Active Sites Derived from Heteroatom Doping in Carbon Materials for Oxygen Reduction Reaction

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Abstract

The oxygen reduction reaction (ORR) is a key cathode reaction in fuel cells. Due to the sluggish kinetics of the ORR, various kinds of catalysts have been developed to compensate for the shortcomings of the cathode reaction. Carbon materials are considered ideal cathode catalysts. In particular, heteroatom doping is essential to achieve an excellent ORR activity. Interestingly, doping trace amounts of metals in carbon materials plays an important role in enhancing the electrocatalytic activities. This chapter describes the recent advancements with regard to heteroatom-doped carbons and discusses the active sites decorated in the carbon matrix in terms of their configurations and contents, as well as their effectiveness in boosting the ORR performance. Furthermore, trace metal residues and metal-free catalysts for the ORR are clarified.

Keywords: oxygen reduction reaction, trace metal residues, active sites, heteroatom doping

1. Introduction

Owing to the limited supply of fossil fuels and increasing number of environmental crises, sustainable energy conversion and storage devices such as fuel cells and metal-air batteries have attracted significant attention [1]. The oxygen reduction reaction (ORR) is a key cathode reaction in such systems [2–4]. The sluggish kinetics of the ORR at the cathode owing to a higher overpotential than in the anode limits the wide commercialization of these devices. Currently, only the state-of-the-art platinum/carbon black catalyst (Pt/C) has been widely used in practical applications of proton exchange membrane (PEM) fuel cells [5]. Unfortunately, the scarcity and high cost of Pt and the poor durability limits the wide commercialization of

these devices. Therefore, the development of low-cost and highly efficient catalysts for the ORR has become a "hot topic".

Earlier studies have focused on tuning the surface structure [6–8] and electronic structure [9] of Pt as well as the electrocatalyst supports [10, 11] to achieve optimum ORR activity by using the least amount of Pt. In addition, various kinds of catalysts, including transition metals and their alloys, transition metal oxides/nitrides/sulfides, as well as mixed-valence metal oxides [12, 13], carbon-based metal-free catalysts [14], and others have been developed to promote the sluggish kinetics of the ORR at the cathode. Among the catalysts studied, heteroatom-doped carbon materials are considered ideal cathode catalysts due to the high surface area, good electrical conductivity, and densely distributed active sites. Presently, carbon black (CB) [15], graphene [16, 17], carbon nanotubes (CNTs) [17, 18], and porous carbon [19] are used as support materials in carbon-based electrocatalysts. Although topological defects contribute to the intrinsic activity of nanocarbon catalysts, various kinds of active sites have been created in nanocarbon catalysts to further enhance their activity [20, 21]. For example, transition metals such as Fe, Co, Ni, Cu, Zn, and Mn display fairly strong adsorption toward oxygen in the ORR, which can enhance the ORR efficiency and performance [22, 23]. Furthermore, metal-free catalysts have also become an intriguing research area. Non-metal heteroatoms, such as N, S, B, and P, in carbon materials can serve as active sites for the ORR. The heteroatoms can alter the electronic distribution of the carbon framework and effectively increase the defects in the carbon structure, contributing to O_2 adsorption and O—O bond breaking during the ORR catalytic reaction and concurrently promoting the catalytic performance of the carbon materials. Although the individual roles of different atoms and their synergistic effects in facilitating the ORR activity are still under debate, numerous achievements have been made toward the rational design and synthesis of carbon materials with a high surface area, high electrical conductivity, and multiple heteroatom doping to achieve extraordinary ORR activities.

In fact, the ORR activity and durability of heteroatom-doped carbon even outperform those of commercially available Pt-based catalysts. Here, we aim to assemble a review of the significant scientific progress in the design and synthesis of carbon-based electrocatalysts. We discuss the activity of different doping sites to provide an understanding of the mode of heteroatom doping and the role of heteroatoms in ORR, especially their content effects in ORR.

