

Fine control on the axial ligand elements improves the oxygen reduction performance of iron phthalocyanine

Qingyi Zhu^{1,§}, Zongyi Wang^{1,§}, Hao Sun²(✉), Xiangrong Jin¹, Keying Tao¹, Yuan Zhang¹, Haocheng Wang¹, Yuyang Zhou¹, Hao Song¹, Yifan Zeng¹, Lu Bai³, Yi Zhao¹, Zheng Chang¹(✉), Jiazhan Li¹(✉), Xiaoming Sun¹(✉)

¹ State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China

² Institute of Intelligent Innovation, Henan Academy of Sciences, Zhengzhou 451162, China

³ CAS Key Laboratory of Standardization and Measurement for Nanotechnology, National Center for Nanoscience and Technology, Beijing 100190, China

[§] Qingyi Zhu and Zongyi Wang contributed equally to this work.

Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94909193>

<https://www.sciopen.com/journal/1998-0124> on Sep. 15, 2026

© The Authors(s)

Just Accepted

This is a “Just Accepted” manuscript, which has been examined by the peer-review process and has been accepted for publication. A “Just Accepted” manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides “Just Accepted” as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, and the page proofs have been corrected, it will be removed from the “Just Accepted” web site and published officially with volume and article number (e.g., *Nano Research*, **2025**, 18, 94906990). Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these “Just Accepted” manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.

Fine control on the axial ligand elements improves the oxygen reduction performance of iron phthalocyanine

Qingyi Zhu ^{1,§}, Zongyi Wang ^{1,§}, Hao Sun ^{2,✉}, Xiangrong Jin ¹, Keying Tao ¹, Yuan Zhang ¹, Haocheng Wang ¹, Yuyang Zhou ¹, Hao Song ¹, Yifan Zeng ¹, Lu Bai ³, Yi Zhao ¹, Zheng Chang ^{1,✉}, Jiazhan Li ^{1,✉}, and Xiaoming Sun ^{1,✉}.

¹ State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China

² Institute of Intelligent Innovation, Henan Academy of Sciences, Zhengzhou 451162, China

³ CAS Key Laboratory of Standardization and Measurement for Nanotechnology, National Center for Nanoscience and Technology, Beijing 100190, China

[§] Qingyi Zhu and Zongyi Wang contributed equally to this work.

Received: 4 August 2026; **Revised:** 14 September 2026; **Accepted:** 15 September 2026

✉ Address correspondence to Hao Sun, sunhao@hnas.ac.cn; Zheng Chang, changzheng@mail.buct.edu.cn; Jiazhan Li, lijiazhan@buct.edu.cn; Xiaoming Sun, sunxm@mail.buct.edu.cn

 **Cite this article:** *Nano Research*, 2026, 19, 94909193 <https://doi.org/10.26599/NR.2026.94909193>

ABSTRACT: Axial coordination was one of the effective strategies for modulating the electronic structure of single-atom catalysts. However, the mechanisms of different axial coordination configurations varied significantly, making it difficult to identify the optimal axial ligand. Here, iron phthalocyanine (FePc) was employed as a model catalyst and loaded onto activated carbon (AC) supports pre-anchored with different heteroatoms (O, N, C) for constructing FePc-based model catalysts with different axial ligand elements. All prepared axial coordination catalysts exhibited excellent activity for the oxygen reduction reaction (ORR), with the performance order of: O>N>C. Through the systematic comparison of these model catalysts, an evaluation of the performance differences in modulating the Fe–N₄ structure by different elements was unified. This work reveals the importance of carbonaceous support for tailoring the performance of macrocyclic molecules in electrocatalysis.

KEYWORDS: iron phthalocyanine; axial coordination; oxygen reduction reaction; model catalysts

1 Introduction

Non-platinum-metal single-atom catalysts (SACs) have emerged as promising alternatives to Pt-based catalysts for the oxygen reduction reaction (ORR) [1-4]. Among them, metal-nitrogen-carbon materials (M–N–C), especially those with an M–N₄ structure, exhibited excellent ORR performance [5-8]. However, the symmetrical structure of M–N₄ limits the optimal adsorption and desorption of oxygen intermediates. Breaking this symmetry became a key strategy to enhance the performance of M–N–C materials. Axial ligand coordination provides an effective approach by disrupting the spatial symmetry of M–N₄ sites and increasing their structural tunability [9-13]. Nevertheless, the complicated structures of traditional axial M–N–C materials obscured the identification of active sites, thereby limiting precise structural control and further improvement in ORR activity.

Metallic macrocyclic compounds overcome the limitations of conventional catalysts owing to their well-defined M–N₄ coordination structure [14-17]. They are regarded as ideal model catalysts for investigating the relationship between active sites and catalytic performance [18-20]. Among them, iron phthalocyanine (FePc) was widely used as a typical model system owing to its well-defined active sites and

highly tunable structure [21-25]. By introducing and anchoring axial ligands on the FePc model, the mechanism by which axial ligands affected the active site was revealed [26-28]. Nevertheless, previous studies have largely focused on individual heteroatom ligands, such as C, N, and O, while a systematic comparison of how different axial ligands affect Fe–N₄ sites remains lacking. Therefore, clarifying the role of axially coordinated heteroatoms in Fe–N₄ structures has become an important scientific issue that requires urgent attention.

Herein, a model system was fabricated via a facile method to systematically explore the regulatory mechanism of axial ligands on Fe–N₄ sites. Ligands with different heteroatoms were anchored to the support and axially coordinated with FePc. Using the oxygen reduction reaction (ORR) as a probe, we systematically compared the effects of C-, N-, and O-based axial ligands on the performance of Fe–N₄. The introduction of axial ligands significantly enhanced the ORR activity of FePc, with O-coordination showing the highest ORR performance, followed by N-coordination. By investigating the roles of different axial heteroatom ligands on a uniform catalyst platform, the lack of cross-comparison in conventional studies was effectively addressed, laying an important experimental foundation for the design and development of electrocatalysts regulated by axial

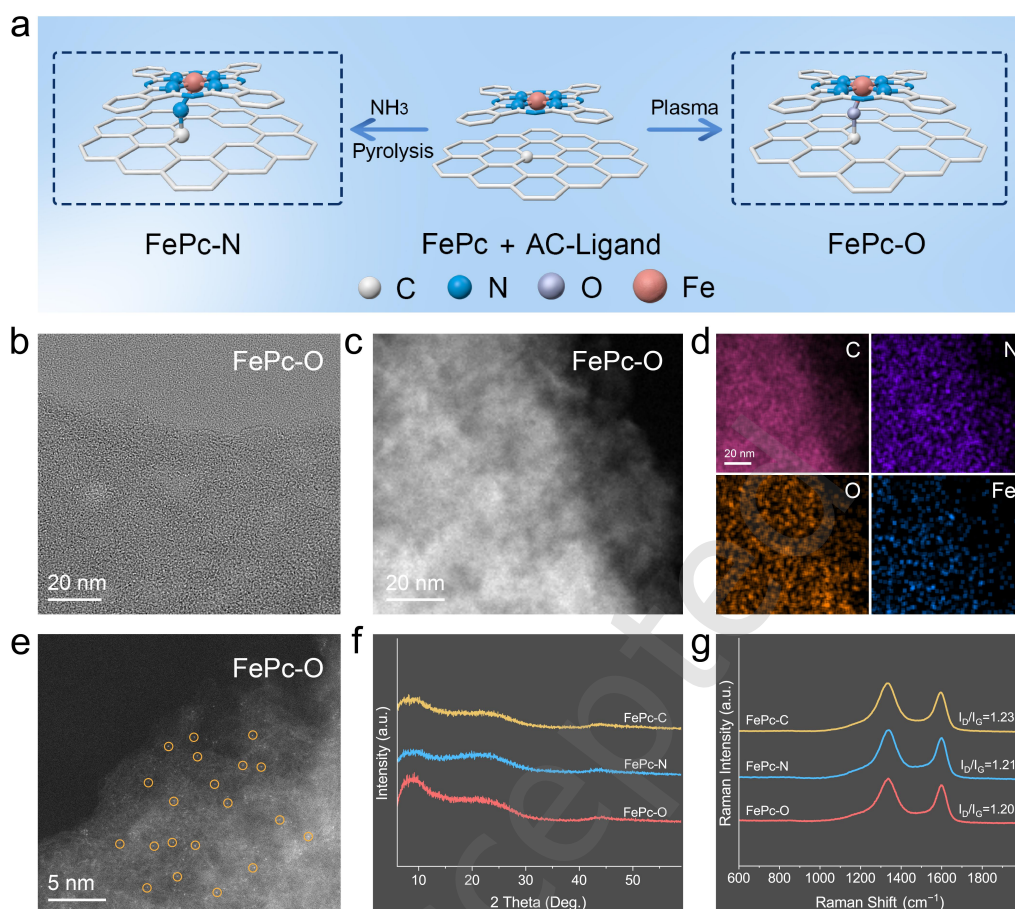


Figure 1 Synthesis and structural characterizations of FePc-ligand materials. (a) Schematic diagram illustrating the synthesis of FePc-ligand catalyst through the solution impregnation method. (b) Representative HRTEM image of FePc-O catalyst. (c-d) HAADF-STEM image (c) and EDS mapping of FePc-O material (d). (e) HAADF-STEM image (d) of FePc-O material. (f) The XRD patterns of FePc-C, FePc-N, and FePc-O materials. (g) Raman spectra of FePc-C, FePc-N, and FePc-O materials.

2.1 Construction of FePc-based model catalysts with axial coordination

As illustrated in Figure 1a, the model catalysts with axial coordination were achieved by the solution impregnation strategy. First, N and O elements were introduced to activated carbon (AC). Specifically, O ligands were constructed on AC through O₂-plasma treatment, yielding AC-O, whereas N ligands were introduced by treatment with NH₃·H₂O followed by evaporation, affording AC-N. Subsequently, iron phthalocyanine (FePc), employed as a molecular model for the Fe-N₄ active site, was uniformly dispersed onto the as-prepared AC support via impregnation using N, N-dimethylformamide (DMF) as the solvent. In this manner, a series of model catalysts with distinct axial ligands (ligand = C, N, O) was constructed, denoted as FePc-C, FePc-N, and FePc-O, respectively.

2.2 Fe-N₄ Sites with Axial Coordination

As shown in Figure S1, the physicochemical properties of AC, AC-N, and AC-O were tested to evaluate the comparability of the supports. Brunauer-Emmett-Teller (BET) measurements revealed comparable porous characteristics and similar pore-size distributions among the AC (2337.2 m²/g), AC-N (2407.6 m²/g), and AC-O (2353.1 m²/g). Raman spectra further reveal comparable I_D/I_G ratios of AC (I_D/I_G=1.21), AC-N (I_D/I_G=1.20), and AC-O (I_D/I_G=1.22), indicating that the degree of graphitic ordering and defect density remain

broadly similar among AC, AC-N, and AC-O (Figure S2). X-ray photoelectron spectroscopy (XPS) further showed highly similar C 1s spectral profiles for AC, AC-N, and AC-O (Figure S3a-3c), while additional N species were identified for AC-N (Figure S3d). Although AC and AC-O exhibited broadly similar O 1s spectral envelopes, the relative distribution of oxygen-containing carbon species differed between AC and AC-O (Figure S3e-3f). Contact angle measurements showed similar wettability for AC and AC-N, and AC-O (Figure S4). Taken together, these results indicate that the three supports retain broadly comparable carbon frameworks and porous structures, while their surface chemical environments are selectively modified by N and O ligands.

