Perspectives on preparation of two-dimensional MXenes

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ABSTRACT
The excellent intrinsic properties of two-dimensional MXenes, such as hydrophilic, good electrical and thermal conductivity, excellent film forming ability, render them potential candidates for many innovations in different areas. High-quality MXene plays an important role in enhancing the devices’ performances in various applications. However, the synthesis of high-quality MXenes has not been well documented. Herein, we summarize the up-to-date preparation strategies of MXene and compare their respective advantages and disadvantages. We particularly outline the criteria of high-quality MXenes, and focus on the influence of different synthetic methods on the surface functional groups, morphology (size and defect), layer spacing of MXene, etc. The challenges on MXenes’ preparation and their future perspectives are also provided. We anticipate this perspective will provide prospective guidance for synthesizing desirable high-quality MXenes.

1. Introduction
Since the successful preparation of two-dimensional (2D) titanium carbide Ti$_3$C$_2$T$_x$, research on etching/delamination of transition metal carbides, nitrides and carbonitrides, so-called MXenes, have become one of the hottest topics within the 2D family [1–10]. The general formula of MXene is described as M$_{n+1}$X$_n$T$_x$, indicating (n + 1) atomic layers of M (early transition metal such as Ti, V, Nb, Cr, Mo, etc) sandwich n atomic layers of X (C and/or N) in an [MX]nM arrangement (Figure 1(a)) [11]. Typically, MXenes are obtained through the selective removal of the A element from their precursor MAX phases (where A represents group 13 or 14 elements such as Al and Si. M and X are same as those of MXenes) via HF-containing solution. As such, resultant MXenes are often terminated with abundant functional groups (– F, – OH, – O, written as T$_x$) [12–16]. The F/O ratio is etching route dependent [17]. In addition, double-M MXenes, either solid solution or ordered phase, are also reported, which greatly enrich this wonder 2D class of materials [18,19].
Figure 1. (a) The family of MXenes (and MAX phases) in Periodic table. (b) Consecutive steps of schematic steps for MXene synthesis from their MAX phase, taking Ti3AlC2 for example; (i–iii) Schematic diagram, atomic structure diagram and SEM images of the stepped MAX phase; (iv–vi) Schematic diagram, atomic structure diagram and SEM images of accordion Ti2C2Tx MXene; (vii–ix) Schematic diagram, atomic structure diagram and TEM images of single-layer Ti3C2Tx MXene. Reproduced with permission from [93], Copyright 2017, American Chemical Society.

Indeed, the advantageous properties of MXenes, including superb electrical conductivity [20], high mechanical strengths [21], attractive optical properties [22], adjusted structure [23] and work function [24], render them as perfect candidates for many different fields, such as biosensing, nanomedicine and environmental remediation and so on [25–32]. For example, MXenes possess excellent electrical conductivity (~20,000 S/cm) [33], which makes them strong candidates for EMI shielding materials [34]. A MXene film with a thickness of 1.35 μm showcases an efficient electromagnetic interference shielding of 50 dB [35]. Due to the excellent electrical and mechanical properties in the delaminated MXene nanosheets, the sprayed MXene film can be employed as electrical contacts (i.e. gate, source and drain) for thin-film transistors [36], bottom electrodes for triboelectronic nanogenerators [37], mechanical reinforcements [38], transparent conductive electrodes [39], etc; furthermore, all the properties could be modified or even manipulated through controlling the surface terminations that are created during the exfoliation and intercalation processes.

For instance, the T-group localization at the surface of the multilayered MXene nanosheets can result in variations in the optical conductivity in the middle of the visible spectrum by up to 40% [40]. In addition, the narrow band gap of Ti3C2T.x with 0.05 and 0.1 eV for – F and – OH functional groups respectively, could be broadened through quantum effects, thus resulting in strong photoluminescence emissions [41]. The spray-coated MXene films endow a higher electrical conductivity, lower contact resistance/sheet resistance, and smaller surface roughness without wrinkles or
porosity [42]. On the side, one can achieve quite low work function-MXenes by surface modifications ending up with a major percent of -OH functionalities [43], because oxygen-terminated MXenes possess a larger work function compared to -F terminated MXenes, followed by bare MXenes and only - OH terminated MXenes [43].

