Guidelines for Synthesis and Processing of Two-Dimensional Titanium Carbide (Ti$_3$C$_2$Tx MXene)

Mohamed Alhabeb, Kathleen Maleski, Babak Anasori, Pavel Lelyukh, Leah Clark, Saleesha Sin, and Yury Gogotsi*

A.J. Drexel Nanomaterials Institute and Department of Materials Science and Engineering, Drexel University, 3141 Chestnut Street, Philadelphia, Pennsylvania 19104, United States

Supporting Information

ABSTRACT: Two-dimensional (2D) transition metal carbides, carbonitrides, and nitrides (MXenes) were discovered in 2011. Since the original discovery, more than 20 different compositions have been synthesized by the selective etching of MAX phase and other precursors and many more theoretically predicted. They offer a variety of different properties, making the family promising candidates in a wide range of applications, such as energy storage, electromagnetic interference shielding, water purification, electrocatalysis, and medicine. These solution-processable materials have the potential to be highly scalable, deposited by spin, spray, or dip coating, painted or printed, or fabricated in a variety of ways. Due to this promise, the amount of research on MXenes has been increasing, and methods of synthesis and processing are expanding quickly. The fast evolution of the material can also be noticed in the wide range of synthesis and processing protocols that determine the yield of delamination, as well as the quality of the 2D flakes produced. Here we describe the experimental methods and best practices we use to synthesize the most studied MXene, titanium carbide (Ti$_3$C$_2$T$_x$), using different etchants and delamination methods. We also explain effects of synthesis parameters on the size and quality of Ti$_3$C$_2$T$_x$ and suggest the optimal processes for the desired application.

INTRODUCTION

Since the isolation of single layer graphene in 2004, 1 two-dimensional (2D) materials have gained tremendous attention because of their distinctive properties relative to their bulk form. The isolation of graphene has become a reference for all 2D materials and opened the possibility to discover even more. Today, there are dozens of new 2D materials, including hexagonal boron nitride, transition metal dichalcogenides, transition metal oxides, clays, etc. 2

In 2011, a new family of 2D materials, named MXenes, were discovered by Drexel University scientists. 3 The MXene family is comprised of transition metal carbides, carbonitrides, and nitrides with a general formula of M$_n$+1AX$_n$-$_x$, where M represents transition metals (such as Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, etc.) and X is carbon and/or nitrogen. 4,5 The name “MXene” was given to describe the similarities between this 2D material family and graphene but also to recognize the parent ternary carbide and nitrides, MAX phases, which MXenes are synthesized from. 3 MAX phases are layered ternary carbides and nitrides with a general formula M$_n$+1AX$_n$-$_x$, where A represents elements from the group 13 and 14 of the periodic table. 3,6

MXenes reported to date are synthesized by wet-chemical etching in hydrofluoric acid (HF) or HF-containing or HF-forming etchants, 7–9 which add surface functionalities such as −F, −OH, or −O−, represented by T$_x$ in this formula as M$_n$+1AX$_n$-$_x$. Etching is required because of strong chemical bonds between A and M elements in MAX phases that make mechanical exfoliation hardly possible. To date, more than 20 members of the MXene family have been synthesized, and dozens more are predicted, making it one of the fastest growing 2D material families. 3 Additionally, the MXene family comes in three atomic structures, ranging from M$_2$X to M$_3$X$_2$ and M$_4$X$_3$, yielding tunability and opportunity to discover and mold materials based on necessary demands. 10,11

In contrast to most other 2D materials, including graphene, MXenes possess hydrophilic surfaces 7 and high metallic conductivities (∼6000–8000 S/cm), 12,13 showing promising performance in energy storage devices, 14–17 water desalination, 18 catalysis, 19 electromagnetic interference shielding, 20 transparent, conducting thin films, 21,22 and many other applications. 7

Since their discovery, production of multilayered MXene flakes was possible through wet-chemical etching with HF, and different MXene compositions were synthesized in this form, such as Ti$_2$CT$_x$, Ti$_3$CNT$_x$, Nb$_2$CT$_x$, and V$_2$CT$_x$ (Figure 1). 3,23,24 However, it was not until 2013 when single-layer MXene flakes were isolated by intercalating large organic molecules and delaminating the sheets from each other, opening the door to exploration of the truly 2D nature of MXenes. 25 In 2014, Ti$_3$C$_2$T$_x$ MXene was produced using a HF-containing etchant such as ammonium bifluoride (NH$_4$HF$_2$) salt, 25 and later in the
same year, Ti₃C₂Tₓ “clay” was synthesized by taking advantage of making in situ HF through addition of lithium fluoride (LiF) salt to hydrochloric acid (HCl), significantly simplifying the synthesis method and improving MXene performance in energy storage applications (Figure 1). With the need for methods to increase the delamination yield, in 2015 additional organic intercalants were used, such as isopropylamine and tetra-butylammonium hydroxide (TBAOH). Moreover, in 2015, two new MXene subfamilies, ordered double-transition metal MXenes, M′′M‴Cₓ where M′ and M″ are two different early transition metals, were discovered, further expanding the 2D family. Each of these evolutionary discoveries has added tunability and diversity to MXene family.

In 2016, larger single Ti₃C₂Tₓ flakes were isolated by using the minimally intensive layer delamination (MILD) method, where manual shaking (no sonication) was used and resulted in larger and less defective single flakes of MXene. The MILD method expanded the opportunities for research on electronic, optical, and size-dependent material properties as well as further enhanced the scalability and production of Ti₃C₂Tₓ MXene. A timeline progress of MXenes is shown in Figure 1.

The exact synthesis conditions used to produce MXenes influence the resulting properties and thus are directly related to the performance of MXenes in their applications. In general, the synthesis of any type of MXene can take from a few hours to a few days, and it depends on at least a few factors: concentration of HF and temperature of etching. For example, in the case of Ti₃C₂Tₓ, we used as low as 3 wt % HF containing etchant and showed the higher the HF content, the higher the concentration of defects in Ti₃C₂Tₓ flakes, which influences the quality, environmental stability, and properties of as-produced MXene. Our group showed that 2 h was enough time to etch aluminum (Al) out of Ti₃AlC₂ with concentrated HF (~50 wt %) at room temperature. Based on the type of MXene and the synthesis conditions, the intercalants may vary as well as the delamination yield. We recently summarized etching and delamination conditions reported in literature for most MXenes known to date, and we encourage the readers to view the referenced review on etching, delamination, and processing protocols for MXenes besides Ti₃C₂Tₓ.

