

Superior Anchoring of Sodium Polysulfides to the Polar C₂N 2D Material: A Potential Electrode Enhancer in Sodium–Sulfur Batteries

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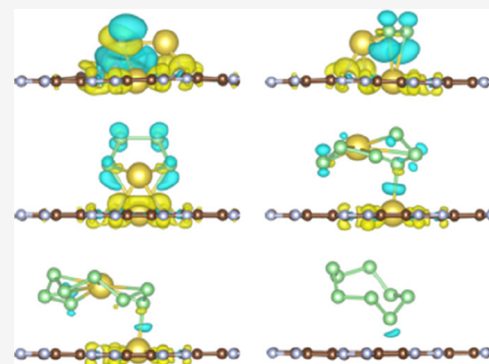


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ABSTRACT: Despite the high theoretical specific energy in rechargeable sodium–sulfur batteries, the shuttle effect severely hampers its capacity and reversibility, which could be overcome by introducing an anchoring material. We, herein, use first-principles calculations to study the low-cost, easily synthesized, environmentally friendly, and stable two-dimensional polar nitrogenated holey graphene (C₂N) and nonpolar polyaniline (C₃N) to investigate their performance as anchoring materials and the mechanism behind the binding to identify the best candidate to improve the performance of sodium–sulfur batteries. We gain insight into the interaction, including the lowest-energy configurations, binding energies, binding nature, charge transfer, and electronic properties. Sodium primarily contributes to binding with the nanosheets, which is in accordance with their characteristics as anchoring materials. Sodium polysulfides (NaPSs) and the S₈ cluster adsorb at the pores of C₂N, where there are six electron lone pairs, one for each N atom. The polar C₂N binds the NaPSs much more strongly than the nonpolar C₃N. In contrast to C₃N, the charge population substantially modifies by adsorbing NaPSs on C₂N, with a substantial charge transfer from the sulfur atoms. The calculated work function of 6.04 eV for pristine C₂N, comparable with the previously reported values, decreases on adsorption of the NaPSs formed from battery discharging. We suggest that the inclusion of C₂N into sulfur electrodes could also improve their issue with poor conductivity.



INTRODUCTION

The damaging effects of nonrenewable energy, like fossil fuels, on humans and the environment have triggered demands of clean renewable energy resources, which has put stress on the existing green energy storage devices like metal-ion (e.g., Li/Na-ion) batteries to keep up with the globe's escalating needs. The low energy density and relatively high cost are other issues limiting the viability of metal-ion batteries for large-scale usage. Lately, alkali metal–sulfur batteries have emerged as a promising option, especially in high energy storage applications. The exceptionally high energy density (2600 Wh/kg) and theoretical specific capacity (1675 mAh/g) of lithium–sulfur batteries are manifold higher than the conventional metal-ion batteries.^{1,2} In addition to higher energy content, low toxicity and comparatively lower operational cost are other salient features associated with this class of batteries.³ However, considering the limited lithium resources in the earth's crust, compared with the more abundant sodium, the utilization of the later could be an economically viable option. Moreover, being a member of the same group, both Li and Na would have similar chemistry. Therefore, sodium–sulfur would be a much cheaper alternative to lithium–sulfur for batteries.^{4,5}

However, the development and commercialization of metal–sulfur batteries are plagued with several critical issues, like large volume expansion, poor electrical conduction of sulfur, and, most importantly, the so-called shuttle effect, where

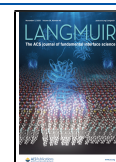
metal polysulfides dissolve into the electrolyte and are transported from the sulfur cathode to the metal anode.⁶ This dissolution of metal polysulfides results in the loss of active materials, and thus the capacity and reversibility of the battery are significantly hampered.⁷ Reduction in the Coulombic efficiency and thermal effects are other pressing issues caused by shuttling of metal polysulfides between the anode and cathode.^{8,9} Therefore, actualization of metal–sulfur batteries relies on the active suppression of the shuttle effect. One of the most effective ways in this regard is the employment of an anchoring material capable of efficiently binding the metal polysulfides.

Two-dimensional (2D) nanostructures have been extensively studied in energy storage applications due to their intriguing properties like large surface area and exceptional structural, electronic, and mechanical properties.^{10–16} Introducing 2D nanostructures not only will help to suppress the shuttle effect by anchoring of metal polysulfides but also can

