First-Principles Study on the Structural, Electronic, and Lithium Storage Properties of Ti$_3$C$_2$T$_2$ (T = O, F, H, OH) MXene

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1. INTRODUCTION

MXenes, known as two-dimensional transition metal carbides, nitrides, and/or carbonitrides, have a general formula of M$_n$X$_m$T$_x$ (n = 1, 2, 3), where M is the transition metal elements (M = Ti, Zr, Hf...), X stands for C and/or N, and $T_x$ represents the surface functional groups such as $-O$, $-F$, $-OH$, and so on. The first MXene, Ti$_3$C$_2$T$_x$, was discovered by Y. Gogotsi and M. W. Barsoum in 2011 by selecting etching Al from Ti$_3$AlC$_2$ with hydrofluoric acid solution at room temperature. To date, more than 50 different configurations of MXenes have been successfully synthesized, while more than 100 potential compositions of MXenes have been predicted. MXenes have excellent thermal stability, conductivity, photoelectric performance, mechanical performance, and theoretical storage capacity, showing a variety of applications in sensing, photocatalysis, electromagnetic shielding, and energy storage.

At present, surface functionalized MXenes are synthesized by almost all experimental processes, while bare MXenes can hardly be synthesized. The surfaces of MXenes prepared by fluoride solution and fluorne-salt etching usually have functional groups such as $-F$, $-O$, and $-OH$. Surface groups such as $-O$ and $-OH$ were introduced into MXenes prepared by hydrothermal assisted alkali etching. Electrochemical etching can introduce groups such as $-Cl$, $-O$, and $-OH$, and MXenes with $-Cl$ and $-O$ terminal groups can be obtained by Lewis acid molten salt etching. In recent years, a large number of studies have shown that the surface functional groups have a great influence on the structures of MXenes and thus can affect their electronic, optical, mechanical, thermal, and electrochemical properties. Hu et al. revealed the thermodynamic stability sequence of MXenes with different groups through Bader charge analysis and thermodynamic calculation, and the results showed that the MXenes had higher thermodynamic stability with the O group. Xie and Kent investigated the structural and electronic properties of Ti$_{3n+1}$C$_n$ and Ti$_{3n+1}$N$_n$ (n = 1–9) with surfaces terminated by O, F, H, and OH groups. Fu et al. studied the influence of different groups (Cl, F, O, and OH) on the mechanical properties, chemical stability, and electronic structure of MXenes by using density functional theory, revealing that Ti$_3$C$_2$O$_2$ MXene had excellent...

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stability and high mechanical strength. Tang et al.\textsuperscript{27} studied the lithium storage performance of Ti$_3$C$_2$F$_2$ and Ti$_3$C$_2$(OH)$_2$ MXenes and found that F and OH terminal groups were not conducive to ion transport and redox reaction and inhibited the ability of MXene to store charge. Although studies on the influence of functional groups on MXenes have never stopped and great achievements have been made, it is undeniable that the influence of laws of many functional groups on various properties are not clear. MXenes have attracted much attention in the study of functional terminals on various surface functional groups. The layered structure can achieve reversible Li$^+$ intercalation, and the functional groups can realize the optimization of electrochemical performance.\textsuperscript{1} Therefore, the effect of functional groups on the lithium storage performance of MXenes needs to be further studied.

In this paper, the structures of bare Ti$_3$C$_2$ and Ti$_3$C$_2$T$_2$ (T = O, F, H, OH) were constructed and optimized; and the effect of T$_2$ (T = O, F, H, OH) on the structural, electronic, and lithium storage properties of Ti$_3$C$_2$ MXene was studied.

### 2. CALCULATION METHODS

In this paper, first-principles calculations were performed using the CASTEP\textsuperscript{28} quantum mechanics program. The functional method\textsuperscript{29} of the generalized gradient approximation (GGA) and the Perdew–Burke–Ernzerhof (PBE) functional is used to deal with the exchange correlation function. The interaction between the electron and nuclear ion adopts the Ultrasoft pseudopotential.\textsuperscript{30} During the structural optimization, the energy deviation per atom is less than $5.0 \times 10^{-6}$ eV, the force per atom is less than 0.01 eV/Å, the maximum displacement deviation is less than 5.0 $\times$ $10^{-4}$ Å, and the maximum stress deviation is less than 0.02 GPa. A $5 \times 5 \times 1$ grid for the Brillouin zone integration was generated using the Monkhorst–Pack\textsuperscript{31} k-point sampling method. The plane wave cutoff energy was set to 450 eV, and the energy convergence was chosen to be $5.0 \times 10^{-7}$ eV. A $2 \times 2 \times 1$ supercell was established to study lithium storage performance.

