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# Supporting Information

# Spin-dependent Active Centers in Fe-N-C Oxygen Reduction Catalysts Revealed by Constant-Potential Density Functional Theory

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## 1 Supplementary calculation methods

In an acidic environment, the overall 4-electron oxygen reduction reaction (ORR) producing $H_2O$ can be written as:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{(S1)}$$

The mechanism of ORR goes through the following elementary steps:

$$O_2 + * + H^+ + e^- \rightarrow OOH^* \quad \text{(S2)}$$

$$OOH^* + H^+ + e^- \rightarrow O^* + H_2O(l) \quad \text{(S3)}$$

$$O^* + H^+ + e^- \rightarrow OH^* \quad \text{(S4)}$$

$$OH^* + H^+ + e^- \rightarrow H_2O(l) + * \quad \text{(S5)}$$

The free energy change of each step after energy correction can be obtained based on the above elementary steps:

$$\Delta G = \Delta E_{ads}^{DFT} - \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} \quad \text{(S6)}$$

where $\Delta E^{DFT}$ is the DFT-determined energy change of each step, T=293.15 K is the room temperature, and ΔS is the entropy change. ZPE is the zero-point energy of OH*, O* and OOH*, which is calculated with the contribution in the free energy expression considering only vibrational entropy frequencies. In this work, to unify the standard, ZPE were calculated with the fixed substrate to obtain ZPE contribution in the free energy expression.

The adsorption energies of ORR intermediates are then calculated by:

$$\Delta G_{OOH^*} = G(OOH^*) - G(*) - \left(2G_{H_2O} - 3/2G_{H_2}\right) \quad \text{(S7)}$$

$$\Delta G_{O^*} = G(O^*) - G(*) - \left(G_{H_2O} - G_{H_2}\right) \quad \text{(S8)}$$

$$\Delta G_{OH^*} = G(OH^*) - G(*) - \left(G_{H_2O} - 1/2G_{H_2}\right) \quad \text{(S9)}$$

where $G(*)$ is the ground state energies of a clean surface, $G(OH^*)$, $G(O^*)$ and $G(OOH^*)$ represent the free energy of surface absorbed with OH*, O* and OOH*, respectively. $G_{H_2O}$ and $G_{H_2}$ are the free energies of $H_2O$ and $H_2$ molecules. All free energies mentioned are obtained by DFT-calculation with correction. Then, the overpotential $\eta$ of ORR is determined by the following equation:

$$\eta_{ORR} = max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}/e + 1.23 \quad \text{(S10)}$$

where $\Delta G_1$, $\Delta G_2$, $\Delta G_3$, $\Delta G_4$ are respectively the free energy change of each elementary reaction step of ORR shown in Reaction S2-S5.

# 2 Supplementary Tables

**Table S1** 3d orbital occupations for Fe ion in bare $FeN_4C_{10}$, $^*OOH/FeN_4C_{10}$, $^*O/FeN_4C_{10}$, and $^*OH/FeN_4C_{10}$.

