Interfacial structure design of MXene-based nanomaterials for electrochemical energy storage and conversion

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Funding information
Zhejiang University of Technology; Natural Science Foundation of Zhejiang Province, Grant/Award Number: LD18E020003; National Natural Science Foundation of China, Grant/Award Number: S1722210; Dartmouth College

Abstract
2D transition metal carbides, carbonitrides, and nitrides known as MXenes possess high electrical conductivity, large redox active surface area, rich surface chemistry, and tunable structures. Benefiting from these exceptional chemical and physical properties, the applications of MXenes for electrochemical energy storage and conversion have attracted increasing research interests around the world. Notably, the electrochemical performances of MXenes are directly dependent on their synthesis conditions, interfacial chemistries and structural configurations. In this review, we summarize the synthesis techniques of MXenes, as well as the recent advances in the interfacial structure design of MXene-based nanomaterials for electrochemical energy storage and conversion applications. Additionally, we provide an in-depth discussion on the relationship between interfacial structure and electrochemical performance from the perspectives of energy storage and electrocatalysis mechanisms. Finally, the challenges and insights for the future research of interfacial structure design of MXenes are outlined.

KEYWORDS
electrocatalysis, electrochemical energy storage, interlayer space, MXene, structure design

1 | INTRODUCTION

With the ever-increasing demands of sustainable energy, considerable attentions have been devoted to the development of novel materials towards high performance electrochemical energy applications for storing renewable electricity from solar and wind.1-4 Two-dimensional (2D) materials including graphene,5 transition metal dichalcogenides (TMDs),6 hexagonal boron nitrides,7 phosphorene,8 metal-organic frameworks (MOFs)9 have been the subjects under extensive research and regarded as superior candidates for electrochemical energy storage and conversion over the past 15 years due to their unique physical and chemical properties.

MXene,10 an emerging family of 2D transition metal carbides, nitrides and carbonitrides was first discovered by the researchers from Drexel University in 2011.11 MXene terminated with OH, O, and F groups can be obtained by etching the MAX phases (M = early transition metal, A = III or IV A-group element, X = carbon (C) or nitrogen (N)) with hydrofluoric acid (HF).12 To date, more than 30 types of MXenes with different compositions, including Ti3C2, Ti2C, Ti4N3, and Mo2C have been successfully synthesized.13-15 Remarkably, MXenes...
have been applied in many fields ranging from energy storage,16-25 environment and catalysis,26-29 electromagnetic interference shielding,30,31 medicine,32 and electronics.33-35 The unique characteristics of MXenes, including high electrical conductivity, large redox active surface area, rich surface chemistry, and tunable structures have rendered them extremely practical for electrochemical energy storage and conversion applications.36 Although there have been some reviews that summarized the synthesis, properties, and applications of MXenes,37-42 less attention has been paid to the underlying structural design principle and regulation mechanisms of MXene-based architectures. Therefore, it is highly desirable to have a comprehensive understanding on the interfacial structure design of MXene-based nanomaterials for electrochemical energy storage and conversion applications.

In this review, we provide an in-depth discussion regarding the recent interfacial structure design of MXene and their electrochemical energy storage and conversion applications. The effect of MXene synthesis techniques and their interfacial structure design on the resulting performance related to electrochemical energy storage and conversion are discussed (Figure 1). In the first section, we go over the synthesis techniques of MXenes, including wet-etching and non-etching methods, as well as the synthesis-dependent structural properties of MXene. In the second section, different interfacial structure design of MXene combined with their electrochemical applications and corresponding performance are summarized. Particularly, a series of structural design of MXene including interlayer structure regulation, hierarchical structure assembly, MXene-based hybrid nanostructures along with the electrochemical energy storage and conversion performance are systematically reviewed. In the last section, the challenges and future prospects on the design of MXene-based nanostructures are presented.

