

Strategies for enhancing catalytic performance of single-atom catalysts in 2e⁻ oxygen reduction reaction: A review

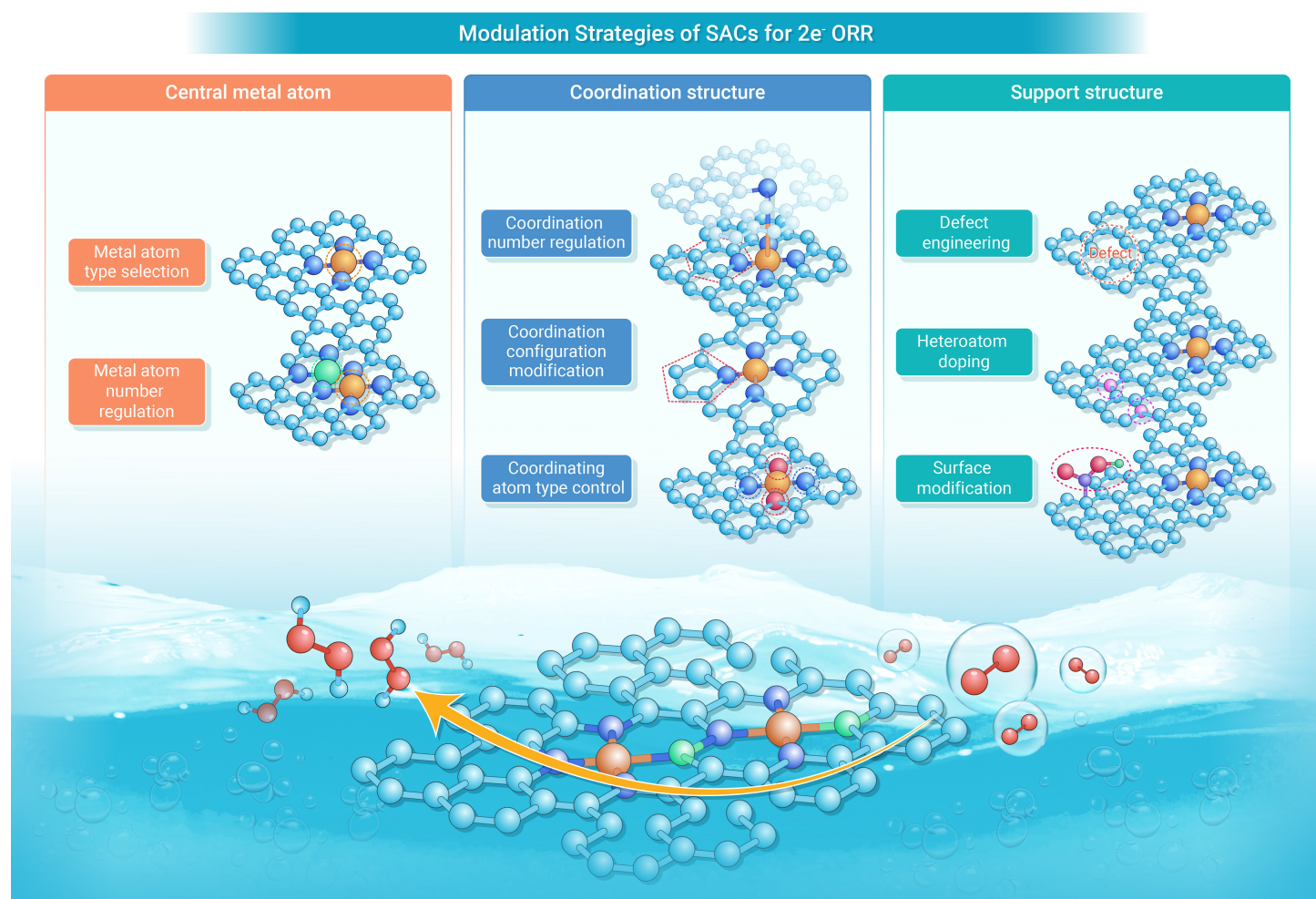
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GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- Summarizing modulation strategies of SACs (Single-Atom Catalysts) for 2e⁻ ORR (oxygen reduction reaction).
- Summarizing the reaction mechanism of 2e⁻ ORR and the recent theoretical advances in SACs' structural design.
- Identifying research gaps and future prospects of SACs for 2e⁻ ORR.

Strategies for enhancing catalytic performance of single-atom catalysts in $2e^-$ oxygen reduction reaction: A review

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The electrocatalytic two-electron oxygen reduction reaction ($2e^-$ ORR) is an effective method for synthesizing hydrogen peroxide under ambient temperature and pressure, which offers advantages such as operational safety and low cost. Single-atom catalysts (SACs) consist of individual metal atoms dispersed on a support, allowing for high structural tunability and cost-effectiveness. Notably, the unsaturated coordination environments and unique electronic structures of SACs significantly enhance their catalytic activity, while isolated active sites improve selectivity for hydrogen peroxide. Consequently, SACs have attracted considerable research interest in the field of $2e^-$ ORR in recent years, leading to significant advancements. This paper first outlines the mechanisms and pathways of the $2e^-$ ORR, as well as the structural design principles of SACs. It then summarizes modulation strategies for SACs, focusing on the selection of metal atoms, optimization of the coordination environment, and modification of the support. Furthermore, the paper discusses how these strategies influence the catalytic activity, selectivity, and stability of SACs. Finally, it highlights the limitations of SACs in $2e^-$ ORR research, including inadequate catalytic performance, insufficient mechanistic studies, and challenges in synthesis, while proposing potential solutions and future research directions.

INTRODUCTION

Hydrogen peroxide ranks among the world's top 100 most critical chemicals. Its widespread applications—including chemical synthesis, environmental remediation, and energy conversion—stem from three key characteristics: strong oxidizing capacity, environmental compatibility, and non-corrosive properties.^{1–3} In recent years, a surge in demand from industries and healthcare sectors has significantly expanded both the application scope and consumption of hydrogen peroxide. In 2022, global market sales for hydrogen peroxide reached approximately 3.9 billion U.S. dollars. Market forecasts indicate that by 2029, this figure is expected to rise to 5.26 billion U.S. dollars, highlighting the indispensable role hydrogen peroxide plays in contemporary industry and everyday life.⁴

The substantial demand for hydrogen peroxide imposes stringent requirements on its production methods. Currently, the anthraquinone process accounts for over 95% of global hydrogen peroxide production.^{5,6} Although offering established advantages—including technological maturity, high automation levels, and precise concentration control—this method presents critical limitations. Specifically, the anthraquinone process is characterized by significant energy consumption and operational complexity.^{7,8} Additionally, its centralized industrial production mode necessitates long-distance transportation of highly concentrated hydrogen peroxide (up to 70 wt%), which increases both the risk of explosion and the costs associated with transportation and storage. These high costs and safety risks ultimately limit the broader application of this production method.

To overcome the limitations of the anthraquinone process and meet industrial demand, researchers have developed alternative hydrogen peroxide synthesis methods, such as direct synthesis from hydrogen and oxygen,^{9,10} photocatalytic oxygen reduction,^{11–14} and electrocatalytic oxygen reduction.^{15,16} Among these methods, direct hydrogen-oxygen synthesis is particularly attractive because of its high reaction selectivity (>95%), environmentally friendly nature (avoiding harmful byproducts), and single-step

streamlined workflow. However, this method also presents several challenges: high explosion risk when hydrogen and oxygen are mixed, high costs and recovery difficulties associated with precious metal catalysts, and low overall reaction efficiency. These factors significantly hinder its widespread industrial application. In contrast, the photocatalytic oxygen reduction method offers notable benefits in terms of environmental sustainability and safety. However, it still faces challenges related to efficiency, stability, and reaction selectivity that need to be addressed for broader adoption.

The two-electron oxygen reduction reaction ($2e^-$ ORR) is a cathodic process converting oxygen to hydrogen peroxide (H_2O_2) in electrolytic cells. Its reaction mechanism follows: $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$. This electrochemical pathway is alternatively termed the oxygen cathodic reduction reaction. This reaction provides an effective method for ambient-condition synthesis of hydrogen peroxide (room temperature, atmospheric pressure). The distributed production mode enabled by this approach mitigates risks linked to storage and transportation, thereby substantially lowering operational costs. Additionally, this method is operationally safe and yields high-purity hydrogen peroxide, making it a promising alternative to the traditional anthraquinone process.¹⁷

Despite its advantages, certain limitations hinder the broader application of the $2e^-$ ORR. Firstly, it faces strong competition from the four-electron oxygen reduction reaction ($4e^-$ ORR), represented by the reaction: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, which produces water as the main product. The equilibrium electrode potential of the $4e^-$ ORR is 1.23 V vs. RHE at pH 0, substantially higher than that of the $2e^-$ ORR (0.68 V vs. RHE at pH 0). This thermodynamic preference for the $4e^-$ ORR over the $2e^-$ pathway consequently leads to diminished H_2O_2 selectivity. Secondly, from a kinetic perspective, the $2e^-$ ORR has a higher energy barrier compared to the $4e^-$ ORR, leading to slower reaction kinetics, which further limits its efficiency in practical applications.^{6,18}

To address the aforementioned challenges, developing catalysts that effectively enhance both reaction activity and selectivity is crucial. Specifically, achieving high catalytic activity requires catalysts that can significantly reduce the high energy barriers associated with the $2e^-$ ORR, thereby optimizing reaction kinetics. On the other hand, to achieve high product selectivity, catalysts must adsorb oxygen and intermediates with the right modes and moderate strengths to favor the desired pathway over competing reactions. Furthermore, an ideal $2e^-$ ORR catalyst should exhibit extremely low activity for the hydrogen peroxide reduction reaction (H_2O_2 RR), ensuring that the produced hydrogen peroxide remains stable over time. This dual focus on enhancing activity while maintaining selectivity is essential for the development of efficient catalysts for the $2e^-$ ORR.^{19,20}

To date, extensively studied $2e^-$ ORR catalysts include carbon-based materials,^{21–25} noble metals,^{26–28} non-noble metals,^{29–31} and single atom catalysts (SACs)^{32–36}. Carbon-based materials offer several advantages, such as abundant availability, low cost, structural tunability, and a low tendency to decompose hydrogen peroxide. However, their inherent catalytic activity is relatively limited, and they often exhibit poor stability under acidic conditions.³⁷ In contrast, noble metal-based catalysts demonstrate superior intrinsic catalytic activity and product selectivity. Nevertheless, their limited availability and high cost hinder widespread application.^{38,39} Non-noble metal materials present tunable and versatile structures, abundant resources, and cost-effectiveness, positioning them favorably for future advancements. However, their catalytic activity, product selectivity, and stability do not match

those of noble metal catalysts, resulting in a gap in fulfilling the demands of practical applications. Addressing these limitations is essential for enhancing the overall viability of non-noble metal catalysts in $2e^-$ ORR processes.³⁸

The limitations of conventional catalysts have driven the development of SACs. Previous experimental and theoretical studies suggest that continuous active sites on metal surfaces tend to favor side-on adsorption of O_2 molecules.^{40–42} This finding indicates that merely increasing the density of active sites does not guarantee enhanced catalytic performance and may, in fact, reduce selectivity for H_2O_2 . The research by Rossmeisl et al. demonstrated that changing the arrangement of surface metal atoms from continuous to isolated sites can significantly enhance product selectivity.⁴³ This finding underscores the potential of tuning the density and distribution of active sites to develop SACs with isolated active sites for hydrogen peroxide electrosynthesis.

SACs serve as an ideal platform for the $2e^-$ ORR, owing to the unique geometric confinement and electronic regulation capabilities of isolated metal sites. These features promote end-on O_2 adsorption, suppress O–O bond cleavage, and lower the reaction energy barrier, thereby steering the reaction toward the $2e^-$ pathway.^{32–36} They combine the advantages of both homogeneous and heterogeneous catalysts, with benefits including but not limited to the following aspects: (1) Superior catalytic performance: The uniform distribution of active sites, unsaturated coordination environments, and unique electronic structures contribute to high catalytic activity. Additionally, the isolated sites on SACs tend to adsorb O_2 and $*OOH$ intermediates in an end-on configuration, which enhances product selectivity. (2) Structural tunability: The strong interactions between metal atoms and the support allow for the modulation of these interactions, leading to further enhancements in catalytic activity, product selectivity, and stability. (3) Cost efficiency: SACs significantly reduce overall catalyst costs by minimizing metal usage and improving atomic utilization efficiency. Recent researches have extensively studied various SACs based on noble and transition metals,^{33–36} confirming their advantages in the $2e^-$ ORR through both theoretical and experimental approaches. Current research efforts are focused on enhancing catalytic performance, exploring novel synthesis methods, and uncovering the underlying catalytic mechanisms. Additionally, scaling up production and reducing costs are key goals to enhance the feasibility of SACs for industrial applications.

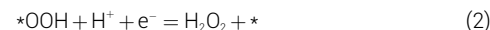
To advance the performance of SACs to the high standards required for industrial production—specifically in terms of activity, selectivity, and stability—researchers have implemented various strategies and achieved significant progress. Although previous reviews have outlined the progress of SACs in the $2e^-$ ORR field,^{19,20,44–51} they often focus on specific aspects or individual strategies, lacking a comprehensive discussion on structural regulation mechanisms. Specifically, there is a notable absence of in-depth analysis on how different strategies impact the structure-performance relationship. To bridge this gap, this paper offers an in-depth review of structural regulation strategies for SACs. It begins by elucidating the reaction mechanisms and pathways for the $2e^-$ ORR, followed by a summary of the latest theoretical advancements in the structural design of SACs. The core focus of the review is on structural regulation strategies, including the selection of metal atoms, optimization of coordination structures, and modification of support materials. It examines how these strategies influence catalytic performance, explores their advantages, challenges, and potential applications. Additionally, it identifies the existing gaps in SACs research for the $2e^-$ ORR and proposes potential directions for future investigation.

REACTION MECHANISM OF THE $2e^-$ ORR

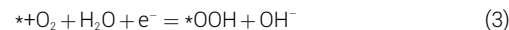
Reaction steps and mechanisms

The $2e^-$ ORR involves a two-step proton-coupled electron transfer process. The specific sequence is as follows: First, an O_2 molecule adsorbs onto the catalyst surface, where it combines with one proton and one electron to form the $*OOH$ intermediate. This intermediate then accepts another electron and proton, producing either H_2O_2 or HO_2^- , which is eventually desorbed from the catalyst surface. Below are the reaction equations for acidic, alkaline, and neutral conditions, respectively.^{8,52}

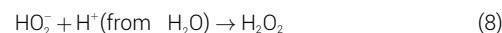
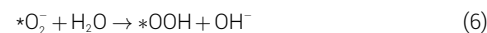
In acidic electrolytes:



In alkaline electrolytes:



In neutral electrolytes:



Key factors of the reaction pathway

Since the $4e^-$ ORR has a higher equilibrium electrode potential (1.23 V vs. RHE, pH = 0) compared to the $2e^-$ ORR (0.68 V vs. RHE, pH = 0),⁵³ it is thermodynamically more favorable.^{6,8,18} Therefore, to achieve efficient H_2O_2 production, catalysts must exhibit high selectivity toward the $2e^-$ ORR to suppress the competing $4e^-$ ORR pathway. The adsorption modes of O_2 are critical factors determining the selectivity. As shown in Figure 1A, the adsorption modes of oxygen on the catalyst include two types: end-on adsorption (Pauling mode) and side-on adsorption (Yeager mode and Griffiths mode). In the Pauling mode, O_2 is adsorbed onto the active site in an end-on configuration, which helps maintain the integrity of the O–O bond. Subsequently, O_2 gains a proton and an electron to form the $*OOH$ intermediate, ultimately leading to the generation of H_2O_2 or HO_2^- , thus facilitating the $2e^-$ ORR, as illustrated in Figure 1B. In contrast, in the Yeager and Griffiths modes, O_2 is adsorbed in a side-on configuration, which tends to activate the O–O bond, promoting the dissociation of $*OOH$ to form $*O$, and ultimately leading to the $4e^-$ ORR. Side-on adsorbed O_2 can react through two pathways: one involves direct O–O bond cleavage after adsorption, generating $*O$, which then combines with protons and electrons to form water; the other involves the formation of the $*OOH$ intermediate first, followed by O–O bond cleavage to form $*O$ and $*OH$, which subsequently combine with protons and electrons to produce water, as shown in Figure 1C. Therefore, the adsorption mode of the oxygen molecule significantly influences the reaction pathway of the ORR. The distribution of active sites on the catalyst surface is a key factor determining the adsorption mode. Isolated active sites favor end-on adsorption, while adjacent active sites tend to favor side-on adsorption.

Additionally, the selectivity of the $2e^-$ ORR is closely related to the catalyst's ability to adsorb the $*OOH$ intermediate. If the adsorption is too weak ($\Delta G(*OOH) < 4.0$ eV), it becomes difficult to bind and activate O_2 ; if the adsorption is too strong ($\Delta G(*OOH) > 4.5$ eV), it leads to O–O bond cleavage. Only a moderate binding energy ($\Delta G(*OOH) \approx 4.2$ eV) is conducive to the $2e^-$ ORR.⁵¹

Furthermore, according to the Sabatier principle, the linear relationship between the adsorption of different intermediates on the catalyst also limits the reaction selectivity.⁵⁴ The $2e^-$ ORR involves the $*OOH$ intermediate, while the $4e^-$ ORR involves intermediates such as $*OOH$, $*O$, and $*OH$. The adsorption linear relationship indicates that while strengthening $*OOH$ adsorption enhances $2e^-$ ORR activity, it concurrently intensifies O and OH adsorption, thereby promoting H_2O formation and compromising selectivity.

