



Fluorine-Doped Nanocarbon-Based Materials for Aqueous Oxygen Electrocatalysis: Synthesis, Mechanisms, Applications, and Perspectives

Yong Zheng^{1,2}, Junpeng Ma², Xinyang He³, Yining Zhang⁴, Yao Wang⁵, Liu Yang¹ (✉), Zhongwei Chen¹ (✉)

¹ Power Battery & Systems Research Center, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

² College of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang 443002, China

³ National & Local Joint Engineering Research Center of Technical Fiber Composites for Safety and Health, School of Textile & Clothing, Nantong University, Nantong 226019, China

⁴ High-Performance Lithium-Ion Battery Research and Development Center, Yulin Innovation Institute of Clean Energy, Yulin 719004, China

⁵ Department of Materials Science and Engineering, College of Chemistry and Materials Science, Jinan University, Guangzhou 511443, China

Nano Research Energy, **Just Accepted Manuscript** • <https://doi.org/10.26599/NRE.2026.9120278>

<https://www.sciopen.com/journal/2791-0091> on Sep. 17, 2026

© The Authors(s)

Just Accepted

This is a “Just Accepted” manuscript, which has been examined by the peer-review process and has been accepted for publication. A “Just Accepted” manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides “Just Accepted” as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, and the page proofs have been corrected, it will be removed from the “Just Accepted” web site and published officially with volume and article number (e.g., *Nano Research Energy*, 2025, 4, e9120191). Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these “Just Accepted” manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.

Fluorine-Doped Nanocarbon-Based Materials for Aqueous Oxygen Electrocatalysis: Synthesis, Mechanisms, Applications, and Perspectives

Yong Zheng^{1,2}, Junpeng Ma², Xinyang He³, Yining Zhang⁴, Yao Wang⁵, Liu Yang¹(✉), Zhongwei Chen¹(✉)

¹ Power Battery & Systems Research Center, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China.

² College of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang 443002, China.

³ National & Local Joint Engineering Research Center of Technical Fiber Composites for Safety and Health, School of Textile & Clothing, Nantong University, Nantong 226019, China

⁴ High-Performance Lithium-Ion Battery Research and Development Center, Yulin Innovation Institute of Clean Energy, Yulin 719004, China

⁵ Department of Materials Science and Engineering, College of Chemistry and Materials Science, Jinan University, Guangzhou 511443, China.

*E-mail: liuyang93@dicp.ac.cn, zwchen@dicp.ac.cn

TABLE OF CONTENTS (TOC)

Fluorine-Doped Nanocarbon-Based Materials for Aqueous Oxygen Electrocatalysis: Synthesis, Mechanisms, Applications, and Perspectives

Yong Zheng^{1,2}, Junpeng Ma², Xinyang He³, Yining Zhang⁴, Yao Wang⁵, Liu Yang^{1,*}, Zhongwei Chen^{1,*}

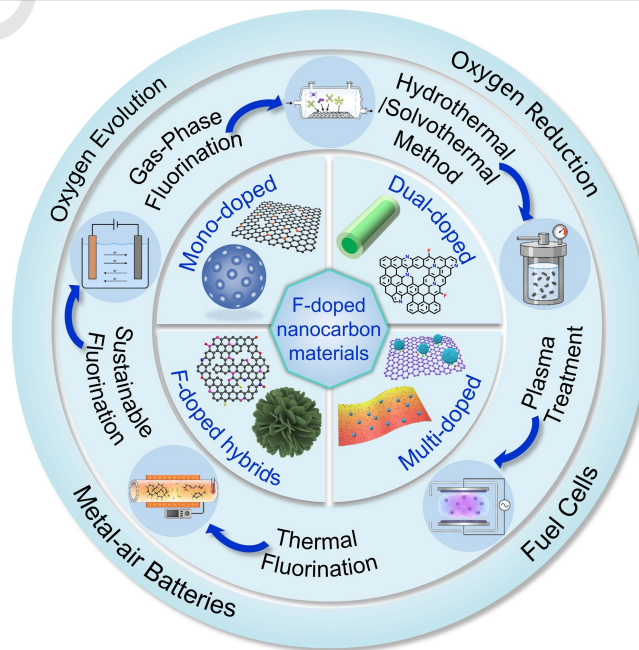
¹Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China.

²China Three Gorges University, China.

³Nantong University, China

⁴Yulin Innovation Institute of Clean Energy, China

⁵Jinan University, China.



This Review highlights recent advances in F-doped nanocarbons for oxygen electrocatalysis, emphasizing F-enabled electronic modulation, defect regulation, and interfacial engineering for enhanced ORR and OER in aqueous energy conversion and H₂O₂ electrosynthesis.



Fluorine-Doped Nanocarbon-Based Materials for Aqueous Oxygen Electrocatalysis: Synthesis, Mechanisms, Applications, and Perspectives

Yong Zheng^{1,2}, Junpeng Ma², Xinyang He³, Yining Zhang⁴, Yao Wang⁵, Liu Yang¹ (✉), and Zhongwei Chen¹ (✉)

¹Power Battery & Systems Research Center, State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

²Country College of Materials and Chemical Engineering, Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, China Three Gorges University, Yichang 443002, China

³National & Local Joint Engineering Research Center of Technical Fiber Composites for Safety and Health, School of Textile & Clothing, Nantong University, Nantong 226019, China

⁴High-Performance Lithium-Ion Battery Research and Development Center, Yulin Innovation Institute of Clean Energy, Yulin 719004, China

⁵Department of Materials Science and Engineering, College of Chemistry and Materials Science, Jinan University, Guangzhou 511443, China

© The Author(s) 2026

Received: 28 July 2026 / Revised: 27 August 2026 / Accepted: 5 September 2026

ABSTRACT

Oxygen electrocatalysis, involving the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), is central to rechargeable metal-air batteries, fuel cells, and electrochemical H₂O₂ production. Fluorine (F)-doped nanocarbon-based materials (F-DNCMs) have emerged as promising alternatives to noble-metal electrocatalysts because the high electronegativity of the F atom enables strong modulation of the electronic structure of carbon frameworks. F incorporation can polarize adjacent carbon atoms, redistribute charge density, regulate the adsorption energetics of oxygen intermediates, and generate defects/edge sites, thereby improving ORR/OER kinetics. Despite these advantages, a comprehensive review of F-doped nanocarbon-based materials (F-DNCMs) for oxygen electrocatalysis remains lacking. This Review systematically summarizes recent progress in the synthesis, structural regulation, catalytic mechanisms, and applications of F-DNCMs. Representative fluorination strategies are presented and compared in terms of their characteristics, advantages, and limitations. F-DNCMs are further classified into F single-doped carbons, F-based dual-doped and multidoped carbons, and F-doped carbon-based hybrids, with emphasis on the effects of C–F bonding configurations, charge polarization, defect engineering, interfacial coupling, and heteroatom synergy on ORR/OER performance. Besides, their applications in metal-air batteries, fuel cells, and electrochemical H₂O₂ production are also highlighted. Finally, key challenges in precise control of F species, identification of active sites, scalable synthesis, and device integration are discussed. This Review aims to establish structure-property-activity relationships and provide practical guidance for the rational design of high-performance F-DNCM electrocatalysts.

KEYWORDS

oxygen electrocatalysis, energy storage and conversion, nanocarbon-based materials, fluorine-doping, electrochemically active sites

1 Introduction

Advanced and sustainable electrochemical energy conversion technologies are increasingly important for addressing the growing demands for efficient energy utilization and ameliorating environmental pollution. Among them, rechargeable metal-air batteries (MABs), fuel cells (FCs), and electrochemical hydrogen peroxide

(H₂O₂) production have attracted considerable attention because of their high theoretical energy efficiency, environmental compatibility, and potential for large-scale applications.^[1–10] Oxygen electrocatalysis plays a central role in these technologies. Specifically, the oxygen reduction reaction (ORR) governs the cathodic process in FCs and the discharge process of MABs, whereas the

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

Address correspondence to Liu Yang, liuyang93@dicp.ac.cn; Zhongwei Chen, zwchen@dicp.ac.cn



oxygen evolution reaction (OER) is crucial for the charging process of rechargeable MABs.^[11] In addition, the two-electron ORR provides an attractive electrochemical route for decentralized and sustainable H₂O₂ production. However, the intrinsically sluggish kinetics of oxygen electrochemistry generally require highly active electrocatalysts. Recently, state-of-the-art oxygen electrocatalysis still relies heavily on noble-metal-based materials, such as Pt/C for ORR and IrO₂/RuO₂-based catalysts for OER, whose high cost, limited abundance, and insufficient long-term durability severely restrict large-scale deployment.^[12-16] Developing efficient, earth-abundant, and robust oxygen electrocatalysts is therefore of both fundamental and technological importance.

Over the past decade, extensive efforts have been devoted to developing alternatives to noble-metal catalysts, including single-atom catalysts, transition-metal oxides/hydroxides/sulfides, high-entropy alloys, metal-free nanocarbons, porous organic polymers, and their composites.^[17-40] Among these candidates, heteroatom-doped carbon nanomaterials have emerged as a particularly attractive class of oxygen electrocatalysts because of their high electrical conductivity, large specific surface area (SSA), structural tunability, tunable surface chemistry, and excellent chemical stability.^[41-47] Incorporating heteroatoms such as N, S, B, P, O, Se, and F can break the electronic symmetry of the carbon lattice and regulate the local charge distribution and spin density, thereby creating active sites and modulating the adsorption of oxygen-related intermediates.^[48-51] Thus, these characteristics make heteroatom engineering an effective strategy for tailoring the intrinsic oxygen electrocatalytic properties of carbon materials.

Among various heteroatoms, fluorine (F) is particularly intriguing because of its exceptionally high

electronegativity (3.98), which enables strong modulation of the electronic structure of neighboring carbon atoms.^[52] F incorporation can redistribute the electron density within carbon frameworks and generate polarized carbon sites, thereby influencing O₂ adsorption and the adsorption/desorption energetics of oxygenated intermediates.^[53] Meanwhile, F doping can induce structural defects, expose additional edge sites, and promote interfacial polarization, all of which may contribute to enhanced oxygen electrocatalysis.^[54] Importantly, the coexistence of ionic, semi-ionic, and covalent C–F bonding configurations offers additional degrees of freedom for regulating the electronic structure, surface chemistry, and catalytic behavior of the carbon matrix.^[55-57] Consequently, F-doped nanocarbon-based materials (F-DNCMs) have emerged as promising platforms for oxygen electrocatalysis (Figure 1) in cutting-edge energy conversion technologies. Nevertheless, F single-doping alone often provides only moderate enhancement in catalytic activity and may be insufficient to meet the requirements of practical energy devices.^[58] F has increasingly been combined with other heteroatoms or metal-containing active species.^[56] Heteroatom co-doping can generate synergistic electronic effects through more pronounced charge redistribution and optimized adsorption energies of oxygenated intermediates,^[59] whereas coupling F-doped nanocarbons with metal-based active sites can further increase active-site density, regulate metal-support electronic interactions, and facilitate charge transfer.^[60, 61] These strategies have substantially broadened the structural and functional diversity of F-DNCMs, allowing them to serve not only as metal-free electrocatalysts but also as versatile supports and functional components in hybrid oxygen electrocatalytic systems.

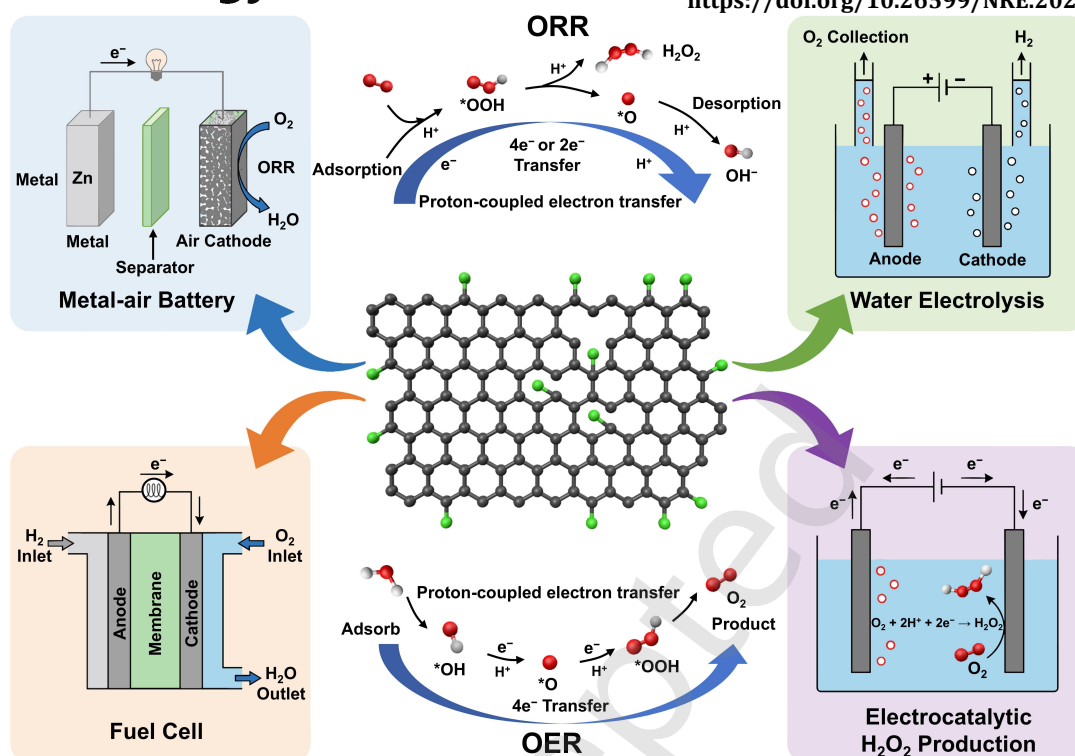


Figure 1. Schematic illustration of the applications and reaction pathways of F-DNCMs in oxygen electrocatalysis.

Since the pioneering report by Sun et al., in which F-doped carbon blacks (CBs) exhibited remarkable ORR activity and delivered a maximum power density exceeding that of commercial Pt/C in alkaline FCs, F-DNCMs have attracted increasing attention for the design and application of F-DNCMs in oxygen electrocatalysis (Figure 2).^[61-69] Subsequent studies have demonstrated substantial progress in controlling F bonding configurations, defect structures, heteroatom interactions, metal-carbon interfaces, and hierarchical architectures, leading to continuously improved ORR/OER performance and expanded applications in energy-conversion devices. However, despite these advances, a systematic review that connects the synthesis, structural chemistry, catalytic mechanisms, and practical applications of F-DNCMs in oxygen electrocatalysis remains lacking. In this Review, therefore provide a

comprehensive overview of recent progress in F-DNCMs, with particular emphasis on their structure-property-activity relationships. We first elucidate the fundamental roles of different F species and local coordination environments in regulating ORR/OER processes, followed by a summary of representative synthetic strategies for constructing F-DNCMs with controllable compositions, bonding configurations, defect structures, and porous architectures. We then discuss recent advances in F-DNCM-based electrocatalysts and their applications in relevant electrochemical energy conversion technologies. Finally, the major challenges and future opportunities in this rapidly developing field are outlined, with the aim of providing mechanistic understanding and practical design principles for next-generation F-DNCM oxygen electrocatalysts.

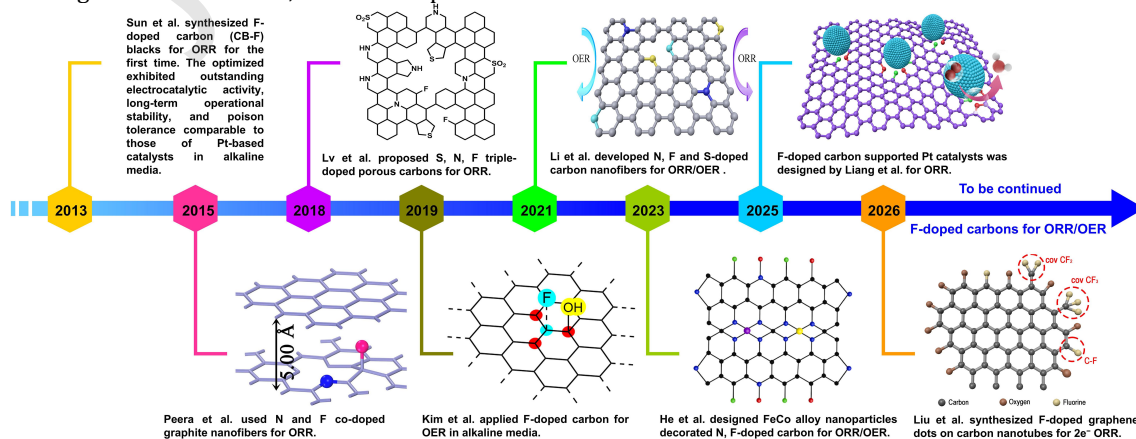


Figure 2. Recent research progress on F-DNCMs for oxygen electrocatalysis over the past decade.^[61-69]



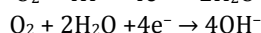
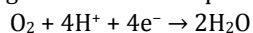
2 Fundamentals of oxygen electrocatalysis on F-Doped nanocarbons

Oxygen electrocatalysis constitutes the fundamental reaction basis of FCs and MABs and largely determines their energy efficiency, reaction kinetics, and long-term durability.^[70] As illustrated in Figure 3a, the cathodic ORR and anodic OER define the polarization behavior of air electrodes. For rechargeable MABs, bifunctional oxygen electrocatalysts are particularly required to promote ORR during discharge and OER during charge (Figure 3b). A mechanistic understanding of the reaction pathways and intermediate adsorption/desorption is therefore essential for the rational design of high-performance F-DNCMs. Both ORR and OER involve multistep interfacial reactions associated with the adsorption, transformation, and desorption of oxygen-containing intermediates, particularly *OOH, *O, and *OH. The binding energy of these intermediates critically determines the reaction pathway, rate-determining step, catalytic activity, and product selectivity. An excessively weak interaction may hinder O₂ activation, whereas excessively strong adsorption can impede intermediate conversion and product desorption. Therefore, rational regulation of the local electronic structure and surface chemical environment of active sites is essential for optimizing oxygen electrocatalysis.

In this circumstance, F-DNCMs provide a distinctive platform for regulating oxygen-intermediate adsorption because the strong electronegativity of F can perturb the local charge/spin distribution of carbon frameworks, generate polarized carbon sites and structural defects, and produce diverse C–F bonding configurations. These structural and electronic effects establish an intrinsic connection between F doping and the key steps of ORR/OER.^[54] Accordingly, a clear understanding of the fundamental oxygen electrocatalytic pathways is necessary before discussing how F species, dopant configurations, and local coordination environments determine the catalytic behavior of F-DNCMs. In the following sections, we first introduce the fundamental mechanisms of ORR and OER and subsequently discuss the structure-activity roles of F doping in regulating these processes.

2.1. Mechanism of oxygen reduction reaction

The ORR typically proceeds through either a four-electron (4e[−]) or two-electron (2e[−]) pathway, depending on the reaction environment, the nature of the catalytic sites, and the binding strength of oxygenated intermediates. The 4e[−] pathway is preferred for FCs and MABs because it enables the complete reduction of O₂ to H₂O in acidic media or OH[−] in alkaline media, thereby delivering higher energy efficiency and suppressing peroxide-related side reactions. The corresponding reactions can be presented as follows:

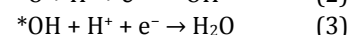
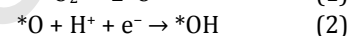


By contrast, the 2e[−] pathway yields H₂O₂ or peroxide

species as intermediates/products, which are undesirable for FCs and MABs because it decreases energy conversion efficiency and can accelerate catalyst degradation. In this regard, it is valuable for disinfection and environmental remediation applications.^[71] In certain cases, ORR may also proceed through an indirect 4e[−] pathway, where H₂O₂ is first formed and subsequently reduced to H₂O or OH[−].

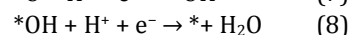
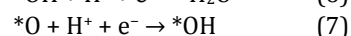
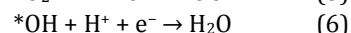
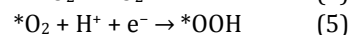
For the direct 4e[−] ORR pathway, two representative mechanisms have been proposed: the dissociative mechanism and the associative mechanism.^[72] The preferred pathway is governed primarily by the O–O bond cleavage barrier and the adsorption strength of oxygenated intermediates on the catalyst surface. In the dissociative pathway, O₂ is first dissociated into adsorbed oxygen species, followed by stepwise proton/electron transfer steps:

Dissociative pathway:



In contrast, in the associative pathway, O₂ remains intact in the initial adsorption stage and is gradually hydrogenated before O–O bond cleavage:

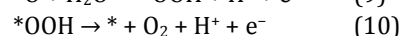
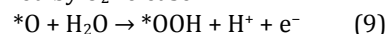
Associative pathway:



Here, * represents an active site on the catalyst surface. The above elementary steps describe the ORR process in acidic electrolyte and alkaline media, where H⁺ is replaced by H₂O and/or OH[−] as the proton source or product.^[73] As illustrated in Figure 3c, the key *O intermediate can be generated through two distinct routes: direct O₂ dissociation at the active site or conversion from the *OOH intermediate. This distinction is crucial because the adsorption energies of *O, *OH, and *OOH critically govern the ORR kinetics and selectivity. For F-doped nanocarbons, F-induced charge redistribution and defects can greatly tune the binding strength of these key intermediates, thereby modulating the preferred ORR pathway.

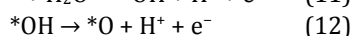
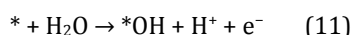
2.2. Mechanism of oxygen evolution reaction

As the reverse counterpart of the ORR, the OER proceeds through multistep proton-coupled electron transfer involving a series of surface-adsorbed oxygenated intermediates.^[74] Similar to ORR, the OER pathway is highly dependent on the surface chemistry of the catalyst and the reaction environment. In acidic media, a representative OER route involves the formation of *OOH from *O, followed by O₂ release:

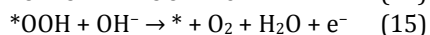
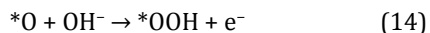


Alternatively, OER may proceed through sequential formation of *OH and *O intermediates, followed by direct coupling of two adsorbed oxygen species:

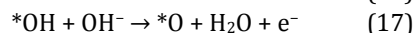
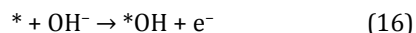




In alkaline media, the corresponding elementary steps are as follows:



Or



Therefore, O_2 evolution involving the $* \text{O}$ intermediate can proceed through two typical routes (Figure 3d): direct O–O bond formation via coupling between adjacent $* \text{O}$ species, or sequential formation of a $* \text{OOH}$ intermediate followed by O_2 release.^[75] The relative preference for these pathways is highly sensitive to the electronic structure of the catalyst and the adsorption thermodynamics of $* \text{OH}$, $* \text{O}$, and $* \text{OOH}$. In this regard, F-doped nanocarbons are

attractive because F incorporation can regulate electron density, defect configuration, and surface polarity, thereby modulating intermediate adsorption and lowering the energy barriers of key OER steps.

Therefore, both ORR and OER are governed by the adsorption, transformation, and desorption of oxygenated intermediates at catalytically active sites. Consequently, the central challenge in designing carbon-based oxygen electrocatalysts is to appropriately regulate the binding strengths of $* \text{OOH}$, $* \text{O}$, and $* \text{OH}$ while maintaining efficient electron transfer and structural stability. For F-doped nanocarbons, these requirements can be addressed through F-induced electronic polarization, defect engineering, and local C–F coordination, which collectively modify the electronic states of neighboring carbon atoms and their interactions with oxygenated intermediates. These mechanistic principles provide the basis for understanding the structure-activity relationships discussed in the following section.

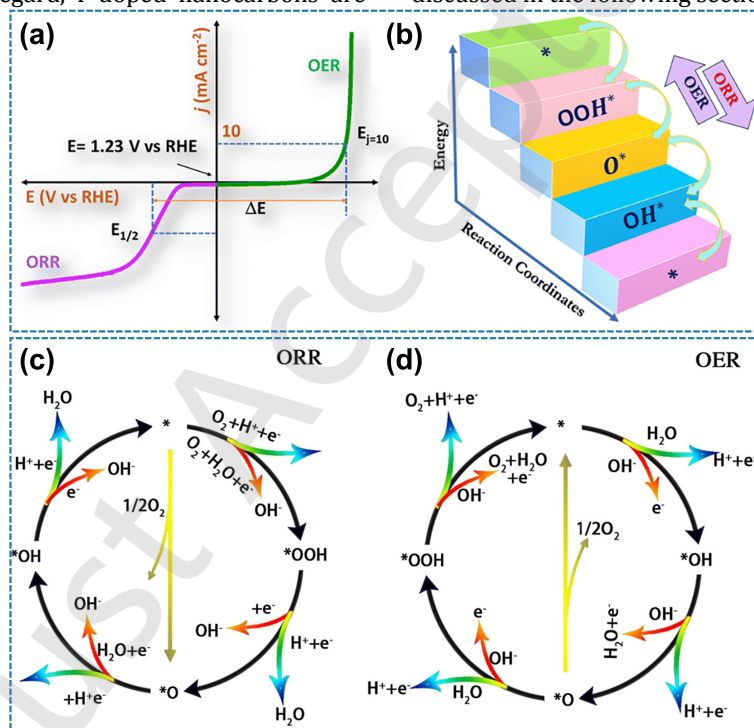


Figure 3. (a) LSV curves of the electrocatalytic ORR and OER processes. (b) The energetics of oxygen redox intermediates.^[75] Reproduced with permission from ref. 75. Copyright Royal Society of Chemistry, 2026. (c-d) ORR and OER mechanisms in acidic and alkaline electrolytes, respectively.^[74] Reproduced with permission from ref. 74. copyright Elsevier, 2021.

2.3. Structure-activity role of fluorine doping in nanocarbons for oxygen electrocatalysis

Based on the ORR/OER mechanisms discussed above, the catalytic performance of nanocarbon materials primarily depends on their ability to regulate oxygen-intermediate adsorption and interfacial electron transfer.^[76] However, pristine carbon frameworks generally possess electronically neutral sp^2 -carbon environments, which provide limited intrinsic activity toward oxygen electrocatalysis. Introducing F into carbon frameworks, including graphene, carbon nanotubes (CNTs), porous carbons, and carbon dots, etc., provides an effective strategy for breaking the electronic symmetry and

generating catalytically active local environments.^[52] Benefiting from its extremely high electronegativity, F can profoundly perturb the electronic environment of the carbon matrix, thereby regulating charge distribution, surface chemistry, and oxygen-intermediate adsorption behavior.^[70] Meanwhile, F-doped nanocarbons retain the intrinsic advantages of carbon-based materials, such as tunable porosity, high conductivity, and stability, which are essential for efficient oxygen electrocatalysis.

As illustrated in Figure 4, the promotional effects of F doping arise from several complementary contributions: (a) the incorporation of F atoms breaks the electroneutrality of the carbon lattice and creates

polarized carbon sites, facilitating O_2 adsorption and activation; (b) F species located at edge or defect sites can modulate the binding strength of oxygenated intermediates, suppress carbon corrosion, and improve catalytic durability; (c) fluorination may weaken interlayer interactions in graphitic domains, expand the interlayer spacing, and exposed more accessible active sites; (d) F

can act synergistically with other heteroatoms or metal-containing active components to further optimize the electronic structure and electrocatalytic environment.^[77] These features establish F doping as a versatile approach for tuning the activity, selectivity, and stability of nanocarbon-based oxygen electrocatalysts.

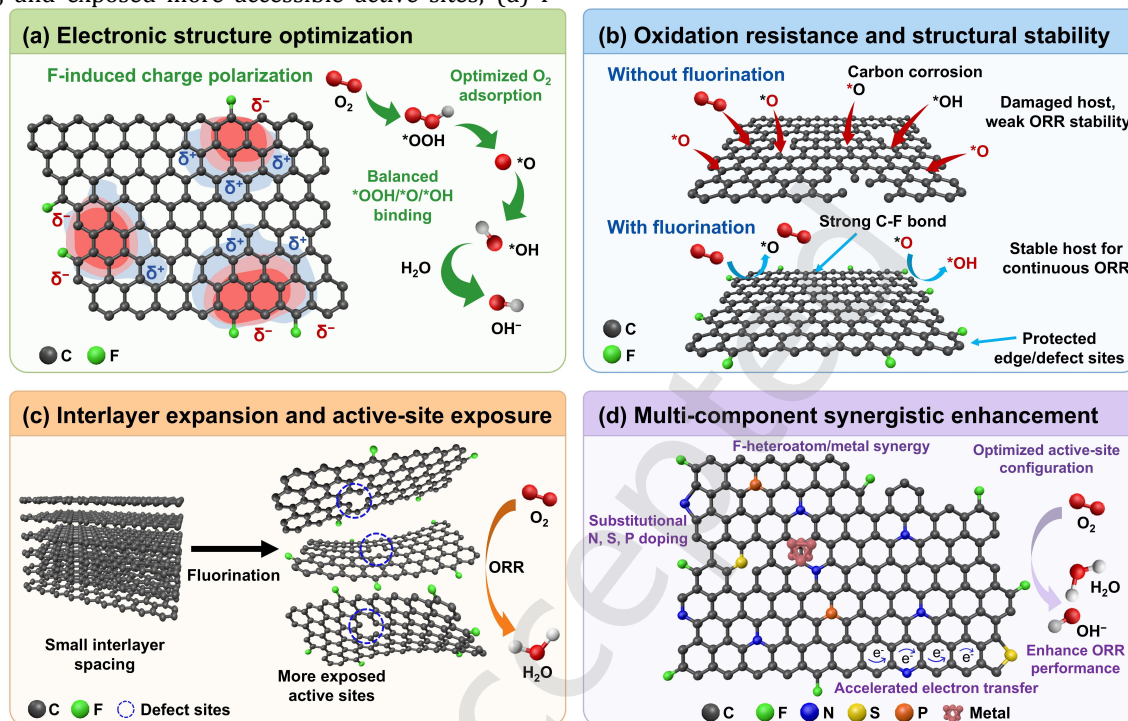


Figure 4. Schematic optimization mechanism of F-DNCMs in ORR.