### 3. RESULTS AND DISCUSSION

#### 3.1. Structural Properties

In this paper, the hexagonal Ti$_3$C$_2$ structure with the space group of P$\bar{3}m1$ (No. 164) is obtained by removing the Al atoms form Ti$_3$AlC$_2$. A schematic diagram of the crystal structure of Ti$_3$C$_2$ and its precursor Ti$_3$AlC$_2$ is shown in Figure 1a–c. The surface functionalized structure of Ti$_3$C$_2$T$_2$ (T = O, F, H, OH) is shown in Figure 1d–e. The functional groups of O, F, H, and OH have three potential sites on the surface of Ti$_3$C$_2$: the TOP site over the Ti atoms at the top surface, the HCP site, and CCP sites above the center of three Ti atoms at the surface, under which there exist one C and Ti atom, respectively.

After structural optimization, the lattice parameters of bare and functionalized Ti$_3$C$_2$T$_2$ (T = O, F, H, OH) are shown in Table 1, in which $a$ is the lattice constant of MXenes, and $h$ represents the thickness of a two-dimensional single-layer of Ti$_3$C$_2$T$_2$. The results show that the lattice constant $a$ of Ti$_3$C$_2$ without surface functionalization is 3.098 Å. The thickness $h$ of

![Figure 1. Crystal structures: (a) bulk Ti$_3$AlC$_2$, (b,c) top and side views of 2D Ti$_3$C$_2$ MXene, (d,e) top and side views of the HCP, CCP, and TOP sites for functionalized Ti$_3$C$_2$T$_2$.](http://pubs.acs.org/journal/acsodf)

| Ti$_3$C$_2$T$_2$ | structure | $a$ (Å) | $h$ (Å) | $d_{C-C}$ (Å) | $d_{C-Ti}$ (Å) | $d_{C-O}$ (Å) |
|---------------|-----------|--------|--------|---------------|---------------|-------------|
| Ti$_3$C$_2$   | present   | 3.098  | 4.629  | 2.220         | 2.048         |
|               | calc.\textsuperscript{32} | 3.058  |        |               |               |
|               | calc.\textsuperscript{33} | 3.085  | 4.742  |               |               |
|               | calc.\textsuperscript{34} | 3.071  | 4.605  |               |               |
| Ti$_3$C$_2$O$_2$ | HCP      | 3.087  | 5.886  | 2.203         | 2.142         | 2.036       |
|               | CCP      | 3.083  | 5.808  | 2.202         | 2.052         | 1.993       |
|               | TOP      | 3.103  | 6.108  | 2.216         | 2.113         | 1.994       |
| Ti$_3$C$_2$F$_2$ | HCP      | 3.091  | 6.062  | 2.211         | 2.070         | 2.216       |
|               | CCP      | 3.089  | 5.965  | 2.207         | 2.055         | 2.184       |
|               | TOP      | 3.109  | 6.125  | 2.215         | 2.060         | 2.181       |
| Ti$_3$C$_2$H$_2$ | HCP      | 3.091  | 5.867  | 2.214         | 2.070         | 2.094       |
|               | CCP      | 3.095  | 5.686  | 2.206         | 2.048         | 2.041       |
|               | TOP      | 3.102  | 6.138  | 2.218         | 2.067         | 2.094       |
| Ti$_3$C$_2$(OH)$_2$ | HCP | 3.090  | 7.007  | 2.208         | 2.081         | 2.210       |
|               | CCP      | 3.087  | 6.957  | 2.190         | 2.062         | 2.180       |
|               | TOP      | 3.110  | 7.832  | 2.219         | 2.069         | 2.195       |
single-layer Ti$_1$C$_2$ is equal to 4.629 Å. The data in this paper are in good agreement with the reported experimental values$^{32}$ and the theoretical values$^{33,34}$

