

# Edge-enriched graphene with boron and nitrogen co-doping for enhanced oxygen reduction reaction

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## ABSTRACT

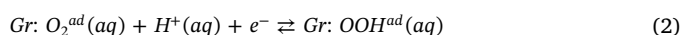
Carbon-based electrocatalysts for oxygen reduction reaction (ORR), especially in anion exchange membrane fuel cells (AEMFCs), have received a lot of attention because they exhibit excellent stability and are comparable to commercial Pt/C catalysts. Currently, to maximize the catalytic activity of carbon-based electrocatalysts, there are two major strategies: heteroatom doping or exposing active edge sites. However, the approach of increasing heteroatomic dopants of active edge sites has been rarely addressed. In this study, we present a simple strategy to prepare edge-enriched graphene catalysts with an increased ratio of heteroatomic dopants suitable for ORR of AEMFCs. The catalysts were prepared under harsh oxidation conditions, followed by a simple co-doping process with boron and nitrogen. The ORR activity of the catalysts was observed to be related to an increase of edge sites with heteroatomic dopants. We believe that the edge-enriched structure leads to accelerated electron transfer with enhanced oxygen adsorption.

## 1. Introduction

Demands for clean and sustainable energy have led to extensive research on fuel cells and metal air batteries [1,2]. The kinetically unfavorable oxygen reduction reaction (ORR) at the cathode in these devices still requires the usage of platinum-group metal (PGM) (e.g., Pd, Pt, Ru, Rh, Os, and Ir) as catalysts. However, this limits the commercialization of fuel cells due to high costs, rarity, and low durability [3,4]. Numerous efforts to replace PGM-based catalysts have been reported using non-precious metals or cost-effective materials [5–8]. According to Sabatier's catalysis principle, the alternatives should have the comparable oxygen adsorption energy as PGM-based catalysts on active surfaces [9]. Furthermore, the number of active sites exposed on the surface should also be maximized [10].

Heteroatom, such as boron (B), nitrogen (N), fluorine (F) and sulfur (S), doped graphene have been highlighted as promising alternatives to PGM catalysts because of their similar catalytic activity in alkaline media and outstanding CO tolerance [11–18]. In particular, anion exchange membrane fuel cells (AEMFCs), which are currently regarded as

advanced fuel cell technology, depend more on graphene-based electrocatalysts than non-platinum or noble-metal catalysts [19]. Generally, ORR mechanism on glassy carbon has been proposed as follows [20]:



As shown in equation (1), the ORR initiates with  $\text{O}_2$  adsorption onto the carbon. In step (2), neutral  $\text{OOH}^{\text{ad}}$  is formed via a proton-coupled electron transfer from the adsorbed oxygen. Then, the  $\text{OOH}^{\text{ad}}$  species has two possible pathways: one is release of  $\text{OH}^-$  by breaking the O–O bond (four-electron process) and the other is release of  $\text{OOH}^-$  by breaking the Grp–O bond (two-electron process). The final product of the former which corresponds to the four-electron reduction pathway is  $\text{H}_2\text{O}$ , and the latter which corresponds to the two-electron reduction pathway is  $\text{H}_2\text{O}_2$ . It is well known that the rate of the ORR is highly related to the oxygen adsorption rate on the graphene surface [21]. This indicates that the ORR performance of graphene-based catalysts significantly depends on how easily oxygen molecules can be adsorbed [22,23]. Currently, there are two strategies to improve the adsorption

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