DFT analysis elementary reaction steps of catalytic activity for ORR on metal-, nitrogen- co-doped graphite embedded structure

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Abstract

Metal-nitrogen coordinated graphite coordination structures are becoming more and more attractive for its novel catalytic activity in oxygen reduction reaction (ORR) at the fuel cells. In this work, single copper atom on graphitic carbon nitride acting as electrocatalyst for ORR have been investigated by using the density functional theory method. Our study results that the Cu site is the active center for all the possible elementary steps of the ORR. Further studies the elementary reaction steps are used to explore the underlying mechanisms to gain insights into ORR. Both the O₂ dissociation and O₂ hydrogenation paths are probably to ORR on the CuN₄-Gra surface. All the possible elementary reaction steps for the ORR are exothermic with small reaction barriers (less than 1.98 eV) for O₂ hydrogenation. Meanwhile, with large reaction barrier (3.16 eV) for O₂ dissociation to go through the rate-limiting steps. The Gibbs free energy for each elementary step of ORR is used to clarify which path determine the ORR/OER on the CuN₄ co-doped graphene. Scaling relation and surface phase diagram are obtained by calculated Gibbs free energy of intermediates at surface active sites with various adsorption species. The different working potentials are also considered for the studied catalysts, as the overpotential of ORR is also an important indexes of the catalytic activities of the catalyst, we calculated the overpotential for each active site on the structures and determined the minimum overpotential for ORR.

Graphic abstract

Keywords CuN₄-Gra coordinated structure · Oxygen reduction mechanism · Activity barrier · Gibbs energy change · Surface phase diagram

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1 Introduction

The metallic and N doped 2D materials embedded structure such as graphitic [1–3], pyridinic [4–6], and pyrrolic N [7, 8] and metal-N heterogeneous structures have been investigated to be as promising catalytic substitutes for oxygen reduction reaction (ORR) and initiate a command in an application to fuel cells in recent years [9, 10]. The metal and N heteroatoms of embedded structure could tune the charge distribution and change catalytic activity of graphite due to the difference in electronegativity between the contiguous N and C atoms. Currently their main usage is focused to as reliable energy storage or energy conversion device applications, [11, 12] the main challenges need to be overcome are related to the storage of O_2 , and energy conversion efficiency. Thanks to the high energy conversion efficiency and storage density of the ORR process for fuel cells, [13] it has been applied massively in portable electronic devices. Metal-N doped graphite catalytic materials have attracted immense attention, due to the high catalytic activity for ORR/OER reactions as power sources for electric vehicles [14]. For example, there are considerable works which reveal that metal-N graphite materials have exhibited a higher ORR activity than non-metallic N-doped graphene; [15, 16] Recently, some theoretical investigations have shown that nitrogen-coordinated transition metals (e.g., Mn, Fe, and Co) in graphene exhibit also good ORR catalytic activity [17, 18]. Bai et al. [19] studied the reaction mechanism for oxygen reduction reaction (ORR) on P-doped graphene through the DFT method, resulting that P-doped graphite could exhibit high electrocatalytic activity, the most favorable reaction pathway is the hydrogenation of O_2 molecule to form OOH, then the hydrogenation of OOH gives H_2O and atomic O in ORR. Liu et al. [20] found that Fe/N-doped graphene could create a promising catalytic activity for ORR, and it can be as guidance for catalytic material design. Lu et al. [21] has studied the formation energy for MnN_4 embedded in graphene with dispersion-corrected density functional theory study for application in fuel cell devices, it is conducive to the design and improvement of catalyst ORR efficiency. Baran et al. [22] have investigated the ORR on metalloporphyrin combined with graphene based on metal MN_4 structures, resulting that there is a sensible scaling relationships between the Gibbs free energies and overpotential of oxygenated species (such as O, OH and OOH) during the ORR process, [23] it implied a volcano plots within overpotential versus adsorption Gibbs free energy of oxygenated species of ORR activity. The free energy of the ORR intermediates can be calculated by using the procedures proposed by Nørskov et al.