In summary, to promote the occurrence of the $2e^-$ ORR, a catalyst with both high selectivity and high activity is required. For high selectivity, the catalyst should adsorb oxygen in an appropriate mode. End-on adsorption is more favorable than side-on adsorption for maintaining the integrity of the O–O bond. Moreover, the catalyst should have a moderate adsorption energy for the $*OOH$ intermediate, facilitating both adsorption and desorption. An ideal catalyst should be able to break the linear relationship of intermediate

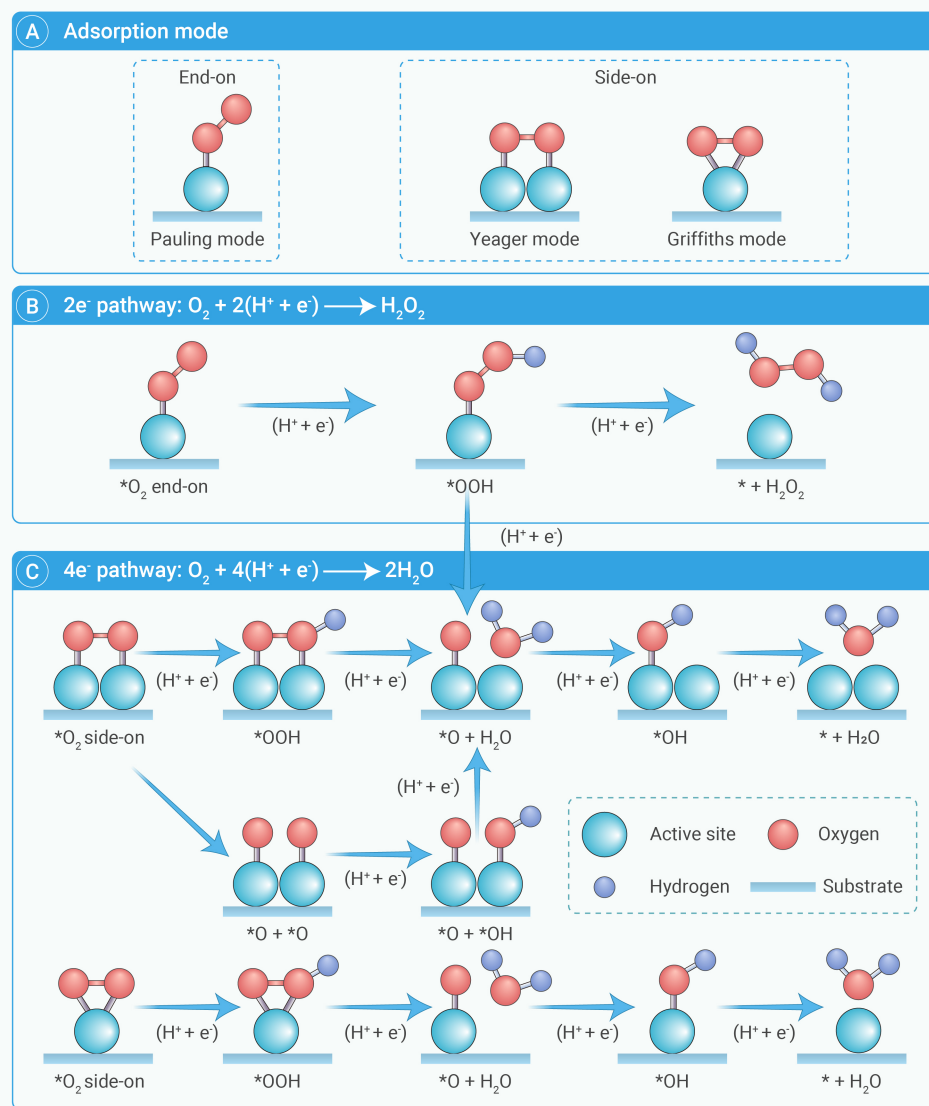
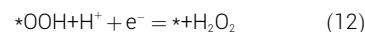
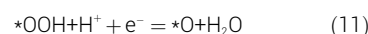
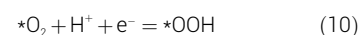


Figure 1. The oxygen adsorption modes at the active sites and the ORR reaction pathways (A) Two modes of oxygen adsorption on metal active sites; (B) and (C) ORR process via two- and four-electron pathways in acidic media.

which results in lower energy barriers for O_2 adsorption and $*OOH$ desorption, while raising the barrier for the dissociation of $*OOH$ into $*O$ and $*OH$. These characteristics enhance the $2e^-$ ORR pathway while suppressing the competing $4e^-$ ORR.⁵⁵ The binding energy and reaction barriers are determined primarily by the electronic structure of the active sites, making the rational design and optimization of these sites critical for improving catalytic performance.



CLASSIFICATION OF SACs

SACs for the $2e^-$ ORR are primarily categorized into two groups: noble metal-based and non-noble metal-based SACs, as shown in Figure 2.

Noble metal-based SACs

In recent years, noble metal-based catalysts (e.g., Pt, Pd, and Au) have emerged as a research hotspot for the $2e^-$ ORR process.^{28,56–58} Compared to non-noble metal alternatives, these materials exhibit superior intrinsic catalytic activity. This enhanced performance

adsorption to achieve the highest selectivity. For high activity, the catalyst should be designed to lower the reaction energy barrier, thereby accelerating the reaction kinetics.

Catalytic mechanism of SACs

Among various catalysts, SACs have emerged as ideal candidates for promoting the $2e^-$ ORR due to their unique structural advantages, particularly the presence of isolated active sites that favor the end-on adsorption of O_2 molecules. Additionally, SACs possess a complex and tunable electronic structure, which facilitates the enhancement of adsorption of different intermediates and breaks the linear relationship of adsorption. The reaction process begins with O_2 adsorption on the active site in an end-on mode, where it combines with one electron and one proton to form the $*OOH$ intermediate, as depicted in reactions (9) and (10) under acidic conditions. From this point, two reaction pathways are possible: (1) The O–O bond in $*OOH$ is cleaved, allowing further combination with an electron and a proton to form H_2O (reaction equation (11)); or (2) the $*OOH$ intermediate reacts with another electron and proton, producing H_2O_2 (reaction equation (12)). The efficiency of these reactions is highly dependent on the adsorption strength at the active site. Too strong adsorption facilitates the cleavage of the O–O bond in $*OOH$, driving the reaction toward H_2O formation, while too weak adsorption hinders O_2 adsorption, reducing overall catalytic efficiency. Thus, only moderate adsorption strength ensures that O_2 adsorbs efficiently while maintaining the integrity of the O–O bond to favor the $2e^-$ ORR.⁴⁸ From a kinetic perspective, an ideal catalyst exhibits moderate binding energy for the $*OOH$ intermediate,

primarily arises from their unique d-band electronic structure, which facilitates efficient charge transfer and accelerates reaction kinetics. Furthermore, their inherent advantages—including high-temperature stability, oxidation resistance, and corrosion durability—make them particularly attractive for electrochemical applications.⁵⁹ However, the intrinsically high catalytic activity of noble metals favors the $4e^-$ pathway, while dispersing them as single atoms can effectively moderate their reactivity, thereby optimizing their performance for selective $2e^-$ ORR. Currently, the most widely studied noble metal-based SACs predominantly feature Pt^{56,60–63} and Pd,^{27,28,57,58,64} which are typically anchored on substrates such as inert metals^{26,27,60,64} carbon-based materials,^{61,62} and metal compounds.⁶³

The use of inert metals (such as Au, Hg, and Ti)^{27,60,64} enables the efficient dispersion of active noble metals (such as Pt and Pd), thereby constructing SACs. Density functional theory (DFT) calculations indicate that on the surfaces of these noble metal SACs, the energy barrier required for the decomposition of $*OOH$ into $*O$ and $*OH$ is relatively high, effectively suppressing the $4e^-$ ORR pathway. For example, Jirkovský et al. prepared Au–Pd SACs, and both theoretical calculations and experimental tests demonstrated that Au-coated Pd SACs with 8% molar Pd concentration significantly enhanced the selectivity for H_2O_2 production, reaching nearly 95%.²⁷ This is attributed to the isolated active sites promoting end-on adsorption of O_2 , thereby avoiding O–O bond cleavage and the subsequent $4e^-$ ORR process.

Meanwhile, carbon-based supports have also become a popular substrate material for constructing noble metal single-atom catalysts due to their low

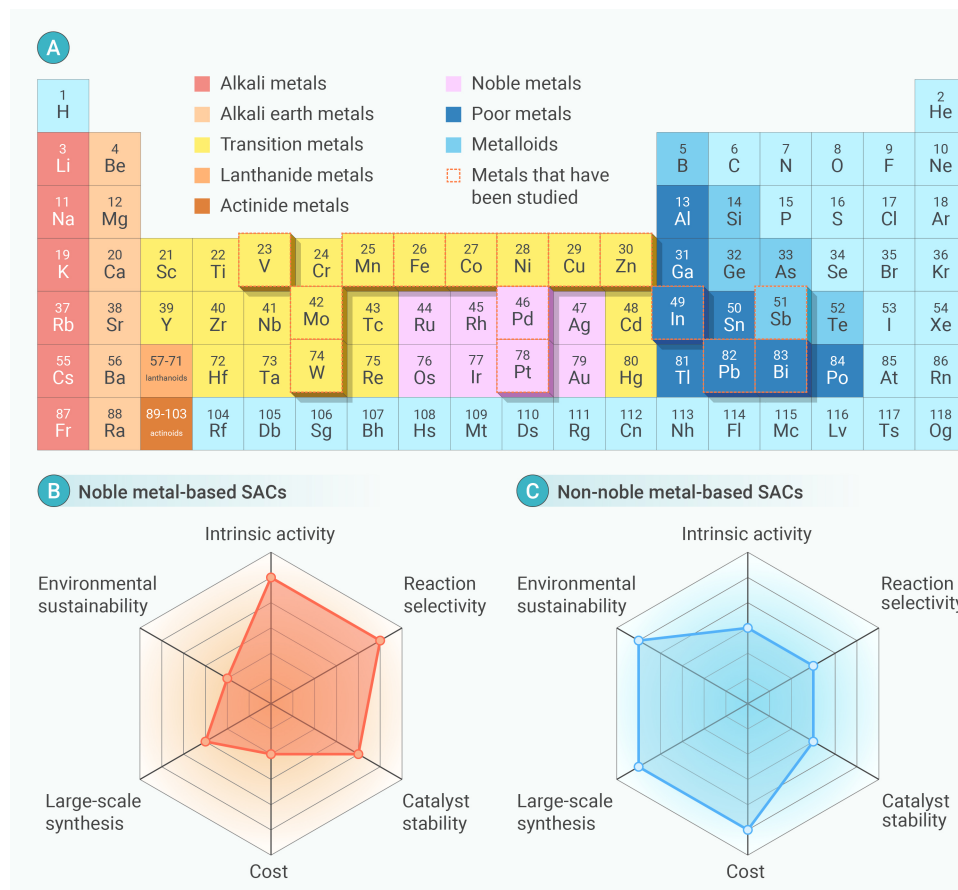


Figure 2. Types of SACs studied for $2e^-$ ORR and performance comparison of noble vs. non-noble metal SACs via radar chart analysis (A) Types of SACs studied for $2e^-$ ORR; (B) Radar Chart for Performance Comparison of Noble metal-based SACs; (C) Radar Chart for Performance Comparison of Non-noble metal-based SACs.

Among the various transition metals, SACs based on Co,⁶⁵⁻⁷⁷ Fe,⁷⁸ Mn,⁷⁹ Ni,^{80,81} and Cu⁸² have been extensively explored. Notably, Co-based SACs have garnered the most attention. Both theoretical calculations and experimental studies have demonstrated that Co single atoms exhibit outstanding $2e^-$ ORR activity and selectivity under specific coordination environments.⁶⁵⁻⁶⁹ Reported Co-based catalysts encompass a wide range of coordination configurations and support types, including single-atom systems (such as Co-N-C,⁶⁶ Co_{SA}-N-CNTs,⁷⁰ Co-N₅C,⁷¹ Co HSACs,⁷² and Co-N₂-C/HO⁷³) and dual-atom systems (such as Co₂-DAC,⁷⁴ Co₂N-C,⁷⁵ CoZn_{SA}@CNTs,⁷⁶ and Co_x-Ni MAC⁷⁷). These studies provide a wealth of structural design paradigms for optimizing the performance of Co-based catalysts.

Additionally, metals such as Mo,⁷⁹ W,⁸⁶ and V⁸⁷ as well as metalloid- and poor metal-based catalysts, are gradually gaining research attention. For example, Yan et al. successfully synthesized a high-density antimony single-atom catalyst (Sb-NSCF) supported on N,S-co-

cost, excellent conductivity, high stability, and abundant defect sites. For instance, Zhao et al. synthesized a series of carbon-based Pt single-atom catalysts and systematically investigated the influence of the local coordination environment on the ORR pathway.⁶¹ The study found that modifying the coordination environment of Pt from Pt-C to Pt-N-C and Pt-S-C promoted the occurrence of $2e^-$ ORR, increasing the selectivity for hydrogen peroxide from 23.3% to 81.4%.

Anchoring noble metal atoms on metal compound substrates and modulating the electronic structure of the noble metals by precisely tuning the composition and structure of these substrates has become another important research focus. Yang et al. compared the regulatory effects of TiC and TiN as substrates on the performance of Pt single-atom catalysts.⁶³ Both experimental results and DFT calculations demonstrated that Pt₁/TiC exhibited exothermic processes in all reaction steps, along with higher selectivity for the $2e^-$ ORR pathway. In contrast, TiN tended to induce O-O bond cleavage due to its strong interaction with oxygen-containing species. This highlights the importance of selecting appropriate substrates for developing efficient noble metal-based single-atom catalysts to achieve targeted electrochemical reactions.

Although noble metal-based SACs demonstrate high intrinsic activity and tunable selectivity toward the $2e^-$ ORR pathway via coordination engineering, their practical deployment faces significant barriers due to the high cost of noble metals, complex preparation processes, and environmental impacts associated with their extraction.⁴⁸

Non-noble metal-based SACs

Compared to precious metal materials, non-noble metal materials are highly favored due to their abundance and low cost. Moreover, their SACs exhibit excellent tunability in composition and structure, making them as a highly promising option among materials for $2e^-$ ORR electrocatalysts.⁴⁸ Currently, non-noble metal SACs in the field of $2e^-$ ORR primarily include transition metal-based SACs,⁶⁵⁻⁸² poor metal-based SACs (such as Pb-N-C⁸³ and Bi-N-C⁸⁴), and metalloid-based SACs (such as Sb-N-C⁸⁵). Among these, transition metal systems are the primary focus of research.

doped carbon nanofibers using nanostructured Sb₂S₃ as a template.⁸⁵ This catalyst demonstrated high selectivity of 97.2% and exceptional mass activity of 114.9 A g⁻¹ at 0.65 V in alkaline media. DFT calculations further revealed that the synergistic effect of the coordination configuration and S doping significantly enhanced the $2e^-$ ORR catalytic performance of the Sb-N₄ sites.

In summary, non-noble metal-based SACs have become a research hotspot in the field of $2e^-$ ORR due to their wide availability, low cost, environmental friendliness, and flexible structural design. However, compared to noble metals, non-noble metals generally exhibit lower intrinsic catalytic activity, often requiring precise structural modulation or ligand modification to enhance their performance. Moreover, under practical reaction conditions, non-noble metal single atoms are prone to aggregation or leaching, leading to reduced catalytic activity and compromised stability, which limits their further application to some extent.⁴⁸

To comprehensively evaluate the catalytic performance of noble metal-based and non-noble metal-based SACs, we systematically scored and compared multiple key metrics and visualized their overall performance using radar charts (as shown in Figures 2B-C). This provides an intuitive representation of their comparative advantages and limitations.

PROGRESS IN THEORETICAL RESEARCH ON SACs FOR THE $2e^-$ ORR

Previous research has shown that isolated metal atoms are typically the active sites of SACs.⁸⁸ Therefore, selecting appropriate metal atoms is the most direct and effective approach to modulating the intrinsic catalytic activity of SACs. Additionally, the coordination structure of SACs can significantly influence their catalytic performance.⁸ Thus, the rational design and screening of metal atoms and their coordination structures are key to achieving superior performance. Besides experimental methods, theoretical calculations can predict and screen suitable SACs structures, significantly saving researchers time and effort while providing clear guidance for subsequent experimental studies. To date, various theoretical calculation methods based on DFT and molecular dynamics have been successfully developed and applied to model SACs. These methods enable the prediction of reaction pathways, rate-determining steps, and other mechanistic details in electro-

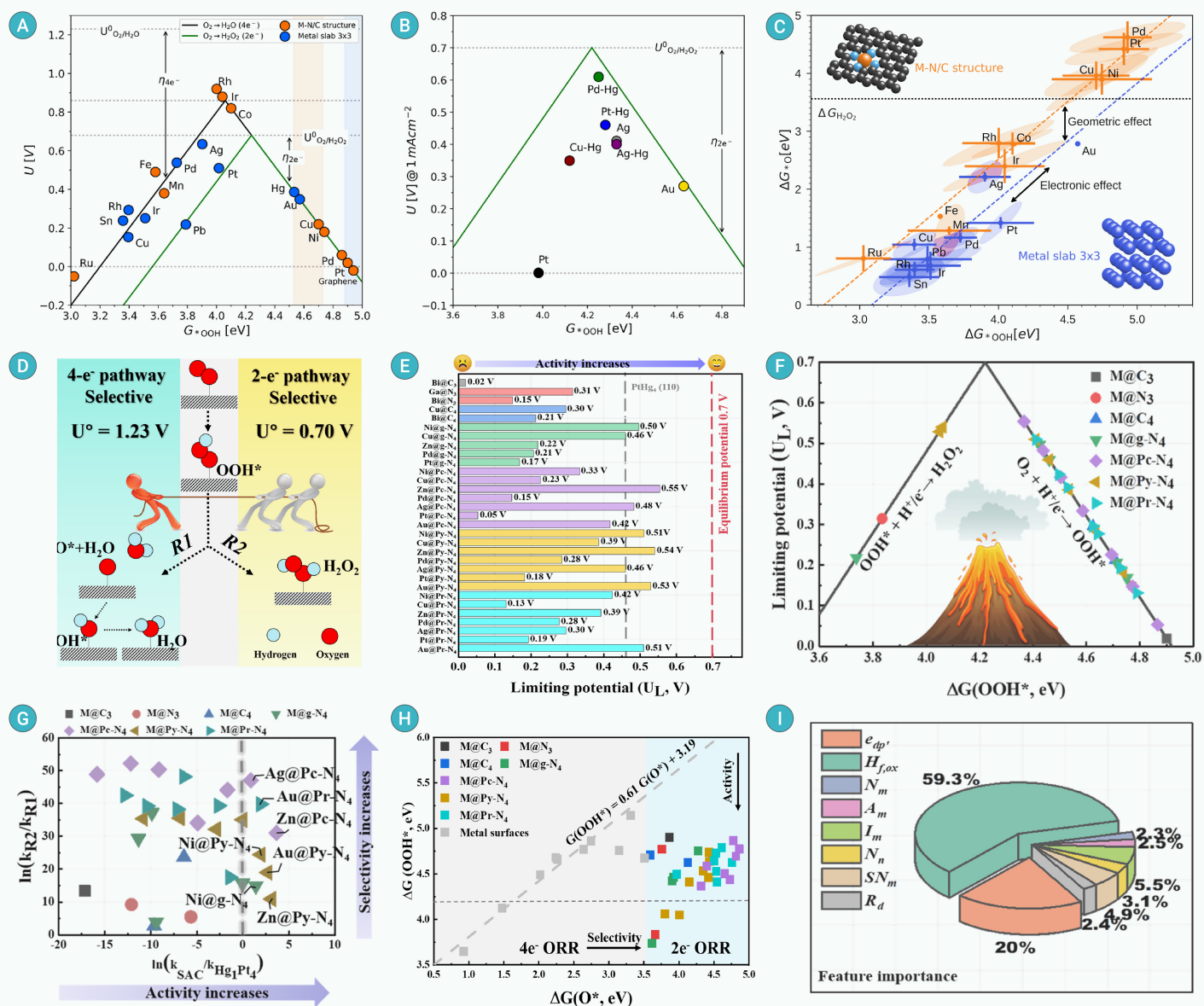


Figure 3. Theoretical research of different types of SACs for 2e⁻ ORR: volcano plots, adsorption trends, and performance evaluation (A) Sabatier volcano plots for electrochemical oxygen reduction for closely packed pure metal slabs (in blue) and M-N/C structures (in red) obtained from DFT calculations. The limiting potential is plotted as a function of ΔG_{OOH} . The green line represents 2-electron reduction, and the black line represents 4-electron reduction. M-N/C catalysts lying to the right of the horizontal red band bind *O sufficiently weak to thermodynamically favor the 2-electron pathway to H₂O₂; pure metal catalysts lying to the right of the horizontal blue band bind *O sufficiently weak to thermodynamically favor the 2-electron pathway to H₂O₂. These boundaries are shown as bands rather than lines to represent the inherent uncertainty in the model; (B) Experiment versus theory for pure metals and metal alloys. The solid line shows the limiting potential from DFT also shown in (A). Circles represent the potential required to reach a kinetic current of 1 mA/cm² on polycrystalline electrodes; (C) Adsorption trend for selected metal slabs and M-N/C catalysts (original data). Reprinted with permission.⁸ Copyright 2018 American Chemical Society; (D) Schematic illustration of the reactions and the equilibrium potentials during the O₂ electroreduction; (E) Computed U_L values of 31 SACs in comparison with the PtH₂(110) benchmark (U_L = 0.46 V); (F) Volcano relation between U_L and ΔG(OOH*) for SACs. The PtH₂(110) was selected as a benchmark for comparison; (G) Variations of activity versus selectivity for SACs. The PtH₂(110) was selected as a benchmark for comparison; (H) Variations of ΔG(O*) and ΔG(OOH*) on the 31 studied SACs. Corrections of -0.02 and 0.17 eV were added to convert the electronic potential into Gibbs free energy for O* and OOH*, respectively; (I) Feature importance of the random forest model for ΔG(O*). Reprinted with permission.⁴² Copyright 2019 American Chemical Society.

chemical reactions.⁸⁹

The adsorption energy of reaction intermediates on catalysts is a crucial determinant of reaction kinetics and pathways. In theoretical calculations, descriptors such as ΔG_{OOH} and ΔG_{OH} assess the feasibility of reactions, facilitating the screening of suitable catalysts. Yang et al. illustrated this concept using a volcano plot, with ΔG_{OOH} values of various metals plotted on the horizontal axis and the thermodynamic limiting potential (U_L) on the vertical axis (as shown in Figure 3A).⁸ This plot predicts catalytic activity for both the 2e⁻ ORR and 4e⁻ ORR.

