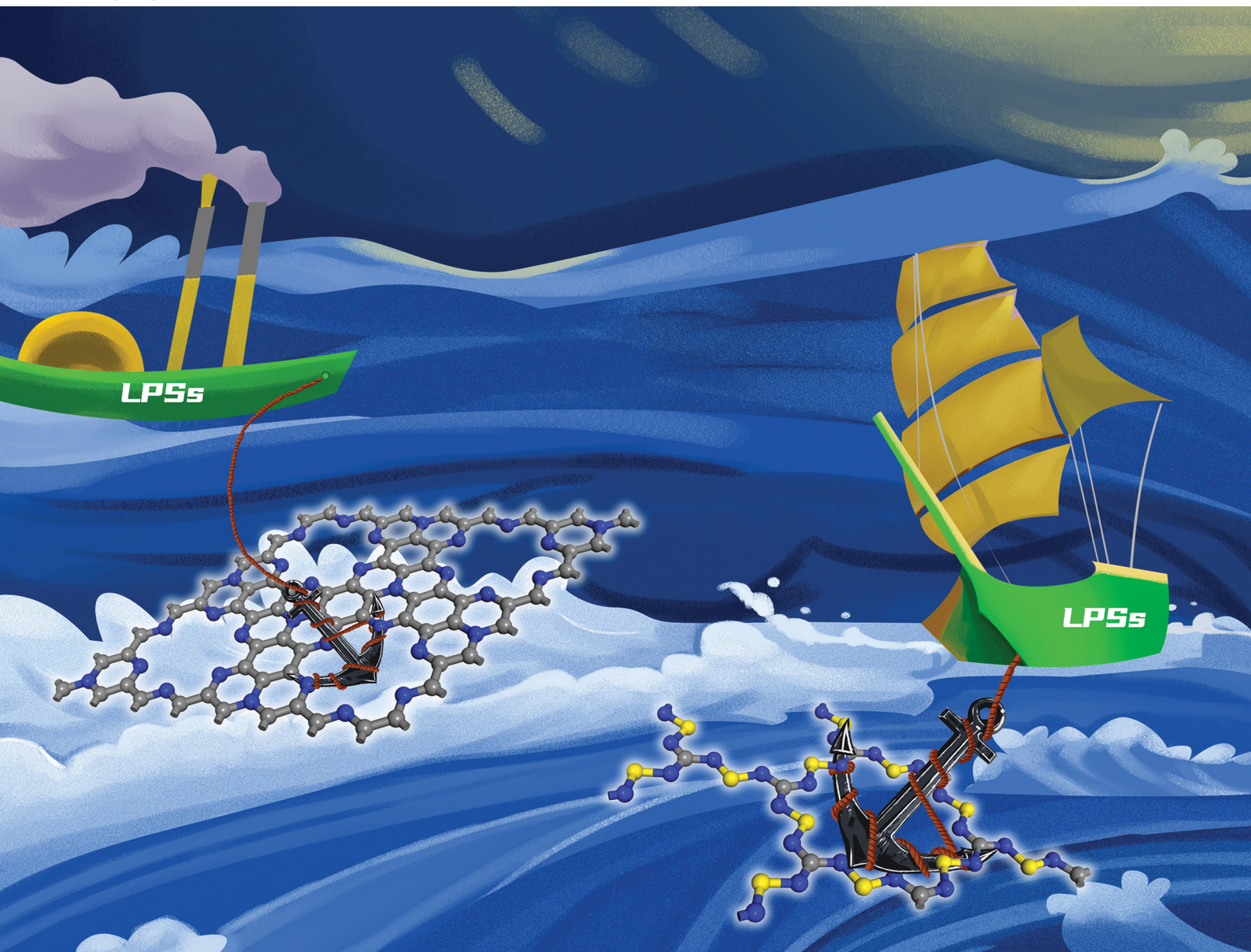


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ISSN 1463-9076

PAPER

Fengyu Li, Jian Gong, Zhongfang Chen *et al.*
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Cite this: *Phys. Chem. Chem. Phys.*,
2021, 23, 12958

C₉N₄ and C₂N₆S₃ monolayers as promising anchoring materials for lithium–sulfur batteries: weakening the shuttle effect *via* optimizing lithium bonds†

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The notorious polysulfide shuttle effect is a crucial factor responsible for the degradation of Li-S batteries. A good way to suppress the shuttle effect is to effectively anchor dissoluble lithium polysulfides (LPSS, Li₂S_n) on appropriate substrates. Previous studies have revealed that Li of Li₂S_n is prone to interact with the N of N-containing materials to form Li–N bonds. In this work, by means of density functional theory (DFT) computations, we explored the possibility to form Li bonds on ten different N-containing monolayers, including BN, C₂N, C₂N₆S₃, C₉N₄, a covalent triazine framework (CTF), *g*-C₃N₄, *p*-C₃N₄, C₃N₅, S-N₂S, and T-N₂S, by examining the adsorption behavior of Li₂S_n (*n* = 1, 2, 3, 4, 6, 8) on these two-dimensional (2D) anchoring materials (AMs), and investigated the performance of the formed Li bonds (if any) in inhibiting the shuttle effect. By comparing and analyzing the nitrogen content, the N-containing pore size, charge transfer, and Li bonds, we found that the N content and N-containing pore size correlate with the number of Li bonds, and the formed Li–N bonds between LPSSs and AMs correspond well with the adsorption energies of the LPSSs. The C₉N₄ and C₂N₆S₃ monolayers were identified as promising AMs in Li-S batteries. From the view of Li bonds, this work provides guidelines for designing 2D N-containing materials as anchoring materials to reduce the shuttle effect in Li-S batteries, and thus improving the performance of Li-S batteries.

Received 8th March 2021,
Accepted 5th May 2021

DOI: 10.1039/d1cp01022k

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1. Introduction

The increasing energy demand, accelerating global climate change, and worsening environment all are calling for the replacement of traditional fossil fuel energy by renewable energies. Lithium-sulfur (Li-S) batteries have a rather high theoretical specific capacity

(1675 mA h g^{−1}) and a high energy density (2600 W h kg^{−1}),¹ as well as a low application cost and abundant natural reserves, and thus are among the most promising renewable energies, especially as the next generation energy storage devices for electric vehicles.^{2–4} However, the development of Li-S batteries has suffered many obstacles, such as low S utilization, poor cycle life, and volume expansion.^{5–9} The polysulfide “shuttle effect”, which originates from the migration of the electrically insulating sulfur and the dissoluble lithium polysulfides (LPSSs, Li₂S_n) between the anode and cathode during charging and discharging processes, is one of the most important unsolved issues that limit the practical application of Li-S batteries.

