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Revolutionizing Fuel Cell Efficiency with Non-Metallic Catalysts for Oxygen Reduction Reactions

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ABSTRACT

Platinum-based catalysts are widely used in oxygen reduction reactions, but platinum's high cost and low reserves have restricted their sustainable development. With continuous in-depth research, it has been found that metal-free catalysts also have better catalytic activity in oxygen reduction reactions and have great potential for development due to the low cost and abundant reserves of metal-free catalysts, which has become a hot research direction. This paper reviews the application of metal-free catalysts in oxygen reduction reactions, including heteroatom-doped carbon-based catalysts, polymeric nitrogen catalysts, and emerging carbon catalysts. This work provides insights into developing non-platinum catalysts for oxygen reduction reactions by comparing the catalytic activity, selectivity, and prolonged stability.

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1. Introduction

With global resources facing depletion and a polluted environment, it is awaiting a solution to explore and investigate clean energy, which can solve the dilemma of insufficient resources. Therefore, the rational use of energy has attracted the attention of various industries and is eventually used in our daily life [1, 2]. Fuel cells have received much attention due to the advantages of high energy utilization and low environmental pollution. The fuel cell is discharged through a reaction that occurs at the anode and cathode, in which electrons are transferred from the anode to the cathode through an external circuit, and cations are produced from the anode and transferred to the cathode through the electrolyte, thus achieving system equilibrium [3]. The slow oxygen reduction reaction at the cathode limits the overall efficiency of the fuel cell [4]. Platinum metal is widely used in fuel cells to improve the overall performance of fuel cells due to its high activity and ability to improve the slow cathode oxygen reduction reaction. However, as research continued, it was found that platinum-based catalysts have some drawbacks that could be more conducive to commercial production because of the high cost and poor stability of the precious metal platinum, which leads to a high overall fuel cell cost. Therefore, developing low-cost and high-activity catalysts has become a key research direction to meet market demand better.

For decades, catalysts have been widely used in oxygen reduction reactions to speed up the reaction process. The catalyst-related research is reflected in these aspects: (1) improve the efficiency of precious metal platinum use in catalysts; (2) develop non-precious metal catalysts to replace precious metal platinum materials; (3) develop metal-free Oxygen reduction reaction (ORR) electrocatalysts to replace platinum-based catalysts. Metal-free electrocatalysts are promising ORR catalysts due to their low cost, abundant reserves, good stability, and tunable structure [5]. This review focuses on heteroatom doping in carbon-based catalysts, including single-atom doping, two-element doping, ternary-doped carbon-based catalysts, etc. It also introduces polymeric nitrogen compounds and emerging advanced catalysts. In addition, this work deals with the use of plasma technology in the metal-free catalytic system. All these catalysts can enhance the catalytic activity of ORR and lay the foundation for further research and development (Fig. **1**).

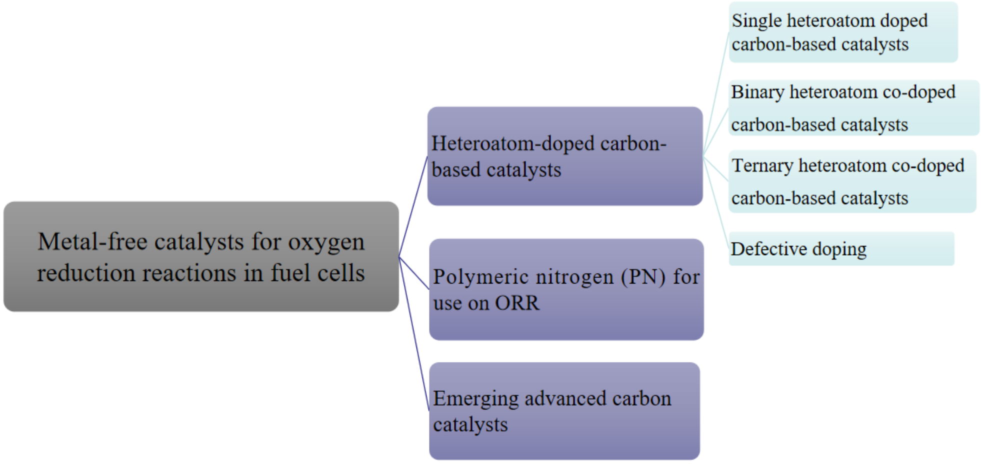

Figure 1: Carbon-based catalysts for ORR.

