**Small Dopants Make Big Differences: Enhanced Electrocatalytic
Performance of MoS₂ Monolayer for Oxygen Reduction Reaction
(ORR) by N- and P-Doping**

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ABSTRACT

The design and development of low-cost and highly efficient electrocatalysts for oxygen reduction reaction (ORR) is crucial to the large-scale commercial application of fuel cells. Herein, by means of comprehensive density functional theory (DFT) computations, we explored the potential of the heteroatom doping (N and P) to activate the basal plane of molybdenum disulfide (MoS_2) monolayer for ORR in acidic medium. Our computations revealed that substituting S in MoS_2 monolayer with N or P atom can introduce high spin density into MoS_2 basal plane, leading to its improved chemical reactivity for the O_2 activation, and the subsequent ORR steps prefer to proceed through a more efficient 4e pathway. Especially, N-doped MoS_2 monolayer exhibits outstanding ORR catalytic performance in terms of its small overpotential (0.67 V) and low energy barrier (0.25 eV), which is comparable (even lower) to those of Pt-based electrocatalysts. In contrast, the catalytic activity of P-doped MoS_2 monolayer is considerably poor due to its very strong interaction with O^* and OOH^* species in the subsequent reactions. Therefore, we expect that N-doped MoS_2 monolayer is a quite promising single-atom-catalyst with high efficiency for ORR in fuel cells.

KEYWORDS : MoS_2 monolayer, doping, oxygen reduction reaction, density functional theory

Graphic Abstract

1. INTRODUCTION

Oxygen reduction reaction (ORR) plays an important role in renewable energy technologies, ranging from fuel cells to metal–air batteries [1-4]. One of the challenges for boosting performance of fuel cells and metal–air batteries is to facilitate the slow kinetics of the ORR at the cathode [5, 6]. Therefore, electrocatalysts are essential to reduce the activation energy barriers of the sluggish ORR. Although platinum (Pt)–based materials have been long known as the most efficient ORR electrocatalysts via the four–electron transfer pathway ($\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$) [7-9], their high cost, scarcity, poor operation durability, and CO–poisoning effect have significantly hampered the large–scale commercialization of fuel cell and metal–air battery technologies [2]. Thus, the search for inexpensive, durable, and effective ORR catalysts for the replacement of Pt–based catalysts is a major target in last decades.

Carbon–based nanostructures, such as carbon nanotubes and graphenes, have recently been regarded as one of the possible alternatives to Pt–based catalysts due to their high durability, great abundance, and low cost [10-15]. Among these candidates, heteroatom-doped graphene materials (e.g., B, N, S, P) have been demonstrated to exhibit excellent catalytic performances [16-20], which is ascribed to the doping–induced modifications of the electronic structures, including the redistribution of the charge density and spin density, and the modulation of energy gap [21-23]. Consequently, the O_2 adsorption on graphene–based materials is obviously improved, leading to the activation of the O–O bonding and thus facilitating the subsequent ORR process.

As an important class of graphene–like two–dimensional (2D) layered materials,

transition-metal dichalcogenides (TMDs) have been widely studied due to their intriguing properties [24-26]. Among 2D layered TMDs, molybdenum disulfide (MoS_2) is one of the most promising semiconductors due to its inherent, thickness-dependent band gap, and abundance in nature as molybdenite. MoS_2 monolayer is formed by a stack of hexagonal layers of molybdenum atoms sandwiched between two layers of sulfur atoms (S–Mo–S) through weak van der Waals forces [27, 28]. Various techniques have been developed to synthesize the ultrathin MoS_2 nanosheets, such as chemical vapor deposition [29] and hydrothermal synthesis [30]. The unique properties render MoS_2 nanomaterials promising applications in catalysis, sensing, energy storage and conversion devices [27, 31, 32]. Especially, the MoS_2 nanosheets doped with various heteroatoms exhibit superior catalytic performance for the hydrogen evolution reaction (HER) [33-50].