A key factor governing the catalytic behavior of F-doped nanocarbons is the chemical nature of the C-F bond. In general, three types of C-F species have been identified in F-doped nanocarbon materials, namely ionic, semi-ionic, and covalent C-F bonds.^[78] Among them, semi-ionic C-F bonding is considered particularly favorable for oxygen electrocatalysis because it offers an effective balance between structural stability and electronic conductivity. In ionic C-F configurations, the C-F interaction is relatively weak, allowing the carbon framework to largely retain its sp^2 -hybridized character.^[79] In contrast, covalent C-F bonding is stronger and usually produces a more stable but less conductive carbon structure. Semi-ionic C-F bonds, which are positioned between these two extremes, can maintain sufficient charge polarization while preserving efficient electron transport, thereby contributing to enhanced catalytic activity and durability. In addition, fluorinated nanocarbons generally exhibit stronger electron-withdrawing characteristics and more acidic surface features, which further influence the adsorption energetics and interfacial charge transfer of intermediates.^[80]

Beyond the bonding configuration, the catalytic activity of F-doped nanocarbons is closely associated with F-induced charge/spin redistribution and defect engineering. F doping-induced intrinsic defects and edge

sites can strongly perturb the surface electronic structure of sp^2 carbon frameworks.^[81] In particular, F-doped defective regions can disrupt π -conjugation and induce pronounced charge polarization on neighboring carbon atoms, thus strengthening interactions with oxygenated intermediates during ORR and OER. These effects are highly dependent on the local atomic configuration, and density functional theory (DFT) studies have provided important insights into the nature of active sites, intermediate stabilization, and pathway preference of F-doped nanocarbons.^[75]

For example, Chang et al. constructed three stable FG configurations and evaluated the ORR activity of F species located at armchair edges, basal planes, and zigzag edges (Figure 5a-c). Their results showed that edge fluorination, particularly at graphene edges, is more effective for promoting ORR than fluorination in the basal plane, highlighting the importance of local atomic configuration in determining catalytic activity.^[82] In a related study, fluorinated graphene nanoribbons were found to exhibit a much lower bandgap than undoped graphene nanoribbons, indicating substantially improved electronic conductivity (Figure 5d-e).^[83] This enhancement was attributed to the strong electronic perturbation induced by F, which facilitates charge transfer within the carbon network. Furthermore, DFT calculations suggested that F sites on graphene can moderately activate O_2 and favor the

associative $4e^-$ pathway, thereby accelerating ORR kinetics (Figure 5f).^[84]

Another important function of F doping is its ability to regulate the local environment of neighboring heteroatoms, especially the N atom. Previous studies have shown that the incorporation of F into pyridinic-N-containing carbon frameworks can markedly increase the charge and spin densities of adjacent carbon atoms, thereby enhancing ORR activity. F doping can also influence the N configuration itself. For instance, it may break graphitic bonding and increase the proportion of pyridinic-N and pyrrolic-N species,^[85] or induce structural rearrangement that converts less active N species into more catalytically favorable pyridinic-N/graphitic-N-dominated motifs.^[86] Experimentally, Zhang et al. demonstrated that F promoted the formation of pyridinic-N and improved the charge/spin density of neighboring Lewis basic carbon sites, enabling the resulting catalyst to deliver a great half-wave potential ($E_{1/2}$) of 0.89 V and 0.75 V vs. RHE in alkaline and acidic media, respectively.^[87] Similarly, Li et al. provided atomic-level evidence that F incorporation during synthesis can direct N reconfiguration toward a pyridinic-N/graphitic-N-dominated structure with a lower theoretical ORR overpotential.^[86]

F can also play a more complex role in metal-containing F-doped nanocarbon systems. On the

one hand, F incorporation has been reported to optimize the electronic structure of Fe-N_x active centers and weaken the adsorption of ORR intermediates. For instance, Tao et al. showed that F atoms on graphitic carbon modulated nearby Fe-N_x sites, resulting in a 30 mV positive shift in $E_{1/2}$.^[88] On the other hand, the influence of F is not universally beneficial. Cherif et al. reported through DFT calculations that fluorination may poison Fe-N_x moieties by strongly coordinating with Fe centers, thereby suppressing ORR activity in certain stacked graphene environments. Notably, this poisoning effect could be reversed after heat treatment at 900 °C, indicating that F-induced deactivation is highly condition-dependent and potentially removable.^[89] These observations emphasize that the role of F in hybrid catalysts is highly sensitive to local coordination environment, F content, and structural characteristics.

Beyond activity enhancement, F doping can also modulate ORR selectivity, particularly in the competition between the $2e^-$ and $4e^-$ pathways. Zeng et al. showed that covalent CF₂ moieties can selectively activate O₂ and facilitate *OOH desorption, thus favoring H₂O₂ production through a $2e^-$ route with a selectivity of 95.7%.^[90] This result highlights that different F species not only modulate catalytic activity but also steer product distribution by tuning the adsorption strength of key intermediates.

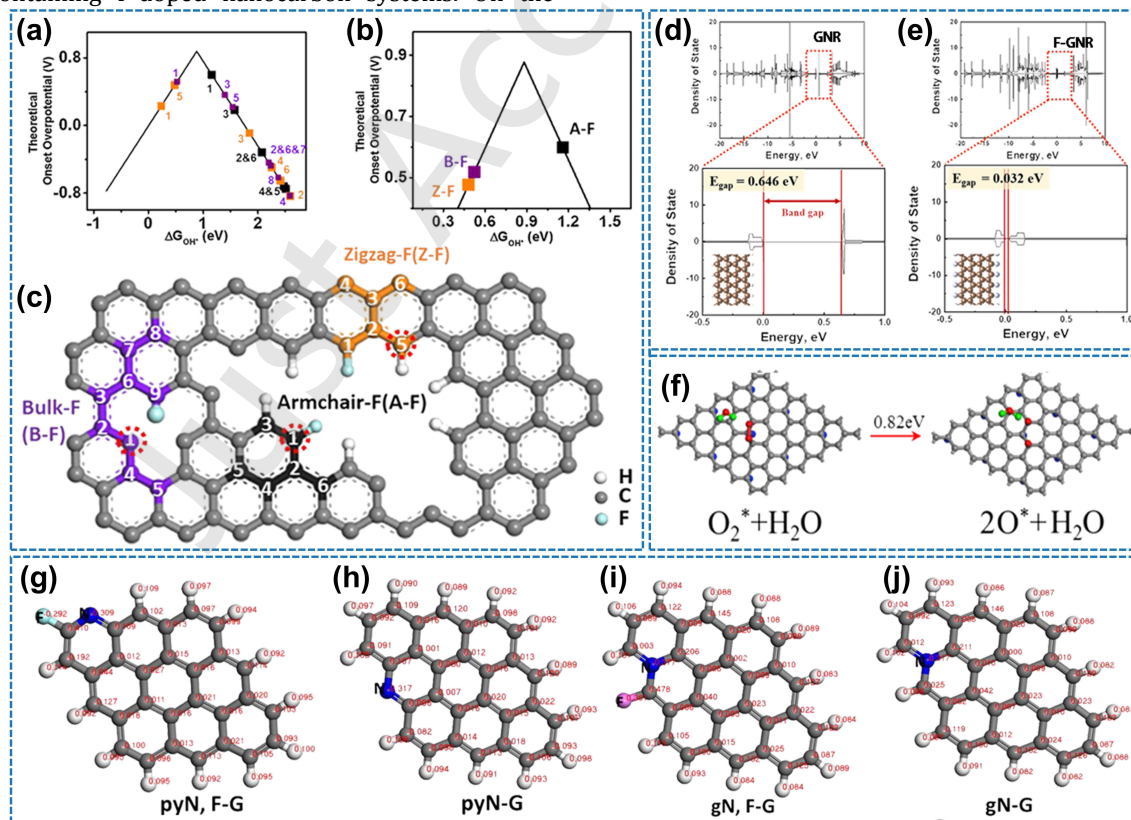


Figure 5. (a) DFT-calculated *OH adsorption energies for various sites and their corresponding locations on the theoretical ORR volcano plot. Purple, black, and orange squares denote the sites related to B-F, A-F, and Z-F, respectively. (b) Overall catalytic activities of A-F, B-F, and Z-F. (c) Structural illustration of A-F, B-F, and Z-F.^[82] Reproduced with permission from ref. 82. Copyright Elsevier B.V., 2021. (d, e) Electronic density of states and band gap of GNR and F-GNR.^[83] Reproduced with permission from ref. 83. Copyright American Chemical Society, 2021. (f) A portion of the minimum energy path for the elementary steps of ORR in an alkaline medium on C₆F graphene at zero potential.^[84] Reproduced with

permission from ref. 84. Copyright Elsevier B.V, 2016. (g-j) atomic configurations and Mulliken charge distributions of (a1) pyN, F-G, (a2) pyN-G, (a3) gN, F-G, and (a4) gN-G.^[91] Reproduced with permission from ref. 91. Copyright Royal Society of Chemistry, 2017.

Beyond ORR, F-mediated electronic regulation also contributes to OER catalysis.^[12] Previous studies have suggested that F is mainly incorporated into nanocarbons in covalent and semi-ionic forms, and the neighboring carbon atoms are often identified as the active sites for OER.^[92] The electron-withdrawing effect of F increases the positive charge density of adjacent carbon atoms, which can strengthen the adsorption and subsequent transformation of oxygenated intermediates. For example, DFT calculations revealed that graphitic-N and F co-modified graphene exhibited the highest carbon atomic charge density among several model structures, which is favorable for optimizing transition state energetics and improving OER activity (Figure 5g-j).^[91] In some cases, the coexistence of F with graphitic or pyridinic-N can further activate paramagnetic centers and reduce the OER reaction barrier.^[55] More recently, Li et al. combined experimental analysis with theoretical calculations to show that F/pyridinic-N codoping activates neighboring carbon atoms for acidic OER and shifts the potential-determining step from *OOH formation to *O generation, leading to improved reaction kinetics.^[93]

Porous architecture is also a key structural parameter governing the oxygen electrocatalytic performance of F-DNCMs, as it directly affects mass transport, active site accessibility, and interfacial reaction kinetics.^[47] Generally, hierarchical porous structures integrating micropores, mesopores, and macropores are more advantageous than architectures dominated by a single pore size. Micropores (<2 nm) provide high specific SSA and abundant defect/edge sites favorable for F incorporation, but excessive microporosity may restrict electrolyte penetration and O₂ diffusion, leaving part of the active surface electrochemically inaccessible. Mesopores (2-50 nm) improve electrolyte infiltration, shorten diffusion pathways, and enhance the utilization of F-related active sites, whereas macropores (>50 nm) serve as rapid transport channels for O₂, electrolyte, and reaction products, particularly under high-current-density conditions. The benefit of hierarchical porosity therefore arises from the synergistic integration of active-site enrichment and multiscale mass transport. Three-dimensional (3D) interconnected pore networks are especially attractive because they can reduce diffusion resistance, minimize isolated pores, and maintain effective gas-liquid-solid interfaces. For F-DNCMs, pore architecture is further coupled with fluorination chemistry, since F incorporation can alter defect density, surface polarity, wettability, and electrical conductivity. Excessive fluorination or uncontrolled pore generation may increase structural disorder while disrupting the sp²-conjugated network, indicating that catalytic performance should not be correlated solely with Brunauer-Emmett-Teller surface area. The optimal pore structure also depends on the targeted reaction. Interconnected meso/macroporous

channels are favorable for sustaining O₂ supply during the 4e⁻ ORR, while open porous frameworks can facilitate electrolyte transport and O₂-bubble removal during the OER.^[82] For the 2e⁻ ORR toward H₂O₂, appropriate mesoporous accessibility may promote rapid product desorption and suppress further reduction or decomposition. Thus, rational pore engineering should focus on maximizing the electrochemically accessible density of F-related active sites while maintaining efficient mass transport. Hierarchical porous F-DNCMs with defect-rich microporous domains interconnected by meso/macroporous transport channels therefore represent a particularly promising architecture for high-performance oxygen electrocatalysis.

In a word, these studies demonstrate that the electrocatalytic role of F cannot be described solely by the total F content. Instead, catalytic activity and selectivity arise from the combined effects of C-F bonding configuration, dopant location, neighboring heteroatoms or metal sites, defect/porous structure, and the resulting interfacial microenvironment. Notably, these structural descriptors are strongly dependent on the fluorination route and processing conditions. Therefore, establishing controllable synthetic strategies capable of regulating F content, bonding state, spatial distribution, and defect configuration is essential for translating the above mechanistic understanding into rational catalyst design. The following section consequently focuses on the major synthesis strategies for constructing F-DNCMs with tailored physicochemical and electrocatalytic properties.

3 Synthesis strategies for Fluorine-doped nanocarbons

Pristine nanocarbons generally exhibit limited intrinsic activity toward the ORR and OER in aqueous electrolytes. F incorporation offers a practical route to overcome this limitation by disturbing the electroneutrality of the carbon lattice, creating polarized carbon sites, and promoting O₂ adsorption and activation. To date, a variety of synthetic approaches have been developed to introduce F into nanocarbon frameworks and tailor their surface chemistry, electronic structure, and defect configuration. As summarized in Figure 6, the preparation of F-DNCMs can be classified into five categories: gas-phase fluorination, hydrothermal/solvothermal fluorination, plasma-assisted fluorination, thermal fluorination, and sustainable fluorination. These strategies differ markedly in the nature and reactivity of the fluorinating species, reaction temperature, fluorination depth, achievable F content, and degree of structural damage to the carbon framework. Consequently, the choice of fluorination route not only determines the amount of incorporated F but also strongly influences the distribution of ionic, semi-ionic, and covalent C-F species, defect density, electronic conductivity, and accessibility of catalytic sites. For oxygen

electrocatalysis, an appropriate synthesis method should therefore balance efficient F incorporation with preservation of the conductive sp^2 -carbon network and controlled generation of catalytically favorable defects.

The following sections discuss these representative methods, focusing on their synthetic characteristics, underlying fluorination processes, key controlling parameters, advantages, and remaining limitations.

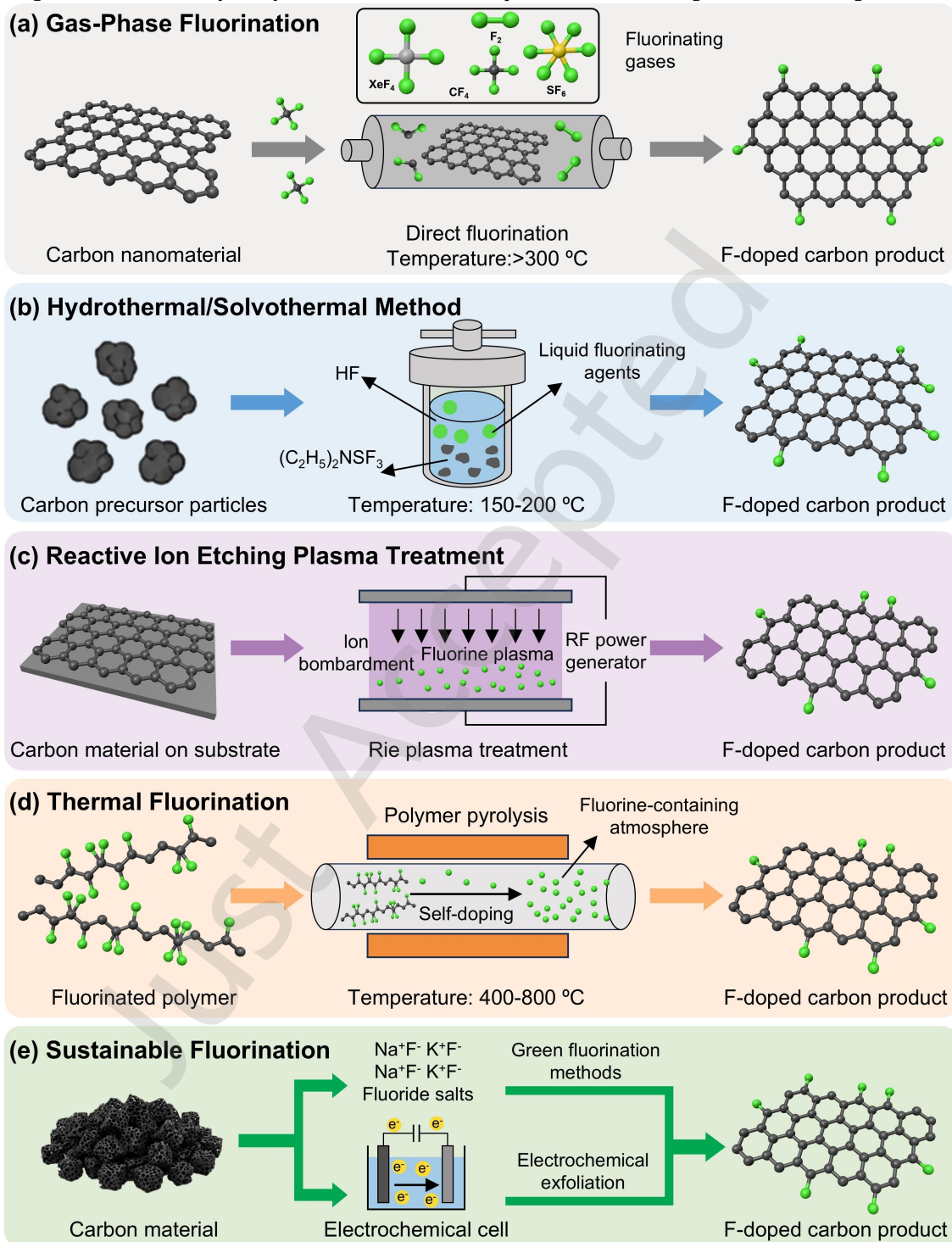


Figure 6. Various strategies for the synthesis of F-DNCMs.

3.1. Gas-phase fluorination

Gas-phase functionalization is widely regarded as an effective and reliable strategy for tailoring the surface properties of nanocarbons.^[94] In particular, F-containing gases such as XeF_4 ,^[95] F_2 ,^[96] CF_4 ,^[97] and SF_6 ,^[98] have been extensively used as fluorination agents for the synthesis of

F-DNCMs. Due to the high reactivity of gaseous F species, this approach enables efficient surface fluorination and relatively precise regulation of the F content and C–F bonding configuration by adjusting the fluorinating-agent concentration, reaction temperature, pressure, and exposure time. The fluorination process generally involves

adsorption of reactive F-containing species on the carbon surface, followed by reaction with exposed carbon atoms, defect sites, edges, or unsaturated bonds. Because edges and structural defects possess higher chemical reactivity than basal-plane carbon atoms, fluorination preferentially occurs at these sites during the initial stage. With increasing fluorination severity, F species can progressively functionalize the basal plane and convert sp^2 -hybridized carbon into more strongly fluorinated configurations. Thus, the extent of fluorination must be carefully controlled because excessive formation of covalent C–F bonds may disrupt the conjugated π -electron network and decrease electrical conductivity, whereas moderate fluorination can generate polarized and defect-rich carbon sites favorable for oxygen electrocatalysis. The diffusion of gaseous fluorinating species into porous carbon architectures is another important factor, particularly for materials with high surface areas or tortuous microporous structures.

For instance, Yazami et al. prepared F-doped carbon nanofibers (CNFs) by exposing CNFs to pure F_2 at 380–480 °C for 16 h, followed by Ar annealing at 1800 °C.^[99] Wheeler et al. employed XeF_2 to fluorinate epitaxial graphene and investigated its suitability for atomic layer deposition of high- κ dielectrics.^[100] In their study, the F dose was controlled by varying the number and duration of XeF_2 pulses. Robinson et al. further showed that XeF_2 could simultaneously etch the Si substrate beneath CVD-grown graphene and fluorinate the graphene film, enabling double-sided fluorination.^[101] They also demonstrated that the fluorinated graphene films could be chemically defluorinated using hydrazine, indicating the reversible nature of fluorination under certain conditions.

Overall, gas-phase fluorination offers several attractive features, including high fluorination efficiency, good controllability, and compatibility with graphitic carbon materials. It is especially useful when uniform surface functionalization or controlled modification of two-dimensional (2D) carbon materials is required. In addition, post-treatment conditions can be used to partially remove weakly bound F species or reconstruct the carbon framework, providing another means of tailoring the final bonding environment. However, the use of highly reactive, hazardous F-containing gases and the requirement for specialized equipment remain a major obstacle to large-scale and safe production. Moreover, excessive fluorination may cause substantial loss of electrical conductivity, while the penetration depth of gaseous species can become limited in densely packed or highly microporous carbon materials. Therefore, achieving a balance among fluorination degree, C–F bonding state, structural integrity, and conductivity remains a key challenge for this strategy.

3.2. Hydrothermal/Solvothermal fluorination

Compared with gas-phase fluorination, hydrothermal and solvothermal methods provide milder and more accessible routes for introducing F into nanocarbons.

Given the toxicity, corrosiveness, and operational complexity of many gaseous fluorinating reagents, liquid-phase fluorination under sealed hydrothermal/solvothermal conditions is often more practical for laboratory and scale-up synthesis.^[102] In these methods, the carbon precursor and F-containing reagent are dispersed in a liquid medium and reacted in a sealed autoclave, where elevated temperature and autogenous pressure enhance mass transfer and promote interactions between the fluorinating species and reactive carbon sites. Oxygen-containing functional groups, vacancies, edges, and other defects in precursors such as graphene oxide (GO) can serve as particularly reactive sites for F incorporation. Compared with direct gas-phase reactions, solution-based processing also provides intimate contact between the fluorinating reagent and dispersed carbon sheets or nanoparticles. The fluorination degree can generally be tuned through parameters such as F-source concentration, solvent composition, reaction temperature, reaction time, and the chemical state of the starting carbon material.

Hydrofluoric acid (HF), despite its strong corrosiveness, remains a low-cost and effective F source. Wang et al. synthesized FG by dispersing GO in HF solution and tuned the C/F ratio by adjusting the reaction conditions.^[103] The as-obtained FG exhibited a sheet-like morphology with a thickness of one to two layers and a tunable bandgap in the range of 1.82–2.99 eV. Zhao et al. reported a mild liquid-phase fluorination of GO using diethylaminosulfur trifluoride, where oxygen-containing groups on GO were converted into different C–F species during the reaction.^[104] Samanta et al. further developed a solvothermal route to produce F-doped reduced graphene oxide (FrGO) from GO, BF_3 -etherate, and 1-heptanethiol.^[105] This process enabled simultaneous reduction and fluorination, affording FrGO with an F content as high as 38 wt%. An important feature of hydrothermal/solvothermal fluorination is that fluorination can occur simultaneously with reduction, defect reconstruction, or heteroatom incorporation, depending on the precursor and reaction medium. This provides opportunities for one-pot construction of multifunctional F-containing carbon materials. However, these coupled chemical processes also make it more difficult to independently control F concentration, carbon reduction degree, defect density, and individual C–F configurations. In addition, incomplete removal of fluorinating reagents or reaction by-products may influence the surface chemistry of the resulting carbon materials and therefore requires careful purification and characterization.

These studies demonstrate that hydrothermal/solvothermal fluorination can provide good solution processability, relatively mild conditions, and tunable F incorporation. The method is particularly suitable for solution-dispersible carbon precursors and offers advantages for batch processing and compositional

modification. Nevertheless, the use of corrosive F-containing liquids and the limited control of specific C-F bonding states remain critical challenges for further optimization. Future development should therefore focus on safer F sources, improved F utilization efficiency, and reaction systems capable of independently regulating F content and bonding configuration while minimizing structural degradation of the carbon matrix.

3.3. Plasma-assisted fluorination

Plasma-assisted fluorination has emerged as a versatile technique for surface functionalization of carbon nanomaterials. In this approach, reactive F radicals and/or F-containing ionic species are generated in plasma and subsequently bonded to carbon surfaces, allowing fluorination that is often confined to near-surface regions. This feature makes the method particularly attractive for thin carbon nanostructures, where short treatment times and controllable fluorination levels are desirable. Unlike conventional thermal or solution-based fluorination, plasma treatment is a nonequilibrium process in which energetic electrons activate F-containing gases and generate highly reactive species at relatively low bulk temperatures. These species interact primarily with exposed surface carbon atoms, allowing rapid functionalization without prolonged high-temperature treatment. The fluorination degree and surface structure can be regulated by plasma power, gas composition, gas pressure, exposure time, substrate position, and treatment temperature. The use of CF_4 , SF_6 , F_2 -containing mixtures, or other F-containing plasma sources can also alter the relative populations of reactive F and CF_x species and thereby influence the resulting surface chemistry.

Plasma fluorination is commonly carried out in a reactive ion etching system. Previous studies have shown that monolayer graphene is more readily fluorinated than bilayer or few-layer graphene, indicating a strong dependence on layer number and surface accessibility. Notably, fluorinated monolayer graphene prepared by plasma treatment can recover its original structure after vacuum thermal annealing at 970 °C for 1 h, suggesting partial reversibility of the plasma-induced C-F bonding. Similarly, Yang et al. synthesized F-doped few-layer graphene via plasma treatment.^[106] Yu et al. prepared FrGO using CF_4 plasma, where the F content was conveniently tuned by adjusting the exposure time.^[107] Tahara et al. further demonstrated controllable fluorination with Ar/F_2 plasma, where XPS analysis confirmed the formation of C-F bonds in the resulting FG.^[108] In addition to F incorporation, energetic plasma species may create vacancies, edge defects, and lattice disorder through ion bombardment. The obtained defects can provide additional active sites and facilitate subsequent fluorination, but excessive plasma power or prolonged exposure may overetch the carbon surface and deteriorate structural integrity and electrical conductivity. Thus, plasma treatment provides a particularly effective means of simultaneously controlling surface fluorination

and defect engineering, provided that the treatment severity is carefully optimized.

Thus, plasma-assisted fluorination offers rapid processing, high surface sensitivity, and tunable fluorination degrees. It also provides spatial and temporal control over surface modification and avoids the need for large quantities of liquid fluorinating reagents. However, it remains limited to near-surface modification and may be less effective for bulk fluorination of thick or densely packed carbon materials. Furthermore, plasma equipment increases processing complexity and cost, while treatment uniformity can become challenging for powders or 3D porous electrodes. These characteristics make plasma fluorination particularly attractive for films, graphene sheets, carbon fibers, and electrode surfaces rather than for high-throughput bulk synthesis.

3.4. Thermal fluorination

Thermal fluorination is one of the most widely used methods for preparing F-doped nanocarbons for oxygen electrocatalysis. In this strategy, F-containing precursors decompose, diffuse, or react with the carbon matrix at elevated temperatures, enabling F species to be incorporated into the carbon framework. Because of its operational simplicity, broad applicability, and relatively facile control over F content, thermal fluorination has become a mainstream route for synthesizing F-DNCMs. Depending on the synthetic design, thermal fluorination can be implemented either by pyrolyzing a carbon precursor together with an external F source or by directly carbonizing an F-containing organic/polymeric precursor. During pyrolysis, decomposition of F-containing compounds generates reactive F species that interact with the evolving carbon framework. Simultaneously, carbonization, graphitization, heteroatom doping, defect formation, and pore evolution may occur, making thermal fluorination particularly suitable for constructing multifunctional electrocatalysts in a single synthetic step.

For carbon materials, this process can couple F incorporation with mild surface etching, thereby increasing surface roughness, generating defect sites, and forming active C-F species for ORR/OER. Various F-containing compounds, such as NH_4F , NH_4PF_6 , polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and F-containing covalent organic polymers, have been used as F sources in this approach.^[109] The final F content and chemical state are strongly dependent on the pyrolysis temperature, heating rate, reaction time, precursor ratio, atmosphere, and thermal stability of the selected F source. In general, insufficient temperature may lead to incomplete carbonization or inefficient precursor decomposition, whereas excessively high temperature can promote the release of volatile F-containing species and reduce the retained F content. Therefore, optimization of the temperature window is essential for balancing F retention, graphitization degree, defect formation, and electrical conductivity. The spatial distribution of F can also be influenced by whether the F source is molecularly

integrated into the carbon precursor or externally mixed with it. Self-doping precursors containing covalently bound F generally provide more intimate precursor-level mixing, whereas external fluorinating agents offer greater flexibility in adjusting the F-source dosage.

For instance, Zheng et al. developed a simple pyrolysis strategy using a stable N, P, and F-containing covalent triazine polymer as a self-doping precursor.^[53] This design avoided complicated post-fluorination steps and yielded N, P, F-tridoped nanocarbons containing semi-ionic and ionic C-F species, which were beneficial for bifunctional ORR/OER electrocatalysis. Despite these advantages, conventional thermal fluorination often requires prolonged heating for sufficient F incorporation.^[110] Moreover, simultaneous carbonization and fluorination make the reaction pathway relatively complex, and F loss at elevated temperatures may lead to discrepancies between the precursor composition and the final F content. Nevertheless, compared with gas-phase and plasma methods, thermal fluorination is generally more compatible with bulk powder production and a wider range of carbon precursors, making it particularly attractive for scalable electrocatalyst synthesis. To overcome the limitation of long processing times, ultrafast deflagration-based synthesis has recently attracted increasing attention. Using a $\text{NaN}_3/\text{C}_5\text{F}_5\text{N}$ deflagration system, Liu et al. synthesized highly graphitized N/F-codoped carbon hollow nanospheres within an extremely short reaction period.^[111] The optimized catalyst displayed excellent ORR activity and long-term stability, even outperforming commercial Pt/C. These ultrafast processes provide transient high-temperature environments that can simultaneously promote precursor decomposition, carbon-framework reconstruction, heteroatom incorporation, and hollow-structure formation, thereby greatly shortening the overall synthesis time. Nevertheless, controlling local reaction temperature, product uniformity, and F retention during such rapid reactions remains important for reproducible synthesis.

These results indicate that thermal fluorination is highly versatile with a broad range of precursor systems. Future advances in this area may focus on shortening processing time, improving F utilization, and achieving finer control of F-containing species during pyrolysis. Particular attention should also be paid to correlating precursor chemistry and thermal history with the final C-F bonding configuration, because these parameters directly determine the electronic structure and catalytic microenvironment of F-DNCMs.

3.5. Sustainable fluorination

Although the above methods have advanced the synthesis of F-DNCMs, many of them still rely on toxic, corrosive, or environmentally problematic fluorinating agents. F_2 and XeF_4 used in gas-phase fluorination, HF and NH_4F used in hydrothermal/solvothermal processes, and SF_6 used in plasma treatment all raise concerns regarding

safety, cost, and environmental impact.^[102] These challenges increasingly motivate the development of sustainable fluorination strategies that use more environmentally friendly F sources. Green fluorination chemistry is therefore becoming an important direction for the synthesis of F-doped nanocarbons. Notably, the sustainability of a fluorination process should not be evaluated solely by the toxicity of the F source. Energy consumption, solvent usage, F atom utilization, generation of corrosive or greenhouse-gas by-products, purification requirements, and process scalability should also be considered. Accordingly, sustainable fluorination aims to replace hazardous fluorinating reagents with stable salts or solid reagents, reduce reaction temperature and processing steps, and improve the utilization efficiency of F-containing precursors.

Aguilar-Bolados et al. reported a feasible graphene fluorination route using a diethylaminodifluorosulfonium salt as a stable solid fluorinating reagent.^[112] In this process, deoxyfluorination occurred through stirring the fluoride salt with graphite oxide at low temperature, offering a safer alternative to conventional fluorination reagents. Zhou et al. further developed a one-step electrochemical exfoliation route to fabricate FG in a two-electrode system using NaBF_4 as the F source.^[113] This approach not only simplified the synthesis process but also provided a safer and potentially scalable route for FG production. Electrochemical routes are particularly attractive because exfoliation and fluorination can potentially be integrated into a single process, while the applied potential/current provides an additional parameter for controlling reaction kinetics. Moreover, the use of stable inorganic fluoride salts can reduce direct handling of highly reactive fluorinating gases or concentrated HF. However, the actual environmental advantage of a given process depends on the overall energy input, electrolyte recovery, product yield, and waste-treatment requirements. Therefore, quantitative evaluation of energy consumption and environmental impact will be necessary for meaningful comparison with conventional fluorination technologies.

Compared with conventional fluorination methods, sustainable strategies are more compatible with the principles of green chemistry and hold considerable promise for large-scale synthesis. However, further work is still needed to enhance F incorporation efficiency, precisely control F bonding configurations, and expand the range of nanocarbon substrates. In addition, developing recyclable fluorinating media, low-temperature processes, and F sources derived from less hazardous and more readily handled compounds will be important for translating these approaches from laboratory demonstrations to practical manufacturing.

3.6. Summary and outlook on synthetic methods

In summary, the synthesis of F-DNCMs is fundamental to the development of high-performance oxygen electrocatalysts, yet no single fluorination strategy

can simultaneously optimize F incorporation, bonding-state control, conductivity, safety, cost, and scalability. Thermal fluorination is the most widely used owing to its versatility and scalability, whereas gas-phase, hydrothermal/solvothermal, plasma-assisted, and sustainable approaches provide complementary advantages in reactivity, processability, surface selectivity, and environmental compatibility, respectively. Therefore, the optimal fluorination route should be tailored to the carbon architecture, fluorination depth, F content and bonding configuration, defect structure, conductivity, and targeted ORR/OER function. Despite substantial progress, challenges including low F utilization, limited control over F bonding states and distribution, processing constraints, and safety concerns remain. Future efforts should focus on safer and more controllable fluorination strategies and on establishing quantitative synthesis-structure-performance relationships to enable the rational and scalable design of next-generation F-DNCM electrocatalysts.

