A General Atomic Surface Modification Strategy for Improving Anchoring and Electrocatalysis Behavior of Ti₃C₂T₂ MXene in Lithium–Sulfur Batteries

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ABSTRACT: Multiple negative factors, including the poor electronic conductivity of sulfur, dissolution and shuttling of lithium polysulfides (Li₂Sₙ), and sluggish decomposition of solid Li₂S, seriously hinder practical applications of lithium–sulfur (Li–S) batteries. To solve these problems, a general strategy was proposed for enhancing the electrochemical performance of Li–S batteries using surface-functionalized Ti₃C₂ MXenes. Functionalized Ti₃C₂T₂ (T = N, O, F, S, and Cl) showed metallic conductivity, as bare Ti₃C₂. Among all Ti₃C₂T₂ investigated, Ti₃C₂S₂, Ti₃C₂O₂, and Ti₃C₂N₂ offered moderate adsorption strength, which effectively suppressed Li₂Sₙ dissolution and shuttling. This Ti₃C₂T₂ exhibited effective electrocatalytic ability for Li₂S decomposition. The Li₂S decomposition barrier was significantly decreased from 3.390 eV to ~0.4 eV using Ti₃C₂S₂ and Ti₃C₂O₂, with fast Li⁺ diffusivity. Based on these results, O- and S-terminated Ti₃C₂ were suggested as promising host materials for S cathodes. In addition, appropriate functional group vacancies could further promote anchoring and catalytic abilities of Ti₃C₂T₂ to boost the electrochemical performance of Li–S batteries. Moreover, the advantages of a Ti₃C₂T₂ host material could be well retained even at high S loading, suggesting the potential of surface-modified MXene for confining sulfur in Li–S battery cathodes.

KEYWORDS: Li–S battery, MXene, Ti₃C₂, surface modification, first-principles calculation

The increasing demand for portable electronics and electric vehicles has driven the development of high-performance rechargeable batteries. In various rechargeable battery systems, lithium–sulfur (Li–S) has attracted increasing attention due to its 5-fold energy density (2600 W·h·kg⁻¹ or 2800 W·h·L⁻¹) with respect to traditional lithium ion batteries (LIBs).¹⁻³ Moreover, sulfur is abundant, inexpensive, and has low toxicity. Although significant advances have been accomplished in recent years, many scientific and technical challenges still hinder the practical application of Li–S batteries. S cathodes experience multiple reduction/oxidation redox during cycling, consequently forming a series of Li₂Sₙ intermediate products. The insulating property of S, its noticeable volume change (80%) upon cycling, and the large decomposition energy of Li₂S cause sluggish reaction kinetics, resulting in large electrode polarization and poor rate capability. In addition, high-ordered lithium polysulfides (LiPSₙ; Li₂Sₙ, n = 4, 6, or 8) formed during dissolution.
discharge are soluble in aprotic electrolytes. A portion of soluble LiPSs shuttle to the Li metal anode and deposit there, resulting in rapid capacity decay.\(^{7,4−8}\)

Four aspects have been considered to address the aforementioned issues of Li–S batteries, including (1) conductive matrix, such as carbon materials\(^ {9−13}\) and metal nanoparticles,\(^ {14,15}\) to facilitate electron transport; (2) confinement framework, such as carbon materials\(^ {16,17}\) and transition metal nitrides\(^ {8,10}\)/sulfides\(^ {18−23}\)/carbides\(^ {6,11,24−26}\)/oxides/\(^ {17,27,28}\) to mitigate the S volume expansion during lithiation and suppress LiPSs dissolution; (3) blocking layer, such as functional interlayers\(^ {3,32}\) and separators,\(^ {30,31}\) to suppress LiPS shuttling; and finally (4) electrocatalysts, such as transition metal sulfides,\(^ {8}\) to improve Li\(_2\)S decomposition kinetics. Two-dimensional (2D) materials, such as graphene and transition metal dichalcogenides, have been studied as host materials for S cathodes and effectively improve the electrochemical performance of Li–S batteries. Besides these materials, 2D transition metal carbides and nitrides with a general formula of \(M\text{C}_{n+1}/M\text{N}_{n−1}\) (\(n = 2−4\)), termed MXenes, where “M” represents an early transition metal, such as Ti, V, Nb, and Mo, have drawn particular attention because of their excellent electronic conductivity, high surface area with abundant active sites, controllable hierarchical structure with high S loading, and physical confinement for electrode volume changes. Liang \textit{et al.} have shown that a S/Ti\(_2\)C composite with 70 wt % S loading exhibits a specific capacity of \(\sim 1200\) mAh-g\(^ {−1}\) at C/5 rate and stable long-term cycling (80% capacity retention over 400 cycles at C/2 rate) due to the strong LiPS interactions with surface Ti atoms.\(^ {25}\) In addition, Ti\(_2\)C/Ti\(_2\)CN nanosheet/carbon nanotube composites enable S cathodes with excellent cycling stability up to 1200 cycles with a low capacity fading rate of 0.043% per cycle.\(^ {11}\)