Compared with the extensive research on HER performance of MoS_2 nanosheets, few experimental studies have explored the potential applications of MoS_2 nanosheets for ORR [51-54]. Very recently, Song and coworkers observed that oxygen (O) or phosphorus (P) incorporation into MoS_2 nanosheet induces a dramatically enhanced ORR activity under alkaline conditions [52, 53].

Encouraged by these above experimental studies on the ORR on MoS_2 -based nanomaterials, in this work, by means of density functional theory (DFT) computations, we doped heteroatoms (N and P) into the basal plane of MoS_2 monolayers (Figure 1), examined their stabilities and electronic structures, and explored their catalytic performance for ORR. Our computations revealed that

1 N-doped MoS₂ monolayer possesses excellent ORR catalytic activity in acidic
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3 conditions and can be a promising candidate for the next-generation of low-cost
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5 ORR catalysts.
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10 11 2. COMPUTATIONAL DETAILS 12 13

14 Our spin-polarized DFT computations employed an all-electron method within a
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16 generalized gradient approximation (GGA) for the exchange-correlation term, as
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18 implemented in the DMol³ code [55, 56]. The double numerical plus polarization
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20 (DNP) basis set and Perdew-Burke-Ernzerhof (PBE) functional were adopted [57].
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22 The accuracy of DNP basis set is comparable to that of Pople's 6-31G** basis set
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24 [58]. To accurately describe the long-range electrostatic interactions of ORR species
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26 with catalysts, the PBE+D2 method with the Grimme vdW correction was employed
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28 [59]. Self-consistent field (SCF) calculations were performed with a convergence
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30 criterion of 10⁻⁶ a.u. on the total energy and electronic computations. The real-space
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32 global orbital cutoff radius was chosen as high as 4.7 Å in all the computations to
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34 ensure high quality results. A conductor-like screening model (COSMO) was used to
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36 simulate a H₂O solvent environment throughout the whole process [60]. The dielectric
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38 constant was set as 78.54 for H₂O solvent.
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50 The adsorption energy (E_{ads}) of ORR species on doped MoS₂ monolayer was
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52 computed by $E_{\text{ads}} = E_{\text{adsorbate/substrate}} - E_{\text{adsorbate}} - E_{\text{substrate}}$, where $E_{\text{adsorbate/substrate}}$, $E_{\text{adsorbate}}$,
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54 in which $E_{\text{substrate}}$ are the total energies of the adsorbate-catalyst, the isolated adsorbate,
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56 and the doped MoS₂ monolayer, respectively. According to this definition, a negative
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E_{ads} indicates exothermic adsorption. The Hirshfeld charge population analysis [61] was adopted to compute the charge transfer and magnetic moment. All the data were obtained under this method unless mentioned otherwise.

We set the x and y directions parallel and the z direction perpendicular to the plane of the doped MoS₂ monolayer, and adopted a supercell length of 15 Å in the z direction. In order to ascertain the reliability of computations in 3×3 supercells, we repeated related computations for MoS₂ nanosheet in 4×4 supercells. The rather small differences between the results of 3×3 and 4×4 supercells guarantee the validity of the conclusions in this work (Table S1 in Supporting Information).

The Brillouin zone was sampled with a $5 \times 5 \times 1$ k points setting in geometry optimizations, and a $12 \times 12 \times 1$ grid was used for electronic structure computations. The transition states were located by using the synchronous method with conjugated gradient refinements. This method involves linear synchronous transit (LST) maximization, followed by repeated conjugated gradient (CG) minimizations, and then quadratic synchronous transit (QST) maximizations and repeated CG minimizations until a transition state is located [62].

