Scalable and sustainable production of Ti₃C₂T₂ MXene and fluorine recovery from wastewater through cryolite precipitation

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Treatment of HF or HCl/LiF etched Ti₃C₂T₂ with 0.05 M NaHCO₃ before water washing reduces the wastewater generated by 75%. When etched with HF, cryolite (Na₃AlF₆) precipitation from spent etching waste effectively removes fluorine from this waste stream, offers insight into the etching chemistry of MAX to MXene, and provides an effective analytical tool for optimization of MXene production. Additionally, washing HF etched multilayered Ti₃C₂T₂ with 0.05 M NaHCO₃ allows for the production of delaminated Ti₃C₂T₂ colloidal suspensions, which typically requires the use of TBAOH or DMSO for intercalation and subsequent delamination. Ti₃C₂T₂ made with HCl/LiF and washed with 0.05 M NaHCO₃ yields a colloidal suspension with a concentration of 18 mg mL⁻¹ and a film conductivity of 1150 S cm⁻¹.

**Introduction**

Traditional synthesis of Ti₃C₂T₂ MXene, most commonly obtained by the selective etching of Al from a Ti₃AlC₂ MAX phase with hydrofluoric acid, HF, requires a large amount of water to obtain a colloidal suspension of few, to single, flake Ti₃C₂T₂. Typically, the amount of water needed is at least 640 mL per gram of MXene as this water is thought to both wash away residual salts formed in the etching process, and to bring the solution pH to neutral at which point a stable colloidal MXene suspension forms. Herein we show that by modifications made to the synthesis process, we can obtain Ti₃C₂T₂ colloidal suspensions with 75% less water utilized in the washing procedure. The fluorine, F, in the remaining wastewater can also be recovered through the precipitation of cryolite.

While MXenes have been shown to be quite promising in terms of their performance across a wide variety of applications, their widescale production has lagged. One of the limiting steps at this time is the large cost of their production and the need for F in the etching medium. Additionally, the treatment of HF-containing wastewater is both a major industrial and environmental concern.*

For MXene production to occur at industrial scales, the large amount of acidic wastewater that is currently a byproduct of its methods of production must be addressed. Furthermore, the presence of F⁻ in this wastewater is problematic as this treatment is quite costly and produces a large amount of industrial waste sludge that becomes difficult to dispose of due to environmental regulations. It was long believed that the main product of the selective etching of Al from Ti₃AlC₂ to yield Ti₃C₂T₂ is AlF₃, which has limited solubility in water (0.5 g/100 g H₂O at 25 °C). However, Cockreham et al. showed that AlF₃ formation only occurs under a range of ionic strength from 8.5 to 10 M and other aluminum/fluorine complex ions are dominant outside this range. It should be noted that this work explored the use of cobalt fluorides (CoF₂/CoF₃) as a source of F, and the applicability to HF or HCl/LiF etching methods has not been demonstrated.

The Ti₃AlC₂ MAX phase is known to form a protective oxide layer which is composed of Al₂O₃ and TiO₂. A product of the reaction between Al-containing species such as alumina comprising this oxide layer, or the aluminum in the MAX structure, and HF is hexafluoroaluminate acid (H₃AlF₆). If H₂AlF₆ is present, then a route to recovering F from the wastewater exists through the addition of sodium cations to form sodium hexafluoroaluminate, otherwise known as cryolite, which can be readily isolated from the spent etching liquor. The yield of precipitated cryolite allows for the calculation of Al etching efficiency, while also being a product of commercial value. In the reaction of the Al in Ti₃AlC₂ with HF, a route for the formation of hexafluoroaluminate acid and cryolite may be as follows:

1. 2Al + 6HF(aq) → 2AlF₃(aq) + 3H₂(g)
2. AlF₃(aq) + 3HF → H₃AlF₆(aq)
3. 2H₃AlF₆(aq) + 3Na₂CO₃ → 2Na₃AlF₆ + 3H₂O + 3CO₂(g)

