

Safe Synthesis of MAX and MXene: Guidelines to Reduce Risk During Synthesis

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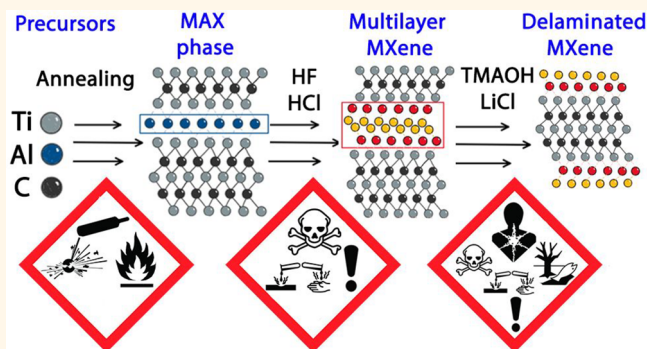
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ABSTRACT: MXenes are proven to be promising materials for a wide variety of applications, from electrochemical energy storage to environmental remediation, leading to their increasing popularity in research. With an influx of new researchers focused on MXenes, it is increasingly important to ensure the safe and reliable production of these materials. Herein, we describe the safe synthesis of MXenes, from their precursors (MAX) to the final product (delaminated MXene), focusing on HF-based etching approaches. Using the synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene as an example, we discuss safety risks associated with each step of the procedure and demonstrate necessary precautions for the safe, reproducible, and reliable synthesis of MXenes. Finally, we overview the most updated research on MXene safety from a cytotoxicity aspect.

KEYWORDS: hydrofluoric acid, two-dimensional materials, MXene, safety, synthesis



INTRODUCTION

In 2011, a large new class of two-dimensional (2D) materials, MXenes, was reported.¹ The MXene family includes 2D carbides, nitrides, and carbonitrides with the general structure of $\text{M}_{n+1}\text{X}_n\text{T}_x$, where M is an early transition metal (Ti, V, Mo, Ta, etc.), X is C and/or N, T_x represents the surface groups (typically = O, -OH, -F, and -Cl), and $n = 1-4$.² To date, there are over 30 stoichiometric MXenes that have been experimentally produced, in addition to a variety of solid solution MXenes.^{2,3} Due to their scalability,^{4,5} hydrophilicity,^{6,7} ease of processing,^{7,8} and desirable optical,^{3,9-13} electrical,^{3,10,14-17} and mechanical properties,¹⁷⁻¹⁹ MXenes have found widespread use in a variety of fields, including electrochemical energy storage,²⁰⁻²⁴ electromagnetic interference shielding,^{25,26} medicine,²⁷⁻²⁹ environmental remediation,³⁰⁻³² etc.³³⁻³⁹ Since this multitude of applications promotes increasing interest in MXene research, it is important for the community to understand how to safely synthesize this family of materials.

During the initial discovery, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene was produced by immersing the $\text{M}_{n+1}\text{AX}_n$ (MAX; A is Al, Si, Ga, etc.) precursor,⁴⁰ Ti_3AlC_2 , into concentrated HF.¹ Following this, many HF-based synthesis routes have been developed, including etching in pure HF,¹ production of *in situ* HF ($\text{LiF} + \text{HCl}$, $\text{FeF}_3 + \text{HCl}$),^{14,41,42} or mixed acid methods (HF/HCl , $\text{HF}/\text{H}_2\text{SO}_4$).^{4,43,44} Even considering the variety of approaches, the majority of MXenes, such as $\text{Mo}_4\text{VC}_4\text{T}_x$,² $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$,⁴⁵ $\text{V}_4\text{C}_3\text{T}_x$,^{46,47} V_2CT_x ,^{48,49} and others,^{3,12,26,50-54} are primarily or

only produced by etching in concentrated HF solution. That being said, there are several promising, alternative synthesis routes that have been demonstrated, including molten salt,^{23,55-58} alkali extractions,^{59,60} or halogenation.^{61,62} However, these approaches are still in early development and have not been as widely studied and used as HF-based synthesis.

After etching, MXenes exist in their multilayer form, which consists of 2D MXene flakes held together in stacks by van der Waals forces. While this form is useful for many applications,^{63,64} many researchers prefer to delaminate the MXene flakes. Delaminated MXene flakes can be studied as individual flakes,^{18,19} as a slurry of both delaminated flakes and multilayer powder, known as MXene "clay",^{65,66} or assembled in a variety of forms, such as free-standing or supported films,^{67,68} aerogels,^{69,70} fibers,⁷¹ composites,⁷²⁻⁷⁴ or others.^{15,16,21,75} There are multiple approaches to delaminate MXene flakes with the help of dimethyl sulfoxide (DMSO),^{6,76} tetramethylammonium hydroxide (TMAOH),^{2,77} lithium chloride (LiCl),^{4,43} or other intercalants.^{14,53,54,78} It is important to note that some of the intercalants used to delaminate MXene will remain on the surface of its flakes, even after washing.^{77,79}