The FePc-based model catalysts were systematically characterized using complementary techniques. As shown in Figure S1, XPS revealed the iron content of 0.32, 0.33 at.% and 0.35 at.% in FePc-C, FePc-N, and FePc-O, respectively. These comparable Fe contents indicate similar loadings of Fe-N₄ moieties across the FePc-ligand catalyst series, thereby satisfying the requirement for comparable active-site densities in model catalysts (Table S1). The high-resolution transmission electron microscope (HRTEM) image showed that FePc-O exhibits an amorphous structure, and no lattice fringes of Fe species are observed, indicating that FePc did not aggregate on the AC-O surface (Figure 1b). Consistently, the HRTEM images of FePc-C and FePc-N, similar to that of FePc-O, demonstrate that the FePc-ligand

materials were an amorphous matrix (Figure S5). Energy-dispersive X-ray spectroscopy (EDS) elemental mapping of FePc-O further revealed a homogeneous spatial distribution of C, O, N, and Fe species, suggesting that FePc was dispersed uniformly throughout the AC-O substrate (Figure 1c, d). Likewise, EDS mapping of FePc-N and FePc-C confirmed the uniform dispersion of FePc on its respective supports (Figure S6). Moreover, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was employed to determine the dispersion state of Fe species. As shown in Figure 1e, the isolated bright spots were clearly observed, indicating that the Fe single atoms were uniformly distributed on the AC-O substrate. The HAADF-STEM image of FePc-N and FePc-C similarly corroborated this conclusion (Figure S7). Furthermore, the X-ray diffraction (XRD) pattern revealed that there were no characteristic diffraction peaks corresponding to Fe^0 in FePc-ligand materials and FePc-C, which was consistent with the results of HAADF-STEM (Figure 1f). All FePc-ligand catalysts display a broad peak at approximately 24° , revealing a feature typical of amorphous carbon with short-range order and long-range disorder. The ID/IG ratios of FePc-O, and FePc-N in Raman are comparable, indicating similar structural defects within the amorphous carbon supports (Figure 1g). Given their similar morphology and structure, the FePc-ligand materials validate that these single-atom catalysts could be employed as a suitable model for further performance studies.

XPS was employed to verify the successful modification of ligand species onto the carbon support. The high-resolution C 1s XPS spectra revealed that there were no significant changes in the major carbon components after FePc loading, indicating that the carbon framework of the supports remained largely preserved (Figure S8). As shown in Figure S9a and S9b, in the high-resolution N 1s XPS spectra, pyridinic N and graphitic N of FePc-N were observed in addition to pyrrolic N and imine N, confirming that pyridinic N along with a small amount of graphitic N had been successfully introduced into the AC support. In addition, the pyridinic N component of FePc-N exhibits a noticeable positive shift in binding energy (+0.3 eV) compared to AC-N, indicating a decrease in the local electron density around pyridinic N (Figure 2a). These results revealed that pyridinic N species are the most probable axial coordination sites. The O 1s XPS spectrum of FePc-O confirmed the introduction of O species. The presence of the Fe-O peak suggested that the O species introduced by plasma treatment were anchored to the AC surface and coordinated to the Fe center in FePc, forming an Fe-O bond (Figure 2b). Moreover, the content of C-O decreased a lot compared to AC-O, indicating that FePc mainly links to C-O (Figure S9c). XPS analysis initially confirmed that heteroatoms were successfully introduced into the AC substrate and interacted with FePc.

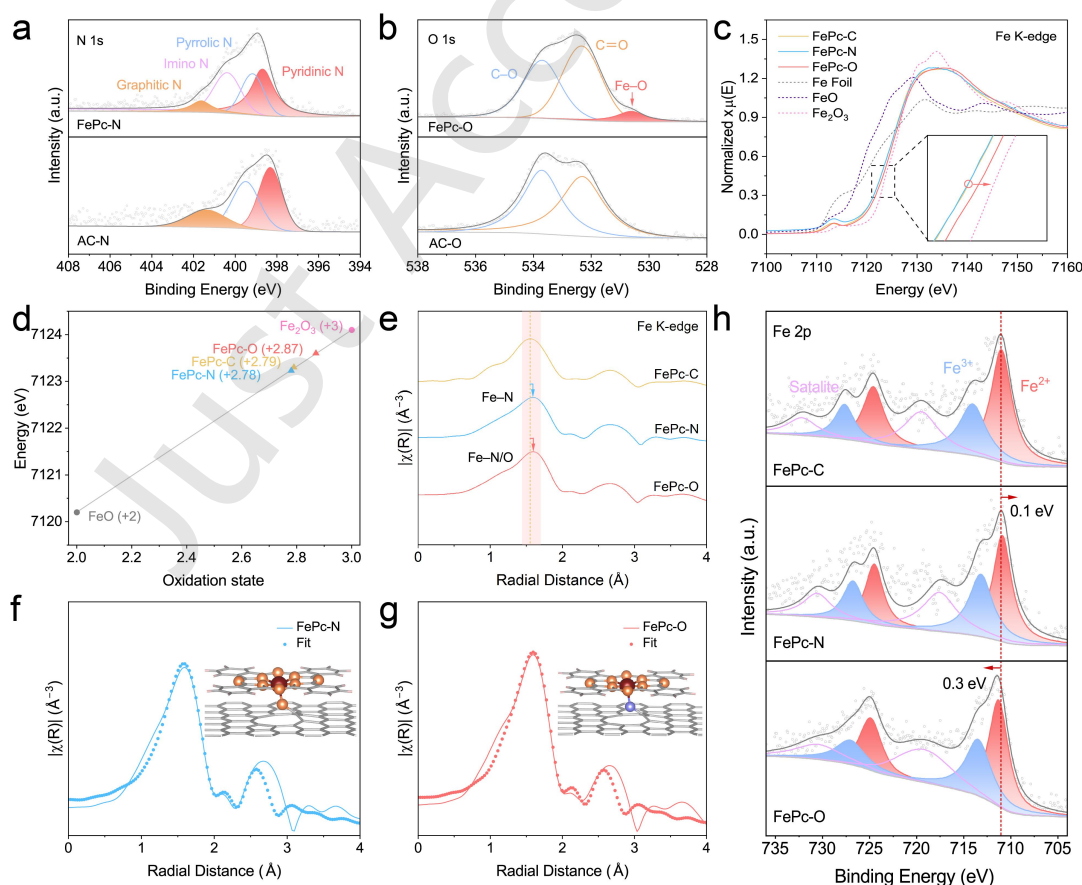


Figure 2 Local coordination environment of Fe in FePc-ligand materials. (a) High-resolution N 1s XPS data of FePc-N and AC-N. (b) High-resolution O 1s XPS data of FePc-O and AC-O. (c) Normalized Fe K-edge XANES spectra of FePc-C, FePc-N, FePc-O, and reference samples (Fe foil, FeO, and Fe₂O₃). Inset: enlarged view of the 7121–7126 eV region. (d) Average iron valence state for FePc-C, FePc-N, and FePc-O materials. (e) Fourier transform of Fe K-edge EXAFS of FePc-C, FePc-N, and FePc-O materials at R-space. (f–g) Fe K-edge EXAFS fitting curves of FePc-N (f) and FePc-O (g) in R-space. Insets

show the corresponding fitting models. (h) High-resolution Fe 2p XPS data of FePc-C, FePc-N, and FePc-O materials.

To further investigate the local coordination environment of Fe and its interaction with heteroatoms, X-ray absorption spectroscopy (XAS) was employed. The Fe K-edge X-ray absorption near-edge spectroscopy (XANES) spectra showed that the absorption edge of the FePc-ligand catalysts was positioned between those of FeO and Fe₂O₃, indicating that the oxidation state of Fe in FePc-ligand ranged from +2 to +3 (Figure 2c). Compared to FePc-C (+2.79), the oxidation state of Fe in FePc-O increased to +2.87, indicating that the introduction of oxygen modulated the electronic configuration of Fe through an electron-withdrawing interaction (Figure 2d). In contrast, the oxidation state of Fe in FePc-N (+2.78) exhibited an average Fe oxidation state comparable to that of FePc-C (+2.79), indicating that axial N coordination does not induce a resolvable change in Fe oxidation. Fourier transform K²-weighted extended X-ray absorption fine structure (FT-EXAFS) spectra were performed to confirm the coordination interaction between the Fe center and heteroatoms. As shown in Figure 2e, FePc-C exhibited a dominant peak at 1.55 Å, which was assigned to the Fe-N/C scattering path. Moreover, the absence of the typical Fe-Fe scattering path at ~2.20 Å provided additional evidence that Fe was atomically dispersed in FePc-ligand catalysts. Notably, the Fe-N scattering paths in the FePc-N and FePc-O samples were longer than that of FePc-C, approximately 1.59 Å, indicating that the interaction between the heteroatoms and FePc led to the elongation of the Fe-N bond. Among them, FePc-N exhibited a longer Fe-N scattering path than pristine FePc, attributable to the formation of axial Fe-N coordination. For FePc-O, axial Fe-O coordination contributed to bond elongation through the combined Fe-N and Fe-O scattering paths. Furthermore,

FePc-ligand catalysts exhibited a maximum intensity in the wavelet-transform EXAFS (WT-EXAFS), which originated from the axial coordination and the Fe-N₄ configuration in the first coordination shell (Figure S10). EXAFS fitting results revealed that the coordination number (CN) of the FePc-ligand catalysts was ~5, indicating that the FePc-ligand catalysts were composed of Fe-N₄ and an axial coordination Fe-N/O. Specifically, FePc-N showed CN of 5.1 for Fe-N (Figure 2f); FePc-O exhibited CN of 4.0 for Fe-N and 0.9 for Fe-O (Figure 2g), and FePc-C performed CN of 3.8 for Fe-N and 1.1 for Fe-C (Figure S11, Table S2). The corresponding k-space fitting results for all models are presented in Figure S12. The high-resolution Fe 2p XPS spectra further verify the local environment of Fe in the Fe-ligand catalysts (Figure 2h). The binding energy of Fe²⁺ in FePc-O was higher than that in FePc-C. In contrast, the Fe 2p XPS spectra of FePc-N showed a lower binding energy of Fe²⁺ than that in FePc-C. Consistent with the XANES findings, the results demonstrated that axial coordination brought about an alteration in the oxidation state of the Fe-N₄ center. In conclusion, the higher oxidation state of Fe in FePc-O was attributed to the electron-withdrawing effect of the axial O. For FePc-N, although no resolvable change in the Fe oxidation state was identified by XANES, the axial Fe-N coordination indicates a perturbation of the local electronic structure of the Fe-N₄ center. Meanwhile, the construction of axial coordination also induces an elongation of the Fe-N bond length. The changes in coordination number, Fe-N bond environment, and complementary XPS features collectively confirm that axial coordination modifies the local coordination and electronic environment of the Fe center.

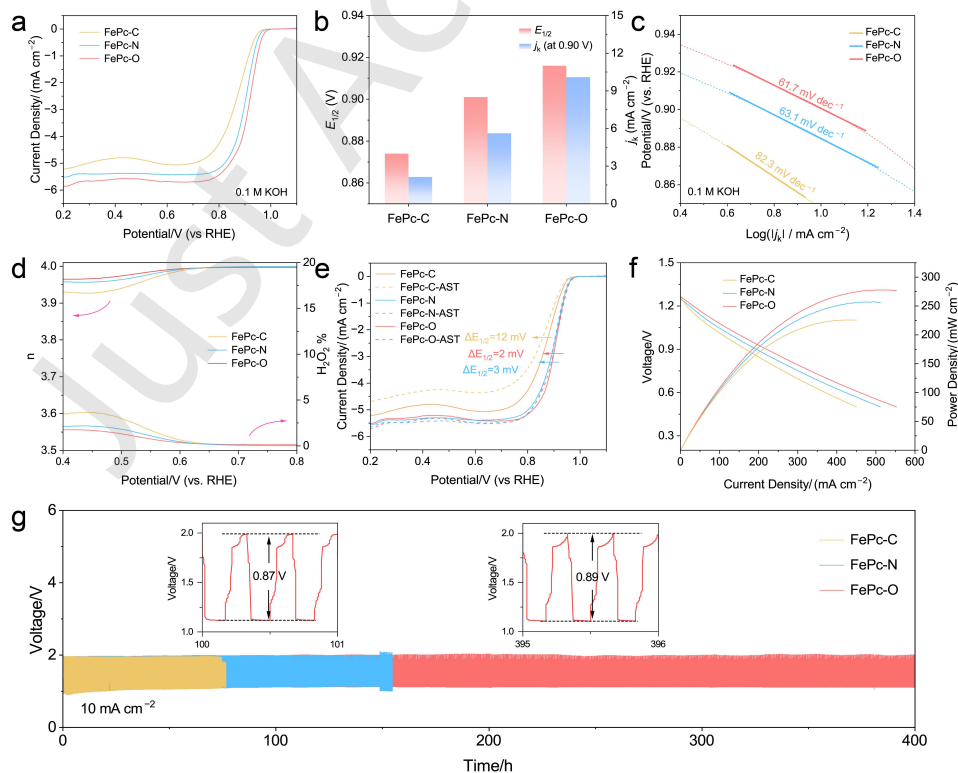


Figure 3 Electrocatalytic ORR performance of the FePc-C, FePc-N, and FePc-O. (a) Linear sweep voltammetry curves of the FePc-C, FePc-N, and FePc-O at the rotation speed of 1600 rpm in 0.1 M KOH solution. (b) $E_{1/2}$ and j_k at 0.90 V for FePc-C, FePc-N, and FePc-O. (c) Tafel plots of FePc-C, FePc-N, and FePc-O. (d) Yield of peroxide (H₂O₂ %) and electron transfer number (n) of FePc-C, FePc-N, and FePc-O. (e) Stability of FePc-C, FePc-N, and FePc-O. (f) Polarization curves of FePc-C, FePc-N, and FePc-O in liquid ZABs. (g) Galvanostatic charge-discharge cycling profiles of Zn-air batteries at 10 mA cm⁻².

