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

Winston Duo Wu and Dan Xu

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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
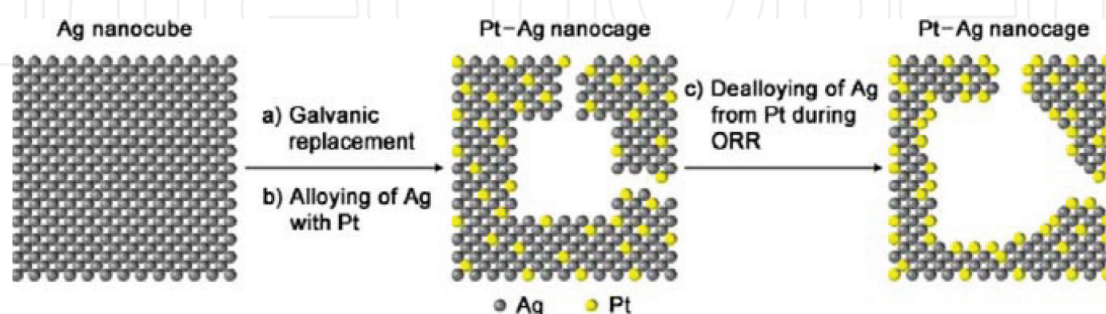


**Figure 1.** Schematic illustration depicting the major steps involved in the formation of Pt—Ag nanocages with high ORR activity: (a, b) alloying of Ag with Pt to generate Pt—Ag nanocages during the galvanic replacement reaction between Ag and a Pt(II) precursor and (c) dealloying of Ag from Pt during 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$_3$C [31, 32], and Fe$_3$O$_4$ [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$_3$C@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$_3$C@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$_3$O$_4$ 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$_3$O$_4$. 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].
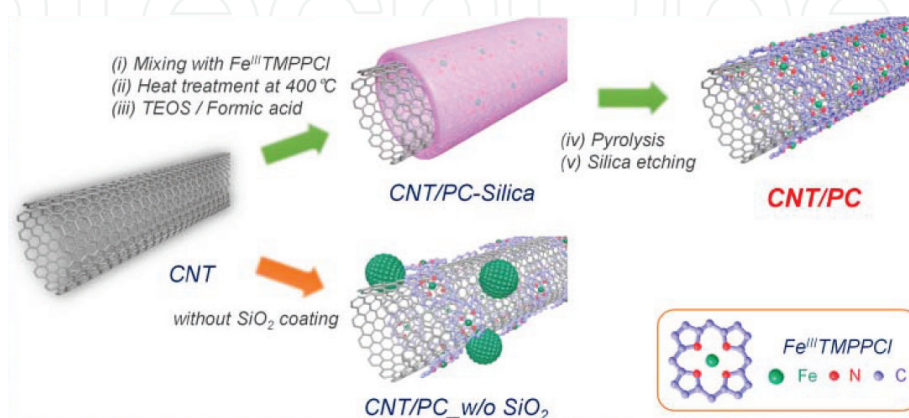


