Theoretical Study on a Nitrogen-Doped Graphene Nanoribbon with Edge Defects as the Electrocatalyst for Oxygen Reduction Reaction

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ABSTRACT: Both theory and experiment show that sp² carbon nanomaterials doped with N have great potential as high-efficiency catalysts for oxygen reduction reactions (ORR). At present, there are theoretical studies that believe that C-sites with positive charge or high-spin density values have higher adsorption capacity, but there are always some counter examples, such as the N-doped graphene nanoribbons with edge defects (ND-GNR) of this paper. In this study, the ORR mechanism of ND-GNR was studied by density functional theory (DFT) calculation, and then the carbon ring resonance energy was analyzed from the perspective of chemical graph theory to elucidate the cause and distribution of active sites in ND-GNR. Finally, it was found that the overpotential of the model can be adjusted by changing the width of the model or dopant atoms while still ensuring proper adsorption energy (between 0.5 and 2.0 eV). The minimum overpotential for these models is approximately 0.36 V. These findings could serve as guidelines for the construction of efficient ORR carbon nanomaterial catalysts.

1. INTRODUCTION

In hydrogen fuel cells, the efficiency of converting chemical energy of hydrogen and oxygen into electrical energy depends on the electrocatalytic performance of the catalyst for sluggish cathodic oxygen reduction reactions (ORR). At present, Pt and Pt-alloy catalysts are the most widely used for commercial purposes, because of their superior ORR activity. Nevertheless, high cost and their lack of abundance hinder the successful commercialization of the hydrogen fuel cells. Moreover, Pt-based catalysts also suffers from severe agglomerations and leaching of the alloy metal, surface-positioning with gaseous molecules such as CO and liquid fuels like methanol, under electrochemical conditions and hence their catalytic performance deteriorates over long term operation. Therefore, it is essential to develop the efficient, cost-effective, and stable catalysts, which can replace the traditional Pt-based catalysts with similar efficiency, and this has been the problem that is being addressed since the last 2 decades. In this regard, the catalyst with no metal component involved (metal-free) is gaining much attention, as they do not possess many of the disadvantages of Pt-based catalysts. Because they do not possess any metallic particles, there is no agglomeration of the nanoparticles. Moreover, they are resistance to CO and methanol species and they are stable under electrochemical conditions. Therefore, attention is being paid on the development of heteroatom-doped catalysts (metal-free catalysts) especially on nitrogen-doped catalysts. It is found by many researches that the doping of N into the sp²-based carbon nanomaterials could be the right choice to engineer the electronic structures of the sp²-based carbon nanomaterials suitable for the ORR catalysis. At the same time, both theory and experiment show that sp² carbon nanomaterials doped with N have great potential as high-efficiency catalysts, by changing the polarity of the adjacent carbon chemical states and dopant bonding configurations. Thanks, to density functional theory (DFT) calculations, which can be used as a fundamental and efficient tool to understand the adsorption energies of O₂ activation barriers for various ORR intermediates, estimation of electronic density on the catalyst surface, and effect of defects on the carbon substrate on the atomic level. DFT calculations also predict
the possible ORR activity of new catalysts and hence are a power tool for many theoretical scientists.

Graphene nanoribbons possess a large aspect ratio and numerous defects along their edge structures and experimentally it is also easy to obtain by the unzipping of carbon nanotubes by various chemical processes. In this article, our calculations show the importance of edge defect sites on N-doped graphene nanoribbon supports, which is due to its influence on the adsorption performance. For the N-doped carbon materials, the ORR reaction proceeds with the adsorption of O₂/H⁺. It is important to have an optimum adsorption of O₂ as weak adsorption lead to a slow ORR process. There are two possibilities by which an ORR reaction can proceed. The first possibility is that oxygen is directly adsorbed on the catalyst and then reduced with (H⁺ + e⁻). The second possibility is that the weakly adsorbed oxygen first combines with the proton to form the precursor OOH⁺ and then the reaction proceeds further with the addition of more protons to form H₂O. Correlation calculations show that if the adsorption process is consistent with the description of the second viewpoint, the adsorption reaction requires certain activation energy. Thus, the adsorption reaction conforming to the first view is more kinetically advantageous. Usually, after doping a small amount of the N element, the direct oxygen adsorption capacity of C nanomaterials is weak, and hence many studies believe that the adsorption reaction is more likely to follow the second possibility.

