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# The heterointerface effect to boost the catalytic performance of single atom catalysts for sulfur conversion in lithium–sulfur batteries†

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Lithium–sulfur (Li–S) batteries are considered as one of the promising next-generation energy storage devices due to their characteristics of high energy density and low cost. However, the shuttle effect and sluggish conversion of lithium polysulfide (LiPs) have hindered their commercial applications. To address these issues, in our previous works, we have screened several highly efficient single atom catalysts (SACs) ( $MN_4@G$ ,  $M = V$ , Mo and W) with atomically dispersed transition metal atoms supported by nitrogen doped graphene based on high throughput calculations. Nevertheless, they still suffer from low loading of metal centers and unsatisfactory capability for accelerating the reaction kinetics. To tackle such problems, based on first-principles calculations, we systematically investigated the heterointerface effect on the catalytic performance of such three  $MN_4@G$  toward sulfur conversion upon forming heterostructures with 5 typical two-dimensional materials of  $TiS_2$ ,  $C_3N_4$ , BN, graphene and reduced graphene oxide. Guided by efficient descriptors proposed in our previous work, we screened  $VN_4@G/TiS_2$ ,  $MoN_4@G/TiS_2$  and  $WN_4@G/TiS_2$  possessing low  $Li_2S$  decomposition barriers of 0.54, 0.44 and 0.41 eV, respectively. They also possess enhanced capabilities for catalyzing the sulfur reduction reaction as well as stabilizing soluble LiPs. More interestingly, the heterointerface can enhance the capability of the carbon atoms far away from the metal centers for trapping LiPs. This work shows that introducing a heterointerface is a promising strategy to boost the performance of SACs in Li–S batteries.

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## 1. Introduction

To reduce the greenhouse gas emission caused by the consumption of fossil fuels stimulates great interest from researchers to develop high-performance energy storage devices. Among these state-of-the-art energy storage devices, lithium–sulfur (Li–S) batteries have garnered significant attention in recent years owing to their high theoretical specific capacity of 1675 mA h g<sup>-1</sup> and high energy density of 2600 W h kg<sup>-1</sup>.<sup>1–5</sup> However, certain issues still exist, weakening the performance of Li–S batteries and thus impeding their commercial applications. The most significant issue among them is the occurrence of the ‘shuttle effect’. During the discharge process, lithium polysulfides (LiPs) formed on the cathode can dissolve into the electrolyte, diffuse through the separator, and accumulate on the lithium anode.

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This phenomenon leads to a decrease in the Coulombic efficiency and capacity degradation of the batteries, thus hindering their cycle performance.<sup>6,7</sup> Moreover, the intrinsic insulation properties of sulfur ( $5 \times 10^{-30}$  S cm<sup>-1</sup>) and  $Li_2S$  ( $10^{-13}$  S cm<sup>-1</sup>) hinder the efficient transfer of electrons, resulting in sluggish electrochemical reactions.<sup>8</sup> Therefore, the rational design of catalysts exhibiting suitable adsorption capability for LiPs and superior catalytic performance for accelerating the reaction kinetics of sulfur redox in Li–S batteries has attracted increasing research attention in recent years.<sup>9–12</sup>

Among the efficient catalysts, carbonaceous materials supported single atom catalysts (SACs) have been widely explored due to their superior catalytic performance for sulfur redox and LiP stabilization.<sup>10,13–15</sup> Nevertheless, the performances of SACs for catalyzing sulfur redox, particularly the sulfur evolution reaction (SER), are still unsatisfactory. Therefore, to further enhance their catalytic performance toward the sulfur conversion is of importance, which might be realized by tailoring the electronic and structural properties of the central metals of SACs. In this regard, significant research efforts have been devoted to the design of SACs with transition metal atoms possessing various coordination environments, which involve

graphene,<sup>13,14</sup> C<sub>2</sub>N<sup>10</sup> and g-C<sub>3</sub>N<sub>4</sub><sup>15</sup> as the supports. In addition to doping strategies, the introduction of heterointerfaces has also been proved to be an efficient strategy to enhance the catalytic performance of electrochemical catalysts for energy storage and conversion, which can be realized by assembling two-dimensional (2D) materials into van der Waals heterostructures.<sup>16</sup> These heterostructures are formed by chemical bonding or physical combination of two or more 2D materials. In recent years, this concept has also been adopted to design electrocatalysts for Li-S batteries, which will incorporate the merits of individual components to neutralize the shortcomings of each building block<sup>17-22</sup> of the heterointerfaces. Nevertheless, there have been no reports on exploring the heterointerface effect on the catalytic performance of SACs for sulfur chemistry.

Up to now, various materials have been investigated for use as electrodes including 2D carbonaceous materials,<sup>23,24</sup> metal sulfides,<sup>25,26</sup> metal oxides<sup>27,28</sup> and Mxenes.<sup>29,30</sup> This implies that the combination of SACs with such materials will give rise to a huge number of heterostructures given the various metal centers of SACs. In this regard, to explore the catalytic performance particularly the SER performance of such heterostructures will be very time consuming, which accordingly requires an efficient descriptor guiding the systematic investigation. In our previous work, we have systematically investigated the descriptors of the Li<sub>2</sub>S decomposition energy barrier on MN<sub>4</sub>@G (typical configuration of SACs containing pyridine-N coordinated transition-metal atoms) and found that some properties could serve as universal descriptors for the rational design of SACs giving rise to a low Li<sub>2</sub>S decomposition barrier, which could predict the activity of the catalyst quickly.<sup>14</sup>

Here, we investigated systematically the performance of heterostructures for sulfur chemistry, which are built by combining SACs with 5 typical 2D materials. For SACs, we utilized three MN<sub>4</sub>@G (M = V, Mo and W) with the highest catalytic activity for Li<sub>2</sub>S decomposition screened in our previous work.<sup>14</sup> The other 5 types of 2D materials are TiS<sub>2</sub>,<sup>31</sup> C<sub>3</sub>N<sub>4</sub>,<sup>32</sup> BN,<sup>33</sup> graphene (G)<sup>34</sup> and reduced graphene oxide (rGO).<sup>35</sup> After examining the extendibility, we selected  $\Delta E$  (energy difference before and after the Li<sub>2</sub>S decomposition) as the efficient descriptor for screening several heterostructures with enhanced catalytic performance for Li<sub>2</sub>S decomposition, which were then further explored for their performance for catalyzing SRR and stabilizing LiPs. Our work will pave a new way for designing electrocatalysts for sulfur chemistry in alkaline metal sulfide batteries.