2.3 Performance optimization of FePc catalysts with different axial coordination

To reveal the influence of the axial heteroatoms for FePc-ligand materials on the ORR performance, electrochemical measurements were conducted. Fe-ligand catalysts and FePc-C were first tested in a three-electrode cell system with 0.1 M KOH electrolyte by linear sweep voltammetry (LSV) (Figure S13). The FePc-C catalyst exhibited a half-potential ($E_{1/2}$) of 0.874 V (vs. RHE), while the FePc-ligand catalysts achieved more positive values (Figure 3a), indicating that axial coordination promotes ORR intrinsic activity. Specifically, FePc-N exhibited only a slight improvement over FePc-C with an $E_{1/2}$ of 0.901 V, FePc-O catalyst demonstrated the highest ORR activity with an $E_{1/2}$ of 0.916 V. These metrics place it as one of the most competitive ORR catalysts reported (Table S3). Given their comparable Fe contents and electrochemically active surface areas (ECSA) (Figure S14), this LSV trend revealed that FePc-O possessed the highest ORR activity among the Fe-ligand catalysts, followed by FePc-N, and finally FePc-C. The kinetic current density (j_k) at 0.90 V follows the above sequence: FePc-C (2.15 mA cm^{-2}) < FePc-N (5.62 mA cm^{-2}) < FePc-O (10.10 mA cm^{-2}) (Figure 3b), demonstrating that the FePc-ligand catalysts accelerate the ORR kinetics. After normalizing the ORR kinetic current density (Figure S15), it was found that the performance still ranked as follows: FePc-C ($6.72 \text{ mA cm}^{-2}(\text{at.\%Fe})^{-1}$) < FePc-N ($17.03 \text{ mA cm}^{-2}(\text{at.\%Fe})^{-1}$) < FePc-O ($28.86 \text{ mA cm}^{-2}(\text{at.\%Fe})^{-1}$). This result is also confirmed by the Tafel slope, as shown in Figure 3c, the Tafel slope exhibits a progressive decrease from 82.3 mV dec^{-1} for FePc-

C to 63.1 mV dec^{-1} for FePc-N, with FePc-O showing the lowest Tafel slope of 61.7 mV dec^{-1} . The progressive decrease in Tafel slope and the progressive increase in j_k consistently indicated that the ORR kinetics accelerated in the order of FePc-C, FePc-N, and FePc-O catalysts. After adding KSCN, the ORR activities of all three catalysts significantly decreased, confirming that the Fe-centered sites are the main active centers (Figure S16). Moreover, FePc-O exhibited a more pronounced inhibitory effect, further indicating that the axially regulated Fe-N₄ sites play a crucial role in enhancing its ORR performance. Furthermore, to determine the ORR pathway of the catalysts, the number of transferred electrons (n) and the H₂O₂ yield (H₂O₂ %) over the potential range of 0.4~0.8 V among those catalysts were measured (Figure 3d). Among them, FePc-O catalyst showed the highest n and the lowest H₂O₂ %, suggesting that FePc-O was more prone to the four-electron ORR pathway than that of the other Fe-ligand catalysts. To evaluate the stability of the Fe-ligand catalysts, the accelerated stability test (AST) was performed. The FePc-O catalyst showed only a 2 mV negative shift in $E_{1/2}$ after 10,000 cycles between 0.6 V – 1.0 V, while the FePc-C catalyst showed an $E_{1/2}$ loss of 12 mV (Figure 3e). The $E_{1/2}$ loss of FePc-N was also much lower than that of FePc-C, indicating that axial coordination effectively enhanced the electrochemical durability of catalyst. The results of XPS and HRTEM after stability tests indicated that the carbon framework and the surface environment, mainly containing heteroatoms, remain basically stable (Figure S17 and S18). These results revealed that the catalyst has good structural and chemical stability in the ORR process.

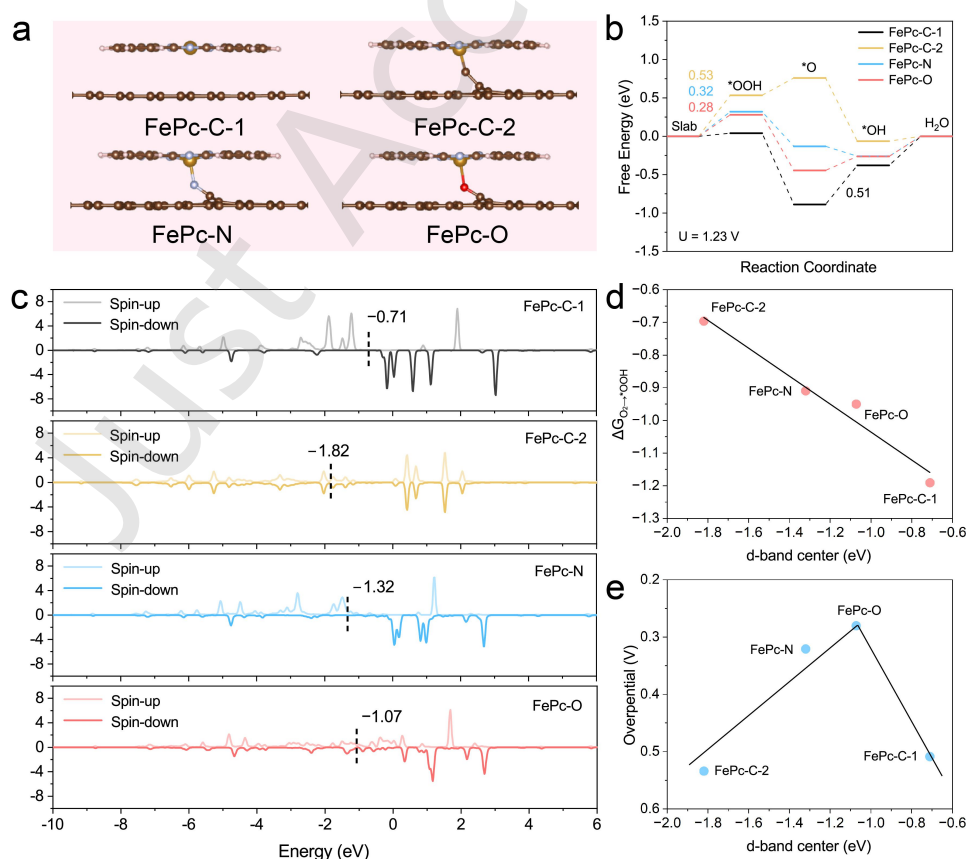


Figure 4 Theoretical calculations for the overall ORR process on FePc/AC-Ligands. (a) Front view of models of FePc-C-1, FePc-C-2, FePc-N, and FePc-O. (b) Gibbs free energy diagrams of the ORR pathways at 1.23 V (vs. SHE). (c) Partial density of states (the dotted line indicates the d-band center). (d) Linear relationship of d-band center with $\Delta G_{O_2 \rightarrow *OOH}$. (e) Linear relationship of d-band center with overpotential.

Zn-air batteries (ZABs) were assembled with Fe-ligand catalysts and FePc-C as the cathode to assess their practical applicability (Figure S19). Firstly, the open-circuit voltages (OCV) of ZABs based on Fe-ligand catalysts were higher than those of the FePc-C-based ZAB, suggesting that axial coordination promotes the device performance. Notably, the ZAB with FePc-O achieved an OCV of 1.43 V, surpassing the FePc-C and other FePc-ligand catalysts, indicating that the axial ligand O enhanced the ORR activity (Figure S20). A substantial improvement in power density was observed with axial O coordination. Under comparable OER performance (Figure S21), the FePc-O-based ZAB (277 mW cm⁻²) delivered excellent performance, which is better than that of the FePc-C-based ZAB (225 mW cm⁻²) (Figure 3f). Moreover, the FePc-N (257 mW cm⁻²) also outperformed FePc-C-based ZAB, collectively demonstrating that axial coordination was beneficial for boosting ZAB performance. The discharge performance of Fe-ligand-based ZABs and FePc-C-based ZAB was evaluated at 2~50 mA cm⁻². FePc-O exhibited the best discharge capacity with excellent rate capability, and the voltage loss of FePc-O was the lowest when the discharge current density returned to 2 mA cm⁻² (Figure S22). Furthermore, the stability of the FePc-ligand catalyst-based ZABs by the galvanostatic charge-discharge cycling (Figure 3g), FePc-O-based ZAB (400 h) displayed markedly superior long-term stability compared to the FePc-C-based ZAB (70 h) at 10 mA cm⁻². Likewise, the introduction of axial ligands in FePc-N (150 h) resulted in greater durability than that of FePc-C, confirming the beneficial role of axial coordination in practical stability. Overall, the introduction of axial ligands promotes the application prospects of FePc in ZAB.

Insights from DFT Calculations

To elucidate how axial coordination regulates Fe-N₄ active sites, density functional theory (DFT) calculations were performed. Guided by the experimental characterization and XAS fitting results, structural models for FePc-C (FePc-C-1 and FePc-C-2), FePc-N, and FePc-O were constructed (Figure 4a). As shown in Figure 4b, FePc-C-1, stabilized by π - π interactions, is limited by *OH formation, whereas axial C coordination in FePc-C-2 shifts the potential-determining step (PDS) to *OOH formation. Upon introducing axial N coordination, the free-energy barrier of the PDS is reduced to 0.32 eV. More notably, FePc-O delivers the lowest PDS barrier of 0.28 eV, suggesting that axial O coordination more effectively tunes the electronic structure of the Fe site, thereby optimizing intermediate adsorption and facilitating the overall ORR process. To uncover the electronic origin of the optimized adsorption, we further analyzed the partial density of states (Figure 4c). Compared with FePc-C-1 (-0.71 eV), axial C coordination in FePc-C-2 downshifts the Fe d-band center to -1.82 eV, which weakens the *OH binding strength but leads to an over-regulation of *OOH adsorption. In contrast, FePc-N (-1.32 eV) and FePc-O (-1.07 eV) shift the Fe d-band center back toward the Fermi level, thereby optimizing *OOH binding without excessively strong *OH adsorption (Figure 4d). A volcano-type relationship between the Fe d-band center and the overpotential was further constructed (Figure 4e), in which FePc-O occupies the apex region. This finding suggests that axial O coordination optimally tunes the electronic structure of the Fe site, enabling balanced oxygen-intermediate adsorption and thereby promoting ORR activity.

3 Conclusion

In summary, a well-defined model system was constructed through a simple strategy to systematically investigate the regulatory mechanism of axial ligands on Fe-N₄ active sites. Heteroatom-containing ligands were anchored onto the surface of the carbon support and subsequently coordinated with FePc in the axial direction. The introduction of axial ligands markedly enhances the ORR activity of FePc, with axial O coordination delivering the highest catalytic performance ($E_{1/2}$ = 0.916 V), followed by axial N coordination and axial C coordination. By systematically comparing the regulatory effects of different axial heteroatom ligands on a structurally comparable catalytic platform, this work elucidates how the axial coordination environment governs the catalytic behavior of Fe-N₄ sites, thereby addressing the lack of direct cross-comparison in conventional studies and providing experimental guidance for the rational design of high-performance electrocatalysts through axial-coordination engineering.

Electronic Supplementary Material: Supplementary material (please provide the brief detail of the ESM) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909193>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (22309008, 22675009, 22539001), the Fundamental Research Funds for the Central Universities (buctrc202401), and the Science and Technology Program of Xinjiang Uygur Autonomous Region (2025A01012).

Declaration of competing interest

All the contributing author(s) report(s) no conflict of interests in this work.

Author contribution statement

Author 1: Data curation, project administration, validation, writing manuscript, experimental design. Author 2: Data curation, experimental design.

