1. Introduction

Two-dimensional (2D) solids—defined as crystals with very high aspect ratios and thicknesses corresponding to a few atomic layers—have garnered tremendous interest recently. By far the most studied is graphene, which is comprised of atomically thin layers of sp²-bonded carbon atoms connected by aromatic in-plane bonds. Since graphene’s outstanding electronic properties were discovered by Novoselov, Geim et al.,[1] other 2D materials, such as hexagonal boron nitrides,[2] transition metal dichalcogenides (TMDs),[3] metal oxides, and hydroxides, have attracted much renewed attention.[4]

Recently, the constellation of 2D materials has been augmented, by a new, potentially quite large, group of early transition metal carbides and/or carbonitrides labeled MXenes. These are produced by the etching out of the A layers from MAX phases.[5–7] The latter are so-called because of their composition: namely, Mₙ₊₁AXₙ, where M is an early transition metal, A is mainly a group IIIA or IVA (i.e., groups 13 or 14) element, X is C and/or N, and n = 1, 2, or 3. Currently more than 60 different pure MAX phases are known,[8] However, given that the MAX phases can also be synthesized with different combinations, or solid solutions, of M atoms, such as (Ti₀.₅,Nb₀.₅)₂AlC,[9] A atoms, such as Ti₃(Al₀.₅,Si₀.₅)C₂,[10] and in the X sites such as Ti₃Al(C₀.₅,N₀.₅),[11] their potential number is quite large indeed.

All known MAX phases are layered hexagonal with P6₃/mmc symmetry, where the M layers are nearly closed packed, and the X atoms fill the octahedral sites. The Mₙ₊₁Xₙ layers are, in turn, interleaved with layers of A atoms.[12] In other words, the MAX phase structure can be described as 2D layers of early transition metal carbides and/or nitrides “glued” together with an A element (Figure 1). The strong M–X bond has a mixed covalent/metallic/ionic character, whereas the M–A bond is metallic.[13] So, in contrast to other layered materials, such as graphite and TMDs,[2] where weak van der Waals interactions hold the structure together, the bonds between the layers in the MAX phases are too strong to be broken by shear or any similar mechanical means. However, as discussed here, by taking advantage of the differences in character and relative strengths of the M–A compared with the M–X bonds, the A layers can be selectively etched by chemical means without disrupting the M–X bonds.

Because the M–A bonds are weaker than the M–X bonds, heating of MAX phases under vacuum,[14] in molten salts,[15,16] or in certain molten metals[17] at high temperatures results in the selective loss of the A element. However, because of the elevated temperature needed, de-twinning of the Mₙ₊₁Xₙ layers takes place which results in formation of a 3D Mₙ₊₁Xₙ rock salt structure.[16,18] On the other hand, the use of strong etchants, such as Cl₂ gas, at temperatures above 200 °C results in the etching of both the A and M atoms, to yield carbide derived carbons (CDC).[19,20] Similarly, reaction of Ti₃AlC with anhydrous hydrofluoric acid (HF) at 55 °C resulted in the formation of a new, ternary metal fluoride phase, Ti₃AlF₉.[21] It follows that, in order to selectively etch the A element, while preserving the 2D nature of the Mₙ₊₁Xₙ layers, a delicate balance between temperature and the activity of the etchant needs to be maintained.

In 2011 we reported, in Advanced Materials, on the selective etching of Al from Ti₃AlC₂ using aqueous HF at room temperature (RT).[4] In this process, the Al atoms are replaced by O, OH and/or F atoms. The removal of the Al layers dramatically weakens the interactions between the Mₙ₊₁Xₙ layers that, in turn, allows them to be readily separated. We labeled these new materials MXenes, to emphasize the loss of the A element from the MAX parent phase and to highlight their 2D nature, which is similar to graphene.

Today, the MXene family includes Ti₃C₂, Ti₃C, Nb₂C, V₂C, (Ti₀.₅,Nb₀.₅)₂C, (V₀.₅,C₀.₅)₂C, Ti₃CN, and Ta₃C₁. Because the n values for the existing Mₙ₊₁AXₙ phases can vary from 1 to 3, the corresponding single MXene sheets consist of 3, 5...
or 7 atomic layers for M<sub>1</sub>X, M<sub>2</sub>X<sub>2</sub> and M<sub>4</sub>X<sub>3</sub>, respectively, (see Figure 1). In all cases, the individual MXene layer thicknesses are less than 1 nm, while their lateral dimensions can reach tens of microns.

With the increased attention to 2D materials beyond graphene, and with MXenes representing a new large family extending the world of 2D materials,[22–24] it is timely to have a progress report on the state of MXene research, covering experimental and theoretical studies related to their synthesis, structure, properties, and potential applications. This article summarizes the current progress in MXene research and outlines the outstanding challenges, both experimental and theoretical. We also provide an outlook of future directions for research of these new and exciting 2D materials.

2. Synthesis

As noted above, MXene synthesis is achieved by selective etching of the A element layers from the MAX phases at room temperature. In this process (Figure 2), the MAX phase powder is stirred in aqueous HF, of a specific concentration, for a given time followed by centrifugation and/or filtration of the mixture to separate the solid from the supernatant with subsequent washing of the solid with deionized water (DI) until the pH of the suspension reaches values of between 4 and 6. As a result of this treatment, solid dense MAX particles (not shown) are converted to a loosely packed accordion-like structure (Figure 3a) resembling exfoliated graphite.[25] Following the convention used in the graphite/nanotube literature, we refer to these loosely packed, stacked particles as multilayer, or ML–MXenes. When the number of stacked layers is less than 5, they will be referred to as few-layer MXenes (FL–MXene). Given that various surface terminations—the exact chemistries of which are still being explored—are possible (see below), a general labeling scheme is needed. Here we denote these surfaces with the general formula: M<sub>Mn</sub>TX<sub>T</sub>, where T stands for surface-terminating functional groups (OH, F, O, H, etc.).

If a MAX phase is fully transformed to MXene, all but the (000l) peaks in the X-ray diffraction (XRD) patterns will weaken or vanish, especially in the case of the thinner M<sub>2</sub>X structures. Furthermore, the (000l) peaks should not only broaden, but downshift to lower angles, an indication of a larger c lattice parameter. If registry along the [0001] direction is lost (see below) then no XRD peaks are expected. Typical results for Nb<sub>2</sub>AlC are shown in Figure 3b, where indeed only (000l) peaks are present after etching. It is important to note that the diffractograms shown in Figure 3b are obtained on samples that were cold pressed to 450 MPa, a procedure that greatly enhances the intensity of the (000l) peaks. Also noteworthy is that in case of incomplete conversion, MAX phase peaks coexist with the MXene (000l) peaks.