2. Active sites in the ORR

The ORR proceeds through two pathways—partial reduction and full reduction—and involves a two-electron pathway and a four-electron pathway, respectively. The four-electron route is highly preferred due to its high efficiency in fuel cell technology. The transformation of O_2 to OOH* is the first step in this route and is also a rate-determining step. The highly active catalytic centers must be favorable to enhance the binding energy between the oxygen intermediates and the catalyst surface but weak enough that the oxygen intermediates dissociate from the catalyst surface to prevent poisoning the catalyst. Therefore, goals for designing an ORR catalyst with high efficiency are to tune the adsorption energies of the

oxygen intermediates and modify the charge/spin distribution of the catalyst. Although, there is strong controversy about the role of active sites and mechanisms, the heteroatoms, even the edges and defects that can function as active sites for the ORR.

2.1. Pt-based active sites

Decreasing the loading amount of Pt and Pt-based materials to enhance the performances of fuel cells is a wise choice. A series of Pt-based catalysts were prepared. For example, Xia et al. reported the synthesis of Pt—Ag alloy nanocages (**Figure 1**) [6]. Due to the ligand effects from the electronegative Ag atoms, the O_2 transition state can be stabilized, demonstrating a high specific activity toward oxygen reduction compared with that of the state-of-the-art commercial Pt/C catalyst. Furthermore, hollow Pt—M (M = Ni, Co) nanoparticle-decorated graphene was designed as an electrocatalyst for the ORR. Due to the hollow interior, the amount of buried nonfunctional precious metal atoms decreased and hence enhanced the electrocatalytic activity and durability toward the ORR [7]. Based on the same mechanism, a hollow structure of a Pt catalyst was also reported by Li and co-workers. The obtained icosahedral Pt-enriched nanocages demonstrated a superior ORR activity [24]. In addition, Pt nanoparticles stabilized by a graphitic step-edge and combined with the effect of nanoscale confinement showed high electrochemical stability outperforming that of a commercial Pt/C [25]. Interestingly, Adzic and co-workers used titanium nickel binary nitride as a support and then several layers of Pt atoms were deposited on the robust support. The obtained catalyst exhibited high mass activity and specific activity compared with the commercial Pt/C catalyst; this result was mainly due to the synergistic effect of Ni doping and the strong interaction between the Pt layer and the support [10]. Mukerjee and co-workers designed a Pt/NbO$_x$/C system as an ORR catalyst and demonstrated that the Pt—O interactions improved the ORR activity [26]. Ultrathin Rh-doped Pt nanowires synthesized by Zeng and co-workers achieved remarkable activity and durability toward the ORR due to the doping of the Rh atoms and high utilization efficiency of the Pt atoms [27]. Furthermore, Pt$_3$Ni nanowires also showed extraordinary activity and stability toward the ORR [8].

All in all, despite numerous progresses made in exploring novel type of ORR catalyst, the state-of-the-art Pt/C catalysts still dominate. Pt-based multimetallic catalysts with various
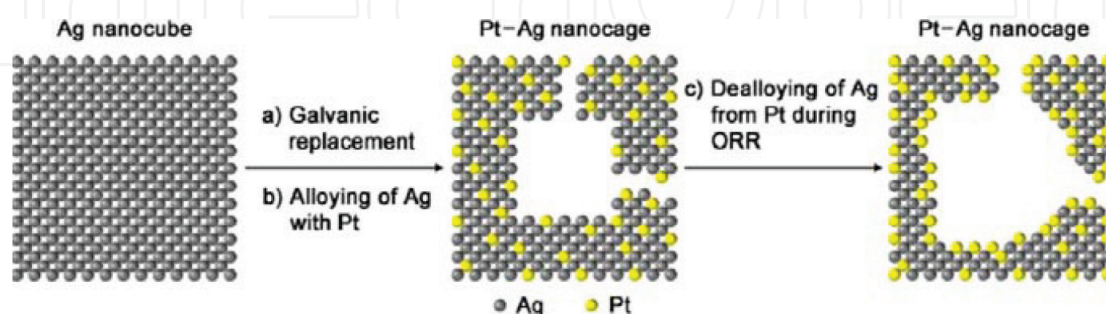

