Mechanism of Oxygen Reduction Reaction on Monolayer WTe_2 with and without S Dopant at Low Coverage

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Transition metal dichalcogenides possess properties such as low cost, easy fabrication, and suitability for various applications. Monolayer WTe_2 is a potential electro-catalytic material for the oxygen reduction reaction (ORR). However, the reaction mechanism on pure and S-doped monolayer WTe_2 remains unknown; therefore, this work is devoted to clarifying the current topic using density functional theory calculations and a thermodynamics model. We found that the ORR mechanism is a four-electron pathway on pure and S-doped monolayer WTe_2 . However, S-doped monolayer WTe_2 increases the thermodynamic barrier of the ORR compared to pure monolayer WTe_2 . Therefore, the S dopant decreases the performance of WTe_2 . The result implies that doping with different elements is not always a method to improve the efficiency of chemical reactions.

Keywords Fuel cell; Catalyst; 2D materials; Density functional theory; Interfaces

I. INTRODUCTION

The development of catalysts for the cathode is a challenge to improve the performance of proton exchange membrane fuel cells and rechargeable metal-air batteries. The oxygen reduction reaction (ORR) on the cathode involves many intermediate steps and has a slow rate. Pure Pt, Pt-based alloys, and carbon-supported Pt nanoparticles were the most efficient catalytic materials [1]. However, they are too expensive to be widely commercialized. Pt-free alloys of less expensive metals such as Pd, Fe, and Co are the alternatives to significantly reduce cost and simultaneously improve the stability of catalysts [2–4]. Their ORR activity is comparable to that of the carbon-supported Pt materials [2]. Single-atom catalysts fabricated by dispersing metal atoms onto macromolecules and carbon-based materials like porphyrin and graphene were also investigated for the ORR [5]. The single-atom catalysts possess the maximum atom utilization efficiency. Besides, transition metal oxides such as cobalt oxides and copper oxides also exhibited a high per-

formance [6]. Recently, transition metal dichalcogenides (TMDs) have attracted much attention for the ORR due to their low cost, high abundance, and high tolerance to organic molecules [7]. Perfect, defective, and doped structures of TMDs could significantly enhance the ORR activity [8–10]. Besides, the ORR mechanisms on WTe_2 , which is a new material of the TMD family, with Te vacancies have been recently investigated [11]. However, there is no research available to elucidate the ORR mechanism and the activity on perfect and doped monolayer WTe_2 . Especially, S is one of the most popular chalcogenide elements, which can form natural compounds like MoS_2 and WS_2 . Hence, S doping in WTe_2 is expected to be thermodynamically favorable. Indeed, we found in this work that the formation energy of S substitution for the Te atom in WTe_2 is significantly negative, which implies that S doping is an exothermic process, and substitution proceeds simultaneously. Other examples of S doping in TMDs such as WSe_2 and MoTe_2 were also found in literature [12–14]. Doping with electron-donating and electron-withdrawing elements is an effective method to

modify the electronic structure of substrates and, therefore, it influences the adsorption strength of ORR intermediates and the efficiency of catalysts. However, due to the complicated nature of the ORR involving many intermediates, understanding the electron-withdrawing S dopant on the overall performance of WTe_2 remains unclarified. For these reasons, the present research will elucidate the ORR mechanisms on the perfect monolayer WTe_2 and S-doped monolayer WTe_2 (abbreviated as WTe_2S) using density functional theory (DFT) calculations and a thermodynamics model.

II. COMPUTATIONAL METHOD

We performed the DFT-based calculations using the Vienna *ab initio* simulation package [15] with the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) functional for exchange-correlation [16, 17] and the projector augmented wave (PAW) method for the core-valence interaction [18–20]. The cut-off energy for the plane-wave basis set expansion was 400 eV. The k -point mesh grid of $3 \times 3 \times 1$ was sampling by the Monkhorst-Pack technique. We took into account the dipole corrections for excluding the interaction of images in periodic supercells.

We modeled the supercell of monolayer WTe_2 by a slab of

Figure 1: Top view (left) and bird view (right) of $\text{O}^* + \text{H}_2\text{O}$ and $\text{HO}^* + \text{H}_2\text{O}$ on WTe_2 (a, b, c, d) and WTe_2S (e, f, g, h). Blue (Te), green (W), yellow (S), red (O), and white (H).

