

# Arsenene, antimonene and bismuthene as anchoring materials for lithium-sulfur batteries: a computational study

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**Abstract:** Finding effective anchoring materials for the immobilization of soluble lithium polysulfides to suppress the shuttling effect has become the key to large-scale application of lithium-sulfur (Li-S) batteries. In this work, the potentials of group-VA two-dimensional (2D) materials including arsenene, antimonene and bismuthene (As, Sb and Bi monolayers) as Li-S battery cathode anchoring materials were systematically investigated by density functional theory (DFT) calculations. The adsorption energies of sulphur ( $S_8$ ) and various lithium polysulfides ( $Li_2S_n$ ,  $n = 8, 6, 4, 2, 1$ ), as well as the diffusion energy barriers for long-chain  $Li_2S_4$  and  $Li_2S_6$  on these three monolayers were studied in detail. The calculated moderate adsorption energies of these monolayers to all polysulfides imply that they can effectively inhibit the shuttling effect. The favorable diffusion barriers for  $Li_2S_4$  and  $Li_2S_6$  ensure the efficient diffusion of polysulfides on monolayer surface. In addition, these 2D materials can keep a balance between the binding strength and the structural integrity of polysulfides. The presented merits demonstrate that As, Sb and Bi monolayers can be the promising cathode anchoring materials to improve the performance of Li-S batteries.

**KEYWORDS:** Li-S batteries, 2D group-VA materials, shuttling effect, DFT

## 1. Introduction

In recent years, with the increasing energy demand of modern society, rechargeable Li-S batteries have attracted widespread attention due to their high theoretical specific energy density (2600 Wh/kg). In addition, sulfur is naturally abundant, low cost, and low toxicity, which makes a lot of researches devoted to Li-S batteries for the next-generation high-energy power systems.<sup>[1-6]</sup> However, their practical application has been still impeded by a series of challenges, such as low ionic and electronic conductivities of sulfur and low-order lithium polysulfides, large volume expansion of sulfur ( ~ 80%) during the reaction. Especially the intermediate polysulfides are easily soluble into the common organic electrolytes, diffusing between anode and cathode and causing the “shuttling effect”, which result in short cycle life, low Coulombic efficiency, and irreversible loss of active materials from the cathode.<sup>[7-12]</sup>

Suppressing the shuttling effect of polysulfides is a critical issue among the above obstacles. Great efforts have been made to deal with this challenge.<sup>[13, 14]</sup> Recently, 2D layered structures as cathode anchoring materials to confine polysulfides have been extensively studied,<sup>[15-21]</sup> since 2D materials have the advantages of superior flexibility, abundant adsorption sites, and large specific surface area. Graphene, as

well as heteroatom-doped graphene, have been theoretically and experimentally proven to improve the electronic conductivity and cycling stability of Li-S batteries.<sup>[22-28]</sup> On the other hand, introducing the metal compounds (such as oxides,<sup>[29, 30]</sup> sulfides,<sup>[31-33]</sup> carbides,<sup>[34, 35]</sup> nitrides<sup>[36, 37]</sup>) into the sulfur cathode is also a novel method to overcome the shuttling effect. Zhang et al. systematically investigated the interaction mechanism between polysulfides and a series of 2D metal oxides, sulfides and chlorides ( $V_2O_5$ ,  $MoO_3$ ,  $TiS_2$ ,  $VS_2$ ,  $ZrS_2$ ,  $NbS_2$ ,  $MoS_2$ ,  $TiCl_2$ ,  $ZrCl_2$ ).<sup>[38]</sup> According to the magnitude of the derived adsorption energies, these three types of materials were classified as strong, moderate, and weak anchoring materials, respectively. They believed that too large adsorption energy would lead to the decomposition of polysulfides, and suggested that anchoring materials with moderate binding strength are the ideal candidates for battery electrodes.

