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Optimization of functional Multilayer and few layer Ti3C2 MXene Synthesis and their characterization as new generation of 2D material for cutting-edge development

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Abstract*--MXene as a new family of 2D structures opens the window for preparing advanced materials which are applicable in different zones.MXenes can be achieved through chemical etching of MAX phases.Since Bonding energy of M-A in various MAX phases are differen, MXenepreaperation procedure should be optimized.Present work gives guidelines about various parameters should be considered to achieve high qualified MXene**from MAX phases which was supplied from foresman company.Two procedures (using HF solution and Fluoride-based salt solution) were applied for Ti_3AlC_2 etching.Investigations proposed that for HF solution**:** concentration, temperature and contact time of 40%, room temperature and 60 h resulted in qualified products according to color change, XRD and FESEM analysis. In the second method using Fluoride-based salt, 50 ˚C and 60 h using 0.5 g Ti_3AlC_2, 0.8 g LiF and 9 M HCl resulted in Ti_3C_2 flakes with desired characteristics.*

Keywords*--2D materials, MAX, MXene, Ti_3C_2, etch.*

I INTRODUCTION

New material structures with compelling characteristics introduce auspicious functional materials in various areas. Two-dimensional (2D) nanomaterials represent significant subgroup of new generation of materials for further augmenting both fundamental studies and practical applications in numerous fields and expanding potentials beyond the existing boundaries. 2D structures are indicative of intriguing category of nanostructures owning sheet like structure possessing thickness of single- or few-atoms thick (typically less than 5 nm) and lateral size of about 100 nm, or up to a few micrometers and even larger[1]. Undeniably, the groundbreaking emergence of graphene and its fascinating applications have been paved the way for appearance of atomically thin postgraphene 2D nanostructures. Graphene as a groundbreaking member of 2D materials was met by Novoselov, Geim and co-workers in 2004, which was indicated the year of ultrathin 2D nanomaterials resurgence. After discovering graphene, researches have been rigorously conducted on postgraphene2D nanomaterials owning to their fascinating characteristics and enriched the exploration of 2D ultrathin family members including metal−organic frameworks (MOFs),graphitic carbon nitride ($g\text{-}C_3N_4$), transition metal dichalcogenides (TMDs), covalent−organic frameworks (COFs), layered double hydroxides (LDHs), hexagonal

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boron nitride (h-BN), layered metal oxides, black phosphorus (BP), silicene, antimonene, inorganic perovskites, and organic−inorganic hybrid perovskites, noble metals and MXene[2]. Pioneered by YuryGogotsi and co-workers[3], researches have been offered MXene as a novel, significant and ever-growing category of 2D materials, monolayer to multilayer and fewlayer, could be produced by chemical etching of MAX phase. Since the first exploration of MXene in 2011, these material have been prompted a flood of research, which thoroughly documented not only on the structure and feature of this sub category of 2D materials, but also the possible application of them have given rise to string of papers was published which can be found in Fig 1 (statistics can be attributed to publication until 27 August 2019 with MXene key words in abtract, Key words and title).MXene words related to the family of transition metal carbide, nitride and carbonitride. MXene structural formula is $M_{n+1}X_nT_x$ (n=1, 2 or 3), where M is a transition metal (such as Sc, Ti, V, Cr, Zr, Hf, Nb, Mo, Ta, and W), X is carbon, nitrogen or carbonitride and T_x is an indicator of surface-terminating functional group (i.e. -OH, -F or -O). $M_{n+1}X_nT_x$ or $M_{n+1}X_n$ was firstly attained by selective elimination of A-element (in majority A is one of the elements of periodic table group 13 or 14) from main phase, layered ternary carbides, named MAX phase. This primary structure (MAX phase) can be determined as $M_{n+1}X_n$ layers with A atoms between the mentioned layers (Fig. 2). In a single $M_{n+1}X_n$ crystalline planar area, M atoms form a hexagonal close pack structure ($p6_3/mmc$ space group) for X atoms to stow octahedral holes. Hitherto, nearly 130 variant MAX phases compound is extant and 30 diverse MXenes have been experimentally discovered with well-known examples of $Ti_3C_2T_x$ and TiC_2T_x.[4]

