Recent Advances in Heteroatom-Doped Graphene Materials as Efficient Electrocatalysts towards the Oxygen Reduction Reaction

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Received April 10, 2016; Revised June 22, 2016

Citation: R. Ma, Y. Ma, Y. Dong and J.-M. Lee, Nano Adv., 2016, 1, 50–61.

The development of cost-effective, efficient and stable electrocatalysts towards oxygen reduction reaction (ORR) has been an aim to overcome the bottleneck of widespread application of fuel cells and rechargeable metal-air batteries. Unique physicochemical properties of heteroatom-doped graphene open up a brand-new avenue for design and application of metal-free electrocatalysts in these electrochemical devices. Given the flourishing research of graphene and electrochemical energy storage, we critically summarize recent progress in the design, synthesis and application of various heteroatom (N, S, P, B, etc)-doped graphene materials as the electrocatalysts towards ORR. The distinctive properties resulting from various dopants and the resultant electrocatalytic activity are highlighted to gain insights into the mechanism of heteroatom-doped graphene for ORR. We conclude this article with some future trends and opportunities of developing heteroatom-doped-graphene-based electrocatalysts in the application of the ORR-related devices.

KEYWORDS: Graphene; Doping; Electrocatalysis; Oxygen reduction reaction; Metal-air battery

1. Introduction

The limited fossil fuels as well as the worsening environmental pollution stimulate worldwide researchers to explore sustainable energy conversion and storage technologies.1 Among the technologies, electrochemical conversion and storage technology is one of simple, efficient and reliable approaches. For example, the fuel cell technology can generate electricity from the electrochemical reaction of hydrogen and oxygen, while electrochemical water splitting produces oxygen and hydrogen gases from water. These technologies, which are highly efficient, cost-effective and environmentally friendly, usually involving the hydrogen evolution reaction (HER), oxygen evolution reaction (OER) or oxygen reduction reaction (ORR) during the electrochemical process. In such a process, a high activation barrier, which is defined by the overpotential or faradic efficiency, has to be overcome with the assistance of electrocatalysts.2 As a result, developing efficient and stable electrocatalysts are central to the efficiency of fuel cells, metal-air batteries and water electrolyzers.2–3

Actually, precious metal-based materials,4 such as PtPd,5 PtCo,6 Ir@Pt/C,7 and AgAu,8 have long been widely investigated as the catalysts towards HER, OER or ORR, due to their highly efficient catalytic activity. However, the scarcity and high cost are an insurmountable bottleneck for mass production. In addition, their susceptibility to time-dependent durability and carbon monoxide (CO) deactivation greatly decreases the cathode potential and reduces efficiency. On the other hand, earth-abundant transition-metal compounds, such as metal oxides/sulfides,9 have been extensively studied as electrocatalysts towards the abovementioned reactions. But they frequently suffer from dissolution and agglomeration during the operation of fuel cells, resulting in a severe degradation. Moreover, the low electrical conductivity of the electrocatalysts is not favourable for the electron transport in the electrodes, constituting a major obstacle for their applications.

With the 2010 Nobel Prize in Physics awarded for ‘ground-breaking experiments regarding the two-dimensional material graphene’,10 graphene, as a building block for carbon materials, has emerged as an attractive candidate for energy applications due to its unique structure and properties.11 Graphene has a carrier mobility up to 10000 cm2 V−1 s−1 and a thermal conductivity of 3000–5000 W m−1 K−1 at room temperature, a high surface area of ~2630 m2 g−1, good optical transparency of ~97.3% and excellent mechanical strength with a Young’s modulus of 1.0 TPa.12 These unique properties, especially the excellent electrical and thermal conductivities and
the huge specific surface area, make graphene either new-generation catalyst supports or catalyst itself. Furthermore, chemical doping with heteroatoms is an important strategy to tailor the electronic property and chemical reactivity of graphene, because the size and electronegativity of the heteroatoms are distinctly different from that of carbon atoms. The introduction of heteroatoms gives rise to new functions for graphene and greatly broadens its applications. Considerable attempts have been made to construct a variety of heteroatom-doped graphene materials or graphene-based nanocomposites, aiming at fully using their excellent properties in their application of electrochemical energy devices.