Almost all synthesized MXenes are terminated with large quantities of functional groups, including O, OH, or F. These functional groups play important roles in electrochemical energy storage and electrocatalytic properties. For example, compared with F and OH, O-functionalized MXenes have exhibited larger capacities in LIBs, while MXenes terminated with O have shown lower activity in hydrogen evolution reactions due to strong interactions between H and surface O.\(^ {32−34}\) Recently, non-native functional groups, such as P, Si, S, and Cl, have been introduced to MXenes, producing positive effects in electrochemical energy storage, such as in LIBs and supercapacitors.\(^ {35−38}\) MXenes have also achieved considerably improved performance in Li–S batteries. However, synergic effects of MXenes in Li–S batteries, including the anchoring ability for LiPSs as well as the catalytic effect for Li\(_2\)S decomposition, have not been clearly established, which has prompted their study at the atomic level. In this study, Ti\(_3\)C\(_2\) was investigated as the host material for S cathodes. The structural stability, electronic conductivity, and anchoring strength for S and Li\(_2\)S, and the catalytic ability for Li\(_2\)S decomposition were comprehensively studied by first-principles calculations. The anchoring strength and catalytic ability of Ti\(_3\)C\(_2\) were modulated by introducing different surface terminating groups (T), including N, P, O, S, F, and Cl, onto Ti\(_3\)C\(_2\) to screen for the best functionalized Ti\(_3\)C\(_2\)T\(_2\) as a S cathode host in Li–S batteries.

**RESULTS/DISCUSSION**

**Why Are Surface Terminating Groups Needed?** As one of the most common MXene materials, Ti\(_3\)C\(_2\) was constructed by sandwiched Ti and C atom layers stacked in a sequence of Ti–C–Ti–C–Ti, which can be described as three Ti layers being interleaved with two C layers, forming edge-shared Ti\(_6\)C octahedral structures (Figure 1a). Calculated electronic structures showed that Ti\(_3\)C\(_2\) has metallic conductivity (Figure 1b). The anchoring effect of Ti\(_3\)C\(_2\) was evaluated by calculating adsorption energies (\(E_{\text{ad}}\)) for S\(_8\) and Li\(_2\)S, according to the equation

\[
E_{\text{ad}} = E_{\text{MXene}} + E_{\text{LiS}} - E_{\text{MXene+LiS}}
\]

where \(E_{\text{MXene+LiS}}\) and \(E_{\text{MXene}}\) are the total energies of Ti\(_3\)C\(_2\) with/without Li\(_2\)S, respectively, and \(E_{\text{LiS}}\) is the total energy of Li\(_2\)S. A positive \(E_{\text{ad}}\) indicated favored adsorption. The \(E_{\text{ad}}\) for S\(_8\) was calculated in the same way. The lowest energy configurations of S\(_8\) and Li\(_2\)S were obtained using the CALYPSO code (Figure 1c), and the results showed that the adsorption strength of S\(_8\) and Li\(_2\)S on bare Ti\(_3\)C\(_2\) was very strong, indicated by the large \(E_{\text{ad}}\) values in the range of S–27 eV (Figure 2a). Under such a large adsorption strength, the S\(_8\) ring decomposed into single S atoms, which were then tightly captured by the outer Ti layer of Ti\(_3\)C\(_2\) (Figure 2b). A similar phenomenon also happened for Li\(_2\)S, where almost all S atoms in Li\(_2\)S were offloaded onto Ti\(_3\)C\(_2\) surfaces. According to these results, it is expected that bare Ti\(_3\)C\(_2\) would be fully terminated by S during preparation of S/Ti\(_3\)C\(_2\) or during initial electrochemical cycling. In other words, bare Ti\(_3\)C\(_2\) cannot be directly used in Li–S batteries. Therefore, in order to achieve reversible Li–S battery operation, surface modification of Ti\(_3\)C\(_2\) was required to obtain suitable adsorption strength with S and Li\(_2\)S.

