



Environmental Stability of MXenes as Energy Storage Materials

Xinliang Li, Zhaodong Huang and Chunyi Zhi*

Department of Materials Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong

In the past decade, MXenes family have undergone considerable development and have been widely investigated in various research fields, relying on their excellent physicochemical properties. Benefiting from the increasingly versatile preparation methods and the continued discovery of new members, their large-scale application has already been underway, with energy storage fields including supercapacitors and batteries leading. The synthesis methods and processing environment of MXenes, which are closely strictly to the microstructure, surface chemistry, and electronic properties, have attracted great attention. In this review, we review the phylogeny of MXenes materials in recent years, mainly focusing on the synthesis process and environmental stability.

Keywords: MXene, environmental stability, energy storage material, electrode, oxidation

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*Correspondence:

Chunyi Zhi
cy.zhi@cityu.edu.hk

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INTRODUCTION

The term MXenes with a formula of $M_{n+1}X_n$, named after other 2D analog materials silicene, graphene, phosphorene, and so on, are synthesized by extracting A atomic layer from ternary MAX ($M_{n+1}AX_n$) ceramics, where M = early transition metal elements (Ti, Zr, Mo, Nb, V, Mn, Sc, Hf, W, and so on), A = group 13 or 14 (Si, Al, Ga, and so on), X = C or/and N (Anasori et al., 2015, 2017). In 2011, Yury's group firstly reported the first MXene material, this is, Ti_3C_2 using HF solution as the etchant and Ti_3AlC_2 as the MAX precursor (Naguib et al., 2011). Ti_3C_2 is generally written as $Ti_3C_2T_X$, where T_X stands for the inevitable surface functional groups, such as =O, -OH, -F, considering its surface chemical properties (Lukatskaya et al., 2013). Subsequently, a series of different MXenes materials, which possesses various M or/and C or/and n, are synthesized and reported using similar wet chemical etching method, and the naming rules follow the convention described above. For example, $Zr_3C_2T_X$, $Ti_4N_3T_X$, $V_4C_3T_X$, $Ta_4C_3T_X$, Ti_2CT_X , V_2CT_X , $Nb_4C_3T_X$, Cr_2CT_X (Naguib et al., 2013; Ghidui et al., 2014b; Urbankowski et al., 2016; Yang et al., 2016; Zhou et al., 2016; Tran et al., 2018; Wu et al., 2018; Xu et al., 2019). In the early stage, MXenes family were roughly classified into the following three categories according to the variable n: M_4X_3 , M_3X_2 , and M_2X (Khazaei et al., 2018). Notable, as the new synthesis methods adopted, recently, the binary transition metal MXenes equipped with different M_1 , M_2 or X_1 , X_2 elements instead of traditional single M or X layer, emerge, thus this discovery dramatically expands the range of MXenes family members and arouses ever-growing attention (Anasori et al., 2015, 2016; Fashandi et al., 2017). Their formula can be expressed as M_1M_2X and MX_1X_2 . $Mo_2TiC_2T_X$ and Ti_3CNT_X should be two good examples. At the same time, etching methods have also made significant progress. For the purpose of avoiding the usage of dangerous HF, alkali solution etching, such as NaOH (hydrothermal condition), NH_4HF_2 , molten salts etching, such as $LiF + NaF + KF$, and especially electrochemical etching were developed one after another (Ghidui et al., 2014a; Urbankowski et al., 2016; Wang X. et al., 2017; Li T. et al., 2018; Yang S. et al., 2018; Li M. et al., 2019). The optimized safe processes significantly facilitate the large-scale preparation and application of MXenes family.

