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PH-Dependent Distribution of Functional Groups on Titanium-Based MXenes

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Ti$_3$C$_2$Al, selective etching with HF removes aluminum atoms (denoted as X), has recently been drawing attention. 2D materials consisting of early transition metals such as Ti, Sc, Zr, Hf, V, Nb, Ta, Cr, Mo (denoted as M), and carbon or nitrogen combine to form a completely new class of 2D materials, called MXenes, where transition metal carbide phases, known as MAX phases, are formed. MXenes are synthesized through etching of layered bulk carbides, Ti$_3$C$_2$ and Ti$_3$C$_2$, using a multiscale modeling scheme. Our scheme is based on calculating Gibbs free energy of formation by a combination of electronic structure calculations with cluster expansion and Monte Carlo simulations. Our calculations show formation of mixtures of O, OH, and F on the surface with the composition depending on pH, temperature, and the work function. On the other hand, our results also suggest a limited stable range of compositions, which challenges the paradigm of a high tunability of MXene properties.

**KEYWORDS:** 2D materials, MXene, multiscale simulation, functional group, density functional theory

**ABSTRACT:** MXenes are a new rapidly developing class of two-dimensional materials with suitable properties for a broad range of applications. It has been shown that during synthesis of these materials the surfaces are usually functionalized by O, OH, and F and further suggested that controlling the surface allows controlling the material properties. However, a proper understanding of the surface structure is still missing, with a significant discrepancy between computational and experimental studies. Experiments consistently show formation of surfaces with mixed terminations, whereas computational studies point toward pure terminated surfaces. Here, we explain the formation of mixed functionalization on the surface of titanium-based two-dimensional carbides, Ti$_3$C$_2$F$_2$ and Ti$_3$C$_2$, using a multiscale modeling scheme. Our scheme is based on calculating Gibbs free energy of formation by a combination of electronic structure calculations with cluster expansion and Monte Carlo simulations. Our calculations show formation of mixtures of O, OH, and F on the surface with the composition depending on pH, temperature, and the work function. On the other hand, our results also suggest a limited stable range of compositions, which challenges the paradigm of a high tunability of MXene properties.
are still far from conclusive. This is a challenging problem as it requires an accurate description of the interactions between the MXene sheet, the functional groups, and the solution and a proper thermodynamic averaging in the case of mixtures. Almost all of the previous formation energy calculations have been carried out for pure terminations and yielded a strong preference for O-termination. In order to model a mixture of terminations, MD simulations were carried out with an explicit solvent and found to yield predominantly F- and OH- terminations, with the exact composition depending on the HF concentration. In addition, global structure optimization methods were employed to find the ground-state structure, in which case the comparison of formation energies showed predominantly O-terminations and no preference for mixing. Only the studies focusing on hydrogenation of O-terminated surfaces seem to suggest that the coverage can be tuned by pH or the electrode potential. Clearly, the surface structure inferred from the calculations is at odds with the experimental data showing a mixture of all three types of terminations. The origin of this discrepancy is still unclear but can arise from ignoring the role of the solvent, an improper treatment of the chemical potential of elements, and absence of thermodynamic sampling. Thus, the important questions still remain: how functional groups are distributed and how the composition depends on the experimental conditions.

Here, we develop a computational scheme to find the composition and distribution of O, OH, and F functional groups on the Ti3C and Ti3C2 monolayers at given experimental conditions. Our multiscale scheme is based on three steps. First, we adopt the cluster expansion (CE) method together with the density functional theory (DFT) to efficiently evaluate the energies of functional group configurations. Second, the CE model together with Monte Carlo simulations enables us to access the configurational free energies and to obtain distributions of the functional groups on the surface. Finally, we calculate the Gibbs free energy of formation in solution over the whole composition range, carefully accounting for the role of experimental factors, such as temperature, pH, and the work function. We also evaluate selected material properties and discuss the degree of tunability over the accessible range of compositions.

RESULTS

Benchmarking Computational Approach. Surface functionalization is a complex process involving different time scales and levels of physics. A proper consideration of surface interaction with adsorbants and solution is needed as the functionalization process happens in an etchant solution. On the other hand, a thermodynamically driven statistical averaging needs to be carried out in the case of mixed terminations. The need of a proper sampling of the configuration space leads us to combine electronic structure calculations and concepts of statistical mechanics and thermodynamics.