It has been pointed out in previous studies that N atoms have larger electronegativity than the carbon and hence N atoms cannot be considered as the O₂ adsorption sites. These studies also indicate that those carbon atoms with positive charge/positive spin density values around the N dopant possess the great adsorption capacities with gaseous O₂. In fact, the adsorption energy depends on the energy changes of the entire system before and after the adsorption process. Thus, the adsorption performance of the active site is not only associated with local characteristics of the catalytic material. In particular, the relationship between the resonance energy associated with the topology (a global characteristic) of the substrate and the adsorption capacity of the substrate is rarely mentioned in previous theoretical studies.

In this study, we used graphene nanoribbons, a common sp² carbon nanomaterial containing the hexagonal lattices doped with N atoms, as the substrate for understanding the ORR mechanism. The doping of the N element and particularly the effect of edge defects has been investigated (this edge defect has been confirmed to exist in experiments). Under the investigated theoretical conditions, N-doped graphene nanoribbons with the edge defect (ND-GNR) ORR process by analyzing various ORR mechanistic parameters. In addition, the change of resonance energy before and after O₂ adsorption of ND-GNR was analyzed from the perspective of chemical graph theory to explain the cause and distribution of active sites in ND-GNR. Finally, the case of changing the width of the model and the doping atoms was also considered and briefly analyzed. The significance of this research is to propose a model that theoretically has both low overpotential and good adsorption performance. In addition, the analysis of the changes in the resonance energy of the substrate can explain the phenomenon that some negatively charged C sites are active. Because it is difficult to directly calculate the difference in resonance energy, qualitative analysis is performed here using chemical graph theory to make the analysis more intuitive. This study provides more ideas for building a model of good ORR activity.

2. COMPUTATIONAL DETAILS

DFT computational simulations were performed using the dmol3 program. The generalized gradient approximation with Perdew Burke Ernzerhof was chosen for the analysis of the exchange–correlation energy. The core treatment parameter used in the calculations was selected as all electron and the basis was the double numerical plus polarization. The track cutoff radius was set as 4.2 Å. A smearing value of 0.005 Ha made the calculations easier to converge. The convergence tolerance of energy, force, and displacement were set as 10⁻⁵ Ha, 0.001 Ha/Å, and 0.005 Å, respectively. The Grimme dispersion correction method was chosen to calculate the interaction between molecules. The conductor-like screening model (COSMO) were used to simulate the aqueous solvent environment for the calculation and the dielectric constant was set as 78.54. The charge distribution is judged by analyzing the Mulliken charge.

The adsorption energy of adsorbed molecules on the substrate is defined by the formula: \( E_{ad} = E_{mol\text{sub}} - E_{mol} - E_{sub} \) where \( E_{sub}, E_{mol\text{sub}}, E_{mol} \) were the total energy of substrate, ORR intermediates, and the most stable adsorption configuration, respectively. Thermodynamic calculations were based on the model proposed by Nørskov et al. The overall free energy change (\( \Delta G \)) is calculated by \( \Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{disp} \) ZPE is zero-point energy and S is the entropy. ZPE and entropy can be obtained by calculating the vibration frequency. \( \Delta G_U \) represents the effect of the electrode potential that is equal to \( -eU \), where \( U \) is the potential difference between the two poles and \( e \) is the basic positive charge. \( \Delta G_{disp} \) is the effect of the solvation environment that is equal to \( -kT \ln10 \times pH \), where \( k \) is the Boltzmann constant and \( T \) is chosen as 298.15 K. This study assumes that the pH of the solution is 0, so the \( \Delta G_{disp} \) is 0 eV in all calculations. The ground state of an oxygen molecule is a triplet state, and it is usually avoided to directly calculate its free energy. Instead, the free energy is calculated indirectly using an equation: \( G_{O_3}(g) = G_{H_2O(l)} - G_{H_2(g)} + 4.92 \text{ eV} \). The \( G_{H_2O(l)} \) can be obtained by calculating \( G_{H_2O(g)} \) at a pressure of 0.035 bar because the pressure of 0.035 bar can equalize the chemical potential of the liquid water molecules and the gaseous water molecules at 298.15 K.

