Exploring an effective oxygen reduction reaction catalyst via 4e⁻ process based on waved-graphene

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ABSTRACT A novel pure and N-doped waved-graphene electro-catalyst with various wavelengths for oxygen reduction reaction (ORR) is explored in acid medium based on the first-principles calculations. The associative and dissociative mechanism are both explored from the O₂ adsorption to the H₂O formation step by step, from which the dissociative mechanism is likely the only way with an effective 4e⁻ process. Furthermore, a very favorable and effective mechanism is proposed for the ORR process, which may provide a guideline on the design of new non-metal electro-catalysts.

Keywords: graphene, oxygen reduction reaction, fuel cell, metal-air cells, non-metal catalyst

INTRODUCTION

Oxygen reduction reaction (ORR) is an important process in various fields, such as fuel cell and metal-air batteries [1,2]. For example, an ORR catalyst in fuel cell can directly generate electricity by electrochemically reducing oxygen and oxidizing hydrogen with water as the only by-product. This energy conversion process is receiving intensive interest for its high energy conversion efficiency, pollution free, and potential large-scale applications. Among the ORR catalysts, platinum (Pt)-based materials are considered as the most efficient catalysts for ORR toward the four-electron transfer pathway ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) [3,4]. Unfortunately, limited natural resources, high cost, and poor CO tolerance hinder its large-scale commercial applications. Therefore, it is urgent to develop new cost-effective electro-catalytic materials to replace the Pt-based catalysts for fuel cell.

Graphene-based ORR catalysts were regarded as one of the possible alternatives to Pt-based catalysts due to their low price, rich abundance, and high stability. However, pure graphene is not good for ORR. A lot of efforts have been done to tune their electronic structures to enhance

their ORR activity by doping a heteroatom [5–9], such as nitrogen (N), phosphorus (P), boron (B), sulfur (S), selenium (Se), antimony (Sb) or their mixtures [10–13]. Another way is to introduce active nonprecious transition metal (e.g., Fe, Co, and Ni) atoms or nanoparticles into heteroatom-doped graphene [14–16]. For example, Fe-N modified carbon electro-catalysts [17] have been reported by Zhu *et al.* [18], Kong *et al.* [19] and Zitolo *et al.* [20] with high ORR activity and good durability in both alkaline and acidic media. However, controlled synthesis of these graphene-based materials is extremely difficult. Moreover, the formed active sites are very few, which will lead to the ORR toward the two electron pathway with the formation of H₂O₂ intermediate ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$). This is because the four-electron reduction pathway requires relatively active catalytic sites to activate O₂ molecules, resulting in the O–O bond breaking and the formation of O–H bond [14]. Because the formation of the graphene basal plane is thermodynamically favorable, it would limit the number of active sites in the graphene-based catalysts.

Fortunately, the waved-graphene (WG) with periodic ripples along one direction, which had been experimentally achieved on a pre-strained substrate [21] (Fig. 1 and Scheme S1), can at least expose 50% active sites, leading to improved catalytic activity due to the enhanced local chemical potential at the curvatures [22]. Also, our previous theoretical study has shown that tunable chemical reactivity can be achieved by simply modulating the local curvatures through compression [22]. Especially, the atoms at the crest of the WG own the highest chemical reactivity due to the largest local curvature and strain energy according to the “ π -orbital axis vector” (POAV) theory [23–27]. Considering its abundant active sites and high chemical reactivity, the WG could be a suitable ORR catalyst. It is well-known that a fuel cell working in an

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Figure 1 The proposed WG for ORR catalysts. For clarity, C atoms of the WG are displayed in two different colours.

acidic medium is of practical significance due to the high CO tolerance during the ORR at the cathode [14,28]. Thus, in this work, we investigate the ORR performance of the WG in the acid medium based on the first-principles calculations. We focus on the armchair WG (thereafter, referred to ac-WG) because that the bending of ac-WG occurring at the bridge between two hexagons has stronger decoupling between the big π bonding states in the neighbouring hexagons and larger charge redistribution [22]. The specific structures can be found in the Supplementary information.