5×5 unit cell and a vacuum of about 13 Å, as shown in Figure 1. S doping at a low coverage was created by replacing one Te atom in perfect monolayer WTe_2 to create the WTe_2S substrate. The substrates have the dimensions of $a = b = 17.61$ Å [11]. All atomic positions in the substrates and the ORR intermediates were fully optimized. The formation energy of -6.64 eV for S doping implies that the process is exothermic and thermodynamically favorable. The formation energy E_f was defined by

$$E_f = E_{\text{Sub}}^{\text{S}} - E_{\text{Sub}}^{\text{V}} - E_{\text{S}}^{\text{i}}. \quad (1)$$

Here, $E_{\text{Sub}}^{\text{S}}$, $E_{\text{Sub}}^{\text{V}}$, and E_{S}^{i} are the total energies of the WTe_2S substrate, the WTe_2 substrate with a Te vacancy, and the isolated S atom, respectively. The formation energy was calculated by Eq. (1), because, in reality, monolayer WTe_2 is not formed from powder but bulk crystal by the mechanical exfoliation technique [21]. The chalcogenide vacancies often occur as an accompanying effect during the fabrication process [22]. Besides, substitutional doping with dopant atoms covalently bonded at vacancy sites is a promising technique [23]. Therefore, the doping process can be interpreted as generating vacancies and updating dopant atoms into the vacancies [24].

The adsorption energy E_a for each ORR intermediate was estimated through the total energy of each component as

$$E_a = E_{\text{Substrate+Intermediate}} - E_{\text{Substrate}} - E_{\text{Intermediate}}. \quad (2)$$

The Gibbs free energy was studied to understand the progress of the reaction steps and the thermodynamic stability of reaction intermediates [25, 26]. The Gibbs free energy was calculated by the formula;

$$\Delta G(U) = \Delta E + \Delta ZPE - T\Delta S + eU. \quad (3)$$

Here, we ignored the contribution of the acid medium by taking $\text{pH} = 0$. The reaction energy, the zero-point energy correction, and the entropy change are denoted as ΔE , ΔZPE , ΔS , respectively. U is the electrode potential relative to the standard hydrogen electrode.

III. RESULTS AND DISCUSSION

Generally, the ORR in an acidic medium, $\text{O}_2 + 4(\text{H}^+ + \text{e}^-) \rightarrow 2\text{H}_2\text{O}$, can proceed through dissociative and associative mechanisms [1, 27] as described in Scheme 1. Both pathways begin with the adsorption of oxygen molecules onto the catalytic surface. The associative mechanism (path $2 \rightarrow 4$) remains the molecular state of the oxygen molecule during the electron and proton transfer, while the dissociative mechanism (path $1 \rightarrow 6 \rightarrow 8$) involves the dissociation of the oxygen molecule to form two oxygen atoms before the hydrogenation steps. Partially, the associative mechanism can turn to the dissociative one at steps 3 and 5. The second hydrogenation step on HOO^* and $\text{O}^* + \text{HO}^*$ will generate $\text{O}^* + \text{H}_2\text{O}$, while the third hydrogenation step on HOOH^* , 2HO^* , and $\text{O}^* + \text{H}_2\text{O}$ will create $\text{HO}^* + \text{H}_2\text{O}$. The last hydrogenation step 12 will form

Scheme 1: ORR possible pathways on perfect WTe₂ and WTe₂S. The asterisk denotes the adsorption site on the substrate surface. Adsorption and vibrational energies (in eV) are presented in red and blue for the intermediates on perfect WTe₂ and WTe₂S, respectively. The vibrational (zero-point) energies are given in the parenthesis.

the by-product of the ORR.

