

## Supporting Information

### Transition-metal single atoms in nitrogen-doped graphene as efficient active centers for water splitting: A theoretical study

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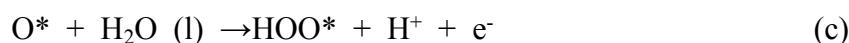
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#### 1. The details for the derivation of Gibbs reaction free energy ( $\Delta G$ ) for each reaction step

The OER is considered to proceed along the  $4e^-$  processes, as below:



where \* stands for an adsorption site on catalysts. l and g refer to liquid and gas phases, respectively. Under electrode potential  $U = 0$  V, the  $\Delta G$  for each step can be calculated by:

$$\begin{aligned} \text{a) } \Delta G_a &= G(HO^*) + G(H^+ + e^-) - G(H_2O) - G(*) \\ &= G(HO^*) + 1/2G(H_2) - G(H_2O) - G(*) \\ &= (E_{HO^*} + ZPE_{HO^*} - TS_{HO^*}) + 1/2(E_{H2} + ZPE_{H2} - TS_{H2}) - (E_{H2O} + ZPE_{H2O} - TS_{H2O}) - E^* \end{aligned}$$

$$\begin{aligned} \text{b) } \Delta G_b &= G(O^*) + G(H^+ + e^-) - G(HO^*) \\ &= G(O^*) + 1/2G(H_2) - G(HO^*) \\ &= (E_{O^*} + ZPE_{O^*} - TS_{O^*}) + 1/2(E_{H2} + ZPE_{H2} - TS_{H2}) - (E_{HO^*} + ZPE_{HO^*} - TS_{HO^*}) \end{aligned}$$

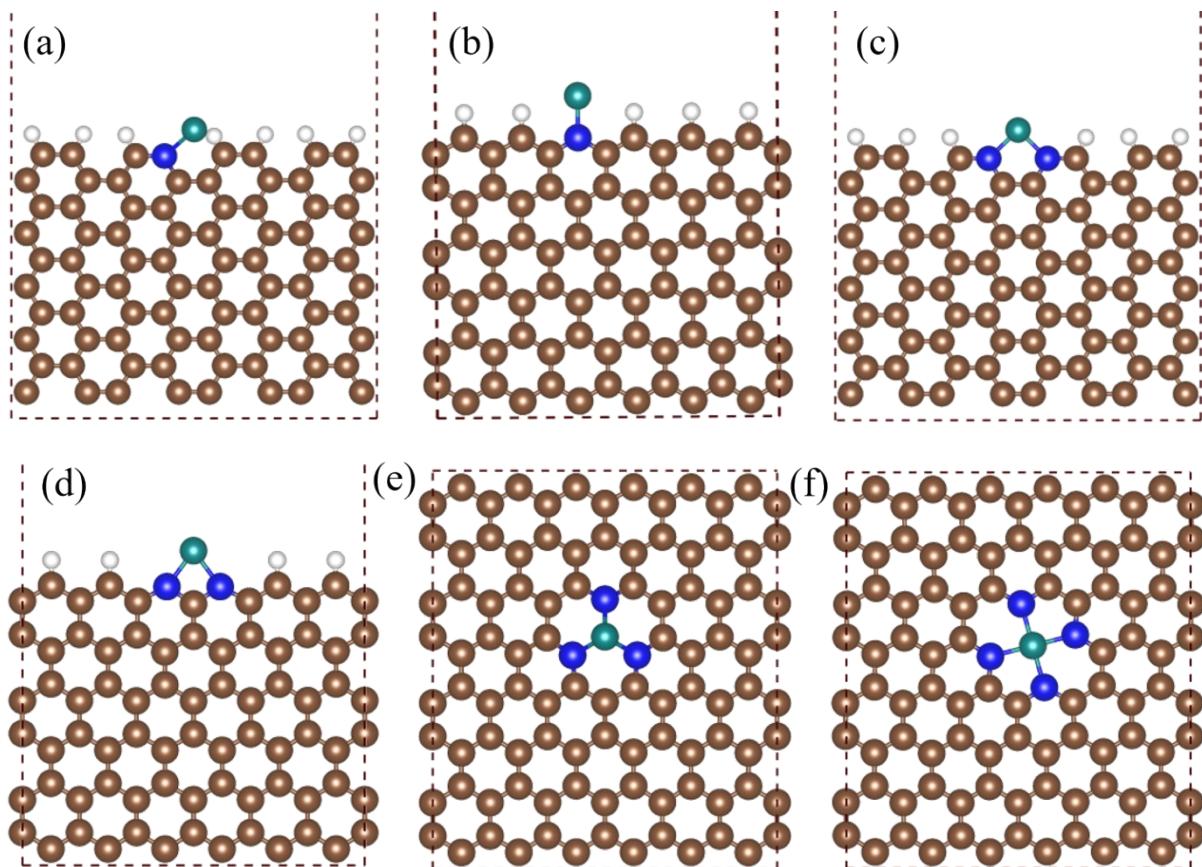
$$\begin{aligned} \text{c) } \Delta G_c &= G(HOO^*) + G(H^+ + e^-) - G(O^*) - G(H_2O) \\ &= G(HOO^*) + 1/2G(H_2) - G(O^*) - G(H_2O) \end{aligned}$$

