

Ab-Initio Studies on Fluorine–Sulfur Coterminated MXene–Reduced Graphene Oxide Composites for Fast Polysulfide Conversion in Flexible Sodium–Sulfur Batteries

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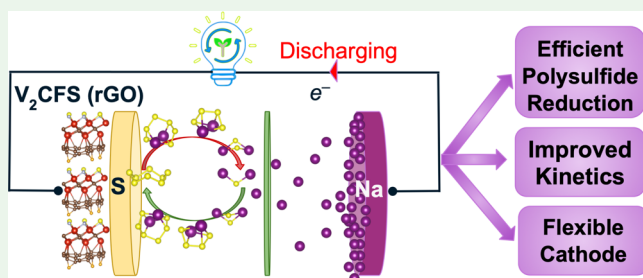
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ABSTRACT: Flexible, high-performance cathodes are essential for realizing practical room-temperature sodium–sulfur (Na–S) batteries, yet sluggish polysulfide conversion, poor retention, and mechanical limitations remain major barriers. Here, we introduce a sulfur/fluorine coterminated vanadium carbide MXene integrated with reduced graphene oxide, $V_2CF_{0.67}S_{0.33}$ (rGO), designed to enhance polysulfide anchoring, catalytic activity, and flexibility simultaneously. First-principles calculations reveal that this mixed-termination MXene–rGO composite exhibits markedly stronger polysulfide adsorption (0.8–3.90 eV) than single-terminated counterparts while preserving structural integrity and metallic conductivity for efficient charge transport. The material achieves the lowest Na_2S decomposition barrier reported for MXene-based Na–S cathodes (0.287 eV) and a reduced Gibbs free energy pathway for the sulfur reduction reaction, enabling faster and more complete sulfur utilization. Charge density difference, partial density-of-states, and crystal orbital Hamilton population analyses confirm substantial charge transfer and strong interfacial chemical bonding with Na_2S_n species. Mechanical stress–strain simulations further demonstrate robust yet flexible behavior, highlighting its promise for wearable energy storage. This work establishes surface-termination engineering in MXene–graphene hybrids as a promising route toward high-capacity, durable, and mechanically compliant Na–S batteries.

KEYWORDS: sodium–sulfur batteries, V_2CT_x MXene, reduced graphene oxide, chemical adsorption, catalytic conversion, flexible cathode, first-principles calculations, surface-termination engineering



1. INTRODUCTION

Metal–sulfur cathodes are among the most promising candidates for next-generation energy storage due to their high theoretical energy density and capacity.^{1,2} For example, Li–S batteries can deliver a theoretical energy density of 2600 Wh kg^{-1} and a capacity of 1675 mAh g^{-1} ,⁴ far exceeding those of conventional Li-ion batteries (155 mAh g^{-1} , 387 Wh kg^{-1}).⁵ However, lithium-ion technology faces limitations such as high cost and restricted lithium availability,^{6,7} raising concerns about long-term sustainability.^{8,9}

Sodium–sulfur (Na–S) batteries have emerged as a cost-effective and sustainable alternative, offering a theoretical energy density of 1274 Wh kg^{-1} at room temperature,¹⁰ low material cost owing to the abundance of sodium and sulfur,^{11,12} and environmental compatibility.^{10,13} Yet, their practical deployment is hindered by poor electrode conductivity, sluggish polysulfide (Na_2S_n) conversion, and severe polysulfide dissolution.¹⁴ Dissolved long-chain polysulfides ($4 \leq n \leq 8$) shuttle to the anode, causing contamination and side reactions,^{15,16} while short-chain species ($1 \leq n \leq 2$) and an $\sim 80\%$ volume change between S and Na_2S ^{17,18} degrade structural integrity. Polar anchoring materials (AMs) such as metal oxides, sulfides,

carbides, phosphides, and borides^{19–21} have been explored to immobilize polysulfides and accelerate their conversion.

Two-dimensional MXenes—transition metal carbides, carbonitrides, and nitrides—have gained particular attention for their electrical conductivity, tunable surface chemistry, and mechanical robustness.^{22–24} Their inherent flexibility makes them promising for wearable and flexible energy storage.^{25–27} However, challenges such as oxidation, defect-induced instability,^{28,29} and self-restacking of nanosheets³⁰ limit their performance, reducing accessible surface area and ion transport pathways. Hybridization with reduced graphene oxide (rGO)³¹ and heteroatom doping are effective strategies to mitigate restacking, enhance conductivity, and improve cycling stability.^{32,69}

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Beyond structural modifications, *surface terminations* critically influence the MXene electrochemical behavior. Different terminations alter ion adsorption energies, diffusion barriers, and cycling stability.^{33,34} For instance, S-terminated Ti_3C_2 reduces Na-ion adsorption barriers by 50% compared to O-terminated surfaces,³⁵ while S-terminated Ti_2C shows triple the specific capacity of pristine Ti_2C for Mg-ion intercalation.³⁵ Although V_2CT_x exhibits superior cycling stability over $\text{Ti}_3\text{C}_2\text{T}_x$ and Mo_2CT_x ,³⁶ the role of mixed terminations remains largely unexplored, particularly for Na–S cathodes.

Here, we address this gap by designing a mixed-terminated S/F V_2C MXene integrated with rGO, $\text{V}_2\text{CF}_{0.67}\text{S}_{0.33}$ (rGO), to synergistically enhance polysulfide anchoring, catalytic conversion, and mechanical flexibility. Using density functional theory (DFT), we reveal that this coterminated MXene-rGO composite achieves markedly higher polysulfide adsorption energies (0.8–3.90 eV) than single-terminated analogues, while preserving metallic conductivity for efficient electron transport. It also exhibits the lowest Na_2S decomposition barrier reported for MXene-based Na–S cathodes (0.287 eV), promoting fast sulfur utilization. Electronic structure and bonding analyses confirm strong interfacial interactions, and stress–strain simulations demonstrate robust flexibility. Our findings highlight surface-termination engineering of MXene–graphene composites as a promising pathway toward high-capacity, durable, and flexible Na–S batteries.