**Structure and Electronic Properties of Ti\(_3\)C\(_2\)T\(_2\).** Based on the above discussion, six surface terminating groups, T = N, P, O, S, F, and Cl, were considered for Ti\(_3\)C\(_2\). The favored sites for terminating groups were determined by performing total energy calculations for T-saturated Ti\(_3\)C\(_2\) monolayers, termed Ti\(_3\)C\(_2\)T\(_2\). There were three possible positions for T, i.e., on top of the Ti(1) atom (site \(\alpha\)), on top of the C atom (site \(\beta\)), and on top of the Ti(2) atom (site \(\gamma\), Figure 1a). Three possible configurations were considered for these terminating groups (Figure S1, Supporting Information), and the total energies of all possible Ti\(_3\)C\(_2\)T\(_2\) phases are listed in Table S1. In mode I, T
groups were at site $\alpha$ on both sides of the Ti$_3$C$_2$ layer; in mode II, at site $\beta$ on both sides of the monolayer; and in mode III, at site $\gamma$ on both sides of the monolayer. For the Ti$_3$C$_2$T$_2$ (T = P, O, S, F, and Cl) phases, mode III had the lowest total energy, while mode II was the lowest energy phase for Ti$_3$C$_2$N$_2$. The binding energies of terminated atoms on Ti$_3$C$_2$ were calculated to verify the thermodynamic stability of functional groups, as listed in Table S2. As a result, all of the terminated atoms could be energetically stable to bind with Ti$_3$C$_2$. In addition, thermal stability of Ti$_3$C$_2$T$_2$ was examined by performing AIMD simulations at 298, 800, and 1000 K. All functionalized Ti$_3$C$_2$T$_2$ maintained their structural integrity after 5 ps of stimulation except Ti$_3$C$_2$P$_2$ (Figure S2). For Ti$_3$C$_2$P$_2$, although the Ti$_3$C$_2$ part retained structural integrity at 298 K, P atoms bonded to each other in some disorder and the distorted structure could not recover the initial configuration after structural relaxation. One possible reason could be that P atoms have the maximum atomic radius (110.5 pm) among all the species of atoms considered, more easily bonding with each other on the limited Ti$_3$C$_2$ surface. What is more, phonon dispersions along the high symmetrical directions of the Brillouin zone for Ti$_3$C$_2$T$_2$ were calculated to determine the lattice dynamic stabilities, as shown in Figure S3. Except for Ti$_3$C$_2$P$_2$, no imaginary frequency phonon was found for Ti$_3$C$_2$T$_2$ (T = N/O/S/F/Cl), indicating the lattice dynamic stability of Ti$_3$C$_2$T$_2$ with a variety of practically relevant terminations. The results were consistent with AIMD simulations. Consequently, P functional groups were not included in the following discussion. Hence, Ti$_3$C$_2$ could be feasibly functionalized by N, O, S, F, or Cl groups, in which O and F are native functional groups born from material preparation and the others can be subsequently introduced with appropriate experimental control.

Calculated electron density of states (DOS) showed that, except for ferromagnetic Ti$_3$C$_2$N$_2$, all functionalized Ti$_3$C$_2$T$_2$ were nonmagnetic by considering spin polarization. For all Ti$_3$C$_2$T$_2$ phases, the majority of electron states at the Fermi level were from Ti-3d states (Figure 3). As a result, the metallic conductivity of Ti$_3$C$_2$ was well retained after surface functionalization. The excellent electronic conductivity of Ti$_3$C$_2$T$_2$ could cure S’s low conductivity and thus improve the electrochemical performance of Li–S batteries. The obvious hybridization between Ti-3d and T(N/O/F)-2p/T(S/Cl)-3p indicated a strong (partial) polar covalent Ti–T bonding.

