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Heteroatom-Doped Carbon Nanotubes as Advanced Electrocatalysts for Oxygen Reduction Reaction

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1.1

Introduction

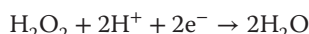
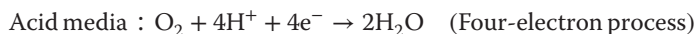
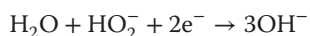
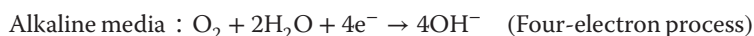
With the diminishing fossil fuels and even increasing demand on energy resources as well as the growing environmental concerns, the development of clean and sustainable energy conversion and storage systems with high efficiency at low cost has attracted intense research interests [1–3]. Fuel cells and metal-air batteries are promising energy devices with unique properties, such as large theoretical specific energy (up to 3600 W h kg^{-1} for Li–O₂ battery). However, implementing these energy technologies in our daily life requires highly effective, but low-cost, electrocatalysts to efficiently reduce O₂ [4]. Specifically, both fuel cells and metal-air batteries involve oxygen reduction reaction (ORR) at the cathode [5–11]. Pt/C catalysts are generally used as electrocatalysts for the sluggish ORR. However, the scarcity and high cost of platinum pose one of the major concerns that have precluded fuel cells from commercial applications [12].

Carbon materials with unique structures, including zero-dimensional (0D) fullerenes, one-dimensional (1D) carbon nanotubes (CNTs), two-dimensional (2D) graphene, and three-dimensional (3D) graphite, are of particular interest because of their desirable properties, including excellent electrical conductivity, controllable porosity, and electrocatalytic activity, and high mechanical strength [13]. Owing to their wide availability, environmental acceptability, corrosion resistance, and unique surface and bulk properties, CNTs are ideal candidates as efficient ORR catalysts [2, 14–17]. In this regard, doping CNTs with nitrogen has been demonstrated to transfer the inert carbon surface to more active electrocatalytic sites for ORR [10, 11]. Recently, substantial progress has been made to understand the doping process associated with doped CNTs. As a result, a number of significant breakthroughs have been witnessed in the development of metal-free carbon-based ORR electrocatalysts [2]. This chapter begins with a brief description of the ORR principles, which is followed by a summary of recent work on the rational preparation of carbon-based ORR electrocatalysts for potential applications. Finally, various heteroatom (N, B, P, S)-doped CNTs are discussed in order to correlate their ORR activities with the syntheses and structures.

1.2

Experimental Evaluation of Electrocatalytic Activity toward ORR

In an aqueous solution, the complete oxygen reduction goes through either a two-electron transfer process with hydrogen peroxide as the intermediate, followed by further reduction to OH^- /water or a more efficient four-electron transfer to produce water directly. As shown below, the two-electron and four-electron reduction processes can occur in both alkaline and acid media [18]:



To evaluate the electrocatalytic activity of catalysts, especially for ORR in aqueous electrolytes, the most commonly used techniques are rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) coupling with linear scan voltammetry (Figure 1.1) [19]. The current of ORR is dependent on the kinetic current (I_k) and diffusion-limiting current (I_d). Kinetic current is determined by the reaction kinetic process. However, the slow mass transport of the reactants (e.g., O_2) from the bulk of electrolyte solution to the electrode surface results in the formation of a concentration profile of the reactants in

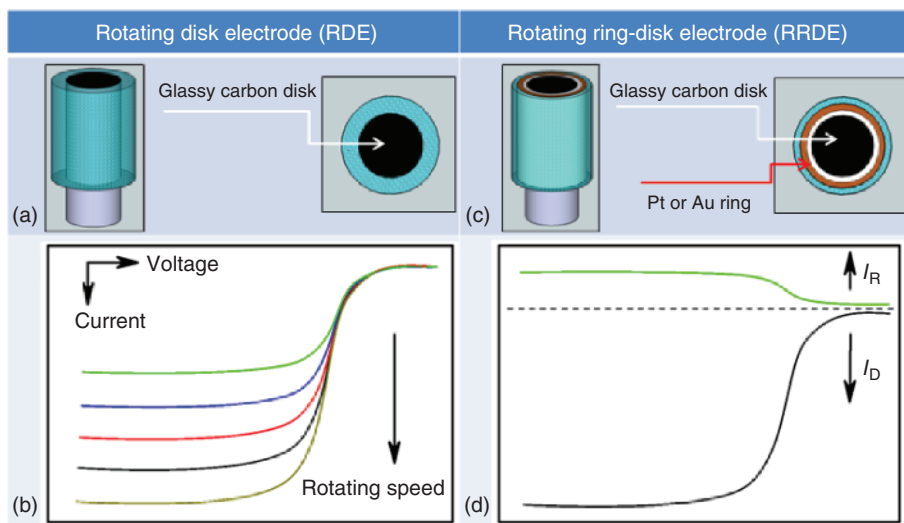


Figure 1.1 Configuration of RDE (a) and RRDE (c). Linear sweep voltammogram (LSV) curves of electrocatalysts in oxygen-saturated electrolyte with different rotating speeds (b). Typical oxygen reduction curves on the disc and ring electrodes, respectively (d).