2. COMPUTATIONAL METHODS

2.1. DFT and Catalysis Calculations. First-principles calculations were performed using the Vienna Ab initio Simulation Package (VASP)³⁷ within the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA),³⁸ with van der Waals interactions treated via the DFT-D3 correction of Grimme.³⁹ The projector augmented wave (PAW) method⁴⁰ was used with a plane-wave cutoff of 415 eV and a $7 \times 7 \times 1$ Monkhorst–Pack k -point mesh.⁴¹ Spin polarization was included in all calculations, and a vacuum gap of 20 Å was applied along the out-of-plane direction. Structures were relaxed until the forces on all atoms were below 0.01 eV Å^{−1}. The V_2C structures were modeled using $p(3 \times 3)$ hexagonal unit cells with a V–C–V trilayer structure (Figure S1). Optimized lattice constants deviated by $\approx 0.4\%$ from experiment and matched prior reports.³³

Surface-functionalized (S, F, and S/F coterminated) V_2C MXenes were investigated in combination with reduced graphene oxide (rGO) substrates and bare monolayer V_2CS surface. A representative mixed-termination model, $\text{V}_2\text{CF}_{0.67}\text{S}_{0.33}$ (rGO), was selected based on experimental evidence indicating partial substitution of F by S terminations after etching and storage.⁴² This composition captures the essential effects of mixed terminations on catalytic behavior, while the systematic variation of F/S ratios will be explored in future work. The adsorption of Na_2S_n ($n = 1, 2, 4, 6, 8$) and S_8 using DFT total energies changes, Gibbs free energy changes for the sulfur reduction reaction (SRR) via vibrational frequency analysis, and Na_2S decomposition barriers using the climbing-image nudged elastic band (CI-NEB) method⁴³ were calculated. Charge transfer was evaluated via Bader analysis,⁴⁴ and bonding interactions were probed with crystal orbital Hamilton population (COHP) calculations.⁴⁵ Full computational parameters, pseudopotentials, supercell specifications, convergence thresholds, and explicit adsorption/free-energy equations are given in the Supporting Information.

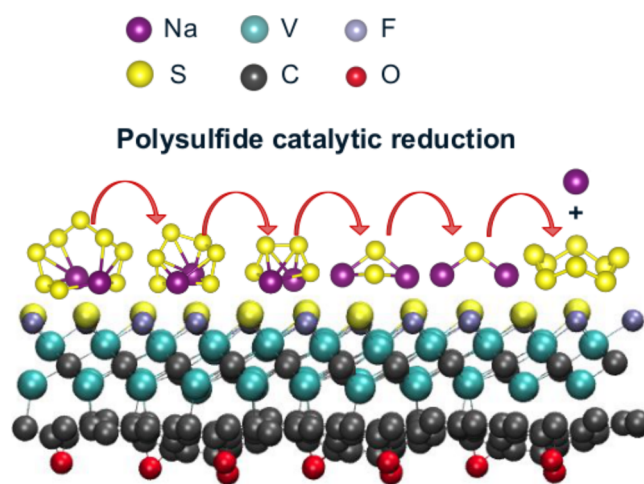
2.2. Mechanical Property Calculations. Mechanical stability and flexibility were evaluated through first-principles stress–strain simulations in the linear elastic regime. Elastic constants (C_{ij}) were obtained from strain–energy relationships, and the corresponding Young’s modulus (Y), shear modulus (G), and Poisson’s ratio (ν) were derived using standard tensor relationships for 2D hexagonal lattices. Calculations were performed in VASP, with input preparation and postprocessing via VASPKIT 1.3.1.⁴⁶ Similar methods have been used

in previous studies to examine the mechanical stability of 2D semiconductor materials,⁴⁷ and the results showed good agreement with available experimental and theoretical data. The complete derivations of the elastic tensor in Voigt notation, strain–energy expressions, definitions of tensile strain, and strain ranges used are detailed in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Adsorption Mechanism of Na_2S_n on VCX. In Na–S batteries, the electrochemical conversion of sulfur is governed by interactions between NaPS and the catalyst surface, a process collectively termed the SRR. This reaction begins during discharge with the adsorption of S_8 molecules onto the VCX monolayer surfaces [V_2CS (bare), V_2CS (rGO), V_2CF (rGO), and V_2CFS (rGO) or $\text{V}_2\text{CF}_{0.67}\text{S}_{0.33}$ (rGO)], started calculation for subsequent reduction steps. The interaction of S_8 with Na ions leads to the formation of long-chain, soluble polysulfides such as Na_2S_8 , Na_2S_6 , and Na_2S_4 . At this stage, a moderate binding affinity between the catalyst and these soluble intermediates is critical for anchoring them on the surface and mitigating the polysulfide shuttle effect, which otherwise results in capacity fading. As the discharge progresses, the reaction pathway advances toward forming short-chain, insoluble species such as Na_2S_2 and Na_2S . Catalysts with suitable activity can accelerate the conversion to these terminal discharge products. Conversely, during the charging process, Na_2S is oxidized and gradually decomposes back to elemental sulfur (S_8), thereby completing the redox cycle. Scheme 1 illustrates the polysulfide reduction process on the V_2CFS (rGO) surface, which ultimately leads to the formation of the S_8 molecule and the release of free sodium ions.

Scheme 1. Schematic Representation of the Polysulfide Reduction Mechanism on the V_2CFS (rGO) Surface



We first determined their ground-state structures in the gas phase to evaluate the adsorption behavior of various polysulfides and sulfur clusters. The most energetically favorable adsorption configurations of S_8 and Na_2S_n ($n = 1, 2, 4, 6$, and 8) on both bare and functionalized MXene surfaces are presented in Figure S2. The corresponding binding energies are listed in Figure 1 and Table S1. Previous studies indicate that interactions of Na_2S_n species with common electrolyte solvents such as DOL, DME, or DMSO are relatively weak (< 1 eV).^{48,49} In comparison, adsorption energies on V_2CFS (rGO) are significantly stronger (2–4 eV), suggesting that solvent effects are unlikely to alter the

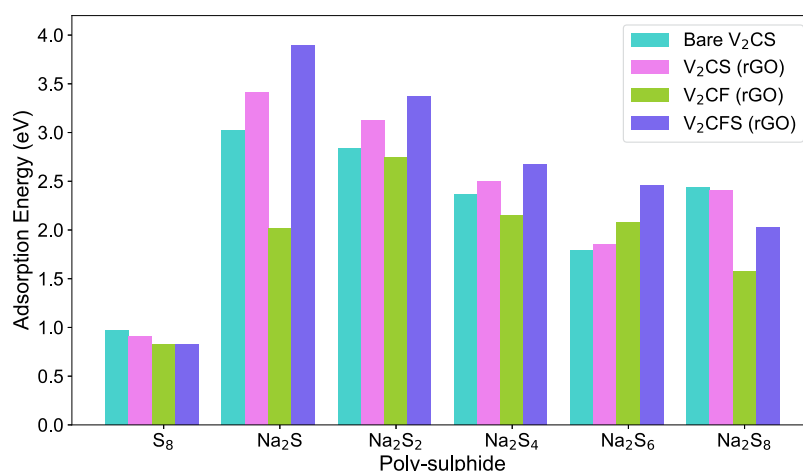


Figure 1. Calculated adsorption energies of S₈ and Na₂S_{*n*} (*n* = 1, 2, 4, 6, and 8) on various surfaces, including bare V₂CS and rGO-supported V₂CS, V₂CF, and V₂CFS, highlighting the influence of surface functionalization and support on adsorption strength.

adsorption trends qualitatively. Therefore, all calculations were performed in the gas phase to capture the intrinsic surface–adsorbate interactions. All sodium polysulfides (NaPS) species adopted three-dimensional cluster-like geometries upon adsorption, which is consistent with the structural features previously reported for lithium polysulfides⁵⁰ and further supported by earlier studies on sodium-based analogs.^{48,49,51} Multiple initial configurations with varied orientations (vertical, tilted, and parallel) and adsorption sites (top, bridge, and hollow) were tested for each Na₂S_{*n*} species. All optimizations consistently converged to the same adsorption motif, with Na atoms oriented toward surface terminations, confirming that the reported structures represent the most stable configurations.

