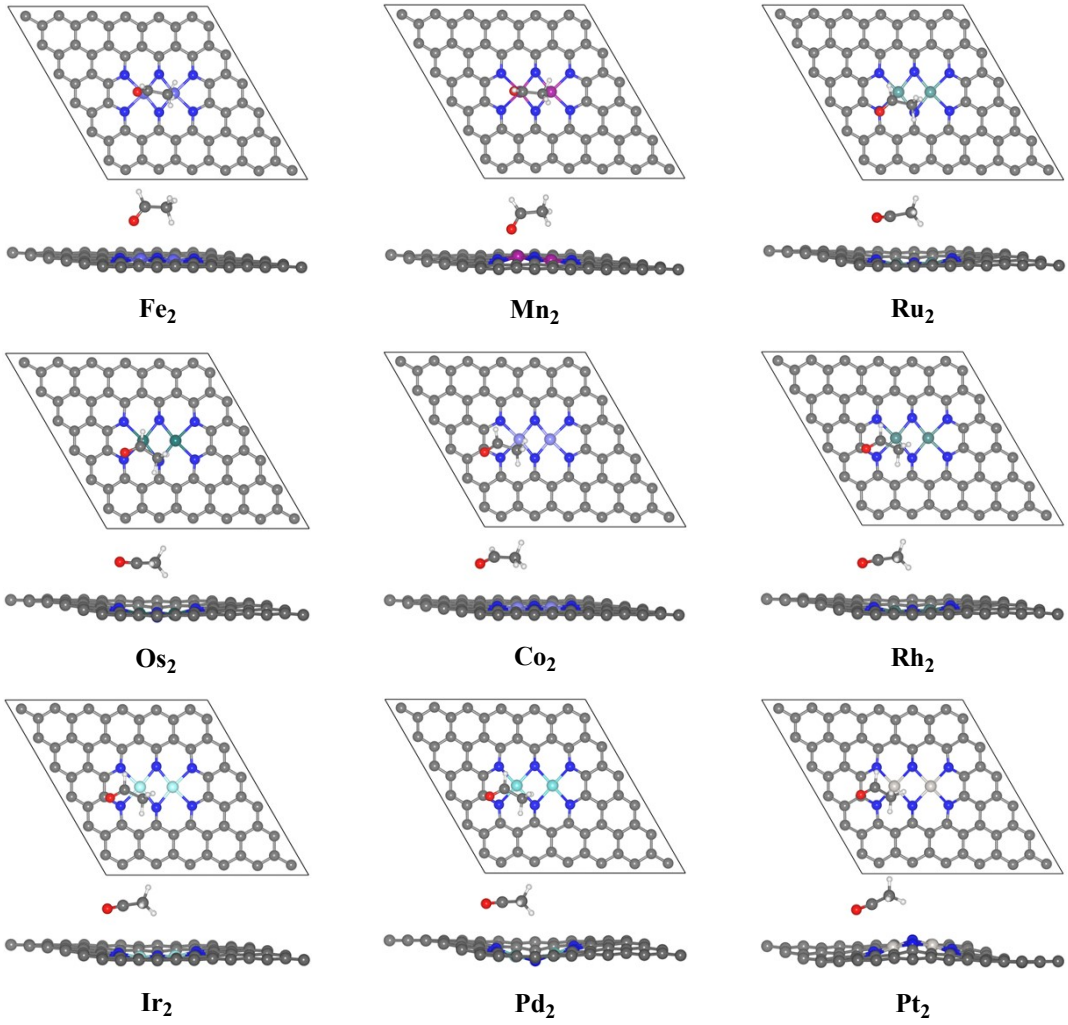

Fig. S12 Top and side views of acetaldehyde absorbed on various TM_2N_6@graphenes.