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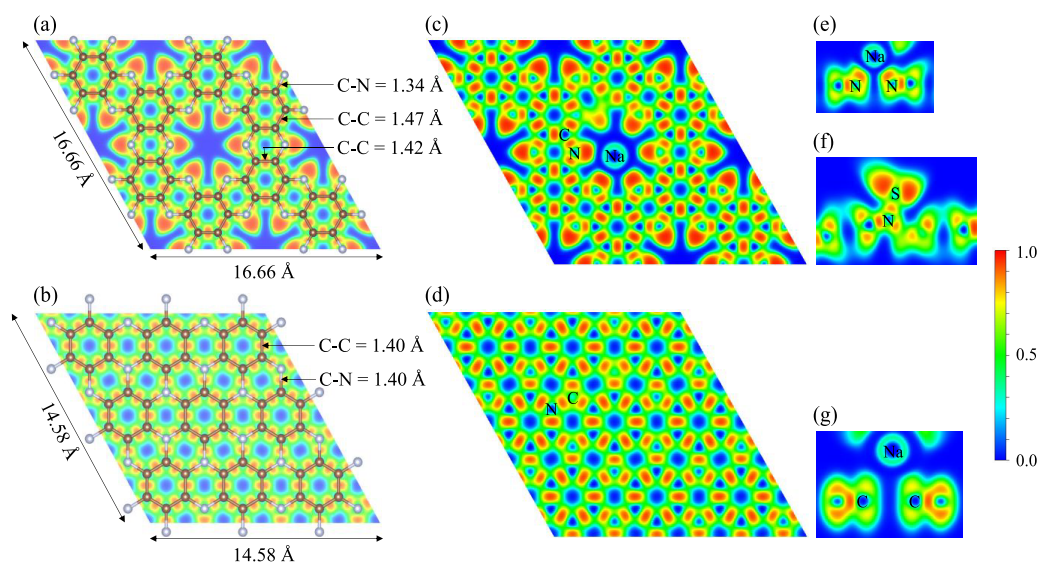


Figure 1. Optimized structure and 2D ELF plots of (a) C_2N and (b) C_3N . Brown and silver spheres represent C and N atoms, respectively. The 2D ELF plots of (c, e, f) Na_2S adsorbed on C_2N and (d, g) Na_2S_2 adsorbed on C_3N . The total in-plane lattice parameters and bond lengths (C–N and C–C) are also indicated.

improve the electric conduction of the sulfur cathode in metal–sulfur batteries. Many recent studies have reported different 2D materials as efficient binders for this purpose for lithium polysulfides. Recently, Li et al. used density functional theory (DFT) calculations combined with the van der Waals (vdW) interaction and solvent models (implicit solvation model and implicit self-consistent electrolyte model)^{17,18} to study the anchoring performance of a novel 2D transition metal–organic framework material, hexaaminobenzene-based coordination polymers (HAB-CPs), concerning intermediate dissolution related to lithium polysulfides.¹⁹ It was found among the studied systems that the vanadium–HAB-CP performed exceptionally well to suppress the shuttle effect in lithium–sulfur batteries. Wang et al. incorporated vdW correction in their DFT simulations to investigate the potential of bare, C- and S-functionalized vanadium carbide as anchoring materials for lithium–sulfur batteries.²⁰ The authors found that V_2CS_2 was the most efficient MXene among the studied systems in binding the polysulfides. Freestanding 1 T MoS_2 /graphene heterostructures, synthesized through a facile one-pot hydrothermal process, are found to be highly efficient electrocatalysts for lithium polysulfides.²¹

Interestingly, very few studies have been conducted to investigate the binding properties of sodium polysulfides (NaPSs), the intermediate products of sodium–sulfur batteries. A handful of combined experimental and theoretical studies report the anchoring characteristics of NaPSs with graphite,⁴ S-terminated $Ti_3C_2T_x$ MXene,²² and bilayer graphene.²³ However, a detailed computational study explaining the intrinsic mechanism of the interaction of NaPSs with anchoring materials is nonexistent. Considering this gap, we have performed first-principles calculations based on DFT to study the anchoring properties of NaPSs (Na_2S , Na_2S_2 , Na_2S_4 , Na_2S_6 , and Na_2S_8) and the S_8 cluster on the experimentally synthesized 2D materials nitrogenated holey graphene (C_2N)²⁴ and polyaniline (C_3N).²⁵ In addition to binding characteristics, structural changes, binding nature, and electronic and charge transfer properties are comprehensively studied.

Computational Details. To explore the anchoring properties of C_2N and C_3N toward the binding of NaPSs, we have performed DFT calculations with the Vienna Ab-initio Simulation Package.²⁶ We have used the generalized gradient approximation exchange–correlation functional of Perdew–Burke–Ernzerhof,²⁷ and plane-wave cutoff energy of 600 eV, using the gamma-centered k-mesh $6 \times 6 \times 1$ ($9 \times 9 \times 1$) for self-consistent (non–self-consistent) calculations. We have employed the empirical DFT-D3 dispersion correction to include vdW interactions.²⁸ The structural relaxation was considered to be converged when the Hellmann–Feynman forces are below 10^{-2} eV/Å for all atoms. We used 2×2 and 3×3 supercells of C_2N and C_3N , respectively, to study the adsorption of the NaPSs and the S_8 cluster. Each model supercell in our study has 72 atoms in the 2D sheet. A vacuum of 20 Å in the out-of-plane direction was used to prevent artificial interactions due to the periodic boundary condition. The binding energies of NaPSs with the commonly used organic electrolytes 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) are also evaluated.