**Anchoring Ability for Li$_2$S$_n$.** Density functional theory (DFT) calculations were performed to study the anchoring effects of Ti$_3$C$_2$T$_2$ (T = N, O, S, F, or Cl) for Li–S batteries. The optimized adsorption conformations of Li$_2$S$_x$ and S$_8$ on Ti$_3$C$_2$T$_2$ are shown in Figure S4. The adsorption strength between Ti$_3$C$_2$T$_2$ and Li$_2$S$_x$ (or S$_8$) was evaluated by $E_{ad}$ based on eq 1. The calculated $E_{ad}$ with vdWs at different lithiation degrees reflected a combination of chemical and physical (vdW) interactions between Ti$_3$C$_2$T$_2$ and Li$_2$S$_x$ (or S$_8$, Figure 4a). For all Ti$_3$C$_2$T$_2$ phases, the $E_{ad}$ for S$_8$ was smaller than that for Li$_2$S$_x$. The calculated $E_{ad}$ 0.75–1.20 eV, was much closer to that of S$_8$ on graphene, transitional metal oxides, and sulfides. With S lithiation, different functional groups showed distinct anchoring effects, which were divided into three classes according to the $E_{ad}$ magnitude. The adsorption strengths for Ti$_3$C$_2$O$_2$ and Ti$_3$C$_2$S$_2$ (at 2.0–4.5 eV) were much stronger...
than the others during the whole lithiation process. The adsorption strengths for Ti$_3$C$_2$Cl$_2$ and Ti$_3$C$_2$F$_2$ were relatively weak, in the range of 0.8−1.4 eV. In comparison, the adsorption strength for Ti$_3$C$_2$N$_2$ was in the middle of those of the five Ti$_3$C$_2$T$_2$ phases. Consequently, the adsorption strength followed the sequence Cl < F < N < O < S. For almost all Ti$_3$C$_2$T$_2$ phases, the evolution of $E_{\text{ad}}$ followed a similar trend, growing stronger with increasing lithiation and reaching a maximum for the fully lithiated Li$_2$S product. The role of surface terminations in suppressing LiPS shuttling was verified by calculating the $E_{\text{ad}}$ and comparison with Li$_2$S$_n$ ($n \geq 4$) binding strength on DOL/DME electrolyte solvent molecules (DOL, 1,3-dioxolane; DME, 1,2-dimethoxyethane, Figure S5). Except for Ti$_3$C$_2$Cl$_2$, all $E_{\text{ad}}$ values were stronger than those for Li$_2$S$_n$ ($n \geq 4$) bonded with DOL/DME (0.74−0.79 eV), which indicated that Ti$_3$C$_2$T$_2$ (T = N, O, S, or F) could be expected to effectively suppress LiPS shuttling. However, based on the crystal structure model, DFT calculations cannot deal with the effect of electrolyte content on the adsorption and anchoring properties of Ti$_3$C$_2$T$_2$ MXenes. The calculations of the binding effects of the two molecular groups (DOL and DME) with polysulfides could only qualitatively evaluate the advantages of S fixation on Ti$_3$C$_2$T$_2$ by a simplified method. Based on the above analysis, the Ti$_3$C$_2$T$_2$ can fix S and Li$_2$S$_n$ on their surfaces and prevent the polysulfide dissolution and shuttling in the electrolyte solvent. These advantages, together with the intrinsic thermal and thermodynamic stabilities of the Ti$_3$C$_2$T$_2$ host materials, may effectively improve the cycle stability of Li−S batteries, resulting in prolonged cycle life.

