Origin of the catalytic activity of phosphorus doped MoS$_2$ for oxygen reduction reaction (ORR) in alkaline solution: a theoretical study

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Phosphorus doped MoS$_2$ nanosheets (P-doped MoS$_2$) have been reported as excellent oxygen reduction reaction (ORR) catalysts with four-electron selectivity in alkaline solution. By performing density functional theory (DFT) calculations, we revealed the detailed reaction mechanism and the key reaction sites on surface of P-doped MoS$_2$ for ORR catalysis. The double P-doped MoS$_2$ (2P-MoS$_2$) is calculated to be more stable than the single P-doped MoS$_2$ (P-MoS$_2$), and the configuration with two P atoms in neighboring sites exhibits the highest stability. The surface of P-doped MoS$_2$ is found highly active for dissociation of O$_2$. Comparative calculations reveal that P-MoS$_2$ is unsuitable as ORR catalyst due to the high dissociation barrier of H$_2$O (1.19 and 2.06 eV for the first and second adsorbed H$_2$O), while the 2P-MoS$_2$ shows good ORR catalytic activity with much lower dissociation barrier of H$_2$O (0.62 eV). Furthermore, we elucidated that the ORR catalytic activity in 2P-MoS$_2$ originates from the activated S$_2$ atom, which provides an extra adsorption site for the first H$_2$O and the following OH group benefited from the enhanced hydrogen bond interaction. Our results illustrate the mechanisms of doped MoS$_2$ based catalysts and provide rational way for designing ORR catalysts with high activity.

Because of the high energy density, high theoretical efficiency, and negligible emission of exhausted gases, fuel cells (FCs) are considered to be one of the most promising energy conversion devices. As the crucial process in FCs, the oxygen reduction reaction (ORR) has been extensively studied. Platinum (Pt) based ORR electro-catalysts are widely used because of their relatively low over-potential in practical applications. However, due to their high cost, less abundance, poor stability in an electrochemical environment, and still sluggish kinetics, there are worldwide research efforts to find precious-metal-free catalysts as replacement to Pt based catalysts, such as nonprecious metals, their alloys or oxides, and nitrogen-coordinated metals. As the ideal candidates, metal-free carbon materials doped with heteroatoms (N, B, Si, P, S and F), have been demonstrated to be effective precious-metal-free ORR catalysts.

Since the discovery of the ultrathin MoS$_2$ monolayer, the electro-catalytic property has attracted great attention. It was reported that with the decrease of monolayer size, MoS$_2$ reveals favorable performance in ORR and hydrogen evolution reaction (HER). By examining nine different layered group 5 metallic transition-metal dichalcogenides (TMDs), Cha et al. identified VTe$_2$ as the best electrocatalyst for the HER in terms of HER overpotential and Tafel slope, at 0.5 V vs. RHE and 55 mV dec$^{-1}$, respectively. Also, other TMDs, such as TaS$_2$, have been found to be efficient catalysts for the ORR due to the onset potentials similar to that of Pt/C catalysts. Luxa et al. held the view that the increased activity of 2HTaS$_2$ may actually stem from the presence of oxides (Ta$_2$O$_5$) formed during the oxidation. Another way to improve the electrocatalysis activity is to transform the TMDs from the semiconducting 2H phase to the metallic 1T phase, such as the improved HER performance on the catalyst MoS$_2$ and WS$_2$ with p-doping Niobium and Tantalum. Both experiments and theoreticians suggested that the band gap of TMDs can be tuned by creating their solid solutions either by having metal dichalcogenides with mixed metal elements (i.e., Mo$_x$W$_{1-x}$S$_2$ (0 ≤ x ≤ 1)) or mixed chalcogenides (i.e., Mo$_y$Se$_{1-y}$S$_2$ (0 ≤ y ≤ 2)), which make a contribution to electrocatalytic properties toward HER. In order to improve the performance in electro-catalysis without the using of precious metal, N- and P-doped MoS$_2$ with few layers were prepared.
The calculated bond energy, the height of P atom and formation energy for pristine, P-MoS\(_2\) and 2P-MoS\(_2\).