In the past decade, on account of the unique intrinsic physical/chemical properties, which include high conductivity, localized layered structure, hydrophilicity, abundant surface terminations, biocompatibility, and so on, 2D MXenes materials have been thoroughly investigated. Many research works witnessed the growth and breakthrough in MXenes family. MXenes can be used in various research fields, including ceramics, conductive polymer, energy storage, sensors, water purification, catalysis, thermoelectric conversion, photothermal conversion, solar cell, biomedicine, and microwave absorption and shielding. Among them, energy storage materials are worth highlighting. Specifically, MXenes had been proven to hold ultra-high volume specific capacity as supercapacitors, exceeding $900 \text{ F}\cdot\text{cm}^{-3}$ (Ghidiu et al., 2014a). Their impressive talent in cation ions storage had also been confirmed by Yury and other researchers, as a series of multivalent ionic capacitors with satisfied performance including Li^+ , K^+ , Na^+ , Mg^{2+} , Zn^{2+} , Al^{3+} (Lukatskaya et al., 2013; Mashtalir et al., 2013; Er et al., 2014; Xue et al., 2017a; Kang et al., 2018; Zhu et al., 2018; Liang et al., 2019; Luo et al., 2019; Ma et al., 2019; Yang et al., 2019a; Zhao et al., 2019). For instance, $\text{Ti}_3\text{C}_2\text{T}_x/\text{TiO}_2$ enabled a capacity of $51 \text{ F}\cdot\text{g}^{-1}$ in the KOH electrolyte (Rakhi et al., 2015). What is more, by their novel microstructure and conductivity (up to $6.76 \times 10^5 \text{ S}\cdot\text{m}^{-1}$), MXenes, as electrodes, both cathode, and anode, still shine brightly in the organic battery system. As to Li-S, Li^+ , Al^{3+} , Mg^{2+} , and K^+ batteries, MXenes sometimes showed even much better electrochemical performance than traditional carbon materials, which was quite impressive considering their much larger density (Naguib et al., 2013; Xie et al., 2014; Kim et al., 2015; Mashtalir et al., 2015; Ahmed et al., 2016; Byeon et al., 2016; Huang et al., 2016, 2017a,b, 2019; Tang et al., 2016; Dong et al., 2017; Liang et al., 2017; VahidMohammadi et al., 2017; Bao et al., 2018; Xu M. et al., 2018; Li H. et al., 2019; Liu R. et al., 2019). For example, as the cathode, about $300 \text{ mAh}\cdot\text{g}^{-1}$ capacity could be delivered in an $\text{Al}/\text{Ti}_3\text{C}_2\text{T}_x$ battery, and $300 \text{ mAh}\cdot\text{g}^{-1}$ was realized in an $\text{Mg}/\text{Ti}_3\text{C}_2\text{T}_x$ battery (VahidMohammadi et al., 2017; Xu M. et al., 2018). Similarly, as anodes, discharge capacity could be up to $1,383 \text{ mAh}\cdot\text{g}^{-1}$ in the Li-S system based on the few-layered $\text{Ti}_3\text{C}_2\text{T}_x$ (Tang et al., 2019). While being loaded other active substances, their natural layered structure coupled with much larger layer spacing than graphene could provide more space and thus superior diffusion kinetics for ions shuttle.

Up to now, more than about 30 different 2D MXenes members have been successfully synthesized, and calculations has predicted the existence of hundreds of other MXenes members due to the emergence of binary MXenes (Anasori et al., 2017). As a rising star in the energy storage field, compared to other monotonous 2D materials, MXenes with the multi-atom layered crystal structure are considered to be star materials. On the one hand, the abundant functional termination that can be adjusted by controlled etching processes, are conducive to their further chemical modification and recombination with other highly active electrode materials, which is also the focus of most researches at present (Hong Ng et al., 2017; Wang et al., 2018; Li M. et al., 2019; Yu et al., 2019). On the other hand, more significantly, the ordered and layered atom arrangement provides more possibilities for researchers to select suitable conditions to

design MXenes derivatives with the favored structure and phase composition that cannot be easily or even impossible to achieve through traditional routes.

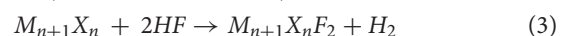
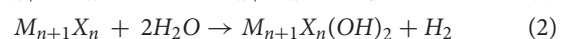
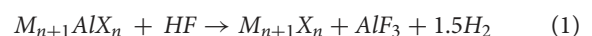
However, in terms of MXenes themselves, natural oxidation phenomenon is an inevitable drawback for electrodes pursuing the stability during cycling (Zhang et al., 2017; Liang et al., 2018; Li H. et al., 2018; Liu et al., 2019a,b; Mo et al., 2019; Seredych et al., 2019; Yang et al., 2019b). This problem is also one of the essential reasons why MXenes-based electrodes are mainly employed in organic electrolytes, in which the absence of water or/and oxygen can effectively avoid their spontaneous oxidation. Interestingly, on the other hand, the results may be reversed if the oxidation products are electrochemically active, even higher than the parent MXenes. The oxidation process, if properly controlled, may mitigate the inevitable decline in battery capacity. In summary, the oxidation behavior of MXenes, whether passive or active, complete or incomplete, is interesting and worthy of in-depth discussion, but rarely focused on. Thus, from the perspective of bare MXenes, we summarized and analyzed the oxidation reactions of MXenes under different environmental conditions and the accompanying structure and phase composition transition.

VARIOUS MXENES AND SYNTHESIS METHODS

Etching methods have been improved over the years, from initially dangerous HF etchant to safe electrochemical etching (Anasori et al., 2015; Wang B. et al., 2017; Pang et al., 2019). The extraction of *A* atomic layers in MAX is often accompanied by the spontaneous formation of functional groups, according to the thermodynamic calculation and experimental confirmation (Naguib et al., 2011). In this regard, different etchants used usually lead to differences in surface terminations, which should further affect the structure, electronic, and chemical properties that are strictly related to energy storage performance. Thus, in this section, we will first review and classify the reported etching methods of MXenes.