2. Heteroatom-Doped Carbon-Based Catalysts

The sp^2 carbon materials are promising catalysts in electron-accepting reactions of free-flowing electrons due to their abundant properties. ORR is a typical representative of a reaction requiring electrons, but carbon materials' inert π-electrons are challenging to use directly [6]. Therefore, activating the π-electrons of carbon is a significant challenge for the practical application of ORR catalysis theory. Currently, with continuous research, it has been found that the electronic structure of carbon-based catalysts can be well modified by heteroatom doping to enhance the activity of the catalysts [7]. Heteroatom-doped carbon materials can improve catalytic activity because π-conjugation breaks the active electrons, providing more active sites [8, 9] (Fig. **2**). We have successfully synthesized carbon-based catalysts doped with single and multiple heteroatoms.

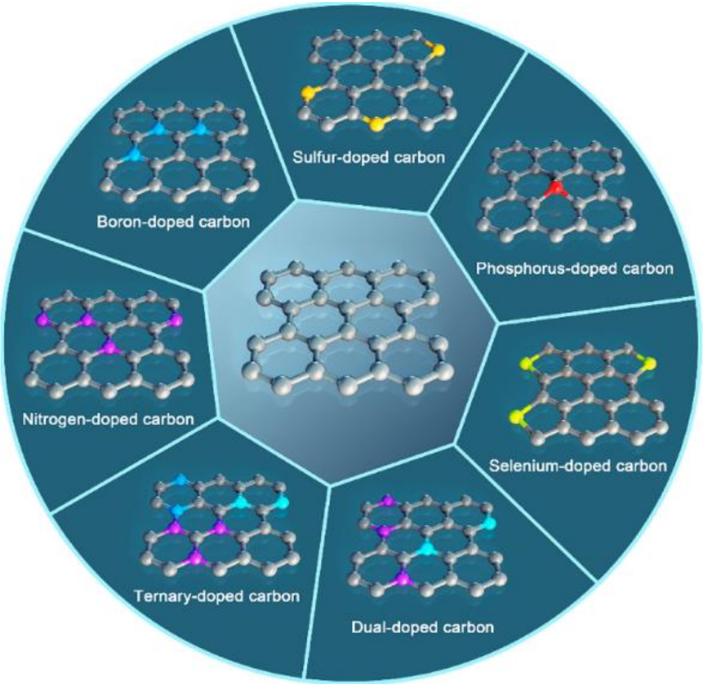

Figure 2: Schematic diagram of heteroatom-doped carbon materials (Reprinted with permission from ref 9. Copyright 2020, American Chemical Society).

2.1. Single Heteroatom Doped Carbon-Based Catalysts

The primary materials in monoatomic doped carbon-based catalysts are doping of N, B, P, and S. These non-metallic elements doping in carbon-based catalysts exhibit better ORR catalytic activity [10]. In various elements doped in carbon materials, N doping is widely studied and applied because the atomic radii of both N and C are similar, and there will be lone electron pairs in the N doping process, which can activate the π electrons in carbon atoms well and show good ORR catalytic activity selectivity and stability [11]. Feng *et al*. [12] reported for the first time that the CN/CNNT electrocatalyst prepared by carbon nitride (CN) and nitrogen-doped carbon nanotubes (CNT) has a relatively large specific area, which shows good ORR catalytic activity and stability. Wang *et al*. [13] investigated the active site of N-doping on graphene. They modified the acetyl groups at pyridine N (N-Ac) and neighboring C atoms (C-Ac) by site-selective methods (Fig. **3a**). It was found that the catalyst exhibited complete inactivity towards ORR when the neighboring C atom was blocked, indicating that the neighboring C on the pyridine ring was the active site. DFT calculations also showed that the significant ORR activity between N-Ac and C-Ac mainly originated from the difference between the positive charge density and the spin density at C-Ac (as shown in Fig. **3b** and **3c**).