As shown in Table 1, the minimum distance between the S₈ molecule and various catalytic surfaces ranges from 3.08 to 3.84

wherein the Na atoms occupy hollow sites of the termination layer, while the S atom resides directly above a surface termination atom. With these configurations, all three atoms form covalent bonds with the substrate termination atoms, except in the case of V₂CF (rGO). Despite forming surface bonds, the Na₂S_{*n*} species maintain their molecular integrity across all surfaces, with only slight structural distortions observed postadsorption (see Figure S2). The preservation of molecular rigidity without dissociation is critical for the reversibility of the redox processes in Na–S batteries.

A general decreasing trend of the Na–S bond lengths is observed across the series of adsorbed Na₂S_{*n*} species (Table 1), with the shortest bond length occurring for Na₂S. As the reduction progresses, this trend signifies increasingly stronger interactions between the AM surfaces and the polysulfide species. Moreover, as illustrated in Figure 1, Na₂S_{*n*} species (*n* = 1, 2, 4, 6) exhibit the most substantial adsorption on the mixed F- and S-terminated surfaces, evidenced by both higher adsorption energies and shorter bond distances relative to bare, singly S-terminated, or F-terminated surfaces. This enhanced interaction suggests that mixed terminations provide the most favorable environment for anchoring polysulfides, offering an effective strategy to suppress the polysulfide shuttle effect.

3.2. Catalytic Conversion of Polysulfide Clusters. One of the primary challenges in sodium–sulfur batteries is the inherently sluggish redox kinetics, which, when combined with the prolonged presence of Na₂S_{*n*} species in the electrolyte, exacerbates the shuttle effect. To address this issue, we systematically investigated how different surface terminations influence the catalytic activity of the electrode and facilitate the reversible electrochemical steps of the SRR. During the discharge process, the SRR involves a series of transformations, ultimately forming Na₂S from elemental sulfur (S₈) and sodium metal. This multistep reaction pathway includes several polysulfide intermediates, as reported in previous studies.^{50,48} Overall, the complete discharge of a Na–S battery involves a total transfer of 16 electrons, culminating in the production of eight Na₂S molecules. Detailed steps are summarized in Section S2.

The complete evolution profile from S₈ to Na₂S is depicted in Figure 2, highlighting the stepwise free energy changes associated with the SRR across different catalytic surfaces. The

Table 1. Minimum Distances (in Å) between Atoms in Adsorbed Polysulfide Species and the Catalyst Surface Indicate the Nature and Strength of Surface–Absorbate Interactions across Different Anchoring Materials

surfaces	S ₈ (S–S)	Na ₂ S ₈ (Na–S)	Na ₂ S ₆ (Na–S)	Na ₂ S ₄ (Na–S)	Na ₂ S ₂ (Na–S)	Na ₂ S (S–S)
V ₂ CS (bare)	3.60	2.91	2.75	2.76	2.64	2.04
V ₂ CS (rGO)	3.38	2.87	2.77	2.81	2.75	2.04
V ₂ CF (rGO)	3.08	2.39	2.36	2.34	2.28	2.34
V ₂ CFS (rGO)	3.84	2.27	2.32	2.25	2.28	2.07

Å, accompanied by adsorption energies between 0.969 and 0.823 eV (see Figure 1 and Table S1). These values and Figure S2 indicate that the S₈ molecule adsorbs onto the surfaces in a parallel orientation, predominantly stabilized by van der Waals interactions, with no evidence of chemical bond formation. This mode of interaction aligns with previous reports on other anchoring materials, where similar parallel adsorption configurations of S₈ have been observed.^{48,49} Furthermore, the puckered ring geometry of the S₈ molecule and the structural integrity of the AM surfaces remain largely preserved following adsorption, suggesting minimal perturbation upon binding.

In contrast, sodium polysulfides (Na₂S_{*n*}, with *n* = 8, 6, 4, 2, 1) display stronger interactions with the surfaces. These species generally adopt configurations in which their Na atoms are oriented toward the substrate, facilitating the formation of Na–S bonds. Notably, Na₂S exhibits a distinct adsorption mode,

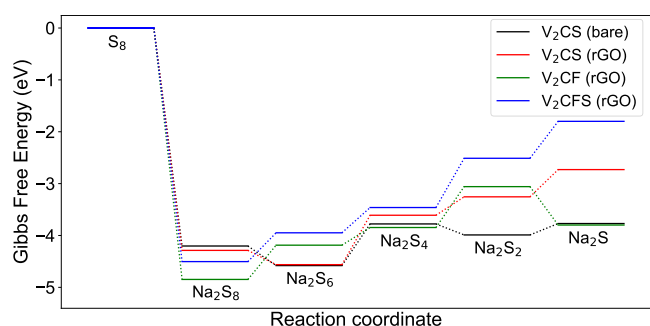


Figure 2. Gibbs free energy profiles of the sulfur reduction reaction during discharge on various V_2C -based catalytic surfaces, illustrating the thermodynamic feasibility and reaction energetics at each intermediate step.

first step, the reduction of S_8 to Na_2S_8 , is found to be spontaneously exothermic on all surfaces, releasing the highest amount of energy ($\Delta G_1 = -4.847$ eV) on the V_2CF (rGO) surface. This strongly exergonic initial step suggests a favorable onset for SRR, especially on fluorine-functionalized systems. In contrast, the second step (ΔG_2), corresponding to the conversion of Na_2S_8 to Na_2S_6 , exhibits apparent surface-dependent behavior. It is endothermic on V_2CF (rGO) and V_2CFS (rGO), requiring 0.660 and 0.555 eV, respectively. However, this same step is exothermic on the bare and V_2CS (rGO) surfaces, with energy releases of -0.377 and -0.275 eV, respectively. This indicates that bare and sulfur-terminated surfaces may stabilize intermediate polysulfides more efficiently during this transition. The third step (ΔG_3), involving the conversion to Na_2S_4 , is endothermic across all surfaces; nonetheless, V_2CF (rGO) requires the least energy input (0.340 eV), reflecting its relatively low thermodynamic barrier for this stage. The fourth step (ΔG_4), which corresponds to the formation of Na_2S_2 , is energetically favorable only on the V_2CS (bare) surface (-0.212 eV), whereas the same transformation remains endothermic on the other three surfaces, suggesting a specific affinity of the bare surface for this intermediate. The final

step (ΔG_5), which represents the crucial solid-to-solid conversion from Na_2S_2 to Na_2S , is significantly endothermic on V_2CS (bare), V_2CS (rGO), and V_2CFS (rGO), with energy requirements of 0.220, 0.525, and 0.712 eV, respectively. In sharp contrast, this step is exothermic on the V_2CF (rGO) surface (-0.740 eV), indicating strong catalytic promotion of this final conversion on the fluorine-functionalized MXene. Overall, the V_2CF (rGO) surface consistently exhibits lower energy barriers for several key steps and notably promotes the terminal conversion to Na_2S , effectively overcoming the thermodynamic bottlenecks typical of SRR. While all of the studied surfaces facilitate the S_8 to Na_2S conversion with an overall exothermic energy profile, the V_2CF (rGO) system stands out in enhancing the thermodynamics of the redox process, thereby offering a promising route to mitigate the sluggish reaction behavior inherent in Na–S batteries.

