Current synthesis routine of Mxene and its applications

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Abstract. 2D transition metal carbides or nitrides are called Mxene, which can be treated as a promising inorganic material which is made up of a few atomic layers of transition metal carbide or nitrides. The properties of Mxene can be determined by the surface groups and the number of layers in the films. The Mxene can be made by top-down strategies which involves HF etching, salt etching, and electrochemical etching. Also, the bottom-up approach is available by using the CVD method. Some typical uses from the wide range of applications of Mxene are included in the article, which include energy storage, gas sensing, and optoelectronic use.

Keywords: 2D Materials, Mxene, Transition Metal Carbides/Nitrites, Energy Storage, Sensor.

1. Introduction

As electrons can only move freely in two dimensions at the nanoscale, the immersion of two-dimensional materials has attracted a great deal of attention due to their unique properties. The concept was brought into public view when single atomic layer graphene was successfully synthesised in 2004. Developing new 2D materials has become a focal point in the related field [1].

The new type of 2D transition metal carbide/nitride, referred to as "Mxene", was synthesised to replace the conventional 2D materials, including graphene-based materials, purposefully. Mxene is usually a 2D metal carbide or nitride with the general formula Mn+1XnTx, where "M" is a transition metal, "X" is carbon or nitrogen, "T" is a functional group like oxygen, hydroxyl, or fluorine, and "n" is an integer [2].

Mxene is formed from the corresponding MAX phase. The MAX phase is a group of ternary carbides and nitrides in a layered structure with a general formula of Mn+1AXn, where "A" represents the A-group element (group from IIIA and IVA from the periodic table). Moreover, n = 1,2,3. When "A" element is removed from the MAX phase using an etchant, n+1 layers of "M" are interleaved with n layers of "X". Then Mxene is formed. However, the functionality of the Mxene surface is based on the chemistry of the etchant agent. Another method of building up Mxene from the bottom has been developed to improve the surface and give better property from a more controlled structure [3]. Because of the unique structure, Mxene has excellent properties, such as metallic conductivity, optical properties, and mechanical properties [1]. With these advantages over traditional materials, many comprehensive kinds of research were done and showed growth in interest in different Mxene potential applications [4].

Rather than concentrating on bulk Mxene, recent research is focusing on single or few layered Mxene (SFL-Mxene). SFL-Mxene has the advantage over bulk Mxene as SFL-Mxene avoids restacking of nanosheets and obtains superior performance and active sites. In contrast to bulk Mxene, SFL-Mxene shows some improved properties, such as low ion-diffuse barrier, low open circle voltage, and high specific area [4]. With all these advantages, Mxene is now one of the most popular research topics in the field.

In this review article, the different synthesis methods and applications of Mxene and SFL-Mxene will be summarised.

2. Synthesis methods

2.1. Top-down method

The top-down method is based on removing the "A" layer element in the MAX phase (e.g., Al, Si, Ga), which produces two-dimensional nanoplates of Mxene with different terminations on the surface treatment [5]. The various surface treatments allow Mxene to have different properties for diverse applications. Also, the Mxene can be designed after treatment to achieve different material properties, such as morphologies and lateral dimensions [4]. The main methods used include acid etching, electrochemical etching, and delamination of bulk Mxene.

Acid etching is the main method used to produce Mxene. And often, HF acid was used for etching and assisted with ultrasonic. The ultrasonic waves not only speed up the etching process, but they also stop the bonding, let stable bonds form, and start the delamination at the same time [6]. The procedure is shown in Figure 1. However, the problem with HF etching is that it fails to etch out the nitride-based sample.[4] For etch nitride-based samples, one example is the molten fluoride salt used to etch Al from Ti_4AlN_3 under 550 ℃ [7]. The difficulty of the synthesis of Mxene using HF acid may be caused for two reasons. The cohesive energy of $Ti_{n+1}N_n$ is lower than the $Ti_{n+1}C_n$ types. The lower cohesive energy gives a less stable structure to the nitride Mxene phase. And the higher formation of $Ti_{n+1}N_n$ indicates that the Al atoms in the MAX phase ($Ti_{n+1}AlN_n$) bonded strongly. Therefore, more energy is required to break the bond for their extraction. Another possible reason could be that the less stable $Ti_{n+1}N_n$ dissolves in the HF aqueous solution. Since a different etchant is required to etch nitride Mxene, which is the fluoride salt [7]. The synthesis steps are shown in Figure 2.

