A Review on Synthesis of 2-Dimensional $M_{n+1}X$ (MXene) materials

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Abstract. The sequence of 2D transition metal carbides, carbonitrides, and nitrides has gained a lot of interest since the discovery of Ti_3C_2 . About thirty new MXene compounds have been identified, with eight different MXene synthesis methods. The presence of surface terminations such as hydroxyl, oxygen, fluorine, or chlorine in the materials described thus far indicates strong hydrophilicity as well as metallic conductivity MXenes are becoming increasingly popular due to their diverse chemistry, which has sparked a surge in academic interest. We will study and examine the many methods of fabricating MXenes in this review, which will cover everything from MAX phase etching to exfoliation, as well as the best approach to synthesise them and their most current applications.

1 Introduction to 2-D materials

Crystallized solids having a thickness of a few atoms or fewer are known as two-dimensional materials. The discovery of graphene, the most well-known two-dimensional (2D) substance, has sparked a renewed interest in two-dimensional (2D) materials among scientists.^[1] There are numerous 2D materials available, each with its own set of characteristics. 2D transition metal dichalcogenides (e.g. MoS_2 , $MoSe_2$, WS_2), hexagonal boron nitride, metal oxides, black phosphorus (BP), silicene (2D silicon), MXenes (2D carbides/nitrides), borophene (2D boron), and germanene (2D germanium) are some of these (2D boron) [2-9]. 2D materials can have diverse optical characteristics, based on their chemical compositions as well as structural configurations (for example. MXenes, graphene, $NbSe_2$ etc), semi metallic behaviour (for example. $PtSe_2$, TiS_2), semiconducting (for example. MoS_2 , WSe_2 , metal oxides). 2D materials may be metallic (e.g. graphene, $NbSe_2$ etc.) or even superconducting (e.g. MoS_2 , WSe_2), (hexagonal boron nitride), (e.g. NbS_2) and feature varying optical characteristics based on their chemical compositions as well as structural configurations.^[10-15] MXenes has different features, which provide exciting avenues for 2D materials and

promote applications in various fields of research such as opto-electronic devices that allow the building of light-emitting appliances in the sensor (chemicals or biologics), catalysing, photovoltaics, spintronics, sensing and energy storage.^[16-23] Assembling multiple 2D materials into one layer vertically produces new artificial materials termed vanderwaal heterostructuring linked by interactions between van der waals. The attributes of each individual may be combined to generate optoelectronic devices with tailored properties by carefully checking the sheet order in the heterostructures.^[24-28] The fabrication of light-emitting electroluminescent appliances and photodetectors for optical image sensors and 2D transistor materials based on flexible computer parts is therefore possible.^[29-31] The combination of these distinct electrical and optical components based on heterostructures from Vanderwaal has amazing potential to produce new flexible electronic devices which could transform existing technology The successful application of 2D materials was driven by control of the growth of 2D materials' size, crystallinity and thickness.

2 Development of MXenes:

Recently, the material science professors Naguib et al & Yuri Gogotsi from Drexel University successfully synthesised a new 2D series of materials containing, mainly, Carbonitrides ($M_{n+1}(C,N)_n$) and nitrides

