Short Communication

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How heteroatoms (Ge, N, P) improve the electrocatalytic performance of graphene: theory and experiment

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The oxygen reduction reactions (ORR) play a crucial role in the electrochemical energy storage devices, such as fuel cell, metal-air batteries^[1-3]. However, their larger scale applications are hindered by the sluggish slow kinetics of the ORR. Up to now, platinum (Pt)-based catalysts are still known as the best ORR electrocatalysts owing to the relatively low overpotential, high catalytic activity and current density^[4]. Nevertheless, the scarcity and high cost of Pt-based materials^[5] limit their wider application. Therefore, the search and development of highly efficient and cost-effective catalysts for ORR is highly desirable. Recently, an enormous amount of research effort goes into the synthesis of carbon-based electrocatalysts doped by heteratoms (e.g., N) to replace Pt-based catalysts. The introduction of N atoms break the sp^2 hybridization of carbon, inducing a lone pair of electrons, thus altering the

charge and spin density of adjacent carbon atoms. Therefore, the modified carbon materials generate active sites for ORR.

Germanium (Ge), as a carbon group element, was regarded as one of the best candidates in carbon-based materials, mainly due to Ge possessed similarly the outmost electron distribution compared with C atom. Despite of the admirable electrical conduction of Ge-doped graphene, it exhibited the unstable structure due to small formation energy^[6]. In contrast, the co-doped system, such as N/P and Ge atom co-doped graphene, owned great formation energy, indicating more stable configurations. She et al. synthesized Ge and N co-doped graphene materials and proved their higher ORR performances experimentally and theoretically^[7]. Li et al.^[3] confirmed that Ge and P co-doped carbon nanotubes showed enhanced ORR catalytic activity and long-term durability. Unfortunately, the work function values of the co-doped samples were relatively large due to the obvious bandgap around Fermi level, making the electron unfavorable to transfer from the carbon surface to the vacuum. This results in the limited improvement of the ORR performance. However, tri-doped systems, such as Ge, N, P-doped graphene, are promising to efficiently decrease the work function values through stronger orbitals hybridization and synergy effect. In view of this, it is important to investigate the Ge, N and P tri-doped system thoroughly.

In this communication, four different structures including Ge-N co-doped defective graphene (Ge-N₄), Ge-P co-doped defective graphene (Ge-P₄), Ge and adjacent N-P tri-doped defective graphene (A-Ge-N₂P₂) and Ge, interphase N-P tri-doped defective graphene (I-Ge-N₂P₂) (**Fig. S1 online**) were investigated by density functional theory (DFT)^[8]. The aims of the present study were as follows: (1) to explore the nature of bonding in Ge, N, P-ternary co-doped graphene, the stability and the transfer of the charge between Ge, N, P atoms and the graphene surface and analyze these models according to the formation energy, the charge density and density of states (DOS); (2) to identify the charge transfer of O₂ molecule adsorbed in various doped systems considering its relation to the differential charge density and Bader charge analysis; (3) to identify the ORR reaction pathway for Ge-N₄, Ge-P₄, A-Ge-N₂P₂ and I-Ge-N₂P₂.

Meanwhile, to verify the DFT results, we synthesized N, P and Ge tri-doped reduced graphene oxide (Ge-N-P-rGO), P and Ge co-doped reduced graphene oxide (Ge-P-rGO), N and Ge co-doped reduced graphene oxide (Ge-N-rGO), respectively. It was found that the tri-doped system displayed much better ORR activity and durability than those of the co-doped system, which is in good agreement with the DFT calculation results.

The optimized models of N₄-Gr (N doped defective graphene), P₄-Gr (P doped defective graphene), A-N₂P₂-Gr (adjacent N and P co-doped defective graphene) and I-N₂P₂-Gr (interphase N and P co-doped defective graphene) are shown in **Fig. S2 (online)**. For the relaxed structures, we calculated the average N–N bond lengths to be 2.659 Å in the relaxed N₄-Gr, 2.703 Å in the relaxed A-N₂P₂-Gr, and the average P–P bond lengths to be 2.261 and 2.294 Å in the optimized P₄-Gr and A-N₂P₂-Gr, respectively (**Table S1 online**). In the I-N₂P₂-Gr structure, the average N–P bonds show the different values of 1.882 and 2.777 Å. Additionally, the average C–C bond lengths are elongated by about 0.027 Å, and the corresponding average bond lengths of P–C and N–C are 1.718 and 1.381 Å, respectively. These changes of bond length are mainly attributed to the introduction of larger sized N or P atoms. Some researchers have proved the stable geometrical structure by means of freezing the plane without the top atom, which can clearly expound the view that the distortion of the configuration leads to the formation of a stable structure^[9]. We also present the optimized structures, calculated bond length and angles for Ge-N₄, Ge-P₄, A-Ge-N₂P₂, and I-Ge-N₂P₂, respectively (**Fig. S1** and **Table S2 online**).

