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Tuning polysulfide adsorption and catalytic activity *via* surface functionalization of Nb₂TiN₂ MXene in Na–S batteries

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Sodium–sulfur (Na–S) batteries are emerging as a promising candidate for large-scale energy storage due to the natural abundance and low cost of sodium and sulfur and their high theoretical energy density. However, the sluggish conversion kinetics of higher-order soluble polysulfides (Na₂S_n, $n > 2$) into lower-order insoluble species (Na₂S₂/Na₂S) lead to severe polysulfide dissolution, insulating discharge products, and rapid capacity fading. MXenes, a type of 2D transition metal carbides and nitrides, are a viable choice for cathode catalysts for Na–S batteries because of their high electrical conductivity and greater affinity towards polysulfides. Hence, in this study, we employ first-principles density functional theory (DFT) calculations to systematically investigate the adsorption characteristics and catalytic behavior of a novel double transition metal (DTM) nitride MXene, Nb₂TiN₂, functionalized with sulfur (S) and oxygen (O) terminal groups (Nb₂TiN₂S₂ and Nb₂TiN₂O₂, respectively). Our results reveal that O-functionalized Nb₂TiN₂O₂ exhibits significantly stronger adsorption of Na₂S_n species, which is expected to mitigate the shuttle effect and improve structural stability compared to its S-functionalized counterpart. Detailed analysis of adsorption energies and charge transfer mechanisms demonstrates that lower-order polysulfides exhibit stronger binding and higher electron transfer on the O-terminated surface. Furthermore, the calculated free energy barriers for the rate-determining step of S reduction reactions are significantly lower on the catalytic surfaces (0.55 eV for Nb₂TiN₂O₂ and 0.75 eV for Nb₂TiN₂S₂), than the barriers for the polysulfides conversion in the gas phase (1.05 eV). These findings suggest that O-functionalization facilitates more favorable reaction kinetics by stabilizing key intermediates and lowering energy barriers compared to S-functionalization. This work provides critical insights for the rational design of advanced cathode hosts to enhance the electrochemical performance and cycle life of Na–S batteries.

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1. Introduction

The growing demand for energy, as well as the environmental damage caused by fossil fuels, underscores the importance of finding sustainable alternatives. Renewable energy sources such as solar and wind provide clean energy; however, their intermittent nature necessitates the development of efficient and cost-effective energy storage systems. Developing such energy storage technology is critical to a sustainable future. Among the available options, rechargeable batteries stand out as the most viable solution to this challenge. Lithium-ion batteries are known for their high energy density. However, the energy density of traditional lithium-ion batteries using insertion-compound cathodes (*e.g.*, LiCoO₂, LiMn₂O₄, and LiFePO₄)

and anode (graphite) is insufficient to meet the needs of electric vehicles and smart grids. As a result, novel battery chemistries are being aggressively investigated.¹

Metal–sulfur (M–S) batteries are attracting increasing interest as next-generation energy storage systems due to their high theoretical specific discharge capacity (1672 mAh g^{−1}), energy density, low cost, and environmental sustainability.^{2–4} Among these, lithium–sulfur (Li–S) chemistry has been extensively explored, with significant advancements achieved over the past decade. However, the high cost, limited availability, and geopolitical concerns surrounding lithium resources limit the scalability of Li–S batteries.^{5–7} From both economic and sustainability perspectives, sodium (Na) presents a more promising alternative to lithium for pairing with sulfur cathodes, owing to its comparable chemical properties and substantially greater natural abundance.⁸ Consequently, Na–S batteries hold strong potential for meeting the energy demands of a wide range of electrochemical applications, particularly large-scale grid energy storage.^{9,10}

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Despite advantages, the performance limiting factors of room temperature Na–S batteries – such as sluggish kinetics, poor rate capability, and rapid capacity degradation limit their practical realization.¹⁰ These issues stem primarily from the shuttle effect and the poor conductivity of sulfur (5×10^{-28} S m⁻¹).¹¹ The former effect reduces the coulombic efficiency, leading to rapid capacity degradation due to the dissolution of soluble polysulfides during the charge and discharge cycles, and the latter slows down the kinetics of the reaction.¹¹ Furthermore, the significant volume expansion of sulfur (170%) disrupts the cathode structure, resulting in low cycle stability.¹² In order to overcome those limitations, it is necessary to develop anchoring materials (AMs) that can trap higher-order polysulfides within the cathode materials and catalyze the polysulfide conversion reactions. This would prevent their dissolution and improve the sluggish kinetics of the reversible conversion of short-chain polysulfides.^{2,13} Various methods have been proposed to address these issues, such as the infusion of sulfur into the carbon matrices,¹⁴ surface coating of sulfur through the introduction of additives into the cathode composition,¹⁵ and optimization of the separators, interlayers, and electrolyte components. While these approaches can hinder polysulfide migration, they remain limited due to the weak chemical interaction between sulfur and nonpolar carbon.

In contrast, polar host materials, which exhibit intrinsic sulfidic properties, form strong chemical bonds with Na₂S_n, effectively preventing polysulfide shuttling. Two-dimensional (2D) materials such as graphene,¹⁶ MoS₂,¹⁷ WS₂,¹⁸ phosphorene,¹⁹ and others have been identified as potential AMs for Na–S batteries due to their high surface-to-volume ratio and tunable electrical properties.²⁰ Another class of 2D materials known as MXenes – with the general formula M_{n+1}X_nT_x – has gained significant attention as potential AMs due to their high electronic conductivity, large surface area rich in active sites, tunable structural properties, and hydrophilicity. Here, M can be a transition metal such as Ti, Cr, V, Mo, or Nb; X can be carbon or nitrogen; and T stands for surface functional groups such as sulfur, oxygen, and fluorine.^{21–24}