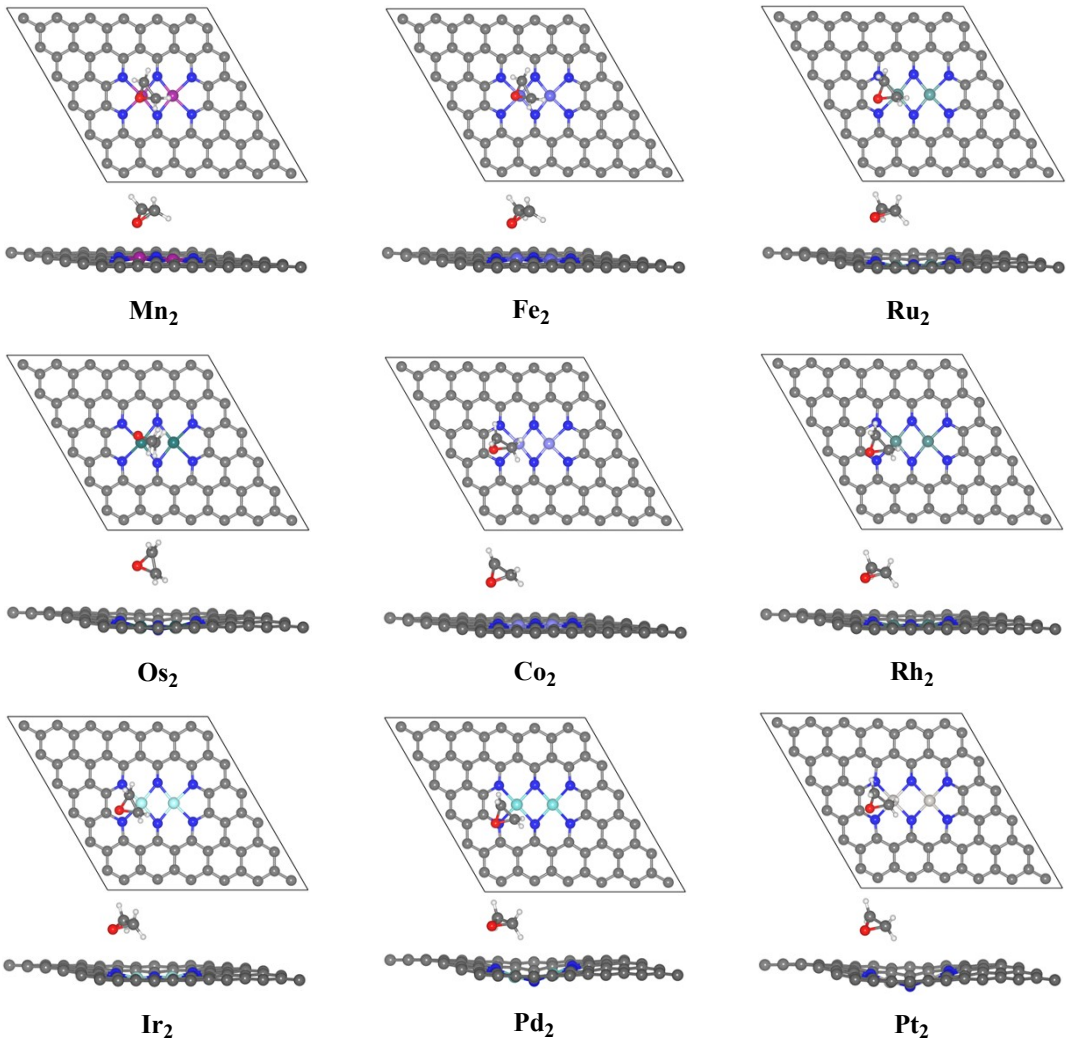

Fig. S13 Top and side views of ethylene oxide absorbed on various TM_2N_6@graphenes.