3.3. Dissociation Mechanism of Na_2S . The reversibility and operational lifespan of sodium–sulfur batteries are critically governed by the catalytic decomposition barrier of the solid redox intermediate Na_2S , which is the final discharge product in the electrochemical cycle.⁵² As Na_2S remains insoluble mainly in the electrolyte during both charge and discharge, its efficient decomposition is essential to sustain redox reversibility. For improved reaction kinetics, a low dissociation barrier is highly desirable. During the charging process, Na_2S undergoes bond cleavage to release sulfur, eventually reforming the elemental cyclo- S_8 . This transformation proceeds via the reaction $Na_2S \rightarrow NaS + Na^+ + e^-$,⁵³ where the liberated Na^+ ions subsequently migrate across the catalytic surface (VCX) along energetically favorable pathways. This decomposition process entails overcoming two key energetic requirements: (i) breaking the Na–S bond at the initial adsorption site and (ii) enabling the diffusion of Na^+ ions to adjacent secondary adsorption sites. This mechanistic pathway is illustrated in Figure 3. Notably, prior experimental investigations have shown that a high decomposition energy barrier can substantially suppress the cell voltage,⁵⁴ underscoring the importance of efficient Na_2S dissociation for maintaining optimal battery performance.

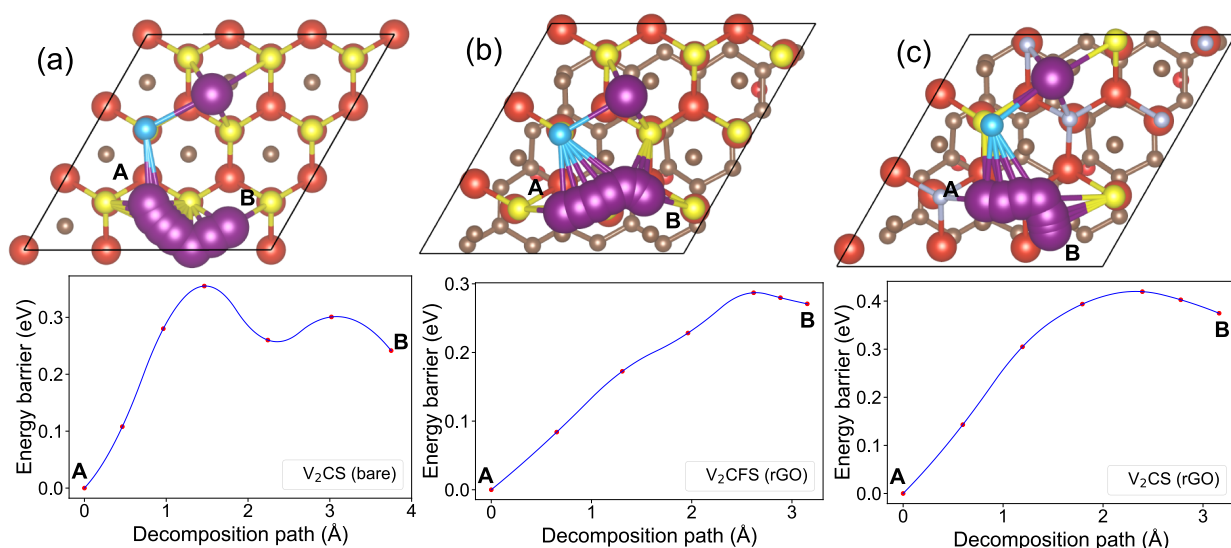


Figure 3. Decomposition energy barriers of Na_2S on (a) V_2CS (bare), (b) V_2CS (rGO), and (c) V_2CFS (rGO) surfaces. Here, the V_2CF (rGO) surface does not show Na_2S decomposition. The top panels depict the reaction pathway involving Na–S bond cleavage and subsequent Na^+ ion migration across the surface. The bottom panels show the corresponding CI-NEB-calculated energy profiles, highlighting the decomposition barriers on each catalytic surface. Color scheme of atoms: V—red; C—brown; S (from AM)—yellow; F—silver; Na—purple; S (from Na_2S)—sky blue.

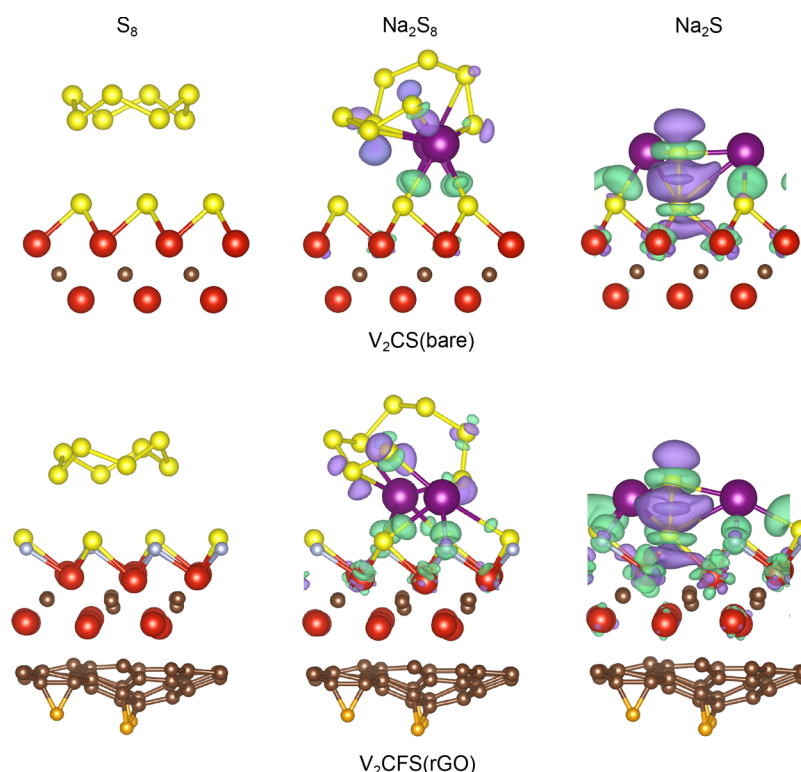


Figure 4. Isosurface plots illustrate charge density differences upon adsorption, with the top panels showing the V_2CS (bare) surface and the bottom panels showing the V_2CFS (rGO) surface. Green and purple regions represent electron accumulation and depletion at an isosurface value of $0.0031 \text{ e}/\text{\AA}^3$. Color scheme of atoms: V, red; C, brown; S, yellow; F, silver; Na, purple; O, orange.

