

Preview

Constructing single-atom Fe sites into defective carbon for efficient oxygen reduction

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Achieving highly efficient oxygen reduction reaction (ORR) catalysts to replace Pt-based materials remains a significant challenge. In the June issue of *Chem Catalysis*, Prof. Wang's group reported a single-atom Fe-carbon catalysis with Fe-C₅ coordination for stable and efficient oxygen electroreduction.

The ORR is an important chemical process in many energy systems, including fuel cells and metal-air batteries, which are vital for a wide range of applications from automotive technologies to renewable energy storage.¹ Currently, platinum (Pt) and Pt-group metals are the predominant choices for ORR catalysts due to their superior catalytic efficiency. However, their high cost, scarcity, and susceptibility to environmental degradation pose significant barriers to widespread adoption and sustainability.²

Given these challenges, there is a critical need for alternative catalysts that are not only cost-effective but also provide comparable or superior performance to Pt-based catalysis. Thus, researchers have increasingly turned their attention to single-atom catalysts (SACs).^{3,4} SACs provide maximum atom utilization and the potential for precise adjustment of electronic properties through careful coordination with their environment, which can result in excellent catalytic activity and selectivity.^{5,6} However, in most SACs, the coordination environment is highly complex due to the diverse nonmetal heteroatoms involved, such as C, N, and O. This complexity makes it challenging to accurately identify the exact active sites.⁷ Thus, a major challenge in the development of SACs for ORR

has been finding a way to effectively integrate active single metal sites into a well-defined structure, which can clearly delineate the active sites and maximize the catalyst's performance.^{8,9}

In this June issue of *Chem Catalysis*, Wang and his colleagues developed a SAC featuring Fe-C₅ coordination within a well-defined pentagon-rich defective carbon (PDC) structure using a chemical vapor deposition (CVD) strategy.¹⁰ This PDC serves as a robust matrix that not only supports the dispersion of single Fe atoms but also induces a favorable electronic structure due to its unique geometry. The resulting Fe-C₅ catalyst demonstrated significantly superior ORR performance compared to N-coordinated sites, and it also exhibited high mass activity and turnover frequency. This research broadens the understanding of the relationship between the atomic structure of catalysts and their performance, contributing valuable insights to the field of SACs used in ORR.¹⁰

In this work, the authors constructed a Fe-C₅ SAC that mainly involves three steps. Initially, the PDC precursor was synthesized using a hydrothermal method. This was followed by high-temperature pyrolysis to remove Zn species from the precursor, yielding

PDC samples. During this phase, a pentagon-rich carbon matrix was created through controlled pyrolysis of phenol-formaldehyde resins mixed with ZnCl₂. This step not only introduced pentagonal defects but also provided precise control over the microstructural properties of the carbon support. Finally, the samples were exposed to FeCl₃ under specific conditions, which facilitated the targeted insertion of Fe atoms at the defect sites, completing the formation of the Fe-C₅ sites (Figure 1A).¹⁰

To verify the structure and composition of the resultant Fe_{SAC}-PDC, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and synchrotron-radiation-based X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were used. As shown in Figure 1B, where numerous bright spots, highlighted with yellow circles, are evident in the HAADF-STEM image, which can be attributed to the Fe atoms. This observation confirms a homogeneous distribution of Fe atoms within the defective carbon matrix. The XANES spectra from the Fe K-edge (Figure 1C) show that the pre-edge positions of the Fe_{SAC}-PDC fall between Fe foil and iron(II) phthalocyanine (FePc), indicating Fe valence is between 0 and 2+. Fe_{SAC}-PDC's pre-edge is notably more negative than Fe_{SAC}-pyrrolic N doped carbon (PON) and Fe_{SAC}-pyridinic N doped carbon (PDN), suggesting a lower Fe oxidation state, likely due to carbon's lower electronegativity compared to nitrogen.