### 2 | SYNTHESIS TECHNIQUES

Unlike most other 2D materials such as graphene, phosphorene, and MoS2, MXenes have the unique properties of high electronic conductivity, hydrophilic and redox-active surface. These unique properties endow MXenes with promising performance in energy storage, catalysis, electromagnetic interference shielding, and many other applications.43 The intrinsic properties of MXenes are closely related to their synthesis techniques.40 Therefore, MXenes synthesis conditions can directly dictate their properties and performances. In general, two primary techniques, wet-etching and nonetching syntheses have been developed to synthesize MXenes.39 Wet-etching synthesis is based on the extraction of M\textsubscript{n}X\textsubscript{n-1} (n = 2, 3, 4) from their ceramic counterpart MAX by removing the A

![Figure 1](image-url)
The possible constituent atoms and the typical structure MAX and MXene phases are shown in Figure 2A-C. So far, more than 70 different kinds of MAX phases have been reported. By removing the A atoms layers, different terminal groups can bond with interfacial M atoms (Figure 2D). Thus, the etchants concentration and etching temperature can strongly influence the quality and properties of as-synthesized MXene. To date, various kinds of etchants (e.g., HF, HCl-LiF, NH₄HF₂, NaOH, and tetramethylammonium hydroxide [TMAOH]) have been developed and some novel fabrication routes have been explored. Meanwhile, non-etching approaches such as chemical vapor deposition (CVD) can also be used for MXene synthesis. Previous research results confirm that ultrathin 2D α-Mo₂C orthorhombic crystals with the lateral size up to 100 μm can be prepared by using methane as the carbon source and bilayer foils, with the substrate being Cu foil sitting above a molybdenum (Mo) foil. Using this method, high-quality MXenes can be produced with a large lateral size and low density of...
defects, which is beneficial for the study of the intrinsic properties.

In this part, we focus on the synthesis techniques of MXene as well as their respective pros and cons (Table 1). We particularly highlight the recent advances in MXene synthesis through wet-etching, and elucidate the relationship between synthesis techniques and structural properties of MXenes.

2.1 | HF etching

Originally, HF etching method was first demonstrated in 2011 for the purpose of delaminating Ti3AlC2 MAX.11 Currently, HF etching method is the most commonly used method for preparing MXenes owing to its flexibility to selectively etch away the A layers from most of MAX phases. Taking Ti3AlC2 as an example, the specific etching reaction of Ti3AlC2 phases by HF can be described by the following equations.11

\[
\begin{align*}
Ti_3AlC_2 + 3HF &= AlF_3 + 3/2H_2 + Ti_3C_2 \quad \cdots \quad (1) \\
Ti_3C_2 + 2H_2O &= Ti_3C_2(OH)_2 + H_2 \quad \cdots \quad (2) \\
Ti_3C_2 + 2HF &= Ti_3C_2F_2 + H_2 \quad \cdots \quad (3)
\end{align*}
\]

The etching condition for various MXenes depends on the structure, atomic bonding, and particle size of MAX phases. In order to achieve a specific MXene formation, etching temperature, HF concentration and reaction time have to be adjusted accordingly.40 According to the previous research results, increasing the atomic number of M and number n in M_{n+1}C_nT_x can lead to a stronger etching and longer etching time.40 The etching of aluminum (Al) from Ti3AlC can be achieved by as little as 10 wt% HF with 10 hours of etching time. Meanwhile, V2C MXene can be obtained by etching V2AlC, which requires 90 hours of etching time and 50 wt% of HF. After HF (≥10 wt%) etching, the accordion-like morphology of multilayered MXene is usually observed (Table 1). The possible reason for the expanded accordion-like structure is the excess amount of escaped gases (eg, H2) during the reaction between A atoms and HF. Additionally, to obtain separated MXene sheets from the multilayered MXene after HF etching, typical intercalation and delamination process is required.48 For the above process, organic molecules (eg, dimethyl sulfoxide [DMSO]) and tetralkylammonium compounds (eg, tetrabutylammonium hydroxide [TBAOH] and tetramethylammonium hydroxide [TMAOH]) are usually used for expanding the interlayer spacing of multilayered MXene, followed by sonication treatment that is required for the case of HF-etched MXene.46-48 However, a disadvantage of HF etching is the highly corrosive nature of HF with the assistance of indispensable sonication can lead to the formation of single MXene flakes with relatively small size and rich structural defects.40 Besides, using HF as etchant can cause hazardous environmental and safety concern, hindering the extensive studies of MXenes.

