Insights into the activity of single-atom Fe-N-C catalysts for oxygen reduction reaction

Kang Liu1,2, Junwei Fu1, Yiyang Lin1, Tao Luo1, Ganghai Ni1, Hongmei Li1, Zhang Lin2 & Min Liu1

1 Hunan Joint International Research Center for Carbon Dioxide Resource Utilization, School of Physics and Electronics, Central South University, Changsha 410083 Hunan, P. R. China. 2 School of Metallurgy and Environment, Central South University, Changsha 410083 Hunan, P. R. China.

Single-atom Fe-N-C catalysts has attracted widespread attentions in the oxygen reduction reaction (ORR). However, the origin of ORR activity on Fe-N-C catalysts is still unclear, which hinder the further improvement of Fe-N-C catalysts. Herein, we provide a model to understand the ORR activity of Fe-N₄ site from the spatial structure and energy level of the frontier orbitals by density functional theory calculations. Taking the regulation of divacancy defects on Fe-N₄ site ORR activity as examples, we demonstrate that the hybridization between Fe 3dz², 3dyz (3dzx) and O₂ π* orbitals is the origin of Fe-N₄ ORR activity. We found that the Fe-O bond length, the d-band center gap of spin states, the magnetic moment of Fe site and *O₂ as descriptors can accurately predict the ORR activity of Fe-N₄ site. Furthermore, these descriptors and ORR activity of Fe-N₄ site are mainly distributed in two regions with obvious difference, which greatly relate to the height of Fe 3d projected orbital in the Z direction. This work provides a new insight into the ORR activity of single-atom M-N-C catalysts.

https://doi.org/10.1038/s41467-022-29797-1
Single-atom Fe-N-C catalysts are considered a candidate to replace the platinum group metals in oxygen reduction reaction (ORR), due to its high activity, anti-toxicity, and metal atom utilization. Advanced Fe-N-C materials show comparable ORR performance to that of benchmark Pt/C. Both theoretical and experimental studies indicate that the Fe-N4 site is the active species of Fe-N-C catalysts. However, the ORR activity of Fe-N4 site on different carbon supports varies greatly, and Fe-N4 ORR activity on curved carbon supports is usually orientation-dependent. The essential of the difference and orientation-dependence of Fe-N4 ORR activity remains unclear. Therefore, understanding the ORR activity of the Fe-N4 site is crucial to further improve the ORR performance of Fe-N-C catalysts.

The intrinsic ORR activity of the Fe-N4 site relates to the electronic structure of carbon supports. Controlling the electronic structure of carbon supports alters the interaction between the supports and the Fe-N4 site, resulting in the activity change of the Fe-N4 site. However, the essential of the change in Fe-N4 ORR activity is still puzzling due to the complex factors affecting it. Some works reported that the electronic structure of carbon supports (electron-withdrawing/donating property) can affect the d-band center or d-orbital level of Fe site. While, others claimed that it regulates the charge state of Fe site. To understand the orientation-dependence and differences of ORR activity at the same Fe-N4 site on different carbon supports, we calculated the binding energy (Ebind) of single-atom Fe site (Fig. 1a). We introduced various divacancy defects around the Fe-N4 site, which include 5-8-5 (6, 8, 9), 555-777 (5a, 6a, 7b, 8a, 9a), and 5-7-7-5 defect (6I, 7I, 8I, 9I, 9I, 10I). The ORR activity on the upper (blue) and lower (red) sides of Fe-N4 configurations were investigated due to surface asymmetry (Fig. 1d). We found that the hydrogenation of O2 is a potential-determining step (PDS) at all Fe-N4 configurations. Divacancy defect can regulate the free energy difference of this step on the Fe-N4 site (Supplementary Table 1). The maximal free energy difference (ΔGmax) of ORR at the perfect FeN4 site is ~0.45 eV, which is consistent with previous studies. Among them, divacancy defects, such as 6, 5a, 6a, 6I, 7I, and 8I, can enhance the activity of the Fe-N4 site, with ΔGmax less than ~0.60 eV (Fig. 1d). For the asymmetric surfaces, the ORR activity of the Fe-N4 site showed orientation-dependence and difference, such as 6I, 7I, 8I, etc. Besides, divacancy defects can control the electron-donating capability of the carbon support, ultimately affecting the charge state and the d-band center of the Fe site (Supplementary Fig. 4). However, these factors are difficult to elucidate the orientation-dependence of the ORR activity of the Fe-N4 site on an asymmetric surface.

