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Industrial & Engineering Chemistry Research

Article

Cite This: Ind. Eng. Chem. Res. 2019, 58, 1570−1579

pubs.acs.org/IECR

Process Safety Analysis for $Ti_3C_2T_x$ MXene Synthesis and Processing

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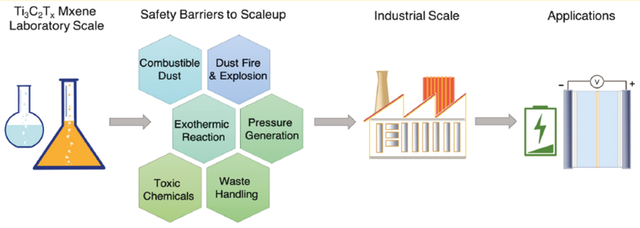
Supporting Information



ABSTRACT: MXenes are two-dimensional metal carbides with promising applications in energy storage and sensors. Guidelines for safe, scalable MXene synthesis are important due to ongoing efforts to scale-up production of these novel nanomaterials. Hazard identification before scale-up will allow for inherently safer designs prior to actual implementation. Here, we investigate hazards associated with MXene production, including MAX phase synthesis from raw materials, etching of the MAX phase to MXene clay, exfoliation to MXene nanosheets, and postprocessing of MXenes with $Ti_3C_2T_x$ as a model species. The major hazards in MXene synthesis are the potential for dust ignition, runaway reactions, and toxic chemical exposure. Because the synthesis of MXenes is a multistep process, safety guidelines for each step are evaluated, including preventive and mitigating measures, best practices, and emergency procedures and responses. This includes handling of combustible powders, exothermic reactions, and harsh chemical etchants. This study is intended to facilitate safer MXene synthesis across various levels of scale-up, from large laboratory batches to commercial production.

1. INTRODUCTION

Nanomaterials are unique because they often present safety hazards in both synthesis and health. Over the last several decades, a number of studies on biological and health hazards of nanomaterials have been published, and these studies are crucial in understanding the effects of nanomaterials on humans and the environment.[1,2] Despite these recent advances, there is a stark absence of research assessing the process safety of nanomaterials synthesis and scale-up. The number of novel nanomaterials synthesized by researchers and small-scale manufacturing companies is increasing; thus, an intimate understanding of the process safety implications during laboratory synthesis and its scale-up is vital for faster and safer implementation of nanomaterials. A number of process safety incidents have occurred during scale-up, including several incidents in laboratories because of a lack of proper hazard identification.[3] For example, in 2010, a graduate student was injured when trying to scale-up a conventional process involving hydrazine perchlorate derivatives synthesis from 300 mg to 10 g.[4]

One of the primary causes of safety incidents in laboratories is a lack of knowledge of safety issues arising during the synthesis route; this is especially true in cases of new materials synthesis and novel processes where the hazards of the reactions are yet to be discovered. While most universities and research laboratories rightfully require researchers to conduct a safety analysis to identify and address potential hazards, these analyses cannot be thorough if the crucial information such as heat and gas generation rate by reaction, byproduct formation, thermal stability, etc. are lacking. This crucial information is not immediately known for novel process development in the laboratory. In addition, the guidance for completing a thorough hazard assessment is often unavailable as the scientific community only recently adopted the concepts of process safety by the means of loss prevention. As a result of these reasons, scaling up novel processes for nanomaterials synthesis can result in catastrophic incidents as hazards can compound if not done correctly. This work is intended to highlight the importance of preventive measures in order to reduce the number and severity of incidents associated with the synthesis and scale-up.

MXenes are a growing family of atomically layered two-dimensional metal carbides and nitrides with the chemical formula $M_{n+1}X_nT_x$, where M is an early transitional metal in the periodic table, X is carbon or nitrogen, and T is a combination of several terminal groups (i.e., −F, −OH, −O, −Cl, etc.). These materials are most frequently etched from $M_{n+1}AX_n$ (MAX) phase powders, which contain post-transition groups 13−15 in the metal layer that are located between M and X layers in their crystal structure. Two-dimensional carbides can have tremendous applications as MXenes have impressive thermal and electrical conductivities. MXenes are currently being evaluated for use in lithium and nonlithium ion energy storage, fuel cell additives, supercapacitors, humidity and pH sensors, and lubricating additives.[5,6] To date, over 60 MAX

Received: November 1, 2018
Revised: January 2, 2019
Accepted: January 4, 2019
Published: January 4, 2019

DOI: 10.1021/acs.iecr.8b05416
Ind. Eng. Chem. Res. 2019, 58, 1570−1579

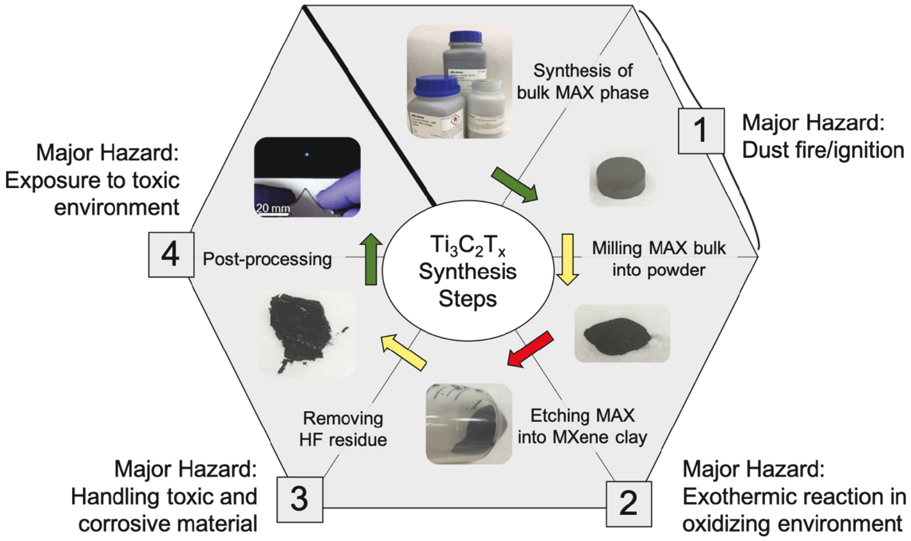


Figure 1. Schematic of $Ti_3C_2T_x$ synthesis from raw materials. Step 1 represents the synthesis and the milling processes of the Ti_3AlC_2 phase, Step 2 is the etching of Al from the Ti_3AlC_2 phase using a strong oxidizing agent such as HF, step 3 is the oxidizing agent (HF) washing, and step 4 is the drying and postprocessing.

phases have been synthesized, plus over 80 MAX phase solid solutions (where the M and/or X layers contain multiple constituents). These "parent materials" can be used to synthesize MXenes via etching, but this etching step typically requires a harsh environment. One frequently used method uses a highly concentrated hydrofluoric acid to dissolve the M−A bonds, releasing heat and hydrogen gas as byproduct. Although it is a relatively recent field, MXenes are a rapidly growing family of materials, and new compositions must often be accompanied by new etching techniques.[7] The etching step is a unique requirement of MXene synthesis compared to that of many other nanomaterials, and each type of MXene may require a slightly different etching procedure.

$Ti_3C_2T_x$ is the best characterized and most studied MXene species because of its relative ease of intercalation and delamination, relatively low financial cost, and excellent conductive properties.[5,8] There is a growing interest in scaling up $Ti_3C_2T_x$ production; in fact, at present, $Ti_3C_2T_x$ is being produced in quantities of 100 g per batch scale.[9] Several publications, including a recent review paper, have neatly outlined various $Ti_3C_2T_x$ synthesis routes and their advantages and disadvantages in terms of product quality.[7,10] However, the process safety analyses associated with different synthesis routes are nowhere to be seen, despite of the serious hazards present in MXene production. $Ti_3C_2T_x$ synthesis is a multistep process that includes handling of combustible powders like aluminum and titanium carbide or graphite to synthesize the Ti_3AlC_2 MAX phase, followed by highly exothermic chemical etching of the Ti_3AlC_2 phase into the desired $Ti_3C_2T_x$ using a strong oxidizing agent. The general, step-by-step synthesis of Ti_3AlC_2 and $Ti_3C_2T_x$ materials from raw materials is depicted schematically in Figure 1 along with the major hazard associated with each step.