In addition, researchers continue to explore the doping of N in other types of carbon materials to verify their catalytic activity. Nitrogen-doped porous carbon (NPC) has attracted focused attention as a promising carbon-based catalyst. Han *et al*. [14] developed a novel NPC material from a pyrrole precursor that exhibited excellent catalytic activity and long-term stability, as well as better selectivity than commercial Pt/C catalysts due to their high specific area, durability, and stability. Ren *et al*. [15] synthesized NPC spheres (NPCS-900) composed of nanosheets by pyrolysis of urea-formaldehyde (UF) resin using a template-free method. It was shown that the NPC spheres have a high surface area and partitioned pore structure, which increase many active sites and improve catalytic performance, long-term stability, and better selectivity for ORR. In addition, the rich nitrogen content also enhanced ORR's catalytic performance.

Compared to N-doping, B-doped carbon materials are also widely used with better ORR catalytic activity [16]. Due to the electron-deficient nature of B atoms, DFT simulations have shown that the electronegativity of carbon atoms is higher than that of boron atoms, inducing positive charges in heteroatoms. In contrast, boron atoms can be effective absorption sites due to the electron-deficient nature of boron atoms inducing charge transfer in carbon

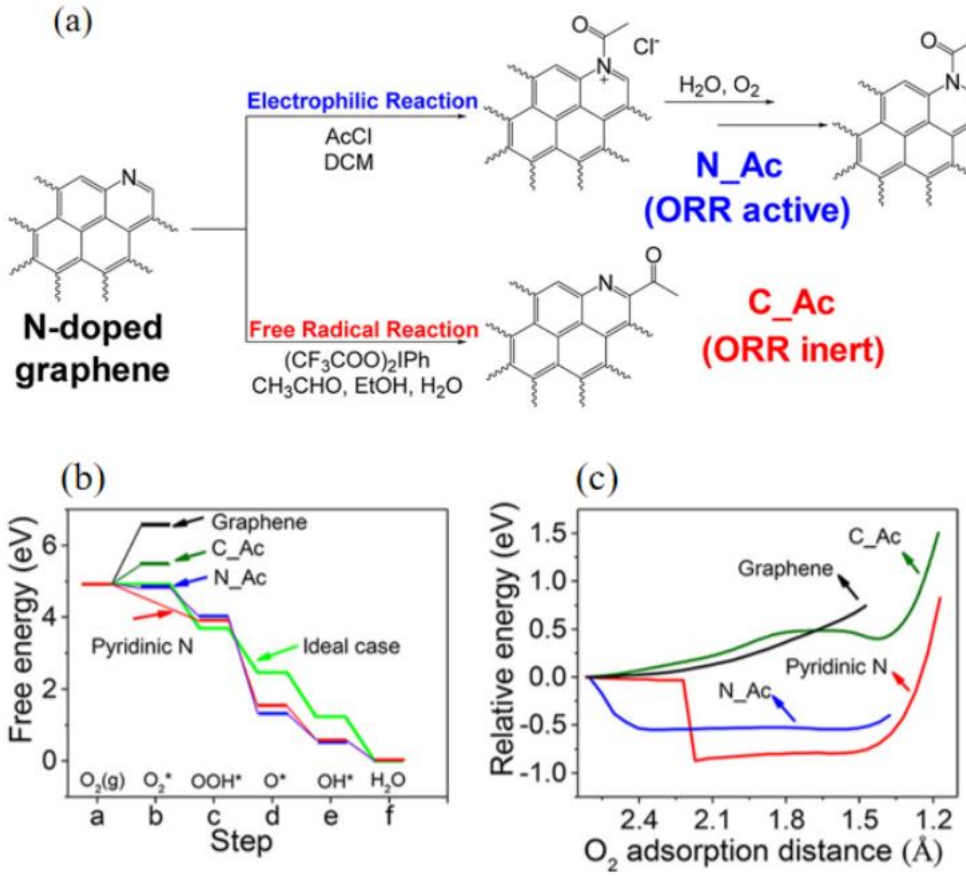

Figure 3: (a) Two selective modifications on N-doped graphene catalysts. (b) ORR free energy distribution on different configurations. (c) Energy variation of O_2 close to different active sites. (Reprinted with permission from ref 13. Copyright 2018, American Chemical Society).