WET CHEMICAL ETCHING

HF solution as an etchant gave birth to the first MXene, $\text{Ti}_3\text{C}_2\text{T}_x$, using Ti_3AlC_2 MAX ceramic as the precursor, and had been widely used to synthesize other many MXenes, such as Nb_2CT_x , V_2CT_x , Ti_3CNT_x . For Al-based MAX, the proposed etching process and associated mechanism could be expressed as the following equations:



In the beginning, as shown in Equation (1), the much weaker metallic M-A bonds compared to M-X (covalent or ionic bonds) broke first, and F ions then combined with the Al ions to form

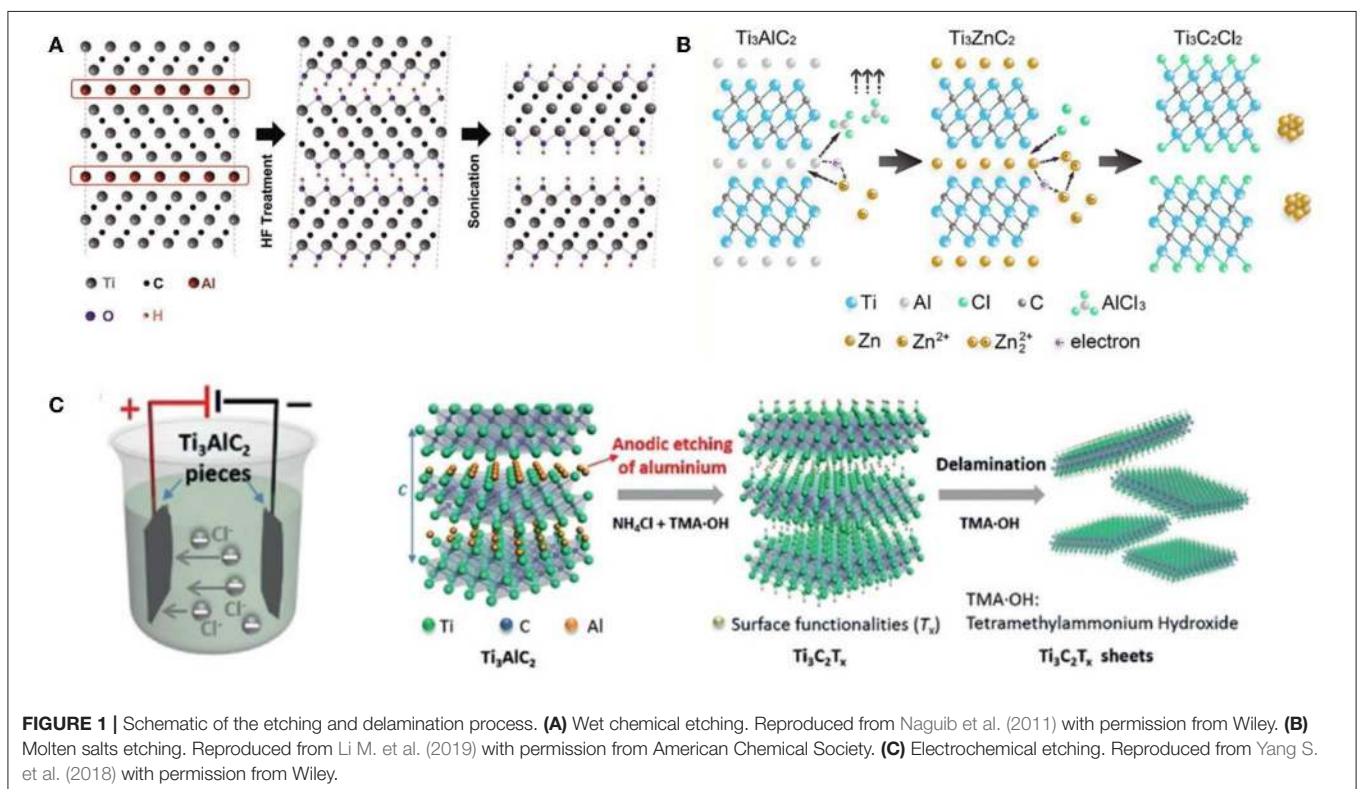
AlF_3 , with the formation and release of H_2 (Naguib et al., 2011; Srivastava et al., 2016; Khazaei et al., 2018). In this way, the Al layer was pulled out of MAX bit by bit, and MXene inherited the hexagonal lattice. At this stage, MXene possessed high activity and could not be stable in water or acid, so it would spontaneously react with H_2O and HF to reduce surface energy by generating $-\text{F}$, $=\text{O}$, and $-\text{OH}$ surface terminations (Figure 1A).