MXenes facilitate the efficient conversion of polysulfide intermediates, enhancing reaction kinetics and improving the electrochemical performance of sulfur-based batteries.^{25,26} According to studies, MXenes can mitigate polysulfide dissolution in Na–S batteries by selectively interacting with sulfur species. Surface modification of MXenes can further enhance their ability to retain and trap polysulfides, effectively reducing the unwanted “shuttle effect”.^{24,27–29} For instance, Liang *et al.* investigated the electrochemical performance of Ti₂C(OH)_x/S sulfur electrodes.³⁰ Bao *et al.* suggested using 3D wrinkled S-doped MXene (S-Ti₃C₂T_x) nanosheets as a sulfur host.³¹ Wang *et al.* systematically studied the electrochemical properties and lithium storage performance of various Ti₃C₂ MXenes where O- and S-functional groups co-exist.³² DTM MXenes have recently garnered increased interest in the energy storage domain due to their unique structures, which feature two distinct transition metals at the M site. These

materials are categorized into – ordered DTM MXenes (metals organized in particular layers, either in or out of plane) and solid solution DTM MXenes (metals scattered randomly).^{33–35} Compared to conventional single-metal MXenes like Ti₃C₂O₂ or Ti₃C₂S₂, recently developed ordered DTM-MXenes offer a significantly broader compositional landscape, facilitating tailored electronic, magnetic, and catalytic properties.^{36,37} The presence of two distinct transition metals introduces synergistic effects, including enhanced structural stability and tunable electronic properties. For instance, in contrast to Ti₃C₂T_x, the behavior of Mo₂TiC₂T_x changes from metallic to semiconducting when Ti is substituted with Mo.³⁸ Also, it is reported that Ti₃C₂T_x and other single transition metal MXenes exhibit limited capacity and cycling inefficiencies when used as Li-ion battery anode.^{39,40} Zhou *et al.* found that ordered DTM-MXenes, such as MoWC and MoWCO₂, had considerably higher capacity and stability as an anode in Na-ion batteries. This improvement is due to the synergistic effect of dual-metal sites and the ordered crystal lattice resulting from unique atomic radii, which gives DTM-MXenes a significant advantage over their single-metal counterparts.⁴¹ We previously investigated carbide-based MXenes, including Ti₃C₂X₂ (where X = S, O, F, and Cl)⁴² and Mo₂Ti₂C₂T₂ (T = S and O)²¹ for anchoring Li/Na polysulfides and polyselenides. Beyond carbide MXenes, nitride or carbonitride MXenes, especially those with DTM, offer superior electrochemical performance due to their higher conductivity, faster ion transport, and improved surface wettability, leading to more active sites for reactions.⁴³ However, the research on DTM-nitride and carbonitride MXene is still limited. In our previous research, we reported the discovery of a novel DTM-nitride based MXene functionalized with S group (Nb₂TiN₂S₂), which demonstrated an excellent anchoring ability for Li₂Se_n species in Li–Se batteries.⁴⁴ Building on this, herein, we investigated the binding mechanism and reaction kinetics of Na₂S_n species on both S- and O-functionalized Nb₂TiN₂ MXenes for Na–S batteries.

In this study, we employ first-principles density functional theory (DFT) to investigate the potential of DTM-nitride MXenes – specifically S and O functionalized Nb₂TiN₂S₂ and Nb₂TiN₂O₂ – as AMs for trapping and catalyzing polysulfides in Na–S batteries. We begin by calculating the adsorption energies of various intermediate polysulfides, followed by an analysis of the charge transfer mechanisms through Bader charge calculations. Additionally, we explore the conductive nature of the AM after Na₂S_n adsorption by evaluating the density of states (DOS). To further understand the sulfur reduction reaction (SRR) during the discharge process, we compute and analyze the Gibbs free energy profiles. This study provides a comprehensive theoretical foundation for future experimental research on DTM-nitride MXenes in energy storage applications.

2. Calculation methodology

The Vienna *Ab initio* Simulation Package (VASP) was utilized to perform spin-polarized DFT calculations. The Perdew–Burke–



Ernzerhof (PBE) functional was employed to evaluate the exchange–correlation energy within the generalized gradient approximation (GGA) framework. The Projector Augmented Wave (PAW) method was applied to account for the influence of core electrons on the valence electron density. A plane-wave kinetic energy cutoff of 520 eV was used for the calculations. To incorporate van der Waals (vdW) interactions, the DFT-D3 method with zero damping (IVDW = 11) and empirical dispersion correction was implemented. A vacuum layer of 25 Å was introduced in the out-of-plane direction to eliminate interactions between periodic images. Geometry optimizations were performed using the conjugate gradient method, allowing for atomic relaxation until the forces acting on all atoms were minimized to below 0.025 eV Å^{−1}, with energy convergence achieved below 1 × 10^{−4} eV. The Monkhorst–Pack grid scheme was employed to sample the Brillouin zone for both electronic structure calculations and atomic relaxations. We employed a 3 × 3 × 1 *k*-point mesh for all the adsorption energy calculations and 11 × 11 × 1 *k*-point mesh for all electronic state calculations. Bader charge analysis was conducted to examine charge transfer between Na₂S_{*n*} and the AMs, with the difference in charge density calculated using the specified equation.

$$\rho_b = \rho_{\text{adsorbed state}} - (\rho_{\text{adsorbate}} + \rho_{\text{AM}})$$

where $\rho_{\text{adsorbed state}}$, $\rho_{\text{adsorbate}}$, and ρ_{AM} represent the charge density of the Na₂S_{*n*} adsorbed AM, the isolated polysulfides, and the adsorption material, respectively. The Gibbs free energy (ΔG) for SRR during the Na–S discharge process is calculated as $\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S$, where ΔE represents the adsorption energy and ΔZPE and $T\Delta S$ denote the zero-point energy difference and entropy difference between the gas phase and adsorbed phase, calculated by using VASPKIT⁴⁵ at 298.15 K. The detail procedure for calculating the SRR free energies are described in our previous publications.² The atomic visualization and charge density differences were carried out with the VESTA code.⁴⁶

3. Results and discussion

3.1. Polysulfide adsorption on Nb₂TiN₂T₂ (T = S and O)

During the discharge phase of the Na–S battery, Na reacts with the elemental S₈, leading to the formation of a series of intermediates, specifically Na₂S_{*n*} (where *n* = 1, 2, 4, 6, 8). To investigate the anchoring characteristics of Nb₂TiN₂T₂ (T = S and O), the adsorption energies of both S₈ and the Na₂S_{*n*} species were computed using $E_{\text{ads}} = E_{\text{Na}_2\text{S}_n} + E_{\text{AM}} - E_{\text{Na}_2\text{S}_n+\text{AM}}$, where $E_{\text{Na}_2\text{S}_n}$, E_{AM} , and $E_{\text{Na}_2\text{S}_n+\text{AM}}$ denote the DFT energies of isolated Na₂S_{*n*}, AM, and the polysulfide adsorbed AM, respectively. The Nb₂TiN₂ monolayer has a quint-layer structure, with two nitrogen (N) layers encasing a Ti atomic layer. Niobium (Nb) layers enclose the N layers on the top and bottom surfaces in the order Nb–N–Ti–N–Nb. The Nb₂TiN₂ monolayer underwent structural relaxation, and the optimal lattice constants were found to be $a = b = 3.01$ Å, with a layer thickness of 5.08 Å (ref. 44) (see Fig. S1). Bare MXenes are reported to exhibit signifi-

cantly high adsorption energies, which can lead to the decomposition of polysulfides.^{31,42} To address this, S and O functional groups are introduced on the surfaces of the Nb layer, and their effects on electrochemical performance were investigated. In our previous research on Nb₂TiN₂-MXene with S group, we determined that the adsorption site directly above the N atom was thermodynamically stable. This conclusion was based on calculated formation energy values for N-top site (approximately −6.0 eV), when compared to the other two sites (*i.e.*, specifically above Ti and Nb). Based on this finding, we considered S and O above the N atom sites for Nb₂TiN₂S₂/O₂.⁴⁴