front of the electrode surface. If the applied overpotential is high enough, every atom/ion reaching the electrode reacts immediately, resulting in nearly zero concentration at the surface, leading to a diffusion-limiting current density, which is only determined by the rate of diffusion. RDE is used to separate the diffusion and the kinetic currents of ORR. In a RDE, rotating movement leads to convection, and subsequently determines the thickness of the diffusion layer. As the diffusion rate is dependent on the rotating speed, the diffusion-limiting current is determined by the rate at which the reactant diffuses to the surface of the electrode, and hence also depends on the rotating speed. When the small effect of a Nafion film on diffusion is neglected for the rotating electrode, the overall measured current, J , can be expressed as being dependent on the kinetic current (J_k) and the diffusion-limiting current (J_d), which can be expressed in terms of the Koutecky–Levich equation as follows [20]:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_d} = \frac{1}{J_k} + \frac{1}{B\omega^{1/2}},$$

where ω is the electrode rotating rate. B is determined from the slope of the Koutecky–Levich plot based on the Levich equation as given below:

$$B = 0.2nF(D_{O_2})^{2/3}\nu^{-1/6}C_{O_2},$$

in which n represents the transferred electron number per oxygen molecule, F is Faraday constant ($F = 96\,485\text{ C mol}^{-1}$), D_{O_2} is the diffusion coefficient of O_2 in electrolyte, ν is the kinetic viscosity, C_{O_2} is the bulk concentration or solubility of O_2 . These parameters are listed in Table 1.1. The constant 0.2 is adopted when the rotation speed is expressed in revolutions per minute.

Figure 1.1b shows the typical linear sweep voltammogram (LSV) curves of ORR tested on RDE at various rotating speeds. The diffusion-limiting current increases with increasing rotating speed, which is associated with the increase of oxygen diffusion to and reduction at the electrode surface. At high overpotentials, the oxygen reduction is fast enough that a flat limiting plateau is achieved (Figure 1.1b). It is explained that the current plateau could be associated to the distribution of the electrocatalytic sites on the electrode surfaces. Typically, the uniform distribution of active sites leads to the well-defined current plateau at the diffusion-limiting region. By contrast, the distribution of active sites is less uniform and the

Table 1.1 The parameters of commonly used electrolytes.

Electrolyte 25 °C, 1 atm O_2	Diffusion coefficient of O_2 ($D_{O_2} \times 10^{-5}$, cm^2s^{-1})	Kinetic viscosity ($\nu \times 10^{-5}$, cm^2s^{-1})	Bulk concentration of O_2 ($C_{O_2} \times 10^{-6}$, mol cm^{-3})	References
0.1 M HClO_4	1.93	1.01	1.26	[21]
0.5 M H_2SO_4	1.40	1.00	1.10	[22]
0.1 M KOH	1.90	1.00	1.20	[23]
0.5 M KOH	1.68	1.06	1.03	[24]
1 M KOH	1.43	1.13	0.84	[24]
1 M NaOH	1.65	1.10	0.84	[25]

electrocatalytic reaction is slower, the current plateau is more inclined [26]. The transferred electron number and kinetically controlled currents can be obtained by Koutecky–Levich plots, in which the diffusion limitations can be eliminated. For the Tafel plot, the kinetic current is calculated from the mass transport correction of RDE by $J_k = J \times J_d / (J_d - J)$.

Alternatively, the RRDE enables to determine the kinetics and the mechanism of ORR. Accordingly, the dominated reaction on the central disc electrode is the direct reduction of O_2 to H_2O (with a four-electron charge transfer) and the potential intermediate species, hydrogen peroxide (H_2O_2), is either oxidized or reduced on the concentric ring electrode, depending on the potential of this electrode (Figure 1.1c, d). Thus, this technology can be used to quantitatively evaluate the molar proportion of produced HO_2^- on ring electrode (platinum or gold). The disc and ring currents (I_D and I_R , respectively) are recorded as a function of the disc electrode potential (Figure 1.1d). The total disk current, I_D , is the sum of the O_2 reduction currents to water, I_{H_2O} , and intermediate (H_2O_2), $I_{H_2O_2}$. The $I_{H_2O_2}$ is related to I_R through a collection efficiency (N) as follows:

$$I_D = I_{H_2O} + I_{H_2O_2} \text{ and } I_{H_2O_2} = I_R/N.$$

The H_2O_2 yield ($H_2O_2\%$) and the electron transfer number (n) are determined by the following equations [19, 27, 28], respectively:

$$H_2O_2\% = 200 \frac{I_R/N}{I_D + I_R/N}$$

$$n = 4 \frac{I_D}{I_D + I_R/N}$$

where N is current collection efficiency of the ring electrode. The collection efficiency is defined as $N = -I_R/I_D$ and is usually determined by using $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox couple [25].

