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Supporting Information for

Electro-epoxidation of ethylene and propylene via atomic active oxygen from

water electrolysis on IrN₄ 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 TMN₄@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
Со	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
Мо	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	Со
$\Delta G_{EO}\left(eV\right)$	-0.24	3.53	3.64	1.61	0.35	0.21	-0.85
$\Delta G_{PO}\left(eV\right)$	-0.33	3.45	3.56	1.52	0.27	0.13	-0.94
metal type	Ni	Cu	Zn	Y	Zr	Nb	Mo
$\Delta G_{\rm EO}\left({\rm eV} ight)$	-1.49	-1.45	-1.42	-0.46	1.69	3.37	3.98
$\Delta G_{PO} \left(eV \right)$	-1.57	-1.53	-1.51	-0.54	1.60	3.28	3.90
metal type	Ru	Rh	Pd	Ag	Hf	Та	W
metal type ΔG _{EO} (eV)	Ru 1.08	Rh -1.09	Pd -1.41	Ag -1.13	Hf 1.68	Ta 4.47	W 4.35
metal type ΔG _{EO} (eV) ΔG _{EO} (eV)	Ru 1.08 1.00	Rh -1.09 -1.17	Pd -1.41 -1.49	Ag -1.13 -1.21	Hf 1.68 1.60	Ta 4.47 4.38	W 4.35 4.27
metal type $\Delta G_{EO} (eV)$ $\Delta G_{EO} (eV)$ metal type	Ru 1.08 1.00 Re	Rh -1.09 -1.17 Os	Pd -1.41 -1.49 Ir	Ag -1.13 -1.21 Pt	Hf 1.68 1.60 Au	Ta 4.47 4.38	W 4.35 4.27
metal type $\Delta G_{EO} (eV)$ $\Delta G_{EO} (eV)$ metal type $\Delta G_{EO} (eV)$	Ru 1.08 1.00 Re 3.52	Rh -1.09 -1.17 Os 1.76	Pd -1.41 -1.49 Ir -0.64	Ag -1.13 -1.21 Pt -1.43	Hf 1.68 1.60 Au -0.99	Ta 4.47 4.38	W 4.35 4.27

represents no corresponding configurations obtained during the optimization. site-1 site-2 metal site-3 0 \mathbf{Sc} 1.79 — 0 ____ Mn 1.47 0 _ Fe 1.34 Co 0 1.11 ____ 0 Ni 0.32 ____ Cu 0 0.27 ____ Zn 0 1.27 ____

1.50

0.89

0

0

0.73

0

0

0

0

0.05

0.33

0

0.09

0.002

Y

Rh

Pd

Ag

Ir

Pt

Au

Table S3. Free energy difference (ΔG , eV) of OH adsorbed at difference sites for 14 TMN₄@graphenes, the "0 eV" represents the most stable OH adsorption site, and "-"



Fig. S1. Top and side views of various TMN₄@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 TMN₄@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-C₂H₄ mode, (c) *O-1-C₃H₆ mode-A, and (d) *O-1-C₃H₆ 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-C₂H₄ mode, (c) *O-1-C₃H₆ mode-A, and (d) *O-1-C₃H₆ mode-B.