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($M_{n+1}N_n$) are early transition metal carbides ($M_{n+1}C_n$) and carbonitrides ($M_{n+1}(C,N)_n$).^[35] MXene is a generic formulation $M_{n+1}X_nT_x$, where M is a transition metal in its earliest state (for example: Sc, Ti, V, Cr, Zr, Hf, Nb, Ta, etc.), X is carbon or nitrogen & T_x stands for terminals (for the -OH, -O, -F) and has a close-packed hexagonal structure.^[36] MXene also can contain more than one metal transition (M) and this structure is available in two forms (1). In the ordered phase, a single-capped or one two-capped of one transition (M) metal (for example, $(Mo_2Ti)C_2$ & $(Ti_2Ta_2)C_3$) type MXenes contains more than two transition metals) is fitted between other transition metals. For a solid solution, two separate transitional metal elements in the M-layers will be randomly distributed (e.g., $(Ti, Nb)_4C_3$). These 2D materials offer a vast range of graphene-like organisms that can be found in three, five or seven nuclear layer-thick combinations. In 2011, $Ti_3C_2T_x$ was the main disclosure for MXene and is usually conductive. To date 19 MXenes have been synthesised by a selective extraction of A element using fluorine-containing etchants made of bulk ternary combinations called the MAX stage, with distinct transition metal or mixed transition metal surfaces. MAX phases belong in particular to a family of solids possessing layer hexagonal structures with symmetry of $P6_3/m$, and their chemical formula is $M_{n+1}AX_n$ where $M = Sc, Ti, V, Zr, Hf$, etc. (early transition, metals), $N = 1-3$.^[37-41] Of the several MXenes, the most extensively utilised MXenes are $Ti_3C_2T_x$ and Ti_2CT_x .^[42] In contrast to other 2D materials, MXenes have strong conductivity, chemical stability, and hydrophilicity. MXenes exhibit a wide variety of uses, including energy storage, triboelectric, diaphragm membranes, optoelectronics, power absorption, catalysis, wireless communication, biosensors, and photothermal therapy. By changing their surfaces, the conductivity of MXenes is regulated.^[43-65] Surface endings like hydroxy, fluorine and oxygen are mainly inserted during MXene synthesis, and predict functional properties, like catalytic performance, magnetism, Li-ion capacity, mechanical properties, to predict superconductivity, when the metal is controlled by insulating transition and subsidising.^[65-75] These anticipate experimental reinforcement effects of impairments. Intercalation also impacts MXene's conductivity. Intercalants do not alter the inherent properties of the MXene, although intercalation of MXene in multi-layer samples can raise resistance of the device by a range of size.^[76-83] This effect deserves the intercalating effect of increased spacing and interflake resistance. $M_{n+1}X_n$ chemistry & intercalation contributes to its electronic conductivity in multi-layered samples of MXene surface endings. The circumvolution of this phenomenon substantially complicates MXene's experimental understanding. Therefore, there is no understanding and control of MXene. We perform an electrical bias of MXenes in situ (up to 775°C) and within TEM in order to meet this problem. The in-situ spectroscopy of energy loss was detected for de-intercalation. We also employ the spectroscopy for low dosage direct electron detection to avoid electron beams that damage the sample.^[84-85] This technique may aid us in the correlation with MXene conductivity between the

defunctionality of terminal species such as -F, -OH & =O. The key purpose of the review is to construct 2D transition layers of metallic carbides, carbonitrides and nitrides i.e. MXenes by various ways^[86]

2.1 Synthesis of MXenes

MXenes can be produced through etchings of A-layers from the layered precursors from MAX phases (MAX phase powders). MAX is a huge category of ternary nitrides and carbides (up to 70 MAX phases reported until now).^[87-91] MAX phases consist mostly of nitrides of metal or of metal carbides of transition ($M_{n+1}X_n$) that are interwoven mostly with layers of A atoms (A = Groups 13 and 14 are the elements that make up this element). Due to the M-A bond's metallic character, it is exceedingly difficult to separate MXenes A-layers by cutting the MAX phases. In contrast to the powerful M-X bonds these M-A bonds are chemically active, making it possible to expel the A layer particularly. A-players & terminations with terminal species, such as -O, -OH, and -F^[91-93], are selectively grafted with Etching's MAX phase. Acidic solution is used to grade the A-layers selectively from MAX phases for the production of MXenes or utilising aq. HF^[94] or through either in situ HF formations, through the HCL & LiF reaction^[95]. In the MAX phase, alone Al has been effectively grafted into MXenes despite the many diverse A components, particularly of group 13 and 14. MXenes from non MAX-phase precursors also can be produced. Mo_2CT_x was first produced by grafting Ga layers of Mo_2Ga_2C , utilising these precursors.^[96-98] This phase, i.e. the non-MAX stage, has two layers of A elements which separate the carbide layers. The $Zr_3C_2T_x$, which is produced from aluminium carbide gravure selectively from $Zr_3Al_3C_5$, was another MXene prepared for these phases. Each layer of metal is divided by a C layer for non-MAX phases. This divides M_2C or M_3C_2 layers into Al-C layers rather than element layers.^[99-100]