A good strategy to suppress the shuttle effect is to introduce polar functional groups¹⁰ or anchoring materials (AMs) to strongly bind the Li₂S_n species, thus reducing the leakage of active material from the cathode.¹¹ For example, vacancy defects and heteroatom-doping can improve the adsorption capability of graphene nanoribbons (GNRs),^{12,13} graphene,^{14,15} and BN.¹⁶ Two-dimensional (2D) carbon-based N-containing materials, such as C₂N¹⁷ and *g*-C₃N₄,^{18–23} demonstrate their good performance as AMs. Note that the interaction between the LPSSs and the AM should be moderate, otherwise it will result in irreversible dissociation of

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† Electronic supplementary information (ESI) available: The most stable configurations of Li₂S_n and S₈ on the AMs; top and side views of the “intact” and decomposed Li₂S₄ on the C₉N₄ and C₂N₆S₃, as well as their relative energies; diffusion paths and migration energy barriers of Li₂S₆ on the BN, C₉N₄, C₂N₆S₃ and CTF monolayers; charge density difference diagrams and the most stable configurations of Li₂S_n and S₈ on different AMs; linear fitting between the adsorption energy of Li₂S_n (*n* = 1–4, 6, 8) and the pore size of the AMs; average length of S–C bond (*d*_{S–C}) and S–N bond (*d*_{S–N}) for different AMs; Li···S distances of the broken Li–S bonds (*d*_{Li···S}, in Å). Data in parentheses denote the number of broken Li–S bonds; average length of the formed S–N bond (*d*_{S–N}) between the Li₂S_n and the ten AMs; variation of adsorption energies (*E*_{ad}), charge transfer (*Δq*) and average length of Li–S/N bond (*d*_{Li–S}, *d*_{Li–N}). See DOI: 10.1039/d1cp01022k

the lithium polysulfides. For example, the excessive strength of the Li–O/Li–S bonds between Li_2S_n and metal oxides/metal sulfides leads to Li_2S_n dissociation, thus weakening the adsorption effect for such metal oxides and metal sulfides.^{11,24,25}

Very recently, the importance of Li bonds^{26,27} in Li–S batteries has gained attention in the battery community. In 2015, for the first time, Goodenough and coworkers reported spectroscopic evidence of the existence of Li bonds between LPSs and the polymer matrix, which resist the dissolution of LPSs and thus ease the shuttle effect in Li–S batteries.²⁸ Shortly afterwards, Zhang and coworkers performed very detailed theoretical and experimental studies from the aspects of the chemical bonds, and provided solid proof of Li bonds in Li–S batteries.²⁹ Ever since, Li bond theory has been widely used to explain the nature and behavior of LPSs–AM interactions, and to gain insights into the fundamental Li chemistry in batteries.³⁰

Considering the importance of Li bonds in inhibiting lithium polysulfides shuttling, some interesting questions are naturally raised: what physicochemical features of the AMs are affecting the strength of the Li bonds? Is there any correlation? Answering these questions can provide us with some guidelines in designing cathode materials for Li–S batteries.

To address the above mentioned questions, in this work, we performed systematic density functional theory (DFT) computations to investigate the adsorption behavior of LPSs and S_8 adsorbed on ten different N-containing 2D materials, namely, C_9N_4 ,³¹ C_2N ,³² BN,³³ a covalent triazine framework (CTF),³⁴ $\text{C}_2\text{N}_6\text{S}_3$,³⁵ $g\text{-C}_3\text{N}_4$,^{36–38} $p\text{-C}_3\text{N}_4$,³⁹ C_3N_5 ,^{40,41} $\text{S-N}_2\text{S}$,⁴² and $\text{T-N}_2\text{S}$.⁴³ These candidate anchoring materials are either experimentally available, or have been theoretically identified as experimentally feasible materials. Among them, $\text{C}_2\text{N}_6\text{S}_3$ and C_9N_4 feature Dirac cones, and their good electrical conductivity is rather beneficial for battery electrode materials. It is known that the overall reaction equation of the discharge process in the Li–S battery is $\text{S}_8 + 16\text{Li} \rightarrow 8\text{Li}_2\text{S}$, which involves multiple steps and Li_2S_n as a product in each step.⁴⁴ Herein, we chose Li_2S_n ($n = 1, 2, 3, 4, 6, 8$) to study the adsorption behavior of LPSs on the ten considered AMs. By comparing and analyzing the stable configuration, adsorption energies, and charge transfer, we found that the N-containing pore size, the chemical environment of the N atoms, and the amount of charge transfer contribute to the adsorption strength of Li_2S_n . Our computations identified C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ monolayers as promising anchoring materials, and highlighted the importance of Li bonds when designing cathode materials for Li–S batteries.

2. Computation methods

Spin-polarized density functional theory (DFT) calculations were carried out using the Vienna ab initio simulation package (VASP).^{45–50} The projector augmented wave (PAW) method⁵¹ was used to describe the electron–ion interactions, and the Perdew–Burke–Ernzerhof (PBE)⁵² functional with the Generalized Gradient Approximations (GGA) was adopted for electron–electron exchange correlations. The energy cutoff and k -point mesh were

set to be 500 eV and $5 \times 5 \times 1$, respectively. The geometric structures were optimized with the convergence criteria of the total energy less than 10^{-5} eV and total force less than $0.01 \text{ eV } \text{\AA}^{-1}$ on each atom. A supercell consisting of $5 \times 5 \times 1$ (BN, $\text{S-N}_2\text{S}$, $\text{T-N}_2\text{S}$) or $2 \times 2 \times 1$ (C_9N_4 , C_2N , CTF, $\text{C}_2\text{N}_6\text{S}_3$, $g\text{-C}_3\text{N}_4$, $p\text{-C}_3\text{N}_4$, C_3N_5) unit cells with the lateral dimensions of 12.56–30.28 Å was adopted. A vacuum region of about 25 Å was applied to the z -direction. Previous studies have shown that the van der Waals (vdW) interaction significantly affects the stable adsorption configuration and adsorption energy of Li_2S_n on AMs.^{11,53} Therefore, the D2 method⁵⁴ is adopted to describe the interaction between Li_2S_n adsorption and AMs to obtain more accurate calculation results. The Bader charge analysis^{55–57} was used to evaluate the charge transfer between the LPSs and AMs. The migration energy barrier of Li_2S_n on these 2D materials was determined using the climbing image nudged elastic-band (CI-NEB) method.⁵⁸

Note that the solvent effect is very important in characterizing the performance of Li–S batteries,⁵³ and in our work, the solvent effect might relate to the detection ability of the N-containing monolayers. Considering the general impact of Li bonds on the shuttle effect, and to save the computation cost, the solvent effect was not involved here.