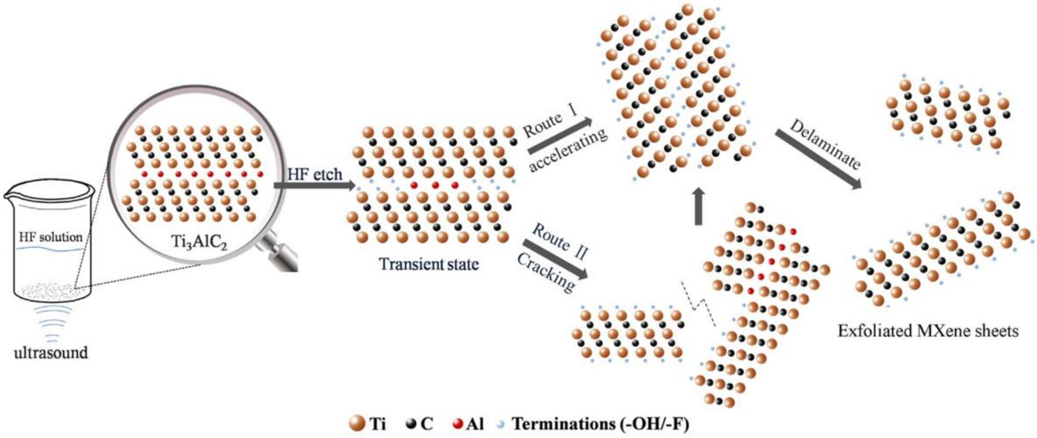

Figure 1. Schematic illustration of the mechanism of accelerated etching and the delaminating process by sonication[6]

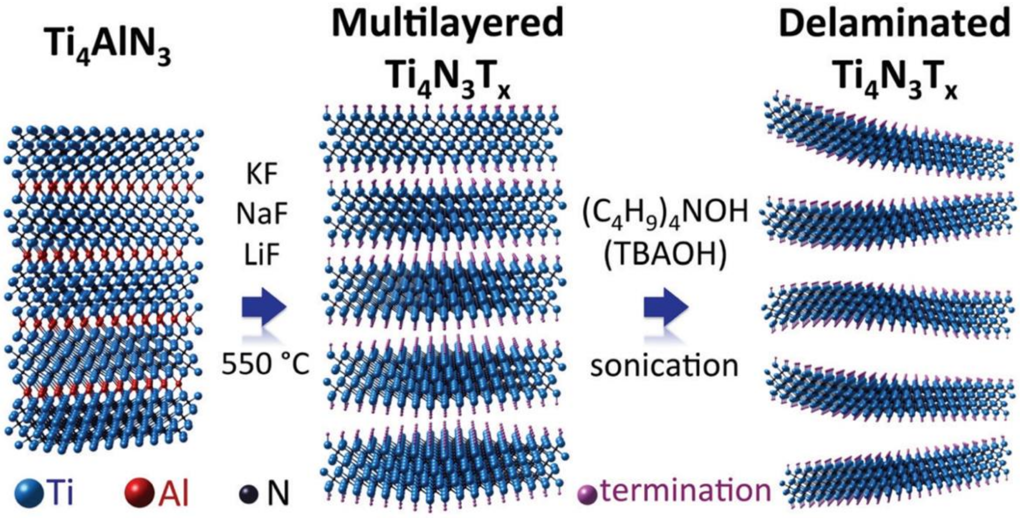

Figure 2. Schematic illustrations of Ti4AlN3 treated with molten fluoride salt under 550 ℃ and following mechanism of the delamination process assisted by sonication [7].

Although the HF acid etching method is very effective for producing Mxene, the HF solution is highly toxic and harmful to humans and the environment. In addition, the aqueous etchants will also create a combination of OH, O, and F groups on the surfaces, making the surface treatment and control of surface termination difficult. Therefore, using the electrochemical method can be a better solution [8].