Based on increasing $E_{\text{ad}}$ with lithiation, the anchoring effects of Ti$_3$C$_2$T$_2$ were expected to mainly derive from chemical interactions between Ti$_3$C$_2$T$_2$ and Li$_2$S$_n$. Interactions between Ti$_3$C$_2$T$_2$ and Li$_2$S$_n$ (or S$_8$) were identified by determining the contributions of chemical and physical (vdW) interactions at different lithiation stages and then evaluated by comparison with adsorption energies without vdW functions (Figure 4b). For all Ti$_3$C$_2$T$_2$ phases, except Ti$_3$C$_2$N$_2$, vdW interactions dominated $S_8$ adsorption at nearly 100%. In other words, no chemical bonds formed between S atoms and Ti$_3$C$_2$T$_2$ (T = O/S/F/Cl). With lithiation, the changing trend of vdW interactions was almost the opposite of that of $E_{\text{ad}}$; that is, vdW interactions gradually decreased with lithiation and reached a minimum value for Li$_2$S. For relatively strongly terminated Ti$_3$C$_2$, such as with O/S/N, vdW interactions decreased linearly with lithiation and chemical interactions increased at the same time. For weakly terminated Ti$_3$C$_2$, such as with F and Cl, vdW interactions dominated the whole lithiation process, to >55% percentage. According to the above discussion, chemical interactions between Ti$_3$C$_2$T$_2$ and Li$_2$S$_n$ (or S$_8$) were mostly derived from intercalated Li$^+$, while vdW interactions were mainly contributed by S.

In assessing the nature of the interaction between Ti$_3$C$_2$T$_2$ and Li$_2$S$_n$ (or S$_8$), the charge density difference was analyzed by the equation.
\[ \Delta \rho = \rho_{TixC_nT_2} - \rho_{LiS} - \rho_{LiS/S} \]  

Here, the adhesion conformations of S8 and Li2S6 on TiC2T2 (T = N, O, S, or Cl) were taken as examples (Figure 4c−1). When S8 was adsorbed on TiC2T2 surfaces, most charge transfer occurred inside S8 clusters and TiC2T2. This indicated that there was no chemical bonding between S8 and TiC2T2 and that the interactions between them mainly depended on vdW adsorption. Only for TiC2N2 was a certain amount of charge transferred between S and Ti, forming Ti−S polar covalent bonds. Meanwhile, when Li2S6 was adsorbed on TiC2T2 (T = N, O, S), electron-rich (green) regions appeared between Li and T, indicating the formation of Li−T bonds. At the same time, Li−S and S−S bonds in Li2S6 were weakened with the increase of electron-deficient regions (blue) between Li (or S) and S, which might have contributed to Li2S decomposition.

Catalytic and Diffusion Kinetic Properties. The final discharge product of Li−S batteries, Li2S, suffers from low electronic conductivity, low Li+ diffusivity, and high decomposition energy, which resulted in high overpotential and low rate capability. Consequently, Li2S decomposition kinetics (Li−S bond breaking) and Li+ diffusion on the substrate were vital for the electrochemical performance of Li−S batteries. Deeper insight into the reaction mechanisms of Li2S decomposition was gained by analyzing Li2S decomposition kinetics on TiC2T2 using the climbing-image nudged elastic band (CI-NEB) method. The decomposition process was drawn from an original Li2S molecule into a LiS cluster and a single Li+, i.e., Li2S → LiS + Li+ + e−. The results showed that the natural Li2S decomposition barrier was as large as 3.390 eV. All considered, TiC2T2 could reduce the Li2S decomposition barrier effectively (Table 1, Figure S6). Among them, TiC2S2 showed the largest decomposition barrier of ~1.5 eV, which could have been due to weak interactions between Li2S and TiC2S2, such that Li−S bond breaking was weakly affected by the substrate. The decomposition barriers on TiC2N2 and TiC2F2 were reduced to 1.0 eV. Furthermore, TiC2S2 and TiC2O2 showed much smaller decomposition barriers, at 0.351 and 0.411 eV, respectively. These values were comparable with those reported for traditional metal disulfides (0.31−0.56 eV). Therefore, these two TiC2T2’s could efficiently catalyze Li2S decomposition and reduce the overpotential of Li−S batteries. The decomposition barrier on TiC2S2 was observed to be much smaller than that on TiC2S2 (~1.51 eV). This indicated that the M/C ratio of MXenes might have influenced the catalytic ability for Li2S decomposition. The efficient catalysis of TiC2T2 for Li2S decomposition helped improve the electrode kinetics of Li−S batteries. Moreover, fast decomposition of Li2S, (n = 4, 6, or 8) was also required because it could shorten the LiPS accumulation time in the cathode and thus reduce LiPS dissolution. Hence, the Li2S decomposition kinetics on TiC2T2 were further studied, and the trend of the Li2S decomposition barrier was found to be like that of Li2S, which was reduced from 3.406 eV (for native Li2S) to 0.180, 0.211, 0.434, 1.208, and 1.532 eV for TiC2S2, TiC2O2, TiC2N2, TiC2F2, and TiC2Cl2, respectively (Figure S7).