In Nb₂TiN₂ structure, the Nb and Ti atoms are arranged in separate layers, with Nb metal occupying the outer layers and the other Ti metal being filled in the inner layers. Fig. 1 show the relaxed configurations for S₈ and Na₂S_{*n*} adsorbed Nb₂TiN₂S₂/O₂. It is clear that during adsorption, the structures of Na₂S_{*n*} species are preserved. With a minimum spacing of approximately 3 to 3.5 Å, the S₈ adsorbed parallel to the AMs. The distance between the S₈ molecule and the Nb₂TiN₂S₂ and Nb₂TiN₂O₂ surfaces is 3.52 and 3.08 Å, respectively, which is greater than the combined atomic radii of S atoms (1.00 Å). This indicates a weak binding dominated by vdW forces. In contrast, other Na₂S_{*n*} molecules adsorb on Nb₂TiN₂T₂ (T = S and O) with their Na atoms oriented toward the S atoms on the surface. The Na–S distances are shown in Table 1. The Na₂S_{*n*} is found to be adsorbed at the bridging site, where each Na atom forms a strong Na–O (in Nb₂TiN₂O₂) and Na–S (in Nb₂TiN₂S₂) bonds with the substrate. Notably, the atomic radii of Na and S atoms are 1.80 Å and 1.00 Å, respectively. Therefore, the Na₂S_{*n*}–Nb₂TiN₂S₂/O₂ distances are close to the sum of these radii, indicating stronger chemical interactions.⁴⁷ The statement is further supported by the calculated adsorption energies (E_{ads}) of S₈ and Na₂S_{*n*} adsorbed on S and O functionalized MXene (Nb₂TiN₂S₂/O₂), as depicted in Fig. 2. As the sodiation process proceeds, the adsorption energies on both substrates show a gradual rise. In particular, the adsorption strength increases approximately linearly from higher-order (*n* = 8) to lower-order (*n* = 1) polysulfides except for Na₂S₆. A consistent trend we observed in metal–S batteries is that lower-order polysulfides like Na₂S and Na₂S₂ exhibit stronger adsorption on MXene surfaces compared to higher-order polysulfides. The shorter chain lengths result in enhanced electrostatic interactions with the negatively charged surface atoms of MXenes.^{42,48}

To gain deeper insights into the effect of surface terminations, we compared the adsorption energies of Na₂S_{*n*} on S and O-functionalized MXenes. These results indicate that lower-order polysulfides, such as Na₂S and Na₂S₂, exhibit stronger adsorption on the O-terminated surface than on the S-terminated counterpart. Notably, the adsorption energies of Na₂S₂ and Na₂S on Nb₂TiN₂O₂ were found to be 4.33 and 4.23 eV, compared to 3.00 and 3.56 eV on Nb₂TiN₂S₂, respectively. Overall, the O-functionalized MXene shows higher binding affinity towards Na₂S_{*n*} than the S-functionalized one. The significantly higher adsorption energy observed for Nb₂TiN₂O₂ MXenes primarily stems from the higher electronegativity of O