More recently, group-VA 2D layered materials including phosphorene, arsenene, antimonene and bismuthene have drawn great attention due to the merits of moderate band gap, high carrier mobility, high theoretical capacity and large surface area. This kind of emerging materials have considerable prospects in the application of field effect transistors, photodetectors, gas sensors, especially Li/Na ion and Li-S batteries.<sup>[39-43]</sup> Phosphorene, first fabricated in 2014, was the most studied material among group-VA 2D materials.<sup>[44-47]</sup> Lots of experiments and theoretical calculations have been done for evaluating of phosphorene in improving the performance of Li-S batteries.<sup>[48-50]</sup> For example, Sun et al. experimentally introduced phosphorene in separator to trap polysulfides for Li-S batteries.<sup>[51]</sup> Zhao et al put forward that black phosphorene ( $\alpha$ -phase of phosphorene ) can be used as the cathode host material for Li-S batteries using first principles calculations.<sup>[52]</sup> The potential applications of defective black phosphorene and blue phosphorene ( $\beta$ -phase of phosphorene) in Li-S batteries have also been predicted through theoretical calculations.<sup>[53-55]</sup> For arsenene, antimonene and bismuthene allotropes, Zhang et al. predicted that all corresponding  $\beta$  phases with the buckled form are the most stable structures.<sup>[56]</sup>  $\beta$ -arsenene,  $\beta$ -antimonene and  $\beta$ -bismuthene have been testified to exist and successfully isolated

from group-VA bulk crystals.<sup>[43, 57]</sup> Although their chemical stability is superior to phosphorene, their researches related to Li/Na ion and Li-S batteries are still in the preliminary stage.<sup>[58-60]</sup> For instance, Guo et al. evaluated the performance of arsenene and antimonene as anode materials in Li/Na ion batteries and Xu et al. developed 2D-Bi nanosheets as electrocatalyst for polysulfides conversion in Li-S batteries.<sup>[61, 62]</sup> However, there are few systematic theoretical studies on the potentials of 2D As, Sb and Bi in Li-S batteries. Herein, these three  $\beta$ -phase monolayers (As, Sb, Bi) were selected as Li-S battery cathode anchoring materials, and the adsorption and diffusion behaviors of various polysulfides on the surfaces were systematically investigated through comprehensive DFT calculations. Our results reveal that the adsorption energies of polysulfides on these monolayers are moderate and their structural integrity is well preserved. These monolayers can also provide favorable diffusion barriers for long-chain polysulfides. Thus, 2D As, Sb and Bi are expected to be promising cathode anchoring materials for high-efficiency Li-S batteries.

## 2. Computational methods

The geometric optimization and electronic properties calculations were implemented in the DMol<sup>3</sup> code.<sup>[63, 64]</sup> The generalized gradient approximation (GGA) with a Perdew–Burke–Ernzerhof (PBE) functional and the double numerical plus polarization (DNP) basis set were adopted.<sup>[65]</sup> Since van der Waals (vdW) interactions play an important role in determining the anchoring effect for soluble Li<sub>2</sub>S<sub>n</sub> species, the DFT-D method with the Grimme correction was employed.<sup>[66]</sup> Self-consistent field (SCF) computations were carried out with a convergence criterion of 10<sup>-6</sup> a.u. on the total energy and electronic computations. The optimal geometric convergence criteria of energy, force, and displacement were 1.0×10<sup>-5</sup> Ha, 0.002 Ha Å<sup>-1</sup>, and 0.005 Å, respectively. The Brillouin zone was sampled with a 4×4×1 k-points setting in structural optimization, and a 10×10×1 grid was used for electronic properties computations. A vacuum region of 20 Å was adopted to avoid interaction between the neighboring layers. All monolayers were built by the slab containing 4×4 primitive cells. The complete LST/QST method was used to search and optimize the diffusion

path of long-chain  $\text{Li}_2\text{S}_n$  ( $n = 4, 6$ ) on anchoring materials surface.<sup>[67]</sup> Electron density difference was computed by CASTEP code.<sup>[68]</sup>

To quantitatively describe the interaction strength between the anchoring materials and  $\text{Li}_2\text{S}_n$  species, the adsorption energy ( $E_{\text{ads}}$ ) was defined as

$$E_{\text{ads}} = E_{\text{AMs}} + E_{\text{Li}_2\text{S}_n} - E_{\text{AMs+Li}_2\text{S}_n} \quad (1)$$

where  $E_{\text{AMs}}$ ,  $E_{\text{Li}_2\text{S}_n}$ , and  $E_{\text{AMs+Li}_2\text{S}_n}$  are the energies of the various anchoring materials, isolated  $\text{Li}_2\text{S}_n$  species, and the adsorbed systems, respectively. According to this definition, the more positive  $E_{\text{ads}}$  indicate the more energetically favorable adsorption interactions between these selected anchoring materials and  $\text{Li}_2\text{S}_n$  species.