To avoid the direct use of toxic HF, the fluoride-contained salts combined with hydrochloric acid were developed into another capable liquid etchant, which was first proposed by Yury's group (Urbankowski et al., 2016). Many experiments showed that MXenes prepared by this modest method tended to acquire much fewer atomic defects and higher conductivity. More importantly, the fluoride salts used were available in a wide range, including LiF, NaF, KF, CaF_2 , CsF, FeF_3 , and so on, while the concentration of HCl ranged from 6 to 12 M (Ghidui et al., 2014a; Wang X. et al., 2017). This etchant endowed the obtained MXenes inherently capable of carrying specific ions pre-intercalation layers, resulting in large interlayer spacing that facilitated subsequent energy storage. Also, the various bifluoride-based solution, including NH_4HF_2 , NaHF_2 , KHF_2 as the etchants had been revealed in recent years (Halim et al., 2014; Feng et al., 2017). $-\text{NH}_3$ and $-\text{NH}_4$ could attack the Al layers in MAX and then inserted into interlayers of the obtained MXenes, which benefited the further delamination of MXenes. The main reaction by-products were verified to be $(\text{NH}_4)_3\text{AlF}_6$, NH_4AlF_4 (Halim et al., 2014). Besides, NH_4F and NaOH solutions came to the fore when more demanding preparation conditions were considered, such as high temperature and pressure. Liu's group successfully synthesized

multi-layered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene by a facile hydrothermal route at 150°C , employing NH_4F as the etching agent (Wang et al., 2016). Wei's group reported the partial etching behavior of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in 1 M H_2SO_4 solution at 80°C , during the hydrothermal process, after undergoing a pre-treatment of precursor Ti_3AlC_2 MAX impregnated in 1M NaOH solution at 80°C for 10 h (Li T. et al., 2018).

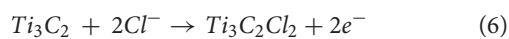
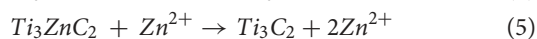
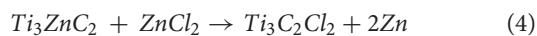
MOLTEN SALTS ETCHING

Nitride MXenes reports lag far behind carbide MXenes. This is due to the difference in the chemical nature of the precursor MAX ceramics of the two, making the latter unsuitable for the mature wet chemical etching method. Their M-A bond energy can be almost the same as or slightly higher than that of the M-X bond. Consequently, the strong etchability of HF or other etchants may open the M-A bonds to etch away Al atoms, and also break M-X (N) bonds to dissolve the MXenes (Urbankowski et al., 2016). Thus, molten salts etching develops into a new method in recent years, which is mainly designed for nitride MXenes members. In 2016, Yury's group proposed the use of molten fluoride-contained salts at high-temperature etchants and successfully synthesized the first nitride MXene member, $\text{Ti}_3\text{N}_4\text{T}_x$ (Urbankowski et al., 2016). In this work, Ti_4AlN_3 MAX was first mixed with the etchant (NaF + KF + LiF mixture) and then sintered at 550°C for 30 min in the Ar flowing, followed by the removal of reaction by-products by 4 M H_2SO_4 solution for 1 h. However, in terms of crystallinity, the results evidenced that the obtained few-layered $\text{Ti}_4\text{N}_3\text{T}_x$



MXene exhibited more surface defects than other HF-etched counterparts. Examining the entire preparation process, this method is far more complicated than the above wet chemistry, although it is sometimes irreplaceable when taking the required high temperature, complex fluoride salts, inert atmosphere, toxic acid solution, into account.

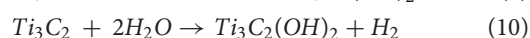
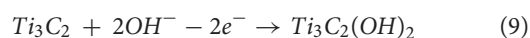
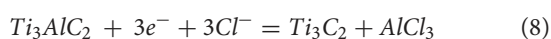
Recent work reported by Huang's group should be highlighted, a general approach was proposed to synthesis halides-terminated MXenes by employing the Zn-based MAX as precursors and only ZnCl₂ salts as the etchant (Li M. et al., 2019; Mian et al., 2019). Thus, a series of MXenes including Ti₃C₂Cl₂ and Ti₂CCl₂, whose surfaces were terminated with only -Cl groups, were synthesized for the first time, after heat treatment at 550°C for 5 h in Ar atmosphere (**Figure 1B**). Remarkably, the simplified etchant, more importantly, the controllable and single functional group, takes the synthesis of MXenes to a new level. The related mechanism involved in the replacement reaction between MAX ceramics and the late transition metal halides were also clarified, as shown in the following equations:



In short, despite the considerable progress, for the moment, the intrinsic drawback described above is likely to make the molten salts etching method less accessible than the wet chemical etching.