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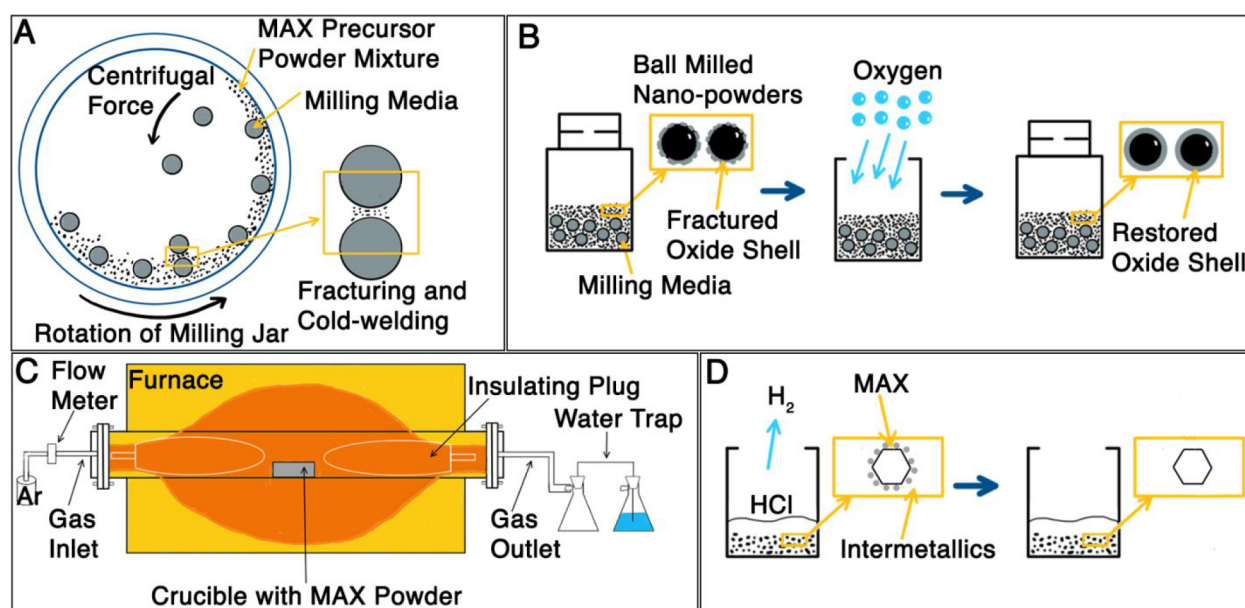


Figure 1. Steps associated with the production of the MAX phase: (A) Ball milling, (B) passivation by oxygen of air, (C) high-temperature synthesis, and (D) acid washing to remove unreacted precursors and side products.

Considering that more than 1500 institutions from nearly 70 countries have already published MXene research in peer-reviewed journals,¹⁵ with new groups continually beginning to study these materials, it is vital to establish safe MXene manufacturing protocols,⁸⁰ including precursor storage and production, safe handling of MXenes, topochemical synthesis, and delamination. While hazards associated with the synthesis of MXene have been previously analyzed,⁸⁰ it provided only general safety considerations for the synthesis of MXene using the *in situ* method ($\text{LiF} + \text{HCl}$). Herein, we are focused on demonstrating how to implement these considerations for the safe synthesis of MXene in a laboratory setting. With this focus in mind, we outline the risks associated with the synthesis of MAX phases and their preparation for MXene synthesis and then shift focus onto MXene synthesis using HF-containing solutions, describe common mistakes and strategies to mitigate them, and review studies of the biocompatibility and cytotoxicity of MXenes themselves.

MAX PHASE SYNTHESIS PROCESS

There are many approaches to synthesize MAX phases, including hot isostatic pressing,^{81–83} self-propagating high-temperature synthesis,^{84–86} spark-plasma sintering,^{87–89} high-temperature synthesis,^{1,2,4} and others.^{46,90–92} Within these techniques, high-temperature synthesis from elements or binary compound precursors is common due to its simplicity, low cost, and scalability; therefore, we will focus on this technique for MAX precursor synthesis.

In a typical procedure for the synthesis of Ti_3AlC_2 ,⁴ TiC, Ti, and Al powders are mixed via ball milling using, e.g., zirconia balls and then annealed in a tube furnace under an argon (Ar) atmosphere at approximately 1400 °C for 2 h with heating and cooling rates of 3 °C min^{-1} . The sintered materials are then crushed, milled, drilled, or ground in a mortar and pestle, depending on the composition, porosity (brittleness of the sintered body), and amount, and then sieved to yield a powder of a desired particle size. If necessary, the annealed powders

can be washed in HCl to remove any remaining metallic or intermetallic impurities before sieving.

While the specific synthesis parameters, such as the ratio of powders ($\text{TiC}:\text{Ti}:\text{Al} = 2:1:1$ atomic ratio⁴ or mass ratio⁹³) or type of precursors used for synthesis,⁴¹ might change depending on the protocol, the hazards which arise during MAX synthesis apply for different MAX compositions and primarily concern the handling and storage of reactive powders (Figure 1A,B), the operation of high-temperature furnaces (Figure 1C), and the use of HCl to wash the MAX powder (Figure 1D).

Due to the pyrophoric nature of fine (especially nanoscale) metal powders, there is a safety risk present when handling and storing the powders necessary to synthesize MAX phases. Nanoparticles are also known to demonstrate unique phenomena^{94,95} which are not observed in coarse powders, caused by the high surface area to volume ratio.⁹⁶ As a result, with variances based on chemical structure, nanopowders have been generally observed to have substantially decreased ignition temperatures/energies indicating higher possibilities of self-ignition and thermal explosions in air.^{95,97} While each nanomaterial has its own safety data sheet (SDS), many are considered pyrophoric, and common precautions for pyrophoric metal powders and nanopowders include the following:^{98,99}

- (1) Keep containers tightly closed in a dry, cool, and well-ventilated place.
- (2) Keep away from heat and sources of ignition (dust can form an explosive mixture in air).
- (3) Wear standard personal protection equipment (PPE), including protective gloves, lab coat, and safety goggles, when handling.
- (4) Ensure adequate ventilation in workspaces and wear a respirator; when handling dusting powders, avoid breathing in dust.⁹⁶
- (5) Keep a Class D fire extinguisher (for use on combustible metals) on hand in case of fire.