Although, in general, all the MAX phase etching techniques are based on electrochemical processes that involve electron transfer during the reaction, the method introduced here is where the anodic sites and cathodic sites are separated. The reaction is driven by bias, unlike a typical reaction where the active spot on the surface partakes in both anodic and cathodic reactions [9]. In contrast to acid etching, which involves fluoride ions, the electrochemical etching method only produces terminal groups of -Cl, -O, and -OH. Therefore, with further treatment, the terminal group does not have fluorine for Mxene [10]. In the experiment done by Sun W et al., the reaction mechanism for electrochemically etching Ti_2AlC was similar to that of acid etching with HF. Instead of HF, 1M concentration of HCl was used, and a +0.6V potential difference was applied to the MAX phase. The -Cl terminal group attached to the Mxene, and Al was oxidised and etched out. The Mxene was then etched further into CDC, and more MAX phase developed into Mxene. Finally, a 3-layered structure was formed. From the outside inwards, there was CDC, Mxene, and an unetched MAX phase [10]. The steps are illustrated in Figure 3 for Mxene synthesis by the electrochemical etching method.

To make SFL-Mxene, delamination of Mxene made from the above methods is important. There are various methods for Mxene delamination. Liyuan L. et al. used molten salt to react with dimethyl sulfoxide, isopropylamine, or tetrabutylammonium hydroxide, followed by sonification to form a colloidal solution of single-layered Mxene [11]. The illustrated steps are shown in Figure 4.

In general, delamination happens in organic molecules or inorganic salts with sonication, mechanical milling, or flash freezing. The sonification method is time-consuming since improvements can be made to reduce the time spent on delamination. The future direction is to utilize the microexplosion approach, which still requires more research. And more studies on optimising the delamination conditions are required for SFL-Mxene synthesis [4].

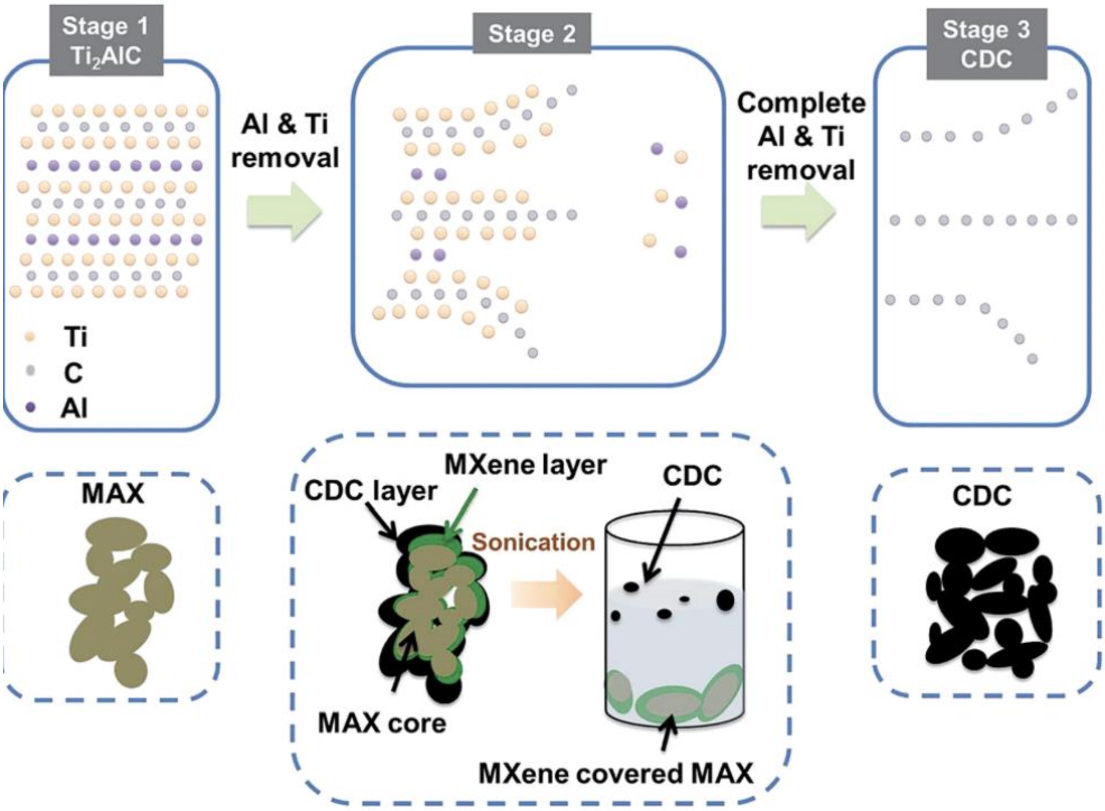

Figure 3. Illustration of electrochemical etching of Ti2AlC in HCl aqueous solution [10].