Factors of ORR activity at the Fe-N4 site. We investigated the ORR process of Fe-N4 configurations from energy, geometry, and electronic structure to explore the origin of Fe-N4 ORR activity. Here, we highlight the results of 6 (5-8-5), 6a (555-777), and 6I (5-7-7-5) models because they can improve the ORR activity of the Fe-N4 site with good thermodynamic stability (Supplementary Fig. 5). The free energy diagram of ORR shows that the ΔG of *O2 formation on 6, 6a, and 6I are ~0.62, ~0.65, and ~0.66 eV (Fig. 2a and Supplementary Fig. 6), respectively. Compared with the perfect FeN4 site (~0.45 eV), divacancy defects (6, 6a, and 6I) can facilitate *O2 conversion to *OOH intermediate. We found that the adsorption energy of *O2 with end-on1 and end-on2 configurations on the FeN4 site are ~0.53 and ~0.41 eV, respectively, and the adsorption energy of *O2 with side-on configuration on the FeN4 site is ~0.01 eV (Supplementary Fig. 7). This result shows that the end-on adsorption is more favorable than the side-on adsorption at the FeN4 site. Among them, the adsorption energies of *O2 on 6, 6a, and 6I are ~0.34, ~0.33, and ~0.38 eV (Fig. 2b), respectively, which are larger than that of the perfect FeN4 site (~0.53 eV). These results suggest the weak adsorption of *O2 on the Fe-N4 site is the key to enhance the ORR activity of the Fe-N4 site. Meanwhile, the O–O bond lengths on the O2@FeN4, O2@6, O2@6a, and O2@6I are 1.284, 1.297, 1.294, and 1.296 Å (Fig. 2b), respectively, which are longer than the bond length of O2 molecule (1.234 Å). Besides, the Fe–O bond lengths on the O2@FeN4, O2@6, O2@6a, and O2@6I are 1.974, 1.745, 1.724, and 1.731 Å (Fig. 2b), respectively. These results reveal that divacancy defects (6, 6a, and 6I) can enhance the interaction between *O2 and Fe site and promote the activation of *O2, thus increasing the Fe-N4 ORR activity.
We studied the electronic structure of the Fe-N4 site and O2 to understand the activation mechanism of O2. Before the adsorption of O2, the projected density of state (PDOS) of the Fe site indicates that the Fe site has spin polarization with a spin magnetic moment of 2μB. The occupied states of the Fe site near the Fermi level consist of localized 3dxz, 3dx2−y2, and 3dz2 (Supplementary Fig. 8). Compared to the PDOS of the FeN4 site, divacancy defects (6, 6a, and 6l) modified the intensity and distribution of Fe 3d states (especially 3dxz and 3dz2). For the O2 molecule, the PDOS of O2 also shows spin polarization with a spin magnetic moment of 2μB. The anti-bonding orbitals (π*) of O2 are mainly composed of the O 2 2pz orbital, and the d-band center of Fe 3d spin state. 

![Fig. 1 Modeling and performance evaluation of single-atom Fe-N4 sites.](image1)

(a) Optimized structure of a perfect FeN4 site.
(b) Divacancy defect models 6, 6a, 6l, and 6II.
(c) The binding energy of Fe site.
(d) The ORR activity of Fe-N4 sites. Blue and red represent upper and lower surface activity, respectively.