Fig. 1 presents the geometric structures of the examined AMs, Li_2S_n and S_8 ; Table S1 (ESI†) lists the N content (η), pore size (d), and the number of bridge N atoms (m) of each AM, where the η , d and x are defined as the percentage of N atoms, the distance between the two farthest N atoms in the same pore region, and the number of two-coordinated N atoms in one pore region, respectively. The adsorption energy (E_{ad}) of the Li_2S_n on the AMs in our work is defined as follows:

$$E_{\text{ad}} = E_{\text{AM}} + E_{\text{Li}_2\text{S}_n} - E_{\text{tot}} \quad (1)$$

where the E_{tot} , E_{AM} and $E_{\text{Li}_2\text{S}_n}$ are the total energy of Li_2S_n adsorbed on the AM, and the energies of pristine AM and isolated Li_2S_n , respectively. According to this definition, a more positive E_{ad} value indicates a stronger binding strength between the AM and the adsorbate.

3. Results and discussion

3.1. Adsorption of Li_2S_n on 2D AMs

First, we examined the adsorption of Li_2S_n at different sites on each AM, and identified the most stable configurations and calculated the corresponding adsorption energies (E_{ad}), as given in Fig. S1 (ESI†), Fig. 2, 3, and Table 1. For Li_2S_n ($n = 1, 2, 3, 4, 6, 8$) and S_8 (Fig. 2), the BN monolayer has the lowest adsorption energies (0.52–1.28 eV), while the CTF shows the highest adsorption strength ($E_{\text{ad}} = 1.25\text{--}6.45 \text{ eV}$). With the increase of n in Li_2S_n , the adsorption energy generally decreases on all examined AMs: the adsorption energy decreases from Li_2S to the lowest value at Li_2S_6 , and then increases slightly for Li_2S_8 (Fig. 2 and Table 1). A similar trend was found for the adsorption of Li_2S_n on the transition metal oxides/sulfides/chlorides²⁵ and phosphorene.⁵⁹

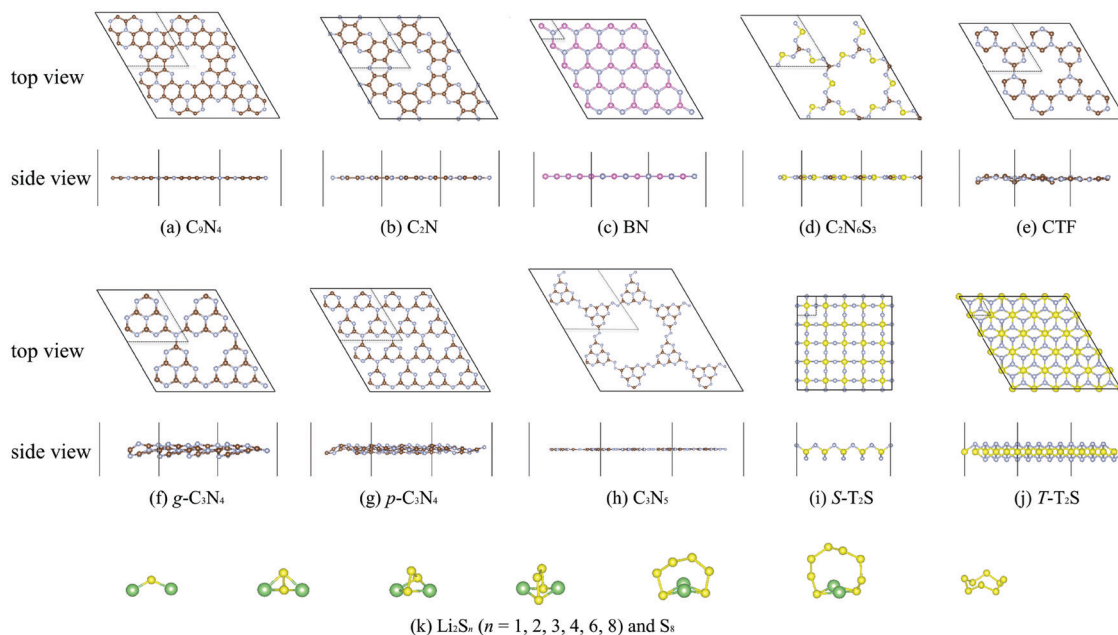


Fig. 1 Structures of 2D AMs (a–j), as well as Li_2S_n and S_8 (k). The black dashed area represents the unit cell. The pink, brown, gray, yellow, and green balls denote boron, carbon, nitrogen, sulfur, and lithium atoms, respectively.

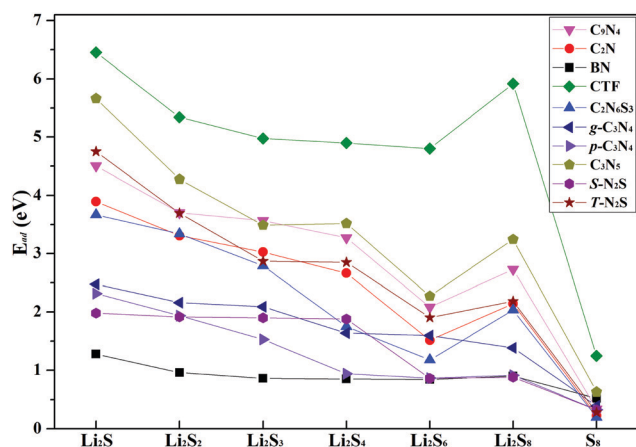


Fig. 2 Adsorption energies of Li_2S_n and S_8 on different AMs.

Then, we carefully analyzed the most stable adsorption configurations of Li_2S_n ($n = 1, 2, 3, 4, 6, 8$) and S_8 on all the examined 2D AMs. For clarity, in the main text, we only presented the energetically most favorable adsorption configurations of Li_2S_n and S_8 on BN and CTF (Fig. 3), while the data for other AMs are given in Fig. S1 (ESI[†]). Note that the BN and CTF monolayers have the lowest and highest adsorption energies towards LPSS among these ten AMs, and thus serve as good representatives.