Along the same lines, and primarily because XRD peak intensities tend to fade with increasing degree of exfoliation (decreasing number of layers in the MXene lamellas), XRD alone cannot be used to quantify the fraction of unreacted MAX phase in a sample. Instead, energy-dispersive spectroscopy (EDS) is used to quantify the A:M atomic ratio. In a fully converted sample, this ratio would be negligible. However, this method tends to overestimate the MAX phase concentration related and other applications. He has co-authored more than 350 journal papers and obtained more than 40 patents. He has received numerous national and international awards for his research and was elected a Fellow of AAAS, MRS, ECS and ACerS and a member of the World Academy of Ceramics.
because, in addition to its presence in the MAX phase, the A element could also be present in the MXene samples in the form of A-element-containing salts, if the etching products are not completely removed during washing. For example, the presence of aluminum fluoride after HF treatment of Ti$_2$AlC$_2$ was confirmed using X-ray photoelectron spectroscopy (XPS).\cite{5,26}

Table 1 summarizes the HF etching conditions needed to synthesize various MXenes, along with their $c$-lattice parameters and the $c$-lattice parameters of their corresponding MAX phases. The MXene yield—defined here as the weight of powders after HF treatment divided by the weight of powders before HF treatment $\times 100$—varied between 60–100%. Note that the atomic weight of Al is close to the combined weight of atoms in (OH)$_2$. If the two are interchanged and if the resulting MXenes do not dissolve in the etchant, little weight loss is expected, as observed. The assumption of replacing each Al atom by two surface groups is reasonable, as one Al layer glues two $M_{n+1}X_n$ layers in the MAX phases (each Al layer is shared by two $M_{n+1}X_n$ layers) so after etching the Al, surface groups terminate the surface of each MXene layer.

The etching times and HF concentrations needed to fully convert a given MAX powder depend primarily on its particle size, time, temperature, and HF concentration.\cite{6,27} Tuning the etching conditions is important for achieving high yields and the complete conversion of MAX into MXene. Prolonged etching can result in the formation of defects, such as the holes observed in Figure 3c in Ta$_4$C$_3$Ti$_x$.\cite{6} Reducing the V$_2$AlC particle size by attrition milling reduces the etching time for complete conversion from 90 h to 8 h.\cite{7}

Although all of the MAX phases listed in Table 1 contain Al as an A element, the etching conditions varied widely, a fact that in part reflects the different M–Al bond energies in the different MAX phases. For example, the Ti–Al and Nb–Al bond energies in Ti$_2$AlC and Nb$_2$AlC have been estimated to be 0.98 eV and 1.21 eV, respectively.\cite{29} This difference, in turn, can explain the experimental finding that the etching of Al from Nb$_2$AlC requires longer times and higher HF concentrations than from Ti$_2$AlC (see Table 1).

Another important variable is the value of $n$ for a given $M_{n+1}AlC_n$ phase. In general the higher the $n$, the more stable the MXene. For example, immersing Ti$_2$AlC powders in 50% HF—the same conditions that yield Ti$_3$C$_2$—resulted in their complete dissolution. It is only by reducing the HF concentration from 50% to 10% that Ti$_2$C was obtained from Ti$_2$AlC.\cite{6}

To date, all attempts to produce nitride-based MXenes, such as Ti$_3$N or Ti$_4$N$_3$, have failed. By contrast, it is possible to selectively etch the Al from Ti$_3$AlCN to produce Ti$_3$CN (see Table 1). Note that the calculated cohesive energies of Ti$_{n+1}N_n$ are less than those of Ti$_{n+1}C_n$, whereas the formation energies of Ti$_{n+1}N_n$ from Ti$_{n+1}AlN_n$ are higher than those of Ti$_{n+1}C_n$ from Ti$_{n+1}AlC_n$.\cite{30} The lower cohesion energy implies lower stability of the structure, whereas the higher formation energy of the MXenes from their corresponding Al containing MAX phases implies that the Al atoms are bonded more strongly in Ti$_{n+1}AlN$ compared to Ti$_{n+1}AlC$, and thus require more energy for their extraction. These two factors may explain why nitride MXenes have to date not been produced. Another distinct possibility is that the Ti$_{n+1}N_n$ layers dissolve in the HF solution due to their lower stability.

The replacement of the strong Al–M bonds by weaker hydrogen or van der Waals bonds allows for the facile delamination of MXene. This is best seen in Figure 3c–g, in which various delaminated MXene layers are imaged in a transmission electron microscope (TEM) and under an optical microscope (OM) (Figure 3h). To obtain the
delaminated MXenes, the HF treated powders are ultrasonicated in isopropyl alcohol or methanol. We note in passing that this technique results in small yields of delaminated flakes.\textsuperscript{5–7} An intercalation approach that dramatically increases the yield is discussed below.\textsuperscript{26} The delaminated layers were found to be transparent not only to the electron beam in TEM (Figure 3c, d) but also to visible light (Figure 3h).\textsuperscript{6} Selected area electron diffraction (SAED) of delaminated MXene (inset in Figure 3g) imaged along [0001] clearly show that the atomic arrangement in the basal planes is identical to that in the parent MAX phase. These results provide further compelling evidence for the 3D to 2D conversion of the material. Furthermore, no evidence for carbide amorphization was observed in the TEM. It is important to note here that the Ti$_3$C$_2$ sheets are significantly more stable than graphene sheets under a 200 kV electron beam in the TEM.\textsuperscript{31,32}

Figure 3e shows a cross-sectional TEM micrograph of two MXene layers, whereas Figure 3f shows their corresponding atomistic model.\textsuperscript{5} During ultrasonication, some of the delaminated layers form scrolls with inner radii of $<20$ nm (Figure 4a–c).\textsuperscript{5} Similar scrolls were also reported for graphene after ultrasonication.\textsuperscript{33,34} In addition to scrolls, MXene nanotubes were also predicted to be stable and to become more stable as their radii increase owing to reduced strain.\textsuperscript{35} In contrast to Ti$_{n+1}$C$_n$(OH)$_2$ MXene sheets, which can be semiconducting (see below), the seamless MXene nanotubes, formed from either Ti$_{n+1}$C$_n$ or Ti$_{n+1}$C$_n$(OH)$_2$ are predicted to have metallic character. The synthesis of seamless MXene nanotubes remains to be demonstrated.

Very recently, Zhang et al.\textsuperscript{36} reported on the exfoliation of Ti$_3$Si$_{0.75}$Al$_{0.25}$C$_2$ by the aid of ultrasonication in various solvents. They suggest that when the A layer is composed of different atoms instead of single elements, breaking the bonds between the carbide layers becomes easier. The resulting ultrathin sheets had thicknesses of $\approx4$ nm and lateral dimension of 100–200 nm. The resulting sheets had the same composition as the parent MAX phase, and the yields were quite low. It was found that the above approach worked only for doped MAX phase; pure Ti$_3$SiC$_2$ could not be exfoliated by this technique.