atoms. Related studies have shown that boron doping can change carbon nanotubes' electrochemical properties and enhance ORR's catalytic activity. Yang *et al*. [17] prepared a catalyst on boron-doped carbon nanotubes (B-CNT) by using a Chemical Vapor Deposition Method(CVD). This catalyst exhibits better catalytic performance, long-term stability, and selectivity. In addition, it was found by further studies that the amount of doped boron has a significant influence on the catalytic performance of ORR, and the catalytic performance is enhanced by increasing the amount of boron. It was shown by (DFT) calculations that B doping could improve the efficiency of this catalyst in oxygen adsorption, and electron transfer could quickly occur, activating the activation of π-electrons on carbon nanotubes and showing good catalytic performance [18].

It can be seen that both electron-deficient B-doping and electron-rich N-doping can activate π-electrons in sp^2-hybridized carbon to give it good catalytic properties [19]. In addition to the two elements N and B, S and P doped carbon materials can exhibit good electrocatalytic properties. The sulfur atom has a larger radius than the nitrogen atom and is a new type of doping element. It was found that S and C combined can form different types of sulfur functional groups around the carbon. Yang *et al*. [20] prepared a carbon-based catalyst of S-doped graphene using graphene oxide and benzyl disulfide (BDS), which exhibited good catalytic performance with folded and folded characteristics. The outermost electron number of both P and N, their chemical properties are similar, the radius of the phosphorus atom is more significant than that of carbon, and the electronegativity is lower than that of carbon. The catalysts prepared by P-doped carbon materials can change the electrochemical properties of carbon materials and show good ORR catalytic activity, long-term stability, and better selectivity [21]. Yang *et al*. [22] prepared a carbon-based catalyst of P-doped ordered mesoporous carbon (POMC) using triphenyl and phenol under a mesoporous silica template, which had a highly ordered pore distribution with a homogeneous distribution of active sites and exhibited better ORR catalytic performance as well as long-term stability. In addition, the lone pair of electrons in the P-doped 3p orbital induces a local charge density that can accommodate the lone pair of electrons from O_2, enhancing the catalytic activity of ORR [23, 24]. Lei *et al*. [25] prepared a carbon-based catalyst of P-doped porous carbon nanosheets (2D-PPCN) using a multiple template method. Using phosphorus pentoxide as the P source and red phosphorus as a self-sacrificing template, the resulting catalyst exhibited excellent stability of ORR catalytic performance with a large number of tiny pores (micropores and mesopores) uniformly distributed and with a high specific area.

2.2. Binary Heteroatom Co-Doped Carbon-Based Catalysts

In addition to studying single atoms, doping two atoms have also been investigated to increase the catalytic activity through the coordination effect between the motions of different heteroatoms to achieve the co-doping of multiple molecules. Since N atom doping would have the nature of lone electron pair and B atom with electron deficiency, the two are combined to form a double atom doping to optimize the catalytic performance of ORR further. Zhao *et al*. [26] prepared two catalysts with N and B heteroatoms co-doped in carbon nanotubes (CNT), one with N and B atoms in the bound state of CNT and the other with N and B atoms in the independent state of CNT, and by studying and analyzing the two catalysts. It was concluded that the bound state form did not change the nature of CNT and did not have better ORR catalytic performance. In contrast, the separated form changed the nature of CNT and showed excellent ORR catalytic performance, long-term stability, and better selectivity. By changing the doping states of both N and B atoms, the activation degree of π-electrons was adjusted, affecting ORR's catalytic performance. Sun *et al*. [27] studied porous B and N copolymer-doped nano-carbon materials prepared by thermolysis of ethylcellulose and 4-(1-naphthyl) phenylboronic acid. The catalysts have interconnected cubic hollow nanocages and abundant carbon defects and contain more porous structures, forming many active sites and exhibiting better ORR catalytic activity. Thus, the synergistic effect of heteroatom co-doping and abundant carbon defects can exhibit excellent electrocatalytic performance.