The lattice constants $a$ of the surface functionalized Ti$_1$C$_2$T$_3$ MXene have changed little and are close to those of Ti$_3$C$_2$. Compared with the lattice constant $a$ of bare Ti$_3$C$_2$ (3.098 Å), the counterpart of the surface functionalized Ti$_1$C$_2$T$_3$ MXene at the HCP site (3.087–3.091 Å) or CCP site (3.083–3.095 Å) decreases, but the counterpart of the surface functionalized Ti$_1$C$_2$T$_3$ at the TOP site (3.102–3.110 Å) increases. Compared with the thickness $h$ of bare Ti$_3$C$_2$ (4.629 Å), the $h$ value of surface functionalized Ti$_1$C$_2$T$_3$ MXene increases. The result showed that the $h$ value slightly increases at the CCP site (5.686–6.957 Å) and increases more at the TOP site (6.108–7.832 Å), and the discrepancy may come from the influence of steric hindrance.$^{35,36}$ In addition, the influence of surface functional groups on structural properties of Ti$_1$C$_2$T$_3$ is also reflected on the bond length between the middle Ti atoms and the C atoms $d_{T1C}$ and the bond length between the surface Ti atoms and the C atoms $d_{T2C}$. Compared with the bond length $d_{T1C}$ = 2.222 Å and $d_{T2C}$ = 2.048 Å in bare Ti$_3$C$_2$, the bond length $d_{T1C}$ (2.190–2.219 Å) almost keeps unchanged, while the $d_{T2C}$ (2.048–2.142 Å) increases significantly in Ti$_1$C$_2$T$_2$ ($T$ = O, F, H, OH). In general, the lattice distortion of functionalized MXene at the CCP position is the smallest among the three potential sites, which is potential evidence for the most stable position of functional groups at the CCP site. In order to determine the structural stability of surface functionalized Ti$_1$C$_2$T$_2$ ($T$ = O, F, H, OH), eq $^{17}$ was used to calculate the formation energies of O, F, H, and OH functional terminals at HCP, CCP, and TOP sites, and the results are plotted in Figure 2:

$$\Delta E_f = E_{\text{tot}}(\text{Ti}_1\text{C}_2\text{T}_2) - E(\text{Ti}_3\text{C}_2) - E(T_2)$$  

where $E_{\text{tot}}(\text{Ti}_1\text{C}_2\text{T}_2)$ represents total energy of the surface functionalized Ti$_1$C$_2$T$_2$, $E(\text{Ti}_3\text{C}_2)$, and $E(T_2)$ are the isolated energy of bare Ti$_3$C$_2$ and functional groups, respectively. It is clear in Figure 2a that the formation energies of all functionalized Ti$_1$C$_2$T$_2$ ($T$ = O, F, H, OH) structures are negative, indicating that these structures are stable. Compared with the formation energies of Ti$_1$C$_2$H$_2$, the counterparts of Ti$_3$C$_2$O$_2$, Ti$_3$C$_2$F$_2$, and Ti$_1$C$_2$(OH)$_2$ are lower, indicating that the structures of Ti$_3$C$_2$O$_2$, Ti$_3$C$_2$F$_2$, and Ti$_1$C$_2$(OH)$_2$ are much more stable. The adsorption energy of the H functional group is the highest among the four functional groups, which provides a reasonable explanation for the rare observation of H-terminated Ti$_3$C$_2$H$_2$ MXene in experiment reports.$^{17,33,38}$ In addition, it is shown in Figure 2 that the surface functional groups tend to be located at CCP sites, with the lowest energy among the three potential sites. This is consistent with the conclusion reported in the literature.$^{25,27,39}$ In the following calculations, the structures of Ti$_3$C$_2$T$_2$ ($T$ = O, F, H, OH) with the functional group located in CCP sites will be discussed.

To further confirm the dynamic stabilities of these MXenes, the phonon spectra were also simulated. As mentioned above, from the perspective of formation energy, Ti$_3$C$_2$O$_2$, Ti$_3$C$_2$F$_2$, and Ti$_1$C$_2$(OH)$_2$ are more stable than Ti$_3$C$_2$H$_2$. So taking the Ti$_1$C$_2$H$_2$ as an example, the calculated phonon dispersion curves are shown in Figure 2b. It can be seen that there is no imaginary phonon frequency in the whole Brillouin zone, indicating that the CCP site of the Ti$_3$C$_2$H$_2$ configuration is dynamically stable. Moreover, the Ti$_3$C$_2$O$_2$, Ti$_3$C$_2$F$_2$, and Ti$_1$C$_2$(OH)$_2$ are also confirmed to be dynamically stable.