With the typical etching procedures using HF or HCl/LiF there is enough HF to fully convert AlF₃ to H₃AlF₆. Furthermore, AlF₆⁻ is believed to be a stable species as the ionic strength of the solution increases. In this reaction, the formation of...
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determination of Al extraction e

carbonate, cryolite can easily be formed and precipitated, similarly treating the waste HF etching liquid with 3 M sodium fluoride to effectively remove F from the wastewater. This reduction in wastewater is achieved independent of the etching method (HF vs. HCl/LiF). By similarly treating the waste HF etching liquid with 3 M sodium carbonate, cryolite can easily be formed and precipitated, according to reaction (3), providing a useful method for the determination of Al extraction efficiency as well as providing a value-added product which effectively removes F from the waste stream.

Results & discussion

The sediments produced by this method were first investigated by XRD to ensure that etching of the MAX phase was complete, and to characterize the obtained MXene. In Fig. 2, XRD patterns of multilayer (ML) MXene obtained by normal washing (DI) water washing, with 8 washes of DI (middle, black), ML MXene after 1 wash with 40 mL 0.05 M NaHCO₃ and 2 washes of DI, (top, red) and the precipitated Na₃AlF₆ from the spent etching liquid. A reference profile for Na₃AlF₆ (dotted bottom red).

H₃AlF₆ may provide a driving force for the continued extraction of Al from Ti₃AlC₂, potentially explaining why HF is the only acid capable of etching the MAX phase to yield MXenes. The structures of hexafluoroaluminic acid and cryolite are shown in Fig. 1.

Sodium hexafluoroaluminate, Na₃AlF₆, more commonly known as cryolite, is insoluble in water, but soluble in sulfuric acid, H₂SO₄, with the evolution of HF. Synthetic cryolite finds widespread industrial use as a flux agent to dissolve alumina, Al₂O₃, in the electrolytic metal extraction process. It is also consumed in the abrasives, ceramic and glass industries.

Many research articles and patents have appeared over the years regarding the production of cryolite, suggesting that if cryolite can be isolated and repackaged as a by-product of MXene production, the economics associated with the scale-up of MXene synthesis may be partially offset. By our calculations, assuming complete etching of Al from Ti₃AlC₂ and complete conversion to cryolite, 1.07 g may be produced from 1 g of Ti₃AlC₂. This may be an attractive method to lower the cost of wastewater treatment and produce a high purity, high value compound, while also providing a quantitative tool for the determination of etching efficiency. The feasibility of this method is supported by the work of Kumar et al. which showed that the recovery of synthetic cryolite from the treatment of synthetic HCl/HF leach liquors comprising H₃SiF₆ and H₃AlF₆ with 3 M Na₂CO₃ was 97.5%.

In this work we demonstrate that by washing the acidified MXene sediment once with a mild solution of low-cost and environmentally benign sodium bicarbonate, BC, colloidal suspensions can be produced using 75% less deionized water than otherwise needed. This reduction in wastewater is achieved independent of the etching method (HF vs. HCl/LiF). By similarly treating the waste HF etching liquid with 3 M sodium carbonate, cryolite can easily be formed and precipitated, according to reaction (3), providing a useful method for the determination of Al extraction efficiency as well as providing a value-added product which effectively removes F from the waste stream.

**Fig. 1.** (a) Structure of hexafluoroaluminic acid, and (b) structure of cryolite, Na₃AlF₆.

**Fig. 2.** XRD patterns of MXene obtained by normal washing 8 times with DI (black – solid line is HF etched ML, dotted line is HCl/LiF etched delaminated films), after 1 wash with 0.05 M NaHCO₃ and 2 times with DI (red – solid line is HF etched ML, dotted line represents HCl/LiF etched delaminated films), Ti₃AlC₂ MAX phase precursor (orange), the precipitated Na₃AlF₆ (blue), and a reference profile for Na₃AlF₆ (dotted bottom red).
with only DI H2O. However after treatment with 0.05 M NaHCO3 (regardless of HF or HCl/LiF etching method), this stability occurred within two rounds of washing, as seen in Fig. 3. Interestingly, a stable suspension is found after just the first wash (Fig. 3a). However in our washing procedure, an additional wash step was carried out that resulted in a darker, more concentrated suspension (Fig. 3b). Washing with DI H2O only, required 640 mL. However with the incorporation of one 40 mL 0.05 M NaHCO3 wash before subsequent DI washes, the volume of water necessary to produce a dark colloidal suspension was 160 mL per gram of Ti3C2Tz sediment. An SEM micrograph of the Ti3C2Tz filtered film after exposure to NaHCO3 can be seen in Fig. 4a and b along with an SEM micrograph of the obtained Na3AlF6 in Fig. 4c.