Heteroatom doping can activate π electrons in carbon materials well and improve the catalytic activity of ORR. Since the outermost electron numbers of N and P are equal and their chemical properties are similar, two elements, N and P, are co-doped with carbon materials to study their electrocatalytic properties. Li *et al*. [28] used high-temperature carbonization for doping. The covalent organic framework (COF) containing N and P was subjected to heat on the CNT surface, which allowed a more uniform distribution and facilitated a good dispersion of the heteroatoms, thus enhancing more active sites while increasing the interaction with oxygen to promote the ORR process, showing good stability, selectivity, and catalytic activity (Fig. **4**). It was shown that the best catalyst activity was obtained by introducing the phosphorus element first and then the nitrogen element [29]. Zhang *et al*. [30] developed an N, P co-doped nano-carbon foam (NPMC), which exhibits better ORR catalytic performance due to its three-dimensional porous structure and better edge effect, which adds a large number of active sites. Yang *et al*. [31] developed a defect-rich N and P codoped carbon nanofoam (NPG-1000), a catalyst made by carbonizing glucose from urea and phytic acid using the hot-blowing method. This catalyst exhibited excellent ORR catalytic performance, long-term stability, and better selectivity due to its large surface area and porous structure, which increased the content of heteroatoms on the surface of the carbon material.

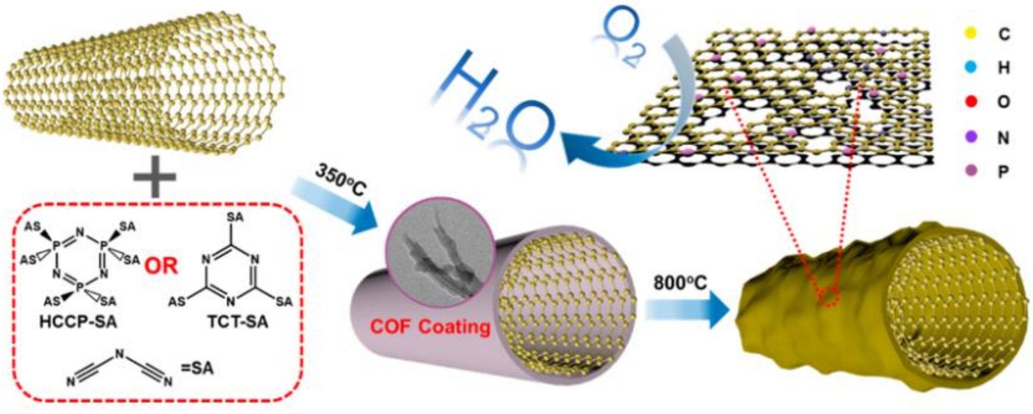

Figure 4: Preparation of N and P codoped carbon materials (Reprinted with permission from ref 28. Copyright 2017, American Chemical Society).

In addition to N, B doping and N, P doping mentioned above, co-doping of N, S, and co-doping of N, F are also studied. Hu *et al*. [32] reported a distinct type of two-dimensional (2D) N, S codoped graphite sheet. The catalyst has a graded architecture of steric pores (SHG), which can deliver many approachable activity spots to promote rapid transport of electrolytes and reactants, high activity for Pt/C catalysts, and possesses higher stability. Kim *et al*. [33] prepared N, S co-doped ORR electrocatalysts (SNBCs) out of the pyrolysis of bamboo and thiourea (Fig. **5**), which have comparable to commercial Pt/C catalysts in terms of half-wave potential and stability due to the well-developed secondary porous architecture that increases the number of active sites. Zhou *et al*. [34] used a rapid explosion combustion method to synthesize N and S co-doped carbon-based catalysts (D-NSOCs), which can generate a certain amount of graphitization on the carbon surface to improve its electrical conductivity by the instantaneous high temperature generated by rapid explosion combustion, and form active catalytic centers by the doping of N and S atoms to improve the catalytic activity and stability of ORR. Zhang *et al*. [35] obtained N and S-codoped carbon materials from rapeseed, which showed excellent ORR catalytic activity, long-term stability, and better selectivity due to the formation of asymmetric charge and self-selected density due to the synergistic effect between the heteroatoms.