References

- [1] Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I. B.; Nørskov, J. K.; Jaramillo, T. F. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* **2017**, *355*, eaad4998.
- [2] Li, J. Z.; Chen, M. J.; Cullen, D. A.; Hwang, S.; Wang, M. Y.; Li, B. Y.; Liu, K. X.; Karakalos, S.; Lucero, M.; Zhang, H. G.; Lei, C.; Xu, H.; Sterbinsky, G. E.; Feng, Z. X.; Su, D.; More, K. L.; Wang, G. F.; Wang, Z. B.; Wu, G. Atomically dispersed manganese catalysts for oxygen reduction in proton-exchange membrane fuel cells. *Nat. Catal.* **2018**, *1*, 935–945.
- [3] Zhao, S. N.; Li, J. K.; Wang, R.; Cai, J.; Zang, S. Q. Electronically and Geometrically Modified Single - Atom Fe Sites by Adjacent Fe Nanoparticles for Enhanced Oxygen Reduction. *Adv. Mater.* **2021**, *34*.
- [4] Li, J. Z.; Zhang, H. G.; Samarakoon, W.; Shan, W. T.; Cullen, D. A.; Karakalos, S.; Chen, M. J.; Gu, D. M.; More, K. L.; Wang, G. F.; Feng, Z. X.; Wang, Z. B.; Wu, G. Thermally Driven Structure and Performance Evolution of Atomically Dispersed FeN Sites for Oxygen Reduction. *Angewandte Chemie-International Edition* **2019**, *58*, 18971–18980.
- [5] Chen, W. W.; Qin, Y. Y.; Heng, C. Q.; Wang, S. F.; Ge, M. S.; Li, Y.

- F.; Wan, X.; Li, X. N.; Shui, J. L.; Su, Y. Q.; Su, D. Degradation of FeNC Electrocatalysts for Acidic and Alkaline Oxygen Reduction. *J. Am. Chem. Soc.* **2025**, *147*, 35730–35741.
- [6] Niu, W. H.; Pakhira, S.; Cheng, G. M.; Zhao, F.; Yao, N.; Mendoza-Cortes, J. L.; Koel, B. E. Reaction-driven restructuring of defective PtSe into ultrastable catalyst for the oxygen reduction reaction. *Nat. Mater.* **2024**, *23*, 1704–1711.
- [7] Jin, X. R.; Chang, M. Y.; Sun, H.; Chang, C. W.; Sendeku, M. G.; Li, Y. J.; Wang, M. Y.; Fang, J. J.; Li, Y. Z.; Zhu, Q. Y.; Li, B. Y.; Yu, J. G.; Liu, Y. F.; Chang, Z.; Zhang, G. X.; Zhuang, Z. B.; Bai, L.; Ma, Q.; Feng, Z. X.; Liu, W.; Li, J. Z.; Sun, X. M. Targeting Synthesis of Diatomic Catalysts by Selective Etching and Sequential Adsorption of Metal Atom. *J. Am. Chem. Soc.* **2025**, *147*, 2689–2698.
- [8] Yu, Y.; Wang, Y.; Yang, F.; Feng, D.; Yang, M. Y.; Xie, P. F.; Zhu, Y. Z.; Shao, M. H.; Mei, Y.; Li, J. C. Meso/Microporous Single-Atom Catalysts Featuring Curved Fe-N Sites Boost the Oxygen Reduction Reaction Activity. *Angewandte Chemie-International Edition* **2025**, *64*, e202415691.
- [9] Chen, C.; Wu, Y.; Li, X.; Ye, Y.; Li, Z.; Zhou, Y.; Chen, J.; Yang, M.; Xie, F.; Jin, Y.; Jones, C.; Wang, N.; Meng, H.; Chen, S. Modulating Fe spin state in FeNC catalysts by adjacent Fe atomic clusters to facilitate oxygen reduction reaction in proton exchange membrane fuel cell. *Applied Catalysis B: Environmental* **2024**, *342*.
- [10] Sun, S. Q.; Cheng, Y. P.; Zhang, H. N.; Lyu, J. M.; Li, X. Y.; Lyu, K.; Sun, M. H.; Yu, S.; Tu, W. M.; Cabot, A.; Chen, L. H. Breaking the ORR Trade-Off via Mg-Steered Fe-N Pyridinic Conversion. *Small* **2026**, *22*.
- [11] Chang, J. W.; Zhang, Q.; Yu, J. K.; Jing, W.; Wang, S. Y.; Yin, G. C.; Waterhouse, G. I. N.; Lu, S. Y. A Fe Single Atom Seed-Mediated Strategy Toward Fe C/Fe-N-C Catalysts with Outstanding Bifunctional ORR/OER Activities. *Advanced Science* **2023**, *10*.
- [12] Han, Z. L.; Chai, S. Y.; Zhu, Y. Q.; Yao, X. Y.; Yang, L. F.; Du, C. L.; Ma, X. L.; Cao, C. B.; Zou, M. S. Pre-coordination anchoring strategy for modulating the coordination structure of iron single atoms and ORR performance. *Chem. Eng. J.* **2024**, *502*.
- [13] Sui, R.; Liu, B.; Chen, C.; Tan, X.; He, C.; Xin, D. Y.; Chen, B. W.; Xu, Z. Y.; Li, J. Z.; Chen, W. X.; Zhuang, Z. B.; Wang, Z. B.; Chen, C. Constructing Asymmetric Fe-Nb Diatomic Sites to Enhance ORR Activity and Durability. *J. Am. Chem. Soc.* **2024**, *146*, 26442–26453.
- [14] Wang, X.; Yi, Z. Y.; Wang, Y. Q.; Wang, D. Molecular Evidence for the Axial Coordination Effect of Atomic Iodine on Fe-N Sites in Oxygen Reduction Reaction. *Angewandte Chemie-International Edition* **2025**, *64*.
- [15] Liu, M. N.; Liu, Y. X.; Zhang, X.; Li, L. F.; Xue, X. Y.; Humayun, M.; Yang, H. W.; Sun, L. B.; Bououdina, M.; Zeng, J. R.; Wang, D. L.; Snyders, R.; Wang, D. S.; Wang, X.; Wang, C. D. Altering the Symmetry of Fe-N-C by Axial Cl-Mediation for High-Performance Zinc-Air Batteries. *Angewandte Chemie-International Edition* **2025**, *64*.
- [16] Su, J. J.; Musgrave, C. B.; Song, Y.; Huang, L. B.; Liu, Y.; Li, G.; Xin, Y. E.; Xiong, P.; Li, M. M. J.; Wu, H. R.; Zhu, M. H.; Chen, H. M.; Zhang, J. Y.; Shen, H. C.; Tang, B. Z.; Robert, M.; Goddard, W.; Ye, R. Q. Strain enhances the activity of molecular electrocatalysts via carbon nanotube supports. *Nat. Catal.* **2023**, *6*, 818–828.
- [17] Chen, C.; Li, Y. F.; Huang, A. J.; Liu, X. R.; Li, J. Z.; Zhang, Y.; Chen, Z. Q.; Zhuang, Z. W.; Wu, Y.; Cheong, W. C.; Tan, X.; Sun, K. A.; Xu, Z. Y.; Liu, D.; Wang, Z. G.; Zhou, K. B.; Chen, C. Engineering Molecular Heterostructured Catalyst for Oxygen Reduction Reaction. *J. Am. Chem. Soc.* **2023**, *145*, 21273–21283.
- [18] Ei Phyu Win, P.; Yang, J.; Ning, S.; Huang, X.; Fu, G.; Sun, Q.; Xia, X.-H.; Wang, J. Molecular architectures of iron complexes for oxygen reduction catalysis—Activity enhancement by hydroxide ions coupling. *Proceedings of the National Academy of Sciences* **2024**, *121*.
- [19] Xie, P. F.; Zhong, H.; Fang, L.; Lyu, Z.; Yu, W. J.; Li, T.; Lee, J.; Shin, H.; Beckman, S. P.; Lin, Y.; Ding, S.; Kim, I. D.; Li, J. C. Molecular Fe–N4 Moieties Coupled with Atomic Co–N4 Sites Toward Improved Oxygen Reduction Performance. *Adv. Funct. Mater.* **2024**, *34*.
- [20] Xu, C. A. L.; Si, Y. J.; Hu, B. B.; Xu, X. R.; Hu, B. H.; Jiang, Y.; Chen, H. F.; Guo, C. Z.; Li, H. L.; Chen, C. G. Promoting oxygen reduction crafting bridge-bonded oxygen ligands on a single-atom iron catalyst. *Inorganic Chemistry Frontiers* **2022**, *9*, 3306–3318.
- [21] Peng, P.; Shi, L.; Huo, F.; Mi, C. X.; Wu, X. H.; Zhang, S. J.; Xiang, Z. H. A pyrolysis-free path toward superiorly catalytic nitrogen-coordinated single atom. *Science Advances* **2019**, *5*.
- [22] Zhang, S. R.; Zhang, R.; Zhang, Z. Y.; Shi, K. F.; Yu, B. Z.; Sun, G. B.; Chen, S. W. Accordion-like multilayered titanium nitride enables FeN-O axial coordination of iron phthalocyanine as efficient catalysts for oxygen reduction reaction. *Chem. Eng. J.* **2024**, *499*.
- [23] Zhu, S.; Ding, L. T.; Zhang, X. H.; Wang, K.; Wang, X.; Yang, F.; Han, G. Y. Biaxially-Strained Phthalocyanine at Polyoxometalate@Carbon Nanotube Heterostructure Boosts Oxygen Reduction Catalysis. *Angewandte Chemie-International Edition* **2023**, *62*.
- [24] Wu, Y.; Liu, J.; Sun, Q. H.; Chen, J. L.; Zhu, X. G.; Abazari, R.; Qian, J. J. Molecular catalyst of Fe phthalocyanine loaded into In-based MOF-derived defective carbon nanoflowers for oxygen reduction. *Chem. Eng. J.* **2024**, *483*.
- [25] Zhang, W. L.; Shu, C. H.; Zhan, J. Y.; Zhang, S. H.; Zhang, L. H.; Yu, F. S. Deep Electronic State Regulation through Unidirectional Cascade Electron Transfer Induced by Dual Junction Boosting Electrocatalysis Performance. *Advanced Science* **2023**, *10*.
- [26] Chen, K. J.; Liu, K.; An, P. D.; Li, H. J. W.; Lin, Y. Y.; Hu, J. H.; Jia, C. K.; Fu, J. W.; Li, H. M.; Liu, H.; Lin, Z.; Li, W. Z.; Li, J. H.; Lu, Y. R.; Chan, T. S.; Zhang, N.; Liu, M. Iron phthalocyanine with coordination induced electronic localization to boost oxygen reduction reaction. *Nat. Commun.* **2020**, *11*, 4173.
- [27] Peng, L. S.; Yang, J.; Yang, Y. Q.; Qian, F. R.; Wang, Q.; Sun-Waterhouse, D.; Shang, L.; Zhang, T. R.; Waterhouse, G. I. N. Mesopore-Rich Fe-N-C Catalyst with FeN-O-NC Single-Atom Sites Delivers Remarkable Oxygen Reduction Reaction Performance in Alkaline Media. *Adv. Mater.* **2022**, *34*.
- [28] Guo, J.; Yan, X. M.; Liu, Q.; Li, Q.; Xu, X.; Kang, L. T.; Cao, Z. M.; Chai, G. L.; Chen, J.; Wang, Y. B.; Yao, J. N. The synthesis and synergistic catalysis of iron phthalocyanine and its graphene-based axial complex for enhanced oxygen reduction. *Nano Energy* **2018**, *46*, 347–355.

© The Author(s) 2026. *Nano Research* published by Tsinghua University Press. The articles published in this open access journal are distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Fine control on the axial ligand elements improves the oxygen reduction performance of iron phthalocyanine

Qingyi Zhu ^{1,§}, Zongyi Wang ^{1,§}, Hao Sun ^{2,✉}, Xiangrong Jin ¹, Keying Tao ¹, Yuan Zhang ¹, Haocheng Wang ¹, Yuyang Zhou ¹, Hao Song ¹, Yifan Zeng ¹, Lu Bai ³, Yi Zhao ¹, Zheng Chang ^{1,✉}, Jiazhan Li ^{1,✉}, and Xiaoming Sun ^{1,✉}.

¹ State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China

² Institute of Intelligent Innovation, Henan Academy of Sciences, Zhengzhou 451162, China

³ CAS Key Laboratory of Standardization and Measurement for Nanotechnology, National Center for Nanoscience and Technology, Beijing 100190, China

[§] Qingyi Zhu and Zongyi Wang contributed equally to this work.