As shown in Figure 3A, the green line represents the volcano plot for the 2e⁻ ORR. On the left side of the peak, smaller ΔG_{OOH} values indicate strong binding of *OOH, which promotes O-O bond cleavage, favoring the 4e⁻ ORR.

In contrast, larger ΔG_{OOH} values on the right side suggest weaker *OOH binding, implying a slow protonation of O₂ molecules in the initial step and leading to low catalytic activity. Catalysts positioned at the peak of the volcano curve exhibit moderate OOH binding energies and thermodynamic limiting potentials (~4.22 eV). These characteristics facilitate both OOH adsorption and desorption, rendering such catalysts optimal for the 2e⁻ ORR pathway.

Experimental studies have confirmed that catalysts near the peak of the volcano plot, such as Pd-Hg SACs,⁸³ show exceptional performance due to their moderate affinity for *OOH. These findings validate theoretical predictions and provide clear guidelines for selecting suitable metal atoms. Gao et al. demonstrated through DFT calculations that the binding energy of *OOH generally correlates with the number of valence electrons at the metal center

in SACs.⁹⁰ They found a gradual increase in binding strength as the number of valence electrons increased from Mn to Fe, Co, Ni, and finally Cu. Their conclusion indicates that binding energies that are either too strong or too weak hinder the preservation and desorption of *OOH, while moderate binding energy results in superior catalytic performance. Among the SACs studied, Co SACs exhibited the most optimal binding energy and the highest catalytic activity for the 2e⁻ ORR.

Furthermore, Federico and coworkers explored metalloporphyrin structures with various metal atoms (Cr, Mn, Fe, Co, Ni, Cu) and ring ligands (H, F, OH, NH₂, CH₃, BH₂).⁹¹ They discovered that strategic selection of these components can disrupt the linear correlation between the binding energies of *OH and *OOH intermediates, enhancing product selectivity in the 2e⁻ ORR. These studies underscore the importance of metal atom selection and coordination structure optimization in SACs for improving intermediate adsorption and enhancing catalytic performance. Collectively, these theoretical calculations deepen our understanding of structure-performance relationships in SACs and expand our knowledge of reaction thermodynamics and kinetics in the 2e⁻ ORR, providing vital theoretical support for catalyst design and optimization.

Recently, Guo and colleagues constructed 210 representative single-atom structures to identify the most suitable candidates for the 2e⁻ ORR, as depicted in Figures 3D-I.⁴² They employed a three-step screening process based on specific criteria related to thermodynamic and electrochemical stability. In the first step, they required the formation energy (E_f) of the SACs to be negative ($E_f < 0$) and the dissolution potential (U_{diss}) to be positive ($U_{\text{diss}} > 0$), which narrowed their selection down to 149 single-atom structures.

In the second step, the researchers focused on product selectivity, further reducing the pool to 31 metal coordination structures. They aimed to ensure that the thermodynamic barrier for H₂O₂ formation was lower than that for the hydrogenation of OOH* to O* and H₂O. They identified two key factors influencing product selectivity: the number of d-electrons in the central metal atom and its coordination environment. Their findings revealed that an increase in the number of d-electrons in the central metal weakened the M-O interaction and raised $\Delta G(*O)$, which facilitates the 2e⁻ ORR process.

Furthermore, they discovered that M-N₄ coordination structures—such as M@Pc-N₄, M@Pr-N₄, M@Py-N₄, and M@g-N₄—exhibited weaker *O adsorption compared to M-C₃, M-C₄, and M-N₃ configurations. This characteristic further promotes the efficiency of the 2e⁻ ORR. In the final screening step, the authors evaluated catalytic activity using thermodynamic and kinetic descriptors. They created a volcano plot to illustrate the relationship between ΔG_{OOH} and the limiting potential (U_L), along with a scatter plot to depict the correlation between activity and selectivity.

Ultimately, they identified seven optimal metal single-atom structures: Ni@g-N₄, Zn@Pc-N₄, Ag@Pc-N₄, Ni@Py-N₄, Zn@Py-N₄, Au@Py-N₄, and Au@Pr-N₄. The study further demonstrated that the coordination structures modulate the electronic structure of the central metal atom, consequently affecting the adsorption energies of intermediates, the rate-determining steps, and the limiting potential (U_L). This influence significantly enhances the catalyst's performance in terms of both selectivity and activity. The authors concluded that the coordination structure and the number of d-electrons in the metal atom of SACs jointly determine the adsorption mode and strength of intermediates, thereby influencing both selectivity and activity. This theoretical research not only confirms the feasibility of SACs as catalysts for the 2e⁻ ORR but also lays a solid theoretical foundation for subsequent experimental studies.

REGULATION STRATEGIES FOR SACs

SACs offer several advantages that enhance their catalytic performance, including uniform active sites, unsaturated coordination environments, unique electronic structures, and high atomic utilization. The isolated active sites promote end-on adsorption of O₂, which helps preserve the integrity of the O-O bond. Furthermore, SACs facilitate the enhancement of catalytic activity, stability, and selectivity more effectively than other low-dimensional materials, primarily through the modulation of metal-support interactions. Therefore, by implementing appropriate regulation strategies, researchers can significantly improve the catalytic performance of SACs.

Both theoretical predictions and experimental studies have confirmed that

the activity and selectivity of SACs in the 2e⁻ ORR are predominantly governed by three key factors: the number of d-electrons, the coordination structure, and the charge transfer capability of the metal centers. These factors collectively influence the adsorption mode and strength of the *OOH intermediate.⁹² By precisely tuning the metal species and their configurations, researchers can optimize the adsorption of the *OOH intermediate. Additionally, the stability of SACs is significantly affected by the interactions between the metal atoms and the support material. To enhance catalytic performance, researchers have developed various regulation strategies, including selecting appropriate metal atoms,^{42,65,75} optimizing coordination structures,^{42,71,73} and modifying support materials.^{70,94-97} These strategies have been shown to effectively improve the catalytic activity, selectivity, and stability of SACs to varying degrees. In the following sections, we will systematically review these strategies, evaluate their effectiveness in optimizing SAC performance, and explore their potential in the design and preparation of SACs, providing a comprehensive reference for future catalyst development. A schematic summary of the regulation strategies of SACs for 2e⁻ ORR is shown in Figure 4. Table 1 provides a summary of the catalytic performance of SACs associated with different regulation strategies discussed below.

Regulation of central metal atoms

Existing research shows that *OOH, O, and OH intermediates typically adsorb on top of metal atoms and interact electronically with them, identifying these metal centers as the actual active sites.⁸⁸ Consequently, the catalytic performance of SACs is directly linked to the selection of metal atoms. Choosing appropriate metal atoms is therefore the most direct and effective way to achieve high intrinsic catalytic activity. Moreover, by introducing additional active centers through the construction of dual-atom or multi-atom structures, it is possible to disrupt the linear relationship in the adsorption of the *OOH, *O, and *OH intermediates. This approach not only enhances catalytic activity but also enables interactions between multiple metal atoms to modulate the electronic structure of the active sites, thereby facilitating the catalytic reaction. As a result, adjusting the species and number of metal atoms stands out as one of the most effective strategies for developing efficient SACs.

Selection of metal atom types

The type of metal atoms significantly influences the catalytic activity and product selectivity of SACs. Early studies have demonstrated that increasing the number of d-electrons in a metal leads to higher adsorption energy ($\Delta G(*O)$) for the *O intermediate. This enhanced adsorption weakens the M-O interaction, thereby favoring the 2e⁻ ORR pathway.⁴² Furthermore, recent research indicates that both the number of d-electrons and the position of the d-band center of the metal atom impact the adsorption of intermediates.

For example, Sun and coworkers synthesized M-N_x-C structures containing various 3d-transition metal single atoms (M = Mn, Fe, Co, Ni, Cu), as illustrated in Figures 5A-E.⁶⁶ Their theoretical calculations and experimental studies revealed that the oxidation state and d-band center position of the metal sites significantly influence their ability to adsorb O₂ and intermediates. Specifically, the electronic density at the metal site determines the oxidation state, which subsequently affects its interactions with O₂ molecules and intermediates. An optimal oxidation state promotes moderate adsorption of intermediates, facilitating the 2e⁻ ORR and enhancing H₂O₂ formation.

Additionally, the position of the d-band center is crucial for catalytic activity. When the d-band center is closer to the Fermi level (E_f), more electronic states are available for bonding with adsorbed molecules. This stronger interaction with adsorbed molecules can make the formation and transformation of *OOH less favorable. Conversely, a d-band center that is farther from the E_f leads to weaker adsorption of oxygen molecules, making the 2e⁻ ORR less favorable. Consequently, both the oxidation state and d-band center of metal sites critically influence O₂ and intermediate adsorption. Optimizing these parameters is essential for achieving high H₂O₂ activity and selectivity.

Notably, findings from these studies indicate that Co-N-C catalysts exhibit the highest catalytic activity for the 2e⁻ ORR. The Co-N-C catalyst, positioned near the peak of the volcano plot, features an optimal d-band center position and moderate adsorption energy for intermediates, contributing to its exceptional catalytic performance. Similarly, Gao et al. synthesized a series of

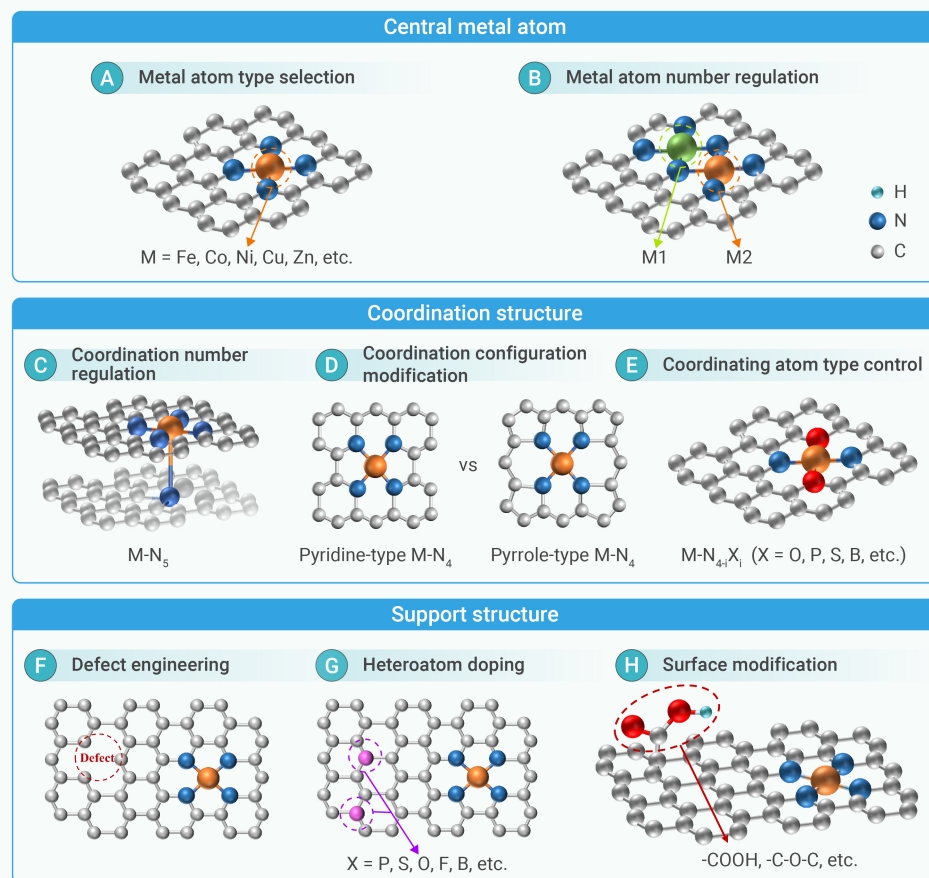


Figure 4. A schematic summary of regulation strategies of SACs for 2e⁻ ORR (A-B) Regulation of central metal atoms; (C-E) Regulation of coordination structures; (F-H) Regulation of support materials.

Firstly, the presence of dual active sites allows DACs to utilize a variety of adsorption modes for O₂ and reaction intermediates, as illustrated in Figure 6A. This diversity in adsorption can be fine-tuned by adjusting the types of metals, coordination elements, and coordination structures used.¹⁰⁰ Moreover, these dual active sites disrupt the linear relationship between the adsorption of different intermediates, which in turn enhances both catalytic activity and product selectivity.

Secondly, the electronic effects and proximity effects between neighboring metal atoms in DACs foster synergistic interactions.¹⁰¹ These interactions can adjust the d-band center position, create asymmetries in the local electronic distribution, and optimize the bonding interactions between active sites and the intermediates. As a result, the energy barriers of the rate-determining steps are lowered, optimizing the overall reaction pathways. Additionally, certain adjacent metal atoms exhibit unique long-range spin coupling effects, which facilitate further synergistic interactions through structural adaptation and electronic transfer.¹⁰² These interactions, whether occurring between heteronuclear or

SACs by anchoring transition metals ranging from Mn to Cu on nitrogen-doped graphene, as shown in Figures 5F-I.⁹⁰ They found that the binding energy of the active sites for oxygen-containing intermediates, such as *OOH, correlates with the number of valence electrons at the metal atoms. As the number of valence electrons increases from Mn to Cu, the d-band center shifts downward relative to the E_f, weakening the binding between metal atoms and oxygen-containing intermediates. Among these catalysts, Co-N-C exhibited superior selectivity for H₂O₂ and minimal activity for the H₂O₂ reduction reaction.

These studies underscore the critical role that the type of metal atoms plays in determining catalytic performance. In addition to the examples provided, various Co-N-C SACs synthesized by different methods have also demonstrated excellent electrocatalytic performance for the 2e⁻ ORR.^{66,70-98} However, it is important to note that not all Co-based SACs are suitable for the 2e⁻ ORR; some exhibit a stronger tendency towards the 4e⁻ ORR.⁹⁹ This observation emphasizes that catalytic activity and product selectivity depend not only on metal type but also on coordination number and configurations. These topics will be discussed in Section 5.2. Additionally, Fe-based⁷⁸ and Ni-based⁸⁰ SACs have also shown promising catalytic activities for the 2e⁻ ORR.

Regulation of the number of metal atoms

Increasing the number and varying the types of metal atoms to construct dual single-atom structures can lead to the development of dual-atom catalysts (DACs). These catalysts retain the isolated active site structure characteristic of SACs while effectively breaking the linear relationship between the adsorption of different reaction intermediates.⁷⁷ This characteristic allows DACs to enhance catalytic performance through multiple strategies, including modulating adsorption modes, leveraging synergistic effects, and increasing metal loading. As a result, DACs offer distinct advantages in the field of the 2e⁻ ORR. Consequently, the regulation of the number and type of central metal atoms has become a prominent research focus.

In catalytic reactions, DACs benefit from two sets of single atoms that can function independently or synergistically to enhance catalytic performance.

homonuclear dual single atoms, help stabilize the metal atoms and reduce the tendency of SACs to agglomerate. Consequently, this stabilization enhances both the metal loading and the mass-specific activity of these catalysts.

DACs can be broadly categorized into three types:¹⁰¹ (1) Strictly Paired DACs: These DACs consist of two sets of identical metal active centers with a symmetrical coordination structure. In these structures, both the spatial arrangement and distance symmetry of the coordination are closely aligned. (2) Generalized DACs: Unlike strictly paired DACs, generalized DACs allow for more flexibility in their coordination structures. While they still contain two sets of metal active centers, there are no stringent requirements regarding the number of coordinating atoms or the symmetry of the coordination structure around each metal atom. In these DACs, carbon or metal atoms in the support material are replaced by two adjacent metal atoms, maximizing functionality through their interactions.¹⁰³⁻¹⁰⁵ (3) Metal-Nonmetal (or Semimetal) DACs: This type of DAC comprises one metal atom and one nonmetal (or semimetal) atom. The distinct electronic structures of the metal and nonmetal (or semimetal) atoms generate synergistic effects that enhance catalytic performance.^{106,107}

The catalytic performance of DACs can be enhanced through metal selection, coordination control, optimization of dual-atom interactions, and adjustment of metal-support interactions. These strategies allow DACs to be applied in diverse fields, including CO₂RR,¹⁰⁸ HER,¹⁰⁹ and 4e⁻ ORR,¹¹⁰ while research on 2e⁻ ORR remains in its early stages. For instance, Du et al. developed a CoIn-N-C dual single-atom catalyst, where Co functions as the active site and In facilitates OOH adsorption on neighboring Co atoms by stabilizing hydroxyl groups.⁷⁵ This catalyst achieved an impressive H₂O₂ yield of 9.68 mol g⁻¹ h⁻¹ in a three-phase flow cell.

Similarly, Huang et al. synthesized a bimetallic cobalt catalyst (Co₂-DAC) using a macrocyclic precursor-mediated method.⁷⁴ This catalyst demonstrated over 95% selectivity for H₂O₂ and a high current density of 2.7 mA cm⁻² in acidic media, achieving an H₂O₂ yield of 11.72 mol g_{cat}⁻¹ h⁻¹ at 400 mA cm⁻². They found that incorporating a second metal into the coordination

Table 1. Summary of electrocatalytic performance under different regulation strategies.