The Gibbs free energy (ΔG) value of each elementary reaction step was computed according to the hydrogen electrode (CHE) model suggested by Nørskov *et al* [63-65]. In detail, the free energy change is defined as $\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\text{pH}} + \Delta G_{\text{U}}$, where ΔE is the reaction energy directly obtained from DFT calculations, ΔE_{ZPE} is the zero-point energy change, T is temperature (298.15 K), and ΔS is the change in entropy. $\Delta G_{\text{U}} = -neU$, where n is the number of electrons transferred and U

is the electrode potential. ΔG_{pH} is the correction of the H^+ free energy by the concentration, $\Delta G_{\text{pH}} = 2.303 k_{\text{B}} T \text{ pH}$, where k_{B} is the Boltzmann constant, and pH is assumed to be zero for acidic medium. Zero-point energies and entropies of the ORR intermediates were computed from the vibrational frequencies. The entropies and vibrational frequencies of molecules in the gas-phase were taken from the NIST database [62], while the vibrational frequencies of adsorbed species were calculated to obtain ZPE contribution in the free energy expression. Only adsorbate vibrational modes were calculated explicitly, while the catalyst sheet was fixed as proposed by previous theoretical studies [65-68].

3. RESULTS AND DISCUSSION

3.1. Geometries and Stabilities of N- and P-Doped MoS_2 Monolayer. For N-doped MoS_2 monolayer, because the radius of N atom is much smaller than that of S atom, N is inward from the top sulfur layer by 0.59 Å, as compared with pristine MoS_2 monolayer (Fig. 1a). As a result, the newly formed Mo–N bond (2.02 Å) is also shorter than that of Mo–S bond in pristine MoS_2 monolayer (2.43 Å), which is in good agreement with the recent DFT study [69]. In contrast, with a very similar atomic radius as S, the P dopant is only slightly outward by 0.03 Å, and the Mo–P bond length is 2.44 Å (Fig. 1b).

To probe the possibility to obtain the N- and P-doped MoS_2 monolayers, we computed their formation energy (E_{f}), which is defined as $E_{\text{f}} = E_{\text{total}}[\text{doped MoS}_2] - E_{\text{total}}[\text{MoS}_2] - \mu_{\text{S}} - \mu_{\text{X}}$, where $E_{\text{total}}[\text{doped MoS}_2]$ and $E_{\text{total}}[\text{MoS}_2]$ are the total energies

of the doped and pristine MoS₂ monolayer, respectively. μ_S and μ_X are the chemical potential of S and N (or P) atoms. μ_X can be computed from X₂ dimers, while μ_S is largely dependent on the experimental growth conditions. For Mo-rich conditions, the Mo chemical potential is obtained from the bulk Mo value, i.e., $\mu_{Mo} = \mu_{Mo-bulk}$, and we assume that $\mu_{MoS_2} = \mu_{Mo} + 2\mu_S$ from the thermodynamic equilibrium condition according to prior DFT computations [70-72] (we also note that although the choice of reference phase is not unique [73], the qualitative conclusion about the doping availability will not change). Then, the chemical potential of S atom under Mo-rich conditions can be computed as: $\mu_S = (\mu_{MoS_2} - \mu_{Mo})/2$, where μ_{MoS_2} is equal to $E_{total}[MoS_2]$ per MoS₂ formula unit. For S-rich conditions, one assume the S₂ gas as the source of S atom, i.e., $\mu_S = \mu_{S_2}$.

According to this definition, the formation energies for N- and P-doped MoS₂ monolayers under Mo-rich conditions are -0.19 and -1.21 eV, respectively, while under S-rich condition, these values are 2.94 and 1.92 eV, respectively. These results are consistent with previous theoretical studies [69]. Clearly, under Mo-rich conditions, N and P dopant can be easily incorporated into the MoS₂ monolayer. A possible strategy is to deliberately produce S vacancy at the post-growth stage and to fill the vacancies with an appropriate dopant. Indeed, very recently, Liu *et al.* prepared N-doped MoS₂ monolayer via a simple two-step method [74], i.e., (1) the preparation of MoS₂ with defects by the hydrothermal method, followed by (2) sintering in a NH₃ atmosphere.