3. Structure

From the outset, modeling has played a crucial part in understanding the structure and properties of MXenes. In fact, the first structure of ML–MXenes—namely, stacked OH-terminated Ti$_3$C$_2$ after prolonged HF treatment. Reproduced with permission.\textsuperscript{5} Copyright 2012, American Chemical Society. c) Transmission electron microscopy (TEM) image of Ta$_4$AlC$_3$ after prolonged HF treatment. Reproduced with permission.\textsuperscript{5} Copyright 2012, American Chemical Society. d) Low-magnification TEM image of Ti$_3$AlC$_2$ after HF treatment. Reproduced with permission.\textsuperscript{5} e) High-resolution transmission electron microscopy (HRTEM) cross-sectional image of Ti$_3$AlC$_2$ after HF treatment. Reproduced with permission.\textsuperscript{5} f) Atomic model of OH-terminated Ti$_3$C$_2$. Reproduced with permission.\textsuperscript{5} g) HRTEM of (Ti$_{0.5}$Nb$_{0.5})_2$AlC after HF treatment and the inset (top left) showing the corresponding SAED pattern. Reproduced with permission.\textsuperscript{5} Copyright 2012, American Chemical Society. h) Optical transmittance micrograph of Ti$_3$CNT$_x$. Reproduced with permission.\textsuperscript{5} Copyright 2012, American Chemical Society. delaminated MXenes, the HF treated powders are ultrasonicated in isopropyl alcohol or methanol. We note in passing that this technique results in small yields of delaminated flakes.\textsuperscript{5–7} An intercalation approach that dramatically increases the yield is discussed below.\textsuperscript{26} The delaminated layers were found to be transparent not only to the electron beam in TEM (Figure 3c, d) but also to visible light (Figure 3h).\textsuperscript{6} Selected area electron diffraction (SAED) of delaminated MXene (inset in Figure 3g) imaged along [0001] clearly show that the atomic arrangement in the basal planes is identical to that in the parent MAX phase. These results provide further compelling evidence for the 3D to 2D conversion of the material. Furthermore, no evidence for carbide amorphization was observed in the TEM. It is important to note here that the Ti$_3$C$_2$ sheets are significantly more stable than graphene sheets under a 200 kV electron beam in the TEM.\textsuperscript{31,32}

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3. Structure

From the outset, modeling has played a crucial part in understanding the structure and properties of MXenes. In fact, the first structure of ML–MXenes—namely, stacked OH-terminated Ti$_3$C$_2$ layers—was proposed on the basis of a density functional theory (DFT) simulation.\textsuperscript{5} The calculated $c$ parameter from the XRD pattern of the geometry-optimized structure of the fully hydroxylated MXene was a close match with the experimental XRD results, despite the fact that a mixture of hydroxyl and fluorine terminations could not be ruled out.\textsuperscript{5} The real situation may be even more complex with incomplete or mixed F, OH, and O terminations present (the presence of both OH and O was confirmed experimentally using XPS).\textsuperscript{5,26} Further complicating the situation is the high probability that water molecules can be present in the interlayer space,\textsuperscript{7} especially in the case of V$_2$C and Nb$_2$C, in which the $c$ values after etching are quite large indeed (see Table 1).
Soon after their discovery, DFT studies\cite{35,37} found two energetically favorable orientations for T in Ti$_3$C$_2$T$_2$, resulting in two distinct configurations: I and II (Figure 5). In configuration I, the T groups are located above the hollow sites between three neighboring C atoms or, said differently, the T groups point directly toward the Ti(2) atoms on both sides of the Ti$_3$C$_2$ layers. In configuration II, the T groups are positioned above the C atoms on both sides of the Ti$_3$C$_2$ layers. A mixed structure, where one side of the sheet is in configuration I, and the opposing side is in configuration II, was also considered and referred to as configuration III. Different authors have used different notations to distinguish between these configurations. For example, a configuration labeled I in one study was labeled “model II” or “conformation A” in another, and so on. Throughout this progress report, we rename the configurations explored in the different studies to be consistent with those shown in Figure 5.

The structural stabilities of different Ti$_3$C$_2$F$_2$ and Ti$_3$C$_2$(OH)$_2$ configurations—estimated by comparing their relative DFT total energies—were found to decrease in the order I > III > II. This suggests that both F and OH groups tend to adopt configuration I. The lowest structural stability of configuration II is ascribed to steric repulsion between T groups and the underlying C atoms.\cite{37} Another possible configuration, where the T terminations are connected to, and positioned just above the Ti(1) atoms of Ti$_3$C$_2$, was shown to be unstable and often transformed into configurations I–III during geometry optimization and will therefore, not be discussed further.\cite{37} It is necessary to emphasize again that MXenes produced to date may have mixed functional groups (such as OH, O, and F) on their surfaces that may affect their configurations. However, no MXenes models with mixed surface functional groups have been published to date.

These configurations, and the order of their stability, for a broader range of T groups, including H, O, OH, and F, have been confirmed in other DFT studies for many MXenes with different n values and elemental compositions,\cite{38,39} including solid solutions (carbonitrides).\cite{40} The relative total energy differences between configuration I, and either II or III, were found not to be very sensitive to the layer thicknesses, with the largest differences observed in case of M$n_{Ti}$X$_n$O$_2$ compared with M$n_{Ti}$X$_n$F$_2$, M$n_{Ti}$X$_n$F, and M$n_{Ti}$X$_n$(OH)$_2$ for X = C or N. Moreover, the energy differences for I–III M$n_{Ti}$X$_n$T$_2$ are smaller than for I–III M$n_{Ti}$C$_n$T$_2$.\cite{39}

The important question of the thermodynamic stability of fully terminated compared to partially terminated structures (that is, M$n_{Ti}$X$_n$H$_2$, M$n_{Ti}$X$_n$F$_2$, and M$n_{Ti}$X$_n$(OH)$_2$ for X = C or N) remains open. Thus far, the only study addressing this question\cite{37} shows that in a wide range of oxygen gas chemical potentials between $-4$ and 0 eV, the fully oxygen terminated Ti$_3$CO$_2$ structure is thermodynamically the most favorable configuration compared with other configurations with lower oxygen contents. Phonon dispersion curves calculated in the same paper for Ti$_3$CO$_2$ have no imaginary frequencies, again signifying that this structure is stable.

Gan et al.\cite{41} found, using both DFT and ab initio molecular dynamics (MD) calculations with the climbing image nudged elastic band method to calculate the energy barriers, that O$_2$ adsorbs on Ti$_3$C surface forming super- and per-oxo species, which then dissociate without any barrier, producing

Table 1. Process conditions and c-lattice parameters for MXene synthesis from MAX phases. Also listed are the c values of the parent MAX phase.

<table>
<thead>
<tr>
<th>MAX Structure</th>
<th>MAX</th>
<th>MXene</th>
<th>RT etching conditions</th>
<th>c lattice parameter, Å</th>
<th>Ref.</th>
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<tr>
<td>211 Ti$_3$AlC</td>
<td>Ti$_3$C$_x$</td>
<td>10 10</td>
<td>13.6 15.04</td>
<td>[6]</td>
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<tr>
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<td>50 8</td>
<td>13.13 23.96</td>
<td>[7]</td>
<td></td>
</tr>
<tr>
<td>Nb$_3$AlC</td>
<td>Nb$_3$C$_x$</td>
<td>50 28</td>
<td>13.88 22.34</td>
<td>[7]</td>
<td></td>
</tr>
<tr>
<td>Nb$_3$(Ta$_3$,Nb$_3$)$_3$AlC</td>
<td>Nb$_3$(Ta$_3$,Nb$_3$)$_3$C$_x$</td>
<td>50 28</td>
<td>13.79 14.88</td>
<td>[6]</td>
<td></td>
</tr>
<tr>
<td>312 Ti$_3$AlC$_2$</td>
<td>Ti$_3$C$_2$T$_x$</td>
<td>50 2</td>
<td>18.42 20.51</td>
<td>[5,6]</td>
<td></td>
</tr>
<tr>
<td>(V$_3$C$_2$)$_3$AlC$_2$</td>
<td>(V$_3$C$_2$)$_3$C$_2$T$_x$</td>
<td>60 59</td>
<td>17.73 24.26</td>
<td>[6]</td>
<td></td>
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<tr>
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<td>(V$_3$C$_2$)$_3$C$_2$T$_x$</td>
<td>30 18</td>
<td>18.41 22.28</td>
<td>[6]</td>
<td></td>
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<tr>
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<td>Ti$_4$C$_3$T$_x$</td>
<td>50 72</td>
<td>24.08 30.34</td>
<td>[6]</td>
<td></td>
</tr>
<tr>
<td>Nb$_3$AlC$_3$</td>
<td>Nb$_3$C$_3$T$_x$</td>
<td>50 50</td>
<td>24.19 30.47</td>
<td>[7]</td>
<td></td>
</tr>
</tbody>
</table>