![Fig. 2 Theoretically study of the origin of Fe-N4 ORR activity.](image2)

(a) Gibbs free energy diagrams of ORR on perfect FeN4 site, 6, 6a, and 6l.
(b) Adsorption energy of *O2, O−O, and Fe−O bond length on the O2@FeN4, O2@6, O2@6a, and O2@6l.
(c) Projected density of states of Fe 3dz2, O2 2pz orbital, and d-band center of Fe 3d spin state.
(d) Maximally localized Wannier functions of Fe 3dz2, O2 2pz orbital.
(e) Charge density difference.
(f) Spin density.
Supplementary Fig. 9). The bond length, the charge state, \( \Delta G \), and \( \Delta L \) are still distributed in stages. For the LDA (CA)–Wang 91 (GGA (PW91))34, strongly constrained and well-behaved functional, the system is more stable and the structure is more realistic. The adsorption energy of \( \text{O}_2 \) on the active Fe-N4 site ranges from 0.95 to 1.02 eV, which is consistent with the result obtained by the LDA (CA)–SCAN and HSE06 functional.

**Descriptors of ORR activity at Fe-N4 sites.** As mentioned above, the adsorption energy of \( \text{O}_2 \), the bond length, the charge state, \( \Delta d \), and the magnetic moment may be related to the ORR activity of the Fe-N4 site (Supplementary Table 2). To gain accurate descriptors for the ORR activity of the Fe-N4 site, we investigated the correlation between these factors and ORR activity (Fig. 3 and Supplementary Figs. 16–18). According to the free energy diagram, the adsorption energy of \( \text{O}_2 \) may be related to ORR activity. The adsorption energy of \( \text{O}_2 \) on the Fe-N4 site ranges from -0.6 to -0.1 eV under the regulation of divacancy defects (Supplementary Fig. 16). The linear fitting results reveal that the coefficient of determination R-square between the adsorption energy of \( \text{O}_2 \) and the ORR activity of the Fe-N4 site is 0.15. No direct correlation between the adsorption energy of \( \text{O}_2 \) and ORR activity at the Fe-N4 site. From the geometric structure, the O–O bond length (L_{O–O}) is related to the activation of O2 molecules, and the Fe–O bond length (L_{Fe–O}) can reveal the strength of the interaction between \( \text{O}_2 \) and Fe-N4 site. Herein, we found that the O–O bond length is distributed between 1.264–1.298 Å by regulating divacancy defects (Supplementary Fig. 17). When the O–O bond length is larger than 1.290 Å, the free energy difference for hydrogenation of \( \text{O}_2 \) is less than -0.6 eV. The coefficient of determination R-square between the O–O bond length and Fe-N4 ORR activity is 0.81, with the relevant formula being \( \Delta G = -9.93 \text{L}_{O–O} + 12.3 \) (Supplementary Fig. 17). Besides, the length of the Fe–O bond is distributed in stages (Fig. 3a). For the active Fe-N4 site (golden circle), the average Fe–O bond length is around 1.737 Å. For the inactive Fe-N4 site (blue circle), the average Fe–O bond length is near 2.013 Å. The coefficient of determination R-square between the Fe–O bond length and Fe-N4 ORR activity is 0.95 (Fig. 3a), indicating that the Fe–O bond length can accurately describe the ORR activity of the Fe-N4 site with the relevant formula \( \Delta G = 0.75 \text{L}_{Fe–O} + 1.94 \).