ELECTROCHEMICAL ETCHING

MXene exfoliation can also be achieved by the electrochemical method. The selection of the electrolyte is critical, which affects not only the completeness and final yield but also the microstructure and surface chemical properties of resulted MXenes. On account of the strong interaction of halogen element Cl with Al, a Cl-contained electrolyte is a hot topic in current research (Yang S. et al., 2018; Pang et al., 2019). Feng's group adopt a binary electrolyte, this is, 1 M NH₄Cl + 0.2 M TMAOH, to etch the Ti₃AlC₂ MAX to obtain the Ti₃C₂T_X MXene with -OH and =O terminations, as shown in **Figure 1C** (Yang S. et al., 2018). Studies had shown that the concentration of hydroxide possessed a direct impact on the etching time and the type of final product (amorphous carbon or MXene). When the value was 0.2, the reaction efficiency was high, and only 10 h was required. Besides, density-functional theory calculation revealed that the etching process occurred when Ti₃AlC₂ was positively charged as the anode. The possible equations were concluded based on the experimental results as follows:



When Cl⁻ ions bonded to Al³⁺ and form AlCl₃, NH₄⁺ in the electrolyte could intercalate the existing MXene, which significantly improved the degree of completion while avoiding the possibility of etching only on the MAX surface (Lukatskaya et al., 2013; Mišković-Stanković et al., 2014). Moving forward, Hao's group improved the above technique and developed a universal thermal-assisted electrochemical etching approach (Pang et al., 2019). The safe and mild route employed pure diluted HCl as the electrolyte without any toxic intercalants, such as tetramethylammonium. The used slight heating procedure promoted the MXenes exfoliation, which had similar effects of other intercalants but completely eliminated the potential hazards. More significantly, the method had been further extended to V₂CTX and Cr₂CT_X MXenes, unlike previous reports that were limited to only Ti-based MXenes, indicating excellent universality. Note that this technology is carried out under ambient conditions, and it can be further promised by optimizing the choice of electrolyte to avoid environmental pollution and health issues. It should be promising in terms of costs and scale in the future.

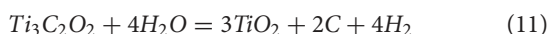
As is well-known, few-layered MXene flakes can be further obtained via the following methods. (1) Sonication; Naguib's group utilized the simple agitation and mild sonication process to delaminate multilayered MXene and obtained flexible Ti₃C₂T_X flakes on a large scale, as depicted in **Figure 1A** (Naguib et al., 2011, 2015). (2) Ions intercalation. Feng and Geng's group reported that the TMA⁺ intercalation would lead to complete delamination of MXenes after etching. Consequently, monolayer or bilayer Ti₃C₂T_X flakes with hydrolyzed Al(OH)₄ surface termination were effectively synthesized (**Figure 1C**) (Xuan et al., 2016; Yang S. et al., 2018).

PHASE AND STRUCTURE TRANSITION UNDER DIFFERENT ENVIRONMENTAL CONDITIONS

Excellent dispersibility enables MXenes to be stably dispersed in water, ethanol, and numerous organic solvents including acetone, ACN, DMSO, DMF, NMP, PC, giving them superior processability and chemical modification. However, MXenes are precisely a class of environmentally sensitive materials. The presence of water and oxygen causes their spontaneous phase transition coupled with microstructure changes, while light and temperature will exacerbate this degradation process. As a result, it is now common to store MXenes colloidal solution at low temperature or/and in the dark or to preserve the dried product in a vacuum or inert atmosphere to isolate moisture and oxygen, especially for few-layered MXenes. Notably, this oxidation behavior is also a direct and effective means of constructing MXene-based composites without the need to introduce any foreign objects. Their fatty elemental composition and ordered layered arrangement provide researchers unlimited operational space. Thus, in this part, we mainly focus on the response behavior and derivatives of MXenes in different environments.