$$\begin{aligned}
&= (E_{OOH^*} + ZPE_{OOH^*} - TS_{OOH^*}) + 1/2 (E_{H_2} + ZPE_{H_2} - TS_{H_2}) - (E_{O^*} + ZPE_{O^*} - TS_{O^*}) - \\
&(E_{H_2O} + ZPE_{H_2O} - TS_{H_2O})
\end{aligned}$$

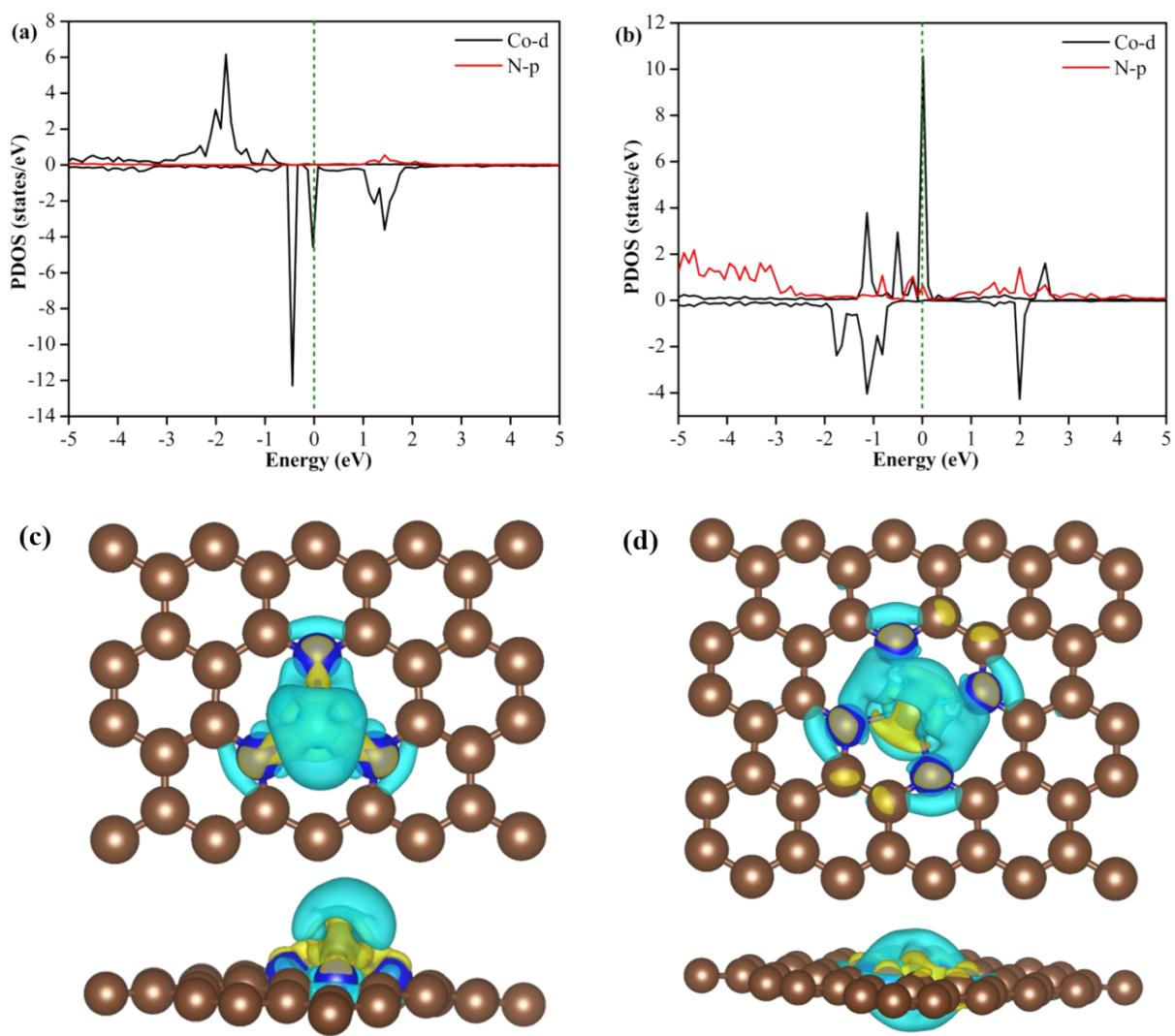
d)  $\Delta G_d = G(O_2) + G(H^+ + e^-) - G(OOH^*)$

