Supporting Information for

Electro-epoxidation of ethylene and propylene via atomic active oxygen from water electrolysis on IrN_4 site in graphene with lower applied potential and wide range

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Table S1. Free energy difference (ΔG, eV) of O atom adsorbed at difference sites for 26 TMN_4@graphenes, the "0 eV" represents the most stable O adsorption site, and "-" represents no corresponding configurations obtained during the optimization.

metal	site-1	site-2	site-3
Sc	0	0.47	0.99
Ti	0	—	—
V	0	—	—
Cr	0	2.87	2.97
Mn	0	1.54	1.65
Fe	0	1.57	1.60
Co	0	0.39	0.45
Ni	1.00	0	0.08
Cu	0.89	0	0.06
Zn	0.15	0.07	0
Y	0.44	0	0.67
Zr	0	—	2.63
Nb	0	4.48	5.08
Mo	0	—	5.22
Ru	0	2.20	2.24
Rh	0	0.23	0.34
Pd	1.34	0	0.07
Ag	0.41	0	0.24
Hf	0	—	2.58
Ta	0	—	—
W	0	—	—
Re	0	4.49	4.62

Os	0	2.76	2.95
Ir	0	0.61	0.69
Pt	1.10	0	0.06
Au	1.66	0	0.19

Table S2. Total Gibbs free energy changes of ethylene and propylene epoxidation reaction starting from the stable *O intermediates to EO and PO on various TMN_4@graphenes.

metal type	Sc	Ti	V	Cr	Mn	Fe	Co
ΔG_{EO} (eV)	-0.24	3.53	3.64	1.61	0.35	0.21	-0.85
ΔG_{PO} (eV)	-0.33	3.45	3.56	1.52	0.27	0.13	-0.94
metal type	Ni	Cu	Zn	Y	Zr	Nb	Mo
ΔG_{EO} (eV)	-1.49	-1.45	-1.42	-0.46	1.69	3.37	3.98
ΔG_{PO} (eV)	-1.57	-1.53	-1.51	-0.54	1.60	3.28	3.90
metal type	Ru	Rh	Pd	Ag	Hf	Ta	W
ΔG_{EO} (eV)	1.08	-1.09	-1.41	-1.13	1.68	4.47	4.35
ΔG_{EO} (eV)	1.00	-1.17	-1.49	-1.21	1.60	4.38	4.27
metal type	Re	Os	Ir	Pt	Au		
ΔG_{EO} (eV)	3.52	1.76	-0.64	-1.43	-0.99		
ΔG_{PO} (eV)	3.43	1.67	-0.72	-1.51	-1.07		

Table S3. Free energy difference (ΔG, eV) of OH adsorbed at difference sites for 14 TMN_4@graphenes, the "0 eV" represents the most stable OH adsorption site, and "-" represents no corresponding configurations obtained during the optimization.

metal	site-1	site-2	site-3
Sc	0	1.79	—
Mn	0	1.47	—
Fe	0	1.34	—
Co	0	1.11	—
Ni	0	0.32	—
Cu	0	0.27	—
Zn	0	1.27	—
Y	0	1.50	—
Rh	0	0.89	—
Pd	0.05	0	—
Ag	0.33	0	—
Ir	0	0.73	—
Pt	0.09	0	—
Au	0.002	0	—