1.3

Doped Carbon Nanotubes for ORR

1.3.1

Carbon Nanotubes Doped with Nitrogen

Carbon-based ORR electrocatalysts are usually obtained by doping sp^2 carbon materials with different dopants [29–32]. As a representative nanocarbon material that has been studied for more than two decades, CNTs offer several notable advantages over carbon blacks as supports for fuel cell electrocatalysts. Those advantages include, but not limited to, the improved mass transfer of reagents/products, enhanced electronic conductivity, and higher resistance to corrosion. The explosion of interest in the carbon-based metal-free ORR catalysts [33–45] started in 2009 when Dai's group [10] reported excellent four-electron ORR performance of vertically aligned nitrogen-doped carbon nanotube (VA-NCNT) arrays (Figure 1.2), which showed comparable onset

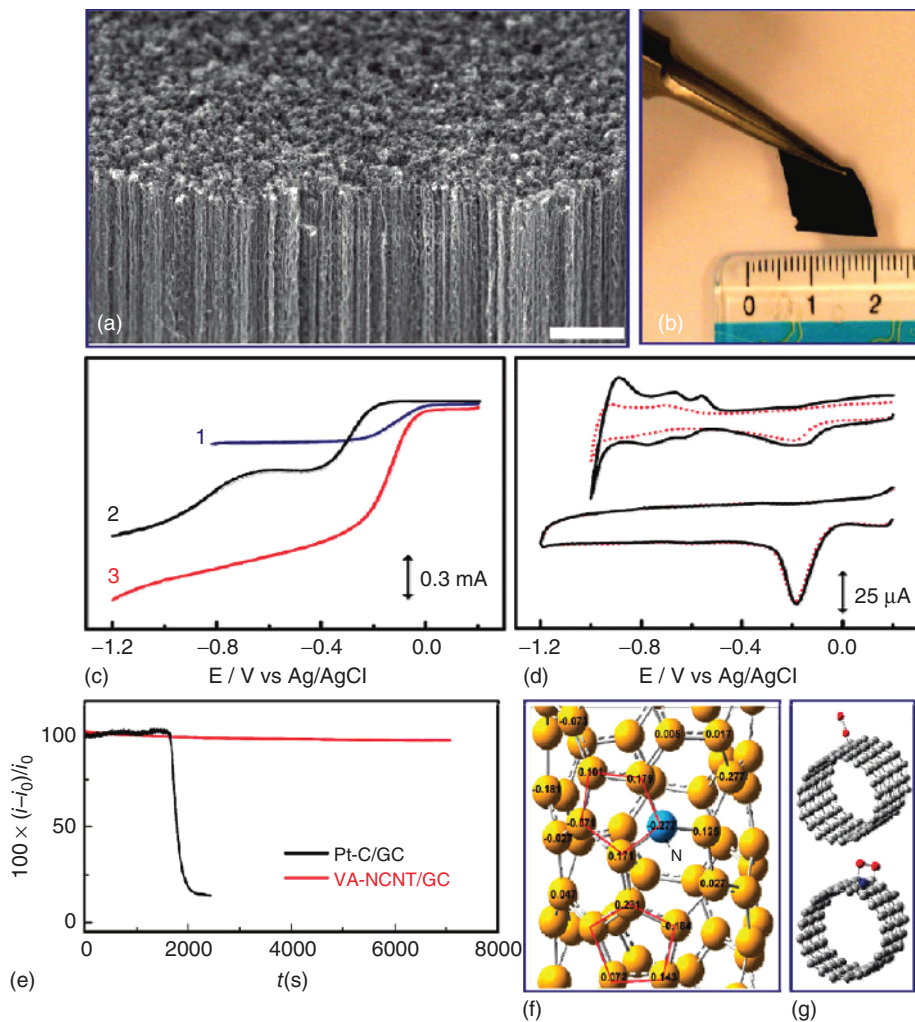


Figure 1.2 (a) SEM image of the as-synthesized VA-NCNTs on a quartz substrate. (b) Digital photograph of the VA-NCNT array after having been transferred onto a PS-nonaqueous CNT conductive nano-composite film. (c) Rotating ring-disk electrode (RRDE) voltammograms for oxygen reduction in air-saturated 0.1 M KOH at the Pt-C (curve 1), vertically aligned all-carbon carbon nanotube (VA-CCNT, curve 2), and VA-NCNT (curve 3) electrodes. (d) Cyclic voltammograms (CVs) for the ORR at the Pt-C (top) and VA-NCNT (bottom) electrodes before (solid curves) and after (dotted curves) a continuous potentiodynamic sweep for

about 100 000 cycles in air-saturated 0.1 M KOH at room temperature ($25 \pm 1^\circ\text{C}$). Scan rates: 100 mV s^{-1} . (e) The CO poisoning effect at the Pt-C (black curve) and VA-NCNT (red line) electrodes, respectively. CO gas of 55 ml/min was first added into the 550 ml/min O_2 flow, and then the mixture gas of $\sim 9\%$ CO (v/v) was introduced into the electrochemical cell at about 1700 s. (f) Calculated charge density distribution for the NCNTs. (g) Schematic representations of possible adsorption modes of an oxygen molecule at the CCNT (top) and NCNT (bottom). (Adapted from Ref. [10].)