These interesting properties endow MXenes quite promising in a variety of applications, including electrochemical energy storage [44–46], electromagnetic interference shielding [47], sensing [48], photodetectors [49], catalysts [50] and so on. For example, Gogotsi et al. showed that the electrolyte-pretreated MXene hydrogel demonstrated excellent volumetric capacitance of 1500 F cm⁻³, which was comparable to that of RuO₂ [51]. Koo et al. reported that a monolayer-thickness film offered ≈20% shielding of electromagnetic waves, while a 24-layer film of ≈55 nm in thickness demonstrated 99% shielding (20 dB) [52]. Ågren et al. showed that as an optical switch for passively mode-locked fiber lasers, ultra-stable pulses can be demonstrated in the telecommunication and mid-infrared regions for Nb₇C MXene [53]. For the catalyst application, both as-synthesized Mo₁₋₀.₃₃₃C and W₁₋₀.₅₃₃C i-MXene exhibited similar over-potential for hydrogen evolution reaction (≈320 mV at a current density of 10 mA cm⁻²) [54].

While these applications are promising, their performances are intrinsically dependent on the quality of MXenes. In other words, the quality of MXene flakes governs their potential applications. For instance, catalysis prefers MXene flakes with more exposed edge sites; therefore, MXene flakes with smaller lateral size favor a higher water splitting kinetics [55]. On the other hand, for transparent conductive electrodes/coatings, larger MXene flakes-based films typically possess much less contact junctions compared to those made of smaller MXene flakes, thus ensuring a much lower sheet resistance [56]. However, for electrochemical energy storage, a balance between the increase in active sites and the loss of electrical conductivity is required, and MXene with median flake sizes performed the best in terms of capacitance or rate performance [57].

These requirements toward different applications highlight the importance of preparation of high-quality MXenes. To date, while most reviews on MXenes or MXene-based composites are focused on their mechanisms and/or applications in electrochemical energy storage, catalysis, EMI shielding and so on, a systematic summary which specially focuses on the preparation of high-quality MXene, has not been reported. As such, here in this work, we summarize the up-to-date preparation strategies of MXene and compare their respective advantages and disadvantages. We outline the criteria of high-quality MXenes, and specially focus on the influence of different synthetic methods on the surface functional groups, morphology (size and defect), layer spacing of MXene, etc. Challenges on MXene synthesis and their future perspectives are also provided. We anticipate this perspective will provide some suggestions for potential synthesis of high-quality MXenes for high-performance applications.

2. Synthesis of MXenes

2.1. Preparation for single-metal MXene

As the precursor of MXenes, MAX phases typically possess a general chemical formula Mₙ₊₁AXₙ, where M is transition metal (Ti, Cr, V, Nb, Mo, etc), n = 1 ~ 4, A is a group 13 or 14 element such as Al, Si, S etc, X is carbon and/or nitrogen (Figure 1(a)). In the MAX atomic structure, M-A bond is weaker than the M-X bond, rendering the ease of selective removal of A and resulting multilayered MXene, terminated with abundant hydrophilic surface groups such as – OH, – O [58] and/or – F, – Cl, – Br, etc [59]. These surface groups are represented with Tₓ. Therefore, MXenes possess a formula Mₓ⁺₁Xₓ⁻₁Tₓ with M atoms located in a close-packed structure and X atoms fill the octahedral interstitial sites, similar to their MAX precursors [60]. The etching process relies on aq. HF brought to the solution or through the in situ formation in LiF/HCl mixture, alkaline solution, molten salts, etc, as schematically shown in Figure 1(b).

Taking Ti₃C₂Tx MXene for example. Ti₃C₂Tx was first obtained in 50% concentrated hydrofluoric acid (HF) at room temperature (RT) for 2 h by Naguib et al. [61]. This method can craft – F and – OH functional groups on the MXene nanosheets and the edges. The key to successfully etching MAX phase is to determine proper parameters such as HF concentration solution, reaction temperature and time. Thereafter, concentrated HF solution has been widely used in etching of other MAX phases to obtain corresponding MXenes, such as Mo₄/₅CTₓ [62], Ti₂NTₓ [63], Nb₂CTₓ [64], Ta₃CₓTx [65], V₂CTₓ [66], etc, as shown in Figure 2(a).