[24] the details about the calculation methods can be found elsewhere [25, 26] by calculation barrier energy can determine the most favorable reaction pathway of elementary reaction steps.

In this study we assume that the temperature is constant at 298.15 K with $pO_2 = 0.1$ bar [27], thus the change in Gibbs free energy caused by the temperature effect is neglected and included only phase state, solvation and hydrogen bonds correction [28]. The scope of this work is to explore the pathway of the reaction mechanism and the thermokinetics of the involved elementary reaction steps for ORR/OER on the CuN_4 active site. To further identify the most favorable pathway for ORR was performed to locate transition states (TS) and obtain barrier energy by CI-NEB method. [29, 30] There are two possible reaction pathways for O_2 . One is O_2 can capture one atomic H to form an OOH species and another is O_2 dissociation. During ORR and OER process, it found that there are several possible elementary reaction steps, such as OH and OOH dissociation, atomic O hydrogenation and OH diffusion. According to the original plan, we shall describe these reaction pathways in detail by the theory developed by Nørskov et al. [24] It can correctly describe the activation energy and reaction energy of Elementary reaction processes [31]. Moreover, the solvation and phase state effects are considered by a correction to the ORR from free energy in the calculations. It can be reflected in our calculations for the adsorption of intermediates, the DFT results show that the catalytic activity of the CuN_4 -graphite is comparable to that of Fe and Mn graphite embedded structure electrocatalysts catalyst, it demonstrates that the ORR on this class of catalysts can proceed via several reaction pathways with barrier and reaction energy.

1.1 Computational detail

All the calculations of geometric and energy are executed within the framework of density functional theory (DFT) method implemented in the VASP code [32, 33]. The Generalized Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof functional (PBE) is used to describe the exchange correlation potential. A cutoff energy of Plane-Wave basis was set with an adequate of 400 eV and accurate precision of convergence for the geometry optimization are set to 10^{-4} eV/Å for energy change, all atomic structures were fully optimized until the forces were smaller than -0.05 eV/Å. The K-point samplings of Brillouin zone integration was as implemented on a grid of $4 \times 4 \times 1$ Monkhorst-Pack method for relaxation calculations and transition state (TS) search by conjugate gradient (CG) method is performed, and a $7 \times 7 \times 1$ grid was used for electronic structure computations (shown in Fig. 1d, e), a periodic ($4 \times 4 \times 1$) supercell of CN_4Cu coordinated

Fig. 1 **a** Geometric structure of CN_4Cu graphene coordinated structure in a $4 \times 4 \times 1$ supercell. The gray and blue balls represent C and N atoms, respectively. **b** For local areas of supercell with 3 carbon atoms between the nitrogen atoms in the active site, and copper atom lies in the center site. **c** A schematic diagram of Brillouin zone, **d, e** band structure and PDOS of CN_4Cu graphene coordinate, respectively

structure graphite were selected for used. The real space thickness in the c direction was set to 15 Å in all the computations in which to ensure there is no interactions within the periodic boundary conditions [34]. The climbing-image nudged elastic band (CI-NEB) method was used to calculate activation energy for each step reaction, there are six images are insert along the favorable path to search for transition states (TS), it employed to locate the saddle points (TS) and reaction path along the smallest energy barrier choose as the reaction pathway [35, 36]. The Gibbs free energy of the ORR intermediates can be calculated from the procedures proposed by Nørskov et al. For each path, the activation energy (ΔE_{act}) and reaction energies (ΔE) were calculated by using formulas: $\Delta E_{\text{act}} = E_{\text{TS}} - E_{\text{IS}}$ and $\Delta E = E_{\text{FS}} - E_{\text{IS}}$, here IS, TS, and FS correspond to the initial state, transition state, and final state, respectively. The Gibbs free energy (ΔG) is given by the follow formula: $\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S$, it needs correction for H-bonds and phase states of the molecule are executed within the VASPKit code. Here, ΔE is the formation energy of intermediates can be obtained from DFT calculations, ΔZPE is the correction of zero point energy and entropic ($T\Delta S$) within 298.15 K, it can be calculated based on the vibrational frequencies [37, 38].