2.2 | Modified fluoride-based acid etching

In order to address the high toxicity associated with HF etching, researchers have made great efforts to explore safer ways to selectively remove A atom layers from MAX precursor. Apart from HF, a mixture solution of a fluoride salt (eg, LiF, NaF, KF, and NH4F) and a strong acid can also be used to etch MAX precursors.44 It is found that fluoride salts and strong acids can react and form in-situ HF to selectively etch A atoms and lead to the intercalation of cations (eg, Li+, Na+, K+, and NH4+) and water between MXene layers, thereby increasing the interlayer spacing of MXene and weakening the interaction of MXene layers. It is noteworthy that both the concentration of strong acid and fluoride salt can influence the quality and size of the final MXene flakes. For example, the as-obtained multilayered Ti3C2 produced via the clay method (5 M LiF/6 M HCl) needs further sonication process to be delaminated into single flakes, which often causes defective and small MXene flakes.40 However, with the use of minimally intensive layer delamination (MILD) method (12 M LiF/9 M HCl), the washing process alone was enough to delaminate multilayered Ti3C2, producing single- or few-layer with larger lateral size and fewer defect.51 Therefore, MILD method has an obvious advantage compared to the HF etching method in terms of maintaining the structures and properties of as-prepared MXene. Besides, difluorides such as KHF2 or NH4HF2 can also be used as the etchant to selectively etch Ti3AlC2.52 Generally, as opposed to HF etching, modified fluoride-based acid etching exhibits different properties: (a) the obtained MXenes have fewer defects and larger sizes; (b) cations intercalation leads to MXenes with large interlayer spacing, facilitating the delamination and further structural regulation; (c) higher content of -O terminal groups; (d) the resulting morphology is not accordion-like (≥10 wt%) (Table 1).

2.3 | Molten salts etching

In addition to HF/fluoride-based acid etching, MXene can also be synthesized by high-temperature treatment of MAX phases, such as treating Ti4AlN3 in a mixture of molten fluoride salt (LiF:NaF:KF = 29:12:59 in weight
| Synthesis techniques | Applicable MAX (obtained MXene) | Reagents | Representative SEM/optical images | Properties (terminations, size, and quality) | Characteristics of technique |
|----------------------|---------------------------------|----------|----------------------------------|---------------------------------------------|-----------------------------|
| Wet etching          | HF etching\(^{40}\)              | Nearly all MXenes | HF | 1) Accordion-like structure with more -F, -OH and -O terminations 2) Small flake size with abundant defects | Merits: High selectivity and acceptable yield Demerits: Abundant defects in the products; hazardous operation |
| Modified fluoride-based acid etching\(^{40}\) | Ti\(_3\)AlC\(_2\) (Ti\(_3\)C\(_2\)) Mo\(_2\)GaC (Mo\(_2\)C) Ti\(_2\)AlC (Ti\(_2\)C) | LiF/NaF/KF +HCl or NH\(_4\)HF\(_2\) | | 1) Large interlayer spacing with high –O termination 2) Large flake size with few defects | Merits: Low defects; less hazardous; large flake size Demerits: higher etching temperature and longer time |
| Molten salts etching\(^{14}\) | Ti\(_2\)AlC (Ti\(_2\)C) Ti\(_4\)AlN\(_3\) (Ti\(_4\)N\(_3\)) | LiF + NaF + KF | | 1) Accordion-like structure with TiO\(_2\) phase 2) Small flake size with many vacancies and defects | Merits: synthesize MXene, which is low stability in HF solution Demerits: high temperature; low crystallinity of MXene |
| Fluoride-free etching\(^{45,46}\) | Ti\(_3\)AlC\(_2\) (Ti\(_3\)C\(_2\)) | NaOH/TMAOH/TMAOH+NH\(_4\)Cl | | 1) For NaOH etching: Compact layered structure only with –OH, -O terminations, and few TiO\(_2\) phase; small and thick flakes 2) For TMAOH etching: Swell Ti\(_3\)C\(_2\) layers terminated with Al(OH)\(_4\)\(^{-}\) and sandwiching TMA\(^{+}\) | For NaOH etching: Merits: less hazardous; no -F termination Demerits: high temperature and high concentration For TMAOH etching: Merits: very efficient etching Al; facilitating delamination; no -F termination Demerits: Al(OH)\(_4\)\(^{-}\) termination may influence the potential applications |
| Nonetching          | CVD\(^{47}\) | Mo\(_2\)C | CH\(_4\) and Cu/Mo foils | 1) Large lateral sizes of high-quality MXene crystals 2) Extremely low defect, disorder, and impurity | Merits: Controlled thickness of MXene crystals; less defect Demerits: Tedious synthesis protocols; Low-efficiency production |
ratio) at 550°C under argon protection to produce Ti₄N₃.¹⁴ The etching process can be completed within a relatively short period of 30 minutes. Because of the lower stability of Ti₉N₉-₁ compared to Ti₉C₉-₁, Ti₉N₉-₁ can be dissolved when using HF or fluoride-based acid as etchant. Therefore, a relatively quick processing time is the advantage of this molten salts etching method. However, extra washing process (by H₂SO₄ and DI water) and further delamination process (in TBAOH solution) are still necessary. Also, the delaminated Ti₄N₃ has lower crystallinity than the MXene obtained by HF etching, as revealed in the XRD patterns of the obtained Ti₄N₃. Besides, TiO₂ phase can be observed in the final product. Overall, compared with HF/fluoride-based acid etching, molten salts etching has an obvious merit of fabricating MXenes with low stability in HF/fluoride-based acid solution. However, this method has disadvantages as followed: (a) The etching process needs high temperature and energy consumption; (b) the obtained MXene has low crystallinity and purity; (c) the obtained MXene has excess vacancies and defects.