An ultimate prerequisite for a material to be an effective catalyst is its stability.

To examine the stability of the N- and P-doped MoS₂ monolayer, we performed first-principles molecular dynamics simulations for 10 ps at 450 K. No notable geometry buckling was observed (Fig. S1), indicating its reasonable thermal stability. Quite recently, Azcatl et al. synthesized N-doped MoS₂ nanosheet through a remote N₂ plasma surface treatment, and they demonstrated that the doping process induced compressive strain in MoS₂, while confirmed the good thermal stability of the Mo–N bond and lack of N desorption upon annealing at 500 C° [69]. Moreover, Huang *et al.* successfully engineered the P atoms into the plane of ultrathin MoS₂ nanosheets [52].

In order to deeply understand the role of N and P dopant for ORR, we studied their electronic properties. These two doped MoS₂ monolayers both have magnetic ground states with a magnetic moment of 1 μ_B , which mainly localizes on the N or P dopant (Fig. S2). Consistent with prior studies [70], our computations also demonstrate that the pristine MoS₂ monolayer is a semiconductor with a band gap of 1.79 eV (Fig. 2a). After the substitutional doping by N atom, a narrow band gap of 0.19 eV is observed in the band structure (Fig. 2b) due to the induced impurity states by N doping. Similarly, P–doped MoS₂ monolayer is also semiconducting, but its band gap is 1.71 eV because its impurity states are rigidly shifted closer to the VBM of the pristine MoS₂ monolayer in both spin channels (Fig. 2c). Overall, the small formation energy, enhanced spin density, and reduced band gap imply the possibility to improve the catalytic performance of MoS₂ monolayer for ORR by introducing N or P dopant.