Typically, Ti3C2Tz produced by etching with HF, only do not yield delaminated flakes (referred to as d-Ti3C2Tz, to insinuate delamination) without the use of a chemical exfoliation agent such as TBAOH or DMSO.5–22 However, with our approach, a colloidal suspension was obtained after NaHCO3 and DI water washing, and a film of d-Ti3C2Tz was produced by vacuum filtration of this suspension (Fig. 4a). A photograph of this colloidal suspension, and the Tyndall effect produced by the d-Ti3C2Tz flakes, is shown as an inset of Fig. 4a. Conductivity measurements were conducted on this film with a four-point probe, and a DC conductivity of 180 ± 10 S cm−1 was measured.

A film was attempted to be produced by the DMSO assisted intercalation and delamination of HF etched, water only washed, Ti3C2Tz, however the concentration of this suspension was so slow that a continuous film was unable to be obtained. Conductivity measurements were attempted on a section of this ‘film’ and a value of 2.25 ± 0.05 S cm−1 was measured.

Conductivity measurements were similarly conducted on HCl/LiF etched films, one washed first with 0.05 M NaHCO3, and the other washed only with water. In the BC washed case, the colloidal suspension had a concentration of 18 mg mL−1 and a film produced from this suspension had conductivity of 1150 ± 27 S cm−1 was measured, while the H2O washed colloidal suspension had a concentration of 15.6 mg mL−1 and the corresponding film had a conductivity of 1330 ± 54 S cm−1.

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Fig. 3 Digital images of post-neutralization washing procedure with NaHCO3. (a) After washing once, and (b) twice with DI water.

Fig. 4 SEM micrograph of, (a) Ti3C2Tz film obtained after 1 wash with 40 mL 0.05 M NaHCO3. Inset: Tyndall effect of delaminated, HF–Ti3C2Tz colloidal suspension after 0.05 M NaHCO3 and H2O washing. (b) Multilayered HF–Ti3C2Tz powders after etching and washing with NaHCO3, demonstrating the accordion-like structure of ML-Ti3C2Tz, and (c) cryolite precipitated from the spent etching liquid. Inset in (c) is picture of obtained cryolite.
Conclusions

In summary, a simple yet effective method of obtaining Ti₃C₂T₂ MXene is presented where the isolated etched sediment is neutralized with a mild solution of sodium bicarbonate. In so doing, the pH can directly be adjusted to neutral without the need of large volumes of DI water. This drastically reduces the amount of wastewater generated, specifically from 640 mL g⁻¹ to 160 mL g⁻¹, a reduction of 75%. This holds for both HF only and HCl/LiF etched Ti₃C₂T₂. Furthermore, when etched with HF, delaminated films of Ti₃C₂T₂ could be produced, provided they were treated with 0.05 M NaHCO₃ before washing with deionized water. Furthermore, films produced by etching with HCl/LiF and then washed once with 0.05 M NaHCO₃, followed by two washes with deionized water resulted in a colloidal suspension with a concentration of 18 mg mL⁻¹. Filtered films made from this suspension had a conductivity of 1,150 ± 27 S cm⁻¹. Additionally, cryolite (Na₃AlF₆) can be formed from this process, which indicates that the etching media used for the extraction of Al from Ti₃AlC₂ must contain hexafluorocarbides, H₃AlF₆. This provides insight into the chemistry of the etching reaction and allows for the recovery of fluoride from the spent etching liquid. The cryolite obtained from this neutralization can be precipitated by treatment with sodium carbonate, further offsetting the cost of MXene production, and providing a quantitative tool for calculating etching efficiency which would allow for the optimization of the etching parameters such as time, temperature, pH and reagent concentrations.