For all these ten N-containing AMs, Li–N bonds are formed between the Li_2S_n and the AMs upon Li_2S_n adsorption. On one hand, Li_2S_n @BN has the longest Li–N bond lengths, and only one or two Li–N bonds are formed between Li_2S_n and the host, which explains well the lowest LPSS adsorption energies on BN among the examined AMs. Note that such small adsorption energies (0.90–1.28 eV) cannot prevent the migration of Li_2S_n ,

and thus the BN monolayer cannot effectively inhibit the shuttle effect. On the other hand, in the case of Li_2S_n @CTF, which has the largest binding energies towards Li_2S_n , besides Li–N bonds, S–C bonds are also formed between the Li_2S_n and the CTF monolayer. Interestingly, with increasing the S content (n) of Li_2S_n , the number of the S–C bonds also increases (Table S2, ESI[†]), indicating the enhanced adsorption strength between Li_2S_n and the CTF host; however, at the same time, the average Li–S bond length of Li_2S_n ($d_{\text{Li-S}}$) increases with the increasing number of S atoms in the Li_2S_n species (Table 2), suggesting the higher tendency for dissociation of the Li_2S_n species. Therefore, as observed in the case of the CTF, very high Li_2S_n adsorption energies can lead to the dissociation of Li_2S_n species. The above analyses revealed that both BN and CTF monolayers are not good AMs for Li–S batteries, and a medium adsorption energy is significant to inhibit the shuttle effect. Such an adsorption should not be too weak in order to prevent the migration of LPSSs, and also should not be too strong so that the dissociation of LPSSs can be avoided.

The general trend between the Li_2S_n -AM interaction strength and the Li–S bond length of Li_2S_n observed for the two extreme cases (BN and CTF) holds true for all the AMs examined in this study. Due to the electrostatic interaction between the Li_2S_n and the AMs, the Li–N (S–N or S–S) bonds are formed, and simultaneously the Li–S bonds are stretched (by 0.02–0.39 Å) or even broken (Table S3, ESI[†]). The average Li–S bond length and the number of the broken Li–S bonds of the Li_2S_n adsorbed on the ten examined N-containing AMs are presented in Table 2 and Table S3 (ESI[†]).

Carefully examining the data in Tables 1 and 2 indicates that, besides BN and CTF, four of the other monolayers, namely, $p\text{-C}_3\text{N}_4$, $S\text{-N}_2\text{S}$, C_3N_5 , and $T\text{-N}_2\text{S}$, can also be ruled out

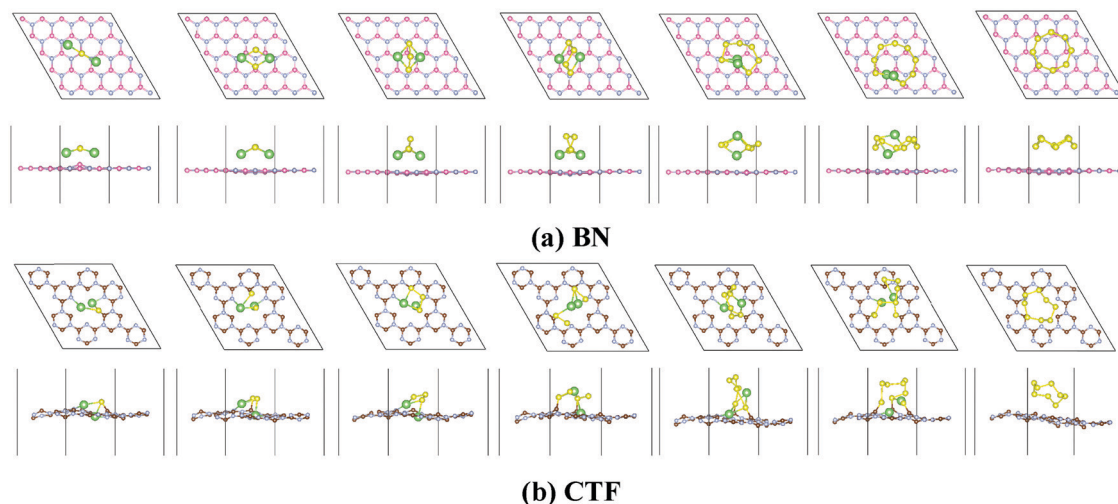


Fig. 3 The most stable adsorption configurations of Li_2S_n and S_8 on the BN (a) and CTF (b) monolayers. Color scheme: B, pink; N, blue; C, brown; Li, green; S, yellow.

as AMs for Li-S batteries. On $p\text{-C}_3\text{N}_4$ and $S\text{-N}_2\text{S}$, the adsorbed Li_2S_n species have similar and intact configurations; however, due to the rather weak adsorption strengths of Li_2S_6 and Li_2S_8 (0.86 and 0.91 eV, respectively, on $p\text{-C}_3\text{N}_4$; 0.86 and 0.88 eV, respectively, on $S\text{-N}_2\text{S}$), the adsorbed Li_2S_n may migrate on these two monolayers. On C_3N_5 , the adsorbed Li_2S_3 and Li_2S_4 , Li_2S_6 , and Li_2S_8 all suffer Li-S bond breaking (the $\text{Li}\cdots\text{S}$ separations range from 2.97 to 4.62 Å). On $\text{T-N}_2\text{S}$, except for Li_2S_3 and Li_2S_4 , Li-S bond breakage occurs for the other four adsorbed Li_2S_n (the $\text{Li}\cdots\text{S}$ distances are in the range of 2.96–4.00 Å, Table S3, ESI[†]); in particular, one S atom dissociates from the Li_2S_2 on the $\text{T-N}_2\text{S}$ surface (Fig. S1, ESI[†]). The dissociation tendency of the adsorbed Li_2S_n suggests that C_3N_5 and $\text{T-N}_2\text{S}$ monolayers are inappropriate AMs for Li-S batteries.

Encouragingly, among the AMs examined in this work, C_2N ($E_{\text{ad}} = 1.52\text{--}3.89$ eV), $g\text{-C}_3\text{N}_4$ ($E_{\text{ad}} = 1.38\text{--}2.47$ eV), C_9N_4 ($E_{\text{ad}} = 2.08\text{--}4.50$ eV), and $\text{C}_2\text{N}_6\text{S}_3$ ($E_{\text{ad}} = 1.18\text{--}3.68$ eV) maintain a balance between the integrity of Li_2S_n and a strong adsorption strength. For the C_2N and $g\text{-C}_3\text{N}_4$ monolayers, our computational results, including the adsorption energies and structural variations of the Li_2S_n adsorption on these monolayers and the general conclusion that both C_2N and $g\text{-C}_3\text{N}_4$ are good AMs for Li-S batteries, agree well with the previous studies.^{17,18} Thus, we will only focus on the other two promising AMs, namely, C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$, in the following sections. Both C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ have medium adsorption energies for LPSS, and the E_{ad} values for specific Li_2S_n species are very close to those on C_2N , which has been proven to be a promising AM for Li-S batteries.¹⁷

Both C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ monolayers can adsorb Li_2S_n species without breaking the integrity of Li-S clusters. It is known that the long-chain Li_2S_n species ($n = 4, 6, 8$) tend to dissociate into smaller clusters.²² However, the adsorption of Li_2S_4 , Li_2S_6 , and even Li_2S_8 (the longest-chain Li_2S_n) on C_9N_4 or $\text{C}_2\text{N}_6\text{S}_3$ monolayers does not break any Li-S bonds (Table 2 and Table S3, ESI[†]). Upon the adsorption of short-chain Li_2S_n species ($n = 1, 2, 3$), the integrity of the Li_2S_n on both C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$

monolayers is well maintained. Interestingly, on the $\text{C}_2\text{N}_6\text{S}_3$ monolayer, in addition to the newly formed Li-N bonds, one S-S bond is formed between each Li_2S_n and the $\text{C}_2\text{N}_6\text{S}_3$ monolayer (the S-S bond length is 2.04, 2.48 and 2.49 Å for $n = 1, 2$ and 3, respectively), and no Li-S bond is broken (except for the adsorption of Li_2S_3 , and one Li-S bond is stretched to 3.68 Å).

