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The effect of fluoride based salt etching in the synthesis of MXene

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Abstract. Here we reported the effect of fluoride-based salt etching in the synthesis of Ti_3C_2 MXene by etching Ti_3AlC_2 MAX phase precursor. Lithium fluoride (LiF) and ammonium fluoride were the fluoride-based salts were chosen as an etching agent in this study. The optimum etchant concentration and etching temperature of the MAX phase were evaluated. The presence of aluminium etched was determined by using the Inducted Couple Plasma Optical Emission Spectrometry (ICP-OES). The initial concentration of aluminium in Ti_3AlC_2 precursor was estimated based on the data from Energy Dispersive X-Ray Analysis (EDX). The study shows that the optimum etchant concentration of LiF is 5M and NH_4F is 3M. Room temperature is the optimum etching temperature due to the exothermic reaction of the process. Compared to LiF, NH_4F is the preferred salt for in-situ HF fluoride-based salt etchant due to the capability of the salt to etch the maximum amount of Al at a low concentration of 3M within 24 hours at room temperature.

Introduction

Since the isolation of single-layer graphene in 2004, two-dimensional (2D) materials have gained tremendous attention because of their distinctive properties relative to their bulk form. The isolation of graphene has become a reference for all 2D materials and opened the possibility of novel discovery [1]. Due to its distinct structural and physical characteristics, a new family of two-dimensional early transition metal carbides and carbon nitrides, known as MXene has recently gained attention [2]. MXenes have important applications in the areas of catalysts [3], sensors [4], super-capacitors [5], and rechargeable batteries [6]. The MXene family comprises of transition metal carbides, carbonitrides, and nitrides with a general formula of $M_{n+1}X_n$, where M represents transition metals, and X is carbon or nitrogen [7]. The name "MXene" was given to describe the similarities between this 2D material family with graphene and to recognize the parent ternary carbide and nitrides, MAX phases, which are the precursor of MXenes [1]. MAX phases are layered ternary carbides and nitrides with a general formula $M_{n+1}AX_n$, where A represents elements from groups 13 and 14 of the periodic table.

Hydrofluoric acid (HF) containing and HF-forming etchants, which add surface functionalities like O, F, or OH, represented by Tx in this formula as $M_{n+1}X_nT_x$, are used to synthesize MXenes [2]. The first method of synthesis MXene was reported in 2011 that Ti_3C_2 MXene was synthesized by immersing Ti_3AlC_2 powders in 50% hydrofluoric acid (HF) [8]. In that method, HF is an essential etchant. However, HF has strong causticity and toxicity. Therefore, it is of great significance to find a new etchant to replace hydrofluoric acid. Since 2014, a new etchant, lithium fluoride (LiF) in hydrochloric acid (HCl), instead of HF, was used to prepare Ti_3C_2. Besides LiF, other fluoride salts in HCl were also reported to produce Ti_3C_2 [9]. Compared with HF, fluoride salts in HCl are milder and safer.

In this study, we discuss the effect of the synthesis parameter of fluoride-based salt etching namely lithium fluoride (LiF) and ammonium fluoride (NH_4F) in the synthesis of $Ti_3C_2T_x$-based MXene. Two synthesis parameters were manipulated, namely concentration and temperature. The amount of aluminium etched from the Ti_3AlC_2-based MAX precursor were measured at different etching interval by using inductively coupled plasma - optical emission spectrometry (ICP-OES).

Experimental

A) Choice of Materials

The Ti_3AlC_2 powder (Purity: 99%) was purchased from Nanoshel. The etching agent LiF and NH_4F were purchased from Sigma-Aldrich. Hydrochloric acid (HCL, 37 wt %) was purchased from Merck.