2 Results and discussion

2.1 Various ORR involved species

In order to make a thoughtful study the mechanism of ORR (O_2) and OER (OH) in both acidic and alkaline media on CuN_4 -graphite surface, firstly we need analyze the adsorption energy of various intermediate structure, it involved possible species in ORR/OER mechanism on the catalytic

active medium, the possible molecule adsorption configurations of the various species on in reaction mechanism, it includes O_2 , O, OH, OOH, and H_2O . For the ORR process, the O_2 molecule adsorption on the catalyst surface is the most essential step in initiating the entire ORR. Meanwhile, the water molecule adsorption is the most important for an OER process. So a suitable O_2 and H_2O adsorption energy are essential for sufficiently active molecules during the reaction process [39]. The optimized geometry and the calculated E_{ads} for both the most stable and some selected stable mono molecular and co-adsorption configurations are summarized in Fig. 2. It is well known that the physical absorption of O_2 and H_2O are the prerequisite whatever the ORR/OER proceed via the 4e transfer process, the other intermediates are chemisorption, it involves O, OH and OOH and their adsorption energy is significantly greater than that of H_2O and O_2 molecule. So the most stable adsorption configuration of O_2 and H_2O is first determined in my study, the corresponding adsorption energy is calculated by the follow equation:

$$\Delta E_{\text{ads}} = E_{\text{adsorbate/Sub}} - E_{\text{Sub}} - E_{\text{adsorbate}} \quad (1)$$

It means that the total energy of the adsorbed configurations subtracting the total energy of the substrate (CN_4Cu surface) and H_2O or O_2 molecule. Meanwhile, stable adsorption systems and the corresponding formation energy for all possible ORR step intermediate products are obtained by the follow methods reports [40, 41].

The intermediates (O, OH and OOH) energetically favorable adsorption configurations are shown in Fig. 2, and the co-adsorption configurations are shown in Figs. 3 and 4. It is found that the OH prefers to stay at the Cu top site and O at the six-member ring or the five-member ring when they co-adsorption, the E_{ads} of the OH in the co-adsorption

Fig. 2 Atomic structures of the relaxed for various ORR intermediates **a** OOH, **b** O, **c** OH, and **d** H₂O on CuN₄-co-doped graphene. The Eads (eV/mol) and adsorption distance (Å) for the related species are marked in the figures

configurations are -2.91 and -3.64 eV with OH and atomic H, respectively. For the OH and H co-adsorption two OH co-adsorption, the Eads's is -4.91 and -4.28 eV, respectively. These results indicate that a strong interaction exists between these species and the catalytic surface. It should be noted that small adsorption energy of H₂O (-0.05 eV). The weak interactions indicate that the water can be easily released as the final production of ORR. It different from the calculation method of adsorption energy of neutral molecules (O₂ or H₂O), the intermediates *O, *OH, and *OOH, must be inferred from the relative to H₂O (l) and H₂ (g) molecules, they are defined as the following formula from Eqs. (2) to (4):

$$\text{GrM} + \text{H}_2\text{O(l)} \leftrightarrow \text{GrM-O} + \text{H}_2\text{(g)} \quad (2)$$

$$\Delta E_{\text{O}} = E_{\text{GrM-O}} - E_{\text{GrM}} - (E_{\text{H}_2\text{O}} - E_{\text{H}_2})$$

$$\text{GrM} + \text{H}_2\text{O(l)} \leftrightarrow \text{GrM-OH} + 1/2\text{H}_2\text{(g)} \quad (3)$$

$$\Delta E_{\text{OH}} = E_{\text{GrM-OH}} - E_{\text{GrM}} - (E_{\text{H}_2\text{O}} - 1/2E_{\text{H}_2})$$

$$\text{GrM} + 2\text{H}_2\text{O(l)} \leftrightarrow \text{GrM-OOH} + 3/2\text{H}_2\text{(g)} \quad (4)$$

$$\Delta E_{\text{OOH}} = E_{\text{GrM-OH}} - E_{\text{GrM}} - (E_{\text{H}_2\text{O}} - 1/2E_{\text{H}_2})$$