Materials & methods

The experimental approach in this work is largely separated into two segments which are focused on: (1) neutralization of the MXene sediment to obtain high quality Ti₃C₂T₂ MLs with less water, and (2) precipitation of cryolite from the spent etching waste.

Two etching methods are explored in this work. Namely, the use of HF acid only as well as the method first reported by Ghidiu et al. utilizing hydrochloric acid and lithium fluoride to produce HF in situ. The latter method is more widely adopted due to the improved handling safety and ability to directly yield delaminated suspensions. However, when considering the precipitation of cryolite through neutralization of the spent etching liquid, the HF only method is a much cleaner system, as there are fewer ionic species present. For the purposes of this work, we demonstrate that cryolite, Na₃AlF₆, can be precipitated from the spent etching media obtained from the HF-only method.

The neutralization of the MXene sediment with 40 mL 0.05 M NaHCO₃ is applicable to both methods of MXene production. Given that the HCl/LiF method is more widely adopted by those that work with MXene, we felt it was important to demonstrate the effectiveness of this washing procedure when working with HCl/LiF etched MXene.

**HF etching of Ti₃AlC₂ to produce HF–Ti₃C₂T₂**

MXene etched by HF acid only, (hereafter referred to as HF–Ti₃C₂T₂) was obtained by etching 1 g of Ti₃AlC₂ MAX phase in 10 mL of 10% HF for 24 h at RT.

**Sodium bicarbonate washing of HF–Ti₃C₂T₂**

After the etching period, the HF–Ti₃C₂T₂ ML sediment is isolated from the etching liquid through centrifugation. The spent liquid portion is then added to cryolite precipitation. After separation, the sediment in each centrifuge tube (0.5 g per tube) was treated with 40 mL of 0.05 M NaHCO₃ so that the pH was adjusted to 7.0. After the initial wash with 0.05 M NaHCO₃, the sediment was washed two times with 40 mL of DI water.

**Delamination of NaHCO₃ washed HF–Ti₃C₂T₂**

20 mL of DI water was added to the sediment obtained after washing with 0.05 M NaHCO₃ and DI water, which was then bath sonicated for 1 h under argon flow. After sonication, the colloidal suspension was isolated by centrifugation at 5000 rpm for 10 minutes. This suspension was then filtered to obtain a film.

**HF-etched, H₂O washed Ti₃C₂T₂**

For comparison to the NaHCO₃ method, a separate 1 g batch of HF–Ti₃C₂T₂ was washed only with DI water. To produce a film of the HF–Ti₃C₂T₂ washed only with water, 12 mL of dimethyl sulfoxide (DMSO) was added to the washed sediment and allowed to mix for 24 h at room temperature (RT). After mixing, the DMSO was separated by centrifugation at 3500 rpm for 5 minutes. 20 mL of DI H₂O was added to the DMSO intercalated sediment, and bath sonicated for 1 h under flowing argon. After sonication, the colloidal suspension was isolated by centrifugation at 5000 rpm for 10 minutes. This suspension was then filtered to obtain a film.

**Precipitation of cryolite from HF–Ti₃C₂T₂ etching media**

Cryolite was precipitated by adding 3 M Na₂CO₃ to the isolated etching liquid until a pH of 4.0. This solution was then kept in a 55 °C oil bath for 1 h, after which the gelatinous liquid was vacuum filtered over a Celgard polypropylene membrane where a white crystalline solid was formed.

**HCl/LiF-etched Ti₃C₂T₂**

To demonstrate the applicability of this method to the more widely used method first reported by Ghidiu et al., two grams of Ti₃C₂T₂ were prepared by etching two grams of Ti₃AlC₂ in 20 mL of 12 M HCl along with two grams of lithium fluoride. This mixture was allowed to mix at 35 °C for 48 h at 300 rpm.

After etching, the contents of the etching bottle were split equally into four centrifuge tubes so that 0.5 g of sediment was in each centrifuge tube. Two of the tubes were washed only with deionized water, while the other two were first washed with...
40 mL of 0.05 M NaHCO₃, followed by two washes with deionized water.