3.2. ORR Species Adsorption. After knowing that N or P doping can effectively

1 tune the electronic properties, we further examined the adsorption of key ORR species,
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3 including O_2 , OOH , OH , O , and H_2O , on these two doped MoS_2 monolayers.
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6 Since ORR initiates by the adsorption of O_2 , and this step greatly impacts the
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8 subsequent steps, we first explored the O_2 adsorption. Two possible adsorption
9 configurations, namely end-on and side-on, were considered, during which the O_2
10 molecule was placed on various sites of doped MoS_2 monolayer, including the central
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20 Our computations showed that the O_2 molecule prefers to locate at the central N
21 or P site. However, the O_2 adsorption configurations differ dramatically on the two
22 doped MoS_2 monolayers (Figure 3). On N-doped MoS_2 monolayer, the end-on
23 configuration is preferred, in which a N–O bond 1.66 Å is formed and the N atom is
24 pulled by about 0.07 Å, while the side-on configuration is not stable at all (converting
25 to the end-on configuration after structural optimization. In contrast, on P-doped
26 MoS_2 monolayer, O_2 molecule can adopt both end-on and side-on adsorptions, but
27 the side-on configuration is 0.12 eV lower in energy. In the side-on configuration, the
28 two P–O bonds are of 1.66 and 1.69 Å (Fig. 3b), while in the end-on configuration,
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47 The computed O_2 adsorption energy on N–doped MoS_2 monolayer is –0.37 eV,
48 and corresponding value on P–doped MoS_2 monolayer is –0.93 eV for side-on
49 configuration and –0.81 eV for end-on configuration. Note that these O_2 adsorption
50 energy values are much more favorable than that on pristine MoS_2 monolayer (–0.11
51 eV). Such adsorptions lead to the elongation of O–O bond (1.26, 1.57, and 1.35 Å,
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1 respectively, for the three located stable configurations, see Figure 3), which can be
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3 understood by the electron donation from the N- or P-doped MoS₂ monolayer to the
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5 half-filled $2\pi^*$ orbitals of O₂ molecule.
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9 Similarly, the adsorption of other ORR species also prefers to locate at the
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11 central N or P atom (Fig. S3). Note that these active sites (the dopants themselves)
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13 have high spin densities. The OOH, O, and OH are strongly chemisorbed on the two
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15 doped MoS₂ monolayer, their adsorption energies are -1.48, -4.19, and -2.76 eV on
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17 N-doped MoS₂ monolayer, and the corresponding values are -2.35, -5.66, and -4.14
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19 eV on P-doped MoS₂ monolayer (see Table 1). In general, a weaker adsorption of O
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21 and OH species on catalysts indicates a higher catalytic activity. Thus, N-doped MoS₂
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23 monolayer is expected to exhibit better catalytic performance for the ORR than
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25 P-doped MoS₂ monolayer. For the product (H₂O), its interaction with both on N- and
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27 P-doped monolayers are weak (the adsorption energies are -0.07 and -0.18 eV,
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29 respectively). Thus, once formed, H₂O can easily desorb from the surface of
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31 electrocatalysts.
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42 For comparison, we also computed the adsorption of these ORR species on the
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44 pristine MoS₂ nanosheet. The adsorption energies of O₂, OOH, O and OH on pristine
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46 MoS₂ nanosheet are -0.11, -0.17, -2.25, and -0.77 eV (Fig. S4), respectively, which
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48 are much smaller than those on N- or P-doped MoS₂ monolayer. Especially, the O₂
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50 and OOH adsorption on the pristine MoS₂ nanosheet is rather weak, suggesting that
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52 O₂ and OOH species cannot be sufficiently activated. Consequently, the pristine MoS₂
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54 monolayer exhibits very poor ORR catalytic activity.
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3.3. ORR on N-doped MoS₂ monolayer. Figure 4 presents the free-energy diagram and various pathways of ORR on N-doped MoS₂ monolayer. As above discussed, the O₂ molecule prefers to bind on the top of the N dopant with adsorption energy of -0.37 eV. When taking ΔE_{ZPE} and entropy into account, however, the ΔG for the O₂ adsorption on N-doped MoS₂ monolayer turns to be 0.32 eV, thus not favorable thermodynamically. However, Choi *et al.*[75] recently revealed that O₂ chemisorption is not essential for ORR occurring on catalyst, in which the first electron directly binds to O₂ molecule at the outer Helmholtz plane (ET-OHP) over a long distance to form OOH⁺, and subsequently adsorbs on the catalytic site as OOH^{*} (*i.e.*, ET-OHP mechanism), which well explains the problem of not finding thermodynamically suitable sites for O₂ binding on N-doped graphene. Thus, we expect that the following oxygen reduction on N-doped MoS₂ monolayer will proceed through the ET-OHP mechanism. This process can be written as $\text{O}_2(\text{g}) + \text{H}^+ + e^- \rightarrow \text{OOH}(\text{aq})$ and $\text{OOH}(\text{aq}) \rightarrow \text{OOH}^*$ and the computed free energy is downhill by 0.61 eV.

After generated via the ET-OHP mechanism, OOH^{*} will be further hydrogenated by adsorbing a proton coupled with an electron transfer. As there are two possible O sites for adsorption of the second hydrogen, the ORR can proceed by two different pathways, one is the four-electron (4e) reduction pathway in which O₂ is reduced to two H₂O molecules, and the other is the two-electron (2e) reduction pathway in which O₂ is reduced to a H₂O₂ molecule. In our work, both reduction pathways were considered.

Along the $4e$ reduction pathway, the second H atom will be attached to the pre-hydrogenated O site in OOH^* species, yielding the O^* species on the central N-dopant with the O–N bond length of 1.25 Å, and releasing one H_2O molecule from N-doped MoS_2 monolayer due to their weak interaction. This process is downhill in the free energy profile by 2.49 eV. The remaining O^* species will be further reduced to an OH^* species with the help of a proton coupled with one electron transfer. In this hydrogenation process, the Gibbs free energy decreases by 0.90 eV. Finally, the second H_2O molecule will be achieved when the OH^* species adsorbs one proton and one-electron. This final step is also downhill in the free energy profile by 0.89 eV (Fig. 4a).