RESULTS AND DISCUSSION

First, we briefly describe the structure of the studied 2D materials. The optimized lattice constant and C–N (two different types of C–C bonds) bond length in the C_2N nanosheet are 8.33 Å and 1.34 Å (1.42 Å and 1.47 Å), respectively. The structure has a uniform distribution of pores and phenyl rings, both surrounded by sp^2 -hybridized N atoms.²⁴ In contrast, the C_3N nanosheet contains only phenyl rings surrounded by sp^2 -hybridized N atoms, such that the optimized lattice constant and C–N (C–C) bond length are 4.86 Å and 1.40 Å (1.40 Å), respectively. These values agree well with those reported previously.^{29–33} The structures and the 2D electron localization function (ELF) for the C_2N and C_3N nanosheets are shown in Figure 1. The ELF shows the in-plane covalent bonding as red regions of localized electrons between the neighboring atoms, in both nanosheets. However, C_2N also has localized electrons (red regions) pointing toward the pores that are electron lone pairs located on the N atoms.

Before finding the suitable binding sites on the nanosheets for the NaPSs and S_8 cluster, it is important to obtain their individual ground-state structure. Figure 2 shows their most

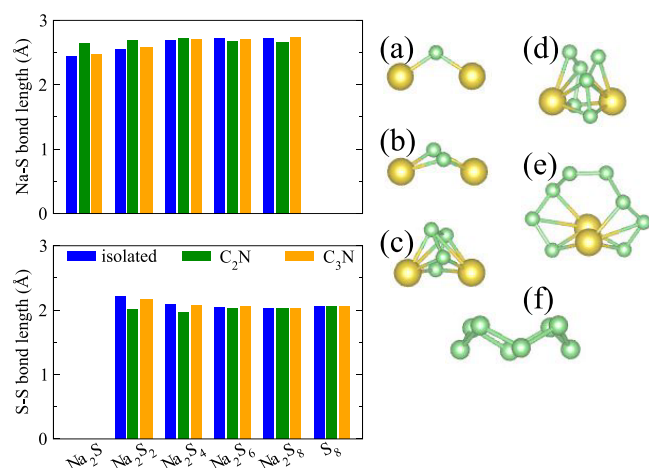


Figure 2. Bond lengths of the isolated and adsorbed NaPSs and S_8 cluster and their relaxed geometries as free species (a) Na_2S , (b) Na_2S_2 , (c) Na_2S_4 , (d) Na_2S_6 , (e) Na_2S_8 , and (f) S_8 . Yellow and green spheres represent Na and S atoms, respectively.

stable geometries and the shortest Na–S and S–S bond lengths in the NaPSs and S_8 cluster. All these species have three-dimensional cluster configurations and are not one-dimensional chains, as is often assumed, which has also been

found in the case of lithium polysulfides.³⁴ As can be seen from the figure, the Na–S bond lengths are getting longer (weaker) with the number of S atoms in the compound, which could play a role in how Na^+ is regenerated from the Na_2S_n series ($n = 1–8$). To find the most stable configuration of the adsorbed Na_2S_n and S_8 cluster, we tried all possible binding sites on the nanosheets C_2N and C_3N with different rotational configurations. The most stable adsorption configurations are shown in Figures 3 and 4, and the corresponding binding energies are reported in Table 1. The binding energy, E_b , has been computed from the energy difference between the adsorbed systems ($E_{nanosheet + NaPSs/S_8}$) and the sum of the pure nanosheet ($E_{nanosheet}$) and isolated Na_2S_n/S_8 species (E_{NaPSs/S_8}), $E_b = E_{nanosheet + NaPSs/S_8} - (E_{nanosheet} + E_{NaPSs/S_8})$. We have used the ELF to determine the nature of binding of the NaPSs and S_8 adsorbed on C_2N and C_3N because ELF is an efficient approach to distinguish between chemical bonding and physical binding.³⁵ We present our findings for Na_2S and Na_2S_2 adsorption on C_2N and C_3N , see Figure 1c–g, but the outlined conclusions are unchanged for the other NaPSs. It can be seen from comparing Figure 1a,c that the absorption of the NaPSs modifies the charge population in the vicinity of the interaction region for C_2N but such modifications of the charge density cannot be seen in C_3N (comparing Figure 1b,d). It is clear that both Na atoms are physically binding with the nanosheets. For C_2N , the NaPSs and S_8 adsorb strongest in and around the pores, which is in line with previous studies of impurity trapping.²⁴ In the case of Na_2S , a S–N covalent bond (1.76 Å) is formed, see Figures 1f and 3a, since the S atom