**Figure 2.** Synthetic scheme for the preparation of CNT/PC catalysts [32].

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
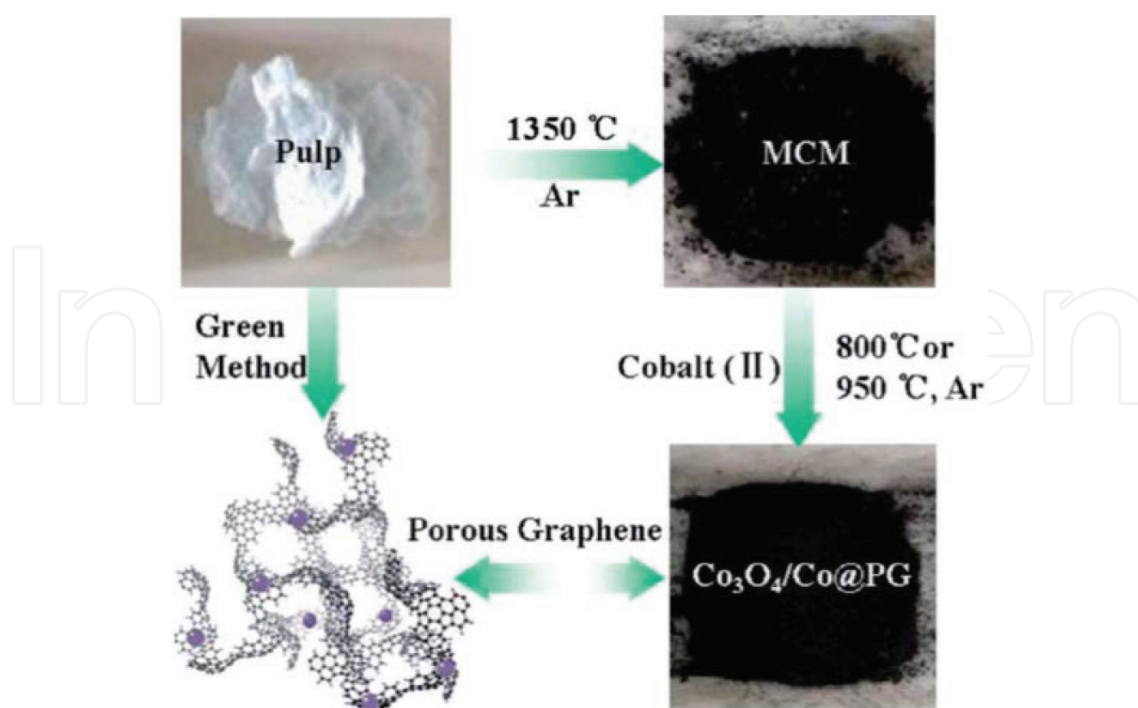


**Figure 3.** Schematic procedure for the preparation of functional porous graphene ($Co_3O_4$/Co@PG) from waste paper (MCM stands for microporous carbonaceous material and PG stands for porous graphene) [40].

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*
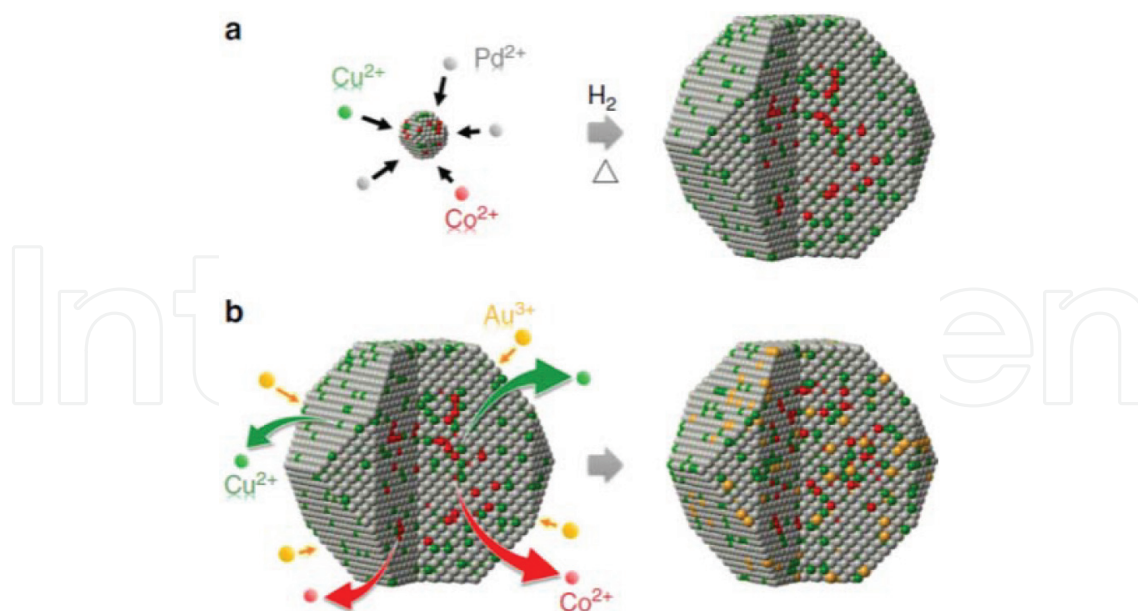
**Figure 4.** Schematic illustration of the formation of Pd$_6$CoCu/C (a) and Au-Pd$_6$CoCu/C (b) [67].