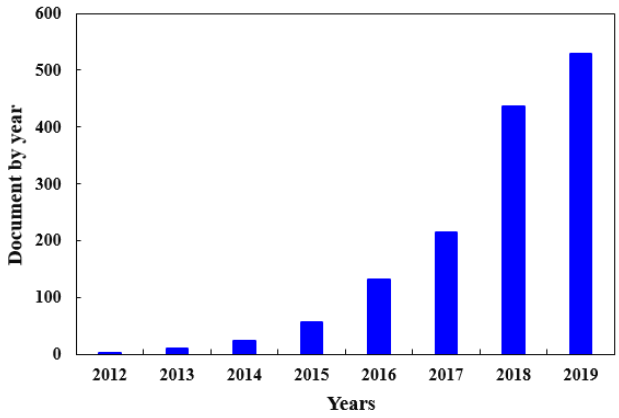

Figure1: Numbers of related to publications with MXene keyword from Scopus until 2018

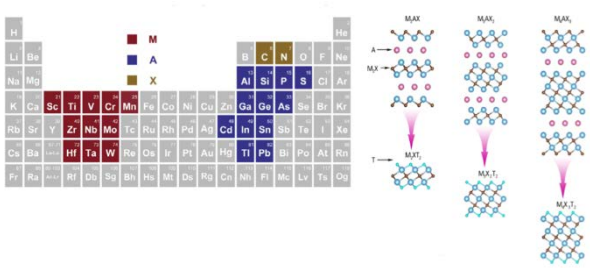

Figure2: Chemical structure of MAX phase

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Presence of metal atomic layers in the structure of MXene endows conductivity to the mentioned materials. Moreover, hydroxyl, oxygen or fluorine are surface functional groups which turn these materials to the hydrophilic one and influencetheir interaction with surrounding. Coexisting of aforesaid features in this material are unique and indispensable to achieve appealing electronic, optical, and magnetic properties. It should be mentioned that metal species and surface traits alter electronic conductivity and magnetism of MXenes[5]. Moreover, favorable luminescent, mechanical properties, tunable band gap and the aforementioned attributes make them the best candidate for development of cutting-edge advanced materials. The above mentioned features have conferred superb application in the fields of sensor, energy storage, water treatment, biomedicine, catalyst and electromagnetic interference shielding[6]. Potential applications of MXene schematically were illustrated in Fig. 3.

As mentioned before MXene can be obtained by chemical etching of MAX phase. The discrepancy of M-A bond energy in different MAX phases results in significant differences in etching conditions. So, several methods which were reported in different publication cannot be applied for different precursors. In this context, optimization of different parameters concerning to chemical etching procedure is crucial during the synthesis. In the present work, we investigated different etching conditions to achieve appropriate MXene from our precursor (MAX phase which was supported from Foresman Company). Furthermore, we tried to delaminate this structure. X-Ray Diffraction (XRD), field emission scanning electron microscopy (FESEM) and Ultraviolet–visible spectroscopy (UV-Vis) analysis were conducted to investigate the obtained MXene.

Figure3: Schematically illustration of MXene application

II EXPERIMENTAL DETAILS

2.1. Materials and analysis

Lithium fluoride (LiF), Hydrochloric acid (HCl, 37%) and Hydrofluoric acid (HF, 48%) were supported from Sigma Aldrich. Ti_3AlC_2 was purchased from Foresman Company.

The morphology of the prepare Ti_3C_2 was studied using field emission scanning electron microscopy (MIRA3TESCAN-XMU FESEM, Oberkochen, Germany). Samples were spin coated on glass and then coated with a gold layer using a sputter coater (Desk sputter coater II Nanostructured coating Co., Iran). UV-Vis

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absorbance spectra were conducted on Lambda 35 UV-spectrophotometer (Perkinelmer, USA).. X-ray diffraction(XRD) patterns were recorded on a Siemens D5000(Germany) diffractometer with monochromatized Cu K_{α}ra-diation.

2.2. Synthesis and characterization of MXene ($Ti_3C_2T_z$)

Predominantly, synthesis of MXene from MAX phase occurred using two main process of HF (hydrofluoric acid) and in-situHF etching (Flouride-based salt). In the present work, Multi-layer and few layer Ti_3C_2 were synthesizes using HF etchant solution and in-situHF etchant solution, respectively.