Providing that the ORR follows the $2e$ reduction pathway, the H atom will react with the O site of OOH species, resulting in the formation of H_2O_2 molecule ($\text{OOH}^* + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O}_2$). The ΔG value of this process, -0.53 eV, is much smaller than that of its reduction to $\text{O}^* + \text{H}_2\text{O}$ in the $4e$ reduction pathway ($\Delta G = -2.49$ eV). Thus, for the occurring ORR on N-doped MoS_2 monolayer, the $4e$ reduction pathway is more energetically favorable rather than the $2e$ reduction pathway, and we will only discuss the $4e$ reduction pathway in the following sessions.

According to the free-energy profile (Figure 4a), the reaction pathway is overall downhill at *zero* potential ($U = 0$ V). By shifting the potential to equilibrium potential ($U = 1.23$ V, corresponding to the maximum thermodynamic potential of the fuel cell), the first (i.e., $\text{O}_2(\text{g}) \rightarrow \text{OOH}^*$), the third (i.e., $\text{O}^* \rightarrow \text{OH}^*$), and the fourth ($\text{OH}^* \rightarrow \text{H}_2\text{O}^*$) steps turn to be uphill in the free energy profile by 0.62, 0.33, and 0.34 eV,

respectively. The rate-limiting step lies in the final step, $\text{OH}^* \rightarrow \text{H}_2\text{O}$, with an overpotential (η) of ($1.23 \text{ eV} - 0.89 \text{ eV} = 0.34 \text{ eV}$), which is an important criterion to evaluate the catalytic performance of a catalyst and is defined as the minimum energy required for the ORR on the catalyst. Considering that the reduction of O^* to OH^* and OH^* to H_2O is uphill at $U = 1.23 \text{ V}$, the minimum energy required for the ORR on N-doped MoS_2 monolayer (i.e, the total overpotential) is $0.33 \text{ eV} + 0.34 \text{ eV} = 0.67 \text{ eV}$, which is much lower than that on some well-known electrocatalysts, such as Co-N co-doped graphene (1.00 eV) [76] and N-doped graphitic materials ($0.43\text{--}0.73 \text{ V}$) [77], and graphene-supported Pt nanoparticles (1.13 eV) [66]. Thus, the N-doped MoS_2 monolayer could be a promising substitute of Pt catalyst for fuel cells from the thermodynamic point of view.

We also considered the effect of pH on the free energies of the ORR on the N-doped MoS_2 nanosheet. According to the equation of the free energies, i.e., $\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\text{pH}} + \Delta G_{\text{U}}$, where $\Delta G_{\text{pH}} = 2.303 k_{\text{B}}T \text{ pH}$ (i.e., $0.06 \times \text{pH}$). At $U = 0 \text{ V}$, as the pH value increases, the energy of each net coupled proton and electron transfer step is decreased (Fig. S5). For example, at $\text{pH} = 1$, the Gibbs free energies of the four elemental steps are decreased to $0.55, 2.43, 0.83$, and 0.84 eV .

Besides the thermodynamics discussed above, we also examined the kinetics by computing the reaction barriers between these elementary steps. Our computations showed that the reduction of OOH^* to $\text{O}^* + \text{H}_2\text{O}$ has a small energy barrier of 0.03 eV (Fig. 5a). In this transition state, the O–O bond is stretched to $1.58 \text{ \AA}$, indicating that the OH group starts to leave OOH^* and form chemical bonding with H (Fig. S6). The

subsequent reductions, O^* to OH^* and OH^* to H_2O , also pass small energy barriers (0.17 and 0.25 eV, respectively, Fig. 5a). Overall, in the whole ORR process on N-doped MoS_2 monolayer, the highest energy barrier (or rate-determining step) is 0.25 eV in the last step ($OH^* \rightarrow H_2O$, Fig. 5a), suggesting the kinetic feasibility of the ORR on N-doped MoS_2 monolayer.