Moreover, we set it for four electronic ORR reaction path processes and shown as follows from stage 5 to stage 8. In the whole ($\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$) process contains four stages as follows formulas, and the Gibbs free energy calculation of its corresponding to intermediate reaction as defined by eqn from Eqs. (5) to (8),

Furthermore, there are some small additional effect on the ORR adsorbates, such as solvation have estimated as 0.3/

Fig. 3 Summary of adsorption intermediates species its dissociation energies and reaction energies of adsorbates on the CuN_4 -graphite surface

eV, phases states have estimated as 0.45/eV and hydrogen bonds in the liquid phase state will be stabilized by 0.30/eV when solvated transfer solution medium, so Gibbs free energy needs correction. In this work, we set to $\Delta G_{\text{O}} = \Delta E_{\text{O}} - 0.30$; $\Delta G_{\text{OH}} = \Delta E_{\text{OH}} + 0.35$; $\Delta G_{\text{OOH}} = \Delta E_{\text{OOH}} + 0.40$ to adsorbed species as reported in Refs. [42, 43]. The term

ΔG_{W} is equal to -2.96 eV for a H_2O molecules form. The total Gibbs free energy ($\Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4$) of full reaction is obtained from the reaction of $\text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O}$, which is -4.92 eV at temperature of 298.15 K with pressure of 0.035 bar.

Fig. 4 Summary of adsorption intermediates species its dissociation energies and reaction energies of adsorbates on the on CuN₄-graphite surface

It is found from Fig. 2 that the central Cu atom serves as the catalytic activity and the most stable adsorption sites for all ORR reaction intermediate species, which agree well with some related previous work [44]. The first stage, O₂ tends to adsorb on the top of the Cu atom and formed a Cu–O bond distance of 2.22 Å with adsorption energy of -0.45/eV, and H₂O adsorbed on the top of Cu atom with a smaller adsorption energy (0.055 eV) than O₂ molecule as shown in Fig. 2a, e, respectively. For the electronic structure of bare surface (see Fig. 1d, e), the extra electrons compel the 2p states of N to Cu3d states which cross to the Fermi energy and activating the adjacent carbon atoms, eventually resulting in the obvious enhanced adsorption properties of adsorbed species. In addition to the hybridization of N2p* states with the C2p state around the Fermi

energy, the hybridization of 2p states of C and N is also observed. This speculation is corroborated by the large binding energy of intermediates, see from Fig. 2, about -2.18 eV for *OH, -3.11/eV for *O, and for -0.92/eV for *OOH, respectively.

2.2 ORR mechanism of O₂

The ORR process of O₂ may occur via two mechanisms. One is direct dissociation into two atomic O and another is associative to form OOH with one atomic H, all the two mechanisms make the adsorbed O₂ molecule sequentially hydrogenates into the final product H₂O. In the associative pathway, a O₂ hydrogenation occurs to form OOH species and then it can be either hydrogenated to form H₂O and

one O atomic, and then the atomic O sequentially hydrogenates into the final product H_2O with two atomic H. In addition, the overall possible reaction pathways are shown in Figure 15 (see from supporting information), where the individual possible reaction step of the dissociative pathways are shown. The relative reaction energy (ΔE) and reaction barrier energy (E_{act}) profiles of all reaction steps for the O_2 molecule with atomic H ORR process are presented in Fig. 3a. As a rule, the total energy of the O_2 adsorbed process on CuN_4 -graphene surface is used as the critical state, the adsorption energy of the states during the reduction steps is $-0.45/\text{eV}$ see in Fig. 2. The detailed data on all potential reaction step reaction energy and barrier energy are summarized in Fig. 3 in the supporting information. According to the calculated reaction barriers, the reaction pathway (as the red line in Fig. 8) is the most favorable pathway (reaction mechanism I) throughout the entire ORR. According to the reaction stages presented above, there are four possible stage for the ORR process on the CuN_4 -gra surface is first stage with the highest reaction barrier of $2.04/\text{eV}$, it corresponding to the hydrogenation process of the O_2 molecule with one atomic H to form the OOH species. Meanwhile, the rate-limiting stage of O_2 dissociation mechanism process with a high reaction barrier energy of $3.16/\text{eV}$, corresponding to the O_2 change into two atomic O.