*[The 8 h treatment of Ti$_3$AlC was carried out on attrition-milled powders; \( Nb_3AlC_3 \) was present as a secondary phase in a \( Nb_3AlC \) sample.]*

Figure 4. a) Ti$_3$C$_2$Tx nanoscroll of about 20 nm in outer diameter. b) Cross-sectional TEM image of a scroll with an inner radius of less than 20 nm. Reproduced with permission.\cite{22} c) Atomic model of OH-terminated Ti$_3$C$_2$ nanotube. Reproduced with permission.\cite{23} Copyright 2012, Elsevier.
Ti$_3$CO$_x$. Once saturation is achieved by forming Ti$_3$CO$_2$, additional O$_2$ is repelled by the surface even at temperatures as high as 550 °C. This suggests that Ti$_3$CO$_2$ is stable and does not form TiO$_2$ in oxidizing environment, in contrast to many transition metal carbide nanoparticles, such as tungsten carbide. The predicted Ti$_3$CO$_2$ stability in these conditions may be important for catalytic applications. It is worth noting that this study was based on perfect Ti$_3$C surfaces (with no defects such as Ti vacancies) which could change the conclusions.

In addition to OH, O, and F surface terminations, Enyashin et al. [42] found—using density-functional tight-binding (DFTB), DFT, and MD calculations—that methoxy-terminated MXenes may be stable. These findings suggest MXenes can be promising catalysts in, e.g., esterification processes.

Most, if not all, DFT calculations to date have been carried out on single, isolated MXene sheets. Experimentally, the latter are the exception rather than the rule. For the most part, the MXene flakes, similar to other 2D materials, are stacked as shown in Figure 3a. Indubitably, the stacking, and just as importantly what is in between the layers, will have a significant effect on the energetics of the system.

4. Intercalation and Large-Scale Delamination of MXenes

Intercalation is a well known phenomenon for many layered materials for which the bonds between the layers are not very strong, such as graphite [43] and clays [44]. The same is true of MXenes: the weak bonds between the M$_n$+X$_n$ layers allow for the intercalation of different species (organic, inorganic, and ionic) between the Ti$_3$C$_2$ layers. [26,45] In case of Ti$_3$C$_2$(OH)$_2$ intercalated with hydrazine (N$_2$H$_4$), a comparison of the experimental and MD derived XRD patterns for different numbers of N$_2$H$_4$ molecules in the interlayer space of Ti$_3$C$_2$(OH)$_2$ showed that the intercalated N$_2$H$_4$ molecules were most probably arranged in an orientation that is parallel relative to the MXene basal planes and formed a complete monolayer (see Figure 6).

Here again the theoretical calculations have to be taken with a grain of salt. For example, owing to the unusual combination of elements in N$_2$H$_4$-intercalated Ti$_3$C$_2$(OH)$_2$, including Ti, C, O, N, and H, a universal force field, which is broad in terms of included elements but not very precise, had to be used in the MD simulations. [26] Configuration III taken from Naguib et al. [5] was used for stacked Ti$_3$C$_2$(OH)$_2$ in these simulations, which as we now know, is not the most stable in the case of Ti$_3$C$_2$(OH)$_2$ monolayers. As noted above, however, nothing is known about the relative stabilities of configurations I to III in multilayer or stacked MXenes.

In most cases, the intercalation results in an increase in the c lattice parameters values. For example, the intercalation induced changes in the c values (Δc) of Ti$_3$C$_2$T$_x$ vary from 0.7 Å for sodium sulfate to 15.4 Å for dimethylsulfoxide (DMSO). [26,45] The large Δc after DMSO intercalation is due to the spontaneous co-intercalation of ambient moisture. Storing DMSO-intercalated Ti$_3$C$_2$T$_x$ samples in air for 3 weeks, resulted in a doubling of the c lattice parameter over its value for Ti$_3$C$_2$T$_x$.

This extraordinary increase of the interlayer spacing further weakens the bonds between the MXene layers to the extent that weak sonication of DMSO intercalated Ti$_3$C$_2$T$_x$ powders in deionized (DI) water for 6 h resulted in further delamination of most of the layers, as schematically shown in Figure 7. [26] It is important to differentiate between as-produced multilayer Ti$_3$C$_2$T$_x$ and delaminated single- or few-layer Ti$_3$C$_2$T$_x$. As MXenes
are hydrophilic, once delaminated, they form stable, surfactant-free colloidal solutions in water (Figure 7 bottom left). To date, the only MXene that has been successfully delaminated in large quantities is Ti$_3$C$_2$T$_x$.

The possibility of intercalating MXenes with various organic molecules goes beyond delaminating MXenes on a large scale. This phenomenon will indubitably play a critical role for a range of MXene applications, from polymer reinforcements to energy storage systems (see below). Furthermore, it was found that the resistivities of cold pressed MXene discs increase by 1–2 orders of magnitude after intercalation with organic compounds. Selectivity to intercalants, and changes in resistivity after intercalation, suggest that MXenes may also work as sensors for various chemicals.

5. Properties

The electronic properties of MXenes are of special interest as they can, in principle, be tuned by changing the MXene elemental composition and/or their surface terminations. The MXenes’ band structure and electron density of states (DOSs) have been extensively studied by DFT. Bare MXene monolayers are predicted to be metallic, with a high electron density near the Fermi level. Interestingly, the electron DOS near the Fermi level ($N(E_f)$) for bare individual MXene layers is higher than in their parent MAX phases. To understand these changes one needs to examine the partial electron density of states of (Figure 8).

In the MAX phases, $N(E_f)$ is dominated by M 3d orbitals. Referring to Ti$_2$AlC (Figure 8a), it is clear that the valence states below $E_f$ group into two sub-bands: sub-band A, which is near $E_f$ and is made up of hybridized Ti 3d-Al 3p orbitals; and sub-band B, which is between $-10$ and $-3$ eV below $E_f$ and is due to hybridized Ti 3d-Al 3p orbitals. In other words, sub-bands A and B give rise to the Ti-Al and Ti-C bonds, respectively. Removal of the A layers results in a redistribution of the Ti 3d states, or “dangling bonds”, from the missing Ti–Al bonds into delocalized Ti–Ti metallic-like bonding states that appear around $E_f$ in Ti$_2$C (Figure 8b). Thus, in MXenes, $N(E_f)$ is 2.5–4.5 times higher than in the corresponding MAX phases for Ti$_n$C$_n$ and Ti$_n$N$_n$ according to Shein et al.; or 1.9–3.2 times higher for Ti$_n$C$_n$ and 2.8–4.8 times higher for Ti$_n$N$_n$ according to Xie et al., where the range of studied $n$ was broader.