*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$_2$S 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$_2$S 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$_{\text{IR-free}}$ 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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## References

[1] Shao MH, Chang QW, Dodelet JP, Chenitz R. Recent advances in Electrocatalysts for oxygen reduction reaction. Chemical Reviews. 2016;**116**:3594-3657. DOI: 10.1021/acs.chemrev.5b00462

[2]  Qiao M, Tang C, Tanase LC, Teodorescu CM, Chen CM, Zhang Q, Titirici MM. Oxygeno-philic ionic liquids promote the oxygen reduction reaction in Pt-free carbon electrocatalysts. Materials Horizons. 2017;**4**:895-899. DOI: 10.1039/c7mh00298j

[3]  Zagal JH, Koper MTM. Reactivity descriptors for the activity of molecular MN4 catalysts for the oxygen reduction reaction. Angewandte Chemie, International Edition. 2016;**55**:14510-14521. DOI: 10.1002/anie.201604311

[4]  Zhang GR, Munoz M, Etzold BJM. Accelerating oxygen-reduction catalysts through preventing poisoning with non-reactive species by using hydrophobic ionic liquids. Angewandte Chemie, International Edition. 2016;**55**:2257-2261. DOI: 10.1002/anie.201508338

[5]  Sui S, Wang XY, Zhou XT, Suc YH, Riffatc S, Liu CJ. A comprehensive review of Pt electrocatalysts for oxygen reduction reaction: Nanostructure, activity, mechanism and carbon support in PEM fuel cells. Journal of Materials Chemistry A. 2017;**5**:1808-1825. DOI: 10.1039/c6ta08580f

[6]  Yang X, Roling LT, Vara M, Elnabawy AO, Zhao M, Hood ZD, Bao SX, Mavrikakis M, Xia Y. Synthesis and characterization of Pt−Ag alloy nanocages with enhanced activity and durability toward oxygen reduction. Nano Letters. 2016;**16**:6644-6649. DOI: 10.1021/acs.nanolett.6b03395

[7]  Zhou YZ, Yang J, Zhu CZ, Du D, Cheng XN, Yen CH, Wai CM, Lin YH. Newly designed graphene cellular monolith functionalized with hollow Pt-M (M = Ni, Co) nanoparticles as the electrocatalyst for oxygen reduction reaction. ACS Applied Materials & Interfaces. 2016;**8**:25863-25874. DOI: 10.1021/acsami.6b04963

[8]  Jiang KZ, Shao Q, Zhao DD, Bu LZ, Guo J, Huang XQ. Phase and composition tuning of 1D platinum-nickel nanostructures for highly efficient electrocatalysis. Advanced Functional Materials. 2017;**27**:1700830. DOI: 10.1002/adfm.201700830

[9]  Jia QY, Ghoshal S, Li JK, Liang WT, Meng GN, Che HY, Zhang SM, Mad ZF, Mukerjee S. Metal and metal oxide interactions and their catalytic consequences for oxygen reduction reaction. Journal of the American Chemical Society. 2017;**139**:7893-7903. DOI: 10.1021/jacs.7b02378

[10]  Tian XL, Luo JM, Nan HX, Zou HB, Chen R, Shu T, Li XH, Li YW, Song HY, Liao SJ, Adzic RR. Transition metal nitride coated with atomic layers of Pt as a low-cost, highly stable electrocatalyst for the oxygen reduction reaction. Journal of the American Chemical Society. 2016;**138**:1575-1583. DOI: 10.1021/jacs.5b11364

[11]  Du L, Du CY, Chen GY, Kong FP, Yin GP, Wang Y. Metal-organic coordination networks: Prussian blue and its synergy with Pt nanoparticles to enhance oxygen reduction kinetics. ACS Applied Materials & Interfaces. 2016;**8**:15250-15257. DOI: 10.1021/acsami.6b02630

[12]  Tong XL, Chen S, Guo CX, Xia XH, Guo XY. Mesoporous $NiCo_2O_4$ nanoplates on three-dimensional graphene foam as an efficient electrocatalyst for the oxygen reduction

reaction. ACS Applied Materials & Interfaces. 2016;**8**:28274-28282. DOI: 10.1021/acsami. 5b10044

[13] Xia Z, An L, Chen P, Xia D. Non-Pt nanostructured catalysts for oxygen reduction reaction: Synthesis, catalytic activity and its key factors. Advanced Energy Materials. 2016;**1600458**:1-29. DOI: 10.1002/aenm.201600458