Therefore, both the Na_2S dissociation energy barrier and the underlying ionic diffusion landscape play pivotal roles in determining the electrochemical efficiency of Na–S batteries.

To gain insights into this critical step, we employed the climbing-image nudged elastic band method⁴³ to evaluate the Na_2S decomposition energy barriers on various catalytic surfaces. As shown in Figure 3, the energy barrier for Na_2S dissociation is remarkably low on the V_2CS (bare) and V_2CS (rGO) surfaces—0.355 and 0.419 eV, respectively—representing a dramatic reduction compared to the barrier in the gas phase (2.199 eV; see Figure S3). Interestingly, among all anchoring materials, V_2CFS (rGO) exhibits the lowest decomposition energy barrier of 0.287 eV (Figure 3c), indicating highly favorable catalytic activity for promoting Na–S bond cleavage. In contrast, the V_2CF (rGO) surface fails to facilitate Na_2S dissociation, emphasizing that dual surface terminations (F and S) are crucial for activating this key transformation. This behavior can be attributed to the weak interaction between the sulfur atom in Na_2S and the V_2CF (rGO) surface, as illustrated in Figure S2. Because no stable bond is formed, the adsorption energy remains relatively low (Table S1), making the dissociation of Na–S bonds energetically unfavorable. As a result, Na_2S tends to remain intact and undissociated. The origin of this weak dissociation pathway is further clarified by the COHP analysis presented in the next section.

Although V_2CFS (rGO) exhibits an endothermic free energy change in the final step ($\Delta G_5 = 0.712 \text{ eV}$), the overall catalytic process remains favorable when both thermodynamics and kinetics are considered. Notably, V_2CFS (rGO) shows the lowest Na_2S decomposition barrier (0.287 eV, Figure 3), enabling a faster regeneration of active sites. In contrast, V_2CF (rGO)—despite its strongly exothermic initial step—does not

effectively facilitate Na_2S dissociation. These results highlight that mixed terminations promote balanced adsorption and superior catalytic activity compared to a single F-termination.

3.4. Electron Density and Bond Interaction Analysis.

Among the studied surfaces, mixed-terminated V_2CFS (rGO) emerged as the most promising Na–S cathode material due to its lowest catalytic decomposition barrier. To gain deeper insight into the decomposition mechanisms of S_8 and Na_2S_n species ($n = 8, 1$) and the associated Na–S and S–S bonding after adsorption, we conducted electronic structure analyses on V_2CFS (rGO) and compared them with bare V_2CS . These included charge density difference, partial density of states (PDOS), and COHP calculations, which together reveal the chemical bonding characteristics between S_8 , Na_2S_8 , and Na_2S and the catalyst surfaces.

We conducted Bader charge analysis to evaluate the extent of charge transfer during adsorption. The results indicate that the nonsodiated S_8 species exhibit weak interactions with both V_2CS (bare) and V_2CFS (rGO) surfaces, with minimal charge transfers of only 0.003 and 0.006 $|e|$, respectively. This limited transfer is primarily attributed to weak S–S interactions. As the discharge process progresses, a greater number of electrons is transferred from Na_2S_n species to the substrate, reflecting stronger interfacial interactions. Specifically, the adsorption of Na_2S_8 and Na_2S results in significant net charge gains on the V_2CS (bare) surface (−0.680 and −1.106 $|e|$) and even higher gains on the V_2CFS (rGO) surface (−0.806 and −1.159 $|e|$), respectively. These results clearly indicate that the V_2CFS (rGO) surface enables a more efficient charge transfer, underscoring its enhanced catalytic activity. The charge transfer distributions for S_8 , Na_2S_8 , and Na_2S adsorbed on both V_2CS (bare) and V_2CFS (rGO) are visualized in Figure 4.

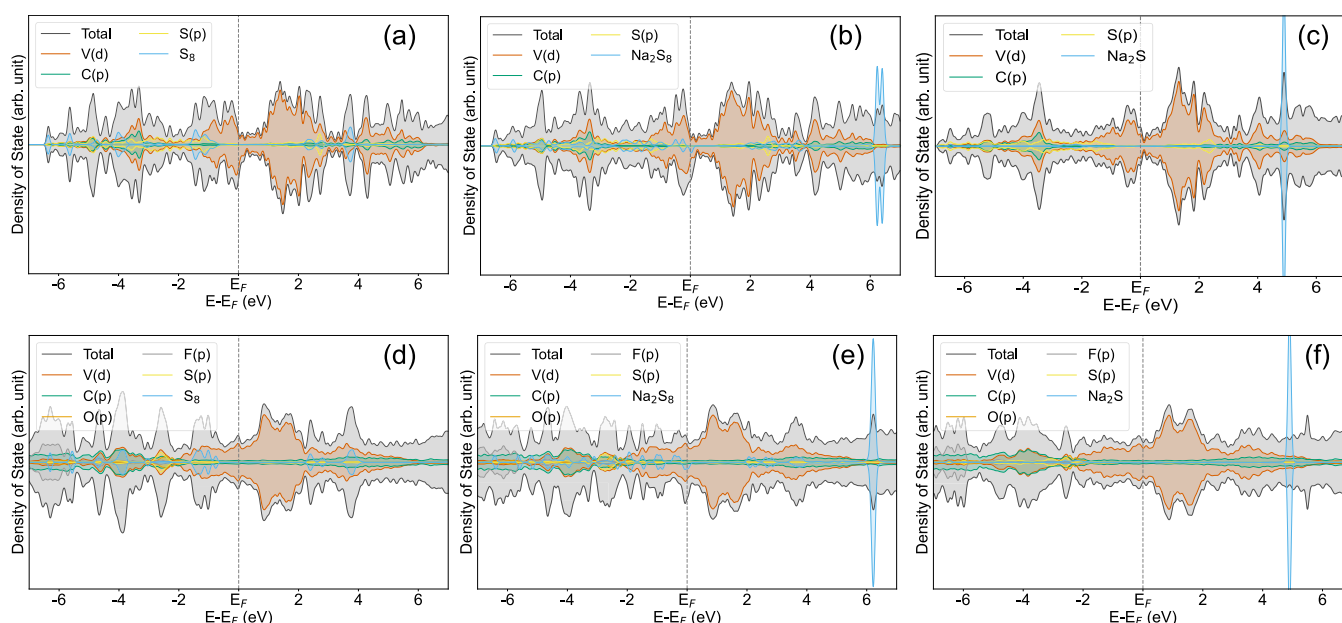


Figure 5. Projected density of states of polysulfides adsorbed on catalytic surfaces. Panels (a–c) show PDOS for S_8 , Na_2S_8 , and Na_2S adsorbed on V_2CS (bare), respectively, while panels (d–f) show the corresponding PDOS for the same species adsorbed on V_2CFS (rGO). The DOS for the pristine systems is shown in Figure S5.