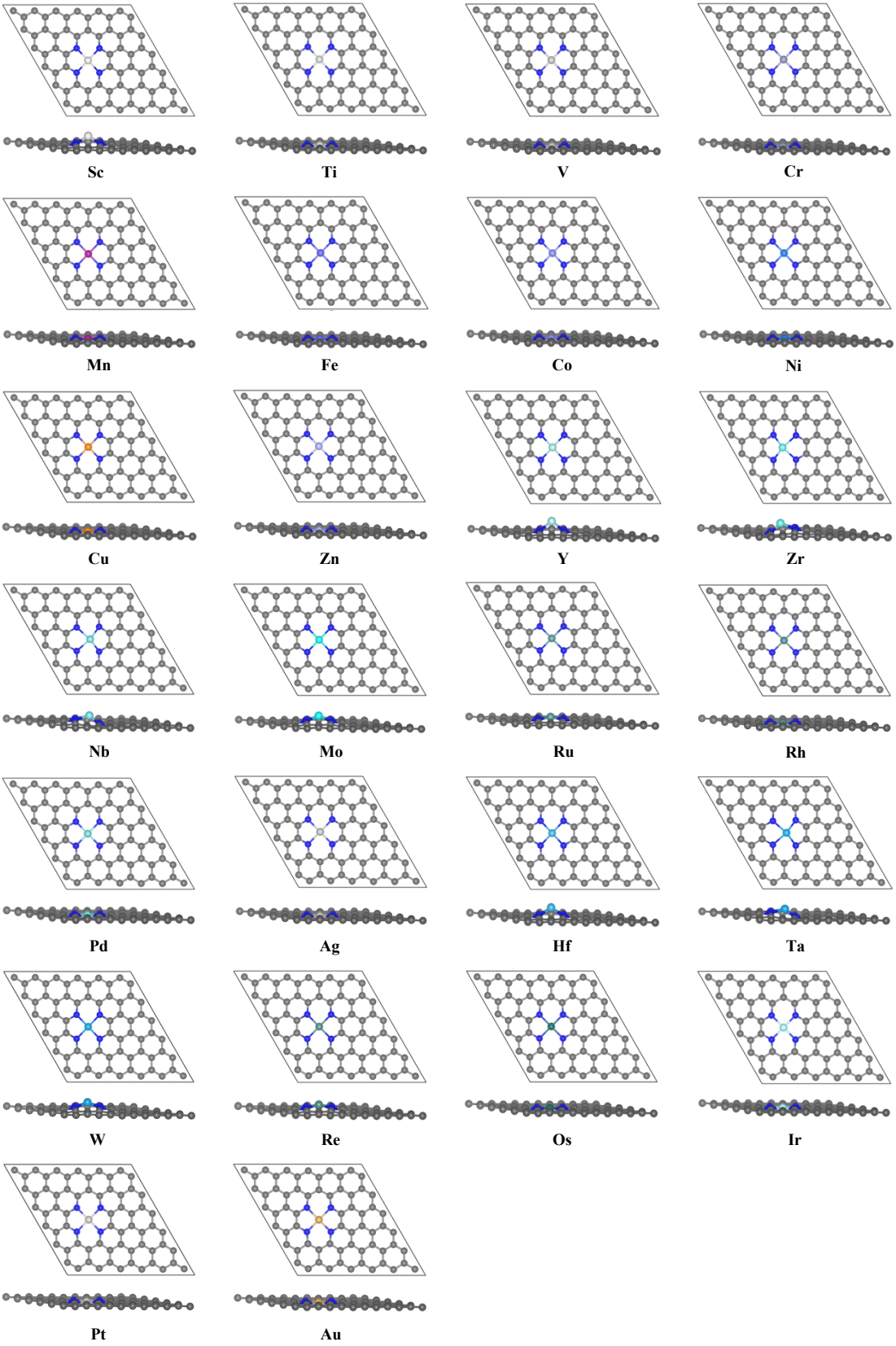

Fig. S1. Top and side views of various TMN_4@graphene SACs.