$$\begin{aligned}
&= \{4.92 + 2G(H_2O) - 2G(H_2)\} + 1/2G(H_2) - G(HOO^*) \\
&= \{4.92 + 2(E_{H_2O} + ZPE_{H_2O} - TS_{H_2O}) - 2(E_{H_2} + ZPE_{H_2} - TS_{H_2})\} + 1/2 (E_{H_2} + ZPE_{H_2} - \\
&TS_{H_2}) - (E_{HOO^*} + ZPE_{HOO^*} - TS_{HOO^*}) \\
&= 4.92 + 2(E_{H_2O} + ZPE_{H_2O} - TS_{H_2O}) - 3/2(E_{H_2} + ZPE_{H_2} - TS_{H_2}) - (E_{HOO^*} + ZPE_{HOO^*} - \\
&TS_{HOO^*})
\end{aligned}$$

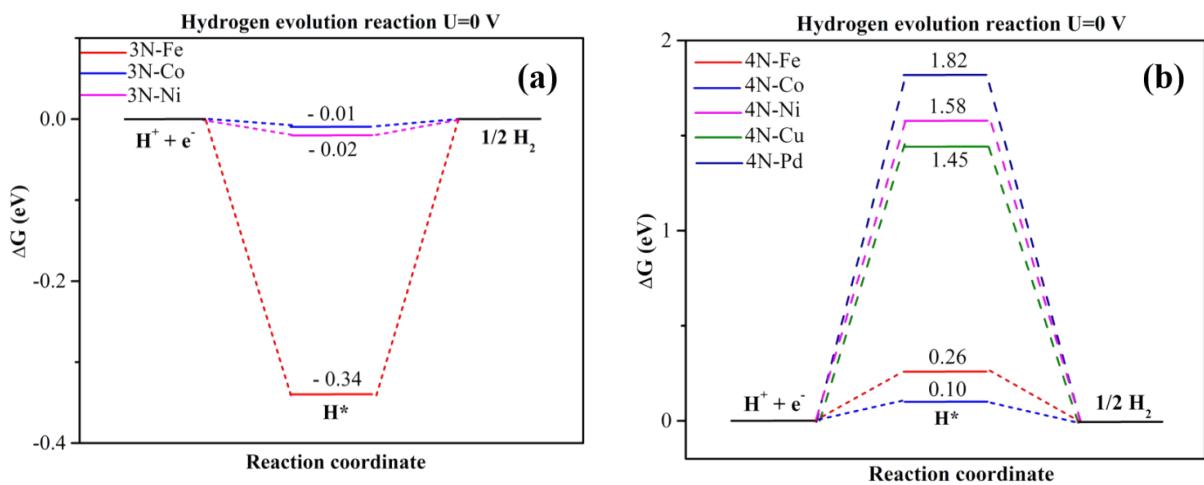
## 2. The Figures in the supporting information (Fig. S1 ~ Fig. S4)



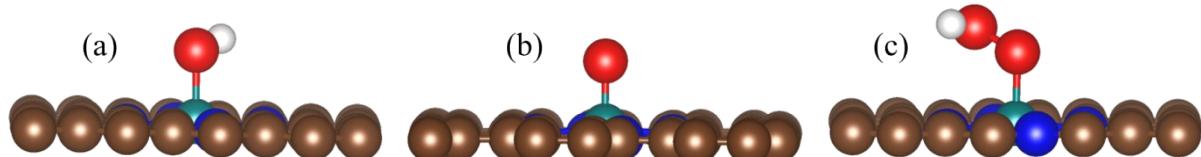
**Fig. S1** The optimized configurations of (a) 1N-AC-Co, (b) 1N-ZZ-Co, (c) 2N-AC-Co, (d) 2N-ZZ-Co, (e) 3N-Co, and (f) 4N-Co. The white, brown, blue, red, and dark cyan balls represent the H, C, N, O, and Co atoms, respectively.