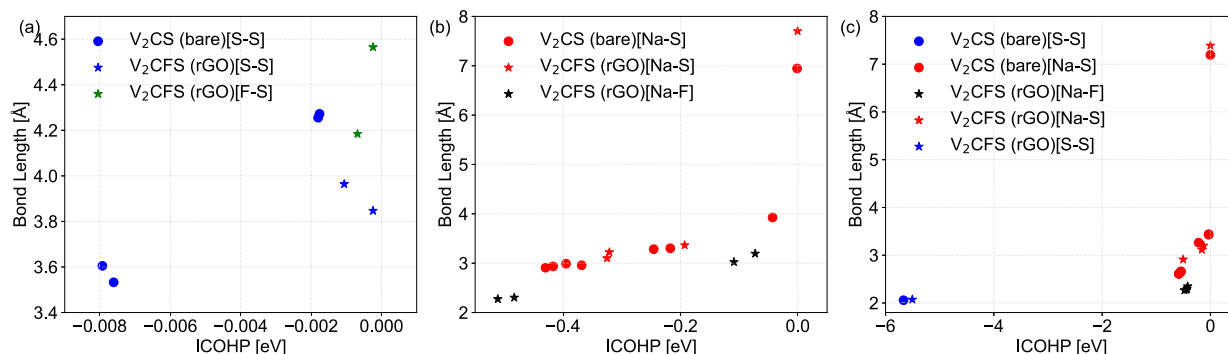


Figure 6. Correlation between the ICOHP values and the interatomic distances for the interactions of polysulfide species—(a) S_8 , (b) Na_2S_8 , and (c) Na_2S —and the V_2CS (bare)/ V_2CFS (rGO) surfaces. Atomic pairs considered (listed in parentheses) are color-coded as follows: S–S (blue), F–S (green), Na–S (red), and Na–F (black).

Furthermore, the corresponding charge density differences along the z -axis, presented in Figure S4, offer an additional visual confirmation of these findings.

The inherently low electronic conductivity of elemental sulfur (S_8) and the intermediate sodium polysulfides formed during the charge/discharge cycles pose a significant challenge to the electrochemical performance of Na–S batteries. This limitation significantly impedes the redox kinetics. In contrast, conductive catalytic surfaces that facilitate electron transfer during redox reactions involving Na_2S_n species can substantially enhance the reaction kinetics. To explore the electronic behavior of such catalytic substrates, we investigated the density of states (DOS) of V_2CS (bare) and V_2CFS (rGO) during the adsorption of S_8 and Na_2S_n species. The projected density of states and total density of states (TDOS), shown in Figure 5a–f, clearly demonstrate that both surfaces exhibit metallic characteristics. Notably, the TDOS comparison before and after the adsorption of S_8/Na_2S_n ($n = 8, 1$), illustrated in Figures S5 and S, respectively, confirm that the metallic nature of V_2CS (bare) and V_2CFS (rGO) is retained even after the adsorption of polysulfide species. This preservation of metallicity highlights

the potential of these surfaces to support efficient electron transport during electrochemical processes in Na–S batteries.

In pristine V_2CS (bare), a high density of states at the Fermi level confirms its intrinsic metallic character and good electronic conductivity (Figure S5). Hybridization with reduced graphene oxide further increases this density, while fluorine and mixed fluorine–sulfur terminations enhance it even more, providing additional states for charge transport. These features align with the stronger adsorption energies and improved catalytic activity observed in the SRR. Adsorption of nonsodiated S_8 (Figure 5) induces only minor changes to the electronic structure, with the Fermi level dominated by states from the catalytic substrates, consistent with its weak binding and minimal charge transfer.

By contrast, Na_2S_8 adsorption introduces additional states near the Fermi level, originating mainly from S– p and Na– s orbitals, indicating charge transfer to the substrate and correlating with its higher adsorption energy. For Na_2S , the Na– s states shift closer to the Fermi level, further facilitating electron transfer. Notably, the emergence of new states near the Fermi level upon Na_2S_8 adsorption strengthens the electronic coupling between the polysulfide species and the substrate.