|          | Mo-P bond energy (eV) | Relative height of P (Å) | Formation energy (eV/atom) |
|----------|-----------------------|--------------------------|---------------------------|
| MoS\(_2\) | -                     | 0                        | -0.052                    |
| P-MoS\(_2\) | 4.847 (Mo-P)        | -0.023                   | -0.070                    |
| 2P-MoS\(_2\)(1) | 4.966 (Mo-P)     | -0.109                    | -0.077                    |
| 2P-MoS\(_2\)(2) | 4.846 (Mo-P)        | -0.089                   | -0.079                    |
| 2P-MoS\(_2\)(3) | 4.881 (Mo-P)        | -0.093                   | -0.079                    |

Table 1. The calculated bond energy, the height of P atom and formation energy for pristine, P-MoS\(_2\) and 2P-MoS\(_2\).

experimentally. The experimental data indicate that N- and P-doped single layered MoS\(_2\) possess wonderful ORR catalytic performance in acidic and alkaline environment, respectively. Soon after, the mechanism about the ORR catalytic effect on N- and P-doped MoS\(_2\) single layer is studied by simulations. However, the catalytic mechanism on the experimental results of P-doped 2D materials as ORR catalysts is not studied, especially the reported generation of extra ORR activity on P-doped MoS\(_2\) nanosheet with four-electron selectivity in alkaline solution, which have been successfully synthesized via the method of pyrolysis. Moreover, Huang and the co-worker have found through the mapping analysis that, P doping on the MoS\(_2\) monolayer can be dispersed on the surface evenly, and with the increase of P-doping amount, the activity of P-doped MoS\(_2\) on ORR can be improved obviously, which reveals that the active site should be related with the P atoms.

In this work by density functional theory (DFT) calculations, we explored the origin of catalytic activity in the P-doped MoS\(_2\) monolayer as the ORR electrocatalyst. Previous theoretical and experimental studies have indicated that, the P-doped MoS\(_2\) monolayer prefers to work as ORR catalyst in alkaline solution rather than acidic solution. According to our simulation results, the P-doped MoS\(_2\) with doping concentration of 5.5% is optimal for reported generation of extra ORR activity on P-doped MoS\(_2\) nanosheet with four-electron selectivity in alkaline solution, which have been successfully synthesized via the method of pyrolysis. More importantly, Huang and the co-worker have found through the mapping analysis that, P doping on the MoS\(_2\) monolayer can be dispersed on the surface evenly, and with the increase of P-doping amount, the activity of P-doped MoS\(_2\) on ORR can be improved obviously, which reveals that the active site should be related with the P atoms.

Table 1. The calculated bond energy, the height of P atom and formation energy for pristine, P-MoS\(_2\) and 2P-MoS\(_2\).
0.16 eV for 2P-MoS$_2$(1)] compared with the pristine MoS$_2$ (1.66 eV). This is mostly due to the introduction of impurity band, which exists as a single band across or above the Fermi level that is splitting from valence band edge. Further analysis from partial density of states (PDOS) tells that the splitting of impurity band origins from the orbital hybridization between Mo and P, as shown from PDOS plots in Fig. 1. The small or zero gap induced by doping of P not only greatly enhances the conductivity of MoS$_2$, but also facilitates the chemical reactivity.

Additionally, the difference of electronegativity between S and P atom also plays important role on the charge population. As shown in Fig. 1, the S atoms (S2–S5) surrounding the doped P atom carry more negative charge (about $-0.11 \text{[e]}$) than that in pristine MoS$_2$ (S1, $-0.099 \text{[e]}$). Meanwhile P atoms carry positive charges (more than $+0.08 \text{[e]}$), which renders the P atom as suitable adsorption site for the nucleophilic species.