3. RESULTS AND DISCUSSION

3.1. ORR Mechanism on ND-GNR. The structure of ND-GNR is shown in the Figure 1. As discussed already, the adsorption gaseous O₂ is the initial step of ORR. By analyzing the possibility of various sites, it can be found that gaseous O₂ is spontaneously adsorbed only on two C carbon atoms (C1 and C1’). Next, the N dopant. As shown in the Figure 2, the adsorption of O₂ on C1 and C1’ carbon atoms can produce two configurations [initial state (IS) and final state (FS) of Figure 2], but one is metastable. The metastable configuration can be converted to the stable configuration after overcoming a small energy barrier (Figure 2). The calculation of adsorption energy only considers the most stable configuration, so the adsorption energy of ND-GNR was about \(-1.08 \text{ eV} \). It is necessary to state that the C1 and C1’ site in the ND-GNR have negative charges (Mulliken charge population, Figure S1),
and some C sites have positive charges (such as the C atom adjacent to the N atom, these sites do not actually adsorb oxygen). Moreover, the electron spin density value of each atom in the calculation results in 0. Therefore, the cause of the adsorption capacity needs to be considered from other aspects.

After the adsorption reaction, adsorbed oxygen will react with \((H^+ + e^-)\). According to previous studies, this reaction may follow two main mechanisms: the dissociation mechanism and the association mechanism.\(^{23}\) For the dissociation mechanism: the adsorbed oxygen dissociates into *O + *O, which further reacts with \((H^+ + e^-)\), where * represents a substrate site. For the association mechanism: adsorbed oxygen does not dissociate, and directly reacts with \((H^+ + e^-)\) to form *OOH. The *OOH formed through the association mechanism has the possibility to produce hydrogen peroxide in the consecutive reaction with \((H^+ + e^-)\), which is an undesired two-electron process. Hence, it is desirable that the catalysts developed should undergo a direct dissociative mechanism to form \(H_2O\) as much as possible, rather than the undesired associative mechanism to form hydrogen peroxide.\(^{23}\)

Our DFT calculation results show that the ORR of ND-GNR follows the dissociation mechanism with a direct four-electron process to form \(H_2O\). The reason is that the dissociation of adsorbed oxygen only needs to overcome a small energy barrier (Figure 3). Moreover, the product of the dissociation mechanism has a hydrogen bond and thus is very stable (Figure 5c). On the other hand, the product of the
association mechanism, *OOH is relatively unstable and can be converted to the above configuration (Figure 4). At the same time, the formation of *OOH releases less energy. When the voltage of the two poles is increased, the potential of e− becomes lower, which is disadvantageous for forming *OOH. Finally, under the dissociation mechanism, according to the free energy of each intermediate product, the ORR of ND-GNR can be divided into the following steps:

\[ \text{O}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{OOH} \]
\[ \text{O} + \text{OOH} \rightarrow \text{H}_2\text{O} \]
\[ \text{O} + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O} \]

According to the above ORR path, a free energy step diagram of ND-GNR can be obtained (Figure 6). In addition, the overpotential of ND-GNR is about 0.45 V, which indicates that ND-GNR has good performance.

![Figure 6](https://dx.doi.org/10.1021/acsomega.9b04146)

In the above discussion, (H+ + e−) in reactions 2−5 acts as the reactant, and (H+ + e−) indicates that H+ and electrons are isolated from each other. In the products of the reactions 2−5, H+ and e− are combined into a hydrogen atom. Previous theoretical studies have shown that there may be two mechanisms for the combination process: the Langmuir–Hinshelwood (LH) mechanism and the Eley–Rideal (ER) mechanism.36 The difference between these two mechanisms is that the sites in the combination process are different. In the LH mechanism, a proton first combines with an electron on the surface of the catalyst to form *H, and then *H reacts with the intermediate product; in the ER mechanism, a proton acquires an electron directly on the oxygen atom in the intermediate product.