From the electronic structure, the charge state of the Fe site (\( \text{Fe}^{2+} \)) can reflect the electronic transfer between Fe and \( \text{O}_2 \), which may have a potential relationship with Fe-N4 ORR activity (Supplementary Fig. 18). The Bader charge state of Fe and \( \text{O}_2 \) are -1.22 to -1.13 e and 0.24 to 0.41 e (Supplementary Fig. 18), respectively, due to the regulation of divacancy defect. The linear fitting results show that the coefficient of determination R-square between the charge state of the Fe site (\( \text{Fe}^{2+} \)) and the ORR activity of the Fe-N4 site is 0.10 (0.58), indicating that they are difficult to describe the ORR activity of Fe-N4 site (Supplementary Fig. 18). In addition, \( \Delta d \) (Fig. 3b), \( \text{M}_{\text{Fe}}, \text{M}_{\text{O2}} \) (Fig. 3c), and \( \text{M}_{\text{O2}} \) (Fig. 3d) are also characteristic symbols for the change of Fe and \( \text{O}_2 \) electronic structure. We found that \( \Delta d \), \( \text{M}_{\text{Fe}} \), and \( \text{M}_{\text{O2}} \) are also distributed in stages (Fig. 3b–d). The smaller their values, the higher the ORR activity of the Fe-N4 site. After the adsorption of \( \text{O}_2 \), the average values of \( \Delta d \), \( \text{M}_{\text{Fe}} \), and \( \text{M}_{\text{O2}} \) on the active Fe-N4 site (golden circle) are 1.755 eV, 1.190 μB, and 0.881 μB, respectively. Correspondingly, the average of \( \Delta G \) is -0.638 eV. For the inactive Fe-N4 sites (blue circle), the average of \( \Delta G \), \( \Delta d \), \( \text{M}_{\text{Fe}} \), and \( \text{M}_{\text{O2}} \) are -0.430 eV, 2.570 eV, 1.756 μB, and 1.177 μB, respectively. These fitting results show that the correlation between \( \Delta d \), \( \text{M}_{\text{Fe}} \), \( \text{M}_{\text{O2}} \), and \( \Delta G \) is nearly linear. The R-squares are 0.95, 0.94, and 0.91 (Fig. 3b–d), indicating that \( \Delta d \), \( \text{M}_{\text{Fe}} \), \( \text{M}_{\text{O2}} \) are promising ORR activity descriptors for the Fe-N4 site. The relevant formulas are \( \Delta G = 0.25 \Delta d - 1.08 \), \( \Delta G = 0.37 \text{M}_{\text{Fe}} - 1.08 \), \( \Delta G = 0.67 \text{M}_{\text{O2}} - 1.22 \), respectively.