In this review, we will focus on the key advancements of heteroatom-doped graphene materials as efficient electrocatalysts towards ORR in the field of electrochemistry. The following sections summarize and discuss recent progress in the synthesis and elucidation of the electrocatalytic properties of heteroatom-doped graphene. Finally, the prospects and opportunities for future research in this field are also discussed.

2. Oxygen reduction reaction (ORR)

2.1 ORR in fuel cells and metal-air batteries

The oxygen reduction reaction (ORR) is an important reaction at the cathode and a major limiting factor of performance for fuel cells and metal-air batteries. As schematically shown in Figure 1, in a typical fuel cell, fuel molecules (e.g., H₂) are oxidized to protons and electrons at the anode (hydrogen oxidation reaction, HOR). In this process, the electrons flow out of the anode to provide electrical power, while protons pass through the electrolyte and react with adsorbed oxygen to produce water at the cathode (ORR). The reverse process is water electrolysis, in which water molecules are oxidized to produce oxygen molecules and release protons and electrons at the anode (OER). Protons traveling through the electrolyte combine with electrons to form hydrogen at the cathode (HER).

For metal-air batteries, the forward and backward processes are very similar to those of fuel cells, except that the metal replaces hydrogen molecules working as “fuel” and electrolytes become solutions containing metal ions. As shown in Figure 2, in the discharge process, the metal at the anode is electrochemically oxidized and releases electrons to the external circuit, while oxygen diffuses into the cathode to accept the electrons from the anode and is reduced to oxygen-containing species. Meanwhile, the dissociated metal ions migrate across the electrolyte and combine with the oxygen-containing species to form metal oxides. When the cell is charged, the process is reversed, in which metal plats at the anode and oxygen evolves at the cathode.

The ORR process involved in fuel cells or metal-air batteries could proceed through either an efficient four-electron pathway (Eq. 1 or 3) or a less efficient two-step two-electron pathway (Eq. 2 or 4). The possible reactions for oxygen reduction in alkaline solution are as follows:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \quad (0.401 \text{ V vs. SHE}) \quad (1) \]

\[ \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^- \quad (-0.076 \text{ V vs. SHE}) \quad (2a) \]

\[ \text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^- \quad (0.878 \text{ V vs. SHE}) \quad (2b) \]

In the four-electron process, the O₂ molecules are directly reduced into OH⁻ at 0.401 V versus Standard Hydrogen Electrode (vs. SHE), followed by combining with a proton into water (Eq. 1). In contrast, in the two-step two-electron pathway, the HO₂⁻ as the intermediate specie is firstly formed, followed by further reduction into OH⁻ (Eq. 2a and 2b).

Similar to the reactions in alkaline medium, there are also two kinds of pathway in the acidic medium, as shown in Eq. 3–4.
O2 + 4H+ + 4e− → 2H2O (1.229 V vs. SHE)  (3)

O2 + 2H+ + 2e− → H2O2 (0.695 V vs. SHE)  (4a)

H2O2 + 2H+ + 2e− → H2O (1.776 V vs. SHE)  (4b)

Oxygen molecules are directly reduced into H2O in the four-electron process (Eq. 3), while intermediate H2O2 is produced in a two-electron process (Eq. 4).

2.2 Electrochemical characterization of ORR

The ORR performance usually is evaluated by the onset potential (Eonset), the electron transfer number (n), half-wave potential (E1/2), overpotential under a specific current density (η), the kinetic-limiting current density (jk), Tafel slope, long-term durability, etc. As mentioned above, the n values per O2 molecule involved in a typical ORR process are of paramount importance for the efficiency of electrocatalysts. So, to rationally evaluate the electrocatalyst, there are two methods to calculate them. One is calculating n value from the slope of the Koutecky–Levich (K–L) plots by using the following equations (Eq. 5–6):

\[ J^{-1} = J_k^{-1} + J_L^{-1} = J_k^{-1} + (Bq^{1/2})^{-1} \]  (5)

\[ B = 0.2nFD_O^2ω^{-1/6}C_O \]  (6)

where J, Jk, and Jl are the measured current density, diffusion-limiting current density and kinetic-limiting current density in sequence, ω is the electrode rotating speed in rpm, B is the reciprocal of the slope, F is the Faraday constant (F = 96485 C mol⁻¹), C_O2 is the concentration of O2, D_O2 is the diffusion coefficient of O2, and ν is the kinematic viscosity of the electrolyte. The coefficient 0.2 is adapted when the rotating speed is expressed in rpm.