For ND-GNR, it is assumed that ORR occurs through the ER mechanism. First, some theoretical research on Pt catalytic materials has roughly shown that the introduction of H atoms in the ER mechanism does not need to overcome a large energy barrier.36 In addition, in the study of this paper, the introduction of hydrogen atoms under the ER mechanism reduces the energy of the system; in the case of the LH mechanism, the energy of the system increases when *H is formed in reactions 2−4 (Table S1). For reaction 5, when protons are converted to *H at Cl or C1’ sites, the energy of the system can be reduced. Unfortunately, reaction *H + *OH → H₂O is less likely to react. This reaction is hardly exothermic and has a reaction barrier of about 1.0 eV. Although this reaction can become exothermic by increasing the width of the model (Figure S2), the reaction barrier of the reaction is hardly reduced. Thus, once the *H + *OH configuration is formed, it may mean that the ND-GNR will lose ORR activity. However, the relevant calculations suggest that the introduction of hydrogen atoms may happen through a special approach. The proton is likely to not directly reach the oxygen atom of the intermediate product. Instead, a special structure is first formed: a proton is linked to the oxygen atom of the intermediate product by hydrogen bonding interactions using several water molecules as bridges, and then under the activation of a certain energy, the hydrogen atom adjacent to the oxygen atom of the intermediate product is converted into a proton.37 This mechanism increases the likelihood that the last step of the reaction will occur through the ER mechanism.

In summary, ORR can be carried out more smoothly under the ER mechanism than the LH mechanism.

### 3.2. Effect of Resonance Energy on Adsorption Energy

The qualitative analysis of resonance energy in this paper draws on the viewpoint of chemical graph theory. The effect of resonance energy on the adsorption energy is as follows: an increase in the resonance energy of the substrate in the adsorption reaction tends to indicate an increase in the adsorption capacity of the substrate. Conversely, a decrease in the resonance energy means that the adsorption capacity of the substrate is decreased. Chemical graph theory believes that the resonance energies of benzene hydrocarbons are mainly from those conjugate circuits, and the contributions of these conjugate circuits are considered to be linearly additive. The conjugate circuit can be understood as: in a certain Kekule valence structure, the conjugate circuit is a circuit composed of several C atoms, and this circuit is connected by a C−C single bond and C−C double bond in turn.38 There is the formula for benzene hydrocarbons:

\[ \text{RE} = \frac{n_1R_1 + n_2R_2 + n_3R_3 + \ldots}{K} \]

where \( n_1, n_2, \) and \( n_3, \ldots \) represent the number of conjugate circuits \( R_1, R_2, \) and \( R_3, \ldots \) respectively, and \( K \) represents the number of Kekule valence structures. \( R_1 \) represents the contribution of a conjugate circuit composed of 6 C atoms to resonance energy, \( R_2 \) represents a contribution of a conjugate circuit composed of 10 C atoms to resonance energy, and \( R_n \) represents the contribution of a conjugate circuit composed of \((4n + 2)\) C atoms to resonance energy.38 In general, the contribution of the conjugate circuit after \( R_1 \) can be ignored. The value of \( R_n \) is an empirical parameter and different values should be taken for different types of systems.

The rigorous approach should be to enumerate the Kekule valence structure of ND-GNR and the conjugate circuits in each of the Kekule valence structures, and finally obtain the approximate RE according to formula 6. A simple analysis method is considered here. For the bond analysis, the resonant representation and the Kekule representation are used (Figure 7). The area enclosed by the dashed line uses the resonant
atoms have only adsorbing oxygen is larger. Therefore, the resonance energy of the ND-GNR after adsorption can provide more conjugate circuits on average.

each Kekule valence structure of ND-GNR after oxygen always contain the resonance regions of ND-GNR, and thus the C1 valence structure, when the structures with large contributions (Figure 7a,c), the resonance regions of ND-GNR are destroyed. It can be seen that in those resonant relatively smaller.

The C1 and C1′ atoms in the ND-GNR have π electrons, while in the ND-GNR after oxygen adsorption, the C1 and C1′ atoms have only σ electrons. Therefore, for each given Kekule valence structure, when the σ electrons on the C1 atom and the C1′ atom become π electrons, some conjugate circuits are always destroyed. It can be seen that in those resonant structures with large contributions (Figure 7a,c,f), the resonance region of ND-GNR after oxygen adsorption can always contain the resonance regions of ND-GNR, and thus each Kekule valence structure of ND-GNR after oxygen adsorption can provide more conjugate circuits on average. Therefore, the resonance energy of the ND-GNR after adsorbing oxygen is larger.

In addition, in the ND-GNR, other C atoms are possible except that the atoms of C1 and C1′ are unlikely to be in the conjugate circuit (Figure 7a,c). When the π electrons of these C atoms in the conjugate circuit are converted into σ electrons (i.e., adsorption reactions occur at these sites), some conjugate circuits are destroyed, which causes the resonance energy of the system to decrease. Therefore, the adsorption capacity of these sites is poor, which is consistent with the detection of previous adsorption sites. For the same reason, if *H is produced at these sites on the reactants of reactions 2–4, the same effect will be produced. This is why the ORR of this model is not well suited to the LH mechanism in reactions 2–4.