HF etchant solution

For HF etching method, 1 gram of MAX phase (Ti_3AlC_2) was added to 10 ml of 40% HF aqueous solution in an ice bath during 30 minute. To optimize the reaction condition, etching processes were conducted in different HF concentrations (10%, 20%, 30%, 40%), various contact times (12 h, 18h, 24h, 36h, 48h, 60h and 72 h) and different temperatures (25 ˚C, 40 ˚C and 50 ˚C). Afterwards produced material was repeatedly centrifuged at 3500 rpm for 5 minute and then washed with DI water (deionized water) till pH of the suspensions reached around 5.

In situ HF(based on Fluoride salt) etchant solution

In this route, hydrofluoric acid is obtained by in situ reaction of 10 ml of 9M HCl andand 0.8 gram (for 20 minute). Subsequently, 0.5 gram of primary MAX phase was slowly added to the above mentioned mixture in ice bath through 20 minute. Optimization of the conditions was performed for various etching times (12 h, 18h, 24h, 36h, 48h, 60h and 72 h) and different temperatures (25 ˚C, 40 ˚C and 50 ˚C). The achieved suspension was frequently centrifuged at 3500 for 5 minute and washed with DI water until pH aroud 5 was attained. For better delamination of these structures, 100 mL DI water was added to the centrifuged suspension, sonication got applied under Ar flow for 40 minute. Centrifugation of suspensions at 3500 rpm for 1 hour separated multilayer Ti_3C_2 from few layer Ti_3C_2. In this case, solution obtained after centrifugation contains few layer Ti_3C_2.

III RESULTS AND DISCUSSION

3.1. Ti_3C_2MXene synthesis

MXene can be achieved through chemical etching of MAX phase in which MXene layers were hold together by strongmetalic M-A bonds. Therefore, exfoliation of MXene is difficult in comparison with other materials bonded together through van der Waals. MXene etching conducts in solutions containing HF. The mentioned solution can be a HF solution or solution in which HF is produced in-situ from the related precursors.

Researches declared that there are differences between exfoliation and delamination in clays and layered materials. So, illustration of these phrases is significant. Exfoliation refers to a process in which largeaggregates turn to smaller particles. On the other hand, delamination demonstrates the separation of the individuallayers. In this context, exfoliation refers to the synthesis of MXene using just HF solution leading to decomposition of MAX phase into small particle and multi-layer MXene. Moreover, delamination process can be attributed to the MXene synthesis using solution in which HF forms via the reaction of precursors (for example solution

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containing LiF and HCl). In the second method, small ions exist in the etchant solution, which can expand interlayer space by intercalation and ion intercalation with sonication process separate layers and delamination occurs.

The process related to the chemical etching of MAX phase (Ti_3AlC_2 in this article)isschematically illustrated in Fig. 4.

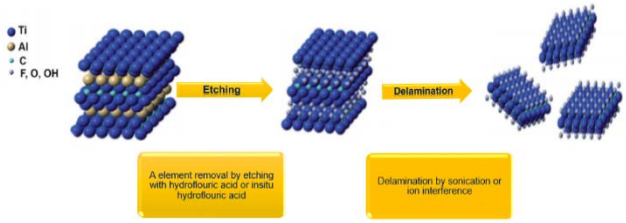

Figure 4: Schematically illusteration belonging the chemical etching of Ti_3AlC_2

Reactions of Ti_3AlC_2 with HF can be summarizes as follow:

$$Ti_3AlC_2 + 3\,HF \longrightarrow AlF_3 + 3/2\,H_2 + Ti_3C_2 \quad (1)$$

$$Ti_3C_2 + 2\,H_2O \longrightarrow Ti_3C_2(OH)_2 + H_2 \quad (2)$$

$$Ti_3C_2 + 2\,HF \longrightarrow Ti_3C_2F_2 + H_2 \quad (3)$$

Exfoliation step attributed to the selective removing Al atoms from the MAX phase is the first step shown in reaction 1. Reactive nature of Ti atoms on the surface follows easy reaction of MXene with water and HF illustrated by reaction 2 and 3[4].