After the washing period, the contents of the tubes were combined so that roughly 1 g of each separately washed powders of Ti₃C₂Tₓ were in each tube. 20 mL of DI H₂O was added to each tube, and these mixtures were bath sonicated for 1 h under flowing argon. After sonication, the colloidal suspensions were collected by centrifugation at 5000 rpm for 10 minutes. These colloidal suspensions were filtered into films by vacuum filtration.

Author contributions

M. C. conducted all experiments and wrote the manuscript along with M. W. B. who oversaw the project.

Conflicts of interest

There are no conflicts to declare.

References

1 M. W. Barsoum, MAX phases: properties of machinable ternary carbides and nitrides, John Wiley & Sons, 2013.
2 M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi and M. W. Barsoum, Adv. Mater., 2011, 23, 4248–4253.
3 M. Ghidiu, M. R. Lukatskaya, M.-Q. Zhao, Y. Gogotsi and M. W. Barsoum, Nature, 2014, 516, 78–81.
4 L. Verger, V. Natu, M. Ghidiu and M. W. Barsoum, J. Phys. Chem. C, 2019, 123, 20044–20050.
5 L. Verger, V. Natu, M. Carey and M. W. Barsoum, Trends Chem, 2019, 1, 656–669.
6 L. Verger, C. Xu, V. Natu, H. Cheng, W. Ren and M. W. Barsoum, Curr. Opin. Solid State Mater. Sci., 2019, 1–15.
7 M. Naguib, V. N. Mochalin, M. W. Barsoum and Y. Gogotsi, Adv. Mater., 2014, 26, 992–1005.
8 C. H. Won, J. Choi and J. Chung, J. Hazard. Mater., 2012, 239–240, 110–117.
9 A. Toyoda and T. Taira, IEEE Trans. Semicond. Manuf., 2000, 13, 305–309.
10 O. Mashtalir, M. Naguib, B. Dyatkin, Y. Gogotsi and M. W. Barsoum, Mater. Chem. Phys., 2013, 139, 147–152.
11 D. R. Lide, CRC Handbook of Chemistry and Physics, CRC press, 2004, vol. 85.
12 C. B. Cockreham, X. Zhang, H. Li, E. Hammond-Pereira, J. Sun, S. R. Saunders, Y. Wang, H. Xu and D. Wu, ACS Appl. Energy Mater., 2019, 2, 8145–8152.
13 M. W. Barsoum, N. Tzenov, A. Procopio and M. Ali, J. Electrochem. Soc., 2001, 148, 551–562.
14 V. Scepanovic, S. Radosavljevic and J. Misovic, J. Fluor. Chem., 1974, 3, 403–408.
15 M. Kumar, M. N. Babu, T. R. Mankhand and B. D. Pandey, Hydrometallurgy, 2010, 104, 304–307.
16 M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi and M. W. Barsoum, Adv. Mater., 2011, 23, 4248–4253.
17 M. S. Corbillon, M. A. Olazabal and J. M. Madariaga, J. Solution Chem., 2008, 37, 567–579.
18 V. D. Jovic, B. M. Jovic, S. Gupta and T. El-raghy, Corr. Sci., 2006, 48, 4274–4282.
19 Z. Akdeniz and M. P. Tosi, Chem. Phys. Lett., 1999, 308, 479–485.
20 O. Mashitalir, M. Naguib, V. N. Mochalin, Y. Dall’Agnese, M. Heon, M. W. Barsoum and Y. Gogotsi, Nat. Commun., 2013, 4, 1716.
21 J. Halim, S. Kota, M. R. Lukatskaya, M. Naguib, M. Zhao, E. J. Moon, J. Pitock, J. Nanda, S. J. May, Y. Gogotsi and M. W. Barsoum, Adv. Funct. Mater., 2016, 26, 3118–3127.
22 P. Urbankowski, B. Ansori, T. Makaryan, D. Er, S. Kota, P. L. Walsh, M. Zhao, V. B. Shenoy, M. W. Barsoum and Y. Gogotsi, Nanoscale, 2016, 8, 11385–11391.