However, HF endangers human health and environment due to its strong toxicity. Instead, mixing lithium fluoride (LiF) with hydrochloric acid (HCl) is able to give HF in situ, thus greatly reduces the potential risks in producing MXenes, featuring a more environmentally green route. In addition, such a LiF-HCl route is also known for the production of high-quality MXenes, best
Figure 2. Preparation method for etching monolayer Group A. (a) Schematic view of the V2AlC pillars construction and HF etching process. Reproduced with permission from [66], Copyright 2020, Royal Society of Chemistry. (b) The reaction between Ti3AlC2 and NaOH water solution under different conditions. Reproduced from [71], Copyright 2018, Wiley Online Library. (c) Proposed E-etching mechanism of Ti3AlC2 in HCl electrolyte. Reproduced with permission from [72], Copyright 2019, American Chemical Society. (d) Etching Ti3AlC2 phase with NH4HF2 in organic solvent. Reproduced with permission from [73], Copyright 2020, Elsevier. (e) (i) Ti3SiC2 MAX phase is immersed in CuCl2 Lewis molten salt at 750 °C; (ii, iii) The reaction between Ti3SiC2 and CuCl2 results in the formation of Ti3C2Tx MXene; (iv) MS-Ti3C2Tx MXene is obtained after further washing in ammonium persulfate (APS) solution. Reproduced with permission from [76], Copyright 2020, Springer Nature. (f) Scheme of the ionothermal synthesis of DES-Ti3C2 MXene. Reproduced with permission from [77], Copyright 2020, Elsevier. (g) Schematic illustration of the synthesis of Ti4 N1Tx by molten salt treatment. Reproduced with permission from [78], Copyright 2016, Royal Society of Chemistry.

evidenced by the reduced amounts of defects or pin-holes on the MXene nanosheets as compared to that of HF etching route. Aside from LiF-HCl combination, non-volatile sulfuric acid (H2SO4) and other fluorides, such as KF, NaF, CsF, FeF3, CaF2, were also used for etching of MAX phase [46], including Ti3CTx [67], V2CTx [68], Ti3CNTx [69], Cr2TiC2T4 [70], etc.

Despite the effective etching of F-containing routes (HF and LiF-HCl routes) in producing MXenes, the involvement of toxic HF (even via in situ formation) and the undesirable -F terminations still pose challenges on scale up the MXene production. By hydrothermal treating the pristine Ti3AlC2 powders in concentrated NaOH solution, the strong interaction between alkali and aluminum allows the latter to be dissolved [71], ending up with fluorine-free Ti3C2Tx MXene, as shown in Figure 2(b). Both hydrothermal temperature and NaOH concentration are key factors that not only control the reaction kinetics but also govern the quality (especially the purity) of resultant MXenes. Nevertheless, such a high temperature hydrothermal treatment in high concentration alkali solutions still pose considerable risks. Instead, electrochemical etching of MAX phase is a mild, harmless yet efficient route. In 2019, a universal strategy based on thermal-assisted electrochemical etching route was developed to synthesize MXenes (Ti3CTx, Cr2CTx, and V2CTx, etc.) (Figure 2(c)) [72]. However, the design of electrolyte, voltage, temperature and time are crucial to selectively remove A layers while preserving the intact 2D structure of MXene, even the architectures of MXene can be constructed by choosing different porous substrate. Although the produce yield (~50%)}
can be slightly higher than that of HF-etched MXenes (~40%) [73], some residue MAX precursors are inevitably retained in the electrochemically etched MXenes. Noteworthy, gentle heating is more conducive to delamination due to the greater current density. And the extent of exfoliation increases with the increase of etching time.