4 Applications of F-Doped Nanocarbon-Based Electrocatalysts

A wide range of F-DNCMs have been explored as efficient ORR/OER electrocatalysts, including single F-doped carbons, dual F-doped carbons, multiple F-doped carbons, and F-doped carbon-based hybrids (Figure 7). Single F-doped and F-based dual-/multi-heteroatom-doped nanocarbons are classified as metal-free carbon frameworks, whereas F-doped carbon-based hybrids are integrated with metal-containing active components. Among these materials, F incorporation not only modifies the intrinsic electronic structure of the carbon matrix but also reshapes interfacial properties, including wettability,

defect distribution, and adsorption behavior of oxygen-containing intermediates. Both theoretical and experimental studies indicate that the strong electronegativity of F enhances the interaction between nanocarbon surfaces and dissolved O_2 , thereby promoting oxygen electrocatalysis. In addition, fluorination can induce surface wrinkling, alter hydrophilicity/hydrophobicity, and expose more accessible active sites, all of which are beneficial for electrocatalytic performance.^[114] Another important feature of F-DNCMs lies in the highly polarized C-F bond, which can interact strongly with metal cations through electrostatic effects.^[115] The interactions help reinforce the coupling between nanocarbons and metal-containing components, while also influencing the morphology of transition-metal compounds on carbon surfaces.^[116] These characteristics provide a versatile foundation for the rational design of advanced oxygen electrocatalysts with enhanced activity and durability. Building on this understanding, the following sections discuss representative applications of different categories of F-DNCMs in oxygen electrocatalysis. The catalysts, test conditions, and corresponding oxygen electrocatalytic performances reported in the literature are summarized in Table 1-3. It should be noted that the reported data were obtained under non-identical experimental conditions, including variations in electrolyte, catalyst loading, rotation rate, and measurement configuration. Thus, the performance metrics listed in these tables should be interpreted as reference values for semi-quantitative comparison rather than as absolute criteria for direct catalyst ranking. These data are primarily intended to identify broad structure-performance relationships and guide the rational design of F-DNCM-based oxygen electrocatalysts.

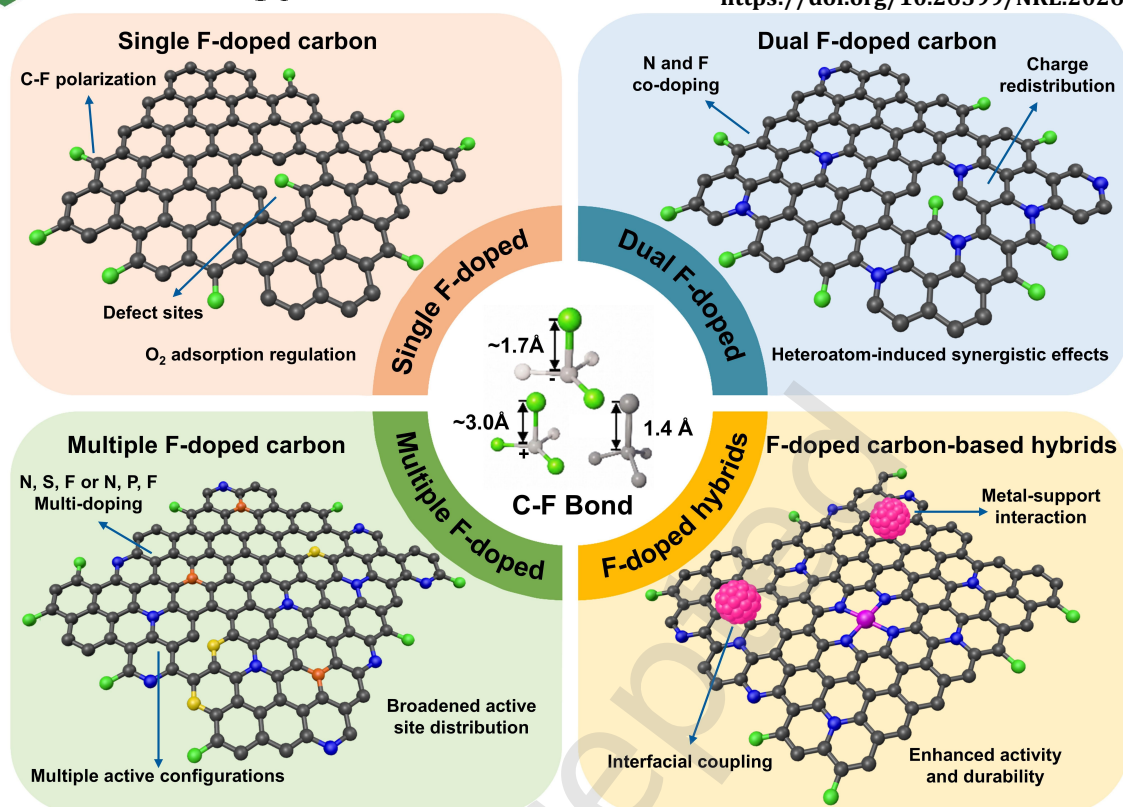


Figure 7. Different types and chemical structures of F-DNCMs.

4.1. Single F-doping nanocarbons

Single F-doping has emerged as an effective strategy for activating nanocarbons toward oxygen electrocatalysis. Although F was once less commonly considered than N, S, or B for doping, its strong electronegativity makes it an effective regulator of both the electronic structure and the interfacial microenvironment. The activity enhancement mainly arises from charge polarization of neighboring carbon atoms, which creates favorable sites for O_2 adsorption and intermediate conversion, while also influencing surface wettability and mass-transport behavior.

For the $4e^-$ ORR pathway, CB-derived materials provide a representative platform because of their low-cost, high conductivity, and structural robustness. Sun and co-workers first reported metal-free F-doped mesoporous CBs through pyrolysis of a mixture of CB with NH_4F .^[62] The optimal BP-18F catalyst exhibited excellent ORR activity, durability, and methanol tolerance in alkaline

media, even outperforming commercial Pt/C catalysts. Different from conventional N-doped carbons, the enhanced ORR activity was primarily attributed to the F-induced charge redistribution, which polarized adjacent carbon atoms and generated active sites. After that, a variety of single F-doped carbons, including F-doped BP 2000,^[117] mesoporous F-doped carbon,^[118] F-doped carbon nanoparticles,^[57] and FG^[119], were reported and exhibited promising ORR activity. In a representative study, Parthiban et al. developed a F-enriched mesoporous carbon (F-MC) as an efficient metal-free ORR catalyst for alkaline FCs.^[120] The optimized F-MC (5:1)-950 exhibited an onset potential (E_{onset}) of -0.10 V vs. SCE and a limiting current density (J_L) of 4.87 mA cm $^{-2}$ in 0.1 M KOH, with an $E_{1/2}$ only ~ 50 mV lower than that of commercial Pt/C. Notably, after 10 000 CV cycles, the $E_{1/2}$ showed only a 10 mV negative shift and excellent methanol tolerance, highlighting the durability advantages of F-doped carbon frameworks.

Table 1. F-doped nanocarbon-based materials for ORR electrocatalysis.

Catalyst	Electrolyte	E_{onset} (V vs. RHE)	$E_{1/2}$ (V vs. RHE)	Tafel slope (mV dec $^{-1}$)	Ref.
BP-18F	0.1 M KOH	-	-	-	[62]
BP-NF	0.1 M KOH	0.77	0.83	-	[54]
BP-18F	0.5 M H_2SO_4	0.9	0.63	-	[117]
N-F-GNF	0.5 M $HClO_4$	-	0.63	-	[63]
NFC@Fe/ Fe_3C -9	0.1 M KOH	-	0.87	57	[121]
FNC	0.1 M KOH	0.98	0.87	76	[122]
F-N-AC-1000	0.1 M KOH	1.04	0.89	-	[87]

F-NPC	0.1 M KOH	0.97	0.86	82	[58]
N, F-Carbon-1000	0.1 M KOH	0.97	0.84	129	[109]
N-F/MWCNTs	0.5M HClO ₄	0.80	0.55	-	[123]
N-F/CTC	0.1 M KOH	-	0.86	-	[124]
BP2000-NF	0.1 M KOH	0.97	0.89	68	[81]
N, F-MCFs-A-1	0.1 M KOH	0.94	0.81	-	[125]
NF@CB	0.1 M KOH	0.95	0.81	73	[126]
GNF-H/N-F	0.1 M KOH	-	0.90	-	[127]
FN-OMC-1000	0.1 M KOH	0.90	0.78	-	[128]
NFCANs-18-1000	0.1 M KOH	0.91	0.83	-	[129]
N-F/RGo	0.1 M KOH	-	0.81	63	[130]
N/F-HC-2	0.1 M KOH	0.82	0.70	-	[111]
NF-4.84	0.1 M KOH	-	0.81	-	[131]
NFPC-800	0.1 M KOH	0.96	0.85	-	[55]
MnPc/FCNT800	0.1 M KOH	-	0.9	60	[132]
F-FeNC-2	0.1 M HClO ₄	-	0.83	-	[88]
C@PVI-(TPFC)Co-800	0.1 M KOH	1.05	0.88	58	[133]
Fe-Co/NF-GNF	0.5 M HClO ₄	0.93	0.77	-	[134]
NFC@Fe/Fe ₃ C-9	0.1 M KOH	-	0.87	57	[135]
CNF-800-5 h-recarb	0.1 M KOH	-	0.87	-	[136]
PtZn i-NPs/F-CNT	0.1 M KClO ₄	-	0.89	-	[137]
Fe@NFC700	0.1 M KOH	0.98	0.83	79	[138]
Fx-Fe/N/C	0.1 M HClO ₄	-	0.81	-	[139]
NiTPP@F-MWCNT	0.1 M KOH	0.86	0.75	62	[140]
F@NC	0.1 M KOH	-	0.9	50	[86]
PFePc/FC	0.1 M KOH	-	0.93	73	[141]
Pt-E6 _{F350}	0.1 M HClO ₄	-	0.92	56	[67]
NFS-700	0.1 M KOH	0.83	0.66	75	[142]
CS ₁₂₋₆₅₀	0.1 M KOH	0.91	0.82	-	[143]
BNFC-800	1 M KOH	-	0.84	56	[144]
IFeNC-2	0.1 M KOH	1.06	0.92	80	[145]
FCNP-4	0.1 M KOH	-	0.85	-	[57]
IM-900	0.1 M KOH	0.9	0.64	-	[146]
F/P-N-C-950	0.1 M KOH	-	0.85	52	[147]
FN ₃ SG	0.1 M KOH	0.99	0.80	96	[148]
NFS-CNF-0.5-1000	0.1 M KOH	0.98	0.91	75	[66]
Co/NSF-C700	0.1 M KOH	-	0.86	90	[149]
SNF-Carbon-1000	0.1 M KOH	0.98	0.86	-	[69]
Tri(Fe/N/F)-doped MCNFs	0.1 M KOH	0.9	0.82	-	[85]
FG-1100	0.1 M KOH	0.91	0.69	-	[119]
FC-900	0.1 M KOH	0.97	0.85	-	[82]
F-CHNS-900	0.1 M KOH	1.06	0.97	-	[150]
Co/FN-C	0.1 M HClO ₄	0.92	0.70	-	[151]
MPFe ₁ Cu ₁ -850	0.1 M HClO ₄	-	0.73	-	[152]
HeNFePt	0.5 M HClO ₄	-	0.78	56	[153]
FeN ₄ -NFS-CNF	0.1 M KOH	-	0.90	55	[154]
Pt@C/F-COOH	0.1 M HClO ₄	1.01	0.91	74	[155]
N/S/F-CNTs	0.1 M KOH	0.9	0.82	-	[156]
NFPC	0.1 M KOH	-	0.82	-	[157]
GO-PANi31-FP	0.1 M KOH	-	0.80	-	[52]
C-F-1000	0.1 M KOH	0.94	0.74	-	[118]
Pt/F-GNR	0.1 M KOH	-	0.85	-	[83]
F-MC (5:1)	0.1 M KOH	0.85	0.73	-	[120]
F-FeNC	0.1 M KOH	-	0.82	-	[158]

In another study, Chang *et al.*^[82] prepared porous F-doped carbon nanosheets using poly(vinylidene fluoride) as precursor and F source, and NaCl as a hard template (Figure 8a). The sample pyrolyzed at 900 °C (FC-900)

displayed excellent ORR activity, which was attributed to its large SSA of $1031 \text{ m}^2 \text{ g}^{-1}$ and abundant accessible active sites (Figure 8b). Under alkaline conditions, FC-900 delivered high ORR and ZABs performance comparable to that of Pt/C. The enhanced activity was attributed to the combined contribution of structural defects and appropriately incorporated F dopants. Interestingly, prolonging the calcination time at 900°C caused only a slight improvement in ORR activity, implying that F doping, rather than defect density, played a more crucial role in this system. To further understand the origin of activity, DFT calculations were performed on three F-doping configurations, namely F located in the basal plane (B-F), at armchair edges (A-F), and at zigzag edges (Z-F), as shown in Figure 8c. The results confirmed the strong dependence of ORR activity on the local fluorination configuration.

Beyond the above $4e^-$ ORR, single F-doped nanocarbons have also attracted extensive attention as selective catalysts for the $2e^-$ ORR toward H_2O_2 electrosynthesis. Compared with the conventional anthraquinone process, electrochemical H_2O_2 production via the $2e^-$ ORR is considered a more sustainable avenue.^[159] In this regard, F doping offers a unique means to tune ORR selectivity by regulating the adsorption/desorption energetics of the $^*\text{OOH}$ intermediate. Zhao *et al.* prepared F-doped porous nanocarbon by carbonizing MIL-53(Al), obtaining an efficient catalyst for electrochemical synthesis of H_2O_2 .^[160] As shown in Figure 8d, the F content had a pronounced influence on H_2O_2 generation. The optimal catalyst with 3.41 at.% F achieved H_2O_2 selectivities of 83.0–97.5% and production rates of $112.6\text{--}792.6 \text{ mmol h}^{-1} \text{ g}^{-1}$ over the potential range from 0.2 to -0.3 V vs. RHE (Figure 8e). Mechanistic analysis indicated that CF_2 species facilitate O_2 adsorption while promoting $^*\text{OOH}$ desorption, thereby favoring the $2e^-$ ORR pathway.

A similar trend was observed in F-modified CNTs. Wang *et al.* used F-doped CNTs as the cathode catalyst in

gas-diffusion electrodes for electrochemical H_2O_2 production.^[161] The F-doped CNT prepared with 0.6 M HF delivered a higher H_2O_2 concentration of 47.6 mg L^{-1} and a current efficiency of 89.5% than those of pristine CNTs (29.6 mg L^{-1} and 70.1%, respectively). This improved performance was attributed to the formation of CF_2 and CF_3 species on the CNT surface, which enhanced both ORR activity and H_2O_2 selectivity. Likewise, Zeng *et al.*^[90] synthesized F-doped carbon in an F_2 atmosphere using a sealed fluidized-bed reactor (Figure 8f). During 3 h of electrolysis, the catalyst produced H_2O_2 at a concentration of 2837.5 mg L^{-1} with a selectivity of 95.7%. Notably, the concentration of H_2O_2 remained constant after 12 cycles, indicating good stability of the catalyst (Figure 8g, h). XPS analysis and DFT calculations suggested that CF_2 moieties facilitate O_2 adsorption and $^*\text{OOH}$ desorption, thereby promoting selective H_2O_2 generation.

In addition to tuning intrinsic activity and selectivity, F doping can also reshape the catalytic microenvironment. Zhao *et al.* further demonstrated that F incorporation into porous carbon not only enhanced the $2e^-$ ORR but also promoted pollutant mineralization through more efficient H_2O_2 production, as evidenced by the increased generation of hydroxyl radicals.^[162] Xing *et al.* subsequently showed that F-doped carbons regulate not only the density of active sites but also the wettability and mass transport within the catalyst layer.^[163] While rotating ring-disk electrode (RRDE) measurements suggested that intrinsic activity increased monotonically with F content, gas-diffusion electrode tests revealed a non-monotonic dependence of H_2O_2 production rate on the doping level. Excessive F doping rendered the carbon surface overly hydrophobic, limiting electrolyte penetration and disrupted the gas-liquid-solid balance in the catalyst layer. These results established a distinct microenvironment effect of F doping, indicating that optimal performance requires a balance between active-site density, gas transport, and ionic accessibility rather than simply maximizing F content.

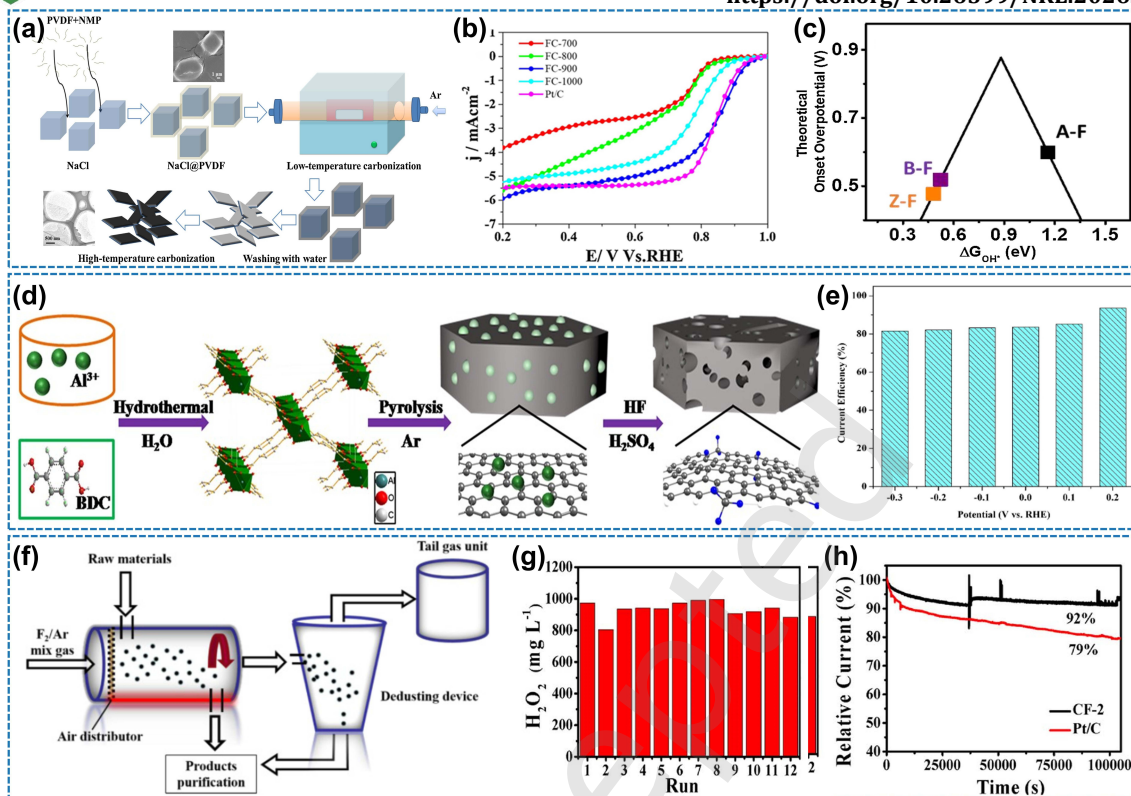


Figure 8. (a) Illustration of the synthesis procedure for FC. (b) Linear sweep voltammograms of the ORR on all samples with a rotating speed of 1600 rpm in O₂-saturated 0.1 M KOH electrolyte. (c) The scheme that depicts the structures of A-F, B-F, and Z-F.^[82] Reproduced with permission from ref. 82. Copyright Elsevier., 2021. (d) Procedure for the synthesis of F-doped hierarchically porous carbon catalysts. (e) The current efficiency of H₂O₂ synthesis by FPC-800 at different applied potentials. Reproduced with permission from ref. 160. copyright Elsevier, 2018.^[160] (f) Schematic diagram of the synthesis device of F-doped carbon. (g) The H₂O₂ concentration of CF-2 catalysts was determined over 12 cycles. (h) Current-time (i-t) chronoamperometric response of CF-2 and Pt/C at -0.1 V vs. RHE. Reproduced with permission from ref. 90. copyright Elsevier, 2022.^[90]

In addition to ORR, F-DNCMs have also emerged as promising metal-free catalysts for the OER in alkaline media. Kim et al. first demonstrated that F-doped carbon black (F-KB), synthesized by pyrolyzing Ketjenblack with Nafion as the F source, exhibited markedly enhanced OER activity compared to pristine CB.^[164] Through XPS analysis and in situ monitoring of evolved O₂, they identified semi-ionic C-F bonds rather than covalent C-F bonds as the key structural motif responsible for the activity enhancement. The positively polarized carbon atoms adjacent to semi-ionic F species were therefore proposed as the active sites for OER.

In a subsequent mechanistic study, the same group combined an RDE setup with a fluorescence-based O₂ sensor to distinguish the true OER current from parasitic processes.^[65] The F-doped carbon showed a Tafel slope of 60 mV dec⁻¹ that was essentially independent of pH with a proton reaction order of -1. These features suggest a pathway involving a pre-equilibrium proton-coupled electron-transfer step, followed by an irreversible chemical rate-determining step. Remarkably, the intrinsic OER activity approached that of RuO₂, highlighting the potential of fluorinated carbon as a noble-metal-free OER catalyst. More recently, Ali et al. developed F-doped CNTs (F-CNTs) through a low-temperature solid-state fusion

route using XeF₂ as the fluorinating reagent.^[92] XPS confirmed the coexistence of covalent and semi-ionic C-F bonds, with a total F content of 5.1 at.%. The resulting F-CNTs acquired an OER overpotential of only 280 mV at 10 mA cm⁻², which was 60 mV and 25 mV lower than those of undoped CNTs and commercial Ir/C, respectively. In addition, the catalyst exhibited excellent stability during 10 h chronopotentiometric testing. These findings further support that F doping, especially in the form of semi-ionic C-F species, can create positively charged carbon sites that promote OH⁻ adsorption and accelerate OER kinetics.

Thus, single F-doped nanocarbons have demonstrated great potential in 4e⁻ ORR for energy conversion, selective 2e⁻ ORR for H₂O₂ electrosynthesis, and alkaline OER. Their performance enhancement stems from multiple cooperative effects, including F-induced charge polarization, regulation of intermediate adsorption, modulation of wettability and mass transport, and the formation of catalytically favorable semi-ionic C-F bonds. These studies establish single F doping as a fundamental yet versatile strategy for engineering nanocarbon-based oxygen electrocatalysts.

4.2. F-based Dual-heteroatom-doped nanocarbons

Compared with single F-doped nanocarbons, dual-heteroatom-doped F-based carbons usually exhibit

higher oxygen electrocatalytic activity. The coexistence of two heteroatoms enables more delicate regulation of local charge distribution, spin density, defect chemistry, and intermediate adsorption. Among the reported works, N, F, and B, F dual-doped nanocarbons have attracted particular attention for the ORR, as heteroatoms with markedly different electronegativities can create highly polarized carbon environments. In N, F-codoped nanocarbons, for example, N typically acts as an electron-donating dopant that modifies the electron density of neighboring carbon atoms, whereas F, owing to its extremely high electronegativity, strongly withdraws electron density and induces pronounced C-F polarization.^[165] The synergistic interaction between these two dopants can therefore generate highly active sites, optimize spin/charge distribution, facilitate O₂ adsorption and activation, thus promoting the efficient ORR process.

Since the pioneering report by Sun and co-workers on N, F-codoped CB as a high-performance metal-free ORR catalyst, a broad range of N, F dual-doped nanocarbons, including CB derivatives, cotton-derived carbons, CNFs, graphene-like nanosheets, and hierarchically porous carbons, have been developed and shown excellent ORR activity and durability.^[168] For example, Liu *et al.* developed N, F co-doped hollow carbon nanospheres (N/F-HC) through an ultrafast NaN₃/C₅F₅N deflagration route (Figure 9a).^[111] During this process, Na nanoclusters served as both sacrificial templates and F scavengers, whereas the intense local heat enabled rapid graphitization and high heteroatom retention within seconds. The optimized N/F-HC-2 catalyst possessed a hollow architecture, an SSA of 386 m² g⁻¹, uniformly

distributed pyridinic-N, pyrrolic-N, graphitic-N, and semi-ionic C-F species. As a result, it delivered an E_{onset} and $E_{1/2}$ comparable to commercial Pt/C in alkaline media. Koutecky-Levich and RDE analyses confirmed an electron transfer number close to 4.0, negligible peroxide yield, and superior durability over 500 cycles. This work highlights the importance of simultaneously controlling graphitization, porosity, and dual-dopant chemistry through ultrafast synthesis. Fu *et al.* synthesized N, F-codoped carbon nanowire aerogels through a template-directed hydrothermal carbonization route using Te nanowires, followed by NH₄F impregnation and high-temperature annealing.^[129] The resulting interconnected nanowire aerogels exhibited a high SSA of 768 m² g⁻¹, dominant mesoporosity, and abundant pyridinic/graphitic N with ionic and semi-ionic C-F species. The optimized catalyst showed an E_{onset} of 0.91 V and $E_{1/2}$ of 0.83 V vs. RHE in alkaline electrolyte, comparable to those of the Pt/C catalyst. Similarly, Gong *et al.*^[125] developed N, F-codoped microporous CNFs (N, F-MCFs) through a multistep electrospinning-hydrothermal and carbonization process, using polyacrylonitrile and poly(vinylidene fluoride) as N and F sources, respectively (Figure 9b). The obtained nanofiber network featured abundant micropores, a high defect density, and a SSA exceeding 700 m² g⁻¹ (Figure 9c). As a result, the N, F-MCFs catalyst delivered an E_{onset} of 0.94 V and an $E_{1/2}$ of 0.81 V vs. RHE with an electron transfer number close to 4.0 (Figure 9d). This study also identified PVDF as an effective and scalable F precursor for ORR-oriented carbon electrocatalyst.

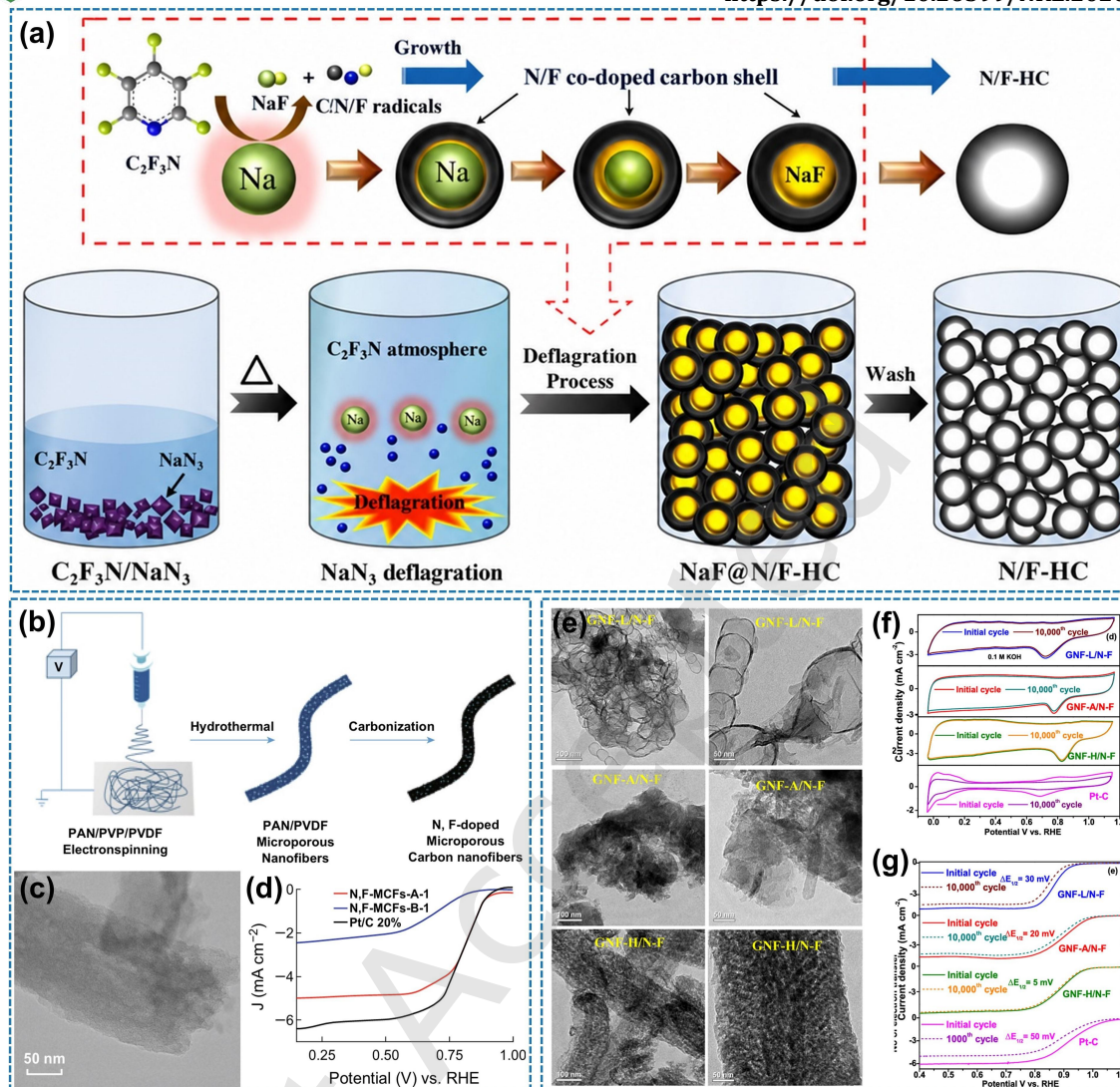


Figure 9. (a) Schematic for the synthesis and formation mechanism of N/F-HC via the NaN_3 deflagration method. Reproduced with permission from ref. 111. copyright The Royal Society of Chemistry, 2018.^[111] (b) Schematic illustration of N, F-MCFs ORR catalysts. (c) TEM images of N, F-MCFs. (d) LSV curves of N, F-MCFs-A; N, F-MCFs-B; and commercial 20% Pt/C in O_2 -saturated 0.1 M KOH electrolyte with a scan rate of 10 mV s^{-1} .^[125] (e) TEM images for GNF-L/N-F, GNF-A/N-F, and GNF-H/N-F at different magnifications. (f) CVs and (g) LSVs for N-F co-doped GNF before and after 10 000 repeated potential cycles, Pt/C before and after 1000 repeated potential cycles in 0.1 M KOH electrolyte. Reproduced with permission from ref. 127. copyright American Chemical Society, 2020.^[127]

The effect of microstructural orientation has also been examined in graphitic CNFs. Akula *et al.* investigated N, F codoping in graphitic CNFs with linear, antler-type, and herringbone platelet arrangements, denoted as GNF-L/N-F, GNF-A/N-F, and GNF-H/N-F, respectively (Figure 9e).^[127] After melamine/ NH_4F -assisted thermal treatment, the herringbone-type nanofibers exhibited more pronounced structural distortion, enlarged interlayer spacing, and abundant open-edge sites enriched with pyridinic/pyrrolic-N and semi-ionic C-F species. The optimized sample displayed excellent ORR kinetics, strong methanol tolerance, and only 5 mV loss in $E_{1/2}$ after 10 000 cycles (Figure 9f, g). These results point to a close interplay between nanofiber morphology and N, F dual-dopant chemistry in determining ORR performance.