2.2 Synthesis of MAX phases:

The MXE precursors i.e. the MAX phases can be synthesised through a variety of methods, e.g. chemical vapour deposition (CVD) by combustion at different temperatures,^[101] high temperature self propagating synthesis (HTS), plasma spark sintering, molten salt or isostatic hot pressure reaction or mechanical alloying, which can speed the A-layer removal. However, relatively few studies were presented on the method of powdered synthesis of MAX stages. In many circumstances, the initial A-layer concentration is little greater than the stoichiometric concentration to prevent binary carbide development of the metal transition.^[102-106] MAX is mainly manufactured utilising titanium, aluminium, titanium carbide and activated c-powders, the powder which is taken into account.^[107] In order to achieve MAX powder, precursors should be used to get appropriate molar values for the MAX phase in the correct molar concentration. Then, for at least 24 hours these precursors are made of ball in alcohol. The 100-mesh screen is sifted in vacuum mixed powder. Then,

MAX particles can flow through the Ar(g) at 30o C/min for 15-60 min at the ultimate temperature of 1200-1500 degree Celsius .Samples of 5-1000 g can be made with this process. This method can be utilised also for the preparation of bulk MAX stages. The final temperature, the synthesised weight and the holding duration will have no effect on the purity. MAX-phase powders can be exfoliated thereafter by immersing them in HF at room temperature. In HF concentration, the solution can vary from 10 to 50 percent wt. by time.^[108-110]The solid MAX phase can be synthesised at a low cost using pressure less sintering. Some researchers are using this technique to sell the MAX stage without pressure support for sintering applications such as hot pressing and hot isostatic pressing .^[111] To exfoliate MXenes production, selective etching of A-atoms from the MAX phase employing HF as a graft is well handled . Not only has HF been used as an etchant for exfoliation, but also LiF + HCl and NH₄HF₂.^[112-114]

2.3 Etching of MAX phase

To make MXene synthesis the MAX stage is employed with the etching of strong fluoride ion-containing grading solutions such ammonium bi, hydrofluoric acid or a fluoride ion combination. Machine exfoliation methods are extremely difficult to utilise with the strong M-A metal bonds in the MAX phase. The M-X bond is a mix of covalent or ionic characteristics and so selective gravure of the atomic layers is better than the MAX phase. As etchant, fluoride-containing acids are often employed. MAX phase powders are then mixed at room temperature with aqueous HF acid for a certain duration. As a result, selective grading of A-layer ensures the MX-layer metal bonds are exchanged through surface endings such as hydroxyl fluoride and oxygen on MXene surface. The resultant solution is then centrifuged and filtered following this etching procedure, to extract the supernatant chased by deionized H₂O, until the pH of the mixture is kept within the 4 - 6 range. This means the acquisition of FL-MXene. A MXene with less than 5 layers is considered to be a small amount of layer.^[115-117]

The fundamental reactions take place The "MA" bond grading is given below in the MAX phase:

Mn+1Xn continues to interact with H₂O (rxn 2), then with HF (rxn 3), after etching A layer (rxn 1), and subsequently forms a surface that includes the functional group OH, F, O and H. The fluorine-containing acid solution such as NH₂HF₂ + (LiF/HCl) mixture is also utilised by similar processes to produce the same usual outcome. In 2014, Ghidui and colleagues showed that a LiF/HCl mix that interacts in situ to produce HF can also be utilised to graze the parent using this equation.

Even yet, with traces of HF in the etched solution, their methods were less harmful. To avoid the use of HF in different ways, (1) electrochemical synthesis in NH₄Cl/N(CH₃)₄ + OH electrolyte at ambient temperature was proposed; (2) hydrothermal synthesis in aqueous NaOH solution at ambient temperature (3) HCl electrochemical synthesis.^[118-121] The process for obtaining MXenes should be both safe and quick to develop. Most MXenes are produced by chemical etching of MAX phases, which takes up to 8 hours of time, high temperatures (always 35°C), and high HF levels, according to previous research . A technology should be devised for producing MXenes that is safe and quick. Electro chemical grafting is less hazardous, and MXenes can even be generated at room temperature out of all of the grafting procedures listed above. In a less hazardous NH₄HF₂ solution at ambient temperatures with different voltages MXenes (Ti₃C₂) can be produced by electrochemical etching of the Ti₃AlC₂ sheet.^[122] MXenes usually demand strong grafting solutions and/or longer grafting times, with a greater atomic number. For instance, n=3 Mo₂Ti₂AlC₃ took longer etching time, twice its Mo₂Ti₂AlC₂ counterpart under the same circumstances and n=2. MXenes may be generated under a variety of etching circumstances, resulting in MXenes with distinct surface chemistry^[123], as shown in the table below:

Method	Etchant	Temp. (°C)	References
HF method	HF H ₂ O ₂ + HF	Room temp. to 550	124 125
Acid with flourine	HCl + LiF HCl+(Na,K,orNH ₄ F) NH ₄ HF ₂	35-55 30-60 RT	125 126 127
Molten salts	LiF+NaF+KF NaOH	550 270	128 129
Hydrother-mal	NaBF ₄ , HCl NH ₄ Cl/TMAOH	180 RT	130 131
Electrochemical	NH ₄ HF ₂	30-60	132
Lewis Acid	ZnCl ₂	550	133

Table 1: Different type of etching methods used to obtain MXenes.