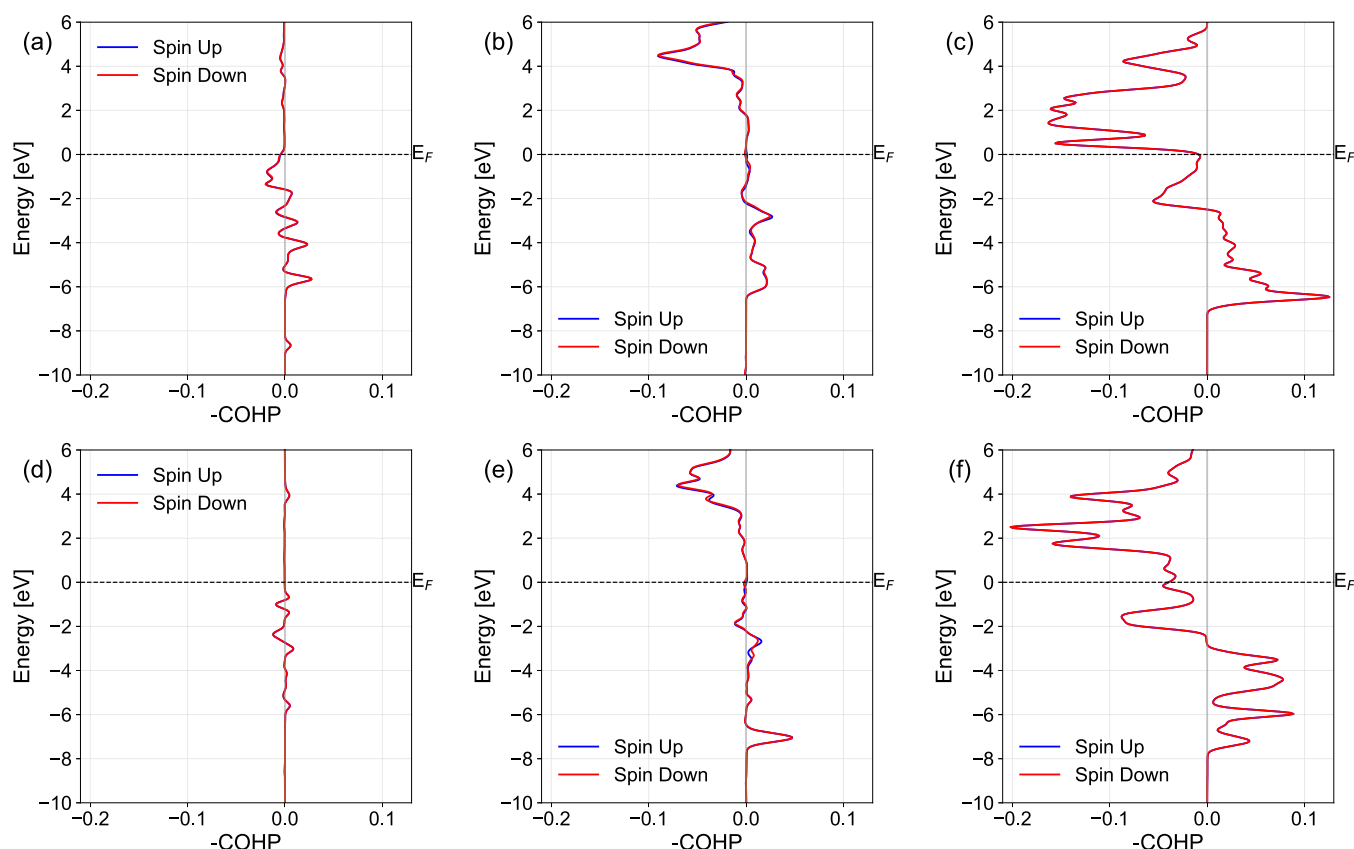


Figure 7. Averaged $-COHP$ plots represent key interactions between the adsorbed species and the catalytic surfaces. Panels (a–c) show interactions for S_8 , Na_2S_8 , and Na_2S on the V_2CS (bare) surface, while panels (d–f) depict the corresponding interactions on the V_2CFS (rGO) surface. The horizontal dashed line at zero marks the Fermi level (E_F).

These states facilitate efficient electron injection into Na–S bonds, thereby reducing the decomposition barrier and accelerating the redox kinetics. This interpretation aligns with the charge-density-difference and Bader analyses, which reveal significant charge transfer and electron localization around Na–S bonds, particularly for the V_2CFS (rGO) surface. In all cases, V $3d$ states of the substrates dominate the upper valence band region, and both V_2CS (bare) and V_2CFS (rGO) retain their metallicity after adsorption, supporting their role as efficient electron-conducting channels during redox transformations. Additional discussions are provided in Section S3.

To further elucidate the bonding between S_8/Na_2S_n ($n = 8, 1$) and V_2CS (bare)/ V_2CFS (rGO), we performed a COHP analysis on the Na–S valence orbitals (Figures 6 and 7). While DOS reveals the distribution of electronic states, COHP decomposes them into bonding, antibonding, and nonbonding contributions based on Hamiltonian matrix elements.⁵⁵ Positive $-COHP$ values denote bonding, negative values indicate antibonding, and values near zero correspond to nonbonding interactions. The integrated COHP (ICOHP) up to the Fermi level provides a quantitative measure of bond strength, with more negative values indicating stronger interactions.⁵⁶

The relationship between the ICOHP and bond lengths is shown in Figure 6. For nonsodiated S_8 , the $S-3p$ orbitals of both catalytic surfaces exhibit weak interactions with the $S-3p$ orbitals of the adsorbate, reflected in small ICOHP values—ranging from -0.00180 to -0.00793 eV/bond for V_2CS (bare) and from -0.00024 to -0.00106 eV/bond for V_2CFS (rGO). The interaction between the F– $2p$ orbitals of V_2CFS (rGO) and the $S-3p$ orbitals of S_8 is even weaker, confirming the

physisorptive nature of this interaction. Quantitative %COHP partitioning shows that S–S and F–S interactions contribute 58.6 and 41.4% of the total bonding, respectively, indicating that while S–S bonds dominate, F–S bonds provide meaningful secondary stabilization at the interface.

For Na_2S_8 adsorption, larger ICOHP values associated with Na–S bonds (-0.00115 to -0.42998 eV/bond on V_2CS and -0.00024 to -0.32516 eV/bond on V_2CFS (rGO)) confirm stronger chemical interactions. Additionally, V_2CFS (rGO) exhibits appreciable Na–F bonding (-0.07261 to -0.51138 eV/bond), demonstrating the involvement of fluorine in interfacial stabilization. The %COHP partitioning indicates that Na–S and Na–F bonds contribute 41.6 and 58.4% of the total interfacial bonding, respectively, underscoring the cooperative role of mixed terminations in modulating interaction strength.

The strongest interactions occur for Na_2S adsorption, where Na– $3s$ and S– $3p$ orbitals form robust bonds on both surfaces, with ICOHP values ranging from -0.00076 to -0.58354 eV/bond for V_2CS and -0.00108 to -0.50433 eV/bond for V_2CFS (rGO). The S–S bonds at the Na_2S –surface interface exhibit the highest ICOHP values (-5.66829 and -5.50632 eV/bond for V_2CS and V_2CFS (rGO), respectively). The corresponding %COHP partitioning shows that Na–S, Na–F, and S–S bonds contribute 9.8, 22.0, and 68.2% of the total interfacial bonding, respectively, confirming that F-containing bonds, while secondary, significantly enhance interfacial stability.

Overall, the quantitative %COHP analysis demonstrates that although S–S bonds dominate interfacial interactions, introducing F-containing terminations provides moderate bonding

contributions that stabilize the interface without causing overbinding. This balanced interaction strength supports efficient catalytic turnover, which is consistent with the Sabatier principle.⁵⁷ The results highlight the importance of mixed terminations in promoting both structural stability and catalytic efficiency for polysulfide conversion on MXene-based electrodes.

The average $-\text{COHP}$ plots presented in Figure 7b,e for Na_2S_8 and Figure 7c,f for Na_2S reveal prominent antibonding states. When these COHP profiles are compared with the corresponding ICOHP values, the observed antibonding peaks can be attributed to charge transfer from the Na-3s orbitals to the high-energy unoccupied S-3p orbitals in V_2CS , as well as to the S-3p and F-2p orbitals in V_2CFS (rGO). Furthermore, Figure 7f highlights a notably larger presence of antibonding orbitals near the Fermi level on the V_2CFS (rGO) surface compared to V_2CS (bare) in the Na_2S -adsorbed phase (Figure 7c). This increased antibonding character near the Fermi level suggests enhanced charge transfer dynamics between Na_2S and the V_2CFS (rGO) substrate. The Bader charge analysis further supports such an interpretation, which quantitatively confirms greater electron transfer in the case of V_2CFS (rGO), thereby reinforcing the role of fluorinated surfaces in improving charge mediation and catalytic behavior.

The dissociation behavior of Na_2S on different surfaces can be rationalized through ICOHP analysis. For the Na–S bonds within Na_2S , the ICOHP value is ≈ -1.12 eV/bond, reflecting a strong internal stabilization that is energetically costly to break. On the F-terminated V_2C surface, the Na_2S –surface interaction is negligible (-0.016 eV/bond), far weaker than the internal Na–S bonding. As a result, the surface cannot compensate for the loss of internal stabilization, leaving Na_2S intact. In contrast, for bare V_2CS , the Na_2S –surface ICOHP is much stronger (-5.67 eV/bond) and remains comparably strong for the mixed S/F termination (-5.50 eV/bond). These values are significantly more negative than the internal Na–S bond, indicating that surface bonding can offset the cost of breaking Na–S interactions and thereby promote sulfur dissociation.