The high $N(E_f)$ values in Ti$_n$X$_n$, contributed by the Ti 3d states, can lead to a magnetic instability, if the Stoner criterion $1-N(E_f) > 1$ (where $I$ is the Stoner exchange parameter, equal to 0.9 eV for 3d elements) is satisfied, resulting in magnetic MXenes. Magnetic MXenes can be both ferromagnetic (such as Cr$_2$C$_2$, Cr$_2$N$_2$ or Ta$_3$C$_2$) or antiferromagnetic (such as Ti$_3$C$_2$ or Ti$_3$N$_3$). The acquired total magnetic moments per unit cell are in the range 2–3 $\mu_B$ for Ti$_n$C$_n$ or fluctuate around 1.2 $\mu_B$ for Ti$_n$N$_n$ as $n$ increases from 1 to 9.

Although magnetism is an important property, for the most part it is only predicted for MXene with bare surfaces. When...
Surface terminations (T, even when T = H) are present, the magnetism disappears due to the formation of p–d bonds between the M atoms and T groups, leading to a partial depopulation of the near Fermi states, which reduces N(E_f) (Ti_2CO_2, Ti_2CF_2, Ti_2CH_2, and Ti_2C(OH)_2 in Figure 8c, d and e, respectively). Prominent exceptions are Cr_2C and Cr_2N, which are predicted to retain significant magnetic moments in their terminated state (T = O, OH, or F) up to nearly room temperature. Unfortunately, to date there have been no reports of experimentally produced Cr_2XT_2 MXenes to test this important prediction.

Surface terminations can influence other MXenes’ electronic properties, such as their bandgaps. In the first MXene paper, it was theoretically shown that although Ti_3C_2 is a metallic conductor, small bandgaps of 0.05 eV and 0.1 eV open up for Ti_2C(OH)_2 and Ti_2C_F_2, respectively. At the time, we suggested that it would be possible to tune the electronic structure of MXenes by varying T. It was further confirmed that the electronic structure of MXenes is sensitive not only to the type of surface terminations, but also to their orientation relative to the MXene sheets. In particular, Ti_2C_F_2 and Ti_2C(OH)_2 in configurations I and III (see above) were shown to be semiconductors with narrow band gaps of 0.04 eV (I-Ti_3C_F_2), 0.03 eV (III-Ti_3C_F_2), 0.05 eV (I-Ti_3C(OH)_2) and 0.07 eV (III-Ti_3C(OH)_2). Interestingly, the same materials in configuration II are predicted to be metals. Although most MXenes are metallic or have small bandgaps, DFT results predict that: Sc_2CF_2 should possess an indirect bandgap of 1.03 eV; Sc_2C(OH)_2 should have a direct bandgap of 0.45 eV; Sc_2CO_2 should have an indirect bandgap of 1.8 eV; Ti_3CO_2 should have an indirect bandgap of 0.24 eV; Zr_2CO_2 should have an indirect bandgap of 0.88 eV; and Hf_2CO_2 should have an indirect bandgap of 1.0 eV. Thus, many MXenes, especially O-terminated ones, are predicted to be semiconducting.

To understand these changes, it is necessary again to examine the partial electron density of states of (Figure 8). In addition to sub-bands A and B, mentioned above, in surface terminated MXenes a new sub-band C, corresponding to Ti–T bonds, is formed below sub-band B, causing a shift of the gap between sub-bands A and B to lower energies and a depletion in the N(E_f). It is the latter effect that reduces the propensity for magnetism in M_{n+1}X_nT_2. This is the basic mechanism through which chemical termination changes the electronic and magnetic properties of MXenes, although additional differences exist between different MXenes. For example, in M_{n+1}N_nT_2, the T contributes to both, the newly formed C sub-band and the existing B sub-band, in contrast to M_{n+1}C_{n+2}, where T contributes only to sub-band C. Note that in the carbonitrides, such as Ti_2C_N_2, the increased electron count due to the presence of the N atoms, may outweigh the withdrawal of electrons by surface groups, thus preserving their metallic character.

Concluding the discussion of computational results, it should be noted that while producing stable and consistent geometries, DFT is known to have issues with predicting bandgaps. Thus, a thoughtful choice of the exchange-correlation functional must be made in order to correctly predict the differences between metals and narrow band semiconductors. A proper inclusion of interlayer van der Waals interactions is also important, as they may not only influence the geometric structures, but may also change the band structures (as has been demonstrated for other materials, for example, see Govaerts et al.[46]. In this context, a comparison of the band gaps of Ti_2C(OH)_2 and Ti_3C_F_2 calculated using the GGA-PBE (Generalized Gradient Approximation–Perdew-Burke-Ernzerhol) and HSE06 (Heyd-Scuseria-Ernzerhol) functionals is instructive. According to GGA-PBE, Ti_2C(OH)_2 and Ti_3C_F_2—in their most stable configurations I—are narrow band semiconductors with band gaps <0.1 eV. However, the same MXenes, in the same configurations, are predicted to be metallic when HSE06 functional is used instead. Another example is Ti_3C_O_2, in configuration I, for which PBE functional predicts a band gap of 0.24 eV, whereas HSE06 gives a value of 0.88 eV. The HSE06 is a hybrid functional, which combines one-quarter of the exact Hartree–Fock exchange energy with three-quarters of an approximate exchange-correlation energy. This combination in general produces more reliable bandgaps than PBE. Therefore, this functional should be preferred over PBE in calculations of electronic properties. In another study,[50] Wu–Cohen (WC) functional within GGA formalism was chosen, because it was deemed superior to PBE, in describing the electronic structure.
The importance of modeling in discovering novel and unexpected properties of MXenes is, and will remain, indispensable. Modeling can also be used for screening different MXenes, some of which have not been synthesized yet and determining which ones have attractive properties, thus guiding experimental efforts.

Some of the predictions have already been confirmed experimentally. The conductivities of MXene free-standing thin discs (thickness around 300 μm)—prepared by cold pressing additive-free MXene powders at RT under a load corresponding to a stress of ~1 GPa—were comparable to those of multilayer graphene.[51] For example, the resistivities of those discs were: 22 Ω · cm for Ti3C2T x to 339 Ω · cm for Ti3CT x depending on their surface chemistry and n (M2X, M3X2, and M4X3). Contact angle measurements of DI water on these cold-pressed MXene discs revealed hydrophilic behavior, with contact angles in the 27 to 41 degrees range.[6] These values are comparable to oxygen terminated carbon surfaces.[52]

MXenes’ 2D morphologies, combined with their metallic electrical conductivities may be beneficial for integration with other layered semiconducting materials, such as MoS2. In these hybrid systems, MXenes may be used as conductive 2D pads. They could also be used to modify the electronic properties of other 2D materials in contact with MXene in vertical hybrid heterostructures. To date, no experimental studies have been carried out in this promising direction, although recent computational results[53] predict that metallic behavior emerges in MoS2 when Ti3C is deposited on it as a consequence of strong chemical bonds formed at the MoS2/Ti3C interfaces. By contrast, the bonding on MoS2/Ti3CF2 and MoS2/Ti3C(OH)2 interfaces is non-covalent (physisorption), preserving the semiconducting nature of MoS2. The bond alignment induces weak and strong n-type doping of the MoS2 in MoS2/Ti3CF2 and MoS2/Ti3C(OH)2 with corresponding n-type Schottky barrier heights of 0.85 and 0.26 eV, respectively.[54]

In another study,[55] high Seebeck coefficients were predicted for MXenes by DFT. The Seebeck coefficients ~1000 μV K−1 predicted for semiconducting Ti3CO2 and Sc2C(OH)2 at ~100 K are comparable to the reported giant Seebeck coefficients of SrTiO3 (850 μV K−1 at ~90 K). This prediction opens a totally new area of potential applications for these surface terminated MXenes.