In order to compare the stabilities of MXene sheets with different surface terminations, we determine their Gibbs free energies of formation, which is obtained by finding the Gibbs free energies for all of the constituents. Here, we define it for the terminated MXT sheet with respect to the bare, unterminated MX sheet as described in the figure.
where \( n_i \) is the number of termination atoms of type \( i \) and \( \bar{\mu}_i \) is their chemical potentials. \( G \) is the “total” Gibbs free energy of the system including configurational and vibrational contributions and the interaction with the solvent. All three contributions are important. They are evaluated here separately and added to the total energies calculated with DFT. The \( \sim \) refers to the standard conditions: room temperature and in solution with pressure \( p = 1 \) atm. The chemical potentials for adsorbed species at these conditions are determined by combining DFT total energies and experimentally determined changes in enthalpy and entropy, as described in detail in Methods.

In order to access the configurational free energies of MXenes with mixed terminations, we construct a lattice-gas Hamiltonian, which is then used in Monte Carlo simulations. For the lattice-gas Hamiltonian, we use the CE defined by a series of interactions between atoms at different lattice sites and multiplied by constant expansion coefficients (effective cluster interactions, ECI). The ECIs in the cluster expansion are usually obtained via fitting the CE energies to those calculated by DFT for a set of configurations. Here, we generate CE for the three-component \((O, OH, F)\) mixture by fitting to a set of 71 and 106 DFT energies for Ti\(_2\)C and Ti\(_3\)C\(_2\), respectively. After evaluating different expansions, we choose for Ti\(_3\)C\(_2\) a CE including pair clusters up to the fourth nearest neighbors and triplet clusters up to the first nearest neighbors, which corresponds to a total of 13 pair clusters and 4 triplet clusters after accounting for the symmetry of the lattice and the dimension of the configuration space in a three-component alloy. The pair clusters up to fourth nearest neighbor were sufficient in the case of Ti\(_2\)C. These choices yielded small cross-validation scores of 0.008 and 0.005 eV/atom for Ti\(_3\)C\(_2\) and Ti\(_2\)C, respectively. Used clusters are illustrated in Figure 1a. The quality of the cluster expansion is demonstrated in Figure 1d, where we compare the DFT energy to the energy predicted using the CE. The ternary compound panel essentially includes all of the structures that were used in the fitting process. In addition, we carried out a separate set of DFT calculations for binary compounds, where each type of compound included a large number of configurations that were not present when training the expansion. The ability for the CE to predict the energies of these previously unencountered configurations illustrates the good transferability of the expansion. Using the obtained CE, we can quickly evaluate the total energies for a large number of configurations or for larger supercells. Figure 1e shows the energies evaluated for a large set of configurations in the O—OH binary system (gray dots). Also shown are the energies expected for the purely random mixtures (yellow crosses) and the average energies (green circles) for the system at room temperature, as obtained from Monte Carlo simulations.

Finally, we highlight the importance of the vibrational free energy contributions in Figure 1b,c. It shows a significant contribution of nearly 1 eV, which obviously cannot be neglected in the calculation of the Gibbs free energy of formation. It mostly arises from the zero-point energy, whereas the change upon approaching room temperature is only about 0.1 eV in all cases. The large difference between OH—versus O— and F-terminations arises from the very high frequency of O—H vibrations. Comparison of the Ti\(_3\)CT\(_2\) and Ti\(_3\)C\(_2\)T\(_2\) results reveals that each termination yields very similar free energy contribution; that is, the differences between the three curves are the same. This suggests that each terminating atom/group has a fixed contribution to the free energy, and thus for a mixed surface, we could use the free energies from the pure terminations weighted according to the composition. This is demonstrated in Figure 1b, which shows the results for the mixed Ti\(_3\)C(O\(_{0.5}\)OH\(_{0.5}\))\(_2\) configuration. Taking the weighted average of pure terminations yields a free energy contribution differing from the explicit calculation by only about 20 meV.