### 2.4 Fluoride-free etching

Although different etching conditions have been confirmed for synthesizing MXenes, HF or fluoride-based compounds are required in most of the synthesis techniques, which can cause the formation of -F and -O terminations on the interface of MXenes.¹¹ Particularly, -F terminations have negative impact on the electrochemical performance of MXenes-based supercapacitors.³⁷ In this case, fluoride-free synthesis techniques are needed to promote decent electrochemical performance. Zhang et al. designed an alkali-assisted hydrothermal etching method to prepare Ti₃C₂ MXene by using NaOH solution as the etchant.⁴⁵ In general, for Ti₃AlC₂ MAX phase, alkali is theoretically feasible as an etchant due to the strong binding between alkali and elemental Al. However, obtaining a multilayered MXene with high purity is still a challenge. In this regard, a high alkali concentration (27.5 M) with a high reaction temperature (270°C) can be applied to etch Al layers and prevent the damage of obtained Ti₃C₂ MXene skeleton, known as Bayer process.⁴⁵ The results confirm that high reaction temperatures and high NaOH concentrations can facilitate the dissolving of high Al (oxide) hydroxides in NaOH, and prevent the oxidation of Ti species. Because of the low water containment in this reaction system, -OH and -O groups can form on the surface of as-prepared Ti₃C₂ MXene without -F groups. As a result, employing Ti₃C₂ film (52 μm) as the electrode for supercapacitor in 1 M H₂SO₄ enabled high gravimetric capacitance of 314 F g⁻¹ and high volumetric capacitance of 511 F cm⁻³ at 2 mV s⁻¹.⁴⁵

Although high-purity Ti₃C₂ MXene can be obtained by the above alkali-assisted hydrothermal etching method, high temperature and pressure hydrothermal condition can also cause safety concerns. Therefore, Geng and her coworkers employed an organic base etching method, in which TMAOH was used as the etchant.⁴⁶ During this reaction, TMAOH can hydrolyze Al and result in Ti₃C₂ MXene terminated by Al(OH)₄⁻ and intercalated by TMA⁺. Based on these results, TMAOH-etched Ti₃C₂ has different properties compared with the ones by HF and NaOH etching. Besides, electrochemical etching can also be used for selective etching process. Feng et al reported the selective electrochemical etching of Al layers from Ti₃AlC₂ using an aqueous electrolyte consisting of 1 M ammonium chloride (NH₄Cl) and 0.2 M TMAOH.⁵³ This electrochemical etching method enables high yield of single or bilayer Ti₃C₂ MXene with large average lateral dimension. The obtained Ti₃C₂ can be used as an electrode for all-solid-state supercapacitors that can deliver a high areal capacitance of 220 mF cm⁻².

Generally, the obtained MXenes are free of -F terminations when created by fluoride-free etching method. Compared with HF and modified fluoride-based acid etching, NaOH etching is less hazardous but still requires high temperature and high concentration of etchant. Moreover, TMAOH etching is very efficient in delamination; however, the obtained Al(OH)₄⁻ terminations in MXenes may influence their potential applications in a negative way.