Figure 5: Preparation and application of SNBC (Reprinted with permission from ref 33. Copyright 2019, American Chemical Society).

According to the relevant literature, it is known that F-doping can induce more defects and active catalytic sites, and the mixture obtained by using carbon black and F precursors under high-temperature pyrolysis is an N and F-codoped carbon-based catalyst [36]. The catalyst exhibits good catalytic performance, long-term stability, and better selectivity due to its high specific surface area and many porous structures (micro- and mesopores), which can provide many accessible active sites and facilitate the rapid transport of electrolytes and reactants. Lu *et al*. [37] prepared an N, F co-doped porous carbon electrocatalyst, in which polyaniline and polytetrafluoroethylene were used as the N and F sources, respectively (Fig. **6**); due to the porous structure, it provides more active sites and exhibits better catalytic performance, selectivity, and stability than that platinum-based catalysts.

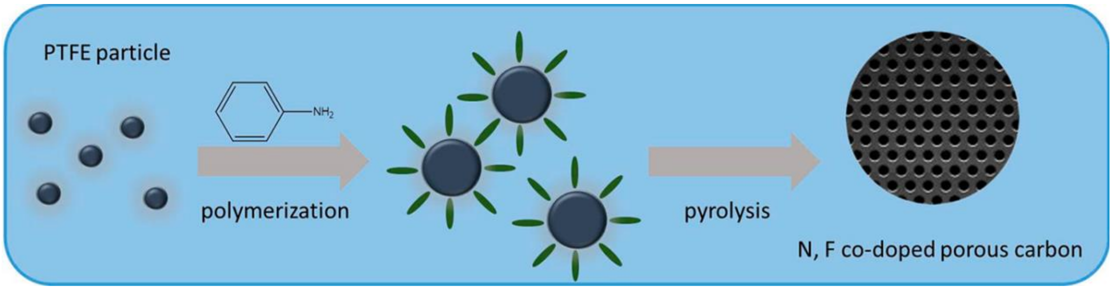

Figure 6: Process of N, F co-doped porous carbon (Reprinted with permission from ref 37. Copyright 2017, American Chemical Society).

2.3. Ternary Heteroatom Co-Doped Carbon-Based Catalysts

Based on the above discussion of binary heteroatom doping, the synergistic effect between these heteroatoms was closely related to the charge-leaving domains. The ternary heteroatom co-doping was found to have excellent ORR activity by studying ternary heteroatom-doped carbon-based electrocatalysts with complex synergistic effects. Inspired by the double heteroatom doping, the synergistic effect between these heteroatoms was found to be closely related to the charge-leaving domain, and by studying ternary heteroatom-doped carbon-based electrocatalysts with complex synergistic effects, it was found that the ternary heteroatom co-doping has excellent ORR activity and long-term stability as well as better selectivity. It was found that introducing more dopants in carbon-based nanocatalysts may trigger similar activity enhancement effects. The in-depth mechanism is complex due to different dopants. Therefore, the detailed mechanisms and optimization associated with various dopants still need further exploration. Zhang *et al*. [38] studied the preparation of a catalyst with three non-metallic elements, N, P, and F, doped with graphene. Polyaniline was used as the N source, and ammonium hexafluorophosphate (AHF) as the P and F sources, and the mixture was obtained by wrapping graphene oxide. Ammonium hexafluorophosphate (AHF), under high-temperature pyrolysis using polyaniline, was the prepared catalyst, which formed a more porous structure and exhibited excellent ORR catalytic activity and long-term stability as well as better selectivity. Long *et al*. [39] synthesized a catalyst containing three elements doped with N, P, and S by pyrolysis using glucose, trithiocyanate, and phosphoric acid, with trithiocyanate as the N and S sources and phosphoric acid as the P source. The catalyst exhibited ORR catalytic activity comparable to that of commercial 40% Pt/C catalysts due to its large specific area and a high number of active sites. Liu *et al*. [40] synthesized defect-rich porous carbon-based electrocatalysts containing three non-metallic elements doped with N, P, and O by a simple pyrolysis method, which exhibited good ORR catalytic activity, selectivity, and stability due to a large number of defect sites. The increase in defect sites and the rapid material transfer triggered the synergistic effect of induced charge movement and self-selective redistribution [41].