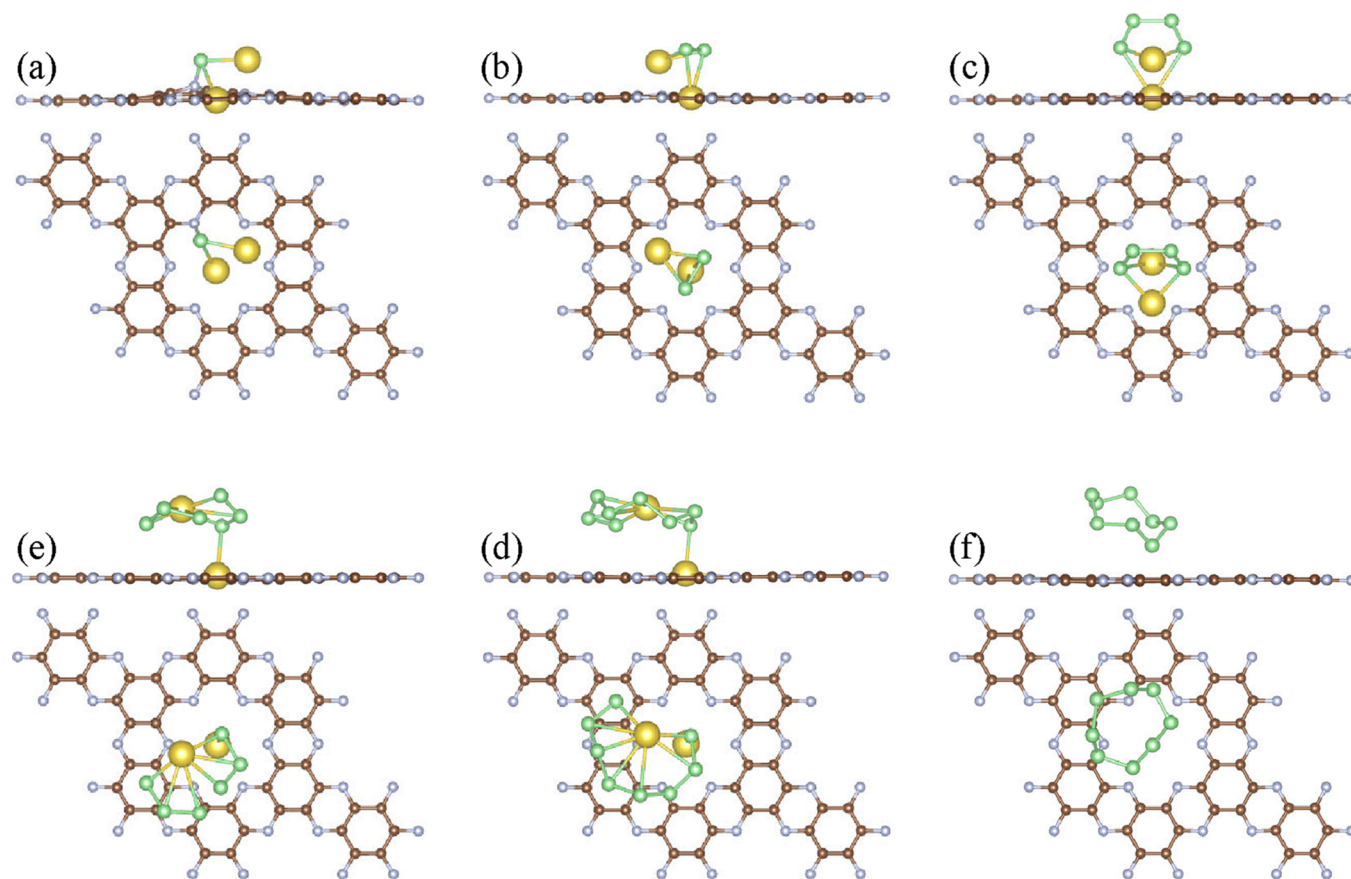


Figure 3. Most stable adsorption configurations on C_2N for (a) Na_2S , (b) Na_2S_2 , (c) Na_2S_4 , (d) Na_2S_6 , (e) Na_2S_8 , and (f) S_8 . Brown, silver, yellow, and green spheres represent C, N, Na, and S atoms, respectively.