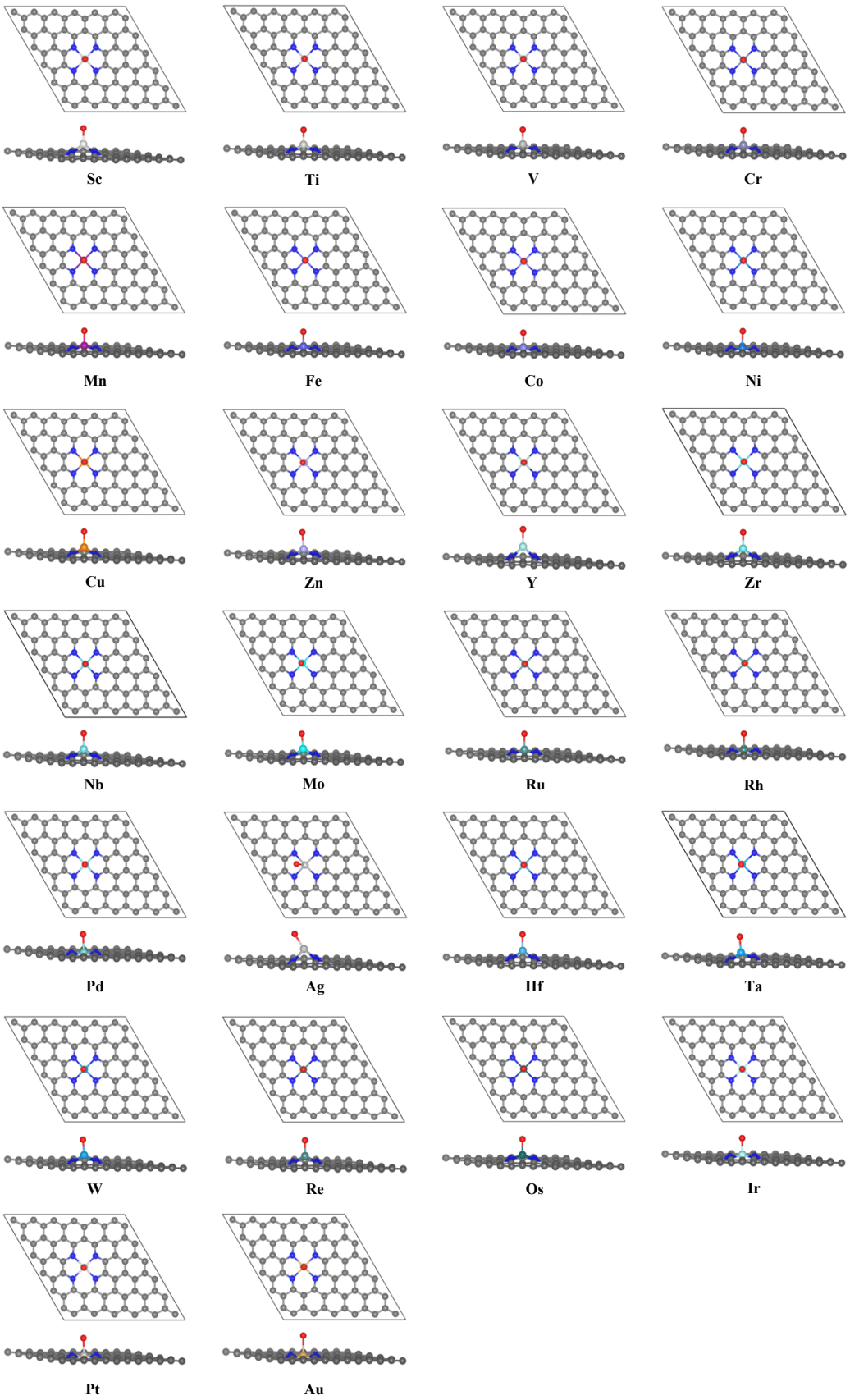

Fig. S2. Top and side views of O atom absorbed at **site-1** on various TMN_4@graphenes.

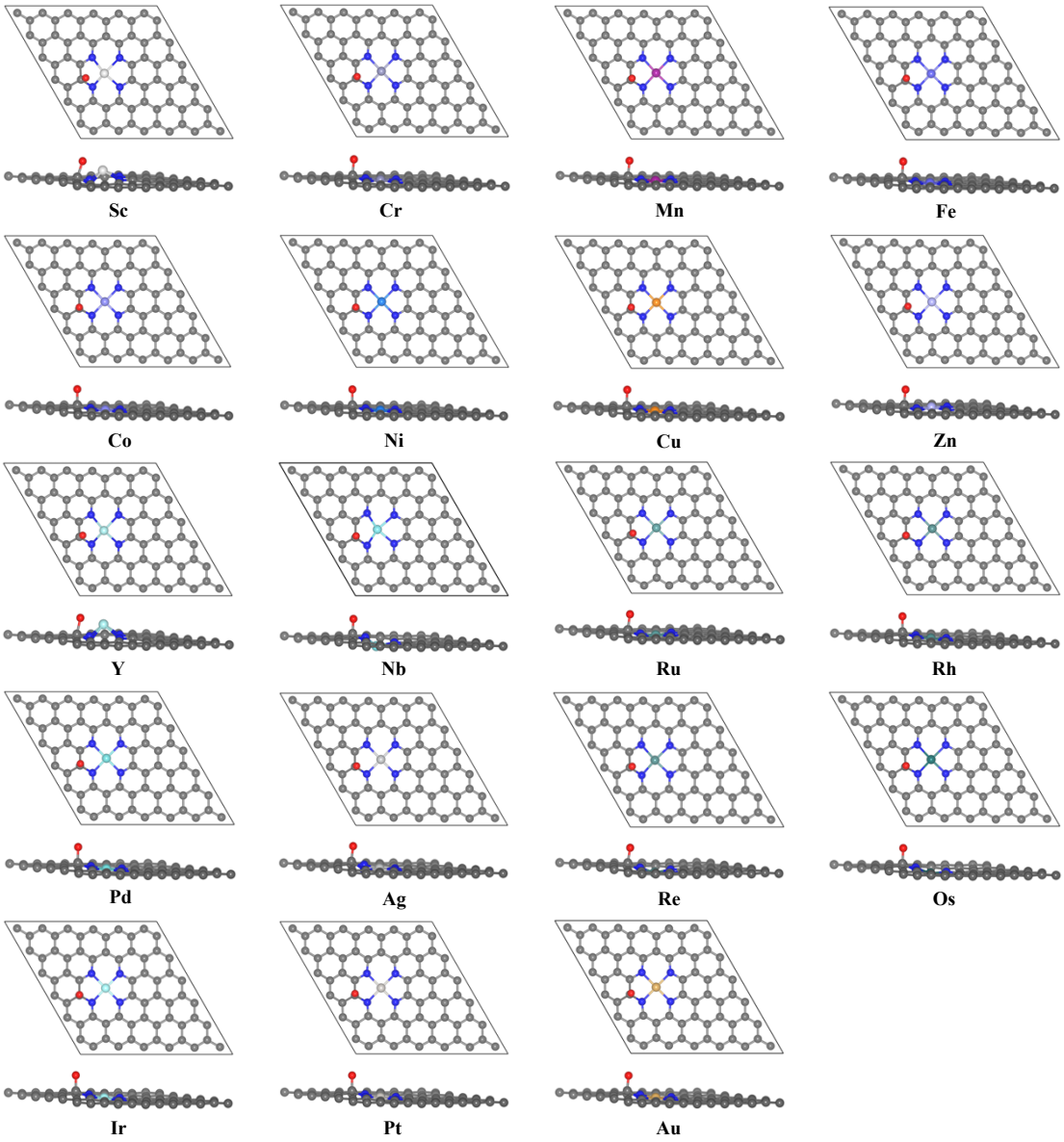

Fig. S3. Top and side views of O atom absorbed at **site-2** on various TMN_4@graphenes.