## 2. Computational details

The DFT simulations were carried out by using the Vienna Ab initio Simulation Package (VASP).<sup>36,37</sup> Additionally, the Perdew-Burke-Ernzerhof functional<sup>38,39</sup> within the generalized gradient approximation (GGA-PBE)<sup>40</sup> was employed to calculate the exchange-correlation energy and the projector augmented wave (PAW) method was used to describe the electron-ion

interactions.<sup>41,42</sup> We employed the DFT-D2 scheme to take the van der Waals interactions into account.<sup>43</sup> To avoid the interaction between two neighboring surfaces, we set the vacuum space to be larger than 20 Å. In all of the calculations, the plane-wave cutoff energy was set to be 520 eV. All the calculations were carried out with the force and energy thresholds of 0.02 eV Å<sup>-1</sup> and 10<sup>-4</sup> eV, respectively. Self-consistent field (SCF) calculations were performed to obtain the energy of the optimized structure while non-self-consistent field (NSCF) calculations were used to gain the electronic density of states (DOS). Three different *k*-point meshes of 2 × 2 × 1, 3 × 3 × 1 and 7 × 7 × 1 were employed in the structural optimizations, and SCF and NSCF calculations. For the Li<sub>2</sub>S decomposition, the minimum energy path (MEP) profiles are obtained by using the climbing image nudged elastic band (CI-NEB) method.<sup>44,45</sup> The formulas for calculating binding energy of heterostructure materials, lattice mismatch of the heterostructure materials, adsorption energy, zero vibration energy, charge density difference and Gibbs free energy changes are labeled as eqn (1)–(10).

The binding energy of heterostructures were calculated according to

$$E_{\text{bin}} = \frac{E_{\text{total}} - E_{\text{ML1}} - E_{\text{ML2}}}{S} \quad (1)$$

where  $E_{\text{total}}$  represent the energies for heterostructures,  $E_{\text{ML1}}$  and  $E_{\text{ML2}}$  stand for the energy of two individual monolayers constituting the heterostructures, respectively,  $S$  is the cross-sectional area at the interface of two monolayers in the simulation box of the heterostructures. Additionally, the lattice mismatch of the heterostructures is calculated by

$$|a - a_h|/a_h \times 100\% \quad (2)$$

where  $a$  and  $a_h$  represent the lattice parameter of the supercell of one component and the double layer heterostructure material, respectively.

The adsorption energy ( $E_{\text{ads}}$ ) is calculated based on the following formula:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{substrate}} - E_{\text{adsorbate}} \quad (3)$$

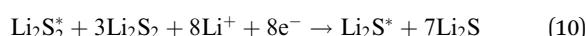
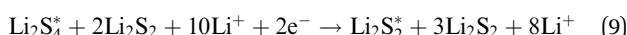
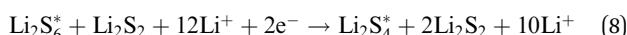
where  $E_{\text{total}}$  is the energy of adsorbed system, while  $E_{\text{substrate}}$  and  $E_{\text{adsorbate}}$  represent the energy of substrate and isolated adsorbate, respectively.

The Gibbs free energy of LiPs and S<sub>8</sub> on substrates are calculated by

$$G = E_{\text{DFT}} + E_{\text{zpe}} - TS \quad (4)$$

where  $E_{\text{DFT}}$  denotes the energy calculated by DFT simulations and  $E_{\text{zpe}}$  is the zero-point energy which is determined as  $ZPE = \frac{1}{2} \sum_i h\nu_i$ ; here  $h$  and  $\nu_i$  are the Planck constant and vibrational frequencies, respectively.  $S$  is the entropy, the entropies of molecules we utilized were acquired from experimental values in the NIST database,<sup>46</sup> while those of the absorbed intermediates were set to zero;  $T$  is the room temperature and is set at 298.15 K.

The elementary reaction steps for sulfur reduction in lithium-sulfur (Li-S) batteries are considered as



The reduction reaction process from  $Li_2S_8$  to  $Li_2S$  is quite complex, which is accompanied with the formation of the by-product  $Li_2S_2$ .<sup>47</sup> The energy of a single Li ion and an electron ( $Li^+ + e^-$ ) pair was treated as the energy of a single crystalline Li atom. The adsorbents with an asterisk “\*” refer to the state of being adsorbed, while the isolated state does not have that mark.

The linear correlations between  $E_b$  and three descriptors  $\Delta E$ ,  $\Delta E(Li)$  and ICOHP were identified in our previous work.<sup>14</sup>

$$E_b = 1.07 \times \Delta E + 0.16 \quad (11)$$

$$E_b = 0.87 \times \Delta E(Li) + 0.38 \quad (12)$$

$$E_b = -1.30 \times ICOHP - 3.49 \quad (13)$$

The difference between  $\Delta E$  and  $\Delta E(Li)$  is shown below,

$$\Delta E = E(Li) - E(Li)$$

where  $E(Li)$  and  $E(Li)$  represent the energies of final and initial states of the  $Li_2S$  decomposition. The asterisk (\*) means the adsorbed state of the adsorbents.

$$\Delta E(Li) = E(Li) - E(Li) - E(Li) \quad (15)$$

where  $E(Li)$ ,  $E(Li)$ ,  $E(Li)$  refer to the total energy of the adsorbed  $LiS$  cluster, energy of single Li atom in the bcc bulk phase and total energy of adsorbed  $Li_2S$ , respectively.

### 3. Results and discussion

#### 3.1 Structure and electronic properties of heterostructures

As shown in Fig. 1, five types of monolayers, which are  $TiS_2$ ,  $g-C_3N_4$ , BN, graphene, and rGO, are selected and combined with  $MN_4@G$  to build heterostructures. Due to the different lattice parameters of those monolayers, various supercells are set up for  $TiS_2$ ,  $g-C_3N_4$ , BN, graphene and rGO to guarantee a small lattice mismatch in the heterostructure. The primitive cell parameters, corresponding supercells, lattice mismatches and the total number of atoms contained in the simulation box of the heterostructures are listed in Table S1 (ESI†). Regarding the model of rGO and  $MN_4@G$ , they are built using a  $6 \times 6 \times 1$  supercell of graphene. rGO is then achieved by introducing two kinds of oxygen-containing defects in the graphene lattice. One type refers to the vacancy defects with hydroxyl saturating the dangling bonds of carbon atoms and the other type includes the epoxide functional groups adsorbed on the carbon atoms while the  $MN_4@G$  are modeled by locating the TM atoms in the N doped graphene with the central metal atoms coordinated with four N atoms, which are accordingly labeled as  $MN_4@G$ . The largest lattice mismatch is 2.354% between  $TiS_2$  and  $MN_4@G$ , and the others are lower than 2% when  $MN_4@G$