In this paper, we identify and discuss hazards in each of these steps for $Ti_3C_2T_x$ synthesis, labeled 1 through 4 in Figure 1. The focus of this paper is to address hazards in small-scale synthesis (grams of $Ti_3C_2T_x$) and consider the implications for scale-up to kilogram quantities. As the scale of $Ti_3C_2T_x$ synthesis increases, a rigorous evaluation is necessary, and we anticipate that this paper will provide a guide on conducting such hazard identification studies for the future. A similar approach can be taken to assess the hazards of other nanomaterials in the MXene family. This paper focuses on the hazards encountered with $Ti_3C_2T_x$, including handling of constituent MAX phase powders, MAX phase synthesis, various etching methods for synthesizing MXenes, and postprocessing methods of exfoliation and optional delamination.

2. METHODOLOGY: THE SAFETY TRIAD: PREVENTION, MITIGATION, RESPONSE

A strong safety program in a laboratory or industry should contain all elements of a robust "safety triad": prevention, mitigation, and response.[11] In addressing safety events, the first priority is to prevent the undesirable events such as spill, fire, explosion, etc. In order to implement preventive measures to avoid such safety incidents, hazards in a process have to be identified throughout the process, for example, identifying synthesis steps with the presence of combustible dust, potential for runaway reaction, toxic gas formation, and others. Only after identification can prevention measures be implemented. If the preventive measures fail and an undesirable event (spill, fire, explosion) occurs, mitigating systems should be employed to minimize the outcome of the undesirable event. Finally, effective response mechanisms need to be planned to minimize the consequence of an undesirable incident.[12,13] The above sequence of considerations is very important to implement in early stages of process development to avoid safety incidents as an incident can have catastrophic effects. The importance of process safety is often undervalued as it has traditionally been seen as an "add-on" component after completion of the process design. However, the inclusion of process safety in the design stage is proven to result in an inherently safer, simpler, and more economical method.[14,15] This paper will discuss the safety triad in the safer synthesis of $Ti_3C_2T_x$ as and when applicable.

2.1. Preventive Measures. Identification of hazards is the first step in applying preventive measures, typically begun by reviewing the safety data sheets (SDS) of each chemical involved in the process; this identifies key hazardous chemicals

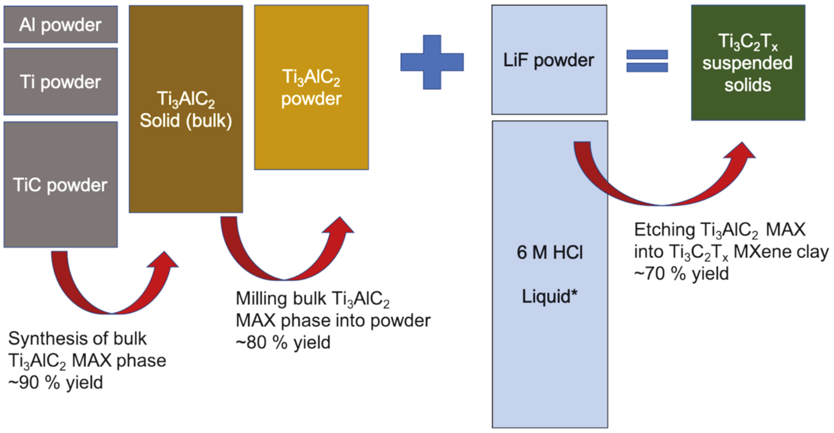


Figure 2. Relative quantities (by mass) of reactant materials required to produce $Ti_3C_2T_x$ MXene. *The quantity of 6 M HCl required is 6 times the amount shown in the figure.

and dangerous situations to avoid. However, the SDS information may not be sufficient because it may not contain all the hazard information, particularly for novel materials such as MXene nanosheets. Instead, the chemical structure, previous incidents with analogous materials, and methodical hazard identification tests should be considered in addition to consulting an SDS. In the next step, the process conditions need to be evaluated, such as heat of reaction, pressure generation rates, temperature range, toxic or instable by-product formation, and thermal stability of materials involved. Once known, these parameters can be managed through several prevention methods.[12]

There are four unique types of hazards preventive measures that can be employed to manage the hazards discussed above: (i) inherently safer designs, (ii) engineering controls, (iii) administrative controls, and (iv) personal protective equipment. These preventive measures are listed in order of decreasing effectiveness. The most effective is the inherently safer design (ISD), and the elements of ISD are to minimize hazards, substitute hazardous materials with less hazardous materials, moderate the amount of hazardous material, and simplify the process. These ISD elements should be utilized whenever possible, but they are more effective when they is employed in the design stage of process development.[16]

In processes requiring use of hazardous materials and operation, engineering controls such as physical protection, a detection system, controllers, and safety interlocks should be implemented. In a laboratory setting, implementing ISD or engineering controls can be quite challenging; therefore, administrative controls such as supervision, proper training, best available work practices, manuals, and procedures should be prioritized. Finally, the use of proper personal protective equipment is the last line of defense should a safety incident occur.

2.2. Mitigation Measures, Emergency Planning, and Response. The main goal of implementing mitigating measures is to reduce the impact of undesirable events that cannot be prevented. Some of the mitigating measures that can be implemented in laboratories are training, familiarization with the surroundings, placement of hood, sensors and alarm systems, and evacuation plans. Automation of the most hazardous steps or maintaining supervision of the operators is key in avoiding safety accidents from occurring.

Finally, emergency response plans are paramount when any significant hazards are present, and these plans must be established before the experiments are carried out. Planning is especially important in scaling up $Ti_3C_2T_x$ synthesis, as hazards such as metal fires and toxic gas release can escalate quickly. The emergency plans should include communicating the hazards and risks present in every step of the process with individuals working directly or indirectly in the facility, access to emergency response personnel, and repair and recovery plans.

3. HAZARDS ANALYSIS OF $Ti_3C_2T_X$ MXENE SYNTHESIS

In this section, each step outlined in Figure 1 is discussed, and as a basis for the study, a laboratory production of $Ti_3C_2T_x$ MXene is investigated. Figure 2 shows relative quantities of material by mass of reactant materials used in the most common $Ti_3C_2T_x$ synthesis route. As seen in Figure 2, significant quantities of raw materials are required to get the final product. The yields below each step are generous estimates, and so, significantly less MXene clay may be produced depending on the available equipment. An optimization of each step to increase the yield will decrease the amount of hazardous materials required on-site for handling. The analysis for each synthesis step is shown in following subsections.

3.1. Hazards Analysis for Ti_3AlC_2 MAX Synthesis. To date, parent MAX phases have been synthesized by nearly a dozen routes, including most notably hot isostatic pressing (HIP), self-propagating high-temperature synthesis (SHS), pulsed electric current sintering (PECS, commonly known as spark plasma sintering SPS), and pressureless sintering.[17] Oxidation of the sample is the primary concern for high-temperature methods such as pressureless sintering, so synthesis should be performed in an inert atmosphere. Pressureless sintering is the most promising technique for commercial scale-up because the process is relatively rapid when compared to other synthesis techniques. However, pressureless sintering is a batch process, and batch processes are inherently not safer because increasing the batch size increases the inventory of hazardous raw materials on-site.[18] An alternative to the current batch process should be studied for safer scale-up. Regardless of the synthesis method selected, powder-handling hazards are the first concerns to address.