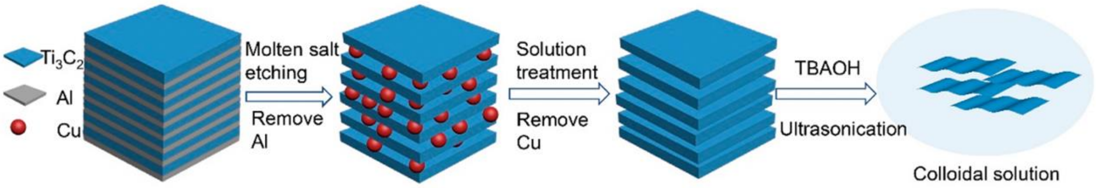

Figure 4. Schematic steps for synthesis and exfoliation of Mxene [11].

2.2. Bottom-up method

A different approach for Mxene synthesis is the bottom-up method, which builds the Mxene directly, unlike the top-down method, which requires delamination of the MAX phase. The bottom-up approach always constructs the structure by connecting atoms and often results in a more controlled and precise structure [4]. This gives the Mxene synthesis more desirable properties.

Chemical vapor deposition (CVD) is a promising technique for achieving large areas and thin layers of Mxene. The growth of Mxene is more uniform and allows for mass production [12]. In the research done by Turker F. et al., thin Mo_2C Mxene was successfully synthesised by CVD. The experiment used N_2 and H_2 as carrier gases and CH_4 as a carbon source. Molybdenum foil was used as the transition metal source, and copper foil was used as the catalyst of carbon capture. The foils were placed in the furnace, and carrier gas filled up the furnace. Then CH_4 flew into the furnace and started the reaction. And Mo_2C was successfully synthesised by CVD [13]. The experiment layout is shown in Figure 5. The thickness of synthesised Mxene can be controlled by varying the CH_4 flow rate, and the H_2/N_2 gas volume ratio can provide the different shapes of Mxene. Therefore, the properties of the

Mxene can be tuned by changing the gas parameters. With fine-tuned properties, the specific application requirements can be achieved [12].

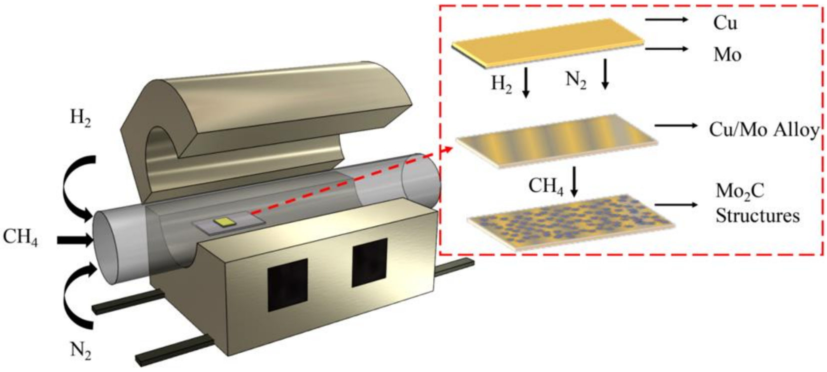

Figure 5. CVD furnace and the reactants for Mo_2C synthesis [13].

Another bottom-up synthesis method is self-assembly. In general, Mxene sheets can be suspended in an aqueous solution because the terminal group is negatively charged on the surface. Therefore, the Mxene is highly hydrophilic and electrostatically repulsive.[14] And in the research done by Mojitabavi, M et al., $Ti_3C_2T_x$ was successfully made via self-assembly at the air/water interface with an ethyl acetate catalyst in the process. Unlike the previous method of self-assembly, which used the Langmuir-Blodgett and Langmuir-Schaefer techniques, the Mojitabavi group used lateral self-assembly at the liquid/liquid interface to synthesise SFL-Mxene instead. The previous method requires delicate control over surface pressure to form monolayer Mxene. The new method provides large-scale and large-area Mxene production [15]. The self-assembly process is shown in Figure 6.