**Simulated Surface Distribution of Functional Groups.** Surface distributions of functional groups for Ti\(_2\)C and Ti\(_3\)C\(_2\) are obtained using Monte Carlo and the CE constructed earlier. We use the canonical ensemble, where the concen-
The concentration of surface adsorbants is fixed. MC simulations are conducted for 12 structures with different compositions: $\text{Ti}_3\text{C}_2-(\text{O}_x\text{OH}_z\text{F}_{1-x})_2$, where $x$ and $z$ vary from 0 to 1 with a step of 0.25. We first show in Figure 2b–e the surface structures for equal concentrations of two functional groups (i.e., a binary mixture) on Ti$_3$C$_2$. We have postprocessed the obtained structures by continuously coloring the first nearest neighbors of the same type (Figure 2b–d). Fairly similar striped patterns are observed in all cases typical for strongly mixing species in a triangular lattice, which is a frustrated system. Figure 2f–h shows the corresponding fractions of the first and second nearest neighbors averaged over the simulation cell. Independent of the constituents, the first nearest neighbor distributions show very similar fractions of about 0.18 between the “like”-terminations and about 0.65 between the “unlike”-terminations. In a random alloy, the values would be 0.25 and 0.5, respectively, meaning that unlike neighbors are overall favored. This, together with the comparison of the energies for the random and MC (SQoS) results in Figure 1e, clearly shows that the surface terminations are not expected to be randomly distributed. The second nearest neighbor fractions show the opposite trend, wherein similar terminations are more likely than in random alloys. This effect is particularly pronounced in the case of O$^{0.5}$F$^{0.5}$, which may explain the slightly different visual appearance.

Figure 3 shows the MC-simulated distribution of functional groups and the nearest neighbor fractions for selected ternary structures. We start off with an equal concentration for each of the three groups, as shown in Figure 3a. Although a binary system in a triangular lattice is frustrated, a ternary (three-state) system is not. As seen in Figure 3a, large areas of the ordered phase, where each O is surrounded by 3 F and 3 OH, etc., arise. This is also reflected in the fractions showing almost completely unlike-terminations in the nearest neighbor sites in Figure 3e. It is interesting to note also the phase boundary structure, as highlighted by the triangles in Figure 3a, where we can identify two types of boundaries: those where the ordering of the terminations is inverted and those where the ordering is the same, but the pattern is shifted between the two grains. Surface distribution for a mixture with excess O [Ti$_3$C$_2$(O$_{0.5}$OH$_{0.25}$F$_{0.25}$)$_2$ in Figure 3b] shows a formation of oxygen containing zigzag stripes, whereas OH and F mostly form triangular structures, where a central atom is surrounded by three atoms of another type. The same kind of arrangement of functional groups can be seen on the surface with excess OH [Ti$_3$C$_2$(O$_{2.5}$OH$_{0.5}$F$_{0.25}$)$_2$ in Figure 3d]. The first and second nearest neighbor fractions show the same tendency for excess O and excess OH (Figure 3f,h), where the first nearest neighbors appear to be unlike-terminated, and the second nearest neighbors are like-terminated. This is fully consistent
Figure 4. We work functions as a function of the composition are shown in MC simulations. The mixing energies, lattice constants, and scheme, which is based on mimicking cluster correlations in MC simulations. The mixing energies, lattice constants, and work functions as a function of the composition are shown in Figure 4. We find large mixing energies in accordance with the mixed distributions in Figures 2, 3, and 1e. The largest energy gain is found with O- and OH-terminations without any F and reaching almost −0.4 eV per unit cell. This is a very large energy gain and clearly much more than \(k_B T\) for temperatures used during etching and delamination. In the case of O/F and F/OH mixings, the maximum energy gains are −0.21 and −0.09 eV, respectively. According to Hu et al., the O- and OH-F-terminations lead to oppositely charged Ti-(O/C/F) octahedra within the MXene sheets, thereby favoring alternating terminations. We propose that there is an additional contribution arising from the fact that in the case of OH the outermost H atom is positively charged, whereas in the case of O and F, the outermost atoms are negatively charged, which leads to attractive electrostatic interaction. Adding the solvation energy to the mixing energy only makes the mixing more favored, as shown in the Supporting Information. In the case of Ti₂C, the energy surface is overall very similar, reaching up to −0.3 eV per unit cell.

The work functions are shown in Figure 4b. The OH functionalization leads to a very low work function, whereas the work function is high for the O-terminated surface. The Ti₃C results are very similar to those for Ti₃C₂F, thereby suggesting that the work function is termination-specific and not material- or composition-specific. The calculated work functions of terminated Ti₃C and Ti₃C₂ coincide with earlier calculated work function values reported in ref 36, where it was also found that the work function has a very weak dependence on the layer thickness; that is, it originates largely from the surface dipole formation due to terminating groups and not from changes in the Fermi level. The high work functions of the O- and F-terminated surfaces are due to charge transfer to these sites, whereas the low work function of OH-terminated surface is due to the intrinsic dipole moment (and possibly due to relaxation effect). There is no obvious correlation between the mixing enthalpy and the work function, which indicates that mixing is not governed by the work function, but it is likely related to the electrostatics between the terminations, as discussed above.