For most Ti_3AlC_2 MAX phase synthesis methods, powders of titanium (Ti), aluminum (Al), and titanium carbide (TiC)

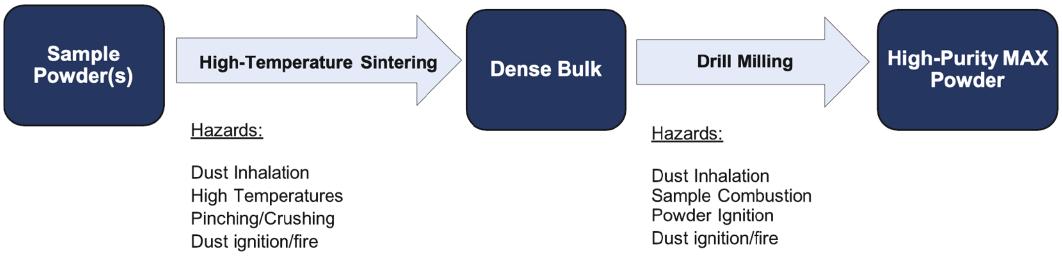


Figure 3. Schematic of MAX, Ti_3AlC_2 phase synthesis, and hazards associated with the steps.

or graphite (C) are thoroughly mixed. These constituent powders present ignition and/or explosion hazards. Fine powders have higher dispersibility and chemical activities, thus increasing the dust explosion risk.[19] The Chemical Safety Board (CSB) recorded 281 dust and explosions incidents in the United States between 1980 and 2005, of which approximately 20% are due to combustible metals dust.[20,21] Specifically, one of the most highly combustible metals is aluminum powder, followed by titanium powder. The inherently safer methods of powder and dust handling are well-known. However, the respective hazard is often not considered, and the appropriate measures are not taken.

The minimum ignition energy (MIE, a measure of the ease of ignition of a suspended dust cloud) for Ti powder of average particle size of 45 μm is 21.91 mJ, but the MIE decreases as the particle size of the powder decreases. Thus, nanoscale Ti powder is more prone to ignition by friction or collision.[22] Finer particle size, though more dangerous, facilitates a higher degree of mixing and generally results in a more phase-pure bulk sample. Thus, a compromise must be made between an inherently safer, larger particle size and purity of the parent Ti_3AlC_2 phase. Significant dust explosion hazards may be present with TiC and C as well, but these systems are not well-studied, and so, their dust explosion parameters (like MIE) have not been reported to date. Consequently, given the numerous potential applicants for MXene, research on these compounds is imperative before scaling up.

In pressureless sintering routes, the mixed reactant powders are placed in a furnace to prepare a porous bulk MAX phase, as shown in Figure 3. Furnace work contains hazards such as potential exposure to high-temperature elements, dust ignition, and, if hoses and fittings are not properly maintained, pressure build-up. To prevent oxidation, the furnace chamber should be an inert atmosphere such as argon. Depending on the synthesis temperature and constituents, some more volatile elements (including aluminum) may evaporate, clogging the inert gas exhaust tube. Furnaces (and inlet/outlet tubing) should be regularly cleaned to maintain an open pathway. Some synthesis methods may contain high-temperature hazards, as in the cases of self-propagating high-temperature synthesis (SHS), pulsed electric current sintering (PECS), hot pressing, and solid-state combustion synthesis (SCS).[23−25] In these synthesis techniques, high temperatures can lead to constituent melting and leaking, so control of the heating rate is critical. Rapid heating rates in SHS and SCS can lead runaway reactions, therefore emergency fire systems, including Class D fire extinguishers, should be accessible at all times. Other methods may contain chemical and/or high-voltage hazards, as in the cases of physical vapor deposition (PVD), chemical vapor deposition (CVD), and PECS.[17,26] In all instances, operators should avoid static buildup and other ignition sources, properly cool and vent the reaction chamber before opening, and wear proper personal protective equipment (PPE).

After removal of this porous bulk material from the furnace, the sample is usually milled into powder to increase the etching rate. There are many different methods of milling, including low- or high-energy ball milling, jet milling, drill milling, and mortar and pestle to name a few.[27,28] Mill selection is crucial to the safety of the MAX phase process, as Ti-based compounds may heat and deform, even igniting the generated fine powders in extreme situations. It is also important to consider dust dispersion to the environment. Dust fires and explosions are usually caused by dust, which has knowingly or unknowingly been dispersed to the surroundings from the process area. Figure 4a shows an example of powder ignition during drill milling of a $Ti_3(AlBi)C_2$ MAX phase in the laboratory. This combustion was facilitated by the low purity of the MAX phase and presence of flammable intermetallic impurities. Though ignition of sample powders is a rare occurrence, it is important to note fires caused by Ti-based compounds cannot be extinguished using water or CO_2-based extinguishing agents (indeed, these may cause the fire to propagate more quickly). Instead, only a Class D fire extinguisher should be used to fight metal fires.

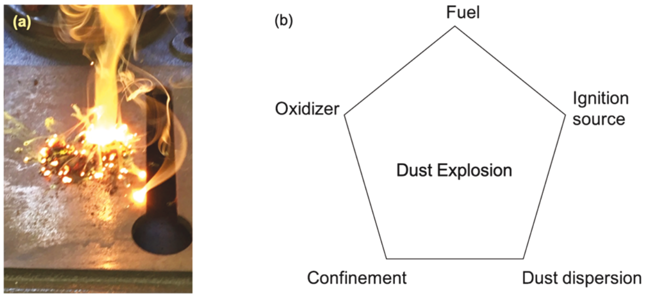


Figure 4. (a) Fire caused by drill milling of $Ti_3(AlBi)C_2$ phase. (b) Schematic representing elements of dust explosion pentagon.

Generally speaking, for a dust explosion to occur, five elements need to be present: a fuel (combustible dust), an oxidizer (oxygen in air), an ignition source, confinement, and dust dispersion (shown in Figure 4b).[29] The dust explosion hazard can be minimized by eliminating one or more of the elements in the pentagon, such as (a) preventing suspension of powder in the air, (b) eliminating all possible ignition sources, and (c) handling all powders in inert environments. In addition to these precautions, wearing proper PPE and equipping the user with firefighting techniques are mandatory.[30] The following preventive measures are recommended as applications of these principles to eliminate one or more elements of the dust explosion pentagon when preparing MAX phase powder for etching into MXenes.

Table 1. Hazards of Ti_3AlC_2 MAX Phase Synthesis

hazard	cause	major effects	corrective/preventive measures in a laboratory scale
spontaneous combustion of reactants	autoignition or introduction of ignition source (static)	potential equipment damage and employee injury	ground the container and minimize dust cloud formation
dust particle inhalation	handling powder reactants	employee injury	work in hood, limit the quantity of toxic reactant, and use proper PPE
combustion of Ti_3AlC_2 phase during drilling	aerosolization of powder during drilling and friction	fire and injury	ground the equipment, drill slowly in inert environment
explosion of ignited sample	extinguishing Al powder using water	fire and injury	use only a Class D fire extinguisher

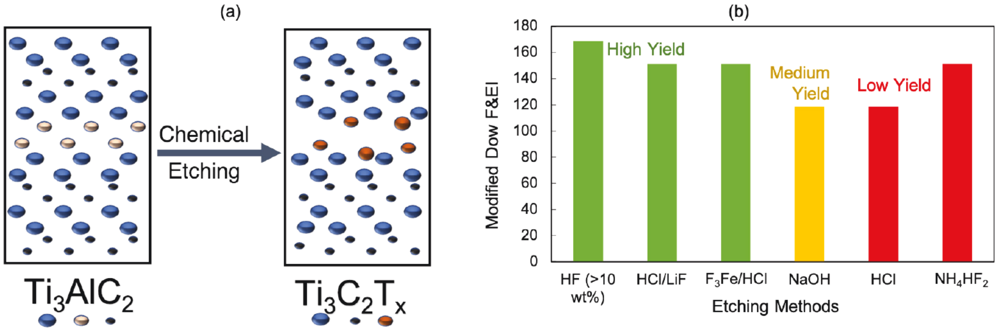


Figure 5. (a) Schematic of Ti_3AlC_2 MAX phase etched to $Ti_3C_2T_x$ MXene. (b) Relative hazards of various etchants used to etch Al from Ti_3AlC_2 phase to $Ti_3C_2T_x$ phase; methods using HF,[32,33] HCl/LiF,[34] and F_3Fe/HCl[36] have a high yield (>55%, green bars), NaOH[37] has a medium yield ($15 < x < 55\%$, orange bars), and HCl[38] and NH_4HF_2[35] have a low yield (less than 15%, red bars), as described by many authors, including Ghidiu et al.[34]

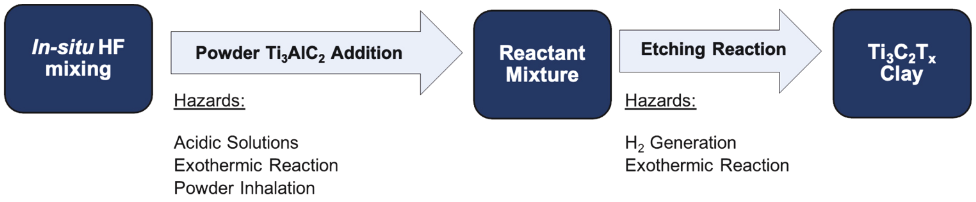


Figure 6. Schematic of $Ti_3C_2T_x$ MXene synthesis using LiF/HCl etchant and the hazards associated with these steps.