### 2.5 Chemical vapor deposition

Apart from the above etching methods, CVD provides a viable route to synthesize high-quality MXene.⁵⁴ In 2015, Ren’s group employed a CVD method to achieve ultrathin α-Mo₂C 2D crystal with the lateral size up to 100 μm by using methane as the carbon source and double metal foils (a Cu foil on a Mo foil) as the substrate.⁴⁷ The CVD-grown MXene single crystals have much larger domain size with much lower density of defects compared to those synthesized via wet-chemical etching methods. Besides, the CVD method can also be used to prepare other ultrathin transition metal carbide, such as WC and TaC crystals. Yet, there is no report on the CVD synthesis of MXene monolayer, indicating further development is still needed. In contrast to wet-chemistry etching method, CVD-grown MXene has a much lower density of defects and disorders as well as lower concentrations of impurities, therefore enabling researchers to
investigate the intrinsic physical, chemical, electrical, and optical properties of MXene.\textsuperscript{47}

3 \hspace{1em} \textbf{INTERFACE STRUCTURE DESIGN AND ELECTROCHEMICAL ENERGY STORAGE AND CONVERSION APPLICATIONS}

Because of their high electrical conductivity, large redox active surface area, rich surface chemistry, and tunable structures, the applications of MXenes for electrochemical energy storage and conversion have gained tremendous momentum. However, the electrochemical performances of pristine MXenes are rather unsatisfactory,\textsuperscript{36} which are caused by multiple reasons. First, small interlayer spacing (~0.98 nm) can restrict the intercalation and storage of charge carrying ions.\textsuperscript{55} Meanwhile, ions transportation and diffusion in electrocatalytic reaction can be affected by the limited layer spacing.\textsuperscript{56} Second, similar to other 2D materials, MXene nanosheets can be easily restacked and agglomerated during the electrochemical reaction process, resulting in poor ionic and electronic transport.\textsuperscript{57} In order to improve the electrochemical performance of MXene, various strategies have been proposed on the interfacial structure design of MXene, including the introduction of interlayer spacers and the assembly of MXene nanosheets into hierarchical structures.\textsuperscript{58} Like most 2D materials, single- or few-layered MXene possesses large surface area and excellent mechanical flexibility, enabling them to act as ideal 2D substrates for realizing high-performance electrochemical energy storage and conversion.\textsuperscript{57}

Therefore, in this section, we focus on the interfacial structure design of MXene and the corresponding electrochemical energy storage and conversion applications (Figure 3). According to different modification methods, the interfacial structure can be classified as follows: layered structure with enlarged interlayer spacing, nanosheet-assembled hierarchical structures, and MXene-based hybrid nanostructures. The relationship between interfacial structure and electrochemical performance are summarized, and the energy storage and electrocatalysis mechanisms are discussed in detail.

3.1 \hspace{1em} \textbf{Layered structure with enlarged interlayer spacing}

By selectively etching A atoms from MAX precursor by HF, MXene with unique layered structure can be obtained. Taking Ti\textsubscript{3}AlC\textsubscript{2} as an example, the corresponding interlayer spacing of Ti\textsubscript{3}C\textsubscript{2} is ~0.98 nm after HF etching, and as-produced interface functional groups (eg, -O\textsubscript{2}, -OH, and -F) endow the MXene with negatively charged interface between the layers.\textsuperscript{55} Although MXene interlayer spacing is larger than that of traditional layer-structured material such as MoS\textsubscript{2} and graphite, the ion intercalation and storage space needed between the layers is still insufficient (especially in organic electrolyte system), which results in unsatisfying electrochemical performance.\textsuperscript{36} Density functional theory (DFT) calculations revealed that the enlarged interlayer spacing of Ti\textsubscript{3}C\textsubscript{2} MXene can stabilize multilayer ions adsorption in the interlayers, thus significantly increasing the theoretical capacity.\textsuperscript{59} Due to the negatively charged interface between the MXene layers, cations can be spontaneously intercalated by electrostatic force, leading to the enlarged interlayer spacing of MXene.\textsuperscript{59,55,60-62} It is worth mentioning that the new chemical bonding between intercalant and MXene can be formed during the intercalation process, which can result in modified interfacial properties and possible change in the terminal groups on the MXene interface.\textsuperscript{63} The specific interfacial modification and their influence on energy storage performance will be discussed in detail later.