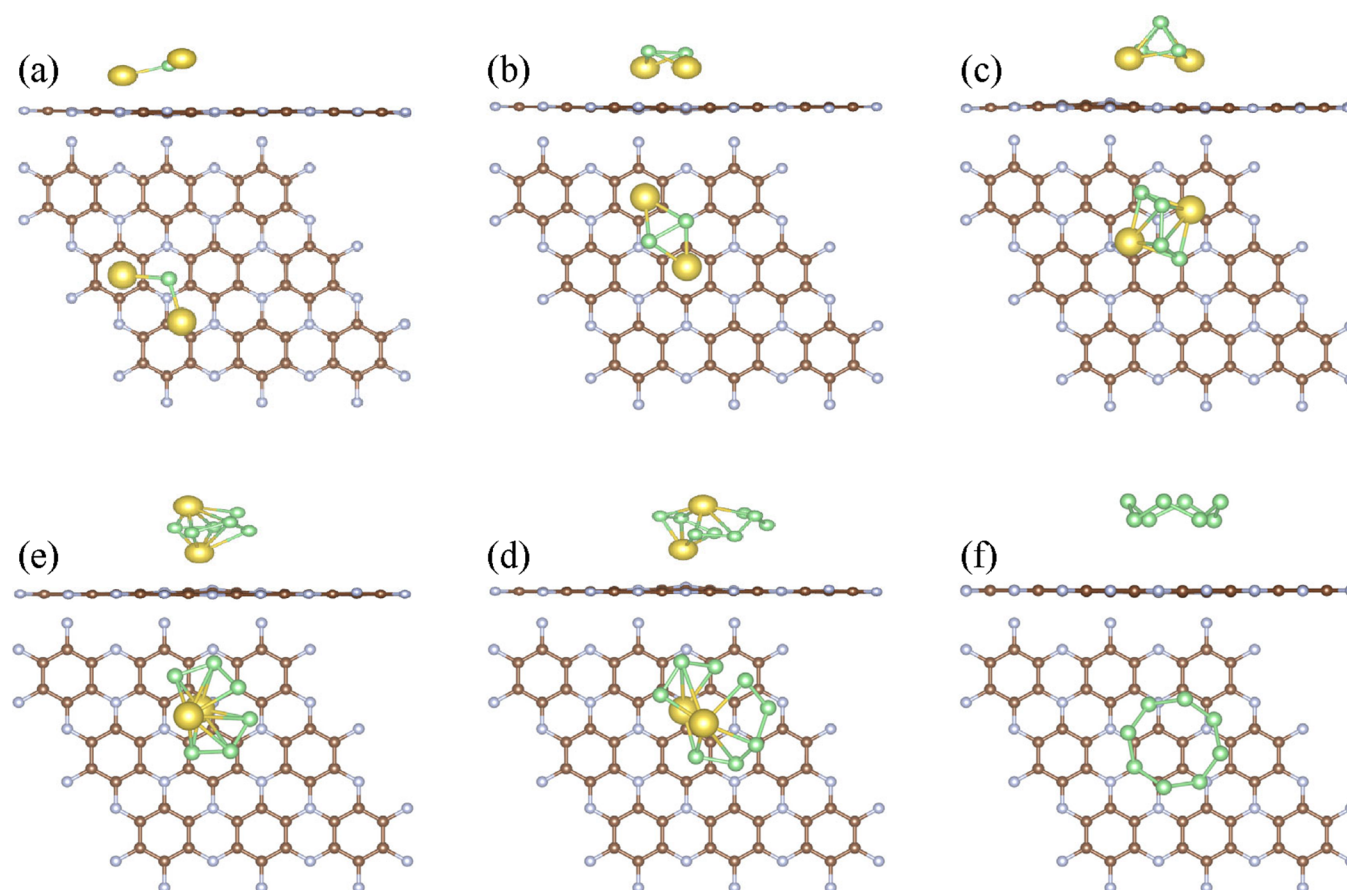


Figure 4. Most stable adsorption configurations on C_3N for (a) Na_2S , (b) Na_2S_2 , (c) Na_2S_4 , (d) Na_2S_6 , (e) Na_2S_8 , and (f) S_8 . Brown, silver, yellow, and green spheres represent C, N, Na, and S atoms, respectively.

Table 1. Calculated Binding Energies (eV) of the NaPSs and S_8 Cluster with the Nanosheets C_2N and C_3N and the Electrolyte Molecules DOL and DME

	Na_2S	Na_2S_2	Na_2S_4	Na_2S_6	Na_2S_8	S_8
monolayer C_3N	−0.56	−0.78	−0.69	−0.53	−0.70	−0.50
monolayer C_2N	−3.09	−3.13	−2.51	−2.39	−2.33	−0.68
bilayer C_2N	−3.11	−3.15	−2.54	−2.41	−2.36	−0.75
DOL	−0.65	−0.82	−0.64	−0.60	−0.65	−0.18
DME	−0.64	−0.88	−0.78	−0.98	−0.42	−0.20