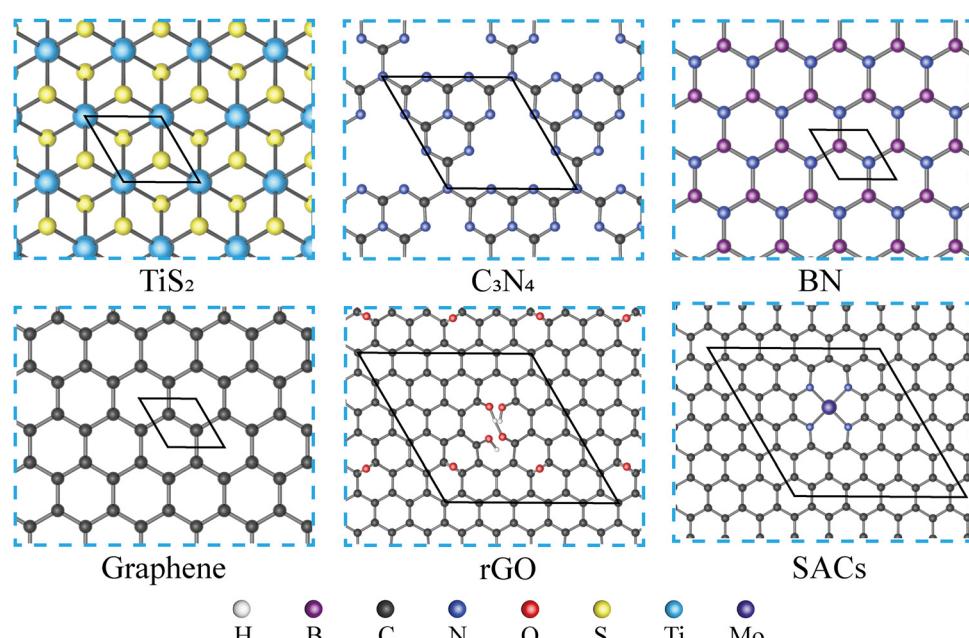


Fig. 1 Top view of  $TiS_2$ ,  $C_3N_4$ , BN, graphene, rGO and SACs. The hexagonal line frames depict the primitive cells of various materials, while the elements represented by spheres of different colors are listed at the bottom of the figure. For SACs,  $MN_4@G$  is selected as an example.

forms heterostructures with  $\text{g-C}_3\text{N}_4$ (1.777%), BN(1.749%), graphene(0.000%) and rGO(1.211%). In order to distinguish those various heterostructures, we named them  $\text{MN}_4@\text{G/ML}$  ( $\text{ML} = \text{TiS}_2, \text{C}_3\text{N}_4, \text{BN}, \text{G}, \text{rGO}$ ), as shown in Fig. S1 (ESI<sup>†</sup>). Moreover,  $\text{MN}_4@\text{G/ML}$  ( $\text{ML} = \text{TiS}_2, \text{C}_3\text{N}_4, \text{G}$  and rGO) and G/BN prefer AB stacking, while the configuration of  $\text{MN}_4@\text{G/BN}$  possesses a mixture of AB- and AA-stacking.

The interaction strength between the components of the heterostructures can be evaluated by the binding energy ( $E_{\text{bin}}$ ), which is calculated by eqn (1) in the ESI<sup>†</sup>. As listed in Table S2 (ESI<sup>†</sup>), the  $E_{\text{bin}}$  values for different heterostructures are between  $-13$  and  $-21$  meV  $\text{\AA}^{-2}$  and close to that for van der Waals interaction,<sup>48</sup> which can also be confirmed by the interlayer distance of  $3.20$ – $3.96$   $\text{\AA}$ . Among them, the largest and smallest  $E_{\text{bin}}$  are  $-26.39$  meV  $\text{\AA}^{-2}$  ( $\text{WN}_4@\text{G/BN}$ ) and  $-7.49$  meV  $\text{\AA}^{-2}$  ( $\text{MoN}_4@\text{G/C}_3\text{N}_4$ ), respectively. Moreover,  $\text{MN}_4@\text{G}$  can bind more strongly with BN than with other monolayers, while the binding strength of  $\text{MN}_4@\text{G}$  with  $\text{TiS}_2$  and  $\text{C}_3\text{N}_4$  are relatively weak. Among  $\text{MN}_4@\text{G/TiS}_2$  or  $\text{MN}_4@\text{G/BN}$ , the interaction strength of monolayers as  $\text{M} = \text{V}$  is stronger than that when  $\text{M} = \text{Mo}$  and  $\text{W}$ , due to the fact that  $\text{V}$  atom tends to sit between the two monolayers by forming chemical bond with two components of the heterostructures, as shown in Fig. S1 (ESI<sup>†</sup>). Note that heterostructures of  $\text{MN}_4@\text{G/rGO}$  have significantly larger interlayer distances than the others due to the presence of functional groups on the surface of rGO.

The formation of heterostructures also induces the charge redistribution in the components, *i.e.*  $\text{MN}_4@\text{G}$  loses charges to the adjacent layers leading to the metal centers more positively charged compared to that in the monolayer of  $\text{MN}_4@\text{G}$ . The diagram of charge density difference of various heterostructures are illustrated in Fig. S1 (ESI<sup>†</sup>). In general, the charge transfer occurs mainly around the  $\text{MN}_4$  moiety and the specific values of charge transfer are listed in Table S2 (ESI<sup>†</sup>). However, for  $\text{MN}_4@\text{G/TiS}_2$ , there is a uniform charge redistribution throughout the interface. In general, the charge transfer between the monolayers in  $\text{MN}_4@\text{G/TiS}_2$  and  $\text{MN}_4@\text{G/C}_3\text{N}_4$  is more pronounced than that in  $\text{MN}_4@\text{G/BN}$  and  $\text{MN}_4@\text{G/G}$  as illustrated in Table S2 (ESI<sup>†</sup>). Moreover, for  $\text{MN}_4@\text{G/TiS}_2$  and  $\text{MN}_4@\text{G/C}_3\text{N}_4$ ,  $\text{M} = \text{V}$  gives rise to more charge transfer than  $\text{M} = \text{Mo}$  and  $\text{W}$ . Taking  $\text{MN}_4@\text{G/TiS}_2$  as an example, the charge transfer in  $\text{MN}_4@\text{G/TiS}_2$  is  $1.48$  e per cell, which is more than those in  $\text{MoN}_4@\text{G/TiS}_2$  ( $1.11$  e per cell) and  $\text{WN}_4@\text{G/TiS}_2$  ( $1.11$  e per cell). Although the total amount of charge transfer for  $\text{MN}_4@\text{G/BN}$  is less than that for  $\text{MN}_4@\text{G/TiS}_2$ , the interaction between the monolayers is still stronger in  $\text{MN}_4@\text{G/BN}$  than that in  $\text{MN}_4@\text{G/TiS}_2$ . This is attributed to the fact that the charge redistribution only occurs around the  $\text{MN}_4$  in the former case while there is wider range of charge redistribution for the rest case.