**Figure 1.** The top view of the optimized structure of (a) pristine MoS$_2$ nanosheets, (b) single P-doped MoS$_2$ nanosheets and (c–e) double P-doped MoS$_2$ nanosheets, respectively. The band structures and corresponding partial density of states (PDOS) are also given. The Hirshfeld charge population of the corresponding atom is also given.
The adsorption of O$_2$ on P-doped MoS$_2$. As the very beginning of ORR, adsorption of O$_2$ is taken into consideration first. By putting O$_2$ molecule on different sites on P-MoS$_2$ and comparing their $E_{\text{ads}}$, we determined the most energetically favorable adsorption configuration as shown in Fig. 2a. As we can see, the O$_2$ molecule chemisorbs to the P-MoS$_2$ by bonding with P atom. The bond length of P-O bonds is about 1.670 Å. And the calculated adsorption energy of O$_2$ on P-MoS$_2$ is up to $E_{\text{ads}} = -1.11$ eV, which is much more favorable than that on pristine MoS$_2$ monolayer ($-0.11$ eV). And the charge transferred from P-MoS$_2$ to O$_2$ is as much as $Q = 0.695 |e|$ (in ref. 33, $E_{\text{ads}} = -0.93$ eV and $Q = 0.30 |e|$). Further results from TS search show that the chemisorbed O$_2$ can be easily dissociated into two O atoms by overcoming a negligible energy barrier (about 0.05 eV). As shown in Fig. 2b, the two dissociated O atoms adsorb on the top site of P atom and the bridge site between P and Mo atoms, respectively. Similarly, the adsorption of other ORR species (OH and H$_2$O) also prefers to adsorb onto the P atom, as displayed in Fig. S1 of Supporting Information.

There are two different occasions for adsorption of O$_2$ molecule on 2P-MoS$_2$. For 2P-MoS$_2$ (1), the O$_2$ molecule binds with the two neighboring P sites with bridged configuration. For 2P-MoS$_2$ (2) and (3), it is found that due to the large distance between the two P atoms, O$_2$ molecule can only separately bind with one P atom as the situation of P-MoS$_2$ (Fig. S1). In the following discussion, we only investigated the adsorption performance of O$_2$ on 2P-MoS$_2$ (1), not only due to its highest stability among the 2P-MoS$_2$, but also for its different binding configuration with O$_2$ compared with P-MoS$_2$. Resulting from the high chemical activity of the two adjacent P atoms, the O$_2$ molecule will directly dissociated and form two P=O bonds without any energy barrier, as shown in Fig. 2c. The bond length of the two P=O bonds are 1.505 Å, which is shorter than the P=O bond (1.515 Å) formed on P-MoS$_2$.

The charge population of P-MoS$_2$ and 2P-MoS$_2$ (1) after dissociation of O$_2$ is also compared. It is found that comparing with the S atoms (S1 and S2) in P-MoS$_2$, the S atoms surrounding dopants (S1, S2, and S3 in Fig. 2c) on 2P-MoS$_2$ carry less negative electron, which may be favorable for the ORR steps as we will discuss in the following parts.

ORR on P-MoS$_2$. Generally, the total reaction in alkaline solution can be expressed as a 4-electron evolution (* denotes the adsorbed surface):

$$\text{O}_2(\text{aq}) + \text{2H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$$

(3)
The elementary reaction steps could be expressed as:

\[ \text{O}_2^* \rightarrow 2\text{O}^* \quad (4) \]
\[ 2\text{O}^* + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{O}^* \quad (5) \]
\[ \text{O}^* + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- \quad (6) \]

After the determination of adsorption and dissociation of O\(_2\), we then proposed the ORR pathway in alkaline environment by taking H\(_2\)O molecule into consideration. Due to the lack of adsorption site, our simulation results indicate that the first H\(_2\)O can only adsorb on the top of P=O bond by hydrogen bond, as shown in Fig. 3a. One of the H atoms in H\(_2\)O will then transfer to the P=O and finally form two adsorbed OH groups as the product. In the most stable configuration of \((2\text{OH}^* + \text{O}^*)\), the bridged O atom will move to form two Mo–O bonds with the breaking of Mo–P bond, as a result of steric repulsion from the two OH groups. The activation barrier for this reaction is 1.19 eV, fairly high for room temperature reaction.

Similarly, the dissociation of second H\(_2\)O molecule also takes place on the top site of the P=O bond, as shown in Fig. 3b. The activation barrier for this reaction is up to 2.06 eV, even higher than the dissociation of first H\(_2\)O. Moreover, this reaction is endothermic with reaction energy of 0.73 eV, which is thermodynamically unstable. The high activation barrier for dissociation of H\(_2\)O demonstrates that the catalytic activity of P-MoS\(_2\) is low for ORR, which mainly due to the strong P=O bond and low reaction activity of H\(_2\)O on P-MoS\(_2\). This is in consistent with the previous theoretical investigations\(^{38}\).