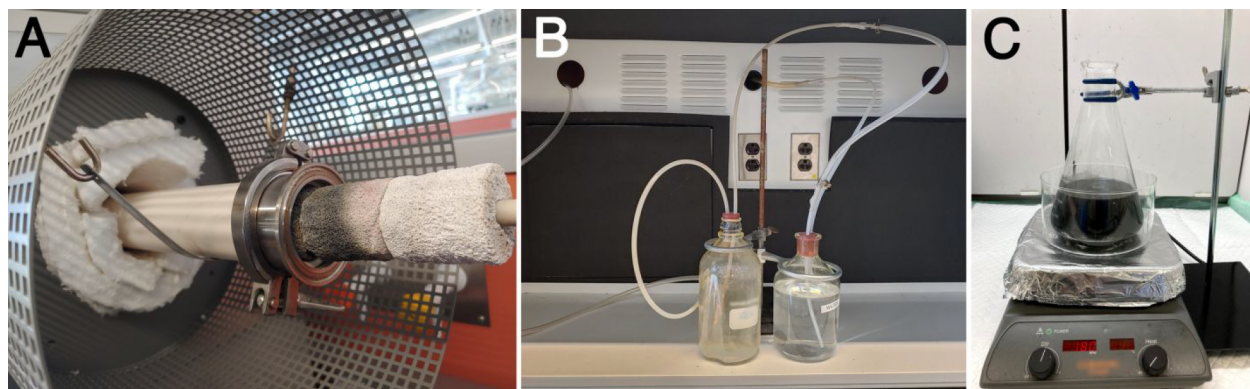


Figure 2. Safety risks associated with MAX synthesis. (A) Photo of a tube furnace with insulating plugs to minimize heat loss and thermal shock. (B) Photo of a two-stage trap system for high-temperature furnaces to capture released gases and monitor Ar flow. (C) Photo of a setup for HCl washing of MAX phase.

These precautions should be taken while handling all of the powders necessary for MAX phases synthesis. Furthermore, the concern of material self-ignition becomes even greater after the powder mixture has been ball milled. High-energy ball milling is a form of mechanical activation, which has been shown to significantly increase the reactivity (decreasing self-ignition temperatures) of the powder mixture.^{100,101} Ball milling fractures the oxide shell present on powders as well as increases the contact surface area between reactants, exposing the raw metal to the environment and resulting in a highly combustible material (Figure 1A). The pyrophoricity of the metallic nanopowders is commonly reduced by chemical passivation (Figure 1B), which reforms the oxide shell that is present in most bulk powders.¹⁰²

Passivation by air (partial oxidation)¹⁰² is the simplest method of reducing the pyrophoricity of nanopowders. The safest way to perform this in a regular lab setting includes the following:

- (1) Designate a fume hood solely for passivation to isolate a possible reaction event.
- (2) Bring the sealed bottles to the fume hood and let them sit undisturbed for an hour to let the agitated particles settle.
- (3) Carefully loosen the cap of the ball-milled powder inside the fume hood.
- (4) Leave powders to slowly oxidize for 1–2 h per cycle, intermittently loosening the cap further over the course of a few hours until the cap is fully removed. Typically, this process takes 8–12 h, depending on the reactivity of the metals being used.

Once the powders have been deemed safe, they can be used for the last step of synthesis, high-temperature reaction sintering (Figure 1C). It typically requires the use of a high-temperature tube furnace under an Ar atmosphere, which involves familiarity with equipment pieces and gas handling to ensure operational safety. While hot pressing or hot isostatic pressing can also be used for MAX phase synthesis, those are less scalable methods that also produce a dense sintered body, which may be difficult to crush. As with normal tube furnaces, the apparatus must be placed in such a way that the ends of the work tube are at least 500 mm away from any adjacent surface, as well as any flammable material. Additionally, thermally insulating plugs are highly recommended on either end of the work tube to minimize any heat loss, as well as to prevent

thermal burns from occurring if any user touches the tube while the furnace is operating (Figures 1C and 2A).

Ar is used to protect the powder mixture from further oxidation that can occur while under high temperatures and is usually flown into the furnace through a gas inlet. To ensure proper gas flow and to clean the outflow gas, a two-stage water trap should be placed at the end of a tube connected to the furnace gas outlet. During the experimental setup, checking the water trap for bubbling ensures that Ar is flowing through the furnace (Figures 1C and 2B). If there is a reverse flow of water into the empty bottle, this would indicate an error in Ar flow, which should be addressed prior to annealing. Common errors include the following:

- (1) Ar tank regulator has not been set to release gas.
- (2) Crack is present in the furnace tube, causing the leaking of Ar and potential oxidation of the reaction mixture.
- (3) The tubes connecting the Ar tank to the furnace leak or are not properly connected. Ar leaking into the lab may cause an asphyxiation hazard (by displacement of oxygen).

Of these issues, 1 and 3 are remedied by leak checking and replacing gas tubes or ensuring that the gas valve is open. Issue 2 is a matter of long-term furnace maintenance, which includes using slow heating and cooling rates¹⁰³ (below 10 °C min⁻¹) to prevent thermal shock to the tube and careful handling of the tube furnace. Once all issues with Ar flow or the tube furnace have been addressed, the MAX powders may be annealed.

As with any high-temperature application, caution must be exercised when removing samples from the furnace after reaction sintering. It is best to be conservative with cooling times and remove materials at the temperature closest to ambient, especially because high-temperature thermocouples used in most furnaces become less accurate at lower temperatures. Additionally, the careful use of crucible tongs to handle materials retrieved from the tube is crucial to prevent burns associated with the high temperatures. Due to the thermal insulation of the furnace, we recommend cleaning the tube the next day after synthesis, as the center of the tube can remain at elevated temperatures (>100 °C) for extended periods of time. If solvents are used to clean the tube during this time, crack formation can readily occur.

If the MAX powder has been observed to have impurities (any residual oxides, metals, or intermetallics), then the powder may be washed in hydrochloric acid (Figures 1D and



Figure 3. PPE required for protection from HF. In addition to close-toed shoes, long pants, and chemical goggles, HF gear include a (A) face shield, (B) HF-resistant gloves with sleeves, and (C) a plastic or rubber apron. (D) Image of a person wearing HF-protective gear.