Measuring of work function is generally challenging, and it is particularly difficult to simultaneously determine the surface termination composition. For Ti₃C, very few experiments are available due its instability: for Ti₃COH₃F₀, a work function of 4.98 eV is reported. Experimental work functions for Ti₃C₂ vary from 3.4 up to 5.28 eV. A work function of 3.4 eV is reported for predominantly OH-terminated sheets. Work functions of 4.37 and 4.6 eV are reported in refs 39 and 40. The highest work function has been reported in ref 16, and although the exact termination is unknown, it was proposed to arise from protonization of OH with the presence of water, resulting in formation of O. Nevertheless, none of these values are close to the calculated limits of 2.0 eV for pure OH-terminated Ti₃C₂ or 6.2 eV for pure O-terminated Ti₃C₂, which suggests that the measured samples feature mixing. We note that when the experimental work function is known, one can extract from Figure 4b a fairly good estimate for the amount of OH, although the O/F balance still remains unknown.

Finally, the lattice constants in Figure 4c appear to closely follow Vegard’s law. Whereas experimentally determined in-plane lattice constant values have been reported in a few papers, comparison is difficult because (i) in calculations, the accuracy of the lattice constants is unknown even though the composition is known exactly, and (ii) in experiments, the composition is often unknown even though the lattice constant might be known fairly accurately.

Gibbs Free Energy of Formation. In the previous section, we obtained large negative mixing energies which strongly pointed toward mixing. However, the mixing energies are not enough to predict the composition under thermodynamic equilibrium. For that, we evaluate the Gibbs free energy of formation with carefully chosen chemical potentials.

While during the functionalization the H atom can be adsorbed from H⁺ or H₂ or H₂O, under equilibrium conditions, the chemical potential for H in all of these different species is the same. The value for the chemical potential will be determined by the amount of dissolved HF (i.e., pH), temperature, the equilibrium with water \([\mu(H_2O) = \mu(O) + 2\mu(H)]\), and the electron chemical potential in the case of ionic species. Chemical potentials as a function of electron chemical potential (work function \(\Phi\)) for two values of pH under ambient conditions are shown in Figure 5, where we only show the lowest energy species at given conditions. Under the conditions present during the MXene synthesis, these correspond to H coming from H₂ or H⁺ depending on conditions, F from F⁻, and O from H₂O. From the crossing point of \(\mu(H)\) lines corresponding to H₂ and H⁺ (pH = 0), we obtain a calculated value for the standard hydrogen electrode (SHE) of −4.7 eV, which is in good agreement with other
computational works\textsuperscript{34,41} and in fair agreement with the experimental value of $-4.44$ V.\textsuperscript{42}

Using the calculated chemical potentials of O, OH, and F, we can construct the formation Gibbs free energies of pure terminations as a function of the electron chemical potential and pH. These are shown in Figure 6, where the calculated work functions are also indicated. Simply finding the lowest energy phase at the respective value of $\Phi$ would seem to indicate the formation of a fully O-terminated surface. This, however, leads to few problems. A work function of 6.1 eV (or $+1.4$ V vs SHE) is extremely high, even outside the stability range of water and thus breaking water to O$_2$. Dissolved O$_2$ molecules are known to lead to oxidation of MXenes to TiO$_2$\textsuperscript{43,44}. Moreover, it is simply at odds with the experimental reality that always shows a mixture of terminations.

However, that is not the only choice for the work function. First of all, it is important to make a difference between the work function of the final fully terminated surface and the work function during etching. One could argue that because the terminating group is adsorbed on a bare surface, the work function of a bare surface would be the most realistic choice. In addition, it is quite likely that the system is not under charge equilibrium. Extra electrons can arise from F$^-$, either upon adsorption or upon AlF$_3$ formation, and from breaking of H$_2$ to 2H$, which are then accumulated to the MXene sheet, thereby lowering the work function. F$^-$ adsorption should occur frequently during the etching, as evidenced by the sizable concentration of F-terminations. The rate of H$_2$ to 2H$^+$ events is not known, but it should only be relevant at a work function higher than SHE. On the other hand, electrons can be depleted by adsorbing H$, either changing the O-termination to the OH one or forming H$_2$, which thereby increases the work function until it reaches SHE. Indeed, etching of MXenes is known to lead to H$_2$ gas formation.\textsuperscript{11,45} Putting both of these aspects together, we suggest that most of the functionalization happens near the SHE conditions. In the end, using our selected etching work function, we obtain the composition and the corresponding work function for the terminated surface, which can be

![Figure 6. Gibbs free formation energy of pure OH-, F-, and O-terminated Ti$_3$C$_2$ depending on work function and pH of the solution.](image)

![Figure 7. Gibbs free energies of formation for mixed terminations at the work function $\Phi = 4.7$ eV including implicit solvents with (a) pH = 0 and (b) pH = 1, as well as the vacuum cases for (c) pH = 0 and (d) pH = 1.](image)
compared to the experimentally measured ones to check for consistency.