As Li+ diffusion on substrate materials is closely related to Li2S nucleation and decomposition, Li+ diffusivity on TiC2T2 was studied by calculating diffusion barriers. The energy profiles along the Li+ diffusion coordinate showed that the minimum Li+ diffusion barriers on TiC2S2, TiC2O2, TiC2F2, and TiC2Cl2 were 0.188, 0.236, 0.187, and 0.196 eV, respectively, which were much lower than that of Li+ on graphene (0.300 eV, Figure S8), with one exception—the Li+ diffusion barrier on TiC2N2 was as large as 0.573 eV. This was because the valence electrons of N formed stronger Li−N ionic bonds, which limited Li+ diffusivity. To summarize, the kinetic properties of TiC2T2 in Li−S batteries, including catalytic effects and Li+ diffusion, followed the priority sequence of TiC2S2 > TiC2O2 > TiC2F2 > TiC2N2 > TiC2Cl2.

Vacancy Effect. MoS2 with sulfur deficiencies has been shown to possess better catalytic ability than stoichiometric MoS2 in Li−S batteries.41 To solve the poor adsorption strength and sluggish electrode kinetics of TiC2Cl2, a small portion of Cl deficiencies were produced to form TiC2Cl2−x (x = 1/16). Here, the vacancy formation energy of one Cl in a 4 × 4 × 1 TiC2Cl2 supercell was calculated to be ~2.866 eV, indicating a Cl vacancy could form on the TiC2Cl2 surface. Compared with intact TiC2Cl2, the Ead of Li2S (S8) increased from 0.7−1.1 eV to 2.5−3.5 eV (Figure 5a). The vdW interaction ratio was decreased to 25−33%, while chemical

Table 1. Calculated Li2S, Li2S6 Decomposition Barriers, and Li+ Diffusion Barriers on TiC2T2

<table>
<thead>
<tr>
<th>substrate</th>
<th>Li2S (eV)</th>
<th>Li2S6 (eV)</th>
<th>Li+ diffusion barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC2O2</td>
<td>0.411</td>
<td>0.211</td>
<td>0.236</td>
</tr>
<tr>
<td>TiC2S2</td>
<td>0.351</td>
<td>0.180</td>
<td>0.188</td>
</tr>
<tr>
<td>TiC2N2</td>
<td>1.101</td>
<td>0.434</td>
<td>0.573</td>
</tr>
<tr>
<td>TiC2F2</td>
<td>0.903</td>
<td>1.208</td>
<td>0.187</td>
</tr>
<tr>
<td>TiC2Cl2</td>
<td>1.625</td>
<td>1.532</td>
<td>0.196</td>
</tr>
</tbody>
</table>

Figure 5. (a) Adsorption energies, (b) ratio of vdW interaction of S8 and Li2S on TiC2Cl2−x (x = 1/16); electron localization functions of the (110) slice of (c) TiC2Cl2−x and (d) TiC2Cl2.
interactions increased (Figure 3b). This could have been due to the Cl vacancy with an electron-rich region (Figure 5c), which could be easily bonded with the S of Li2S4 (S8). In addition, the adsorption strength for Li2S4 was much stronger than the bonding energy with DOL/DME, which greatly suppressed the shuttling effect. In addition, decomposition barriers for Li2S and Li2S4 on Ti3C2T2 declined dramatically, to 0.316 and 0.537 eV (Figure S9), respectively, which were even lower than those on the optimal Ti3C2S4. Consequently, it was speculated that appropriate functional group vacancies would further promote the anchoring and catalytic capabilities of Ti3C2T2 to boost the electrochemical performance of Li–S batteries.