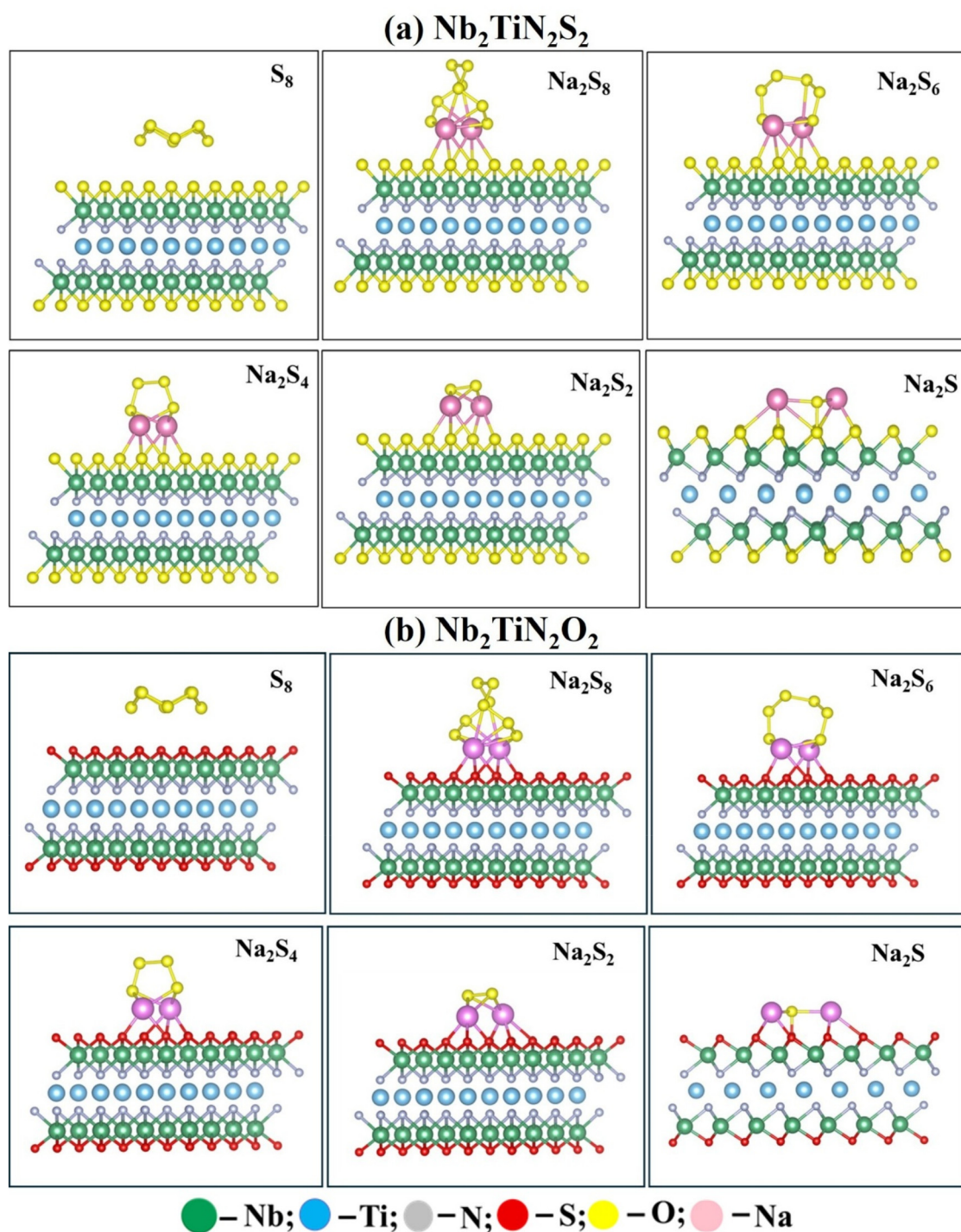


Fig. 1 Optimized geometric configurations of S₈ and Na₂S_n adsorbed on (a) Nb₂TiN₂S₂; (b) Nb₂TiN₂O₂.

compared to S. On the Pauling scale, O and S have electronegativities of 3.44 and 2.58, respectively.⁴⁹ This higher electronegativity means that O atoms more effectively attract electron density from the underlying transition metal MXene framework (such as Nb and Ti), leading to a more negatively charged surface. This increased negative charge enhances electrostatic interactions with the positively charged sodium present in

Na₂S_n species, leading to stronger adsorption. As a result, these interactions reduce the dissolution of polysulfides and provide a mechanism for suppressing the shuttle effect.

To evaluate the effectiveness of Nb₂TiN₂T₂ (T = S and O) in mitigating the shuttle effect, the adsorption energies of Na₂S_n with common electrolyte solvents such as 1,3-dioxolane (DOL) and 1,2-dimethoxymethane (DME) were calculated and com-



Table 1 Calculated variation in the average Na–S bond distance ($\Delta d_{\text{Na-S}}$) in Na_2S_n and the minimum distance between the $\text{S}_8/\text{Na}_2\text{S}_n$ species ($d_{\text{Na}_2\text{S}_n\text{-AM}}$) (in Å) and the $\text{Nb}_2\text{TiN}_2\text{S}_2/\text{O}_2$ substrates

Na_2S_n	$\Delta d_{\text{Na-S}}$		$d_{\text{Na}_2\text{S}_n\text{-AM}}$	
	$\text{Nb}_2\text{TiN}_2\text{S}_2$	$\text{Nb}_2\text{TiN}_2\text{O}_2$	$\text{Nb}_2\text{TiN}_2\text{S}_2$	$\text{Nb}_2\text{TiN}_2\text{O}_2$
S_8	—	—	3.52	3.08
Na_2S_8	3.01	3.07	2.86	2.36
Na_2S_6	2.95	2.88	2.94	2.35
Na_2S_4	2.84	2.93	2.78	2.33
Na_2S_2	2.80	3.17	2.80	2.32
Na_2S	2.78	2.80	2.70	2.34

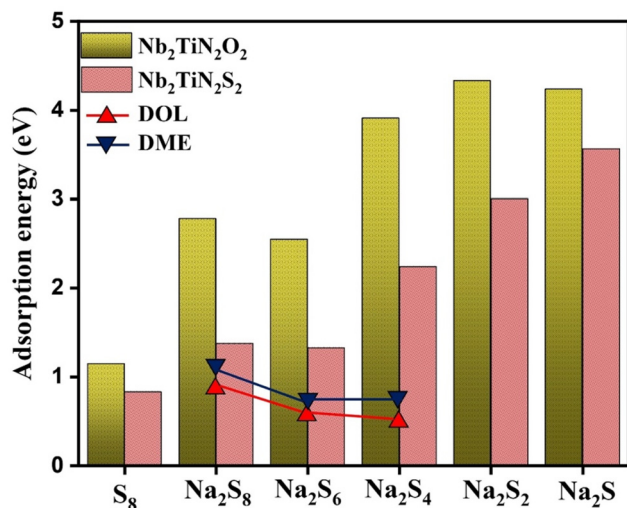


Fig. 2 The calculated adsorption energies of S_8 and Na_2S_n adsorbed on $\text{Nb}_2\text{TiN}_2\text{S}_2$. The binding energies of higher-order Na_2S_n with the electrolyte solvents DOL and DME are taken from ref. 2

pared. The comparatively higher binding energy values with the AMs, as opposed to those of Na_2S_n with DME and DOL, effectively ensure the inhibition of the shuttle effect. The configurations of DOL and DME adsorbed structures, which involve higher-order M_2X_n interactions through a single bond, were previously reported in our previous works.^{50,51} Since $\text{Nb}_2\text{TiN}_2\text{S}_2$ contains transition-metal d orbitals, typically GGA with a Hubbard U correction is necessary to properly account for on-site Coulomb interactions. However, our previous studies on $\text{Mo}_2\text{TiC}_2\text{T}_2$ ($\text{T} = \text{O}, \text{S}$), $\text{Ti}_3\text{C}_2\text{T}_2$ ($\text{T} = \text{O}, \text{S}, \text{F}, \text{Cl}$), VS_2 , and MoS_2 have demonstrated that inclusion of U parameters has a negligible effect on the binding energies of polychalcogenides.^{2,21,42,51} To further assess this effect, we calculated the polysulfides binding energies on $\text{Nb}_2\text{TiN}_2\text{S}_2$ ($\text{T} = \text{O}, \text{S}$) using $U = 4.0$ eV for Ti and 2.0 eV for Nb, consistent with prior studies.^{52–54} As shown in Fig. S2, the results demonstrate that incorporating U parameters has an insignificant influence on polysulfide interactions. Therefore, we conclude that the PBE functional without U corrections is adequate to describe Na_2S_n adsorption on $\text{Nb}_2\text{TiN}_2\text{S}_2$ surfaces. To further examine solvation effects, we performed simulations using the conti-

num solvation model in VASPsol considering the dielectric constant of DME ($\epsilon = 7.2$). The results are presented in Fig. S3 reveal that implicit solvation has a negligible effect on the predicted polysulfide binding energies on $\text{Nb}_2\text{TiN}_2\text{S}_2$ ($\text{T} = \text{O}, \text{S}$). Therefore, we find that gas-phase calculations are sufficient to describe polysulfide interactions.

