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Heteroatom doped germanene and stanene as anchoring materials for lithium-sulfur batteries: a density functional theory study

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Abstract: **With a high theoretical energy density, lithium sulfur (Li-S) batteries become one of the most promising candidates for next-generation energy storage devices. Effectively anchoring Li2Sn species on specific substrate is an important method to suppress the "shuttle effect". In this work, we have explored the adsorption and decomposition of Li2Sn species on heteroatom doped germanene and stanene monolayer using DFT computations. The results revealed that all Li2Sn species can be effectively adsorbed on the given substrates. Furthermore, the Li2Sn species on B-doped germanene can keep intactness, which suggest that the B-doped germanene is the most promising anchoring materials for Li-S batteries.**

Keywords: Lithium sulfur batteries; density functional theory; shuttle effect; 2D materials

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1. Introduction

As one of the most promising candidates for energy storage devices, lithium sulfur (Li-S) batteries have gained great attention to fulfill the ever-increasing demand of electronic devices due to their high theoretical energy density (2600Wh/Kg), which have exceed the currently state-of-the-art lithium ion batteries [1-3]. Severing as the cathode of the Li-S batteries, sulfur has multiple advantages such as naturally abundant, inexpensive, and environmentally friendly [4]. However, there are still numerous obstacles hindering the developing of the practical application of Li-S batteries. Firstly, sulfur and the discharge products Li_2S/Li_2S_2 are insulating, which cause the low active material utilization and reduce the transmission rate of electrons. Secondly, during lithiation, the cathode sulfur would proceed volume expansion (about 80%), which produce solid Li_2S and Li_2S_2 detaching the conductive scaffold [2]. Finally, the discharge intermediates easily dissolve into the electrolyte forming the lithium polysulfides (Li_2S_n), which causes "shuttle effect" between cathode and anode. This "shuttle effect" would greatly influence the cycling and stability performance of Li-S batteries. In addition, these Li_2S_n species would uncontrollable deposite during the charge and discharge process resulting in the fast capacity fading and low coulombic efficiency [4].

For the above mentioned issues, numerous efforts have been made to meet these challenges. Firstly, impregnating sulfur into the porous carbon, such as carbon nanotube (CNT), carbon fiber and graphene, is one of the most effective approaches to increase the conductivity of the battery and restrict Li_2S_n species into nanohole via physical adsorption [5]. However, this weak physical interaction between nonpolar anchor materials (AM) and polar Li_2S_n species would cause the detachment of Li_2S_n species from the carbon surface [6-9]. Hence, it is very important to introduce polar materials to form a chemical interaction between polar Li_2S_n species and nonpolar anchor materials. Introducing heteroatoms, such as oxygen, nitrogen, sulfur, phosphorous, and boron, or co-doping into nanomaterials is an effective method for constructing polar functional groups, thereby increasing the immobilization of Li_2S_n species on the AM. The two most used dopants are electronegative N and B, which considered as Lewis-bases reacting with Lewis acids severed by Li atoms in Li_2S_n species. Yang et al. using boron-doped porous carbon materials as the cathode could deliver much higher initial capacity, exhibiting high conductivity and allowing chemisorption of Li_2S_n species due to the existence of B. Recently, two-dimensional (2D) materials with high surface-volume ratio have been regarded as one of the most promising candidates of anchoring material. For example, graphene and doped graphene can act as potential anchor materials verified theoretically and experimentally. And the other 2D structures, including metal oxide, sulfides, Mxene, phosphorene, silicene, and germanene ect, also can deliver more stronger chemical binding energies between Li_2S_n species and AM than nonpolar carbon materials.

In this study, the DFT computations were performed to investigate the feasibility of the nonmetallic elements (P and B) doped germanene (Ge) and stanene (Sn) as anchoring materials (AM) in Li-S batteries. The binding energies between Li_2S_n species and AM and the intactness of the Li_2S_n species can provide a powerful tool to deeply understand the anchoring effects of the given 2D materials. The calculated results show that the Li_2S_n species have chemical interaction with AM to suppress the "shuttle effect" while keeping intact configurations. This indicates that the doped germanene and stanene will be potential to improve the performance of Li–S batteries.

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2. Computational methods

All calculations were based on the density functional theory (DFT), using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional in the framework of the general gradient approximation (GGA) implemented in the DMol^3 package. All-electron double numerical basis set with polarization functions (DNP basis set) was used. Self-consistent field (SCF) calculations were performed with a convergence criterion of 10^{-6} a.u. and the K-point was set to 4x4x1. To simulate the adsorption and diffusion process of Li_2S_n species, the unit cell were designed by taking 4x4 supercell including 31 pristine atoms and one doped atom, and the vacuum layer along the normal direction was set to 20Å, which was examined to be large enough to avoid an unexpected interaction between atoms in different super cells.

