Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

Mechanism of Oxygen Reduction Reaction Catalyzed by Fe(Co)−N_x/C

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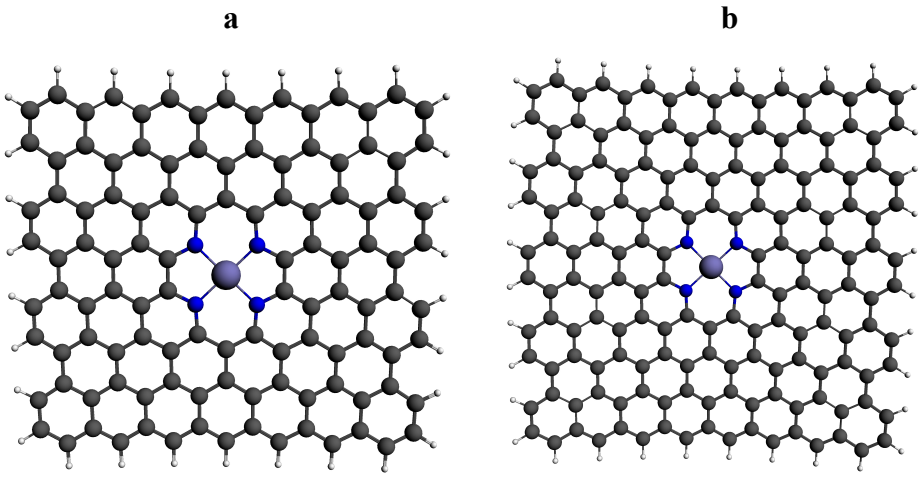

Supplementary Figure S1. Optimized structures of different size for Fe−N_4 sites in graphene sheet. (a) 2.2 nm and (b) 2.7 nm.

Supplementary Table S1. Calculated electronic energies with different multiplicity.

Structure	Multiplicity	Electronic energy (eV)
Co−N_1C_3	1	−512.78373
	3	−512.68619
	5	−512.43110
Fe−N_1C_3	2	−513.00721
	4	−513.15558
	6	−513.00221
Co−N_2C_2 (2, 3)	2	−513.60608
	4	−513.45928
	6	−513.06279
Co−N_2C_2 (3, 4)	2	−513.32971
Co−N_2C_2 (2, 4)	2	−513.17696
Fe−N_2C_2	1	−513.89284
	3	−513.92486
	5	−513.93226
Co−N_3C_1	1	−514.09329
	3	−514.07548
	5	−513.75070
Fe−N_3C_1	2	−514.56304
	4	−514.47208
	6	−514.25894
Co−N_4	2	−514.49698
	4	−514.52353
	6	−513.01473
Fe−N_4	1	−515.07790
	3	−515.13058
	5	−515.10776

Supplementary Table S2. Calculated reaction energy changes

System	Structure	ΔE (eV)
Internal sites	Co−N_1C_3	−3.10
	Fe−N_1C_3	−2.69
	Co−N_2C_2	−4.62
	Fe−N_2C_2	−3.74
	Co−N_3C_1	−3.70
	Fe−N_3C_1	−2.96
	Co−N_4	−3.71
	Fe−N_4	−3.11
Adge sites (zigzag edge)	Co−N_2	−1.48
	Fe−N_2	−0.97
Adge sites (armchair edge)	Co−N_2	−1.75
	Fe−N_2	−1.06

Supplementary Table S3. Calculated key bond lengths, R (Å), for all the steps in the O_2 reduction catalyzed by Co−N_1C_3

State	$R_{Co(1)–N(2)}$	$R_{Co(1)–C(3)}$	$R_{Co(1)–C(4)}$	$R_{Co(1)–C(5)}$	$R_{Co(1)–O(6)}$	$R_{O(6)–O(7)}$
A_0	1.990	1.930	1.918	1.935		1.246
A_1	2.061	1.977	1.921	1.975	1.940	1.341
A_2	2.069	2.001	1.921	1.958	1.893	1.494
A_3	2.061	1.897	1.910	2.103	1.936	2.793
A_4	2.055	1.985	1.934	1.946	1.831	
A_5	2.003	1.934	1.927	1.947	2.386	

Supplementary Table S4. Calculated key bond lengths, R (Å), for all the steps in the O_2 reduction catalyzed by Co−N_2C_2