COMPUTATIONAL SECTION

Computational method

We studied the catalytic properties of the WG (with or without doping) by the first-principles calculations, which is based on the density functional theory (DFT) [29] and the Perdew-Burke-Eznerh of generalized gradient approximation (PBE-GGA) [30]. The projector augmented wave (PAW) scheme [31–33] as incorporated in the Vienna *ab initio* simulation package (VASP) [31] was employed. The Monkhorst and Pack scheme of k point sampling was used for integration over the first Brillouin zone [34]. A $1 \times 1 \times 1$ grid for k-point sampling for geometry optimization, and an energy cut-off of 500 eV was consistently used for the WG in our calculations. Good convergence was obtained with these parameters and the total energy was converged to 1.0×10^{-5} eV/atom.

Optimization of WG

WG was constructed based on the calculated lattice parameter of the graphene (C–C bond length is 1.427 Å).

The starting wavelength of flat graphene is about 25 Å (referring to the supercell's length of the flat graphene along armchair/zigzag direction). WG with shrunk wavelength was realized by compression. The top view and side view of the ac-WG with 30%, 40% and 50% compression are provided in Figs S1 and S2, respectively.

Formation energy computation

The formation energy for a nitrogen dopant, E_f , was calculated by $E_f = E_{\text{N-doped-WG}} + m\mu_{\text{C}} - (E_{\text{WG}} + m\mu_{\text{N}})$, where $E_{\text{N-doped-WG}}$ is the total energy of the supercell with N-doped WG, and E_{WG} is the total energy of the pristine WG; μ_{C} is the chemical potential of carbon defined as the total energy of graphene per carbon atom and μ_{N} is the chemical potential of N taken as one-half the total energy of N_2 molecule. And m is the number of nitrogen atoms in the model.

Adsorption energy computation

The adsorption energy (E_{ad}) of the adsorbates on WG was calculated as $E_{\text{ad}} = E_{\text{WG/intermediate}} - E_{\text{WG}} - E_{\text{intermediate}}$, where E_{WG} and $E_{\text{intermediate}}$ are the energies of adsorption substrate (WG) and the isolated adsorbate molecules, respectively, and $E_{\text{WG/intermediate}}$ is the total energy of the molecule adsorbed on WG. Based on the definition, the negative E_{ad} indicates the exothermic adsorption processes, which means the energetically favorable configurations.

Free energy computation

The free energy change (ΔG) is defined by $\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S + \Delta G_{\text{pH}} + \Delta G_{\text{U}}$, which was based on a standard hydrogen electrode (SHE) model suggested by Nørskov *et al.* [35], and ΔE is the electronic energy change directly, ΔZPE is the zero-point energy change, T is temperature (298.15 K), and ΔS is the entropy change, respectively. The vibrational frequencies were calculated to determine ZPE and the entropy contributions. ΔG_{pH} is the correction of H^+ free energy by the concentration $\Delta G_{\text{pH}} = kT \ln 10 \times \text{pH}$, where k is the Boltzmann constant and pH is assumed to be 0 for acidic environment. $\Delta G_{\text{U}} = -neU$, where n is the number of transferred electrons, e is the elementary charge, and U is the electrode potential referenced to SHE. As indicated by the computational hydrogen electrode (CHE) model, the free energy change ΔG is a function of the applied electrical potential (U) [14,36]. The free energy of ($\text{H}^+ + \text{e}^-$) in solution at standard conditions was assumed as the energy of $1/2 \text{ H}_2$ according to a computational hydrogen electrode model suggested by Nørskov *et al.* [35] Taking the reaction $\text{HO}^* + \text{H}^+ + \text{e}^- \rightarrow * + \text{H}_2\text{O}$ as an example, at $U = 0 \text{ V}$, $\Delta G = \mu(\text{H}_2\text{O}) + \mu(*) -$

$\mu(\text{HO}^*) - \mu(\text{H}^+ + \text{e}^-) = \mu(\text{H}_2\text{O}) + \mu(^*) - \mu(\text{HO}^*) - \mu(1/2\text{H}_2(\text{g}))$, where μ is the chemical potential. At an applied potential of $U = 1.23$ V, $\Delta G = \mu(\text{H}_2\text{O}) + \mu(^*) - \mu(\text{HO}^*) - \mu(\text{H}^+ + \text{e}^-) - eU = \mu(\text{H}_2\text{O}) + \mu(^*) - \mu(\text{HO}^*) - \mu(1/2\text{H}_2(\text{g})) - eU$, where $e = 1$ since there is only one proton-electron transfer ($\text{H}^+ + \text{e}^-$). Thus, if there are two ($\text{H}^+ + \text{e}^-$), e would be 2.