✉ Address correspondence to Hao Sun, sunhao@hnas.ac.cn; Zheng Chang, changzheng@mail.buct.edu.cn; Jiazhan Li, lijiazhan@buct.edu.cn; Xiaoming Sun, sunxm@mail.buct.edu.cn

Supporting information to <https://doi.org/10.26599/NR.2026.94909193>

Experiment

Chemicals. Activated carbon (YP80F) was purchased from Guangdong Canrd New Energy Technology Co., Ltd. Iron(II) phthalocyanine (FePc, 98%) was purchased from Energy Chemical. N, N-dimethylformamide (DMF, $\geq 99\%$) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Ammonia solution ($\text{NH}_3\cdot\text{H}_2\text{O}$, 28.0%~30.0% NH_3 basis) was purchased from Aladdin. All chemicals were from commercial sources and used without further purification.

Synthesis of FePc-C. 30 mg FePc was added to 15 mL DMF, after ultrasonic treatment for 30 minutes, and the solution was centrifuged to obtain supernate A. 20 mg AC was added to 15 mL DMF. After ultrasonic dispersion to achieve uniformity, supernate A was added to the solution, stirred at room temperature for 24 hours, centrifuged the solution, and dried at 60°C overnight. FePc-C was obtained.

Synthesis of FePc-N. AC was placed in a porcelain vessel and heated in a high-temperature tube furnace at 700°C for 1 hour under flowing NH_3 , and the AC-N was obtained. FePc-N was prepared following the same procedure as for FePc-C, with the only modification being the substitution of AC by AC-N.

Synthesis of FePc-O. AC-O was synthesized by decorating with O by O_2 -plasma treatment for 30 min. FePc-O was prepared following the same procedure as for FePc-C, with the only modification being the substitution of AC by AC-O.

Characterizations. Brunauer-Emmett-Teller (BET) surface areas and pore size distributions were analyzed by Micromeritics ASAP 2460 at 77 K. The powder X-ray diffraction (XRD) patterns were recorded by MeasSrv F9XDZ42. Raman spectra were measured by VERTEX 70v Fourier Infrared Reflectometer. The high-resolution transmission electron microscope (HRTEM) images were recorded on the JEOL 2100 high-resolution transmission electron microscope with a working voltage of 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and Energy Dispersive Spectrometer (EDS) mapping images were obtained on a JEOL COM high-resolution transmission electron microscope at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on the Axis Supra, and binding energies (BE) were calibrated by setting the measured BE of C 1s to 284.8 eV. X-ray absorption spectroscopy (XAS) measurements were conducted on the 1W1B station of the Beijing Institute of High Energy Physics.

Electrochemical measurements. The electrochemical measurements were performed using a three-electrode system controlled by a Corrtest electrochemical Workstation at room temperature. The working electrode was a coated glass-carbon rotating disk electrode (RDE) (area: 0.1960 cm^2) and a rotating ring disk electrode (RRDE) (disk area: 0.2475 cm^2 , ring area: 0.1866 cm^2), while the counter electrode was a graphite rod. A saturated calomel electrode (SCE) served as the reference electrode in a 0.1 M KOH solution. The reported potentials were calibrated to the reversible hydrogen electrode (RHE) scale according to the following equation: $E(\text{RHE}) = E(\text{SCE}) + 0.241 + 0.059 \times \text{pH}$. The formulation of the catalyst ink is as follows: 5 mg of the catalyst is dispersed in a mixture of 500 μL of IPA and 15 μL of 5 wt.% Nafion solution, ultrasound was performed for 1 hour, resulting in a uniform ink. The catalyst was loaded at 0.5 mg cm^{-2} for electrochemical testing. In a 0.1 M KOH solution with oxygen saturation, cyclic voltammetry (CV) measurements were carried out at a rate of 50 mV per second, while the linear sweep voltammetry (LSV) tests were conducted at a rate of 5 mV per second under the condition of a rotational speed of 1600 rpm. Kinetic parameters were derived from the Koutecky-Levich (K-L) equation (1) and (2):

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K} \quad (1)$$

$$B = 0.62nFC_0D_0^{2/3}V^{-1/6} \quad (2)$$

where j , j_L , and j_K represent the measured, diffusion-limiting, and the kinetic current density, respectively, ω is the angular velocity of the disk. n represents the electron transfer number; F is the Faraday constant (96500 C mol^{-1}). C_0 is the bulk concentration of O_2 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$). D_0 is the diffusion coefficient of O_2 ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$). V is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$).

The hydrogen peroxide yield ($\text{H}_2\text{O}_2\%$) and electron transfer number (n) were calculated from RRDE polarization curves using the following equations:

$$n = 4 \times \frac{I_{\text{disk}}}{\frac{I_{\text{ring}}}{N} + I_{\text{disk}}} \quad (3)$$

$$\text{H}_2\text{O}_2(\%) = 200 \times \frac{I_{\text{ring}}/N}{(I_{\text{ring}}/N) + I_{\text{disk}}} \quad (4)$$

Where I_{disk} is the disk current, and I_{ring} is the ring current. N is the H_2O_2 collection coefficient at the Pt ring, which is 0.37. The ORR polarization curves were obtained by subtracting the background currents measured in N_2 -saturated 0.1 M KOH from those in O_2 -saturated solution to eliminate capacitive contributions.

The Tafel slope was achieved from the Tafel equation:

$$E = a + b \log(j_K) \quad (5)$$

Electrochemically active surface area (ECSA) can be calculated using the following equations:

$$i_c = vC_{\text{dl}} \quad (6)$$

$$A_{\text{ECSA}} = \frac{C_{\text{dl}}}{C_s} \quad (7)$$

i_c is the charging current, v is the scan rate, and C_s is the specific capacitance ($40 \mu\text{F cm}^{-2}$). Cyclic voltammetry in the potential range of 0.98 to 1.11 V (vs. RHE) with scan rates of 10 to 50 mV s^{-1} was tested. Then, the double-layer capacitance (C_{dl}) was determined by plotting $1/2\Delta j$ (where $\Delta j = j_a - j_c$, representing the difference between anodic and cathodic current densities at 1.04 V vs. RHE) against scan rate, with the resulting slope corresponding to C_{dl} .

Zinc-Air battery tests. The catalyst and the zinc plate were used as the cathode and anode, respectively. 3 mg cm⁻² of catalyst and 50 µL Nafion were added to 1 mL isopropanol to prepare the catalyst ink. The catalyst was ultrasonically dispersed for 2 hours at 25°C. Then, the catalyst ink was sprayed onto a 1 cm² gas diffusion electrode carbon paper. After the catalyst dried, the carbon paper and the gas diffusion layer were combined to form the cathode. The electrolyte used in the test was 6 M KOH. The battery performance evaluation was conducted using the LAND test system.

Computation method. Spin-polarized DFT calculations were carried out by using the Vienna ab initio simulation package (VASP)[1] with the projector augmented wave (PAW)[2] method. The Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA)[3] was used to describe the exchange–correlation functional. The DFT-D3 method[4] was used to describe the van der Waals interactions between intermediate and catalyst. The kinetic energy cutoff was set as 450 eV and convergence thresholds of energy and atomic forces were set as 1×10⁻⁵ eV and 0.05 eV/Å, respectively. Gamma-centered 2×2×1 and 4×4×1 k-point mesh was used for the first Brillouin zone sampling to optimize geometry and calculate electronic property. A vacuum layer of 15 Å along z-axis was set to avoid interaction between neighbor unit.

Supplementary figures and tables

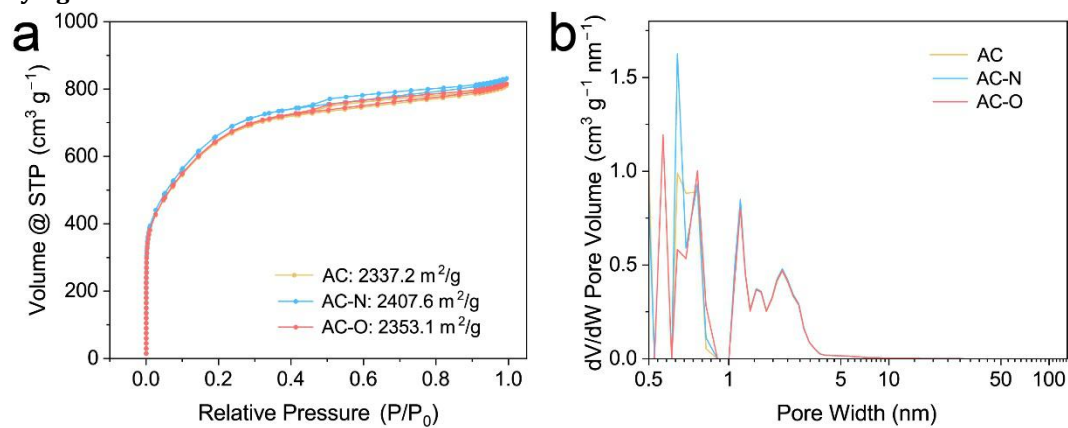


Figure S1. Nitrogen adsorption/desorption isotherms (a) and the corresponding pore size distributions (b) of AC, AC-N, and AC-O.

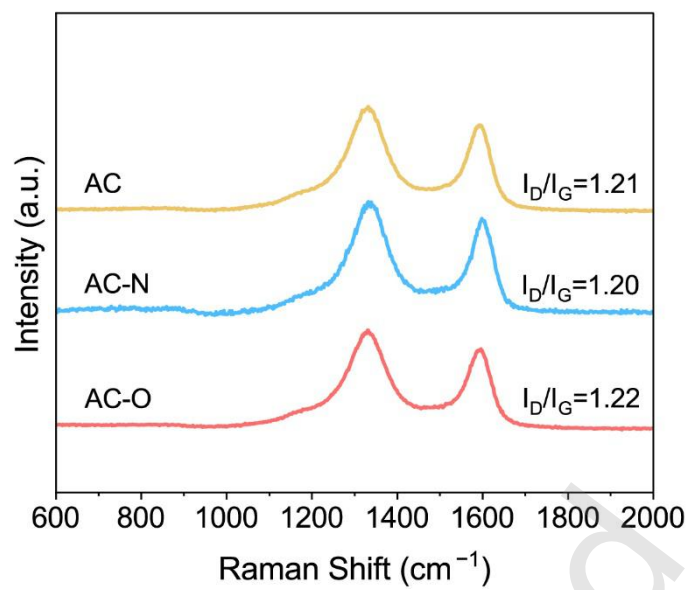


Figure S2. Raman spectra of AC, AC-N, and AC-O.

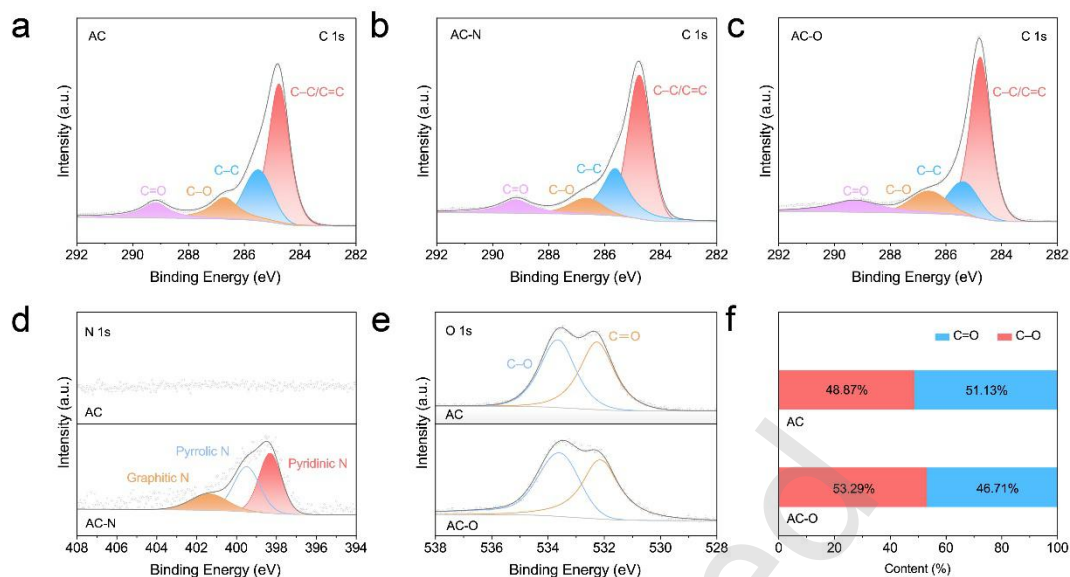


Figure S3. (a-c) High-resolution C 1s XPS data of AC (a), AC-N (b), and AC-O (c). (d) High-resolution N 1s XPS data of AC and AC-N. (e) High-resolution O 1s XPS data of AC and AC-O. (f) The distribution of O species in AC and AC-O.