Here, we discuss the best practices used in our lab and provide step-by-step guidance for room temperature synthesis of titanium carbide (Ti₃C₂Tₓ), the most studied and widely used MXene. We categorize currently used etchants for selective removal of Al from Ti₃AlC₂ structure into two types: synthesis protocols using HF and protocols using in situ formed HF. Moreover, we provide a guideline on how to delaminate as-synthesized materials into colloidal solutions even without sonication. We also discuss storage, processing, and deposition techniques to make different types of conductive Ti₃C₂Tₓ MXene films.

### DISCUSSION OF METHODS

There are many different protocols for synthesizing MXene materials reported in literature, and one synthesis route may be better for one application but not suitable for another application. When synthesizing any kind of MXene, one must be aware of the end goal, the properties desired, and the materials warranted, to develop the best material for the job.

Synthesis of MXene begins with etching the A-element atomic layers (for example, aluminum) in a MAX phase (for example, Ti₃AlC₂) from the Mₓ/></ref> elements adjacent to the A-element layers. The etching process results in terminated multilayered MXene powders (for example, Ti₃C₂Tₓ) with the 2D layers held together by hydrogen and van der Waals bonds.
After the etching is finished (that is, the complete removal of the A-element layers), washing is required to remove residual acid and reaction products (salts) and achieve a safe pH (~6). Washing is normally done by repeated centrifugation to separate multilayered MXene from acidic solution and decantation of the acidic supernatant (Figure S1a, Supporting Information). After the pH is increased to ~6, the multilayered flakes can be collected, e.g., via vacuum-assisted filtration (Figure S1b, Supporting Information) and dried in vacuum (Figure S1c, Supporting Information). For the rest of this study, we will focus on synthesis and processing of one type of MXene, Ti$_3$C$_2$T$_x$.

**General Synthesis and Processing of Ti$_3$C$_2$T$_x$ MXene.** Figure 2 describes a general map for the synthesis of Ti$_3$C$_2$T$_x$ at room temperature with HF or in situ HF and delamination of the impurity phases. A common impurity in Ti$_3$AlC$_2$ is Ti$_2$AlC. One method to distinguish Ti$_3$AlC$_2$ from Ti$_2$AlC is its peak (002) because Ti$_3$AlC$_2$ has a (002) peak at ~13°. Other peaks of Ti$_3$AlC$_2$ are distinguishable from one another, and details are presented in Figure S2a, Supporting Information. The coexistence of Ti$_3$AlC MX phase in Ti$_3$AlC$_2$ can lead to a mixed phase MXene of Ti$_3$C$_2$T$_x$ with Ti$_2$CT$_x$, which often leads to changes in properties (conductivity, optical absorbance spectra, etc.) of the resulting MXene and most importantly can influence the interpretation of the reported results. Also, diluted colloidal solutions of Ti$_3$C$_2$T$_x$ optically exhibit green color while Ti$_3$CT$_x$ solutions have a purple/magenta color. The UV–vis spectra of Ti$_3$CT$_x$, Ti$_3$C$_2$T$_x$, and mixed phase Ti$_3$CT$_x$/Ti$_3$C$_2$T$_x$ are distinguishable from one another, and details are presented in Figure S2b–d, Supporting Information. The effect of sintering conditions of MAX phase on the resulting MXene is yet to be studied, and it is out of the scope of this paper. We only used one batch of Ti$_3$AlC$_2$ in this study, which was synthesized from TiC:TiAl with the 2:1:1 stoichiometric ratio for synthesis details, see Supporting Information).

**Choice of Etchants and Intercalants.** Hydrofluoric acid (HF, 49.5 wt%) was purchased from Acros Organics. ammonium hydrogen fluoride (NH$_4$HF$_2$, 95% grade) powder, tetramethylammonium hydroxide (TMAOH, 25 wt % in water), and Al$_2$O$_3$. 

**Supporting Information.** However, based on the previously reported studies, Ti$_3$AlC$_2$ can be made from different starting mixtures, for example, Ti, Al, and C; Ti, Al, and C; or even TiO$_2$, Al, and C, under proper conditions. In the earlier studies of MAX phases, pressure was used (for example, hot pressing or hot isostatic pressing) to obtain fully dense MAX phase samples. When Ti$_3$AlC$_2$ powder is needed, no pressure is required, since a less dense block of MAX phase is easier to mill into powder. In general, Ti$_3$C$_2$T$_x$ MXene can be made from Ti$_3$AlC$_2$ regardless of the MAX phase sintering route. However, the sintering conditions of each MAX phase can result in different impurities in Ti$_3$AlC$_2$, such as TiC, Ti$_3$AlC, and Al$_2$O$_3$. 

**Figure 2.** General map for Ti$_3$C$_2$T$_x$ synthesis from Ti$_3$AlC$_2$ discussed in this paper. For the etching, there are two routes, HF and in situ HF. In the HF route, three different concentrations with different durations were used, all sufficient to synthesize Ti$_3$C$_2$T$_x$. In situ HF is the alternative way compared to the direct use of hazardous HF in which the resulting Ti$_3$C$_2$T$_x$ multilayered powder behaves like clay in comparison to powders produced by NH$_4$HF$_2$. Delamination of Ti$_3$C$_2$T$_x$ powder depends on the chosen synthesis routes. In the case of the HF route or a salt (NH$_4$HF$_2$), delamination can be achieved by introduction of large organic molecules such as dimethyl sulfoxide (DMSO) or tetramethylammonium hydroxide (TMAOH) followed by sonication, if required. In the case of lithium fluoride/hydrochloric acid (LiF/HCl), the resulting Li$^+$ intercalated Ti$_3$C$_2$T$_x$ clay can be delaminated by sonication (clay) or without sonication (MILD) depending on the concentration of LiF and HCl used to prepare the etchant.
and tetrabutylammonium hydroxide (TBAOH, 40 wt % in water) were purchased from Sigma-Aldrich. Lithium fluoride (LiF, 98.5% grade) powder and hydrochloric acid (HCl, 37 wt %) were purchased from Alfa Aesar, and all the above chemicals were used as received. Deionized water (DI H2O) used in this study was purified using Elix Essential 3 UV, Millipore.