B) Varying Synthesis Temperature

To study the effect of temperature on the amount of Al etched, 1L of 6M hydrochloric acid (HCL) solution was prepared by diluting with deionized water [2]. Then, LiF salt was added to the HCl solution to prepare 5M of in-situ HF etchant solution. An oil bath was set up to heat the etchant solution to the desired temperature. The solution was soaked in the oil bath and simultaneously stirred at a rate of 130 rpm. Then, 4 g of Ti_3AlC_2 powder were slowly added into the solution under continuous stirring for 7 hours. The solution was then separated from the solid precursor and tested for the presence of Al by using ICP-OES. The experiment was repeated at different temperatures (40°C, 50°C and 60°C). The same experimental method was repeated for NH_4F salt. However, a lower concentration of 3M NH_4F-based etchant solution in 6M HCl solution was selected.

C) Varying Concentration of Etchant Solutions

To study the effect of salt concentration on the amount of Al etched, different weight of Li-based salts (LiF and NH_4F) was added to 1L of diluted HCl (6M). The solutions were left under continuous stirring at 100 rpm for 30 minutes by using a magnetic hotplate stirrer. 4 g of Ti_3AlC_2 powder were then added gradually to the etchant solution. The concentration of aluminium in the sample at different time intervals (1 hour, 7 hours, 22 hours, and 24 hours) was measured by using ICP-OES. The overall steps were repeated by using different concentrations (4M to 7M) of LiF and NH_4F salts in a diluted HCl solution.

Result and Discussion

A) EDX Analysis of MAX phase

Fig. 1 shows the Energy Dispersive X-Ray Analysis (EDX) of the Ti_3AlC_2-based MAX precursor sample. The analysis confirms the presence of titanium, aluminium and carbon elements that represent the Ti_3AlC_2 structure. The analysis shows that the sample is consist of 58.14 wt% of Ti element, 16.32 wt% of C element, 14.12 wt% of Al element and 11.42 wt% of O element. The presence of O elements could be due to the oxidation of the sample. The mass and initial concentration of aluminium was calculated as below:

$$Weight\ \% = \frac{mass\ of\ Al}{total\ mass} x\ 100\% \tag{1}$$

$$Concentration_{i(Al)} = \frac{mass\ of\ Al}{volume\ of\ solution} \tag{2}$$

From the calculation, the initial concentration of the aluminium presence in the MAX precursor isabout 7060 mg/L.

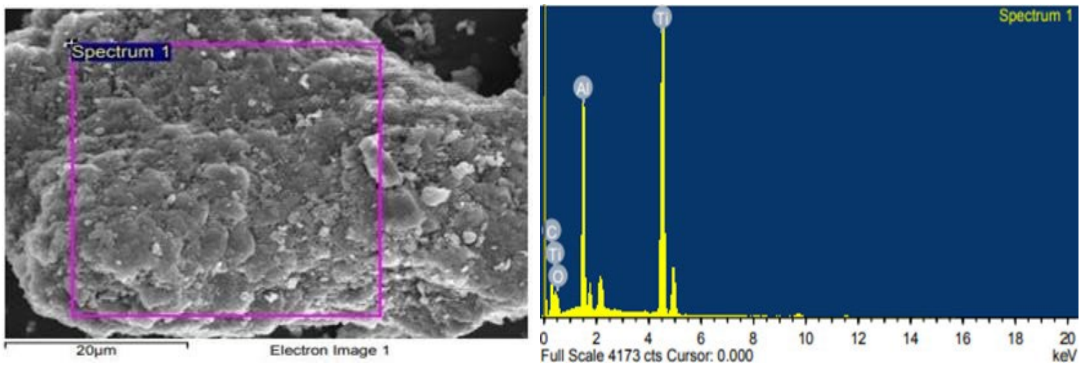

Fig. 1. The composite of Ti3AlC2 structure

B) The Effect of Synthesis Temperature on the Amount of Aluminium Etched
Fig. 2 and Fig. 3 show the amount of Al etched at different etching temperatures by using LiF and NH_4F salt, respectively. Regardless of the type of salt etchant, increase the synthesis temperature results in decreasing the amount of Al etched from the MAX precursor. Etching at room temperature results in the highest amount of AL etched. The reduce amount of Al etched could be due to the reduce the flowability of the salt solution into the lattice of MAX phase. The etching process of Al is an exothermic reaction, where the heat is release because of the chemical reaction between the acid and the MAX precursor. Introduce heat during the etching process resulting in increase the temperature of the etching solution close to the boiling point of the solution thus reduce the capability of the salt solution to penetrate the lattice of the MAX precursor. However, detail study must be conducted to prove the theory. The findings indicate that heating is not required in the synthesis of MXene by using in-situ HF fluoride-based salt etchant. Compared the amount of Al etched at room temperature, 5M of LiF solution able to extract about 26.85 mg/L while NH_4F salt solution can etch higher amount of Al (403 mg/L)even at lower concentration of 3M.