We have searched the adsorption site and configuration for the possible intermediates of the ORR on WTe₂ and WTe₂S by designing their geometric structures and performing the DFT optimization. Scheme 1 listed the adsorption energy for the most stable configuration of intermediates. The positive adsorption energy of the ORR intermediates in the pathways 2 → 4 and 1 → 6 → 8 implies that adsorption of the ORR intermediates is thermodynamically unfavorable, which is in good agreement with the work of Liu *et al.* [28]. Even with HOO* on WTe₂S, the adsorption energy is negative, although the vibrational (zero-point) energy is much higher than its adsorption energy. This result indicates that HOO* is unstable on the WTe₂S surface due to a large fluctuation. Notably, only two intermediates, i.e., O* + H₂O and HO* + H₂O adsorb stably with significant negative adsorption energies on WTe₂ and WTe₂S. The analysis of the adsorption energy suggests that the ORR should proceed through the chain: O₂ → O* + H₂O → HO* + H₂O → 2H₂O, i.e., pathway 7 → 10 → 12. Furthermore, the adsorption energy of O* and HO* in the absence of water (the gas phase intermediates) was also presented in Scheme 1 for comparison with O* + H₂O and HO* + H₂O. It exhibits that these ORR intermediates on the same substrate in the presence of water adsorb stably than those without water. Also, the adsorption energy of O* and HO* with and without H₂O is more negative on WTe₂S than on WTe₂. The result implies that the S dopant increases the adsorption strength of O* and HO*.

Figure 1 shows the most favorable adsorption site of the two stable intermediates, O* + H₂O and HO* + H₂O, for which O* of these intermediates preferentially locates on top of the Te atom of WTe₂ and WTe₂S [Figure 1(a–d, g, h)] except for O* + H₂O on WTe₂S [Figure 1(e, f)] with O*

Table 1: Bond lengths (Å) and bond angles (°) for O* + H₂O and HO* + H₂O at the most favorable adsorption site on the monolayer WTe₂ and WTe₂S substrates.

Substrate	O* + H ₂ O	HO* + H ₂ O
WTe ₂	Te–O* = 1.856 Å O*–O = 3.053 Å	Te–O* = 2.238 Å O*–H = 0.98 Å (for HO*) Te–O*–H = 102° (for HO*) O*–O = 2.818 Å
WTe ₂ S	S–O* = 1.509 Å O*–O = 3.243 Å	Te–O* = 2.235 Å O*–H = 0.98 Å (for HO*) Te–O*–H = 105° (for HO*) O*–O = 2.783 Å

favorable on top of the S atom. Furthermore, HO* + H₂O is also stable on top of the S atom of WTe₂S with an adsorption energy of −0.683 eV. However, this value is less than that of −1.228 eV on the Te site of WTe₂S. Therefore, although the S atom site is not the most favorable one, it is still an active adsorption site for HO* + H₂O on WTe₂S. Also, both gas-phase O* and HO* intermediates adsorb most favorably on top of the Te atom for perfect WTe₂ and the S atom for WTe₂S. Noticeably, the structure of O* + H₂O and HO* + H₂O intermediates in their most favorable adsorption configuration on WTe₂ is similar to WTe₂S. However, the geometric parameters are different. Table 1 shows that the Te–O* bond length between O* + H₂O and WTe₂ is longer than the S–O* bond length between O* + H₂O and WTe₂S, which incorporate well with the trend in adsorption energy of the intermediate on the substrates. O* is sticking stronger on WTe₂S than on WTe₂. The O*–O distance between O* and O of the water molecule becomes elongated when the O* + H₂O intermediate adsorbs on WTe₂S. For HO* + H₂O, the bond distances remain almost the same except for the angle Te–O*–H of HO* increases by 3° upon S doping.

The density of state (DOS) structure exhibits that for the O* + H₂O intermediate (the left column of Figure 2), the O* p_x orbital is more dominant than the O* p_z orbital around −2.0 eV, which mainly interacts with the Te p_x and p_z states of the WTe₂ and WTe₂S substrates due to the overlapping with the DOS of the Te atoms. However, the O* p_z orbital is more significant than the O* p_x orbital at lower energies. Contrastingly, for WTe₂S, there are the peak resonances of the O* p_z orbital with the S p_z orbital and the O* p_x orbital with the S p_x orbital around −6.5 eV. For HO* + H₂O (the right column of Figure 2), the DOS of O* disperses in a broad range of energy, and they are similar for both the WTe₂ and WTe₂S substrates. The S p orbitals do not show a resonance with the O* p orbitals because the most favorable configuration of the HO* + H₂O intermediate locates far away from the S atom. Even though, we have to note that the S atom site is the second most favorable position of HO* + H₂O on the WTe₂S substrate.