**Fig. S2** Calculated PDOS for the d orbital of Co and p orbital of N atoms for the (a) 3N-Co and (b) 4N-Co, include their corresponding top view of optimized configurations. The Fermi level is set at the zero of energy (dashed line in figures). The top and side view of charge density difference for the (c) 3N-Co, and (d) 4N-Co. The brown, blue, and dark cyan balls represent the C, N, and Co atoms, respectively. The yellow areas mean that the accumulation of electrons and the blue region exhibits the depletion of electrons (the isosurface value is  $\pm 0.002 \text{ e/ A}^3$ ).



**Fig. S3** The calculated free energy diagram for (a) 3N-TM, and (b) 4N-TM systems for HER at a potential  $U = 0$  relative to the ideal catalyst.



**Fig. S4** The optimized configurations of (a) HO\* adsorbed on the 4N-Co, (b) O\* adsorbed on the 4N-Co, and (c) HOO\* adsorbed on the 4N-Co. The white, brown, blue, red, and dark cyan balls represent the H, C, N, O, and Co atoms, respectively.

### 3. The Tables in the supporting information (Table S1 ~ Table S6)

**Table S1** Vibrational frequencies of the intermediates adsorbed on 3N-Co and 4N-Co catalysts.

System	Vibration Frequencies (cm <sup>-1</sup> )
H*-3N-Co	1763, 413, 407
HO*-4N-Co	3693, 899, 456, 160, 142
O*-4N-Co	609, 174, 168
HOO*-4N-Co	3541, 1226, 905, 462, 326

**Table S2** The zero-point energy (ZPE) and entropic corrections (TS) in determining the free energy of reactants, intermediates, and products adsorbed on catalysts at 298K. For the adsorbates, the ZPE value is not sensitive to the metal and coordination since they have the close value.

Species	ZPE(eV)	TS(eV)
H <sub>2</sub> O	0.56	0.67
H <sub>2</sub>	0.27	0.41
H*	0.16	0
O*	0.05	0
HO*	0.34	0
HOO*	0.44	0

**Table S3** Binding energies (eV) of TM atoms adsorbed on different coordinated number of xN-TM catalysts.

Metal	1N-AC	1N-ZZ	2N-AC	2N-ZZ	3N	4N
Fe	-1.85	-1.73	-3.08	-2.94	-4.79	-7.57
Co	-2.15	-2.07	-3.44	-3.16	-5.17	-7.99
Ni	-2.62	-2.47	-3.88	-3.41	-4.87	-8.14
Cu	-1.39	-1.71	-2.87	-2.55	-3.39	-5.50
Pd	-1.46	-1.72	-2.49	-2.22	-2.76	-6.23

**Table S4** Bond lengths (*d*) for the optimized xN-TM geometries. *d*<sub>N-C1</sub> and *d*<sub>N-C2</sub> are the bond distances among N and their two C nearest neighbors, *d*<sub>TM-N</sub> is the distance between TM atom

and its nearest N atom. Q refers to charges transfer from TM atoms to substrate obtained by Bader charge analysis; the positive value indicates that the charge is transferred from TM atoms to the substrates.

System	$d_{N-C1}$ (Å)	$d_{N-C2}$ (Å)	$d_{TM-N}$ (Å)	Q (e)
4N-Pd	1.37	1.37	1.95	0.72
4N-Cu	1.37	1.37	1.91	0.93
4N-Ni	1.38	1.38	1.87	0.84
4N-Co	1.39	1.38	1.87	0.90
4N-Fe	1.39	1.38	1.89	1.10
3N-Pd	1.36	1.36	2.11	0.49
3N-Cu	1.36	1.36	1.91	0.68
3N-Ni	1.36	1.36	1.84	0.78
3N-Co	1.37	1.37	1.84	0.82
3N-Fe	1.37	1.37	1.88	0.98
2N-zigzag-Pd	1.36	1.39	2.16	0.38
2N-zigzag-Cu	1.37	1.39	2.01	0.57
2N-zigzag-Ni	1.36	1.40	1.95	0.57
2N-zigzag-Co	1.37	1.41	1.93	0.66
2N-zigzag-Fe	1.37	1.40	1.98	0.75
2N-armchair-Pd	1.37	1.33	2.13	0.36
2N-armchair-	1.38	1.32	1.93	0.59
Cu				
2N-armchair-Ni	1.34	1.38	1.90	0.55
2N-armchair-	1.34	1.38	1.91	0.62
Co				
2N-armchair-Fe	1.34	1.38	1.96	0.76
1N-zigzag-Pd	1.38	1.38	2.04	0.13
1N-zigzag-Ni	1.40	1.40	1.80	0.27
1N-zigzag-Fe	1.40	1.39	1.91	0.46