### 3. Results and discussion

#### 3.1. Structures of $\text{S}_8$ , $\text{Li}_2\text{S}_n$ species and anchoring materials

As theoretically and experimentally demonstrated, some S-related intermediates, including  $\text{S}_8$ ,  $\text{Li}_2\text{S}_8$ ,  $\text{Li}_2\text{S}_6$ ,  $\text{Li}_2\text{S}_4$ ,  $\text{Li}_2\text{S}_2$ , and  $\text{Li}_2\text{S}$  species, represent the critical lithiation stages during the charging and discharging process of Li-S batteries.<sup>[69]</sup> Among them, the long-chain  $\text{Li}_2\text{S}_n$  ( $n=8, 6, 4$ ) species could be soluble in electrolytes, such as 1, 2-dimethoxyethane (DME) and 1, 3-dioxolane (DOL), thus inducing the so-called shuttling effect and resulting in fast capacity fading of Li-S batteries. The optimized most stable configurations for these species are presented in Figure 1A. Our results reveal that all optimized S-containing species are in three-dimensional cluster shapes except for  $\text{Li}_2\text{S}$ , which is a chain-like structure. Furthermore, with the decreasing number of S atoms in polysulfides, the Li-S bond lengths of these  $\text{Li}_2\text{S}_n$  species shorten, while the distances between two S atoms increase, indicating that long-chain  $\text{Li}_2\text{S}_n$  species are more easily ionized into Li cation and polysulfide anion in the electrolytes than short-chain  $\text{Li}_2\text{S}_2$  or  $\text{Li}_2\text{S}$ , which are consistent with previous simulation works.<sup>[70-73]</sup>

The optimized structures of As, Sb and Bi monolayers are displayed in Figure 1B. These 2D materials with buckled structures contain 32 As/Sb/Bi atoms and each atom is covalently bonded to three neighboring atoms. The lattice parameters of these

monolayers are  $a = b = 3.83 \text{ \AA}$ ,  $4.32 \text{ \AA}$ ,  $4.47 \text{ \AA}$  and the buckling heights are  $1.36 \text{ \AA}$ ,  $1.62 \text{ \AA}$ ,  $1.73 \text{ \AA}$  for 2D As, Sb and Bi, respectively. Moreover, the measured As-As, Sb-Sb, and Bi-Bi bond lengths are  $2.59 \text{ \AA}$ ,  $2.98 \text{ \AA}$ ,  $3.10 \text{ \AA}$  and the bond angles are  $95^\circ$  (As),  $93^\circ$  (Sb),  $92^\circ$  (Bi), respectively. The above obtained values are similar to previous studies.<sup>[74, 75]</sup>

### 3.2 Adsorption of $S_8$ and $Li_2S_n$ species on the anchoring materials

A rational cathode anchoring material for Li-S batteries should be able to immobilize polysulfides effectively. Therefore, the adsorption energies of various S-containing species on As, Sb and Bi monolayers were calculated. To search for the most energetically favorable adsorption sites, we considered a series of distinct translational and rotational configurations of  $S_8$  and  $Li_2S_n$  species over these high-symmetry sites of monolayers. The adsorption of  $Li_2S_6$  on As, Sb and Bi monolayers was used as the representative. The optimized configurations and adsorption energies of  $Li_2S_6$  with various orientations and sites on these monolayers are shown in Figure S1-S3. Through the detailed sampling, the most stable adsorption configurations of all polysulfides on As, Sb and Bi monolayers are shown in Figures 2, and Figure S4-S5. The corresponding adsorption energies, shortest distances and charge transfer values for the adsorption systems are summarized in Table 1.

Take the adsorption of polysulfides on arsenene as an example, the adsorption energy of unlithiated  $S_8$  over arsenene is  $1.03 \text{ eV}$ , and only  $0.04$  electrons transfer from arsenene to  $S_8$ .  $S_8$  is almost parallel to the surface with the shortest distance of  $3.30 \text{ \AA}$  (Table 1). It can be inferred that the adsorption of  $S_8$  over arsenene surface mainly originates from vdW physical interaction and there is no chemical bond formation between them. As plotted in Figure 3A, once the lithiation begins, the adsorption energies of polysulfides would enhance to different extent (in the range of  $2.09 \sim 3.60 \text{ eV}$ ), which are much higher than those on graphene ( $E_{\text{ads}} = 0.68 \sim 1.09 \text{ eV}$ ).<sup>[76]</sup>  $Li_2S_6$  with adsorption energy of  $2.09 \text{ eV}$  is the smallest among all  $Li_2S_n$  species. It should also be noted that the adsorption energy of  $S_8$  is significantly lower

than other  $\text{Li}_2\text{S}_n$  species due to the lack of lithium participating in bonding. The variation trend of adsorption energy of polysulfides is similar with those on the phosphorene surface.<sup>[52]</sup> In addition, the adsorption energies of polysulfides on the antimonene and bismuthene also follow the same variation trend. The moderate binding strength between polysulfides and these monolayers preliminarily indicates that the As, Sb, and Bi monolayers can be ideal anchoring materials for Li-S batteries.  
[38]