Gogotsi and coworkers investigated the relationship between intercalation of different cations (eg, Li\textsuperscript{+}, Na\textsuperscript{+}, Mg\textsuperscript{2+}, K\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, and Al\textsuperscript{3+}) into Ti\textsubscript{3}C\textsubscript{2} MXene and the corresponding capacitance for supercapacitor.\textsuperscript{60} The results show that an increase in the interlayer spacing (~0.25 nm) leads to a notable improvement on intercalation capacitances. When Ti\textsubscript{3}C\textsubscript{2} is treated by NaOH solution, binder-free Ti\textsubscript{3}C\textsubscript{2} paper can deliver a high volumetric capacity of up to 350 F cm\textsuperscript{-3}, far outperforming those results on activated graphene and carbide-derived carbon electrodes. The NaOH treatment can not only increase the interlayer spacing of MXene, but also alter the terminal groups between MXene layers. Peng and co-workers et al. confirmed that the alka-

realized the Sn\textsuperscript{4+} pillared MXene through the use of alkali metal ions to pre-pillar Ti\textsubscript{3}C\textsubscript{2} MXene, followed by the ion-exchange interaction between Sn\textsuperscript{4+} and pre-intercalated alkali metal ions. The intercalation of Sn\textsuperscript{4+} between MXene layers increases the interlayer spacing of Ti\textsubscript{3}C\textsubscript{2} from 0.98 to 1.28 nm by forming strong Ti-O-Sn bonding. With the help of polyvinylpyrrolidone (PVP), the amorphous Sn(IV) nanocomplex with a lateral size smaller than 7 nm can be homogeneously anchored in the Ti3C2 matrix. As an anode of lithium-ion batteries, this PVP assisted Sn\textsuperscript{4+} pillared Ti\textsubscript{3}C\textsubscript{2} (PVP-Sn(IV)@Ti3C2) exhibits a high volumetric capacity (~1400 mAh cm\textsuperscript{-3}).63 In a similar manner, Song et al. synthesized Co\textsuperscript{2+} intercalated V\textsubscript{2}C MXene (V\textsubscript{2}C@Co), and the corresponding interlayer spacing can be increased from 0.74 to 0.95 nm after Co\textsuperscript{2+} intercalation via strong V-O-Co bonds.65 Due to the unique layered structure and pseudocapacitive contribution of Co species, the as-obtained V\textsubscript{2}C@Co exhibits a high capacity and an excellent rate performance as a promising electrode for Li\textsuperscript{+} capacitors.

Although metal ions can be intercalated between MXene layers, the increments of interlayer spacing are limited due to their small size. Recently, our group proposed the introduction of large volume cationic surfactants with long chain hydrophobic tail as the intercalation agent to intercalate into the interlayer of Ti3C2 MXene to increase the interlayer spacing.55 Remarkably, the interlayer spacing of Ti3C2 can reach to 2.71 nm, a nearly 177% increase compared with that of pristine Ti3C2 (0.98 nm). The intercalated cationic surfactants between MXene layers can provide the ion-exchange sites for other cations. Therefore, different...
pillared structure MXene can be obtained by a facile cationic surfactant pre-pillaring followed by subsequent cations pillaring method. Our group successfully synthesized Sn^{4+} pillared Ti_3C_2 MXene (CTAB-Sn(IV)@Ti_3C_2) by using liquid phase CTAB prepillaring and subsequent Sn^{4+} pillaring. As an anode for lithium-ion storage, the as-obtained CTAB-Sn(IV)@Ti_3C_2 electrode delivers a high reversible capacity of 765 mAh g^{-1} at 0.1 A g^{-1} after 100 cycles, which is much higher than that of CTAB pillared Ti_3C_2 (248 mAh g^{-1}). As the weight ratio of Sn in CTAB-Sn(IV)@Ti_3C_2 is only 10%, it can be concluded that the main capacity contribution of CTAB-Sn(IV)@Ti_3C_2 can be attributed to the “pillar effect”. During the lithiation process, the alloying reaction between intercalated Li^+ and Sn(IV) nanocomplex causes the volume expansion, and this can effectively prop the MXene layers open and endow the MXene with incremental interlayer space for Li^+ storage, namely the “pillar effect”. Coupling the CTAB-Sn(IV)@Ti_3C_2 anode with commercial activated carbon (AC) cathode,
the assembled Li-ion capacitor exhibits high energy density of 239.50 Wh kg$^{-1}$ (Figure 4F). Apart from the application of pillared MXene for lithium-ion storage, our group also designed Sn$^{2+}$ pillared MXene (CT-Sn[II]@Ti$_3$C$_2$) that serves as a stable matrix for Na metal anode (Figure 4G).$^{66}$ In this work, intercalated Sn$^{2+}$ not only induces Na to nucleate and grow between Ti$_3$C$_2$ MXene layers, but endows Ti$_3$C$_2$ with larger interlayer space to accommodate the deposited Na under the "pillar effect", thus resulting in the uniform Na deposition.