We calculated the Gibbs free energies of formation for the SQoS structures obtained earlier at a fixed work function and pH. Figure 7a,b shows the ternary diagrams of Gibbs free energy of formation for mixed surface terminations at a fixed work function equal to 4.7 eV and (a) pH = 0 or (b) pH = 1, which are typical values during the MXene synthesis. For comparison, we also show in Figure 7c,d the same cases, but in vacuum, that is, excluding the solvation energy contribution. Inspecting the numbers around the energy minimum reveals that the solvation energy contribution is relatively minor, some tens of millielectronvolts, but it tends to lower the energy of mixed configurations relative to the pure constituents. Generally, in all cases, the energy minima are found inside the triangles and are quite significantly lower in energy than those for the pure terminations. In vacuum, the O$_{0.5}$F$_{0.5}$ structure has the lowest Gibbs free energy at pH = 0, but the energy surface is very flat between this point and O$_{0.5}$OH$_{0.5}$. The change of pH to 1 shifts the minimum energy to the O$_{0.5}$F$_{0.25}$OH$_{0.25}$ mixture. When solvation is included, the energy minimum lies in both cases close to O$_{0.5}$F$_{0.25}$OH$_{0.25}$. Due to the flatness of the energy surface between O$_{0.5}$F$_{0.5}$ and O$_{0.5}$OH$_{0.5}$, even a small solvation energy contribution is sufficient to shift the location of the energy minimum. Such sensitivity means that our calculations may not be able to predict the exact composition but only the dominant stability region.

In Figure 8a, we show how the composition at a fixed $\Phi$ changes as pH is varied. The OH concentration remains near 0.25, but for pH >1, the concentration of O increases and that of F decreases; that is, the minimum of Gibbs free energy shifts to the composition O$_{0.75}$OH$_{0.25}$. This is consistent with the hydrogenation study by Zhan et al., showing H coverage of about 0.3 when the point of zero charge is close to SHE. $^{29}$ Finally, we have also varied the work function $\Phi$ from 4.4 to 5.4 eV and plotted the composition in Figure 8b. At low work function values, we obtain O$_{0.5}$OH$_{0.5}$, largely independent of pH (also see Figure 6). At very large work function values, the pure O-terminated surface is obtained. Only at intermediate values is it possible to obtain mixtures with marked F concentrations.

**DISCUSSION**

In this study, we have combined multiple theoretical approaches to simulate functionalization of the Ti$_2$C$_x$ and Ti$_2$C surfaces. Surface distributions of functional groups over distinct concentrations have been obtained. We have shown that functional groups are equally distributed without any segregation regardless of the concentration or the type of the adsorbant. Our simulation results align with recent experimentally measured data, $^{17,25}$ where random distributions of terminations were reported. The preference toward mixing arises from the significant energy gain by mixing and has been obtained by accounting only structural factors (Figure 4a). On the other hand, the lowest energy composition of the functional groups on the surface varies with the electro-chemical factors such as the electron chemical potential $\Phi$, pH, and temperature. We showed that the lowest energy composition is sensitive to these parameters, but when choosing values similar to those in experiments, we obtained similar mixtures of all three components as reported in experiments. Now, taking the obtained compositions and referring to Figure 4b, the low $\Phi$ composition, O$_{0.5}$OH$_{0.5}$, corresponds to a work function of about 3.5 eV, which is close to the lower limit obtained in experiments. $^{38}$ The composition O$_{0.5}$F$_{0.25}$OH$_{0.25}$ would result in a work function of about 4.5 eV, which is consistent with those reported in refs 39 and 40, whereas the high $\Phi$ or high pH composition O$_{0.75}$OH$_{0.25}$ leads to a work function closer to 5 eV, similar to that reported in ref 16.