To mitigate the risk of ignition, high-energy milling should only be performed on samples with a lubricating solvent and under an inert atmosphere. All electrical equipment should be grounded to prevent any ignition due to static discharge both during and after milling. Dust dispersion to the environment should be prevented, or the accumulation dust should be thoroughly removed. Once a sufficiently fine and pure powder has been obtained, the MXene synthesis can begin. However, on an industrial scale, it is difficult to mitigate all static sources or prevent dust accumulation. The titanium industry, which deals with highly flammable dust particles, has incorporated alternative safer designs, and this could be a starting point for design safer large-scale MAX drilling processes.[31]

The hazards present in Ti_3AlC_2 synthesis and processing are summarized in Table 1 along with causes, major effects, and corrective and/or preventive actions. Some causes listed in this table and subsequent tables such as leaks or loss of controls cannot be avoided all of the time in all the equipment. Therefore, during scaling up, processes should be designed such that they do not depend heavily on equipment controls or instrumentations. Although controls and instrumentation can be a layer to prevent negative incidents, the key to safer processes is to make the processes inherently safer at the design stage.

3.2. Hazards Analysis for Ti_3AlC_2 MAX Phase Etching Process. MXenes are produced by etching the A layer from the powdered MAX phase, as shown in Figure 5a. In the most typical case of Ti_3AlC_2, the Al layer is removed by using an aqueous solution of hydrogen fluoride (HF), which can be introduced at varying concentrations or produced in situ from a fluoride-based compound and an acid, such as LiF and HCl, respectively. The etching reaction is highly exothermic and produces H_2 gas and H_2O vapor. This section investigates the process safety issues with this step, especially the reaction exotherm and byproducts formation.

A total of seven $Ti_3C_2T_x$ etching routes were identified, and their relative hazards were ranked. These seven methods include $Ti_3C_2T_x$ synthesis using 10 wt % HF or higher[32,33] and in situ mixing of LiF and HCl to form HF,[34] NH_4HF_2,[35] F_3Fe/HCl,[36] NaOH,[37] and HCl.[38] The Dow Fire and Explosion Index was used to rank the relative hazard level of each method.[39] Details on conditions and assumptions used to develop the index for each process are provided in the Supporting Information (SI). As seen in Figure 5b, the synthesis route using 10 wt % or higher HF is the most hazardous, and the routes using in situ production of HF using LiF and HCl, F_3Fe, and HCl are relatively less hazardous. Etching with HCl and NaOH is the least hazardous. However, it is important to note the quality and yield of $Ti_3C_2T_x$ produced varies significantly between these methods. There is no standard method to report the yield of $Ti_3C_2T_x$; nevertheless, in this paper, the yield from each synthesis route

DOI: 10.1021/acs.iecr.8b05416
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is estimated using experimental masses and final concentrations reported, but the terminal group compositions and final volumes were assumed using previously reported XPS results of similar etching methods and yield images. The yields were categorized relative to each other as high (>55%), medium (15 to 55%), or low (<15%). The synthesis routes using HF and in situ HF (i.e., HCl/LiF, and F_3Fe/HCl) have the highest yields, methods using NaOH have medium yields, and methods using HCl and NH_4NF_3 have the lowest comparative yields.

The most common method of $Ti_3C_2T_x$ synthesis from Ti_3AlC_2 is via HCl and LiF as this method retains a high yield of MXenes and minimizes handling of HF during the etching process. However, it should be noted that HF is still present in the reaction as a byproduct in this method, and HF hazards are discussed in subsequent section. The process is summarized in Figure 6, where 6 M HCl solution is charged in a Teflon reactor with a 5 M equivalent of LiF, and powdered Ti_3AlC_2 phase is added to the solution slowly to minimize bubbling of the reaction (this procedure is described by many authors, including Ghidiu et al.).[34] This reaction is exothermic, and Sharma et al. determined the heat of reaction (ΔH_{rxn}) from the Ti_3AlC_2 phase to $Ti_3C_2T_x$ using a calorimeter.[40] The study reported ΔH_{rxn} to be −1775 kJ/mol of Ti_3AlC_2 (equivalent to −9.12 kJ/g of Ti_3AlC_2) phase. On the basis of this reaction enthalpy, if all of the Ti_3AlC_2 MAX phase is added to the reaction mixture at once, the adiabatic temperature increase is estimated at 270 °C of the solution. This temperature increase was estimated using eq 1, where m is the mass of a small industrial-scale reaction mixture (500 g of Ti_3AlC_2 phase) using the HCl/LiF in situ method. The heat capacity of solution, C_p, used for calculation is same as that of 37 wt % HCl (2.46 kJ·K/kg) because in a typical synthesis around 86 wt % of the reaction mass is HCl solution, and $\Delta T_{(ad)}$ is the adiabatic temperature increase.

$$\Delta H = mC_p\Delta T \tag{1}$$

The $\Delta T_{(ad)}$ is beyond the boiling point of HF solution, which is between 98 °C (for 5 wt % HF) and 110 °C (for 50 wt % HF). If the reaction is carried out at room temperature (around 23 °C), the $\Delta T_{(ad)}$ is sufficient to trigger violent boiling off of the reaction mixture, releasing HF vapor into the environment. To avoid uncontrollable temperature increases during the etching step, the feed rate of the Ti_3AlC_2 MAX phase into the reaction mixture and the cooling capacity will be critical. This is especially true when scaling up this reaction as increasing the scale of reaction will likely decrease the reactor surface-area-to-volume ratio, thereby reducing the heat of reaction dissipation. In the case of uncontrollable temperature increase, the use of overhead condenser to cool vapor can also help mitigate release of hazardous vapor into the environment. The condenser should be appropriately sized and designed based on the scale of the reactor mass and volume. An additional hazards analysis, including a detailed kinetics analysis to understand the reaction pathways, is necessary if the presented $Ti_3C_2T_x$ synthesis method is to be scaled up.

Additionally, the etching reaction produces H_2 gas and water vapor as the byproduct. The etching reaction can be described by the following reaction pathway[41]

$$Ti_3AlC_2 + 3HF \rightarrow AlF_3 + Ti_3C_2 + \frac{3}{2}H_2$$

$$Ti_3C_2 + 2H_2O \rightarrow Ti_3C_2(OH)_2 + H_2$$

$$Ti_3C_2 + 2HF \rightarrow Ti_3C_2F_2 + H_2$$

The etching reaction produces 3.5 moles of H_2 for every mole of Ti_3AlC_2. To accommodate the generated pressure, the reaction is performed in vented containers. Figure 7 shows the estimated pressure generated by the reaction for a known container volume in an isothermal condition. It should be noted that the gas generated (H_2) is highly flammable at 4 to 75 vol %, and a static spark is enough to ignite the gas in these conditions.[42] Moreover, hydrogen gas is the one of lightest gases, making it easy to escape into the surrounding environment unknowingly. Hydrogen gas burns with an invisible flame, and an incident involving hydrogen gas can propagate quickly. Therefore, special care should be taken to vent the H_2 gas produced. The rate of H_2 production during the etching process has not been measured at the lab scale, but this will be critical during any sort of scale-up, both for safety and for emissions purposes. Table 2 shows the hazards in the etching step along with recommended corrective and preventive measures in a laboratory scale. As mentioned in the Introduction of the paper, there are a number of ways MXenes can be synthesized. This paper focuses on the hazard analysis technique for one synthesis method in detail. A similar approach can be taken to conduct hazard analyses for other synthesis routes to design safer MXene operating procedures.