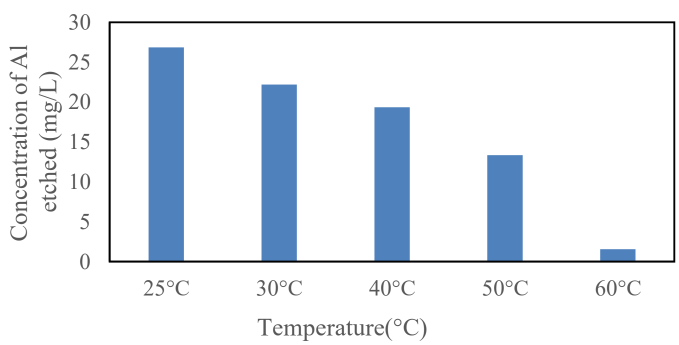

Fig. 2. Temperature vs concentration of Al etched

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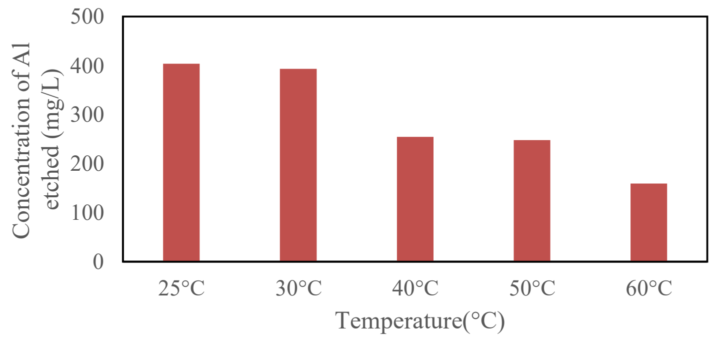
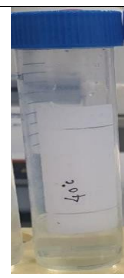
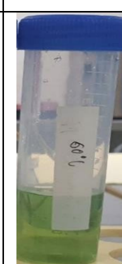


Fig. 3. Temperature vs concentration of Al etched

Table 1 shows the images of the etchant solution after 7 hours of the etching process at different etching temperatures by using 5M of LiF and 3M of NH_4F salt solutions. The images show that there is a significant change in the colour of the sample as the etching temperature increases. Regardless of the type of salt, the solution exhibit almost colourless at an etching temperature of 30°C. The colour change from pale yellow to green when the temperature increases from 40°C to 60°C. However, an obvious colour change is observed when the temperature is increased to 50°C and 60°C. It is suggested that detailed analysis must be conducted to evaluate the presence of any elements that contribute to the change in the colour of the solution.

Table 1. Change of the etchant colour at different temperature

Temp.	30°C		40°C		50°C		60°C	
Label	**LiF**	**NH_4F**	**LiF**	**NH_4F**	**LiF**	**NH_4F**	**LiF**	**NH_4F**
Sample								

C) The Effect of Aluminium Concentration at Different Etchant Concentrations

Fig. 4 and Fig. 5 show the amount of Al etched by using different concentrations of the salt solution measured at different time intervals at room temperature. Regardless of the type of fluoride-based salt solution, increasing the etching time results in increasing the amount of Al etched. Based on Fig 5, the concentration of salt solution has slightly affected the amount of Al etched. After 24 hours of etching time, 4M and 5M of LiF-based salt solution exhibit the highest amount of Al etched. Further increasing the concentration of LiF salt solution to 6M and 7M result in reducing the concentration of Al presence in the etched solution. The same trends were also observed for NH_4F-based salt solution, where the sample with the lowest concentration of3M exhibits the highest amount of Al etched. Further increasing the concentration results in reducing the amount of Al etched. Based on the analysis, etching process by using 3M of NH_4F solution at room temperature can etch almost all Al element presence in the MAX precursor sample.