[14] Paraknowitsch JP, Thomas A. Doping carbons beyond nitrogen: An overview of advanced heteroatom doped carbons with boron, sulphur and phosphorus for energy applications. Energy & Environmental Science. 2013;**6**:2839-2855. DOI: 10.1039/c3ee41444b

[15] Perivoliotis DK, Tagmatarchis N. Recent advancements in metal-based hybrid electrocatalysts supported on graphene and related 2D materials for the oxygen reduction reaction. Carbon. 2017;**118**:493-510. DOI: 10.1016/j.carbon.2017.03.073

[16] Hu PG, Liu K, Deming CP, Chen SW. Multifunctional graphene-based nanostructures for efficient electrocatalytic reduction of oxygen. Journal of Chemical Technology and Biotechnology. 2015;**90**:2132-2151. DOI: 10.1002/jctb.4797

[17] Lee WJ, Maiti UN, Lee JM, Lim J, Han TH, Kim SO. Nitrogen-doped carbon nanotubes and graphene composite structures for energy and catalytic applications. Chemical Communications. 2014;**50**:6818-6830. DOI: 10.1039/c4cc00146j

[18] He YF, Gehrig D, Zhang F, Lu CB, Zhang C, Cai M, Wang YY, Laquai F, Zhuang XD, Feng XL. Highly efficient electrocatalysts for oxygen reduction reaction based on 1D ternary doped porous carbons derived from carbon nanotube directed conjugated microporous polymers. Advanced Functional Materials. 2016;**26**:8255-8265. DOI: 10.1002/ adfm.201603693

[19] Zhu CZ, Li H, Fu SF, Du D, Lin YH. Highly efficient nonprecious metal catalysts towards oxygen reduction reaction based on three-dimensional porous carbon nanostructures. Chemical Society Reviews. 2016;**45**:517-531. DOI: 10.1039/c5cs00670h

[20] Tang C, Wang HF, Chen X, Li BQ, Hou TZ, Zhang BS, Zhang Q, Titirici MM, Wei F. Topological defects in metal-free nanocarbon for oxygen electrocatalysis. Advanced Materials. 2016;**28**:6845-6851. DOI: 10.1002/adma.201601406

[21] Tang C, Zhang Q. Nanocarbon for oxygen reduction electrocatalysis: Dopants, edges, and defects. Advanced Materials. 2017;**29**:1604103. DOI: 10.1002/adma.201604103

[22] Suna T, Tian BB, Lu J, Su CL. Recent advances of Fe (or co)/N/C electrocatalysts for oxygen reduction reaction in polymer electrolyte membrane fuel cells. Journal of Materials Chemistry A. 2017;**5**:18933-18950. DOI: 10.1039/c7ta04915c

[23] Fu SF, Zhu CZ, Song JH, Du D, Lin YH. Metal-organic framework-derived non-precious metal nanocatalysts for oxygen reduction reaction. Advanced Energy Materials. 2017;**7**:1700363. DOI: 10.1002/aenm.201700363

[24] He DS, He DP, Wang J, Lin Y, Yin PQ, Hong X, Wu YE, Li YD. Ultrathin icosahedral Pt-enriched nanocage with excellent oxygen reduction reaction activity. Journal of the American Chemical Society. 2016;**138**:1494-1497. DOI: 10.1021/jacs.5b12530

[25] Gimenez-Lopez MC, Kurtoglu A, Walsh DA, Khlobystov AN. Extremely stable platinum-amorphous carbon electrocatalyst within hollow graphitized carbon nanofibers for the oxygen reduction reaction. Advanced Materials. 2016;**28**:9103-9108. DOI: 10.1002/adma.201602485

[26] Jia QY, Ghoshal S, Li JK, Liang WT, Meng GN, Che HY, Zhang SM, Ma ZF, Mukerjee S. Metal and metal oxide interactions and their catalytic consequences for oxygen reduction reaction. Journal of the American Chemical Society. 2017;**139**:7893-7903. DOI: 10.1021/jacs.7b02378