Figure 2: Electronic density of states (DOS): Left and right columns are for $O^* + H_2O$ and $HO^* + H_2O$, respectively, and the first and second rows are for WTe_2 and WTe_2S , respectively. The O p_x and p_z orbitals are those of O^* . For $O^* + H_2O$, although we do not show the DOS of the S atom, there are the peaks of the S p_x and p_z orbitals around -6.5 eV.

Table 2: The Bader point charge (e^-) of the atoms in the systems of $O^* + H_2O$ and $HO^* + H_2O$ intermediates with WTe_2 and WTe_2S . The positive and negative signs indicate the charge accumulation and donation, respectively.

System	O^*	O	ΣH^a	ΣW	ΣTe	S
$(O^* + H_2O)/WTe_2$	1.77	2.02	-2.0	-25.10	23.31	
$(HO^* + H_2O)/WTe_2$	1.58	2.02	-3.0	-25.10	24.50	
clean WTe_2S				-24.82	23.61	1.21
$(O^* + H_2O)/WTe_2S$	2.01	1.95	-2.0	-26.43	25.09	-0.62
$(HO^* + H_2O)/WTe_2S$	2.02	1.57	-3.0	-26.50	24.75	1.16

^a Each hydrogen atom donates charge of $1e^-$. Charge of H_2O is the contribution of O and 2H.

The interaction of the DOS between the substrates and the intermediates leads to charge rearrangement. We calculated the point charge of the atoms in the substrate-intermediate systems by the Bader partition technique to understand the charge exchange tendency. Table 2 shows that the W atoms donate while the Te atoms accumulate charge. The H_2O molecule in $O^* + H_2O$ and $HO^* + H_2O$ on WTe_2 has a total charge of $0.02e^-$. Therefore, the water molecule almost remains neutral charge state during the adsorption of O^* and HO^* on WTe_2 . The O^* atom of $O^* + H_2O$ and $HO^* + H_2O$ intermediates gains charge from WTe_2 . However, the H atom of HO^* compensates a part of the charge to the Te atoms. Therefore, the Te atoms of WTe_2 gain a higher charge

value for the adsorption of $HO^* + H_2O$ than $O^* + H_2O$.

For clean WTe_2S , the S atom gains charge, which is in good agreement with its electron-withdrawing nature. The O^* atom of $O^* + H_2O$ and $HO^* + H_2O$ accumulates a higher portion of the charge from the WTe_2S substrate and the H atoms relative to the case of WTe_2 . Hence, the adsorption strength of $O^* + H_2O$ and $HO^* + H_2O$ is stronger on WTe_2S than on WTe_2 .

The ORR intermediate steps are proposed based on the stable adsorption intermediates $O^* + H_2O$ and $HO^* + H_2O$ on WTe_2 and WTe_2S as follows:

Table 3: Gibbs free energy (eV) for the proposed mechanism.

Medium	Quantity	WTe ₂ S		WTe ₂	
		$U = 0$ V	$U = 1.23$ V	$U = 0$ V	$U = 1.23$ V
with H ₂ O	$\Delta G_1(U)$	0.40	1.63	-0.25	0.98
	$\Delta G_2(U)$	-2.25	-1.02	-2.45	-1.22
	$\Delta G_0(U)$	-1.85	0.61	-2.70	-0.24
without H ₂ O	$\Delta G_1(U)$	0.47	1.70	-0.39	0.85
	$\Delta G_2(U)$	-2.33	-1.10	-2.56	-1.33
	$\Delta G_0(U)$	-1.86	0.60	-2.95	-0.49

Equation (4) involves transferring of two protons and two electrons at once. We can imagine that O₂ (gas phase) combines with two protons and two electrons during approaching the surface of WTe₂ and WTe₂S to form the stable intermediates, while the common dissociative and associative ORR mechanisms always start with adsorption of the oxygen molecule.