| Fe spin states | Majority spin | | | | | Minority spin | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $d_{xy}$ | $d_{xz}$ | $d_{yz}$ | $d_{z^2}$ | $d_{x^2-y^2}$ | $d_{xy}$ | $d_{xz}$ | $d_{yz}$ | $d_{z^2}$ | $d_{x^2-y^2}$ |
| **bare $FeN_4C_{10}$** | | | | | | | | | | |
| HS-1 | 0.9498 | 0.9657 | 0.9696 | 0.9631 | 1.0111 | 0.9220 | 0.0591 | 0.0561 | 0.0779 | 0.1878 |
| HS-2 | 0.9602 | 0.9458 | 0.9570 | 0.9370 | 1.0533 | 0.1044 | 0.0231 | 0.0428 | 0.8345 | 0.3121 |
| HS-3 | 0.9604 | 0.9389 | 0.9597 | 0.9501 | 1.0700 | 0.0207 | 0.8695 | 0.0477 | 0.0488 | 0.3086 |
| IS-1 | 0.9500 | 0.9112 | 0.9501 | 0.9320 | 0.4343 | 0.8709 | 0.8279 | 0.0465 | 0.1108 | 0.3390 |
| IS-2 | 0.9487 | 0.9233 | 0.9445 | 0.9130 | 0.4232 | 0.9406 | 0.0263 | 0.0395 | 0.8917 | 0.3287 |
| IS-3 | 0.9499 | 0.9270 | 0.9335 | 0.9257 | 0.4213 | 0.7510 | 0.0262 | 0.8946 | 0.2434 | 0.3297 |
| LS | 0.9055 | 0.8780 | 0.5007 | 0.5258 | 0.3849 | 0.9023 | 0.8772 | 0.4295 | 0.5997 | 0.3854 |
| **$^*OOH/FeN_4C_{10}$** | | | | | | | | | | |
| HS | 0.9604 | 0.9734 | 0.9817 | 0.9977 | 1.0343 | 0.0256 | 0.1485 | 0.1645 | 0.3602 | 0.3109 |
| IS | 0.9535 | 0.9602 | 0.9688 | 0.9871 | 0.5056 | 0.9373 | 0.1402 | 0.1314 | 0.2842 | 0.3233 |
| LS | 0.9462 | 0.9087 | 0.968 | 0.6785 | 0.4034 | 0.9267 | 0.8475 | 0.1132 | 0.2773 | 0.3284 |
| **$^*O/FeN_4C_{10}$** | | | | | | | | | | |
| HS | 0.9565 | 0.9987 | 1.0010 | 0.9216 | 1.0162 | 0.0133 | 0.3000 | 0.2748 | 0.3886 | 0.2248 |
| IS | 0.9484 | 0.9811 | 0.9919 | 0.6901 | 0.4387 | 0.9410 | 0.3062 | 0.2948 | 0.4945 | 0.3344 |
| LS | 0.9448 | 0.6659 | 0.6580 | 0.5742 | 0.3809 | 0.9448 | 0.6666 | 0.6569 | 0.5742 | 0.3809 |
| **$^*OH/FeN_4C_{10}$** | | | | | | | | | | |
| HS | 0.9598 | 0.9805 | 0.9882 | 0.9989 | 1.0288 | 0.0188 | 0.1342 | 0.1583 | 0.3576 | 0.3047 |
| IS | 0.9529 | 0.966 | 0.9781 | 0.9881 | 0.5157 | 0.9375 | 0.0896 | 0.1356 | 0.2936 | 0.3108 |
| LS | 0.9452 | 0.9206 | 0.9679 | 0.6499 | 0.4019 | 0.9271 | 0.8534 | 0.1091 | 0.2659 | 0.3278 |
| **$^*O_2/FeN_4C_{10}$** | | | | | | | | | | |
| HS | 0.9608 | 1.0073 | 0.9959 | 0.9758 | 1.0142 | 0.1363 | 0.3365 | 0.1849 | 0.1688 | 0.2254 |
| IS (end-on) | 0.9537 | 0.9509 | 0.9636 | 0.9742 | 0.4978 | 0.9404 | 0.094 | 0.0689 | 0.433 | 0.342 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| IS (side-on) | 0.9538 | 0.9757 | 0.9672 | 0.9767 | 0.4961 | 0.9441 | 0.3373 | 0.0761 | 0.1548 | 0.322 |

# 3 Supplementary Figures

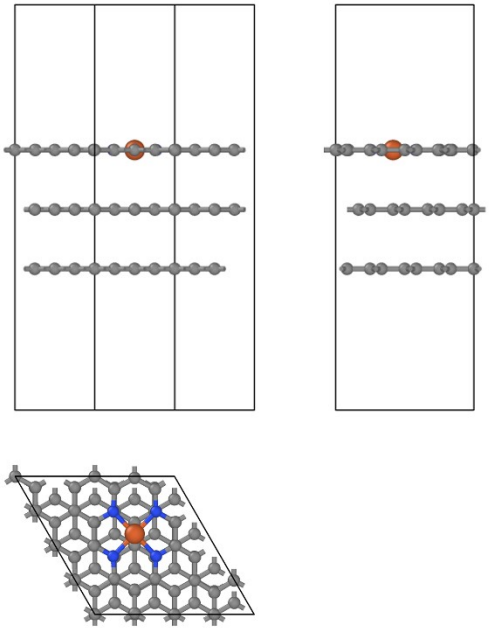

**Figure S1:** Slab model of Fe-$N_4$ site-embedded three-layer graphene in this work. Gray, blue and orange balls represent C, N, Fe atoms, respectively.