2D N, F-codoped graphene-like sheets and carbon nanosheets provide another important platform because

they expose a high density of edge sites and basal-plane defects while maintaining rapid in-plane electron transport. Qiao *et al.*^[130] reported N, F co-doped reduced graphene oxide (GO) prepared by one-step thermal annealing of GO with NH_4F , achieving uniform incorporation of N of 2.5 at% and F of 0.7 at% without compromising electrical conductivity. The obtained N-F/rGO possessed a high SSA of $412 \text{ m}^2 \text{ g}^{-1}$, abundant slit-shaped mesopores, and a large proportion of semi-ionic C-F bonds. These structural features enhanced charge polarization around N sites and promoted O-O bond activation. As a result, N-F/rGO delivered a positive E_{onset} of 0.96 V vs. RHE, a low Tafel slope of 63 mV dec^{-1} , an electron transfer number of ~ 3.9 –4.0, peroxide yields below 6%, and improved stability/methanol tolerance.

Hierarchically porous carbon frameworks represent an effective architecture for ORR, because interconnected

hierarchical pores can simultaneously improve active-site exposure, electrolyte infiltration, and oxygen transport. Wang *et al.*^[128] synthesized F, N co-doped ordered mesoporous carbon (FN-OMC) via a hard-template route using SBA-15 and resorcinol, with ammonium fluoride serving as the heteroatom source (Figure 10a). The optimized FN-OMC-1000 exhibited a high SSA of $671 \text{ m}^2 \text{ g}^{-1}$, ordered mesoporous channels of $\sim 6.2 \text{ nm}$, and homogeneously distributed pyridinic/graphitic N with ionic and semi-ionic C-F species (Figure 10b, c). The ORR activity of FN-OMC-1000 is comparable to commercial Pt/C in an alkaline electrolyte (Figure 10d), along with superior durability and methanol tolerance. In another study, Lv *et al.* developed N, F-codoped porous carbons from a PTFE/polyaniline (PANI) composite precursor (Figure 10e).^[166] This strategy enabled more stable F retention during carbonization than volatile F salts. After pyrolysis at 1000°C , the resulting N, F-Carbon-1000 showed a high SSA of $838 \text{ m}^2 \text{ g}^{-1}$, hierarchical micro/mesoporosity, and dominant pyridinic/graphitic N species coupled with F dopants. The catalyst achieved an E_{onset} of 0.97 V and an $E_{1/2}$ of 0.84 V vs. RHE, nearly

identical to 20 wt% Pt/C (Figure 10f), and followed a near $4e^-$ ORR pathway.

Beyond porosity and morphology, F can also directly reshape the atomic configuration of N species during pyrolysis. Li *et al.* revealed that F introduction selectively weakens edge C-N bonds, converting a large fraction of the pyrrolic-N into more stable graphitic-N while preserving pyridinic-N (Figure 10g-k).^[86] This F-induced rearrangement maximized the fraction of catalytically favorable pyridinic-N and graphitic-N species and destabilized the π -conjugated network, thereby creating a more localized electronic structure that favored O_2 adsorption and O-O bond cleavage. The resulting urchin-like F@NC superstructure, composed of radially aligned carbon nanorods with uniformly distributed N and F, exhibited an outstanding $E_{1/2}$ of 0.90 V vs. RHE and a low Tafel slope of 50 mV dec^{-1} , surpassing both Pt/C and the F-free counterpart (Figure 10l). This work demonstrates that F doping can serve not only as an electronic modulator but also as an atomic-level driver for constructing more active N configurations in metal-free ORR catalysts.

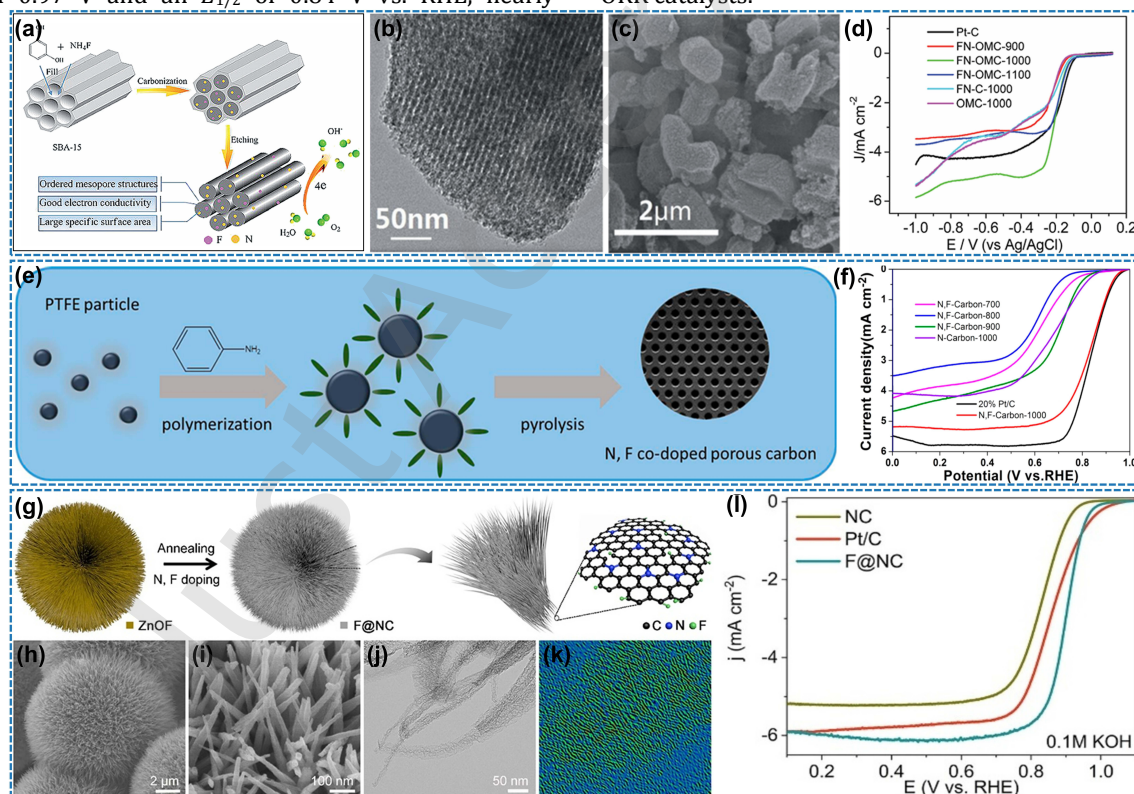


Figure 10. (a) Illustration of the preparation of FN-OMC as a catalyst for ORR. (b) TEM and (c) SEM images of mesoporous FN-OMC-1000. (d) RDE polarization curves recorded on FN OMC-1000 and Pt/C catalysts at 1600 rpm. Reproduced with permission from ref. 128. copyright The Royal Society of Chemistry, 2016.^[128] (e) Synthesis illustration of N, F-doped carbon as an ORR electrocatalyst. (f) Rotating-disk voltammograms of four N, F-Carbon catalysts and 20% Pt/C in O_2 -saturated 0.1 M KOH with a sweep rate of 5 mV s^{-1} at the rotating rate of 1600 rpm. Reproduced with permission from ref. 166. copyright American Chemical Society, 2017.^[166] (g) synthesis illustration, (h-k) morphology of the F@NC, (l) LSV curves of the corresponding samples. Reproduced with permission from ref. 86. copyright American Chemical Society, 2025.^[86]

Besides, biomass-derived carbons provide a sustainable platform for constructing N, F-codoped ORR catalysts while preserving the advantages of low-cost, high scalability, and inherited porous architectures. Zhao *et al.* reported a high-throughput strategy to prepare N,

F-codoped porous carbons from nearly 30 types of biomass, including alfalfa, banana peel, and willow leaves (Figure 11a).^[131] In this synthesis, NH_4F was used as the N and F source, while Zn-based species acted as sacrificial porogens. The resulting carbons exhibited fluffy 3D

porous frameworks, large SSA of 1000–1400 m² g^{−1}, and tunable N and F contents and ratios. The optimized catalyst delivered an $E_{1/2}$ comparable to Pt/C, a dominant 4e[−] pathway, excellent durability, and methanol tolerance in an alkaline electrolyte. Notably, this study proposed a “treasure-map” concept to correlate heteroatom chemistry with ORR activity (Figure 11b), thereby offering a design guide for biomass-derived carbon catalysts. After that, Akula *et al.* reported N, F co-doped porous carbon derived

from silk cotton fibers through carbonization, followed by melamine and NH₄F post-doping.^[124] The intrinsic porous structure of silk-cotton-derived carbon was retained, while dual doping increased defect density, SSA, and the fraction of pyridinic-N and semi-ionic C-F species. The optimized catalyst exhibited an E_{onset} and $E_{1/2}$ close to Pt/C, an electron transfer number of ~ 3.9 –4.0, negligible peroxide formation, and strong resistance to methanol and CO poisoning over 10 000 cycles.

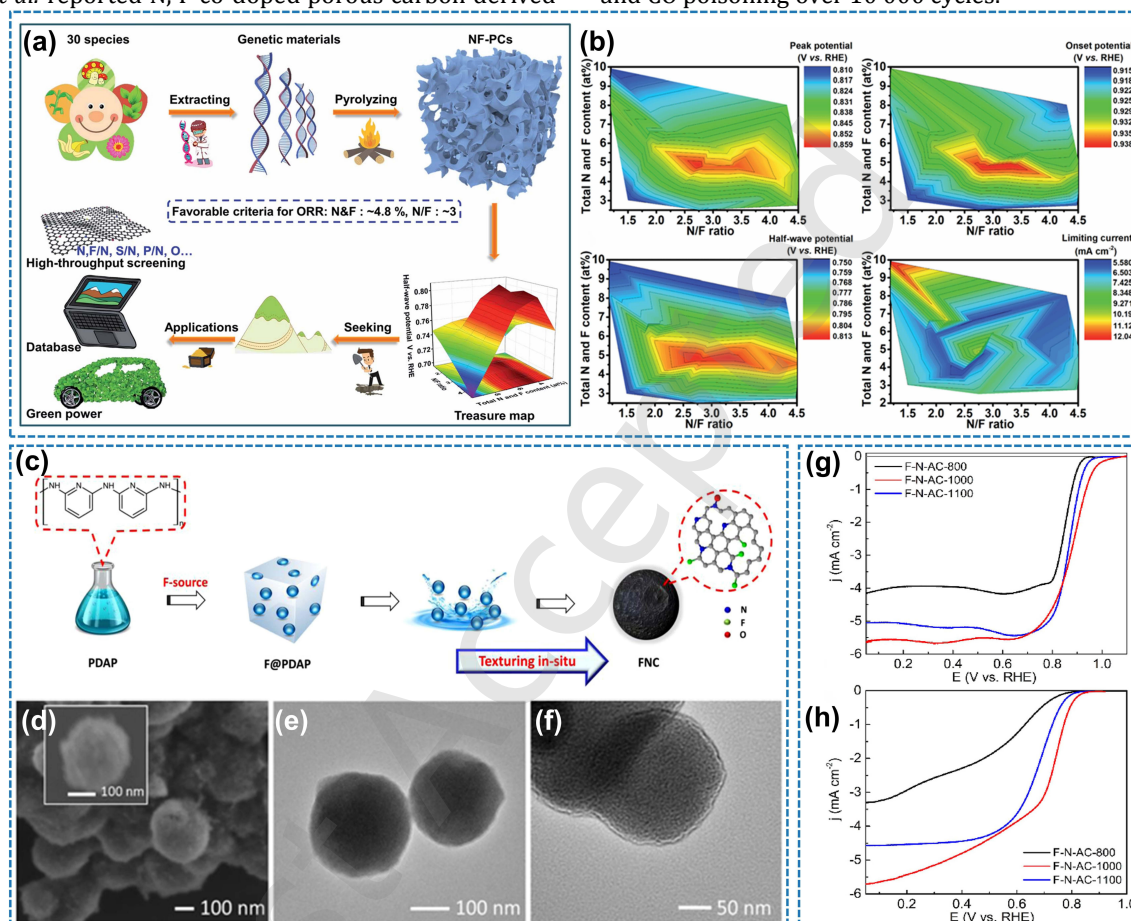


Figure 11. (a) Schematic illustration of the synthesis of NF-PCs. (b) The contour plots of peak potential, E_{onset} , $E_{1/2}$, and limiting current density as functions of total N and F content and N/F ratio. Reproduced with permission from ref. 131. copyright The Royal Society of Chemistry, 2021.^[131] (c) Schematic illustration for the synthesis of FNC. (d) SEM images and (e, f) TEM images of FNC at different magnifications. Reproduced with permission from ref. 122. copyright Elsevier, 2021.^[122] LSV curves of F-N-ACs in (g) alkaline and (h) acid electrolyte. Reproduced with permission from ref. 87. copyright Elsevier, 2022.^[87]

Although metal-free carbon catalysts typically perform better in alkaline media, several N, F-codoped systems have also shown impressive ORR activity in acidic electrolytes. Peera *et al.*^[63] synthesized N, F co-doped graphite nanofibers (N-F/GNFs) via high-temperature pyrolysis of oxidized GNFs using melamine and NH₄F as N and F sources, respectively. The optimized N-F/GNF catalyst exhibited ORR activity comparable to Pt/C in 0.5 M HClO₄, outstanding tolerance to methanol and CO, and negligible activity decay after 20 000 cycles. Moreover, when used as the cathode catalyst in an H₂/O₂ polymer electrolyte FC, it achieved a peak power density of 165 mW cm^{−2}. DFT calculations suggested that N, F codoping enlarged the graphite interlayer spacing and generated highly polarized carbon sites, where pyridinic/graphitic N

and semi-ionic C-F bonds synergistically facilitated O₂ adsorption and facilitated the 4e[−] reduction pathway. Akula *et al.* extended this concept to multiwalled CNTs, where oxidative pretreatment followed by melamine/NH₄F pyrolysis induced partial unzipping into graphene-like nanosheets rich in edge defects.^[123] The resulting N-F/MWCNT catalyst showed an $E_{1/2}$ relative to single-doped controls, a dominant 4e[−] ORR mechanism, and exceptional stability over 10 000 cycles in acidic electrolyte. These results indicate that F-assisted structural transformation is a highly effective strategy to simultaneously enhance intrinsic activity and stability under acidic conditions.

Dual-doped carbon catalysts can even maintain strong ORR performance across both alkaline and acidic

media, which is highly desirable for practical deployment but remains difficult to achieve. Shah *et al.*^[122] reported mesoporous N, F-codoped carbons synthesized via a salt-assisted gas-liquid interfacial strategy using poly-diaminopyridine and NH_4F (Figure 11c). The in situ decomposition of NH_4F induced simultaneous F incorporation and pore formation, resulting in a catalyst with high SSA and abundant edge defects (Figure 11d-f). The optimal FNC catalyst delivered an E_{onset} of 0.98 V and $E_{1/2}$ of 0.87 V vs. RHE in alkaline electrolyte, while still retaining an $E_{1/2}$ of 0.78 V in acidic medium. The ORR proceeded mainly through a $4e^-$ ORR pathway with peroxide yield below 2% and excellent stability over 8000 cycles. Similarly, Zhang *et al.* developed F-modified N-based activated carbons with an F-enhanced pyridinic-N configuration and hierarchical porosity.^[87] The optimized catalyst exhibited $E_{1/2}$ of 0.89 V vs. RHE in alkaline and 0.75 V vs. RHE in acidic electrolyte (Figure 11g, h), outperforming most reported metal-free catalysts and even surpassing the Pt/C catalyst in durability and methanol tolerance. DFT calculations revealed that F incorporation into the pyridinic-N motif significantly

enhanced charge and spin density of adjacent carbon atoms, thereby strengthening Lewis base sites and optimizing the adsorption energies of ORR intermediates.

In addition to the $4e^-$ ORR, dual-doped F-based nanocarbons have also been applied to the $2e^-$ ORR toward H_2O_2 electrosynthesis. Chokradjaroen *et al.* synthesized undoped, B-doped, and B, F dual-doped carbon nanoparticles via a one-step solution plasma process at room temperature and atmospheric pressure (Figure 12a).^[167] This route generated turbostratic carbon nanoparticles with abundant structural defects and semi-ionic C-F bonds without requiring high-temperature pyrolysis. Electrochemical tests revealed that the obtained nanocarbons catalyze ORR predominantly through a $2e^-$ pathway, with n mainly in the range of 2.0-2.7 and HO_2^- yields up to 80% (Figure 12b-d). Notably, undoped and B-doped samples displayed the highest peroxide selectivity, whereas B, F dual doping slightly increased the n and suppressed peroxide production, suggesting that the influence of F depends strongly on the local bonding environment and defect structure (Figure 12e).

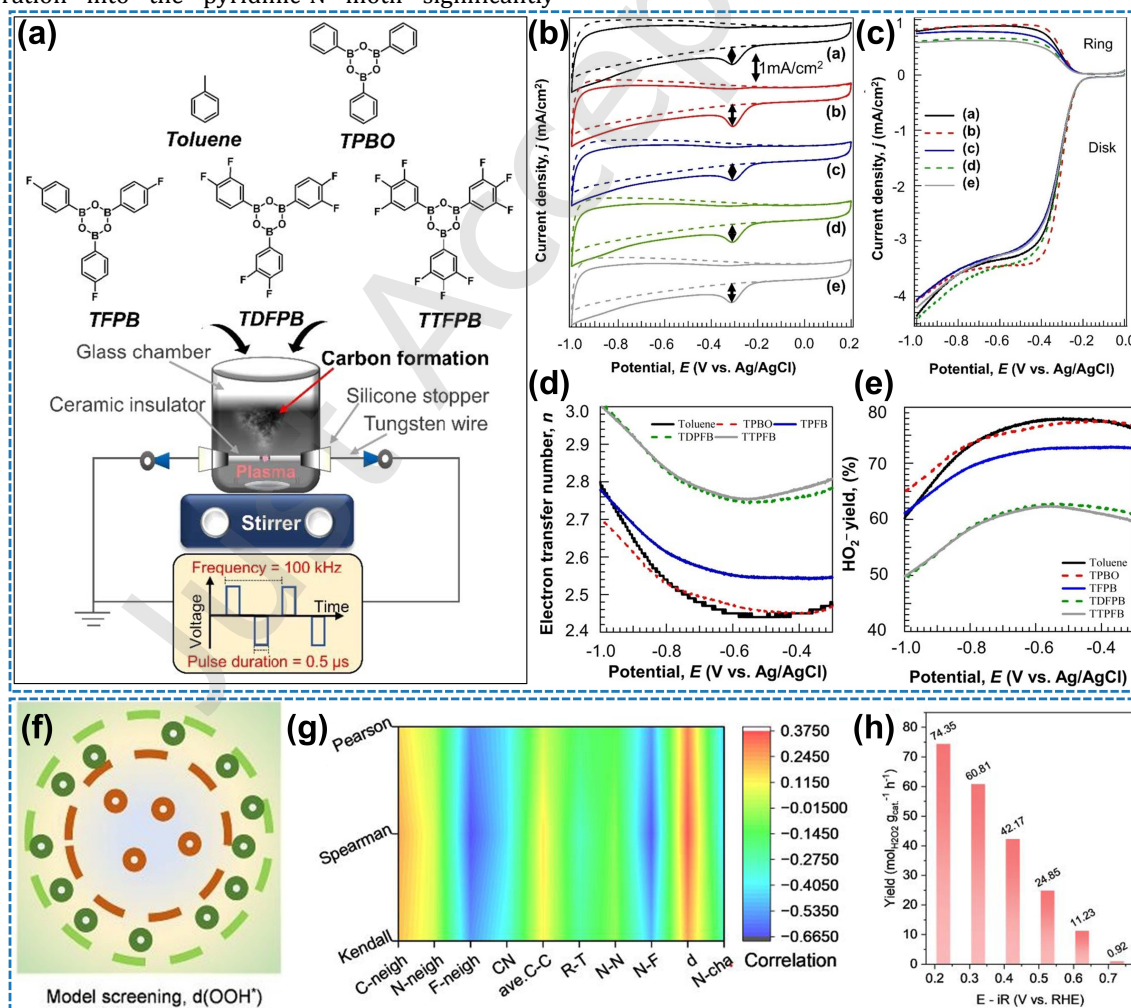


Figure 12. (a) Illustration of the solution plasma setup for the synthesis of B, F dual-doped carbon nanoparticles. (b) CV curve and (c) LSV curves of the B, F dual-doped carbon nanoparticles in N_2 - and O_2 -saturated 0.1 M KOH solution. (d) n values and (e) HO_2^- yields of the B, F dual-doped carbon nanoparticles. Reproduced with permission from ref. 167. Copyright The Royal Society of Chemistry, 2020.^[167] (f, g) Statistical screening of active sites and ΔG_{OOH^*} correlation. (h) Summary of the total yield of H_2O_2 at varying potentials. Reproduced with permission from ref. 71.

copyright Springer Nature, 2026.^[71]

Recently, Yu et al. reported that F, N codoped carbon could achieve nearly 100% H₂O₂ selectivity at 0.5 to 0.65 V vs. RHE, with over 95% selectivity over a wide potential range from 0.01 to 0.65 V.^[71] Statistical analysis of 66 possible active sites revealed that F doping, especially with adjacent F atoms, substantially lowered the absolute $\Delta G^{\circ}_{\text{OOH}}$, thereby optimizing *OOH binding (Figure 12f, g). During fluorination, a denitrogenation cascade occurred, decreasing the N content from 2.56 to 1.18 at.% while increasing the F content to 7.55 at.%. This process passivated deep defect sites and suppressed the competing 4e⁻ pathway. As a result, the water-formation current decreased by 85% compared with N-doped carbon. Under industrially relevant conditions, the catalyst sustained 300 mA cm⁻² for 105 h with a Faradaic efficiency of 95% and an H₂O₂ production rate of 74.35 mol g_{cat}⁻¹ h⁻¹ (Figure 12h). In another study, Liu et al. reported an FG quantum dot-decorated CNT, in which abundant sp²-carbon edge sites and electron-withdrawing CF_x moieties cooperatively promoted *OOH desorption and selective 2e⁻ ORR.^[168] As a result, the obtained FGQD/CNT achieved a H₂O₂ selectivity of 90.7 % at 0.75 V

vs. RHE, outperforming pristine CNT and GQD/CNT. In situ ATR-SEIRAS confirmed facile *OOH desorption from the catalyst surface, supporting the proposed 2e⁻ ORR pathway. When applied in a value-added-reaction-assisted ZAB system, the catalyst delivered both high H₂O₂ productivity and practical device-level feasibility.

Beyond ORR, N, F dual-doped nanocarbons are also attractive for the OER, where sluggish multistep proton-coupled electron transfer requires finely regulated electronic structures and intermediate adsorption energetics. Li et al. reported that the F, N-codoped carbon matrix with a low overpotential of 345 mV clearly outperforms single N-doped and F-doped samples.^[93] Theoretical calculations revealed that the synergistic interaction between pyridinic-N and F species lowers the energy barrier for the *O to *OOH transition, shifts the potential-limiting step from *OOH formation to *O generation, and enhances charge transfer during OER. Long-term electrochemical testing further confirmed its excellent stability, demonstrating that dual-heteroatom engineering can simultaneously improve the activity and durability of metal-free carbon catalysts.

Table 2. F-doped nanocarbon-based materials for OER electrocatalysis.

Catalyst	Electrolyte	Catalyst loading (mg cm ⁻²)	Overpotential (mV)	Tafel slope (mV dec ⁻¹)	Ref.
F-NPC	0.1 M KOH	-	420	181	[58]
NF@CB	0.1 M KOH	0.61	379	69	[126]
WO ₃ @F _{0.1} -GS	0.1 M KOH	0.20	298	94	[68]
N,F-Co(OH) ₂ /GO	1 M KOH	-	228	53	[169]
FeNi@CNTs-400-F-300	1 M KOH	0.20	391	42	[170]
CISC-Ag-5%	1 M KOH	0.28	380	54	[171]
F-carbon	0.1 M KOH	0.2	390	62	[65]
F-doped CNTs	1 M KOH	-	280	75	[92]
FeN ₄ -NFS-CNF	0.1 M KOH	-	270	55	[154]
NFS-700	1 M KOH	0.21	370	116	[142]
FCDs/FeCoSe-VSe/NF	1 M KOH	-	258	35	[172]
GO-PANi31-FP	1 M KOH	-	390	136	[173]
BNFC-800	1 M KOH	0.50	313	56	[144]
NFS-CNF-0.5-1000	1 M KOH	0.64	380	67	[66]

Because rechargeable Zn-air batteries (ZABs) rely on ORR during discharge and OER during charge, bifunctional oxygen electrocatalysis is particularly important for dual-doped F-based nanocarbons. Sun et al. reported N, F-codoped porous carbons derived from an F-containing covalent organic framework (COF) via one-step carbonization (Figure 13a).^[55] The optimized NFPC-1100 catalyst exhibited an ORR E_{onset} of 0.96 V and an $E_{1/2}$ of 0.85 V vs. RHE, outperforming commercial Pt/C, while also showing lower OER onset potential and higher current density than Pt/C and RuO₂ (Figure 13b). When used as

the air cathode of a ZAB, the catalyst delivered a peak power density of 157 mW cm⁻², exceeding the Pt/C + RuO₂ benchmark (Figure 13c). DFT calculations based on representative N, F-codoped structures suggested that the f-graphitic N-F configuration possessed the lowest free-energy barriers for both ORR and OER (Figure 13d-f), thereby explaining the excellent bifunctional activity and long-term cycling stability. Subsequently, Zhu *et al.* N, F co-doped CB (NF@CB) was synthesized through ball-milling and pyrolysis of CB, melamine, and PTFE.^[126] The optimized NF@CB catalyst exhibited an ORR $E_{1/2}$ of

0.81 V vs. RHE and a low OER overpotential of 379 mV at 10 mA cm^{-2} , comparable to commercial Pt/C + RuO₂ catalysts. When employed as the air cathode in a ZAB, the NF@CB catalyst delivered a small charge-discharge voltage gap and excellent cycling stability over 49 h. More recently, Li *et al.*^[174] reported a COF-derived F, N-codoped porous carbon (F-NPC) with uniformly distributed heteroatoms and abundant hierarchical porosity (Figure 13g). The resulting F-NPC also exhibited outstanding

bifunctional activity with an $E_{1/2}$ of 0.86 V vs. RHE and an OER potential of 1.65 V at 10 mA cm^{-2} . The ZAB with the F-NPC catalyst showed a high peak power density of 206.3 mW cm^{-2} and long-term cycling durability (Figure 13h). DFT calculations further indicated that F doping broadened the distribution of spin and charge density on neighboring carbon atoms and optimized the adsorption free energies of *OOH, *O, and *OH intermediates, thereby accelerating both ORR and OER kinetics.

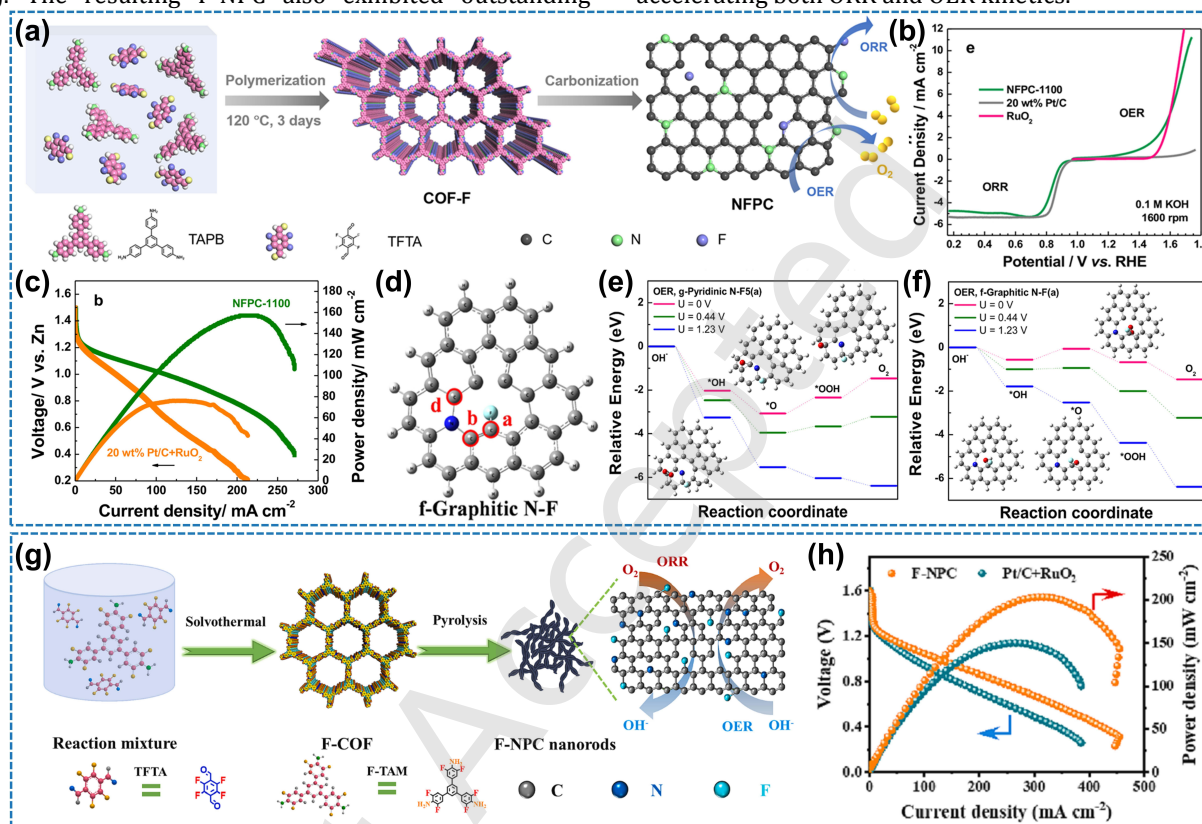


Figure 13. (a) Schematic illustration for the synthesis of NFPC. (b) ORR and LSV Curves. (c) ZAB polarization and power density of the samples. (d-f) DFT active structures and free-energy diagrams of NFPC. Reproduced with permission from ref. 55. Copyright Elsevier, 2021.^[55] (g) Schematic illustration of the synthesis of F-NPC-T. (h) Discharge polarization curves and the corresponding power density curves of ZABs based on F-NPC and Pt/C + RuO₂ catalysts. Reproduced with permission from ref. 174. copyright Elsevier, 2023.^[174]

Overall, F-based dual-heteroatom-doped nanocarbons represent one of the most powerful directions in metal-free oxygen electrocatalysis. Compared with single F-doped carbons, dual-doped systems offer a more versatile platform for regulating local electronic structure, active-site configuration, pore architecture, and catalytic microenvironment. Among them, N, F-codoped carbons are by far the most extensively studied and have demonstrated excellent performance in oxygen electrocatalysis. Moreover, recent advances have shown that the performance of these materials depends not only on the presence of N and F, but also on their exact bonding motifs, spatial arrangement, and coupling with hierarchical structure. Therefore, future efforts should move toward atomic-level control of dopant configuration, quantitative identification of true active sites, and more deliberate integration of intrinsic activity with mass-transport and interfacial microenvironments.