The other is measuring ring and disc currents from a rotating ring-disc electrode (RRDE) followed by the calculation according to the following equation (Eq. 7). By this method, the peroxide (H2O2) yield can also be obtained on the basis of Eq. 8.

\[ n = 4 \times \frac{I_R}{I_R + I_D} \]  (7)

\[ \% (H_2O_2) = 200 \times \frac{I_R/N}{I_R + I_D/N} \]  (8)

where IR and ID are the ring and disk currents, respectively, and N is the current collection efficiency of the Pt ring electrode (N = 0.37, from the reduction of K,Fe(CN)6). Further insights into the dynamics of ORR may be obtained from the slope of the Tafel plot. The Tafel slope is calculated according to the Tafel equation as follows:

\[ \eta = b \cdot \log(j/j_0) \]  (9)

where η is the overpotential, b is the Tafel slope, j is the current density, and j0 is the exchange current density. For oxygen electrocatalytic reduction, the Tafel slopes are typically found at 60 mV dec⁻¹ or 120 mV dec⁻¹, where the former corresponds to a pseudo two-electron reaction as the rate determining step, and in the latter the rate determining step is presumed to be the first-electron reduction of oxygen.15

3. Single-doped graphene

Single-doped graphene has made exceptional progress over the past decade either by in-situ doping during the graphene synthesis or through post-treatment of graphene with heteroatom-containing precursors. Comparative study of single-doped graphene towards ORR has also been extensively conducted, providing guideline for designing and fabricating heteroatom-doped graphene.16 And experimentally, the promising single-doped graphene materials as efficient, stable electrocatalysts towards ORR have also been demonstrated.

3.1 Nitrogen-doped graphene (NG)

The nitrogen doping modifies materials intrinsically, which tailors electronic properties, manipulates surface chemistry and produces local changes to the elemental composition of host materials. Thus, this doping can consequently improve the electrocatalytic activity. There are usually several N-containing species in NG, including pyridinic N (~398.7 eV), pyrrolic N (~400.3 eV), quaternary N (~401.2 eV), and N-oxides of pyridinic N (~402.8 eV) as shown in Figure 3.17 Pyridinic N refers to N atoms at the edges or defects of graphene, which contribute one π electron to the aromatic π system. Pyrrolic N atoms with higher binding energy bond to two carbon atoms and contribute two π electrons to the π system, which are incorporated into five-membered heterocyclic rings. Quaternary N atoms are incorporated into the graphene layer by substituting carbon atoms within the hexagonal ring, which are assigned to N-Q-center (graphitic N) and N-Q-valley. N-oxides of pyridinic N, pyridinic-N′-O′, are N atoms bonded to two carbon atoms and one oxygen atom.18 Among these nitrogen types, pyridinic N and quaternary N are sp² hybridized and pyrrolic N is sp³ hybridized. By N doping, the spin density and charge distribution of carbon atoms will be influenced by the neighbour N dopants, which
provide more active sites on the graphene surface and facilitate the electron transfer.\textsuperscript{19} Moreover, nitrogen doping in the monolayer graphene induces the Fermi level shifting above the Dirac point and suppresses the density of state near the Fermi level, thus opening the band gap between the conduction band and valence band.