**Choice of the Synthesis Method.** For Ti3C2Tx, the choice of a synthesis method directly influences the resulting properties in terms of surface terminations,13 size,29 and quality of the flakes (for example, number and type of defects).13

**HF Etching Protocol.** When handling hazardous HF, independent of the concentration, it is extremely important to be aware of the risk assessment and required safety protocols (see safety section, Supporting Information). Most synthesis protocols reported in literature use 10 or 50 wt % HF,3,7,25 although a lower concentration of HF, as discussed later, is sufficient to achieve complete removing Al can be achieved with as low as 5 wt % and that an etching time of 5 h is enough in the case of using a concentration ≥30 wt % HF (Figure 2). For all three HF concentrations, the synthesis of Ti3C2Tx can be done as follows:

1. A total of 0.5 g of Ti3AlC2 powder was added gradually (in the course of 5 min) to 10 mL of etchant while stirring with the help of a Teflon magnetic bar (Movie S1, Supporting Information). The gradual addition of Ti3AlC2 powder is necessary to minimize excessive bubbling formed due to the exothermic nature of this reaction (For detailed instruction see Movie S1, Supporting Information).

2. The reaction was then allowed to proceed at room temperature (~23 °C) for 5, 18, and 24 h for 30, 10, and 5 wt % HF, respectively. These etching times for different HF concentrations are sufficient to achieve complete etching, as discussed below.

3. Each powder was washed separately five times (that is equivalent to the total volume of 1000 mL of deionized H2O) via centrifugation (5 min per cycle at 3500 rpm).

   a. After each centrifuge cycle, Ti3C2Tx powder settled at the bottom of the centrifuge tube as sediment separated from water-like supernatant.

   b. The supernatant after the first washing cycle exhibited acidic pH (Figure S1a, Supporting Information) and was decanted into waste.

   c. The sedimented Ti3C2Tx was redispersed with an additional 150 mL of deionized H2O followed by another centrifugation cycle. The washing cycles were repeated until the pH of the supernatant became ~6. A total of five centrifugation cycles were enough for washing Ti3C2Tx in the case of washing 0.5 g of powder and using a 175-mL graduated conical tube (see Figure S1a, Supporting Information).

4. The Ti3C2Tx sediments were rewash with 1000 mL of deionized H2O via vacuum-assisted filtration using a polyvinyl difluoride (PVDF) filter membrane with 0.22 μm pore size (Durapore, Millipore) before collection of the remaining materials.

The MXene powders (Figure S3, Supporting Information) were dried in vacuum at 80 °C for 24 h. The resulting powders were labeled as 30F-Ti3C2Tx, 10F-Ti3C2Tx, and 5F-Ti3C2Tx, for 30, 10, and 5 wt % HF, respectively. All three MXene powders were stored in vacuum before any further processing or analysis.

As shown in Figure S3, the resulting Ti3C2Tx MXene powders exhibited distinctive color differences (dark gray to black) from the graphitic-gray color of Ti3AlC2 powder. The 30F-Ti3C2Tx powder exhibited similar color to Ti3C2Tx previously synthesized with 50 wt % HF;3 however, it looked darker than both 10F-Ti3C2Tx and SF-Ti3C2Tx which exhibited a similar color (Figure S3, Supporting Information).

We compare the scanning electron microscopy (SEM) images of all the powders in this study in Figure 3. Ti3AlC2 powders show compact, layered morphology (Figures 4a and S4 in Supporting Information) as expected for a bulk layered ternary carbide.5 However, the multilayered Ti3C2Tx powders look different depending on the etchant concentration (compare Figure 3b–d). 30F-Ti3C2Tx powders exhibit an accordion-like morphology (Figures 3b and S5 in Supporting Information) even when etching in 30 wt % HF was used for low etching times (5 h).

Morphology such as this was previously observed as a feature of Ti3C2Tx MXene synthesized with 50 wt % HF.3,7 For lower HF concentrations such as 10 wt % HF (Figures 3c and S6 in Supporting Information), the accordion-like structure was not as prevalent as in the case of using 30 wt % HF. Additionally, the accordion-like morphology was not observed in Ti3C2Tx powder synthesized with 5 wt % HF, as the resulting Ti3C2Tx is barely discernible from MAX powder (Figures 3d and S7 in Supporting Information). This expanded accordion-like structure can possibly be ascribed to the larger amount of escaped gases (H2 in this case) because of exothermic nature of HF reaction with Al.3

Interestingly, low concentrations of HF (5 wt %) for 24 h were still sufficient for selectively etching aluminum, similar to the higher concentrations (10 wt % HF for 18 h and 30 wt % HF for 18 h), as confirmed by energy dispersive X-ray (EDX) analysis (Table S1). This was further confirmed by a shift of the (002) peak of Ti3AlC2 at 9.5° to 9.0° for the Ti3C2Tx in XRD patterns (Figure 4a) and no residual peaks of Ti3AlC2 after etching for SF-, 10F-, and 30F-Ti3C2Tx. The lower peak shift of the basal planes (such as (002) peak) is due to the removal of Al in the Ti3AlC2 and introduction of surface terminations.
Methods/Protocols

drying of the HF etched Ti3C2T, such as NH4HF2. In situ HF formation from hydrogen fluoride salts, such as NH4HF2, result in Ti3C2T, selective etching. Low concentration of HF (≤10 wt % HF) is preferred over higher concentrations (≥5 wt % HF) for MXene synthesis.

In situ HF Formation. As reported in most MXene literature, concentrated HF has been often the etchant of choice to selectively remove Al from Ti3AlC2.7,38 However, one way to avoid using unnecessarily high HF concentrations is to use dilute etchant with 5 wt % HF, as shown in the previous section. The alternative method can be through in situ HF formation from hydrogen fluoride or fluoride salts such as NH4HF221,39 or LiF15,15 to prepare etchants containing 3–5 wt % HF.