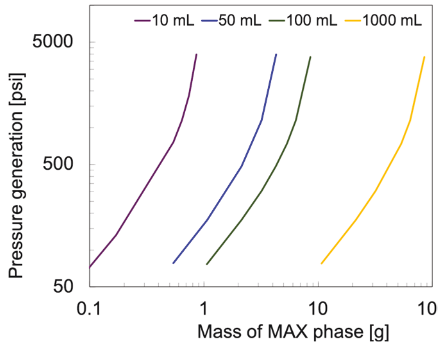

Figure 7. Estimated pressure generation during etching process for various container sizes assuming isothermal conditions. The etching reaction should be carried out in a vented container to relieve pressure buildup and to contain the reaction products.

3.3. Hazards Analysis for Postprocessing $Ti_3C_2T_x$ MXenes.

The $Ti_3C_2T_x$ product slurry obtained after etching is washed with DI water in a filtration unit (or in a centrifugation unit) to remove unreacted HF and water-soluble salts. The washing with DI water is repeated until the pH of the solution is at least 6 to mitigate risk during handling. This bulk product is labeled as $Ti_3C_2T_x$ clay, and there are several postprocessing techniques for $Ti_3C_2T_x$ clay discussed in prior literature.[10] The postprocessing includes delamination to yield MXene nanosheets and further processing for an application. The selection of postprocessing techniques depends on the applications of $Ti_3C_2T_x$. Some methods can involve direct handling of the undelaminated $Ti_3C_2T_x$ clay, such as paint coating.[34] $Ti_3C_2T_x$ can be freeze-dried for long-term oxidation-free storage,[43] spray-dried to "crumple" the morphology, thereby increasing the surface area,[44] or vacuum-dried to create free-standing $Ti_3C_2T_x$ films. Figure 8 shows different forms of $Ti_3C_2T_x$ used in various applications.

Table 2. Hazards of Etching Process

hazard	cause	major effects	corrective/preventive measures in a laboratory scale
exothermic reaction	rapid addition of Ti_3AlC_2 to HF solution	HF gas, H_2 gas, equipment damage	slow addition of Ti_3AlC_2 to limit the temperature increase, adequate cooling capacity
toxic gas release (H_2)	loss of etching reaction controls	flammable environment	the reaction should be conducted in a negative pressure hood with good ventilation
HF exposure	outlined in next section		

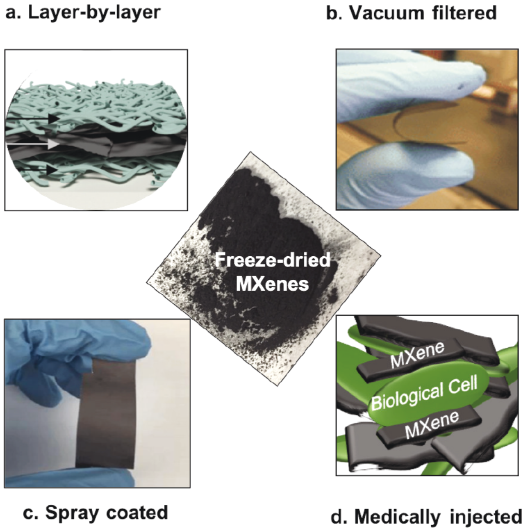

Figure 8. Reproduction of images showing $Ti_3C_2T_x$ processed for current applications. (a) Layer-by-layer (for wearable electronics),[6] reproduced with permission from reference #6, copyright 2018, AAAS. (b) Vacuum-filtered (for free-standing films and polymer composites),[10,45,46] reproduced with permission from reference #46. (c) Painted or spray-coated (for thin film coatings),[10,47] reproduced with permission from reference #47, copyright 2018, AAAS. (d) Medically injected (as antibiotics, drug delivery, and cancer therapy),[48−50] reproduced with permission from reference #48, copyright 2016, ACS.

Delamination of the accordion-like clay yields MXene nanosheets, which are currently the most used form of MXenes. Specifically, $Ti_3C_2T_x$ can be delaminated into a thick colloidal suspension of nanosheets then assembled layer-by-layer into flexible biometric sensors.[5,6] This thick colloidal suspension can also be diluted and mixed with additives (such as platinum nanoparticles) and used in dip and evaporative coatings.[51] The most popular method of delamination is intercalation with dimethyl sulfoxide (DMSO) followed by sonication after exfoliation as this method is relatively quick and can be varied to produce nanosheets of different sizes.[34,52−54] Other wet chemical etchants include urea,[52] tetrabutylammonium hydroxide (TBAOH), choline hydroxide, and *n*-butylamine[55] for MXene delamination.

The solvents used for both exfoliation and delamination are vital in selecting the composition of terminal groups of the MXenes,[56] but of more direct pertinence to this paper are the safety concerns associated with each solvent. DMSO and urea are the safest chemical solvents to implement, with the primary hazard associated with both being irritation from inhalation, ingestion, or eye contact. Possible absorption through skin is a special safety concern, particularly for DMSO, as all of these solvents may bring nanoparticles or other chemical constituents with them. MXenes have not had a long-term biological impact study performed, so operators should avoid contact with skin. Harsher solvents like TBAOH, choline hydroxide, and *n*-butylamine cause severe burns when exposed to skin or eyes. Further, all of these harsher solvents, especially *n*-butylamine, can prove fatal if inhaled. All chemical solvents listed range from slightly to highly flammable, and so, exposure to electrical sparks or other ignition sources should be carefully avoided. Moreover, disposal hazards should also be considered.

Inadequate washing of $Ti_3C_2T_x$ solution can expose researchers and lab equipment to HF during the postprocessing steps. Furthermore, F^- ions can propagate in the final product such as paints, powder, and films. Precautions should be taken when handling any nanomaterials, especially in powder form as fine powder can disperse in the environment without detection. Several in vivo and ecotoxicological studies have shown noncytotoxic behavior of several MXenes, including $Ti_3C_2T_x$, but a long-term systematic analysis is still needed. MXenes are a promising chemosynergistic and photothermal conversion material for cancer treatment, but control of the terminal groups and complete removal of −F ions is paramount. Despite these promising findings, biological interactions of MXenes are still not yet fully known.[57−60]

3.4. Hazards Analysis for HF Handling and Removal.

The medium- and high-yield MXene methods are obtained by etching via HF, either from stock solution or produced in situ. As a result of the relatively common usage of HF, it is important to look at its hazards individually. HF is an extremely corrosive chemical, able to penetrate through skin, muscle tissue, and bones. In the presence of naturally occurring cations in the human body (such as calcium and magnesium), HF dissociates into hydrogen ion and fluoride ion. These ions can cause harm in two ways: (1) corrosive burns due to hydrogen ions and (2) chemical burns in skin and bone because of fluoride ions.[61] More importantly, these ions can affect the biological distribution of electrolytes, causing death.[62] For example, in 1994, a lab technician died due to fluoride poisoning when he spilled 100 mL of 70 wt % HF.[63] The spill covered about 10% of his body. At least 20 incidents of HF exposure have occurred since 1998.[64]

HF must be securely contained, which can pose a major challenge due to its corrosive nature. HF corrodes common materials of construction for laboratory equipment such as stainless steel and glass. Few materials are compatible with HF: for laboratory purposes, PTFE (or Teflon) is known to be the most resistant to HF, followed by HDPE (high-density polyethylene).