To reveal the underlying anchoring mechanism, the contributions of chemical and physical vdW interactions of polysulfides over monolayers were evaluated. The ratio for vdW interaction was calculated and determined as

$$R = (E_b^{\text{vdW}} - E_b^{\text{no vdW}}) / E_b^{\text{vdW}} \quad (2)$$

where  $E_b^{\text{vdW}}$  and  $E_b^{\text{no vdW}}$  represent the adsorption energies of adsorbed systems with and without vdW corrections, respectively. As shown in Figure 3B, the R values of different lithiation stages are different for all the studied monolayers, although the profile generally maintains a downward trend. For long-chain polysulfides, the physical interaction plays a major role, while the chemical interaction is dominant for short-chain polysulfides. This is also the reason why the adsorption energy of  $\text{Li}_2\text{S}_8$  is greater than that of  $\text{Li}_2\text{S}_6$ . Because  $\text{Li}_2\text{S}_8$  has more S atoms close to monolayer compared with  $\text{Li}_2\text{S}_6$ , which will increase the physical binding strength of  $\text{Li}_2\text{S}_8$ . The above observations agree well with previous works.<sup>[55, 77]</sup> Taking these into account, the physical vdW interaction can not be negligible in the calculation process to search for favorable cathode anchoring materials more accurately.

To further confirm their bonding nature, we compared the shortest distances between  $\text{Li}_2\text{S}_n$  species and anchoring materials. For  $\text{Li}_2\text{S}_n$  ( $n = 8, 6, 4, 2$ ) species, Li atoms are closer to the As, Sb and Bi atoms of substrates than S atoms (Figure 2, S4, S5). The shortest distances between these  $\text{Li}_2\text{S}_n$  species and As, Sb and Bi monolayers



are about 2.70, 2.90 and 3.00 Å, respectively (Table 1), which are close to the sum of the covalent radii between Li atom and As/Sb/Bi atoms. Therefore, the above  $\text{Li}_2\text{S}_n$  species and the monolayers tend to form Li-As, Li-Sb and Li-Bi bonds, which further confirms that the anchoring effect in these adsorption systems has a partial contribution from the chemical interaction. Particularly, for the adsorption of  $\text{Li}_2\text{S}$  on the As, Sb, and Bi monolayers, the shortest  $d_{\text{Li-AMs}}$  are 2.64, 2.86, 2.88 Å and the shortest  $d_{\text{S-AMs}}$  are 2.26, 2.60, 2.74 Å, respectively. These values indicate that both Li and S atoms of  $\text{Li}_2\text{S}$  tend to form bonds with the monolayer atoms, thereby effectively fix  $\text{Li}_2\text{S}$ . Thus, the chemical interaction between  $\text{Li}_2\text{S}$  and surface is the strongest in the entire lithiation stages, which is also in line with the ratio for vdW profile in Figure 3B. To verify the aforementioned description, the electron density of  $\text{Li}_2\text{S}_4$  and  $\text{Li}_2\text{S}$  adsorbed on three anchoring materials was illustrated in Figure 4. As shown in the figure, the S atom in  $\text{Li}_2\text{S}$  obviously interacts with monolayer atom, while the S atom in  $\text{Li}_2\text{S}_4$  does not exhibit this behavior. This is also the reason why the adsorption energy of  $\text{Li}_2\text{S}$  is much higher than that of  $\text{Li}_2\text{S}_4$ .