Bifluoride-Based Etchants. HF salts, such as NH4HF2, have been used at room temperature either for a few hours to etch thin coatings of Ti3AlC221 or for a longer time of 5 days to etch Ti3AlC2 powder at room temperature (60 °C).39 Here we describe this approach and delamination protocols (discussed later in detail) of MXene powders synthesized using NH4HF2. The synthesis of NH4HF2 etched Ti3C2T, can be done as follows:

1. A total of 0.5 g of Ti3AlC2 powder was added to 10 mL of 2 M NH4HF2 under continuous stirring, and the reaction was left to run for 24 h at room temperature (∼23 °C).

2. Similar to earlier described washing processes, the mixture product was washed with deionized H2O via centrifugation at 3500 rpm (5 times per 5 min per cycle). Further washing was performed using vacuum-assisted filtration by filtering the Ti3C2T, product over a PVDF filter membrane with 0.22 μm pore size and rinsing with 1000 mL of deionized water through the filtration setup.

3. The powder was dried at 120 °C for 24 h in a vacuum oven. MXene produced by this route is referred to as NH4-Ti3C2T,.

The morphology of multilayered NH4-Ti3C2T, powders shown in Figure 3e (also see Figure S8, Supporting Information) resembles Ti3C2T, multilayered powders produced with lower concentrations of HF (Figure 3c,d). Here, the selective removal of Al can be confirmed by complete disappearance of Ti3AlC2 peaks (for example, no (002) at 9.5°) in the XRD pattern (Figure 4a). This was also supported by EDX results showing the removal of Al (Table S1, Supporting Information). NH4-Ti3C2T, showed basal plane peaks shift to a lower 2θ-angle—from ∼9.5° in the Ti3AlC2 precursors to 8.5° and 7.15°, which correspond to d-spacings of 10.35 and 12.37 Å, respectively. The larger d-spacing after drying can be explained by the presence of confined/intercalated (NH4+ ions and water molecules in between the MXene layers.21,40 NH4-Ti3C2T,x, unlike the HF-etched Ti3C2T, needs a longer duration or higher temperature vacuum drying to completely remove the intercalated water molecules from the powder. Similar behavior was observed for other in situ HF etched Ti3C2T, samples, as discussed in the following section.

Fluoride-Based Salt Etchants. When performing synthesis with fluoride-based salts, it is crucial to understand that the concentration of LiF and HCl used to prepare in situ HF will change the quality, size, and ability to process Ti3C2T, flakes.
improved when the LiF:Ti3AlC2 molar ratio was increased from 5 to ≥7.5 (that is equivalent to change of the LiF:Ti3AlC2 mass ratio from 0.67 to ≥1, respectively) as well as the concentration of HCl from 6 to 9 M. Although a LiF/HCl mix was used in both (5 M LiF/6 M HCl) and (7.5 M LiF/9 M HCl) methods, the concentration optimization of these two ingredients (LiF and HCl) in the latter method enhanced the quality (fewer defects) as well as the size of produced Ti3C2T flakes which enabled studying and quantification of defects in single-layer flakes of Ti3C2T. Freestanding films produced from larger size Ti3C2T flakes showed high electrical conductivity (6000–8000 S/cm—higher than other solution-processed inorganic materials) and enabled use of MXene in many important applications.

As previously reported, multilayered Ti3C2Tx produced by the clay method (5 M LiF/6 M HCl) (Figure 2) were isolated into single flakes via sonication, which often created small and defective MXene flakes (Figure 1). However, hand-shaking was enough to isolate Ti3C2Tx multilayered powder, produced by (7.5 M LiF/9 M HCl), into single and obviously large flakes. To distinguish this optimized method from the clay LiF/HCl method, we called this method minimally intensive layer delamination (MILD) to stress the fact that a minimal and less milder route was used to produce single and larger flakes with fewer defects (Figure 1).

MILD method has been the choice for studies/applications where larger flake size is favorable. Here we report on an optimized MILD synthesis method using (12 M LiF/9 M HCl) instead of (7.5 M LiF/9 M HCl) at room temperature as follows:

1. The etchant was prepared by adding 0.8 g of LiF to 10 mL of 9 M HCl and left under continuous stirring for 5 min.
2. A total of 0.5 g of Ti3AlC2 powder was gradually added (over the course of 5 min) to the above etchant, and the reaction was allowed to run for 24 h at room temperature.
3. The acidic mixture was washed with deionized H2O via centrifugation (5 min per cycle at 3500 rpm) for multiple cycles. After each cycle, the acidic supernatant was decanted as waste followed by the addition of fresh deionized H2O before another centrifuging cycle. These washing cycles were repeated until pH 4–5 was achieved. This range of pH was observed after two cycles (when a 175-mL centrifuge tube was used) or seven cycles (when a 50-mL centrifuge tube was used).
4. When pH ≥ 5, there are two important observations: first, a dark-green supernatant is observed, which is stable even when centrifugation time is increased from 5 min to 1 h (see Figure S9, Supporting Information) indicating delamination has already started during washing with no further processing steps. Second, the Ti3C2Tx sediment settled at the bottom of the centrifuge tube, after collecting the supernatant, is found to be swollen to almost twice the volume compared to the previous washing cycles, when no delamination occurred. The swollen sediment exhibits a distinctive black layer of Ti3C2Tx slurry above a grayish layer of nonetched Ti3AlC2/Ti3C2Tx mixture (Figure 4b).
5. The black Ti3C2Tx slurry was carefully collected, separately from Ti3AlC2/Ti3C2Tx, with a spatula and vacuum-filtered producing a thick black cake (Figure 4b, top right inset). A thick film was formed after drying in vacuum at 120 °C for 24 h. All these steps are shown in Figure S10a-d, Supporting Information. It is worth noting here that the film made from the Ti3C2Tx sediment (Figure S10d) was flexible.