[27] Huang HW, Li K, Chen Z, Luo LH, Gu YQ, Zhang DY, Ma C, Si R, Yang JL, Peng ZM, Zeng J. Achieving remarkable activity and durability toward oxygen reduction reaction based on ultrathin Rh-doped Pt nanowires. Journal of the American Chemical Society. 2017;**139**:8152-8159. DOI: 10.1021/jacs.7b01036

[28] Wang BW, Wang XX, Zou JX, Yan YC, Xie SH, Hu GZ, Li YG, Dong AG. Simple-cubic carbon frameworks with atomically dispersed iron dopants toward high-efficiency oxygen reduction. Nano Letters. 2017;**17**:2003-2009. DOI: 10.1021/acs.nanolett.7b00004

[29] Ren SB, Wang J, Xia XH. Highly efficient oxygen reduction electrocatalyst derived from a new three-dimensional polyporphyrin. ACS Applied Materials & Interfaces. 2016;**8**:25875-25880. DOI: 10.1021/acsami.6b05560

[30] Chen PZ, Zhou TP, Xing LL, Xu K, Tong Y, Xie H, Zhang LD, Yan WS, Chu WS, Wu CZ, Xie Y. Atomically dispersed iron–nitrogen species as electrocatalysts for bifunctional oxygen evolution and reduction reactions. Angewandte Chemie, International Edition. 2017;**56**:610-614. DOI: 10.1002/anie.201610119

[31] Kim JH, Sa YJ, Jeong HY, Joo SH. Roles of Fe−Nx and Fe−Fe$_3$C@C species in Fe−N/C electrocatalysts for oxygen reduction reaction. ACS Applied Materials & Interfaces. 2017;**9**:9567-9575. DOI: 10.1021/acsami.6b13417

[32] Sa YJ, Seo DJ, Woo JW, Lim JT, Cheon JY, Yang SY, Lee JM, Kang DW, Shin TJ, Shin HS, Jeong HY, Kim CS, Kim MG, Kim TY, Joo SH. A general approach to preferential formation of active Fe−Nx sites in Fe−N/C electrocatalysts for efficient oxygen reduction reaction. Journal of the American Chemical Society. 2016;**138**:15046-15056. DOI: 10.1021/jacs.6b09470

[33] Wang HT, Wang W, Xu YY, Dong S, Xiao JW, Wang F, Liu HF, Xia BY. Hollow nitrogen-doped carbon spheres with Fe$_3$O$_4$ nanoparticles encapsulated as a highly active oxygen-reduction catalyst. ACS Applied Materials & Interfaces. 2017;**9**:10610-10617. DOI: 10.1021/acsami.6b15392

[34] Xiao JW, Xia YT, Hu CC, Xi JGB, Wang S. Raisin bread-like iron sulfides/nitrogen and sulfur dual-doped mesoporous graphitic carbon spheres: A promising electrocatalyst for the oxygen reduction reaction in alkaline and acidic media. Journal of Materials Chemistry A. 2017;**5**:11114-11123. DOI: 10.1039/c7ta02096a

[35] Hu K, Tao L, Liu DD, Huo J, Wang SY. Sulfur-doped Fe/N/C nanosheets as highly efficient electrocatalysts for oxygen reduction reaction. ACS Applied Materials & Interfaces. 2016;**8**:19379-19385. DOI: 10.1021/acsami.6b02078

[36]    Zhang JW, Xu D, Wang CC, Guo JG, Yan F. Rational design of $Fe_{1-x}S/Fe_3O_4$/nitrogen and sulfur-doped porous carbon with enhanced oxygen reduction reaction catalytic activity. Advanced Materials Interfaces. 2018;**5**:1701641. DOI: 10.1002/admi.201701641

[37]    Yu HY, Fisher A, Cheng DJ, Cao DP. Cu,N-codoped hierarchical porous carbons as electrocatalysts for oxygen reduction reaction. ACS Applied Materials & Interfaces. 2016;**8**:21431-21439. DOI: 10.1021/acsami.6b04189

[38]    Volosskiy B, Fei HL, Zhao Z, Lee S, Li MF, Lin ZY, Papandrea B, Wang C, Huang Y, Duan XF. Tuning the catalytic activity of a metal-organic framework derived copper and nitrogen co-doped carbon composite for oxygen reduction reaction. ACS Applied Materials & Interfaces. 2016;**8**:26769-26774. DOI: 10.1021/acsami.6b08320