DEGRADATION AT ROOM TEMPERATURE

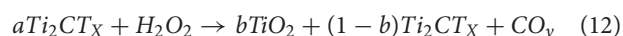
MXenes are unstable in an open environment, even at room temperature. Yury's group took few-layered $Ti_3C_2T_x$ MXenes as an example, the most studied and commonly used representative, systematically investigated and reported the oxidation behavior of its colloidal solution (Zhang et al., 2017). Results showed that the freshly prepared $Ti_3C_2T_x$ MXenes colloidal solution placed in the open vial was degraded by 42% after 5 days, and ultimately degraded after 15 days (Figure 2A). The color of the solution gradually faded from black to pure white. Further XRD data confirmed that the resulting final product was TiO_2 with the anatase crystal structure, after a period of $Ti_xC_yTi_3C_2T_x/TiO_2$ composites. From the structural point of view, the oxidation phenomenon started from the edge sites of MXenes, and as time progressed, it gradually expanded toward the inside of the flakes and eventually invaded the whole. What is more, the degradation rate had a negative correction with the size of the flakes, the smaller the flakes, the faster the degradation. The proposed reaction mechanism was revealed by the following equation:



Obviously, the inert carbon layer was retained after degradation. As to the few-layered Ti_2CT_x MXene, its oxidation process and reaction product was similar to the above, only becoming more intense and rapid. Degradation occurred after a few hours and completed after only about 1 day, the color of the Ti_2CT_x

colloidal solution completely turned brown to white, meaning the complete transition at this moment.

Additionally, the situation changed a lot when the sample was placed in an Ar atmosphere. After more than 3 weeks of storage, the degradation of the colloidal solutions was still very weak, and it became less obvious as the temperature decreased. In this stage, the inevitably little dissolved oxygen in the water was the main influencing factor. On the other hand, filtrating MXenes film by a simple vacuum process was very effective in retarding the degradation rate because of the shielding effect of the dense structure on the external moisture. Barsoum's group also proved the above oxidation mechanism was applicable to multilayer MXenes (Mashtalir et al., 2014). Furthermore, Alshareef's group explored the effect of oxidants on the oxidation behavior of MXenes (Ahmed et al., 2016). The following showed the possible reaction equation:



Apparently, this could be regarded as incomplete oxidation. The usage of H_2O_2 was able to accelerate the oxidation process without changing the final product significantly. By adjusting the oxidant content and reaction time, this was, the oxidation degree, the original layered structure could be selectively retained.

DEGRADATION AT HIGH TEMPERATURE

The oxidation behavior of MXenes at high-temperature conditions mainly depends on the treatment temperature

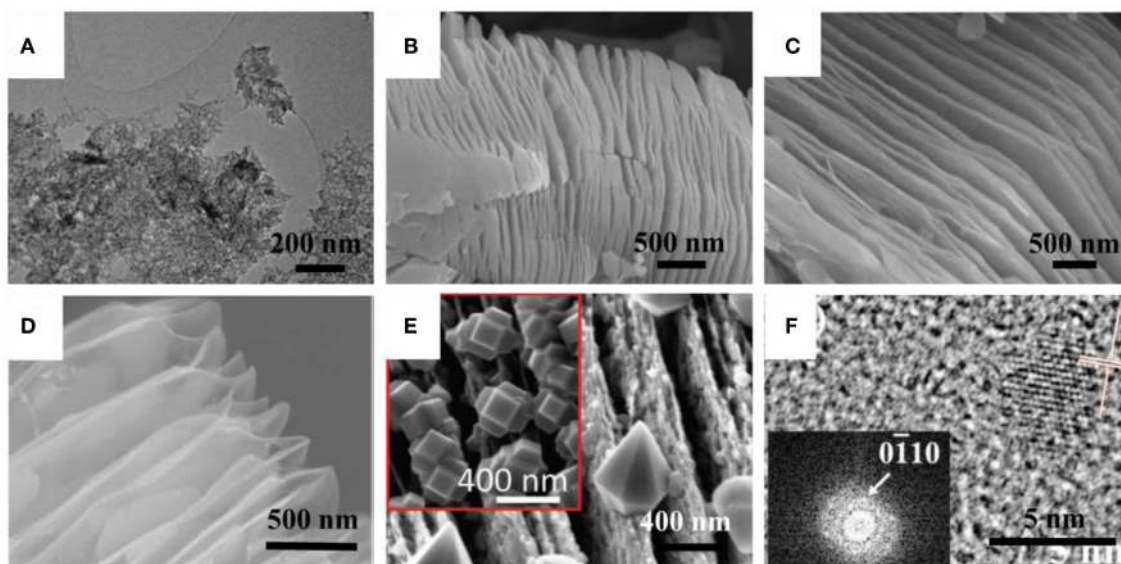


FIGURE 2 | (A) TEM images of MXene flakes of aged d- $Ti_3C_2T_x$ solutions in Air@RT for 7 days. Reproduced from Zhang et al. (2017) with permission from American Chemical Society Wiley. SEM images of $Ti_3C_2T_x$ MXene (B) before annealing and (C) after annealing in Ar@800°C for 2 h. Reproduced from Han et al. (2016) with permission from American Chemical Society. (D) SEM images of as-synthesized C/ TiO_2 hybrids in CO_2 @800°C for 1 h. Reproduced from Han et al. (2017) with permission from American Chemical Society. (E) SEM image of $Ti_3C_2T_x$ flakes after oxidation in Air@1150°C for 30 s. Reproduced from Naguib et al. (2014) with permission from American Chemical Society. (F) HRTEM and FFT pattern of $Ti_3C_2T_x$ quantum dots at 150°C. Reproduced from Xue et al. (2017b) with permission from Wiley.