Although the predicted adsorption energies of sodium polysulfides on DTM-MXenes are relatively high—raising potential concerns about strong adsorption and hindered SRR kinetics—literature evidence indicates that these values remain within the desirable range. According to the Sabatier principle, adsorption should be neither too weak (leading to polysulfide shuttling) nor too strong (causing site poisoning). In our study, the reported binding energies fall within this optimal window. For example, Nahian *et al.* reported comparable binding energies (~ 4.0 – 4.5 eV) for lower-order polysulfides (Na_2S_2 and Na_2S) on $\text{Mo}_2\text{TiC}_2\text{O}_2$ surfaces, which yet correlated with enhanced SRR activity.²¹ Similarly, Deng *et al.* found binding energy values in the range of 3–7 eV for metal-MOF centres.⁵⁵ Recently, Song *et al.* reported Na_2S_4 binding energies up to 7.53 eV for Fe- N_x catalysts for Na–S batteries with enhanced sulfur utilization (81.4% at 167.5 mA g^{-1}), superior rate performance ($1003.0 \text{ mAh g}^{-1}$ at 1675 mA g^{-1}), and stable long-term cycling (83.5% retention over 450 cycles).⁵⁶ Additionally, our computed reaction free-energy profile clearly demonstrates that SRR occurs more effectively on DTM MXenes than under vacuum conditions. Together, these results confirm that the adsorption energies reported here are not expected to retard SRR.

3.2. Charge transfer analysis for the polysulfides adsorption on $\text{Nb}_2\text{TiN}_2\text{O}_2$ and $\text{Nb}_2\text{TiN}_2\text{S}_2$

To examine the charge transfer process during the adsorption of S_8 and Na_2S_n species on $\text{Nb}_2\text{TiN}_2\text{S}_2/\text{O}_2$ substrates, Bader charge analysis was conducted, and the results are shown in Fig. 3. This electron transfer is critical for understanding binding strength and covalent interactions between Na_2S_n and the AM. The positive charge transfer values indicate electron transfer from S_8 and Na_2S_n species to the AMs. Our results showed a clear pattern of increased charge transfer from S_8 to lower-order polysulfides (Na_2S), indicating stronger interactions as the polysulfide chain shortens. An exception to this trend occurs with Na_2S_6 on $\text{Nb}_2\text{TiN}_2\text{O}_2$, where the charge transfer ($\sim 1.1e$) is slightly lower than that of Na_2S_8 ($\sim 1.29e$). The charge transfer from S_8 to $\text{Nb}_2\text{TiN}_2\text{S}_2$ ($0.145e$) and $\text{Nb}_2\text{TiN}_2\text{O}_2$ ($0.26e$) is relatively low in both cases, indicating a weak electrostatic interaction between the S_8 molecule and the substrate. The minimal charge redistribution indicates that physisorption takes precedence over strong chemisorptive binding, indicating a limited adsorption strength of S_8 on both surfaces. However, the O-functionalized $\text{Nb}_2\text{TiN}_2\text{O}_2$ surface has slightly greater charge transfer, indicating stronger adsorption compared to the S-functionalized counterpart. This is likely owing to enhanced electronic affinity introduced by the O-terminal groups.



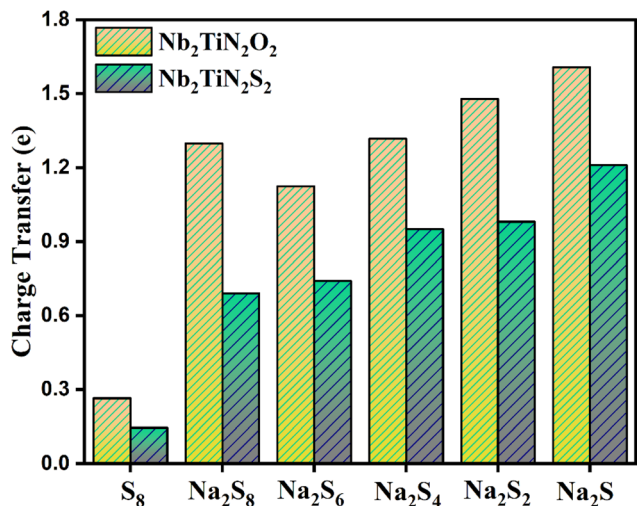


Fig. 3 Computed charge transfer for S₈ and Na₂S_n adsorbed on Nb₂TiN₂S₂/O₂.

Across all sulfur species investigated, Nb₂TiN₂O₂ consistently exhibits a higher degree of charge transfer compared to Nb₂TiN₂S₂. Specifically, for higher-order polysulfides such as Na₂S₈ and Na₂S₆, the charge transfer on Nb₂TiN₂O₂ is approximately 1.29|e| and 1.13|e|, respectively, which is markedly higher than the corresponding values of ~0.69|e| and ~0.74|e| observed for Nb₂TiN₂S₂. This trend continues through the intermediate species Na₂S₄ and Na₂S₂, where Nb₂TiN₂O₂ exhibits charge transfer values of 1.30|e| and 1.50|e|, respectively, in con-

trast to 0.95|e| and 0.98|e| observed for Nb₂TiN₂S₂. The disparity becomes most pronounced with Na₂S, for which Nb₂TiN₂O₂ reaches a peak charge transfer of ~1.60|e|, significantly surpassing the ~1.20|e| observed on Nb₂TiN₂S₂. Higher charge transfer indicates a stronger electronic coupling between Nb₂TiN₂O₂ and Na-polysulfides, which leads to improved adsorption and catalysis during electrochemical processes.

This conclusion is reinforced by the differential charge density analysis as shown in Fig. 4. The figure illustrates various Na₂S_n (Na₂S₈, Na₂S₆, Na₂S₄, Na₂S₂, Na₂S) adsorbed on the Nb₂TiN₂S₂/O₂ catalyst, with yellow regions indicating charge accumulation and cyan regions showing depletion. Our findings reveal that charge transfer from the Na₂S_n species to the catalyst was primarily driven by S atoms rather than metal ions in both the O and S functionalized substrates, which emphasizes the specific mechanism behind this interaction. This aligns with our previous research on Na-S battery systems employing Mo₂TiC₂S₂ MXene as an AM.² Furthermore, the extent of charge transfer is found to be more pronounced on the O-functionalized substrate than on the S-functionalized one, which corroborates the stronger electronic interactions and affinity of S atoms in polysulfides towards the more electronegative O-functionalized AM. Overall, Nb₂TiN₂O₂ demonstrates a stronger binding than Nb₂TiN₂S₂ as revealed through the charge transfer analysis.