3.4. ORR on P-doped MoS_2 monolayer. Now we turn to investigate the mechanisms of the ORR on P-doped MoS_2 monolayer. As shown in Fig. 4b, the free energy of the molecular O_2 adsorption on P-doped MoS_2 monolayer is -0.24 eV, thus leading to the activation of the O_2 molecule. Remarkably, the chemisorbed O_2 molecule can be dissociated into two separated O^* species with a small energy barrier of 0.11 eV (Fig. 5b), followed by their hydrogenation to H_2O . Alternatively, the adsorbed O_2 molecule is more preferable to be hydrogenated into OOH^* species by reacting with ($H^+ + e^-$) with a zero energy barrier. Similarly, the formed OOH^* species could also be dissociated or further hydrogenated.

Providing that the OOH^* species dissociates on P-doped MoS_2 monolayer, its OH^* species still locates on the P dopant with the O-P bond length of 1.63 Å, while the O^* species is inserted into the Mo-P bridge, forming Mo-O and P-O bonds (2.29 and 1.55 Å, respectively). The energy barrier for the OOH^* dissociation, 0.75 eV, is much higher than that for its hydrogenation (i.e., $OOH^* + H^+ + e^- \rightarrow O^* + H_2O$, 0.08 eV), indicating that the hydrogenation of OOH^* species to H_2O is more favorable kinetically. After H_2O is released from the P-doped MoS_2 monolayer surface, the remaining O atom on the central P dopant (P-O bond length of 1.51 Å) can further

interact with another proton to yield OH^* species by crossing a small energy barrier of 0.09 eV, and concomitantly the P–O bond is elongated to 1.62 Å (Fig. 3c). Note that the final step ($\text{OH}^* + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O}$) needs to overcome a barrier energy of 1.20 eV (Fig. 5b), implying that kinetically this process is unlikely to proceed at working temperature, no matter which pathway the oxygen reduction follows due to the OH–poisoning effect.

To further evaluate the oxygen–reduction activity of P–doped MoS_2 monolayer, we computed the free energies of the ORR via the kinetically more favorable OOH associative mechanism (Fig. 4b). At the *zero* electrode potential ($U = 0$ V), Gibbs free energies of all the reaction steps are downhill except for the last step ($\text{OH}^* + \text{H}^+ + e^- \rightarrow \text{H}_2\text{O}$). This endothermic step is the rate–determining one in the ORR, and could arise from the strong interaction of OH^* species with P–doped MoS_2 monolayer ($E_{\text{ads}} = -4.14$ eV). At the equilibrium potential ($U = 1.23$ V), free energies in all ($\text{H}^+ + e^-$) transfer steps are uphill except for the hydrogenation of OOH^* species to O^* species. The minimum energy required for the ORR to occur on P–doped MoS_2 monolayer (namely overpotential) is 2.05 eV, which is larger than that of on Pt–based catalysts. Thus, P–doped MoS_2 monolayer is not a good candidate as the ORR electrocatalyst.

Another important issue is that other lattice sites, such as interstitial sites, could affect the catalytic performance of MoS_2 nanosheet. Thus, we also considered the ORR on the interstitial sites of N- and P-doped MoS_2 nanosheets (Fig. S7). Our computations revealed that O_2 molecule can be interstitially adsorbed on N-doped MoS_2 nanosheet with the adsorption energy of -0.38 eV, while O_2 adsorption on the P