and atmosphere, and further according to whether the oxidation product contains MXenes, it can be divided into complete oxidation and incomplete oxidation. First, in the air atmosphere, most of the MXenes cannot be stably present, and the corresponding transition metal oxides will be formed, while the carbon layers are oxidized to CO_2 or CO . For example, the team of Zhou presented the different responses of $\text{V}_2\text{CT}_\text{X}$ and $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ at selected temperatures (Wu et al., 2018). After a period of stability, within 150°C , vanadium oxide began to form. At $1,000^\circ\text{C}$, and the layered structure was utterly broken, and the phase was converted entirely to V_2O_5 . As for the $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ MXene, within 200°C , the layered structure remained unchanged, and only a small portion of the anatase was formed between the layers. At $1,000^\circ\text{C}$, $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ was no longer present, leaving only a high temperature stable phase of rutile. Furthermore, with the protection of inert atmospheres, such as Ar, N_2 , or He, MXenes were able to retain their original layered structure over a range of temperatures, but still produced a small amount of oxide (Li et al., 2015; Rakhi et al., 2015; Han et al., 2016; Seredych et al., 2019; Xu et al., 2019). At the same time, the inert carbon layers were kept. When the temperature continued to rise, the crystal structure would change to a high-temperature stable type. For instance, Yin's group explored the thermal stability of $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ within 800°C (Han et al., 2016). The layered structure was almost constant except that the sheet was thinned, and a small amount of invisible titanium dioxide was formed therein. Also, Yury's group revealed the non-negligible effect of surface terminations on the thermal stability of $\text{Ti}_3\text{C}_2\text{T}_\text{X}$, $\text{Nb}_2\text{CT}_\text{X}$, $\text{Mo}_2\text{CT}_\text{X}$ MXenes in the He atmosphere (Seredych et al., 2019). At $1,500^\circ\text{C}$, $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ was confirmed to converted to the TiC phase. As to the NH_3 atmosphere, the oxidation behavior was similar to that of the inert atmosphere, but some nitrogen atoms would partially replace the carbon atoms in carbide MXenes to form N-doped MXenes (Wen et al., 2017; Bao et al., 2018). Wang's group managed the synthesis of N-doped MXenes with 1.7–20.7 at% surface N concentrations by annealing $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ at 200 – 700°C in the NH_3 atmosphere (Wen et al., 2017). Meanwhile, no signal of titanium oxide was detected, and original morphology stayed, similar to the results of the few-layered $\text{Ti}_3\text{C}_2\text{T}_\text{X}$.

Also, for a highly reducing atmosphere, such as H_2 , H_2/Ar , or H_2/N_2 , the localized laminated structure can be well-maintained, and the amount of oxide formed is much smaller than that in the above conditions. Yin's group work showed that the $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ MXene flakes ($\text{Ti}_3\text{C}_2\text{T}_\text{X}$ and $\text{Ti}_2\text{CT}_\text{X}$) had even become smoother after undergoing heat treatment at 500 – 800°C in H_2/Ar condition, as displayed in **Figures 2B,C** (Li et al., 2017b; Xu et al., 2019). For the oxidizing atmosphere, such as CO_2 , the oxidation behavior of MXene should be divided into two types, as shown in **Figures 2D,E** (Naguib et al., 2014; Chen et al., 2015; Rakhi et al., 2015; Zhang et al., 2016; Han et al., 2017; Li et al., 2017a). At lower temperatures, both MXenes phase and layered structure can be reserved. Barsoum's group fabricated the $\text{TiO}_2/\text{Ti}_2\text{CT}_\text{X}/\text{C}$ and $\text{Nb}_2\text{O}_5/\text{Nb}_2\text{CT}_\text{X}$ composites using the flash sinter process (Naguib et al., 2014). Besides, Yury's group synthesized the $\text{Nb}_2\text{O}_5/\text{Nb}_4\text{C}_3\text{T}_\text{X}$ (or $\text{Nb}_2\text{CT}_\text{X}$) and $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_\text{X}$ composites by post-etch annealing at 850°C in flowing CO_2 (Zhang

et al., 2016). Remarkably, at higher temperatures, the oxidation behavior becomes completely different. The transition metal layers were oxidized while the middle carbon layer was wholly stripped, and thus MXene disappeared utterly, resulting in the pure C/TiO_2 composite with a highly ordered sandwich-like layered structure (Han et al., 2017; Li et al., 2017a).