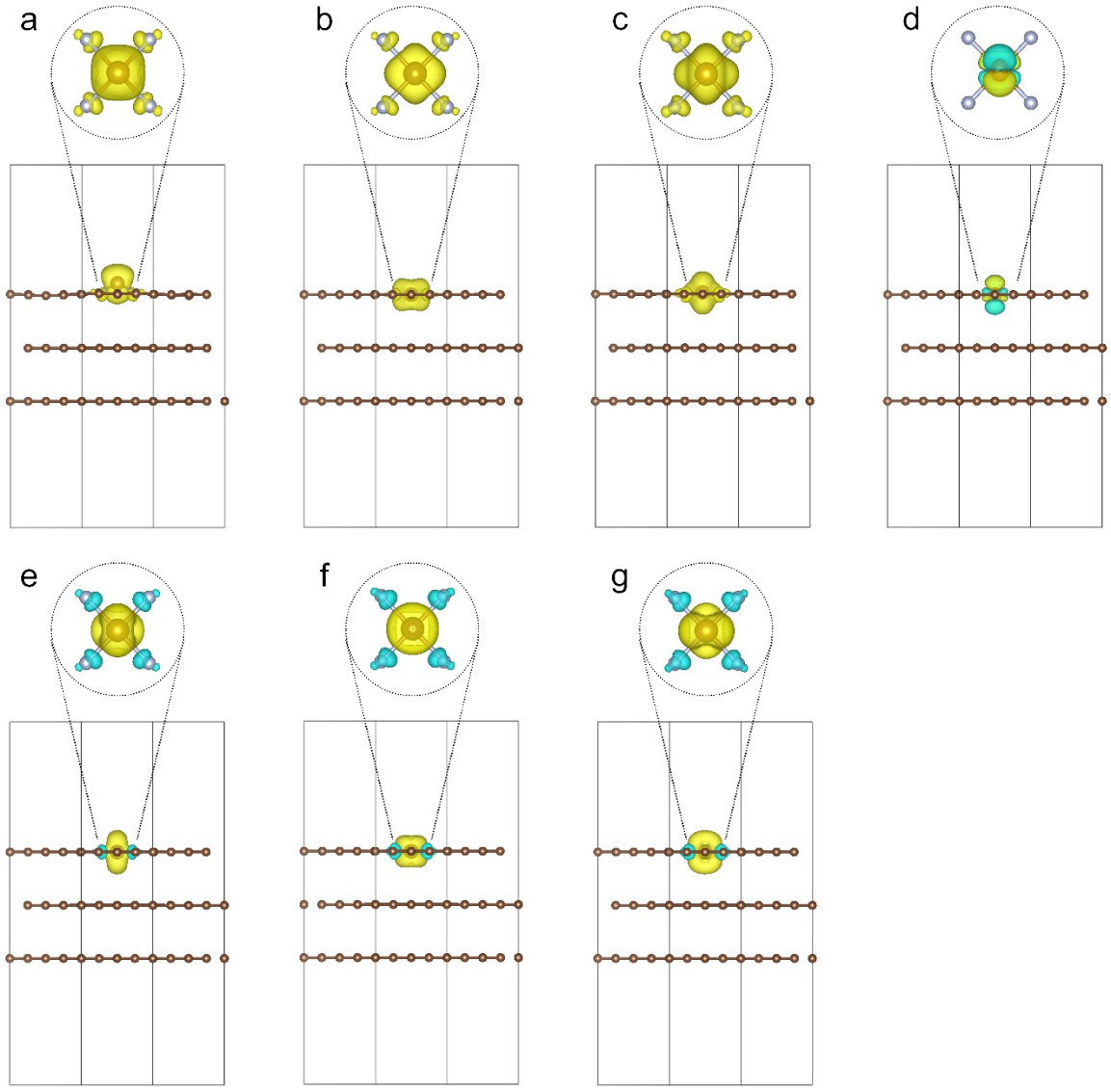


**Figure S2:** Spin density plots of bare $FeN_4C_{10}$ of various spin states (a) HS-1, (b) HS-2, (c) HS-3, (d) LS, (e) IS-1, (f) IS-2, and (g) IS-3. Yellow and blue areas represent electron spin-up and spin-down occupations, respectively.