3. Application

The applications for Mxene are various, such as gas sensing, energy storage, optoelectronics, etc. In this article, some of the most studied aspects are discussed.

3.1. Gas sensor

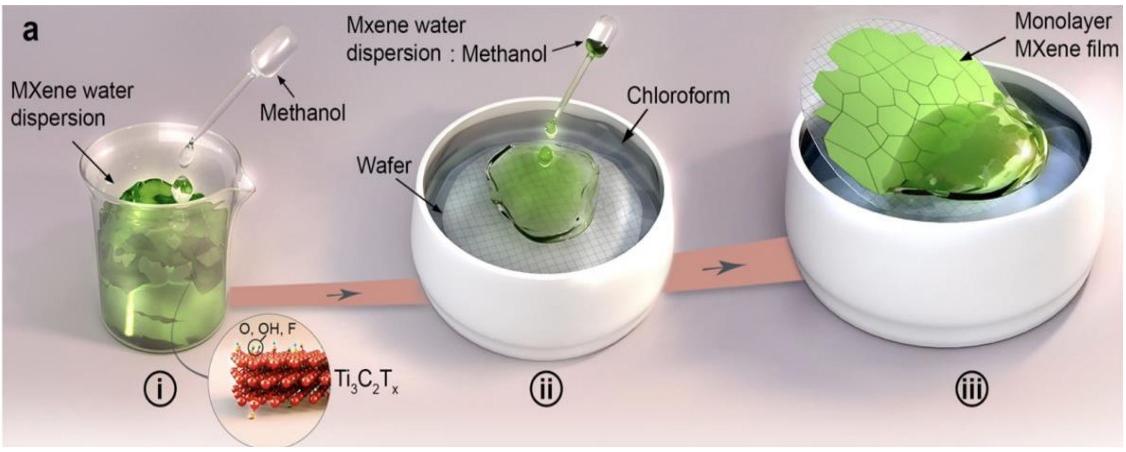

Figure 6. Schematic illustration of self-assembly at a liquid/liquid interface and transfer steps of monolayer Ti3C2Tx film [15].

Gas-sensing devices are essential nowadays. The demand for reliability, high sensitivity, and selective gas-sensing ability requires new materials. And more research found that 2D materials, such as graphene, transition metal dichalcogenides, and transition carbides (Mxene), are a good fit for the application. The structural parameters and surface treatment can be adjusted to meet the requirements of different gas sensors. The most influential factors for gas sensing are structural defects, surface terminated groups, surface functions, and dopants [16].

Among all the 2D materials, Mxene and Mxene-based materials have gained more attention for gas sensing. The gas sensing property is achieved based on the metal oxides depending on the surface reaction of gas molecules with pre-adsorbed oxygen species. However, the gas sensing mechanism of Mxene relies on the charge transfer process, which is the physisorption of gas molecules on the surface of terminated groups without absorbing oxygen species. In Figure 7, the example mechanism for ammonia sensing is illustrated [16].

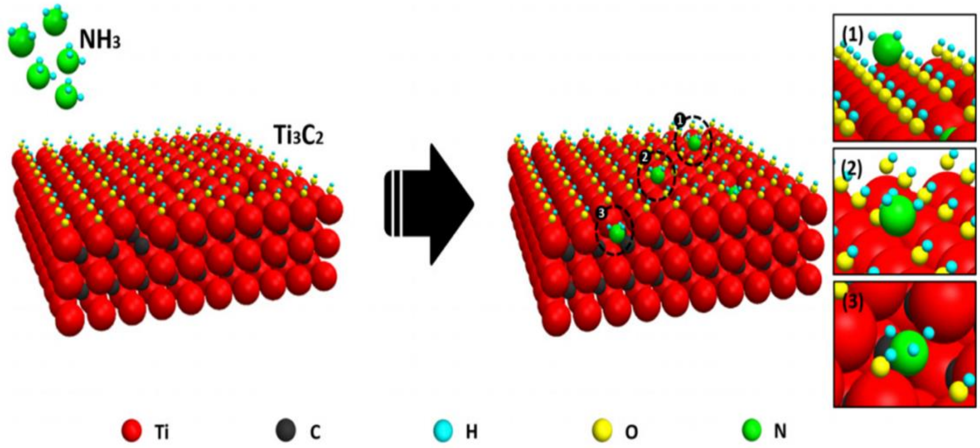

Figure 7. Illustration of ammonia sensing by adsorption/desorption process on Mxene [16].