Other large ions such as amine ions can also be selected as intercalation agents.$^{49}$ Gogotsi’s group developed isopropylamine (i-PrA) intercalation method to delaminate Nb$_2$C. When mixing Nb$_2$C with i-PrA solution, the formed cation R-NH$_3^+$ can potentially intercalate between MXene layers with the assistance of electrostatic forces, thereby increasing the interlayer spacing of Nb$_2$C from 1.04 to 2.27 nm. After i-PrA intercalation, Nb$_2$C can be successfully delaminated with the assist of mild sonication in water. Nb$_2$C MXene can be assembled layer-by-layer with carbon nanotube (CNT) by vacuum filtration, and the obtained CNT/MXene composite “paper” electrode shows a high volumetric capacitance of 325 F cm$^{-3}$ as electrode for Li-ion capacitor.$^{49}$

Additionally, some polymers that have decent solubility in water/organic solvent have been proved to be promising intercalation agents for MXenes.$^{66-70}$ Ling et al mixed the single-layer Ti$_3$C$_2$ MXene with polydiallyldimethylammonium chloride (PDDA) and polyvinyl alcohol (PVA) to produce Ti$_3$C$_2$/polymer composites.$^{69}$ The intercalation and confinement of the above two kinds of polymers between MXene layers not only can increase the electrode flexibility, but also improve the volumetric capacitance. MXene/PVA-KOH composite film shows an impressive volumetric capacitance of 530 F cm$^{-3}$. In addition, electrochemically active polymers, such as polypyrrole (PPy), can intercalate between Ti$_3$C$_2$ layers by constantanous intercalation and alignment. Polymerization of monomer and pyrrole can expand the interlayer space of MXene for rapid charge transport.$^{70}$ The PPy/Ti$_3$C$_2$ composite delivers a high volumetric capacity of 1000 F cm$^{-3}$ and high capacitance retention of 92% after 25 000 cycles. In addition to the metal free polymerization as described above, electrochemical polymerization can also be used to prepare PPy intercalated Ti$_3$C$_2$ MXene electrode. Zhi et al utilized the electrochemical polymerization to intercalate PPy into layered Ti$_3$C$_2$.$^{68}$ The results show that the strong chemical bonding between PPy chains and Ti$_3$C$_2$ interface can provide pathways for charge carriers transport, which is favorable for the pseudocapacitive process. Electrochemical testing results show that the as-prepared free-standing PPy/Ti$_3$C$_2$ films exhibit an excellent capacitance of 35 mF cm$^{-2}$ with a consistently stable performance at any bending states after 10 000 cycles. Furthermore, facile precursor intercalation and annealing processes to realize heteroatom intercalated MXene were demonstrated for MXene-based nanostructure with enlarged interlayer spacing.$^{67,71}$ Recently, our group successfully intercalated sulfur (S) atoms into the Ti$_3$C$_2$ MXene interlayer by a facile CTAB pretreatment, thermal diffusion with elemental S, and subsequent annealing process (Figure 4H).$^{67}$ After annealing, a desirable interlayer-expanded structure of S atoms pillared Ti$_3$C$_2$ via Ti-S bonding can be developed, which has larger interlayer spacing (1.37 nm) than that of CTAB pretreated Ti$_3$C$_2$ after annealing (1.15 nm). The strong Ti-S bonds not only can react with the intercalated Na that contributed to the “pillar effect”, but also can provide stable double-layer Na ions adsorption and configuration that is confirmed by DFT calculation. At an annealing temperature of 450°C, the obtained S atoms pillared Ti$_3$C$_2$ MXene (CT-S@Ti$_3$C$_2$-450) delivers an improved Na$^+$ storage capacity of 550 mAh g$^{-1}$ at 0.1 A g$^{-1}$ ($\approx$120 mAh g$^{-1}$ at 15 A g$^{-1}$) and excellent cycling stability over 5000 cycles at 10 A g$^{-1}$. Coupling CT-S@Ti$_3$C$_2$-450 anode with commercial AC cathode enables Na-ion capacitor with a high energy density of 263.2 Wh kg$^{-1}$. Wang and co-workers synthesized N-doped Ti$_3$C$_2$ MXene (N-Ti$_3$C$_2$) by annealing Ti$_3$C$_2$ in ammonia (NH$_3$).$^{71}$ During the annealing process, N is introduced as a heteroatom between Ti$_3$C$_2$ layers, leading to increased interlayer spacing of Ti$_3$C$_2$ from 0.96 to 1.23 nm upon NH$_3$ treatment at 200°C. Interestingly, the obtained N-doped Ti$_3$C$_2$ shows improved electrochemical capacitances of 192 F g$^{-1}$ in 1 M H$_2$SO$_4$ electrolyte as an electrode for supercapacitor. Overall, annealing is often required in the heteroatoms intercalation process, hence the increased interlayer spacing by introducing heteroatoms between MXene layers is always smaller than that of ions intercalation. In addition to the above methods of intercalating the intercalants into MXene layers, layer by layer assembly and electrostatic self-assembly can also be used to fabricate MXene-based nanostructures with enlarged interlayer spacing. Gogotsi and his coworkers demonstrated layer by layer assembly method to prepare flexible and free-standing sandwich-like MXene/CNT paper.$^{72}$ After CNT intercalation, the interlayer spacing of MXene increases from 1.21 to 1.42 nm with the increment of layer spacing being 0.21 nm, thus forming the sandwich-like MXene/CNT paper with improved rate performance as an electrode for supercapacitor. Yan et al prepared the MXene/reduced graphene oxide (rGO) hybrid electrode films through an electrostatic self-assembly process.$^{73}$ After electrostatic assembly, rGO nanosheets can be successfully inserted in-between MXene layers with an interlayer
spacing of 1.67 nm. As a supercapacitor electrode, MXene/rGO exhibits a volumetric capacitance of 1040 F cm$^{-3}$ and impressive rate capability.

