



## Research Paper

# The synergy effect and reaction pathway in the oxygen reduction reaction on the sulfur and nitrogen dual doped graphene catalyst



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## ABSTRACT

The first-principle calculations are performed to explore the synergy effects between two dopants (N, S) and the detailed reaction pathway of oxygen reduction reaction (ORR) on the graphene catalysts. The co-doping N and S induces the significant spin density and has a strong chemical bonding with oxygen molecule which is not observed on the mono-doped cases. Three different reaction pathways are revealed from the calculations. Due to the large barrier of the O–O breaking, the hydrogenation of the adsorbed oxygen molecule is kinetically more favorable. The free energy change of reaction under different electrode potential is also evaluated.

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With the fast growth of the global economy and the dwindling fossil resource, the searching for the alternative energy source becomes a worldwide pressing challenge. The fuel cells and metal-air batteries, are promising technologies to power automobiles and portable devices [1]. The oxygen reduction reaction (ORR) at the cathode is one of the determining factor in these electrochemical process due to its sluggish kinetics [2]. Conventionally, the platinum is the best catalysts for ORR. However the high price and the scarcity of platinum hinder a sustainable development. One way to circumvent this obstacle is to alloy Pt with non-noble metal which can reduce the amount of Pt in catalyst and increase the intrinsic catalytic reactivity [3]. On the other hand, Jasinski found that N4-chelate complex with the non-precious metal center such as Fe is also an efficient ORR catalyst which has the comparable performance with Pt catalyst [4–6].

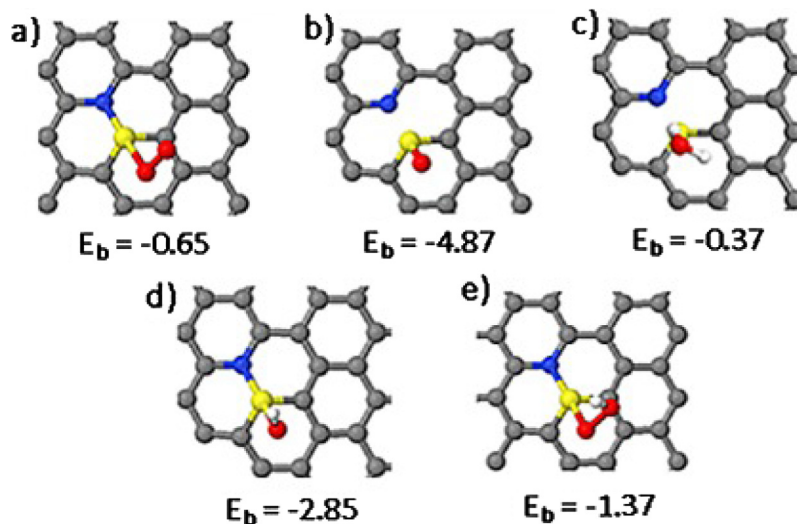
One major breakthrough for ORR catalysts is reported by Dai and his co-workers in 2009 [7]. They used the metal-free nitrogen-doped carbon nanotube as ORR catalyst and the catalytic performance is close to the noble metal catalyst. The metal-free nanostructured carbon catalyst has the obvious advantages in the environmental protection and economical saving compared with the metal catalysts. Therefore the numerous studies on the doped nanostructured carbon catalysts for ORR are reported in recent years [8]. Not only nitrogen but also boron, sulfur, and phosphorus doped carbon catalysts have been shown remarkable performance in ORR [2]. Recently, a new trend emerges for the doped carbon catalysts in ORR by using dual dopants such as B, N or N,

S [8,9]. Qiao and his co-workers for the first time applied the sulfur and nitrogen dual doped graphene (SN-G) catalyst in ORR [10]. They found the performance from dual doped graphene catalyst is significantly increased than the single element (nitrogen or sulfur) doped catalyst. The enhanced ORR reactivity is explained by the synergy effects between nitrogen and sulfur dopants. Furthermore, the dual doped graphene catalyst has the very low onset potential which is  $-0.06$  eV in alkaline medium and the transfer electron number is nearly four. They also conclude that the active sulfur in ORR has a thiophene-like structure. Due to its extraordinary performance in ORR, the S-N dual doped carbon catalysts draw much attentions after Qiao's work. Various S-N dual doped carbon catalysts have been explored in ORR including carbon nanotube [11], graphene [12–15], graphene oxide [16], and graphitic carbon [17] and the promising catalytic performance with the low onset potential, the high current, and the direct 4e pathway are reported. Moreover the S-N dual doped carbon catalysts have the impressive stability even in acid medium which is crucial for the commercial applications [11,18]. Overall, the S-N dual doped carbon materials exhibit the great potential as the metal-free ORR catalysts.