The primary sources of HF exposure during $Ti_3C_2T_x$ synthesis are during the etching reaction itself and the transfer of the HF solution during washing. According to ISD principles, there is a present need to find a high-yield etching method without using HF. However, to mitigate exposure to HF using current methods, time spent adding and removing HF solution should be minimized or automated. During direct handling, proper personal protection equipment (PPE) is vital. The recommended PPE to handle HF solutions is neoprene gloves, an acid-resistant face shield, a full-body acid-resistant suit, and leather boots. In case of HF exposure, it is important

Table 3. Hazards with HF Handling and Removal

hazard	cause	major effects	corrective/preventive measures in a laboratory scale
HF exposure (in solution or fume)	improper handling of HF solution during transfer	exposure to HF can lead to serious injury or death	proper PPE (HF-rated gloves, facemask, full sleeve clothing)
	improper handling of HF waste		easy access to calcium gluconate ointment near work area in case of HF exposure
	failure of reaction or storage container	exposure to human	use HF compatible containers and sealant, use secondary container

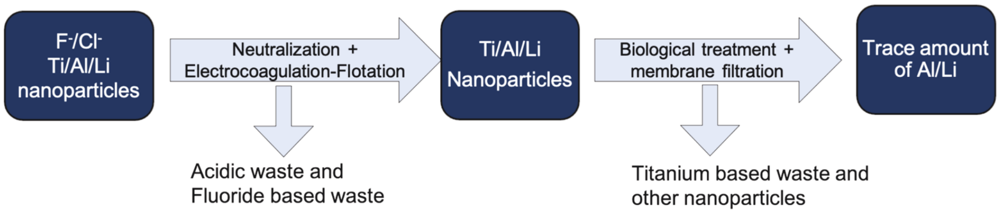

Figure 9. Schematic showing wastewater treatment technology from $Ti_3C_2T_x$ MXene synthesis.

to neutralize the fluoride ions with calcium or magnesium ions: application of a 10 wt % calcium gluconate solution is recommended in the exposed area. Best laboratory practices should also be followed to avoid and minimize HF exposure. Table 3 summarizes the hazards with HF, including the recommended corrective and preventive measures.

Inhalation of HF vapor can also cause harm to human health. HF inhalation could be a result of exposure to HF solution (>50 wt %), exposure in a confined space, or exposure through contaminated clothing. According to the EPA, the 15 min STEL (short-term exposure limit) for HF vapors is 6.0 ppm for 15 min, and OSHA regulates the 8 h TWA (time-weighted average) to 3 ppm.[65] At concentrations of 30 ppm, it is considered immediately dangerous to life and health (IDLH).[66] To adhere to the OSHA and the EPA standards, the $Ti_3C_2T_x$ solution needs to be washed to pH 6 or higher for safer handling of the solution.

3.5. Waste Treatment. An important aspect of process scale-up is also considering waste disposal. The etching and washing steps in $Ti_3C_2T_x$ produce a considerable amount of waste, though exact quantities of various elements in the waste stream are not known. On the basis of the synthesis scheme, there are three different classes of waste produced during $Ti_3C_2T_x$ synthesis: acidic waste from LiF/HCl (majority), metal waste from Ti and Al, and solid particulate such as C and under or overetched Ti_3AlC_2 particles. Any waste treatment facility would have to be prepared to deal with these three kinds of waste and their associated hazards. Hu et al. proposed that using calcium salt to neutralize acidic water and then using an electrocoagulation−flotation technique where sodium dodecyl sulfate as an anodic surfactant is best to remove fluoride-based waste.[67] Similarly, Westerhoff et al. suggested that Ti-based and nanoparticle waste can be trapped using a biological treatment and then settling and removing using a membrane filtration.[68] A typical amount of Al and Li in the waste stream from the $Ti_3C_2T_x$ etching process is not known, but these metals can be recovered on a larger scale, if necessary. Figure 9 shows a schematic of wastewater treatment scheme, there are three different classes of waste produced during $Ti_3C_2T_x$ MXene synthesis.

4. CONCLUSIONS AND FUTURE OUTLOOK

In conclusion, this study has identified the hazards associated with $Ti_3C_2T_x$ laboratory production and discussed the prevention, mitigation, and emergency response plan. In MAX phase synthesis, most hazards are associated with dust handling, including both reactant and postsynthesis processing. Alternative milling methods could drastically increase safety, though the high hardness of the bulk sample prevents many conventional methods. Additionally, the combustible dust property of the Ti_3AlC_2 MAX phase is not known. Further study is required to understand the probability of and risk associated with dust explosions of Ti_3AlC_2 MAX phase before this process can be scaled up.

Etching the aluminum layer from MAX phase to synthesize $Ti_3C_2T_x$ MXenes is highly exothermic and thus poses a significant hazard even in small batch sizes. If the Ti_3AlC_2 MAX phase is added too quickly, the increase in reaction temperature can cause the reaction to become violent and HF (or other chemical etchant) to boil, resulting in corrosive splashing and increasing the concentration of toxic fumes produced. Mechanism and kinetics are not fully understood for etching MXenes, and thus, many hazards may not be fully addressed. For example, if the etching reaction produces thermally unstable byproducts, the ability to mix and cool the reaction becomes paramount for scaling up to industrial batch sizes. The etching methods with the highest reported yields to date use HF, but an alternative method needs to be explored because HF is extremely toxic and unsafe. However, if HF is selected as the etchant, containment of HF is paramount but challenging as it corrodes most conventional containers, particularly in industry. A detailed worst-case scenario should be considered, and an effective emergency response plan should be in place.

Further, if the $Ti_3C_2T_x$ clay is not properly washed, HF hazards may persist through every step of the postprocess. Finally, more research is required to fully understand the long-term biological impact of MXenes. As suggested by Fadeel et al., an increase in the surface area of a nanostructure, especially with hazardous functional groups such as fluorine, may cause severe inflammation and irritation in and on human tissues.[2]

This study only provides general process safety considerations for the most commonly used MXene. Each application may elicit different synthesis methods, and specific processing steps may be more hazardous than those typical steps described above. Specifically, different compositions (i.e., using a different parent MAX phase) often require different

DOI: 10.1021/acs.iecr.8b05416

etching conditions, which can increase the hazards associated with handling and washing.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b05416.

> Details on development of Dow F&EI and gas generation (PDF)

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■ ACKNOWLEDGMENTS

The authors thank Dr. Wanmei Sun and Smit Alkesh Shah for their valuable input and guidance, Zeyi Tan, Yexiao Chen, and Xaiofei Zhao for their tireless efforts, and Dr. Hyosung An for his encouragement and feedback. The funding was provided by the Mary Kay O'Connor Process Safety Center (MKOPSC) at Texas A&M University, the United States National Science Foundation (Grant CMMI-1760859), and the TAMU Energy Institute.

■ REFERENCES

(1) Guiney, L. M.; Wang, X.; Xia, T.; Nel, A. E.; Hersam, M. C. Assessing and Mitigating the Hazard Potential of Two-Dimensional Materials. *ACS Nano* **2018**, *12*, 6360.

(2) Fadeel, B.; Farcal, L.; Hardy, B.; Vázquez-Campos, S.; Hristozov, D.; Marcomini, A.; Lynch, I.; Valsami-Jones, E.; Alenius, H.; Savolainen, K. Advanced tools for the safety assessment of nanomaterials. *Nat. Nanotechnol.* **2018**, *13*, 537.

(3) American Industrial Hygiene Association. Lessons Learned. https://www.aiha.org/get-involved/VolunteerGroups/LabHSCommittee/Pages/Lessons-Learned.aspx (accessed May 2018).

(4) U.S. Chemical Safety and Hazard Investigation Board. Texas Tech University Chemistry Lab Explosion. https://www.csb.gov/texas-tech-university-chemistry-lab-explosion/ (accessed May 2018).

(5) Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y. 25th anniversary article: MXenes: a new family of two-dimensional materials. *Adv. Mater.* **2014**, *26*, 992−1005.