The swelling of Ti3C2Tx sediment after washing was only observed in our previous report as well as shown in the optimized MILD described above. This swelling behavior of Ti3C2Tx during washing cycles after synthesis was not observed in the earlier “clay” synthesis using LiF/HCl (5 M of LiF:Ti3AlC2) with both 6 M HCl and 12 M HCl. This is another important difference between the two methods, and it confirms that there is a minimum concentration of Li+ required, besides a certain concentration of HCl, when performing etching at room temperature for ≤24 h. Cross sectional SEM images of the film (Figure S9d) made by vacuum-assisted filtration of the black layer of Ti3C2Tx slurry (Figure 4b, top inset) are shown in Figure S11, Supporting Information. The XRD pattern of this black slurry sediment MILD-Ti3C2Tx thick film after vacuum drying at 120 °C exhibited only the (000) peaks of Ti3C2Tx MXene with the (002) peak centered at 8.6° (Figure 4c, top pattern). The SEM image of the thick film made by filtering Ti3C2Tx slurry sediment Figure S9d is very similar to that of the rolled/sheared film of the Ti3C2Tx clay, and the XRD pattern is very similar to that of the films made from delaminated single- to few-layer Ti3C2Tx reported before.

In other words, the as-separated/collected Ti3C2Tx slurry sediment does not require any type of mechanical vibration or shearing and only addition of deionized H2O to the Ti3C2Tx slurry, followed by gentle shaking, is needed to make the delaminated MILD Ti3C2Tx film possibly due to presence of solvated Li ions between the MXene layers. The XRD pattern of the dried gray material from the bottom of the tube (Figure 4b, bottom inset) showed a mixture of nonetched Ti3C2Al2 and Ti3C2Tx (Figure 4c, bottom pattern). SEM image of this layer shows that it contains Ti3C2Tx particles (Figure 3f), similar to that of Ti3C2Tx produced by etching in low-concentrations of HF (Figure 3d). Thus, we recommend separation of the black Ti3C2Tx slurry sediment from the gray sediment containing a mixture of nonetched and etched particles, as explained in step 4 of this section (Figure 4b).

**Choice of Intercalation Method.** Using intercalating compounds to expand the interlayer spacing of Ti3C2Tx flakes has proven to be a key step for weakening the interactions between 2D layers and delaminating MXene into separate 2D sheets. The intercalation and delamination process typically requires a suitable solvent for the material and intercalant, a mixing step where the intercalant is introduced between 2D sheets, occasionally a sonication step depending on desired flake size and concentration, and a centrifugation step to isolate the delaminated material from the material which is multilayered (nondelaminated). The final colloidal solution will contain dispersed 2D sheets of electrostatically stabilized MXene, which are stable against aggregation, or clumping, and are processable and functional. Moreover, the sonication step is highly dependent on the etching method and the desired application, as well as the required concentration. Sonication for longer times and higher powers will exhibit smaller flakes with more defects and may yield concentrations different than those which are not sonicated. The concentration of MXene sheets in solution also depends on different parameters such as the synthesis methods and type of intercalants used to weaken the
interlayer interaction between MXene sheets. In this section, we report on the advantages and disadvantages in processing of \( \text{Ti}_3\text{C}_2\text{T}_x \) MXenes using different intercalants that cause delamination with or without sonication.

**Dimethyl Sulfoxide (DMSO).** Large, organic molecules, such as dimethyl sulfoxide (DMSO), were some of the first intercalants used for expanding the interlayer spacing of \( \text{Ti}_3\text{C}_2\text{T}_x \) MXenes synthesized with HF.\(^\text{25}\) Additionally, DMSO or other organic solvents can be used to disperse \( \text{Ti}_3\text{C}_2\text{T}_x \) sheets in solution, and without sonication, the multilayered sheets will fall to the bottom of the vial as sediment (first vial from the left in Figure 5a). Flake sizes produced by these methods are usually on the order of a few hundred nanometers.

**Tetraalkylammonium Hydroxides.** Tetraalkylammonium compounds, such as tetrabutylammonium hydroxide (TBAOH), have been used to exfoliate 2D layered oxides.\(^\text{46}\) This delamination technique is based on ion exchange between protons (H\(^+\)) and the bulky tetraalkylammonium ions (TMA\(^+\) or TBA\(^+\)) leading to swelling and delamination with manual shaking, when used on different materials, such as layered oxides.\(^\text{46}\) TBAOH has also been used to exfoliate MXenes, such as \( \text{Ti}_3\text{C}_2\text{N}, \text{Mo}_2\text{C}, \text{V}_2\text{C} \) and \( \text{Nb}_2\text{C} \). However, TBAOH could not delaminate \( \text{Ti}_3\text{C}_2\text{N} \) even with sonication.\(^\text{27}\) In another study, \( \text{Ti}_3\text{C}_2\text{T}_x \) was claimed to be synthesized and delaminated using TMAOH after pre-treatment of \( \text{Ti}_3\text{AlC}_2 \) surface using 20–30 wt % HF for a short time.\(^\text{47}\) However, we have not been able to reproduce the results by only using TMAOH as etchant and we were only able to delaminate \( \text{Ti}_3\text{C}_2\text{T}_x \) into single- and few-layers when HF was used as an etchant and TMAOH was used as an intercalant, regardless of HF concentration.

Here, we used TMAOH to delaminate all the HF-synthesized and \( \text{NH}_4\text{HF}_2 \)-synthesized \( \text{Ti}_3\text{C}_2\text{T}_x \) samples in this study. Delamination of 100 mg of each material resulted in darker and more concentrated colloidal solutions for HF-etched \( \text{Ti}_3\text{C}_2\text{T}_x \) in comparison to \( \text{NH}_4\text{HF}_2 \)-synthesized \( \text{Ti}_3\text{C}_2\text{T}_x \). The detailed process of delaminating multilayered \( \text{Ti}_3\text{C}_2\text{T}_x \) powders with the help of TMAOH can be described as follows:

1. A total of 100 mg of each MXene powder (SF-\( \text{Ti}_3\text{C}_2\text{T}_x \), 10F-\( \text{Ti}_3\text{C}_2\text{T}_x \), 30F-\( \text{Ti}_3\text{C}_2\text{T}_x \) or \( \text{NH}_4\text{Ti}_3\text{C}_2\text{T}_x \)) was mixed separately with 10 mL of deionized \( \text{H}_2\text{O} \) containing 100 mg of TMAOH in a 20-mL glass vial, and the mixture was stirred for 12 h at room temperature.

2. The basic mixture (~pH 10) was washed twice via centrifugation (3500 rpm, 5 min per cycle) using 50 mL tubes to bring the pH to ~7.