Figure S4. (a-c) Contact angle measurements of AC (a), AC-N (b), and AC-O (c).

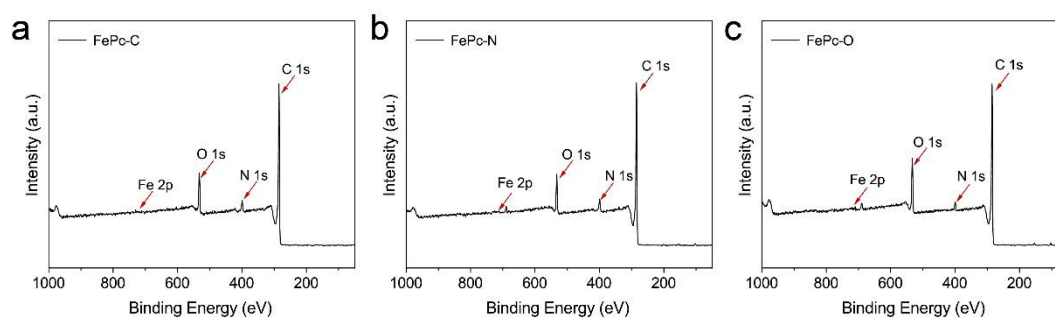


Figure S4. (a–c) X-ray photoelectron spectra of FePc-C (a), FePc-N (b), and FePc-O (c).

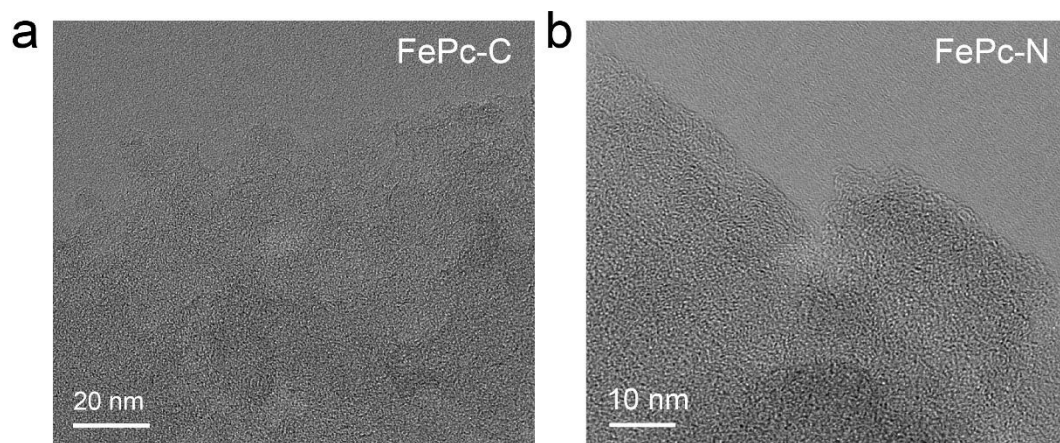


Figure S5. The HRTEM images of the FePc-C (a) and FePc-N (b) materials.

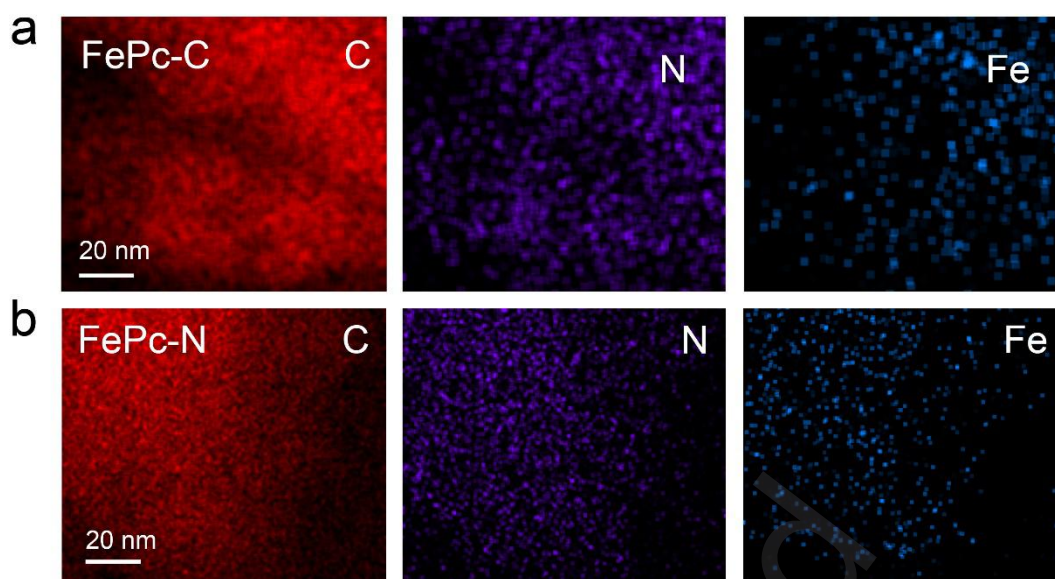


Figure S6. The EDS mapping of the (a) FePc-C and (b) FePc-N materials.

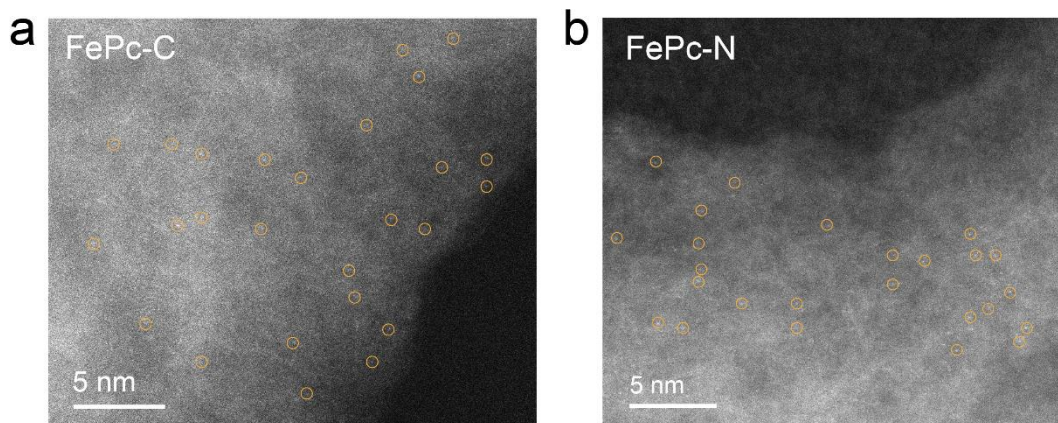


Figure S7. The HAADF-STEM images of the (a) FePc-C and (b) FePc-N materials.

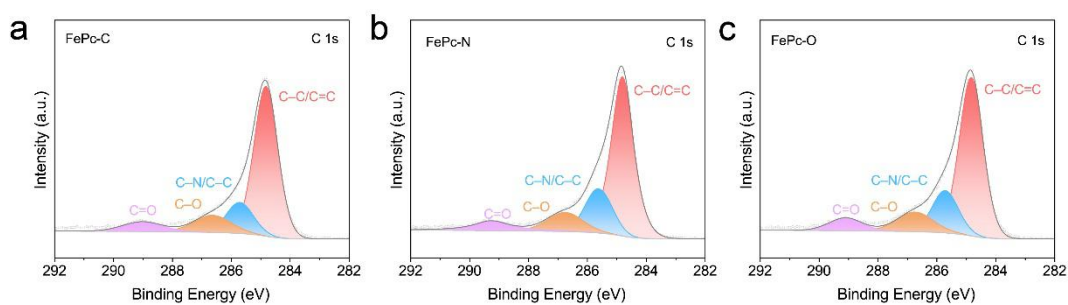


Figure S8. (a–c) High-resolution C 1s XPS data of FePc-C (a), FePc-N (b), and FePc-O (c) materials.

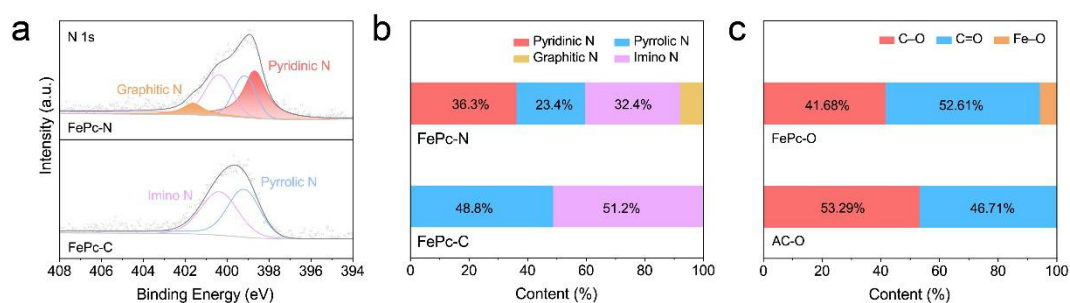


Figure S9. (a) High-resolution N 1s XPS data of FePc-C and FePc-N. (b) The distribution of N species in FePc-C and FePc-N. (c) The distribution of O species in FePc-O and AC-O.

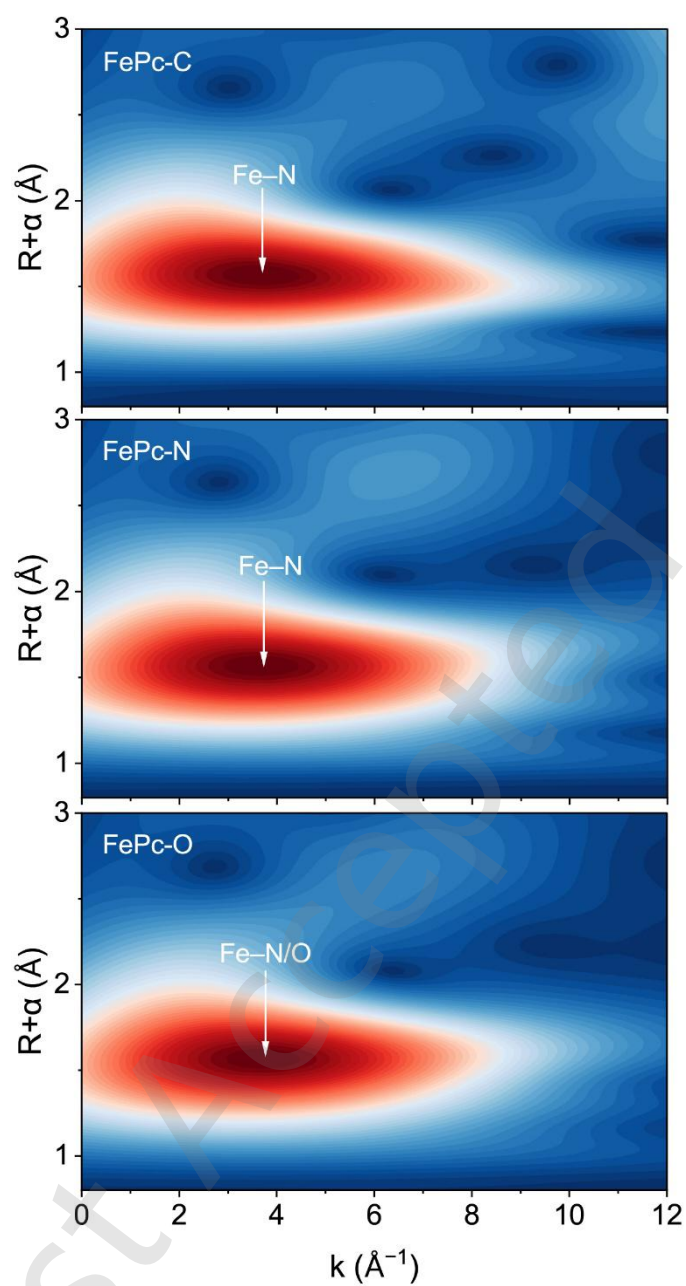


Figure S10. The WT-EXAFS of FePc-C, FePc-N, and FePc-O materials.