Figure 1. Schematic illustration depicting the major steps involved in the formation of Pt—Ag nanocages with high ORR activity: (a, b) alloying of Ag with Pt to generate Pt—Ag nanocages during the galvanic replacement reaction between Ag and a Pt(II) precursor and (c) dealloying of Ag from Pt during the accelerated durability test [6].

finely tuned morphologies will represent a promising research area of ORR catalyst, due to the scarcity of Pt and the unsatisfactory long-term stability.

2.2. Non-noble metal-based active sites

The search for Pt-free alternative catalysts with excellent ORR performance has attracted much attention. Accordingly, extensive efforts have been directed toward the design and synthesis of nonprecious metal-based catalysts for potential applications in fuel cells. Particularly, the co-doping of transition metals and non-metal heteroatoms have also been extensively studied due to their combined advantages. Fe—N—C catalysts have been broadly studied. Atomically dispersed Fe [28], Fe—N_x [29, 30], Fe_3C [31, 32], and Fe_3O_4 [33] are all considered ORR active sites. Dong and co-workers demonstrated that atomically dispersed Fe (1–2 wt%) played a pivotal role in promoting the ORR performance [28]. Joo et al. prepared a catalyst consisting of Fe—N_x and Fe—$Fe_3C@C$ species (Fe content of 6.3 wt%) [31]. The experimental results indicated that the Fe—N_x sites played a dominant role in promoting the ORR via a 4-electron pathway, whereas the Fe—$Fe_3C@C$ sites played an auxiliary role. The authors also prepared a CNT/porphyrinic carbon (PC) catalyst with densely distributed active Fe—N_x sites (**Figure 2**). The Fe contents of the CNT/PC were 2.9 wt%. This catalyst showed very high ORR activity in both alkaline and acidic media [32]. Xia and co-workers prepared Fe_3O_4 nanoparticles encapsulated in hollow core-shell structured N-doped carbon spheres. The obtained catalyst exhibited an excellent catalytic performance toward the ORR [33].

In addition to Fe—N—C catalysts, S-doped Fe—N—C catalysts have also been systematically studied. For example, Wang and co-workers found that iron sulfides/nitrogen and sulfur dual-doped mesoporous graphitic carbon spheres demonstrated excellent electrocatalytic activities toward the ORR in alkaline and acidic media. The remarkable catalytic performance was ascribed to the iron sulfide nanocrystals with an iron content of 5.9 wt% [34]. Similarly, multi-source-derived S—Fe/N/C with the atom contents of Fe 1.38% has been reported by Wang and co-workers. Five types of Fe were detected: Fe, FeS, FeN, FeC, and Fe_3O_4. Although the nature of the active sites was uncertain for the Fe/N/C, the S—Fe/N/C catalyst showed a highly efficient ORR activity [35, 36].
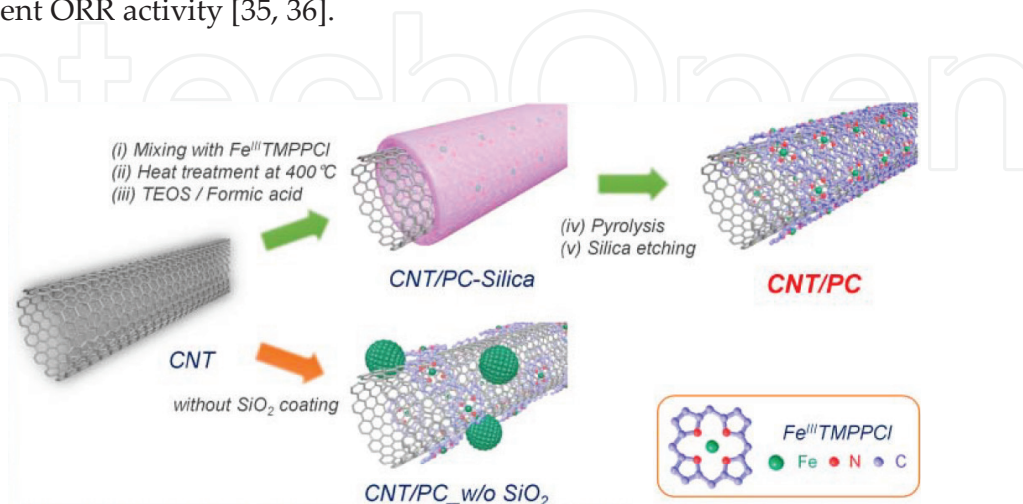