3.3. Sulfur reduction reaction (SRR)

During the discharge process of Na-S batteries, we investigated the complete reaction pathway, including the formation of

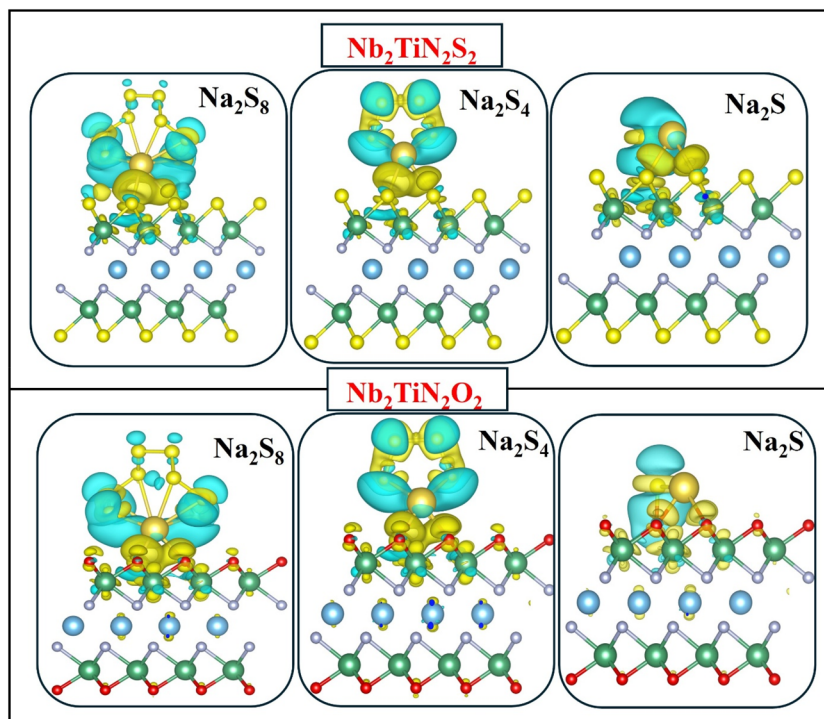


Fig. 4 Charge density differences of Na₂S₈, Na₂S₄ and Na₂S on Nb₂TiN₂S₂/O₂. The isosurface level is set at 0.001 e Å⁻³.



Na_2S_n from S_8 and bulk Na, to gain insight into the SRR kinetics on $\text{Nb}_2\text{TiN}_2\text{S}_2$ and $\text{Nb}_2\text{TiN}_2\text{O}_2$ surfaces. We computed the free energy change (ΔG) for each intermediate reaction step, both in the gas phase and on $\text{Nb}_2\text{TiN}_2\text{S}_2/\text{O}_2$ substrates. By determining the extent to which the $\text{Nb}_2\text{TiN}_2\text{S}_2/\text{O}_2$ surface reduces energy barriers and stabilizes important intermediates in comparison to the gas phase baseline, this comparative analysis enabled us to evaluate the catalytic efficacy of the substrates. In Na–S batteries, the conversion of high-order soluble polysulfides to low-order insoluble polysulfides is often limited by sluggish reaction kinetics, which contributes to the polysulfide shuttling effect.⁵⁷ Fig. 5 illustrates the ΔG profile along the reaction pathway from S_8 to Na_2S . It is evident from the figure that the initial step, involving the reduction of S_8 to Na_2S_8 , is spontaneously exothermic in all three cases, with the ΔG values calculated as -4.28 eV in the gas phase, -4.93 eV on $\text{Nb}_2\text{TiN}_2\text{S}_2$, and -5.05 eV on $\text{Nb}_2\text{TiN}_2\text{O}_2$. Similarly, the conversion of Na_2S_8 to Na_2S_6 is also exothermic, with ΔG values of -0.05 eV and -0.01 eV on S and O-functionalized surfaces, respectively. In contrast, the same step is uphill in the gas phase with a positive ΔG of 0.14 eV. Furthermore, the Na_2S_6 to Na_2S_4 conversion shows an increasing trend in free energy in the gas phase (ΔG rising from 0.14 to 0.82 eV), whereas it proceeds spontaneously with negative ΔG values on both $\text{Nb}_2\text{TiN}_2\text{S}_2$ (-0.19 eV) and $\text{Nb}_2\text{TiN}_2\text{O}_2$ (-0.57 eV) AMs. Between the two AMs, the O-functionalized surface demonstrates faster reaction kinetics, as evident from the lower energy barriers.

Since Na_2S_4 is a soluble liquid-phase species and Na_2S_2 precipitates as an insoluble solid product,⁵⁸ the conversion of Na_2S_4 to Na_2S_2 emerges as the rate-determining step. This step exhibits ΔG values of 0.75 eV and 0.55 eV on S and O-functionalized surfaces, respectively, indicating a transition from exothermic polysulfide conversion reactions to endothermic behavior depending on the surface chemistry. Though

both functionalized materials effectively promote the early stages of polysulfide conversion, a kinetic bottleneck arises at this critical step, which limits the overall reaction rate and battery performance. However, compared to the gas phase, the $\text{Nb}_2\text{TiN}_2\text{S}_2$ surface reduces the energy barrier for the Na_2S_4 to Na_2S_2 conversion by 48%, and $\text{Nb}_2\text{TiN}_2\text{O}_2$ achieves an even greater reduction of 66%, highlighting their significant role in enhancing the electrochemical performance of the Na–S system. The final conversion step from Na_2S_2 to Na_2S exhibits an uphill trend in the free energy profile, indicating an endothermic process across all three phases. The positive ΔG associated with this step suggests that it is non-spontaneous and requires an external thermodynamic driving force to proceed. This behavior may arise from the relative stabilization of Na_2S_2 intermediates or the comparatively weaker interaction of Na_2S with the AM. Overall, the SRR is more thermodynamically favorable in the presence of AMs than under gas-phase conditions. Among the two functionalized surfaces, the O-terminated Nb_2TiN_2 consistently outperforms the S-functionalized counterpart by more effectively lowering the activation barriers at each intermediate stage, thereby promoting faster SRR kinetics during the Na–S battery discharge. We calculated the Gibbs free energies for all reaction steps on $\text{Nb}_2\text{TiN}_2\text{S}_2/\text{O}_2$ substrates and then compared them to gas phase data (Fig. 5). A detailed description of the Gibbs free energy calculation methodology can be found in our previous study.²