(6) An, H.; Habib, T.; Shah, S.; Gao, H.; Radovic, M.; Green, M. J.; Lutkenhaus, J. L. Surface-agnostic highly stretchable and bendable conductive MXene multilayers. *Science advances* **2018**, *4*, No. eaaq0118.

(7) Anasori, B.; Lukatskaya, M. R.; Gogotsi, Y. 2D metal carbides and nitrides (MXenes) for energy storage. *Nature Reviews Materials* **2017**, *2*, 16098.

(8) Sinha, A.; Dhanjai; Zhao, H.; Huang, Y.; Lu, X.; Chen, J.; Jain, R. MXene: An emerging material for sensing and biosensing. *TrAC, Trends Anal. Chem.* **2018**, *105*, 424.

(9) Gogotsi, A. Y. Anasori Applications 2D Carbides, Nitrides and Carbonitrides (MXenes) Applications 2D Carbides, Nitrides and Carbonitrides (MXenes). *CIMTEC Conference*, Perugia, Italy, 2018.

(10) Alhabeb, M.; Maleski, K.; Anasori, B.; Lelyukh, P.; Clark, L.; Sin, S.; Gogotsi, Y. Guidelines for Synthesis and Processing of Two-Dimensional Titanium Carbide (Ti3C2T x MXene). *Chem. Mater.* **2017**, *29*, 7633−7644.

(11) Mannan, M. S. Director's Corner. *Centerline - Mary Kay O'Connor Process Safety Center* **2018**, *22*.

(12) Hazard Identification and Evaluation Task Force of the American Chemical Society's Committee on Chemical Safety. *Identifying and Evaluating Hazards in Research Laboratories*; 2015.

(13) Occupational Safety and Health Administration. *Job Hazard Analysis*; OSHA 3071; 2002.

(14) Edwards, D. W.; Lawrence, D. Assessing the inherent safety of chemical process routes: is there a relation between plant costs and inherent safety? *Process Safety and Environmental Protection: Transactions of the Institution of Chemical Engineers* **1993**, *71*, 252−258.

(15) Ade, N.; Liu, G.; Al-Douri, A. F.; El-Halwagi, M. M.; Mannan, M. S. Investigating the effect of inherent safety principles on system reliability in process design. *Process Saf. Environ. Prot.* **2018**, *117*, 100−110.

(16) Kletz, T. A.; Amyotte, P. *Process plants: A handbook for inherently safer design*, 2nd ed.; CRC Press, 2010.

(17) Eklund, P.; Beckers, M.; Jansson, U.; Högberg, H.; Hultman, L. The Mn+ 1AXn phases: Materials science and thin-film processing. *Thin Solid Films* **2010**, *518*, 1851−1878.

(18) Kletz, T. *Plant Design for Safety: A User-Friendly Approach*, 1st ed.; Hemisphere Publishing Corporation: New York, 1990.

(19) Cashdollar, K. L. Overview of dust explosibility characteristics. *J. Loss Prev. Process Ind.* **2000**, *13*, 183−199.

(20) Blair, A. S. Dust explosion incidents and regulations in the United States. *J. Loss Prev. Process Ind.* **2007**, *20*, 523−529.

(21) Occupational Safety and Health Administration. Combustible Dust: An Explosion Hazard. https://www.osha.gov/dsg/combustibledust/index.html (accessed June 2018).

(22) Wu, H.-C.; Chang, R.-C.; Hsiao, H.-C. Research of minimum ignition energy for nano titanium powder and nano iron powder. *J. Loss Prev. Process Ind.* **2009**, *22*, 21−24.

(23) Hendaoui, A.; Andasmas, M.; Amara, A.; Benaldjia, A.; Langlois, P.; Vrel, D. SHS of high-purity MAX compounds in the Ti-Al-C system. *Int. J. Self-Propag. High-Temp. Synth.* **2008**, *17*, 129−135.

(24) Wang, X.; Zhou, Y. Solid−liquid reaction synthesis of layered machinable Ti 3 AlC 2 ceramic. *J. Mater. Chem.* **2002**, *12*, 455−460.

(25) Yeh, C.; Kuo, C.; Chu, Y. Formation of Ti3AlC2/Al2O3 and Ti2AlC/Al2O3 composites by combustion synthesis in Ti−Al−C−TiO2 systems. *J. Alloys Compd.* **2010**, *494*, 132−136.

(26) Högberg, H.; Hultman, L.; Emmerlich, J.; Joelsson, T.; Eklund, P.; Molina-Aldareguia, J. M.; Palmquist, J.-P.; Wilhelmsson, O.; Jansson, U. Growth and characterization of MAX-phase thin films. *Surf. Coat. Technol.* **2005**, *193*, 6−10.

(27) Fecht, H.; Hellstern, E.; Fu, Z.; Johnson, W. Nanocrystalline metals prepared by high-energy ball milling. *Metall. Trans. A* **1990**, *21*, 2333.

(28) Nykamp, G.; Carstensen, U.; Müller, B. Jet milling—a new technique for microparticle preparation. *Int. J. Pharm.* **2002**, *242*, 79−86.

(29) Amyotte, P. R.; Eckhoff, R. K. Dust explosion causation, prevention and mitigation: An overview. *J. Chem. Health Saf.* **2010**, *17*, 15−28.

(30) Benson, J. M. Safety considerations when handling metal powders. *Journal of the South African Institute of Mining and Metallurgy* **2012**, *112*, 563.

(31) Poulsen, E. Safety-related problems in the titanium industry in the last 50 years. *JOM* **2000**, *52*, 13−17.

(32) Lai, S.; Jeon, J.; Jang, S. K.; Xu, J.; Choi, Y. J.; Park, J.-H.; Hwang, E.; Lee, S. Surface group modification and carrier transport properties of layered transition metal carbides (Ti2CTx, T:−OH,−F and−O). *Nanoscale* **2015**, *7*, 19390−19396.

(33) Yoon, Y.; Lee, M.; Kim, S. K.; Bae, G.; Song, W.; Myung, S.; Lim, J.; Lee, S. S.; Zyung, T.; An, K.-S. A Strategy for Synthesis of

Carbon Nitride Induced Chemically Doped 2D MXene for High-Performance Supercapacitor Electrodes. *Adv. Energy Mater.* **2018**, *8*, 1703173.

(34) Ghidiu, M.; Lukatskaya, M. R.; Zhao, M.-Q.; Gogotsi, Y.; Barsoum, M. W. Conductive two-dimensional titanium carbide 'clay'with high volumetric capacitance. *Nature* **2014**, *516*, 78.

(35) Feng, A.; Yu, Y.; Jiang, F.; Wang, Y.; Mi, L.; Yu, Y.; Song, L. Fabrication and thermal stability of NH4HF2-etched Ti3C2MXene. *Ceram. Int.* **2017**, *43*, 6322−6328.

(36) Wang, X.; Garnero, C.; Rochard, G.; Magne, D.; Morisset, S.; Hurand, S.; Chartier, P.; Rousseau, J.; Cabioc'h, T.; Coutanceau, C.; Mauchamp, V.; Celerier, S. A new etching environment (FeF 3/HCl) for the synthesis of two-dimensional titanium carbide MXenes: a route towards selective reactivity vs. water. *J. Mater. Chem. A* **2017**, *5*, 22012−22023.

(37) Li, T.; Yao, L.; Liu, Q.; Gu, J.; Luo, R.; Li, J.; Yan, X.; Wang, W.; Liu, P.; Chen, B.; Zhang, W.; Abbas, W.; Naz, R.; Zhang, D. Fluorine-Free Synthesis of High-Purity Ti3C2Tx (T= OH, O) via Alkali Treatment. *Angew. Chem., Int. Ed.* **2018**, *57*, 6115−6119.

(38) Sun, W.; Shah, S.; Chen, Y.; Tan, Z.; Gao, H.; Habib, T.; Radovic, M.; Green, M. Electrochemical etching of Ti 2 AlC to Ti 2 CT x (MXene) in low-concentration hydrochloric acid solution. *J. Mater. Chem. A* **2017**, *5*, 21663−21668.