The mechanical properties of MXenes are also of great interest as the M–C and/or M–N bonds are some of the strongest known. At this juncture the only information available on how MXenes would respond to stress, are the elastic constants when they are stretched along the basal planes, i.e., c11. An early DFT study of Ti3C2(OH)2 predicted a c11 ~300 GPa.[56] A follow up study[57] predicted that the c11 values of different, bare, or unfunctionalized, M3XnC layers would be higher than in their parent MAX phases (Table 2). This could be due to the strengthening of the M–X bonds when the A atoms are removed and the electron density is more concentrated within the M3XnC layer. However, the enhanced mechanical properties could also be due to the difficulty in accurately estimating the exact thickness of a MXene layer.

And although the c11 values for MXenes are lower than those of graphene, the bending rigidity, which scales as ~t4, where t is the layer thickness, should be significantly higher than for graphene, as many MXenes consists of at least 3 atomic layers. Moreover, t and the consequent elastic rigidity anisotropies can also be readily tuned by varying n in M3n+1Xn.[58]

### 6. Applications

The rich chemistries and unique morphologies of MXenes, in addition to their good electronic conductivities, render them strong candidates for many applications that range from sensors and electronic device materials to catalysts in the chemical industry, conductive reinforcement additives to polymers, electrochemical energy storage materials, among many others. For the most part many of those applications are still hypothetical. The few experimental results that exist to date have explored the use of MXenes in energy storage applications such as lithium ion batteries, LIBs, electrochemical capacitors (supercapacitors), and fuel cells.[59, 60, 61, 62]

Early DFT calculations on Li intercalation into multilayer Ti3C2 predicted the formation of Ti3C2Li2 in Li rich environments, with a slightly positive enthalpy explained by the larger size of Li versus Al atoms.[60] The theoretical Li capacity in that case was found to be 320 mAh g−1. Soon afterwards, DFT was again used to study the adsorption and diffusion of Li on monolayers of Ti3C2, Ti3C2F2 and Ti3C2(OH)2.[61] The most favorable Li adsorption sites for all three materials, in their most stable configuration I, were the positions above the C atoms of the carbide sheets. The adsorbed Li atoms become partially or fully ionized due to charge transfer between Li and Ti3C2, I-Ti3C2F2 or I-Ti3C2(OH)2. This charge transfer suggests that the adsorbed Li strongly interacts with MXenes via coulombic interactions. The calculated Li adsorption energies on Ti3C2, I-Ti3C2F2, and I-Ti3C2(OH)2 monolayers were found to be 0.50, −0.95, −0.20 eV per Li atom, respectively. The Li diffusion rates follow the order I-Ti3C2 > I-Ti3C2F2 > I-Ti3C2(OH)2, thus, bare Ti3C2 monolayers

<table>
<thead>
<tr>
<th>Layer</th>
<th>a, Å</th>
<th>c11, GPa MXene (MAX)</th>
<th>DOS at E= eV−1 atom−1</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>3.007</td>
<td>636 (312)</td>
<td>2.63</td>
</tr>
<tr>
<td>Vc</td>
<td>2.869</td>
<td>718 (338)</td>
<td>1.45</td>
</tr>
<tr>
<td>CrC</td>
<td>2.787</td>
<td>690 (340)</td>
<td>2.55</td>
</tr>
<tr>
<td>ZrC</td>
<td>3.238</td>
<td>594 (261)</td>
<td>1.77</td>
</tr>
<tr>
<td>HfC</td>
<td>3.239</td>
<td>658 (291)</td>
<td>2.25</td>
</tr>
<tr>
<td>TaC</td>
<td>3.138</td>
<td>788 (334)</td>
<td>0.89</td>
</tr>
<tr>
<td>MoC2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiC</td>
<td>3.071</td>
<td>523 (368)</td>
<td>2.19</td>
</tr>
<tr>
<td>TaC</td>
<td>3.196</td>
<td>575 (368)</td>
<td>1.44</td>
</tr>
<tr>
<td>TaC</td>
<td>3.066</td>
<td>512 (403)</td>
<td>1.83</td>
</tr>
<tr>
<td>TaC</td>
<td>3.172</td>
<td>633 (437)</td>
<td>0.56</td>
</tr>
</tbody>
</table>
should possess the highest Li transport rates. The higher Li diffusion barriers on the \( \text{I-Ti}_3\text{C}_2\text{F}_2 \) and \( \text{I-Ti}_3\text{C}_2\text{O} \text{(OH)}_2 \) surfaces were ascribed to steric hindrances induced by the surface F and OH groups.

The open circuit voltages were predicted to be 0.62, 0.56, and 0.14 V for \( \text{Ti}_3\text{C}_2\text{Li} \), \( \text{I-Ti}_3\text{C}_2\text{F}_2\text{Li} \) and \( \text{I-Ti}_3\text{C}_2\text{O} \text{(OH)}_2\text{Li} \), respectively. The corresponding theoretical specific capacities were found to be 320, 130, and 67 mAh g\(^{-1}\), respectively. All in all, the authors\(^{[37]} \) conclude that bare 2D \( \text{Ti}_3\text{C}_2 \) monolayers would be better anode materials for LIBs than \( \text{TiO}_2 \) due to their enhanced electronic conductivity (metallic character), smaller open circuit voltage, and improved Li storage capacity. Also, the predicted diffusion barrier (0.07 eV) for an isolated Li atom on a \( \text{Ti}_3\text{C}_2 \) surface was much lower than that in anatase \( \text{TiO}_2 \) (0.35–0.65 eV) or graphite (\( \approx 0.3 \) eV), meaning that \( \text{Ti}_3\text{C}_2 \) should sustain higher charge/discharge rates than these materials, rendering it promising for high power batteries. However, as noted above, all MXenes produced to date are terminated with surface groups, which may affect their performance as LIBs anodes. It follows that modeling will probably continue to have a pivotal role in identifying optimal MXene compositions and surface terminations for ion intercalation, as well as in uncovering new important details of the mechanisms of these processes.