2C). We wash it for 18 h, but the time depends on grain size, content of impurities, and other parameters. HCl is not as life-threatening as HF, but it is still a corrosive and volatile substance that can cause severe burns and respiratory irritation. Precautions that must be followed with any experiment involving HCl are listed below:

- (1) Work in a fume hood with exhaust ventilation to minimize airborne concentrations of vapor.
- (2) Ensure that safety showers and emergency eyewash stations are immediately available.
- (3) Use standard PPE as well as nitrile gloves, or other gloves made of acid-resistant material.
- (4) Properly and immediately dispose of any contaminated gloves or pipettes.
- (5) Never add water to acid (significant heat generation), always add acid to water.
- (6) Use a proper glove removal technique to ensure that your bare hands are not exposed to the outer surface of used gloves.
- (7) Wash hands thoroughly and immediately after handling HCl.

In addition to the normal safety hazards surrounding HCl use, since MAX powders contain metal and intermetallic impurities, there must be extra caution related to heat generation and gas evolution. Prior to the addition of MAX powder, the bottle should be placed into an ice-bath to address rapid heat generation and should be secured tightly by a clamp to avoid any spillage (Figure 2C). In addition to heat generation, HCl reacting with metals in the presence of water forms hydrogen gas, which is highly flammable and explosive when mixed with air. For this reason, MAX powder must be added slowly (~ 1 g/min) to the acid solution to control the rate of hydrogen evolution and heat being formed, and to prevent any violent runaway reactions. In our experience, this reaction (and the etching reaction discussed below) has an induction period, and the gas evolution does not immediately start after adding the MAX powder. The rate at

which powder should be added depends on MAX composition and reactivity, but a cautiously slow rate is encouraged for optimal safety. When all MAX powder has been added, there must be a vent port or other unrestricted gas evolution route to accommodate the controlled gas evolution. Afterward, the HCl-washed powder should be repeatedly washed by deionized (DI) water until neutral pH, which can be done with repeated centrifugation, by sedimentation, or by filtration.

■ MXENE SYNTHESIS PROCESS

Hydrofluoric Acid Safety/Exposure. Hydrofluoric acid is one of the primary components for MXene synthesis, whether in its pure HF form or produced *in situ* by reaction of another acid with a metal fluoride, such as LiF. Therefore, it is vital to understand how to properly handle HF, focusing on how to prevent or treat accidental exposure. All HF burns are classified as severe. HF burns are defined by concentration, surface area of burns, and duration of exposure.¹⁰⁴ If exposed, minimizing these three variables will lessen harm, however, even with medical care, it is not uncommon for HF burns to result in disability or even death.

To understand the severity of HF burns, it is necessary to examine why HF is so deadly.^{105,106} HF simultaneously causes tissue damage based on two mechanisms; the first is through high concentrations of hydrogen (hydronium) ions, leading to standard acid burns, similar to HCl or H_2SO_4 . The second mechanism, which is much more deadly, is the release of fluoride ions. These free fluoride ions are highly lipophilic and will penetrate deeply into human tissue, which rapidly leads to liquefactive necrosis in the affected area.^{107,108} High exposure ($>1\%$ total body surface area) can lead to multiple organ failure, hyperkalemia, hypocalcemia, and hypomagnesemia.^{107,109,110} To further compound on the danger of HF exposure, depending on the concentration, different physiological pain responses will occur. With high concentrations ($>50\%$), the burn will be almost immediately apparent; at concentrations from 21% to 50%, it may take up to 24 h for

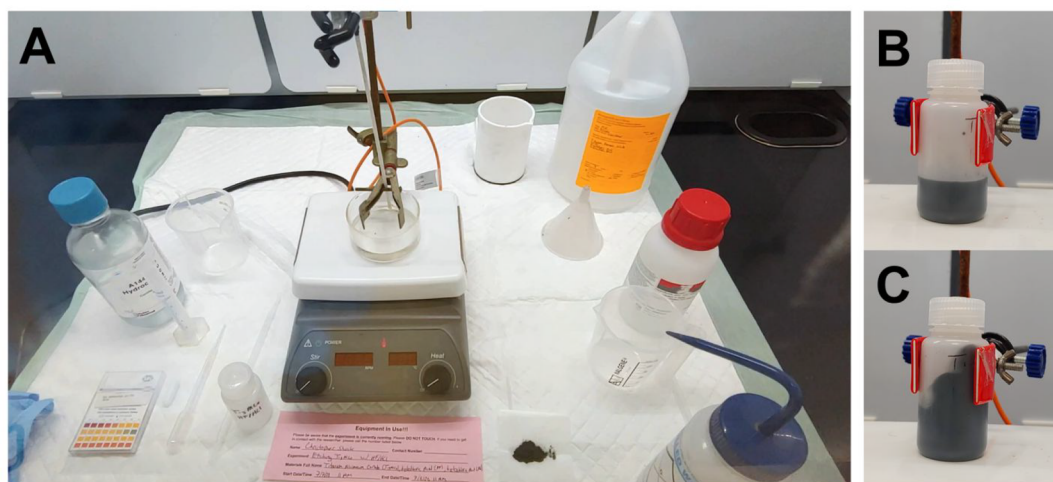


Figure 4. Etching setup. (A) Image of a workstation prepared for etching. Photos of an etching bottle with proper (B) and improper (C) stirring.

pain to occur and exposure to be noted, and for concentrations below 21%, it can take even longer for exposure to be noted.^{104,111} In all cases, however, HF exposure can be dangerous if left untreated.^{104,105,112–114}

The exposure response generally consists of the removal of the chemical, treatment of systemic toxicity, systemic supportive treatments, and treatment of tissue damage. In the laboratory setting, exposure response begins with immediate use of the emergency shower (or eyewash station for ocular exposure) to massively flush the exposed area and remove all surface HF, during which the researcher removes all exposed clothing. Following this, topical treatment of the exposed area using calcium gluconate gel or solution/slurry is necessary.^{115,116} Calcium ions from the calcium gluconate will bind to fluoride ions to prevent further damage. After immediate response, it is necessary to urgently go to a hospital for professional treatment.^{106,110,111,117,118} For inhalation exposure (even concentrations below 10% pose an inhalation toxicity risk), the person must be immediately taken to a hospital for treatment.