When comparing our calculated composition to experimental ones, the problem is that one can find experimental report to support any computational finding; similar concentration of all three terminations in ref 46, O dominance in ref 18, F dominance in refs 12 and 15, equal O and F versus small OH concentration in ref 20, equal F and OH versus small O concentration in ref 19. Perhaps the most useful reports are those which report composition changes upon changing synthesis conditions. For instance, according to Wang et al., going from a 10% HF concentration to 48%, the O/F ratio decreases from 1.4 to 0.8, $^{19}$ which qualitatively agrees with our result that lower pH increases the F concentration. Although the high sensitivity of the functional group composition to the experimental conditions may explain part of the results, there are some discrepancies. Our calculations always resulted in an O concentration of 50% or more and a relatively small F concentration of 25% or less. The possible reasons could include local variations in the solution (content of F$^-$ ions, trapped H$_2$, etc.), kinetic factors related to etching, and inaccuracies in our computational approach.
Although it seems that the surface composition can be tuned, even if only within a limited range, how would that affect the material properties, such as the electrical conductivity? We show the total and atom-projected densities of states in Figure 9, where we have also indicated the atomic origins of all the main features. The Fermi level moves down as the concentration of O increases, as expected due to its large electronegativity and oxidation state. Nevertheless, the Fermi level is always confined inside the Ti-d band, and moreover, this band is largely unaffected by the surface terminations and appears fairly similar in all cases. Thus, there is likely no dramatic changes in the density of states at the Fermi level or consequently in the electrical conductivity (assuming it is governed by the former), especially if considering only the limited range of compositions. The situation is again very similar in the case of Ti2C (Figure S7). Whereas pure O-terminated Ti2CO2 should open a band gap at the Fermi level, this band is largely unaFFECTED.

CONCLUSIONS

In this study, we have shown that functional groups form mixed compositions at Ti2C and Ti1.5C2 surfaces. Our large-scale simulations show that mixed functional groups are equally distributed at the surfaces and form ordered arrangements for certain concentrations. Furthermore, we have constructed Gibbs free energy diagrams for different concentrations of functional groups depending on pH and the work function. The analysis shows that formation of mixed terminations is favorable. Our results show that the tunability of the surface composition by pH and temperature is limited, and it does not lead to dramatic changes in electronic properties. Our multiscale modeling approach for determining the distribution and composition of functional groups on a surface should be straightforward to apply to other MXene systems in order to more accurately predict their structures and properties. Moreover, many other systems, other than MXenes, can be considered, especially those of solvated nanoparticles.

METHODS

Free Energy Calculations. The Gibbs free energy of formation is given in eq 1. The free energy of the sheet should include the vibrational contributions as well as the interaction with the solution. We assume that the two contributions do not depend on each other and thus

\[
G^\circ(MXT) = E(MXT) + \Delta_{vib} F(MXT) + \Delta_{sol} E(MXT)
\]  

where \(E(MXT)\) is the DFT total energy, \(\Delta_{vib} F\) is the phonon contribution to the free energy at room temperature evaluated in vacuum, and \(\Delta_{sol} E\) is the solvation energy evaluated at \(T = 0\) using implicit solvation models. (The \(pV\) term can be ignored at \(p = 1\) atm.)

The choice of chemical potentials \(\mu\) depends on the conditions around the MXene sheet and the reactions on the surface. Taking as an example one of the most studied MAX phases, Ti3AlC2, when the etching is done in water solutions of HF, the following three simplified reactions have been proposed to take place:

1. \(\text{Ti}_3\text{AlC}_2 + 3\text{HF} = 3\text{AlF}_3 + \frac{3}{2}\text{H}_2 + \text{Ti}_2\text{C}_2\)
2. \(\text{Ti}_3\text{C}_2 + 2\text{H}_2 = \text{Ti}_3\text{C}_2(\text{OH})_2 + \text{H}_2\)
3. \(\text{Ti}_3\text{C}_2 + 2\text{HF} = \text{Ti}_3\text{C}_2\text{F}_2 + \text{H}_2\)

In these reactions, hydrogen is always assumed to be in the form of \(\text{H}_2\). However, considering that HF dissociates in water to \(\text{H}^+\) (or \(\text{H}_3\text{O}^+\)) and \(\text{F}^-\) ions, it seems plausible that the reactions could involve just the ions, an aspect that has not been accounted for in the previous studies on MXenes. In this work, we will consider both scenarios, which, thanks to the adopted method, is only reflected in the choice of the chemical potentials.