**Figure 3.** The top and side views of optimized reactant and product as well as the reaction energy barrier for the dissociation of (a) first H\(_2\)O and (b) second H\(_2\)O. \(E_b\) in the diagram represents the barrier energy for each step. The dash line between O atom and H in H\(_2\)O represents the effect of hydrogen bonding.
Same with the P-MoS$_2$, H$_2$O molecule physisorbs on 2P-MoS$_2$, mostly relying on the hydrogen bonds between H atoms in H$_2$O and P=O bonds, as shown in Fig. 4c. However, the adsorption of H$_2$O on 2O adsorbed 2P-MoS$_2$ (1) is obviously strengthened as listed in Table 2. It is found that the decrease of charge assigned on S2 (Fig. 2c) accounts for the improved adsorption performance of H$_2$O. As we can see in Fig. 2c, due to the strong electronegativity of O, the presence of dissociated O atoms will decrease the negative charge of the surface S atoms. Interestingly, the S2 in 2O adsorbed 2P-MoS$_2$ (1) exhibits much less negative charge (−0.068 |e| as marked in Fig. 2c) other than that in 2O adsorbed P-MoS$_2$ (−0.098 |e| as marked in Fig. 2b). It is the charge decrease as well as stronger hydrogen bond caused by the two nearby P–O bonds [as depicted in structure (2) of Fig. 4] together enhance the adsorption performance of H$_2$O on the S2 site. Combined with the fact that the adsorption of H$_2$O is strengthened, we assumed that it is this S2 atom that makes 2P-MoS$_2$ (1) different, and further simulations confirm our proposal. We found that this S2 site can also serve as an adsorption site for OH group, which makes it active during the reaction. As the structure (2) displayed in Fig. 4, accompanied with the hydrogen bond interaction from two P=O bonds, the first added H$_2$O molecule could be easily dissociated into two adsorbed OH groups, one binds with the P and the other one adsorbs onto the S2 site. The corresponding activation barrier for the dissociation of first H$_2$O is 0.62 eV, a moderate value for reaction under room temperature. As comparison, both the two dissociated OH groups in P-MoS$_2$ can only adsorb onto the P atom, leading to significant structural distortion and a high barrier of 1.19 eV.

Following that, the formed OH groups would combine with the electron provided from the electrode and solve into the solution as OH$^−$. And then, the exposed P atom will be the most active site on the surface of 2P-MoS$_2$ (1). Both of the strong reaction activity of P atom and the negative charge on O atom contribute to the dissociation of the second H$_2$O without energy barrier. Also, the possibility of the breaking of P=O bond and the

| E$_{\text{ads}}$/eV | MoS$_2$ | P-MoS$_2$ | O- P-MoS$_2$ | 2O- P-MoS$_2$ | 2P-MoS$_2$ | O-2P-MoS$_2$ | 2O-2P-MoS$_2$
|------------------|--------|----------|-------------|-------------|-------------|-------------|--------|
|                  | −0.151 | −0.129   | −0.305      | −0.256      | −0.120      | −0.372      | −0.319 |

Table 2. The adsorption energy of H$_2$O molecule on the substrates of pristine MoS$_2$, P-MoS$_2$, 2P-MoS$_2$, single O atom adsorbed P-MoS$_2$ and 2P-MoS$_2$, as well as two O atoms adsorbed P-MoS$_2$ and 2P-MoS$_2$, respectively.
MoS$_2$ is then obtained by substituting a surface S atom in MoS$_2$ with a doping concentration of 3.7 atom%. The structures of MoS$_2$ prepared experimentally. Meanwhile, among the 2P-MoS$_2$ nanosheets, type 1 is the most energetically favorable. The double P-doped MoS$_2$ nanosheet (2P-MoS$_2$) is obtained by substituting two surface S atoms in the first H$_2$O is greatly lowered compared with the P-MoS$_2$ (0.62 eV for 2P-MoS$_2$ and 1.19 eV for P-MoS$_2$). Associated with the fact that the formation energy for 2P-MoS$_2$ is almost the same with the P-MoS$_2$ (Table 1), it is much easier for 2P-MoS$_2$ to be prepared experimentally. Meanwhile, among the 2P-MoS$_2$ nanosheets, type 1 is the most energetically favorable (Table S1). Based on the comparison results, we confirm that the activated S atom in 2P-MoS$_2$ is the origin of ORR catalytic activity of P-doped MoS$_2$ in alkaline solution. Notably, it is not accident that the 2P-MoS$_2$ we modeled shows improved ORR catalytic performance. As we have stated, the doping concentration of 2P-MoS$_2$ is 5.5%, which is quite close to the optimal doping concentration observed experimentally (4.7%)$^{37}$. It is the special structure of 2P-MoS$_2$ that activates the S$_2$ site and facilitates the adsorption of H$_2$O molecule and the extra OH group, which well explains why the MoS$_2$ with a P doping concentration of 4.7% exhibits the best ORR performance in experiments.