### 3.2 Catalytic performance of $\text{MN}_4@\text{G/ML}$ for SER

We next explored the catalytic performance of the heterostructures for SER. In the charging cycles of Li–S batteries, the decomposition of  $\text{Li}_2\text{S}$  is a crucial step for SER requiring efficient electrocatalysts to accelerate the reaction kinetics. This

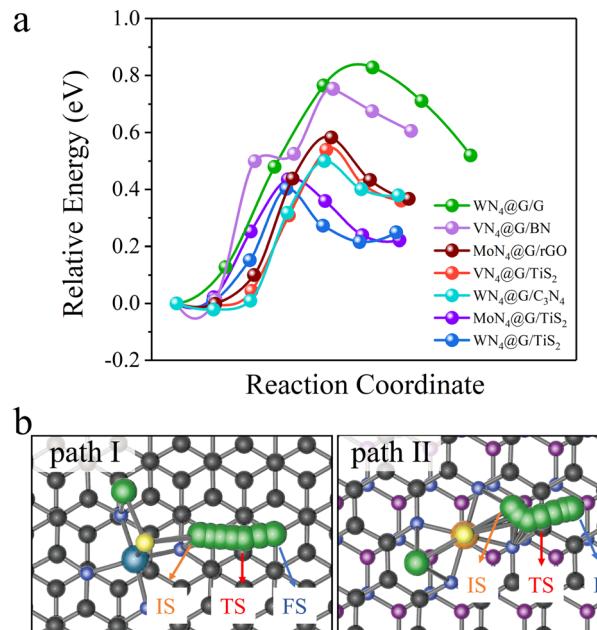
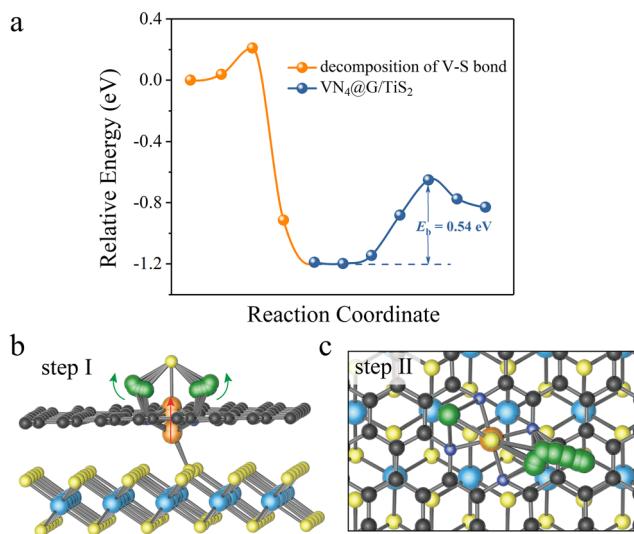


Fig. 2 (a) The energy profiles of  $\text{Li}_2\text{S}$  decomposition on selected heterostructures. (b) Two different energetically preferable  $\text{Li}_2\text{S}$  decomposition pathways. IS, TS, FS represent the initial, transitional, and final states of  $\text{Li}_2\text{S}$  decomposition on the heterointerfaces, respectively.

is usually evaluated by the energy barrier ( $E_b$ ) of  $\text{Li}_2\text{S}$  decomposition, which can be achieved based on the nudged elastic band (NEB) method.<sup>14</sup>

We selected some heterostructures as representatives and explored the decomposition of  $\text{Li}_2\text{S}$  on them. The energy profiles of  $\text{Li}_2\text{S}$  decomposition on  $\text{WN}_4@\text{G/G}$ ,  $\text{VN}_4@\text{G/BN}$ ,  $\text{MoN}_4@\text{G/rGO}$ ,  $\text{WN}_4@\text{G/C}_3\text{N}_4$ ,  $\text{MoN}_4@\text{G/TiS}_2$  and  $\text{WN}_4@\text{G/TiS}_2$  with the energetically preferable decomposition pathways are illustrated in Fig. 2. It can be seen from Fig. 2a that the  $E_b$  of  $\text{Li}_2\text{S}$  decompositions on all heterostructures are lower than  $1.0$  eV. The lowest and the highest  $E_b$  are observed on  $\text{WN}_4@\text{G/TiS}_2$  ( $0.41$  eV) and  $\text{WN}_4@\text{G/G}$  ( $0.83$  eV), respectively. The catalytic performances of the heterostructures for the  $\text{Li}_2\text{S}$  decomposition follow the order  $\text{WN}_4@\text{G/TiS}_2 > \text{MoN}_4@\text{G/TiS}_2 > \text{WN}_4@\text{G/C}_3\text{N}_4 > \text{VN}_4@\text{G/TiS}_2 > \text{MoN}_4@\text{G/rGO} > \text{VN}_4@\text{G/BN} > \text{WN}_4@\text{G/G}$ , and the corresponding  $E_b$  values are  $0.41, 0.44, 0.50, 0.54, 0.58, 0.75$  and  $0.83$  eV respectively. It should be noted that those heterostructures possess more enhanced capability for catalyzing SER than individual  $\text{MN}_4@\text{G}$ , such as  $\text{VN}_4@\text{G}$  ( $E_b = 0.70$  eV),  $\text{MoN}_4@\text{G}$  ( $E_b = 0.58$  eV),  $\text{WN}_4@\text{G}$  ( $E_b = 0.55$  eV) and  $\text{CoN}_4@\text{G}$  ( $E_b = 1.37$  eV).<sup>13,14</sup> Overall, the catalytic performance of  $\text{MN}_4@\text{G}$  for the SER will be significantly improved when forming the heterostructures with  $\text{C}_3\text{N}_4$ ,  $\text{TiS}_2$  and rGO. Moreover, due to the different adsorption configurations of  $\text{Li}_2\text{S}$ , two different  $\text{Li}_2\text{S}$  decomposition pathways are identified as shown in Fig. 2b. And the cleavage of the Li–S bond on  $\text{WN}_4@\text{G/G}$  is along the path I, while for the rest cases it follows the relatively short path II.

It should be noted that the decomposition of  $\text{Li}_2\text{S}$  on  $\text{VN}_4@\text{G/TiS}_2$  is a bit complex as reflected by the energy profiles of  $\text{Li}_2\text{S}$  decomposition (see Fig. 3a). This is due to the specific