To generalize the correlations between electronic structure and Fe-N4 ORR activity, we calculated the electronic structure of \( \text{O}_2@\text{Fe-N4} \) by using other theoretical approximations, including local density approximation (LDA (CA))32,33, Perdew–Wang 91 (GGA (PW91))34, strongly constrained and appropriately normed semilocal density functional (meta-GGA (SCAN))35, and Heyd–Scuseria–Ernzerhof screened hybrid density functional (HSE06)36,37. The results show that the type of DFT exchange-correlation functional can affect the absolute value of the spin magnetic moment of Fe (\( \mu_{\text{Fe}} \)), the spin magnetic moment of \( \text{O}_2 \) (\( \mu_{\text{O2}} \)), and the d-band center gap of spin state (\( \Delta d \)), but the variation tendency of the value is consistent (Supplementary Figs. 19–22 and Supplementary Tables 3–5). There is still a nearly linear correlation between electronic structure and Fe-N4 ORR activity in the theoretical framework of LDA (CA) + U, GGA (PW91) + U, meta-GGA (SCAN), and HSE06 (Supplementary Figs. 20–22). \( \text{M}_{\text{Fe}}, \text{M}_{\text{O2}}, \) and \( \Delta d \) are still distributed in stages. For the LDA (CA) + U, GGA (PW91) + U, meta-GGA (SCAN), and HSE06, the R-square between \( \text{M}_{\text{Fe}} \) and \( \Delta G \) are 0.93, 0.95, 0.91, and 0.91.
In this work, we investigated the origin and descriptors of ORR activity on the Fe-N₄ site using DFT calculation. We explored divacancy defects on carbon supports that could modulate the ORR activity of the Fe-N₄ site. The first electron step ($^\cdot$O₂ + H⁺ + e⁻ $\rightarrow$ *OH) is the potential-determining step (PDS) on all Fe-N₄ configurations. Fe-N₄ site on 6, 5a, 6a, 6I, 7I, and 8I showed high ORR activity with $\Delta G_{\text{max}}$ less than −0.60 eV. The ORR activity of Fe-N₄ sites on the asymmetric surface showed orientation-dependence. We demonstrated that the hybridization between Fe 3dz², 3dyz (3dxz) and O₂ π* orbital is the origin of Fe-N₄ ORR activity by studying the electronic structure. The Fe–O bond length, $\Delta d$, $M_{\text{Fe}}$, and $M_{\text{O}}$ are also due to the above factors. Therefore, the Fe-N₄ ORR activity is origin from the activation of O₂, that is, the hybridization between Fe 3dz² (3dyz or 3dxz) and *O₂ π* orbital. The Fe–O bond length, $\Delta d$, $M_{\text{Fe}}$, and $M_{\text{O}}$ are the specific symbols describing hybridization.
Fe-N₄ site. There is a nearly linear correlation between Δd, M₊, M₋, and the Fe–O bond length from geometry and electronic structure. Importantly, we elucidate that the Fe–O bond length, Δd, M₊, and M₋ are essentially hybrids between Fe 3d2 (3dyz) and O₂ π* orbitals from the spatial distribution and energy level of the frontier orbital. The height of the Fe 3d projected orbital is related to the activation of O₂. For the active Fe-N₄ sites, the strong hybridization of 3d2 and 3dyz (or 3dxz) with O₂ π* orbital results in the short Fe–O bond length (1.737 Å), low Δd (1.755 eV), M₊ (1.190 μB), and M₋ (0.881 μB). For the inactive Fe-N₄ site, the strong hybridization of 3d2 with O₂ π* orbital and the negligible hybridization of 3dyz (3dxz) with O₂ π* orbital lead to the long Fe–O bond length (2.013 Å), high Δd (2.570 eV), M₊ (1.756 μB), and M₋ (1.177 μB). This work offers insights into the Fe-N₄ ORR activity and provides guidelines for designing the high-performance Fe-N-C catalysts.

**Methods**

**DFT calculations.** Our spin-polarized density functional theory simulation was calculated using the Vienna ab initio simulation package (VASP)³⁹. The PAW potentials and the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) were employed to describe the interaction of electron-ion and the electron-electron exchange and correlation functional, respectively⁴⁰,⁴¹. After the test, the cutoff energy was set at 400 eV, and Monkhorst–Pack mesh with a 2 × 2 × 1 grid was used in our calculations after testing (Supplementary Fig. 24). van der Waals (VDW) forces were corrected with the D2 method of Grimme⁴². The convergence criterion was set at 0.02 eV Å⁻¹ for the force and 1 × 10⁻⁴ eV per atom for energy. We used the correlation energy (U) of 4 eV and the exchange energy (I) of 1 eV for Fe 3d orbitals⁴³,⁴⁴. We built a super-cell (7 × 8) carbon substrate as a model, which includes 106 C atoms, 4 N atoms, and 1 Fe atom. The lattice parameters of this slab are a = 17.31 Å and b = 16.98 Å after optimization. The lattice constants are optimized again due to the introduction of divacancy defects in the system. The vacancy layer was set at 15 Å. Maximal localized Wannier functions (MLWFs) methods are applied by Wan-nier90 to calculate the spatial distribution of Fe 3d and O₂ 2p orbital⁴⁵,⁴⁶. We also considered the effect of solvent on the ORR activity of the Fe-N₄ site by employing an implicit solvent model⁴⁸,⁴⁹. To confirm the generalization validity of the correlation between electronic structure and Fe-N₄ ORR activity, local density approximation with the Ceperly–Alder functional (LDA (CA))⁵⁰, Perdew–Wang 91 (GGA (PW91))⁵¹, strongly constrained and appropriately normed semilocal density functional (meta-GGA (SCAN))⁵², and Heyd–Scuseria–Ernzerhof screened hybrid density functional (HSE06) were used to evaluate the electronic structure⁵³,⁵⁴. In the framework of LDA (CA) and GGA (PW91), we also consider the Coulomb interaction between Fe 3d orbital electrons, and the Hubbard U value is 3 eV. First-principles Born–Oppenheimer molecular dynamics (BOMD) simulation was performed in the canonical ensemble with Nosé–Hoover heat bath schemes⁵⁵,⁵⁶. During the simulation, spin polarization is not considered, and the Brillouin zone integrations were performed using the Gamma-point grid. The total simulation time is 5 ps with a time step of 1 fs at 300 K. We also used the VESTA package to visualize the structures and charge density differences⁵².