potential to that of commercial Pt/C with a much higher reduction current density. Furthermore, the VA-NCNT catalyst exhibited high tolerance to CO poisoning and methanol oxidation (crossover effect). According to the experimental observations and theoretical calculations by B3LYP hybrid density functional theory (DFT), the improved catalytic performance is contributed to the electron-accepting ability of the nitrogen atoms, which creates net positive charge on adjacent carbon atoms in the CNT plane of VA-NCNTs (Figure 1.2f). More importantly, the nitrogen-induced charge delocalization could also change the chemisorption mode of O_2 from the usual end-on adsorption (Pauling model) at the nitrogen-free CNT surface (top, Figure 1.2g) to a side-on adsorption (Yeager model) onto the NCNT electrodes (bottom, Figure 1.2g). The N-induced charge transfer from adjacent carbon atoms could lower the ORR potential while the parallel diatomic adsorption could effectively weaken the O–O bonding, facilitating ORR at the VA-NCNT electrodes. Meanwhile, doping CNTs with nitrogen heteroatoms could also efficiently create the metal-free active sites for electrochemical reduction of O_2 . Like the doping-induced intramolecular charge transfer, intermolecular charge transfer induced by adsorption of polyelectrolyte onto all-carbon CNTs could also impart ORR catalytic activities [46]. Uncovering this ORR mechanism in the nitrogen-doped CNT electrodes is significant as the same principle could be applied to the development of various other metal-free efficient ORR catalysts for ORR applications. This seminal work is followed by many studies in order to broaden the diversity of carbon-based electrocatalysts [2, 47]. Recent research activities carried out in many laboratories, including our own one, have not only confirmed the aforementioned findings, but also further proved the important role of heteroatom doping, which has a large impact on the design and development of new catalytic materials for fuel cell applications and even beyond fuel cells [2, 14, 41–45, 48, 49].

Apart from the VA-NCNTs, a wide range of other N-doped carbon nanostructures, including graphene, carbon nanocups, and carbon nitrides, have also been developed with different morphologies and structural characteristics for ORR applications. For instance, Qu *et al.* [50] have prepared N-graphene films using a nitrogen-containing reaction gas mixture and a Ni-coated SiO_2/Si substrate. The resultant N-graphene film could be readily etched off from the substrate by dissolving Ni catalyst layer in an aqueous solution of HCl, allowing the freestanding N-graphene sheets to be transferred onto various substrates suitable for electrochemical investigation. Being only single or a few layers of graphene, the N-graphene sheets were flexible and transparent. More importantly, the N-graphene was demonstrated to act as a metal-free electrode with a much better electrocatalytic activity, long-term operation stability, and tolerance to crossover effect than platinum for oxygen reduction via a four-electron pathway in alkaline fuel cells. In addition, Shao *et al.* [51] have also synthesized nitrogen-doped graphene by exposing graphene to nitrogen plasma. It was found that N-graphene thus prepared exhibited higher ORR activity than that of Pt/C and was free from the methanol crossover effect, indicating the possibility of replacing expensive Pt with low-cost N-graphene. Star and coworkers [52]

compared the ORR activity of nitrogen-doped carbon nanotube cups (NCNCs) to those of commercial Pt-decorated multiwalled CNTs (Pt/CNTs). These NCNCs were composed of individual nanocups stacked together to form long nanofibers with a nitrogen content of 2–7 wt% and diameters in the range of 12–40 nm. NCNCs exhibited a comparable ORR electrocatalytic activity to that of Pt/CNTs in alkaline medium. Lyth *et al.* [53] have found that carbon nitride materials exhibited a higher ORR catalytic activity in acidic media than their N-free counterparts, though their current density for oxygen reduction was still low. Through uniform incorporation of carbon nitride into a mesoporous carbon to enhance the electron transfer efficiency of carbon nitride, Zheng *et al.* [41] have prepared metal-free carbon nitride@carbon composite that showed a significantly improved oxygen reduction current density for a four-electron ORR process.