Considering the risks associated with HF, for all HF-based MXene synthesis protocols, it is imperative that emergency showers, eyewash stations, and calcium gluconate are readily available in the laboratory. All laboratory personnel who handle HF, or those who are in the immediate proximity, must know the exposure response plan and the locations of nearby hospitals equipped to treat HF burns. Ideally, no exposure should occur; we have not had a case in more than 10 years of regular HF use by a large number of researchers, but preparing for exposure is crucial. Additionally, HF-specific personal protective equipment (PPE) should be worn during use of HF, along with an experimental procedure that minimizes exposure risk. More details on the specific preparation and procedure to prevent or minimize exposure will follow below. However, it is important that the risks of HF exposure are well understood prior to conducting MXene synthesis. The authors recommend reading the above literature and especially the SDSs associated with HF prior to planning and executing experiments.¹¹⁹

Personal Protective Equipment for Hydrofluoric Acid Usage. Prior to discussing the synthesis procedure itself, it is imperative to understand proper PPE usage (Figure 3). Using proper PPE while handling HF-containing solutions is crucial to avoid injury. For eye protection, the researcher should wear

laboratory goggles and a plastic face shield when working with HF (Figure 3A,D). Safety glasses with side shields do not provide adequate eye protection alone. For body protection, the researcher should wear an apron made of Neoprene, Viton, or natural rubber over a lab coat, long pants, and closed-toe shoes (Figure 3C,D). When working with concentrated solutions of HF and/or large volumes, special gloves with sleeves that cover the hands, wrists, and forearms should be worn (Figure 3B,D). Wearing a thin disposable glove underneath the thicker glove is recommended to maintain the cleanliness within the HF gloves. Thick PVC or neoprene gloves provide good resistance to HF but may reduce manual dexterity due to their bulkiness. Therefore, wearing a second layer of thin disposable polyethylene gloves on top of the thick HF gloves helps to improve dexterity. Moreover, the thick HF gloves should be checked periodically for holes or signs of degradation before use. According to the Quick Selection Guide to Chemical Protective Clothing,¹²⁰ the following gloves will provide protection from hydrofluoric acid (30–70%) for 4 h or more: butyl rubber, neoprene rubber, Viton/butyl rubber, Barrier (PE/PA/PE), Silver Shield/4H (PE/EVAL/PE), Trelchem HPS, Trelchem VPS, Tychem SL (Saranex), Tychem CPF3, Tychem BR/LV, 4 Tychem Responder, and Tychem TK.

Disposal of Hydrofluoric Acid Waste. HF-containing waste, including solutions from *in situ* HF formation, must be placed in a chemically compatible container (never use glass!) and labeled to identify the contents. The bottle should not be filled completely in order to allow the gas formation and release without creating pressurized waste bottles. The lid should be sealed, and the waste bottle should be stored using a secondary container in its designated area until it is properly disposed of, e.g., picked up by Environmental Health and Safety (EHS) staff. Gloves or other solid waste not contaminated with HF may be disposed of as regular trash, whereas disposable equipment that is contaminated (e.g., gloves) or reusable equipment that is contaminated and cannot be safely decontaminated should be disposed of as hazardous solid waste.

Etching. *Disclaimer: Follow all chemical hygiene, storage, spill, and waste disposal procedures as defined by your institution. The following procedures serve as an example and may need adjustment to adhere to national or institutional guidelines.*

Additionally, the following procedures do not account for chemical spillage. If a chemical spill occurs, alert others in the area and safely address the spill as defined by your institutional safety standards. Lastly, become fully familiar with the procedure before initiating the etching procedure in practice. While in practice, progressing through procedural steps while a colleague reads them may prove helpful. All experiments involving HF and other acids should always be performed with another person nearby.

To synthesize lab-scale quantities of $\text{Ti}_3\text{C}_2\text{T}_x$ by etching MAX in HF/HCl, the following procedure is typically described:^{4,43,44} 1 g of the Ti_3AlC_2 is slowly added over 5 min into a 60 mL polypropylene bottle containing 20 mL of solution composed of 2 mL of 29 M (49 wt %) HF, 6 mL of DI H_2O , and 12 mL of 12 M HCl. The reaction is allowed to continue for 24 h while at 35 °C and stirring at 500 rpm. Execution of the etching procedure can be viewed in [Video S1](#). Modification of this protocol can be used for the etching of other MXenes as well.^{2,3,12,26,45–54}

The first step of this protocol is to prepare the workstation. Prior to experimentation, it is important to locate the closest eyewash station, safety shower, spill kit, and medical kit with calcium gluconate. It is equally important to ensure that all of the equipment used in this experiment is functioning correctly, including the hot plate, thermocouple, and fume hood where the experiment is performed. It is also advisable to gather all of the necessary plasticware (graduated cylinder, spatula, etching plastic bottle with screw cap, stir bar, secondary containers) and disposal container (chemical waste container) and prepare all chemicals to minimize extraneous movement and spill risks ([Figure 4A](#)).