The adsorption energy (E_{ads}) of lithium polysulfides (Li_2S_n) on a host material is calculated by $E_{ads} = E_{total} - E_{AM} - E_{Li_2S_n}$, where E_{total}, E_{AM}, and $E_{Li_2S_n}$ are the total energies of the adsorbed system, doped germanene or stanene, and isolated Li_2S_n species respectively. According to this definition, a more negative value indicates a more energetically favorable interaction between Li_2S_n species and the doped germanene or stanene monolayer surface.

Charge density difference calculations were performed to gather insight into the electronic interactions between the Li_2S_n species and the AM surface. The charge density difference ($\Delta\rho_{ads}$) for each system was calculated using the following equation:

$$\Delta\rho_{ads} = \rho_{total} - \rho_{Li_2S_n} - \rho_{AM}$$

Where ρ_{total} is the charge density of AM upon adsorption of the Li_2S_n species of interest, ρ_{AM} is the charge density of free standing doped germanene or stanene, and $\rho_{Li_2S_n}$ is the charge density of the isolated Li_2S_n species of interest.

3. Results and discussion

3.1. Structural analysis of Li_2S_n species and AM

Theoretically, the pristine germanene or stanene monolayer are atomic thick materials with hexagonal honeycomb structures similar to that of graphene. However, they are not flat but have a periodically buckled topology. Figure 1 displays the P-doped germanene, in which P atom with two adjacent atoms (Ge_1 and Ge_2) on different planes. The bond angle along Ge_1-P-Ge_2 and the adjacent P-Ge_1 bond length are 112.67° and 2.38 Å respectively. while for B-doped Ge, they are 118.99° and 2.06Å, and for P-doped Sn (B-doped Sn) are 111.65° (118.11°) and 2.60 Å (2.26 Å), respectively. The configurations of polysulfides are also shown in Fig.1. They are three-dimensional shapes, rather than chains with Li atoms on the terminals. S_8 molecule is symmetrical wrinkled ring structure, where S-S bond and S-S-S angles are 2.09Å and 109.16°, respectively.

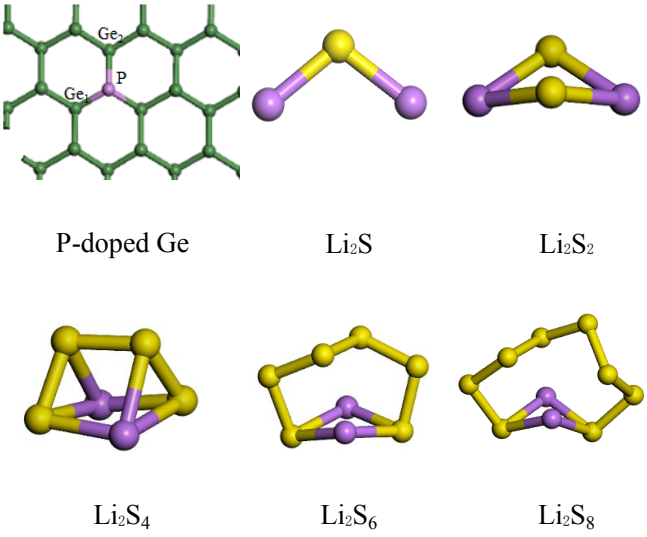

Figure 1. The optimized structures of P-doped germanene and Li_2S_n species.

In addition, as shown in Figure 2, the S-S bond lengths of Li_2S_n species shorten and the Li-S bond elongate as the number of S atoms in Li_2S_n increases, suggesting that soluble long-chain Li_2S_n (such as Li_2S_4, Li_2S_6, Li_2S_8) is easily ionized into Li and polysulfide ions in electrolyte than insoluble short-chain Li_2S or Li_2S_2, consistent with previous studies [10].

3.2. Adsorption of Li_2S_n species on AM surfaces

Firstly, we studied the interaction strength between the polysulfides and AM. Various adsorption configurations of Li_2S_n on AM were considered and the most stable ones were illustrated in Figure 3. The corresponding adsorption energies were exhibited in Figure 4. Take Li_2S for example, the adsorption on B-doped Sn with 4.95eV is large than other AM, which suggests the formation of strong covalent bonds. While for that of Li_2S_8, the adsorption energy is lower than those of P-doped Sn and P-doped Ge monolayer. In

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contrast, the binding of Li_2S on P-doped Ge has lowest strength with 3.43eV and has the most weak interaction for Li_2S_6 (2.17eV) among all systems. And the B-doped Ge and P-doped Sn have the medium strength. The adsorption of Li_2S_2 has the same tendency and as well as large than that of other soluble polysulfides. In other words, the insoluble Li_2S and Li_2S_2 exhibit strongest interaction with AM. At the same time, the configurations of AM occur slight change. For example, P-Ge bond length increased to 2.52Å and the angle become 120.84° after adsorbed Li_2S due to the strong strength. On the other hand, the binding energies of soluble Li_2S_n species adsorbed on AM are ranging from 2.17eV to 4.14eV, much larger than those between electrolyte solvents and Li_2S_n clusters (e.g. DME and DOL, the binding energy are range from 0.94 to 1.06 eV). Hence, introducing heteroatom into Ge and Sn can anchor Li_2S_n species effectively thus may suppress the so-called "shuttle effect".