As the CVD growth processes for the preparation of VA-NCNTs and N-graphene involve metal catalysts (e.g., Fe and Ni), considerable care has been taken during the electrode preparation to completely remove the catalyst residue [10, 42, 50]. Even though VA-NCNTs electrode was purified by electrochemical oxidation [10], possible effects of metal contaminants on the observed superb ORR performance could still be a matter of controversy unless nitrogen-doped carbon nanomaterials with excellent ORR electrocatalytic activities can be produced by a metal-free preparation procedure. In order to address this issue, Yu *et al.* [47] developed a simple, but very effective, plasma-etching approach for the metal-free growth of undoped and nitrogen-doped single-walled carbon nanotubes (SWCNTs). In contrast to undoped SWCNTs, the metal-free nitrogen-containing SWCNTs thus synthesized were demonstrated to show high electrocatalytic activity and long-term stability toward ORR in an acidic medium. Using a metal-free nanocasting approach, Liu *et al.* [43] have also reported a superior ORR electrocatalytic performance to platinum for nitrogen-doped ordered mesoporous graphitic arrays (NOMGAs). Because of the metal-free preparation procedure in this case, the reported electrocatalytic activity can be exclusively attributed to the incorporation of nitrogen in NOMGAs. Metal-free N-doped MWCNTs or ordered mesoporous carbons (OMCSs) have also been prepared through carbonization of a MWCNT-supported polyaniline (PANI) coating [37] or via NH_3 activation to show high ORR activities even in acidic media [44].

Since N-doping plays an essential role in forming the active sites for oxygen reduction catalysts, it is necessary to understand the influence of nitrogen content and its chemical nature on the ORR activity. In order to examine the chemical nature of active sites and optimize the content of nitrogen in carbon lattices for ORR, recent research activities carried out in many laboratories have led to the synthesis of NCNTs with different nitrogen contents from different precursors [45]. For instance, NCNTs with higher nitrogen contents have been obtained by increasing the precursor ratio (pyridine to ethanol) in CVD process [54]. Such NCNTs exhibited a positive correlation between nitrogen content and the electrocatalytic activity toward ORR. The nitrogen contents in NCNT arrays can

also be adjusted by changing the pyrolysis temperature. The NCNTs with a high content of pyridinic-type nitrogen have been demonstrated to show an excellent activity toward ORR and a much better activity in an alkaline medium than that in an acidic medium [55].

Theoretical simulations indicated that the presence of nitrogen could reduce the barrier to ORR at a neighbor carbon atom [56]. The pyridinic-type nitrogen in the C-N_x catalysts would contribute to the conjugation effect of the nitrogen lone-pair electrons on the nitrogen and graphene π -system, leading to enhanced ORR activity [38, 57]. By contrast, Niwa *et al.* [58] revealed that carbon nanomaterials containing a high concentration of graphite-like nitrogen have a high ORR activity via X-ray absorption analysis. The influence of nitrogen concentration in the NCNTs on the electronic, structural, and electrochemical properties has been examined, showing an increase in bulk electrical conductivity and the density of states at the Fermi level with the increased nitrogen doping in CNTs [57, 59]. This may stem from the existence of an electron-rich nitrogen site, for example, pyridinic nitrogen possesses a lone pair of electrons in addition to a donated electron in the conjugated π -system (mixed σ - π valence states) [59]. The nitrogen doping in CNTs would result in chemically active, localized areas of higher electron density to promote the electrocatalysis of ORR. However, detailed understanding of the catalytic roles for each nitrogen atoms with different doping configurations requires further study through the combined experimental and theoretical approaches.

1.3.2

Carbon Nanotubes Doped with Heteroatoms Other Than Nitrogen

In addition to doping CNTs with nitrogen, CNTs have been doped with other heteroatoms, such as boron, sulfur, and phosphorus, to tune the electron-donating properties for enhancing the ORR activity. Depending on the chemical nature of the heteroatoms and the local structures, the heteroatom doping could either increase the oxygen reduction current or decrease the onset overpotential by means of (1) facilitating the O₂ adsorption, (2) increasing the total number of active sites, and (3) improving the surface hydrophilicity. In this context, Yang *et al.* [60] have recently extended the doping atoms to include boron with a lower electronegativity than that of carbon. The experimental results revealed that doping CNTs with the electron-deficient boron could also turn CNTs into metal-free ORR catalysts with a positively shifted potential and enhanced reduction current, as well as a high stability and good resistance toward methanol crossover and CO poisoning. DFT calculations have revealed that the larger electronegativity of carbon in comparison to the boron atom leads to the formation of positively charged boron due to the polarization in B-C hybridization bonds, which is favorable for the chemisorption of O₂ on boron dopant (Figure 1.3). By contrast, O₂ was adsorbed on the carbon atoms neighboring the nitrogen dopant in nitrogen-doped CNTs [10, 61]. These experimental and theoretical results suggest that the doping-induced charge redistribution, regardless whether the

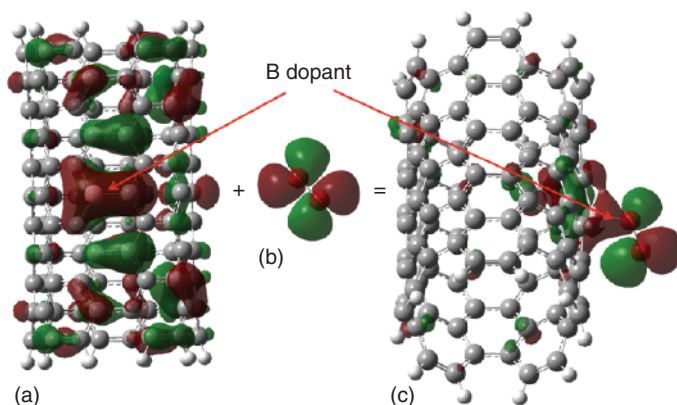


Figure 1.3 Important molecular orbitals involved in the O_2 adsorption on BCNT (5,5). (a) Spin-down HOMO-1 of BCNT(5,5); (b) LUMO of triplet O_2 ; and (c) Spin-down HOMO-2 of O_2 -BCNT(5,5). (Adapted from Ref. [60].)