The free energy of O_2 was obtained from the free energy change of the reaction $\text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O}$, which is -4.92 eV at 298.15 K and a pressure of 0.035 bar. The free energy of H_2O was calculated in the gas phase with a pressure of 0.035 bar, which is the equilibrium vapor pressure of H_2O at 298.15 K. The free energy of OH^- was derived from the reaction $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$, which is in equilibrium in water solution [37,38]. The entropies and vibrational frequencies of the adsorbates in the gas phase were taken from the NIST database. Zero-point energy and entropies of the adsorbed species were calculated explicitly from the vibrational frequencies, while the WG substrate was fixed.

RESULTS AND DISCUSSION

The first step in the ORR process is the adsorption of O_2 molecule on the catalyst, which is very critical to both dissociative and associative mechanisms [39]. Several possible adsorption sites are considered near the crest of ac-WG (Figs S1, S2) under different compression to obtain the most stable adsorption configuration. It turns out that O_2 molecule preferably adsorbs on the top of C–C bond in parallel. The O_2 adsorption energy E_{ad} is calculated to be -0.09 , -0.36 , -0.62 eV for the WG under 30%, 40% and 50% compression, respectively (Table 1), where the negative values indicate the exothermic process. We see that the bigger compression, the stronger adsorption of O_2 molecule on the WG. Due to the lower adsorption energies of O_2 molecule (not shown here) on WGs under flat, 10% and 20% compression, only the WGs under 30%, 40% and 50% compression are considered in the following (presented as p-30, p-40 and p-50, and p represents pure). Previous studies have shown that N-doping of graphene is considered to be an effective method to enhance the ORR

performance due to the charge redistribution among surrounding C atoms caused by the higher electro-negative of N atom than C atom [5,40–42]. First, we have calculated the formation energy E_{f} of the N-doped WG under 30%, 40% and 50% compression (presented as N-30, N-40 and N-50, respectively, as shown in Fig. S3) listed in Table S1. It can be seen that nitrogen atom prefers to substitute the carbon atom in pure WG. Furthermore, taking p-50 and N-50-doped WG as examples, the two C atoms adjacent to the doped N atom (Fig. S3 and Table S2) have changed from negative state to positive state, which would benefit the O_2 molecule adsorption. Thus, the adsorption of O_2 molecule on the N-doped WG is also calculated and the adsorption energies are shown in Table 1. Surprisingly, the E_{ad} on the N-doped WG are greatly enhanced with E_{ad} of -0.83 , -1.05 and -1.22 eV, respectively, comparing with the p-WG (Fig. S3), which is also much larger than the planar N-doped graphene [37,43,44]. Accordingly, the bond of O–O is elongated to 1.509–1.518 Å from the original 1.21 Å upon adsorption on the six kinds of WG (Table 1). Also, the charge transfer from the WG to the O_2 molecule is as much as ~ 1 e, which is much higher than that of the planar N-doped graphene [44], suggesting an obvious chemisorption. Similarly, the higher compression, the more charge transfer from the pure WG or N-doped WG to O_2 molecule. Therefore, we conclude that both thermodynamically favourable adsorption energy and large O–O bond stretching due to excess charge transfer to the O_2 molecule result in the first step toward the catalytic ORR.

In the acid medium, the ORR process can proceed in two ways: associative way and dissociative way D1 or D2 (Fig. 2) [39]. For the associative mechanism, the first step involves the formation of an O–OH structure when capturing the first H^+ and an additional electron after O_2 molecule adsorption on the WG. Interestingly, after the geometry relaxation of the WG–O–OH configuration, we obtain a WG–OHO complex (Fig. 2c1 and 2c2, 0.01 eV in energy difference) with H atom in the middle of the two O atoms, which ascribes to the strong and favourable

Table 1 The adsorption energy E_{ad} (eV) of O_2 molecule (in singlet (s) and triplet (t)) and OHO intermediate on WG. The O–O distance (Å) of the adsorbed O_2 molecule and the corresponding separated O–O. The charge transfer C (e^-) from the WG to O_2 molecule.