State	$R_{Co(1)–N(2)}$	$R_{Co(1)–N(3)}$	$R_{Co(1)–C(4)}$	$R_{Co(1)–C(5)}$	$R_{Co(1)–O(6)}$	$R_{O(6)–O(7)}$
A_0	1.979	1.979	1.870	1.870		1.246
A_1	2.001	2.002	1.896	1.897	1.866	1.295
A_2	2.035	2.037	1.905	1.901	1.865	1.472
A_3	2.116	2.125	1.914	2.006	1.875	2.431
A_4	2.043	2.041	1.908	1.907	1.865	
A_5	1.992	1.992	1.888	1.889	2.337	

Supplementary Table S5. Calculated key bond lengths, R (Å), for all the steps in the O_2 reduction catalyzed by Fe−N_3C_1

State	$R_{Fe(1)–N(2)}$	$R_{Fe(1)–N(3)}$	$R_{Fe(1)–N(4)}$	$R_{Fe(1)–C(5)}$	$R_{Fe(1)–O(6)}$	$R_{O(6)–O(7)}$
C_0	1.925	1.974	1.953	1.889		1.246
C_1	2.023	2.047	2.021	1.912	1.848	1.406
C_2	1.986	2.031	1.962	1.898	1.838	1.502
C_3	2.015	2.001	1.965	1.919	1.649	2.898
C_4	2.002	2.022	1.964	1.902	1.837	
C_5	1.966	1.985	1.938	1.900	2.407	

Supplementary Table S6. Calculated key bond lengths, R (Å), for all the steps in the O_2 reduction catalyzed by Fe−N_4

State	$R_{Fe(1)–N(2)}$	$R_{Fe(1)–N(3)}$	$R_{Fe(1)–N(4)}$	$R_{Fe(1)–N(5)}$	$R_{Fe(1)–O(6)}$	$R_{O(6)–O(7)}$
D_0	1.934	1.935	1.923	1.932		1.246
D_1	1.935	1.935	1.942	1.943	1.897	1.314
D_2	1.947	1.942	1.940	1.946	1.808	1.502
D_3	1.958	1.959	1.958	1.959	1.670	
D_4	1.941	1.938	1.936	1.941	1.842	
D_5	1.927	1.928	1.938	1.938	2.471	

Supplementary Table S7. Calculated MDC−q charges, ΔQ, in the entire O_2 reduction steps for Co−N_1C_3, Co−N_2C_2, Fe−N_3C_1, Fe−N_4 and Fe−N_4'

Molecule	$\Delta Q(O_2)$	$\Delta Q(OOH)$	$\Delta Q(OH–OH/O)$	$\Delta Q(OH)$	$\Delta Q(H_2O)$
Co−N_1C_3	−0.186	−0.162	−0.209	−0.214	0.081
Co−N_2C_2	−0.206	−0.223	−0.464	−0.267	0.105
Fe−N_3C_1	−0.384	−0.251	−0.486	−0.271	0.079
Fe−N_4	−0.283	−0.279	−0.405	−0.278	0.075
Fe−N_4'	−0.268	−0.269	−0.522	−0.202	0.078

Supplementary Methods

For the above models, the size of the investigated graphene sheet is about 1.4 nm, and for all of the above models, the edge carbon atoms of the graphene are terminated by hydrogen atoms. In order to evaluate the size effect on the mechanism of ORR, we further built two larger graphene sheets which contain Fe−N_4/C sites. One is about 2.2 nm and the other is 2.7 nm.

The chemical potential (the free energy per H) for the reaction ($H^+ + e^-$) can be related to that of $1/2H_2$ in the gas phase by use of the standard hydrogen electrode.[1,2] Therefore, at standard conditions (U=0, pH=0, p=1bar, T=298K), the energy difference of a reaction $*AH \rightarrow A + H^+ + e^-$, can be calculated via the reaction $*AH \rightarrow A + 1/2H_2$. Thus, the energy change (ΔE) for each oxygen reduction step could be obtained. Furthermore, the adsorption energy (AE) for O_2 and the reaction intermediates is defined as the energy difference between the adsorption and the isolated systems. Here, the energy of the isolated system refers to the sum of the energies of the relaxed $Me-N_x/C$ and the individual adsorbate molecules. Therefore, the negative AE values indicate that the adsorbate molecule would be energetically favorable to be adducted to the surface of the $Me-N_x$ active sites in graphene sheets.

Supplementary References

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2. G. S. Karlberg, J. Rossmeisl and J. K. Nørskov, *Phys. Chem. Chem. Phys.*, 2007, **9**, 5158−5161.