2.4. Defective Doping

It is well known that there are almost no crystals without any defects in the world, and defects can lead to changes in the arrangement of some atoms, forming lattice distortions and affecting their electronic structure, which can be adjusted to change the ORR activity [42, 43]. Among the numerous defect types, the two most common are edge and topological defects, respectively, which are considered the active centers of ORR and can enhance catalytic activity. Wang *et al*. [44] prepared edge-defective graphene using the Ar plasma etching route. The analysis of the study showed that the structure of the plasma-treated graphene did not change significantly, but many small pores were found on the surface of the graphene. These pores provided more active sites for ORR catalysis and showed better catalytic activity. Topological defects can break the original hexagonal network in the carbon skeleton and cause the redistribution of off-domain orbitals. In contrast, pentagonal defects are a common topological defect that exhibits excellent catalytic activity and has attracted focused attention and research. It has been found that plasma technology has fewer introduced impurities, the higher catalytic activity of products, and shorter reaction time compared with traditional synthesis methods. The plasma technology is more suitable for the preparation and treatment of carbon-based nanomaterials by improving the plasma source to enhance its stability and efficiency on the one hand and improving the physicochemical properties of carbon-based nanomaterials by compounding with different heterogeneous nanomaterials on the other hand. The plasma treatment process for carbon materials can affect their surface groups depending on the plasma energy and the plasma atmosphere. The plasma energy can be divided into plasma removal of the surface groups of carbon materials and the change of the structure of the carbon material itself. The reduction of groups on the surface of carbon nanomaterials and the grafting of new groups on the surface of carbon nanomaterials can be classified according to the atmosphere used. The gas-liquid microplasma method uses the precursor solution as the reactant, and the energetic electrons and active particles (e.g., ions, radicals, sub-stable atoms, radiative photons, etc.) in the plasma interact directly with the reactant to prepare nanomaterials. Ma *et al*. [45] used citric acid solution as the carbon source and ethylenediamine as the nitrogen source. The gas-liquid microplasma reactor was constructed with a stainless acid capillary as the cathode and a platinum sheet inserted into the electrolyte as the ground electrode. Both electrodes were connected to a negatively biased DC power supply to generate the plasma. It was found that the average particle size of carbon quantum dots increased from 3.10 to 5.98 nm by extending the plasma treatment time (1~2 h). With the increase of operating voltage (3~5 kV), the discharge volume was enlarged, more high-energy electrons were generated, and then the condensation reaction between reactants was more intense, which accelerated the carbon nucleation and growth, resulting in an increase of the mass fraction of carbon in the graphite structure from 40% to 51%. In addition, the average yield of carbon quantum dots synthesized at 0.25 mm stainless steel tube electrode (0.42%) is slightly higher than that of

0.50 mm (0.31%) due to the current density and electron density increase with the decrease of the microplasma tube diameter. Mu *et al*. [46] prepared fullerenes with pentagonal defects by using an in situ etching route, and after DFT calculations showed that a large number of pentagonal defects in fullerene molecules would facilitate band gap narrowing and local electron redistribution, with better binding affinity and catalytic reaction characteristics. Yao *et al*. [47] found that the pentagonal defect showed long-term stability and better selectivity. Table **1** summarizes the advantages and disadvantages of various preparation methods in the metal-free catalytic ORR system.

Table 1: Advantages and disadvantages of different preparation methods.

Prepared Methods	Advantages	Disadvantages
Chemical Vapor Deposition	The process is simple; the degree of densification is easy to control accurately, and there is no damage to the fiber.	The preparation cycle is too long, and the production efficiency is low
No Template Method	Reduced preparation cost, with green, environmental protection, and low-cost advantages	Poor performance in precisely controlling the morphology and porous structure of the material
Pyrolysis Method	The equipment process is simple and easy to operate, saving costs	Low catalytic efficiency
Deflagration Method	Quick response, good effect	With a certain degree of danger
Plasma Method	Less introduction of impurities, the higher catalytic activity of products, shorter reaction time	The treatment process is complex and improper control can damage the material's surface.