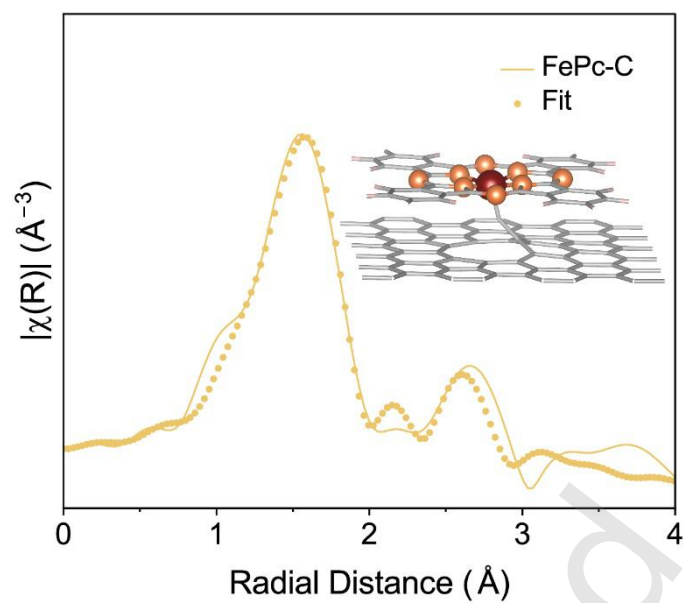


Figure S11. Fe K-edge EXAFS fitting curves of FePc-C in R-space. Insets show the corresponding fitting models.

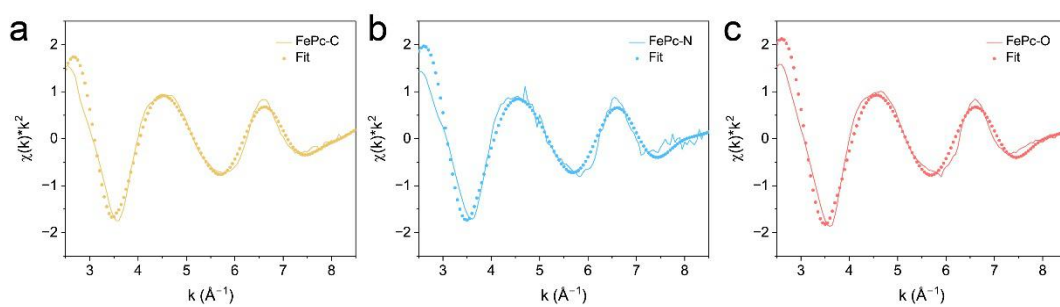


Figure S12. (a-c) Fe K-edge EXAFS fitting curves for FePc-C (a), FePc-N (b), and FePc-O (c) at K-space.

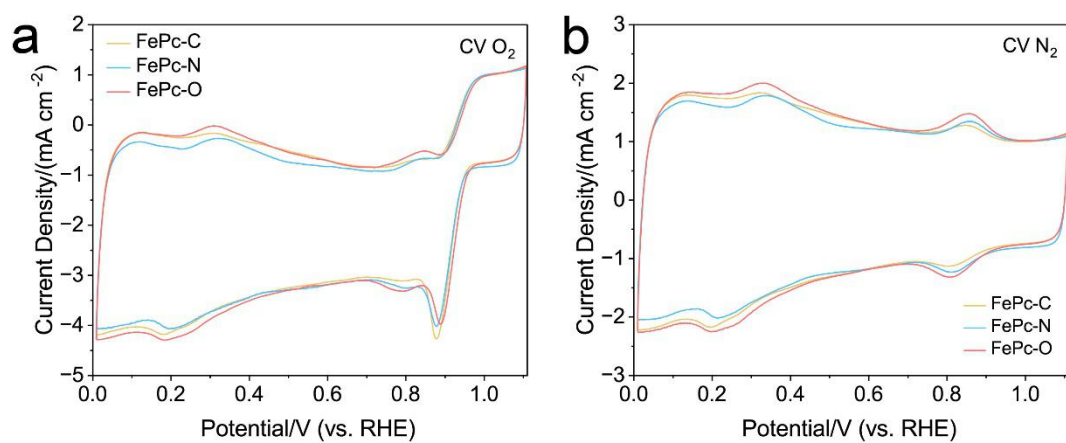


Figure S13. (a) The CV of FePc-C, FePc-N, and FePc-O catalysts under O_2 atmosphere in 0.1 M KOH solution. (b) CV of FePc-C, FePc-N, and FePc-O catalysts under N_2 atmosphere in 0.1 M KOH solution.

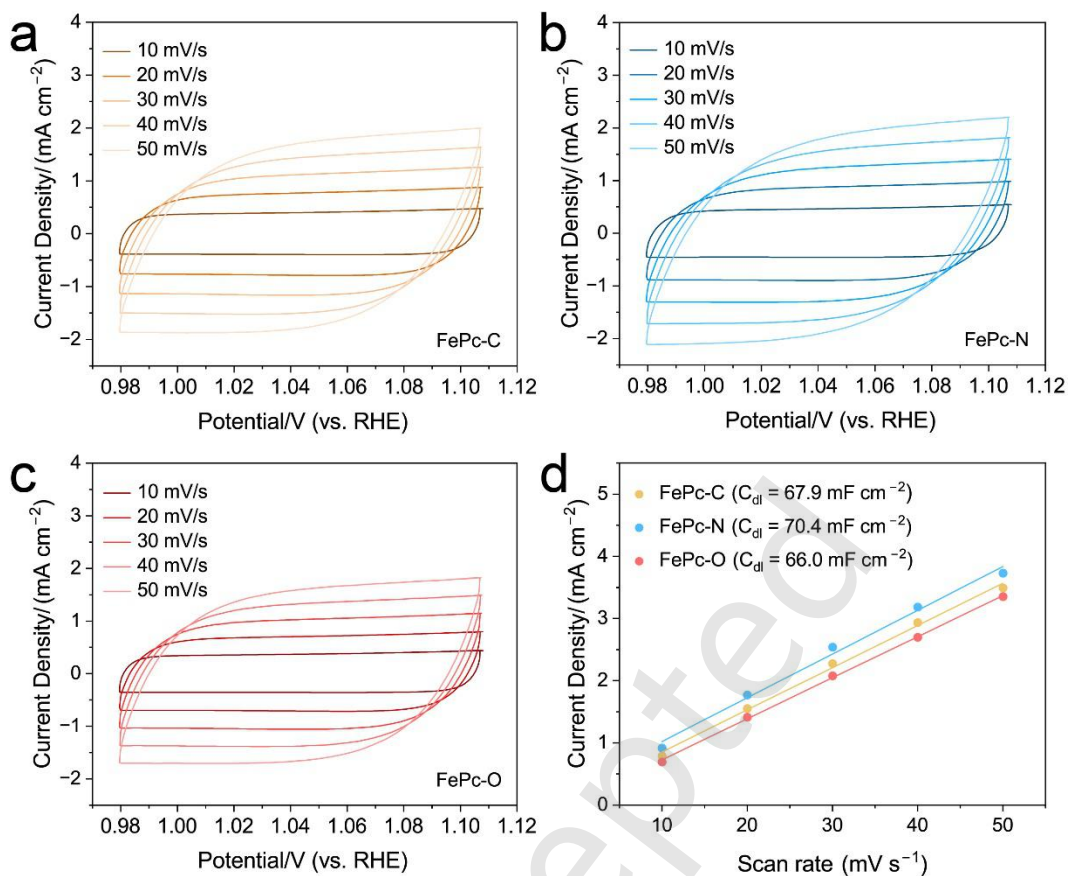


Figure S14. (a–c) CV curves of FePc-C (a), FePc-N (b), and FePc-O (c) catalysts at different scan rates from 10 to 50 mV s^{-1} in the potential range from 0.98 V to 1.11 V (vs. RHE) in 0.1 M KOH solution. (d) Calculated C_{dl} at 1.04 V (vs. RHE) of FePc-C, FePc-N, and FePc-O catalysts.

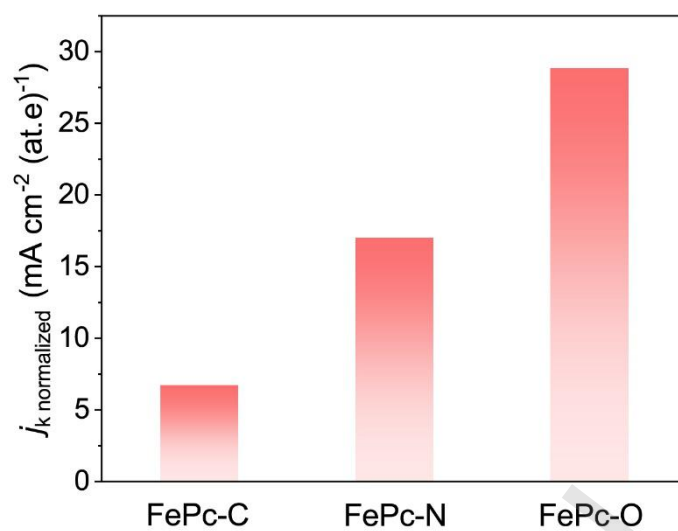


Figure S15. j_k at 0.90 V after normalization of FePc-C, FePc-N, and FePc-O.

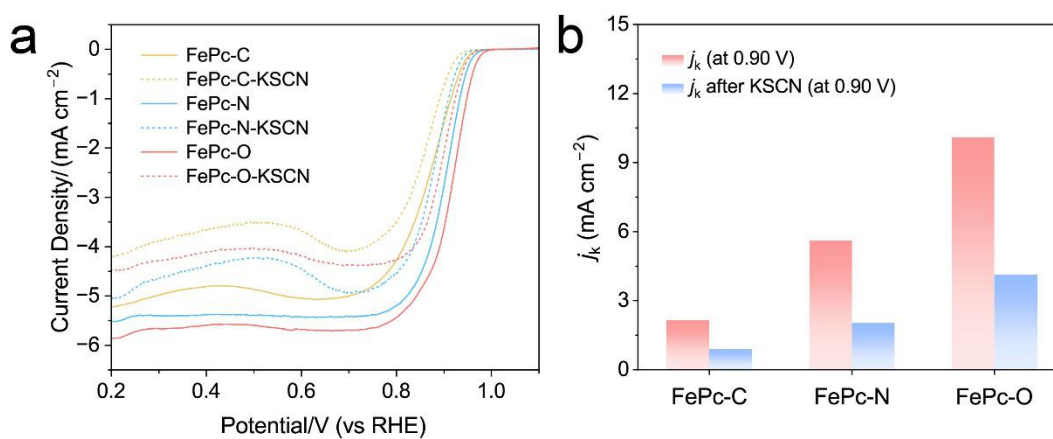


Figure S16. (a) Linear sweep voltammetry curves of the FePc-C, FePc-N, and FePc-O before and after KSCN poisoning. (b) j_k at 0.90 V for FePc-C, FePc-N, and FePc-O before and after KSCN poisoning.

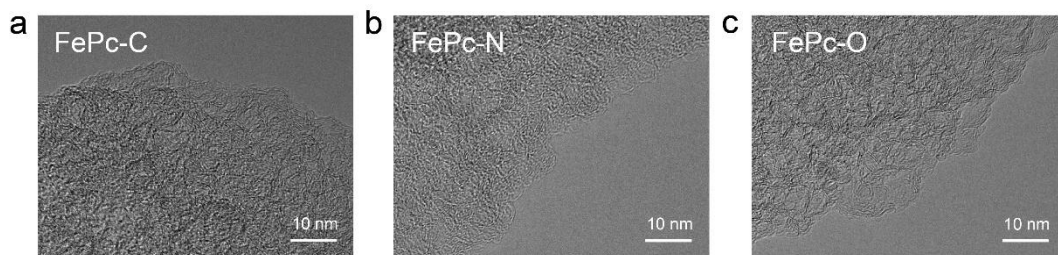


Figure S17. The HRTEM images of the FePc-C (a), FePc-N (b), and FePc-O (c) materials.

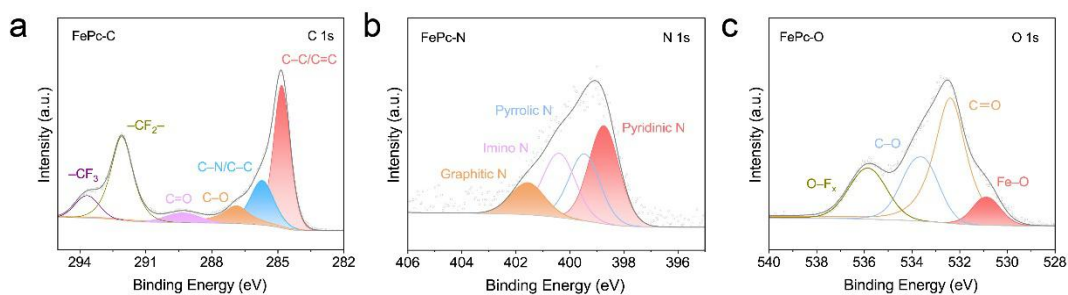


Figure S18. (a) High-resolution C 1s XPS data of FePc-C. (b) High-resolution N 1s XPS data of FePc-N. (c) High-resolution O 1s XPS data of FePc-O.