In accordance with the same procedure described in the previous works^[4,9], we computed the formation enthalpies of the ternary (N, P, Ge) co-doped defective graphene. We predicted with the DFT method that there is an order of N₄-Gr (-4.61 eV) > I-N₂P₂-Gr (-4.19 eV) > A-N₂P₂-Gr (-4.14 eV) > P₄-Gr (-3.52 eV) for N and P doped defective graphene, which are listed in **Table S3 (online)**. The negative formation enthalpies indicate that these doped structures are energetically favorable to be embedded in the defective sites. Quite evidently, the formation enthalpy is reduced

again after the doping of Ge. For instance, the most stable configuration is A-Ge-N₂P₂ with a value of -8.01 eV, followed by the I-Ge-N₂P₂ configuration with a lower value of -7.75 eV. The formation enthalpy of Ge-P₄ and Ge-N₄ was -5.12 and -6.47 eV, respectively. The values of formation enthalpy are comparable to previous computations for Co and Fe defect motifs^[10].

To investigate the electronic structures of the doping effect, we also calculated the electronic densities of the configurations above-mentioned. As shown in **Fig. S3 (online)**, for the pristine graphene, the π electrons show inertness and most of the electrons are uniform around the C-C bond^[10], while the defect sites with two removed carbon atoms are losses electron regions. The red area represents the attraction of electrons, while the blue area represents the losses of electrons. We noticed that the attraction region of electrons around N atoms and the losses region of electrons around P atoms were formed after the introduction of Ge atom in N and P co-doped defective graphene. At the same time, Ge atom also presents losses of electrons. As a supplement, in order to determine the role of each atom, the Bader charge was used for further analyzing the electron loss/gain of each atom (**Table S4 online**). The Bader charge populations of the Ge, N and P atoms are 0.90, -1.25, and 0.94 |e| for A-Ge-N₂P₂ and 0.69, -1.22, 0.97 |e| for I-Ge-N₂P₂, respectively. Apparently, there is electrons transfer between doped atoms and graphene, indicating strong coupling between heteroatoms and C atom. The electrons always transfer from Ge and P atoms to the N atoms since Ge and P have a lower electronegativity than N. Additionally, taking O₂ adsorption on the four models as an example, there was 0.90, 0.46, 0.25 and 0.47 |e| charge transfer from the Ge atom to O₂, which occupied antibonding $2\pi^*$ orbitals of O₂. Compared with Ge atom, the charge transfer of N and P atoms plays a secondary role. As a result of the synergy effect for co-doped systems, the redistribution of electrons created more active sites which would be beneficial to the ORR process. Moreover, A-Ge-N₂P₂ (**Fig. S3d online**) is favorable for the electron loss with N and the electron gain of P compared with I-Ge-N₂P₂ (**Fig. S3c online**). Therefore, A-Ge-N₂P₂ could be considered as better candidate as an ORR

catalyst.

Oxygen molecules adsorbed onto the surface of catalyst is the primary condition for the occurrence of ORR. In order to obtain the optimal geometrical configurations, we placed the O_2 molecule above the $Ge-N_4$, $Ge-P_4$, $A-Ge-N_2P_2$, and $I-Ge-N_2P_2$, including the end-on and the side-on adsorption configurations. After the optimizations, the end-on configuration was found to be the more favorable, which is consistent with previous studies^[7]. Given that the catalytic activity of ORR electrocatalysts was highly dependent on O_2 adsorption energy on catalyst surface, the O_2 adsorption energy on different relaxed structures was used to evaluate the catalytic performance. The calculated O_2 adsorption energies on $Ge-N_4$, $Ge-P_4$, $A-Ge-N_2P_2$ and $I-Ge-N_2P_2$ are -0.28, -0.15, -0.19 and -0.21 eV, respectively. Analogy to previous studies, the DFT computed O_2 adsorption energies are less than that of $Fe-P_4-C$ and $Co-P_4-C$ (-1.03 and -0.85 eV, respectively)^[7]. Still, the adsorbed O_2 molecule can also be well activated. For example, for the adsorbed O_2 on $Ge-N_4$, $Ge-P_4$, $A-Ge-N_2P_2$ and $I-Ge-N_2P_2$, the O–O bond are elongated from the 1.21 Å of the free O_2 to 1.34-1.40 Å, which is a typical value for peroxide species.