does not have any other neighbors (cf. Na_2S_2 in Figure 3b). The rest of the polysulfides absorb through physisorption via ionic and vdW dispersion binding, as seen from Figure 1c,e,g. For all the NaPSs, one of the two Na atoms resides inside the big pore, and it is in accordance with the characteristics of using it as an anchoring material for which the pores interact with the metal atoms.⁶ The Na atom sitting inside the pore is not precisely at the center but has asymmetric binding distances with the N atoms. In the case of Na_2S_n ($n = 1, 2$, and 4), the second Na atom is physically bound with two neighboring N atoms at the pore rim, which as a result are slightly pulled out from their equilibrium positions (most prominent in the Na_2S case). For Na_2S_2 and Na_2S_4 , the Na $\cdots$ N distances are equivalent (2.55 and 2.61 Å, respectively), but for Na_2S , they are slightly different (2.42 and 2.48 Å). This strong interaction with the pore rim is the cause for the higher binding energies relative to those found for Na_2S_6 and Na_2S_8 , where the second Na atom is only interacting with one N atom

at a considerably longer distance due to steric hindrance by the larger number of S atoms. In contrast, the binding of the Na_2S_n and S_8 cluster to C_3N is substantially weaker. This can be attributed to the polar nature of C_2N ; as clear from Figure 1, each big pore has six N atoms with electron lone pairs, making them efficient for impurity trapping as has also been shown experimentally.²⁴ Therefore, we have found that C_2N is a much better choice compared with C_3N , to effectively retard the shuttle effect during the charging–discharging cycling of sodium–sulfur batteries. The strong binding of the NaPSs on C_2N affects the absorbents, which can be seen in their prominent geometrical distortion compared with that on C_3N (cf. Figures 3 and 4). It is also reflected by the Na–S bond length elongations when bound to C_2N (see Figure 2). The effect is most pronounced for Na_2S and Na_2S_2 and becomes less significant for $n = 4, 6$, and 8, which could be important for Na^+ regeneration. The weakest binding appears for the unsodiated S_8 cluster with a binding energy of 0.68 eV (see Table 1) through vdW dispersion only (see discussion below). Accordingly, it undergoes hardly any geometrical distortion with the S–S bond lengths (2.06 Å) remaining unchanged after adsorption. This is slightly larger than that of the S_8 bound to C_3N (0.50 eV), where it is parallel to the nanosheet while it is tilted toward the pore in C_2N , such that the minimum binding distances are 3.85 and 3.43 Å, respectively. We have found that the bond lengths within the NaPSs do not change significantly after adsorption on C_3N , reflecting their weak binding. Based on the spin-polarized calculations, we found that a negligible amount of total magnetic moment

(0.10–0.32 μ_B) appears for the three cases of Na_2S , Na_2S_2 , and Na_2S_4 adsorbed on C_2N . We have also investigated if the binding strength of the NaPSs is affected by the thickness of the nanosheet with bilayer C_2N . Fortunately, we find that the binding energies are very similar to that of the monolayer (see Table 1) and are even increased by 0.02 to 0.07 eV. For bilayer C_2N , we consider the lowest energy stacking as obtained in refs.^{30,31} and the most stable adsorption configurations are shown in Figure S1.

In sodium–sulfur batteries, during the electrochemical process, the polar electrolytes (DME and DOL) may cause undesirable shuttling of soluble NaPSs. Thus, the binding of the polysulfides with DME and DOL should be weaker than that with the anchoring materials; otherwise, they will dissolve into the electrolytes. The ground-state structural geometries of the NaPSs and S_8 cluster with the electrolytes are given in Figure S2. Table 1 shows that the NaPSs are bound much stronger (more than three times) with the C_2N nanosheet than with the electrolytes. On the other hand, C_3N fails to meet this criterion. Thus, we suggest that C_2N nanosheets would be an efficient anchoring material by limiting the solvation of NaPSs and immobilize them to alleviate the shuttle effect.

Because C_2N outperforms C_3N , we further explored the former nanosheet interaction with the NaPSs and S_8 cluster in depth. To study the charge transfer, we have performed the Bader analysis³⁶ and found that the NaPSs donate the electronic charge of between 0.34 and 1.48 e to C_2N on adsorption (see Table 2). We have found that the charge is

Table 2. Charge Rearrangement (in Electrons, e) on the Constituents of NaPSs/ S_8 Species before (after) Adsorption on C_2N ^a

	ΣS	Na1	Na2	Σ
Na_2S	−1.48 (−0.26)	0.74 (0.86)	0.74 (0.88)	(1.48)
Na_2S_2	−1.72 (−0.76)	0.86 (0.87)	0.86 (0.88)	(0.99)
Na_2S_4	−1.70 (−0.71)	0.85 (0.88)	0.85 (0.86)	(1.03)
Na_2S_6	−1.71 (−1.30)	0.85 (0.88)	0.86 (0.85)	(0.43)
Na_2S_8	−1.70 (−1.39)	0.85 (0.88)	0.85 (0.86)	(0.34)
S_8	(0.01)			(0.01)