### 3.2. Electronic Property

Band structure plays an important role in studying electronic properties of materials. The calculated band structures of Ti$_3$C$_2$T$_2$ ($T$ = O, F, H, OH) with the high-symmetry point path of Γ−M−K−Γ are plotted in Figure 3. The electronic properties of Ti$_3$C$_2$T$_2$ MXene are strongly associated with the surface terminations. The results show that there are substantial electron states crossing the Fermi level and there is no band gap, indicating that Ti$_3$C$_2$T$_2$ ($T$ = O, F, H, OH) is metallic. Therefore, the metalliclicity of Ti$_3$C$_2$T$_2$ MXene is not changed by the surface functional groups, which is consistent with reported conclusion that the band structure of the bare Ti$_3$C$_2$ MXene is characterized as a metal.$^{27,40–43}$ This is mainly due to the low energy level of the outer layer of the surface functional groups, which mainly affects the valence band whose energy is much lower than the Fermi level but has a weak influence on the band near the Fermi level.

Total density of states (DOS) and partial density of states (PDOS) for the bare Ti$_3$C$_2$ and functionalized Ti$_3$C$_2$T$_2$ are shown in Figure 4. It can be seen in Figure 4a that there are four main peaks where electronic states are concentrated ($−10$ eV, $−6$ eV, $−4$ eV to $−2$ eV, $0$–$3$ eV), named as $P_1$–$P_4$. Peak $P_1$ and $P_2$ in the valence band are dominated by the C-2p and Ti-3d states, indicating the hybridization of C-2p and Ti-3d orbitals; $P_{III}$ near the Fermi level and $P_{IV}$ in the conduction band are dominated by the Ti-3d states. It is shown in Figure 4b–e that surface functional groups have significant effect on the $P_{I−IV}$ peaks in the valence band and have a slight effect on the $P_{III}$ and $P_{IV}$ peak. In addition, it is clear that the peak $P_{II}$ and peak $P_{III}$ move to the left after surface functionalization, and the peak $P_1$ and peak $P_{IV}$ are still in the original positions. In addition, compared with the functional groups of O, F, and OH, the H-
The Mulliken population provides an objective criterion for the bonding. The Mulliken population of bare Ti$_3$C$_2$ and functionalized Ti$_3$C$_2$T$_2$ (T = O, F, H, OH) are calculated to quantify the bond overlap as well as the change transfer among Ti, C, and T atoms, and the results are shown in Table 2. It is shown that the charge transfer from Ti to C atoms after bonding is 1.50 electrons in bare Ti$_3$C$_2$. Therefore, bare Ti$_3$C$_2$ exhibits an ionic bonding feature with a strong directional bonding between Ti and C atoms. Different surface functional groups have different effects on the Mulliken population, mainly because of the different electronegativity of functional groups. Surface functional groups have little effect on the C atoms, while they have a significant effect on Ti atoms. Even more, surface functional groups mainly affect the surface Ti atoms, resulting in a charge transfer of 0.69–1.03 electrons from surface Ti atoms to C atoms and functional groups, while the charge transfer is only 0.37 from surface Ti atoms to C atoms in bare Ti$_3$C$_2$. This result in Table 2 is consistent with the functional groups having a significant effect on the bond length between surface Ti with C atoms ($d_{Ti-C}$), as mentioned in section 3.1.

### 3.3. Lithium Storage Performance

Adsorption energy plays an important role in determining suitable adsorption sites for lithium ion storage. Equation 2 is used to calculate the adsorption energies of lithium ions at HCP, CCP, and TOP sites:

$$\Delta E_{ab} = E_{\text{sub} + x\text{Li}} - E_{\text{sub}} - xe(Li)$$  \hfill (2)

![Figure 3](http://pubs.acs.org/journal/acsodf)

**Figure 3.** Band structure of Ti$_3$C$_2$T$_2$: (a) Ti$_3$C$_2$O$_2$, (b) Ti$_3$C$_2$F$_2$, (c) Ti$_3$C$_2$H$_2$, and (d) Ti$_3$C$_2$(OH)$_2$. (The red line represents the energy band contributed by Ti$_3$C$_2$, and the blue line represents the energy band contributed by functional group T$_2$.)

![Figure 4](http://pubs.acs.org/journal/acsodf)

**Figure 4.** Density of states of Ti$_3$C$_2$T$_2$: (a) Bare Ti$_3$C$_2$ MXene, (b) Ti$_3$C$_2$O$_2$, (c) Ti$_3$C$_2$F$_2$, (d) Ti$_3$C$_2$H$_2$, and (e) Ti$_3$C$_2$(OH)$_2$.
where $E_{\text{sub}+x\text{Li}}$ represents the total energy of bare Ti$_3$C$_2$ or Ti$_3$C$_2$T$_2$ (T = O, F, H, OH) MXenes adsorbed with lithium ions, $x$ is the number of adsorbed lithium ions, $E_{\text{sub}}$ is the isolated energy of bare Ti$_3$C$_2$ or Ti$_3$C$_2$T$_2$ MXene, and $E(Li)$ represents the average energy of lithium ions.

