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B, N co-doping graphene nanoribbons as effective oxygen reduction electrocatalyst

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Abstract

In this study, a facile method was used to synthesize B, N co-doped graphene nanoribbons (BN-GNRs), with g-C₃N₄ as a source of N and boric acid as a source of B, for use as an effective electrocatalyst for the oxygen reduction reaction (ORR). Numerous wavy edges are exposed in GNRs, and these exposed wavy edges provide doping positions for N and B atoms. Compared with single doping of B or N, co-doping of B and N with opposite electronegativity can increase the doping amounts. Thus, the obtained BN-GNRs catalyst has tremendous graphitic- and pyridinic-N active sites, which are beneficial to oxygen adsorption and desorption and to electron mass transfer.

Additionally, the interaction between nearby N and B can promote the ORR’s catalytic process and conversion efficiency. BN-GNRs demonstrate strong ORR performance, better selectivity, and stability. Moreover, their half-wave potential can reach 0.852 V in alkaline electrolyte, similar to that for Pt/C. This study shows that BN-GNRs can be employed as an effective metal-free ORR catalyst to replace commercial Pt/C.

1. Introduction

Because the issues of energy depletion and environmental damage caused by the burning of fossil fuels are becoming worse, it is crucial to evolve green technology for storing and converting energy sustainably [1–4]. The widespread oxygen reduction reaction (ORR) with retard kinetics has gravely hindered the use of batteries made of metal-air and fuel cells [5–7]. At present, Pt-based materials are the most popular ORR catalyst, but due to the high price and scarce reserves of Pt, Pt-based materials cannot be applied on a large scale [8, 9]. Therefore, it is extremely important to prepare a cheap, easily available, and environmentally friendly catalyst [10–12]. As a kind of widely sourced and environmentally friendly material, carbon materials have become the most promising substitutes for Pt-based materials. By adding heteroatoms as a substitute for carbon lattice atoms, the charge density near the carbon atoms can be changed to effectively adjust the work function and promote the reactant adsorption at particular sites [13–15].

Owing to their small weight, graphene nanoribbons (GNRs) have attracted intense interest from researchers. Their high specific area, good electrical conductivity, and numerous uneven wavy edges provide many doping positions [16–18]. GNRs are obtained by longitudinally cutting multi-walled carbon nanotubes (MWCNTs), exposing many uneven wavy edges at the fracture edges. As shown in figure S1 of the Supplementary Information, after the carbon nanotubes are cut the lattice fringes of carbon at the edges are distributed in a step-like pattern, indicating a large number of wavy edges. Compared to the base surface, the margins of exposed heteroatomic doping GNRs have a higher tendency to adsorb oxygen, so it is clear that the edges of heteroatomically doped GNR catalysts have higher ORR performance, while the base surface still remains virtually
NRs, N-GNRs, B-GNRs, and BN-GNRs in scanning- and 2. Results and discussion

ORR-inactive [19]. Therefore, heteroatomic doping of GNRs with abundant edges will contribute to more catalytic active sites, which enhances the ORR catalytic activity. Since the groundbreaking research of Dai et al. on N-doped carbon nanotube arrays, the catalytic capabilities of these catalysts have been thoroughly investigated by altering the electronic structure of carbon-based catalysts by doping heteroatoms (e.g., N, B, P, or S) [20–22]. At present, the single doping of heteroatoms for GNRs has been widely researched. However, several problems remain, such as a low doping amount and difficult doping control, which limit the enhancement of the catalytic process. Therefore, co-doping of heteroatoms with different electronegativities is proposed to realize a more controllable method to enhance the catalytic effectiveness, due to the synergistic outcome of electron interactions between dissimilar dopants [23].

N, B co-doped carbon materials are some of the first that show synergistic effects of different heteroatoms. The interplay between neighboring B and N atoms can further boost the ORR’s catalytic activity and conversion efficiency. Zeng et al. produced ordered mesoporous carbon with B and N co-doping using a straightforward self-assembly process, carbonization, and a catalyst with good ORR performance [24]. Gong et al. built a three-dimensional structure using graphene oxide nanoribbons as the building blocks and prepared a B,N co-doped GNR gas condensate with rich edge defects [25] The obtained catalyst had excellent ORR electrocatalytic performance, originating from the abundant edges, which greatly reduced the energy barrier for the ORR’s rate-determining step. However, the aggregation-induced mass transfer and few active sites still make it very difficult to realize practical use of the catalyst. Designing and constructing a highly efficient catalyst with a suitable structure is therefore of great importance [26–28].