Regulation of Central Metal Atoms	Catalysts	Electrolyte (RRDE)	E_{onset} vs RHE	H_2O_2 selectivity (%)	H_2O_2 yield	FE (%)	Ref
Metal Atom Type Selection	Co-N-C	0.5 M H_2SO_4	0.83	~80	$90.9 \text{ mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$	—	66
	$\text{Co}_{\text{SA}}\text{-N-CNTs}$	0.5 M H_2SO_4	0.7	~95	$974 \pm 25 \text{ mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$	80~86	70
	Co-NC	0.1 M HClO_4	0.7	~90	$275 \text{ mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$ (0.4V)	>90	90
Metal Atom Number Regulation	CoIn-N-C	0.1 M HClO_4	0.7	~94	$9.68 \text{ mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	—	75
	$\text{Co}_2\text{-DAC}$	0.1 M HClO_4	0.72	~95	$11.72 \text{ mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	85~100	74
	$\text{CoZn}_{\text{SA}}\text{@CNTs}$	0.1 M KOH	0.82	>90	$7.50 \text{ mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	95	76
	$\text{Co}_x\text{-Ni MAC}$	0.1 M HClO_4	0.75	~80	$28.96 \text{ mol L}^{-1} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$	—	77
Regulation of Coordination Structures	Catalysts	Electrolyte (RRDE)	E_{onset} vs RHE	H_2O_2 selectivity (%)	H_2O_2 yield	FE (%)	Ref
Metal Atoms Coordination Number Regulation	Co- N_5C	0.5 M H_2SO_4	0.7	~65	$6.78 \text{ mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	57.7 (at 0.3 V)	71
	Co HSACs	0.1 M KOH	0.85	~95	—	90	72
	Co- $\text{N}_2\text{-C/HO}$	0.1 M KOH	0.801	~91.3	~1000mg L^{-1} within 1h	90	73
Coordination Configuration Modification	Co-N SAC _{DP}	0.1 M HClO_4	0.3	~94	$664 \text{ mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$	90	98
Coordinating Atom Type Control	In SACs/NSBC	0.1 M KOH	0.65	~95	$6.49 \text{ mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	90	142
	Fe-CNT	0.1 M KOH	0.822	~95	—	—	119
	Ni- N_2O_2	0.1 M KOH	0.4	~96	$5.9 \text{ mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	91	115
	$\text{W}_1/\text{NO-C}$	0.1 M KOH	0.815	~90	$1.23 \text{ mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	95	86
Support Regulation	Catalysts	Electrolyte (RRDE)	E_{onset} vs RHE	H_2O_2 selectivity (%)	H_2O_2 yield	FE (%)	Ref
Defect Engineering	DPC0.5-5	0.1 M KOH	0.75	~90	$115.32 \text{ mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$	89	130
Heteroatom Doping	Sb-NSCF	0.1 M KOH	0.76	~97.2	$7.46 \text{ mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	80~94.7	85
	$\text{CoN}_4\text{-PC}$	0.1 M KOH	0.81	~97	$11.2 \text{ mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	80~92	131
	Co- $\text{N}_5\text{-O-C}$	0.1 M KOH	0.801	~85.6	$11.3 \text{ mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	~80	112
	Co-N SAC _{DP}	0.1 M HClO_4	0.3	~94	$664 \text{ mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$	~90	125
Surface Modification	Co-N SAC _{DP}	0.1 M HClO_4	0.3	~94	$664 \text{ mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$	~90	125
Others	$\text{Co}_1\text{-NG (O)}$	0.1 M KOH	0.815	~82	$418 \pm 19 \text{ mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$	—	65
	Co- $\text{O}_4\text{@PC}$	0.1 M KOH	0.73	98.8	$0.25 \text{ mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	84.8~92.4	126
	Co-F-CNT	0.1 M KOH	0.7	~80	$18.6 \text{ mol g}_{\text{cat}}^{-1} \text{h}^{-1}$	90	124
	h-Pt ₁ -CuS _x	0.1 M HClO_4	0.68	~96	$546 \pm 30 \text{ mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$	—	128
	Pt1/TiC	0.1 M HClO_4	0.2	~68	—	—	56

sphere of the cobalt atom shifted its d-band center downward, which reduced its affinity for *OH and *HOOH intermediates. This adjustment effectively prevents the cleavage of the O-O bond and suppresses the further reduction of H_2O_2 .

Additionally, Yang et al. synthesized a heteronuclear CoZn dual single-atom catalyst ($\text{CoZn}_{\text{SA}}\text{@CNTs}$) encapsulated in N/O-doped hollow carbon nanotubes through a spatially confined growth strategy, as shown in Figures 6B-D.⁷⁶ This material exhibits exceptional performance in synthesizing H_2O_2 across the entire pH range. The remarkable performance is attributed to the synergistic effect between adjacent Co and Zn single atoms, which optimizes the electronic structure and facilitates electron transfer between them via long-range interactions. This reduces the energy barrier of the reaction and enhances catalytic activity. Furthermore, the abundant defects and multiple active sites within the material create a favorable microenvironment for the adsorption and enrichment of oxygen, thereby improving product selectivity. The successful synthesis of these catalysts highlights the significant potential and promising future of DACs in the 2e^- ORR field at the experimental level.

Building on the concept of DACs, researchers have developed complex multi-single-atom catalysts (MSACs) that provide substantial advantages in regulating the microenvironment of active sites and optimizing their interactions with intermediates. The versatile atomic arrangements and intricate synergistic effects of these catalysts enable more effective catalytic processes.⁷⁷ A notable example is the work by Tong et al., who synthesized a series of MSACs tailored for the 2e^- ORR, as illustrated in Figures 6E-H.⁷⁷ Among these, the Co_2NiN_8 tri-single-atom structure (Co-O-Co-N-Ni) demonstrated remarkable catalytic activity, achieving a rate of 28.96 mol/L/g/h and high selectivity (>80%) for H_2O_2 in both acidic and neutral conditions. This pioneering research marks a significant advancement in the application of multi-single-atom catalysts for the 2e^- ORR.

Regulation of coordination structures

In SACs, the coordination structure of the metal, in addition to the type of metal atom, significantly influences the geometric and electronic structures. These factors subsequently affect the adsorption of intermediates, ultimately impacting catalytic performance. Coordination structure regulation targets

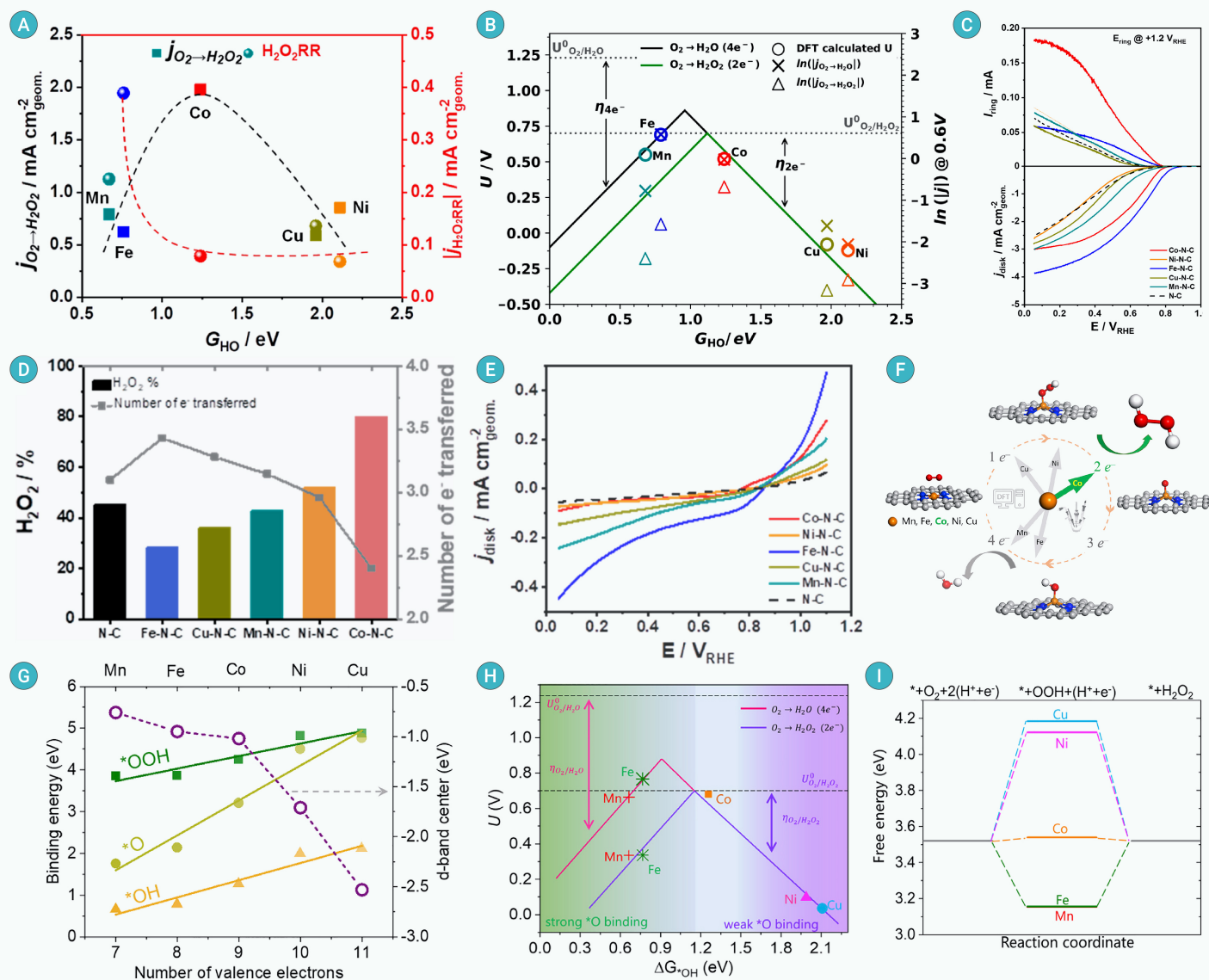


Figure 5. ORR pathways and H_2O_2 selectivity in different transition metal SACs: binding energy and activity volcano relationships (A) H_2O_2 production current as a function of the binding energy of the $\ast\text{OH}$ intermediate; (B) Thermodynamic relations (volcano) lines for the two- (green solid line) and four-electron ORR (black solid line); (C) Linear sweep voltammetry (LSV) in a rotating ring-disk electrode (RRDE) setup with the Pt ring held at $+1.2 \text{ V}_{\text{RHE}}$; (D) H_2O_2 selectivity ($\text{H}_2\text{O}_2 \%$) and the number of electrons (n) at $+0.1 \text{ V}_{\text{RHE}}$ derived from RRDE data; (E) Background-corrected $\text{H}_2\text{O}_2\text{RR}$ performance in N_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ electrolyte containing $1 \text{ mM H}_2\text{O}_2$. Reprinted with permission.⁶⁵ Copyright 2019 American Chemical Society; (F) Schematic of ORR along the 2e^- or 4e^- pathway on transition metal SACs ($\text{M} = \text{Mn, Fe, Co, Ni, and Cu}$) anchored in N-doped graphene; (G) Binding energy of $\ast\text{OOH}$, $\ast\text{O}$, and $\ast\text{OH}$ on M-SAC ($\text{M} = \text{Mn, Fe, Co, Ni, and Cu}$) and d-band center (open circle) of M atom in M-SAC ($\text{M} = \text{Mn, Fe, Co, Ni, and Cu}$); (H) Activity-volcano curves of ORR via the 2e^- or 4e^- pathway. The limiting potential is plotted as a function of $\Delta G_{\ast\text{OH}}$. The gradual change in color indicates the catalyst window for producing H_2O_2 ; (I) Free energy diagrams of 2e^- ORR on the SACs at $U = 0.7 \text{ V}$ versus RHE.⁹⁰ Copyright 2019 Elsevier Inc.

two microscopic-level features in single-atom catalysts: (i) the first coordination shell (e.g., N/O/S atoms and their coordination number), and (ii) the second shell (e.g., next-nearest neighbors and spatial configurations). This approach directly interacts with the metal active center through strong electronic interactions, optimizing its local electronic structure and thus enhancing catalytic performance. In the selection of supports for SACs, carbon-based substrates are widely used due to their high specific surface area and excellent conductivity. While metal atoms are typically supported on carbon, the relatively weak chemical bonds between the metal and carbon can lead to the aggregation or detachment of metal atoms from the support. This loss of active sites results in a decline in catalyst performance. Unlike carbon, nitrogen atoms exhibit higher electronegativity, stronger coordination stability, and broader coordination geometries. These advantages render nitrogen-doped carbon materials ideal supports for SACs, with nitrogen atoms serving as direct ligands to metal centers. Theoretical studies have demonstrated that the electronic structure of the coordinating atoms influences the bonding capability between the metal and the intermediates.¹¹⁸ Therefore, regulating

the coordination structure of metal atoms is essential for enhancing catalytic activity and product selectivity, which can involve adjustments to the coordination number, configuration, and types of coordinating atoms.

The coordination number of metal atoms significantly influences the catalytic performance of SACs by affecting their coordination configuration. When the coordination number is ≤ 4 , the metal atoms and coordinating atoms typically form a planar configuration. In contrast, when the coordination number is ≥ 5 , metal atoms bond with additional coordinating atoms in the out-of-plane axial direction, resulting in hyper-coordinated structures. Early theoretical calculations suggested that the M-N_4 coordination structure is more favorable for the 2e^- ORR compared to M-C_3 , M-C_4 , and M-N_3 structures.⁴² This preference arises because the M-N_4 structure weakens the adsorption of the intermediate $\ast\text{O}$, thereby preventing the cleavage of the O-O bond. However, subsequent research has indicated that the M-N_4 coordination structure does not consistently provide optimal intermediate adsorption or catalytic activity.¹¹⁹ Consequently, efforts have been made to enhance the catalytic performance by regulating the coordination structure of metal

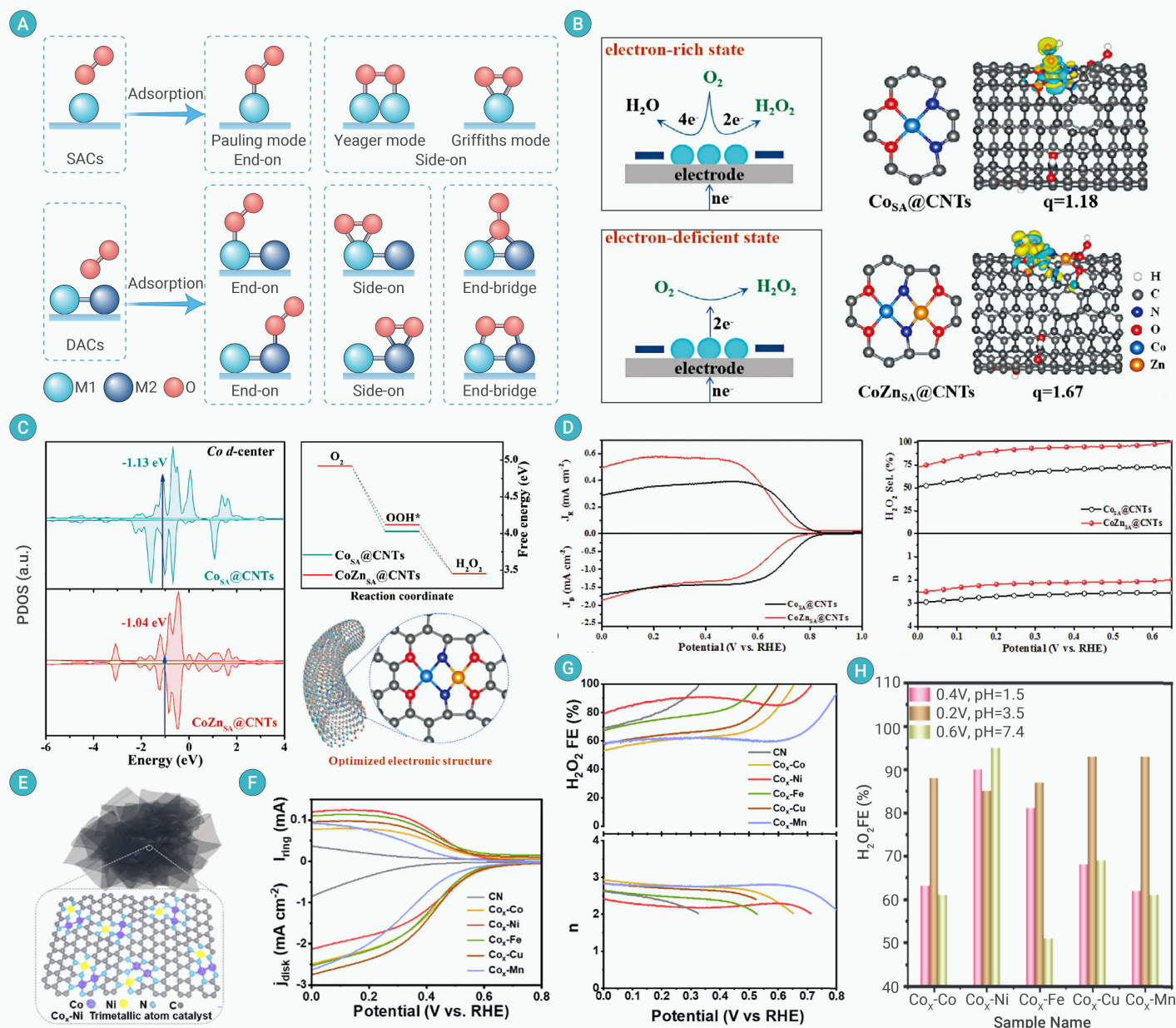


Figure 6. Different DACs for $2e^-$ ORR: adsorption modes, electronic structure, and pH-dependent H_2O_2 selectivity (A) Distinct adsorption modes of oxygen molecules on single-metallic and bimetallic sites; (B) Illustration of model specification and their differential partial charge densities with OOH^* adsorption (side view) for $Co_{SA}@CNTs$ and $CoZn_{SA}@CNTs$, respectively; (C) PDOS of Co 3d orbital and Gibbs free energy diagrams of two-electron ORR of $Co_{SA}@CNTs$ and $CoZn_{SA}@CNTs$, respectively; (D) LSV curves based on RRDE, along with H_2O_2 selectivity and electron transfer number (n) for $Co_{SA}@CNTs$ and $CoZn_{SA}@CNTs$, respectively.⁷⁶ Copyright 2024 The Author(s); (E) Structural diagram of Co_x-Ni MAC; (F) RRDE polarization curves in O_2 -saturated 0.1 M $HClO_4$; (G) H_2O_2 selectivity and electron transfer number calculated from the polarization curves; (H) H_2O_2 selectivity in 0.1 M $HClO_4$ (pH = 1.5; potential = 0.4 V), 0.1 M CH_3COONa buffer solution (pH = 3.5; potential = 0.2 V), and 0.1 M phosphate buffer saline (pH = 7.4; potential = 0.6 V).⁷⁷ Copyright 2023 The Authors. *Carbon Energy* published by Wenzhou University and John Wiley & Sons Australia, Ltd.

atoms, particularly by increasing the coordination number.

Certain hyper-coordinated structures, such as the five-coordinated $M-N_5$ structure, exhibit superior electrocatalytic performance compared to the $M-N_4$ structure, primarily due to their asymmetric electronic configuration. This advantage has been demonstrated in multiple electrochemical reactions, such as CO_2RR ,¹¹³ $4e^-$ ORR,⁹² and sulfur redox chemistry in Li-S batteries.¹¹⁴ Recently, the benefits of the $M-N_5$ structure have also been confirmed in the $2e^-$ ORR field.⁷¹ For instance, Fan et al. successfully synthesized a SAC featuring Co- N_5 coordination through axial coordination between pyridine groups and cobalt phthalocyanine (CoPc) molecules, as shown in Figures 7A–C.⁷² This innovative design resulted in excellent catalytic activity and product selectivity for the $2e^-$ ORR. The performance enhancement stems from axial coordination disrupting Co- N_4 planar symmetry in CoPc. This breaks charge symmetry and shifts the Co d-band center. This adjustment optimizes the

adsorption and activation of the $*OOH$ intermediate.