In the present work, Multilayer Ti_3C_2MXene was synthesized by exfoliation of Ti_3ALC_2 MAX phase in HF solution. Bonding energies of M-A bonds in different MAX phase precursors are various. So, Optimization of etching time, temperature and acid concentration should be considered which were performed in the present work.Supplimentary analysis were done to approve synthesis.

Optimization of Ti_3C_2 synthesis using HF solution and their characterization

Literature review shows that concentration of etchant reagent, time and temperature are crucial parameters through synthesis. Changing the color of etchant solution from gray to black can be thethefirst sign of possible successful etching process. Complematary assessments regarding the synthesis should be accomplished using XRD and FESEM analysis. For the first step, HF solution wih different concentrations (10%, 20%, 30%, 40%) were applied as etchant solution for different contact times (12 h, 18 h, 24 h, 36 h, 48 h, 60 h and 72 h). Etching in HF solutions with low concentrations (10%, 20% and 30%) for all contact timesindicated approximately same results. Results of color change, XRD pattern for low concentrations represented that etching process was not complete. XRD of Ti_3AlC_2(Fig. 5a) and XRD of the resultant powder using low concentrations of HF (Fig. 5b) were shown in Fig. 5. Since outputs for concenterations lower than 40% for all contact times represented same trends, one XRD patterns for these three concentrations in different contact time was shown to avoid reporting repetitive results. Distinguished peaks at 9.5˚, 19.3˚, 34.02˚, 36.8˚, 39.2˚, 41.8˚, 48.6˚, 52.5˚, and 56.7˚ of Ti_3AlC_2 are relevant to (002), (004), (101), (103), (104), (105), (107), (108), and (110) planes, which can be recognized at Fig 5a. Chemical exfoliation of Ti_3AlC_2 giving rise to MXeneis accompanied by vanishing the high intensity peak situated at 39.2˚ along with the introducing of new peak nearby 27˚[7]. As can be

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distinguished from Fig 5b, XRD peak at 39.2˚ didn't vanished completely declaring existence of Ti_3AlC_2 and incomplete etching of Ti_3AlC_2. So, it could be stated that the mentioned concentrations weren't appropriate.

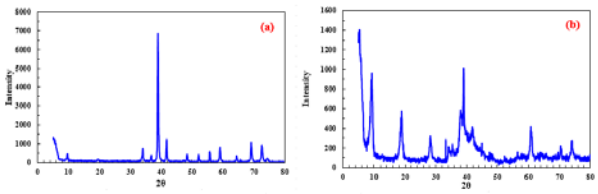

Figure5: XRD pattern of (a): Ti_3AlC_2 and (b): incomplete etching of Ti_3AlC_2 in lower concentrations (10%, 20% and 30%)

Moreover, morphological investigation of Ti_3AlC_2 and incomplete etching of Ti_3AlC_2 can be found in SEM imagese shown in Fig. 6.Bulk structure of Ti_3AlC_2 with flat surface can be identified pursuant to the SEM images (Fig 6a). Loosely stacked "accordion" structure of MXene are expected from etched structure which results from Al removing of Ti_3AlC_2. However, the mentioned structure isn't obvious in Fig 6b due to the incomplete etching and relatively low removing of Al.

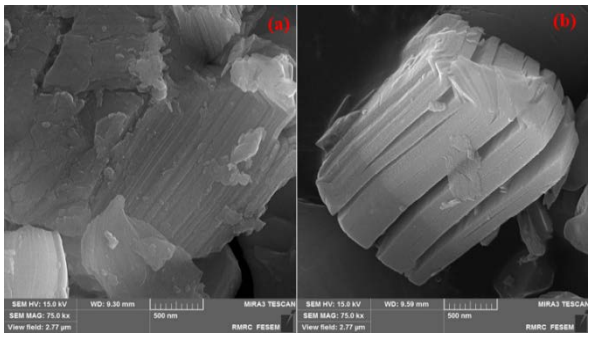

Figure 6: SEM images of (a): Ti_3AlC_2 (b): Ti_3C_2 achieved with lower concentrations

According to outputs of solution color, XRD and FESEM results, etching process wasn't complete with 40% HF solutions at contact times of 12h, 18h, 24h, 36h and 48 h which was identical with results of using 10%, 20% and 30% acid concentrations shown in Fig. 5 and 6.