Very recently, it has been reported that metal-free N-doped carbons exhibit excellent ORR catalytic activity, which is comparable to or better than commercial Pt/C catalysts,\textsuperscript{28, 34} illustrating an exceptional progress on metal-free catalysts used in metal-air batteries or fuel cells. For example, Ding et al. presented a novel strategy for the selective synthesis of pyridinic- and pyrrolic-nitrogen-doped graphene (NG) by the use of layered montmorillonite (MMT) as a quasi-closed flat nanoreactor, as shown in Figure 4.\textsuperscript{17} The as-prepared NG exhibits the excellent electronic conductivity, high ORR activity, and good stability in acidic electrolyte. Table 1 gives a summary of N-graphene materials recently used as efficient electrocatalysts toward ORR. Pyridinic and quaternary N species are generally considered as the active functionalities in NG. Wang et al. proposed that the activity of N-doped graphite arises from the electronic states near Fermi level due to the doping of N atoms.\textsuperscript{35} This is helpful for the electron transfer from the band of graphite to the anti-bonding orbitals of O\textsubscript{2}, which leads to weakening or breaking of the O–O bond and to the reduction of O\textsubscript{2}. Moreover, Ožkan’s group found that gross nitrogen content did not play a role in ORR activity and N was incorporated into the graphitic matrix, not attached as part of a surface functional group. Luo et al. further investigated N-doped graphene with

<table>
<thead>
<tr>
<th>Table 1. Summary of the ORR performance of various N-doped graphene materials.</th>
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<tbody>
<tr>
<td><strong>Samples</strong></td>
</tr>
<tr>
<td>PANI/RGO</td>
</tr>
<tr>
<td>PPy/RGO</td>
</tr>
<tr>
<td>BN-RGO</td>
</tr>
<tr>
<td>N-RGO-1000</td>
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<tr>
<td>NG1000</td>
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<tr>
<td>NCS-800 (N-doped carbon nanosheets)</td>
</tr>
<tr>
<td>NGSHs (N-doped graphene/single-walled CNT hybrids)</td>
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<tr>
<td>NCM58 (N-doped)</td>
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<tr>
<td>NC-900</td>
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<tr>
<td>NG-A</td>
</tr>
<tr>
<td>red-N-GOQD (reduced N-doped Graphene Oxide Quantum Dots)</td>
</tr>
<tr>
<td>GQD-GNR hybrid (Graphene Quantum Dots Supported by Graphene Nanoribbons)</td>
</tr>
<tr>
<td>NDCN-22 (N-Doped Carbon Nanosheets)</td>
</tr>
<tr>
<td>N-MG (N-doped mesoporous graphene)</td>
</tr>
<tr>
<td>dN-C (~100V) (N-doped carbon films deposited at -100V)</td>
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<tr>
<td>NG-1000</td>
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<td>NG-800</td>
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XPS (X-ray photoelectron spectroscopy) and UPS (ultraviolet photoelectron spectroscopy), and concluded that the pyridinic N efficiently changed the valence band structure of graphene, including the raising of density of π states near the Fermi level and the reduction of work function, thus greatly boosting the ORR activity.\(^\text{38}\) Qiao group examined three multilayer graphene samples prepared from graphene oxide using different nitrogen sources and doping methods for different nitrogen doping configurations and concentrations.\(^\text{37}\) They found that the carbon atom neighbouring pyridinic nitrogen plays an important role in the ORR process and should be the main active sites. Kim \textit{et al.} reported that the outermost graphitic nitrogen sites in particular enhanced the oxygen adsorption, the first electron transfer, and also the selectivity toward the four-electron reduction pathway, but there is an inter-conversion between the graphitic and pyridinic sites via the ring-opening of a cyclic C–N bond in the next electron and proton transfer reaction.\(^\text{38}\) Ruoff’s group synthesized a series of NG with different N states as shown in Figure 5 and studied the catalytic active center for ORR.\(^\text{39}\) They pointed out that the electrocatalytic activity of N-containing metal-free catalysts is highly dependent on the graphitic N content while pyridinic N species improve the onset potential for ORR. They also found that the total atomic content of N in the metal-free, graphene-based catalyst did not play an important role in the ORR process.