Besides the experimental studies, the first principle calculations are also performed to uncover the origin of the superior ORR reactivity for the S-N dual doped carbon catalysts [19–21]. In their seminal work, Qiao and his co-workers analyze the spin density and charge density of the S, N and the surrounding carbon atoms [10]. They relate the ORR reactivity with the induced spin density after S, N doping. Denis et al. carry out DFT calculations to study the various configurations of the S-N dual doped graphene. The calculations reveal that S, N pair replaces a C–C bond, however the

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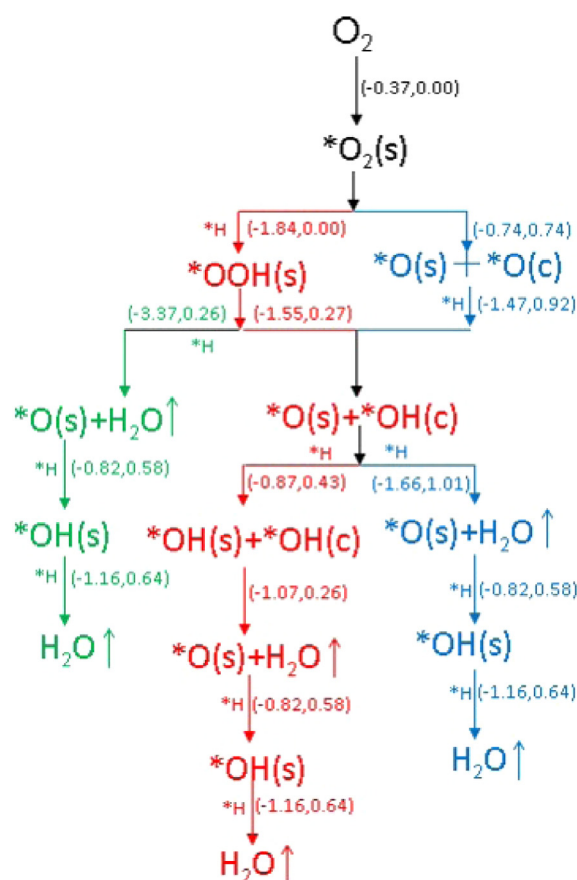
**Fig. 1.** The optimized structures and the binding energy ( $E_b$ , eV) of reactants, intermediates, and products on SN-G catalysts. (a)  $O_2$  (b) O (c)  $H_2O$  (d) OH (e) OOH. Color code: oxygen is red, hydrogen is white, carbon is gray, nitrogen is blue, and sulfur is yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

distance between S and N is over 2.5 Å and not forming a covalent bond [22,23]. They also found that the oxygen molecule can dissociate at the sulfur site on S-N doped graphene. Zhao and Xia carefully examine the various dopants pairs including N, S, P, Cl, B by using graphene ribbon model. The descriptor to enable rational design for ORR reactivity is proposed based on the free energy and onset potential calculations [9].

Although considerable progress have been made for S-N dual doped carbon catalysts in ORR, there are still a few questions remaining unanswered. In current work, the first principle calculations are performed to resolve these pending issues. Firstly, the synergy effect is very often invoked to explain the observed ORR reactivity for dual doped carbon catalysts. However, the accountable explanations on the synergy effects are still absent. Therefore we aim to give a clear description on this effect by the comparison between dual and single doped catalysts. Secondly, the different pathways on the SN-G in ORR are examined and the most favorable pathway is proposed. Both kinetic and thermo limited steps are identified along the reaction pathway. These information obtained from the calculations are indispensable to correctly understand the reaction mechanism. In the end, the conclusions from the current work not only lay out the concrete base for the further optimization of the S-N doped carbon catalysts but also shed light on the mechanism of the other dual doped carbon catalysts in ORR.

To determine the most stable configuration of SN-G, the positions of S and N are varied and the relative stability is compared. It turns out that S and N occupying the ortho sites is the most stable structure as shown in Fig. S1. The distance between S and N is 2.55 Å which is significantly longer than the bond distance in nitrogen sulfide (1.49 Å). Therefore the chemical bond is not formed between sulfur and nitrogen. Moreover, the sulfur protrudes from the graphene basal plane. The most stable structured predicted from current work is consistent with the experimental XPS measurements. The XPS indicates that the sulfur is most likely in a thiophene-like structure and the sulfur and nitrogen does not form a bond [10]. The similar structure is also predicted in previous computational study [23].

The optimized structures of the reactants, intermediates, and products on SN-G are shown in Fig. 1. It is generally accepted that the first step of ORR is the adsorption of oxygen molecule. Several different binding sites are tested for the  $O_2$  molecule. It turns out that most stable configuration is that the  $O_2$  molecule directly



**Fig. 2.** The reaction pathway of ORR on SN-G catalyst revealed from DFT calculations. The two values in parenthesis is the reaction energy (first one, eV) and the reaction barrier (second one, eV). The negative reaction energy means exothermic. The asterisk indicates the adsorbed species on surface.

interact with the S dopant on the graphene as shown in Fig. 1a. The bond distance between S and the adsorbed oxygen molecule is 2.08 Å and the binding energy is -0.65 eV. On the other hand,  $O_2$  adsorptions on the mono-doped (N and S) graphene are also

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