4.3 F-based Multi-heteroatom-doped nanocarbons

Compared with single-doped and dual-doped nanocarbons, F-based multi-heteroatom-doped carbons offer a broader platform for oxygen electrocatalysis. Their catalytic behavior arises from cooperative electronic regulation rather than from a single dominant active site. The simultaneous incorporation of F with other heteroatoms, such as N, S, P, or B, enables more refined tuning of local charge density, spin density, and Fermi-level alignment, thereby creating a wider distribution of active sites. In addition, multi-doping can generate diverse active configurations, including heteroatom-adjacent carbon defects, semi-ionic C-F moieties, and coupled heteroatom domains. These sites can synergistically optimize O₂ adsorption, facilitate O–O bond activation, and stabilize key oxygenated intermediates. These complementary effects are often difficult to achieve in single- or double-doped systems. Moreover, the coexistence of heteroatoms with different electronegativities and atomic sizes can intensify defect

generation and interfacial polarization, thereby improving active-site accessibility, charge transfer, and catalytic robustness. As a result, F-based multi-doped nanocarbons often achieve a more balanced combination of activity, selectivity, and long-term stability than their single- or dual-doped counterparts.

Previous studies have demonstrated the potential of this multi-heteroatom-doping strategy. For instance, Yang et al. reported N, S, F tri-doped CNTs through pyrolysis of a polydopamine derivative, which exhibited excellent ORR activity and stability, highlighting the role of F in strengthening the electronic modulation of interfacial active sites.^[156] Subsequently, Wang and colleagues developed N, B, F tri-doped carbon fibers with an efficient $4e^-$ ORR pathway and an open-circuit voltage (OCV) of 1.46 V in ZABs, underscoring the important contribution of F to charge transport and device-level performance.^[64] Cao et al. further reported S, N, F tri-doped porous carbon with an E_{onset} of 0.98 V and an $E_{1/2}$ of 0.86 V vs. RHE, comparable to commercial Pt/C. These results further confirm the benefit of ternary heteroatom doping in electrocatalysis.^[69]

Multi-heteroatom-doped F-based carbons also show clear advantages over single- and dual-doped analogues because multiple dopants can simultaneously tune adsorption energetics and broaden the distribution of active sites. Li et al.^[148] constructed F-modified carbon nanosheets by combining thermal fluorination with structural defect engineering (Figure 14a). The obtained N, F, and S tri-doped porous graphene (FN₃SG) possessed

expanded interlayer spacing, abundant edge defects, and a conductive sp^2 -carbon framework with highly exposed active sites. The FN₃SG delivered an $E_{1/2}$ of 0.83 V vs. RHE, rapid reaction kinetics, excellent methanol tolerance, and stable activity over thousands of cycles in an alkaline electrolyte. The enhanced activity was attributed to F-induced electronic redistribution and defect polarization, which create electron-deficient carbon centers favorable for O₂ chemisorption while avoiding excessive *OH adsorption. Similar effects were reported by Cui et al.^[146], who synthesized N, P, F-tridoped mesoporous carbon through one-step pyrolysis of melamine and the ionic liquid BmimPF₆. The ionic liquid simultaneously served as the carbon source and P and F dopant precursor, enabling direct formation of a mesoporous carbon framework without post-treatment. The optimized catalyst showed strong ORR activity, excellent methanol tolerance, and long-term durability in an alkaline medium. The enhanced performance was attributed to the cooperative electronic effects of N, P, and F, which induced charge delocalization, defect enrichment, and strong C-F/C-P polarization. In another example, Li et al. prepared an F, P, N-codoped carbon catalyst by pyrolyzing poly(3-fluoroaniline)-coated g-C₃N₄ with phytic acid.^[147] The optimal F/P-N-C-950 catalyst showed an $E_{1/2}$ of 0.85 V vs. RHE, surpassing that of commercial Pt/C. Its high activity was associated with the cooperative regulation of graphitic-N, pyridinic-N, and ionic/semi-ionic C-F species, which strengthened O₂ chemisorption and lowered the ORR energy barrier.

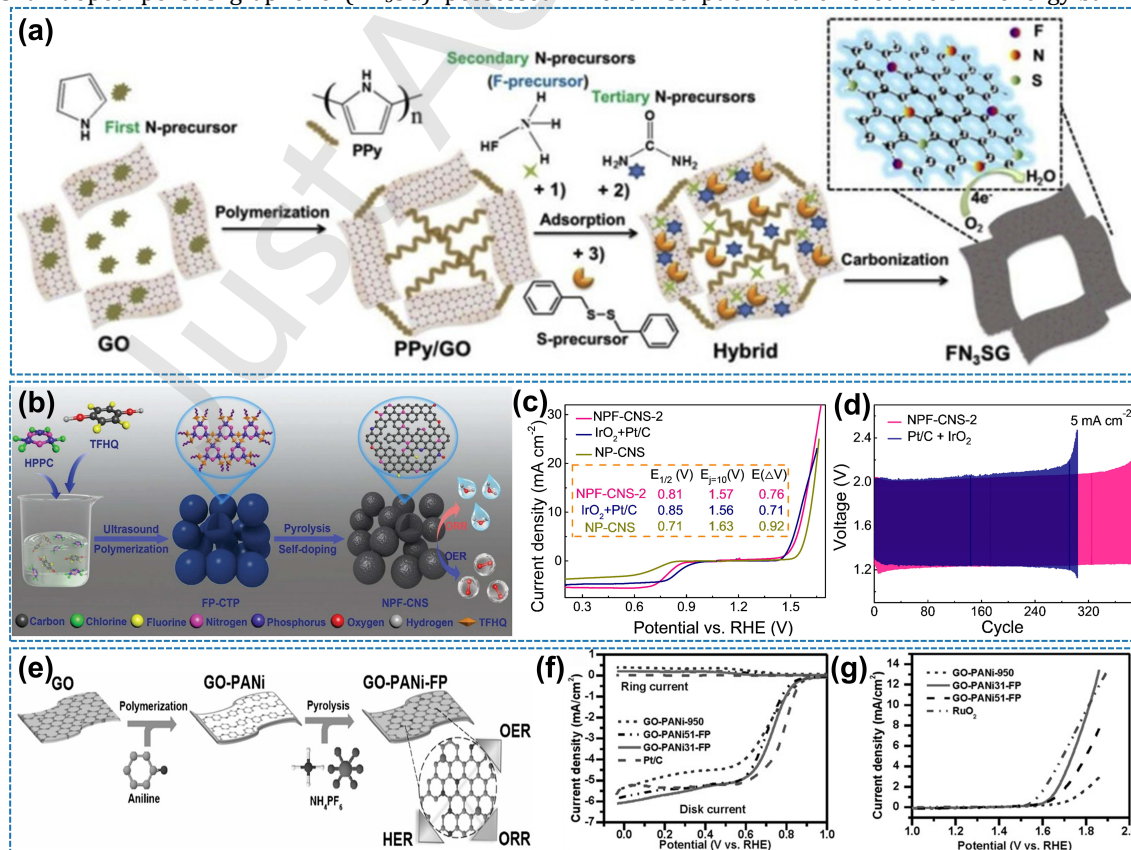


Figure 14. (a) Schematic representation of the synthesis process of FN₃SG. Reproduced with permission from ref. 148, copyright Elsevier, 2023.

^[148] (b) Schematic illustration of the preparation procedure of NPF-CNSs. (c) ORR and OER LSV curves of the samples. (d) Galvanostatic charge and discharge cycling curves of rechargeable ZABs with NPF-CNS-2 and commercial Pt/C + IrO₂ cathodes. Reproduced with permission from ref. 175. copyright Wiley, 2020.^[175] (e) The preparative process for N, O, S, F co-doped porous carbon vesicles. (f) The ORR curves of the obtained catalysts. (g) The OER curves of the obtained catalysts. Reproduced with permission from ref. 52. copyright Wiley, 2016.^[52]

Beyond ORR, multi-heteroatom doping is particularly attractive for constructing efficient ORR/OER bifunctional oxygen electrocatalysts, which are critical for rechargeable ZABs. In these systems, F not only polarizes the carbon lattice but also works together with N, P, S, O, or B to tune the adsorption free energies of *OOH, *O, and *OH intermediates. Zheng *et al.*^[175] developed N, P, F tri-doped carbon nanospheres (NPF-CNS) through self-templated carbonization of a heteroatom-enriched covalent triazine polymer (Figure 14b). Because N, P, and F were introduced from a single precursor, the resulting catalyst displayed uniform heteroatom distribution and excellent ORR/OER bifunctional performance. The optimized NPF-CNS-2 exhibited outstanding ORR activity in pH-universal media and excellent OER performance in an alkaline electrolyte. When used as the air cathode of a ZAB, it delivered a peak power density of 144 mW cm⁻² and long-term cycling stability over 385 charge-discharge cycles (Figure 14c-d). The enhanced activity was attributed to the synergistic effect of pyridinic/graphitic N, P-C bonds, and ionic/semi-ionic C-F species, which collectively promoted charge redistribution, improved oxygen adsorption, and accelerated interfacial charge transfer.

Zhang *et al.* reached a similar conclusion using N, P, F-tridoped graphene prepared by thermal activation of polyaniline-coated GO with ammonium hexafluorophosphate (AHF), as shown in Figure 14e.^[52] During pyrolysis, AHF served both as the heteroatom source and as a porogen through gas evolution. The resulting material also exhibited excellent bifunctional ORR/OER activity (Figure 14f-g). Ma *et al.* Also synthesized N, O, S, F co-doped porous carbon vesicles via a self-template pyrolysis strategy.^[176] The resulting catalyst showed improved ORR and OER kinetics, low

overpotentials, high discharge capacities, and long-term cycling stability. DFT calculations suggested that semi-ionic C-F species play a central role in regulating charge redistribution and intermediate adsorption, thereby lowering the energy barriers of oxygen electrocatalysis. In another study, Zhang *et al.* reported B, N, F-tridoped nanocarbons prepared from ionic-liquid-treated cigarette butts, affording a catalyst with an $E_{1/2}$ of 0.836 V vs. RHE and a low OER overpotential of 313 mV.^[144] When assembled into a ZAB, the catalyst delivered a peak power density of 127 mW cm⁻² and stable operation over 2300 cycles, further confirming the value of multi-heteroatom synergy for bifunctional oxygen catalysis. Previous studies further emphasize that the advantage of F-based multi-doping lies in atomic-level regulation of the electronic environment, rather than in simple accumulation of dopants content. Zheng *et al.* reported an ultrasound-triggered self-assembly strategy followed by pyrolysis to synthesize N, P, and F tri-doped porous carbon flowers (NPF@CNFs), as illustrated in Figure 15a.^[53] SEM reveals the characteristic flower-like morphology assembled from interconnected nanosheets (Figure 15b). As expected, the optimal NPF@CNF-800 exhibits superior ORR/OER bifunctional electrocatalytic activity with an $E_{1/2}$ of 0.85 V vs. RHE and a low overpotential of 330 mV at 10 mA cm⁻² (Figure 15c). When used as the air cathode in a ZAB, it maintained stable operation for more than 810 charge-discharge cycles. These findings indicate that F cooperates with N and P to generate highly polarized carbon centers with optimized oxygen-intermediate binding, thereby improving both intrinsic activity and device-level durability.

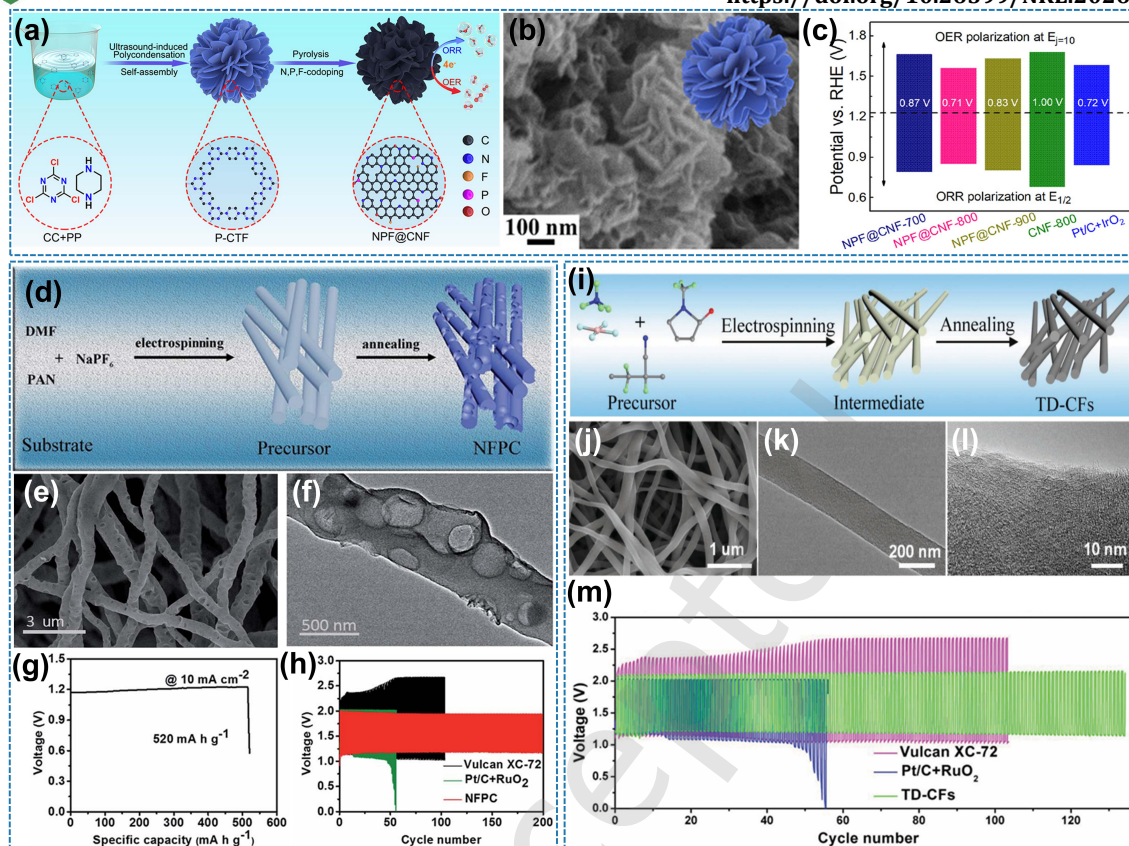


Figure 15. (a) Schematic illustration of ultrasound-triggered synthesis of NPF@CNFs. (b) SEM of NPF@CNF-800. (c) Bifunctional ΔE comparison of the corresponding catalysts. Reproduced with permission from ref. 53. copyright American Chemical Society, 2021.^[53] (d) The synthesis process of N, F, P ternary-doped macroporous carbon fibers. (e) SEM and (f) TEM images of the as-synthesized NFPC. (g) Specific capacities at a current density of 10 mA cm^{-2} for the NFPC-based primary ZAB. (h) Cycling curves of the batteries based on NFPC as air cathodes at a current density of 10 mA cm^{-2} . Reproduced with permission from ref. 157. copyright The Royal Society of Chemistry, 2018.^[157] (i) Schematic illustration of the preparation process of the TD-CFs. (j) SEM, (k) TEM, and (l) HR-TEM images of TD-CFs. (m) Discharge/charge cycling curves of ZAB using TD-CFs catalyst for the air cathode. Reproduced with permission from ref. 64. copyright Wiley, 2018.^[64]

Wu *et al.* synthesized N, F, P ternary-doped macroporous CNFs (NFPC) via electrospinning followed by thermal annealing (Figure 15d).^[157] Polyacrylonitrile and sodium hexafluorophosphate were used as carbon and heteroatom sources, respectively. The obtained electrospun fibers were subsequently carbonized and acid-washed to form a 3D porous nanofiber network. The resulting NFPC exhibited a high SSA of $1230 \text{ m}^2 \text{ g}^{-1}$ with interconnected macro/microporosity and uniform heteroatom distribution (Figure 15e, f). In an alkaline electrolyte, the NFPC showed high ORR activity, with a positively shifted reduction peak of 0.82 V vs. RHE and $E_{1/2}$ comparable to that of Pt/C. For OER, it showed a low

E_{onset} and high catalytic current density, clearly outperforming undoped CNFs. When integrated into ZABs, the NFPC afforded a high OCV of 1.46 V , a large discharge capacity of 520 mAh g^{-1} , and stable charge-discharge cycling over 200 cycles (Figure 15g, h). The excellent performance was attributed to the synergistic electronic coupling of N, F, and P dopants, which induce strong charge polarization and defect formation within the carbon lattice. This effect creates highly active sites that optimize adsorption/desorption of oxygenated $\ast\text{OOH}$ intermediates. Meanwhile, the macroporous nanofiber network enhances mass transport and electron conduction, enabling efficient ORR and OER catalysis.

Table 3. F-doped nanocarbon-based materials for ORR/OER electrocatalysis.

Catalyst	$E_{1/2}$ (V vs. RHE)	E_{10} (V vs. RHE)	ΔE (V)	Electrolyte	Ref.
F-NPC	0.86	1.65	0.79	0.1 M KOH	[58]
NF@CB	0.81	1.61	0.80	0.1 M KOH	[126]
FeN_4 -NFS-CNF	0.90	1.50	0.60	0.1 M KOH/1 M KOH	[154]
NFS-700	0.66	1.60	0.94	0.1 M KOH/1 M KOH	[142]
BNFC	0.84	1.54	0.70	0.1 M KOH/1 M KOH	[144]
NFS-CNF-0.5-1000	0.91	1.61	0.70	0.1 M KOH/1 M KOH	[66]



Wang *et al.*^[64] reported N, F, B ternary-doped carbon fibers (TD-CFs) prepared by electrospinning PAN with NH_4BF_4 followed by thermal carbonization (Figure 15i). The resulting TD-CFs have fibrous networks with uniform multi-dopant incorporation and defect-rich carbon frameworks (Figure 15j-l). Compared to single-doped carbon fibers, the TD-CFs exhibited enhanced ORR activity with a more positive E_{onset} and efficient $4e^-$ selectivity. The TD-CFs also showed improved OER performance, as reflected by a lower OER E_{onset} and higher catalytic current densities than control samples. When used as air cathodes in rechargeable ZABs, TD-CFs showed small charge-discharge voltage gaps, high power output, and superb long-term cycling stability, outperforming Pt/C + RuO_2 cathodes (Figure 15m). These results demonstrate that N, F, and B multi-heteroatom doping can create robust bifunctional carbon electrocatalysts.

Polymerized ionic liquids (PILs) have also emerged as appealing precursors for constructing multi-heteroatom-doped F-based carbons, because they inherently contain multiple heteroatoms, offer molecular-level tunability, and can be converted directly into defect-rich conductive carbon frameworks. Li *et al.*^[66] reported a PILs-derived N, F, S tri-doped CNF obtained through electrospinning followed by pyrolysis (Figure 16a). SEM and TEM results revealed flexible and 3D interconnected nanofibrous networks with uniform morphology and predominantly amorphous carbon architecture. (Figure 16d-e). The resulting porous freestanding nanofiber network contained uniformly distributed N, F, and S species and showed excellent

ISSN 2791-0091 (print); 2790-8119 (online)
<https://doi.org/10.26599/NRE.2026.9120278>
bifunctional activity, with an $E_{1/2}$ of 0.91 V vs. RHE, a low OER overpotential of 380 mV at 10 mA cm^{-2} , and outstanding durability. When directly employed as a binder-free air cathode in ZABs, the catalyst enabled an OCV of 1.47 V, a maximum power density of 127.5 mW cm^{-2} , a high specific capacity of 826.4 $\text{mAh g}_{\text{Zn}}^{-1}$, and stable cycling over 80 h (Figure 16f-h). DFT calculations revealed that N, F, and S tri-doping synergistically tailors the charge density distribution of the carbon lattice and optimizes the adsorption free energies of $^*\text{OOH}$, $^*\text{O}$, and $^*\text{OH}$ intermediates, thereby promoting both ORR and OER kinetics.

In a word, multi-heteroatom-doped F-based nanocarbons represent a further evolution beyond single- and dual-doped systems. Their key advantage lies in the simultaneous regulation of electronic structure, defect chemistry, and oxygen-intermediate adsorption through multiple heteroatoms. In most reported systems, F plays a unique role as a strong electron-withdrawing dopant that amplifies local polarization, activates C-centered active sites, and helps stabilize favorable bonding environments created by N, P, S, B, or O codopants. These materials have therefore shown compelling performance in bifunctional oxygen electrocatalysis for rechargeable ZABs. Nevertheless, the individual contribution of each dopant and the exact active motifs in multi-doped systems remain insufficiently resolved. Further progress will require more precise synthesis, quantitative structure-activity analysis, and operando characterization to distinguish the roles of different heteroatom configurations under realistic working conditions.

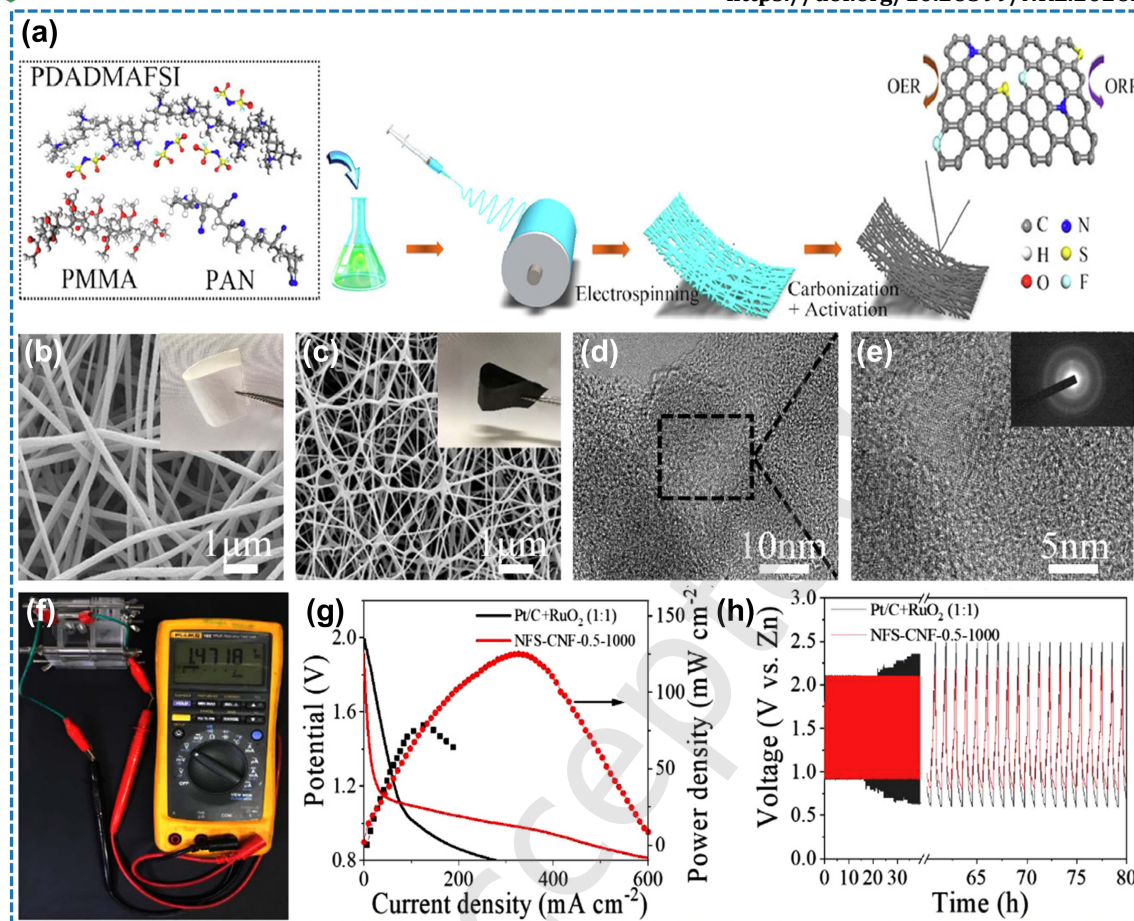


Figure 16. (a) Schematic illustration of the preparation procedure of NFS-CNF. SEM images of the NFS-CNF-0.5-1000 nanofibers (b) before and (c) after pyrolysis at 1000 °C. (d, e) HR-TEM images of the NFS-CNFs-0.5-1000. (f) Photograph of the ZAB showing OCV. (g) Specific capacity for ZABs. (h) Discharge curve and corresponding power density curves of NFS-CNF-0.5-1000 cells. Reproduced with permission from ref. 66. copyright Elsevier, 2021.^[66]

4.4 F-doped carbon-based hybrid materials

Although metal-free F-doped nanocarbons have shown considerable progress in oxygen electrocatalysis, further enhancement of intrinsic activity and operational durability often requires the integration of F-doped carbon frameworks with additional active components.^[177] F-doped carbon-based hybrid materials, including materials coupled with metal components (e. g., single atoms, nanoparticles, nanoclusters, compounds, etc.), have emerged as a particularly important class of ORR/OER electrocatalysts.^[178] In these hybrids, F is not merely a passive dopant in the carbon support. Owing to its strong electron-withdrawing ability and highly polarized C-F bonding, F can tune the electronic structure of adjacent active sites, strengthen metal-support interactions, regulate intermediate adsorption, and improve resistance to carbon corrosion. As a result, F-doped carbon supports provide a versatile platform for constructing hybrid electrocatalysts with enhanced activity, selectivity, and durability.^[134]

One important direction involves anchoring atomically dispersed metal sites on F-doped carbon substrates. In these systems, the long-range electronic influence of F can regulate the coordination environment

of metal centers, optimizing their catalytic behavior while maintaining high atomic utilization. Li and coworkers reported a hollow N, F, and S tri-doped CNF-supported Fe single-atom catalyst synthesized via coaxial electrospinning using ionic liquids and zeolitic imidazolate frameworks (ZIFs) as precursors.^[154] The resulting catalyst combined atomically dispersed Fe sites with a conductive heteroatom-rich carbon matrix and delivered an $E_{1/2}$ of 0.90 V vs. RHE and a low overpotential of 270 mV for OER. The outstanding performance was attributed to the fully exposed Fe single-atom sites and the electronic redistribution induced by the surrounding N, F, and S dopants, which modulated the charge state of the Fe centers. Similarly, Yang and colleagues developed an F self-doped porous Fe-N-C catalyst through oxidative polymerization and pyrolysis using fluoroaniline as both the F and N source.^[158] The F self-doping was shown to modulate the Fe-N_x coordination structure through long-range electronic interactions, promoting the formation of dense Fe-N_x active sites. As a result, the obtained catalyst exhibited an $E_{1/2}$ of 0.82 V vs. RHE in an alkaline medium and exceptional cycling stability in flexible ZABs. Yoon and coworkers synthesized an N, F-coordinated Fe-N-C catalyst utilizing a synergistic

chelating precursor of ethylenediamine and hexafluoroacetylacetone.^[138] After annealing at 700 °C, the optimal catalyst delivered an E_{onset} of 0.981 V vs. RHE, outperforming the F-free counterpart. This work proved the critical role of semi-ionic C-F bonds in accelerating ORR kinetics. He et al. further reported a F, N-codoped Fe-N-C catalyst derived from Fe-ZIF-8, NH_4F , and melamine.^[179] The obtained sample exhibited a high E_{onset} of 0.95 V vs. RHE, $E_{1/2}$ of 0.84 V vs. RHE, J_L of 5.5 mA cm^{-2} , and J_K of 28.1 mA cm^{-2} at 0.8 V, surpassing commercial Pt/C. These results confirm that the coupled regulation of Fe centers, F, N dopants, and the carbon matrix can substantially enhance ORR performance.

The advantages of F-regulated Fe-based hybrids become even more evident under acidic ORR conditions, where carbon corrosion and strong intermediate adsorption pose greater challenges. Tao et al. synthesized micropore-rich F-doped Fe-N-C from perfluorotetradecanoic acid-modified metal organic frameworks (Figure 17a).^[88] Advanced spectroscopy confirmed atomically dispersed FeN_4 centers with uniform

N and F distribution (Figure 17b). The optimal F-FeNC-2 catalyst exhibited an $E_{1/2}$ of 0.83 V vs. RHE in acidic media, outperforming the pristine FeNC (Figure 17c). This study showed that the strong electron-withdrawing effect of F lowers the adsorption energy of oxygenated intermediates on Fe-centered active sites, thereby enhancing acidic ORR kinetics. Similarly, Wu *et al.* employed a supramolecular polymer precursor to construct B, N, F, and Fe co-doped hollow carbon shells for efficient ORR.^[143] The optimized sample exhibited excellent ORR activity with an E_{onset} of 0.91 V vs. RHE and an $E_{1/2}$ of 0.82 V vs. RHE in an alkaline electrolyte. The ORR mainly proceeded with a dominant $4e^-$ transfer pathway, low peroxide yield, high durability for more than 1000 cycles, and strong methanol tolerance. The enhanced ORR performance was attributed to the synergistic electronic coupling between heteroatoms. The pyridinic and graphitic-N created electron-rich active centers, B induced electron-deficient sites, while F induced pronounced C-F polarization and defect formation.

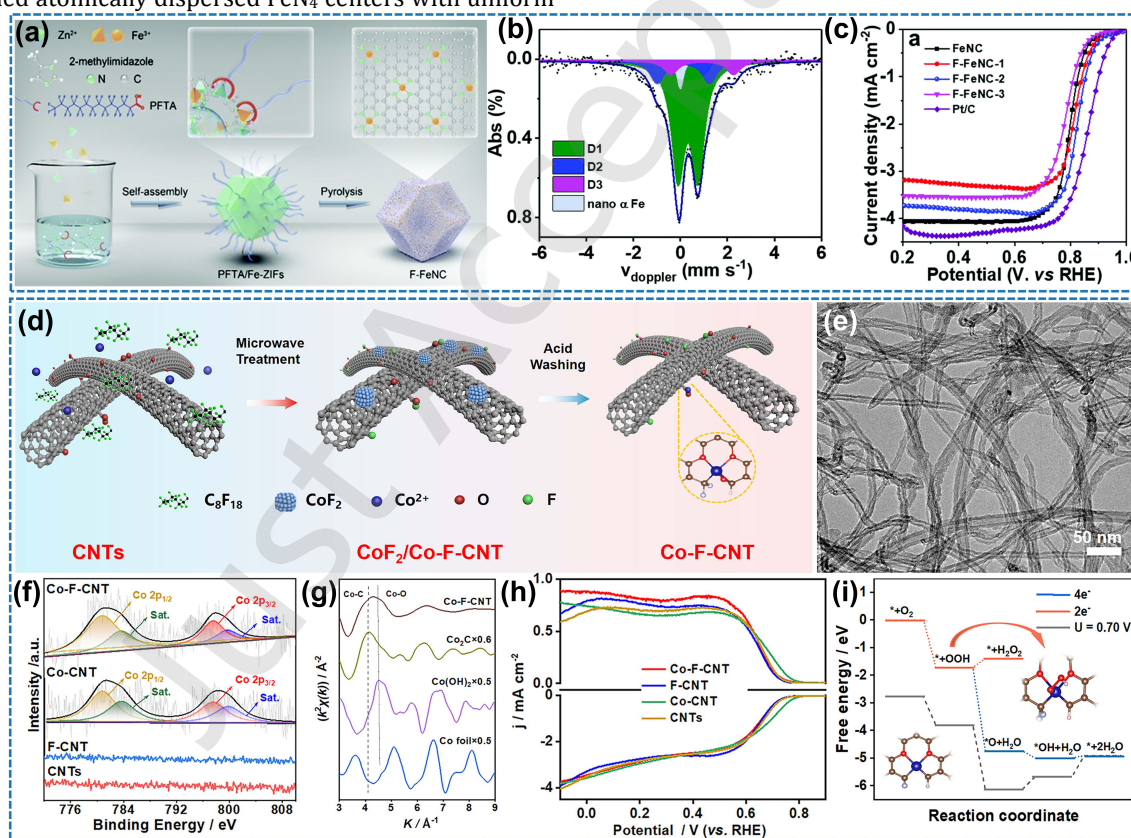


Figure 17. (a) Preparation of F-FeNC via pyrolysis of perfluorotetradecanoic acid-modified Fe-ZIFs. (b) Room-temperature ^{57}Fe Mössbauer spectra. (c) ORR polarization curves of the catalysts. Reproduced with permission from ref. 88. copyright The Royal Society of Chemistry, 2022.^[88] (d) Schematic illustration of Co-F-CNT preparation. (e) HR-TEM image of Co-F-CNT. (f) High-resolution Co 2p XPS spectra; (g) k-space EXAFS spectra for Co-F-CNTs. (h) Polarization curves of samples. (i) Gibbs free energy diagram of $2e^-$ transfer ORR pathways on Co-F/C-CNT. Reproduced with permission from ref. 180. copyright Wiley, 2022.^[180]

In addition to the $4e^-$ ORR, F-doped carbon-supported single-atom systems have also shown great promise for the $2e^-$ ORR toward H_2O_2 synthesis. Tian and co-authors reported an ultrafast microwave-assisted strategy to synthesize F-regulated Co SAs supported on CNTs (Figure 17 d-g).^[180] The synthesized Co-F-CNT

catalyst achieved a H_2O_2 yield of 18.6 $\text{mol g}^{-1} \text{h}^{-1}$ with a Faradaic efficiency of 90% at -0.04 V vs. RHE (Figure 17h). Experimental results and DFT simulations reveal that F regulation converts the active centers from a single Co atom to multiple surrounding C atoms, thereby favoring a highly efficient $2e^-$ ORR pathway (Figure 17i). The

Co-F-CNT also presented robust durability, reaching an accumulative H_2O_2 concentration of 5.2 g/L after 20 h of electrocatalysis. This work illustrated that, in hybrid catalysts, F not only optimizes isolated metal sites but also reshapes the broader electronic landscape of the support and redirects ORR selectivity.