We carried out density functional theory (DFT) calculations of the active sites and the overall possible reaction pathways are illustrated in Fig. 8, where the individual

microsteps of the dissociative pathway and associative pathway. In a word, it is seen from all the possible reaction pathways that for O_2 dissociation, the favorable pathway is the process $\text{O}_2 \rightarrow 2^*\text{O} \rightarrow 2^*\text{OH} \rightarrow ^*\text{O}$ and $\text{H}_2\text{O} \rightarrow ^*\text{O} \rightarrow ^*\text{OH} \rightarrow \text{H}_2\text{O}$ form with the rate determining step of O_2 dissociation (barrier activity $3.16/\text{eV}$). It need note that $^*\text{OH} + ^*\text{OH} \rightarrow ^*\text{O} + \text{H}_2\text{O}$ with a barrier energy of 0.62 eV and $^*\text{OH} + ^*\text{OH} + \text{H}^+ \rightarrow ^*\text{OH} + \text{H}_2\text{O}$ with a similar barrier energy ($0.59/\text{eV}$). It indicates that they are competitive pathways. Nonetheless, we also noted that the second atomic $^*\text{O}$ hydrogenation to form OH have the smallest energy barriers (0.26). On the other hand, the O_2 hydrogenation is the process a O_2 hydrogenation $\rightarrow ^*\text{OOH}$ dissociation $\rightarrow$ atomic $^*\text{O}$ and $\text{OH} \rightarrow ^*\text{O}$ hydrogenation $\rightarrow ^*\text{OH}$ hydrogenation $\rightarrow \text{H}_2\text{O}$ form with the rate-determining step of O_2 hydrogenation (barrier energy 1.98 eV) preferred due to a smaller energy barrier than O_2 dissociation (3.16 eV). The formed OH species is stable on the Cu site, H atom would diffuse from the five ring site and form OH with a 1.48 barrier energy and high exothermic reaction energy ($-3.34/\text{eV}$). For the OOH dissociation, producing an atomic O adsorbed on Cu with a exothermic reaction energy of $0.94/\text{eV}$ (See in Fig. 3e). The formed OH diffuses easily from the five-member ring to the Cu top site of the six-member ring with a reaction barrier of $0.69/\text{eV}$ and a small exothermic reaction energy of -0.36 , as presented in Fig. 4d.

The free energy diagram for the complete O_2 reduction at different potentials as shown in Fig. 5, direct dissociation of O_2 molecule into two atomic O atoms, it requires

Fig. 5 The possible ORR and OER pathways on single copper doped graphite, the free energy profiles for the ORR pathway (a, b) and the OER pathway (c, d) on CuN_4 -graphite surface for the complete O_2 reduction/oxidation at different potentials