[39]    Tong Y, Chen PZ, Zhou TP, Xu K, Chu WS, Wu CZ, Xie Y. A bifunctional hybrid electrocatalyst for oxygen reduction and evolution: Cobalt oxide nanoparticles strongly coupled to B,N-decorated graphene. Angewandte Chemie, International Edition. 2017;**56**:1-6. DOI: 10.1002/anie.201702430

[40]    Xu D, Xie Y, Song YJ, Deng WQ. A green and facile method toward synthesis of waste paper-derived 3D functional porous graphene via in situ activation of cobalt(II). Journal of Materials Chemistry A. 2015;**3**:16072-16078. DOI: 10.1039/c5ta03220b

[41]    Yin PQ, Yao T, Wu Y, Zheng LR, Lin Y, Liu W, Ju HX, Zhu JF, Hong X, Deng ZX, Zhou G, Wei SQ, Li YD. Single cobalt atoms with precise N-coordination as superior oxygen reduction reaction catalysts. Angewandte Chemie, International Edition. 2016;**55**:10800-10805. DOI: 10.1002/anie.201604802

[42]    Li B, Nam H, Zhao J, Chang J, Lingappan N, Yao F, Lee TH, Lee YH. Nanoreactor of nickel-containing carbon–shells as oxygen reduction catalyst. Advanced Materials. 2017;**29**:1605083. DOI: 10.1002/adma.201605083

[43]    Schöfberger W, Faschinger F, Chattopadhyay S, Bhakta S, Mondal B, Elemans JAAW, Müllegger S, Tebi S, Koch R, Klappenberger F, Paszkiewicz M, Barth JV, Rauls E, Aldahhak H, Schmidt WG, Dey A. A bifunctional electrocatalyst for oxygen evolution and oxygen reduction reactions in water. Angewandte Chemie, International Edition. 2016;**55**:2350-2355. DOI: 10.1002/anie.201508404

[44]    Song P, Luo M, Liu XZ, Xing W, Xu WL, Jiang Z, Gu L. Zn single atom catalyst for highly efficient oxygen reduction reaction. Advanced Functional Materials. 2017;**27**:1700802. DOI: 10.1002/adfm.201700802

[45]    Ma M, You SJ, Wang W, Liu GS, Qi DP, Chen XD, Qu JH, Ren NQ. Biomass-derived porous $fe_3c$/tungsten carbide/graphitic carbon nanocomposite for efficient electrocatalysis of oxygen reduction. ACS Applied Materials & Interfaces. 2016;**8**:32307-32316. DOI: 10.1021/acsami.6b10804

[46]    Wei C, Feng ZX, Scherer GG, Barber J, Shao-Horn Y, Xu ZJ. Cations in octahedral sites: A descriptor for oxygen electrocatalysis on transition-metal spinels. Advanced Materials. 2017;**29**:1606800. DOI: 10.1002/adma.201606800

[47] Xue HR, Tang J, Gong H, Guo H, Fan XL, Wang T, He JP, Yamauchi Y. Fabrication of PdCo bimetallic nanoparticles anchored on three-dimensional ordered N-doped porous carbon as an efficient catalyst for oxygen reduction reaction. ACS Applied Materials & Interfaces. 2016;**8**:20766-20771. DOI: 10.1021/acsami.6b05856

[48] Chen Y, Chen Y, Ding D, Ding Y, Choi YM, Zhang L, Yoo S, Chen DC, deGlee B, Xu H, Lu QY, Zhao B, Vardar GL, Wang JY, Bluhm H, Crumlin EJ, Yang CH, Liu J, Yildiz B, Liu ML. A robust and active hybrid catalyst for facile oxygen reduction in solid oxide fuel cells. Energy & Environmental Science. 2017;**10**:964-971. DOI: 10.1039/c6ee03656b

[49] He B, Ren ZJ, Qi CZ, Yan SK, Wang ZH. Synthesis of nitrogen-doped monolayer graphene with high transparent and n-type electrical properties. Journal of Materials Chemistry C. 2015;**3**:6172-6177. DOI: 10.1039/C5TC01046B

[50] Li OL, Chiba S, Wada Y, Panomsuwan G, Ishizaki T. Synthesis of graphitic-N and amino-N in nitrogendoped carbon via a solution plasma process and exploration of their synergic effect for advanced oxygen reduction reaction. Journal of Materials Chemistry A. 2017;**5**:2073-2082. DOI: 10.1039/c6ta08962c