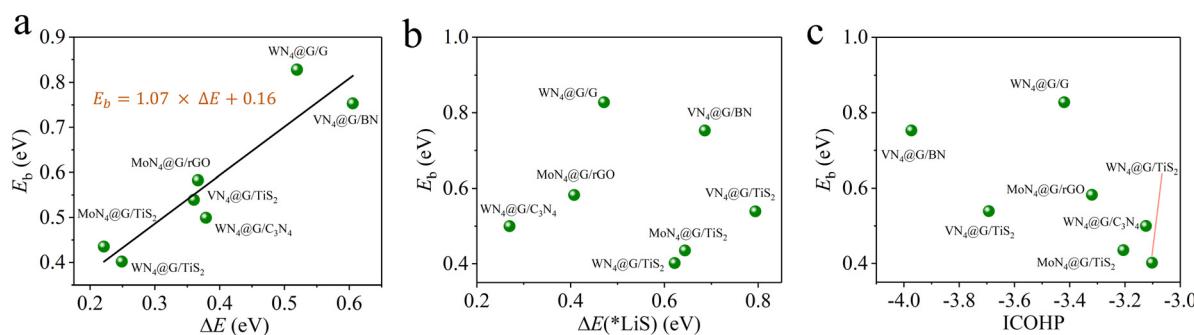
**Fig. 3** (a) The energy profiles of  $\text{Li}_2\text{S}$  decomposition on  $\text{VN}_4@\text{G/TiS}_2$ . (b) The structural evolution before the  $\text{Li}_2\text{S}$  decomposition on  $\text{VN}_4@\text{G/TiS}_2$ . (c) The decomposition process of  $\text{Li}_2\text{S}$  on  $\text{VN}_4@\text{G/TiS}_2$ . The migration of  $\text{V}$  atom follows the direction of the red arrow while the change of angle of  $\text{Li}-\text{S}-\text{Li}$  is marked with green arrows.

structural configuration of  $\text{VN}_4@\text{G/TiS}_2$ , for which the V atom sits between the graphene layer and  $\text{TiS}_2$  (see Fig. 3b). This further leads to the weak interaction between  $\text{Li}_2\text{S}$  and the V atom upon the adsorption of  $\text{Li}_2\text{S}$  on  $\text{VN}_4@\text{G/TiS}_2$  since the S atom of  $\text{Li}_2\text{S}$  cannot form a chemical bond with the V atom with only the Li atoms binding to N/C atoms from the N doped graphene. Overall, the whole process of  $\text{Li}_2\text{S}$  decomposition on  $\text{VN}_4@\text{G/TiS}_2$  can be divided into two subprocesses. Firstly, before the breakage of Li-S bonds in adsorbed  $\text{Li}_2\text{S}$ , the V atom moves back to the center of the N edged hole and binds to the S atom of adsorbed  $\text{Li}_2\text{S}$ , leaving the V-S (S from  $\text{TiS}_2$ ) bond broken (see Fig. 3b). This process just requires overcoming a very small energy barrier of 0.21 eV as shown in Fig. 3a. Meanwhile, the angle of Li-S-Li bond gradually increases from  $85.01^\circ$  to  $139.29^\circ$  and the bond length of Li-S also expands from 2.25 Å to 2.39 Å. It is then followed by the second subprocess of  $\text{Li}_2\text{S}$  decomposition accompanied by the Li-S bond breakage as shown in Fig. 3c (consistent with the

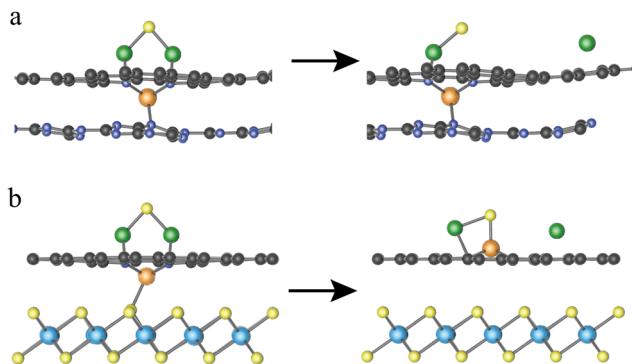
decomposition pathway II in Fig. 2b), which necessitates surmounting an energy barrier of 0.54 eV.

It is time-consuming to calculate directly the  $E_b$  values for 15 heterostructures using the CI-NEB method. In our previous works, we have identified three descriptors  $\Delta E$ ,  $\Delta E(^*{\text{LiS}})$  and ICOHP correlating well with  $E_b$  for  $\text{MN}_4@G$ , where  $\Delta E$  refers to the energy difference between the initial and final states of the  $\text{Li}_2\text{S}$  decomposition,  $\Delta E(^*{\text{LiS}})$  stands for the reaction energy of the  $\text{Li}_2\text{S}$  decomposition and ICOHP means the integral value of the crystal orbital Hamilton population for evaluating the binding strength of Li-S in adsorbed  $\text{Li}_2\text{S}$ .<sup>14</sup> And the corresponding functions describing the linear correlations between  $E_b$  and  $\Delta E$ ,  $\Delta E(^*{\text{LiS}})$ , ICOHP are shown in the computational details. Among them,  $\Delta E$  performs the best in predicting  $E_b$  values. Based on the available data from the current study, we next explored the predictive capability of  $\Delta E$ ,  $\Delta E(^*{\text{LiS}})$ , ICOHP for determining  $E_b$  and then to screen high performance  $\text{MN}_4@G/\text{ML}$  for  $\text{Li}_2\text{S}$  decomposition. As shown in Fig. 4a, all the data points of  $E_b$  fall near the line, implying the robustness of the functional of  $E_b = 1.07 \times \Delta E + 0.16$  proposed in our previous work.<sup>14</sup> The minimum percentage error of  $E_b$  between the  $\Delta E-E_b$  prediction and the CI-NEB calculation occurs in  $\text{VN}_4@G/\text{TiS}_2$ , which is only 2.22%. The largest percentage error is observed in  $\text{WN}_4@G/\text{C}_3\text{N}_4$ , reaching 14%, but the specific difference is only 0.07 eV. The percentage errors of the predicted values with respect to those obtained from CI-NEB calculations for the remaining structures are all below 10%. In contrast, the  $\Delta E(^*{\text{LiS}})-E_b$  and ICOHP- $E_b$  relationships from the current study do not follow the trend described by those linear functions obtained from previous works (see Fig. 4b and c). The corresponding data of predicted  $E_b$  values based on  $\Delta E$ ,  $\Delta E(^*{\text{LiS}})$  and ICOHP are listed in Table S3 (ESI<sup>†</sup>). Overall, these results show that  $\Delta E$  can serve as the best descriptor and provide efficient theoretical guidance for fast screening of active  $\text{MN}_4@G/\text{ML}$  toward  $\text{Li}_2\text{S}$  decomposition based on the equation of  $E_b = 1.07 \times \Delta E + 0.16$ .