an high energy barrier of 3.16 eV, then one atomic on top Cu hydrogenates with one H atomic to form $^*\text{O}$ and $^*\text{OH}$ co-absorption system, and then with another H atom spontaneous form two $^*\text{OH}$, one located on top of Cu and another was situated above one carbon atom of the six member ring. The rate limiting stage is the O_2 dissociation with the reaction barrier of 3.16 eV, the hydrogenation of the atomic O on top of Cu with first atomic H to form OH, and then the second H would diffuse to the O atom to form $\text{O} + \text{H}_2\text{O}$ binding to the Cu, for the other O atom hydrogenated form OH with a 0.05 eV energy barrier to the top carbon atom of the six member ring, a high exothermic reaction energy ($-3.01/\text{eV}$). Subsequently, the OH species adsorbed on the Cu to H_2O form with a H atom adsorbed on Cu. The OOH species dissociates with a negligible barrier (1.06/eV) and high exothermic reaction energy (0.94/eV) (see in Fig. 3e). Moreover, the second OH diffuses easily from the five-member ring to the Cu top site with a diffusion barrier of 0.69/eV, and a small exothermic reaction energy of $-0.36/\text{eV}$ as presented in Fig. 4d. As $^*\text{O} + ^*\text{OH} + ^*\text{H}$ spontaneously transforms into two OH radicals and transform into O and H_2O with the reaction barrier of 0.59 eV. Here, the transition states (TS) are marked by the color dashed rectangular box, the corresponding reaction barrier (ΔE_{TS}) and reaction energy (ΔE) by calculated the change energy between products and reactants) are also presented below the TS. The hydrogenation process of $^*\text{OH}$ and $^*\text{O}$ with one atomic H may have two different pathways. The first is defined as $^*\text{OH} + ^*\text{O} + \text{H} \rightarrow 2^*\text{OH}$ and $^*\text{OH} + ^*\text{O} + \text{H} \rightarrow ^*\text{O} + \text{H}_2\text{O}$. For the first step, 2^*OH desorbing from the surface occurs rather efficiently with an activation barrier of less than zero eV, it can not be directly

formed $^*\text{O}$ and H_2O whereas it has a high activation barrier (0.62/eV) and high reaction energy (0.55 eV). 2^*OH take one atomic H to form O and H_2O , and then the $^*\text{O}$ takes H from another OH on top Cu, and finally forms the final product H_2O . The H_2O molecule formed shows small adsorption energy ($-0.055/\text{eV}$) on top Cu atom with a distance of 2.99 Å, indicating that it easy desorption from the surface. This is an exothermic process with reaction energy of $-3.34/\text{eV}$ and an activation barrier of 1.48/eV sees in Fig. 3c. Then, it follows the $\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$ resulting in the final product H_2O with reaction energy of $-2.26/\text{eV}$ and a barrier energy of 0.21/eV.

2.3 Thermodynamics analysis

To gain further explore of the ORR/OER process at an atomic level. First we convert free energy into Gibbs free energy by correcting, such as solvation correction, hydrogen bonds, phase state and so on. It can be observed in Fig. 6, it showed a constant separation catalytic activity of 0.2/eV between the energy levels of $^*\text{O}$ and $^*\text{OOH}$, while that of much more large-scale separation activity site of about 1 eV between $^*\text{OH}$ and $^*\text{OOH}$, it is consistent with that of previous analyses which concluded that the energy levels of $^*\text{OH}$ and $^*\text{OOH}$, there have a constant separation of 0.2–3.2/eV on a wide range of catalytic surface. This constant separation has been attributed to the similarities between $^*\text{O}$ and $^*\text{OOH}$ with the surface. It is obvious from Fig. 7b (surface phase diagram) that the reduction of OH into H_2O is the most occurred step which the potentials higher than 0.82/V, indicating that the protonation of OH into H_2O is more easily along the whole reaction

Fig. 6 Volcano plots for **a** OER and **b** ORR on different sites of CuN_4 -graphene surface, and volcano plots of overpotential η versus the difference of binding energy of **c** $^*\text{O}$ versus $^*\text{OH}$ and **d** $^*\text{OOH}$ versus $^*\text{O}$, respectively

linear scaling relations are determined by the Gibbs free energy of binding, the intercept of these relations appears to be determined by the absorption strength of intermediates. All intermediates have only at top binding available, resulting in similar scaling relations. Nevertheless, graphite materials are probably more stable in acidic environments has great importance properties. Moreover, the fact that experimentally the active sites are created in the interstices between graphite layers in porous materials could, in principle improve the ORR/OER activities. [45]