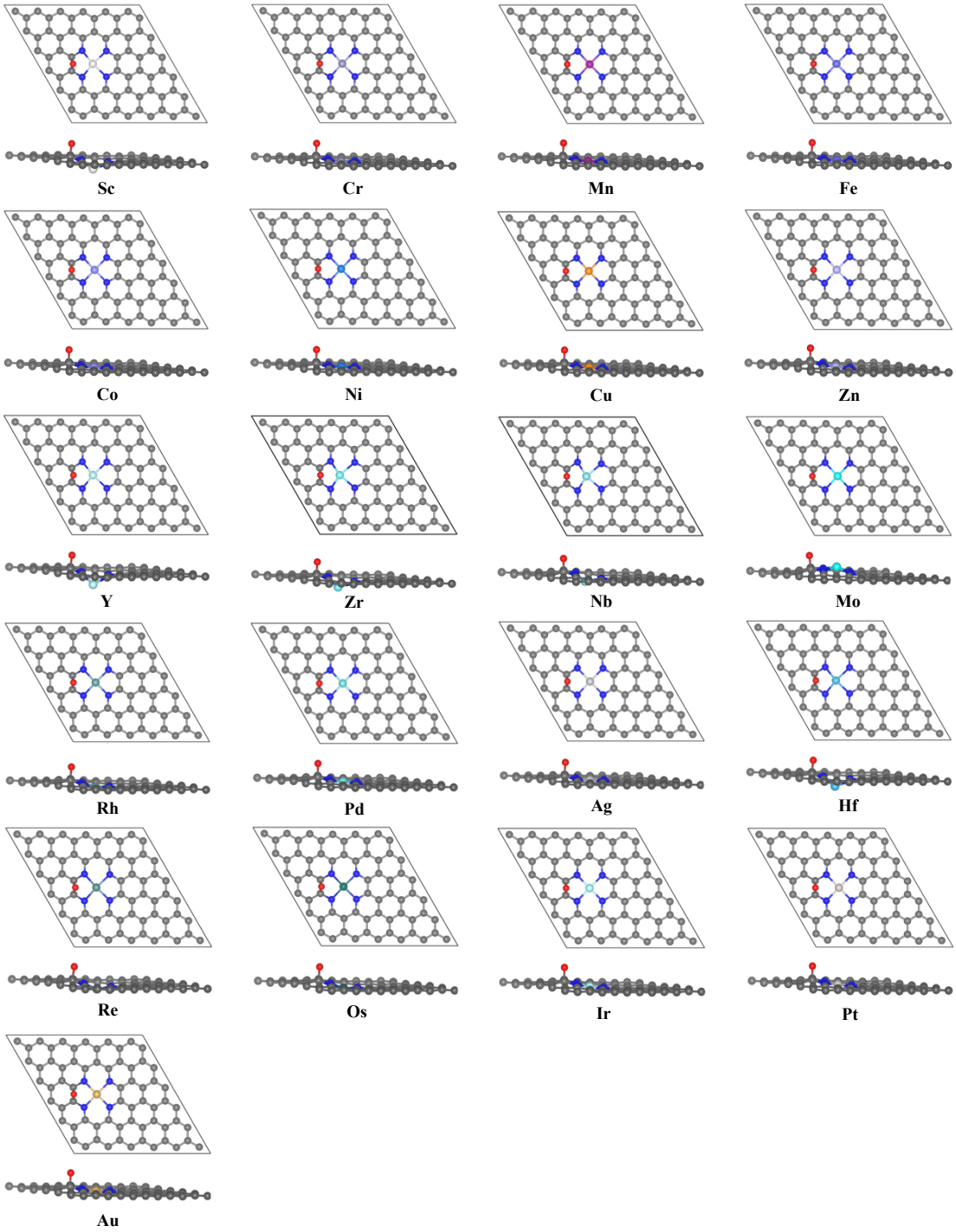

Fig. S4. Top and side views of O atom absorbed at **site-3** on various TMN_4@graphenes.