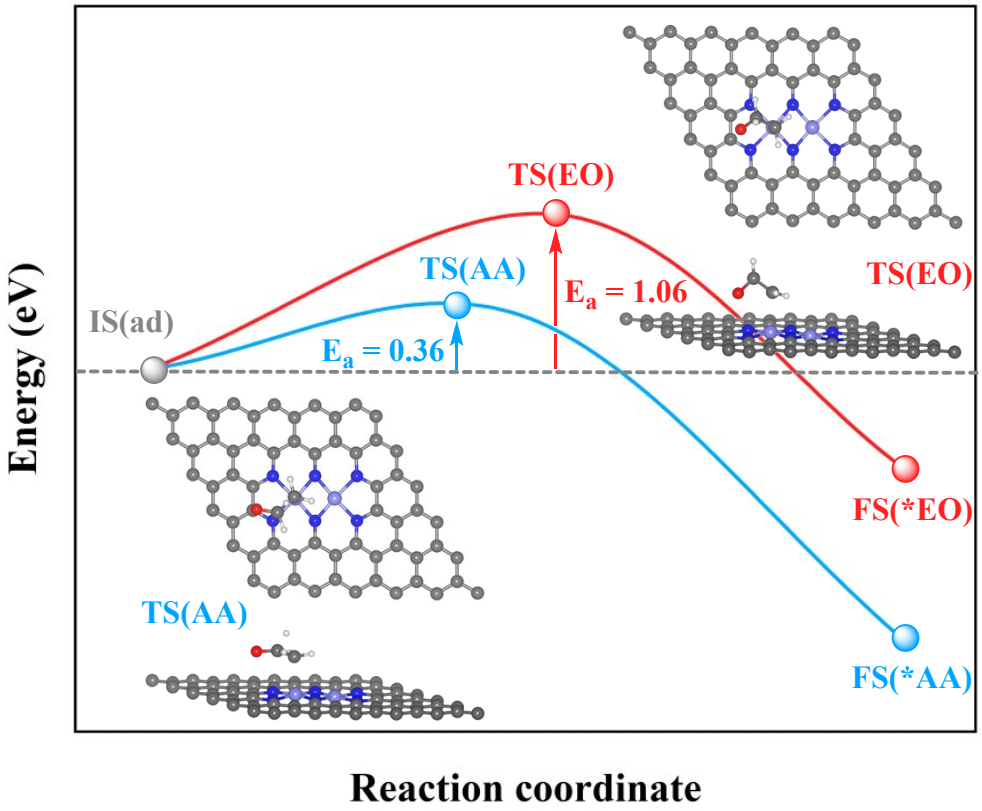

Fig. S14 Kinetic energy barriers and transition state structures of AA and EO generation through C-TM mechanism on Co_2N_6@graphenes.