As listed Table S3 (ESI†), the  $E_b$  values are predicted based on the linear function  $E_b = 1.07 \times \Delta E + 0.16$  for 15 hetero-structures which are built by combining 3  $MN_4@G$  with 5 monolayers. Among them,  $MoN_4@G/TiS_2$  and  $WN_4@G/TiS_2$  give rise to significantly low  $E_b$  values of 0.40 and 0.43 eV,



**Fig. 4** Calculated values of  $E_b$  using the CI-NEB method (green balls) for representative heterostructures as a function of  $\Delta E$  (a),  $\Delta E(\text{*LiS})$  (b) and ICOHP (c). In (a), the linear relationship (black lines), obtained in our previous works for graphene supported SACs was included for comparison.<sup>14</sup>



**Fig. 5** Initial and final structures of  $\text{Li}_2\text{S}$  decomposition on  $\text{VN}_4\text{G}/\text{C}_3\text{N}_4$  (a) and  $\text{VN}_4\text{G}/\text{TiS}_2$  (b). The orange, yellow, green spheres represent the V, S and Li atoms.

which are accordingly highly efficient for catalyzing the SER. In contrast, the worst SER performance is found for  $\text{VN}_4\text{G}/\text{C}_3\text{N}_4$  with  $E_b = 2.24$  eV since the V center does not participate in activating the Li-S bond. As shown in Fig. 5a, in  $\text{VN}_4\text{G}/\text{C}_3\text{N}_4$  the V atom tends to sit between the graphene and  $\text{C}_3\text{N}_4$  monolayers leading to the absence of S-V bonds upon the  $\text{Li}_2\text{S}$  deposition indicating that there is no direct interaction between  $\text{Li}_2\text{S}$  and the V center. Moreover, this holds for the whole process of  $\text{Li}_2\text{S}$  decomposition. Therefore, the catalytic performance of  $\text{VN}_4\text{G}/\text{C}_3\text{N}_4$  for  $\text{Li}_2\text{S}$  decomposition is rather worse compared to the rest of the heterostructures. It should be noted that, in the  $\text{VN}_4\text{G}/\text{TiS}_2$  the V atom remains between graphene and  $\text{TiS}_2$  monolayers after the  $\text{Li}_2\text{S}$  adsorption. However, during the  $\text{Li}_2\text{S}$  decomposition the V atom can move back the N-edged hole and form a chemical bond with S from  $\text{Li}_2\text{S}$  by overcoming a low energy barrier of 0.21 eV (see Fig. 2a). This S-V bond even remains when the Li-S bond is eventually broken as shown in Fig. 5b. Therefore,  $\text{VN}_4\text{G}/\text{TiS}_2$  still shows efficient SER performance by giving rise to a low  $E_b$  of 0.54 eV.

We next analyzed the heterointerface effect on the catalytic performance of  $\text{MN}_4\text{G}$  for SER. To this end, three SCAs of  $\text{WN}_4\text{G}$ ,  $\text{MoN}_4\text{G}$ , and  $\text{VN}_4\text{G}$ , screened by our previous work<sup>14</sup> were considered to explore the changes of  $E_b$  before and after forming the heterointerfaces. Table 1 shows a comparison of  $E_b$  values between  $\text{MN}_4\text{G}$  and  $\text{MN}_4\text{G}/\text{ML}$  ( $\text{M} = \text{V}$ ,  $\text{Mo}$  and  $\text{W}$ ;  $\text{ML} = \text{TiS}_2$ ,  $\text{C}_3\text{N}_4$ ,  $\text{BN}$ ,  $\text{G}$  and  $\text{rGO}$ ). The energy barriers of  $\text{Li}_2\text{S}$  decomposition over  $\text{MN}_4\text{G}$  are decreased when forming the heterostructures with  $\text{TiS}_2$ ,  $\text{C}_3\text{N}_4$  and  $\text{rGO}$ . Among them,  $\text{TiS}_2$  provides the best effect on surface regulation leading to enhanced SER performance of  $\text{MN}_4\text{G}$  by giving rise to  $E_b$  of 0.41, 0.44 and 0.54 for  $\text{WN}_4\text{G}/\text{ML}$ ,  $\text{MoN}_4\text{G}/\text{TiS}_2$  and  $\text{VN}_4\text{G}/\text{TiS}_2$ , respectively, while the effect of  $\text{C}_3\text{N}_4$  and  $\text{rGO}$  on enhancing the catalytic activity for SER was significantly weak. In contrast,  $\text{BN}$  and  $\text{G}$  actually increased the  $E_b$  on  $\text{VN}_4\text{G}$  and  $\text{WN}_4\text{G}$ , respectively, indicating decreased SER performances. Note that the  $\text{VN}_4\text{G}/\text{C}_3\text{N}_4$  gives rise to the  $E_b$  value of 2.24 eV significantly larger than that of 0.70 eV given by  $\text{VN}_4\text{G}$ . This is due to the fact that the V atom does not participate in catalyzing the  $\text{Li}_2\text{S}$  decomposition. As shown in Fig. 5a, during the whole process of  $\text{Li}_2\text{S}$  decomposition, no chemical bond is formed

**Table 1** Comparison of  $E_b$  (eV) between heterostructures and their corresponding  $\text{MN}_4\text{G}$

	Heterostructures	$\text{MN}_4\text{G}$
$\text{WN}_4\text{G}/\text{TiS}_2$	0.41 <sup>a</sup>	0.55
$\text{MoN}_4\text{G}/\text{TiS}_2$	0.44 <sup>a</sup>	0.58
$\text{VN}_4\text{G}/\text{TiS}_2$	0.54 <sup>a</sup>	0.70
$\text{WN}_4\text{G}/\text{C}_3\text{N}_4$	0.50 <sup>a</sup>	0.55
$\text{MoN}_4\text{G}/\text{C}_3\text{N}_4$	0.57 <sup>b</sup>	0.58
$\text{VN}_4\text{G}/\text{C}_3\text{N}_4$	2.24 <sup>b</sup>	0.70
$\text{WN}_4\text{G}/\text{BN}$	0.62 <sup>b</sup>	0.55
$\text{MoN}_4\text{G}/\text{BN}$	0.63 <sup>b</sup>	0.58
$\text{VN}_4\text{G}/\text{BN}$	0.75 <sup>a</sup>	0.70
$\text{WN}_4\text{G}/\text{rGO}$	0.54 <sup>b</sup>	0.55
$\text{MoN}_4\text{G}/\text{rGO}$	0.58 <sup>a</sup>	0.58
$\text{VN}_4\text{G}/\text{rGO}$	0.79 <sup>b</sup>	0.70
$\text{MoN}_4\text{G}/\text{G}$	0.74 <sup>b</sup>	0.55
$\text{WN}_4\text{G}/\text{G}$	0.83 <sup>a</sup>	0.58
$\text{VN}_4\text{G}/\text{G}$	0.79 <sup>b</sup>	0.70

<sup>a</sup>  $E_b$  values obtained based on the NEB method. <sup>b</sup>  $E_b$  values predicted by the  $E_b$ - $\Delta E$  relationship.

between the  $\text{Li}_2\text{S}$  cluster and the atomically dispersed V atom sitting between  $\text{VN}_4\text{G}$  and  $\text{C}_3\text{N}_4$ .