Figure 2. Synthetic scheme for the preparation of CNT/PC catalysts [32].

Other earth-abundant non-noble metal-based electrocatalysts are also emerging as a new generation of low-cost and high-performance alternatives [37–44]. For example, the ORR electrocatalyst properties of Cu, N-co-doped hierarchical porous carbon with a copper content of 2.67 wt% were almost equal to those of a commercial Pt/C catalyst [37]. CoO_x nanoparticles@B, an N-decorated graphene hybrid material, was prepared by Wu and co-workers. Abundant Co—N—C active sites and high electron transfer capacity made this hybrid active in the ORR in an alkaline medium [39]. Recently, Deng and co-workers prepared Co_3O_4/Co-decorated porous graphene derived from waste paper (**Figure 3**) [40]. In this work, the cobalt(II)acetate-1,10-phenanthroline complex was selected as a precursor of both the catalyst and etcher; the control of the feed ratio of the complex, as well as the pyrolysis temperature and chemical compositions (Co_3O_4/Co) of the active sites could be finely tuned. This cost-efficient and green catalyst exhibited an efficient ORR activity with a performance comparable to that of a Pt/C catalyst due to the synergistic catalytic effects between Co_3O_4 and graphene combined with the hierarchical porous structure of the matrix. Lee and co-workers designed a nickel-containing nanoreactor (Ni@N-CNCs) [42]. Ni particles were encapsulated in N-decorated carbon nanocapsules. X-ray photoelectron spectroscopy (XPS) analysis showed the formation of N—C and Ni—N bonds in the nanoreactor and these two types of active sites significantly improved the catalytic activity. In addition, a nanoconfined effect improved the reaction rate. The electron transfer number of Ni@N-CNCs reached nearly 4.0 comparable to that of Pt/C. Successively, a manganese corrole complex [43] and ZnN_x/C catalysts [44] were explored as efficient ORR catalysts.