Employing a relatively mild etchant ensures a gentler etching of MAX phase; the resultant MXenes are expected to possess much less defects/pinholes. NH₄HF₂ is a weak yet efficient etchant for MAX phase. Indeed, this etching route allows the non-aqueous preparation of MXenes, which eradicates the potential oxidation of MXenes since MXenes tend to be slowly oxidized in aqueous medium [74]. According to Barsoum et al., by dispersing Ti₃AlC₂ and NH₄HF₂ (mass ratio = 1) in 10 ml of propylene carbonate (PC) solvent, and reacting at 35°C for 196 h, multilayered MXenes can be obtained with PC molecules intercalated in the interlayers [75], as shown in Figure 2(d). The d-spacing in the multilayered MXene after etching (without washing) can be up to 50.7 Å in N, N-dimethylformamide [75]. Therefore, organic polar solvents-induced etching in the presence of ammonium dihydrogen fluoride allows in situ intercalation of organic molecules (solvents beyond PC, for example, acetonitrile, DMSO, NMP, etc.) and rich fluorine terminations on the resultant MXenes. It’s also noted that through washing with acidic propanol, the intercalated organic species and/or NH₄⁺ can be exchanged with the protons presented in the acidic propanol. This opens vast opportunities for tuning the intercalative chemistry of MXenes, providing alternative routes to obtain highly fluorinated MXenes (i.e. in a glove box) and especially suitable for applications that are water-sensitive.

Aside from solution etching strategies, molten salts etching represents an efficient method not only in the selective removal of A element from various MAX phases, but also in the capability in tuning the terminated surface functionalities. In particular, the MAX phases go beyond Ti₃AlC₂, with A element being Zn, Si, Ga etc. and the surface groups being –Cl, –Br, –I, etc. Such a method is so-called Lewis acidic etching, which is general and regulates the functional groups grafted on the MXene nanosheets according to the type of salt (Figure 2(e)) [76]. The Lewis acidic etching also allows the preparation of some novel MXenes which is impossible via the traditional HF or LiF-HCl routes, thus drastically broadens the MXene family. In addition, Wu, et al. [77] developed a water-free ionothermal synthesis of 2D Ti₃C₂ MXene via etching Ti₃AlC₂ in low-cost choline chloride and oxalic acid based deep eutectic solvents (DES) in the presence of NH₄F, thus it is highly safe and convenient to the effective mass production of few-layer flakes and the design of MXene electrodes with high charge storage performance (Figure 2(f)).

Etching nitrides MXenes is almost impossible from the HF route (despite the usage of highly concentrated HF solution), due to the higher formation energy of Tiₙ₋₁Nₙ (the Al atoms in Tiₙ₋₁AlNₙ are stronger bonded than carbon-based MAX phase) and its ease dissolution in HF acid [78]. Instead, through etching in the molten salt mixtures (KF, NaF and LiF) at 550°C, Ti₃AlN₃ was successfully converted to Ti₃N₅Tₓ under an argon atmosphere (Figure 2(g)) [78]. Through further intercalation of large organic base molecules, such as tetrabutylammonium hydroxide, TBAOH assisted by sonication, multilayered Ti₃N₅Tₓ particles can be delaminated, forming colloidal solutions which enriched with predominately single-layer Ti₃N₅Tₓ flakes. Similarly, other 2D transition metal nitrides can also be prepared through such a molten salts etching route [79].

2.2. Preparation method of MXene from non-MAX phase

In addition to the MAX phase precursor, non-MAX phases are also used as precursors to give MXenes, thus greatly enlarging this 2D family of materials. Non-MAX phase has a general formula of (MC)n [Al(A)]mCₘ₋₁, where n is similar in MAX; m usually equals to 3, 4, etc.; and A usually is Si or Ge [80]. For instance, Feng et al. obtained Mo₂C MXene by two methods (LiF/HCl and HF) based on Mo₂Ga₃C and showcased that Mo₂C MXene was an intriguing material with excellent photothermal-conversion efficiency for the first time [81], as shown in Figure 3(a).