On the basis of abundant results, this work fully summarizes and analyzes the ORR/OER process of CuN_4 -Gra surface from Fig. 8. For the O_2 dissociation pathway, the favorable pathway is the process an $\text{O}_2 \rightarrow * \text{O}$ with the rate determining step of OH dissociation (barrier activity 3.16 eV). While the O hydrogenation of O_2 pathway is OOH form $\rightarrow$ transformation into $* \text{O}$ and $\text{H}_2\text{O} \rightarrow * \text{O}$ formation within $\text{H}^+ \rightarrow$ generate OH and OH with the last H with the H_2O form, the rate-determining step of OOH form (the energy barrier of diffusion is 1.98 eV). However, the formation of OOH and H_2O is a spontaneous process for ORR with negative reactions energy, suggesting that OOH hydrogenation is more easily than OOH dissociation (barrier energy 4.03 eV). The hydrogenation of OH and atomic $* \text{O}$ with a barrier of 0.31 eV and 0.05 eV, respectively. See from Fig. 8, the reaction pathway of H_2O split, there are two pathways of reaction mechanism, the favorable pathway is the process a H_2O dissociation $\rightarrow$ OH dissociation $\rightarrow * \text{OOH}$ formation of atomic $* \text{O}$ with a H_2O molecule $\rightarrow$ OOH dissociation into O_2 and H with the rate-determining step of OH dissociation (energy barrier 4.83 eV) (see Figure S3). Meanwhile, the favorable pathway is $2\text{H}_2\text{O}$ split into 2OH and then dissociation to two atomic $* \text{O}$. Finally the two atomic $* \text{O}$ transform into O_2 with a energy barrier of 0.95 eV indicating that the O_2 hydrogenation is much easier than O_2 dissociation and very difficult to spite for water and OH of OER process of CuN_4 -graphite surface. Atomic O is the main intermediates species on the catalyst surface not only but also for OER and ORR process.

3 Conclusions

Theoretical calculations revealed that the CuN_4 co-doped graphene, it would improve the catalytic activity for the ORR process. This coordination structure has delivered a superior performance compared to conventional metal for catalyzing ORR in fuel cells. First, we calculated the adsorption energy of ORR intermediates, and then calculated reaction energy and barrier energy by using climbing image nudged elastic band (CI-NEB) method to search transition state of all of the ORR elementary reaction steps, indicating that the CuN_4 co-doped graphene as efficient

catalyst for ORR. The intermediate molecules are always chemisorption at the top of Cu site on the CuN_4 co-doped graphene, it implies that the N-chelated transition metal with carbon plays an important role in the ORR/OER process, the transition metal is the active center for all the possible elementary steps of the ORR. The most favorable pathway is the O_2 hydrogenation to OOH form. OOH from the calculation of barrier energy for all elementary reaction steps, the hydrogenation of O_2 is more easily than O_2 dissociation pathways. According to the scaling relations between the Gibbs free energy and the separation activated site gap value expected from the scaling-relationships, the free energy of oxygenated intermediates ($* \text{OOH}$, $* \text{O}$, and $* \text{OH}$), in ORR approximately linearly scale with each other, it can analysis and known how to work for metals and oxides of the ORR adsorbates and also has great influence on reaction pathways due to the different active sites. Indicating that the O_2 hydrogenation is much easier than O_2 dissociation. Therefore, our study revealed that the single atomic metallic Cu can improve the catalytic activity of graphite for the ORR without OER process. Since the hydrogenation of O_2 molecule to form $* \text{OOH}$ and the hydrogenation of $* \text{OOH}$ to form H_2O and atomic $* \text{O}$, it can be happened spontaneously with a negative reactions energy, this step plays an extremely important role in ORR. It predicted that the reduction and oxidation potential for U_{ORR} is 0.279 V and U_{OER} is 2.76 V, respectively. Our theoretical research is helpful for designing novel efficiency catalysts for fuel cells.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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