The binding energy of the Fe site (Ebind) on the carbon supports can be calculated by

$$E_{\text{bind}} = E_{\text{Fe/CUB}} - E_{\text{Fe}} - E_{\text{CUB}}$$

where $E_{\text{Fe/CUB}}$ is the total energy of the Fe atom embedded in the carbon supports; $E_{\text{Fe}}$ and $E_{\text{CUB}}$ are the energies of the substrate and single Fe atom in the Fe bulk, respectively.

The Gibbs free energy can be expressed as

$$\Delta G = \Delta E + AZPE - T \cdot \Delta S$$

where $\Delta E$, AZPE, and $\Delta S$ are the reaction energy calculated by the DFT methods, the changes in zero-point energies, and the entropy during the reaction, respectively⁵⁷–⁵⁹. $T$ is the temperature (298.15 K, in our work).

The d-band center gap of spin state (Δd) can be defined as

$$\Delta d = |e_{\uparrow} - e_{\downarrow}| = \int \frac{1}{\sqrt{\pi}} n_{\uparrow}(\epsilon) d\epsilon - \int \frac{1}{\sqrt{\pi}} n_{\downarrow}(\epsilon) d\epsilon$$

where $e_{\uparrow}$ and $e_{\downarrow}$ are the d-band center of the Fe 3d spin-up projected density of states and $\Delta d$ is the d-band center of the Fe 3d spin-down projected density of states⁵⁶.

The magnetic moment (M) is defined as

$$M = N(\text{spin-up}) - N(\text{spin-down})$$

where $N(\text{spin-up})$ and $N(\text{spin-down})$ represent the number of electrons in the spin-up and spin-down occupied state, respectively⁶⁰,⁶¹. $M(3dyz)$, $M(3dz^2 - y^2)$, $M(3dxz)$, $M(3dxc)$, and $M(3dz^2)$ represent the projected of magnetic moments on Fe 3dyz, 3dz²−y², 3dxz, 3dxc, and 3dz², respectively.

**Data availability**

The data that support the findings of this study are available from the corresponding author on reasonable request.

**Code availability**

The computational codes used in this work are available from the corresponding author on reasonable request.
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Acknowledgements
The authors gratefully thank the International Science and Technology Cooperation Program (Grant No. 2017YFE0127800 and 2018YFE0203400), Natural Science Foundation of China (Grant No. 21872174 and U1932148), Hunan Provincial Science and Technology Program (Grant No. 2017XK2026), Shenzhen Science and Technology Innovation Project (Grant No. JCYJ20180307151313532), and Postdoctoral Research Fund of Central South University (Grant No. 140050047).

Author contributions
M.L. and H.L. conceived the project, and K.L. demonstrated the idea and collected all the data. K.L. and J.F. wrote the paper. K.L., J.F., Y.L., T.L., G.N., and Z.L. analyzed the results. All authors read and commented on the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-29797-1.

Correspondence and requests for materials should be addressed to Min Liu.

Peer review information Nature Communications thanks Jun Jiang and the other anonymous reviewer(s) for their contribution to the peer review of this work.

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