In order to investigate whether LPSS can easily dissociate or not on C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$, we calculated the relative energies of “intact” and “decomposed” Li_2S_4 on the surface of C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ (Fig. S2, ESI[†]). The “decomposed” Li_2S_4 on C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ has a higher energy (0.83 and 1.24 eV, respectively) than its “intact” counterpart, indicating that the system of “intact” Li_2S_4 on either the C_9N_4 or $\text{C}_2\text{N}_6\text{S}_3$ monolayer is energetically more favorable. In other words, LPSS are energetically reluctant to dissociate on C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ monolayers.

Good conductivity is an essential requirement of an AM for Li-S batteries, thus we investigated the electronic properties of C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ before and after the adsorption of the LPSS. According to the density of states (DOS) of two AMs before and after the adsorption of LPSS (Fig. S3, ESI[†]), one can see that both AMs retain the metallic feature after the adsorption of the LPSS, and dominate the contribution of the total DOS (TDOS). Therefore, both C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ have excellent electrical conductivity during the whole process of electrode reaction, which will significantly improve the performance of Li-S batteries.

3.2. Migration of Li_2S_6 on C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ monolayers

To give a standard of “weak” and “suitable” adsorption energy, we calculated the migration energy barrier of the LPSSs on the AMs, and Li_2S_6 was taken as the representative on BN, C_9N_4 , $\text{C}_2\text{N}_6\text{S}_3$ and CTF, where BN/CTF has small/large adsorption energy, C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ have medium adsorption energy. Among the three considered migration paths of Li_2S_6 on these AMs (Fig. S4, ESI[†]), path 2 has the lowest barriers (Table S5, ESI[†]), and the migration energy barriers were calculated to be 0.18, 0.81, 0.44 and 2.01 eV (Fig. S5, ESI[†]), respectively, on BN,

Table 1 Adsorption energy (E_{ad}), the average length of the Li–N bond ($d_{\text{Li–N}}$), and the amount of charge transfer (Δq) of Li_2S_n and S_8 on different AMs. Data in parentheses denote the number of Li–N bonds

	Li_2S	Li_2S_2	Li_2S_3	Li_2S_4	Li_2S_6	Li_2S_8	S_8
E_{ad}/eV							
C_9N_4	4.50	3.70	3.57	3.28	2.08	2.73	0.33
C_2N	3.89	3.31	3.03	2.66	1.52	2.14	0.22
BN	1.28	0.96	0.86	0.85	0.84	0.90	0.52
CTF	6.45	5.34	4.98	4.90	4.80	5.92	1.25
$\text{C}_2\text{N}_6\text{S}_3$	3.68	3.34	2.79	1.75	1.18	2.03	0.20
$g\text{-C}_3\text{N}_4$	2.47	2.16	2.09	1.64	1.60	1.38	0.39
$p\text{-C}_3\text{N}_4$	2.32	1.94	1.53	1.25	0.86	0.91	0.33
C_3N_5	5.66	4.28	3.60	3.52	2.27	3.24	0.63
$\text{S-N}_2\text{S}$	1.98	1.92	1.90	1.88	0.86	0.88	0.33
$\text{T-N}_2\text{S}$	4.75	3.70	2.87	2.85	1.90	2.18	0.28
$d_{\text{Li–N}}/\text{\AA}$							
C_9N_4	1.93	1.95	2.02	2.02	2.15	2.03	—
	(4)	(4)	(4)	(4)	(4)	(4)	—
C_2N	1.95	2.04	2.09	2.00	2.17	2.07	—
	(4)	(4)	(4)	(4)	(4)	(4)	—
BN	2.10	2.22	2.26	2.26	2.22	2.14	—
	(2)	(2)	(2)	(2)	(1)	(1)	—
CTF	1.99	2.00	1.99	2.06	2.21	2.04	—
	(2)	(2)	(2)	(1)	(1)	(1)	—
$\text{C}_2\text{N}_6\text{S}_3$	2.03	2.04	2.07	2.08	2.13	2.08	—
	(4)	(4)	(4)	(4)	(2)	(4)	—
$g\text{-C}_3\text{N}_4$	2.00	2.03	2.13	2.34	2.32	2.33	—
	(4)	(4)	(4)	(4)	(2)	(2)	—
$p\text{-C}_3\text{N}_4$	1.98	2.06	2.06	2.14	1.98	2.02	—
	(4)	(4)	(2)	(2)	(1)	(1)	—
C_3N_5	2.02	2.05	2.08	2.07	2.14	2.10	—
	(4)	(4)	(4)	(4)	(4)	(4)	—
$\text{S-N}_2\text{S}$	2.02	2.02	2.11	2.19	2.24	2.18	—
	(2)	(2)	(2)	(2)	(2)	(2)	—
$\text{T-N}_2\text{S}$	2.09	2.15	2.25	2.21	2.25	2.15	—
	(6)	(4)	(6)	(5)	(6)	(5)	—
$ \Delta q / e $							
C_9N_4	1.38	1.21	1.03	1.07	0.80	0.85	0.05
C_2N	1.32	0.97	0.95	0.99	0.71	0.75	0.07
BN	0.39	0.16	0.11	0.10	0.06	0.07	0.04
CTF	1.43	1.05	1.21	0.87	0.93	1.50	0.04
$\text{C}_2\text{N}_6\text{S}_3$	1.19	0.84	0.88	0.89	0.49	0.75	0.10
$g\text{-C}_3\text{N}_4$	0.86	0.60	0.59	0.45	0.28	0.20	0.07
$p\text{-C}_3\text{N}_4$	0.70	0.42	0.19	0.14	0.09	0.12	0.08
C_3N_5	1.51	1.28	1.18	1.19	0.77	1.17	0.10
$\text{S-N}_2\text{S}$	0.99	0.97	0.94	0.86	0.46	0.50	0.16
$\text{T-N}_2\text{S}$	2.08	1.85	1.48	1.60	1.86	2.88	0.20

C_9N_4 , $\text{C}_2\text{N}_6\text{S}_3$ and CTF, which indicates that the AM with the small adsorption energy of LPSSs is “weak” to anchor the LPSSs, while the AM with a medium adsorption energy of LPSSs is “suitable” to hold the LPSSs, in line with the Sabatier principle.⁶⁰

The migration barrier is also related to the diffusion constant (D).⁶¹ According to the formula:⁶² $D \sim \exp\left(\frac{E_a}{k_B T}\right)$, the diffusion constant mainly depends on the value of the migration barrier without an external electric field, where E_a , k_B and T are the migration barrier, Boltzmann constant and temperature, respectively. Typically, the larger migration barrier prevents the diffusion of Li_2S_6 along Paths 1 and 3 on the C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ monolayers. Moderate adsorption energies and migration energy barriers endow C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ with a good adsorption effect on the LPSSs, which is beneficial to inhibit the shuttle effect.