Effects of S Loading Amount. According to the above analysis, Ti3C2T2, particularly with T = O and S, can improve the electrochemical properties of the sulfur cathode. However, it should be noted that the electrochemical performance of Li–S batteries is strongly affected by the S loading amount in the cathode. The structure model used in the above analysis, one S8 (or Li2S4) molecule adsorbed on a 4 × 4 × 1 supercell, only corresponded to a small S loading (0.9–6.5 wt %) in the MXene host material, which does not reflect the real Li–S batteries. Hence, in order to evaluate the practical application of Ti3C2T2 in Li–S batteries, we further studied the influence of S loading on the anchoring effect and electronic and catalytic properties of Ti3C2S4, which has been predicted to possess the best performance among all Ti3C2T2 MXenes under investigation.

First, we studied the anchoring ability of the Ti3C2S4 monolayer for the S and Li2S4 electrodes with different S contents, i.e., S8 (35.7 wt %), Li2S4 (30.3 wt %), Li2S4 (32.6 wt %), and Li2S (14.7 wt %). As shown in Table 2, all the adsorption energies for the above species (ΔE1) were negative, indicating that the Ti3C2S4 host material could effectively anchor sulfur and suppress the dissolution of LiPSs. Especially, the adsorption energies (ΔE2) became even more negative with further adsorption of an additional S4 (or Li2S4) molecule on the Ti3C2S4 substrate. This indicated that the anchoring effect of Ti3C2S4 could be well retained under high S loading. On the above basis, we further calculated the electronic structures of the Ti3C2S4 host material with/without S and Li2S4 adsorption. The S4 molecule has an intrinsic insulator property (Figure 6a), while the Ti3C2S4 host material is obviously metallic (Figure 6b). The electronic structure of the Ti3C2S4/S4 composite exhibited sizable electron states crossing the Fermi level, which indicated that the insulating property of pristine S4 has been successfully changed by the Ti3C2S4 host (Figure 6c). In addition, all the Ti3C2S4/Li2S4 (n = 6, 4, 1) composites also showed metallic properties (Figure 6d–f). This indicates that the electrode can maintain high electronic conductivity during the whole lithiation/delithiation process, which is very helpful for the rate capability and cycle stability of the Li–S battery cells. Finally, we studied the Li2S decomposition barriers on the Ti3C2S4 surface with different S loading contents. CI-NEB calculations showed that the decomposition barrier of Li2S increased from 0.351 eV to 1.900 eV when the Li2S concentration increased from 1/16 (corresponding to a S loading of 0.9 wt %) to 19/16 (corresponding to a S loading of 14.7 wt %) per Ti3C2S4. However, all these decomposition barriers were much lower than the original decomposition barrier of 3.390 eV for bare Li2S (Figure 6g). The results showed that the catalytic capacity of the Ti3C2S4 host material could be well maintained even at high S loading contents.

CONCLUSIONS

In this work, Ti3C2 MXenes were systematically studied as the S cathode host for Li–S batteries by first-principles calculations. It was shown that bare Ti3C2 cannot be directly used in Li–S batteries because of excessively strong interactions between Li2S4/Li2S4 and Ti3C2-induced decomposition of S8 and Li2S4. Ti3C2 terminated with functional groups can achieve high performance in Li–S batteries. Among various functional groups, S and O were identified as the best choices for Ti3C2 surface modification, in which O was a native moiety derived from material preparation and S was introduced secondarily with appropriate experimental control. The improved Li–S battery performance benefited from using Ti3C2T2 as the host material for the following reasons: (1) metallic properties of Ti3C2T2 conferred high electronic conductivity to the S cathode, (2) the moderate surface adsorption strength effectively suppressed Li2S4 dissolution and shuttling, and (3) the electrocatalytic ability of Ti3C2T2 accelerated the electrode reaction kinetics for Li2S decomposition. These advantages can be well retained even at high S loading, supporting the practical application of Ti3C2T2 as a host material for Li–S batteries. Also, appropriate vacancies in surface terminations further promoted the anchoring and electrocatalytic ability of Ti3C2T2 to boost the electrochemical performance of Li–S batteries. This study provides a general strategy for enhancing the electrochemical properties of Li–S batteries by atomic surface modification of MXenes.