Recently, we also synthesized a series of NG materials by introducing pyrrole into a Wurtz-type reductive coupling reaction as shown in Figure 6.\(^\text{26}\) We found that a remarkable evolution of N-species from pyrrolic N to pyridinic N upon annealing, together with improved electrocatalytic activity happens with a relatively stable content of graphitic N. By correlating the ORR measurements with the XPS analysis, we proposed that the pyridinic N plays a more important role than pyrrolic N and graphitic N in largely improving the catalytic activity.

### 3.2 Sulfur-doped graphene

Sulfur-doped graphene also demonstrated improved electrocatalytic activity toward ORR, compared to its undoped counterpart. But, different from the mechanism of N-doped graphene, the enhanced ORR activity of S-doped graphene is usually attributed to the modifications in spin density instead of changes in atomic charge density ascribed to N doping, because sulfur has electronegativity close to that of carbon.\(^\text{16c,39}\) Sulfur atoms have been usually incorporated into the sp\(^2\) carbon lattice by two procedures: (I) chemical vapour deposition (CVD) technique using liquid organics\(^\text{40}\) and (II) thermal reaction of GO and sulfur-containing precursors.\(^\text{21,41}\) Pumera’s group synthesized a series of sulfur-doped graphene via thermal exfoliation of graphite oxide in H\(_2\)S, SO\(_2\), or CS\(_2\) gas as shown in Figure 7.\(^\text{45}\) The shift of the reduction potential by 40 mV from undoped graphene to S-doped graphene shows that S-doped graphene provides an electrocatalytic surface of ORR.
Recently, we also fabricated sulfur-doped graphene by a one-step magnesiothermic reduction strategy to transform greenhouse gas CO$_2$ (in the form of Na$_2$CO$_3$) in the presence of small amount of Na$_2$SO$_4$ as an inorganic S source to form S-doped graphene, as shown in Figure 8. At high temperatures, Mg metal could reduce carbon in the oxidation state of +4 in CO$_2$ to form black graphene products, while the SO$_4^{2-}$ ions could supply S atoms to build C$-$S sp$^3$ bonds integrated into the graphene lattice. The as-formed S-doped graphene materials demonstrate good electrocatalytic activity for ORR with a dominant four-electron reaction pathway as well as excellent durability. Sulfur-doped graphene derived from cycled lithium–sulfur batteries was also obtained by Wang and co-workers, showing a positive shift of about 60 mV and higher current density compared to the undoped graphene. The doping mechanism is believed to be similar to other electrochemical doping methods, but further investigation is still required to fully understand it.

### 3.3 Boron-doped graphene

B-doped graphene exhibits tunable band gaps and transport properties through controllable doping content, especially tunable p-type electrical properties, which could arise from the strong electron-withdrawing capability of B atom (electronegativity: 2.04 on the Pauling scale).

The increased carrier concentration and charge polarization in B-doped graphene highly improve the electrical conductivity and create more active sites favourable for O$_2$ adsorption. B doping could boost the reactivity of graphene with oxygen to form covalently bound bulk borates (BO$_x$–G) in oxygen-rich conditions. These species are highly important intermediates for breaking O=O bond in the reduction process of O$_2$ to form H$_2$O. The as-obtained BG shows an excellent bifunctional electrocatalytic activity toward ORR and OER with a four-electron pathway, high methanol tolerance, high stability, and low yields of side products, which makes B-doped graphene on par with Pt/C electrode.
3.4 Phosphorus-doped graphene

Phosphorus, an element of the nitrogen group, often shows the similar chemical properties due to the same number of valence electrons as N. But it has lower electronegativity (2.19) and larger covalent radius (107±3 pm) than N. Therefore, the polarity of the C–P bond is opposite to that of the C–N bond and favours the sp³-orbital configuration in molecules with larger structural distortion. The larger P–C bond length (1.79 Å) than 1.42 Å for C–C sp² bonds combined with the difference in bond angles, forces P to protrude from the graphene plane. These different features also facilitate the adsorption of O₂ and result in improved reaction rate of the overall oxygen reduction process. Poyato and co-workers showed that the four-electron transfer mechanism is the thermodynamically predominant pathway in the ORR on the studied P-doped graphene surfaces because the two-electron transfer mechanism is energetically less favourable. The comparative study of the ORR on N-doped, B-doped, and P-doped graphene surfaces demonstrates that the highest efficiency is obtained for the P-doped surface.¹⁶ᵃ