### 3.3.1. Adsorption Properties of Monolayer Lithium Ions

According to crystal structure and symmetry, there are also three
potential sites for lithium-ion adsorption on the surface of bare Ti$_3$C$_2$ and functionalized Ti$_3$C$_2$T$_2$ (T = O, F, H, OH), as shown in Figure S5a,b. The 2 × 2 × 1 supercells are built, and the adsorption energies of single lithium ions on the bare Ti$_3$C$_2$ and functionalized Ti$_3$C$_2$T$_2$ (T = O, F, H, OH) are calculated. It is revealed in Figure S5c that different surface terminal groups have different effects on adsorption energy. In the bare Ti$_3$C$_2$, 2 × 2 × 1 supercell, the adsorption energy of a single lithium is −0.53 eV at the HCP site, −0.52 eV at the CCP site, and −0.38 eV at the TOP site. According to the lowest energy principle, HCP is the most suitable adsorption site of a single lithium ion on the Ti$_3$C$_2$ surface. Compared with the bare Ti$_3$C$_2$, the terminal group O always reduces the adsorption energies of Li ions at HCP (−1.63 eV), CCP (−1.95 eV), and TOP (−0.95 eV), respectively. Inversely, the terminal groups of F, H, and OH inhibit the adsorption of lithium ions. The lithium ion can only stably adsorb at the HCP site (−0.37 eV) of the three potential sites on the surface of Ti$_3$C$_2$F$_2$, and none of the three potential sites can adsorb lithium ions stably when the surface groups are H and OH. In conclusion, the most suitable adsorption site of a single lithium ion is HCP for bare Ti$_3$C$_2$ (−0.53 eV) and CCP for Ti$_3$C$_2$O$_2$ (−1.95 eV) as well as Ti$_3$C$_2$F$_2$ (−0.37 eV).

The models labeled as Ti$_3$C$_2$(2 × 2)_8Li, Ti$_3$C$_2$O$_2$(2 × 2)_8Li, and Ti$_3$C$_2$F$_2$(2 × 2)_8Li are built (Figure S5d–f). In the Ti$_3$C$_2$(2 × 2)_8Li model, the Li atoms are adsorbed on the HCP sites on both sides of 2D Ti$_3$C$_2$ MXene with a Li–Ti bond length of 3.07 Å. In the Ti$_3$C$_2$O$_2$(2 × 2)_8Li and Ti$_3$C$_2$F$_2$(2 × 2)_8Li models, the Li atoms are adsorbed on the CCP sites on both sides of 2D Ti$_3$C$_2$O$_2$ or Ti$_3$C$_2$F$_2$ MXene with a Li–O bond length of 1.94 Å and a Li–F bond length of 1.88 Å. The average adsorption energies are calculated to be −0.47 eV, −1.12 eV, and −0.11 eV per Li atom, respectively.

3.3.2. Adsorption Properties of Bilayers of Lithium Ions. Previous work has shown that Li may form more than one layer on bare Ti$_3$C$_2$ and Ti$_3$C$_2$O$_2$ surfaces to enhance the Li capacity.\cite{1,44–46} In order to further study the lithium storage performance of Ti$_3$C$_2$ and Ti$_3$C$_2$O$_2$ MXene, the adsorption of a single lithium ion on the Ti$_3$C$_2$(2 × 2)_8Li and Ti$_3$C$_2$O$_2$(2 × 2)_8Li structures is calculated and shown in Figure 6a,b. Similarly, there exist three types of high-symmetry sites: HCP, CCP, and TOP. As shown in Figure 6c, the absorption energies of single lithium ions on the Ti$_3$C$_2$(2 × 2)_8Li and Ti$_3$C$_2$O$_2$(2 × 2)_8Li structures at the three potential sites are negative, indicating that these structures are stable. The most suitable adsorption sites for lithium ions are CCP sites of both the Ti$_3$C$_2$(2 × 2)_8Li and Ti$_3$C$_2$O$_2$(2 × 2)_8Li structures, and the absorption energies are calculated to be −0.38 eV and −0.95 eV (≈ −0.90 eV\textsuperscript{45}), respectively. The structures of the full lithium bilayers formed on the surfaces of the bare Ti$_3$C$_2$ and Ti$_3$C$_2$O$_2$ are presented in Figure 6d,e. The distances between two lithium layers are 2.46 and 2.95 Å (2.80 Å\textsuperscript{46}) for the interlayer-expanded bare Ti$_3$C$_2$ and Ti$_3$C$_2$O$_2$, respectively.