We computed the electron transfer via charge density difference and Bader analysis to better analyze the chemical bonding between O_2 molecule and catalyst. According to **Fig. S4a-d (online)**, with the introduction of O_2 molecule, the accumulation (yellow region) of O-2p orbitals upon interaction with the substrates is observed from the charge density difference plot. It is balanced in the charge density increased of the Ge–N and/or Ge–P bonds on the calculated co-doped system, mainly due to the lone electron pair of the N and P atoms. Moreover, based on Bader analysis, there was 0.91, 0.46, 0.46 and 0.25 |e| charge transfer from the Ge atom to antibonding $2\pi^*$ orbitals of O_2 in the sequence of $Ge-N_4 > Ge-P_4 > A-Ge-N_2P_2 > I-Ge-N_2P_2$. Therefore, the interaction between O_2 and Ge atom can certainly facilitate the ORR reaction process.

Following the O_2 adsorption on the catalysts, the active O_2 molecules firstly react with hydrogen proton forming OOH species which will be adsorbed on the Ge site in all the models (**Figs. S5 and S6**). This step can be defined as OOH* formed from chemisorbed O_2^* . With the continuous introduction of hydrogen, the second hydrogen

proton may be adsorbed on another O site of OOH* to form adsorbed HOOH species. According to the calculated results, we find that it is difficult for the HOOH species to maintain its molecular adsorption configuration on the Ge-N₄ and Ge-P₄ center and would spontaneously decompose into O* + H₂O species after structural optimization. The calculated adsorption energies of the HOOH molecules anchored on Ge-N₄ and Ge-P₄ are -3.06 and -2.85 eV. For A-Ge-N₂P₂ and I-Ge-N₂P₂, it exhibited the same result for the process of dissociation. Obviously, the favorable process is the formation of O* and H₂O rather than two OH species. This indicates that it prefers a 4e pathway rather than 2e pathway. When the H₂O molecule was released, the O adsorbate was still retained on the Ge site and the other protons were combined to form OH species. Ultimately, the second H₂O molecule was formed and escaped away from the plane because of its weaker binding energy.

Given that the ORR was occurred in a solution phase, the solvent effect was also considered. One of the important factors is water effect on the adsorption stabilities of intermediates in electrochemistry system^[11]. This is because all the oxygen-containing adsorbed species can form hydrogen bonding with H₂O molecules. To explore the water effect for each adsorbed species, we adopted 30 H₂O molecules to simulation the water environment, as shown in **Fig. S7 (online)**. The initial configuration of water layers was set as that of ice. We carried out molecular dynamics (MD) calculations to relax the water molecules until the total energy of the system was stabilized (~30 ps). To the end, we obtained one most stable configuration to compute the effect of water on the adsorbed species in comparison with the system without water. The free energy change for each species in the presence of water was defined as ΔG_{water} . The difference between ΔG and ΔG_{water} can be regarded as the stabilization energy. Obviously, the hydrogen bonding originated from water molecules can enhance the stability of adsorbed species. Especially for the O₂ species, it exhibited the lower stabilization formation, which was favorable to reaction kinetics for ORR.

We also plotted the free energy profile to describe the ORR sub-steps on active sites of the models. Apparently, some of intermediate pathways started to move uphill

in this process from zero to equilibrium potential (**Fig. 1**). For the relaxed Ge-P₄ and Ge-N₄, the overpotential was 0.74 and 0.65 eV, while there are overpotentials of 0.34 and 0.39 eV for the A-Ge-N₂P₂ and I-Ge-N₂P₂ catalysts. For comparison, previous studies on ORR catalytic performance for doped graphene were list in **Table S6 (online)**. From the thermodynamic point of view, it indicated that the lower the overpotential is, the higher the ORR catalytic activity is. The calculated results demonstrated that the three heteroatoms-doped A-Ge-N₂P₂ and I-Ge-N₂P₂ exhibited the better ORR catalytic performance.