dopants have a higher (as N) or lower (as B) electronegativity than that of carbon, could create charged sites (C^+ or B^+) that are favorable for O_2 adsorption and subsequent reduction process [45]. For the pristine CNTs, this process could not be achieved as there is no charged site on the tube, and the ground-state triplet O_2 would have repulsion force with spin-singlet pristine CNTs owing to orbital mismatch [60].

Hu and coworkers [60] prepared B-doped CNT by CVD with benzene, triphenylborane, and ferrocene as the precursors and catalyst. The shapes of the BCNTs evolved from straight to bamboo-like, and eventually to twisted nanotubes with an increasing amount of B-dopant in the range of 0%–2.13%. It should be noted that doping of carbon materials with B is more difficult than N-doping. For example, the highest reported B-doping level (2.13%) is far less than that in the case of N (12%), and B-doping is often accompanied by a high O content because of the strong affinity between O and B. The ORR onset- and peak-potentials shifted positively and the current density increased noticeably with increasing boron content, indicating a strong dependence of the ORR performance on the boron content. By extension, various CNT-based metal-free electrocatalysts could be prepared by doping CNTs with other heteroatoms (other than N and B) of electronegativities different from that of carbon.

The aforementioned results have confirmed that the doping-induced charge transfer plays a key role in oxygen reduction on the carbon-based metal-free ORR catalysts [11]. Apart from the aforementioned charge transfer, electron spin is also an important factor influencing oxygen reduction process on metal-free electrocatalysts. Theoretically, Zhang and Xia [62] concluded that dopant-induced redistribution of spin density and charge density on the graphene strongly affected the formation of the intermediate species (e.g., OOH) in ORR, O_2 adsorption, O–O bond breakage, and/or water formation. Anderson and coworkers [56] have also demonstrated that the adsorption bond strengths of adsorbate radicals

(e.g., H and OOH) exhibited a correlation with the spin density. Therefore, spin density could be regarded as a factor determining the positional selectivity of radical adsorption while charge density determined the attractive force with charged moieties. Experimentally, Jeon *et al.* [63] reported that edge-selectively sulfurized graphene nanoplatelets (SGnPs) could be produced by simple, but efficient, dry ball milling graphite in the presence of sulfur. The resultant SGnPs have been used as efficient metal-free ORR electrocatalysts. Furthermore, oxidation of the SGnPs into SOGnPs further improved the ORR capability to surpass the commercially available Pt/C electrocatalyst. In order to investigate the origin of the observed high ORR activities, theoretical calculations were conducted and showed that the electronic spin density, in addition to generally considered charge density, played a key role in the high ORR activities arising from the SGnPs and SOGnPs. On the other hand, Yang *et al.* [64] synthesized sulfur-doped graphene by directly annealing graphene oxide (GO) and benzyl disulfide (BDS) in argon. The sulfur-doped graphene (S-graphene) thus prepared exhibited an excellent ORR catalytic activity, long-term stability, and high methanol tolerance in alkaline media. Graphene doped with another element of a similar electronegativity as carbon (e.g., selenium; electronegativity: 2.55) showed also a similarly high ORR catalytic activity as S-graphene. Given that sulfur has a close electronegativity to that of carbon and that the C–S bonds are predominantly at the edge or the defect sites, the change of atomic charge distribution for the S-graphene is relatively small with respect to N (B, or P)-doped carbon materials. As such, the charge transfer alone cannot explain the observed high ORR electrocatalytic activities for S-/Se-graphene. Therefore, the spin density was considered to be the dominant factor to regulate the observed ORR activity in the S-/Se-graphene.

It is also interesting to note that Yao *et al.* [65] prepared iodine-doped graphene by annealing GO and iodine in argon, which exhibited better catalytic activity and long-term stability than a commercial Pt/C catalyst. Similarly, Liu *et al.* [66] synthesized the phosphorus-doped CNTs by the thermolysis of CNTs. The phosphorus doping significantly improved the electrocatalytic activity of CNTs for the ORR in alkaline media. Compared to the Pt/C catalyst, CNTs doped with small amounts of phosphorus exhibited a higher electrocatalytic activity and stability. The ORR activity of the N-doped carbon catalysts was increased by 11%–15% due to the additional B-doping, but there was an increase of 100%–108% in the case of additional P-doping. Thus, further understanding the crucial role of the doping microstructure in ORR performance enhancement is of significance in designing and optimizing advanced metal-free carbon-based electrocatalysts. The heteroatom doping changed not only the carbon surface chemistry, like basicity and hydrophilicity/oleophilicity, but also the electronic structure by donating a lone pair of electrons to shift the neutralized charge distribution on carbon atoms. The altered distribution of charge density and spin density of carbon atoms and heteroatoms played a critical role in the chemisorption of oxygen molecules and their derivatives.