Several MXenes (\( \text{Ti}_3\text{C}_2\text{T} \), \( \text{Ti}_3\text{C}_2\text{T} \), \( \text{V}_2\text{CT} \), and \( \text{Nb}_2\text{CT} \)) were experimentally investigated as electrode materials in LIBs. Among these compounds, in non-delaminated forms, \( \text{V}_2\text{CT} \) showed the highest capacity (280 mAh g\(^{-1}\) at a cycling rate of 1 C and 125 mAh g\(^{-1}\) at 10 C). Although Nb atoms are heavier than Ti, the gravimetric capacity of \( \text{Nb}_2\text{CT} \) is higher than that for \( \text{Ti}_3\text{C}_2\text{T} \) at the same cycling rates (180 mAh g\(^{-1}\) for \( \text{Nb}_2\text{CT} \) versus 110 mAh g\(^{-1}\) for \( \text{Ti}_3\text{C}_2\text{T} \) at 1C). An in situ XRD study on \( \text{Ti}_3\text{C}_2\text{T} \) showed that the mechanism governing lithiation and delithiation was Li intercalation and de-intercalation between the layers, respectively.\(^{[55,59]} \) For a given chemistry, \( \text{M}_2\text{X} \) electrodes will have higher gravimetric capacities than their \( \text{M}_3\text{X}_2 \) and \( \text{Nb}_2\text{CT} \) counterparts. For example, the gravimetric capacity of \( \text{Ti}_3\text{C}_2\text{T} \) was \( \approx 1.5 \) times higher than that of \( \text{Ti}_3\text{C}_2\text{T} \) for the simple reason that the former has the least number of atomic layers per MXene sheet.

More recently, we showed that each MXene has its own active voltage window. For example, more than two-thirds of the reversible lithiation capacity of \( \text{Nb}_2\text{CT} \) is below 1 V; for \( \text{V}_2\text{CT} \) more than two-thirds of the reversible delithiation capacity is above 1.5 V.\(^{[7]} \) Considering the rich chemistry of MXenes and solid solution compositions, it may in principle be possible to fine-tune and design the MXenes for specific battery applications. Thus, some MXenes could function as anodes and some could be used as cathodes for lithium ion and other batteries.

As noted above, \( \text{Ti}_3\text{C}_2\text{T} \) can be readily delaminated, resulting in a colloidal solution of single- and few-layer \( \text{Ti}_3\text{C}_2\text{T} \) flakes, by sonication of a suspension of DMSO-intercalated \( \text{Ti}_3\text{C}_2 \) in DI water. Filtration of this solution yields additive-free, flexible paper that detaches readily from the anodic aluminum oxide filter membranes. This paper was in turn used to fabricate electrodes that were tested as LIB electrodes.\(^{[26]} \) As shown in Figure 9, such an electrode yielded a reversible capacity of 410 mAh g\(^{-1}\) at 1 C (\( \approx 4 \) times higher than the capacity of the cast \( \text{Ti}_3\text{C}_2\text{T} \) film that has binder and carbon additives), and possessed excellent ability to handle extremely high cycling rates (110 mAh g\(^{-1}\) at 36 C after 700 cycles).\(^{[26]} \) Although the MXenes’ gravimetric capacities are not as high as \( \text{Si} \),\(^{[57]} \) they have the great advantage of combining high cycling rates with good capacities. The cycling rates reported are as good as, and probably better than, lithium titanium oxide (LTO) based anodes.\(^{[28]} \)

These comments notwithstanding, first cycle irreversibility is a challenging problem in all tested MXenes so far. The exact reasons for the irreversibilities are not clear but could be due to solid-electrolyte interphase (SEI) formation or irreversible reactions between Li and the MXene surface groups. This problem, in principle, can be solved by prelithiation of the MXene electrodes, similar to what was reported for other nanostructured materials.\(^{[39]} \)

All the work to date on MXene electrodes in LIBs was carried out on as-synthesized materials, with no tailoring of their surface chemistries. Thus, many opportunities for enhancing the performance and reducing first cycle irreversibility remain unexplored. For example, and as noted above, bare MXene surfaces are predicted to perform better than terminated ones in LIBs.\(^{[37]} \) Delaminating other MXenes may increase their Li uptake, similar to what was reported for \( \text{Ti}_3\text{C}_2 \).\(^{[26]} \) Thin and lightweight \( \text{M}_2\text{X} \) MXenes are of special interest for this purpose. Similar to other 2D materials, further optimization and enhancement can be achieved by engineering electrode architectures using different additives.\(^{[60–62]} \)

The capability of MXenes to handle high cycling rates renders them good candidates for use in asymmetric, non-aqueous energy storage devices (hybrid cells), that combine the high energy densities characteristic of LIBs and the high power densities of electrical double layer capacitors (EDLCs). Typically, in Li-ion capacitors activated carbon (AC) and a Li host material are used as the positive and negative electrodes,
respectively. When $\text{Ti}_3\text{CT}_x$ was used as the negative electrode, an energy density of 30 Wh kg$^{-1}$ at 930 W kg$^{-1}$ for 1000 cycles was obtained.\cite{53}

Spontaneous chemical intercalation of different cations between $\text{Ti}_3\text{CT}_x$ layers from aqueous salt solutions resulted in outstanding supercapacitors.\cite{45} Reversible capacities—stable for more than 10 000 cycles—of more than 330 F cm$^{-3}$ were achieved when $\text{Ti}_3\text{CT}_x$ paper was tested in a KOH electrolyte, using a current of 1 A g$^{-1}$.\cite{45} This capacitance is higher than the volumetric capacitance of the best all-carbon EDLCs.\cite{66}

$\text{Ti}_3\text{C}_2$ paper electrodes showed better performance in supercapacitors than their multilayer counterparts made from MXene powders in a conventional way (i.e., rolling films of active material with binder and conductive additive).\cite{45} The difference, however, was not as dramatic as observed when they were used as electrodes in LIBs. The better performance can in part be attributed to the better overall electronic conductivity of the $\text{Ti}_3\text{C}_2$-paper electrodes, because they are additive-free, while the powder electrodes contained a nonconductive polymer binder. Spontaneous intercalation of cations between MXenes’ layers makes each layer accessible for ion adsorption. Electrochemical intercalation of Na$^+$ and multivalent ions, such as Mg$^{2+}$ and Al$^{3+}$, suggests MXenes can be promising host materials in multivalent ion batteries beyond Li.

Very recently, Xie et al.\cite{56} used $\text{Ti}_3\text{C}_2\text{T}_x$ as a supporting material for platinum nano particles (Pt NPs) for fuel cell applications. They found that the Pt/$\text{Ti}_3\text{C}_2\text{T}_x$ combination was more durable and more electrochemically stable than the Pt/C catalysts that are conventionally used. For example, after 10 000 cycles, the Pt/$\text{Ti}_3\text{C}_2\text{T}_x$ catalyst lost 15.7% of its initial Pt electrochemical surface area; the Pt/C electrode lost 40.8%.