Another major category of F-doped carbon-based hybrids involves metal nanoparticles or nanoclusters supported on fluorinated carbon substrates. Compared with conventional carbon supports, F-doped carbons typically provide stronger resistance to electrochemical oxidation, more controllable wettability, and metal-support interactions.^[181] These features are particularly valuable for Pt-group-metal catalysts, whose

activity and durability are highly sensitive to the electronic structure of the metal surface and the transport microenvironment near the catalyst/support interface. Jin et al. reported Pt nanoparticles supported on fluorinated graphene nanoribbons (Pt/F-GNRs), prepared by thermal fluorination of graphene nanoribbons followed by polyol deposition of Pt (Figure 18a, b).^[83] Compared to Pt/rGNR, the Pt/F-GNR showed slower performance decay and higher mass-activity retention after accelerated durability testing. The improved durability was attributed to the hydrophobic fluorinated support, suppressed carbon corrosion, and better stabilization of Pt nanoparticles on the F-modified carbon surface.

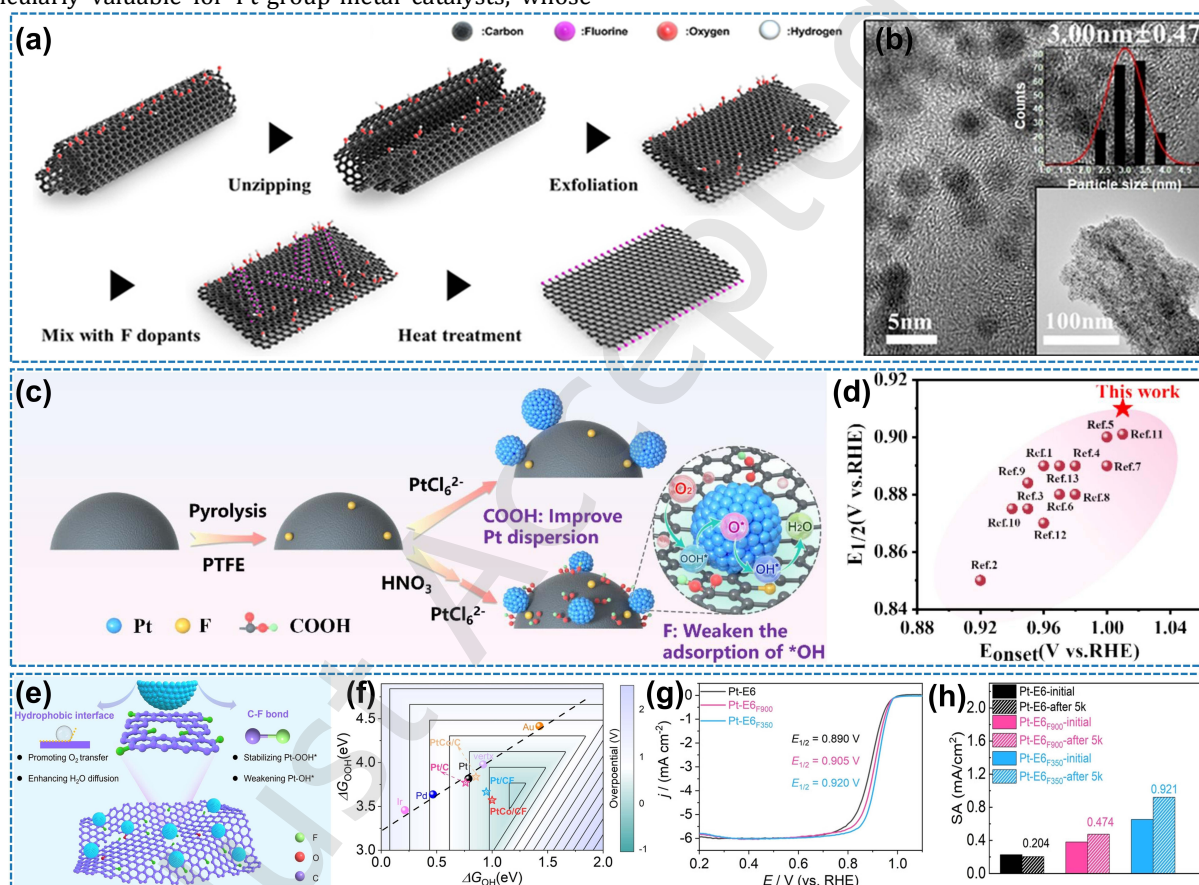


Figure 18. (a) Schematic illustration of Pt/F-GNR. (b) TEM image of Pt/F-GNR. Reproduced with permission from ref. 83. copyright American Chemical Society, 2021.^[83] (c) Schematic of the synthesis of Pt@C/F and Pt@C/F-COOH. (d) Comparison of the performances of Pt@C/F-COOH and other reported Pt-based catalysts. Reproduced with permission from ref. 155. copyright Elsevier, 2025.^[155] (e) Schematic illustration of the promoting effect of the hydrophobic and polar C-F bond on ORR. (f) Calculated chemisorption energies of $^*\text{OOH}$ and $^*\text{OH}$, and a volcano plot exhibiting the scaling relationship. (g) ORR polarization curves of the catalysts in O_2 -saturated 0.1 M HClO_4 . (h) Variations of active surface area-specific activities, mass activities, and specific activities before and after the accelerated stress test. Reproduced with permission from ref. 182. copyright Wiley, 2024.^[182]

Recently, Wang and coworkers synthesized F- and O co-doped carbon-supported Pt nanocatalysts through nitric acid oxidation followed by pyrolysis (Figure 18c).^[155] Compared with other Pt-based catalysts, the designed Pt@C/F-COOH exhibited more positive E_{onset} and $E_{1/2}$. (Figure 18d). Theoretical calculations indicated that the strong inductive effect of C-F groups triggered electron redistribution within the Pt nanoparticles, downshifting the d-band center. In another study, Pt nanoparticles

supported on F-doped carbon showed enhanced ORR activity because C-F bonding stabilized $^*\text{OOH}$ while weakening $^*\text{OH}$ adsorption, creating a local superhydrophobic interface that deviated from conventional adsorption scaling relations (Figure 18e-f).^[182] The Pt/CF showed an $E_{1/2}$ of 0.92 V vs. RHE, 30 mV more positive than Pt/C, and a smaller Tafel slope and improved cycling durability (Figure 18g-h). These studies indicate that fluorinated carbon supports

can simultaneously regulate the intrinsic activity of Pt sites and the mass-transport environment at the catalyst/electrolyte interface.

F-doped carbon supports can also cooperate with alloy or intermetallic nanoparticles to enhance ORR performance under FC-relevant conditions. Li et al. proposed an oxygen-trapping effect using PtZn intermetallic nanoparticles supported on F-doped CNTs.^[137] The F dopants induced significant negative charge accumulation on the carbon surface, forming an electronic confinement structure with the charge-deficient metal particles. This interaction created a macroscopic energy-level potential well for O₂, thus promoting oxygen enrichment around the metal active sites. In proton exchange membrane FCs (PEMFCs), the catalyst reached a peak power density of 1.49 W cm⁻² and showed only a 7.4% degradation after 30 000 accelerated stress-test cycles. Akula et al. similarly investigated Pt electrocatalysts supported on N, F-codoped graphitic carbon nanofibers and found that the synergistic N, F modification strengthened the Pt-support interface and improved long-term stability.^[153] The optimal catalyst exhibited a mass activity of 101.9 mA mg_{Pt}⁻¹ and an $E_{1/2}$ of 0.78 V vs. RHE. After 20 000 CV cycles, the $E_{1/2}$ decreased by only 20 mV, with a degradation rate of 0.33 mV h⁻¹, outperforming the commercial Pt/C. These enhancements further support the role of F-containing carbon supports in reinforcing metal-support coupling while preserving favorable transport properties.

F-modified carbon matrix has also been extended to nonprecious metal nanoparticle systems. Yang et al. reported Co nanoparticles supported on N, S, and F tri-doped carbon (Co/NSF-C) via one-step pyrolysis.^[149] The optimal Co/NSF-C700 exhibited an $E_{1/2}$ of 0.855 V vs. RHE, followed by a dominant 4e⁻ ORR pathway, and retained 88% of its current after a 20 000 s durability test in 0.1 M KOH. Karuppannan et al. reported N, F-doped carbon-encapsulated Fe/Fe₃C catalysts through solvent-free mechanochemical polymerization followed by pyrolysis and acid leaching.^[135] The obtained NFC@Fe/Fe₃C-9 exhibited an $E_{1/2}$ of 0.870 V and 0.730 V vs. RHE in 0.1 M KOH and 0.1 M HClO₄, respectively, with only 26 mV decay over 50 000 CV cycles in alkaline medium and 27 mV decay after 30 000 CV cycles in acidic media. Promising performance was also achieved in both PEMFC and AEMFC single-cell tests, demonstrating that F-doped graphitized carbon shells can enhance electron transfer, methanol tolerance, and overall durability.

Beyond ORR, F-doped carbon-based hybrids have also emerged as effective OER catalysts when combined with transition-metal compounds. In these systems, fluorinated carbons can accelerate charge transfer, stabilize active phases, and promote the in situ reconstruction of active metal oxyhydroxides. Zhu et al. reported an FeNi alloy supported on F-doped CNTs through in situ growth and F-doping.^[170] The catalyst acquired an overpotential of only 272 mV at 10 mA cm⁻²

and showed a low Tafel slope of 41.64 mV dec⁻¹. The enhanced OER performance was attributed to the etching effect of fluorination and the strong ionic nature of C-F bonds, which increased surface roughness and accelerated the reconstruction of active oxyhydroxide species. In another study, Dai and colleagues decorated F-doped carbon dots onto vacancy-rich FeCoSe nanosheets for efficient OER in seawater electrolysis.^[172] The intimate interfacial coupling between the fluorinated carbon dots and the defect-rich FeCoSe substrate optimized oxygen adsorption energetics, affording an overpotential of 258 mV at 200 mA cm⁻² in 1 M KOH and strong resistance to chloride corrosion in both simulated and natural seawater. Lu et al. also developed F-doped graphite sheets decorated with ultrasmall WO₃ nanoparticles (WO₃@F-GS) via a plasma-induced assembly method.^[68] The optimal WO₃@F_{0.1}-GS exhibited an overpotential of 298 mV at 10 mA cm⁻², a Tafel slope of 77.6 mV dec⁻¹, and impedance comparable to commercial RuO₂. Combined characterization and DFT analysis confirmed that F-doping and WO₃ loading synergistically lowered the OH deprotonation barrier. Muthukumar et al. reported N, F-doped Co(OH)₂ and GO nanocomposites synthesized via a hydrothermal method, which exhibited significantly enhanced OER performance compared to undoped Co(OH)₂ or Co(OH)₂/GO.^[169] The N, F-Co(OH)₂/GO catalyst required an overpotential of 228 mV to reach 10 mA cm⁻², markedly lower than 370 mV for N, F-Co(OH)₂ and 325 mV for Co(OH)₂/GO, with a Tafel slope of 52.6 mV dec⁻¹ and a charge transfer resistance of 4.7 Ω. These examples highlight that fluorinated carbon components can play multiple roles in hybrids for OER, including electronic regulation, stabilization of active centers, and facilitation of interfacial reconstruction.

F-doped carbon supports are also highly attractive for hybrid catalysts containing encapsulated or supported transition-metal nanoparticles for bifunctional ORR/OER catalysis. Singhal et al.^[183] employed a related strategy by embedding Co nanoparticles in N, F-doped porous CNFs, achieving bifunctional ORR/OER activity with a potential gap (ΔE) of 0.785 V. Yan et al. also reported N, F-doped bimetallic carbide composites that exhibited an $E_{1/2}$ of 0.873 V vs. RHE, only 3 mV loss over 60 000 CV cycles, and retention of 95.9 % of the initial peak power density in H₂/O₂ FCs.^[184] These results indicate that F-containing carbon matrices can effectively cooperate with metal or metal-compound phases to enhance activity, stability, and practical device performance.

A distinct yet increasingly important branch of F-doped carbon-based hybrids involves molecular catalysts immobilized on fluorinated conductive substrates. Metal macrocyclic compounds such as metallophthalocyanines and metalloporphyrins possess well-defined M-N_x coordination configurations, but their poor conductivity and aggregation tendency often limit their direct use in oxygen electrocatalysis. Coupling these molecules with F-doped carbon supports provides an

effective solution by improving electronic communication, adjusting the local hydrophobic/hydrophilic microenvironment, and modulating the electronic structure of the central metal sites. For instance, Yang *et al.* developed a polymerized iron phthalocyanine molecular catalyst assembled on a high F-content carbon substrate through noncovalent interactions (Figure 19a, b).^[141] In situ electrochemical impedance measurements revealed that F engineering of the substrate not only modulated the interfacial microenvironment but also induced the downshift of the d-band center of Fe-Nx active sites, thus weakening the overly strong adsorption of oxygenated intermediates. The obtained PFePc/FC catalyst achieved $E_{1/2}$ of 0.93 V and 0.74 V vs. RHE in alkaline and acidic media, respectively. (Figure 19c). When integrated into ZABs and PEMFCs, it delivered maximum power densities of 163 mW cm⁻² and 196 mW cm⁻², highlighting its substantial commercial potential (Figure 19d). Furthermore, Xu *et al.* anchored an F-containing Co corrole complex onto polyvinylimidazole-functionalized CB through axial coordination, yielding an F-doped Co-N-C composite catalyst (Figure 19e).^[133] This catalyst achieved a remarkably positive $E_{1/2}$ of 0.88 V vs. RHE, and a kinetic current density of 20.3 mA cm⁻² at 0.85 V, outperforming both the F-free counterpart and commercial Pt/C (Figure 19f). In practical ZAB tests, it delivered a peak power density of 141 mW cm⁻² and an OCV of 1.45 V. Mechanistic analyses suggested that the strong electron-withdrawing capability of the F atom reduced the electron density of the central Co atom, thereby favoring the adsorption of oxygen species and accelerating the catalytic cycle. Subsequently, Rathour *et al.* immobilized nickel tetraphenylporphyrin molecules onto F-doped multi walled CNTs.^[140] The F-doping not only modified the electrochemical double-layer microenvironment of the

CNTs but also generated abundant semi-ionic C-F bonds at the interface, greatly promoting the activation of O₂ at the Ni centers. RRDE measurements confirmed an increased electron-transfer number, strongly suppressed H₂O₂ yield, and a more positive ORR onset potential. In another related example, Fan *et al.* developed an Fe, N, and F co-doped CNT catalyst by thermally transforming Fe phthalocyanine with fluorinated CNTs.^[185] The yielded FePc/FCNT800 catalyst exhibited an E_{onset} of 1.05 V and an $E_{1/2}$ of 0.90 V vs. RHE, with a dominant 4e⁻ pathway and a low Tafel slope of 73.3 mV dec⁻¹. These results emphasize that F-containing carbon supports are not only conductive matrix, but also active interfacial regulators for molecularly defined catalytic sites.

Overall, F-doped carbon-based hybrids extend the functionality of fluorinated nanocarbons by coupling F-induced electronic polarization and interfacial regulation with the high intrinsic activity of atomically dispersed metals, nanoparticles, metal compounds, or molecular catalysts. In these hybrid systems, F can tune metal-support interactions, modify the adsorption energetics of oxygenated intermediates, balance the interfacial hydrophobicity/hydrophilicity, improve carbon corrosion resistance, and even redirect the effective catalytic centers from the metal site to neighboring carbon atoms. Thus, F-doped carbon-based hybrids have delivered remarkable ORR/OER performance in H₂O₂ production, ZABs, and FCs. Nevertheless, the exact electronic role of F at hybrid interfaces remains insufficiently resolved, especially in systems containing multiple active motifs. Future studies should combine well-defined model catalysts, operando spectroscopy, and theoretical descriptors to clarify how F influences charge transfer, intermediate binding, and active-site evolution under realistic operating conditions.

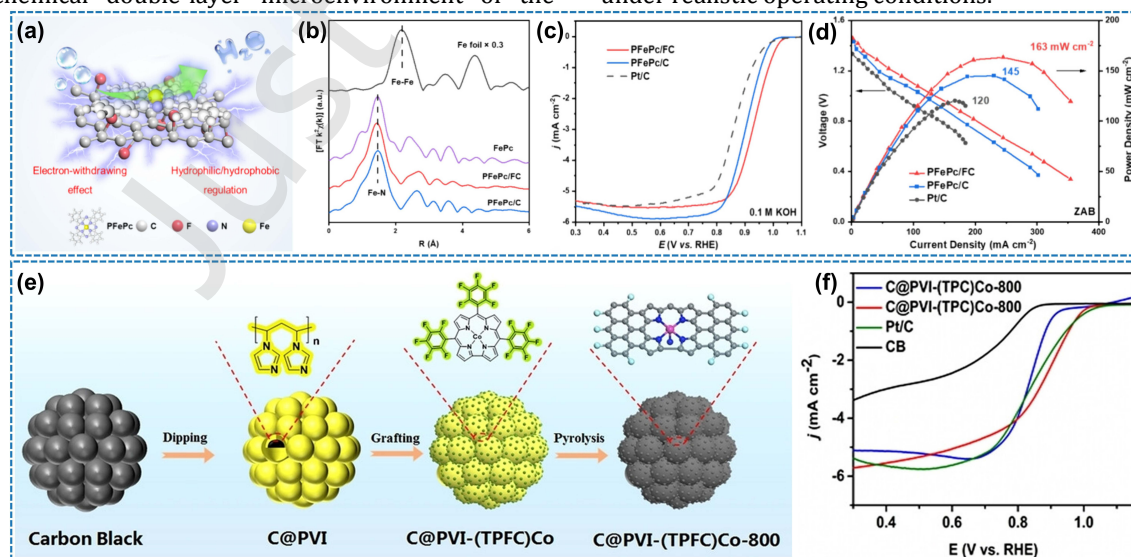


Figure 19. (a) Structural illustration of PFePc/FC. (b) Fourier-transformed Fe K-edge EXAFS spectra of the samples. (c) ORR polarization curves of the samples in an O₂-saturated 0.1 M KOH solution. (d) Discharge polarization curves and the corresponding power densities of the samples in PEMFCs. Reproduced with permission from ref. 141. copyright American Chemical Society, 2025.^[141] (e) Schematic illustration of the C@PVI-(TPFC)Co-800 catalyst. (f) LSV curves of corresponding catalysts in an O₂-saturated 0.1 M KOH solution. Reproduced with permission from ref. 133. copyright Wiley, 2023.^[133]

5 Conclusions and Perspectives

F has emerged as a particularly powerful heteroatom for engineering nanocarbon-based oxygen electrocatalysts, owing to its exceptional electronegativity, strong electron-withdrawing capability, and the high thermochemical stability of C-F bonds. As summarized in this Review, F incorporation can modulate the electronic structure of carbon frameworks, redistribute local charge density, tailor the adsorption energetics of oxygenated intermediates, and enhance the chemical robustness of carbon-based catalysts. These characteristics render

F-doped nanocarbon-based materials (F-DNCMs) attractive for diverse oxygen electrocatalytic applications, including H_2O_2 electrosynthesis, MABs, and FCs. Nevertheless, despite substantial progress, several fundamental and practical challenges continue to hinder the transition of F-DNCMs from laboratory-scale demonstrations to practical applications. As summarized in Figure 20, future efforts should focus on four closely related aspects: controllable and sustainable synthesis, mechanistic understanding and active-site identification, morphology/structure-performance optimization, and device-oriented validation.

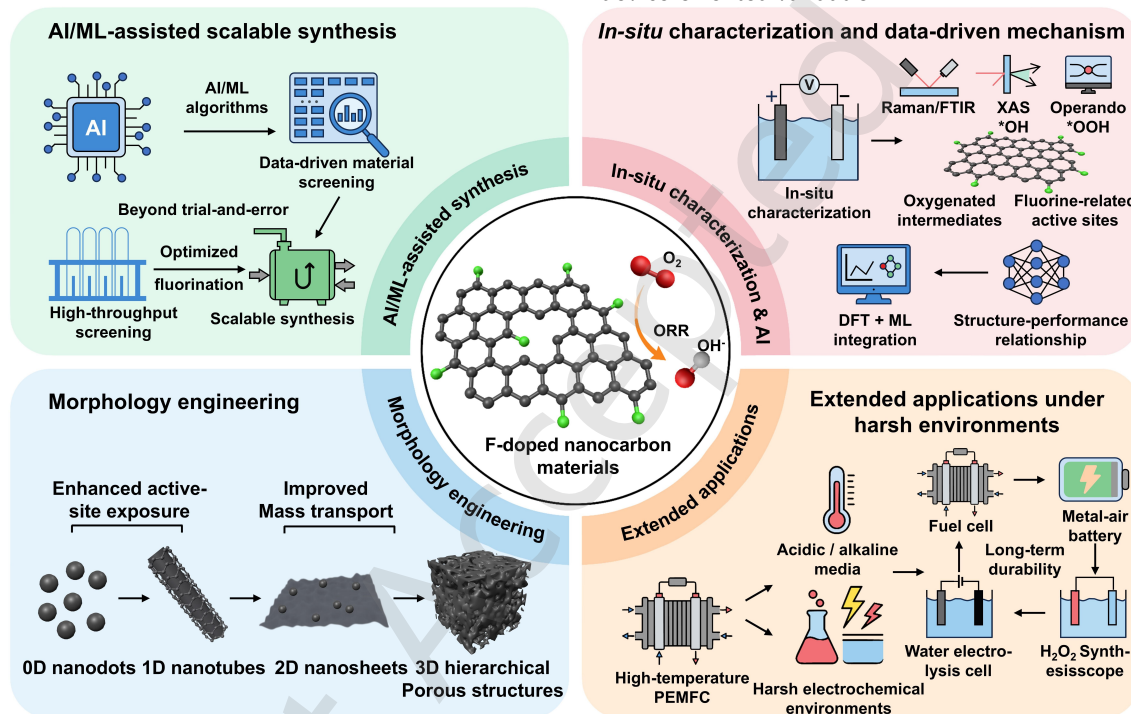


Figure 20. The perspectives and outlook for future F-DNCMs for oxygen electrocatalysts.

5.1 Controllable, sustainable, and scalable synthesis

A primary challenge lies in the controllable, reproducible, and scalable synthesis of F-DNCMs. Current fluorination strategies, including solvothermal, thermal, plasma-assisted, and gas-phase methods, often provide limited control over F content, bonding configuration, and spatial distribution. Moreover, the synthesis of these emerging materials frequently relies on toxic fluorinated precursors or harsh high-temperature pyrolysis conditions, which compromise environmental compatibility, reproducibility, and industrial scalability. Therefore, sustainable synthetic protocols capable of precisely regulating F-doping levels and C-F bonding configurations are urgently needed. Beyond the total F content, future synthesis should enable independent regulation of ionic, semi-ionic, and covalent C-F species, their spatial distribution, and the associated defect structures, because these structural parameters directly influence conductivity, intermediate adsorption, and catalytic stability.

In this regard, the integration of data-driven tools,

such as machine learning (ML) and artificial intelligence (AI), with high-throughput experimentation and DFT calculations could accelerate the identification of suitable fluorination conditions, dopant configurations, and target structures. This integrated strategy would help move the field beyond conventional trial-and-error optimization toward predictive materials design. Equally important will be the development of safer F sources, lower-temperature processing, improved F utilization efficiency, and synthetic protocols compatible with large-batch or continuous production.

5.2 Identification of active sites and operando mechanistic understanding

A comprehensive mechanistic understanding of F-DNCMs is equally essential for further improving their oxygen electrocatalytic performance. Although numerous studies have suggested that F doping enhances oxygen electrocatalysis through electronic polarization, defect regulation, and interfacial microenvironment modulation, direct experimental evidence under realistic operating conditions remains limited. At present, mechanistic

interpretations still rely heavily on ex situ characterization, particularly X-ray photoelectron spectroscopy, and on theoretical calculations, whereas operando validation remains insufficient, especially for light-element dopants such as F.

Consequently, several fundamental questions remain unresolved, including the exact identity of catalytically relevant C-F species, the dynamic evolution of F-containing active sites during operation, and the extent to which F modulates neighboring metal centers or heteroatom sites through local or long-range electronic interactions. Another important issue is whether F itself participates directly in catalytic active motifs or predominantly activates neighboring C, heteroatom, or metal sites through electronic and structural modulation. Distinguishing these possibilities is essential for establishing reliable structure-activity relationships.

Addressing these questions will require advanced in situ and operando characterization techniques, such as synchrotron-based spectroscopy, operando Raman spectroscopy, in situ infrared spectroscopy, and other time-resolved methods capable of monitoring intermediate evolution and local structural reconstruction during catalysis. When coupled with multiscale simulations and ML-assisted data analysis, these approaches could establish a more reliable and predictive understanding of the correlations among F chemistry, carbon structure, electrolyte environment, and catalytic performance.

5.3 Morphology engineering and structure-performance optimization

Morphological engineering represents another critical yet still underexplored dimension for optimizing the performance of F-DNCMs. 1D F-doped carbon nanofibers and nanotubes can provide continuous electron-transport pathways, while hierarchical features such as herringbone stacking and open-edge cavities may simultaneously promote electrolyte penetration and expose abundant edge-type active configurations. 2D ultrathin F-doped carbon nanosheets can maximize accessible active-site density through high SSA and shortened ion-diffusion pathways. 3D interconnected porous frameworks can facilitate efficient oxygen transport and rapid removal of reaction intermediates or products.

Beyond individual morphologies, the rational construction of heterostructured or multidimensional hierarchical architectures offers an opportunity to synergistically integrate these structural advantages. Notably, future studies should move beyond simple correlations between morphology and catalytic performance and establish quantitative relationships among dimensionality, pore architecture, F distribution, accessible active-site density, mass transport, and intrinsic activity. Achieving predictive morphological design, rather than empirical optimization, will require closed-loop feedback between morphology-resolved operando

characterization and computational screening of structure-dopant-performance relationships.

5.4 Device-oriented validation and expansion of application scenarios

Beyond catalyst design, expanding the application scenarios of F-DNCMs is also crucial. Most current studies focus on alkaline ORR/OER systems and zinc-air batteries, whereas more demanding electrochemical environments remain much less explored. The strong C-F bond and enhanced corrosion resistance of fluorinated carbons suggest considerable potential for operation under harsh conditions, such as acidic fuel cells and high-temperature proton-exchange membrane fuel cells (HT-PEMFCs). In these systems, catalyst durability, interfacial stability, and resistance to chemical attack are as important as intrinsic catalytic activity.

Future studies should therefore move beyond proof-of-concept evaluations and place greater emphasis on device-relevant testing, long-term operation, and performance assessment under realistic working conditions. Standardized evaluation protocols should also be considered to facilitate meaningful comparisons among different F-DNCM systems, including catalyst loading, electrolyte composition, mass-transport conditions, durability criteria, and full-cell operating parameters. In addition, greater attention should be paid to integrating catalyst design with electrode architecture and catalyst-electrolyte interfaces, since high intrinsic activity does not necessarily translate directly into high device-level performance.

In summary, the future development of F-DNCMs requires a transition from empirical materials optimization toward mechanism-guided and application-oriented catalyst design. An integrated research framework combining controllable fluorination chemistry, advanced in situ/operando characterization, multiscale theoretical modeling, high-throughput experimentation, and AI/ML-assisted analysis will be essential for establishing predictive synthesis-structure-property-performance relationships. Particular attention should be paid to how F incorporation regulates the interfacial solvation environment, water network, local dielectric properties, and electron-transfer kinetics under realistic operating conditions. Meanwhile, scalable and environmentally responsible synthesis must be coupled with rigorous device-level validation. With coordinated advances in these directions, F-DNCMs are expected to evolve from promising model electrocatalysts toward practically relevant materials for next-generation electrochemical energy conversion and storage technologies.

Acknowledgements

We are grateful for the financial support from the National Natural Science Foundation of China (22405161, 22302205), the Strategic Priority Research Program of the Chinese Academy of Science (XDB0600000, XDB0600100),

the Young Talents in Science and Technology Program of Hubei Province (2025DJA041), the China Postdoctoral Science Foundation (2024M763200), and the Key Research and Development Program of Shaanxi Province (Grant No.2024CY-GJHX-25).

Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

Data availability

No primary research results, software or code have been included and no new data were generated or analyzed as part of this review.