	$E_{\text{ad-O}_2\text{-s}}$	$E_{\text{ad-O}_2\text{-t}}$	$E_{\text{ad-OHO}}$	D_{O_2}	$D_{\text{O-O}}$	C
p-50	−0.62	0.47	−3.87	1.518	2.825	1.01
p-40	−0.36	0.77	−3.36	1.516	2.774	0.95
p-30	−0.09	1.01	−2.81	1.515	2.727	0.93
N-50	−1.22	−0.14	−5.88	1.517	2.655	0.94
N-40	−1.05	0.03	−5.42	1.514	2.609	0.92
N-30	−0.83	0.25	−4.88	1.509	2.567	0.90

Figure 2 The ORR process based on the dissociative mechanism D1 or D2 and the proposed mechanism in red dashed arrows.

O---HO hydrogen bond. For the second step, a H₂O molecule should be formed and desorbed from the substrate after capturing the second H⁺ ion and an additional electron. However, a WG-OH-OH (Fig. 2e1) or WG-HO-HO (Fig. 2e2) structure is gained with the two OH group linked by O---HO hydrogen bond. In other words, the complex d1 or d2 (Fig. 2) cannot be obtained based on our calculations. Thus, we conclude that the associative mechanism cannot take place on the novel WG ORR electrocatalyst.

Alternatively, as for the dissociative mechanism (the 4 e⁻ process), when adding the second H⁺ ion and an additional electron, e1 and e2 are formed with very small energy difference (0.01 eV) by considering different attack-direction of proton. After capturing the third H⁺ ion, the first H₂O molecule is formed and desorbed from the WG (Fig. 2f1 and 2f2). The second H₂O molecule would form after capturing the fourth H⁺ ion and an electron. Ultimately, two H₂O molecules are formed (Fig. 2g). The optimized structures with the lowest energy in each elemental step of ORR process are provided in Fig. 3 (for p-50 and N-50-doped WG), and Tables S3–S6. It should be noted that O-WG-O structures are obtained with the distance of two O atoms elongated to 2.567–2.825 Å after slightly disturbing the chemically adsorbed O₂ molecule (Table S6). Unfortunately, the transition state from the O₂-WG to O-WG-O configuration is not observable due to the larger deformation of the C atoms adsorbed by O atoms. This behavior could be caused by the high strain energy in the crest of WG and high repulsion of the two O

atoms (Fig. S3). In the view of thermal stability, the ORR process would not proceed through the O-WG-O way. In fact, the structure c1, c2, e1, e2, f1, f2 and g can also be obtained from the O-WG-O complex by capturing H⁺ and e⁻ one by one. In fact, another possible way is through the formation of H₂O₂ molecule. However, e1 or e2 is formed after geometry optimization of WG-H₂O₂ complex, indicating that the molecule H₂O₂ would decompose into OH---OH group on the surface of WG. To be concluded, the dissociated mechanism (4 e⁻ process) is very likely the only efficient way for the novel pure and N-doped WG electrocatalyst for ORR in acid.

To better understand the overall ORR process, we plot the reaction free energy diagram in Fig. 4 for p-50 and N-50 doped WG. The reference level of free energy values is set as that of the final product (*+ 2H₂O). We see that the p-50-WG consumes 0.79 eV (in triplet) energy to chemisorb O₂ molecule in the first step of ORR process; then all the elementary steps are exothermic occurring spontaneously in the following ORR steps. Notably, only 0.19 eV energy is needed to chemisorb O₂ molecule (triplet state) on the N-50-doped WG. However, it is uphill (1.1 eV) for the step O-HO-WG (c) → OH-OH-WG (e) for the N-50-doped WG at *U* = 0 V, suggesting it is the rate-determine-step due to the highest OHO (adjacent to the N atom and Fig. 3) adsorption energy (−5.88 eV and Table 1). When *U* = 1.23 V, all the steps become uphill except the desorption of the second H₂O molecule for p-50 WG electro-catalyst. As for the N-50-doped WG, however, there are two uphill steps. One is the same step O-HO-WG (c) → OH-OH-WG (e) as that at *U* = 0 V. The other step is the desorption of the second H₂O molecule with a Δ*G* = 0.31 eV. Overall, it is hard to proceed the ORR for the N-50-doped WG due to large free energy consumption (1.1 eV) in the step O-HO-WG (c) → OH-OH-WG (e). Thus, the p-50 WG is superior to the N-50-doped WG electrocatalyst in this case. Remarkably, the maximum potential is 0.5 V, at which all the reactions are still exothermic for the pure WG. Thus, in acidic media, the onset potential would be 0.5 V for pure WG ORR electrocatalyst. The similar free energy trends can be found for the p-40 (30) and N-40(30)-doped WG, which are provided in Fig. S4. For the p-30 and p-40 WG, all the elementary steps are exothermic after the chemisorption of O₂ molecule with 0.6 V onset potential for ORR, which is comparable to the N-doped graphitic materials. For the 30-N and 40-N-doped WG, it must overcome 0.05 and 0.33 eV free energy for the step O-HO-WG (c) → OH-OH-WG (e), which is much lower than the 50-N-doped WG.