3.4. Electronic structure analysis

For the Na–S system on a $\text{Nb}_2\text{TiN}_2\text{S}_2/\text{O}_2$ substrate, partial density of states (PDOS) analysis provides important information on the electronic structure and interactions in the system. Fig. 6 and 7 show a detailed understanding of PDOS for S_8 and Na_2S_n on a $\text{Nb}_2\text{TiN}_2\text{S}_2$ and $\text{Nb}_2\text{TiN}_2\text{O}_2$ substrate, respectively. For S-functionalized MXene, significant electronic states are present in the system at the Fermi level, suggesting that metallic behavior and strong electronic conductivity are two essential components needed for improving charge transfer in Na–S batteries. The extent of orbital overlap between the Na–S system and AM was assessed by examining PDOS contributions from S(3p), Ti(3d), Nb(4d), and N(2p) atoms. PDOS analysis was performed for each polysulfide (both soluble and insoluble) and observed that key contributions near the Fermi level arise primarily from the Ti-3d orbitals, suggesting Ti's dominant role in determining the electronic properties of the system. In addition, Nb-4d orbitals also contribute near the Fermi level, indicating the importance of this Nb atom in shaping the overall electronic structure and establishing covalent interactions with S atoms. When Na_2S_n is adsorbed, peaks appear below the Fermi level, indicating charge transfer from Na_2S_n to $\text{Nb}_2\text{TiN}_2\text{S}_2$. This transfer is primarily attributed to the hybridization between the p orbitals of Na and S.

For the O-functionalized counterpart, $\text{Nb}_2\text{TiN}_2\text{O}_2$, a similar metallic character is retained post Na_2S_n adsorption. However, in this case, the PDOS reveals a dominant contribution from the Nb-4d orbitals, accompanied by nearly equivalent contri-

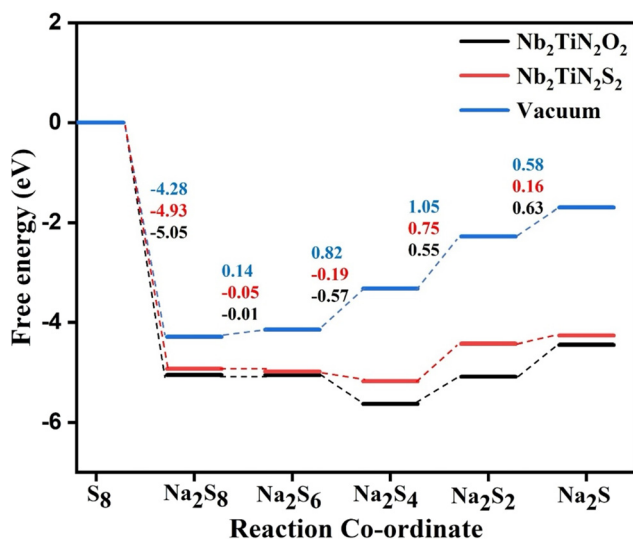


Fig. 5 Gibbs free energy profile of sulfur reduction reaction in vacuum and on $\text{Nb}_2\text{TiN}_2\text{S}_2/\text{O}_2$.



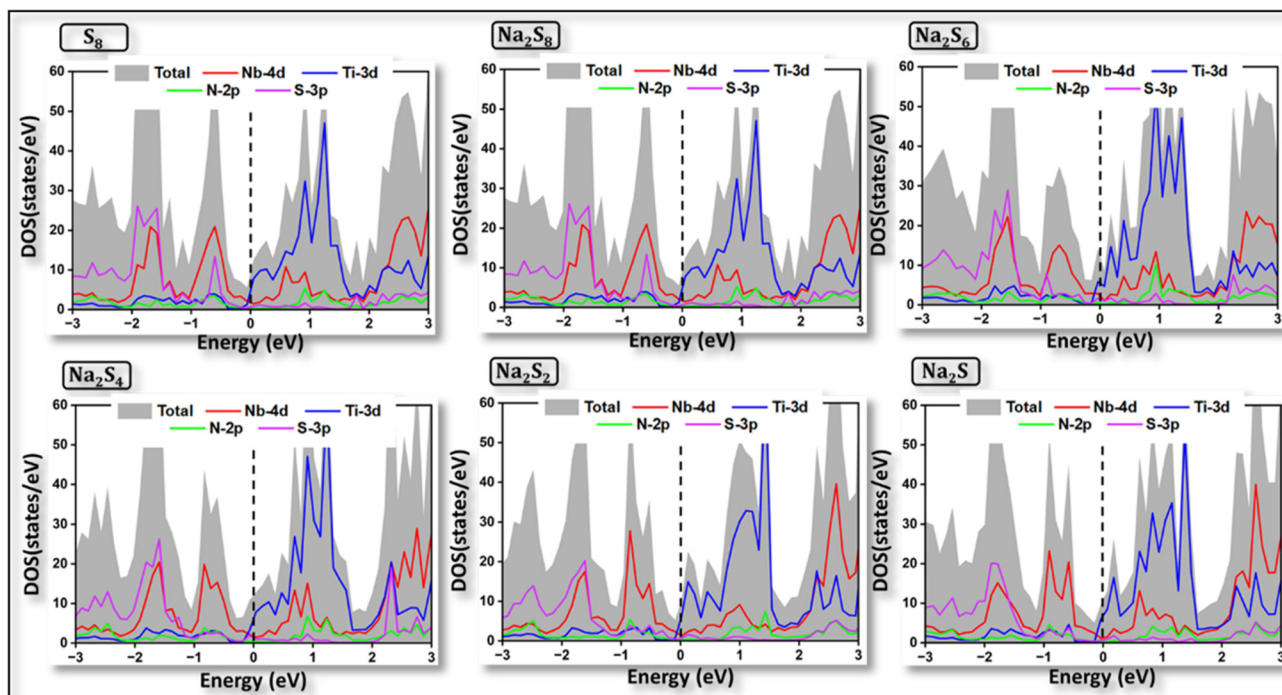


Fig. 6 PDOS of S_8 and Na_2S_n adsorbed on $Nb_2TiN_2S_2$. The Fermi level is denoted by vertical lines.