Ouputs illustrated that etching trend was successfully accomplished in HF solution with 40% concentration and 60h contact time. In this context, results of color change, XRD and FESEM analysis were the great approval exhibited in Fig 7. Elimination of XRD peak at 39.2˚ and introducing of new peak nearby 27˚ were the best sign of prosperous elimination of Al from MAX phase (Fig 7a). Furthermore, FESEM result approved XRD resultant pattern and exhibited accordion morphology verifying successful synthesis of Multilayer Ti_3C_2MXene (Fig 7b).

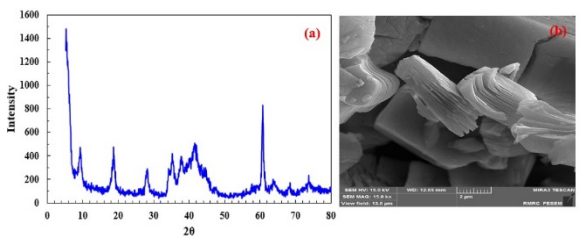

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Figure 7: XRD pattern and FESEM image of etched $Ti_3AlC_2$with HF 40% and 60 h

Etching results of 40% HF concentration were the same for both 72h and 60h contact time. On the otherhand, long time can decompose the layered structure and have undesirable effect on the structure of outputs. By considering the mentioned reasons and to concise this process, etching time was optimized to 60 h for multilayer Ti_3C_2.

The efffect of temperature (25 ˚C, 40 ˚C, 50 ˚C) was also investigated. The results indicated that room temperature was the best temperature for etching process. High temperatureconditions led to oxidation of Ti_3C_2 resulting degradation of Ti_3C_2 and producing TiO_2 and carbon byproducts. etchant solution color was changed to brown in this case[8].

Optimization of Ti_3C_2 synthesis using in-situ HF (Fluoride-basedsalt)and their characterization

In-situ HF production can be attained from reaction of LiF and HCl and this proceducere was selected as the second procedure to delaminate MXene structure and introduce few layered Ti_3C_2. Since small ions like Li^+ are present in the etchant solutions (Fluoride-based salt), these ions can penetrate between layers and enlarge distance of layers,which is assistance of achieving few layer Ti_3C_2.In Fluoride-based salt etchants, concentration of the applied LiF and HCl and molar ratio of LiF to HCl are step forward toward to synthesize 2D nanocrystal with on demand size and quality. In particular, changing molar ratio of LiF:Ti_3AlC_2 from 0.67 to ≥1 along with increasing concentration of HCl from 6 to 9 M improved the quality and the size of Ti_3C_2 flakes[9]. So, the best aspect ratio which was mentioned in the experimental section was chosen for future experiments. In this matter, the effect of temperature (25 ˚C, 40 ˚C and 50 ˚C)on the etching process with the above mentioned concentrations for componenets (Ti_3AlC_2: 0.5 g, LiF: 0.8 g, HCl: 9M and 24 h) was monitored. Trends of XRD schema for the mentioned temperature of etchant solution were described in Fig 8. Evidence expressed that etching didn't perform in 25 ˚C.There was no discrepancy in XRD pattern of Ti_3AlC_2 (Fig 5a) and XRD pattern of etched powder in 25 ˚Cconforming to Fig 8a. Result of XRD analysis remarked that this temperature isn't advisable. So, other temperatures (40 ˚C and 50 ˚C) were considered. XRD analysis of provided samples in the marked temperatures were displayed in Fig 8b and 8c. Peak weaking at 39.2˚ expressed initiation of etching process and existence of the remained characteristic peak declared imperfect etching. However, trends of XRD announced that 50 ˚C can be a good choice for etching process. XRD pattern of $Ti_3C_2T_x$ and Ti_3AlC_2were compared and they revealed that (002) peak was shifted to smaller angle in Ti_3C_2 XRD pattern expressing increase in distance of layers.