DEGRADATION UNDER HYDROTHERMAL CONDITION

Unlike the conditions described above, the high temperature and pressure environment derived from the hydrothermal process, promote not only MXene phase transition, but also rich and varied structural evolution, especially in the presence of various regulators. Barsoum's group implemented the hydrothermal treatment at 150 – 250°C under 1–5 MPa pressure and obtained $\text{Ti}_3\text{C}_2\text{T}_\text{X}/\text{TiO}_2/\text{C}$ composites, which owned a similar microstructure to that obtained by thermal treatment in CO_2 (Naguib et al., 2014). Also, Mei's group explored the layer-stacked $\text{Ti}_3\text{C}_2\text{T}_\text{X}/\text{TiO}_2$ phase via a similar process at 200°C (Tang et al., 2016). Moreover, Cao's group recorded the formation of spherical TiO_2 on the surface of $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ at 180°C (Gao et al., 2015). But, in the alkalization environment, results changed significantly. As highlighted by Bao's group, after introducing $\text{KOH} + \text{H}_2\text{O}_2$ and $\text{NaOH} + \text{H}_2\text{O}_2$, the original accordion-like particles evolved into intertwined flexible nanobelts, and $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ MXenes were also totally converted into $\text{K}_2\text{Ti}_4\text{O}_9$ and $\text{NaTi}_{1.5}\text{O}_{8.3}$, respectively (Dong et al., 2017). Furthermore, when the regulator changed to $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O} + \text{H}_3\text{PO}_4 + \text{H}_2\text{O}_2$, Na^+ , and PO_3^{2-} reacted with existed TiO_2 that had been formed, to generate $\text{NaTi}_2(\text{PO}_4)_3$ at 160°C (Yang Q. et al., 2018). During the reaction, TiO_2 acted as the seed layer to guide the uniform nucleation and growth of $\text{NaTi}_2(\text{PO}_4)_3$.

Moreover, hydrothermal is also an effortless facile way of synthesizing MXenes quantum dots. Zhi's group adopt $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ MXenes as the precursor to manufacture quantum dots with different size, and quantum yield was up to about 10% (Xue et al., 2017b). It is worth noting that the resulting quantum dots were monolayer and water soluble. Their size was tailored to the reaction temperature. The average lateral size reached about 2.9, 3.7, and 6.2 nm, corresponding to the reaction temperature of 100, 120, and 150°C , respectively, showing an apparent positive correlation. Unfortunately, with the increase of heat, the loss of Ti atoms on the surface of $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ quantum dots also deteriorated. At 150°C , the crystallinity was inferior to the low-temperature products, and even a small number of carbon quantum dots were detected (**Figure 2F**). Besides, Xu's group designed 2D N-doped quantum dots based on $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ via the hydrothermal process combined with HNO_3 pre-treatment (Xu Q. et al., 2018). Specifically, the precursor $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ was nitrified using nitric acid for 5 h at 100°C and then subjected to a hydrothermal step at 160°C for 2 h, with the addition of NaOH and ethanediamine. XPS revealed that some nitrogen atoms and carbon atoms were chemically bonded, suggesting the successful nitridation of $\text{Ti}_3\text{C}_2\text{T}_\text{X}$ quantum dots. The lateral size was concentrated at 3.4 nm. The quantum dots yield of up to

18.7% in this work was sufficient to demonstrate the effectiveness of this proposed method.

CONCLUSION

In summary, the etching process and subsequent processing environment definitely have a significant impact on the phase composition and microstructure and the associated physical/chemical properties of MXenes. The increasingly mature synthesis methods lay the foundation for their large-scale application. The controllable microstructure and rich surface chemistry are also primarily important to determine the properties of MXenes. At low temperatures, the dark condition and vacuum and inert atmosphere are effective ways to isolate moisture and oxygen and then prevent the oxidation behavior, especially for few-layered MXenes. At high temperatures, this oxidation behavior tends to occur and associated transition metal oxides are formed. The phase transition temperature and products usually depend on the composition of MXenes and atmosphere conditions. At hydrothermal condition that provides high temperature and pressure, more varied microstructural transformations even MXenes quantum dots can be obtained

except for the above phase transition by adjusting the additives with different pH. Unique electronic and chemical properties are making MXenes stand out in many fields, in particular, energy storage. It is foreseeable that the wide variety of MXenes derivate available in different environments will offer considerable possibilities for future expansion. Therefore, while developing new MXenes, profoundly exploring their transformation behavior in extensive settings should be worthy and necessary.

AUTHOR CONTRIBUTIONS

XL and ZH wrote the manuscript. CZ supervised and communicated the manuscript.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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