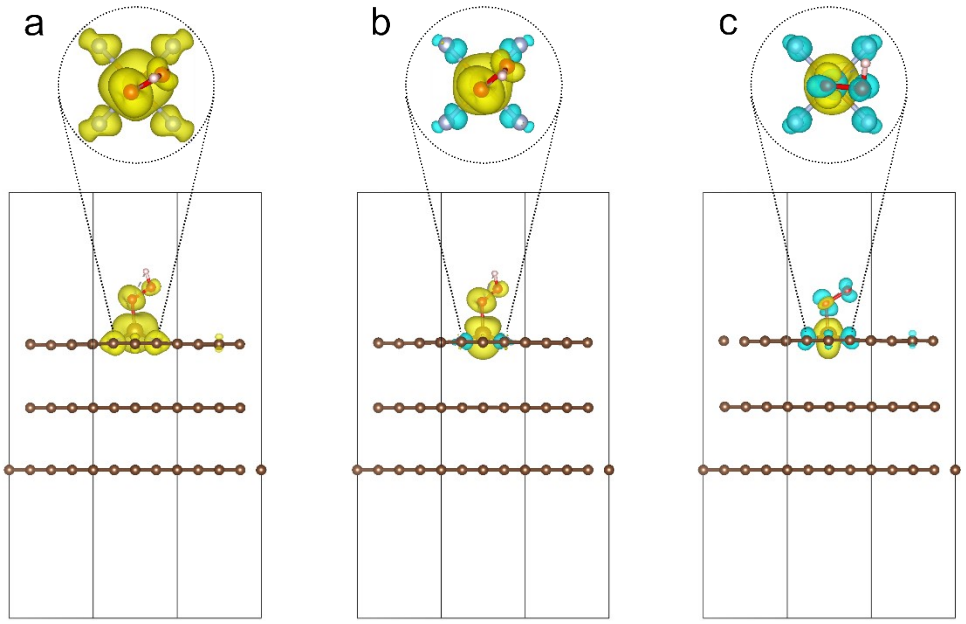


**Figure S3:** Spin density plots of $^{*}$OOH/$FeN_4C_{10}$ of various spin states (a) HS, (b) IS, and (c) LS. Yellow and blue areas represent electron spin-up and spin-down occupations, respectively.

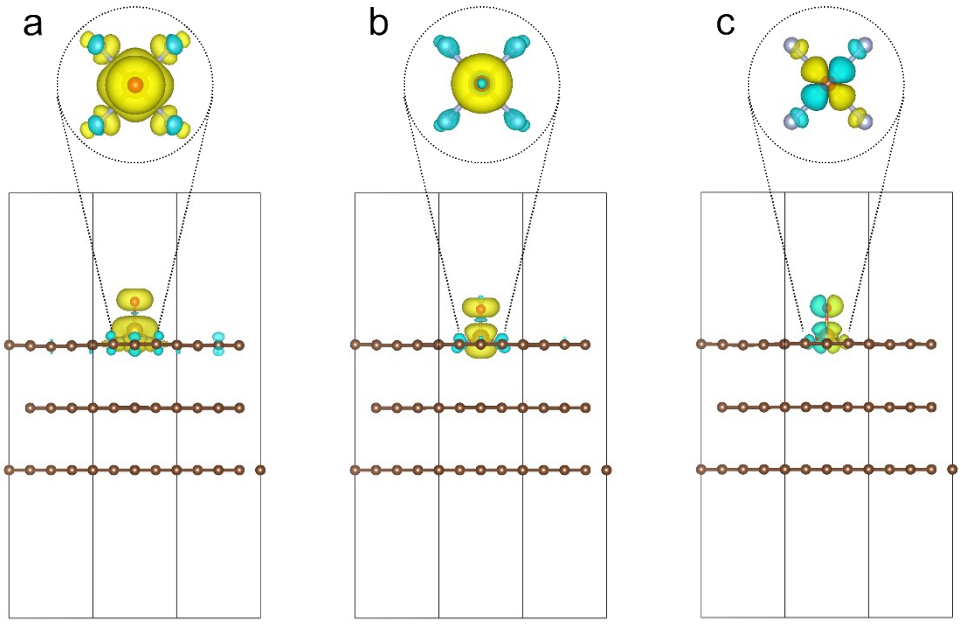


**Figure S4:** Spin density plots of $^{*}O/FeN_4C_{10}$ of each spin states (a) HS, (b) IS, and (c) LS. Yellow and blue areas represent electron spin-up and spin-down occupations, respectively.