References

- [1] Zhao, Y.; Wan, J.; Ling, C.; Wang, Y.; He, H.; Yang, N.; Wen, R.; Zhang, Q.; Gu, L.; Yang, B.; Xiang, Z.; Chen, C.; Wang, J.; Wang, X.; Wang, Y.; Tao, H.; Li, X.; Liu, B.; Zhang, S.; Wang, D. Acidic oxygen reduction by single-atom Fe catalysts on curved supports. *Nature* **2025**, *644*, 668–675.
- [2] Luo, M.; Zhao, Z.; Zhang, Y.; Sun, Y.; Xing, Y.; Lv, F.; Yang, Y.; Zhang, X.; Hwang, S.; Qin, Y.; Ma, J.-Y.; Lin, F.; Su, D.; Lu, G.; Guo, S. PdMo bimetallic for oxygen reduction catalysis. *Nature* **2019**, *574*, 81–85.
- [3] Sun, W.; Wang, F.; Zhang, B.; Zhang, M.; Küpers, V.; Ji, X.; Theile, C.; Bieker, P.; Xu, K.; Wang, C.; Winter, M. A rechargeable zinc-air battery based on zinc peroxide chemistry. *Science* **2021**, *371*, 46–51.
- [4] Li, Y.; Huang, A.; Zhou, L.; Li, B.; Zheng, M.; Zhuang, Z.; Chen, C.; Chen, C.; Kang, F.; Lv, R. Main-group element-boosted oxygen electrocatalysis of Cu-N-C sites for zinc-air battery with cycling over 5000 h. *Nat. Commun.* **2024**, *15*, 8365.
- [5] Yuan, C. Sustainable battery manufacturing in the future. *Nat. Energy* **2023**, *8*, 1180–1181.
- [6] Luo, F.; Roy, A.; Silviali, L.; Cullen, D. A.; Zitolo, A.; Sougrati, M. T.; Oguz, I. C.; Mineva, T.; Teschner, D.; Wagner, S.; Wen, J.; Dionigi, F.; Kramm, U. I.; Rossmeisl, J.; Jaouen, F.; Strasser, P. P-block single-metal-site tin/nitrogen-doped carbon fuel cell cathode catalyst for oxygen reduction reaction. *Nat. Mater.* **2020**, *19*, 1215–1223.
- [7] Liu, Z.; Peng, B.; Tsai, Y.-H. J.; Zhang, A.; Xu, M.; Zang, W.; Yan, X.; Xing, L.; Pan, X.; Duan, X.; Huang, Y. Pt catalyst protected by graphene nanopockets enables lifetimes of over 200,000 h for heavy-duty fuel cell applications. *Nat. Nanotechnol.* **2025**, *20*, 807–814.
- [8] Zeng, Y.; Qi, M.; Liang, J.; Hermann, R. P.; Yu, H.; Zachman, M. J.; Chang, C.-W.; Lucero, M.; Feng, Z.; Cullen, D. A.; Myers, D. J.; Dodelet, J.-P.; Wu, G. Regulating in situ gaseous deposition to construct highly durable Fe-N-C oxygen-reduction fuel cell catalysts. *Nat. Catal.* **2026**, *9*, 196–210.
- [9] Tang, B.; Zhou, Y.; Ji, Q.; Zhuang, Z.; Zhang, L.; Wang, C.; Hu, H.; Wang, H.; Mei, B.; Song, F.; Yang, S.; Weckhuysen, B. M.; Tan, H.; Wang, D.; Yan, W. A Janus dual-atom catalyst for electrocatalytic oxygen reduction and evolution. *Nat. Synth.* **2024**, *3*, 878–890.
- [10] Li, J.; Liang, H.; Li, S.; Sun, J.; Zhang, Y.; Mei, S.; Wang, S.; Zheng, Y. Coaxial nano-multilayered C/SnO₂/TiO₂ composites as anode materials for lithium-ion batteries. *Rare Met.* **2025**, *44*, 7118–7135.
- [11] Cao, Q.; Wan, L.; Xu, Z.; Kuang, W.; Liu, H.; Zhang, X.; Zhang, W.; Lu, Y.; Yao, Y.; Wang, B.; Liu, K. A Fluorinated Covalent Organic Framework with Accelerated Oxygen Transfer Nanochannels for High-Performance Zinc-Air Batteries. *Adv. Mater.* **2023**, *35*, 2210550.
- [12] Cai, S.; An, Y.; Feng, Y.; Duan, L.; Zhang, H.; Zhang, M.; Wu, J.; Tang, H. Recent progress in porous carbon-supported materials as efficient oxygen electrocatalysts for zinc-air batteries. *Sci. China Mater.* **2023**, *66*, 3381–3400.
- [13] Wang, F.; Li, H.; Zhang, S.; Duan, B.; Huang, N.; Zheng, Y.; Jia, B.; Xu, S.; Liu, W.; Ye, L. Protonation-enhanced H₂O₂ electrosynthesis: high-selectivity and high-yield with a noble-metal-free CTF/BHN composite. *J. Catal.* **2026**, *454*, 116616.
- [14] Huo, L.; Lv, M.; Li, M.; Ni, X.; Guan, J.; Liu, J.; Mei, S.; Yang, Y.; Zhu, M.; Feng, Q.; Geng, P.; Hou, J.; Huang, N.; Liu, W.; Kong, X.; Zheng, Y.; Ye, L. Amorphous MnO₂ Lamellae Encapsulated Covalent Triazine Polymer-Derived Multi-Heteroatoms-Doped Carbon for ORR/OER Bifunctional Electrocatalysis. *Adv. Mater.* **2024**, *36*, 2312868.
- [15] Xie, Z.; Liang, X.; Kang, Z.; Zou, Y.; Wang, X.; Wu, Y. A.; King, G.; Liu, Q.; Huang, Y.; Zhao, X.; Chen, H.; Zou, X. High-Porosity, Layered Iridium Oxide as an Efficient, Durable Anode Catalyst for Water Splitting. *CCS Chem.* **2025**, *7*, 216–228.
- [16] Zhang, Y.; Sun, J.; Wang, Y.; Wu, Y.; Huang, C.; Zhang, C.; Liu, T. A Radiative-Cooling Hierarchical Aligned Porous Poly(vinylidene fluoride) Film by Freeze-Thaw-Promoted Nonsolvent-Induced Phase Separation. *Chin. J. Polym. Sci.* **2024**, *42*, 976–983.
- [17] Wan, K.; Chu, T.; Li, B.; Ming, P.; Zhang, C. Rational Design of Atomically Dispersed Metal Site Electrocatalysts for Oxygen Reduction Reaction. *Adv. Sci.* **2023**, *10*, 2203391.
- [18] Zheng, Y.; Chen, S.; Lu, H.; Zhang, C.; Liu, T. 3D honeycombed cobalt, nitrogen co-doped carbon nanosheets via hypersaline-protected pyrolysis towards efficient oxygen reduction. *Nanotechnology* **2020**, *31*, 364003–3644011.
- [19] Chen, S.; Zheng, Y.; Zhang, B.; Feng, Y.; Zhu, J.; Xu, J.; Zhang, C.; Feng, W.; Liu, T. Cobalt, Nitrogen-Doped Porous Carbon Nanosheet-Assembled Flowers from Metal-Coordinated Covalent Organic Polymers for Efficient Oxygen Reduction. *ACS Appl. Mater. Interfaces* **2019**, *11*, 1384–1393.
- [20] Zheng, Y.; Li, M.; Wang, Y.; Huang, N.; Liu, W.; Chen, S.; Ni, X.; Li, K.; Xiong, S.; Shen, Y.; Liu, S.; Zhou, B.; Khan, N. A.; Ye, L.; Zhang, C.; Liu, T. Floret-like Fe-N_x nanoparticle-embedded porous carbon superstructures from a Fe-covalent triazine polymer boosting oxygen electroreduction. *Front. Chem. Sci. Eng.* **2023**, *17*, 525–535.
- [21] Li, M.; Lv, M.; Zheng, Y.; Zhu, M.; Feng, Q.; Guan, J.; Yu, X.; Shen, Y.; Hou, J.; Lu, Y.; Huang, N.; Ye, L. Bimetallic-Coordinated Covalent Triazine Framework-Derived FeNi Alloy Nanoparticle-Decorated Coral-Like Nanocarbons for Oxygen Electrocatalysis. *ACS Appl. Mater. Interfaces* **2024**, *16*, 633–642.
- [22] Wang, Y.; Qian, J.; Zheng, J.; Li, J.; Sun, A.; Xing, J.; Liu, L.; Zheng, Y. In situ, fast constructing interface/doping-engineered NiCo bimetal-based composites boosting electrocatalytic oxygen reduction for zinc-air battery. *J. Alloys Compd.* **2024**, *1004*, 175821.
- [23] Huang, J.; Xu, X.; Yan, Y.; Zheng, Y.; Yao, Y.; Li, Z.; Yan, Y.; Hui, K. N.; Zou, J.; Liu, M. Facile Microwave Synthesis of Kilogram-Scale Electrocatalysts with Nanocarbons Bridged Cobalt Active Sites for Enhanced Oxygen Electrocatalysis. *Adv. Energy Mater.* **2025**, *15*, 2500360.
- [24] Lei, Z.; Liu, M.; Zhang, Y.; Li, L.; Zang, S.-Q.; Zheng, Z. Covalent triazine frameworks: Fabrication for energy conversion.

- Coord. Chem. Rev.* **2025**, 537, 216703.
- [25] Yang, Y.; Guo, L.; Wang, X.; Li, Z.; Zhou, W. Halogen modified organic porous semiconductors in photocatalysis: mechanism, synthesis, and application. *Adv. Powder Mater.* **2024**, 3, 100178.
- [26] Dai, L.; Xue, Y.; Qu, L.; Choi, H. J.; Baek, J. B. Metal-free catalysts for oxygen reduction reaction. *Chem. Rev.* **2015**, 115, 4823–92.
- [27] Xiang, Z.; Cao, D.; Huang, L.; Shui, J.; Wang, M.; Dai, L. Nitrogen-doped holey graphitic carbon from 2D covalent organic polymers for oxygen reduction. *Adv. Mater.* **2014**, 26, 3315–20.
- [28] Li, Y.; Zhao, Y.; Cheng, H.; Hu, Y.; Shi, G.; Dai, L.; Qu, L. Nitrogen-Doped Graphene Quantum Dots with Oxygen-Rich Functional Groups. *J. Am. Chem. Soc.* **2012**, 134, 15–18.
- [29] Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. Nitrogen-Doped Carbon Nanotube Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Science* **2009**, 323, 760–764.
- [30] Cui, P.; Zhao, L.; Long, Y.; Dai, L.; Hu, C. Carbon-Based Electrocatalysts for Acidic Oxygen Reduction Reaction. *Angew. Chem. Int. Ed.* **2023**, 62, e202218269.
- [31] Wang, S.; Yu, D.; Dai, L. Polyelectrolyte functionalized carbon nanotubes as efficient metal-free electrocatalysts for oxygen reduction. *J. Am. Chem. Soc.* **2011**, 133, 5182–5.
- [32] Jeon, I.-Y.; Zhang, S.; Zhang, L.; Choi, H.-J.; Seo, J.-M.; Xia, Z.; Dai, L.; Baek, J.-B. Edge-Selectively Sulfurized Graphene Nanoplatelets as Efficient Metal-Free Electrocatalysts for Oxygen Reduction Reaction: The Electron Spin Effect. *Adv. Mater.* **2013**, 25, 6138–6145.
- [33] Shui, J.; Wang, M.; Du, F.; Dai, L. N-doped carbon nanomaterials are durable catalysts for oxygen reduction reaction in acidic fuel cells. *Sci. Adv.* **2015**, 1.
- [34] Zhang, J.; Zhao, Z.; Xia, Z.; Dai, L. A metal-free bifunctional electrocatalyst for oxygen reduction and oxygen evolution reactions. *Nat. Nanotechnol.* **2015**, 10, 444–452.
- [35] Zhao, Z.; Li, M.; Zhang, L.; Dai, L.; Xia, Z. Design Principles for Heteroatom-Doped Carbon Nanomaterials as Highly Efficient Catalysts for Fuel Cells and Metal–Air Batteries. *Adv. Mater.* **2015**, 27, 6834–6840.
- [36] Wu, L.; Wang, Y.; Shao, C.; Sun, F.; Wang, L.; Li, B. Unraveling microenvironment modification in an atomically dispersed bimetallic FeCu catalyst in the oxygen reduction reaction. *Chem. Sci.* **2025**, 16, 8082–8091.
- [37] Cui, P.; Zhao, L.; Long, Y.; Dai, L.; Hu, C. Carbon-Based Electrocatalysts for Acidic Oxygen Reduction Reaction. *Angew. Chem. Int. Ed.* **2023**, 62, e202218269.
- [38] Chen, X.; Guan, J.; Zheng, Y.; Chen, R.; Lv, M.; Yan, Y.; Chen, M.; Liu, M.; Tian, X.; Ye, L. Multi-Heteroatom-Doping and Defect Co-Engineered Hollow Carbon Nanocages for Ultralong-Cycle Zinc–Air Batteries. *Nano Lett.* **2025**, 25, 11713–11722.
- [39] Liu, M.; Dong, H.; Wang, G.; Zhao, J. Enhancing Zinc–Air Flow Batteries: Single-Atom Catalysis within Cobalt-Encapsulated Carbon Nanotubes for Superior Efficiency. *Nano Lett.* **2024**, 24, 12102–12110.
- [40] Rao, P.; Wu, D.; Wang, T.-J.; Li, J.; Deng, P.; Chen, Q.; Shen, Y.; Chen, Y.; Tian, X. Single atomic cobalt electrocatalyst for efficient oxygen reduction reaction. *eScience* **2022**, 2, 399–404.
- [41] Feng, X.; Chen, G.; Cui, Z.; Qin, R.; Jiao, W.; Huang, Z.; Shang, Z.; Ma, C.; Zheng, X.; Han, Y.; Huang, W. Engineering Electronic Structure of Nitrogen-Carbon Sites by sp^3 -Hybridized Carbon and Incorporating Chlorine to Boost Oxygen Reduction Activity. *Angew. Chem. Int. Ed.* **2023**, 63, e202316314.
- [42] Zheng, Y.; Khan, N. A.; Ni, X.; Zhang, K. A. I.; Shen, Y.; Huang, N.; Kong, X. Y.; Ye, L. Emerging covalent triazine framework-based nanomaterials for electrochemical energy storage and conversion. *Chem. Commun.* **2023**, 59, 6314–6334.
- [43] Guan, J.; Dong, D.; Khan, N. A.; Zheng, Y. Emerging Pt-based intermetallic nanoparticles for the oxygen reduction reaction. *Chem. Commun.* **2024**, 60, 1811–1825.
- [44] Li, R.; Fan, W.; Rao, P.; Luo, J.; Li, J.; Deng, P.; Wu, D.; Huang, W.; Jia, C.; Liu, Z.; Miao, Z.; Tian, X. Multimetallic Single-Atom Catalysts for Bifunctional Oxygen Electrocatalysis. *ACS Nano* **2023**, 17, 18128–18138.
- [45] Li, H.; Di, S.; Niu, P.; Wang, S.; Wang, J.; Li, L. A durable half-metallic diatomic catalyst for efficient oxygen reduction. *Energy Environ. Sci.* **2022**, 15, 1601–1610.
- [46] Hu, C.; Paul, R.; Dai, Q.; Dai, L. Carbon-based metal-free electrocatalysts: from oxygen reduction to multifunctional electrocatalysis. *Chem. Soc. Rev.* **2021**, 50, 11785–11843.
- [47] Hu, C.; Dai, L. Carbon-Based Metal-Free Catalysts for Electrocatalysis beyond the ORR. *Angew. Chem. Int. Ed.* **2016**, 55, 11736–58.
- [48] Chen, X.; Feng, P.; Zheng, Y.; Li, H.; Zhang, Y.; Shen, Y.; Yan, Y.; Liu, M.; Ye, L. Emerging Nitrogen and Sulfur Co-doped Carbon Materials for Electrochemical Energy Storage and Conversion. *Small* **2025**, 11, 2412191.
- [49] Zheng, Y.; Chen, S.; Yu, X.; Li, K.; Ni, X.; Ye, L. Nitrogen-doped carbon spheres with precisely-constructed pyridinic-N active sites for efficient oxygen reduction. *Appl. Surf. Sci.* **2022**, 598, 153786.
- [50] Zheng, Y.; Chen, S.; Song, H.; Guo, H.; Zhang, K. A. I.; Zhang, C.; Liu, T. Nitrogen-doped hollow carbon nanoflowers from a preformed covalent triazine framework for metal-free bifunctional electrocatalysis. *Nanoscale* **2020**, 12, 14441–14447.
- [51] Xu, X.; Wu, H.; Yan, Y.; Zheng, Y.; Yan, Y.; Qiu, S.; Liang, T.; Deng, C.; Yao, Y.; Zou, J.; Liu, M. Electronic Structure Modulation in N, P, S Tri-Doped Nanofibers with Interpenetrated Pores for Enhanced Oxygen Reduction Reaction. *Adv. Energy Mater.* **2025**, 15, 2405236.
- [52] Zhang, J.; Dai, L. Nitrogen, Phosphorus, and Fluorine Tri-doped Graphene as a Multifunctional Catalyst for Self-Powered Electrochemical Water Splitting. *Angew. Chem. Int. Ed.* **2016**, 55, 13296–13300.
- [53] Zheng, Y.; Chen, S.; Zhang, K. A. I.; Zhu, J.; Xu, J.; Zhang, C.; Liu, T. Ultrasound-Triggered Assembly of Covalent Triazine Framework for Synthesizing Heteroatom-Doped Carbon Nanoflowers Boosting Metal-Free Bifunctional Electrocatalysis. *ACS Appl. Mater. Interfaces* **2021**, 13, 13328–13337.
- [54] Meng, K.; Liu, Q.; Huang, Y.; Wang, Y. Facile synthesis of nitrogen and fluorine co-doped carbon materials as efficient electrocatalysts for oxygen reduction reactions in air-cathode microbial fuel cells. *J. Mater. Chem. A* **2015**, 3, 6873–6877.
- [55] Sun, Y.-N.; Yang, J.; Ding, X.; Ji, W.; Jaworski, A.; Hedin, N.; Han, B.-H. Synergetic contribution of nitrogen and fluorine species in porous carbons as metal-free and bifunctional oxygen electrocatalysts for zinc–air batteries. *Appl. Catal. B Environ.* **2021**, 297, 120448.
- [56] Zhao, Z.; Li, M.; Zhang, L.; Dai, L.; Xia, Z. Design Principles for Heteroatom-Doped Carbon Nanomaterials as Highly Efficient Catalysts for Fuel Cells and Metal–Air Batteries. *Adv. Mater.* **2015**, 27, 6834–40.
- [57] Panomsuwan, G.; Saito, N.; Ishizaki, T. Simple one-step synthesis of fluorine-doped carbon nanoparticles as potential alternative metal-free electrocatalysts for oxygen reduction reaction. *J. Mater. Chem. A* **2015**, 3, 9972–9981.
- [58] Li, W.; Wang, J.; Jia, C.; Chen, J.; Wen, Z.; Huang, A. Covalent organic framework-derived fluorine, nitrogen dual-doped carbon as metal-free bifunctional oxygen electrocatalysts. *J. Colloid Interface Sci.* **2023**, 650, 275–283.
- [59] Wang, X.; Li, K.; Yang, D.; Yang, X.; Xiao, M.; Zheng, L.; Xing, W.; Liu, C.; Zhu, J. F Doping-Induced Multicomponent Synergistic Active Site Construction toward High-Efficiency

- Bifunctional Oxygen Electrocatalysis for Rechargeable Zn–Air Batteries. *Small* **2024**, *20*, 2310250.
- [60] Wang, M.; Cao, L.; Du, X.; Zhang, Y.; Jin, F.; Zhang, M.; Li, Z.; Su, K. Highly Dispersed Co-, N-, S-Doped Topological Defect-Rich Hollow Carbon Nanoboxes as Superior Bifunctional Oxygen Electrocatalysts for Rechargeable Zn–Air Batteries. *ACS Appl. Mater. Interfaces* **2022**, *14*, 25427–25438.
- [61] Sun, X.; Zhang, Y.; Song, P.; Pan, J.; Zhuang, L.; Xu, W.; Xing, W. Fluorine-Doped Carbon Blacks: Highly Efficient Metal-Free Electrocatalysts for Oxygen Reduction Reaction. *ACS Catal.* **2013**, *3*, 1726–1729.
- [62] Peera, S. G.; Sahu, A. K.; Arunchander, A.; Bhat, S. D.; Karthikeyan, J.; Murugan, P. Nitrogen and fluorine co-doped graphite nanofibers as high durable oxygen reduction catalyst in acidic media for polymer electrolyte fuel cells. *Carbon* **2015**, *93*, 130–142.
- [63] Wang, L.; Wang, Y.; Wu, M.; Wei, Z.; Cui, C.; Mao, M.; Zhang, J.; Han, X.; Liu, Q.; Ma, J. Nitrogen, Fluorine, and Boron Ternary Doped Carbon Fibers as Cathode Electrocatalysts for Zinc-Air Batteries. *Small* **2018**, *14*, e1800737.
- [64] Kim, J.; Fukushima, T.; Zhou, R.; Murakoshi, K. Revealing High Oxygen Evolution Catalytic Activity of Fluorine-Doped Carbon in Alkaline Media. *Materials* **2019**, *12*, 211.
- [65] Li, H.; Ha, T. A.; Jiang, S.; Pozo-Gonzalo, C.; Wang, X.; Fang, J.; Howlett, P. C.; Wang, X. N. F and S doped carbon nanofibers generated from electrospun polymerized ionic liquids for metal-free bifunctional oxygen electrocatalysis. *Electrochim. Acta* **2021**, 377.
- [66] Liang, J.; Liang, L.; Zeng, B.; Feng, B.; Du, L.; Qiu, X.; Wang, Y.; Song, H.; Liao, S.; Shao, M.; Cui, Z. Fluorine-Doped Carbon Support Enables Superfast Oxygen Reduction Kinetics by Breaking the Scaling Relationship. *Angew. Chem. Int. Ed.* **2024**, *63*, e202412825.
- [67] Lu, K.; Wang, Z.; Wu, Y.; Zhai, X.; Wang, C.; Li, J.; Wang, Z.; Li, X.; He, Y.; An, T.; Yang, K.; Yang, D.; Yu, F.; Dai, B. Synergistic effect of F doping and WO₃ loading on electrocatalytic oxygen evolution. *Chem. Eng. J.* **2023**, *451*, 1.
- [68] He, X.; Chang, L.; Wu, H.; Liu, G.; Zhang, Y.; Zhou, A. Design of ZIF-67-derived Fe, N and F co-doped porous carbon material and evaluation of its ORR and OER performance. *J. Alloys Compd.* **2023**, *967*, 171709.
- [69] Lv, Y.; Yang, L.; Cao, D. Sulfur, Nitrogen and Fluorine Triple - Doped Metal - Free Carbon Electrocatalysts for the Oxygen Reduction Reaction. *ChemElectroChem* **2018**, *6*, 741 – 747.
- [70] Peera, S. G.; Menon, R. S.; Das, S. K.; Alfantazi, A.; Karuppasamy, K.; Liu, C.; Sahu, A. K. Oxygen reduction electrochemistry at F doped carbons: A review on the effect of highly polarized C-F bonding in catalysis and stability of fuel cell catalysts. *Coord. Chem. Rev.* **2024**, *500*, 215491.
- [71] Yu, A.; Bi, H.; Joshua, F.; Lyons, M.; Rangavajjula, A.; Dhungana, B.; Park, H.; Cui, Y.; Ponnusamy, V. S.; Kumar, S.; Liu, S.; Zhang, Q.; Du, Y.; Zhai, L.; Seal, S.; Guo, J.; Feng, Z.; Lin, Z.; Yang, Y. Active site design enables industrial scale H₂O₂ electrosynthesis with metal-free catalysts. *Nat. Commun.* **2026**, *17*, 4474.
- [72] Liang, Z.; Lei, H.; Zheng, H.; Wang, H.-Y.; Zhang, W.; Cao, R. Selective two-electron and four-electron oxygen reduction reactions using Co-based electrocatalysts. *Chem. Soc. Rev.* **2025**, *54*, 5248–5291.
- [73] Zhao, Y.; Adiyeri Saseendran, D. P.; Huang, C.; Triana, C. A.; Marks, W. R.; Chen, H.; Zhao, H.; Patzke, G. R. Oxygen Evolution/Reduction Reaction Catalysts: From In Situ Monitoring and Reaction Mechanisms to Rational Design. *Chem. Rev.* **2023**, *123*, 6257 – 6358.
- [74] Wang, J.; Kong, H.; Zhang, J.; Hao, Y.; Shao, Z.; Ciucci, F. Carbon-based electrocatalysts for sustainable energy applications. *Prog. Mater. Sci.* **2021**, *116*, 100717.
- [75] Kumar, G.; Das, M.; Dey, R. S. Recent progress in covalent organic frameworks for bifunctional oxygen electrocatalysis in rechargeable zinc–air batteries. *Chem. Commun.* **2026**, *62*, 322–340.
- [76] Zhang, H.-B.; Meng, Y.; Fang, L.; Yang, F.; Zhu, S.; Li, T.; Yu, X.; Rong, J.; Chen, W.; Su, D.; Mei, Y.; Hou, P.-X.; Liu, C.; Shao, M.; Li, J.-C. A thermal evaporation–trapping strategy to synthesize flexible and robust oxygen electrocatalysts for rechargeable zinc–air batteries. *Energy Environ. Sci.* **2024**, *17*, 9375–9382.
- [77] Wang, G.; Jia, S.; Gao, H.; Shui, Y.; Fan, J.; Zhao, Y.; Li, L.; Kang, W.; Deng, N.; Cheng, B. The action mechanisms and structures designs of F-containing functional materials for high performance oxygen electrocatalysis. *J. Energy Chem.* **2023**, *76*, 377 – 397.
- [78] Nakajima, T.; Koh, M.; Gupta, V.; Žemva, B.; Lutar, K. Electrochemical behavior of graphite highly fluorinated by high oxidation state complex fluorides and elemental fluorine. *Electrochim. Acta* **2000**, *45*, 1655–1661.
- [79] Lee, J. H.; Koon, G. K. W.; Shin, D. W.; Fedorov, V. E.; Choi, J.-Y.; Yoo, J.-B.; Özyilmaz, B. Property Control of Graphene by Employing “Semi-Ionic” Liquid Fluorination. *Adv. Funct. Mater.* **2013**, *23*, 3329–3334.
- [80] Zhou, J.; Lian, J.; Hou, L.; Zhang, J.; Gou, H.; Xia, M.; Zhao, Y.; Strobel, T. A.; Tao, L.; Gao, F. Ultrahigh volumetric capacitance and cyclic stability of fluorine and nitrogen co-doped carbon microspheres. *Nat. Commun.* **2015**, *6*, 8503.
- [81] Sun, X.; Song, P.; Zhang, Y.; Liu, C.; Xu, W.; Xing, W. A class of high performance metal-free oxygen reduction electrocatalysts based on cheap carbon blacks. *Sci. Rep.* **2013**, *3*, 2505.
- [82] Chang, Y.; Chen, J.; Jia, J.; Hu, X.; Yang, H.; Jia, M.; Wen, Z. The fluorine-doped and defects engineered carbon nanosheets as advanced electrocatalysts for oxygen electroreduction. *Appl. Catal. B Environ.* **2021**, 284.
- [83] Jin, S.; Yang, S. Y.; Lee, J. M.; Kang, M. S.; Choi, S. M.; Ahn, W.; Fuku, X.; Modibedi, R. M.; Han, B.; Seo, M. H. Fluorine-Decorated Graphene Nanoribbons for an Anticorrosive Polymer Electrolyte Membrane Fuel Cell. *ACS Appl. Mater. Interfaces* **2021**, *13*, 26936–26947.
- [84] Zhao, J.; Cabrera, C. R.; Xia, Z.; Chen, Z. Single-sided fluorine-functionalized graphene: A metal-free electrocatalyst with high efficiency for oxygen reduction reaction. *Carbon* **2016**, *104*, 56–63.
- [85] Lee, Y.-G.; Ahn, H.-J. Tri(Fe/N/F)-doped mesoporous carbons as efficient electrocatalysts for the oxygen reduction reaction. *Appl. Surf. Sci.* **2019**, *487*, 389–397.
- [86] Li, Y.; Cao, Z.; Chen, C.; Zhao, G.; Abou-Hamad, E.; Wu, Z.-P.; Wang, Z.; Li, Q.; Rueping, M.; Han, Y.; Cavallo, L.; Zhang, H. Atomic Exploration of the Fluorination-Driven Structural Rearrangement of Carbon Electrocatalysts toward Efficient Oxygen Reduction Reactions. *J. Am. Chem. Soc.* **2025**, *147*, 34933–34943.
- [87] Zhang, F.; Zhang, D.; Liu, W.; Li, X.; Chen, Q. Fluorine enhanced pyridinic-N configuration as an ultra-active site for oxygen reduction reaction in both alkaline and acidic electrolytes. *Carbon* **2022**, *187*, 67–77.
- [88] Tao, X.; Lu, R.; Ni, L.; Gridin, V.; Al-Hilfi, S. H.; Qiu, Z.; Zhao, Y.; Kramm, U. I.; Zhou, Y.; Mullen, K. Facilitating the acidic oxygen reduction of Fe-N-C catalysts by fluorine-doping. *Mater. Horiz.* **2022**, *9*, 417–424.
- [89] Cherif, M.; Dodelet, J.-P.; Zhang, G.; Glibin, V. P.; Sun, S.; Vidal, F. Non-PGM Electrocatalysts for PEM Fuel Cells: A DFT Study on the Effects of Fluorination of FeN_x-Doped and N-Doped Carbon Catalysts. *Molecules* **2021**, *26*, 7370.
- [90] Zeng, S.; Wang, S.; Zhuang, H.; Lu, B.; Li, C.; Wang, Y.; Wang, G. Fluorine-doped carbon: A metal-free electrocatalyst for oxygen