^aPlus and minus signs are referred to as charge lost and charge gained. The first column is the sum of charges on the S atoms, and the last column equals the total charge donated to C_2N .

mainly accumulated (depleted) on S (Na) before absorption, whereas it is transferred substantially from the S atoms after absorption such that the charge on Na remains unaltered, except for a 0.12–0.14 e decrease in the case of Na_2S . The charge transfer between the NaPSs and C_2N enables ionic binding, responsible for the high binding energies (−3.09 to −2.33 eV). In the case of the unsodiated S_8 cluster, an insignificantly small charge is transferred, and hence, it has the lowest binding energy (no ionic binding).

Such massive charge transfer from the NaPSs to C_2N leads to considerable changes in their respective charge densities, which can be seen with the help of charge density differences using the relation $\Delta\rho = \rho_{\text{C}_2\text{N} + \text{NaPSs}/\text{S}_8} - (\rho_{\text{C}_2\text{N}} + \rho_{\text{NaPSs}/\text{S}_8})$, where $\rho_{\text{C}_2\text{N} + \text{NaPSs}/\text{S}_8}$, $\rho_{\text{C}_2\text{N}}$, and $\rho_{\text{NaPSs}/\text{S}_8}$ are the electron densities of the adsorbed system, pure C_2N , and isolated NaPSs/ S_8 species, respectively. As can be seen in Figure 5, there is charge rearrangement not only within C_2N and the NaPSs but also between them, and this effect is largest when the charge transfer is largest. Thus, it is most prominent for the

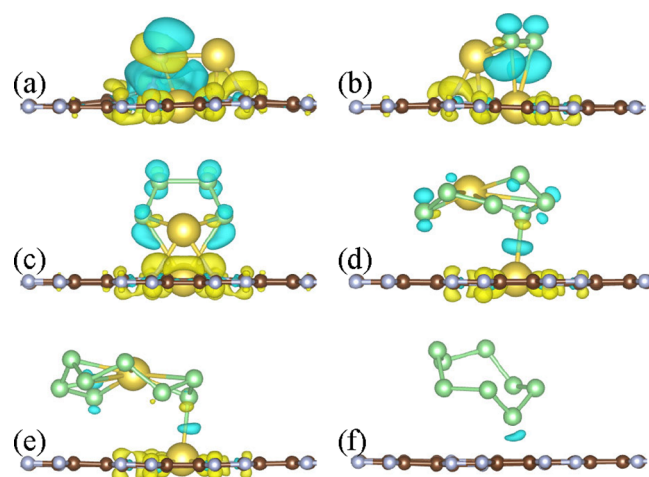


Figure 5. Charge density difference after and before (a) Na_2S , (b) Na_2S_2 , (c) Na_2S_4 , (d) Na_2S_6 , (e) Na_2S_8 , and (f) S_8 adsorbed on C_2N . Yellow and cyan colors correspond to charge accumulation and depletion, respectively. The isosurface value is $3 \times 10^{-3} \text{ e}\text{\AA}^{-3}$.

small NaPSs and is consistent with the higher binding energies (ionic binding). In addition, the charge depletion located along the Na–S bonds show that they are weakened while the accumulation between Na and N is a result of the charge transfer. As expected, the charge density difference (CDD) contribution is smaller for S_8 . However, because CDD has to be computed with the separated constituents at frozen structures from the adsorption, it is known that it can give results that are hard to interpret, especially when the interaction is unusually strong or very weak. For example, the ELF analysis shown in Figure 1c–g is needed to deduce if the polysulfides are bound chemically (only Na_2S) or physically, which is difficult to tell from the CDD analysis.

It is worth mentioning that the adsorption of the NaPSs alters the electronic properties of C_2N , which has been studied through the electronic density of states (DOS). Figure 6 shows the total DOS of pristine C_2N and that with NaPS adsorption. The pristine system has an energy band gap of 1.66 eV, which is consistent with the previously predicted value at the same level of DFT.^{37,38} Concentrating on the DOS, the adsorption of the NaPSs shifts the conduction band states below the Fermi level, causing an n-type doping effect due to charge transferred from the NaPSs to C_2N , as found from the Bader analysis. Among others, poor conductivity of the sulfur cathodes is one of the most critical problems for the realization of efficient metal–sulfur batteries. We have found that C_2N becomes metallic when adsorbed with NaPSs (as observed from the DOS values in Figure 6 a–e). This is very important because C_2N anchoring layers incorporated into the sulfur cathode not only would suppress the shuttle effect but also could improve the conductivity of the sulfur cathode. Thus, C_2N could potentially overcome another unwanted issue in metal–sulfur batteries. No prominent influence on the DOS is observed upon S_8 adsorption, consistent with its weak vdW bonding and small charge transfer. It has already been shown in scanning Kelvin probe microscopy experiments that graphene experiences a substantial shift in the work function after molecular adsorption.^{39,40} To have a deep insight into the electronic properties of C_2N , we calculated the work function (ϕ) of pristine C_2N and that with NaPS adsorption, see Figure 7, using $\phi = V_{\text{vacuum}} - E_F$, where V_{vacuum} and E_F are referred to