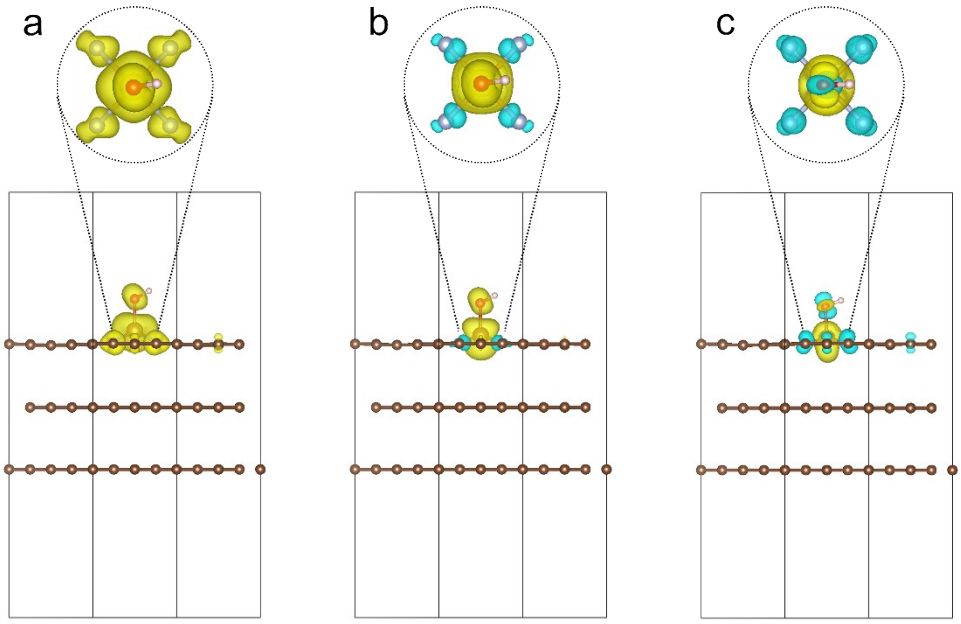


**Figure S5:** Spin density plots of $^{*}OH/FeN_4C_{10}$ of each spin states (a) HS, (b) IS, and (c) LS. Yellow and blue areas represent electron spin-up and spin-down occupations, respectively.

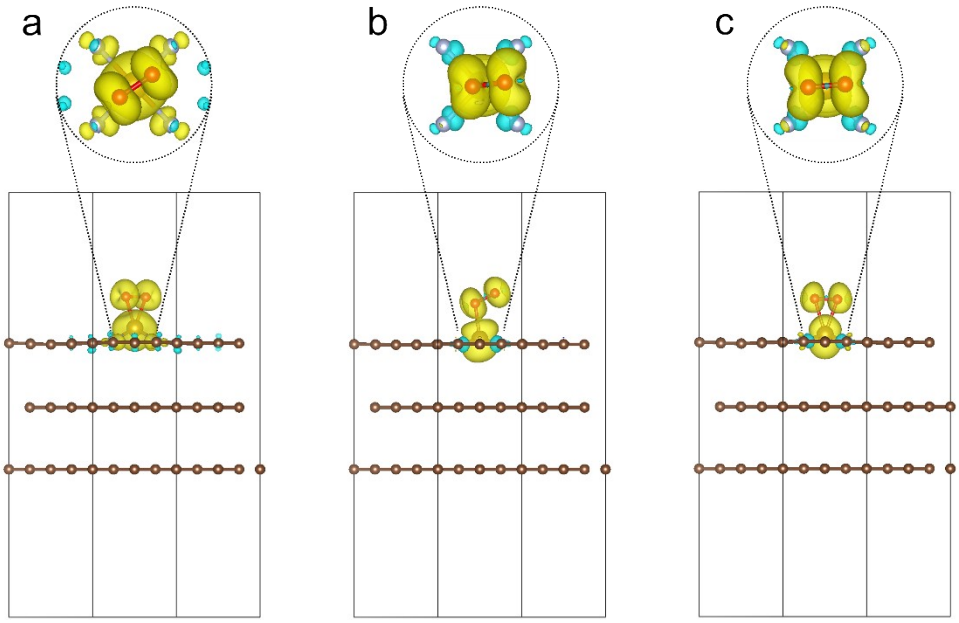


**Figure S6:** Spin density plots of $^{*}O_2/FeN_4C_{10}$ of each spin states (a) HS, (b) IS (end-on), and (c) IS (side-on). Yellow and blue areas represent electron spin-up and spin-down occupations, respectively.