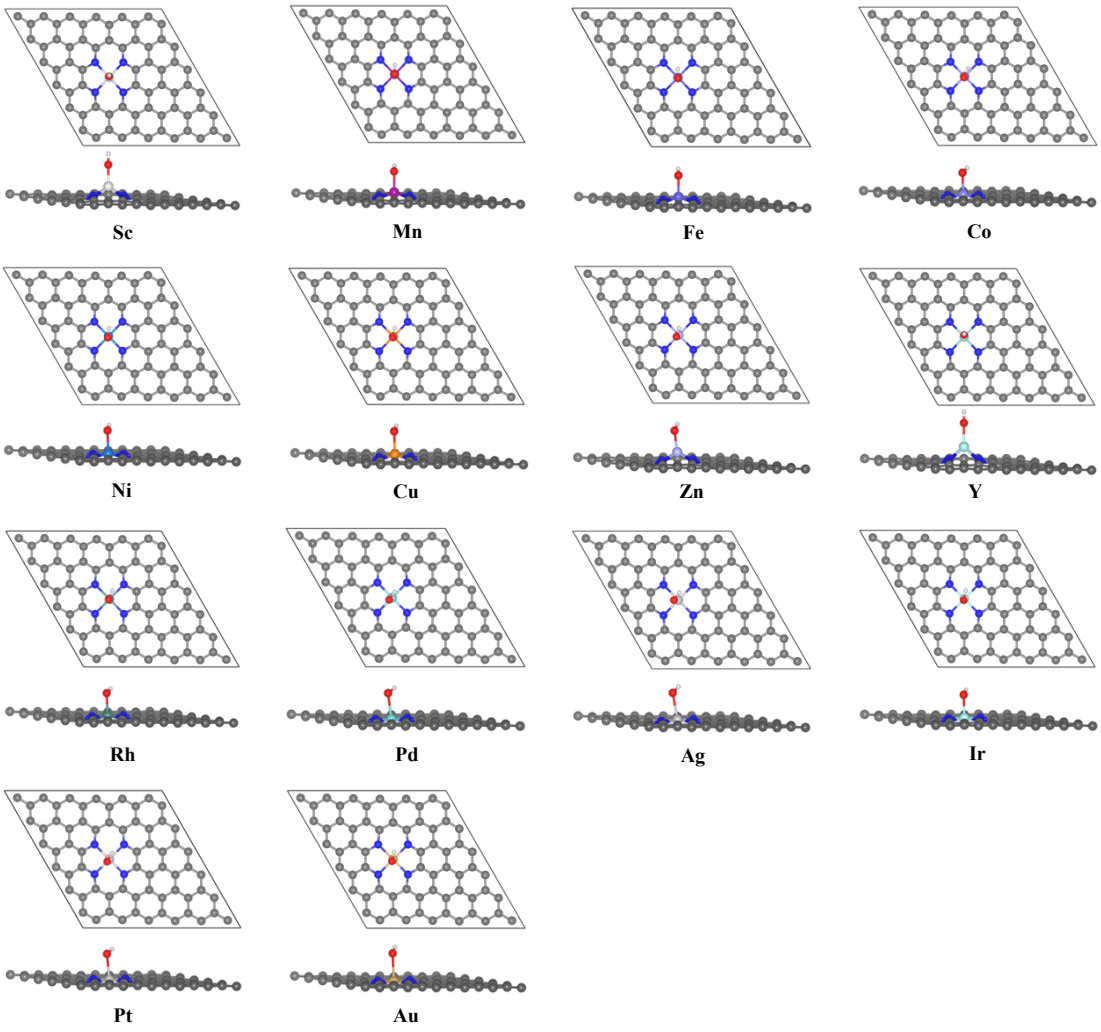

Fig. S5. Top and side views of OH absorbed at **site-1** on various TMN_4@graphenes.