Recently, Qiao and coworkers [67] investigated the origin of ORR electrocatalytic activity for graphene doped with different heteroatoms, including N, B, O, S, and P elements, respectively, using both electrochemical measurements and DFT calculations (Figure 1.4). The ORR activities at these doped graphene sheets were evaluated in terms of four electrochemical descriptors: exchange current density, onset potential, reaction pathway selectivity, and kinetic current density. The measured exchange current densities for each synthesized graphene surface can be obtained from the respective Tafel plot, as shown in Figure 1.4a. These current densities formed a volcano-shaped plot versus the adsorption

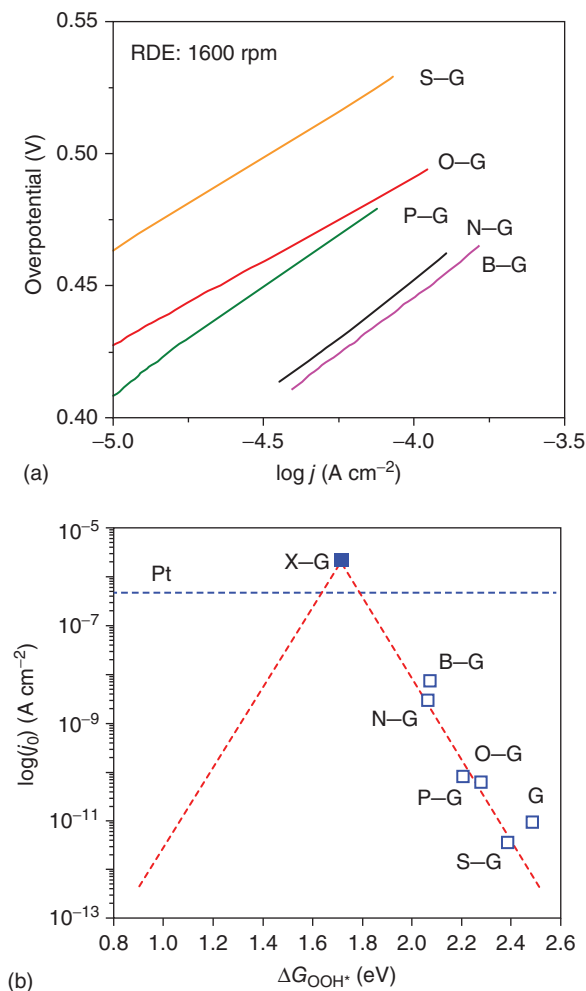


Figure 1.4 (a) Experimentally determined Tafel plots for different catalysts from ORR polarization curves and (b) volcano plot between j_0 (theory) and ΔG_{OOH^*} with charge transfer coefficient $\alpha = 0.5$. (Adapted from Ref. [67].)

free energies of the intermediate OOH^* (ΔG_{OOH^*}) with other electrochemical quantities being also related well to ΔG_{OOH^*} on the catalyst surface. Therefore, the adsorption free energies of intermediate OOH^* probably play important roles in determining the oxygen reduction activity of doped carbon materials.

Co-doping CNTs with two heteroatoms, one with higher and another with lower negativity than that of carbon, was found to significantly enhance their ORR electrocatalytic activities with respect to the single-atom-doped CNTs [68, 69]. In particular, we have successfully prepared vertically aligned CNTs containing both nitrogen and boron heteroatoms (VA-BCN). Figure 1.5a, b shows SEM and TEM images of the resultant VA-BCN nanotubes. Because of a synergetic effect arising from the co-doping of CNTs with boron and nitrogen, the VA-BCN nanotubes exhibited a higher electrocatalytic activity for ORR in alkaline medium than those of vertically aligned carbon nanotubes (VA-CNTs) doped with either boron or nitrogen only [69]. This approach has