Additionally, bimetallic catalysts are promising candidates for the ORR. You and co-workers synthesized Fe_3C/tungsten carbide/graphitic carbon in which the Fe_3C acted as the active
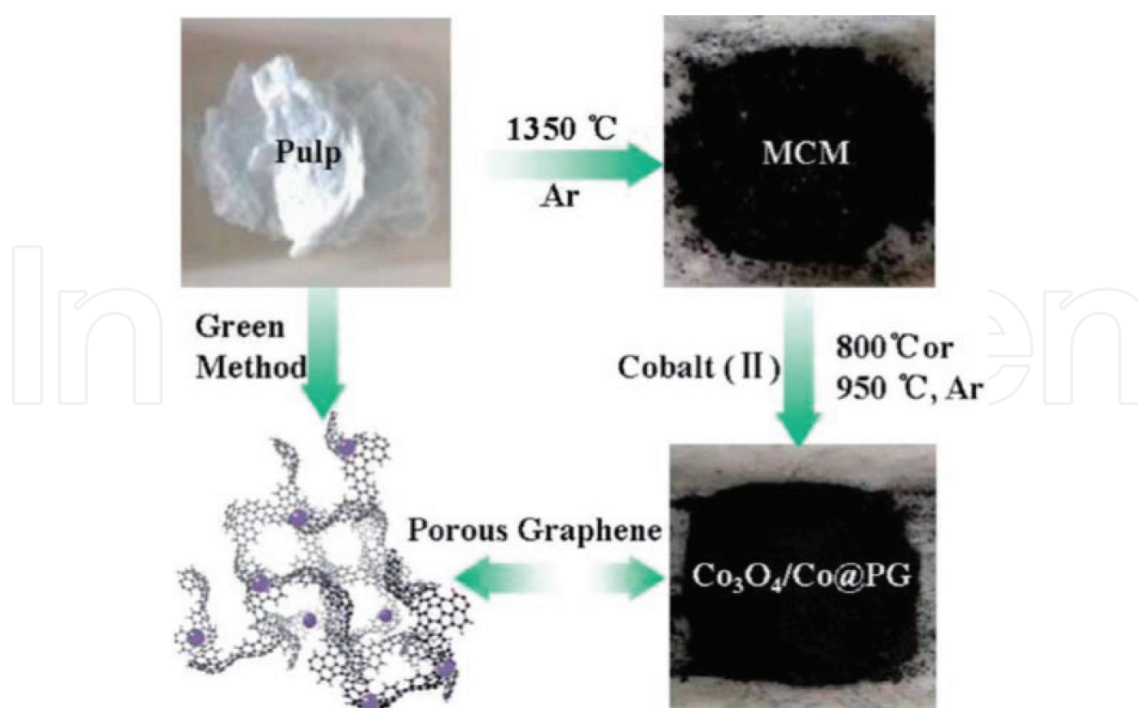

Figure 3. Schematic procedure for the preparation of functional porous graphene (Co_3O_4/Co@PG) from waste paper (MCM stands for microporous carbonaceous material and PG stands for porous graphene) [40].

sites. Meanwhile, graphitic layers and tungsten carbide nanoparticles can improve the surface chemical stability of the Fe_3C phase. The nanocomposite demonstrated high ORR efficiency via a four-electron pathway in a pH-neutral electrolyte [45]. Xu and co-workers used transition-metal spinels as a descriptor to identify the active sites in $MnCo_2O_4$ for catalyzing the ORR. Mn cations played an important role in the ORR because of the Mn valence in the octahedral sites [46]. Moreover, PdCo bimetallic nanoparticle (~8 wt%)-decorated N-doped porous carbon was fabricated by Yamauchi and co-workers. Due to the existence of the PdCo nanoparticles, the O—O bonds can be easily broken. More importantly, the three-dimensional ordered porous structure disperses the PdCo nanoparticles uniformly in the matrix. Therefore, this composite exhibited similar electrocatalytic activity to that of commercial Pt/C in alkaline media [47]. One step beyond is to further dope metal into the bimetallic catalysts. A cathode catalyst composed of a conformal film of the $PrNi_{0.5}Mn_{0.5}O_3$ and exsoluted PrO_x nanoparticles was designed by Liu and co-workers. Oxygen-vacancy-rich surfaces of the catalyst facilitated the electron transfer and hence dramatically enhanced the ORR kinetics and durability [48].

Now, the non-noble metal-based ORR catalysts have received more concern, due to their low cost and earth abundance. Although the deep insights of the active sites are not clear, non-noble metal-based ORR catalyst can outperform the catalytic performance of Pt/C. However, most synthetic strategies involved the random mixing of carbon precursors and dopants, followed by pyrolysis. Therefore, it is hard to tune the porous structures and the distribution of active sites. Future research should focus on the control of the morphology, composition, and active sites of the non-noble metal-based catalysts in high precision.