The chemical potentials are obtained by first evaluating the Gibbs free energies of the elemental phases using DFT and then using experimentally determined thermochemical quantities to evaluate Gibbs free energy of the solutes and the solution. Taking \(\text{O}_2\) as an example, the DFT energy \(E_{\text{DFT}}(\text{O}_2)\) sets the (absolute) energy scale, which allows us to write the (absolute) enthalpy and Gibbs free energy of the molecule as

\[
H^\circ(\text{O}_2) = E_{\text{DFT}}(\text{O}_2) + E_{\text{vib}}(\text{O}_2) + \Delta H^\circ(\text{O}_2)
\]

\[
G^\circ(\text{O}_2) = H(\text{O}_2) - T S^\circ(\text{O}_2)
\]

where \(E_{\text{vib}}\) and \(\Delta H^\circ\) are the zero-point vibrational energy and the enthalpy of formation, respectively. Then, the Gibbs free energy, or the chemical potential, of water is obtained as \(\mu(\text{H}_2\text{O}) = \mu(\text{O}) + 2\mu(\text{H}) + \Delta G_0(\text{H}_2\text{O})\), where the formation energy is obtained from the NIST-JANAF tables. On the other hand, if \(H\) is in the form of \(\text{H}^+\) ions, we also need to consider the electron chemical potential. The potential energy of \(\text{H}^+\) ion is written as

\[
\Delta G(\text{H}^+) = \Delta G^\circ(\text{H}^+) - \mu(\text{H}) + \mu
\]
where \( \mu_s \) is given with respect to vacuum, that is, \( \mu_s = \mu_s^0 - \mu^0 \). The energy of solvated ions is obtained from the ion heat of formation in the gas phase plus the hydration energy. The ion heats of formation are taken from the NIST-JANAF thermochemical tables and the hydration energies from refs 47 and 48. We may also connect this to pH, which is directly related to the \( \text{H}^+ \) concentration in the solution:

\[
c_{\text{H}^+} = c_0 \exp\left(-\Delta G(\text{H}^+)/k_BT\right) = 10^{-\Phi/2.303}
\]

where \( c_0 = 55.55 \text{ mol/L} \) is the concentration of the \( \text{H}_2\text{O} \) molecules in water. Equations for \( \Phi \) are similar. A full account of the chemical potential calculations and a list of all the thermochemical quantities are given in Supporting Information.

**Computational Details.** Our density functional theory calculations were carried out in the framework of projector-augmented waves as implemented in the VASP software package. For the exchange-correlation functional, we wanted to choose one that properly reproduces the formation energies of MXenes. However, because experimental values are not available, we used \( \text{TiO}_2 \) and water properly reproduces the formation energies of MXenes. Therefore, the MXene sheets were then calculated using the PBEsol functional. The optimal plane-wave cutoff energy was chosen as \( 550 \text{ eV} \) according to a convergence test. The set of \( 15 \times 15 \times 1 \text{ k-points} \) was found to be sufficient for the unit cells of \( \text{Ti}_2\text{C} \) and \( \text{Ti}_3\text{C}_2 \).

The calculated lattice constants and work functions are in good agreement with previous calculations for the fully terminated \( \text{Ti}_3\text{C}_2 \) and \( \text{Ti}_2\text{C}_2 \). The calculated lattice parameters and work functions are listed in Table 1. The lattice constant has been measured for \( \text{Ti}_3\text{C}_2 \) and is equal to \( 3.050 \text{ Å} \).

**Table 1. Calculated Lattice Parameters for Terminated \( \text{Ti}_2\text{C} \) and \( \text{Ti}_3\text{C}_2 \) Sheets**

|       | \( \text{Ti}_2\text{C} \) | \( \text{Ti}_2\text{C} \) | \( \text{Ti}_2\text{C} \) | \( \text{Ti}_2\text{C} \) |
|-------|----------------|----------------|----------------|----------------|
| \( a \) | 3.040 | 3.006 | 3.040 | 3.026 |
| \( \Phi \) | 4.59 | 5.84 | 1.96 | 4.88 |

|       | \( \text{Ti}_3\text{C}_2 \) | \( \text{Ti}_2\text{C} \) | \( \text{Ti}_2\text{C} \) | \( \text{Ti}_2\text{C} \) |
|-------|----------------|----------------|----------------|----------------|
| \( a \) | 3.081 | 3.016 | 3.057 | 3.050 |
| \( \Phi \) | 4.47 | 6.16 | 1.99 | 4.77 |

Phonons and thermal properties were calculated using Phonopy.\(^{59}\) The force constants were evaluated using a \( 5 \times 5 \) supercell and the thermal properties integrated in 1000 \( \times 1000 \) \( \text{k-point} \) mesh.