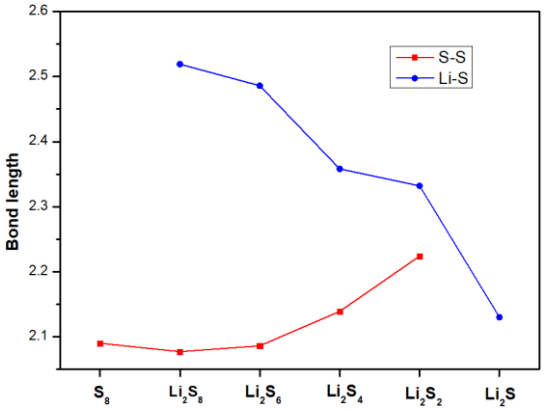

Figure 2. The lengths of S-S and Li-S bonds in Li_2Sn species.

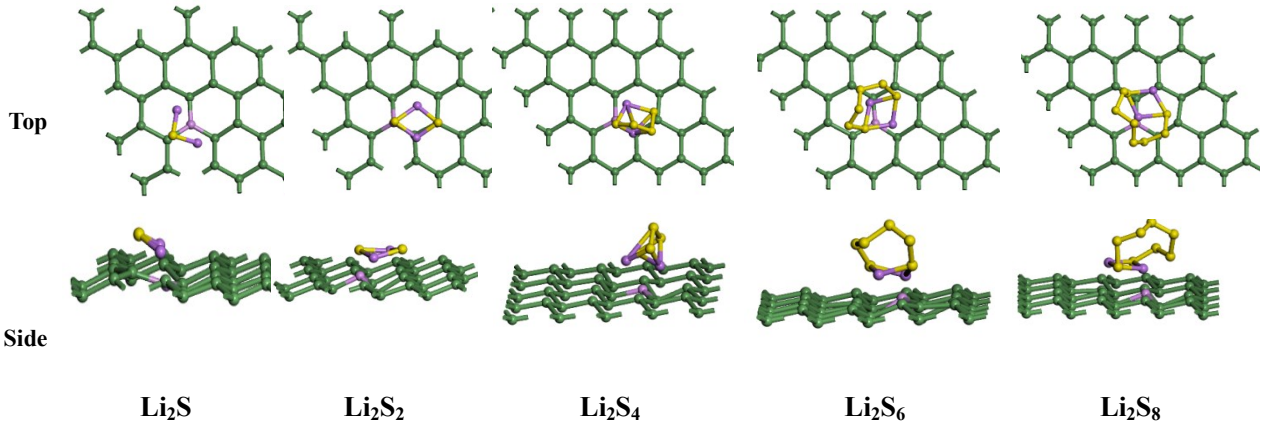

Figure 3. The top and side views of the optimized configurations of Li_2S, Li_2S_2, Li_2S_4, Li_2S_6, Li_2S_8 adsorbed on AM.

To clarify the underlying mechanism of dopant-induced strong immobilization of Li_2S_n species, the shortest distances between the adsorbed Li_2S_n species and AM monolayer were analyzed, in which Li_2S_n species on P-doped Ge was chosen as an example. From the value of bonding energy, it is obvious that the anchoring effect of P-doped Ge mainly originates from chemical interaction between Li or S atoms in Li_2S_n species with P or Ge. As seen from the value, the distance between S atom in Li_2S and Ge is 2.27 Å and form Ge-S bond.

For others Li_2S_n, the S-Ge distances are 2.22, 2.34, 2.42 and 2.57 Å. In addition, there are S • • • P interaction between Ge monolayer and Li_2S_n except Li_2S, with the average distance of 2.0 Å. Therefore, it is chemical interaction between Li_2S_n species and AM to adsorb polysulfides thereby improving the performance of Li-S batteries.

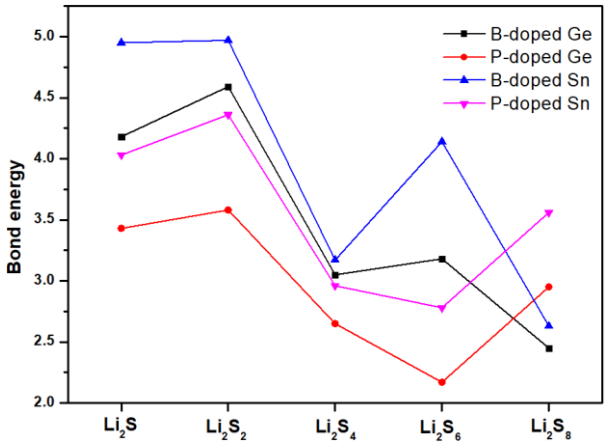

Figure 4. The binding energies for Li-S composites on different AMs.