Liu et al. demonstrated the synthesis of P-doped graphite layers by pyrolysis of toluene and triphenylphosphine with improved electrocatalytic activity toward ORR. Hou’s group also showed that P-doped graphene exhibits remarkable catalytic activity, outstanding tolerance to methanol crossover effect and excellent long-term stability. Li et al. reported metal-free P-doped graphene nanosheets by annealing a homogeneous mixture of graphene oxide and an ionic liquid (BmimPF₆), as shown in Figure 10.⁵³ P atoms in the as-prepared PG are partially oxidized and existed as tetrahedral forms such as C₃PO, C₃PO₂, and CPO₂. The O atom with the higher electronegativity will first make the P atom polarized, and then withdraw electrons from the carbon atoms with the polarized P atom as a bridge, creating a net positive charge on the carbon atoms adjacent to the P atom. As a result, the positively charged carbon atoms become the active sites favourable adsorption of O₂, weakening the O–O bonding, and attracting electrons from the anode to facilitate the reduction of O₂ to H₂O through an efficient four-electron pathway. A latest article reports that ORR on P-doped graphene could proceed firstly by a 2e⁻ process to form an OOH intermediate, followed by a 4e⁻ process to break the O–O bond of OOH.⁵² Along this reaction path, the reduction of the second OH to H₂O is the rate-limiting step with the largest barrier of 0.88 eV.

3.5 Halogen-doped graphene

Halogen-doped graphene can be obtained by several strategies, including CVD,⁵³ liquid-phase exfoliation,⁵⁴ mechanical exfoliation,⁵⁵ etc. Recently, Jeon et al. synthesized edge-halogenated graphene nanoplatelets (ClGnP, BrGnP, and IgnP) and demonstrated remarkable electrocatalytic activities toward ORR with a high selectivity, good tolerance to methanol crossover/CO poisoning effects, and excellent long-term cycle stability, as shown in Figure 11.⁵⁶ The order of ORR activities is ClГnP ≪ BrGnP < IgnP, which seems to be contradicted to the doping-induced charge-transfer mechanism (electronegativity: Cl = 3.16, Br = 2.96, and I = 2.66).

But it can be explained that the atomic sizes of Br and I are larger than that of Cl, and hence the valence electrons of Br and I are much loosely bound than those of Cl for facilitating charge polarization in the BrGnP and IgnP electrodes. Unlike Cl, Br and I can form partially ionized bonds of −Br⁻ and −I⁻ to...
further enhance the charge-transfer because of their relatively large atomic sizes. Gentle and co-workers also reported that both Br-RGO and I-RGO facilitated a more efficient ORR than Cl-RGO and the undoped RGO at a higher reaction onset potential.\(^{57}\) Yao et al. showed that I-doped graphene by utilizing GO and iodine at 500–1100 °C in Ar has a long-term stability and an excellent resistance to crossover effects for ORR, suggesting that the formation of the I3 structure plays a crucial role for enhancement of the ORR activity of graphene.\(^{58}\)

4. Dual-doped graphene

Dual doping of foreign atoms into pristine graphene could induce a unique electronic structure in graphene and create a synergistic coupling effect between heteroatoms. From this point of view, dual doping is a promising approach to tailor the physical and chemical properties of graphene for obtaining excellent metal-free electrocatalysts. Several kinds of dual-doped graphene have been demonstrated to possess better electrocatalytic activity than those single-doped counterparts, which will be discussed below.