### 3.3 Heterointerface effect on the performance of $\text{MN}_4\text{G}$ for catalyzing SRR and stabilizing LiPs

Since the catalytic performance of SCAs for catalyzing  $\text{Li}_2\text{S}$  decomposition will be significantly enhanced when being combined with  $\text{TiS}_2$ , we next chose the heterostructures of  $\text{MN}_4\text{G}/\text{TiS}_2$  to further investigate their binding strengths to LiPs and  $\text{S}_8$  as well as their SRR performance, which are also crucial for suppressing the shuttle effect as well. In this regard, both sides of the heterostructures were explored. To indicate the specific surface where the adsorbates locate, it is necessary to redefine the nomenclature for the heterostructures. The bilayer consisting of monolayers of ML1 and ML2 can be named ML1/ML2 or ML2/ML1, representing the adsorbate being adsorbed on the side of the ML1 or ML2. For example,  $\text{MoN}_4\text{G}/\text{TiS}_2$  means that  $\text{MoN}_4$  provides the active sites for adsorbing the LiPs and  $\text{S}_8$  while it means the opposite when it is represented by  $\text{TiS}_2/\text{MoN}_4\text{G}$ .

As shown in Fig. 6a and Table S4 (ESI†), the adsorption energies of LiPs on  $\text{MN}_4\text{G}/\text{TiS}_2$  ( $\text{M} = \text{Mo}$  and  $\text{W}$ ) are both below  $-3.00$  eV, which are lower than those on the organic electrolyte molecules such as 1,3-dioxynaphthalenes (DOL) and 1,2-dimethoxy ethane (DME) within the range of  $-1.00$  to  $-0.80$  eV.<sup>49</sup> This implies the advantages of such heterointerfaces in suppressing the shuttle effect because the host material exhibits stronger adsorption performance than the organic electrolyte molecules. Moreover,  $\text{WN}_4\text{G}/\text{TiS}_2$  possesses more enhanced capability in trapping LiPs than  $\text{MoN}_4\text{G}/\text{TiS}_2$ . In detail, the adsorption energies of LiPs ( $\text{Li}_2\text{S}_x$ ,  $x = 1, 2, 4, 6, 8$ ) and  $\text{S}_8$  on the  $\text{WN}_4\text{G}/\text{TiS}_2$  interface are  $-5.21$ ,  $-5.15$ ,  $-4.17$ ,  $-4.17$ ,  $-4.33$  and  $-2.52$  eV, respectively. They are lower than the corresponding values on  $\text{MoN}_4\text{G}/\text{TiS}_2$ , which are  $-4.67$ ,  $-3.72$ ,  $-3.71$ ,  $-3.35$ ,  $-3.28$  and  $-2.11$  eV, respectively. Note that the adsorption energies on individual  $\text{TiS}_2$  and  $\text{MN}_4\text{G}$  are higher than those on the heterostructures as shown in

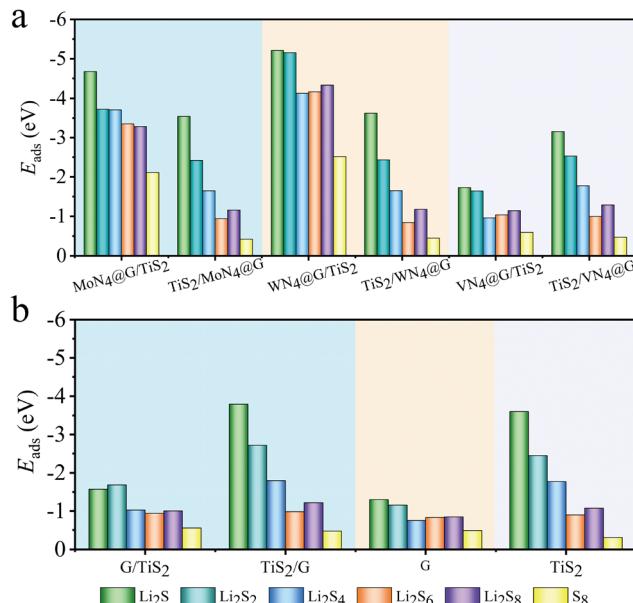


Fig. 6 The bar chart of adsorption energies of LiPs and  $S_8$  on  $MN_4@G/TiS_2$  (a),  $G/TiS_2$ , graphene (G) and  $TiS_2$  (b). ML1/ML2 indicates the adsorption site is on ML1.

Table S4. Therefore, the capabilities of  $MoN_4@G$  and  $WN_4@G$  in stabilizing LiPs are generally enhanced when combined with  $TiS_2$ . In contrast, the adsorption strength of  $VN_4@G/TiS_2$  to LiPs and  $S_8$  are weaker than that for  $MN_4@G/TiS_2$  ( $M = Mo$  and  $W$ ). The lowest adsorption energy observed on  $VN_4@G/TiS_2$  is merely  $-1.73$  eV for  $Li_2S$  adsorption, which means that the adsorption strength of  $VN_4@G$  to LiPs is significantly weakened upon forming a heterointerface with  $TiS_2$ . This can be attributed to the formation of V-S bonds in the interlamination of  $VN_4@G/TiS_2$ . When the reaction intermediates are adsorbed on  $VN_4@G/TiS_2$ , the lack of V atoms on the surface of  $VN_4@G/TiS_2$  leads to the absence of chemical bond between V atoms and LiPs/ $S_8$ , indicating a relatively weak interaction strength between the heterostructure and LiPs/ $S_8$ .

We also considered the binding strength of  $TiS_2$  of three heterostructures to the adsorbates and found that the adsorption energies of various clusters on  $TiS_2/MN_4@G$  ( $M = V, Mo$  and  $W$ ) are very similar. Furthermore, the values are comparable to the adsorption on pure  $TiS_2$ , suggesting that  $MN_4@G$  has a tiny impact on the adsorption performance of  $TiS_2$  in heterostructures.

The application of  $MN_4@G$  is often constrained by the low loading density of metal atoms and heterogeneous distribution of doping sites. In the region without dopants, the local structure of  $MN_4@G$  retains the carbon lattice of pure graphene. Therefore, we set up a model of  $G/TiS_2$  in order to further examine the regulatory role of  $TiS_2$  on the performance of such carbon atoms far away from the metal centers. As shown in Fig. 6b and Table S4,  $G/TiS_2$  possesses enhanced trapping capabilities for LiPs with respect to G. Moreover, the adsorption energies of  $Li_2S_4$ ,  $Li_2S_6$  and  $Li_2S_8$  on  $G/TiS_2$  are  $-1.03$ ,  $-0.94$  and  $-1.01$  eV, respectively, which are lower than