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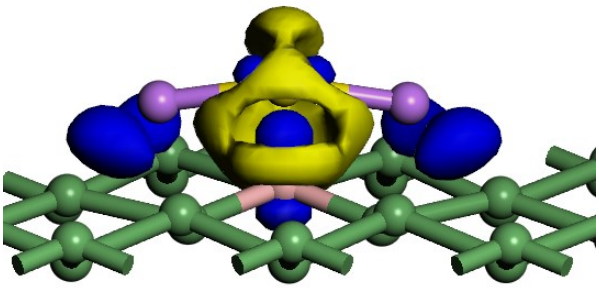


Figure 5. Charge transfers when Li2S adsorbs on B-doped Ge. Blue (yellow) is the spatial regions gain (loss) in charge.

3.3. Charge distribution

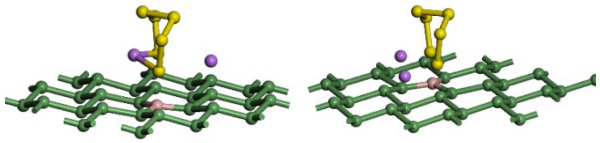
To gain deeply understanding of the chemical interaction between Li_2S_n species and AM, the Mulliken charge transfer (take Li_2S as example) between them are investigated. There are 0.05, 0.2, 0.01 and 0.02e electron transferred from Li_2S to AM, respectively. In this respect, they have fewer charge transfer except B-doped Ge monolayer, illustrating lack of the ability to attract electrons. In contrast, the charge transfer between Li_2S and B-doped Ge monolayer can facilitates the enhancement of the anchoring effects.

For more detailed description of charge transfer between Li_2S and AM (taking Li_2S adsorbed on B-doped Ge for example), we also calculated the charge density difference between them (Fig. 5). B-doped Ge lost electrons and transferred to S atom for Li_2S. On the contrary, sulfur lost electrons and transferred to B-doped Ge for Li_2S due to the electronegativity of sulfur is greater than that of boron (2.58 and 2.04 for sulfur and boron elements, respectively).

3.4. Stability of Li_2S_n species

The stability of Li_2S_n adsorbed on AM is also an important issue to evaluate the anchoring materials. Therefore, we calculated the binding energies of decomposed and intact Li_2S_n species adsorbed on AM (Figure 6). Two kinds of decomposed structures are considered, including Li + LiS_n and 2Li + S_n (Li represents isolated atom, n=6 is chosen as a representative), and their energy differences are denoted as ΔE_1 and ΔE_2. Negative value suggests that the intact structure owns lower energy than decomposed one. The result shows that ΔE_1 and ΔE_2 are negative values (-0.39 and -0.55eV, respectively), illustrating the intact structure is energetically favorable. The other AM all have positive ΔE_1 and negative ΔE_2, suggesting that they have a tendency to decompose to Li + LiS_6.

Li + LiS_6 2Li + S_6



(a)

	ΔE_1	ΔE_2
Ge-P	**0.47**	**-0.56**
Ge-B	**-0.39**	**-0.55**
Sn-P	**0.55**	**-0.47**
Sn-B	**0.57**	**-0.54**

(b)

Figure 6. (a) Li + LiS_6 and 2Li + S_6 adsorbed on B-doped Ge. (b) Energy differences between intact Li_2S_6 and decomposed Li_2S_6 adsorbed on AM. Here, $\Delta E1 = E(Li_2S_6 + AM) - E(Li + LiS_6 + AM)$, and $\Delta E2 = E(Li_2S_6 + AM) - E(2Li + S_6 + AM)$, respectively.

Through the above discussions, we excepted that the B-doped germanene is a promising material for anchoring polysulfieds due to the strong interaction to restrain "shuttle effect" and intactness of the structure.

4. Conclusions

The potential of utilizing heteroatom doped germanene or stanene as anchoring material of Li_2S_n species in Li-S batteries was systematically researched by means of DFT computations. The results revealed that heteroatom doped germanene or stanene could provide strong interaction with polysulfides to avoiding the dissolution of Li_2S_n species into electrolyte and hence suppress "shuttle effect". Especially, the structure of Li_2S_n adsorbed on B-dope germanene can keep intactness. We hope that our research could inspire more investigations and theoretical studies on exploring the potential of other 2D materials for Li-S batteries.

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