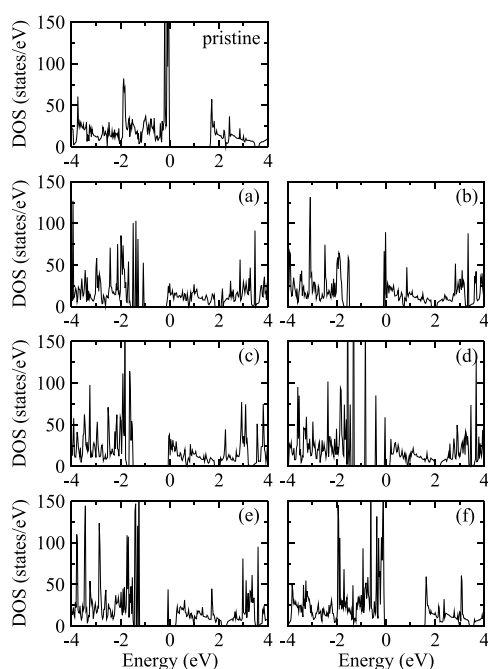


Figure 6. Total DOS of pristine C_2N (top panel) and adsorbed with (a) Na_2S , (b) Na_2S_2 , (c) Na_2S_4 , (d) Na_2S_6 , (e) Na_2S_8 , and (f) S_8 . The Fermi level is set at 0 eV.

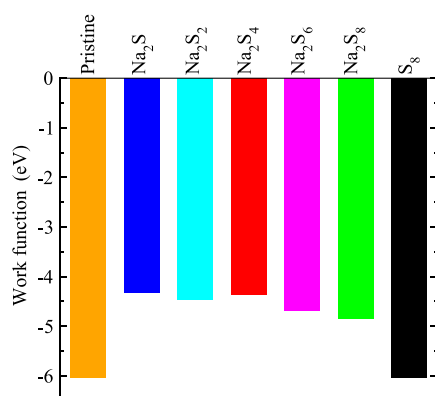


Figure 7. Calculated work functions of the pristine and the polysulfide-adsorbed C_2N nanosheets.

as the electrostatic potential and the Fermi level. V_{vacuum} is calculated from the planar average of the electrostatic potential sufficiently far from the surface along the c -direction. We find that ϕ turns out to be 6.04 eV for pristine C_2N , which is comparable with previously reported values (5.80 eV³⁷ and 6.20 eV⁴¹). The adsorption of NaPSs renders significant changes in the electron density and the occupation due to the charge transfer. Hence, ϕ substantially decreases. In contrast, the S_8 cluster adsorption does not lead to significant changes in ϕ as the charge transfer is minimal (0.01 e).

CONCLUSIONS

The anchoring role of polar C_2N and nonpolar C_3N nanosheets has been investigated by studying the entire sodiation process through computations at the DFT level. We have used the ELF to show that physical binding dominates at all the stages of sodiation except for Na_2S adsorption on C_2N , where a covalent bond is formed between the S atom and an N atom at the pore rim. The polar C_2N outperforms the nonpolar

C_3N in terms of binding strength, which is attributed to more charge transfer to the former nanosheet, that is, between 0.34 and 1.49 e . This results in strong ionic binding contributions with binding energies between -2.33 and -3.09 eV. Bilayer C_2N , instead of the monolayer, improves the anchoring behavior, but the improvement is limited as the binding energies do not increase substantially (0.02 to 0.07 eV). Charge density difference shows that the charge rearrangement occurs in both C_2N and NaPSs and between them. The charge depletion located along with the Na–S bond shows that the bond is softened after adsorption. The adsorption of NaPSs gives rise to n -type doping in C_2N and, hence, could be used to improve the conductivity of the sulfur cathode, whereas the S_8 cluster does not modify the electronic features of the nanosheet. Considering the role of electrolytes, NaPSs weakly bind with DME and DOL than C_2N , suggesting that the NaPSs will not dissolve into these electrolytes. The present study paves the way for a cost-effective C_2N nanosheet as an anchoring material for high-energy and high-capacity sodium–sulfur batteries.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.langmuir.0c02616>.

Most stable adsorption configurations on bilayer C_2N for the sodium polysulfides and binding configurations of the sodium polysulfides with electrolytes (DME and DOL) (PDF).

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Notes

The authors declare no competing financial interest.

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