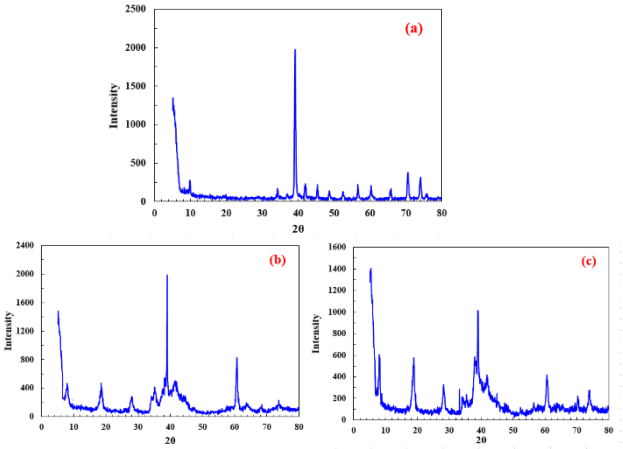

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Figure 8:XRD pattern of powder resulted from in-situ HF solutions in (a) 25 ˚C, (b): 40 ˚C and (c): 50 ˚C

In the next step, various contact times (36 h, 48 h and 60 h) at 50 ˚C were assessed to attain the perfect Ti_3C_2. These assessments ascertained that 36 h and 48 h weren't enough time for complete etching and the results of XRD experiments were similar to XRD reported in Fig 8b and 8c. XRD outcomes for etching time of 60 h exhibited that the the most intense peak of Ti_3AlC_2 situated at $2\theta \approx 39.0°$ (104) was vanished in XRD pattern of Ti_3C_2(Fig 9a). Shifting and broadening of (002) peak in XRD pattern of Ti_3C_2 obtained at 60 h infered increase in the d-spacing and successful intercalation of ions within the Ti_3C_2 layer. In this procedure, sonication of obtained powder under Ar atmosphere delaminated the products to few layer structure[10].

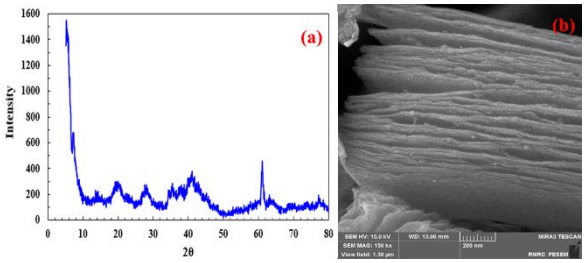

Figure 9. (a): XRD pattern and (b): FESEM image of powder resulted from in situ HF solutions in

For complimentary analysis, Uv-Vis absorbances of the diluted Ti_3C_2etched by the mentioned procedures (HF solution and in-situ HF solution) had the same trend which exhbited in Fig 10 which is compatible with the reported results.

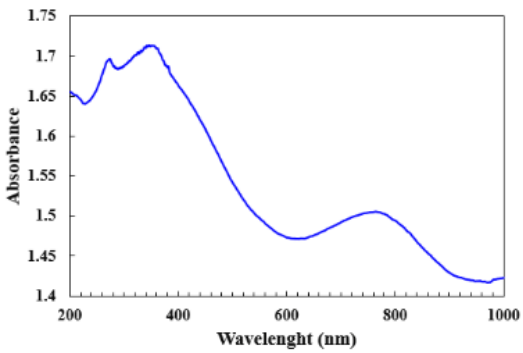

Figure 10: UV-Vis absorbance of Ti_3C_2

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IV CONCLUSIONS

It should be mentioned that exfoliation and delamination of Ti_3C_2 is a step forward unto the development of advanced materials in different areas such as sensor, energy storage, water treatment, catalyst, electromagnetic interference shielding and biomedicine. Since MAX phases produced with different procedures possess various M-A bonding energy, applied conditions for etching process are different and should be optimized. In the present work, two procedures using HF and in-situ HF were assessed and effect of fundamental parameters was determined. Assessments suggested that for HF solution, concentration, temperature and contact time of 40%, room temperature and 60 h resulted in qualified products according to color change, XRD and FESEM analysis. For the second method using Fluoride-based salt, 50 ˚C and 60 h using 0.5 g Ti_3AlC_2, 0.8 g LiF and 9 M HCl resulted in Ti_3C_2 flakes with desired characteristics.

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