In another study, Yan et al. employed a sacrificial template strategy to embed a Co- N_5 structure within graphite-3R carbon, constructing a hierarchical pore structure.⁷¹ This catalyst featured axial nitrogen ligands that effectively modulated the d-band center of the Co atom, optimizing the binding energy of the $*OOH$ intermediate. As a result, the catalyst achieved a remarkable H_2O_2 yield of 6.78 mol/g_{catalyst}/h at 0.0 V (vs. RHE). Both theoretical and experimental findings highlight the benefits of adjusting the coordination number to enhance the catalytic activity of SACs. Beyond $M-N_4$ and $M-N_5$ structures, studies have also reported SACs with $M-N_3$ and $M-N_6$ coordination configurations,^{72,73} further reinforcing the feasibility and advantages of this approach in improving catalytic performance. These studies provide valuable insights and references for future efforts to tune catalytic performance. Nevertheless, maximizing the coordination number in SACs does not

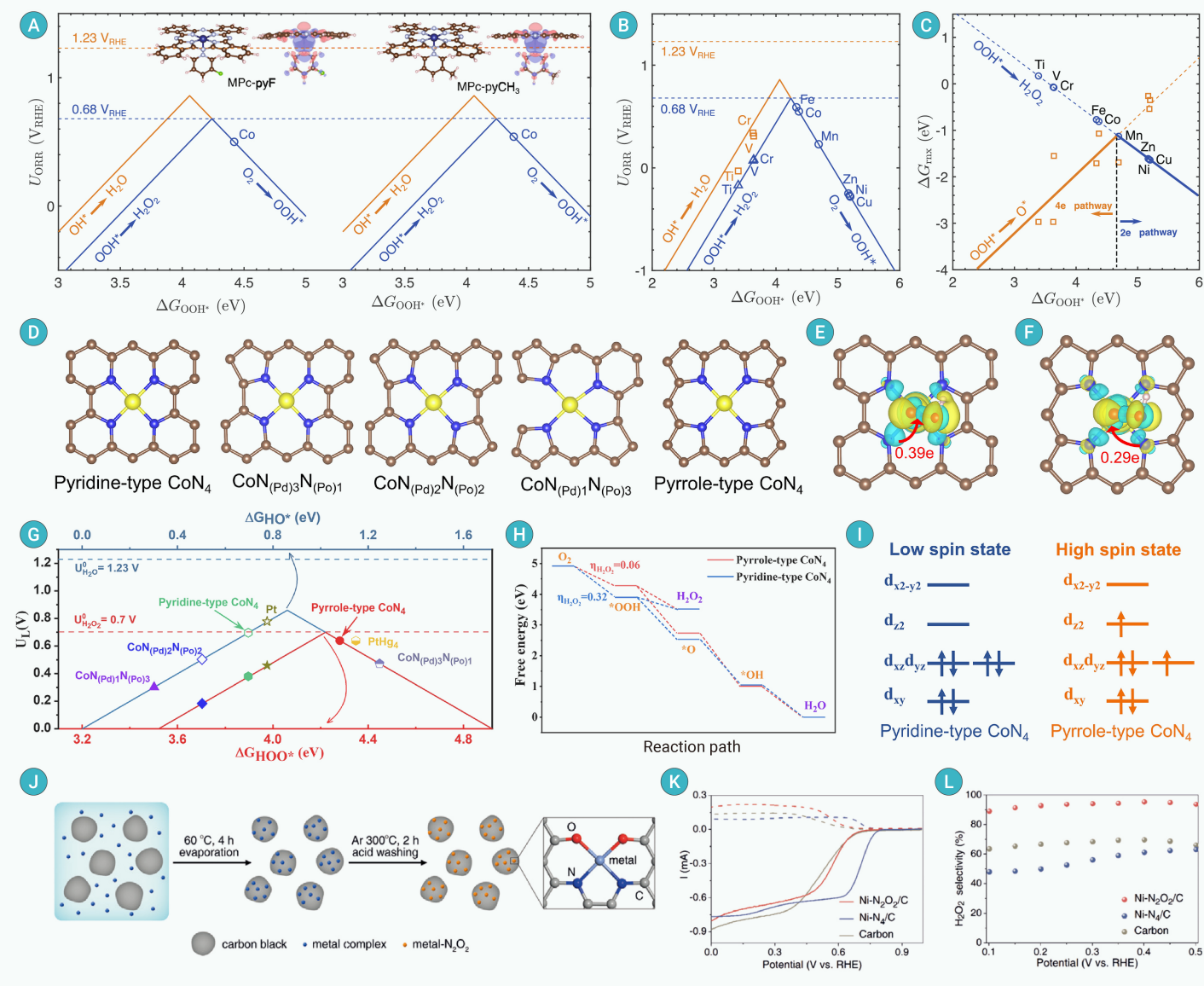


Figure 7. Regulation of coordination structures of SACs for $2e^-$ ORR pathways: volcano activity, H₂O₂ selectivity, and electronic structure modulation (A) Calculated catalytic activity volcano plot for the $2e^-$ and $4e^-$ reaction pathways of ORR over Co HSACs-F and Co HSACs-CH₃; (B) Calculated catalytic activity volcano plot for the $2e^-$ and $4e^-$ reaction pathways of ORR over M HSACs; (C) Calculated selectivity plot of ORR over M HSACs.⁷² Copyright 2023, The Author(s); (D) Simulated different CoN₄ coordination structures; (E) Differential charge distribution on the pyridine-type CoN₄ with adsorption of HOO*; (F) Differential charge distribution on the pyrrole-type CoN₄ with adsorption of HOO*; (G) Volcano plot depicting the Gibbs free energy of reaction intermediates (ΔG_{HO^*} and ΔG_{HOO^*}) on different Co-N coordination structures; (H) Free energy diagram of ORR on the pyridine-type and pyrrole-type CoN₄; (I) 3d electron configuration of pyridine-type and pyrrole-type CoN₄ with adsorption of HOO*.⁹⁸ Copyright 2022 The Authors.; (J) Synthesis of Ni-N₂O₂/C; (K) RRDE polarization curves at 1600 rpm in O₂-saturated 0.1 m KOH with the ring current shown in upper part (dashed lines) and disk current shown in lower part (solid lines); (L) H₂O₂ selectivity as a function of the applied potential.¹¹⁵ Copyright 2020 Wiley - VCH Verlag GmbH & Co. KGaA, Weinheim

universally improve catalytic performance. Increased coordination numbers enhance stability via strengthened metal-support bonds. However, excessive coordination can over-stabilize the electronic states of active sites, thereby impairing reactant adsorption and reducing catalytic activity. Consequently, rational optimization of SACs' coordination numbers is critical for balancing competing activity-stability requirements. State-of-the-art high-throughput computational screening and machine learning techniques now allow for quantitative structure-activity relationship (QSAR) modeling, revealing the fundamental mechanisms that connect coordination number with catalytic behavior. This integration will unravel the mechanistic interplay between coordination number and SACs' performance, while providing a theoretical foundation for the precise design of highly active and stable single-atom catalysts.

Modifying the coordination configuration of SACs is a crucial strategy for enhancing their catalytic performance. While the coordination number and ligand types in the first shell are critical, the second coordination shell's environment can induce distinct electronic configurations that significantly

modulate catalytic performance. In this section, we will primarily discuss how changes in the coordination configuration, while maintaining fixed coordination numbers and types in the first shell, impact the catalytic performance of SACs. It has been observed that SACs with the same Co-N₄-C structure exhibit varying sensitivities; some show enhanced reactivity toward the $2e^-$ ORR, while others are more favorable for the $4e^-$ ORR.^{70,116,117} This suggests that, in addition to the number and spatial arrangement of nitrogen atoms in the first coordination shell, other factors—such as the arrangement of nitrogen atoms in the second coordination shell and their spin states—also significantly influence performance. Theoretical and experimental studies reveal that in M-N₄ structures, the coordinating nitrogen atoms in the second shell can adopt various spatial arrangements, such as phthalocyanine-type, pyrrole-type, pyridine-type, and graphite-type.^{42,98} These different nitrogen atom coordination configurations significantly influence the catalytic performance of SACs. For instance, Chen et al. demonstrate that pyrrole-type Co-N₄-C is favorable for the $2e^-$ ORR, while pyridine-type Co-N₄-C is advantageous for the $4e^-$ ORR, as illustrated in Figures 7D-I.⁹⁸ This distinction arises

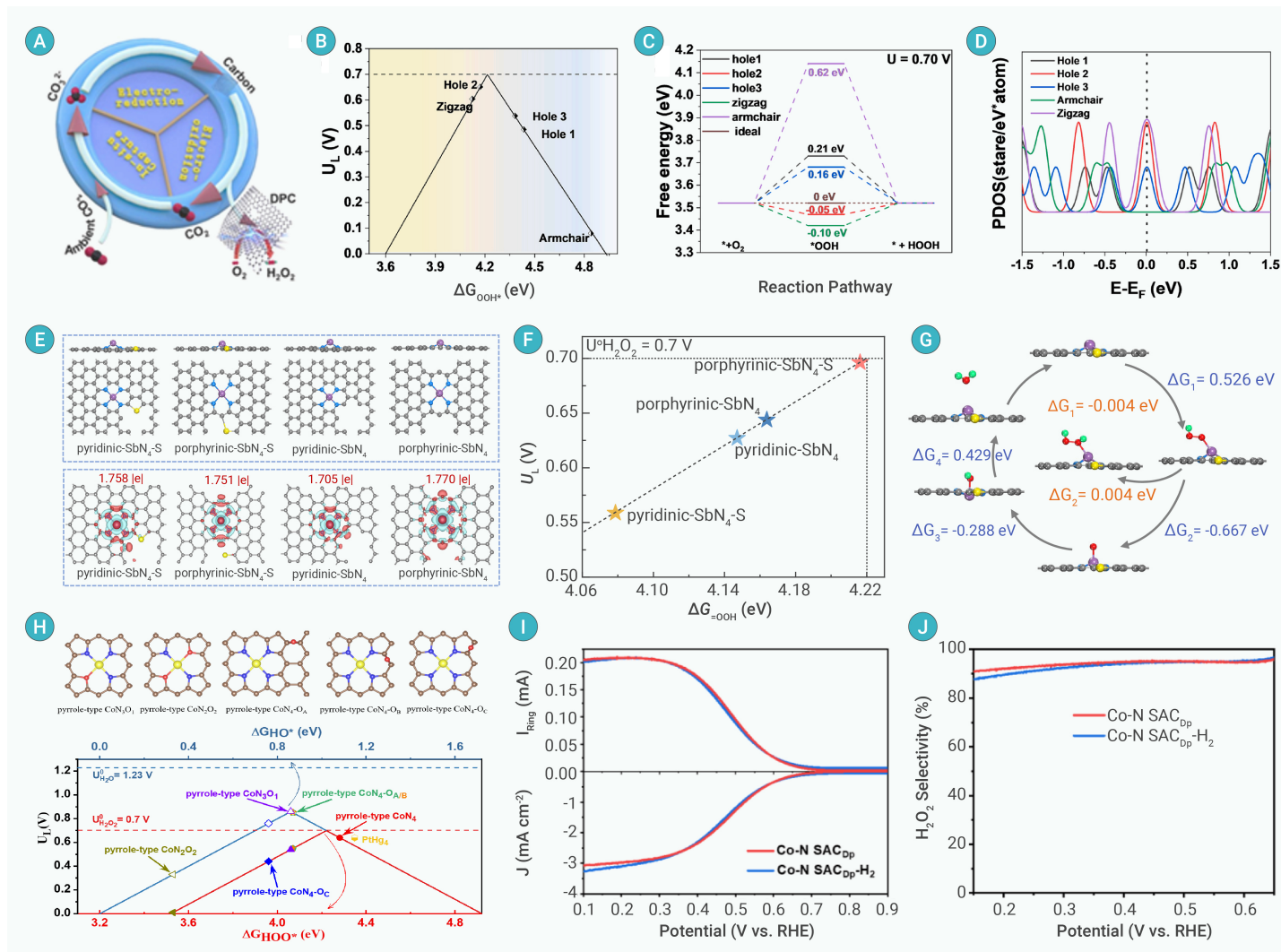


Figure 8. Theoretical calculations and performance analysis of $2e^-$ ORR for SACs with engineered support materials (A) Schematic diagram of the DPC Synthesis Strategy; (B) Calculated $2e^-$ ORR-related volcano plot for the electro-reduction of O_2 to H_2O_2 displayed with the limiting potential plotted as a function of ΔG_{OOH^*} . The equilibrium potential for the $2e^-$ ORR is shown as a dashed black line; (C) Free-energy diagram of hole1, hole2, hole3, zigzag and armchair defects for oxygen reduction to H_2O_2 ; (D) Density of states for armchair, zigzag, hole1, hole2 and hole3 defects carbon site and the final adsorption energy of OOH^* .¹³⁰ Copyright 2022 Elsevier B.V.; (E) Side and top views of optimized structural models of pyridinic-SbN₄-S, porphyrinic-SbN₄-S, pyridinic-SbN₄ and porphyrinic-SbN₄ and the calculated charge density difference for the corresponding structural models; (F) Limiting potentials (U_L) as a function of ΔG_{OOH^*} for the four models; (G) The $2e^-$ and $4e^-$ ORR reaction pathways on the porphyrinic-SbN₄-S configuration.⁸⁵ Copyright © 2023, The Author(s); (H) The pyrrole-type CoN₄ with C-O-C at different positions and the corresponding volcano plot for ΔHO^* and ΔHOO^* ; (I) ORR polarization curves of RRDE for Co-N SAC_{Dp} and Co-N SAC_{Dp-H₂}; (J) H_2O_2 selectivity for Co-N SAC_{Dp} and Co-N SAC_{Dp-H₂}.¹²⁵ Copyright 2022 The Authors.

from variations in the spin states of the nitrogen ligands, which affect the electronic structure of cobalt. The Pyrrole-type Co-N₄-C exhibits a weak interaction with O_2 / *OOH , promoting the production of hydrogen peroxide. Similarly, Ha et al. found that in Co-N₄-C SACs, the configuration of nitrogen ligands, in addition to their number, significantly influences catalytic performance.¹¹⁸ They developed a Co-N₄-C SAC in which cobalt atoms are primarily anchored to pyridinic nitrogen (Co-pyridinic N-C). DFT calculations showed that the presence of pyridinic nitrogen greatly reduces electron localization around the cobalt atom, increases the binding energy with *OOH , and lowers the energy barrier for the $4e^-$ ORR, thereby facilitating this reaction. These findings underscore the critical role of coordination configuration in determining catalytic performance. Consequently, designing and synthesizing optimal coordination configurations for SACs can substantially enhance their catalytic activity and product selectivity.

Controlling the types of coordinating atoms is another strategy to enhance the catalytic performance of SACs. Currently, many studied SACs primarily feature M-N_x structures, where nitrogen is the main coordinating atom. However, other elements such as oxygen,^{86,119} carbon,^{71,119} boron,¹²⁰ and sulfur¹²¹ can also serve as coordinating atoms. Changing the type of coordinating atom around a given metal single atom can significantly impact its electronic structure and, consequently, its catalytic activity. Notably, certain

non-metal coordinating atoms may play a more critical role in catalytic reactions compared to nitrogen, potentially acting as active sites for catalysis. This highlights the importance of exploring a broader range of coordinating atoms to optimize SAC performance. For instance, Wang et al. developed a Ni-N₂O₂ SAC that shows higher selectivity for hydrogen peroxide (H_2O_2) compared to conventional Ni-N₄ SACs, as shown in Figures 7J-L.¹¹⁵ This improvement is largely due to the simultaneous presence of Ni-N and Ni-O bonds, which optimize the adsorption of OOH on the nickel atom, significantly enhancing selectivity for H_2O_2 . Additionally, Zhang et al. employed a coordination polymer pyrolysis method to create a tungsten SAC (W-N₁O₂) anchored on porous carbon nanosheets doped with oxygen and nitrogen.⁸⁶ The catalytic activity of W-N₁O₂ was markedly enhanced, achieving over 90% selectivity for H_2O_2 and a yield of up to 1.23 mol g_{cat}⁻¹ h⁻¹, outperforming W-O₃ or W-N₃ structures. DFT calculations revealed that carbon is the primary active site, with tungsten crucial for optimizing the binding energy of the HOO intermediate.

Furthermore, Jiang and colleagues synthesized an Fe-C₃O₁ catalyst and found that its $2e^-$ ORR catalytic activity significantly exceeded that of the Fe-N₄ structure, achieving over 95% selectivity for H_2O_2 under both alkaline and neutral conditions.¹¹⁹ DFT calculations revealed that the *OOH intermediate binds to the catalyst through the carbon site, while electron transfer between

the iron and oxygen atoms enhances catalytic performance. These results illustrate that the choice of coordinating atoms can influence the electronic structure of the metal atoms to which they are bound, thereby affecting the adsorption of O_2 and intermediates. In conclusion, controlling the types of coordinating atoms is a crucial measure for improving the catalytic activity and product selectivity and of SACs.

Modification of support materials

Beyond the two aforementioned modulation strategies, support modification operates at the structural level by introducing defects (e.g., vacancies, edges), surface functional groups (e.g., -OH, -COOH), and heteroatom dopants (e.g., B, P, S). These modifications indirectly tune the catalyst's electronic properties, thereby influencing the catalytic behavior of metal active sites. Isolated metal atoms in SACs are anchored to the support through coordinating atoms, which facilitate electronic interactions between the metal atoms, the coordinating atoms, and the support material. These interactions allow the support to regulate the electronic structure of the metal and affect its stability.⁴² Additionally, the support can provide catalytic active sites that modulate the adsorption behavior of reactants and intermediates, further contributing to catalytic activity.⁹⁶ At the macroscopic level, an ideal support features a high specific surface area, superior electrical conductivity, and high hydrophilicity, which facilitate efficient mass transfer and accelerate the reaction. Therefore, selecting an appropriate support can significantly enhance the catalytic performance of SACs. In recent years, various strategies have been developed to modulate the structure of supports to optimize their coordination with metal atoms and maintain their dispersion.

To elucidate the interaction between metal atoms and supports, extensive research has been conducted. The interaction between the support material and the metal is referred to as the metal-support interaction (MSI), a fundamental concept in catalysis that significantly influences the activity, stability, and selectivity of catalysts. MSI primarily includes four categories: covalent metal-support interaction (CMSI), electronic metal-support interaction (EMSIs), oxidative strong metal-support interaction (OMSI), and strong metal-support interaction (SMSI).¹²² CMSI and EMSI are dominant MSI mechanisms in SACs. Through synergistic effects, these interactions stabilize isolated metal atoms and modulate their electronic structures, enabling high activity and selectivity.

Covalent Metal-Support Interaction (CMSI) refers to the formation of partial or complete covalent bonds between metal atoms and surface atoms of the support (e.g., N, O, S). This chemical bonding not only effectively anchors the metal atoms but also regulates their electronic structures, thereby influencing the activity and selectivity of catalytic reactions. CMSI effectively suppresses metal aggregation while simultaneously tailoring the electronic structure via precise control of charge distribution and d-band center modulation. This electronic structure regulation significantly affects reactant adsorption, activation, and intermediate stability, thereby enhancing catalytic activity and selectivity. Precise modulation of CMSI configurations (e.g., Ni-N₄-O₂, Ni-N₄-O₁) enables selective control over ORR pathways ($2e^-$ or $4e^-$), offering new strategies for catalyst design and optimization.¹²³

The concept of Electronic Metal-Support Interaction (EMSIs), proposed by Campbell,⁹⁷ is also a common MSI in SACs. It involves electron transfer between metal and support, driven by chemical potential differences.⁹⁶ This interaction finely tunes the electron density of metal sites, affecting the adsorption mode and strength of reactants (e.g., O_2), thereby reducing reaction energy barriers and accelerating reaction kinetics. Additionally, EMSI improves reaction selectivity by stabilizing intermediates. The EMSI effect is influenced by both the intrinsic properties of the support and the geometric position of single metal atoms on the support. Strong metal-support interactions induce greater electron transfer from metal to support/coordinating atoms, which increases the positive charge on the metal. This phenomenon affects the adsorption of intermediates on the catalyst, thereby influencing catalytic activity. It is important to note that catalytic reactions have specific requirements for the electron density of metal atoms; excessively high or low electron density can hinder the smooth progression of the reaction. Therefore, selecting an appropriate support and modulating its structure to alter the bonding state and distribution of metal atoms on the support and thereby tune the electronic structure of the metal atoms will be more conducive to the



Figure 9. Summary and perspectives on SACs for $2e^-$ ORR.

$2e^-$ ORR catalytic reaction.

In practical catalytic systems, CMSI and EMSI often act synergistically to influence the catalytic process. CMSI provides structural stability by anchoring single metal atoms through covalent bonds, while EMSI optimizes electronic structures by regulating electron transfer and d-band centers between the metal and support. This dual interaction synergistically stabilizes active sites and precisely controls reaction pathways.