- reduction to peroxide. *Electrochim. Acta* **2022**, 420.
- [91] Yue, X.; Huang, S.; Cai, J.; Jin, Y.; Shen, P. K. Heteroatoms dual doped porous graphene nanosheets as efficient bifunctional metal-free electrocatalysts for overall water-splitting. *J. Mater. Chem. A* **2017**, 5, 7784–7790.
- [92] Ali, Z.; Mehmood, M.; Ahmad, J.; Fatima, A.; Ali, M. Fluorine doped CNTs for efficient OER activity outperforming iridium supported carbon electrocatalyst. *J. Appl. Electrochem.* **2021**, 51, 1573–1581.
- [93] Li, Y.; Chen, C.; Zhao, G.; Huang, H.; Ren, Y.; Zuo, S.; Wu, Z. P.; Zheng, L.; Lai, Z.; Zhang, J.; Rueping, M.; Han, Y.; Zhang, H. Unveiling the Activity Origin of Electrochemical Oxygen Evolution on Heteroatom-Decorated Carbon Matrix. *Angew. Chem. Int. Ed.* **2024**, 63, e202411218.
- [94] Lee, W.-K.; Robinson, J. T.; Gunlycke, D.; Stine, R. R.; Tamanaha, C. R.; King, W. P.; Sheehan, P. E. Chemically Isolated Graphene Nanoribbons Reversibly Formed in Fluorographene Using Polymer Nanowire Masks. *Nano Lett.* **2011**, 11, 5461–5464.
- [95] Nair, R. R.; Ren, W.; Jalil, R.; Riaz, I.; Kravets, V. G.; Britnell, L.; Blake, P.; Schedin, F.; Mayorov, A. S.; Yuan, S.; Katsnelson, M. I.; Cheng, H.-M.; Strupinski, W.; Bulusheva, L. G.; Okotrub, A. V.; Grigorieva, I. V.; Grigorenko, A. N.; Novoselov, K. S.; Geim, A. K. Fluorographene: A Two-Dimensional Counterpart of Teflon. *Small* **2010**, 6, 2877–2884.
- [96] Ahmad, Y.; Dubois, M.; Guerin, K.; Hamwi, A.; Flahaut, E. High energy density of primary lithium batteries working with sub-fluorinated few walled carbon nanotubes cathode. *J. Alloys Compd.* **2017**, 726, 852–859.
- [97] Valentini, L.; Puglia, D.; Armentano, I.; Kenny, J. M. Sidewall functionalization of single-walled carbon nanotubes through CF₄ plasma treatment and subsequent reaction with aliphatic amines. *Chem. Phys. Lett.* **2005**, 403, 385–389.
- [98] Poh, H. L.; Sofer, Z.; Klímová, K.; Pumera, M. Fluorographenes via thermal exfoliation of graphite oxide in SF₆, SF₄ and MoF₆ atmospheres. *J. Mater. Chem. C* **2014**, 2, 5198–5207.
- [99] Yazami, R.; Hamwi, A.; Guérin, K.; Ozawa, Y.; Dubois, M.; Giraudet, J.; Masin, F. Fluorinated carbon nanofibres for high energy and high power densities primary lithium batteries. *Electrochem. Commun.* **2007**, 9, 1850–1855.
- [100] Wheeler, V.; Garces, N.; Nyakiti, L.; Myers-Ward, R.; Jernigan, G.; Culbertson, J.; Eddy, C.; Kurt Gaskill, D. Fluorine functionalization of epitaxial graphene for uniform deposition of thin high-κ dielectrics. *Carbon* **2012**, 50, 2307–2314.
- [101] Robinson, J. T.; Burgess, J. S.; Junkermeier, C. E.; Badescu, S. C.; Reinecke, T. L.; Perkins, F. K.; Zalalutdniov, M. K.; Baldwin, J. W.; Culbertson, J. C.; Sheehan, P. E.; Snow, E. S. Properties of Fluorinated Graphene Films. *Nano Lett.* **2010**, 10, 3001–3005.
- [102] Wang, T.; Zang, X.; Wang, X.; Gu, X.; Shao, Q.; Cao, N. Recent advances in fluorine-doped/fluorinated carbon-based materials for supercapacitors. *Energy Storage Mater.* **2020**, 30, 367–384.
- [103] Wang, Z.; Wang, J.; Li, Z.; Gong, P.; Liu, X.; Zhang, L.; Ren, J.; Wang, H.; Yang, S. Synthesis of fluorinated graphene with tunable degree of fluorination. *Carbon* **2012**, 50, 5403–5410.
- [104] Zhao, F.-G.; Zhao, G.; Liu, X.-H.; Ge, C.-W.; Wang, J.-T.; Li, B.-L.; Wang, Q.-G.; Li, W.-S.; Chen, Q.-Y. Fluorinated graphene: facile solution preparation and tailorable properties by fluorine-content tuning. *J. Mater. Chem. A* **2014**, 2, 8782–8789.
- [105] Samanta, K.; Some, S.; Kim, Y.; Yoon, Y.; Min, M.; Lee, S. M.; Park, Y.; Lee, H. Highly hydrophilic and insulating fluorinated reduced graphene oxide. *Chem. Commun.* **2013**, 49, 8991–8993.
- [106] Yang, H.; Chen, M.; Zhou, H.; Qiu, C.; Hu, L.; Yu, F.; Chu, W.; Sun, S.; Sun, L. Preferential and Reversible Fluorination of Monolayer Graphene. *J. Phys. Chem. C* **2011**, 115, 16844–16848.
- [107] Yu, X.; Lin, K.; Qiu, K.; Cai, H.; Li, X.; Liu, J.; Pan, N.; Fu, S.; Luo, Y.; Wang, X. Increased chemical enhancement of Raman spectra for molecules adsorbed on fluorinated reduced graphene oxide. *Carbon* **2012**, 50, 4512–4517.
- [108] Tahara, K.; Iwasaki, T.; Matsutani, A.; Hatano, M. Effect of radical fluorination on mono- and bi-layer graphene in Ar/F₂ plasma. *Appl. Phys. Lett.* **2012**, 101, 16.
- [109] Lv, Y.; Yang, L.; Cao, D. Nitrogen and Fluorine-Codoped Porous Carbons as Efficient Metal-Free Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells. *ACS Appl. Mater. Interfaces* **2017**, 9, 32859–32867.
- [110] Zheng, Y.; Song, H.; Chen, S.; Yu, X.; Zhu, J.; Xu, J.; Zhang, K. A. I.; Zhang, C.; Liu, T. Metal-Free Multi-Heteroatom-Doped Carbon Bifunctional Electrocatalysts Derived from a Covalent Triazine Polymer. *Small* **2020**, 16, 2004342–2004352.
- [111] Liu, Y.; Huang, B.; Peng, S.; Wang, T.; Ji, G.; Yang, G.; Ramakrishna, S. Deflagration synthesis of nitrogen/fluorine co-doped hollow carbon nanoparticles with excellent oxygen reduction performance. *Inorg. Chem. Front.* **2018**, 5, 1307–1313.
- [112] Aguilar-Bolados, H.; Contreras-Cid, A.; Yazdani-Pedram, M.; Acosta-Villavicencio, G.; Flores, M.; Fuentealba, P.; Neira-Carrillo, A.; Verdejo, R.; López-Manchado, M. A. Synthesis of fluorinated graphene oxide by using an easy one-pot deoxyfluorination reaction. *J. Colloid Interface Sci.* **2018**, 524, 219–226.
- [113] Zhou, F.; Huang, H.; Xiao, C.; Zheng, S.; Shi, X.; Qin, J.; Fu, Q.; Bao, X.; Feng, X.; Müllen, K.; Wu, Z.-S. Electrochemically Scalable Production of Fluorine-Modified Graphene for Flexible and High-Energy Ionogel-Based Microsupercapacitors. *J. Am. Chem. Soc.* **2018**, 140, 8198–8205.
- [114] Bi, Z.; Kong, Q.; Cao, Y.; Sun, G.; Su, F.; Wei, X.; Li, X.; Ahmad, A.; Xie, L.; Chen, C.-M. Biomass-derived porous carbon materials with different dimensions for supercapacitor electrodes: a review. *J. Mater. Chem. A* **2019**, 7, 16028–16045.
- [115] O'Hagan, D. Understanding organofluorine chemistry. An introduction to the C–F bond. *Chem. Soc. Rev.* **2008**, 37, 308–319.
- [116] Chen, Y.; Qu, B.; Hu, L.; Xu, Z.; Li, Q.; Wang, T. High-performance supercapacitor and lithium-ion battery based on 3D hierarchical NH₄F-induced nickel cobaltate nanosheet–nanowire cluster arrays as self-supported electrodes. *Nanoscale* **2013**, 5, 9812–9820.
- [117] Sun, X.; Song, P.; Chen, T.; Liu, J.; Xu, W. Fluorine-doped BP 2000: highly efficient metal-free electrocatalysts for acidic oxygen reduction reaction with superlow H₂O₂ yield. *Chem. Commun.* **2013**, 49, 10296–8.
- [118] Wang, H.; Kong, A. Mesoporous fluorine-doped carbon as efficient cathode material for oxygen reduction reaction. *Mater. Lett.* **2014**, 136, 384–387.
- [119] Guo, J.; Zhang, J.; Zhao, H.; Fang, Y.; Ming, K.; Huang, H.; Chen, J.; Wang, X. Fluorine-doped graphene with an outstanding electrocatalytic performance for efficient oxygen reduction reaction in alkaline solution. *Soc. Open Sci.* **2018**, 5, 10.
- [120] Parthiban, V.; Bhuvaneshwari, B.; Karthikeyan, J.; Murugan, P.; Sahu, A. K. Fluorine-enriched mesoporous carbon as efficient oxygen reduction catalyst: understanding the defects in porous matrix and fuel cell applications. *Nanoscale Adv.* **2019**, 1, 4926–4937.
- [121] Karuppannan, M.; Park, J. E.; Bae, H. E.; Cho, Y.-H.; Kwon, O. J. A nitrogen and fluorine enriched Fe/Fe₃C@C oxygen reduction reaction electrocatalyst for anion/proton exchange membrane fuel cells. *Nanoscale* **2020**, 12, 2542–2554.
- [122] Shah, S. S. A.; Najam, T.; Nazir, M. A.; Wu, Y.; Ali, H.; Rehman, A. U.; Rahman, M. M.; Imran, M.; Javed, M. S. Salt-assisted gas-liquid interfacial fluorine doping: Metal-free defect-induced electrocatalyst for oxygen reduction reaction. *Mol. Catal.* **2021**, 514.
- [123] Akula, S.; Parthiban, V.; Peera, S. G.; Singh, B. P.; Dhakate, S. R.;

- Sahu, A. K. Simultaneous Co-Doping of Nitrogen and Fluorine into MWCNTs: An In-Situ Conversion to Graphene Like Sheets and Its Electro-Catalytic Activity toward Oxygen Reduction Reaction. *J. Electrochem. Soc.* **2017**, *164*, F568-F576.
- [124] Akula, S.; Balasubramaniam, B.; Varathan, P.; Sahu, A. K. Nitrogen-Fluorine Dual Doped Porous Carbon Derived from Silk Cotton as Efficient Oxygen Reduction Catalyst for Polymer Electrolyte Fuel Cells. *ACS Appl. Energy Mater.* **2019**, *2*, 3253–3263.
- [125] Gong, T.; Qi, R.; Liu, X.; Li, H.; Zhang, Y. N, F-Codoped Microporous Carbon Nanofibers as Efficient Metal-Free Electrocatalysts for ORR. *Nano-Micro Lett.* **2019**, *11*, 9.
- [126] Zhu, P.; Gao, J.; Chen, X.; Liu, S. An efficient metal-free bifunctional oxygen electrocatalyst of carbon co-doped with fluorine and nitrogen atoms for rechargeable Zn-air battery. *Int. J. Hydrogen Energy* **2020**, *45*, 9512–9521.
- [127] Akula, S.; Sahu, A. K. Structurally Modulated Graphitic Carbon Nanofiber and Heteroatom (N,F) Engineering toward Metal-Free ORR Electrocatalysts for Polymer Electrolyte Membrane Fuel Cells. *ACS Appl. Mater. Interfaces* **2020**, *12*, 11438–11449.
- [128] Wang, H.; Ding, J.; Zhang, J.; Wang, C.; Yang, W.; Ren, H.; Kong, A. Fluorine and nitrogen co-doped ordered mesoporous carbon as a metal-free electrocatalyst for oxygen reduction reaction. *RSC Adv.* **2016**, *6*, 79928–79933.
- [129] Fu, S.; Zhu, C.; Song, J.; Engelhard, M. H.; Xiao, B.; Du, D.; Lin, Y. Nitrogen and Fluorine-Codoped Carbon Nanowire Aerogels as Metal-Free Electrocatalysts for Oxygen Reduction Reaction. *Chemistry* **2017**, *23*, 10460–10464.
- [130] Qiao, X.; Liao, S.; Wang, G.; Zheng, R.; Song, H.; Li, X. Simultaneous doping of nitrogen and fluorine into reduced graphene oxide: A highly active metal-free electrocatalyst for oxygen reduction. *Carbon* **2016**, *99*, 272–279.
- [131] Zhao, Y.; Liu, Y.; Chen, Y.; Liu, X.; Li, X.; Gao, S. A treasure map for nonmetallic catalysts: optimal nitrogen and fluorine distribution of biomass-derived carbon materials for high-performance oxygen reduction catalysts. *J. Mater. Chem. A* **2021**, *9*, 18251–18259.
- [132] Zhou H., Liu H., Sun Y., Jiang L., Xiao J., Zhang H., Xie H., Li L., Wang S., Han L., Synergistic Effect of Single Atomic Ce Sites and CeO₂ Nanoparticles for Boosting Oxygen Reduction Reaction. *Adv. Energy Mater.* **2025**, *15*, 2404689.
- [133] Xu, C.; Guo, P. P.; Yang, K. Z.; Lu, C.; Wei, P. J.; Liu, J. G. F - Doped Co-N-C Catalysts for Enhancing the Oxygen Reduction Reaction in Zn - Air Batteries. *ChemCatChem* **2023**, *15*, e202300404.
- [134] Peera, S. G.; Arunchander, A.; Sahu, A. K. Cumulative effect of transition metals on nitrogen and fluorine co-doped graphite nanofibers: an efficient and highly durable non-precious metal catalyst for the oxygen reduction reaction. *Nanoscale* **2016**, *8*, 14650–64.
- [135] Karuppannan, M.; Park, J. E.; Bae, H. E.; Cho, Y. H.; Kwon, O. J. A nitrogen and fluorine enriched Fe/Fe₃C@C oxygen reduction reaction electrocatalyst for anion/proton exchange membrane fuel cells. *Nanoscale* **2020**, *12*, 2542–2554.
- [136] Taniguchi, Y.; Kokuryo, S.; Takada, R.; Yang, X.; Miyake, K.; Uchida, Y.; Nishiyama, N. Fluoropyridine-mediated zeolite templating method for N/F co-doped carbon with high electrocatalytic performance on oxygen reduction reaction. *Electrochem. Commun.* **2024**, *160*, 107665.
- [137] Li, C.; Mao, Y.; Qiu, J.; Wang, X.; Miao, J.; Min, Y.; Zhou, W.; Shao, Z. A potential well effect for efficient oxygen reduction and corrosion resistance under the operating temperature conditions of PEMFCs. *J. Mater. Chem. A* **2024**, *12*, 31214–31222.
- [138] Yoon, H. S.; Park, H.-Y.; Jung, W. S. Synergistic effects of fluorine and nitrogen dopants in fluorine/nitrogen-coordinated iron-co-doped carbon catalysts for enhanced oxygen reduction in alkaline media. *Int. J. Hydrogen Energy* **2024**, *60*, 1092–1100.
- [139] Park, S.-H.; Park, D.-H.; Byeon, J.-H.; Kim, M.-H.; Gu, Y.; Lim, D.-M.; Kim, J.-H.; Jang, J.-S.; Hong, C.-E.; Seo, D.-G.; Han, J.-I.; Park, K.-W. Tri-doped mesoporous carbon nanostructures prepared via template method for enhanced oxygen reduction reaction. *Carbon* **2024**, *218*, 118666.
- [140] Rathour, V.; Singh, S.; Ganesan, V. Enhancing Four-Electron Selective Oxygen Reduction via Fluorine-Doped Multiwalled Carbon Nanotubes: Synergistic Interaction with Nickel Tetraphenylporphyrin. *Langmuir* **2025**, *41*, 30116–30123.
- [141] Yang, K.-Z.; Su, Y.-Z.; Xu, C.; Guo, P.-P.; Zhao, Y.-M.; Liu, X.; Jia, L.; Yang, Y.; Zhu, H.-N.; Wei, P.-J.; Liu, J.-G. Boosting Oxygen Reduction Reaction through Substrate Fluorination-Mediated d-Band Center Tuning and Microenvironment Optimization of Molecular Catalysts. *ACS Catal.* **2025**, *15*, 8114–8124.
- [142] Zhang, R.; Huang, M.; Shi, L.; Deng, W.; Yao, Z.; Peng, M.; Wang, J.; Wu, J.; Jin, F.; Hu, M. High power density and Ultra-Long stability of N, F, S tri-doped carbon black catalysts for Zinc-Air batteries and water Splitting applications. *Chem. Eng. Sci.* **2026**, *324*, 123314.
- [143] Wu, Y.; Li, Y.; Mao, J.; Wu, H.; Wu, T.; Li, Y.; Zeng, B.; Xu, Y.; Yuan, C.; Dai, L. Metallosupramolecular Polymer Precursor Design for Multi-Element Co-Doped Carbon Shells with Improved Oxygen Reduction Reaction Catalytic Activity. *Catalysts* **2019**, *9*, 102.
- [144] Zhang, Q.; Luo, F.; Ling, Y.; Xiao, S.; Li, M.; Qu, K.; Wang, Y.; Xu, J.; Cai, W.; Yang, Z. Identification of functionality of heteroatoms in boron, nitrogen and fluorine ternary-doped carbon as a robust electrocatalyst for nitrogen reduction reaction powered by rechargeable zinc-air batteries. *J. Mater. Chem. A* **2020**, *8*, 8430–8439.
- [145] Luo, S.; Hu, J.; Guo, S.; Yu, D.; Dong, P.; Xu, M.; Han, L.; Li, M.; Lin, Y.; Liu, F.; Zhang, C.; Zhang, Y. Ionic liquid-derived Fe, N, S, F multiple heteroatom-doped carbon materials for enhanced oxygen reduction reaction. *Nanotechnology* **2021**, *32*, 39.
- [146] Cui, F.; Deng, Q.; Zhao, H.; Jiang, Y.; Li, J. Ionic liquid promoted synthesis of nitrogen, phosphorus, and fluorine triple-doped mesoporous carbon as metal-free electrocatalyst for oxygen reduction reaction. *Ionics* **2020**, *26*, 4609–4619.
- [147] Li, M.; Ye, Q.; Hou, S.; Yang, J.; Chi, B.; Deng, Y.; Tian, X. Fluorine and phosphorus atoms cooperated on an N-doped 3D porous carbon network for enhanced ORR performance toward the zinc-air batteries. *J. Mater. Chem. A* **2023**, *11*, 8730–8738.
- [148] Li, Y.; Wen, H.; Yang, J.; Zhou, Y.; Cheng, X. Boosting oxygen reduction catalysis with N, F, and S tri-doped porous graphene: Tertiary N-precursors regulates the constitution of catalytic active sites. *Carbon* **2019**, *142*, 1–12.
- [149] Guangzhi, Y.; Chen, B.; Zhao, W.; Xu, M.; Lu, Y.; Xue, Y.; Zhang, H.-J. Nitrogen, Sulfur and Fluorine Tri-Doped Carbon Supporting Cobalt Nanoparticles for Oxygen Reduction Catalysis. *J. Electrochem. Soc.* **2022**, *169*, 3.
- [150] Jiang, R.; Zhi, Q.; Liu, W.; Gao, Z.; Zhan, X.; Jin, Y.; Wang, K.; Sun, T.; Li, W.; Jiang, J. F-doped carbon hollow nanospheres for efficient electrochemical oxygen reduction. *J. Mater. Sci.* **2022**, *57*, 5924–5932.
- [151] Ma, Y.; Sung, K. W.; Ahn, H. J. MOF-Derived Co Nanoparticles Catalyst Assisted by F- and N-Doped Carbon Quantum Dots for Oxygen Reduction. *Nanomaterials (Basel)* **2023**, *13*, 2093.
- [152] Liu, S.; Yang, H.; Yao, L.; Peng, H.; Huang, P.; Lin, X.; Liu, L.; Zhang, H.; Cai, P.; Wen, X.; Zou, Y.; Xiang, C.; Xu, F.; Sun, L.; Kannan, P.; Ji, S. Design of Fe and Cu bimetallic integration on N and F co-doped porous carbon material for oxygen reduction reaction. *Int. J. Hydrogen Energy* **2022**, *47*, 7751–7760.
- [153] Akula, S.; Varathan, P.; Kesh, A.; Tammeveski, K.; Peera, S. G.;

- Panda, S. K.; Balasubramaniam, B.; Sahu, A. K. Morphological influence of graphitic carbon nanofibers by N-F dual-doping on Pt electrocatalytic activity and stability for oxygen reduction reaction in polymer electrolyte membrane fuel cells. *Int. J. Hydrogen Energy* **2022**, *47*, 20617–20631.
- [154] Li, H.; Zhao, H.; Yan, G.; Huang, G.; Ge, C.; Forsyth, M.; Howlett, P. C.; Wang, X.; Fang, J. Ternary Heteroatomic Doping Induced Microenvironment Engineering of Low Fe-N₄-Loaded Carbon Nanofibers for Bifunctional Oxygen Electrocatalysis. *Small* **2023**, *20*, e2304844.
- [155] Wang, M.; Sun, E.; Zhao, S.; Sun, Y.; Zhang, S.; Li, Z.; Wu, M. Elucidating the mechanistic synergy of fluorine and oxygen doping in boosting platinum-based catalysts for proton exchange membrane fuel cells. *J. Colloid Interface Sci.* **2025**, *682*, 115–123.
- [156] Yang, J.; Niu, L.; Zhang, Z.; Yan, L.; Chou, L. Preparation and Study of Multi-Heteroatom Carbon Nanotube as Excellent Electrocatalyst for Oxygen Reduction Reaction Using Polydopamine Derivative. *Adv. Mater. Sci. Eng.* **2018**, 1734040, 1–6.
- [157] Wu, M.; Wang, Y.; Wei, Z.; Wang, L.; Zhuo, M.; Zhang, J.; Han, X.; Ma, J. Ternary doped porous carbon nanofibers with excellent ORR and OER performance for zinc-air batteries. *J. Mater. Chem. A* **2018**, *6*, 10918–10925.
- [158] Yang, T.; Chen, Y.; Tian, M.; Liu, X.; Zhang, F.; Zhang, J.; Wang, K.; Gao, S. Engineering the electronic structure of Fe-N/C catalyst via fluorine self-doping for enhanced oxygen reduction reaction in liquid and all-solid-state Zn-air batteries. *Electrochim. Acta* **2023**, 443.
- [159] Xu, X.; Gao, Y.; Yang, Q.; Liang, T.; Luo, B.; Kong, D.; Li, X.; Zhi, L.; Wang, B. Regulating the activity of intrinsic sites in covalent organic frameworks by introducing electro-withdrawing groups towards highly selective H₂O₂ electrosynthesis. *Nano Today* **2023**, *49*, 101792.
- [160] Zhao, K.; Su, Y.; Quan, X.; Liu, Y.; Chen, S.; Yu, H. Enhanced H₂O₂ production by selective electrochemical reduction of O₂ on fluorine-doped hierarchically porous carbon. *J. Catal.* **2018**, *357*, 118–126.
- [161] Wang, W.; Lu, X.; Su, P.; Li, Y.; Cai, J.; Zhang, Q.; Zhou, M.; Arotiba, O. Enhancement of hydrogen peroxide production by electrochemical reduction of oxygen on carbon nanotubes modified with fluorine. *Chemosphere* **2020**, *259*, 127423.
- [162] Zhao, K.; Quan, X.; Chen, S.; Yu, H.; Zhang, Y.; Zhao, H. Enhanced electro-Fenton performance by fluorine-doped porous carbon for removal of organic pollutants in wastewater. *Chem. Eng. J.* **2018**, *354*, 606–615.
- [163] Xing, Z.; Shi, K.; Parsons, Z. S.; Feng, X. Interplay of Active Sites and Microenvironment in High-Rate Electrosynthesis of H₂O₂ on Doped Carbon. *ACS Catal.* **2023**, *13*, 2780–2789.
- [164] Kim, J.; Zhou, R.; Murakoshi, K.; Yasuda, S. Advantage of semi-ionic bonding in fluorine-doped carbon materials for the oxygen evolution reaction in alkaline media. *RSC Adv.* **2018**, *8*, 14152–14156.
- [165] Yang, N.; Li, L.; Li, J.; Ding, W.; Wei, Z. Modulating the oxygen reduction activity of heteroatom-doped carbon catalysts via the triple effect: charge, spin density and ligand effect. *Chem Sci* **2018**, *9*, 5795–5804.
- [166] Lv, Y.; Yang, L.; Cao, D. Nitrogen and Fluorine-Codoped Porous Carbons as Efficient Metal-Free Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells. *ACS Appl. Mater. Interfaces* **2017**, *9*, 32859–32867.
- [167] Chokradjaroen, C.; Kato, S.; Fujiwara, K.; Watanabe, H.; Ishii, T.; Ishizaki, T. A comparative study of undoped, boron-doped, and boron/fluorine dual-doped carbon nanoparticles obtained via solution plasma as catalysts for the oxygen reduction reaction. *Sustain. Energy Fuels* **2020**, *4*, 4570–4580.
- [168] Liu, T.-T.; Aulia, S.; Chen, K.-H.; Rinawati, M.; Yu, S.-W.; Chang, L.-Y.; Adem, L. H.; Lin, S. D.; Huang, W.-H.; Yeh, M.-H. Regulating *OOH intermediate adsorption via F-doped graphene quantum dots modulated carbon nanotubes for selective 2e⁻ oxygen reduction reaction in value-added reaction-assisted Zn-air battery. *J. Energy Storage* **2026**, *146*, 120187.
- [169] Muthukumar, P.; Nantheeswaran, P.; Mariappan, M.; Pannipara, M.; Al-Sehemi, A. G.; Anthony, S. P. Enhancing the oxygen evolution reaction of cobalt hydroxide by fabricating nanocomposites with fluorine-doped graphene oxide. *Dalton Trans* **2023**, *52*, 3877–3883.
- [170] Zhu, X.-Y.; Jiang, X.-T.; Pang, Z.-H.; Guo, J.-C.; Zhang, X.-S.; Li, W.-Z.; Luan, J.; Liu, Y. Effective synergy of fluorine-doped in situ growth FeNi@CNTs/C-F catalyst for the oxygen evolution reaction. *Int. J. Hydrogen Energy* **2025**, *149*, 150117.
- [171] Li, X.; Zhu, G.; Xiao, L.; Liu, Y.; Ji, Z.; Shen, X.; Kong, L.; Shah, S. A. Loading of Ag on Fe-Co-S/N-doped carbon nanocomposite to achieve improved electrocatalytic activity for oxygen evolution reaction. *J. Alloys Compd.* **2019**, *773*, 40–49.
- [172] Dai, J.; Zhang, L.; Zhang, Z.; Chen, H.; Hu, Y.; Li, G.; Han, L. Fluorine-doped carbon dots decorated on iron-cobalt selenide nanosheets as superior electrocatalysts for oxygen evolution in seawater. *Appl. Surf. Sci.* **2025**, *680*, 161456.
- [173] Zhang, J.; Dai, L. Nitrogen, Phosphorus, and Fluorine Tri-doped Graphene as a Multifunctional Catalyst for Self-Powered Electrochemical Water Splitting. *Angew. Chem. Int. Ed.* **2016**, *55*, 13296–13300.
- [174] Li, W.; Wang, J.; Jia, C.; Chen, J.; Wen, Z.; Huang, A. Covalent organic framework-derived fluorine, nitrogen dual-doped carbon as metal-free bifunctional oxygen electrocatalysts. *J. Colloid Interface Sci.* **2023**, *650*, 275–283.
- [175] Zheng, Y.; Song, H.; Chen, S.; Yu, X.; Zhu, J.; Xu, J.; Zhang, K. A. I.; Zhang, C.; Liu, T. Metal-Free Multi-Heteroatom-Doped Carbon Bifunctional Electrocatalysts Derived from a Covalent Triazine Polymer. *Small* **2020**, *16*, e2004342.
- [176] Ma, S.; Yao, H.; Li, Z.; Liu, Q. Tuning the nucleation and decomposition of Li₂O₂ by fluorine-doped carbon vesicles towards high performance Li-O₂ batteries. *J. Energy Chem.* **2022**, *70*, 614–622.
- [177] Qi, D.; Zhang, H.; Shao, G.; Wang, C.; Peng, Y.; Wang, H.; Li, Y.; Jin, H.; Luo, J.; Wang, S.; Xu, J.; Yuan, Y. Fluorine-Mediated Engineering of Stable High-Valence Single-Atom Catalysts. *Angew. Chem. Int. Ed.* **2026**, *65*, e1641171.
- [178] Yang, H.; Wu, H.; Yao, L.; Liu, S.; Yang, L.; Lu, J.; Peng, H.; Lin, X.; Cai, P.; Zhang, H.; Xu, F.; Zhang, K.; Sun, L. One-Step Synthesis of a Non-Precious-Metal Tris (Fe/N/F)-Doped Carbon Catalyst for Oxygen Reduction Reactions. *Molecules* **2023**, *28*, 2392.
- [179] He, X.; Chang, L.; Li, K.; Wu, H.; Tang, Y.; Gao, F.; Li, X.; Zhang, Y.; Zhou, A. Preparation of F and N Co - Doped Fe-N-C Catalyst and Evaluation of its Oxygen Reduction Performance. *Energy Technol.* **2022**, *11*, 2200992.
- [180] Tian, Y.; Chen, R.; Liu, X.; Yin, L.; Yang, D. a.; Hou, F.; Liang, J. Fluorine - regulated carbon nanotubes decorated with Co single atoms for multi - site electrocatalysis toward two - electron oxygen reduction. *EcoMat* **2023**, *5*, e12336.
- [181] Das, B.; Toledo - Carrillo, E. A.; Li, L.; Ye, F.; Chen, J.; Slabon, A.; Verho, O.; Eriksson, L.; Göthelid, M.; Dutta, J.; Åkerman, B. Cobalt Electrocatalyst on Fluorine Doped Carbon Cloth – a Robust and Partially Regenerable Anode for Water Oxidation. *ChemCatChem* **2022**, *14*, e202200538.
- [182] Liang, J.; Liang, L.; Zeng, B.; Feng, B.; Du, L.; Qiu, X.; Wang, Y.; Song, H.; Liao, S.; Shao, M.; Cui, Z. Fluorine-doped Carbon Support Enables Superfast Oxygen Reduction Kinetics by Breaking the Scaling Relationship. *Angew. Chem.* **2024**, *63*,

e202412825.

- [183] Singhal, R.; Kalra, V. Cobalt Nanoparticle-Embedded Porous Carbon Nanofibers with Inherent N- and F-Doping as Binder-Free Bifunctional Catalysts for Oxygen Reduction and Evolution Reactions. *ChemPhysChem* **2017**, *18*, 223–229.
- [184] Yan, Z.; Cui, J.; Jiang, D.; Xie, J.; Zhang, M.; Wei, W.; Zhao, X. Nitrogen- and fluorine-doped bimetallic carbide as active and stable oxygen reduction reaction electrocatalyst. *J. Colloid Interface Sci.* **2024**, *660*, 345–355.
- [185] Fan, Y. T.; Du, P.; Xu, P. F.; Wang, Y. G.; Fan, D. Y.; Pan, X. C.; Wang, R. Y.; Zhang, R. Iron, nitrogen and fluorine co-modified carbon nanotubes as an effective catalyst for oxygen reduction reaction. *Mater. Lett.* **2021**, *304*, 130617

Just Accepted



Yong Zheng is an Assistant Professor at China Three Gorges University (CTGU). He received his Ph.D. from Donghua University in 2021 and conducted collaborative research at Fudan University from 2019 to 2021. From 2024 to 2026, he worked as a postdoctoral researcher at the Dalian Institute of Chemical Physics, Chinese Academy of Sciences (CAS). His research interests include the rational design of micro-/nanostructured covalent organic polymers and single-atom-based nanohybrids for photocatalytic and electrocatalytic applications.



Junpeng Ma is a postgraduate student at China Three Gorges University under the supervision of Dr. Yong Zheng. His research focuses on photocatalytic hydrogen peroxide production for sustainable energy and environmental applications.



Xinyang He received his Ph.D. degree from Donghua university and conducted joint doctoral research at the National University of Singapore. He is currently an associate professor at Nantong University. His research interests focus on smart textiles, wearable electronics and thermoelectric fibers.



Yining Zhang received his Ph.D. from the Dalian Institute of Chemical Physics, Chinese Academy of Sciences (DICP, CAS), and subsequently stayed at the institute as a faculty member, serving as an Associate Professor and Master's supervisor. He later worked at the University of Waterloo in Canada for eight years. His research directions include fuel cells, lithium batteries, flow batteries, and electrochemical sensors, with emphasis on their industrialization and commercialization.



Yao Wang received his M.Eng. degree from the National University of Singapore. He is currently pursuing a Ph.D. in Mechanical Engineering at Texas A&M University. His research interests focus on additive manufacturing, wearable electronics, and thermoelectric materials.



Liu Yang is an Associate Professor at the Dalian Institute of Chemical Physics, Chinese Academy of Sciences (DICP, CAS). She received her Ph.D. from Beijing University of Chemical Technology in 2020 and completed postdoctoral training at Beijing University of Chemical Technology from 2020 to 2022, during which she conducted joint postdoctoral research at the University of Waterloo. Her research focuses on the design, development, and application of key materials for fuel cells and water electrolysis devices.



Zhongwei Chen is a Professor and Doctoral Supervisor, Fellow of the Royal Society of Canada and Fellow of the Canadian Academy of Engineering, and Vice President of the International Academy of Electrochemical Energy Science (IAOEES). He currently serves as Director of the State Key Laboratory of Catalysis at the Dalian Institute of Chemical Physics, Chinese Academy of Sciences. He has long been devoted to the research and industrialization of electrochemical energy materials and systems, including fuel cells, lithium/sodium-ion batteries, solid-state batteries, zinc-air batteries, hydrogen hybrid power systems, and AI + electrochemical energy storage.

Just Accepted