3. The stable MXene colloidal solutions were collected after 1 h of centrifugation at 3500 rpm, and the sediments were collected via vacuum assisted filtration and dried in vacuum at 120 °C.

Using this method, all three HF-etched samples can be delaminated, and stable colloidal solutions are formed. The TMA\(^+\) delaminated colloidal solution of SF-\( \text{Ti}_3\text{C}_2\text{T}_x \) MXene (labeled as TMA-SF-\( \text{Ti}_3\text{C}_2\text{T}_x \)) is black and stable (Figure 5a) with concentration of ~0.5 mg/mL. When the solution was analyzed via dynamic light scattering (DLS), the size of the flakes collected after an hour of centrifugation at 3500 rpm was in the range of 0.2 to 0.7 μm (Figure 5b), which is similar to the flake size reported for the sonicated LiF/HCl clay method.\(^\text{41}\) This shows that delamination of MXene with stirring in TMAOH can break the flakes into smaller sizes. The breakage of flakes due to intercalation of TMAOH was previously observed in layered 2D oxides even with stirring, and larger flakes were only obtained with gentle shaking.\(^\text{46}\)

The intercalation of TMA\(^+\) into SF-\( \text{Ti}_3\text{C}_2\text{T}_x \) was confirmed by the (002) peak shift from 9.0° to 6.0° 2θ-angle (Figure 5c) for SF-\( \text{Ti}_3\text{C}_2\text{T}_x \) which corresponds to a d-spacing shift of 9.7 Å to 14.7 Å. This shows that TMA\(^+\) intercalated the \( \text{Ti}_3\text{C}_2\text{T}_x \) flakes and stayed in between the layers even after 120 °C drying in vacuum. A higher temperature is needed to remove the intercalated molecules, as the decomposition temperature of TMAOH exceeds 200 °C.\(^\text{48,49}\)

Similarly, a stable but less concentrated colloidal solution of \( \text{Ti}_3\text{C}_2\text{T}_x \) MXene can be made by intercalation of TMAOH into \( \text{NH}_4\text{Ti}_3\text{C}_2\text{T}_x \) powder followed by sonication. The intercalated \( \text{NH}_4\text{Ti}_3\text{C}_2\text{T}_x \) powder (labeled as TMA-NH4-\( \text{Ti}_3\text{C}_2\text{T}_x \)) showed similar (001) peak positions as the TMA-SF-\( \text{Ti}_3\text{C}_2\text{T}_x \).
The (002) peak is at 5.9°, which is slightly shifted further to the left and corresponds to 14.86 Å interlayer spacing (Figure 5c).

This successful delamination of Ti$_3$C$_2$T$_x$ due to intercalation of TMA$^+$, regardless of HF content, suggests that intercalation of larger ions like TBA$^+$ is possible with more prolonged stirring time. To test our hypothesis, we stirred 0.2 g of 30F-Ti$_3$C$_2$T$_x$ in 20 mL of deionized H$_2$O containing 0.2 g of TBAOH for 2.5 days. This long time of stirring resulted in a stable and concentrated colloidal solution after sonication (Figure S12, Supporting Information), collected after 1 h of centrifugation at 3500 rpm.

Lithium Ions. When etchants containing lithium are used, such as LiF/HCl, in both clay and MILD methods, delamination is driven by the intercalation of solvated Li$^+$ ions. However, sonication of the intercalated Ti$_3$C$_2$T$_x$ was required in the case of the clay method and was optional in the case of the MILD method (Figure 2). In the following, we describe the effect of intercalant (Li$^+$) used in the MILD method for delamination of Ti$_3$C$_2$T$_x$ flakes (MILD-Ti$_3$C$_2$T$_x$). Because no sonication is needed, these flakes are larger with fewer defects. However, to prepare high-quality, large flakes in high concentrations the following notes should be considered:

1. The mass ratio of LiF to Ti$_3$AlC$_2$ should be ≥1 (corresponding to molar ratio of ≥7.5) as the Li$^+$ content and the H$^+$ provided by HCl plays a major role in the differences between the clay and MILD methods described in Figure 2.

2. In the case of in situ HF formation from LiF and HCl, the LiF must be the limiting reagent (no excess of LiF can be present) when added to HCl, not vice versa. This reaction produces lithium chloride (LiCl), and copious washing with deionized H$_2$O is required to completely wash the LiCl salt away.

3. The excess HCl remaining in the etchant results in a higher concentration of protons (H$^+$) and enables ion exchange with Li$^+$, resulting in swollen clay-like Ti$_3$C$_2$T$_x$ (Figure 4b) which can be delaminated by manual shaking. This is confirmed by higher concentration of the delaminated solution of MXene when 9 M HCl was used instead of 6 M HCl.

Considering all these parameters, here is the best method, to our knowledge, to delaminate MILD-Ti$_3$C$_2$T$_x$ and obtain a stable colloidal solution:

1. As explained in the etching section, after the third centrifuge wash for 1 h using a 175-mL graduated conical tube (Figure S9), a stable dark-green supernatant is produced. This supernatant can be collected as a stable colloidal solution with MXene concentration of ~1 mg/mL, without any further processing.

2. As mentioned earlier, because this method results in swollen black Ti$_3$C$_2$T$_x$ slurry with some nonetched Ti$_3$AlC$_2$ (Figure 4b), separation of Ti$_3$C$_2$T$_x$ from nonetched Ti$_3$AlC$_2$ must be performed before delamination. The separation process was either done as mentioned above in step 5 of the MILD method or by the addition of 50 mL of deionized H$_2$O to the whole sediment (Ti$_3$C$_2$T$_x$ slurry and the nonetched Ti$_3$AlC$_2$) followed by manual shaking until all the sediment was redispersed. Then, we separate the nonetched Ti$_3$AlC$_2$ (gray sediment in Figure 4b) via centrifugation at 3500 rpm for 2 min followed by collection of the dark concentrated supernatant of Ti$_3$C$_2$T$_x$ flakes. Centrifuging the collected supernatant for 1 h at 3500 rpm resulted in a black clay sediment (Figure S10a, Supporting Information) and stable dark supernatant (Figure 5b) mainly consisting of single-layer flakes of Ti$_3$C$_2$T$_x$. The average concentration of this colloidal solution is about 1–2 mg/mL, which is higher than that of TMA delaminated solutions (<0.5 mg/mL).