Moreover, Zhou et al. alloyed a small amount of silicon into the ternary Hf-Al-C carbide with Si on Al sites to create the Al-C sublayer and weaken the interfacial adhesion between Hf-C and Al-C units [82]. Upon the selective etching of the [Al(Si)]-C sublayer in concentrated hydrofluoric acid (HF), Hf₅C₄Tₓ MXene was achieved due to the more valence electrons of Si than Al, which weaken the adhesive energy of the etching interface (Figure 3(b)) [82]. Unlike the non-MAX phase Hf₁Al₇C₁₀, Zr₁Al₇C₁₀ is easier to be etched with hydrofluoric acid to remove the (AlC)ₓ unit and obtain Zr₁C₁₀Tₓ MXene [83], as shown in Figure 3(c). Based on the large family of (MC)n [Al(A)]mCₘ₋₁ compounds, this non-MAX etching route further broadens the MXenes family, and the efficient technique of forming solid solution to manipulate the sublayer adhesion, like Hf₁[Al(Si)]C₁₀, will provide a novel mentality to etch the MAX phase with high binding sublayer.
2.3. Preparation of double metal MXene

Double metal MAX phases can be generally classified into two general categories: ordered and solid solutions, depending on the atomic arrangement of two metals [84]. The double-metal solid solution phases (The elements in solid solution MAX phases are infinitely soluble with each other, and the M elements are randomly distributed in the M layer), for instance (Ti,V)₂AlC, (Ti,Nb)₂AlC, (Mo,V)₂AlC₃, (Nb,Zr)₂AlC₃ and (Nb,V)₂AlC have been etched and corresponding (Ti,V)₂CTₓ, (Ti,Nb)₂CTₓ, (Mo,V)₂CTₓ, (Nb,Zr)₂CTₓ and (Nb,V)₂CTₓ MXenes were synthesized, respectively through the above etching method of single-M MAX phase. On the side, ordered MAX phases can be divided into out-of-plane ordering (o-MAX) and in-plane ordering (i-MAX). For the o-MAX structure, two M elements in a ratio of 2 to 1 form a phase with out-of-plane chemical order through alternating layers composed of one type of M element. Currently, four o-MAX (Mo₂TiAlC₂, Mo₂Ti₂AlC₃, Cr₂TiAlC₂, and Cr₂VaIc₂) have been successfully converted to MXene (Mo₂TiC₂Tₓ, Mo₂Ti₂C₃Tₓ, Cr₂TiC₂Tₓ, and Cr₂VC₂Tₓ) [85]. Anasori et al. [70] verified the electrochemical-energy potential of Mo₂TiC₂Tₓ MXene and confirmed its unique behavior by etching out-of-plane Mo₂TiAlC₂ with 48 ~ 51% aqueous HF solution for 48 hours (Figure 4(a)). However, in i-MAX, M’ and M” elements arrange in-plane ordering in the atomic ratio of 2:1 in M₂AX phase, therefore, upon the selective removal of M” as well as A elements, i-MXene with a general formula of M’₁₂₋₃ₓTₐ is typically obtained featuring ordered divacancies left by the removal of M” [86]. Meshkian et al. [54] produced Mo₁₂₋₃ₓC MXene with divacancy ordering by using 48% HF or a combination of LiF and HCl to remove Al and Sc atoms. Interestingly, the volumetric capacitance of the as-synthesized Mo₁₂₋₃ₓC is 65% higher than its counterpart, Mo₂C which is in the absence of vacancies and possesses a high electrical conductivity (Figure 4(b)). Such a conclusion suggests that through manipulating the atomic arrangement of double M, the performance of resultant devices can be tuned accordingly. The synthesis of o-MXene and i-MXene rise interest in possibilities for chemically ordered MXenes and expand the MXene family.