To conclude this section, we note that although no MXene dispersion in polymers has been reported so far, Zhang et al.\cite{57} used ultrathin nanolaminates of $\text{Ti}_3\text{Si}_{0.75}\text{Al}_{0.25}\text{C}_2$, as a conductive additive to poly(methyl methacrylate) (PMMA). The composites possessed excellent mechanical and thermal properties that were comparable to PMMA/graphene composites.\cite{67} As the in-plane elastic properties of MXenes (Table 2) were found to be even higher than their parent MAX phases,\cite{58} MXenes can potentially be used as additives to polymers to fabricate composites with outstanding mechanical properties and good electrical conductivities. As noted above, an important advantage of MXenes over the MAX phases is that the former have surface functional groups that should enhance the matrix-filler interface strengths and even allow for covalent bonding of the polymer to the MXenes layers, similar, for example, to nanodiamond–polymer composites.\cite{68} These considerations certainly suggest that the use of MXenes in polymer matrices should pay large dividends.

### 7. Summary and Outlook

In summary, a new family of 2D materials comprised of early transition metal carbides and carbonitrides has been produced by selectively etching the Al layers (A layers in MAX) with HF at room temperature. The replacement of the strong primary Al–M bonds in the $\text{M}_{\text{M}+1}\text{AX}_3$ phases with O, OH and F surface terminations allows for the conversion of a 3D—one albeit a layered one—solid to a 2D solid. This new family of 2D materials has been labeled “MXenes” to denote the loss of the A element from the MAX phases and to emphasize their 2D structure. To date, the following MXenes have been produced: $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{Ti}_2\text{C}_3$, $\text{Nb}_2\text{C}_3$, $\text{V}_3\text{C}_3$, ($\text{Ti}_{0.5}\text{Nb}_{2.5}\text{C}_3$), $\text{Ti}_3\text{CN}$, $\text{Tb}_3\text{C}_3$, and $\text{Nb}_3\text{C}_3$. Many more have been predicted theoretically.

XPS and EDS results indicate that MXenes are terminated with a mixture of O, OH, and/or F groups. The as-synthesized MXenes are simultaneously electronically conducting and hydrophilic, an uncommon combination. Sonication can be used to separate the 2D $\text{M}_{\text{M}+1}\text{X}_3$ layers from each other and produce single-layer and few-layered flakes. Sonication also results in nanoscrolls with inner radii less than 20 nm.

The yields are high and the process is simple and readily scalable. This comment notwithstanding, other synthesis techniques need to be explored. For example, it would be beneficial to identify etchants that are safer than HF. The use of non-aqueous etchants could in principle avoid O or OH termination of the MXene sheets. Furthermore, the etching of A elements other than Al needs to be explored to cover all possible transition metal carbides that form the MAX phases. For example, Al-containing Mo, Zr, and Hf-based MAX phases currently do not exist. If other A elements can be etched out, it would be possible to synthesize MXenes based on these metals.\cite{72}

As described above, some of the etching by-products can coexist with the MXene after etching the A element. The effect of these etching reaction by-products and surface contaminations on the performance and properties of various MXene layers need to be well investigated, understood and ultimately controlled.

The space between the MXene sheets is extremely versatile and amenable to a host of compounds and cations. For example, $\text{Ti}_3\text{C}_2\text{T}_x$ can be intercalated with various organic molecules as well as inorganic salts dissolved in water. In principle, ionic liquids and other intercalants can also be utilized. Sonication of DMSO intercalated $\text{Ti}_3\text{C}_2\text{T}_x$ in DI water resulted in the large-scale delamination into single- and few $\text{Ti}_3\text{C}_2\text{T}_x$ layers. Filtration of the latter resulted in thin, free-standing MXene paper that was flexible, hydrophilic, and conductive.

MXenes’ 2D morphology and their good electronic conductivities render them promising electrode materials for LIBs, hybrid cells, and supercapacitors. They offer excellent capability to handle high cycling rates in LIBs, and outstanding volumetric capacitance in supercapacitors.

The majority of current publications on MXenes are theoretical studies, mostly using DFT, as well as classical and ab initio molecular dynamics. However, many challenges remain for modeling as well, and the research in this area will likely continue at an increasing pace. First of all, we still need to fully understand the surface chemistry of the MXenes. Which functional groups are present on their surfaces after synthesis, and how the latter change over time when MXenes are stored or treated needs to be studied and understood. Upon drying of MXenes, a fraction of OH groups may be converted into O terminations by H$_2$O elimination. Most current models assume complete termination by F, OH, or O groups. However, the coverage may well be incomplete or nonuniform or both, i.e., different functional groups may coexist with bare areas on the surface of a single MXene particle. In addition, water may...
be present on the surface and between the layers, forming hydrogen bonds and affecting MXene interlayer interactions. How these factors affect the predicted structural, electronic, magnetic, and other properties of MXenes remains an open question.

Although DFT showed that fully terminated M$_{n+1}$X$_n$T$_x$ monolayers may exist in three different configurations with one of them being energetically favored, it is still not clear which (if any) of these configurations would be favored in stacked multilayer MXenes. The properties of multilayer MXenes comprised of M$_{n+1}$X$_n$T$_x$ monolayers stacked in different geometric configurations have never been probed by DFT. Despite its clear importance, this problem is likely to pose a significant challenge for DFT, which is inherently poor in describing weak interactions, such as the van der Waals and hydrogen bonds that are believed to hold the MXene monolayers in stacks. Recent developments in DFT for weakly interacting systems may prove useful in this situation. Many other properties of monolayer, few layers and multilayered MXenes need to be modeled. For example vibrational spectra, especially Raman, which can be easily compared with experiments, need to be calculated. Interpreting Raman spectra of MXenes is one of the challenges faced by experimentalists, and an area where modeling can provide considerable insights.

Besides monolayers and stacks, other MXene structures, such as MXene nanotubes and nanocables need to be further studied. We currently know very little about their geometry, electronic structure, and properties. Finally, the development of a reliable classical force field for MXenes is urgently needed. Many practical phenomena such as intercalation, ion exchange, interactions and dynamics of polymers in MXene composites can only be studied by classical techniques. Therefore, the development of reliable classical force fields for MXenes (similar to ClayFF or ReaxFF) will open new possibilities for studying these prohibitively large/complex systems/phenomena important for development of future applications.

Despite the fact that MAX thin films have been well studied as of yet no work has been published on the exfoliation of such thin films. Furthermore, some MAX phases, such as Ti$_3$GeC$_6$, have only been synthesized in thin film form. Producing MXenes from thin films is key for the fabrication and characterization of MXene-based electronic devices.

Experimentalists working with this emerging family of 2D materials should focus on addressing the following:

- Controlling and modifying MXenes’ surfaces.
- Establishing the exact structure of M$_{n+1}$X$_n$T$_x$ as a function of T and n.
- Detailing and understanding the structure and properties of MXenes intercalated with various compounds/ions.
- Determining the chemical and thermal stabilities of MXenes in different environments.
- Large-scale delamination of MXenes other than Ti$_3$C$_2$T$_x$.
- Finding alternative, robust, and safe routes of MAX phase exfoliation and MXene delamination.
- Synthesizing MXenes without surface functional groups.
- Direct gas phase synthesis of single-layer MXene films.
- Characterizing single-layer MXenes, including electronic, magnetic, optical, thermal, and mechanical properties.
- Exploring MXenes in various applications, such as composite reinforcement, catalysis, transparent electronic conductors, sensors, etc.
- Expanding the family through synthesis of new MXenes.

Success in addressing these points should lead to numerous applications. These comments notwithstanding, the discovery of MXenes is an exciting development that greatly expands the family of 2D materials.

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