It is noteworthy that the colloidal solutions of MILD-Ti$_3$C$_2$T$_x$ often contain larger flakes (>2 μm) as shown in Figure 5b. We also drop casted diluted delaminated solutions of both MILD-Ti$_3$C$_2$T$_x$ and TMA-5F-Ti$_3$C$_2$T$_x$ on a porous alumina membrane and compared the flake size distributions in SEM. The flakes of MILD-Ti$_3$C$_2$T$_x$ have larger sizes (Figure 6a,b) in comparison to MXene flakes in colloidal solution prepared via TMAOH intercalation (Figure 6c,d). Additionally, the MILD-Ti$_3$C$_2$T$_x$ flakes have distinctive and straight edges, mimicking the original shape of the Ti$_3$AlC$_2$ crystalline grains. In contrast, in the case of TMAOH delamination, flakes are broken into small fragments, and their edges appear to contain more defects, showing that stirring or intense shaking when using organic base intercalants, such as TMAOH, leads to fractured flakes. This strong or excessive shaking after intercalation of TMAOH or TBAOH, even for a short time, has been shown to cause breakage of flakes in 2D layered oxides.\textsuperscript{46,50} Thus, it is advised to perform gentle shaking if larger flakes are desired when using TMAOH or TBAOH, similar to the protocol previously adapted for delamination of 2D layered oxides.\textsuperscript{46,50}

As explained, synthesis of MXene is a top-down method and therefore the flake size produced in the MILD method is directly related to the grain size and shape of the starting MAX powder. Thus, large crystals of MAX phases are needed to achieve larger MXene flakes.

It is important to note that the synthesis protocols described above are applicable not just to small laboratory samples characterized in this study but also to large scale manufacturing. We can produce up to 100 g of MXene per batch using a reactor designed for us by the Materials Research Center (Kiev, Ukraine). Control of the synthesis conditions becomes even more important when large amounts of MXenes are manufactured.
Processing, Deposition, and Storage. MXenes can be processed, deposited, and stored in a variety of ways. Once the material has been processed by delamination, size selection, or sonication, it can be deposited as freestanding film or thin film, printed, or sprayed on diverse substrates depending on the application. However, MXene flakes have been shown to degrade in the presence of a water containing dissolved oxygen, especially at elevated temperatures and under sunlight, making storage in aqueous solutions challenging.51,52

So far we have presented different routes to etch and delaminate Ti₃C₂Tx as well as prepare stable high-concentration colloidal solutions with controlled flake sizes. In the following, we are going to discuss the current practices to process, deposit, and store MXenes, based on our experience and the available published information.

Sonication and Size Selection. The size of the flakes can be controlled by performing cascading centrifugation to isolate and fractionate flakes based on lateral size or by decreasing the flakes by bath or probe/tip sonication, and some of these processing techniques have been used in protocols for other 2D materials.8 Figure S13 shows flake sizes of colloidal solution of MILD-Ti₃C₂Tₓ can be separated by size via centrifugation for 2 min at 2500, 5000, and 10000 rpm, and the collected colloidal solution contained flake sizes as large as 2 μm after 2500 rpm, ~1 μm after 5000 rpm and as small as ~200 nm after 10000 rpm.

When performing sonication, it is critical to monitor the power output of the sonicator as well as the time spent sonicating. Each of these parameters will change the resulting concentration, the quality of flakes, and their lateral size distribution. For example, it has been shown that bath sonication of a MILD-Ti₃C₂Tₓ can change the flake size from ~4 μm to less than 1 μm.39 When performing bath sonication, it is desired to keep the bath at a constant temperature and avoid exposing the material to elevated temperatures, to prevent oxidation. We monitor the water in the bath to ensure the temperature is constant, and we may periodically add ice to the bath. Furthermore, to prevent oxidation during sonication, we bubble argon (Ar) through the solution. When performing sonication by a tip or probe sonicator, we use pulse sonication where the probe is on for 8 s and off for 2 s, and we also use a cooling system surrounding the sample, keeping the solution temperature ~ 5 °C, similar to the temperature of a refrigerator.

Deposition of Flakes. Solution-processed MXenes can be deposited using a variety of methods, including vacuum-assisted filtration,20,34 spin coating,12,34,35 spray coating,22,41 or rolling15,56 as shown in Figure 7. Each technique can be tailored for a specific application. For example, spin coating may produce even, uniform, thin coatings for optics or electronics,12,35 whereas vacuum-assisted filtration and rolling are more suitable for making battery or electrochemical capacitor electrodes,57 while spray coating is convenient for producing large-area films for electromagnetic interference shielding.20

Other techniques, such as screen printing, inkjet printing or slurry rolling, can be employed. Rolling of MXene slurry with a clay-like rheology can provide a way to quickly deposit material and produce thick films for electrode applications.54 Printing MXene allows for precise control over the pattern, increasing the amount of material by increasing the number of layers; however, it requires ink formulation for optimal results.

In the most simplistic manner, nanosheets can be vacuum-filtered to create freestanding films.20 A vacuum-filtration setup of any size can work, assuming a filtration membrane (typically a porous polymer such as Celgard or PVDF) can fit over the Büchner funnel and the pore size is small enough to prevent MXene flakes from passing through the filter. Using this method, freestanding films with controlled thickness can be made of delaminated MXenes and their hybrids with other nanomaterials, such as carbon nanotubes.58

These colloidal solutions of delaminated MXenes can also be deposited onto substrates by spin or spray coating for thinner coatings compared to vacuum-assisted filtration. Spray deposition has obvious advantages; it is easy to use, can cover large areas, and can be done on any surface, also outside the lab. However, the coating is less uniform and often produces rougher films22,41 compared to spin coating.12 Spin coating has the potential to create even, uniform, and optical quality films, for applications where thickness and transparency are important.12

Substrate Functionality. Titanium-based MXenes have been successfully deposited on simple substrates such as paper,56 plastic (PET) substrates,20,41 glass55 and silicon.12 Because MXenes are inherently hydrophilic and negatively charged, the nature of the chosen substrate in terms of hydrophobicity versus hydrophilicity and surface charges is important. Based on our experience, hydrophilic surface treatments such as UV/ozone or O₂ plasma may be used to make the substrate surface hydrophilic, or one may use liquid treatments such as Piranha solution on glass or silicon.22,55