2.3. N-, S-, B-, and P-based active sites

Along with great progress made in metal-based catalysts, metal-free catalysts have attracted significant attention. Due to their high catalytic performance, long-term stability, and durability, electronegative N-doped carbon materials have been broadly studied. Pyridinic-N and graphitic-N were found to be the most highly active sites for the ORR. It is still under debate which configuration contributes more to the ORR. In fact, it is difficult to determine the role of a single N-type because high-temperature pyrolysis tends to introduce a mixture of N types. Surprisingly, synthetic strategies favorable for obtaining specific types of C—N bonding have been developed [49, 50]. Specifically, Zhang and co-workers prepared pyridinic-N dominated graphene aerogels by the etching effect of NH_3. The authors found that a long annealing time at 900°C was favorable for obtaining pyridinic-N. An N content of up to 12.2 at% with 90.4% pyridinic nitrogen has been achieved [51]. Furthermore, g-C_3N_4 is an ideal nitrogen dopant with an N content of 57.1 at%. A series of studies have been reported using g-C_3N_4 as both the template and nitrogen source [52–54]. Yan and co-workers reported a facile strategy for the synthesis of nitrogen-doped porous carbon with an N content of 10.49 at% [53]. Polypyrrole was used as the carbon and heteroatom sources and g-C_3N_4 acted as a sacrificial template and nitrogen sources. The XPS spectra of N 1 s indicated the existence of pyridinic-N, pyrrolic-N, graphitic-N, and oxidized-N. Due to the high specific surface area and N content as well as massive edges and defects, the obtained porous carbon exhibited excellent ORR activity. In addition, nitrogen-doped carbon nanoparticle−carbon nanofiber composites prepared by Ishizaki and co-workers demonstrated long-term durability and high tolerance to methanol. This can be attributed to the high conductivity of the carbon nanofibers and the largely

exposed active sites [55]. Task-specific tubular nanoporous polycarbazole-derived N-doped carbon nanotubes [56] and highly pyridinic nitrogen (up to 14.9 wt%)-doped ultra-hollow carbon frameworks [57] have also been reported. The design of carbon structures with multi-component active centers can in principle enhance the ORR activity. Two-dimensional N- and S-co-doped graphitic sheets with abundant interfacial active sites showed catalytic activity comparable to that of the commercial Pt/C [58]. In addition, N- and P-co-doped porous carbon networks showed high activities and excellent durability for ORR [59]. More interestingly, an N- and S-doped carbon nanofiber network coated with N- and P-doped carbon nanoparticles showed superior ORR performance due to the integration of N, S, and P in the carbon hybrid [60]. Zhi and co-workers studied the ORR activity of B-, P-, and S-doped g-C_3N_4. The XPS results suggested the formation of B—N, P—N, and S—C bonds. The experimental results indicated that S- and P-doping enhanced the electrocatalytic performance of ORR, whereas B-doping deactivated the ORR process. The authors proposed that B, S, and P atoms are active sites in the ORR with the catalytic activity trend of S-doped > P-doped > g-C_3N_4 > B-doped g-C_3N_4 [61].

Now, metal-free catalysts, commonly decorated with N, B, P, or S, have emerged as promising catalysts in ORR, due to the high methanol tolerance and excellent long-term stability. In fact, design and synthesis of metal-free catalysts with satisfactory ORR performance in pH-universal electrolyte is still a challenge.

2.4. Trace metal-based active sites

It has been reported that metallic impurities within sp^2 carbon nanomaterials may dominate the electrochemistry of the materials [62, 63]. Jiang and co-workers prepared sulfur, trace nitrogen, and iron co-doped porous carbon foams with an Fe content of 0.27 at%. They proposed that C—S moieties and the synergistic effect of sulfur, the trace amount of nitrogen, and iron contributed to the efficient electrocatalytic properties [64]. Wang and co-workers decorated Pd_3V bimetallic alloy nanoparticles with Pt (Pt to Pd nominal atomic ratio at 1:30). With the exposure of more active sites of the Pt, the obtained catalyst showed high catalytic activity and stability in the ORR with a 30-mV positive half-wave potential ($E_{1/2}$) comparable to that of commercial Pt/C [65]. Surprisingly, the presence of trace Au (Au/Pt atomic ratio = 0.0005) can significantly enhance the ORR durability of a PtCu alloy [66]. Similarly, incorporating trace amounts of gold (Au:Pd = 1:100) in Pd_6CoCu nanocatalysts can markedly improve the durability of the ORR (**Figure 4**). Synchrotron X-ray absorption spectroscopy showed that gold replaced cobalt and copper on the surface and in the interior of the nanoparticles. This study developed a new strategy for enhancing the stability of fuel-cell catalysts [67].