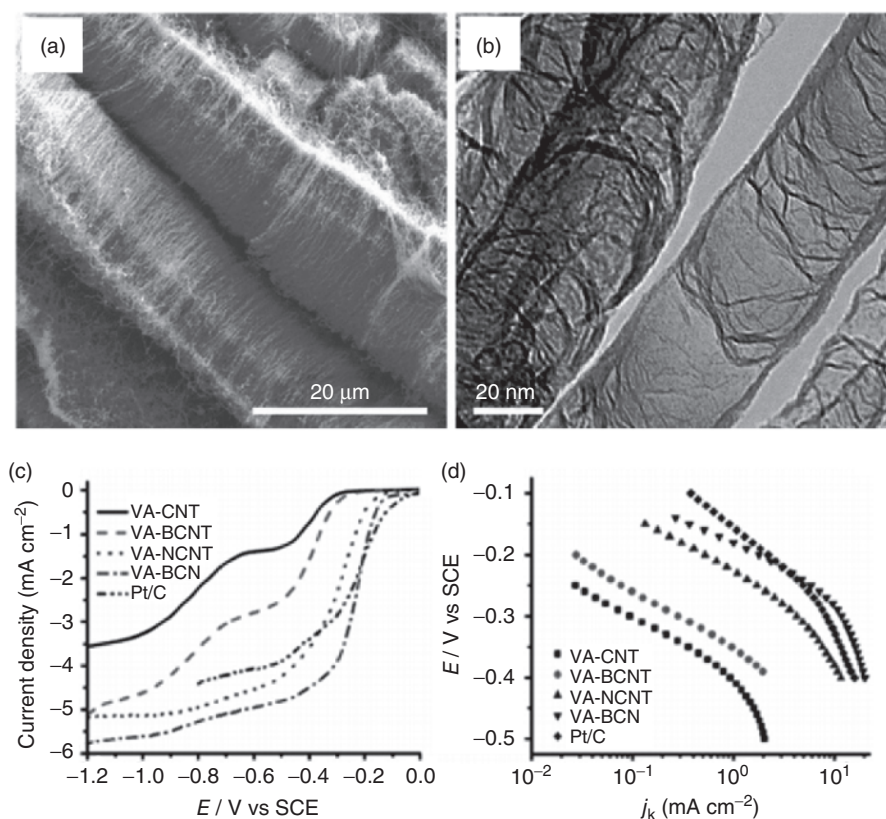


Figure 1.5 (a) SEM and (b) TEM images of VA-BCN nanotubes. (c) Linear sweep voltammetry curves of various electrodes in O_2 -saturated 0.1 M KOH electrolyte at a scan

rate of 10 mV s^{-1} at a rotation speed of 1000 rpm. (d) Tafel plots derived from (c) in the low-current region. (Adapted from Ref. [69].)

been extended to VA-CNT co-doped with phosphorus (P) and nitrogen (N) as high-performance electrocatalysts for ORR [70]. The observed superior ORR performance with a good methanol and CO tolerance and excellent durability in comparison to the commercial Pt/C electrode opens up novel avenues for designing efficient metal-free ORR catalysts by co-doping carbon nanomaterials with more than one heteroatoms with electronegativities different from that of carbon atom. However, different doping configurations could lead to different ORR electrocatalytic activities. For instance, co-doping of CNTs with dominantly separated (B–C and N–C) can turn the inert CNTs into efficient ORR catalysts whereas the bonded boron and nitrogen (B–N–C) cannot [71].

Theoretical calculations revealed that neutralization between the extra electron from N and the vacant orbital from B for the bonded case led to unfavorable chemisorption of O_2 on the co-doped CNTs. Fortunately, the neutralization can be prevented by separating B from N to maintain the conjugation with the carbon π -system as in the mono-doped CNT, leading to the improved ORR activities. Recent studies reported by Hu and coworkers [71] and Qiao and coworkers [72] indicated that sequential doping of B and N, and hence the separated dopant location, into carbon materials provided an enhanced synergistic coupling effect that could significantly facilitate the electrocatalytic ORR. These results, once again, demonstrated the crucial role of the doping microstructure on ORR performance, providing new insights into the molecular design and feasible synthesis of advanced carbon-based metal-free catalysts for potential applications in fuel cells and metal-air batteries. Even though excellent ORR performance, particularly in alkaline media, has been demonstrated for many of the carbon-based ORR catalysts discussed earlier, the performance evaluation of these nanocarbon catalysts in actual fuel cells has been much less discussed in literature. Xiong *et al.* [73] have investigated nitrogen-doped CNT arrays as an ORR catalyst in a PEMFC-analogous acidic medium and demonstrated a strong ORR signal at the favorably positive potential. Rao and Ishikawa [74] evaluated the VA-NCNT metal-free electrocatalysts in anion-exchange membrane fuel cells (AEMFCs), while Feng *et al.* [49, 75] fabricated a microbial fuel cell (MFC) with an air-cathode single chamber and carbon fiber brush anode to efficiently produce electricity with a good durability.

1.4

Conclusions

Recently, heteroatom-doped CNTs have been intensively investigated as efficient ORR electrocatalysts. It was found that doped CNTs exhibited even a higher electrocatalytic activity and better long-term operation stability than those of commercially available platinum-based electrodes for ORR. On the basis of the theoretical simulation, it was concluded that the altered distributions of charge density and/or spin density of carbon atoms due to the heteroatom doping played critical roles for improving catalytic activities of CNTs. Co-doping of carbon

nanomaterials with more than one heteroatoms could create synergistic effects for facilitating ORR. However, more studies are needed to understand the nature of the active sites and the ORR mechanisms on the (co-)doped carbon nanomaterials. Even though some recent studies on the doped carbon nanomaterials in acidic medium have indicated their potential applications in practical cells, the catalytic performance of these reported N-doped carbon nanomaterials still needs to be further improved.

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