It should be confirmed that all containers are compatible with the synthesis conditions. First, they should be plastic, such as PTFE or HDPE, as glass is not HF-compatible. Second, they should be of sufficient volume. To ensure no spillage will occur from stirring, even with heat or gas release, we recommend that the etchant solution volume is less than 1/3 of the etching bottle volume. The secondary container, a large high-walled plastic beaker, should be the same height and twice the volume of the etching bottle. It is also important to check the temperature rating of the etching bottle and large high-walled plastic beaker such that they are heat-tolerant at the desired etching temperature. The synthesis of some MXenes, for instance, $\text{Mo}_2\text{TiC}_2\text{T}_x$, $\text{Mo}_2\text{Ti}_3\text{C}_3\text{T}_x$, and $\text{Nb}_4\text{C}_3\text{T}_x$ ²⁶ requires temperatures of up to 50 °C, and not all of the plastic containers are compatible with these temperatures. It is important to check the stir bars prior to usage; over time, stir bars will wear away and produce contamination of MXene.

As it is demonstrated in [Video S1](#) and [Figure 4A](#), we typically fill the secondary container with mineral oil in order to maintain the reaction temperature, but the level of mineral oil is lower than the etchant volume. Please note that the transparent glass container used in [Video S1](#) and in [Figure 4](#) is for demonstration only; a compatible plastic beaker should be used for these experiments. We also recommend paying attention to the thermocouple, which should be properly secured with a dedicated clamp with the height adjusted so that the thermocouple tip is submerged in the mineral oil bath and located next to the etching bottle, but not touching the bottom of the high-walled beaker. This will ensure that the temperature measured by the thermocouple is accurate. The accuracy of the temperature could be confirmed by a separate thermometer or thermocouple. If the thermocouple is not properly secured, it possesses a risk of uncontrolled heat,

degradation of the etching container, and potential spillage of HF-containing solution.

When preparing the etching solution, we recommend adding HF at the very last step, after the required volumes of H_2O and then HCl have been added to the etching bottle. At this point, the HF safety gear discussed above and demonstrated in [Figure 3](#) should be worn. After preparing the etching solution, all of the excess acids should be disposed into the chemical waste, and all used plasticware and the secondary containers should be carefully rinsed with water. To confirm that rinsing is complete, the pH should be measured using pH strips. Checking gloves regularly is essential. If gloves are dirty (i.e., oil, chemicals, etc.), replace them with fresh gloves.

When the etching solution is prepared, MAX powder can be added. With the MAX powder in one hand and the spatula in the other, scoop MAX powder into the etching bottle at a rate of $\sim 0.2 \text{ g min}^{-1}$. Both adding acid to water during the previous step and adding MAX phase to the etching solution are exothermic processes. Using such a slow rate of adding the MAX phase to the solution ensures proper control of the reaction temperature. In some cases, for instance Ti_2AlC and V_2AlC , the reaction is more exothermic when added to HF, and an ice bath should be used after preparing the etching solution and while adding the MAX powder.

During etching, there will be H_2 gas formation, which will be noticed as gas bubble accumulation on the sides of the etching bottle.¹ These bubbles will grow and rise to the surface. However, if the bubbles become frequent, resembling simmering or boiling, immediately turn off the hot plate heating and close the fume hood sash. After the MAX powder is added to the etching bottle (approximately 5 min for 1 g of Ti_3AlC_2), the etching bottle lid can be placed onto the etching bottle. It is important to ensure that there is a way for the generated gas to escape, which could be done by either unscrewing the lid by a 1/2 turn (the lid is not tightly closed) or making a small hole in the lid. It is worth noting that significant amounts of H_2 gas will be generated during the synthesis process. Depending on the specific surface terminations, the amount of H_2 gas per mole of Ti_3AlC_2 can range from 2.5 mol of H_2 (for a purely stoichiometric F- or OH-terminated surface) up to 3.5 mol of H_2 (for a purely stoichiometric O-terminated surface). Furthermore, the MXene surface can deviate from perfect stoichiometry and be over- or undersaturated with surface termination groups.¹²¹ This means that etching 1 g of Ti_3AlC_2 will produce at least $\sim 0.3 \text{ L}$ of H_2 gas.

After these steps, the hot plate stirring speed can be increased to the value necessary for proper mixing. The stirring speed should be limited such that the etching solution height is lower than 2/3 of the etching bottle height ([Figure 4B,C](#); note that secondary containment is not shown to illustrate the effect on solution height), and there is no splashing inside of the etching bottle, while still providing proper mixing of the solution.

Before taking off the HF safety gear, we recommend checking the top pair of gloves to ensure that no HF contamination has occurred. We usually take off the HF safety gear starting with the thick HF gloves, then sleeves, then the face shield, and then the rubber apron. After a period of time, we also recommend ensuring that the hot plate temperature is still stable, and the stirring speed is consistent.

For safely etching larger amounts than a few grams of MAX, we recommend using commercial reactors with a Teflon

etching container placed inside a stainless-steel outer container, which provides an automated powder feed and temperature control (water cooling/heating), such as described in ref 4.

Washing. Once the etching procedure is complete, the etchant must be neutralized by centrifugation using DI water (Figure S1). This is typically done by repeated cycles of centrifugation at 3500 rpm (2550 rcf) to settle the powders and decanting the acidic supernatant until the supernatant reaches neutral pH. Execution of the washing procedure can be viewed in Video S2.

Strict safety precautions must be taken while handling the etchant solution. To minimize HF exposure, all HF safety gear must be worn during the washing procedure (Figure 3). Prior to washing, it is recommended to gather all supplies, including DI water, centrifugation tubes, pH strips, and disposable graduated plastic pipettes. Transferring the HF-containing solutions should be performed within the fume hood over a chemical spill pad or a plastic tray, which will contain spills if they accidentally happen. We recommend using a pipette to transfer the etching solution from the etching bottle into the centrifugation tubes because of the magnetic stir bar, which can cause splashing when the solution is poured. Both the centrifuge tubes and the etching bottle should be secured using an appropriate holder or clamp in order to avoid accidentally knocking the containers over and spilling the solution, as was reported in a recent accident.¹²²

In order to follow the “add acid to water” rule, we recommend adding DI water to the centrifugation tube before transferring the etching solution. After all solution is removed, the remaining solids (MXene and unreacted MAX) can be transferred by carefully redispersing them in DI water and then pipetting it into the centrifugation tubes. After all solids are removed from the etching bottle, the centrifugation tubes should be sealed tightly and the etching bottle rinsed thoroughly with DI water until neutral pH (confirmed with pH strips), while disposing the solution into the chemical waste using the pipette. Then, the magnetic stir bar can be removed and the etching bottle disposed into the chemically contaminated waste disposal container.