Impressively, Schuhmann and co-workers systematically investigated the influence of trace metal residues on the ORR activity. They prepared a metal-free catalyst and then deliberately incorporated metal precursors into the catalyst. The experimental results indicated that the addition of Fe with 0.05 wt% to the metal-free catalyst significantly improved its ORR activity [68]. Pumera and co-workers found that a Mn content of 0.0018 wt% in graphene was sufficient to enhance the electrocatalytic properties toward the ORR. In addition, they claimed that the elemental analysis of the metal contents should be provided to prove that the catalyst is "metal-free" [69]. Recently, we prepared a catalyst for the ORR derived from *Gentiana scabra*
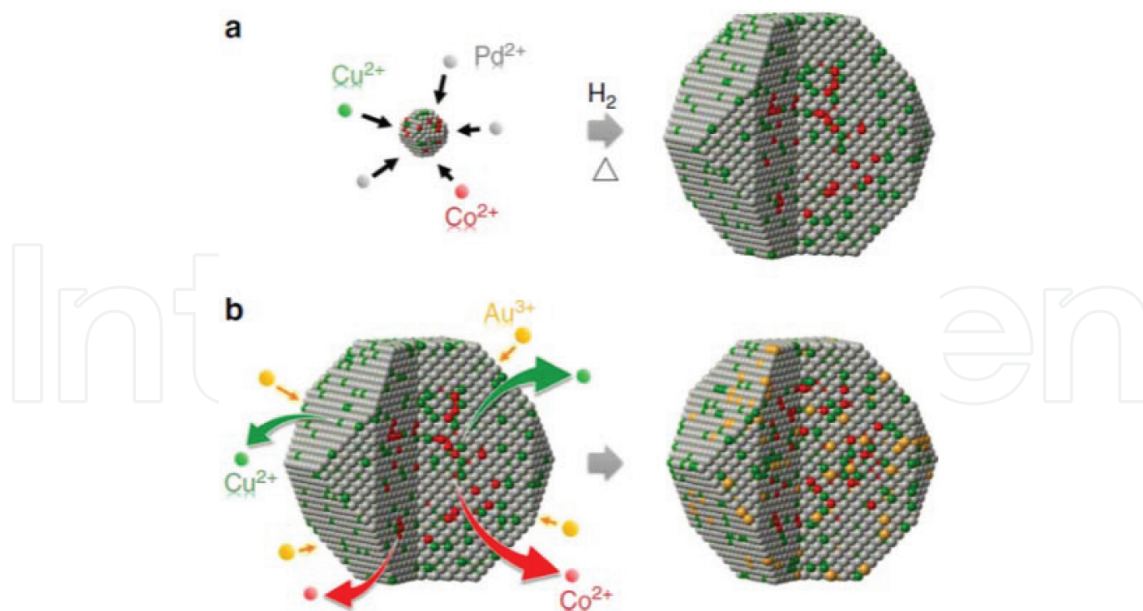
Figure 4. Schematic illustration of the formation of Pd_6CoCu/C (a) and $Au-Pd_6CoCu/C$ (b) [67].

Bunge (natural biomass) (**Figure 5**). Notably, the obtained catalyst showed an enhanced ORR activity compared with other biomass-derived carbon materials [70]. This could be partly due to the presence of intrinsic Fe species (about 744 mg kg^{-1}). Fe not only facilitates the formation of catalytically active N—C sites but also increases the graphitization degree of carbon. Another possible reason is that trace levels of Fe residues (0.07 wt%) in carbon can dramatically enhance the ORR properties.