4.1 N, B-doped graphene

Dai’s group demonstrated that N, B-doped graphene (NBG), which was synthesized by thermal annealing graphene oxide in the presence of boric acid under ammonia atmosphere, showed ORR electrocatalytic activities even better than the commercial Pt/C electrocatalyst and also investigated the electrocatalytic activity theoretically by density functional theory (DFT) calculations.\(^{59}\) Compared to pure graphene, the substitution of C by B and N leads to a smaller energy gap, but over-doping of B and N resulting in a significant increase in the energy gap is not favourable for the electrocatalytic activity. Therefore, a modest N- and B-doping level is necessary to improve the catalytic activity of graphene.\(^{60}\)

Qiao and co-workers also incorporated N and B sequentially into selected sites of graphene domain to facilitate the electrocatalytic ORR.\(^{60}\) The resultant NBG exhibited much improved electrochemical performance as compared to that of single-doped graphene and the hybrid electrodes, suggesting a synergistic coupling effect between N and B atoms as shown in Figure 12. Dual doping of N and B atoms could cause offset of asymmetric charge density because N and B atoms have higher and lower electronegativity than C atoms, respectively. However, the dual doping could bring out high asymmetric spin density of C atoms, which plays a much more important role than the atomic charge density in determining the catalytic active sites.\(^{61}\) Agnoli and co-workers attributed the better performance of N, B co-doped graphene than that of N or B doped counterparts to two factors (i) the twice higher concentration of active sites for ORR (B atoms and C atoms neighbouring to N) and (ii) an enhanced positive charge on B caused by the electron withdrawing properties of N.\(^{27}\)
4.2 N, S-doped graphene

N, S co-doped graphene (NSG) is usually synthesized by CVD method or thermal reaction of graphene oxide and solid/gaseous N/S-containing precursors (e.g., thiourea or NH3/H2S gas). The synergistic effect between heteroatoms was also reported for N and S dual-doped graphene, which is beneficial for improving the ORR. For example, Qiao’s group displayed a very high ORR onset potential of NSG (−0.06 V vs. Ag/AgCl), very close to that of commercial Pt/C (−0.03 V vs. Ag/AgCl) and much more positive than that of NG, SG or G at 1600 rpm. DFT calculations indicate that simultaneously incorporating of S and N into graphene induces a substantially uplift of spin density, indicating higher ORR catalytic performance. Recently, Jeon and co-workers prepared a series of heteroatoms (N and/or S) doped graphene in different ratios from various doping precursors (pyridine, thiophene and bithiophene combined separately with dipyrrolemethane as single N and/or S precursor) by thermal reaction. They found that the N and S dual-doped graphene has better catalytic activity.

Table 2. Summary of electrochemical performance of NSG.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Precursors</th>
<th>Onset Potential</th>
<th>( \Delta E_{1/2} = E_{1/2(\text{Sample})} - E_{1/2(\text{Pt/C})} )</th>
<th>n</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNGL-20</td>
<td>GO, pyrimidine and thiophene</td>
<td>−0.11 V vs. Ag/AgCl</td>
<td>10 mV</td>
<td>3.7</td>
<td>62b</td>
</tr>
<tr>
<td>NSG-700</td>
<td>GO and thiourea</td>
<td>−0.12 V vs. SCE</td>
<td>−150 mV</td>
<td>3.91</td>
<td>63</td>
</tr>
<tr>
<td>NSG</td>
<td>GO, melamine and benzyl disulfide</td>
<td>−0.06 V vs. Ag/AgCl</td>
<td>−156 mV</td>
<td>3.6</td>
<td>64</td>
</tr>
<tr>
<td>NSG</td>
<td>GO and 2-aminothiophenol</td>
<td>−0.09 V vs. Ag/AgCl</td>
<td>-</td>
<td>2.9–3.2</td>
<td>67</td>
</tr>
<tr>
<td>NSG</td>
<td>GO, cysteine and polydopamine</td>
<td>−0.002 V vs. Hg/HgO</td>
<td>−65.8 mV</td>
<td>2.98–3.36</td>
<td>68</td>
</tr>
<tr>
<td>NSG-1000</td>
<td>GO, and poly [3-amin-5-mercapto-1,2,4-triazole]</td>
<td>−0.1 V vs. SCE</td>
<td>−70 mV</td>
<td>3.59–3.63</td>
<td>69</td>
</tr>
</tbody>
</table>
on ORR than only N-doped graphene, probably due to the synergistic effect of dual-doping and superiority of S than N with two lone-paired electrons. The improved electrocatalytic activity caused by N and S atoms paves the way of practical application of NSG in the Li-air batteries, as demonstrated by Kim et al.\textsuperscript{56} The electrochemical performance of NSG reported in recent years is summarized in Table 2.