3.3.3. Lithium Storage Capacity. The theoretical storage capacity (C) depends on the number of lithium ions adsorbed by MXene (x) and can be calculated according to eq 3:\textsuperscript{37}

\[
C = \frac{x \times z \times F \times 10^3}{4W}
\]

where z is the valence number (z = 1 for Li), F is the Faraday constant (26.810 Ah/mol), and W is the atomic mass (167.62 g/mol for Ti$_3$C$_2$), 199.62 g/mol for Ti$_3$C$_2$O$_2$, and 205.62 g/mol for Ti$_3$C$_2$F$_2$). Figure 7a shows the change of adsorption energy as the number of adsorbed lithium ions of bare Ti$_3$C$_2$ and functionalized Ti$_3$C$_2$T$_2$ (T = O, F) increases. When the number of lithium ions is less than eight, the lithium ions are adsorbed in the first layer, and the lithium ions are adsorbed in the second layer when the number is more than eight. The results show that the average adsorption energy increases with the increasing number of lithium ions for all of the bare Ti$_3$C$_2$ and functionalized Ti$_3$C$_2$T$_2$. The single-layer lithium storage capacity on bare Ti$_3$C$_2$, Ti$_3$C$_2$O$_2$, and Ti$_3$C$_2$F$_2$ MXene, as Figure 7b shows, is calculated to be 319.89 mAh/g (320 mAh/g\textsuperscript{19}), 268.61 mAh/g (268.53 mAh/g\textsuperscript{19}), and 130.77 mAh/g (130.39 mAh/g\textsuperscript{19}), respectively. When the number of adsorbed lithium ions increases, the bilayer adsorption of lithium atoms can improve the capacities to 639.78 mAh/g and 537.22 mAh/g (410.00 mAh/g\textsuperscript{19}).

4. CONCLUSIONS

In this paper, DFT calculations are conducted to study the effect of surface functionalization on the structural, electronic and lithium storage properties of Ti$_3$C$_2$ MXene. Oxidized, fluorinated, hydrogenated, and hydroxylated surfaces are considered. The results show that the surface terminals can cause lattice distortion of Ti$_3$C$_2$T$_2$ (T = O, F, H, OH). The degree of lattice distortion mainly depends on the adsorption position of functional groups and the types of surface functional groups. The degree of lattice distortion caused by surface functional groups is H < O < F < OH; and the order of lattice distortion mainly depends on the types of surface functional groups is as follows: HCP > TOP > CCP. The adsorption
energies of all functional groups at three potential locations are calculated, and the values are all negative with the lowest energy at the CCP site, indicating the CCP site to be the most stable adsorption site. The results of band structure and DOS show that the metallicity of Ti$_3$C$_2$T$_2$ MXene follows the series of Ti$_3$C$_2$O$_2$ < Ti$_3$C$_2$F$_2$ < Ti$_3$C$_2$H$_2$ < Ti$_3$C$_2$(OH)$_2$ < Ti$_3$C$_2$. In terms of lithium storage, the oxygen functional groups will reduce the adsorption energy of lithium atoms, while the fluorine functional groups will limit the adsorption of lithium atoms, and the lithium atoms cannot even stably adsorb on the surface of Ti$_3$C$_2$H$_2$. In addition, surface functionalization affects the starting site of lithium atom adsorption. In the bare Ti$_3$C$_2$T$_2$, lithium atom adsorption starts from the HCP position, while functionalized Ti$_3$C$_2$T$_2$ MXene starts from the CCP position. Compared with the adsorption energy of bare Ti$_3$C$_2$T$_2$ (−0.53 eV) for the lithium ion, the adsorption energy of Ti$_3$C$_2$O$_2$ (−1.95 eV) and Ti$_3$C$_2$F$_2$ (−0.37 eV) will decrease and increase, respectively. Finally, the theoretical capacities of Ti$_3$C$_2$T$_2$ (639.78 mAh/g), Ti$_3$C$_2$O$_2$ (537.22 mAh/g), and Ti$_3$C$_2$F$_2$ (130.77 mAh/g) were calculated.

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**Notes**

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