3.3. Effect of the Model Width and Doping Element.
First, the influence of model width on the adsorption performance of ND-GNR is discussed. It can be speculated that as the width of the model increases, the magnitude of the fluctuation of the adsorption energy gradually becomes smaller and eventually approaches a certain value (Figure S4). The values of the adsorption energy of these models are still in the appropriate range, indicating that the change in width can adjust the adsorption energy to some extent. In addition, the change in width also affects the free energy of other ORR steps, thus changing the overpotential of the model. It is worth mentioning that ND-GNR1 has a lower overpotential of 0.36 V, which is lower than the theoretical overpotential (0.45 V) of the Pt catalytic material. The overpotential depends on the one with the least exotherm in the reactions 2–5, and the total exothermic amount of the reactions 1–5 is 4.92 eV, so the adsorption energy also affects the overpotential. Because of this trend of adsorption energy, the relationship between the overpotential and the width of the model becomes unclear (Table 1).

| Substrate | adsorption energy (eV) | overpotential (eV) |
|-----------|-----------------------|------------------|
| ND-GNR    | −1.08                 | 0.45             |
| ND-GNR1   | −0.89                 | 0.36             |
| ND-GNR2   | −0.76                 | 0.40             |
| BD-GNR    | −0.91                 | 0.40             |
| PD-GNR    | −1.19                 | 0.52             |

To further extend our understanding the effect of B and P dopants, the N atoms in the ND-GNR1 is replaced with B atoms or P atoms (Figure 8e,g). When B atoms are doped, B atoms can also act as adsorption sites. For ease of comparison, the ORR that occurs on the B atom is ignored here. Moreover, according to previous studies, P atoms are easily passivated by oxygen, which are described in both experimental and theoretical calculations. Because the electronegativity of the P atom and the B atom is small, the doping effect of these atoms is different from that of the N atom doping. Finally, compared with ND-GNR1, although the exothermic heat of reaction 2 of PD-GNR and BD-GNR is reduced, the exothermic heat of reaction 4 is also reduced, which causes the overpotential to rise. Although the adsorption energy and overpotential of these models have changed, they are all within the appropriate range, which indicates that such models have good controllability and great potential.
4. CONCLUSIONS

Some of the carbon sites in the nonconjugated circuit can be made active by the synergy of edge defects and dopant atoms, and this effect is discussed from the perspective of chemical graph theory. When screening highly active C sites, after enumerating the resonance structures with larger contributions, attention should be paid to those C atoms that are not on any conjugate circuit. In addition, by calculating the ORR path, it is found that the ND-GNR not only has suitable adsorption energy, but also has a low overpotential. Changing the width of the model or changing the doping element can appropriately adjust the ORR activity of the model. From the calculation results of this paper, as the width increases, the fluctuation of the adsorption energy value of the model decreases and gradually approaches a certain value. Because of this tendency to adsorb energy, it is difficult to judge the change in overpotential as the width of the model increases. However, it was found by calculation that the overpotential of

Figure 8. ND-GNR1 (a) and its free energy step diagram (b); ND-GNR2 (c) and its free energy step diagram (d); BD-GNR (e) and its free energy step diagram (f); and PD-GNR (g) and its free energy step diagram (h).
some models can reach 0.36 V. The influence of doping elements is more complicated. According to the calculation results, the doping of elements with lower electronegativity than carbon will reduce the exotherm of reaction 2, but will also reduce the exotherm of reaction 4, which makes reaction 4 the least exothermic reaction. Therefore, BD-GNR and PD-GNR also have high potential. These findings could serve as guidelines for the construction of efficient ORR carbon nanomaterial catalysts. Theoretical calculations show that ND-GNR has good ORR activity but this infinite-cycle structure is an ideal structure. Combined with the actual situation, ND-GNR can be transformed into a carbon nanotube structure, thereby inheriting the important attributes of ND-GNR. In addition, you can also get good ORR activity by adjusting the width or doping the atoms.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04146.

Mulliken charge of ND-GNR, free energy of $\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$, energy required to form $\text{H}_2\text{O}$, resonance structure with large contribution in ND-GNR1,2, and adsorption energy varies with model width (PDF)

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