Storage of Material. Once synthesized, the material may need storage before use. Elimination of dissolved oxygen is the first step to suppress oxidation, and this can be done by storing the solution in argon-sealed vials. Second, refrigeration can also suppress the oxidation by decreasing the temperature and eliminating UV radiation. A detailed study on the shelf life of Ti₃C₂Tₓ and Ti₃CTₓ has been published recently.52

Based on our experience, the rate of degradation and quality of the solution can be monitored by ultraviolet—visible absorbance (UV—vis) spectroscopy over time and noting the change in absorbance of the main peak (e.g., 700–800 nm for Ti₃C₂Tₓ).52 Aqueous solutions that are kept in open vials at room or elevated temperatures start degrading almost immediately, with large amounts of TiO₂ forming a week after synthesis. By placing the aqueous colloidal solution in the refrigerator, the oxidation process can be slowed dramatically. When the solution is kept refrigerated in vials sealed under Ar, the degradation is minimal over the course of 24 days.52

Figure 7. Fabrication of Ti₃C₂Tₓ, MXene electrically conducting films via vacuum assisted filtration (left), spray-coating (middle), and painting (right) of MXene ink over various flexible substrates.
Additionally, because the aqueous solutions may cause degradation of the samples, storing MXenes in organic solvents can be advantageous, due to the stabilizing solvation shell which is provided by the organic solvent. A dark supernatant remained stable even after months of dispersing the material in protic organic solvents, suggesting that this may be the best way when long-term storage of the material in solution is needed. Additionally, since MXenes can be redispersed in different solvents, another practice to store MXenes is to filter the colloidal solution and store the resulting film under vacuum. When colloidal solution is needed, MXene film can be redispersed in the solvent of choice by either manual shaking or sonication, depending on the solvent/material combination. Note that drying the film at elevated temperature may lead to strong bonding between the layers, making redispersion difficult.

**Characterization Methods.** Despite the differences in methods and protocols reported in many papers throughout the 2D materials community, basic characterization protocols are necessary to ensure reproducibility. To characterize MXene flakes, many methods are used to probe the structure and morphology of the flakes, such as XRD, SEM, transmission electron microscopy (TEM), and Raman spectroscopy. Elemental composition of Ti3C2Tx MXene powder/films can be characterized by EDX. We use a Zeiss Supra 50VP SEM, and EDX spectra were collected from 5 different locations at 250x magnification (an area of almost 0.5 x 0.5 mm²) for 30 s. A powder diffractometer (Rigaku Smart Lab, U.S.A.) with Cu Kα radiation was used to collect the XRD patterns of MXene powders/films and MAX powders at a step size of 0.03° with 0.5 s dwelling time. MXene powders are placed on a 2 cm × 2 cm engraved or flat glass substrates for XRD analysis. We pressed the powder with a glass slide manually to intensify the (00l) peaks and monitored if the (002) peak of nonetched Ti3AlC2 appears in the XRD pattern. The lateral size of flakes can be measured using SEM by depositing colloidal solution of MXenes on porous alumina substrate (Anodisc, 0.1 μm pore size, Whatman) or by using dynamic light scattering (DLS) on the colloidal solution to confirm the particle size (Zetasizer Nano ZS, Malvern Instruments, U.S.A.). Ideally, more than one technique should be used to obtain reliable data. For example, it is necessary to use DLS in conjunction with SEM to confirm particle size distributions, as shown in Figures 5 and 6. Measuring the properties derived from a specific synthesis route can be used to quantify differences between the methods and select the synthesis method for a specific application. For example, the electrical conductivities of spray/spin coated, vacuum-filtered, or painted films of Ti3C2Tx MXene can be measured using a four-point probe (ResTest v1, Jandel Engineering Ltd., Bed fordshire, U.K.) with a probe distance of 1 mm. Free-standing films produced by the MILD method exhibit high electrical conductivity of ~8000 S/cm in comparison to films produced through TMAOH intercalation (~200 S/cm).

**SUMMARY**

In this Methods and Protocols paper, we have described best practices used to synthesize and process Ti3C2Tx MXene at room temperature, as well as various techniques for making thin coatings or free-standing films of MXene. We showed that as low as 5 wt % HF can etch aluminum out of the Ti3AlC2 MAX phase, but the accordion-like morphology of particles is usually observed when ≥10 wt % HF solutions are used. When in situ HF formation was used (NH4HF2 and LiF/HCl etchants), similar MXene particle morphologies were observed. In the case of LiF/HCl, which is the least harsh etchant, some residual nonetched particles may remain. However, the MILD-LiF/HCl method offers the largest flake size and best quality (least defects) among all etching methods. Moreover, many properties, such as electrical conductivity of Ti3C2Tx films, are synthesis and processing dependent. For example, Ti3C2Tx films produced from colloidal solutions made via TMAOH intercalation showed high resistivity in comparison to films produced by the MILD method. Therefore, we recommend using MILD synthesis in applications where high electrical conductivity, larger flake sizes, environmental stability, or mechanical properties are important and alternative methods, such as “clay” or HF etched Ti3C2Tx, where smaller or more defective flakes are necessary (for example, for catalysis and selected electrochemical or biomedical applications).

Furthermore, we summarized the best practices to process, deposit, and store MXene films and colloidal solutions. We have explained our methods for characterization of these materials by performing microscopy, diffraction, performance testing (for example, conductivity), and light scattering.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b02847.

Additional figures, details, and photographs (PDF)

Movie S1: Synthesis of Ti3C2Tx MXene showing and describing the process that should be followed when adding Ti3AlC2 powder to an etchant (MP4)

**AUTHOR INFORMATION**

*Corresponding Author*

E-mail: gogotsi@drexel.edu (Y.G.).

**ORCID**

Mohamed Alhabeb: 0000-0002-9460-8548
Kathleen Maleski: 0000-0003-4032-7385
Babak Anasori: 0000-0002-1955-253X
Yury Gogotsi: 0000-0001-9423-4032

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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