Figure 3. (a) Schematics showing the preparation and delamination process of Mo₂C MXenes based on a 3D layer-structure (top) and ball-and-stick (below) model. Reproduced with permission from [81], Copyright 2019, Wiley Online Library. (b) The fabrication process of the Hf₂C₂Tₓ MXene form Hf₂[Al(Si)₂]C₆. Reproduced with permission from [82], Copyright 2017, American Chemical Society. (c) The unit cell of Zr₂AlC₃ and their two structural models. Reproduced with permission from [83], Copyright 2016, Wiley Online Library.
3. The quality control of MXenes

The above sections describe effective ways for MXene preparation summarized according to the categories of precursor. Indeed, both the etching (the synthesis of MXene begins by etching the parent layered precursor, which can be a MAX phase or non-MAX phase precursor) [85] and intercalation (the choice of the intercalated cation and the intercalated molecules, etc.) strategies play a key role in the quality of as-prepared MXene. Therefore, it is important to provide the definition of high-quality as well as factors that govern the synthesis of high-quality MXenes.

High-quality MXene should be rationally designed with different functional groups, interlayer spacing, defects, lateral size and so on towards different applications. Said otherwise, different applications may require MXenes with different features (i.e. defects, size, thickness, surface groups, etc.), and only those MXenes which satisfy the desired application performance can be considered as high-quality. For instance, fluoride-free MXenes can be considered as high-quality MXenes for Li-ion batteries, as they deliver much higher capacity and better rate performance than fluoride-containing $\text{Ti}_3\text{C}_2\text{T}_x$ when storing Li ion [87], and MXene with a larger interlayer spacing has higher specific surface area and more exposed active sites [88]. Moreover, the single-layer MXene with fewer defects and larger size has higher conductivity [89]. Therefore, for those applications requiring highly conductive MXenes, synthesis of single-layer large MXene nanosheets is of particular interest. The following are the factors affecting the preparation of high-quality MXene based on the above definition.

Primarily, the maximum size of MXene nanosheets is limited by the size of the precursor MAX phase, so it is an effective and simple strategy to tailor the size of the precursor to tune the lateral size of resultant nanosheets. Zhang et al. [90] synthesized single-layer $\text{Ti}_3\text{C}_2\text{T}_x$ flakes with average lateral size of 10 ± 2.1 μm using a modified minimally intensive layer delamination (MILD) method, by pre-selecting large $\text{Ti}_3\text{AlC}_2$ MAX phase particles (those greater than 10 μm) from the as-received MAX phase prior to the selective etching step, as illustrated in Figure 5(a). These predominantly large MX particles require the etching conditions to be slightly modified from the MILD method to improve the etching efficiency and yield. Moreover, the interlayer spacing of MXene can be enlarged by pre-intercalating cations before dispersing multi-layer MXene. The difference of hydration enthalpy of cations leads to different number of water-molecules
layers. In 2016, Ghidiu et al. [91] studied the intercalative chemistry via thermogravimetric analysis of the dehydration behavior of these materials, and showed the humidity response associated with cation-exchanged varieties in Ti$_3$C$_2$ MXene (Figure 5(b)).

In addition, it is extremely important for guaranteeing the dispersion of the MXene nanosheet by intercalating with various polar protic and aprotic solvents, such as ethanol, N-methyl-2-pyrrolidone, dimethyl sulfoxide, N, N-dimethylformamide and propylene carbonate [92]. By measuring the concentration and absorption spectra of MXene in organic solvents as well as correlating the concentration to solvent physical properties, Maleski et al. [92] revealed the dispersive behavior of Ti$_3$C$_2$Tx MXene in organic media and potentially developed the criteria of solvent selection. It’s worth noting that the overall dispersibility changes when varying the surface chemistry or synthesis method (Figure 5(c)). This strategy of organic solvents replacement expands the opportunities for processing techniques. Simultaneously, when stored as solutions, liquid medium type also has large impacts on the oxidation rate [74].