Currently, the supports utilized for SACs include inert metals, carbon-based materials, and metal compounds. Inert metals are preferred supports for noble metal SACs to mitigate intermediate over-adsorption (Section 3.1). Non-noble SACs typically use carbon-based or metal compound supports. While both types of materials effectively disperse single metal atoms, each has distinct advantages. Carbon-based materials, because of their high specific surface area, abundant defects, and ease of heteroatom doping, are widely used in SACs. Common carbon-based materials include graphene,⁵⁵ CNTs,¹²⁴ amorphous carbon,¹²⁵ and porous carbon.¹²⁶ Two-dimensional carbon-based materials, represented by graphene, have become commonly used supports for SACs due to their excellent conductivity, good structural stability, and thermal stability. For instance, in 2020, Hyeon and Sung et al. designed and synthesized a catalyst with Co-N₄ active sites supported on N-doped graphene for the electrocatalytic production of H_2O_2 .⁶⁵ This catalyst exhibited outstanding performance, achieving a current density of $2.8 \pm 0.2 \text{ mA cm}^{-2}$ (0.65 V vs. RHE), a mass activity of $155 \pm 6 \text{ A g}^{-1}$ (0.65 V), and electrochemical stability for up to 110 hours. Furthermore, three-dimensional carbon-based materials, such as MOF-derived carbon, have also attracted significant attention due to their high volumetric surface area and 3D structure, which promote mass transfer. Zhang et al. synthesized a Co-O₄@PC single-atom catalyst (SAC) by embedding cobalt into a metal-organic framework (MOF)-derived graphene-like carbon matrix.¹²⁶ Carbon vacancies, porosity, and high surface area in this structure contributed to enhanced $2e^-$ ORR selectivity and activity. At 0.6 V, it achieved a selectivity of 98.8% for H_2O_2 , with an onset potential of 0.73 V. DFT calculations revealed that tuning the electronic structure of the Co sites through carbon vacancies reduced the d-band center, leading to a lower Gibbs free energy and optimized *OOH adsorption, thereby boosting H_2O_2 production. Additionally, CNTs are excellent supports for SACs due to their high surface area, superior conductivity, large π -electron system, ease of modification and doping, and tunable surface functionalization. Tian et al. constructed a Co SAC (Co-F-CNT) on fluorine-doped carbon nanotubes (F-CNTs).¹²⁴ By utilizing the long-range

coupling effect between the F and Co atoms, they modulated the surface charge distribution of the Co single atoms. This modulation successfully turned the active sites from individual Co atoms to multiple adjacent carbon atoms, thereby not only increasing the number of active sites but also enhancing the catalyst's electrochemical stability. The H_2O_2 yield reached $18.6 \text{ mol g}^{-1} \text{ L}^{-1}$ with a Faradaic efficiency of 90%. Theoretical calculations confirmed that the optimal adsorption of $\ast\text{OOH}$ on these carbon sites lowered the kinetic energy barrier of the reaction.

As another class of supports for SACs, metal compounds show considerable promise in the 2e^- ORR field. Their remarkable metal-support interactions provide unique advantages in dispersing and stabilizing active centers. These interactions, combined with their tunability in crystal phase, composition, and crystal facets, further enhance the overall catalyst's performance. Moreover, these supports endow catalysts with superior thermal and chemical stability, which are crucial for maintaining long-term catalytic efficiency under harsh conditions. The mechanisms for anchoring metal atoms in these supports are as follows:¹²⁷ (i) Cation vacancies, which provide sufficient space for atom adsorption and regulate the electronic density at the interface, thereby activating local metal atoms to promote reaction kinetics; (ii) Anion vacancies (including O, S, Se, and P), which serve as anchoring sites for metal atoms through spatial confinement or charge attraction, thereby enhancing metal-metal and metal-support interactions in SACs to boost their catalytic activity; (iii) Crystal facet dependence and strain-induced strong interactions, which induce synergistic enhancement of catalytic behavior. These insights demonstrate that incorporating metal compound supports can simultaneously improve the catalytic activity, product selectivity, and durability of single metal atoms. Shen et al. prepared a CuS_x -supported Pt SAC for the 2e^- ORR via ion exchange.¹²⁸ The strong interaction between CuS_x and Pt (through Pt-S bonds) helps modulate the electronic structure of Pt atoms while inhibiting side reactions, thereby optimizing overall catalytic performance. Yang et al. loaded Pt atoms onto titanium carbide (TiC) and titanium nitride (TiN) supports using the impregnation method, resulting in Pt/TiC and Pt/TiN catalysts.⁵⁶ Experimental results indicated that the Pt/TiC catalyst exhibited higher activity and selectivity for H_2O_2 in the 2e^- ORR compared to Pt/TiN. This difference is attributed to TiN's tendency to promote the cleavage of the O-O bond in oxygen molecules, reducing selectivity for H_2O_2 . The TiC support stabilizes Pt single atoms and prevents their clustering. The TiC-Pt interactions modify the electronic structure of Pt, which tunes O_2 adsorption and thereby enhances catalytic activity. Additionally, compared to TiN, TiC demonstrated better stability during electrochemical reactions, which may stem from TiC's greater resistance to oxidation under reaction conditions, helping maintain the catalyst's long-term performance. Currently, research on non-noble metal compound-based SACs for the 2e^- ORR is limited, presenting vast opportunities for future exploration.

Currently, strategies for optimizing SAC supports for the ORR include introducing defects,^{95,129,130} doping with heteroatoms,^{69,85,124,131,132} and surface modification with functional groups.^{125,133,134} For instance, in carbon-based supports,⁷⁰ both defect introduction and heteroatom doping can create additional anchoring sites that stabilize individual metal atoms. Furthermore, modifications to the coordination environment can significantly alter the electronic structure of the active metals, enhancing the adsorption strength of oxygen-containing intermediates and thereby improving catalytic activity and product selectivity. Additionally, surface modification and localized tuning of the support can further enhance catalytic performance.

Defect engineering is recognized as an effective method for enhancing the catalytic activity of SACs. In carbon-based supports, defects such as edge sites and in-plane topological defects can create additional electronic states near the Fermi level. This leads to charge localization that modulates the local electronic environment of the metal atoms, activating their inherent catalytic activity.^{95,129} Additionally, these defects can serve as anchoring sites for stabilizing metal atoms. As a result, defect engineering is frequently employed to improve the performance of carbon-based catalysts. For instance, Yu et al. synthesized porous carbon with holes and edge defects, achieving over 90% selectivity for H_2O_2 , as shown in Figures 8A-D.¹³⁰ DFT calculations further confirmed that defect tuning strategies effectively enhance overall catalytic activity. Although this approach has been widely applied to carbon-based catalysts, its use in regulating carbon-based supports for SACs in the 2e^-

ORR field remains relatively uncommon. If successfully implemented in SAC supports, this strategy has the potential to significantly improve catalytic performance.

Furthermore, heteroatom doping is recognized as an effective strategy to enhance the catalytic activity and product selectivity of SACs. On one hand, it optimizes the charge distribution and spin states of the metal atoms through long-range delocalization effects.¹³⁵⁻¹³⁸ On the other hand, carbon-based supports doped with heteroatoms provide additional active centers to facilitate the 2e^- ORR.¹³⁹⁻¹⁴¹ This occurs because adjacent heteroatoms alter the spin density and charge distribution of the carbon atoms. Additionally, heteroatom doping enhances the interfacial contact between the catalyst surface and the electrolyte, which boosts the overall reaction rate by increasing the catalyst's hydrophilicity and reducing charge transfer resistance.^{121,142} These advantages collectively contribute to the enhanced catalytic activity of SACs. To date, doping with elements such as F,¹²⁴ S,⁸⁵ P,¹³¹ O¹³² and B⁶⁹ has been confirmed as an effective method for enhancing the activity of SACs in the 2e^- ORR. For instance, Liu et al. prepared a Co-N-PC catalyst by doping the carbon support with phosphorus.¹³¹ This P doping elongates the Co-N bond and reduces the electron density of Co, optimizing the adsorption of $\ast\text{OOH}$. Consequently, this catalyst exhibited excellent catalytic activity and product selectivity, demonstrated by a high onset potential of 0.81 V vs. RHE and H_2O_2 selectivity exceeding 90%. Similarly, Yan et al. dispersed high-density antimony (Sb) atoms onto layered, porous N/S-doped carbon nanofibers (Sb-NSCF), as illustrated in Figures 8E-G.⁸⁵ Theoretical calculations revealed that the localized coordination environment created by S doping effectively adjusted the electronic structure of the metal sites, achieving optimal adsorption energy for the $\ast\text{OOH}$ intermediate. This significantly enhanced 2e^- ORR performance, yielding high product selectivity (97.2%) and a yield of $7.46 \text{ mol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ in a flow cell under alkaline conditions.

In addition to defect engineering and heteroatom doping, surface modification of supports can effectively regulate the catalytic performance of SACs. For instance, modifications with surface functional groups (such as O-containing,¹²⁵ N-containing,¹³³ and S-containing groups¹³⁴) significantly influence the hydrophilicity of the catalyst, the adsorption of O_2 molecules, and the binding energies with reaction intermediates. Notably, the same functional groups can produce different effects depending on the specific single-atom structure. For example, Chen et al. found that in the pyridine-type Co- N_4 single-atom structure, the introduction of C-O-C functional groups enhanced selectivity for hydrogen peroxide, as shown in Figures 8H-J.¹²⁵ Conversely, for the pyrrole-type Co- N_4 structure, the same functional group resulted in decreased selectivity for hydrogen peroxide. This variation highlights the need for further investigation into how different surface functional groups affect catalytic performance and the underlying mechanisms involved.

SUMMARY AND PERSPECTIVES

In recent years, SACs have garnered significant attention in the field of the 2e^- ORR due to their unique structural advantages—uniform active sites, unsaturated coordination environments, and distinctive electronic structures. The isolated active sites in SACs facilitate the adsorption of O_2 via the end-on mode, effectively preserving the O-O bond and preventing the occurrence of the four-electron ORR (4e^- ORR), thereby leading to high selectivity for H_2O_2 . Furthermore, the highly tunable structure of SACs allows for the modulation of metal-support interactions, which improves overall catalytic performance.

In this review, we outline the reaction mechanisms and potential pathways for the 2e^- ORR and summarize the latest research advancements that combine the structural characteristics of SACs with findings from DFT calculations. We then focus on strategies for modulating the catalytic performance of SACs, including altering metal atoms, tuning coordination structures, and modifying support materials. We also explore the advantages, challenges, and potential applications of these modulation strategies across various dimensions, including research perspectives, mechanistic analysis, and case studies.

Despite the significant advancements in the electrocatalytic synthesis of H_2O_2 using SACs in recent years, several challenges remain in enhancing catalytic performance, achieving controllable catalyst preparation, elucidating catalytic mechanisms, and theoretically predicting catalysts. Future research should focus on the following key areas (as shown in Figure 9):

Overcoming the trade-off between activity, selectivity, and stability

An ideal $2e^-$ ORR catalyst should possess excellent catalytic activity, high product selectivity, and good stability. High H_2O_2 selectivity demands precise pathway control to avoid O_2^-/H_2O formation. SACs' isolated sites enable linear adsorption of intermediates ($*OOH$, $*O$, $*OH$), aligning with the Sabatier principle. If the adsorption energies of these intermediates are too similar, competitive reaction pathways may be activated, leading to reduced product selectivity. This implies that enhancing the adsorption strength for $*OOH$ might inadvertently increase the adsorption of $*O$ and $*OH$, meaning that improvements in catalytic activity often come at the expense of product selectivity. Moreover, the performance of SACs is significantly influenced by the electronic metal-support interaction (EMSI) between the single metal atom and the support. When the EMSI is strong, the metal atom binds more tightly to the support, stabilizing the single-atom state. However, this strong binding results in the transfer of a significant amount of electrons from the metal atom to the coordinating atoms and the support, which in turn reduces the electron density of the metal atom and greatly decreases its catalytic activity. Conversely, if the EMSI is weak, the metal atom binds less tightly to the support, making it prone to aggregation and potentially diminishing its catalytic effectiveness. These limitations make it challenging for SACs to simultaneously achieve optimal catalytic activity, product selectivity, and stability. Therefore, overcoming the trade-off among these factors is crucial for developing high-performance SACs. One potential solution to these challenges is the construction of multi-metal atom catalysts.

Enhancing the understanding of catalysis through advanced characterization and theoretical methods

At present, our understanding of the fundamental nature of single-atom catalysis remains limited, primarily due to two factors: limitations of characterization techniques and inaccuracies in theoretical calculations. Existing characterization techniques (TEM, EELS, AFM, XAS) are limited by low resolution and the inability to monitor dynamic reaction processes in real time.

To elucidate the catalytic mechanism, high-resolution techniques such as aberration-corrected TEM (AC-TEM) and synchrotron XAS can resolve active sites and structural details, enabling mechanistic studies. Furthermore, high time-resolution characterization techniques, particularly in-situ or operando methods, can track the adsorption and desorption processes of reactants and intermediates, as well as dynamic changes in the active sites during reactions, thereby revealing the reaction mechanisms. This approach also facilitates the investigation of the deactivation of active sites and the mechanisms underlying catalyst degradation, providing theoretical guidance for extending the lifespan of catalysts. The application of these advanced methods contributes to uncovering the behavior of catalysts at the atomic and molecular levels, offering a solid theoretical foundation for designing more efficient catalysts.

Theoretical calculations, particularly DFT, are essential for predicting and understanding the electronic structure, adsorption energies, and energy changes in catalytic processes. However, DFT calculations are constrained by computational resources and often rely on simplified models that neglect environmental factors, which may lead to inaccuracies in modeling complex catalytic systems. Additionally, their computational efficiency is insufficient to meet the demands of large-scale catalyst screening. To address these limitations, researchers are exploring new methods to improve both the accuracy and efficiency of theoretical predictions. By employing multi-scale modeling approaches (e.g., QM/MD coupling and phase-field simulations), researchers can comprehensively account for the complex coordination environments of catalysts, thereby significantly improving the accuracy of theoretical predictions. Furthermore, integrating machine learning and high-throughput computing techniques optimizes catalyst design and bridges the gap between theory and experiment, offering new possibilities for screening and predicting high-performance SACs. For example, Professor Teng Li's group has demonstrated that combining machine learning with first-principles calculations allows for rapid performance predictions of SACs, achieving speeds 130,000 times faster than traditional DFT methods.¹⁴³ The adoption of these advanced theoretical tools, along with the development of improved computational methods, will significantly reduce the time and effort required by researchers, thereby providing clear guidance for subsequent experimental studies.

Developing controllable synthesis strategies for SACs

The synthesis methods of SACs critically influence their properties, including metal loading, spatial distribution, aggregation resistance, and coordination structure. Additionally, the structure and coordination environment of the support (such as defects, heteroatom doping, and surface functional groups) play a significant role. By employing different synthesis strategies to regulate these structural features, researchers can significantly influence the electronic structure and catalytic performance of SACs. Currently, the synthesis methods of SACs can be broadly categorized into three main approaches: bottom-up strategies, top-down strategies, and quantum dot crosslinking/self-assembly strategies.¹⁴⁴ Specific methods for SACs include pyrolysis,^{145,146} wet-chemical methods,^{147,148} atomic layer deposition,^{149,150} and chemical vapor deposition,^{151,152} among others. While each method has its advantages, they also share common limitations, such as difficulty in controlling the anchoring position, distribution, and coordination structure of the metal atoms, low metal loading, complex preparation processes, and low yields. These drawbacks hinder their applicability for industrial-scale production. Therefore, developing controllable, simple, and high-yield synthesis methods to obtain SACs with tunable structures and high metal loadings is a pressing issue for future research. In recent years, various new methods such as gas migration,^{153,154} ion implantation,¹⁵⁵ photochemical synthesis,^{156,157} and electrochemical deposition^{158,159} have been developed for synthesizing SACs. Gas migration involves migrating and depositing metal precursors in the gas phase onto the surface of the support. This method allows for the deposition of metal atoms at relatively low temperatures, which helps preserve the isolated state of the metal atoms. Ion implantation, on the other hand, directly injects metal ions into the support using ion implantation technology. This approach enables precise control over both the implantation depth and the distribution of atoms by adjusting parameters such as energy and dosage. Its excellent batch consistency and reproducibility make it suitable for industrial production. Photochemical synthesis utilizes electron-hole pairs generated by light irradiation to reduce metal precursors, forming stable single-atom sites on the support. By adjusting parameters such as light intensity, duration, and wavelength, researchers can precisely control the reduction process of the metal precursors. Electrochemical deposition applies an electric field in an electrolyte to deposit metal ions or other compounds onto the surface of a conductor. This method allows for fine control over the amount and distribution of the deposited metal by tuning parameters like current density, potential, and time. Furthermore, electrochemical deposition can regulate the reduction and deposition of metal precursors at the molecular level, which facilitates a high degree of dispersion of metal atoms.

In summary, the judicious selection and optimization of synthesis methods are of paramount importance for enhancing the catalytic performance of single-atom catalysts in the context of $2e^-$ ORR. As research continues to advance, it is anticipated that a variety of innovative synthesis strategies will emerge, offering novel solutions to the current challenges in synthesis, and further propelling the field forward.