3. Polymeric Nitrogen (PN) for Use on Our

Poly(nitrogen) (PN) compounds are three-dimensional crystal structures containing nitrogen atoms [48]. Because of the high-power consumption, the large amount of heat emitted, and the non-polluting gas nitrogen produced, it has received much attention. Wu *et al*. [49] prepared polymeric nitrogen ions for the first time using cyclic voltammetry (CV). They stabilized them on multi-walled carbon nanotubes, and the synthesized PNs exhibited excellent ORR catalytic activity. Shi *et al*. [50] found that the multi-nitrogen chain N_8 can be inserted into graphene layers and remain stable under specific environments. Graphene can be used for electron transport, and the doping of heteroatoms can change the structure of its surface and the nature of electrons, which can improve the catalytic activity of ORR [51]. Since the atomic radii of B and C are very similar, but the electronegativity of B is lower than that of carbon, PN-BG catalysts were prepared by depositing multi-nitrogen N_8 on boron-doped graphene [52]; the catalyst exhibits better ORR catalytic activity than commercial Pt/C catalysts. Yao *et al*. [53] further attempted to change the polymeric nitrogen substrate and prepared N_8-polymeric nitrogen stabilized on it using nitrogen-doped carbon nanotubes (CNT) as a substrate, which exhibited good stability and catalytic activity.

4. Emerging Advanced Carbon Catalysts

As researchers continue to study in-depth, in addition to the types of carbon materials that can be doped with heteroatoms, new types of carbon materials have been studied, and the nature of carbon materials affects the catalytic performance of ORR. Gao *et al*. [54] reported a novel nitrogen-doped carbon foam (CF) based carbon catalyst. This catalyst exhibited excellent ORR catalytic activity with sp^3 and sp^2 carbons and a three-dimensional (3D) structure. Through further studies, it was found that the catalyst exhibited excellent catalytic performance due to the dominance of sp^3 carbon and the doping of N [55]. Currently, the research is still primarily focused on sp^2 carbon, while graphene, as a new star of carbon materials, is composed of unique sp hybridized carbon atoms, which is expected to bring new nitrogen-doped configurations [56]. Zhao *et al*. [57] reported a novel sp-hybridized N-doped graphite acetylene-based carbon catalyst. Compared with sp^2 carbon and sp^3 carbon materials, sp hybridized carbon atoms can attract more positive charges, which promotes the adsorption and activation of oxygen and is more favorable for electron transfer, improving the catalytic performance of ORR. The different hybridization types of carbon materials, which exhibit different ORR activities, broaden the idea of studying metal-free catalysts and provide new research directions for the future development of metal-free catalysts.

5. Conclusion and Outlook

Carbon-based catalysts have a wide range of applications, from renewable energy to environmental protection, due to their excellent catalytic properties. While metallic platinum is not conducive to commercial production due to its scarce reserves and high price, non-metallic catalysts are considered promising ORR catalysts due to their lower cost, chemical stability, and tunable structure. This paper focuses on various heteroatom-doped carbon-based catalysts, polymeric nitrogen compounds, and emerging advanced catalysts, which provide research directions to replace Pt-based catalysts in the future and draw focused attention to non-metallic heteroatomic carbon-based catalysts. However, the stability of the structure and performance of carbon-based catalysts is an important factors limiting their practical application. Therefore, we still need to continuously improve the catalyst structure and stability to meet the market demand and conduct continuous research on metal-free carbon-based catalysts to better understand fuel cells' practical effects. Metal-free catalysts have the advantages of low price, comprehensive source, environmental friendliness, and good stability. On the other hand, they also have the disadvantages of chemical instability and low catalytic efficiency. The author hopes that through continuous thinking, research, and exploration, with the joint efforts of researchers, ORR catalysts with better performance can be developed to accelerate the development of hydrogen fuel cell catalysts.

Acknowledgements

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