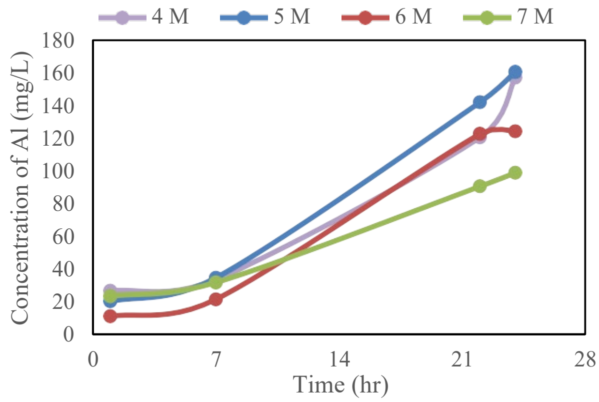


Fig. 4. Aluminium etched in different concentrations of LiF

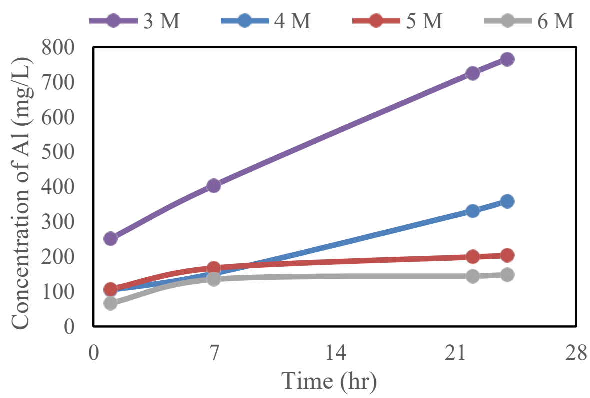


Fig. 5. Aluminium etched in different concentration of NH4F

Table 2 and Table 3 show the difference in etchant colour after etching for 7 hours by using different concentrations of LiF and NH_4F-based salt solution. The images show that the colour of the LiF-based salt etching change from colourless to green when the concentration increase from 4M to 6M. In different, NH_4F-based salt solution exhibit colourless solution at lowconcentrations of 3M to 4M. The solution change to pale yellow when the concentration increases to 5M and 6M. The greenish solution produced when the etched solution is filtered is likely to be a titanium (III) complex of fluoride and potentially chloride [10]. The greenish colouris not formed by a complex of chloride alone, because titanium produces a blue or purple compound when it reacts with chloride alone [11]. As the concentration of etchant increases, the intensity of the green colour in the sample increases which results in the increase in titanium concentration.

Table 2. Change of the etchant colour at different concentration of LiF

Description	4 M	5 M	6 M	7 M
Samples				
Colour	Colourless	Pale yellow	Pale green	Darker green

Table 3. Change of the etchant colour at different concentration of NH4F

Description	3 M	4 M	5 M	6 M
Samples				
Colour	Colourless	Colourless	Pale yellow	Pale yellow

Conclusion

In conclusion, two-dimensional MXene Ti_3C_2 can be synthesized from Ti_3AlC_2 MAX precursor via in-situ HF fluoride-based salt etching, namely LiF and NH_4F in HCl solution. Based on the study conducted, the optimum etchant concentration of LiF is 5 M and NH4F is3M, where the highest amount of aluminium is etched. Room temperature is the optimum etchingtemperature due to the exothermic reaction of the etching process. An increase in the etching temperature results in reduces the efficiency of the etching process due to the reduction of the penetration of the solution into the lattice of the MAX precursor. Moreover, NH_4F shows a better etchant compared to LiF since it etched more aluminium within 24 hours of the etching process.

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