METHODS

First-principles calculations were performed within the framework of DFT, as implemented in the Vienna ab initio simulation package.42 The projector-augmented wave potential was used with a plane-wave cutoff energy of 600 eV.43 Exchange-correlation energy was described by the generalized gradient approximation in the scheme proposed by Perdew–Burke–Ernzerhof.44 Spin alignments were studied by spin-polarized calculations. For geometry optimization, the Brillouin-zone integration was performed using a Monkhorst-Pack grid of k-point sampling.45 Considering the strong correlation in titanium (Ti), the electronic structure was calculated using a generalized gradient approximation (GGA) plus Hubbard U (GGA +U) method with a U value of 4.2 eV.46,47 Geometry optimizations were performed using the conjugated gradient method, with the convergence threshold set at 1 × 10−5 eV-atom−1 in energy and 0.01 eV-Å−1 in force. A vacuum distance of >20 Å was employed to avoid interactions of neighboring images. The configurations of S8 and Li2S4 (n = 1, 2, 4, 6, and 8) were predicted by the advanced swarm-intelligence structure prediction method implemented in the CALYPSO code.48,49 For all cases, structural searching simulations for each calculation were stopped after generating over 500 structures (e.g., ~20–30 generations).
The van der Waals forces between Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2} and Li\textsubscript{2}S\textsubscript{n} were accurately dealt with using the vdW-inclusive DFT-D3 method, which introduced empirical dispersion corrections implemented by Grimme.\textsuperscript{50} The different sulfur amount configurations were based on a 4×4×1 supercell of Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2}. Furthermore, the CI-NEB method was applied for computing diffusion and decomposition barriers.\textsuperscript{51} The force convergence criterion for optimization was set at 0.01 eV Å\textsuperscript{−1}. Ab initio molecular dynamics (AIMD) simulations were performed at different temperatures of 298, 800, and 1000 K. AIMD simulations in an NVT ensemble using the Nosè−Hoover heat method lasted for 5 ps with a time step of 1.0 fs. The phonon spectra were calculated using the PHONOPY package.\textsuperscript{52}

Figure 6. Density of states for S\textsubscript{8}, Ti\textsubscript{3}C\textsubscript{2}S\textsubscript{2}, Ti\textsubscript{3}C\textsubscript{2}S\textsubscript{2}/S\textsubscript{8}, Ti\textsubscript{3}C\textsubscript{2}S\textsubscript{2}/Li\textsubscript{2}S\textsubscript{n}, Ti\textsubscript{3}C\textsubscript{2}S\textsubscript{2}/Li\textsubscript{2}S\textsubscript{n}, and Ti\textsubscript{3}C\textsubscript{2}S\textsubscript{2}/Li\textsubscript{2}S (a, b, c, d, e, f, respectively). The Fermi level is set to zero. (g) Decomposition barriers of bare Li\textsubscript{2}S (black) and Li\textsubscript{2}S on the Ti\textsubscript{3}C\textsubscript{2}S\textsubscript{2} supercell with 1/16 (green) and 19/16 (red) Li\textsubscript{2}S to Ti\textsubscript{3}C\textsubscript{2}S\textsubscript{2} ratios.

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.9b03412.

Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2} configurations and snapshots of the equilibrium structures after AIMD simulation, adsorption configurations of Li\textsubscript{2}S\textsubscript{n} and S\textsubscript{8} on Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2}, configurations and binding energies of Li\textsubscript{2}S\textsubscript{n} (n = 4, 6, 8) bound with DME and DOL, energy profiles for the decomposition of Li\textsubscript{2}S and Li\textsubscript{2}S\textsubscript{n} in a vacuum and on Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2}, Li\textsuperscript{+} diffusion on Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2} (PDF)

### Associated Content

#### Notes

The authors declare no competing financial interest.

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