Conclusions

In summary, we performed comprehensive studies on the origin of the ORR catalytic activity of P-doped MoS$_2$ in alkaline solution through DFT calculations. The 2P-MoS$_2$ with doping concentration of 5.5% is calculated to be more stable than the P-MoS$_2$ with doping concentration of 3.7%, which is consistent with the optimal doping concentration of 4.7% from the experiments$^{37}$. And the configuration with two P atoms in neighboring sites is found to possess the highest stability among the possible configurations of 2P-MoS$_2$. The surface of P-doped MoS$_2$ exhibits highly reactive activation for dissociation of O$_2$.

Except the doping on MoS$_2$ plane, we also discuss the influence of phosphorus present on edge of MoS$_2$. The detailed structure configuration and energy values have been given in Fig. S6. For the two edge S sites that can be placed by P (Mo edge and S edge as shown in Fig. S6 (a)), the P prefer doping in S edge site rather than Mo edge site considering the relative energy difference up to 0.97 eV. For the O$_2$ adsorption on the P-doped MoS$_2$ on the edge site, two adsorption sites are considered (shown in Fig. S6 (b)). The positive adsorption energy on the S site indicated that P-doped on the edge site can't activate the S site around P atom. While on the edge P site, the adsorbed O$_2$ would dissociated directly, which is same with single P atom doped on MoS$_2$ plane (Fig. 2 (b)). And the adsorption for H$_2$O is $-0.13$ eV, which is also the same with the P-MoS$_2$ ($-0.129$ eV, as shown in Table 2). Thus, based on our calculation results, we concluded that the doping of P in the basal plane and edge sites will exhibit similar adsorption performance for adsorption of H$_2$O and dissociation for O$_2$.

Further comparative calculations reveal that P-MoS$_2$ is unsuitable as ORR catalyst due to the strong P-O bond and high dissociation barrier of H$_2$O on P-MoS$_2$ ($1.19$ eV and $2.06$ eV for the first and second adsorbed H$_2$O). In comparison, the 2P-MoS$_2$ shows good ORR catalytic activity. The dissociation barrier of the first H$_2$O on 2P-MoS$_2$ (0.62 eV) is much lower than that of P-MoS$_2$. And the dissociation of O$_2$ and the second H$_2$O on 2P-MoS$_2$ is even spontaneous without any activation barriers. While for the two other types of 2P-doped MoS$_2$, not only the stability is less than the neighboring doped 2P-MoS$_2$, but also the reaction mechanism is similar with the single P doped MoS$_2$. By checking the charge population and adsorption performance of the ORR intermediates, we elucidated that the ORR catalytic activity in 2P-MoS$_2$ originates from the activated S$_2$ atom with increased charge that affected by the two neighboring P-O bonds, which provides an extra adsorption site for the first H$_2$O and the following OH group with the help from the enhanced hydrogen bond interaction. Our results reveal the detailed reaction mechanism of MoS$_2$ based catalysts and provides instructive suggestions for designing ORR catalysts with high performance.