The charge transfer values between all polysulfides and anchoring materials were calculated by Mulliken population analysis to gain a deeper understanding of their interactions. The charges on the arsenene surface are 0.04, 0.11, 0.08, 0.08, -0.03 and -0.31 e for the systems including  $\text{S}_8$ ,  $\text{Li}_2\text{S}_8$ ,  $\text{Li}_2\text{S}_6$ ,  $\text{Li}_2\text{S}_4$ ,  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$ , respectively (see Table 1). This means that with the lithiation to  $\text{Li}_2\text{S}_4$ , the electrons transfer from arsenene to polysulfides, while the electrons transfer in the opposite direction during  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  stages. We can speculate that as the lithiation progresses, the quantity of electrons accumulated on arsenene increases with the gradually enhanced interaction strength between polysulfides and arsenene. For antimonene, the electrons transfer from antimonene to polysulfides with the lithiation to  $\text{Li}_2\text{S}_2$ , while the electrons transfer in the opposite direction in the  $\text{Li}_2\text{S}$ -Sb adsorption system. For bismuthene, the electrons transfer from bismuthene to polysulfides during the entire lithiation stages. Hence, the above charge redistribution indicates that arsenene has the strongest electron attraction ability among these three anchoring materials, followed

by antimonene and bismuthene, which are consistent with the electronegativity change rule of group-VA elements.

The electron density difference of three anchoring materials at different lithiation stages were plotted to visually describe the charge transfer between polysulfides and monolayers. This can be defined as

$$\Delta\rho = \rho_{\text{AMs+Li}_2\text{S}_n} - \rho_{\text{AMs}} - \rho_{\text{Li}_2\text{S}_n} \quad (3)$$

where  $\rho_{\text{AMs+Li}_2\text{S}_n}$ ,  $\rho_{\text{AMs}}$ ,  $\rho_{\text{Li}_2\text{S}_n}$  are the electron densities for adsorbed systems, various anchoring materials, and isolated  $\text{Li}_2\text{S}_n$  species, respectively. As shown in Figures 5, S6 and S7, the red and blue regions represent electron density accumulation and depletion, respectively. For all  $\text{S}_8$  adsorption systems, there are little electron exchange due to the weak vdW physical interaction. In the arsenene adsorption systems of Figure 5, as lithiation to  $\text{Li}_2\text{S}_4$ , the electrons lost on the monolayer side, whereas accumulate around Li atoms and lost around S atoms of polysulfides. In the  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  stages of arsenene, more electrons accumulate on the monolayer side and lost on the polysulfides side. For antimonene in Figure S6, more electrons lost on the monolayer side with lithiation to  $\text{Li}_2\text{S}_2$ , and accumulate on the monolayer side in the  $\text{Li}_2\text{S}$  stage. For bismuthene in Figure S7, the electrons lost on the monolayer side throughout the lithiation stages. These are consistent with the data obtained by Mulliken population analysis in Table 1 and the charge transfer direction judged above. It is also worth noting that the red regions between Li atoms and monolayers mean the formation of new chemical bonds, which also confirms our discussions in the preceding paragraphs.

Moreover, density of states (DOS) of  $\text{S}_8$  and  $\text{Li}_2\text{S}_n$  ( $n = 8, 6, 4, 2, 1$ ) species adsorbed on three anchoring materials were calculated to understand their electronic properties. As shown in Figures 6, S8 and S9, the DOS of isolated monolayers are also presented for comparison. It can be seen that in all adsorption systems, the electron states mainly come from the contribution of monolayers. The reduced band gaps of these monolayers after the adsorption of polysulfides are also observed. According to the following formula<sup>[52]</sup>

$$\sigma \sim \exp(-\Delta E/k_B T) \quad (4)$$

where  $\Delta E$  is the band gap, the reduced band gap will be beneficial for increasing the electrical conductivity of adsorption systems, which can further improve the Coulombic efficiency of Li-S batteries.

As mentioned above, the long-chain  $\text{Li}_2\text{S}_n$  ( $n = 8, 6, 4$ ) species are easily soluble in organic electrolyte solvents (such as DME or DOL), leading to the rapid capacity fading of Li-S batteries. Therefore, the interaction between the above three  $\text{Li}_2\text{S}_n$  species and two electrolytes (DME and DOL) were calculated, the optimized structures and the corresponding adsorption energies are presented in Figure S10. It can be seen that Li atoms in  $\text{Li}_2\text{S}_n$  species tend to combine with O atoms in DME and DOL molecules due to the attraction between negatively charged O atoms and positively charged Li atoms. The adsorption energies of three selected anchoring materials and two electrolytes are visually compared in Figure 3A. Obviously, the adsorption energies of the long-chain  $\text{Li}_2\text{S}_n$  species on these monolayers (more than 1.50 eV) are larger than those of electrolytes ( $E_{\text{ads}} = 1.00 \sim 1.14$  eV). That is to say, these polysulfides can be effectively trapped by As, Sb and Bi monolayers, rather than dissolved into the electrolytes. In addition, the average variances of Li-S bond length ( $\Delta d_{\text{Li-S}}$ ) and S-S bond length ( $\Delta d_{\text{S-S}}$ ) of polysulfides upon adsorption on these three monolayers are plotted in Figure S11. The bond lengths of polysulfides change to certain extent in all adsorption systems. This suggests that there will be a certain degree of structural deformation after adsorption, which agrees well with the work of Qie and coworkers.<sup>[78]</sup>