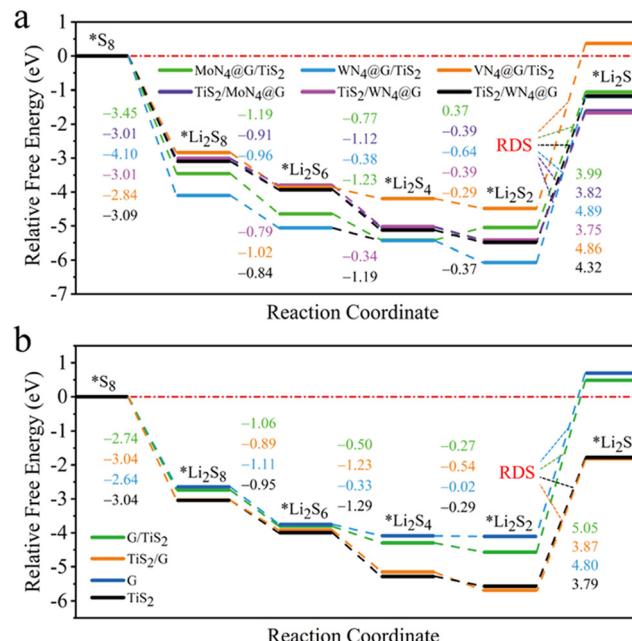


Fig. 7 Gibbs free energy profiles for SRR on  $MN_4@G/TiS_2$  (a),  $G/TiS_2$ , graphene (G) and  $TiS_2$  (b). Regarding heterostructures (ML1/ML2), ML1 represents the surface for adsorbing the adsorbates. The numbers with different colors are the Gibbs energy differences between the two adjacent states during SRR.

those for organic electrolyte ( $-1.00$  to  $-0.80$  eV). Therefore, combining with  $TiS_2$  can enhance the adsorption performance of the entire region of  $MN_4@G$  monolayers for LiPs, which will help overcome the disadvantages of low loading of atomically dispersed atoms in  $MN_4@G$ .

We have also investigated the SRR performance of those heterostructures by calculating the Gibbs free energy changes ( $\Delta G$ ) profile as depicted in Fig. 7. For  $MoN_4@G/TiS_2$  and  $WN_4@G/TiS_2$  (see Fig. 7a), the  $\Delta G$  values of overall SRR are  $-1.06$  and  $-1.19$  eV, respectively, which are lower than those of  $-0.41$  and  $-0.33$  eV for  $MoN_4@G$  and  $WN_4@G$ , respectively. Moreover, the  $\Delta G$  of rate-determining step ( $\Delta G_{RDS}$ ) for the transition from  $Li_2S_2$  to  $Li_2S$  are  $3.99$  and  $4.89$  eV, lower than the corresponding values of  $4.25$  and  $4.36$  eV for individual  $MoN_4@G$  and  $WN_4@G$ , respectively. These results imply the positive effect of heterointerface on enhancing the SRR performance of  $MN_4@G$  ( $M = Mo$  and  $W$ ). In contrast, the overall  $\Delta G$  of SRR on  $VN_4@G/TiS_2$  is  $0.37$  eV, which is larger than  $-0.82$  eV for  $VN_4@G$ . Such an increase of  $\Delta G$  can be attributed to the structural feature of  $VN_4@G/TiS_2$  with the V atom located between  $VN_4@G$  and  $TiS_2$  and formation of the V-S bond. It means that the single V atom in  $VN_4@G/TiS_2$  will not participate in forming chemical bonds with LiPs and  $S_8$  during the SRR process leading to decreased SRR performance compared to individual  $VN_4@G$ . When it turns to  $TiS_2/MN_4@G$  ( $M = Mo, W$  and  $V$ ), the overall  $\Delta G$  of SRR are  $-1.61$ ,  $-1.66$ , and  $-1.17$  eV, respectively, while the related  $\Delta G_{RDS}$  values are  $3.82$ ,  $3.75$  and  $4.32$  eV. These values are comparable to the corresponding values for individual  $TiS_2$ . This shows that the heterointerface

effect on the SRR performance of  $\text{TiS}_2$  is relatively weak. Regarding G and G/TiS<sub>2</sub>, they exhibit even worse performance for SRR, as reflected by the  $\Delta G$  values of 0.69 and 0.48 eV for the overall SRR, respectively (see Fig. 7b). This also implies that the SRR performance of carbon atoms far away from the metal centers in  $\text{MN}_4@\text{G/TiS}_2$  (M = Mo, W and V) is relatively worse, which is still better than that for pristine graphene. Nevertheless, based on the above analysis, we believe that both sides of  $\text{MN}_4@\text{G/TiS}_2$  possess promising performance for SRR. Overall,  $\text{MN}_4@\text{G/TiS}_2$  (M = Mo and W) show good performance in stabilizing LiPs and accelerating the kinetics of SER/SRR as confirmed by the low values of adsorption energies for LiPs/S<sub>8</sub>,  $\Delta G$  for overall SRR,  $\Delta G_{\text{RDS}}$  and  $E_b$  for  $\text{Li}_2\text{S}$  decomposition, which demonstrate that they are promising candidates electrocatalysts for sulfur chemistry in Li-S batteries.

## 4. Conclusions

Using DFT calculations, we explored the heterointerface effect on the catalytic performance SACs toward sulfur conversion in Li-S batteries. To this end, 15 heterostructures were constructed by combining  $\text{MN}_4@\text{G}$  (M = Mo, W and V) with 5 different 2D materials of  $\text{TiS}_2$ ,  $\text{C}_3\text{N}_4$ , BN, graphene and rGO. We then investigated their electronic properties, adsorption capabilities for LiPs/S<sub>8</sub> and catalytic activities for sulfur redox. Using previously proposed descriptors of  $\Delta E$ , we firstly screened three heterointerfaces  $\text{MN}_4@\text{G/TiS}_2$  (M = Mo, W and V) due to their low values of  $E_b$  of 0.54, 0.44, and 0.41 eV, respectively, indicating the enhanced SER performance of  $\text{MN}_4@\text{G}$  caused by the interface effect. This effect also induces the increased binding strength to LiPs/S<sub>8</sub> beneficial for suppressing the shuttle effect as reflected by the low adsorption energies. Moreover, our DFT calculations demonstrate that both sides of  $\text{MN}_4@\text{G/TiS}_2$  (M = Mo and W) possess enhanced SRR performance compared to the individual components of heterostructures. These can be confirmed by those competitive values of low values of adsorption energies for soluble LiPs ( $< \sim -3$  eV),  $\Delta G$  for the overall SRR ( $-1.66$  to  $0.37$ ) and  $\Delta G_{\text{RDS}}$  ( $3.82$  to  $4.89$ ). Interestingly, the interface effect even strengthens the binding strength of the carbon atoms far away from the metal centers and soluble LiPs, which will probably address the issue of low loading rate of atomically dispersed metal atoms. This study paves a new way of designing novel electrocatalyst for sulfur chemistry for Li-S batteries and even other alkali-ion-chalcogen batteries.

## Author contributions

H. Liang and Z. Zeng performed the calculations and the data analysis and H. Liang prepared the draft of the manuscript. Z. Qiao and Y. Li initialize the project and proposed the supervision. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

The authors declare no competing financial interest.

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