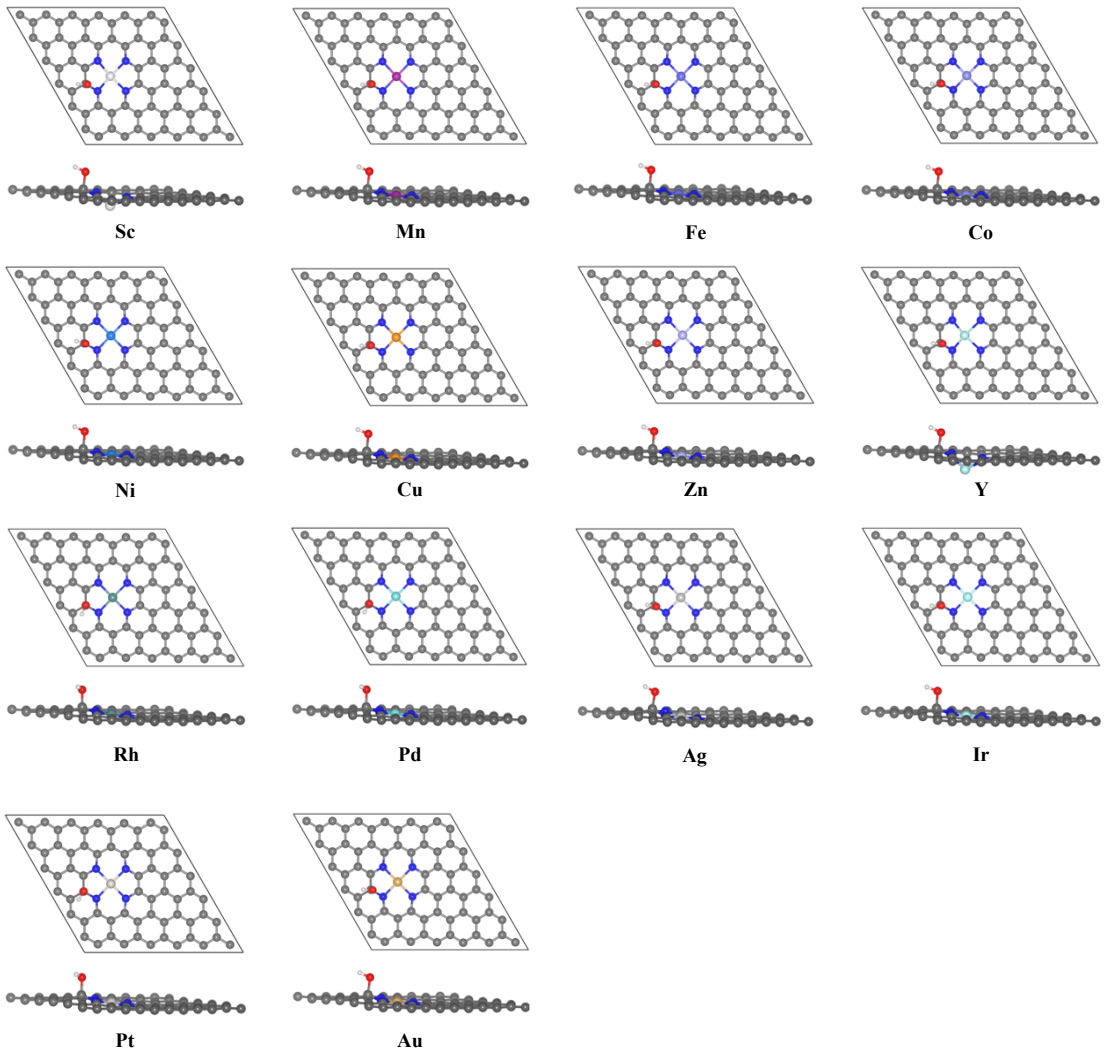

Fig. S6. Top and side views of OH absorbed at **site-2** on various TMN_4@graphenes.