Fig. 1 Schematic free energy diagrams and all relaxed intermediate models for ORR pathway in alkaline condition on Ge-P₄ (a), Ge-N₄ (b), I-Ge-N₂P₂ (c) and A-Ge-N₂P₂ (d). In the configuration, dark brown, blue, green, purple, red and white balls represent C, N, P, Ge, O and H atoms, respectively.

To clearly understand the activity and stability of all the optimized structures for ORR, we calculated the partial density of states (PDOS) to qualitatively interpret the nature change of electronic structures after doping with Ge, N, and P. As shown in **Fig. S8a, b (online)**, the p-orbitals of P and Ge atoms had a distinct hybridization effect for Ge-P₄ and so did the N and Ge atoms in Ge-N₄. However, the interaction with Ge,

N and P atoms can efficiently promote the ORR reaction process, especially the donation of the p orbitals for co-doping of N and P atoms (**Fig. S8c, d online**). Moreover, the DOS value of N p-orbitals was higher than that of P p-orbitals atom near the Fermi level, indicating the donated electronic capability of the N atoms was stronger than that of P, which was favorable to promote the ORR reaction process.

Alternatively, the band structures were also calculated to disclose their ability for electron transfer. As displayed in **Fig. S9a (online)**, the Ge-N₄, Ge-P₄ and I-Ge-N₂P₂ models have a relatively larger bandgap at G point compared with A-Ge-N₂P₂, indicating that the electron transfer need extra energy from valence band to conduction band and it results in the poor electrocatalytic performance. The A-Ge-N₂P₂ has almost no bandgap (**Figs. S8d and S9d online**), so it shows the best electrocatalytic activity among all the structures.

Inspired by the DFT calculations, we also prepared Ge-N-P-rGO, Ge-P-rGO and Ge-N-rGO in experiment. As shown in the elemental mapping of Ge-N-P-rGO (**Fig. S10 online**), Ge, N and P were distributed uniformly on the rGO substrate. We also found that the N-Ge (398.1 eV)^[7], P-Ge (134.1 eV)^[4], P-C (132.4 eV)^[13] and C-N bonds (288.7 eV)^[13] from the XPS data for Ge-N-P-rGO. (**Fig. S11 online**) Their ORR electrocatalytic activities were investigated in O₂-saturated of 0.1 mol L⁻¹ KOH with rotating disk electrode (RDE) measurement. As indicated in the linear sweep voltammetry (LSV) polarization curves (**Fig. 2a**), Ge-N-P-rGO exhibits superior electrocatalytic activity to those of Ge-N and Ge-P in terms of onset potential (E_{onset}), half-wave potential ($E_{1/2}$), and limiting current. The E_{onset} and $E_{1/2}$ of Ge-N-P-rGO is 0.94 and 0.84 V, respectively, which are more positive than those of Ge-P-rGO (E_{onset} = 0.87 V, $E_{1/2}$ = 0.76 V), Ge-N-rGO (E_{onset} = 0.88 V, $E_{1/2}$ = 0.75V) and Pt/C (E_{onset} = 0.92 V, $E_{1/2}$ = 0.83 V). Besides, it also shows a comparable limiting current density (−5.1 mA cm⁻²) to that of Pt/C (−5.3 mA cm⁻²). The LSV polarization curves at different electrode rotation rates (**Figs. 2b and S12 (online)**) were measured. The electron transfer numbers (n) of the samples were conducted on the basis of the Koutecky-Levich (K-L) plots towards ORR. As shown in **Fig. 2c**, the n values towards Ge-P-rGO and Ge-N-rGO are 3.3 and 3.4 during ORR at 0.5 V vs. reversible

hydrogen electrode (RHE), respectively. However, the n value of Ge-N-P-rGO is as high as 4.0, indicating an enhanced selectivity to ORR. The electrocatalytic durability of Ge-N-P-rGO (**Fig. 2d**) was assessed by chronoamperometric measurement at the overpotential of 0.4 V vs. RHE. The current density of Ge-N-P-rGO exhibited only 16% decrease after 10 h reaction, whereas Pt/C reduced by 26% from its initial current^[7]. Obviously, the Ge-N-P-rGO indicates the excellent stability towards ORR. As demonstrated by the experimental results, the Ge-N-P-rGO also exhibited the better ORR catalytic activity than other samples as well, which in good agreement with the DFT results.