4.3 N, P-doped graphene

Dual doping of N and P atoms into graphene is also a promising approach to improve the electrocatalytic activity of graphene towards ORR. Heteroatomic P, N defect is more stable than the P defect in graphene, which creates localized electronic states that modify the electron transport properties by acting as scattering centers.\textsuperscript{48} Similar to N, B and N, S doping, the incorporation of N and P atoms also induces asymmetric spin density of C atoms, making C atoms more active for adsorption of O\textsubscript{2} molecule. It was reported that the P, N co-doped graphene synthesized by a CVD route exhibits a remarkably stable n-type behaviour at ambient conditions and reasonable charge carrier mobility.\textsuperscript{70} Woo’s group reported N, P co-doped graphene exhibits the higher activity towards ORR in acidic medium compared with single N-doped graphene.

We also fabricated N, X (X = B, S or P) dual-doped graphene by a simple solvothermal method, which is facile and scalable, as shown in Figure 13.\textsuperscript{71} We found that the electrocatalytic activity is in the order of NSG < NBG < NPG, which is consistent with the reported theoretical and experimental results. The improved electrochemical performance of all co-doped graphene samples indicates that dual doping actually exerts a positive influence on the electrochemical activity. Such influence could be regarded as the so-called synergistic effect, namely, N atom polarizes the adjacent C atom, while X (S, P, or B) atom facilitates the adsorption of and bonding with HO\textsubscript{2}.\textsuperscript{60} Furthermore, additional doping of B or P into N-doped graphene could also result in the improvement of asymmetry of charge distribution, a facile electron transfer on the basal plane of graphene, and a decrement of energy gap between highest occupied molecular orbital and lowest unoccupied molecular orbital.

5. Ternary-doped graphene

Earlier study shows that ternary doping of B and P with N into carbon induces remarkable performance enhancement, due to the charge delocalization of the carbon atoms and increase of edge sites of the carbon.\textsuperscript{64} Recently, Yu and co-workers incrementally doped P atoms into N, S co-doped graphene to achieve a ternary (N, S and P)-doped graphene, demonstrating an excellent ORR activity, which is 2 times better than that of binary (N and S)-doped RGO, and 5 times better than that of single (P)-doped graphene and even exceeds the commercial Pt in alkaline medium.\textsuperscript{72}

6. Summary and perspectives

In this review, we have summarized recent advances in the development of heteroatom-doped graphene towards ORR. The discussion of electrocatalysis has focused on the influence of heteroatoms on the electrochemical properties and performance of graphene. Doping-induced charge/spin redistribution make the C atoms in the graphene more active for O\textsubscript{2} adsorption to facilitate the ORR process, which make doped graphene promising in the electrocatalysis, either as a catalyst support or catalyst itself. In this exciting field of heteroatom-doped graphene materials, although significant progress has been made, challenges are still remained. Firstly, large-scale and low-cost fabrication method is a prerequisite to utilize graphene in the electrocatalytic reactions, because most of synthetic methods are involved in high temperature or toxic precursors, which increase the cost and difficulty for mass production. Secondly, reaction mechanism of doped graphene is still further elucidated by exactly controlling the doping configuration experimentally and carefully model construction and simulation by quantum calculation theoretically. At last but not least, the exploration of doped graphene used in practical fuel cells and metal-air batteries still needs to be extended, because most reports put emphasis on the estimation of sole ORR performance. We believe that the ever-increasing understanding and exploration of heteroatom-doped graphene will open up avenues for the development of future energy systems.

\textsuperscript{59} LSV curves of various graphene products at 1600 rpm in O\textsubscript{2}-saturated 0.1 M KOH solution.\textsuperscript{71}
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Notes and references