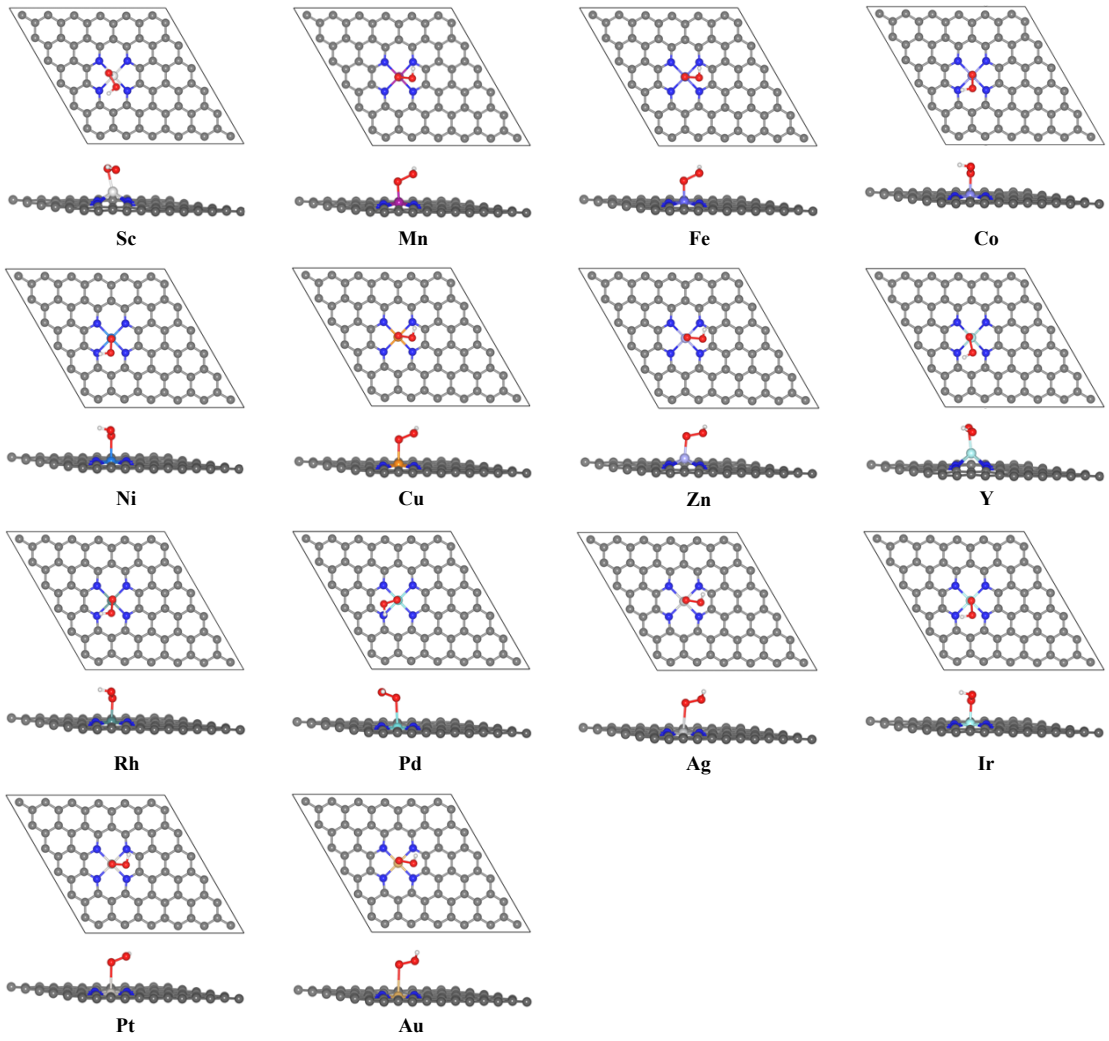

Fig. S7. Top and side views of OOH absorbed on various TMN_4@graphenes.

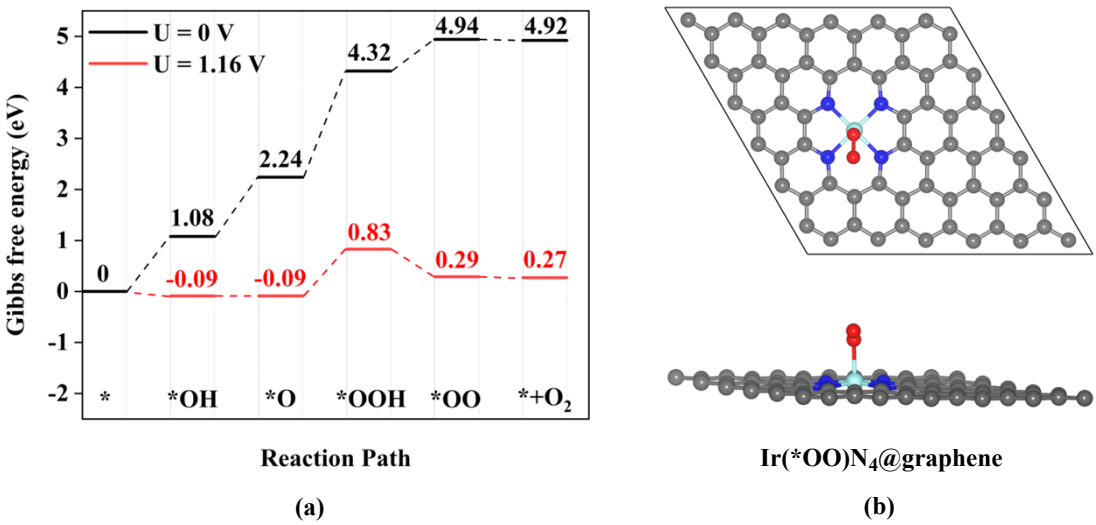

Fig. S8. (a) Gibbs free energy changes of complete electrolysis water reaction at 0 V and 1.16 V on IrN_4@graphene. (b) Top and side views of Ir(*OO)N_4@graphene intermediates.