In the work reported herein, we synthesized B, N-co-doped graphene nanoribbons (BN-GNRs) as an efficient metal-free ORR catalyst, employing g-C3N4 with a high N content as the N source and environmentally benign boric acid as the B source for BN–GNRs with irregular edges that provide N- and B-atom doping sites. Thus, the obtained BN-GNRs catalyst has a huge number of pyridinic-N, graphitic-N, and B-N active sites, which are beneficial to oxygen adsorption and desorption and electron mass transfer. Excellent ORR performance, improved stability, and selectivity are all displayed by BN-GNRs. Their half-wave potential \( E_{1/2} \) is similar to that of Pt/C at 0.852 V.

2. Results and discussion

GNRs, N-GNRs, B-GNRs, and BN-GNRs in scanning- and (SEM) transmission-electron-microscopy (TEM) images are shown in figure 1, exhibiting a typical curved irregular nanoribbon morphology, which indicates the successful decompression of MWCNTs and the successful preparation of GNRs. At the same time, by introducing N, B, and BN co-doping into GNRs for tuning, we fully utilized the edges of GNRs to obtain high-performance oxygen reduction catalysis. B-GNRs show a slight adhesion phenomenon of the strips (figures 1(i)–(j)), while N-GNRs show a looser topographic structure (figures 1(e), (f)), which may be caused by the ammonia gas generated by the decomposition of g-C3N4. In the TEM images, N-GNRs exhibit a looser GNR structure, while B-GNRs also exhibit a slight band adhesion phenomenon, in agreement with the SEM images (figures 1(g)–(h) and (k)–(l)). As shown in figures 1(m)–(n), BN-GNRs display a lamellar structure at low magnification and a loose and porous structure at high magnification. The TEM images of BN-GNRs (figures 1(o)–(p)) also show special GNR morphology, i.e., irregular edges and pores, which is in satisfactory agreement with the SEM results. The elemental mapping images are recorded by using energy dispersive x-ray spectroscopy analysis (EDS), the outcome demonstrates that the C and N elements are evenly distributed in N–GNRs (Figure S2), the C and B elements are uniformly dispersed (Figure S3) in B–GNRs and the C, N and B elements are unevenly dispersed in BN–GNRs (Figure S4), demonstrating N and B’s successful doping.

For all samples, the x-ray diffraction (XRD) patterns shown in figure 2(a) exhibit two peaks that, respectively, correspond to the (100) and (002) facets of graphite carbon. Since GNR is a carbon material with more carbon content and less N and B doping, it is not obvious in XRD, and only the peak of carbon is obvious. But in XPS, C, N, and B elements can be measured precisely, and with precise atomic content. (Table S1). X-ray Photoelectron Spectroscopy (XPS) results further indicate the effective N doping, B doping and N, B co-doping for N-GNRs, B-GNRs and BN-GNRs, respectively (figure 2(b)). Table S1 shows the elemental content of three samples, i.e., N–GNRs and B–GNRs show very low N and B doping amounts, while BN–GNRs show increased doping amounts of the two dopants, which is caused by the dual active centers created by N- and B-synergistic coordination interaction. The high-resolution B 1s spectrum for the BN–GNRs sample is shown in figure 2(c). Four peaks can be discerned from the B 1s spectral peak, which are centered at 190.8 eV, 191.9 eV, 192.8 eV and 196.8 eV corresponding to the BC2O, BCO3, B-N and BC3 structures. The BC3 structure is a basal configuration formed by substituting B atoms for C atoms without destroying the bond configuration. Owing to the low electronegativity of N atoms, the B-atom electrons can be transferred to the carbon side. The bonding structure of BCO3 and BC2O is mainly located at the edges of BN–GNRs, which will reduce their electrical conductivity.
However, these bonds may have better interactions with oxygen intermediates and can exhibit stronger adsorption during electrocatalysis. There is a synergistic effect between B and N that can form diatomic active centers in defective carbon materials, which plays a positive role in the ORR reaction and promotes the reaction \[29\]. The atomic content revealed by x-ray photoelectron spectroscopy (XPS) also proves that B,N co-doping can significantly increase the content of B and N, which is beneficial to improving the catalytic activity of ORR. The presence of a high proportion of B-N bonds in the spectrum verifies the interaction of the B and N components, enhancing the electronically catalytic activity of the BN-GNRs sample. It is possible to further deconvolute the N 1s peaks in BN-GNRs into five peaks that correspond to pyridinic N (398.2 eV), N-B (398.7 eV), pyrrolic N (399.6 eV), graphitic N (400.7 eV) and oxidized N (403.6 eV) (figure 2(d)). The polarization of B and N atoms will be greatly increased when B and N atoms are simultaneously doped into carbon, which is advantageous to increasing the ORR performance of the BN-GNRs catalyst. We can conclude from the XPS atomic content analysis of GNRs, N-GNRs, and B-GNRs that, after single doping by N or B atoms, all three are less doped with N or B atoms: only 2.7% and 3.1%, respectively. However, the content of doped N and B atoms in BN-GNRs increased significantly after B, N co-doping, reaching 4.6% and 5.1%, respectively (Table S1).