The resistance of Mxene under gas exposure always increases and is not affected by gas type, unlike semiconductor-based gas sensors, which strongly depend on electron acceptor/donor properties and charge carrier type [16].

3.2. Electric conductor

Mxene has high electrical conductivity and a large specific surface area. Surface chemistry allows functionalisation and good dispersion in a solvent. Most importantly, electrochemically conductive for energy storage properties [17].

Electrical conductivity is crucial for electrical storage efficiency. And the conductivity of Mxene can be improved by using graphite as a carbon source and excessive aluminium powder when making Ti_3AlC_2 MAX phase precursor for $Ti_3C_2T_x$ Mxene. Synthesis of large surface area leads to fewer defects. Mxene can also improve conductivity. The surface treatment, which removes -OH and -F termination groups, also produces Mxene with higher conductivity [18].

3.3. Supercapacitors

Mxene can be used to build supercapacitors because of the high surface area, and the structure provides high electrical double-layer capacitance. Also, the pseudocapacitance is increased due to the intercalation mechanism by accommodating different cations. With surface treatment and removal of -OH and -F termination groups and replacement with -S groups, the pseudocapacitance increases because of the adsorption of counter-ions. Also, doping can change the band gap and add more counter-ions, which, when carefully treated, the synergy between different atoms can improve the electrode properties as well as the interaction with the electrolyte to produce higher capacitance. But the excess doping will cause a decline in capacitance [17].

3.4. Batteries

Mxene can also be built into lithium batteries. Mxene was first used as an anode material with a high surface area and weak interlayer forces with surface functional groups. Because of Mxene's special composition, it can be tuned to achieve better performance, such as the specific capacitance of $Ti_2C<Nb_2C<V_2C$. And the voltage profile is different among different Mxene compositions. Therefore, Mxene can be used for both anode and cathode [17]. Besides, Mxene can also be implemented in sodium batteries as Na ions intercalate in Mxene nanosheets and increase the interlayer distance. Which traps the Na ions and acts as the pillar and penetrated solvent molecules uptake in the interlayer and keeps the distance the same during sodiation/desodiation process. As a result, Mxene reduces sodium diffusion and improves the battery storage capacity [19].

3.5. Optoelectronics

The electronic band of Mxene is calculated, which in theory is metallic when without surface terminated group. But with surface groups, Mxene can acquire semi-conductor like or semi-metallic properties, which is suitable for making optoelectronics. The transparency of Mxene makes it suitable for being implemented as an electrode in optoelectronics [20]. As Mxene has good conductivity, transparency, tunable band gap, and hydrophilicity, it is suitable in solar cell applications, mainly used as electron/hole transport layers, light absorbing layers, and electrodes. Both Mxene and Perovskite are suitable for perovskite solar cells, organic solar cells, silicon-based solar cells, and QD sensitized solar cells. In addition, implementation of Mxene is all improved or has comparable properties compared to other techniques [20], which showed Mxene has high potential in optoelectrical applications. With more research and development, Mxene in the future can be a promising material for optoelectronics.

4. Conclusion

This review included the recent progress in the synthesis of Mxenes. Also, the applications in gas sensing, energy storage, and the optoelectronic potential. The applications are limited by the synthesis process, which need to be improved. The large-scale synthesis is always required. The optimization of synthesis routines is also important, and more research are focused on that prospect. Mxene is also in a research phase, where new applications and synthesis methods will be discovered. In addition, Mxene already showed improvement in different applications while replacing the traditional or current used materials. And with Mxene implementation, such as in the lithium battery, the energy storage properties are improved. Therefore, Mxene can be treated as the next prospective material and more research will be done on it in the future. And eventually, large-scale industrial applications will be achieved.

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