We obtained the Gibbs free energy for the intermediate steps, i.e., Eqs. (4) to (6), from the calculated zero-point energy, total energy, and the thermodynamics model [25, 26] at the electrode potential of 1.23 V, pH = 0, the pressure of 1 bar, and the temperature of 300 K. The Gibbs free energy for the proposed intermediate steps were calculated by the following formulae:

$$\begin{aligned} \Delta G_1(U) &= G_{\text{HO}^* + \frac{1}{2}\text{H}_2 + \text{H}_2\text{O}}(U) - G_{\text{O}^* + \text{H}_2 + \text{H}_2\text{O}}(U) \\ &= \Delta G_1(0) + eU, \end{aligned}$$

$$\begin{aligned} \Delta G_2(U) &= G_{\text{H}_2\text{O}}(U) - G_{\text{HO}^* + \frac{1}{2}\text{H}_2 + \text{H}_2\text{O}}(U) \\ &= \Delta G_2(0) + eU, \end{aligned}$$

$$\begin{aligned} \Delta G_0(U) &= G_{\text{H}_2\text{O}}(U) - G_{\text{O}^* + \text{H}_2 + \text{H}_2\text{O}}(U) \\ &= \Delta G_0(0) + 2eU, \end{aligned}$$

where, $\Delta G_i(0)$ ($i = 0, 1, 2$) obtained from Eq. (3) with $U = 0$. The corresponding values of the Gibbs free energy were listed in Table 3.

The Gibbs free energy diagram in Figure 3(a) shows that, in the presence of H₂O, both steps of the O* and HO* formation on WTe₂ are going uphill. In Figure 3(b), the step of the O* formation on WTe₂S is downhill before uphill again at the step of the HO* formation. The reason for going downhill is due to the stronger adsorption of the O* intermediate upon the S doping. In the presence of H₂O, we find on both substrates that the first step transfers two protons and two electrons at the same time. This process is different compared to the first hydrogenation step with only one hydrogen atom at a time for various catalytic materials in the literature [1, 11, 27]. The second step is the rate-limiting step of the reaction, which is the transfer of the third proton and electron. This result is also different com-

Figure 3: Gibbs energy diagram for the ORR in the absence (red) and presence (blue) of water on perfect WTe₂ (a) and WTe₂S (b) at the electrode potential of 1.23 V, pH = 0, the pressure of 1 bar, and temperature of 300 K. The thermodynamic barriers are 1.22 and 1.63 eV for the ORR in the presence of H₂O on WTe₂ and WTe₂S, respectively.

pared to the literature in that the first proton and electron transfer is the rate-limiting step of the reaction [1, 11, 25, 27]. The activation barrier for the whole process in the forward direction from left to right of the Gibbs free energy diagram was calculated by the energy difference between two steps of the HO* formation and O₂ + 4H for WTe₂ and between two steps of the HO* and O* formation for WTe₂S. The barriers of 1.22 and 1.63 eV were obtained for the ORR in the presence of H₂O on WTe₂ and WTe₂S, respectively. The result implies that S doping decreases the performance of WTe₂ toward the ORR, which also agrees with literature for other electron-withdrawing elements or p-type doping [29–31]. Furthermore, the presence of H₂O decreases the activation barrier by 0.1 eV compared to the absence of H₂O on both WTe₂ and WTe₂S substrates. The ORR mechanism involves four electrons in the current work.

IV. CONCLUSION

In summary, the density functional theory calculations and the thermodynamics model revealed that the ORR mechanism on perfect monolayer WTe_2 and S-doped monolayer WTe_2S begins with a simultaneous transfer of two protons and two electrons to dissociate and stabilize O_2 in the form of $\text{O}^* + \text{H}_2\text{O}$. The second step, i.e., the transfer of the third proton and electron, is the rate-limiting step with the thermodynamics barrier of about 1.22 and 1.63 eV for WTe_2 and WTe_2S , respectively. The final step forms water, the by-product of the ORR. We have to emphasize that the mechanism does not start with the adsorption of the oxygen molecules. Also, the rate-determining step is not the first hydrogenation step as the common dissociative and associative mechanisms. Interestingly, the ORR proceeds via a four-electron process on the transition-metal dichalcogenides. The S dopant harms the ORR performance of WTe_2 because it enhances the adsorption strength of O^* and HO^* intermediates and leads to the increase of the ORR thermodynamics barrier.

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