When the solution transfer is finished, it is important to confirm that there is no solution on the outside of the filled centrifugation tube. Since the centrifugation tube should not be opened outside of the fume hood, we recommend weighting this tube while tightly sealed and filling a separate clean centrifugation tube with water to counterbalance the weight. Centrifugation at 3500 rpm (2550 rcf) for 5–10 min will be sufficient at this stage to settle all of the powders; then, the clear supernatant can be carefully decanted from the centrifuge tube into the chemical waste. Use of a plastic funnel will help with pouring into the chemical waste and reduce spilling. The centrifuge tube with solids sedimented on the bottom should be refilled with DI water and sealed, and then, the sediment should be fully redispersed (Figure S2). The centrifugation procedure should be repeated until the pH of the supernatant is >6, which takes approximately 5 washing cycles.

After the neutral pH is reached, HF safety gear can be removed. Similar to the etching step, it is important to check the top pair of gloves to ensure that no HF contamination has occurred and then dispose of them. Remove the HF safety gear, in order of the thick rubber gloves, then sleeves, then the face shield, and then the rubber apron. From here, the MXene can be collected and used as multilayer MXene or can be

delaminated and used as a colloidal solution of single-layer or few-layer flakes.

Transferring Etching Solutions between Rooms. If the HF-containing etchant needs to be transferred from one lab to another, it should be done with proper precautions. First, the solution should be stored in a chemically compatible container, and the container lid should be closed. It is also crucial to use a chemically compatible secondary container to contain a possible spill. Clean gloves should be used to avoid possible contamination while moving from one lab to another. All containers used for transferring should be rinsed with water.

Delamination. After the etching process, MXenes are in a multilayer (also known as powder) form, where the individual MXene sheets are held together by van der Waals forces. Delamination is the process where the multilayer MXene is separated into individual MXene sheets. Within the MXene literature, there are many approaches to delaminate MXenes,¹⁷ including the use of organic or inorganic intercalants, solvents, or mechanical force, each of which results in colloidal dispersions with varying yields and different properties. In-depth protocols for the different delamination approaches will not be provided due to the similarity with the washing protocol. Herein, attention will be focused on the safety risks associated with the most popular delamination agents.

Lithium Chloride. LiCl only is a feasible delaminant when a Ti-based MXene, for instance, $\text{Ti}_3\text{C}_2\text{T}_x$ or Ti_2CT_x , is etched with the HF/HCl method. A visual depiction of delamination of $\text{Ti}_3\text{C}_2\text{T}_x$ with LiCl is shown in Figures S3–S5. LiCl is one of the most hygroscopic salts known;¹²³ therefore, LiCl should be stored in a tightly-closed container sealed with a self-sealing thermoplastic or paraffin, in a cool, dry, ventilated area. For delamination, LiCl dissolved in DI water is added to the sediment after washing. However, regardless of the ratio, when LiCl is added to water, a significant amount of heat is generated. Additionally, aqueous LiCl solution is known to be a skin and eye irritant. Therefore, proper PPE, including glasses, a lab coat, and gloves, should be worn when handling LiCl powder and aqueous LiCl solutions. Adequate ventilation should be used, and inhalation should be avoided.

Tetrabutylammonium Hydroxide and Tetramethylammonium Hydroxide. Tetrabutylammonium hydroxide (TBAOH) or tetramethylammonium hydroxide (TMAOH) are mostly used to delaminate MXenes other than $\text{Ti}_3\text{C}_2\text{T}_x$, such as Ti_3CNT_x , Mo_2CT_x , V_2CT_x , Nb_2CT_x , etc.^{2,3,12,26,77,124} Generally, TMAOH is the more common intercalant, with the 25 wt % (or diluted 10 wt %) aqueous TMAOH solution typically used. This leads to ion exchange between protons (H^+) and the tetraalkylammonium ions (TBA^+ or TMA^+) and results in intercalation and subsequent delamination of the MXene.¹⁴

Alkylammonium hydroxides are strong bases and should be treated as such. Similar to other alkali solutions, such as NaOH or KOH, alkylammonium hydroxides can cause severe chemical burns upon exposure. In addition to its alkalinity, the tetramethylammonium cation ($(\text{CH}_3)_4\text{N}^+$ or TMA^+) is also toxic and primarily affects nerves and muscles.¹²⁵ TMA^+ is destructive to eyes, skin, and mucous membrane tissue; thus, exposure will result in severe damage. TMAOH is readily and rapidly absorbed through the skin, and fatal systemic and acute toxicity may be observed if dermal absorption occurs. Several injuries and deaths have been reported even after exposure to dilute TMAOH solutions.^{126,127} Therefore, not only should safety glasses, a lab coat, and disposable nitrile gloves be worn

when handling TMAOH, but the use of a chemical-resistant apron, chemical splash goggles or face protection, and nitrile gloves (4 mil or 100 μm) with long gauntlets is also highly recommended. The TMAOH container should be kept tightly closed in a dry and well-ventilated place, and the container should be carefully resealed after use. Lastly, it should be noted that when TMAOH is used for delamination, the MXene sometimes may need to undergo a heating treatment up to 500 $^{\circ}\text{C}$ under an inert atmosphere for several hours to remove the TMAOH intercalants.^{2,77} Under heating, TMAOH can produce many toxic and flammable volatile compounds, such as trimethylamine, dimethyl ether, and methanol,¹²⁸ which necessitate corresponding safety precautions.