Linear sweep voltammetry (LSV) and Cyclic voltammetry (CV) were used to assess the electrocatalytic performance of the samples in 0.1 M KOH solution. It is evident from figure 3(a) that under Ar saturation, the CV curves of the samples have no reduction peak. Under O\_2 saturation, obvious reduction peaks are observed at 0.87 V, 0.83 V, 0.82 V, 0.82 V (versus RHE) for BN-GNRs, N-GNRs, B-GNRs, and GNRs, respectively, which reveals that the BN-GNRs sample has the best ORR performance. In the ORR test, the LSV curve was measured under saturated oxygen conditions, we obtained the \(J_L\) value, and the corresponding voltage value at half of the \(J_L\) value was determined as the half-wave potential of the material. It is evident from figure 3(b) that the half wave-
Figure 2. (a) XRD of GNRs, B-GNRs, N-GNRs and BN-GNRs. (b) XPS of B-GNRs, N-GNRs and BN-GNRs. (c) B 1s spectrum of BN-GNRs. (d) N 1s spectrum of BN-GNRs.

Figure 3. (a) CV curves of several catalysts in O2 and Ar-saturated 0.1 M KOH solutions. (b) Various catalysts LSV curves at 1600 rpm. (c) LSV curves at different speed ranges of 400–1600 rpm in BN-GNR. (d) K-L plots for different potentials of BN-GNRs.
potentials \((E_{1/2})\) of BN-GNRs, N-GNRs, B-GNRs and GNRs are 0.852 V, 0.822 V, 0.837 V and 0.82 V, respectively, the four samples all show ORR catalytic activity, especially BN-GNRs. Additionally, as the rotating rate increases, it is evidently seen that the current density of BN-GNRs increases, indicating a first-order reaction toward oxygen reduction (figure 3(c)). The ORR catalytic activity is assessed using the electron transfer number \((n)\) generated from the Koutechy-Levich (K-L) plots. From the K-L plots (figure 3(d)), The sample from BN-GNRs shows good linearity between \(j^{-1}\) and \(\omega^{-1/2}\) at the potential range from 0.4 V to 0.7 V, and the \(n\) value is about 3.85, recommending an effective 4e\(^{-}\) ORR route with \(H_2O\) as the primary product. To learn more about the ORR process’s \(H_2O_2\) yield and electron transfer number, RRDE experiments were conducted at 1600 rpm rotation speed in an aqueous solution of 0.1 M KOH that was \(O_2\)-saturated (figure 4(a)). The \(n\) value of BN-GNRs is 3.93, significantly superior to those of other catalysts. The BN-GNRs sample has the highest doping amounts and ORR occurs in 4e\(^{-}\) pathway, showing excellent electrocatalytic performance. The Tafel slope of BN-GNRs is 67 mV dec\(^{-1}\), smaller than those of other comparison samples and the Pt/C, demonstrating quicker ORR kinetics of BN-GNRs (figure 4(b)). As shown in figure 4(c), the \(E_{1/2}\) value of BN-GNRs only has a negative shift of 10 mV after 5000 cycles, indicating its eminent stability. In figure 4(d), when 1 M methanol is injected into \(O_2\)-saturated 0.1 M KOH at 200 s, the current of Pt/C shows sharp decline while the addition of methanol had no impact on BN-GNRs, manifesting that the BN-GNRs sample is immune to methanol crossover.

The reasons for the better performance of the BN-GNRs catalyst compared with other catalysts are the following.

1. The co-doping of B and N causes the doping amounts of B and N to increase, compared with the single doping of N or B, and thus the number of catalytic active sites is increased.

2. The co-doping of B and N generates B-N active sites, and the synergistic effect of B and N leads to a further increase in catalytic performance.

3. Conclusion

In conclusion, simple hydrothermal and pyrolysis processes can be used to create BN-GNRs with outstanding ORR characteristics. Compared with single doping of B or N, co-doping of B and N can increase the doping
amount and thus increase the number of active sites. In addition, the interaction between adjacent B and N atoms can further improve the conversion efficiency and catalytic activity of ORR. In alkaline electrolyte, BN-GNRs exhibit high ORR performance, superior methanol resistance, and excellent stability compared with other single-doped and undoped samples. This study shows that BN-GNRs can be used as an efficient metal-free ORR catalyst to replace commercial Pt/C.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of interest statement

The authors affirm that they do not have any competing interests.

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