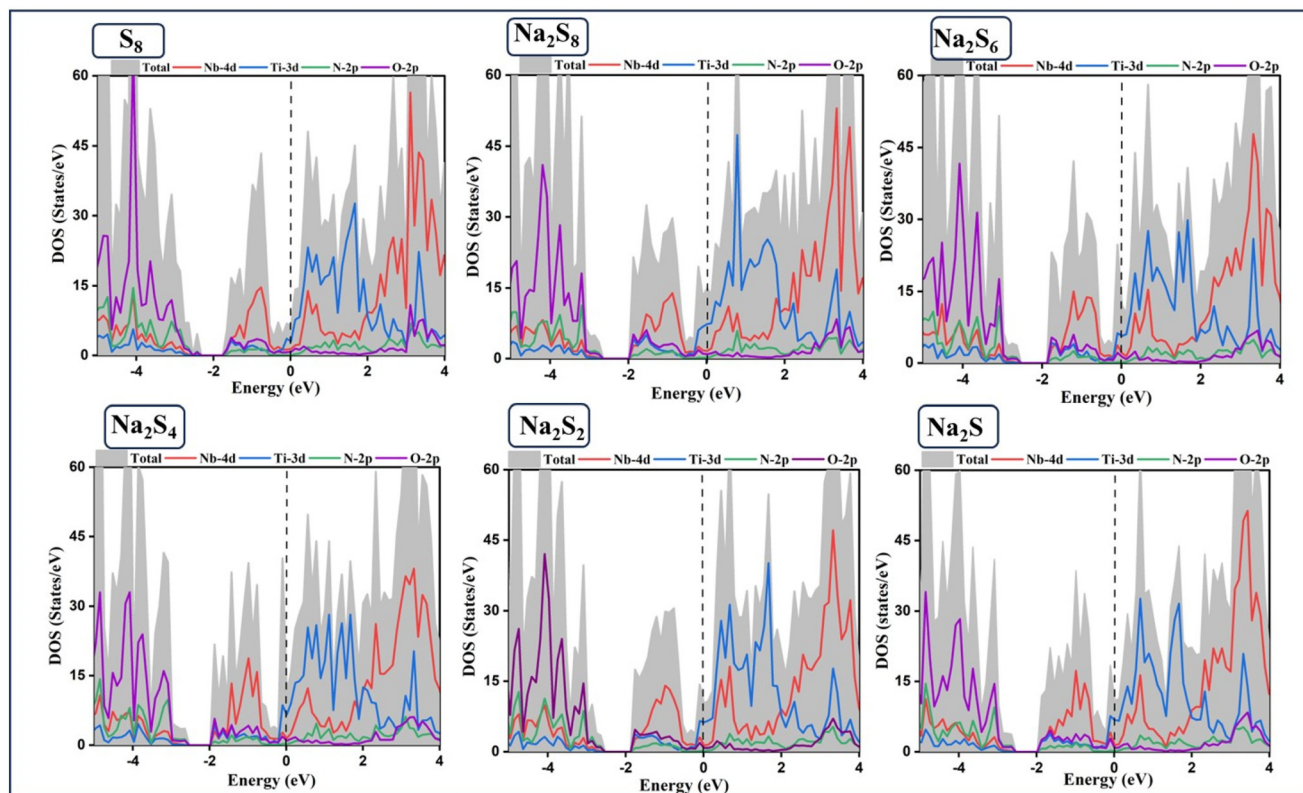


Fig. 7 PDOS of S_8 and Na_2S_n ($n = 1, 2, 4, 6$, and 8) adsorbed on $Nb_2TiN_2O_2$. The Fermi level is denoted by vertical lines.



butions from Ti-3d orbitals. This indicates that in the O-functionalized system, both Nb and Ti play synergistic roles in defining the electronic properties and enhancing interfacial bonding. The PDOS analysis indicates that the Na-S system retains its metallic character upon adsorption on both Nb₂TiN₂S₂ and Nb₂TiN₂O₂ substrates, predominantly due to Ti-3d states in the S-functionalized case, and due to combined contributions from Nb-4d and Ti-3d states in the O-functionalized case.

4. Conclusion

The widespread utilization of the Na-S system is restricted by the shuttle effect and sluggish reaction kinetics. To address this issue, we employed DFT calculations to investigate the adsorption energy and reaction kinetics of Na₂S_n species on our computationally discovered S and O-functionalized Nb₂TiN₂T₂ (T = S, O) substrates.⁴⁴ Adsorption energy calculation revealed that both the surface group exhibits strong interaction with Na₂S_n; however, Nb₂TiN₂O₂ exhibits superior binding energies compared to Nb₂TiN₂S₂. Thus, Nb₂TiN₂O₂ is expected to effectively mitigate the shuttle effect. Furthermore, upon Na₂S_n adsorption, both substrates maintain their structural rigidities without any structural deformation, which is crucial for ensuring high reversibility during the redox reactions. Bader and charge density difference analysis further revealed a significant amount of electrons transferred from Na₂S_n to both the substrates, especially for lower order insoluble polysulfides, with the O-surface exhibiting a strong covalent interaction due to higher charge redistribution. Gibbs free energy, ΔG , profiles for the SRR revealed that the rate-determining step (Na₂S₄ → Na₂S₂) is more favorable on both Nb₂TiN₂S₂ and Nb₂TiN₂O₂ substrates compared to the gas phase, with the O-functionalized surface exhibiting superior catalytic performance by achieving 66% reduction barrier improvement *versus* 48% for the S-functionalized counterpart. Besides, PDOS study revealed that Nb₂TiN₂S₂/O₂ AM retains their metallic nature post Na₂S_n adsorption. Which is essential for effective charge transfer during battery operation. In conclusion, both Nb₂TiN₂S₂ and Nb₂TiN₂O₂ substrates demonstrate strong potential as AM for Na-S batteries *via* offering enhanced binding strength, increased charge transfer, and faster kinetics. Among them, the O-functionalized Nb₂TiN₂O₂ outperforms the S-functionalized, highlighting the importance of surface termination in tuning MXene-based materials for high-performance and stable metal-S batteries.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The authors confirm that the data required to reproduce the findings of this study are available within the article and can be reproduced by density functional theory calculations.

Supplementary information includes the optimized geometric configurations of pristine and surface-functionalized DTM-MXenes, comparison of adsorption energies of S₈ and Na₂S_n (*n* = 2, 4, 6, and 8) for O- and S-functionalized groups employing Hubbard corrections (PBE and PBE+*U*), and comparison of polysulfide adsorption energies between the gas phase and the implicit solvation model. See DOI: <https://doi.org/10.1039/d5nr03030g>.

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