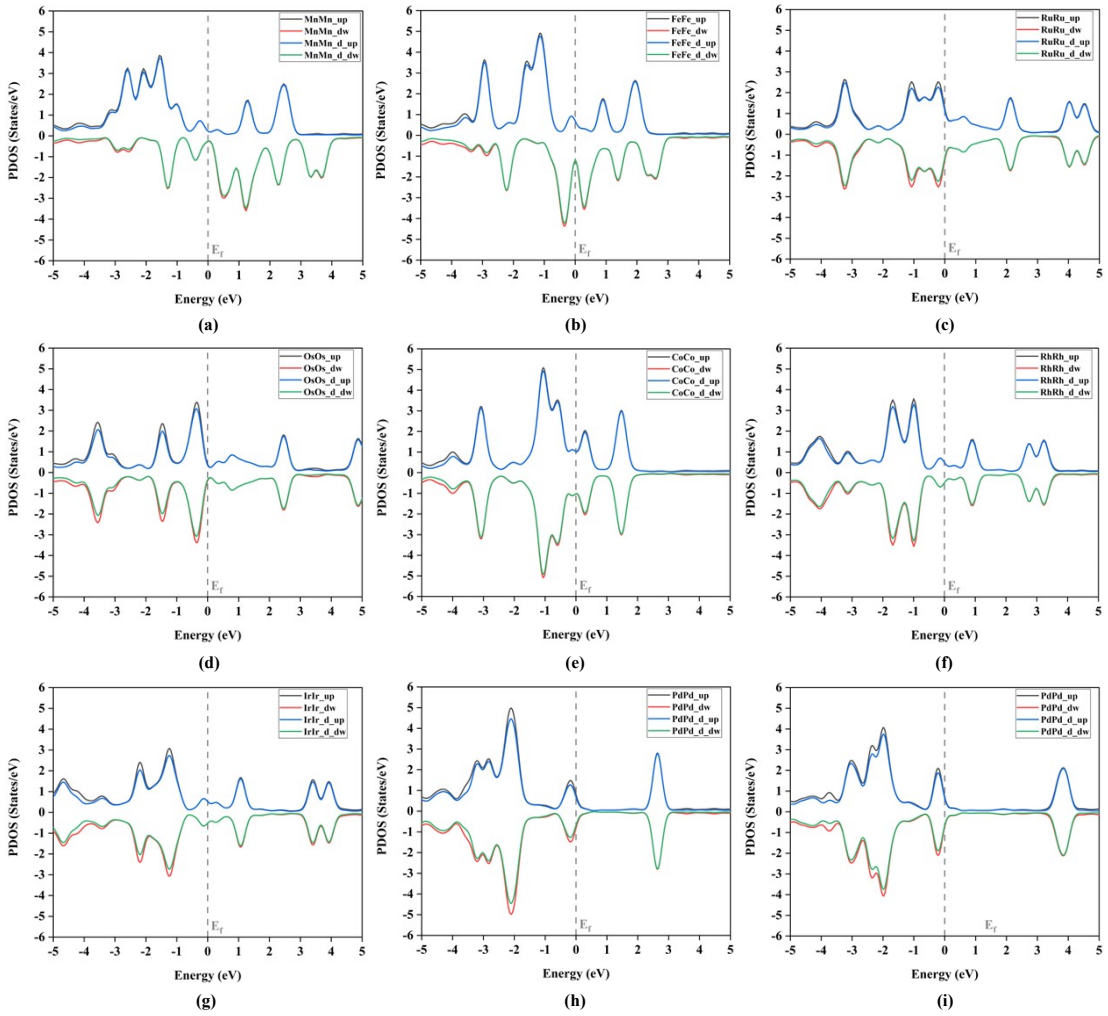

Fig. S15 Projected density of states (PDOS) of the d orbitals of the two metals in TM_2N_6@graphenes.