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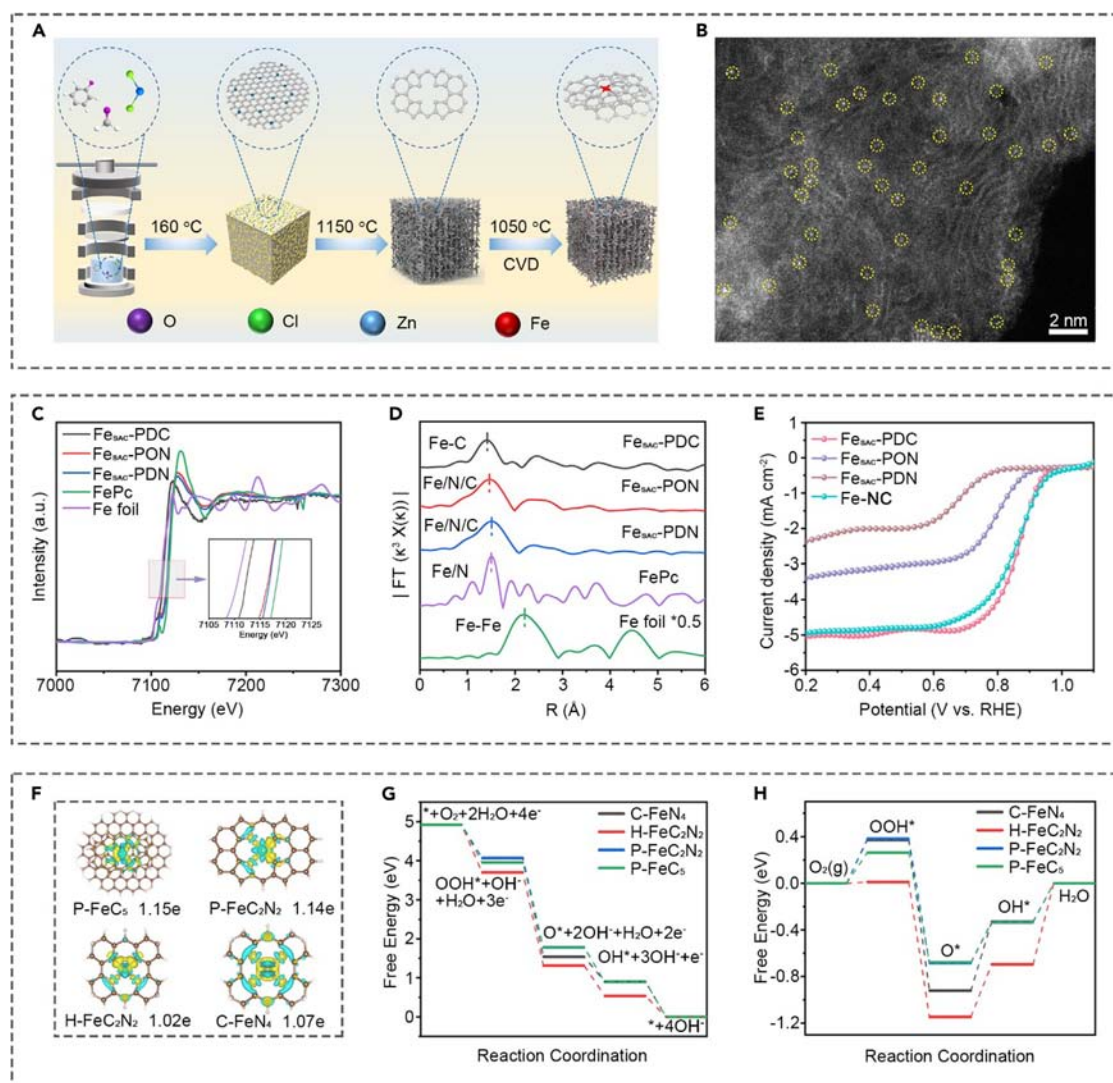


Figure 1. Schematic illustration of the syntheses of single-atom Fe-C₅ catalysis and its ORR application

(A) Schematic illustration of the preparation of FeSAC-PDC.

(B) AC-HAADF-STEM image of FeSAC-PDC.

(C) Fe K-edge XANES spectra of FeSAC-PDC, FeSAC-PON, FeSAC-PDN, FePc, and Fe foil references.

(D) k₃-weighted Fourier transform curves derived from EXAFS spectra at R space.

(E) Linear sweep voltammograms of FeSAC-PDC, FeSAC-PON, FeSAC-PDN, and Fe-NC in O₂-saturated 0.1 M potassium hydroxide.

(F) The charge density difference in the model of FeSAC-PDC, FeSAC-PON, FeSAC-PDN, and Fe-NC (the colors yellow and cyan represent the charge accumulation and depletion, respectively).

(G and H) The Gibbs free energy diagram of the 4e⁻ oxygen reduction process of different models at (G) U = 0 V and (H) U = 1.23 V is calculated.

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The EXAFS R-space plots confirm the Fe-N/C coordination sphere at ~ 1.5 Å, aligning with Fe-N distances in FePc and prior reports (Figure 1D).¹⁰

Electrochemical evaluation of the catalysts reveals that the Fe-C₅ configured sites exhibit significantly higher catalytic activity compared to N-coordi-

nated Fe sites, which have been the focus of previous studies. Figure 1E presents the polarization curves for different Fe single atomic samples. Notably, FeSAC-PDC demonstrates superior ORR activity, achieving a half-wave potential of 0.866 V vs. RHE (reference hydrogen electrode) and a limiting current density of

5.06 mA cm⁻². These results not only surpass the other samples but also match the performance of the 20% Pt/C catalyst.¹⁰