Dimethyl Sulfoxide. Dimethyl sulfoxide (DMSO) is one of the first organic molecules used to intercalate $\text{Ti}_3\text{C}_2\text{T}_x$.⁷⁶ While DMSO is a relatively nontoxic solvent, it readily penetrates the skin carrying with it any dissolved substances. Therefore, proper gloves, such as thick rubber gloves, should be worn when handling DMSO. When using DMSO or other organic solvents for delamination, a sonication step is often required, which should be performed in a safe manner. We recommend following standard safety protocols when working with sonication baths. Regular PPE should be worn by the researcher while handling DMSO. It is suggested not to wear contact lenses since they may absorb and concentrate irritants. Also, DMSO should be used only in well-ventilated areas and kept away from sources of ignition. Breathing its vapor and contact with skin, eyes, and clothing should be avoided.

■ TOXICITY OF MXENES

While it is possible to safely produce MXenes, there remains the question of whether MXenes themselves are toxic. Within the 2D-material community, this question is important and relevant for both laboratory personnel and for commercialization.^{129–131} Since the discovery of graphene, there have been continual questions regarding the safety and toxicity of 2D materials. The same nanoscale thickness and 2D structure that make these materials so desirable raise questions regarding how they will differ from their bulk counterparts when exposure does happen. For large families of 2D materials that have a variety of chemistries, such as MXenes or transition metal dichalcogenides (TMDs), it stands to reason that some chemistries may be safe, while others are not.^{129–131} Since MXenes are not infinitely stable, it is important to consider both pristine MXenes as well as their degradation products.^{132–134}

While there are more than 30 stoichiometric MXene compositions experimentally synthesized,² with numerous proposed applications that interact with the body,^{27,135,136} only a few ($\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x ,^{29,44,78,137–148} Nb_2CT_x ,^{149,150} $\text{Nb}_4\text{C}_3\text{T}_x$,²⁹ $\text{Ta}_4\text{C}_3\text{T}_x$,^{28,29,151,152} $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$,²⁹ and Mo_2CT_x ¹³³) compositions have been tested for their toxicity and environmental effects.²⁷ In all studies thus far, there has been no reported acute toxicity or negative influence of MXenes on human or animal cells. For example, it was shown that $\text{Ti}_3\text{C}_2\text{T}_x$ does not generate any reactive oxygen species or induce cytotoxicity in quantities up to 500 $\mu\text{g mL}^{-1}$.¹⁴⁷ Extended exposure (48 h) of breast cancer cells to $\text{Ti}_3\text{C}_2\text{T}_x$ showed no cytotoxicity in high concentrations (600 $\mu\text{g mL}^{-1}$).¹⁴⁸ Furthermore, extended tests with zebrafish models confirmed the nontoxicity, allowing the material to be classified as “practically nontoxic”.¹⁴⁶ In addition to Ti-based MXenes, similar results were shown with Mo_2CT_x ; no apparent

cytotoxicity was detected with normal (L929) or cancer (4T1) cell lines after extended (48 h) exposure at 400 $\mu\text{g mL}^{-1}$ concentrations.¹⁵³ Regardless of the etching approach, there appears to be no toxicity directly associated with the investigated MXenes.

However, considering that there are still many chemistries and structures that have not been studied, it is not possible to claim that all MXenes will show no toxicity. While for the most studied MXenes, such as $\text{Ti}_3\text{C}_2\text{T}_x$, safety information is available (SDS is provided in the [Supporting Information](#)), other compositions are less studied. Thus, it is important that new MXene chemistries, structural modifications, and synthetic approaches are systematically investigated to examine and identify the associated risks inherent in MXenes, if any. To fully understand and characterize any toxicity, additional studies must be conducted with a variety of MXene compositions (including single M, ordered double M, solid-solution, and divacancy MXenes), etching approaches that affect surface chemistry, intercalants, higher concentrations (to study the possibility of contamination during production or spillage), and extended exposure times.

■ CONCLUSIONS

Herein, we have described safe processes and procedures for the synthesis of MXenes, using the $\text{Ti}_3\text{C}_2\text{T}_x$ etched with HF/HCl method as an example. Beginning with the synthesis of Ti_3AlC_2 , the primary safety hazards are pyrophoric powder and HCl-washing. When synthesizing $\text{Ti}_3\text{C}_2\text{T}_x$ from Ti_3AlC_2 using HF-based etchants, the main safety concern is handling and usage of HF or HF-containing solutions.

While there are multiple approaches to synthesize MXenes, and multiple MXene chemistries and structures possible, we have focused on the most common MXene, $\text{Ti}_3\text{C}_2\text{T}_x$, using the most up-to-date method of synthesis. Each different MXene and synthesis approach necessitates the critical examination of all risks involved. Moreover, while experimentation on the biotoxicity of MXenes is underway, many MXenes have not been studied in this regard yet, and the available studies are not exhaustive for all conditions and sizes. Thus, we caution researchers to minimize exposure whenever possible and to always utilize PPE when handling MXenes, their precursors, or any intermediate or final product.

It is crucial to fully understand all risks prior to experimentation, wear proper PPE, utilize engineering controls when possible, and always perform experimentation with others in the laboratory. By following the procedures outlined here, researchers will be able to produce high-quality MXenes in a safe and reproducible manner.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chas.1c00051>.

Additional notes regarding etching, washing, and delamination of MXenes to achieve high-quality material; and images of each step of the etching, washing, and delamination of $\text{Ti}_3\text{C}_2\text{T}_x$ using LiCl ([PDF](#))

Safety data sheet (SDS) of $\text{Ti}_3\text{C}_2\text{T}_x$ ([PDF](#))

Video S1: how to properly set up MXene etching ([MP4](#))

Video S2: how to wash the MXene after etching ([MP4](#))

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Notes

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