1 interstitial site is not energetically favorable, as the P atom will be pulled away from
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3 the MoS₂ nanosheet by the O₂ molecule (Fig. S8). Furthermore, we examined the free
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5 energies of each ORR elementary step on N interstitial site at U = 0 and 1.23 V (Fig.
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9 S9). The minimum energy required (or overpotential) for the ORR on this kind of
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11 doped MoS₂ monolayer is 0.78 eV, which is slightly larger than that of the
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13 substitutionally doped site (0.67 eV). In other words, substitutionally doping N into
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15 MoS₂ nanosheet can induce a better catalytic activity for the ORR.
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20 Overall, by comparing the computed energy barriers and overpotential of the
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22 ORR, we predict that the N-doped MoS₂ monolayer exhibits much higher catalytic
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24 activity than P-doped MoS₂ monolayer both kinetically and thermodynamically.
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27 Clearly, although P-doped MoS₂ monolayer has a higher reactivity towards O₂
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29 activation in the initial reaction process, the exceptional stability of O* and OH*
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31 species on its surface hinders the formation of production species (e.g., H₂O) in
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33 subsequent steps. This observation is well consistent with the Sabatier principle: an
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35 ideal catalyst should not bind with the reaction species too strongly or too weakly
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37 (which prevents reaction intermediates from drifting away from the catalytic center).
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47 4. CONCLUSIONS

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50 In summary, we investigated the ORR activity of N- and P-doped MoS₂
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52 monolayers in acidic medium by means of systematical DFT computations. Our
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54 computations revealed that N doping renders MoS₂ monolayer better catalytic
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56 performance than P doping due to its moderate binding strength with ORR species.
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Especially, the energy barrier and overpotential of the ORR on N-doped MoS₂ monolayer is even lower than those on Pt-based catalysts. The improved catalytic activity of MoS₂ monolayer mainly originates from the induced suitable spin density due to N and P doping. Thus, introducing other dopants (such as F, Cl, Re, Ru, Rh, Ag, Cd, and Pd) that can endows MoS₂ monolayer enhanced spin densities may also lead to optimal binding strength with oxygenated species, and achieve suitable MoS₂-based catalysts for ORR. We are encouraging more efforts to explore the potential of 2D MoS₂ nanosheets as single-atom catalysts for the ORR.

5. AUTHOR CONTRIBUTIONS

Huiying Zhang and Yu Tian contributed equally.

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SUPPORTING INFORMATION

The test of the employed supercell, spin density, adsorption configurations of ORR on N- and P-doped MoS₂ monoalyer, and the involved transition states of each elementary step on N-doped MoS₂ monoalyer.

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Table 1. Adsorption energy (E_{ads}) values of ORR intermediates on doped MoS₂ monolayers. All results are in unit of eV.

	O ₂	OOH	O	OH	H ₂ O
N-doped	-0.37	-1.48	-4.19	-2.76	-0.07
P-doped	-0.93	-2.35	-5.66	-4.14	-0.18

Figure Captions

Figure 1. The top and side views of the optimized structures of (a) N-□ and (b) P-doped MoS₂ monolayers.

Figure 2. The computed spin-polarized band structures of (a) pristine, (b) N-, and (c) P-doped MoS₂ monolayer. The Fermi level is set as zero in red dash line. The left and right denote spin-up and spin-down band structures, respectively.

Figure 3. The stable configurations of O₂ adsorption on (a) N- and (b,c) P-doped MoS₂ monolayer. a and c are end-on configurations, while b is of side-on configuration. The key bond lengths (in Å), the adsorption energies (E_{ads} , eV), and the electron donation from the doped MoS₂ monolayer to the $2\pi^*$ orbitals of O₂ molecule (Q , |e|) are also given.

Figure 4. The computed free□energy diagram of ORR on (a) N- and (b) P-doped MoS₂ monolayers. Black and red lines represent reactions at zero electrode potential ($U = 0$ V) and the equilibrium potential ($U = 1.23$ V), respectively.

Figure 5. Various possible reaction pathways for ORR on the (a) N- and (b) P-doped MoS₂ monolayer. The activation energies and reaction energies (in units of eV) are given in parentheses. The kinetically most favorable pathway of the ORR on P-doped MoS₂ monolayer is marked in red.

Figure 1

(a)

(b)

Figure 2

Figure 3

Figure 4

Figure 5