REFERENCES

1. Agarwal N., Freakley S. J., McVicker R. U., et al. (2017). Aqueous Au-Pd colloids catalyze selective CH_4 oxidation to CH_3OH with O_2 under mild conditions. *Science* **358**:223–227. DOI:10.1126/science.aan6515
2. Hage R. and Lienke A. (2006). Applications of transition-metal catalysts to textile and wood-pulp bleaching. *Angew. Chem. Int. Ed.* **45**:206–222. DOI:10.1002/anie.200500525
3. Jeon T. H., Kim B., Kim C., et al. (2021). Solar photoelectrochemical synthesis of electrolyte-free H_2O_2 aqueous solution without needing electrical bias and H_2 . *Energy Environ. Sci.* **14**:3110–3119. DOI:10.1039/D0EE03567J
4. https://www.sohu.com/a/727956610_121172584 (accessed 13 October 2023).
5. Yi Y., Wang L., Li G., et al. (2016). A review on research progress in the direct synthesis of hydrogen peroxide from hydrogen and oxygen: Noble-metal catalytic method, fuel-cell method and plasma method. *Catal. Sci. Technol.* **6**:1593–1610. DOI:10.1039/C5CY01567G
6. Li M., Song P., Hou M., et al. (2024). Atomic-level functionalized carbon-based materials for effective electrosynthesis of hydrogen peroxide: A review. *Chem. Eng. J.* **479**:147608. DOI:10.1016/j.cej.2023.147608
7. Campos-Martin J. M., Blanco-Brieva G. and Fierro J. L. G. (2006). Hydrogen peroxide synthesis: An outlook beyond the anthraquinone process. *Angew. Chem. Int. Ed.* **45**:6962–6984. DOI:10.1002/anie.200503779

8. Yang S., Verdager-Casadevall A., Arnanson L., et al. (2018). Toward the decentralized electrochemical production of H_2O_2 : A focus on the catalysis. *ACS Catal.* **8**:4064–4081. DOI:10.1021/acscatal.8b00217
9. Edwards J. K., Freakley S. J., Lewis R. J., et al. (2015). Advances in the direct synthesis of hydrogen peroxide from hydrogen and oxygen. *Catal. Today* **248**:3–9. DOI:10.1016/j.cattod.2014.03.011
10. Lunsford J. H. (2003). The direct formation of H_2O_2 from H_2 and O_2 over palladium catalysts. *J. Catal.* **216**:455–460. DOI:10.1016/S0021-9517(02)00070-2
11. Fuku K., Miyase Y., Miseki Y., et al. (2017). Photoelectrochemical hydrogen peroxide production from water on a $WO_3/BiVO_4$ photoanode and from O_2 on an Au cathode without external bias. *Chem. Asian J.* **12**:1111–1119. DOI:10.1002/asia.201700292
12. Fuku K. and Sayama K. (2016). Efficient oxidative hydrogen peroxide production and accumulation in photoelectrochemical water splitting using a tungsten trioxide/bismuth vanadate photoanode. *Chem. Commun.* **52**:5406–5409. DOI:10.1039/C6CC001605G
13. Shiraishi Y., Kanazawa S., Kofuji Y., et al. (2014). Sunlight-driven hydrogen peroxide production from water and molecular oxygen by metal-free photocatalysts. *Angew. Chem. Int. Ed.* **53**:13454–13459. DOI:10.1002/anie.201407938
14. Fukuzumi S., Lee Y. M. and Nam W. (2018). Solar-driven production of hydrogen peroxide from water and dioxygen. *Chemistry* **24**:5016–5031. DOI:10.1002/chem.201704512
15. Fellinger T.-P., Hasché F., Strasser P., et al. (2012). Mesoporous nitrogen-doped carbon for the electrocatalytic synthesis of hydrogen peroxide. *J. Am. Chem. Soc.* **134**:4072–4075. DOI:10.1021/ja300038p
16. Lu Z., Chen G., Siahrostami S., et al. (2018). High-efficiency oxygen reduction to hydrogen peroxide catalysed by oxidized carbon materials. *Nat. Catal.* **1**:156–162. DOI:10.1038/s41929-017-0017-x
17. Melchionna M., Fornasiero P. and Prato M. (2019). The rise of hydrogen peroxide as the main product by metal-free catalysis in oxygen reductions. *Adv. Mater.* **31**:e1802920. DOI:10.1002/adma.201802920
18. Ciriminna R., Albanese L., Meneguzzo F., et al. (2016). Hydrogen peroxide: A key chemical for today's sustainable development. *ChemSusChem* **9**:3374–3381. DOI:10.1002/cssc.201600895
19. Zhang H., Xu H., Yao C., et al. (2024). Metal atom–support interaction in single atom catalysts toward hydrogen peroxide electrosynthesis. *ACS Nano* **18**:21836–21854. DOI:10.1021/acsnano.4c07916
20. Zhu W. and Chen S. (2020). Recent progress of single-atom catalysts in the electrocatalytic reduction of oxygen to hydrogen peroxide. *Electroanalysis* **32**:2591–2602. DOI:10.1002/elan.202060334
21. Xu S., Gao Y., Liang T., et al. (2022). N, O-coupling towards the selectively electrochemical production of H_2O_2 . *Chin. Chem. Lett.* **33**:5152–5157. DOI:10.1016/j.ccllet.2022.01.057
22. Zhao K., Su Y., Quan X., et al. (2018). Enhanced H_2O_2 production by selective electrochemical reduction of O_2 on fluorine-doped hierarchically porous carbon. *J. Catal.* **357**:118–126. DOI:10.1016/j.jcat.2017.11.008
23. Pang Y., Wang K., Xie H., et al. (2020). Mesoporous carbon hollow spheres as efficient electrocatalysts for oxygen reduction to hydrogen peroxide in neutral electrolytes. *ACS Catal.* **10**:7434–7442. DOI:10.1021/acscatal.0c00584
24. Ri K., Pak S., Sun D., et al. (2024). Boron-doped rGO electrocatalyst for high effective generation of hydrogen peroxide: Mechanism and effect of oxygen-enriched air. *Appl. Catal. B Environ.* **343**:123471. DOI:10.1016/j.apcatb.2023.123471
25. Fan M., Wang Z., Sun K., et al. (2023). N-B-OH site-activated graphene quantum dots for boosting electrochemical hydrogen peroxide production. *Adv. Mater.* **35**:2209086. DOI:10.1002/adma.202209086
26. Pizzutillo E., Freakley S. J., Cherevko S., et al. (2017). Gold–palladium bimetallic catalyst stability: Consequences for hydrogen peroxide selectivity. *ACS Catal.* **7**:5699–5705. DOI:10.1021/acscatal.7b01447
27. Jirkovský J. S., Panas I., Ahlberg E., et al. (2011). Single atom hot-spots at Au-Pd nanoalloys for electrocatalytic H_2O_2 production. *J. Am. Chem. Soc.* **133**:19432–19441. DOI:10.1021/ja206477z
28. Verdager-Casadevall A., Deiana D., Karamad M., et al. (2014). Trends in the electrochemical synthesis of H_2O_2 : Enhancing activity and selectivity by electrocatalytic site engineering. *Nano Lett.* **14**:1603–1608. DOI:10.1021/nl500037x
29. Sheng H., Hermes E. D., Yang X., et al. (2019). Electrocatalytic production of H_2O_2 by selective oxygen reduction using earth-abundant cobalt pyrite (CoS_2). *ACS Catal.* **9**:8433–8442. DOI:10.1021/acscatal.9b02546
30. Sheng H., Janes A. N., Ross R. D., et al. (2022). Linear paired electrochemical valorization of glycerol enabled by the electro-Fenton process using a stable $NiSe_2$ cathode. *Nat. Catal.* **5**:716–725. DOI:10.1038/s41929-022-00826-y
31. Ross R. D., Sheng H., Parihar A., et al. (2021). Compositionally tuned trimetallic thiospinel catalysts for enhanced electrosynthesis of hydrogen peroxide and built-in hydroxyl radical generation. *ACS Catal.* **11**:12643–12650. DOI:10.1021/acscatal.1c03349
32. Yang X.-F., Wang A., Qiao B., et al. (2013). Single-atom catalysts: A new frontier in heterogeneous catalysis. *Acc. Chem. Res.* **46**:1740–1748. DOI:10.1021/ar300361m
33. Choi C. H., Kim M., Kwon H. C., et al. (2016). Tuning selectivity of electrochemical reactions by atomically dispersed platinum catalyst. *Nat. Commun.* **7**:10922. DOI:10.1038/ncomms10922
34. Wang Y. L., Gurses S., Felvey N., et al. (2019). In situ deposition of Pd during oxygen reduction yields highly selective and active electrocatalysts for direct H_2O_2 production. *ACS Catal.* **9**:8453–8463. DOI:10.1021/acscatal.9b01758
35. Kattel S. and Wang G. (2013). A density functional theory study of oxygen reduction reaction on $Me-N_4$ ($Me = Fe, Co, or Ni$) clusters between graphitic pores. *J. Mater. Chem. A* **1**:10790–10797. DOI:10.1039/C3TA12142A
36. Jin Q., Shen Y., Ma L., et al. (2019). Novel TiO_2 catalyst carriers with high thermostability for selective catalytic reduction of NO by NH_3 . *Catal. Today* **327**:279–287. DOI:10.1016/j.cattod.2018.04.038
37. Zhang B., Xu W., Lu Z., et al. (2020). Recent progress on carbonaceous material engineering for electrochemical hydrogen peroxide generation. *Trans. Tianjin Univ.* **26**:188–196. DOI:10.1007/s12209-020-00240-0
38. Tian Y., Deng D., Xu L., et al. (2023). Strategies for sustainable production of hydrogen peroxide via oxygen reduction reaction: From catalyst design to device setup. *Nano-Micro Lett.* **15**:122. DOI:10.1007/s40820-023-01067-9
39. Zhuang Z., Huang A., Tan X., et al. (2023). p-Block-metal bismuth-based electrocatalysts featuring tunable selectivity for high-performance oxygen reduction reaction. *Joule* **7**:1003–1015. DOI:10.1016/j.joule.2023.04.005
40. Montemore M. M., van Spronsen M. A., Madix R. J., et al. (2018). O_2 activation by metal surfaces: Implications for bonding and reactivity on heterogeneous catalysts. *Chem. Rev.* **118**:2816–2862. DOI:10.1021/acs.chemrev.7b00217
41. Wang N., Zhao X., Zhang R., et al. (2022). Highly selective oxygen reduction to hydrogen peroxide on a carbon-supported single-atom Pd electrocatalyst. *ACS Catal.* **12**:4156–4164. DOI:10.1021/acscatal.1c05633
42. Guo X., Lin S., Gu J., et al. (2019). Simultaneously achieving high activity and selectivity toward two-electron O_2 electroreduction: The power of single-atom catalysts. *ACS Catal.* **9**:11042–11054. DOI:10.1021/acscatal.9b02778
43. Karamad M., Tripkovic V. and Rossmeisl J. (2014). Intermetallic alloys as CO electroreduction catalysts—role of isolated active sites. *ACS Catal.* **4**:2268–2273. DOI:10.1021/cs500328c
44. Song M., Liu W., Zhang J., et al. (2023). Single-atom catalysts for H_2O_2 electrosynthesis via two-electron oxygen reduction reaction. *Adv. Funct. Mater.* **33**:2212087. DOI:10.1002/adfm.202212087
45. Liu K., Chen P., Sun Z., et al. (2023). The atomic interface effect of single atom catalysts for electrochemical hydrogen peroxide production. *Nano Res.* **16**:10724–10741. DOI:10.1007/s12274-023-5823-7
46. Huang H., Sun M., Li M., et al. (2023). Recent advances in single-atom catalysts for electrocatalytic synthesis of hydrogen peroxide. *Green Energy Resour.* **1**:100031. DOI:10.1016/j.gerr.2023.100031
47. Cheng Y., Wang H., Song H., et al. (2023). Design strategies towards transition metal single atom catalysts for the oxygen reduction reaction – A review. *Nano Res. Energy* **2**:e9120082. DOI:10.26599/NRE.2023.9120082
48. Chen K.-Y., Huang Y.-X., Jin R.-C., et al. (2023). Single atom catalysts for use in the selective production of hydrogen peroxide via two-electron oxygen reduction reaction: Mechanism, activity, and structure optimization. *Appl. Catal. B Environ.* **337**:122987. DOI:10.1016/j.apcatb.2023.122987
49. Zhang J., Yang H. and Liu B. (2021). Coordination engineering of single-atom catalysts for the oxygen reduction reaction: A review. *Adv. Energy Mater.* **11**:2002473. DOI:10.1002/aenm.202002473
50. Sun K., Xu W., Lin X., et al. (2021). Electrochemical oxygen reduction to hydrogen peroxide via a two-electron transfer pathway on carbon-based single-atom catalysts. *Adv. Mater. Interfaces* **8**:2001360. DOI:10.1002/admi.202001360
51. Jiang K., Zhao J. and Wang H. (2020). Catalyst design for electrochemical oxygen reduction toward hydrogen peroxide. *Adv. Funct. Mater.* **30**:2003321. DOI:10.1002/adfm.202003321
52. Yu A. and Yang Y. (2025). Atomically dispersed metal catalysts for oxygen reduction reaction: Two-electron vs. four-electron pathways. *Angew. Chem. Int. Ed.* **64**:e202424161. DOI:10.1002/anie.202424161
53. Zhang L., Jiang S., Ma W., et al. (2022). Oxygen reduction reaction on Pt-based electrocatalysts: Four-electron vs. two-electron pathway. *Chin. J. Catal.* **43**:1433–1443. DOI:10.1016/S1872-2067(21)63961-X
54. Gao W., Chen Y., Li B., et al. (2020). Determining the adsorption energies of small molecules with the intrinsic properties of adsorbates and substrates. *Nat. Commun.* **11**:1196. DOI:10.1038/s41467-020-14969-8
55. Mase K., Ohkubo K. and Fukuzumi S. (2013). Efficient two-electron reduction of dioxygen to hydrogen peroxide with one-electron reductants with a small overpotential catalyzed by a cobalt chlorin complex. *J. Am. Chem. Soc.* **135**:2800–2808. DOI:10.1021/ja312199h
56. Yang S., Tak Y. J., Kim J., et al. (2017). Support effects in single-atom platinum catalysts for electrochemical oxygen reduction. *ACS Catal.* **7**:1301–1307. DOI:10.1021/acscatal.6b02899
57. Chang Q. W., Zhang P., Mostaghimi A. H. B., et al. (2020). Promoting H_2O_2 production

- via 2-electron oxygen reduction by coordinating partially oxidized Pd with defect carbon. *Nat. Commun.* **11**:2178. DOI:10.1038/s41467-020-15843-3
58. Wei Z., Deng B., Chen P., et al. Palladium-based single atom catalysts for high-performance electrochemical production of hydrogen peroxide. *Chem. Eng. J.* **428**:131112. DOI:10.1016/j.cej.2021.131112.
59. Luo E., Yang T., Liang J., et al. (2024). Selective oxygen electroreduction to hydrogen peroxide in acidic media: The superiority of single-atom catalysts. *Nano Res.* **17**:4668–4681. DOI:10.1007/s12274-024-6505-9
60. Shin S., Kim J., Park S., et al. (2019). Changes in the oxidation state of Pt single-atom catalysts upon removal of chloride ligands and their effect for electrochemical reactions. *Chem. Commun.* **55**:6389–6392. DOI:10.1039/C9CC01593K
61. Zhao J., Fu C., Ye K., et al. (2022). Manipulating the oxygen reduction reaction pathway on Pt-coordinated motifs. *Nat. Commun.* **13**:685. DOI:10.1038/s41467-022-28346-0
62. Song X. Z., Li N., Zhang H., et al. (2019). Promotion of hydrogen peroxide production on graphene-supported atomically dispersed platinum: Effects of size on oxygen reduction reaction pathway. *J. Power Sources* **435**:226771. DOI:10.1016/j.jpowsour.2019.226771
63. Yang S., Kim J., Tak Y. J., et al. (2016). Single-atom catalyst of platinum supported on titanium nitride for selective electrochemical reactions. *Angew. Chem. Int. Ed.* **55**:2058–2062. DOI:10.1002/anie.201509241
64. Fortunato G. V., Pizzutilo E., Mingers A. M., et al. (2018). Impact of palladium loading and interparticle distance on the selectivity for the oxygen reduction reaction toward hydrogen peroxide. *J. Phys. Chem. C* **122**:15878–15885. DOI:10.1021/acs.jpcc.8b04262
65. Jung E., Shin H., Lee B.-H., et al. (2020). Atomic-level tuning of Co–N–C catalyst for high-performance electrochemical H₂O₂ production. *Nat. Mater.* **19**:436–442. DOI:10.1038/s41563-019-0571-5
66. Sun Y., Silvili L., Sahraie N. R., et al. (2019). Activity–selectivity trends in the electrochemical production of hydrogen peroxide over single-site metal–nitrogen–carbon catalysts. *J. Am. Chem. Soc.* **141**:12372–12381. DOI:10.1021/jacs.9b05576
67. Yuan J., Yin H., Ge X., et al. (2023). Superior efficiency hydrogen peroxide production in acidic media through epoxy group adjacent to Co–O/C active centers on carbon black. *Chem. Eng. J.* **465**:142691. DOI:10.1016/j.cej.2023.142691
68. Lee C.-S., Jeon T. H., Jang Y. H., et al. (2023). Cobalt single-atom catalyst as a multifunctional electrocatalyst for boosting radical generation. *Chem. Eng. J.* **481**:148431. DOI:10.1016/j.cej.2023.148431
69. Yang L., Sun G., Fu H., et al. (2023). Isolation of cobalt single atoms on hollow B, N co-doped defective carbon nanotubes for hydrogen peroxide production and tandem reagent-free electro-Fenton oxidation. *Chem. Eng. J.* **472**:145052. DOI:10.1016/j.cej.2023.145052
70. Liu W., Zhang C., Zhang J., et al. (2022). Tuning the atomic configuration of Co–N–C electrocatalyst enables highly-selective H₂O₂ production in acidic media. *Appl. Catal. B Environ.* **310**:121312. DOI:10.1016/j.apcatb.2022.121312
71. Yan L., Wang C., Wang Y., et al. (2023). Optimizing the binding of the *OOH intermediate via axially coordinated Co–N₅ motif for efficient electrocatalytic H₂O₂ production. *Appl. Catal. B Environ.* **338**:123078. DOI:10.1016/j.apcatb.2023.123078
72. Fan W., Duan Z., Liu W., et al. (2023). Rational design of heterogenized molecular phthalocyanine hybrid single-atom electrocatalyst towards two-electron oxygen reduction. *Nat Commun* **14**:1426. DOI:10.1038/s41467-023-37066-y
73. Gong H., Wei Z., Gong Z., et al. (2022). Low-coordinated Co–N–C on oxygenated graphene for efficient electrocatalytic H₂O₂ production. *Adv. Funct. Mater.* **32**:2106886. DOI:10.1002/adfm.202106886
74. Huang H., Sun M., Li S., et al. (2024). Enhancing H₂O₂ electrosynthesis at industrial-relevant current in acidic media on diatomic cobalt sites. *J Am Chem Soc* **146**:9434–9443. DOI:10.1021/jacs.4c02031
75. Du J., Han G., Zhang W., et al. (2023). CoIn dual-atom catalyst for hydrogen peroxide production via oxygen reduction reaction in acid. *Nat Commun* **14**:4766. DOI:10.1038/s41467-023-40467-8
76. Yang L., Cheng H., Li H., et al. (2024). Atomic confinement empowered CoZn dual-single-atom nanotubes for H₂O₂ production in sequential dual-cathode electro-fenton process. *Adv Mater* **36**:e2406957. DOI:10.1002/adma.202406957
77. Tong Y., Liu J., Su B.-J., et al. (2024). High-rate electrochemical H₂O₂ production over multimetallic atom catalysts under acidic–neutral conditions. *Carbon Energy* **6**:e378. DOI:10.1002/cey.2.378
78. Wu Y., Ding Y., Han X., et al. (2022). Modulating coordination environment of Fe single atoms for high-efficiency all-pH-tolerated H₂O₂ electrochemical production. *Appl. Catal. B Environ.* **315**:121578. DOI:10.1016/j.apcatb.2022.121578
79. Tang C., Jiao Y., Shi B., et al. (2020). Coordination tunes selectivity: Two-electron oxygen reduction on high-loading molybdenum single-atom catalysts. *Angew. Chem. Int. Ed.* **59**:9171–9176. DOI:10.1002/anie.202003842
80. Cheng X., Hu J., Shang W., et al. (2024). Asymmetrically ligated single atomic nickel sites for efficient hydrogen peroxide electrosynthesis. *Nano Res.* **17**:1094–1100. DOI:10.1007/s12274-023-5899-0
81. Zhang B., Han B., Guan C., et al. (2023). Highly selective oxygen reduction to H₂O₂ on π -d conjugated coordination polymers: The effect of coordination atoms. *Chem. Eng. J.* **460**:141688. DOI:10.1016/j.cej.2023.141688
82. Xu J., Zheng X., Feng Z., et al. (2021). Organic wastewater treatment by a single-atom catalyst and electrolytically produced H₂O₂. *Nat. Sustain.* **4**:233–241. DOI:10.1038/s41893-020-00635-w
83. Zhang X., Wang C., Chen K., et al. (2023). Optimizing the Pd sites in pure metallic aerogels for efficient electrocatalytic H₂O₂ production. *Adv. Mater.* **35**:2211512. DOI:10.1002/adma.202211512
84. Zhu P., Feng W., Zhao D., et al. (2023). p-Block bismuth nanoclusters sites activated by atomically dispersed bismuth at tandem boosting electrocatalytic hydrogen peroxide production. *Angew. Chem. Int. Ed.* **62**:e202304488. DOI:10.1002/anie.202304488
85. Yan M., Wei Z., Gong Z., et al. (2023). Sb₂S₃-templated synthesis of sulfur-doped Sb–N–C with hierarchical architecture and high metal loading for H₂O₂ electrosynthesis. *Nat. Commun.* **14**:368. DOI:10.1038/s41467-023-36078-y
86. Zhang F., Zhu Y., Tang C., et al. (2022). High-efficiency electrosynthesis of hydrogen peroxide from oxygen reduction enabled by a tungsten single atom catalyst with unique terdentate N₃O₂ coordination. *Adv. Funct. Mater.* **32**:2110224. DOI:10.1002/adfm.202110224
87. Li D., Guo Y., Sun Y., et al. (2024). Efficient industrial-current-density H₂O₂ production in neutral medium via external-shell boron regulation on single-atom VN₄ sites. *Chem. Eng. J.* **494**:153211. DOI:10.1016/j.cej.2024.153211
88. Siahrostami S., Verdaguer-Casadevall A., Karamad M., et al. (2013). Enabling direct H₂O₂ production through rational electrocatalyst design. *Nat. Mater.* **12**:1137–1143. DOI:10.1038/nmat3795
89. Zheng C., Zhang X., Zhou Z., et al. (2022). A first-principles study on the electrochemical reaction activity of 3d transition metal single-atom catalysts in nitrogen-doped graphene: Trends and hints. *eScience* **2**:219–226. DOI:10.1016/j.esci.2022.02.009
90. Gao J., Yang H. b., Huang X., et al. (2020). Enabling direct H₂O₂ production in acidic media through rational design of transition metal single atom catalyst. *Chem* **6**:658–674. DOI:10.1016/j.chempr.2019.12.008
91. Calle-Vallejo F., Krabbe A. and García-Lastra J. M. (2017). How covalence breaks adsorption-energy scaling relations and solvation restores them. *Chem. Sci.* **8**:124–130. DOI:10.1039/C6SC02123A
92. Zhao C.-X., Li B.-Q., Liu J.-N., et al. (2021). Intrinsic electrocatalytic activity regulation of m–n–c single-atom catalysts for the oxygen reduction reaction. *Angew. Chem. Int. Ed.* **60**:4448–4463. DOI:10.1002/anie.202003917
93. Zhang Q., Zhou M., Ren G., et al. (2020). Highly efficient electrosynthesis of hydrogen peroxide on a superhydrophobic three-phase interface by natural air diffusion. *Nat. Commun.* **11**:1731. DOI:10.1038/s41467-020-15597-y
94. Tauster S. J., Fung S. C. and Garten R. L. (1978). Strong metal-support interactions. Group 8 noble metals supported on titanium dioxide. *J. Am. Chem. Soc.* **100**:170–175. DOI:10.1021/ja00469a029.
95. Liu Y., Bao J., Li Z., et al. (2022). Large-scale defect-rich iron/nitrogen co-doped graphene-based materials as the excellent bifunctional electrocatalyst for liquid and flexible all-solid-state zinc-air batteries. *J. Colloid. Interface Sci.* **607**:1201–1214. DOI:10.1016/j.jcis.2021.09.070
96. Liu D., He Q., Ding S., et al. (2020). Structural regulation and support coupling effect of single-atom catalysts for heterogeneous catalysis. *Adv. Energy Mater.* **10**:2001482. DOI:10.1002/aenm.202001482
97. Campbell C. T. (2012). Catalyst-support interactions: Electronic perturbations. *Nat. Chem.* **4**:597–598. DOI:10.1038/nchem.1412
98. Chen S., Luo T., Li X., et al. (2022). Identification of the highly active Co–N₄ coordination motif for selective oxygen reduction to hydrogen peroxide. *J. Am. Chem. Soc.* **144**:14505–14516. DOI:10.1021/jacs.2c01194
99. Wu F., Pan C., He C.-T., et al. (2020). Single-atom Co–N₄ electrocatalyst enabling four-electron oxygen reduction with enhanced hydrogen peroxide tolerance for selective sensing. *J. Am. Chem. Soc.* **142**:16861–16867. DOI:10.1021/jacs.0c07790
100. Li R. and Wang D. (2022). Superiority of dual-atom catalysts in electrocatalysis: One step further than single-atom catalysts. *Adv. Energy Mater.* **12**:2103564. DOI:10.1002/aenm.202103564
101. Hu Y., Li Z., Li B., et al. (2022). Recent progress of diatomic catalysts: General design fundamentals and diversified catalytic applications. *Small* **18**:2203589. DOI:10.1002/smll.202203589
102. Zhang W., Chao Y., Zhang W., et al. (2021). Emerging dual-atomic-site catalysts for efficient energy catalysis. *Adv. Mater.* **33**:2102576. DOI:10.1002/adma.202102576
103. Zhang Y., Chou J. B., Li J., et al. (2019). Broadband transparent optical phase change materials for high-performance nonvolatile photonics. *Nat. Commun.* **10**:4279. DOI:10.1038/s41467-019-12196-4
104. Guan E., Ciston J., Bare S. R., et al. (2020). Supported metal pair-site catalysts. *ACS Catal.* **10**:9065–9085. DOI:10.1021/acscatal.0c02000
105. Tian S., Wang B., Gong W., et al. (2021). Dual-atom Pt heterogeneous catalyst with excellent catalytic performances for the selective hydrogenation and epoxidation.