The strong interaction between polysulfides and anchoring materials, and the deformation of polysulfides after adsorption may cause the decomposition of polysulfides. Here, we compared the energy differences of the intact and decomposed configurations of two  $\text{Li}_2\text{S}_n$  ( $n=4, 6$ ) species adsorbed on the three anchoring materials, the decomposed configurations including  $\text{Li} + \text{LiS}_n$  and  $\text{Li} + \text{Li} + \text{S}_n$ . The energy differences were defined as

$$\begin{aligned}\Delta E_1 &= E_{\text{AMs+Li}_2\text{S}_n} - E_{\text{AMs+Li+LiS}_n} \\ \Delta E_2 &= E_{\text{AMs+Li}_2\text{S}_n} - E_{\text{AMs+Li+Li+S}_n}\end{aligned}\quad (5)$$

where  $E$  and  $\Delta E$  represent the energy and energy difference of adsorption system, respectively. A negative value indicates that the intact configuration has lower energy than the decomposed one, meaning that the intact polysulfides are more stable when adsorbed. The optimized configurations of  $\text{Li} + \text{LiS}_n$  and  $\text{Li} + \text{Li} + \text{S}_n$  ( $n=4, 6$ ) adsorbed on arsenene, and all the energy differences studied are given in Figure 7.

Obviously, for the adsorption of  $\text{Li}_2\text{S}_4$  and  $\text{Li}_2\text{S}_6$ , all  $\Delta E$  values are negative. In other words, the intact configurations are energetically preferable for these anchoring materials. Hence, these polysulfides can preserve their complete configurations during adsorption process, and avoid the capacity fading of Li-S batteries.

### 3.3 Diffusion of $\text{Li}_2\text{S}_n$ species on the anchoring materials

The effective diffusion of polysulfides is critical to the charge and discharge performance of Li-S batteries. To better assess the applicability of these 2D materials as Li-S battery cathode anchoring materials, we further probe the diffusion properties of polysulfides on these monolayers. The diffusion of long-chain  $\text{Li}_2\text{S}_n$  ( $n=4, 6$ ) species along the armchair and zigzag directions of anchoring materials was considered, in which they would diffuse from the most favorable adsorption site to a similar adjacent site. The computed diffusion energy barriers on three monolayers are listed in Table 2. Our results indicate that the diffusion of polysulfides along the zigzag direction is more favorable than that of the armchair direction. For instance, the diffusion barriers along the armchair direction are 0.73 eV and 1.02 eV for  $\text{Li}_2\text{S}_4$  and  $\text{Li}_2\text{S}_6$  on arsenene, respectively. However, the barriers in the zigzag direction are smaller than those of armchair direction, which are 0.66 eV and 0.49 eV, respectively. The same trend can be observed for antimonene, bismuthene, and blue phosphorene.<sup>[55]</sup> These minimum diffusion barriers are comparable or even lower than those of other 2D materials, such as  $\beta_{12}$ -borophene, boron-phosphide monolayer and phosphorene-like MX ( $M = \text{Ge}, \text{Sn}; X = \text{S}, \text{Se}$ ).<sup>[79-81]</sup> As a result, the diffusion barriers for  $\text{Li}_2\text{S}_4$  and  $\text{Li}_2\text{S}_6$  are determined to be favorable for the effective diffusion of

polysulfides on these anchoring materials.

#### 4. Conclusions

In conclusion, the adsorption and diffusion behaviors of polysulfides on the 2D group-VA arsenene, antimonene and bismuthene were systematically investigated by means of DFT calculations, to explore their potentials as Li-S battery cathode anchoring materials. On the basis of our calculation, these monolayers possess moderate binding strength with all polysulfides and provide favorable diffusion barriers for long-chain polysulfides. In particular, they can not only suppress the shuttling effect effectively, but also maintain the structural integrity of polysulfides well. Consequently, these anchoring materials are promising on the immobilization of the polysulfides. We predict that these anchoring materials can be applied in Li-S battery cathode and improve battery performance. In future, more 2D layered materials should be screened to explore their potentials as Li-S battery hosts.

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