Moreover, modifying the synthesis recipe triggers huge effect on the resultant MXene quality. It is been reported that by adjusting the molar ratio of LiF and HCl to MAX phase, through the minimally intensive layer delamination (MILD) process, the MAX can be successfully etched and delaminated in the absence of high-power sonication, the as-obtained MXene flakes possess less defects/pin-holes with much larger lateral size. This enables the fundamental study of monolayer single-flake MXene properties and the MXene dispersions with higher concentrations, due to the enhanced delamination by increasing the concentration of Li$^+$ cations and protons. For example, Lipatov et al. [17] prepared the substantially larger MXene flakes with
more uniform size, cleaner surfaces and less defects by increasing the molar ratio of LiF to Ti3AlC2 from 5 to 7.5 (Figure 5(d)). However, the obtained MXenes have a wide size distribution between a few nanometers to few microns for all the reported synthesis methods. To produce MXene flakes with controlled average sizes and narrow size distributions, delamination methods such as sonication [10] and centrifugation [93] can be applied to separate the flakes based on their size, so-called cascade method. Maleski et al. [57] compared the effects of ultrasound and non-ultrasound samples on the size distribution of the MXene nanosheets, and indicated that the average size of the nanosheets decreased by more than 70% after 15 minutes of ultrasound, as shown in Figure 5(e).

4. Influence mechanism of etching and delamination routes on MXenes

To sum up, the above etching methods and delamination methods have great effects on the functional groups, size, localized defects and crystal structure of MXenes, which are closely related to the physical and chemical properties of MXene. However, the lack of understanding based on accurate theoretical predictions of these effects on desired properties makes it a great challenge for MXene to be accurately designed using optimized synthesis methods for high-performance applications. Herein, the influence of etching methods and delamination methods to the mechanism (how defects, structure, and functional groups influence various functional properties of MXenes) should be investigated with more detail.

The randomly anchored surface termination of MXenes obtained by various methods is vital to the property of MXenes including electronic structure, energy storage performance, catalytic performance, and other physiochemical properties. Thus, an increased attention has been paying to tuning the surface reformation of MXene [94,95], Lai et al. processed the exfoliated Ti2CTx with thermal annealing, and indicated that the energy band gap can be regulated by simply functional group modification [94]. Huang et al. [96] obtained MXenes with only single Cl termination by a green and viable Lewis acid etching method. The Cl-terminated MXenes were expected to be more stable and excellent electrochemical behavior than the F-terminated MXenes, which implicated promising applications such as energy storage. Talapin et al. [59] successful synthesized MXenes with oxygen, imido, sulfur, chlorine, selenium, bromine and tellurium surface terminations through molten inorganic salts strategy, as well as bare MXenes (no surface termination). They confirmed that the surface groups controlled the superconductivity of niobium carbide MXenes, also the surface groups controlled interatomic distances in the MXene lattice, and Ti_{n+1} C_n MXenes terminated with telluride (Te^{2−}) ligands showed a giant (>18%) in-plane lattice expansion compared with the unstrained titanium carbide lattice (Figure 6(a)).

The size of MXene materials is micron or even smaller, which limits its application in electronic, photonic and electrochemical devices. Hong et al. [97] studied the size- and edge-dependent properties of MXene nanoribbons, and indicated that the bandgap evolution as a function of the ribbon size of the armchair nanoribbons exhibited significant even-odd oscillations at small sizes, but the gaps converged to that of the 2D sheet at large sizes. Maleski et al. [57] controlled and sorted 2D titanium carbide (Ti3C2T x) MXene flakes based on density gradient centrifugation. The Ti3C2Tx electrodes from lateral sizes flakes (>1 μm) showed the best capacitance and rate performance (Figure 6(b)).

During etching of the A layer, the M-layer and X-layer atoms would inevitably be stripped due to the complex chemical reaction, which can form atomic-scale vacancies and/or severe hole [62,98–100]. The defects play an important role in their electronic properties, optical properties, and magnetic properties the electronic and electrochemical properties of the nanosheets. Therefore, controllable preparation of defective MXene has become an important topic, in order to develop the application potential of nanosheets. For example, water desalination can be enhanced due to the nanopores on MXene which can influence ion transport properties [97]. Moreover, defective Ti3CNTx nanosheets displayed an obvious enhancement of electrochemical activity compared to defect-free Ti3CNTx nanosheets sheets [101], because the active sites are generally located on the edge and defect position of Ti3CNTx. However, the defects in MXene tends to promote its oxidation (Figure 6(c)) [102], because the electric field at flake ripples and/or edges can drive the nucleation and growth of TiO2 by prompting Ti cation diffusion. As a surface area dependent two-dimensional material, broadening the available surface area of MXene is undoubtedly an important means to enhance the catalytic, electrochemical energy storage and sensing properties. In addition, the effective area of MXene can be increased by removing the functional groups during annealing [103]. Hu et al. [104] reported that the MXene with larger interlayer spacing and a greater amount of water led to not only high capacitance but also excellent cycling performance due to the more high-mobility H2O molecules between the Ti3C2Tx layers facilitated more protons to have access to the active sites (Figure 6(d)).