- Nat. Commun.* **12**:3181. DOI:10.1038/s41467-021-23517-x
106. Li H., Di S., Niu P., et al. (2022). A durable half-metallic diatomic catalyst for efficient oxygen reduction. *Energy Environ. Sci.* **15**:1601–1610. DOI:10.1039/D1EE03194E
 107. Chen Z., Su X., Ding J., et al. (2022). Boosting oxygen reduction reaction with Fe and Se dual-atom sites supported by nitrogen-doped porous carbon. *Appl. Catal. B Environ.* **308**:121206. DOI:10.1016/j.apcatb.2022.121206
 108. Hu C., Wang Y., Chen J., et al. (2022). Main-group metal single-atomic regulators in dual-metal catalysts for enhanced electrochemical CO₂ reduction. *Small* **18**:2201391. DOI:10.1002/smll.202201391
 109. Yang Y., Qian Y., Li H., et al. (2020). O-coordinated W-Mo dual-atom catalyst for pH-universal electrocatalytic hydrogen evolution. *Sci. Adv.* **6**:eaba6586. DOI:10.1126/sciadv.aba6586
 110. Zhong X., Ye S., Tang J., et al. (2021). Engineering Pt and Fe dual-metal single atoms anchored on nitrogen-doped carbon with high activity and durability towards oxygen reduction reaction for zinc-air battery. *Appl. Catal. B Environ.* **286**:119891. DOI:10.1016/j.apcatb.2021.119891
 111. Yang X., Zeng Y., Alnough W., et al. (2022). Tuning two - electron oxygen - reduction pathways for H₂O₂ electrosynthesis via engineering atomically dispersed single metal site catalysts. *Adv. Mater.* **34**:2107954. DOI:10.1002/adma.202107954
 112. Zhang W., Choi J. W., Kim S., et al. (2023). Penta nitrogen coordinated cobalt single atom catalysts with oxygenated carbon black for electrochemical H₂O₂ production. *Appl. Catal. B Environ.* **331**:122712. DOI:10.1016/j.apcatb.2023.122712
 113. Wu Y., Chen C., Yan X., et al. (2021). Boosting CO₂ electroreduction over a cadmium single - atom catalyst by tuning of the axial coordination structure. *Angew. Chem. Int. Ed.* **60**:20803–20810. DOI:10.1002/anie.202105263
 114. Xiao H., Li K., Zhang T., et al. (2023). High loading atomically distributed Fe asymmetrically coordinated with pyridinic and pyrrolic N on porous N-rich carbon matrix driving high performance of Li-S battery. *Chem. Eng. J.* **471**:144553. DOI:10.1016/j.cej.2023.144553
 115. Wang Y., Shi R., Shang L., et al. (2020). High-efficiency oxygen reduction to hydrogen peroxide catalyzed by nickel single-atom catalysts with tetradentate N₂O₂ coordination in a three-phase flow cell. *Angew. Chem. Int. Ed.* **59**:13057–13062. DOI:10.1002/anie.202004841
 116. Zhang J., Mou Y., Suo W., et al. (2024). Single-atomic Co-N-C sites anchored on helical carbonaceous nanotubes for the oxygen reduction reaction. *Adv. Funct. Mater.* **35**:2417621. DOI:10.1002/adfm.202417621
 117. Hu J., Shang W., Xin C., et al. (2023). Uncovering dynamic edge-sites in atomic Co-N-C electrocatalyst for selective hydrogen peroxide production. *Angew. Chem. Int. Ed.* **62**:e202304754. DOI:10.1002/anie.202304754
 118. Ha Y., Fei B., Yan X., et al. (2020). Atomically dispersed Co-pyridinic N-C for superior oxygen reduction reaction. *Adv. Energy Mater.* **10**:2002592. DOI:10.1002/aenm.202002592
 119. Jiang K., Back S., Akey A. J., et al. (2019). Highly selective oxygen reduction to hydrogen peroxide on transition metal single atom coordination. *Nat. Commun.* **10**:3997. DOI:10.1038/s41467-019-11992-2
 120. Pan J., Fang Q., Xia Q., et al. (2021). Dual effect of the coordination field and sulphuric acid on the properties of a single-atom catalyst in the electrosynthesis of H₂O₂. *Phys. Chem. Chem. Phys.* **23**:21338–21349. DOI:10.1039/D1CP03189A
 121. Zhang E., Tao L., An J., et al. (2022). Engineering the local atomic environments of indium single-atom catalysts for efficient electrochemical production of hydrogen peroxide. *Angew. Chem. Int. Ed.* **61**:e202117347. DOI:10.1002/anie.202117347
 122. Li Z. and Yu C. (2024). Chapter 3 - Structure-performance relationship of nanomaterials. Li Z. and Yu C. (eds). *Nanostructured materials* (Elsevier), pp:43-92. DOI:10.1016/B978-0-443-19256-2.00006-5.
 123. Xiao C., Cheng L., Zhu Y., et al. (2022). Super-coordinated nickel N₄Ni₂O₂ site single-atom catalyst for selective H₂O₂ electrosynthesis at high current densities. *Angew. Chem. Int. Ed.* **61**:e202206544. DOI:10.1002/anie.202206544
 124. Tian Y., Chen R., Liu X., et al. (2023). Fluorine-regulated carbon nanotubes decorated with Co single atoms for multi-site electrocatalysis toward two-electron oxygen reduction. *EcoMat* **5**:e12336. DOI:10.1002/eom.2.12336
 125. Chen S., Luo T., Li X., et al. (2022). Identification of the highly active Co-N₄ coordination motif for selective oxygen reduction to hydrogen peroxide. *J. Am. Chem. Soc.* **144**:14505–14516. DOI:10.1021/jacs.2c01194
 126. Zhang S., Tao Z., Xu M., et al. (2024). Single-atom Co-O₄ sites embedded in a defective-rich porous carbon layer for efficient H₂O₂ electrosynthesis. *Small* **20**:e2310468. DOI:10.1002/smll.202310468
 127. Gong F., Liu Y., Zhao Y., et al. (2023). Universal sub-nanoreactor strategy for synthesis of yolk-shell MoS₂ supported single atom electrocatalysts toward robust hydrogen evolution reaction. *Angew. Chem. Int. Ed.* **62**:e202308091. DOI:10.1002/anie.202308091
 128. Shen R., Chen W., Peng Q., et al. (2019). High-concentration single atomic Pt sites on hollow CuS_x for selective O₂ reduction to H₂O₂ in acid solution. *Chem* **5**:2099–2110. DOI:10.1016/j.chempr.2019.04.024
 129. Lei H., Cui M. and Huang Y. (2022). S-doping promotes pyridine nitrogen conversion and lattice defects of carbon nitride to enhance the performance of Zn-air batteries. *ACS Appl. Mater. Interfaces* **14**:34793–34801. DOI:10.1021/acsami.2c09019
 130. Yu A., Ma G., Zhu L., et al. (2022). Conversion of CO₂ to defective porous carbons in one electro-redox cycle for boosting electrocatalytic H₂O₂ production. *Appl. Catal. B Environ.* **307**:121161. DOI:10.1016/j.apcatb.2022.121161
 131. Liu J., Wei Z., Gong Z., et al. (2023). Single-atom CoN₄ sites with elongated bonding induced by phosphorus doping for efficient H₂O₂ electrosynthesis. *Appl. Catal. B Environ.* **324**:122267. DOI:10.1016/j.apcatb.2022.122267
 132. Zhang W., Choi J. W., Kim S., et al. (2023). Penta nitrogen coordinating cobalt single atom catalysts with oxygenated carbon black for electrochemical H₂O₂ production. *Appl. Catal. B Environ.* **331**:122712. DOI:10.1016/j.apcatb.2023.122712
 133. Ramaswamy N., Tylus U., Jia Q., et al. (2013). Activity descriptor identification for oxygen reduction on nonprecious electrocatalysts: Linking Surface science to coordination chemistry. *J. Am. Chem. Soc.* **135**:15443–15449. DOI:10.1021/ja405149m
 134. Mun Y., Lee S., Kim K., et al. (2019). Versatile strategy for tuning orr activity of a single Fe-N₄ site by controlling electron-withdrawing/donating properties of a carbon plane. *J. Am. Chem. Soc.* **141**:6254–6262. DOI:10.1021/jacs.8b13543
 135. Chen Z., Su X., Ding J., et al. (2022). Boosting oxygen reduction reaction with Fe and Se dual-atom sites supported by nitrogen-doped porous carbon. *Appl. Catal. B Environ.* **308**:121206. DOI:10.1016/j.apcatb.2022.121206
 136. Yin H., Yuan P., Lu B.-A., et al. (2021). Phosphorus-driven electron delocalization on edge-type FeN₄ active sites for oxygen reduction in acid medium. *ACS Catal.* **11**:12754–12762. DOI:10.1021/acscatal.1c02259
 137. Chen Z., Niu H., Ding J., et al. (2021). Unraveling the origin of sulfur-doped Fe-N-C single atom catalyst for enhanced oxygen reduction activity: Effect of Fe-spin state tuning. *Angew. Chem. Int. Ed.* **60**:25404–25410. DOI:10.1002/anie.202110243
 138. Shao C., Wu L., Zhang H., et al. (2021). A versatile approach to boost oxygen reduction of Fe-N₄ sites by controllably incorporating sulfur functionality. *Adv. Funct. Mater.* **31**:2100833. DOI:10.1002/adfm.202100833
 139. Gu J., Magagula S., Zhao J., et al. (2019). Boosting ORR/OER activity of graphdiyne by simple heteroatom doping. *Small Methods* **3**:1800550. DOI:10.1002/smdt.201800550
 140. Wang Y., Gan R., Zhao S., et al. (2022). B, N, F tri-doped lignin-derived carbon nanofibers as an efficient metal-free bifunctional electrocatalyst for ORR and OER in rechargeable liquid/solid-state Zn-air batteries. *Appl. Surf. Sci.* **598**:153891. DOI:10.1016/j.apsusc.2022.153891
 141. Kang Y., Wang W., Li J., et al. (2021). Ultrathin B, N co-doped porous carbon nanosheets derived from intumescent flame retardant for rechargeable Zn-air battery. *J. Power Sources* **493**:229665. DOI:10.1016/j.jpowsour.2021.229665
 142. Zhang E., Tao L., An J., et al. (2022). Engineering the local atomic environments of indium single-atom catalysts for efficient electrochemical production of hydrogen peroxide. *Angew. Chem. Int. Ed.* **61**:e202117347. DOI:10.1002/anie.202117347
 143. Wu L., Guo T. and Li T. (2021). Machine learning-accelerated prediction of overpotential of oxygen evolution reaction of single-atom catalysts. *iScience* **24**:102398. DOI:10.1016/j.isci.2021.102398
 144. Shujuan S., Nannan Z., Haokun P., et al. (2025). Research progress on preparation methods of single-atom catalysts. *J. Inorg. Mater.* **40**:113–127. DOI:10.15541/jim20240302
 145. Chang J., Jing W., Yong X., et al. (2024). Synthesis of ultrahigh-metal-density single-atom catalysts via metal sulfide-mediated atomic trapping. *Nat. Synth.* **3**:1427–1438. DOI:10.1038/s44160-024-00607-4
 146. Chen K., Sun W., Huang J., et al. (2024). Batch preparation of Fe single-atom catalysts for ultrahigh power density zinc-air batteries. *CCS Chem.* **7**:1–12. DOI:10.31635/ccschem.024.202404606
 147. Liu P., Zhao Y., Qin R., et al. (2016). Photochemical route for synthesizing atomically dispersed palladium catalysts. *Science* **352**:797–800. DOI:10.1126/science.aaf5251
 148. Zhang Z., Zhu J., Chen S., et al. (2023). Liquid fluxional ga single atom catalysts for efficient electrochemical CO₂ reduction. *Angew. Chem. Int. Ed.* **62**:e202215136. DOI:10.1002/anie.202215136
 149. Yan H., Cheng H., Yi H., et al. (2015). Single-atom Pd₁/graphene catalyst achieved by atomic layer deposition: Remarkable performance in selective hydrogenation of 1,3-butadiene. *J. Am. Chem. Soc.* **137**:10484–10487. DOI:10.1021/jacs.5b06485
 150. Zhang L., Si R., Liu H., et al. (2019). Atomic layer deposited Pt-Ru dual-metal dimers and identifying their active sites for hydrogen evolution reaction. *Nat. Commun.* **10**:4936. DOI:10.1038/s41467-019-12887-y
 151. Lin Y., Xia C., Zhu Z., et al. (2024). Carbon nanocage supported asymmetrically coordinated nickel single - atom for enhanced CO₂ electroreduction in membrane electrode assembly. *Angew. Chem. Int. Ed.* **64**:e202414569. DOI:10.1002/anie.202414569
 152. Li H., Wan Q., Du C., et al. (2021). Vapor-phase self-assembly for generating thermally stable single atom catalysts. *Chem.* **8**:731–748. DOI:10.1016/j.chempr.2021.11.002
 153. Pereira-Hernández X. I., DeLaRiva A., Muravev V., et al. (2019). Tuning Pt-CeO₂ interactions by high-temperature vapor-phase synthesis for improved reducibility of lattice oxygen. *Nat. Commun.* **10**:1358. DOI:10.1038/s41467-019-09308-5

154. Zhang L., Wan S., Du C., et al. (2024). Generating active metal/oxide reverse interfaces through coordinated migration of single atoms. *Nat Commun* **15**:1234. DOI:10.1038/s41467-024-45483-w
155. Prussin S., Margolese D. I. and Tauber R. N. (1985). Formation of amorphous layers by ion implantation. *J. Appl. Phys.* **57**:180-185. DOI:10.1063/1.334840.
156. Fu W., Wan J., Zhang H., et al. (2022). Photoinduced loading of electron-rich Cu single atoms by moderate coordination for hydrogen evolution. *Nat. Commun.* **13**:5496. DOI:10.1038/s41467-022-33275-z
157. Zhang H., Dong Y., Zhao S., et al. (2020). Photochemical preparation of atomically dispersed nickel on cadmium sulfide for superior photocatalytic hydrogen evolution. *Appl. Catal. B Environ.* **261**:118233. DOI:10.1016/j.apcatb.2019.118233
158. Shen S., Zhao L. and Zhang J. (2022). Promising approach for preparing metallic single-atom catalysts: electrochemical deposition. *Front. Energy* **16**:537–541. DOI:10.1007/s11708-022-0837-5
159. Zhang Z., Feng C., Liu C., et al. (2020). Electrochemical deposition as a universal route for fabricating single-atom catalysts. *Nat. Commun.* **11**:1215. DOI:10.1038/s41467-020-14917-6

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DECLARATION OF INTERESTS

The authors declare no competing interests.

DATA AND CODE AVAILABILITY

Data are available from the corresponding author upon reasonable request.