Fig. 2 ORR performance for Ge-N-P-rGO, Ge-P-rGO and Ge-N-rGO. (a) LSV polarization curves of the samples; (b) LSV polarization curves of Ge-N-P-rGO at different electrode rotation rates from 400 to 2,500 r min⁻¹. (c) K-L plots of three samples at an overpotential of 0.5 V vs. RHE. (d) The time-dependent current density curve of Ge-N-P-rGO at 0.4 V vs. RHE.

In summary, we have performed density functional theory calculations to investigate the origin and mechanism of ORR occurring on N, P and Ge-ternary co-doped defective graphene, together with experimental verifications. According to

free energy profiles, the Ge, N and P tri-doped defective graphene (A-Ge-N₂P₂ and I-Ge-N₂P₂) have lower overpotential (0.34 and 0.39 eV). So, both of them exhibit better electrocatalytic activity due to a very small energy difference of 0.05 eV. Furthermore, the experimental results reveal the Ge-N-P-rGO exhibits the best ORR catalyst performance compared with Ge-N-rGO and Ge-P-rGO, which is in good agreement with the calculation results. These findings will stimulate further interest in research area and open avenues in the development of the combination between theory and experiment aspect for ORR.

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

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References

- [1] Jia Y, Zhang L, Du A, et al. Defect graphene as a trifunctional catalyst for electrochemical reactions. *Adv Mater* 2016; 28; 9532-9538.
- [2] Cao R, Lee JS, Liu M, et al. Recent progress in non-precious catalysts for metal-air batteries. *Adv Energy Mater* 2012; 2; 816-829.
- [3] Wang S, Jiang S. Prospects of fuel cell technologies. *Natl Sci Rev* 2017; 4;163-166.
- [4] Li Q, Yuan F, Yan C, et al. Germanium and phosphorus co-doped carbon nanotubes with high electrocatalytic activity for oxygen reduction reaction. *RSC Adv*. 2016; 6; 33205-33211.
- [5] Zhao W, Yuan P, She X, et al. Sustainable seaweed-based one-dimensional (1D) nanofibers as high-performance electrocatalysts for fuel cells. *J Mater Chem A* 2015; 3; 14188-14194.
- [6] Dai X, Li Y, Xie M, et al. Structural stability and electronic, magnetic properties of

Ge adsorption on defected graphene: a first-principles study. *Phys E* 2011, 43; 1461-1464.

[7] She X, Li Q, Ma N, et al. Creation of Ge-N_x-C_y configures in carbon nanotubes: origin of enhanced electrocatalytic performance for oxygen reduction reaction. *ACS Appl Mater Interfaces* 2016; 8; 10383-10391.

[8] Kohn W, Sham L.J. Self-consistent equations including exchange and correlation effects. *Phys Rev* 1965; 140; A1133-A1138.

[9] Feng L, Liu Y, Zhao J. Fe- and Co-P4-embedded graphenes as electrocatalysts for the oxygen reduction reaction: theoretical insights. *Phys Chem Chem Phys* 2015; 17; 30687-30694.

[10] Kattel S, Atanassov P, Kiefer B. Stability, electronic and magnetic properties of in-plane defects in graphene: a first-principles study. *J Phys Chem C* 2012; 116; 8161-8166.

[11] Jiang H, Zhao T, Shi L, et al. First-principles study of nitrogen-, boron-doped graphene and co-doped graphene as the potential catalysts in nonaqueous Li-O₂ batteries, *J Phys Chem C* 2016; 120; 6612-6618.

[12] Yu L, Pan X, Cao X, et al. Oxygen reduction reaction mechanism on nitrogen-doped graphene: a density functional theory study. *J Catal* 2011, 282; 183-190.

[13] Zhao S, Liu J, Li C, et al. Tunable ternary (N, P, B)-doped porous nanocarbons and their catalytic properties for oxygen reduction reaction. *ACS Appl Mater Interfaces* 2014; 6; 22297-22304.

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