[51] Cui XY, Yang SB, Yan XX, Leng JG, Shuang S, Ajayan PM, Zhang ZJ. Pyridinic-nitrogen-dominated graphene aerogels with Fe-N-C coordination for highly efficient oxygen reduction reaction. Advanced Functional Materials. 2016;**26**:5708-5717. DOI: 10.1002/adfm.201601492

[52] Yu HJ, Shang L, Bian T, Shi R, Waterhouse GIN, Zhao YF, Zhou C, Wu LZ, Tung CH, Zhang T. Nitrogen-doped porous carbon nanosheets templated from g-$C_3N_4$ as metal-free electrocatalysts for efficient oxygen reduction reaction. Advanced Materials. 2016;**28**:5080-5086. DOI: 10.1002/adma.201600398

[53] Li Q, Xu D, Guo JN, Ou X, Yan F. Protonated g-$C_3N_4$@polypyrrole derived N-doped porous carbon for supercapacitors and oxygen electrocatalysis. Carbon. 2017;**124**:599-610. DOI: 10.1016/j.carbon.2017.09.029

[54] Li Q, Xu D, Ou X, Yan F. Nitrogen-doped graphitic porous carbon nanosheets derived from in situ formed g-$C_3N_4$ templates for the oxygen reduction reaction. Chemistry, an Asian Journal. 2017;**12**:1816-1823. DOI: 10.1002/asia.201700586

[55] Panomsuwan G, Saito N, Ishizaki T. Nitrogen-doped carbon nanoparticle–carbon nanofiber composite as an efficient metal-free cathode catalyst for oxygen reduction reaction. ACS Applied Materials & Interfaces. 2016;**8**:6962-6971. DOI: 10.1021/acsami.5b10493

[56] Zhu X, Zhu YH, Tian CC, Jin T, Yang XJ, Jin XB, Li CZ, Wang HL, Liu HL, Dai S. Pyrolysis of conjugated nanoporous polycarbazoles to mesoporous N-doped carbon nanotubes as efficient electrocatalysts for the oxygen reduction reaction. Journal of Materials Chemistry A. 2017;**5**:4507-4512. DOI: 10.1039/c6ta09604b

[57] He B, Liu F, Yan S. Temperature-directed growth of highly pyridinic nitrogen doped, graphitized, ultra-hollow carbon frameworks as an efficient electrocatalyst for the oxygen reduction reaction. Journal of Materials Chemistry A. 2017;**5**:18064-18070. DOI: 10.1039/c7ta04685e

[58] Hu CG, Dai LM. Multifunctional carbon-based metal-free electrocatalysts for simultaneous oxygen reduction, oxygen evolution, and hydrogen evolution. Advanced Materials. 2017;**29**:1604942. DOI: 10.1002/adma.201604942

[59] Zhang JT, Qu LT, Shi GQ, Liu JY, Chen JF, Dai LM. N,P-Codoped carbon networks as efficient metal-free bifunctional catalysts for oxygen reduction and hydrogen evolution reactions. Angewandte Chemie, International Edition. 2016;**55**:2230-2234. DOI: 10.1002/anie.201510495

[60] Mulyadi A, Zhang Z, Dutzer M, Liu W, Deng YL. Facile approach for synthesis of doped carbon electrocatalyst from cellulose nanofibrils toward high-performance metal-free oxygen reduction and hydrogen evolution. Nano Energy. 2017;**32**:336-346. DOI: 10.1016/j.nanoen.2016.12.057

[61] Pei ZX, Gu JX, Wang YK, Tang ZJ, Liu ZX, Huang Y, Huang Y, Zhao JX, Chen ZF, Zhi CY. Component matters: Paving the roadmap toward enhanced electrocatalytic performance of graphitic $C_3N_4$-based catalysts via atomic tuning. ACS Nano. 2017;**11**:6004-6014. DOI: 10.1021/acsnano.7b01908

[62] Banks CE, Crossley A, Salter C, Wilkins SJ, Compton RG. Carbon nanotubes contain metal impurities which are responsible for the "Electrocatalysis" seen at some nanotube-modified electrodes. Angewandte Chemie, International Edition. 2006;**45**:2533. DOI: 10.1002/anie.200600033