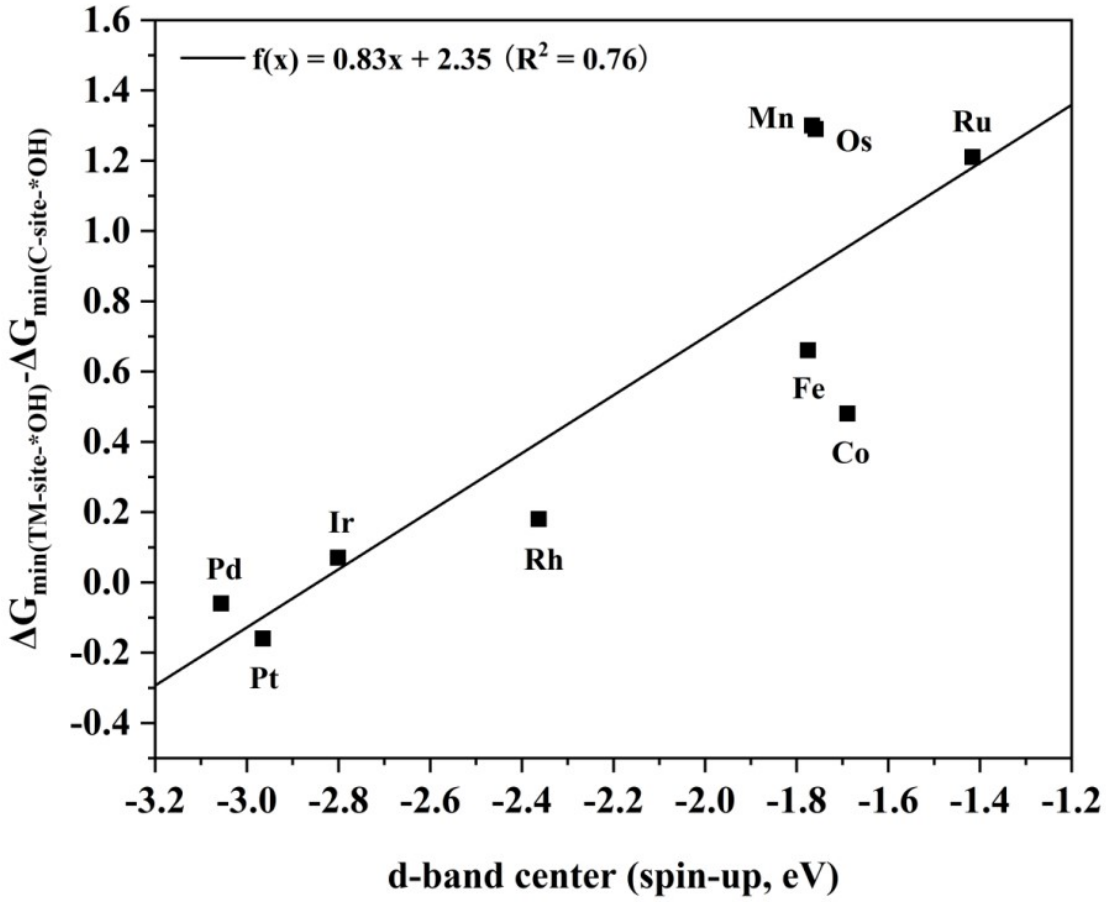

Fig. S16 Linear relationship between d-band center of metals in TM_2N_6@graphenes and energy difference of the most stable OH adsorption sites between metal and C sites.

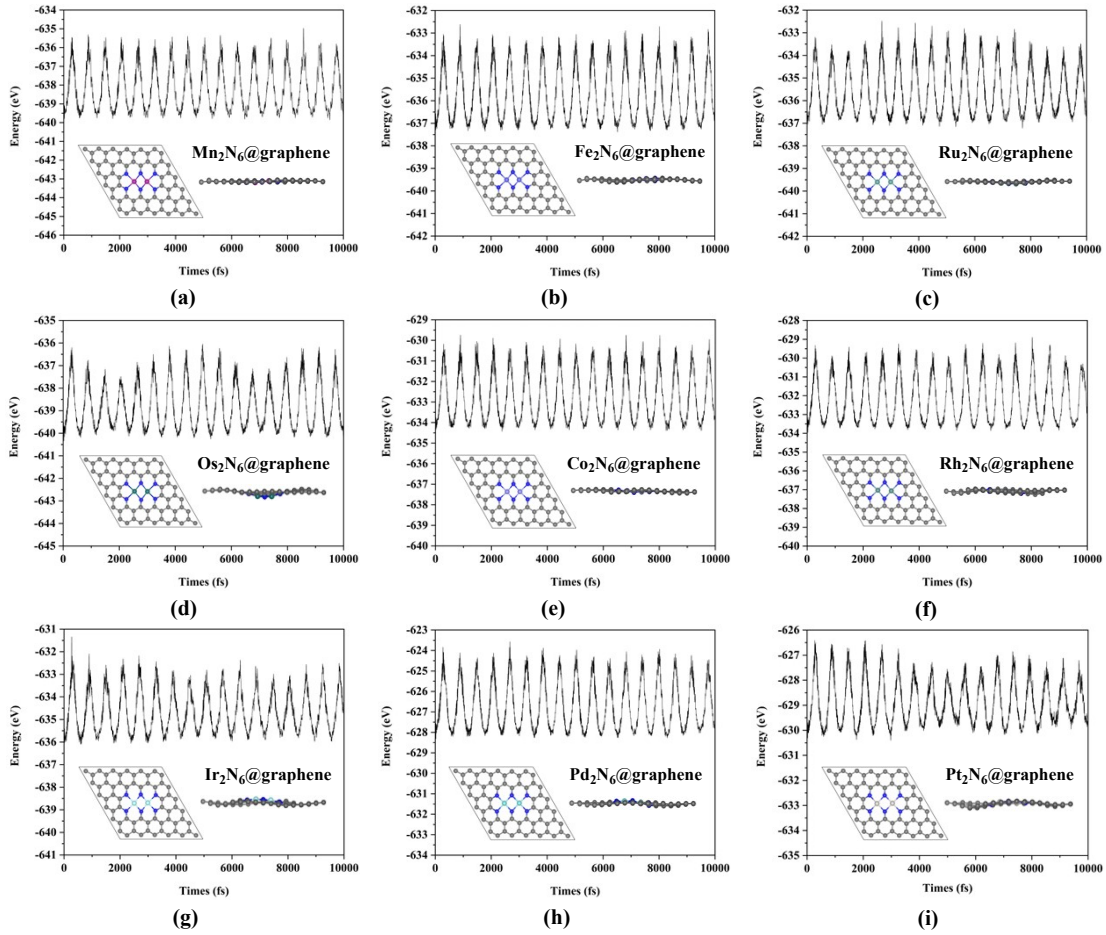

Fig. S17 Evolution of the total energy of 9 TM_2N_6@graphene at 300 K, and the total times duration 10 ps. Snapshots of structures at the end of AIMD simulations are also shown.