In fact, controversy still exists over whether metal ions can function as active sites or just facilitate the formation of active sites. An understanding of active sites has been gained from experimental data and theoretical calculations [71]. An in situ poisoning experiment confirmed the existence of a metal-centered active site. For example, in the presence of CN^-, the redox couple of Co(III)/Co(II) dramatically changed because CN^- coordinated with the transition metal in the axial position. The blocking effect prevented the interaction of O_2 with the transition metal and hence reduced the electrocatalytic activity [72]. Similarly, H_2S has also been used in an in situ poisoning experiment. A significant deactivation of Fe—N—C catalysts for ORR was observed after the H_2S treatment due to the formation of Fe—S bonds. In addition, the XPS characterization indicated the existence of Fe—S type bonds. These results showed that Fe was indeed active sites in catalyzing ORR [73].

The experimental results indeed proved that trace metal residues enhanced the ORR activity. Here comes the question: "How metal-free are metal-free catalysts?" [68]. Pumera and co-workers investigate the electrochemical response of carbon nanotubes with different metallic impurities. They found that 100 ppm of Fe impurities (close to the detection limit) still dominated the electrochemical behavior of a CNT sample [74]. Therefore, definitive proof of metal-free catalysts is necessary. In addition, we highly suggest that there is no need to argue whether trace metal residue promotes the ORR activity. The abovementioned results clarify this.

Figure 5. Schematic procedure for the synthesis of heteroatom doped porous carbon materials derived from Gentiana scabra Bunge [70].

Trace metal as active sites in ORR depending more on the nanostructure of carbon matrix. It is time to take the step forward toward exploration of ORR electrocatalyst with uniform open cavities and ordering distribution of the trace metal.

3. Conclusion(s)

Cathode catalysts meet the criteria of promising ORR performance, high stability, high durability, and low cost and are highly desirable for automotive applications. The development of novel strategies for the rational design and synthesis of catalysts for meeting these performance goals is very important. Furthermore, it is significantly important to develop a theoretical and experiment-based in-depth understanding of the nature of active sites together with the underlying mechanism of the ORR. Close attention should be paid to catalysts with high ORR activities under alkaline, acidic, and neutral conditions.

Metal atoms, metal alloys, metal oxide/nitride/sulfide nanoparticles, non-metal heteroatoms (e.g., N, S, B, and P), and even topological defects and edges of the carbon support can serve as potential active sites. Assisted by theoretical calculations, the catalytic mechanism of the ORR can be easily predicted; thus, the rational design and synthesis of catalysts become more efficient. In addition, the composition, size, dispersion, morphology, and structure of the nanoparticles, the contents of the heteroatoms, as well as the nanostructure of the carbon support are probably influential in the ORR. Therefore, the precise control of the structure, electronic state, and density of the active sites at the atomistic level are favorable for achieving an optimum ORR performance. Probing the role of trace metals in the ORR further guides future research activities, thereby reducing the cost and dramatically improving the ORR performance.

For practical applications, the reduction in the cost of electrocatalyst is an important factor. Future studies should focus on the design and synthesis of platinum group metal (PGM)-free cathode catalysts achieving high efficiency and durability along with low costs. The 2020 target for PGM-free catalyst activity proposed by the Department of Energy (DOE) is to achieve 0.044 A/cm^2 @ 0.9 V$_{IR\text{-free}}$ and a durability of 5000 h [75]. Overall, a bright future awaits for cathode catalysts.

Acknowledgements

Acronyms and abbreviations

ORR	Oxygen reduction reaction
PEM	Proton exchange membrane
Pt/C	Platinum/carbon black catalyst
CB	Carbon black
CNT	Carbon nanotube
XPS	X-ray photoelectron spectroscopy

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