Table 2 Average length of Li–S bonds ($d_{\text{Li–S}}$, in $\text{\AA}$) in free and adsorbed Li_2S_n . Data in parentheses denote the number of Li–S bonds

	Li_2S	Li_2S_2	Li_2S_3	Li_2S_4	Li_2S_6	Li_2S_8
Li_2S_n	2.09	2.23	2.33	2.38	2.40	2.38
	(2)	(4)	(4)	(4)	(4)	(4)
$\text{Li}_2\text{S}_n@ \text{C}_9\text{N}_4$	2.39	2.47	2.51	2.51	2.47	2.69
	(2)	(4)	(3)	(3)	(3)	(4)
$\text{Li}_2\text{S}_n@ \text{C}_2\text{N}$	2.37	2.56	2.46	2.60	2.45	2.43
	(2)	(4)	(3)	(4)	(3)	(3)
$\text{Li}_2\text{S}_n@ \text{BN}$	2.17	2.26	2.36	2.39	2.42	2.42
	(2)	(4)	(4)	(4)	(4)	(4)
$\text{Li}_2\text{S}_n@ \text{CTF}$	2.53	2.46	2.52	2.69	2.62	2.63
	(2)	(3)	(3)	(3)	(4)	(3)
$\text{Li}_2\text{S}_n@ \text{C}_2\text{N}_6\text{S}_3$	2.69	2.45	2.50	2.49	2.49	2.46
	(2)	(4)	(3)	(4)	(4)	(4)
$\text{Li}_2\text{S}_n@ g\text{-C}_3\text{N}_4$	2.23	2.40	2.42	2.53	2.41	2.50
	(2)	(4)	(3)	(3)	(3)	(3)
$\text{Li}_2\text{S}_n@ p\text{-C}_3\text{N}_4$	2.27	2.49	2.40	2.44	2.45	2.43
	(2)	(4)	(4)	(4)	(4)	(4)
$\text{Li}_2\text{S}_n@ \text{C}_3\text{N}_5$	2.56	2.61	2.53	2.61	2.44	2.35
	(2)	(4)	(2)	(2)	(2)	(2)
$\text{Li}_2\text{S}_n@ \text{S-N}_2\text{S}$	2.74	2.51	2.51	2.50	2.48	2.41
	(2)	(4)	(4)	(4)	(4)	(4)
$\text{Li}_2\text{S}_n@ \text{T-N}_2\text{S}$	2.77	2.44	2.58	2.58	2.57	2.77
	(1)	(2)	(4)	(4)	(3)	(1)

Our above analyses indicate that the metallic C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ monolayers are potential AM candidates for Li–S batteries.

3.3. Charge transfer analysis

To gain a deeper insight into the adsorption behavior of Li_2S_n on each AM, we examined the charge density difference and the charge transfer. The BN and CTF AMs were taken as the representatives again, and their charge distributions are displayed in Fig. 4, and the results for other systems are shown in Fig. S6 (ESI†). In general, for a given AM, as the adsorption energy decreases, the charge accumulation region between the Li_2S_n and AM also decreases.

Table 1 summarizes the charge transfer (Δq) between the adsorbates and the AMs. Among all the considered ten AMs, $\text{T-N}_2\text{S}$ has the largest amount of charge transfer with the adsorbed Li_2S_n , while the least charge transfer happens on BN. Upon adsorption, Li_2S_n loses electrons to the AM. In order to analyze the adsorption effect more intuitively, we checked the relationship between the absolute value of the charge transfer and the Li_2S_n adsorption energies as well as the Li–N bond lengths. As shown in Table 1, the greater charge transfer corresponds to a shorter Li–N bond length and a higher adsorption energy with the exception of $\text{T-N}_2\text{S}$ (the average bond length of the Li–N formed on $\text{T-N}_2\text{S}$ is the longest for Li_2S_n ($n = 1, 2, 3, 6$); however, the largest amount of charge transfer contributes to the largest number of Li–N bonds (Table 1) and S–N bonds (Table S4, ESI†)). For example, for the adsorption of Li_2S_n on C_9N_4 and C_2N , the same number of Li–N bonds is formed, while the average Li–N bond lengths (amount of charge transfer) on C_9N_4 are slightly shorter (larger) than for C_2N . As a result, the adsorption energies are slightly larger on C_9N_4 than those on C_2N . To summarize, charge transfer analysis indicates that Δq is related to Li bonds, and corresponds to the adsorption strength. In addition to combining the charge density

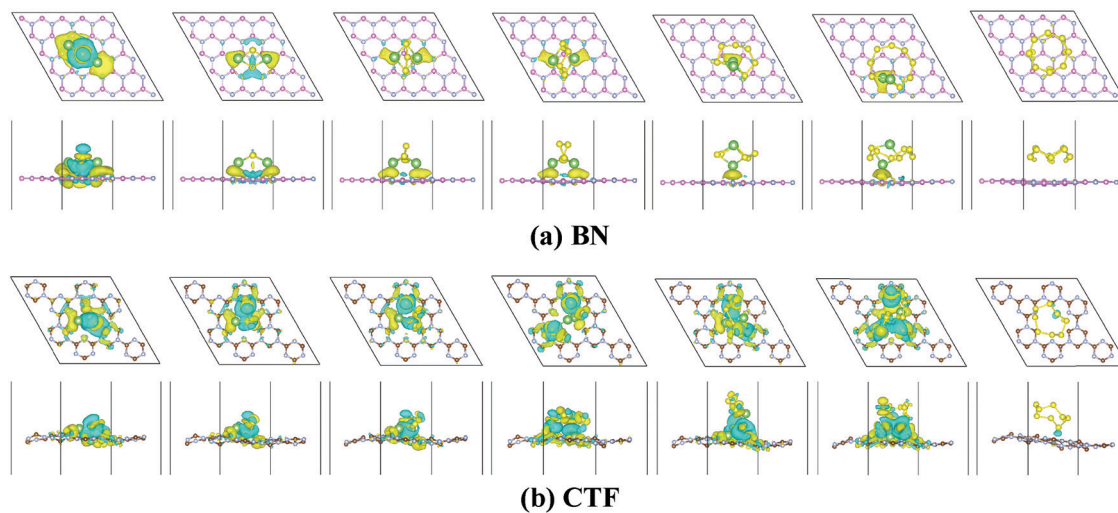


Fig. 4 Charge density difference diagrams of Li_2S_n and S_8 on BN (a) and CTF (b). The yellow and blue regions represent charge accumulation and depletion, respectively.