Methods

All the calculations are carried out by DMol$^3$ program. The electronic exchange and correlation effects are described by the generalized gradient approximation with Perdew–Burke–Ernzerhof (GGA-PBE) functional$^{39}$. In order to accurately describe the van der Waals forces, dispersion correction (DFT-D) is adopted by Grimme approach$^{40}$. The all-electron double numerical atomic orbital including polarized p-function (DNP)$^{41}$ is chosen as the basis set with orbital cutoff of 4.9 Å. The convergence threshold values for energies, gradient and displacement are specified as $1 \times 10^{-5}$ Ha, $1 \times 10^{-3}$ Ha/Å, and $5 \times 10^{-3}$ Å, respectively, while the self-consistent-field (SCF) convergence threshold value is $1 \times 10^{-6}$ Ha. To enhance SCF convergence efficiency during optimization, an electron thermal smearing value of 0.002 Ha is employed for all the calculations. The conductor-like screening model (COSMO)$^{42}$ is used to simulate the aqueous environment, where the dielectric constant is set as 78.54 (water). All the stably existed species during the ORR process are confirmed no imaginary frequencies by performing frequency analysis. To determine the activation barriers ($E_a$), transition state (TS) searches are conducted by using the complete linear synchronous transit/quadratic synchronous transit (LST/QST) method. All the obtained TS structures exhibit only one imaginary frequency throughout the potential surface, and are ensured to directly connect corresponding reactants and products by nudged elastic band (NEB) algorithm$^{43}$.

The unit cell of 2H-MoS$_2$ is optimized by using $9 \times 9 \times 1$ Monkhorst–Pack k-point grids. The single P doped MoS$_2$ is then obtained by substituting a surface S atom in MoS$_2$ (3 $\times$ 3 supercell) into P atom, with a doping concentration of 3.7 atom%. The structures of MoS$_2$ (3 $\times$ 3 supercell and single P-doped MoS$_2$ nanosheet (P-MoS$_2$) are depicted in Fig. 1(a,b). The double P-doped MoS$_2$ nanosheet (2P-MoS$_2$) is obtained by substituting two surface...
S atoms in MoS₂, $2\sqrt{3} \times 2\sqrt{3}$ supercell into P atoms, with a doping concentration of 5.5 atom%. Differing from the relative positions between the two doped P atoms, there are three possible configurations that are taken into consideration. That is, neighboring sites (type 1), spaced by a Mo atom (type 2), and spaced by a S atom (type 3), as shown in Fig. 1(c–e). Considering the close atomic volume between P and S atom, the influence of doping on lattice size is neglected. Brillouin zone of MoS₂, $3 \times 3$ supercell and the P-doped MoS₂ structures are sampled by $3 \times 3 \times 1$ Monkhorst-Pack k-point grids during the geometry optimization, which is tested converging for total energy. Population analysis of electron is performed by assigning Hirshfeld charges for the optimized structures.

In this article, the adsorption energy ($E_{ads}$) is defined as

$$E_{ads} = E_{mol/sub} - E_{mol} - E_{sub}$$

(7)

Where $E_{mol}$ and $E_{sub}$ represent the total energies of the isolated adsorbate and adsorption substrate, and $Emol/sub$ represents the total energy of the adsorption system. Here, the negative $E_{ads}$ means exothermic process for the adsorption. The more negative $E_{ads}$ is, the more stable the adsorption system is. The triplet is taken as the ground state of O₂ during the calculation.

In order to calculate the Gibbs free energy of reactions involving electron/proton transfer, the computational hydrogen electrode (CHE) model introduced by Nørskov and co-workers was used. The reaction free energies ($\Delta G$) can be computed as follows:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_{ph} + \Delta G_U$$

(8)

where the $\Delta E$ was the reaction total energy directly obtained from Dmol3 calculation, $\Delta ZPE$ is the change in the zero-point energy, $T$ is the temperature (298.15 K), and $\Delta S$ is the change in entropy. $\Delta G_{ph} = -nF \times \ln10 \times pH$ represents the free energy contribution due to the variation in the H₂ concentration and the pH value in this work was assumed to 14 in the alkaline medium. $\Delta G_U = -neU$, where $n$ was the number of electrons transferred and $U$ was the applied electrode potential. The entropy values are taken from the physical chemistry table considering H₂ and H₂O in gaseous form at room temperature and atmospheric pressure whereas the entropy of the adsorbed state is considered to be negligible. ZPE of the free molecules are estimated from our DFT calculations considering vibrational frequencies of the molecules in the harmonic approximation. The details of calculation steps to plot Free energy profile are demonstrated in the supporting information.

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Author Contributions

H.D. and Y.L. conceived the main idea. C.L. performed all the calculation work. C.L. and H.D. analyzed the results and wrote the paper. Y.L. and T.H. joined the discussion. All authors contributed to the final version. Y.L. supervised the project.

Additional Information

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