Even at high temperatures, MXenes were also synthesised. During 2016, this technique synthesis was utilised to create the first nitride base MXene in which the 59% potassium fluoride fluoride melting mixture was used, 29% lithium fluoride and 12% sodiums in an inert atmosphere such as Ar(g) at 550°C, which grazed the Al-layer in Ti₄AlN₃ (MAX phase polder).^[134] Another technique to make nitride MXene is to undertake an ammonia treatment at 550°C starting from carbide using NH₃(g). This was a successful surgery Mo₂NT_z and V₂NT_z respectively of Mo₂CT_z and V₂CT_z Alkaline based, etc., conditions in an autoclave are severe i.e. 27.5M of sodium hydroxide, which makes it

difficult to escalate. The process of molten salt utilised for producing Ti_4N_3 alone requires relatively low temperatures ($550^\circ C$). The electrochemical procedure that reports a return of roughly 90 % is thus the most liberal approach to obtaining huge quantities of MXene made by the Yang & colleague. ^[136]

2.4 Exfoliation of MAX phases:

The A-layers that have disintegrated are replaced by different endings (ionic, organic species) following the etching of MAX powders, resulting in a multi-layered material consisting of $M_{n+1}X_nT_z$. The method of exfoliation used depends on the conditions for etching. MXene sheets, for example, accommodate ions of Li^+ that intersperse between layers to increase the interlayer distance and also aid the exfoliation of fluorine (HCl/HF) by sonifying or just shaking solution. If HF is employed as a grafting material but only through the contact between the layers of exfoliation is feasible organic species that increases the distance between the layers and weakens the connections of the links. Incorporation between the laying configurations of ions or molecules in materials with Transition metal dichalcogenides like MoS2 have weak Interactions between hydrogen and van der Waals. The exfoliation process frequently depends on the nature of the chemical MXene. ^[138]

2.5 Overall synthesis of MXenes

In HF etching, the first step is stacked MAX stages. The surface terminations O, F, and/or OH are substituted (M_2XT_z) after the grading of the M_2AX atomic layers. The multilayer exfoliation in single 2D flakes is possible through intercalation, organic compounds. Following the exfoliation process, MXene colloidal suspensions can be treated in a variety of ways in water: spin coating, Spraying, vacuum filtration ^[138]

3 Conclusion

MXenes were produced in the past 8 years by the etching & exfoliation of layered precursors i.e MAX phases which forms a large family of 2-Dimensional materials. The synthesis of new MAX phases (more layered ternary metal carbides & nitrides) can lead to the formation of new 2D-MXenes with different compositions. Non-terminated MXenes can be incorporated by the bottom up methods such as Chemical vapor deposition (CVD), physical vapor deposition (PVD). For instance, MXenes obtained by CVD method contains no terminal (Tx) groups & hence shows excellent conductivity. Although, max of the MXene samples have been synthesized by the top down approach. But there are very few attempts in growing the monolayers of MXene by bottom-up approach, so amount of work have to be done in this region. A major challenge which scholars faced in this research is the storage capacity of MXene dispersions in aq. medium. Presently, to give them longer a longer life those

dispersions have been stored in subzero temperatures. However this type of solution is not possible in the real practice. Thus for storing MXenes solution & preventing them from oxidation, new & better techniques need to be explored. Also applications of MXene such as super capacitors, hydrogen storage, desalination, batteries etc. are still in their initial stages, thus devoted work needs to be done to its applications both industrially as well as in research. Out of all the synthesis methods discussed, electrochemical method is far more elegant than others because in this method NH_4HF_2 aq. solution has been used as the etchant which is less harmful, so in the low F-solution MXenes can be obtained rapidly at the room temperature. However, basic understanding of synthesis of MXene & its scale up is required if MXenes have to be utilized commercially. All these challenges needs to be optimized in time.

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