[63] Wong CHA, Chua CK, Khezri B, Webster RD, Pumera M. Graphene oxide nanoribbons from the oxidative opening of carbon nanotubes retain electrochemically active metallic impurities. Angewandte Chemie, International Edition. 2013;**52**:8685. DOI: 10.1002/anie.201303837

[64] Guo ZY, Jiang CC, Teng C, Ren GY, Zhu Y, Jiang L. Sulfur, trace nitrogen and iron codoped hierarchically porous carbon foams as synergistic catalysts for oxygen reduction reaction. ACS Applied Materials & Interfaces. 2014;**6**:21454-21460. DOI: 10.1021/am506459f

[65] Liu SF, Han LL, Zhu J, Xiao WP, Wang J, Liu HF, Xin HL, Wang DL. Enhanced electrocatalytic activity and stability of $Pd_3V/C$ nanoparticles with a trace amount of Pt decoration for the oxygen reduction reaction. Journal of Materials Chemistry A. 2015;**3**:20966-20972. DOI: 10.1039/c5ta05202e

[66] Lu BA, Sheng T, Tian N, Zhang ZC, Xiao C, Cao ZM, Ma HB, Zhou ZY, Sun SG. Octahedral PtCu alloy nanocrystals with high performance for oxygen reduction reaction and their enhanced stability by trace Au. Nano Energy. 2016;**33**:65-71. DOI: 10.1016/j.nanoen.2017.01.003

[67] Wang DL, Liu SF, Wang J, Lin RQ, Kawasaki M, Rus E, Silberstein KE, Lowe MA, Lin F, Nordlund D, Liu HF, Muller DA, Xin HL, Abruña HD. Spontaneous incorporation of gold in palladium-based ternary nanoparticles makes durable electrocatalysts for oxygen reduction reaction. Nature Communications. 2016;**7**:11941. DOI: 10.1038/ncomms11941

[68] Masa J, Zhao AQ, Xia W, Sun ZY, Mei B, Muhler M, Schuhmann W. Trace metal residues promote the activity of supposedly metal-free nitrogen-modified carbon catalysts for the oxygen reduction reaction. Electrochemistry Communications. 2013;**34**:113-116. DOI: 10.1016/j.elecom.2013.05.032

[69] Wang L, Ambrosi A, Pumera M. "Metal-free" catalytic oxygen reduction reaction on heteroatom-doped graphene is caused by trace metal impurities. Angewandte Chemie, International Edition. 2013;**52**:13818-13821. DOI: 10.1002/anie.201309171

[70] Wang CC, Wu WD, Wang Y, Xu D, Yan F. Nitrogen doped carbon materials derived from Gentiana scabra Bunge as high-performance catalysts for the oxygen reduction reaction. New Journal of Chemistry. 2017;**41**:7392-7399. DOI: 10.1039/c7nj01178d

[71] Malko D, Kucernak A, Lopes T. Performance of Fe-N/C oxygen reduction Electrocatalysts toward $NO_2$-, NO, and $NH_2OH$ electroreduction: From fundamental insights into the active center to a new method for environmental nitrite destruction. Journal of the American Chemical Society. 2016;**138**:16056-16068. DOI: 10.1021/jacs.6b09622

[72] Gupta S, Fierro C, Yeager E. The effects of cyanide on the electrochemical properties of transition-metal macrocycles for oxygen reduction in alkaline-solutions. Journal of Electroanalytical Chemistry. 1991;**306**:239-250. DOI: 10.1016/0022-0728(91)85233-F

[73] Singh D, Mamtani K, Bruening CR, Miller JT, Ozkan US. Use of $H_2S$ to probe the active sites in FeNC catalysts for the oxygen reduction reaction (ORR) in acidic media. ACS Catalysis. 2014;**4**:3454-3462. DOI: 10.1021/cs500612k

[74] Pumera M, Miyahara Y. What amount of metallic impurities in carbon nanotubes is small enough not to dominate their redox properties? Nanoscale. 2009;**1**:260-265. DOI: 10.1039/b9nr00071b

[75] Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan. November 2016. https://www.energy.gov/sites/prod/files/2017/05/f34/fcto_myrdd_fuel_cells.pdf