The key to MXene successful delamination is to weaken the interactions between adjacent layers [25,105]. Many researchers expand the interlayer
spacing by intercalating big organic molecules (tetrabutylammonium hydroxide, choline hydroxide and n-butylamine, etc), monovalent cation (Li⁺, Na⁺, K⁺ and NH⁴⁺), multivalent cation (Mg²⁺, Co²⁺ and Sn⁴⁺), or polar solvents (dimethyl sulfoxide, urea, and hydrazine, etc.), due to the greatly weakened

Figure 6. (a) Effect of surface functional groups on MXene. Reproduced with permission from [59], Copyright 2020, Science. (b) (i) Dynamic light scattering of the 6–3 mL fraction (blue) composed of larger flakes (~1.7 μm lateral flake size) and the 12–9 mL fraction (black) composed of smaller flakes (~400 nm lateral flake size); (ii) cross-sectional SEM showing the thicknesses of 6–3 electrode (top, scale bar 100 nm) and the 12–9 electrode (bottom, scale bar 200 nm); (iii) CV profiles collected in 3 M H₂SO₄ at 20 and 2000 mV/s scan rates. Reproduced with permission from [57], Copyright 2018, American Chemical Society. (c) Ambient oxidation of Ti₃C₂ MXene initialized by atomic defects; (i) Ti-vacancies (dark contrast marked by yellow arrowheads) and Ti-rich areas (bright contrast marked by red arrowheads); (ii) schematic of the internal electric field, with the positive side formed around a hole with many Ti-vacancies and the negative side with the accumulation of electrons on the convex particle. Reproduced with permission from [102], Copyright 2019, Royal Society of Chemistry. (d) Surface functional groups and interlayer water determine the electrochemical capacitance of Ti₃C₂Tx MXene. Reproduced with permission from [104], Copyright 2018, American Chemical Society.
interlayer forces between adjacent layers [103]. For instance, the c-lattice parameter (c-LP) of the pristine Ti$_3$C$_2$T$_x$ boosts up from 19.5 Å to 44.8 Å in DMSO/water co-intercalate [106]. And the LiF–HCl etching route spontaneously enables the insertion of Li$^+$ ions at the same time as etching [107].

5. Conclusions and perspectives

In summary, we reviewed the major synthesis methods and compared these synthesis strategies from a perspective of MXene quality control. This perspective is a guide for researchers to further understand the structure and properties of MXenes, and it is of great guiding significance for the selection of suitable MXene preparation regimens for different application fields. In order to obtain MXene with stronger catalytic activity, electrochemical storage capacity, antioxidation capacity and electromagnetic shielding performance, tailoring functional groups, interlayer spacing, defects, size, etc. of MXene is particularly important by different preparation methods and treatment methods. Based on this, high-quality MXene are expected with enhanced application performance.

Since the discovery of the 2D MXene materials, many scholars have done outstanding work on the preparation of high-quality MXene, however, there are still many challenges need be considered and solved. In the aspect of synthesis, (i) many MXenes such as Sc$_2$C, Hf$_2$C, W$_2$C and so on are predicted to be thermodynamically stable, but their precursors have not yet been produced. Therefore, a novel preparation method needs to be proposed to expand the MXene family. (ii) It is highly desirable to develop new methods for synthesizing high-quality MXenes combining large lateral dimensions, fewer defects and controlled surface terminations. (iii) The notorious oxidation problem urgently needs to be solved for the long-term preservation of MXene. In the aspect of treatment methods, precise anchoring functional groups in a certain position, preparing bare MXene without functional groups, realizing the controllable preparation of defect sites for synthesizing MXene with specific properties still need to be solved.

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Disclosure statement

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