Solvation energies were calculated using VASPsol.\(^{50,61}\) A high cutoff energy is required to properly describe the interfacial region between the implicit solution and the surface, in particular, to construct an appropriate grid for the cavity surface, and therefore, these calculations are carried out using a cutoff energy of \( 1000 \text{ eV} \). We keep the atomic positions fixed to those obtained from vacuum calculations. For the pure terminations, the solvation energies are very small: \(-50, -8, -40, \) and \(-9 \text{ meV} \) for \( \text{Ti}_2\text{C} \), \( \text{Ti}_2\text{C}_2 \), \( \text{Ti}_2\text{C}_2 \), and \( \text{Ti}_2\text{C}_2 \) respectively. For the mixed configurations, we did not assume that the solvation energy contributions could be obtained using the pure terminations and averaging them according to the composition. Instead, we carried out explicit calculations for the solvation energies of the SQoS structures with the atomic structure fixed to that in vacuum.

The electron chemical potential \( \mu_s^0 \) is evaluated from the work function of the unsolvated sheets (in vacuum) for each of the three surface terminations.

**Cluster Expansion of Alloy Energies, Monte Carlo Simulations, and Special Quasi-ordered Structures.** Cluster expansion study for the mixture of surface terminations was carried out using ATAT.\(^{62,63}\) In order to sample the configuration space, we generate CE for the three-component (\( \text{O}, \text{OH}, \text{F} \)) mixture by fitting to a set of 71 and 106 DFT energies for \( \text{Ti}_2\text{C} \) and \( \text{Ti}_3\text{C}_2 \), respectively. In addition to atomic positions, we also optimized the lattice constants. However, accurate effective cluster interactions require high-quality DFT data as well as the right selection of the number and type of clusters. For \( \text{Ti}_2\text{C}_2 \), we have considered clusters with 3, 6, 10, and 13 pairs and 4 triplets, as well. The set of 3 pair clusters includes only the first near neighbor interactions and basically resembles the Ising model. The sets of 6 and 10 clusters include interactions of the lateral first nearest neighbors as well as interactions between nearest neighbors on the opposite sides of the slab. The set of 13 pairs and 4 triplets includes lateral pair interactions up to the second nearest neighbor and the first nearest neighbor on the opposite sides of the slab. CE predicted energies are fitted using the least-squares method to the calculated DFT energies. The fitting quality was evaluated by the cross-validation (CV) score and by the residual distribution. Residuals were normally distributed in all cases. A small CV was obtained when including a set of 13 pair and 4 triplet clusters, that is, 0.008 eV/atom for \( \text{Ti}_2\text{C}_2 \) and 0.005 eV/atom for \( \text{Ti}_2\text{C}_2 \) when including a set of 13 pair clusters.

Using the obtained CE effective interactions, we carried out Monte Carlo simulations using the program MultiComponent Easy Monte Carlo Code (Mecmc2) of ATAT. Statistical samplings were performed in the canonical ensemble (i.e., fixed composition) within a \( 40 \times 40 \times 1 \) supercell containing 3200 surface atoms. The Monte Carlo simulations were performed with target precision of 1 meV in the average energy. We started the simulation from high temperatures (5000 K) and gradually approached room temperature (300 K) with a temperature step of 200 K. These are used to study the distribution of adsorbants on the surface.

In order to evaluate the mixing and Gibbs free energies, work function, and lattice constants of the structures within different concentrations of functional groups, we generated representative supercell models and carried out separate DFT calculations for those. Following the same construction principles as in generating special quasi-random structures, but employing the correlations from the MC simulations instead of random correlations, we generated representative special quasi-ordered structures (SQoS) with 4 \( \times \) 4 supercells.\(^{50,60}\) These SQoS supercells are used to evaluate the final material properties.

**ASSOCIATED CONTENT**

**S Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano.9b03511.

ATAT files (ZIP)

Additional details and all numerical values needed for the determination of chemical potentials of solutes; benchmarking of exchange-correlation functionals and the size of the cluster expansion; surface structures and energies for \( \text{Ti}_2\text{C}_2 \) similar to those for \( \text{Ti}_3\text{C}_2 \) presented in the main text (PDF)

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**Notes**

The authors declare no competing financial interest.

Computational data generated in this study have been submitted to NOMAD repository and are available at http://dx.doi.org/10.17172/NOMAD/2019.07.02-1.
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