difference diagrams (Fig. 4 and Fig. S6, ESI†) and the amount of charge transfer (Table 2) to judge the charge distribution of AMS-adsorbed Li_2S_n , the visualized planar average charge density difference can also be used to describe the charge transfer.⁶³

3.4. Effect of the N content and pore size on the Li bonds

Considering that the Li–N bonds correlate with the adsorption strength of the Li_2S_n clusters, and the Li–N bonds are formed at the pore region, we examined the effect of N content and pore size of the N-containing AMs on the Li–N bonds. Fig. 5 illustrates the variation of adsorption energy with the N content and pore size.

The relationship between the N-content and the adsorption energy of the LPSs on the AMs is a bit complicated. For C_9N_4 , C_2N , $\text{C}_2\text{N}_6\text{S}_3$ and $g\text{-C}_3\text{N}_4$, they have the same number of bridge N atoms ($m = 6$) in one pore, and the E_{ad} value for the Li_2S_n species decreases as the N content increases (Fig. 5a). For $g\text{-C}_3\text{N}_4$

and $p\text{-C}_3\text{N}_4$ with equal N contents, the larger pore size of $g\text{-C}_3\text{N}_4$ allows the formation of more Li–N bonds, leading to the stronger adsorption strength. In general, the N content and number of bridge N atoms impacts on the adsorption strength.

Generally speaking, for a given Li_2S_n , the adsorption energy increases as the pore size increases (Fig. 5b), and the abrupt increase for $T\text{-N}_2\text{S}$ is due to the highest number of Li–N and S–N bonds being formed, since it has the largest N content (66.67%); the abnormal jump for CTF can be understood by the S–C bonds formed at the pore region; the deviation for $\text{C}_2\text{N}_6\text{S}_3$ is attributed to the lower charge transfer, which originates from the smaller electronegativity difference of S between $\text{C}_2\text{N}_6\text{S}_3$ and the Li_2S_n .

The effect of pore size on the Li bonds can also be understood by the adsorbed configurations of the Li_2S_n species. As shown in Fig. S1 (ESI†), in general, an AM with a larger pore size provides sufficient space to form more Li–N bonds, thus enhancing the adsorption strength and reducing the Li_2S_n shuttle effect.

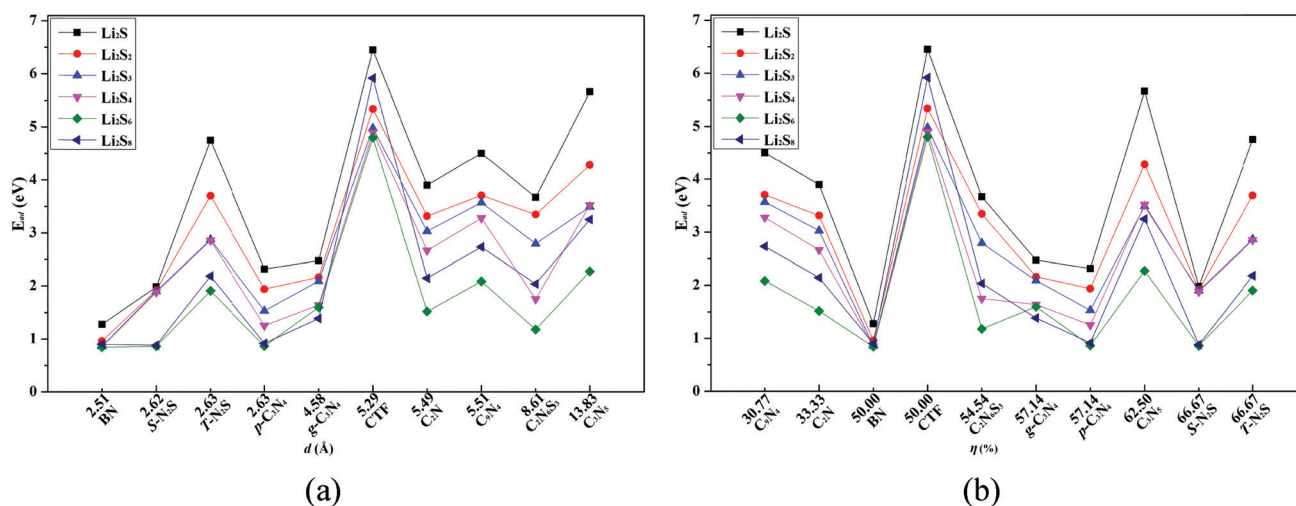


Fig. 5 Variation of the adsorption energy of Li_2S_n ($n = 1-4, 6, 8$) with the N content (a) and pore size (b) of the AMs. The diameters of the pore size and the values of the N contents are given in the x-axis for each AM.