1N-zigzag-Cu	1.38	1.38	1.87	0.41
1N-zigzag-Co	1.39	1.39	1.82	0.46
1N-armchair-Pd	1.34	1.38	2.08	0.16
1N-armchair-Ni	1.34	1.38	1.90	0.47
1N-armchair-Fe	1.34	1.39	1.95	0.69
1N-armchair-	1.34	1.38	1.91	0.36
Cu				
1N-armchair-	1.34	1.38	1.91	0.57
Co				

**Table S5** Computed adsorption free energies of oxygenated intermediates ( $\Delta G_{HO^*}$ ,  $\Delta G_{O^*}$ ,  $\Delta G_{HOO^*}$ ) and hydrogen ( $\Delta G_{H^*}$ ) as well as overpotentials for OER ( $\eta^{OER}$ ) on stable SACs catalysts. The unit for  $\Delta G$  is eV, while for  $\eta$  is V.

System	$\Delta G_{HO^*}$	$\Delta G_{O^*}$	$\Delta G_{HOO^*}$	$\Delta G_{H^*}$	$\eta^{OER}$	$\varepsilon_d$
4N-Pd	2.39	4.58	5.31	1.82	1.16	-2.96
4N-Cu	1.83	3.83	4.84	1.45	0.77	-2.90
4N-Ni	2.04	4.28	5.09	1.58	1.01	-2.27
4N-Co	1.04	2.52	4.14	0.09	0.38	-1.37
4N-Fe	0.66	1.26	3.74	0.26	1.25	-1.28
3N-Ni	-0.21	0.93	3.15	-0.02	0.98	-3.59
3N-Co	-0.60	0.23	2.43	-0.01	1.26	-1.93
3N-Fe	-0.65	-0.55	0.63	-0.34	3.06	-1.18

**Table S6** For comparison, the calculated hydrogen adsorption free energies ( $\Delta G_{H^*}$ ) and overpotentials for OER ( $\eta^{OER}$ ) on the metal centered graphene and nitrogen-coordinated graphene are listed. The unit for  $\Delta G$  is eV, while for  $\eta$  is V.

Composites	Methods	$\Delta G_{H^*}$	$\eta^{OER}$	Reference
Fe-pyridine-N <sub>4</sub>	VASP/PBE	-0.25	1.95	1
Co-pyridine-N <sub>4</sub>		0.10	0.37	

Ni-pyridine-N <sub>4</sub>	0.22	0.33	
Pd-pyridine-N <sub>4</sub>	0.91	1.31	
CoN <sub>3</sub>	MS/DMol <sup>3</sup>	-	1.33
CoN <sub>4</sub>		-	0.69
Fe@3		-	1.41
Fe@4		-	1.83
Co@3		-	1.35
Co@4		-	0.93
Ni@3	VASP/PBE	0.38	0.87
Ni@4		-	0.40
Cu@3		-	0.70
Cu@4			2.68
Pd@3		-	0.59
Pd@4		-	0.41
3N-Fe		-0.34	3.06
3N-Co		-0.01	1.26
3N-Ni		-0.02	0.98
4N-Fe	VASP/PBE	0.26	1.25
4N-Co		0.10	0.38
4N-Ni		1.58	1.01
4N-Cu		1.45	0.77
4N-Pd		1.82	1.16

- Ref: 1. H. X. Xu, D. J. Cheng, D. P. Cao and X. C. Zeng, *Nat.Catal.*, 2018, **1**, 339–348.  
 2. X. L. Zhang, Z. X. Yang, Z. S. Lu and W. C. Wang, *Carbon.*, 2018, **130**, 112-119.  
 3. G. P. Gao, S. Bottle and A. J. Du, *Catal. Sci. Technol.*, 2018, **8**, 996-1001.