Importantly, considering abundant H⁺ ions in the acid

Figure 3 Typical ORR process from O₂ adsorption to two H₂O molecule desorption from the catalyst p-50 and N-50-doped WG. Upper panel and lower panel are pure and N-doped WG structures with the lowest energy, respectively.

Figure 4 Free energy diagrams (at different electrode potentials) for the ORR on p-50 and N-50-doped WG electrocatalyst in an acidic medium. Dissociative mechanism D1 or D2 (left panel, red line is for p-50 WG at 0.5 V potential) and the proposed mechanism (right panel). The labels are: initial = O₂ + * + 4H⁺ + e⁻, a = O₂* + 4H⁺ + e⁻, c = O-HO* + 3H⁺ + e⁻, e = HO-HO* + 2H⁺ + e⁻, f = HO* + H₂O + H⁺ + e⁻, g = 2H₂O + *, respectively.

medium, thus, we proposed a mechanism that the two O atoms of chemisorbed O₂ molecule can be attacked by H⁺ ion simultaneously. In this case, the mechanism is initial → a → e (e1 or e2) → g (red dashed line in Fig. 2).

Accordingly, we have plotted free energy diagram for the pure and N-doped WG electrocatalyst for ORR in Fig. 4 and Fig. S5, respectively. Based on this mechanism, all the ORR process can proceed smoothly for all p-50/40/30 and

N-50/40/30-doped WG from $U = 0$ V and $U = 1.23$ V with a slight energy demand (0.09 eV at 1.23 V) for N-50-doped WG. If the O–WG–O pathway is considered, the onset potential for the p-30/40 and N-30/40 doped WG are 0.7/0.4 and 0.4/0.5 V (Fig. S4), respectively.

CONCLUSIONS

In summary, we explore the ORR process based on novel WG. The first-principles calculations suggest that the ORR process can proceed *via* the desired 4e^- dissociative mechanism on WG. For pure WG, it can proceed smoothly with the onset potential 0.6 V. However, for the N-doped-WG, it must overcome 1.1, 0.33 and 0.05 eV in the step O–HO–WG (c) $\rightarrow$ OH–OH–WG (e), respectively. Alternatively, we propose a mechanism: $\text{O}_2\text{--WG} \rightarrow \text{O--O--WG}$ or $\text{O---O--WG} \rightarrow \text{HO--HO--WG}$ or $\text{OH--OH--WG} \rightarrow \text{H}_2\text{O---WG}$, considering the two O atoms attacked by two H^+ ions simultaneously. Importantly, O_2 molecule can be adsorbed chemically on the novel WG catalyst, which is a prerequisite in the following ORR steps. Thus, our novel WG catalyst can also find applications in other reactions involving activating some molecules like O_2 [45], N_2 [46,47], NO [48], CO [49–50], etc. We also hope the results can provide necessary mechanism information for future experiments on WG for ORR.

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波浪型石墨烯作为高效四电子氧气还原反应电催化剂的探索

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摘要 本文基于第一性原理, 针对一种本征或氮掺杂的石墨烯在不同晶胞参数压缩比和在酸性条件下的氧气还原反应机理进行了探索. 文章假设了两种不同的反应机理, 并逐步分析了从氧气吸附到水分子形成的整个过程, 结果表明基于氧气分子解离机理的四电子过程是唯一有效的路径. 文章进一步提出了一种有效的氧气还原反应机理, 这为设计新的非金属电催化剂提供了新的思路.