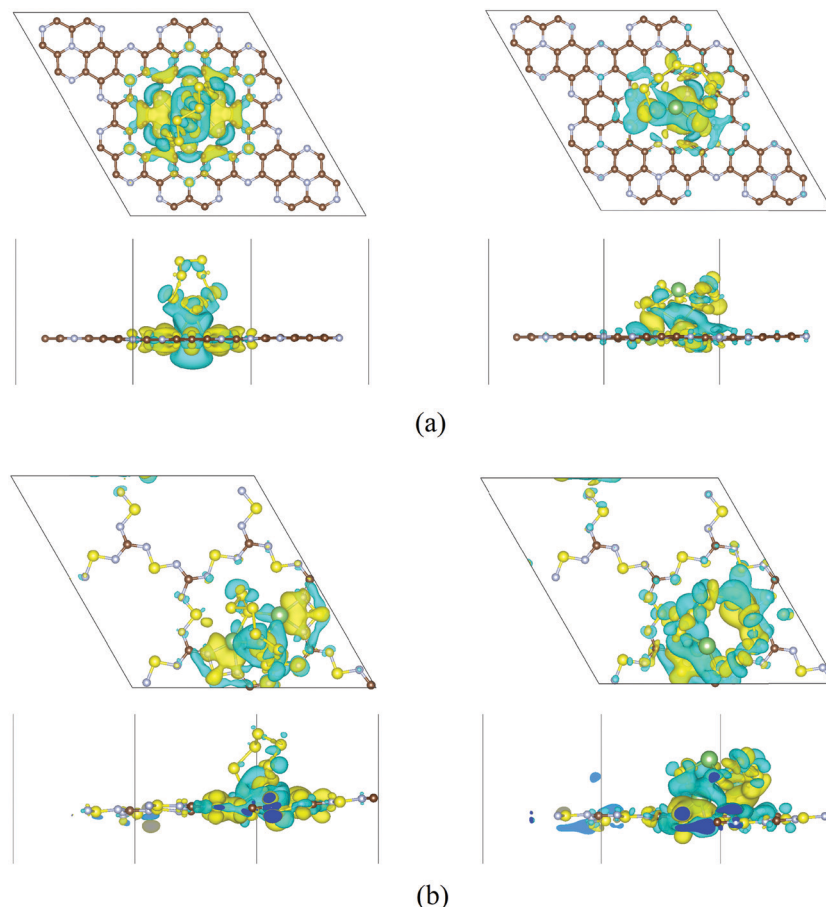


Fig. 6 Charge density difference diagram of Li_2S_8 on non-Li-trapped (left) and Li-trapped (right) C_9N_4 (a) and $\text{C}_2\text{N}_6\text{S}_3$ (b).

We found that there is a quasi-linear relationship between the adsorption energy and the pore size for eight out of the ten AMs examined in this work (except for CTF and $T\text{-N}_2\text{S}$) (Fig. S7, ESI†). The slope decreases from Li_2S to the lowest value for Li_2S_6 , and then increases slightly for Li_2S_8 . This trend is consistent with the variation of adsorption energy as discussed in Section 3.1.

3.5. Adsorption of Li_2S_8 on Li-preadsorbed C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$

The adsorption of Li_2S_n on the AMs involves lots of complicated processes, *e.g.*, Li-trapping in the AMs.^{64,65} Thus, we investigated the effect of trapping one Li atom on the adsorption of the LPSs on the AMs. The C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$ monolayers were chosen as representative AMs due to their distinguished performance, and Li_2S_8 was selected as a delegate of the Li_2S_n since the long chain Li_2S_8 shows a dissociative tendency.

We compared the adsorption behavior of Li_2S_8 on non-/Li-trapped C_9N_4 and $\text{C}_2\text{N}_6\text{S}_3$. Fig. 6 illustrates the energetically most favorable configuration and charge density difference diagram for Li_2S_8 on Li-trapped $\text{C}_9\text{N}_4/\text{C}_2\text{N}_6\text{S}_3$ and pristine $\text{C}_9\text{N}_4/\text{C}_2\text{N}_6\text{S}_3$ monolayers. For the case of Li-trapped $\text{C}_9\text{N}_4/\text{C}_2\text{N}_6\text{S}_3$, charges are accumulated at the Li atom of the Li_2S_8 near $\text{C}_9\text{N}_4/\text{C}_2\text{N}_6\text{S}_3$, the two N atoms of the $\text{C}_9\text{N}_4/\text{C}_2\text{N}_6\text{S}_3$ monolayer, the S atom at the end of the S ring of Li_2S_8 , and the precaptured Li atom. The adsorption energy and amount of

charge transfer of Li_2S_8 on Li-trapped $\text{C}_9\text{N}_4/\text{C}_2\text{N}_6\text{S}_3$ are 1.87/1.46 eV and 0.08/0.17 $|e|$ (Table S6, ESI†) respectively, which are lower than those on the pristine C_9N_4 monolayer ($E_{\text{ad}} = 2.73/2.03$ eV, $\Delta q = 0.85/0.75 |e|$). For Li-trapped $\text{C}_9\text{N}_4/\text{C}_2\text{N}_6\text{S}_3$, the charge of the Li atom precaptured by $\text{C}_9\text{N}_4/\text{C}_2\text{N}_6\text{S}_3$ compensates for the charge of the two S atoms at the end of the S ring in Li_2S_8 , thus the total charge transfer amount of Li_2S_8 is reduced. The adsorption orientation of Li_2S_8 is “parallel” to Li-preadsorbed $\text{C}_9\text{N}_4/\text{C}_2\text{N}_6\text{S}_3$, compared with the “perpendicular” configuration in the pristine $\text{C}_9\text{N}_4/\text{C}_2\text{N}_6\text{S}_3$. Upon adsorption on the Li-trapped $\text{C}_9\text{N}_4/\text{C}_2\text{N}_6\text{S}_3$, the Li-S bond in the Li_2S_8 cluster is shortened from 2.69/2.46 to 2.44/2.35 Å without any dissociation tendency; the Li-N bonds nearly remain the same length (changing from 2.03/2.08 to 2.04/2.11 Å), while the number of Li-N bonds is reduced from 4/4 to 2/2. All these factors correspond to the decrease in adsorption energy. Therefore, it is very likely that the preadsorption of Li is beneficial for effective adsorption of Li_2S_n without dissociating long chain LPSs.

4. Conclusions

By means of comprehensive computations and comparison of the adsorption behavior of Li_2S_n ($n = 1, 2, 3, 4, 6, 8$) on ten N-containing monolayers (BN, C_2N , $\text{C}_2\text{N}_6\text{S}_3$, C_9N_4 , CTF, $g\text{-C}_3\text{N}_4$,

p-C₃N₄, C₃N₅, *S*-N₂S and *T*-N₂S) as anchoring materials (AMs), we found that the Li bonds contribute to inhibiting the shuttle effect in Li-S batteries: the length and number of Li-N bonds are related to the pore size and N content of the 2D N-containing AMs, and correlate with the charge transfer between Li₂S_n and 2D AMs and the adsorption strength of LPSs on the 2D N-containing AMs. Among the ten considered AMs, the C₉N₄ and C₂N₆S₃ monolayers outperform the others as promising AMs for Li-S batteries, due to their metallic feature and “optimal” Li bonds: their moderate adsorption strength, and the “intact” configuration of the adsorbed LPSs, especially for the long chain clusters. Moreover, the porous framework and the high specific surface area of the C₉N₄ and C₂N₆S₃ monolayers will also provide fast ion transport and a broad reaction interface of the sulfur cathode, facilitating the high capacity output and superior rate performance of Li-S batteries. Thus, by taking advantage of Li bonds, we may reduce the notorious polysulfide shuttle effect, and facilitate the rational designing of 2D AMs for Li-S batteries.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (11828401, 11964022) and Startup Project of Inner Mongolia University (21200-5175101), and in the USA by NSF Center for the Advancement of Wearable Technologies (Grant 1849243) and NASA (Grant Number 80NSSC19M0236).

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