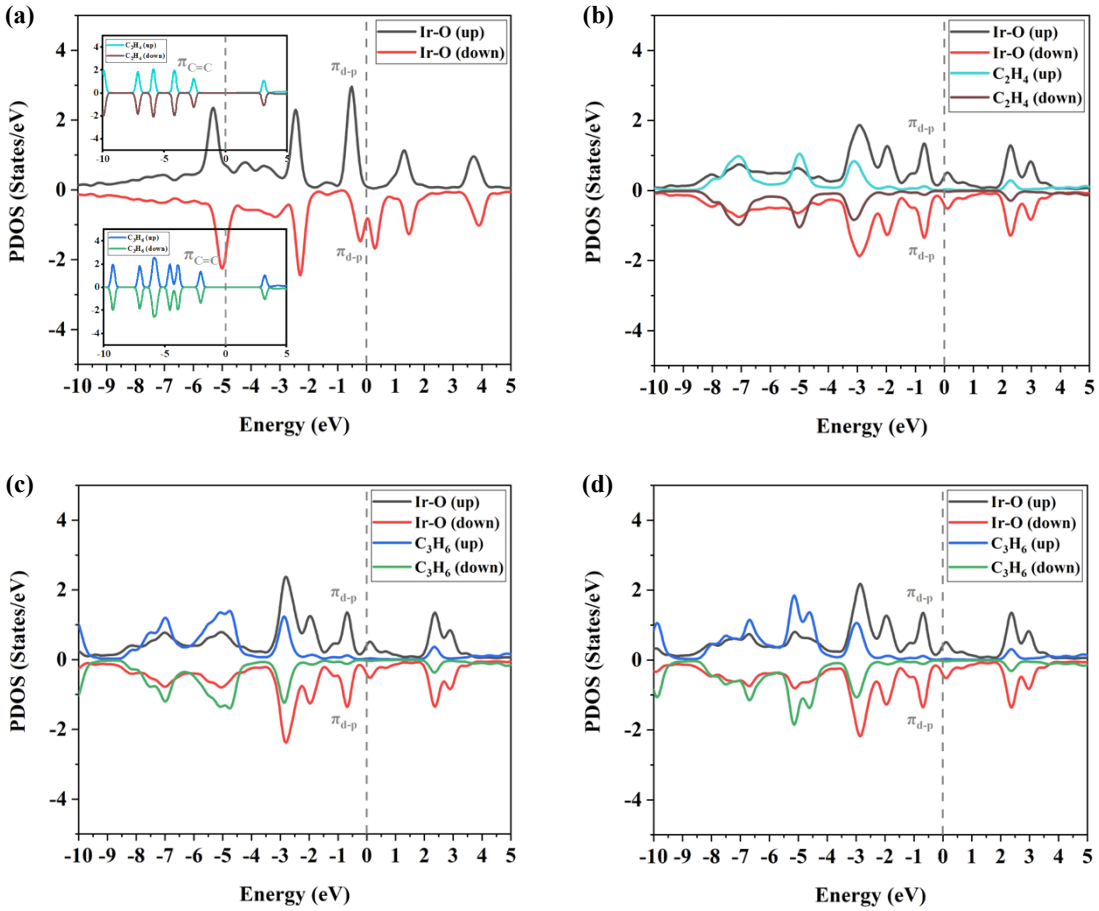

Fig. S9. The PDOS of Ir-O bond, ethylene, and propylene before (a) and after (b, c, and d) co-adsorption of ethylene and propylene on the Ir(*O)N_4@graphene. The PDOS of (a) the Ir(*O)N_4@graphene, and free ethylene and propylene molecules are also inserted in. The corresponding PDOS in (b) *O-1-C_2H_4 mode, (c) *O-1-C_3H_6 mode-A, and (d) *O-1-C_3H_6 mode-B.

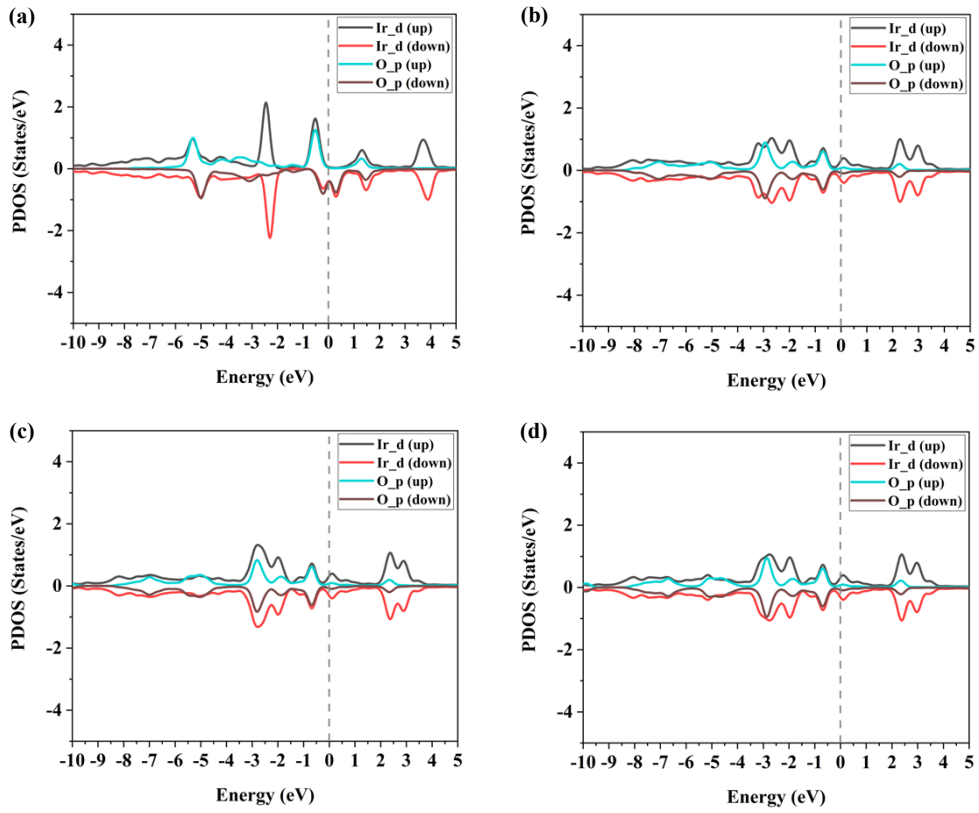

Fig. S10. The PDOS of d-orbital of Ir and p-orbital of O before (a) and after (b, c, and d) co-adsorption of ethylene and propylene on Ir(*O)N_4@graphene. The PDOS of (a) the Ir(*O)N_4@graphene intermediate, and the corresponding PDOS in (b) *O-1-C_2H_4 mode, (c) *O-1-C_3H_6 mode-A, and (d) *O-1-C_3H_6 mode-B.