Comparable trends have been reported in previous studies,⁵⁸ where DFT-predicted strong polysulfide adsorption on MXenes such as $\text{V}_4\text{C}_3\text{T}_x$ was later validated experimentally through visual polysulfide sequestration and diffusion tests, confirming effective suppression of the shuttle effect via combined physical confinement and chemical anchoring. Given the close structural and electronic resemblance between $\text{V}_4\text{C}_3\text{T}_x$ and the present V_2CFS (rGO) system, a similar correspondence between theoretical predictions and experimental observations can be reasonably anticipated. This consistency underscores the reliability of our computational findings and their relevance to practical Na–S battery applications. To comparatively benchmark the present work with previously reported MXene-based cathodes (as shown in Table S2), this confirms the lowest decomposition barrier and strong binding of Na_2S on V_2CFS (rGO), helping to improve its catalytic activity and facilitate efficient polysulfide conversion.

While the present study focuses on theoretical insights into the interfacial and electronic mechanisms governing polysulfide conversion, experimental validation through cycling stability and rate capability measurements remains an important next step. The computational findings presented here are expected to guide future experimental efforts toward realizing and evaluating V_2CFS (rGO)-based cathodes in practical Na–S battery systems.

3.5. Mechanical Stability of V_2CS (Bare) and V_2CFS (rGO) Layer. To evaluate the suitability of the material for flexible applications, it is essential to understand its mechanical properties. The relationships between the elastic constants and mechanical moduli were determined by using the stress–strain method. A summary of the calculated mechanical properties is outlined in Table 2. It can be observed that both V_2CS (bare)

Table 2. Calculated Mechanical Properties of V_2CS (Bare) and V_2CFS (rGO) Composites, Including Elastic Constants (C_{11} , C_{12}), Young's Modulus (Y), and Shear Modulus (G), Highlighting Their Structural Stability and Mechanical Flexibility

property	V_2CS (bare)	V_2CFS (rGO)
Young's modulus (Y) (N/m)	143.036	218.782
shear modulus (G) (N/m)	55.102	105.799
Poisson's ratio, ν	0.298	0.034
elastic constants, C_{ij} (N/m)	$\begin{pmatrix} C_{11} = 156.968 \\ C_{12} = 46.763 \end{pmatrix}$	$\begin{pmatrix} C_{11} = 219.035 \\ C_{12} = 7.437 \end{pmatrix}$

and V_2CFS (rGO) satisfy the Born criteria for elastic stability,⁵⁹ which can be defined as $C_{11} > 0$ and $C_{11} > |C_{12}|$. Young's modulus has been previously reported to range from 380 to 470 GPa for ordered graphene oxides, depending on the degree of oxygen functional group coverage.⁶⁰

The calculated Young's modulus of the V_2CFS (rGO) composite is 218.78 N/m, which is slightly lower than the experimentally reported values for monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ (318 N/m) and graphene (335 N/m).⁶¹ This moderate reduction in stiffness indicates enhanced mechanical flexibility, making the composite a promising candidate for use in flexible cathodes. While the incorporation of rGO into the MXene matrix improves electronic properties and interfacial interactions compared to the bare V_2CS system, the synergistic combination with functionalized MXene reduces rigidity relative to stand-alone rGO. This balance of moderate stiffness ($Y \sim 219$ N/m) and low shear resistance ($G \sim 106$ N/m) positions V_2CFS (rGO) as a promising candidate for flexible electronics, where mechanical compliance must coexist with robust electronic performance. Moreover, despite the increase in modulus compared to that of bare V_2CS (143.036 N/m), the composite remains considerably more flexible than pristine rGO, confirming the mechanical advantage conferred by MXene integration. The elastic stability of the material, reflected in the condition $C_{11} \gg |C_{12}|$, further ensures its structural integrity under deformation—an essential characteristic for next-generation flexible and wearable device platforms.

Moreover, a dry anhydrous etching strategy was recently proposed to synthesize fluorine-rich and hydroxyl-free $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes.⁶² Similarly, a dry molten salt method employing sulfur substitution has been demonstrated for the synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$, effectively eliminating the need for harsh acid treatments and complex procedures.⁶³ This strategy could be adapted to synthesize the proposed V_2CT_x MXenes. Moreover, the synthesis of MXene–rGO (reduced graphene oxide) composites can be carried out using freeze-drying or vacuum filtration methods, followed by thermal annealing if necessary, as demonstrated in previous studies,^{64–66} which supporting the experimental feasibility of the materials proposed in this work. Despite their promise, MXenes face practical challenges related to oxidation and long-term durability. V_2CT_x is susceptible to air and aqueous oxidation,^{67,68} which can degrade its layered

structure and compromise stability. Nevertheless, strategies such as composite formation with conductive carbon frameworks, surface modification, or doping to strengthen polysulfide anchoring and pillared or hierarchical architectures have been shown to mitigate these issues.^{69,70} Implementing these approaches may help unlock the full potential and practical applications of V_2CT_x for durable Na–S battery applications.

4. CONCLUSIONS

We have demonstrated that sulfur/fluorine coterminated MXene composites integrated with reduced graphene oxide—specifically $V_2CF_{0.6}S_{0.33}$ (rGO)—offer a powerful platform for high-performance, flexible room-temperature Na–S batteries. First-principles calculations reveal that this mixed-termination design markedly strengthens polysulfide anchoring, achieving adsorption energies of 0.8–3.90 eV, while preserving structural integrity and metallic conductivity for efficient electron transport.

The V_2CFS (rGO) composite exhibits the lowest Na_2S decomposition barrier reported for MXene-based Na–S cathodes (0.287 eV) and a thermodynamically favorable sulfur reduction pathway, enabling faster and more complete sulfur utilization. Electronic structure analyses (charge density difference, PDOS, and COHP) confirm that its superior performance arises from strong interfacial chemical bonding and substantial charge transfer with Na_2S_n species. Stress–strain simulations further demonstrate mechanical robustness combined with flexibility, underscoring its potential for a wearable energy storage devices.

These findings establish surface-termination engineering of MXene–graphene composites as a general strategy for suppressing polysulfide shuttling, enhancing redox kinetics, and delivering high-capacity, durable, and flexible Na–S batteries, with broader applicability to other metal–sulfur electrochemical systems.

■ ASSOCIATED CONTENT

Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.5c04042>.

Additional computational details, the structure of V_2C monolayer, optimized geometries of Na_2S_n species adsorbed on V_2CT_x surface, decomposition energy barrier, charge density difference plots, total and partial DOS, and computed adsorption energies (PDF)

Atomic coordinates of individual species and surface configurations provided in a separate compressed file in POSCAR format (ZIP)

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Author Contributions

R.S. and A.M. conceived the research idea. R.S. performed all simulations. R.S. and A.M. analyzed the data and interpreted the results. R.S. and A.M. cowrote and revised the manuscript.

Notes

The authors declare no competing financial interest.

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