Kinetic analyses show that the Fe-C₅ sites facilitate a more favorable interaction with O, leading to enhanced ORR performance. The study also

employs density functional theory calculations to explore how different Fe coordination environments affect ORR activity and catalytic mechanisms. Four models were analyzed: P-FeC₅, P-FeN₂C₂, H-FeN₂C₂, and C-FeN₄ (Figure 1F). Charge density analyses show that the P-FeC₅ model has the highest electron transfer to the Fe center, suggesting a more effective ORR process. Gibbs free energy calculations reveal that all models exhibit spontaneous ORR reactions at 0 V, becoming endothermic at higher potentials. For most models, except C-FeN₄, the rate-determining step in the ORR process occurs during the desorption of *OH from active sites. (Figures 1G and 1H).¹⁰

In conclusion, Wang et al. introduced a single-atom Fe-carbon catalysis with Fe-C₅ coordination for stable and efficient oxygen electroreduction via pyrolysis-CVD strategy.¹⁰ The findings significantly advance the field of electrocatalysis by demonstrating a viable pathway to enhance ORR performance without relying on precious metals. The innovative approach of using pentagonally coordinated single-atomic Fe sites embedded in a defective carbon matrix not only achieves outstanding catalytic performance but

also paves the way for further advancements in the development of sustainable and efficient catalytic materials.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

- Zhang, H., Zhou, W., Chen, T., Guan, B.Y., Li, Z., and Lou, X.W.D. (2018). A modular strategy for decorating isolated cobalt atoms into multichannel carbon matrix for electrocatalytic oxygen reduction. *Energy Environ. Sci.* *11*, 1980–1984. <https://doi.org/10.1039/c8ee00901e>.
- Chinese Society of Electrochemistry (2024). The Top Ten Scientific Questions in Electrochemistry. *J. Electrochem.* *30*, 2024121. <https://doi.org/10.61558/2993-074x.3444>.
- Zhang, H., Zhou, W., Lu, X.F., Chen, T., and Lou, X.W.D. (2020). Implanting Isolated Ru Atoms into Edge-Rich Carbon Matrix for Efficient Electrocatalytic Hydrogen Evolution. *Adv. Energy Mater.* *10*, 2000882. <https://doi.org/10.1002/aenm.202000882>.
- Zhao, Q., Zhang, C., Hu, R., Du, Z., Gu, J., Cui, Y., Chen, X., Xu, W., Cheng, Z., Li, S., et al. (2021). Selective Etching Quaternary MAX Phase toward Single Atom Copper Immobilized MXene (Ti₃C₂Cl_x) for Efficient CO₂ Electroreduction to Methanol. *ACS Nano* *15*, 4927–4936. <https://doi.org/10.1021/acsnano.0c09755>.
- Zhang, D., Wang, S., Hu, R., Gu, J., Cui, Y., Li, B., Chen, W., Liu, C., Shang, J., and Yang, S. (2020). Catalytic Conversion of Polysulfides on Single Atom Zinc Implanted MXene toward High-Rate Lithium-Sulfur Batteries. *Adv. Funct. Mater.* *30*, 2002471. <https://doi.org/10.1002/adfm.202002471>.
- Gu, J., Zhu, Q., Shi, Y., Chen, H., Zhang, D., Du, Z., and Yang, S. (2020). Single Zinc Atoms Immobilized on MXene (Ti₃C₂Cl_x) Layers toward Dendrite-Free Lithium Metal Anodes. *ACS Nano* *14*, 891–898. <https://doi.org/10.1021/acsnano.9b08141>.
- Li, Y., Zuo, S., Wei, F., Chen, C., Zhang, G., Zhao, X., Wu, Z., Wang, S., Zhou, W., Rueping, M., et al. (2024). Boosted hydrogen evolution kinetics of heteroatom-doped carbons with isolated Zn as an accelerant. *Proc. Natl. Acad. Sci.* *121*, e2315362121. <https://doi.org/10.1073/pnas.2315362121>.
- Pei, Z., Zhang, H., Guo, Y., Luan, D., Gu, X., and Lou, X.W.D. (2024). Atomically Dispersed Fe Sites Regulated by Adjacent Single Co Atoms Anchored on N-P Co-Doped Carbon Structures for Highly Efficient Oxygen Reduction Reaction. *Adv. Mater.* *36*, 2306047. <https://doi.org/10.1002/adma.202306047>.
- Tian, X., Lu, X.F., Xia, B.Y., and Lou, X.W.D. (2020). Advanced Electrocatalysts for the Oxygen Reduction Reaction in Energy Conversion Technologies. *Joule* *4*, 45–68. <https://doi.org/10.1016/j.joule.2019.12.014>.
- Wang, X., Sun, H., He, T., Guo, P., Huang, R., Mao, Z., Han, C., Liu, X., Huang, M., and Wang, L. (2024). Precisely Constructing Pentagon Trapped Single-Atomic Iron Sites in Defective Carbon for Efficient Oxygen Electroreduction. *Chem Catal.* *4*, 101007.