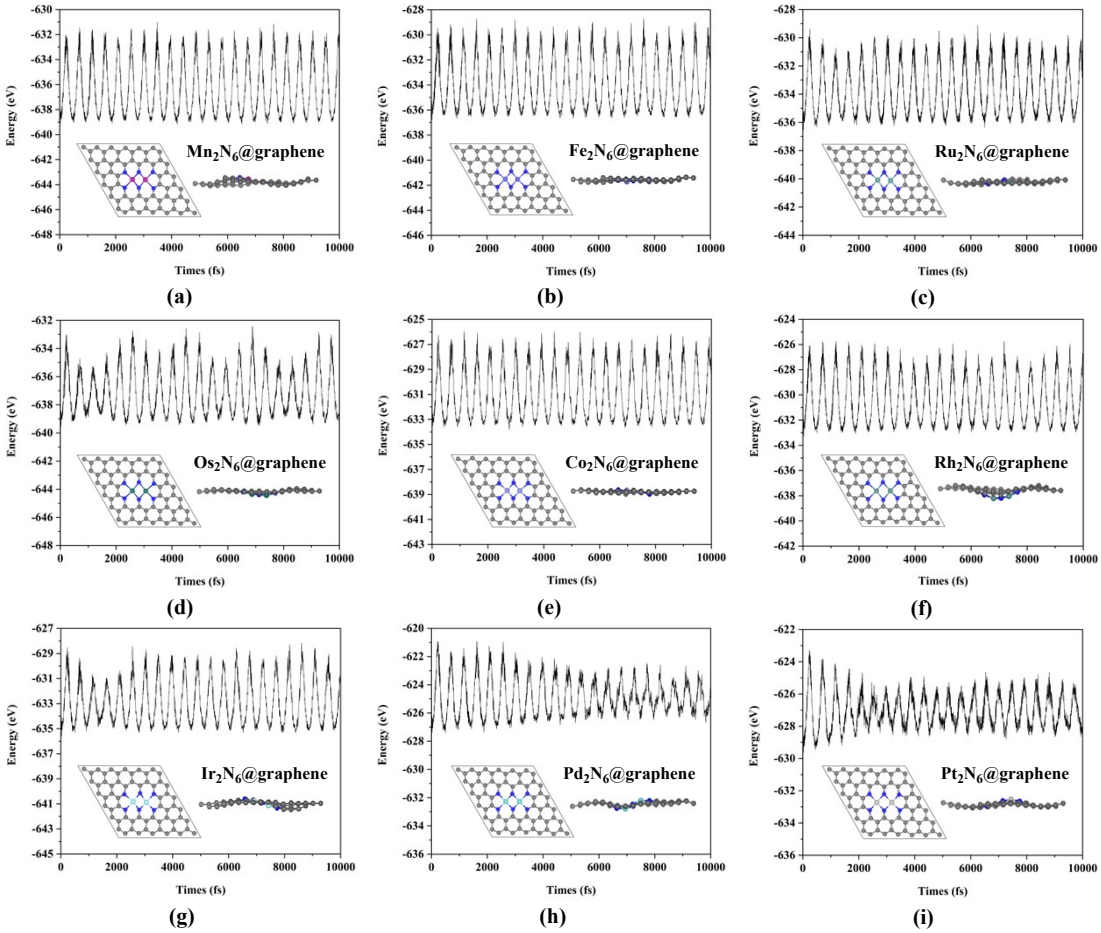

Fig. S18 Evolution of the total energy of 9 TM_2N_6@graphene at 500 K, and the total times duration 10 ps. Snapshots of structures at the end of AIMD simulations are also shown.