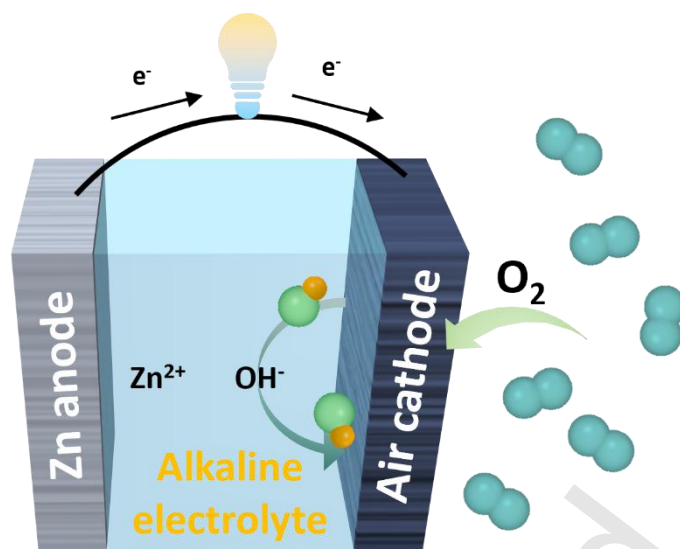


Figure S19. The schematic illustration of a Zn-air battery.

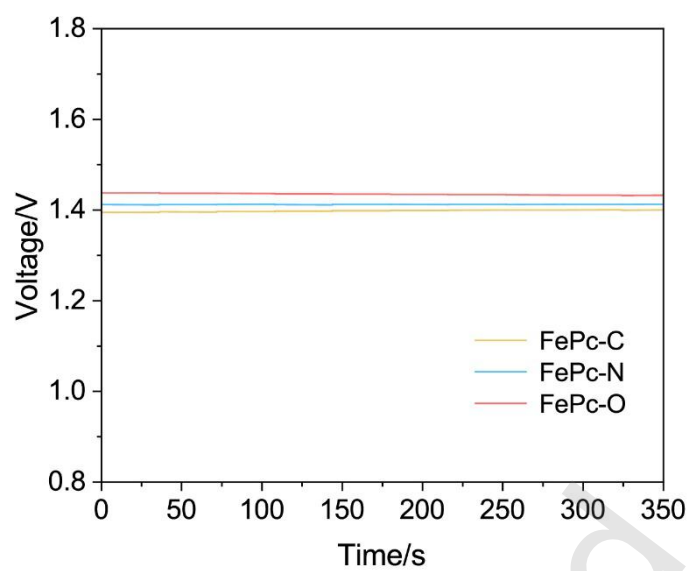


Figure S20. The OCP of the FePc-C, FePc-N, and FePc-O catalysts in Zn-air batteries.

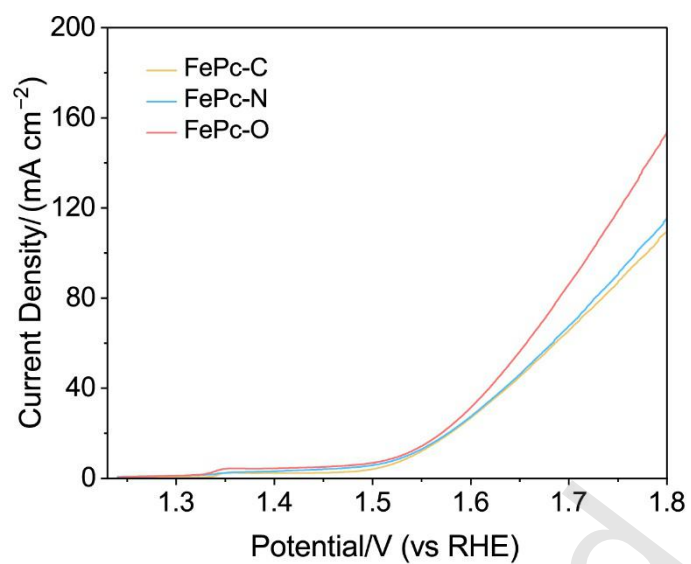


Figure S21. The Linear sweep voltammetry curves of the FePc-C, FePc-N, and FePc-O catalysts in 0.1 M KOH.

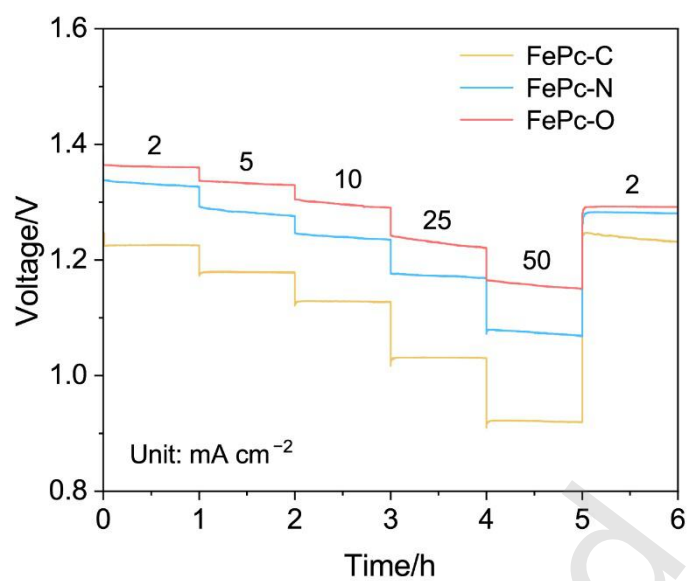


Figure S22. Galvanostatic discharge curves of ZABs with FePc-C, FePc-N, and FePc-O catalysts at different current densities.

Table S1. Element analysis of FePc-C, FePc-N, and FePc-O based on C 1s XPS characterizations.

Sample	C 1s (at.%)	N 1s (at.%)	O 1s (at.%)	Fe 2p (at.%)
FePc-C	84.78	4.43	10.47	0.32
FePc-N	88.16	5.80	5.71	0.33
FePc-O	84.46	2.92	12.27	0.35

Table S2. Fitting parameters of the EXAFS refinement. (CN: coordination number; R: distance; σ^2 : mean-square disorder; E_0 : energy shift). The single number in the bracket for R, σ^2 , and E_0 is the last digit error. The numbers in parentheses for CN are the full errors.

Sample	Edge	Scattering Path	CN	R (Å)	σ^2 (Å ²)	E ₀ (eV)	R Factor
FePc-C	Fe K	Fe-C	1.1	1.49 (9)	0.005	13.6 (1.9)	0.015
		Fe-N	3.8	2.01 (1)	0.006		
		Fe-N-C	2.9	3.01 (4)	0.001		
FePc-N		Fe-N1	1.2	1.87 (1)	0.001	13.6 (1.9)	0.017
		Fe-N2	3.9	2.01 (2)	0.006		
		Fe-N-C	8.9	2.97 (4)	0.001		
FePc-O		Fe-N	4.1	2.01 (3)	0.007	13.8 (3.0)	0.020
		Fe-O	0.9	1.80 (2)	0.002		
		Fe-N-C	0.6	2.97 (5)	0.001		

Table S3. Comparison of the ORR catalytic performance of various reported axial coordination FePc catalysts in a rotating ring-disk electrode in 0.1 M KOH solution.

Catalysts	$E_{1/2}$ (V vs. RHE)	Refs.
FePc- $\{PW_{12}\}$ /NT	0.90	<i>Angew. Chem. Int. Ed.</i> 2023[5]
FePc/DG	0.90	<i>Applied Catalysis B: Environ.</i> 2021[6]
FePc@N-CNSs	0.88	<i>Nanoscale</i> 2024[7]
Ti ₄ N ₃ Cl _x /FePc	0.91	<i>Adv. Energy Mater.</i> 2025[8]
FePc-10 %Cu-ZIS	0.91	<i>Nano Energy</i> 2025[9]
FePc NTs-rGO	0.88	<i>Proc. Natl. Acad. Sci.</i> 2023[10]
CoSAC@FePc	0.904	<i>Adv. Funct. Mater.</i> 2024[11]
FePc-P/MWCNTs-A	0.902	<i>Chem. Eng. J.</i> 2022[12]
FePc@CNF	0.875	<i>Chem. Eng. J.</i> 2024[13]
<i>pf</i> SAC-Fe-0.2	0.91	<i>Sci. Adv.</i> 2019[14]
FePc-N	0.901	This Work
FePc-O	0.916	This Work

References

- [1] Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* **1993**, *47*, 558–561.
- [2] Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953–17979.
- [3] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [4] Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- [5] Zhu, S.; Ding, L. T.; Zhang, X. H.; Wang, K.; Wang, X.; Yang, F.; Han, G. Y. Biaxially-Strained Phthalocyanine at Polyoxometalate@Carbon Nanotube Heterostructure Boosts Oxygen Reduction Catalysis. *Angewandte Chemie-International Edition* **2023**, *62*.
- [6] Yu, X. Z.; Lai, S. J.; Xin, S. S.; Chen, S.; Zhang, X. L.; She, X. L.; Zhan, T. R.; Zhao, X. L.; Yang, D. J. Coupling of iron phthalocyanine at carbon defect site via π - π stacking for enhanced oxygen reduction reaction. *Applied Catalysis B-Environment and Energy* **2021**, *280*.
- [7] Zhang, X. L.; Zheng, R.; Chang, Q. F.; Ma, Z. J.; Yang, Z. X. Regulating the frontier orbital of iron phthalocyanine with nitrogen doped carbon nanosheets for improving oxygen reduction activity. *Nanoscale* **2024**, *16*, 8036–8045.
- [8] Zhang, S. R.; Han, Y. T.; Zhang, R.; Zhang, Z. Y.; Sun, G. B. Regulating Fe Intermediate Spin States via FeN-Cl-Ti Structure for Enhanced Oxygen Reduction. *Adv. Energy Mater.* **2025**, *15*.
- [9] Dong, X.; Tao, S.; Wang, G.; Chen, J.; Wang, R.; Zhang, J. Microenvironment regulation of asymmetric Fe coordination centers through designing p-n junction toward highly efficient oxygen reduction for rechargeable zinc-air batteries. *Nano Energy* **2025**, *134*.
- [10] Win, P. E. P.; Yang, J.; Ning, S.; Huang, X.; Fu, G.; Sun, Q.; Xia, X.-H.; Wang, J. Molecular architectures of iron complexes for oxygen reduction catalysis—Activity enhancement by hydroxide ions coupling. *Proceedings of the National Academy of Sciences* **2024**, *121*.
- [11] Xie, P. F.; Zhong, H.; Fang, L.; Lyu, Z.; Yu, W. J.; Li, T.; Lee, J.; Shin, H.; Beckman, S. P.; Lin, Y.; Ding, S.; Kim, I. D.; Li, J. C. Molecular Fe–N₄ Moieties Coupled with Atomic Co–N₄ Sites Toward Improved Oxygen Reduction Performance. *Adv. Funct. Mater.* **2024**, *34*.
- [12] Mei, Z.-y.; Cai, S.; Zhao, G.; Zou, X.; Fu, Y.; Jiang, J.; An, Q.; Li, M.; Liu, T.; Guo, H. Boosting the ORR active and Zn-air battery performance through ameliorating the coordination environment of iron phthalocyanine. *Chem. Eng. J.* **2022**, *430*.
- [13] Wu, Y.; Liu, J.; Sun, Q. H.; Chen, J. L.; Zhu, X. G.; Abazari, R.; Qian, J. J. Molecular catalyst of Fe phthalocyanine loaded into In-based MOF-derived defective carbon nanoflowers for oxygen reduction. *Chem. Eng. J.* **2024**, *483*.
- [14] Peng, P.; Shi, L.; Huo, F.; Mi, C.; Wu, X.; Zhang, S.; Xiang, Z. A pyrolysis-free path toward superiorly catalytic nitrogen-coordinated single atom. *Science Advances* **2019**, *5*.