(39) Jensen, N. Modifying the Dow Fire & Explosion Index for Use in Assessing Hazard and Risk of Experimental Setups in Research Laboratories. *12th International Symposium on Loss Prevention and Safety Promotion in the Process Industries*, Edinburgh, Scotland, UK, 2007.

(40) Sharma, G.; Naguib, M.; Feng, D.; Gogotsi, Y.; Navrotsky, A. Calorimetric Determination of Thermodynamic Stability of MAX and MXene Phases. *J. Phys. Chem. C* **2016**, *120*, 28131−28137.

(41) Naguib, M.; Mashtalir, O.; Carle, J.; Presser, V.; Lu, J.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-dimensional transition metal carbides. *ACS Nano* **2012**, *6*, 1322−1331.

(42) Mazloomi, K.; Gomes, C. Hydrogen as an energy carrier: prospects and challenges. *Renewable Sustainable Energy Rev.* **2012**, *16*, 3024−3033.

(43) Habib, T.; Shah, S.; Chen, Y.; Sun, W.; An, H.; Lutkenhaus, J.; Radovic, M.; Green, M. Oxidation Stability of Ti3C2Tx (MXene) Nanosheets in Solvents, Films, and Composites. **2018**; Submitted.

(44) Shah, S.; Habib, T.; Gao, H.; Gao, P.; Sun, W.; Green, M.; Radovic, M. Template-free 3D titanium carbide (Ti 3 C 2 T x) MXene particles crumpled by capillary forces. *Chem. Commun.* **2017**, *53*, 400−403.

(45) Zhang, H.; Wang, L.; Chen, Q.; Li, P.; Zhou, A.; Cao, X.; Hu, Q. Preparation, mechanical and anti-friction performance of MXene/polymer composites. *Mater. Des.* **2016**, *92*, 682−689.

(46) Li, C.; Kota, S.; Hu, C.; Barsoum, M. On the Synthesis of Low-Cost, Titanium-Based MXenes. *J. Ceram. Sci. Technol.* **2016**, *7*, 301−306.

(47) Sarycheva, A.; Polemi, A.; Liu, Y.; Dandekar, K.; Anasori, B.; Gogotsi, Y. 2D titanium carbide (MXene) for wireless communication. *Science advances* **2018**, *4*, No. eaau0920.

(48) Rasool, K.; Helal, M.; Ali, A.; Ren, C. E.; Gogotsi, Y.; Mahmoud, K. A. Antibacterial Activity of Ti3C2T x MXene. *ACS Nano* **2016**, *10*, 3674−3684.

(49) Huang, K.; Li, Z.; Lin, J.; Han, G.; Huang, P. Two-dimensional transition metal carbides and nitrides (MXenes) for biomedical applications. *Chem. Soc. Rev.* **2018**, *47*, 5109.

(50) Lin, H.; Wang, X.; Yu, L.; Chen, Y.; Shi, J. Two-dimensional ultrathin MXene ceramic nanosheets for photothermal conversion. *Nano Lett.* **2017**, *17*, 384−391.

(51) Lorencová, L.; Bertok, T.; Filip, J.; Jerigová, M.; Velic, D.; Kasák, P.; Mahmoud, K. A.; Tkac, J. Highly stable Ti3C2Tx (MXene)/Pt nanoparticles-modified glassy carbon electrode for H2O2 and small molecules sensing applications. *Sens. Actuators, B* **2018**, *263*, 360−368.

(52) Mashtalir, O.; Naguib, M.; Mochalin, V. N.; Dall'Agnese, Y.; Heon, M.; Barsoum, M. W.; Gogotsi, Y. Intercalation and delamination of layered carbides and carbonitrides. *Nat. Commun.* **2013**, *4*, 1716.

(53) Lukatskaya, M. R.; Mashtalir, O.; Ren, C. E.; Dall'Agnese, Y.; Rozier, P.; Taberna, P. L.; Naguib, M.; Simon, P.; Barsoum, M. W.; Gogotsi, Y. Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide. *Science* **2013**, *341*, 1502−1505.

(54) Ling, Z.; Ren, C. E.; Zhao, M.-Q.; Yang, J.; Giammarco, J. M.; Qiu, J.; Barsoum, M. W.; Gogotsi, Y. Flexible and conductive MXene films and nanocomposites with high capacitance. *Proc. Natl. Acad. Sci. U. S. A.* **2014**, *111*, 16676−16681.

(55) Naguib, M.; Unocic, R. R.; Armstrong, B. L.; Nanda, J. Large-scale delamination of multi-layers transition metal carbides and carbonitrides "MXenes. *Dalton transactions* **2015**, *44*, 9353−9358.

(56) Dall'Agnese, Y.; Lukatskaya, M. R.; Cook, K. M.; Taberna, P.-L.; Gogotsi, Y.; Simon, P. High capacitance of surface-modified 2D titanium carbide in acidic electrolyte. *Electrochem. Commun.* **2014**, *48*, 118−122.

(57) Jastrzębska, A.; Szuplewska, A.; Wojciechowski, T.; Chudy, M.; Ziemkowska, W.; Chlubny, L.; Rozmysłowska, A.; Olszyna, A. In vitro studies on cytotoxicity of delaminated Ti3C2MXene. *J. Hazard. Mater.* **2017**, *339*, 1−8.

(58) Nasrallah, G. K.; Al-Asmakh, M.; Rasool, K.; Mahmoud, K. A. Ecotoxicological assessment of Ti 3 C 2 T x (MXene) using a zebrafish embryo model. *Environ. Sci.: Nano* **2018**, *5*, 1002−1011.

(59) Yu, X.; Cai, X.; Cui, H.; Lee, S.-W.; Yu, X.-F.; Liu, B. Fluorine-free preparation of titanium carbide MXene quantum dots with high near-infrared photothermal performances for cancer therapy. *Nanoscale* **2017**, *9*, 17859−17864.

(60) Liu, G.; Zou, J.; Tang, Q.; Yang, X.; Zhang, Y.; Zhang, Q.; Huang, W.; Chen, P.; Shao, J.; Dong, X. Surface Modified Ti3C2MXene Nanosheets for Tumor Targeting Photothermal/Photodynamic/Chemo Synergistic Therapy. *ACS Appl. Mater. Interfaces* **2017**, *9*, 40077−40086.

(61) Hatzifotis, M.; Williams, A.; Muller, M.; Pegg, S. Hydrofluoric acid burns. *Burns* **2004**, *30*, 156−159.

(62) McKee, D.; Thoma, A.; Bailey, K.; Fish, J. A review of hydrofluoric acid burn management. *Plastic Surgery* **2014**, *22*, 95−98.

(63) Muriale, L.; Lee, E.; Genovese, J.; Trend, S. Fatality due to acute fluoride poisoning following dermal contact with hydrofluoric acid in a palynology laboratory. *Ann. Occup. Hyg.* **1996**, *40*, 705−710.

(64) Occupational Safety and Health Administration. Accident Search Results. https://www.osha.gov/pls/imis/AccidentSearch.search?acc_keyword= (accessed May 2018).

(65) Occupational Safety and Health Administration. OSHA Annotated Table Z-2. https://www.osha.gov/dsg/annotated-pels/tablez-2.html (accessed December 2018).

(66) Occupational Safety and Health Administration. OSHA Hazard Information Bulletins: Use of Hydrofluoric Acid in the Petroleum Refining Alkylation Process. https://www.osha.gov/dts/hib/hib_data/hib19931119.html (accessed December 2018).

(67) Hu, C.; Lo, S.; Kuan, W.; Lee, Y. Removal of fluoride from semiconductor wastewater by electrocoagulation−flotation. *Water Res.* **2005**, *39*, 895−901.

(68) Westerhoff, P.; Song, G.; Hristovski, K.; Kiser, M. A. Occurrence and removal of titanium at full scale wastewater treatment plants: implications for TiO 2 nanomaterials. *J. Environ. Monit.* **2011**, *13*, 1195−1203.

DOI: 10.1021/acs.iecr.8b05416