Based on the examples mentioned above, we summarize the state-of-the-art works about adjusting the interlayer spacing of MXene via the introducing of intercalation agents (Table 2). Overall, the intercalation agents can be divided into the following categories: (a) heteroatoms; (b) alkali metal ions; (c) nonalkali metal ions; (d) polymers; (e) large cations; (f) 1D/2D nanomaterials. The main synthetic methods of MXene having enlarged interlayer spacing include: (a) liquid phase pre-pillaring and pillaring; (b) precursor intercalation and annealing; (c) layer by layer assembly. After the insertion of intercalation agents, MXene with enlarged interlayer spacing exhibits two main advantages for energy storage: (a) MXene equips with large space for charge carrying ions intercalation and storage; (b) MXene exhibits excellent ion transport property due to shorter diffusion pathways. Besides, according to our recent research, the controlled and fine-tuned interlayer spacing of MXenes (from 1 to 2.7 nm) can be designed by creating pillared structure based on the spontaneous intercalation of cationic surfactant.\cite{36} This design method of pillared MXene helps to achieve uniform surface terminations for controllable modification of MXene layers, and offers new perspectives in the field of electrochemical energy storage.\cite{36} Furthermore, these breakthrough can provide guidance for the development of electrode materials for the next-generation electrochemical energy storage and conversion devices.

### 3.2 | Nanosheet-assembled hierarchical structures

Like most 2D materials, MXene nanosheets are prone to be restacked and agglomerated via van der Waals (vdW) attraction and hydrogen bonding during the electrochemical reaction process.\cite{74} This shortcoming causes the

### Table 2 | Comparison of different MXenes with enlarged interlayer spacing

| Intercalation agent types | Materials | Intercalation agent precursors | Methods (Temperature/°C) | After intercalation spacing (nm) | added value (Δd) | Refs |
|--------------------------|-----------|-------------------------------|--------------------------|---------------------------------|-----------------|------|
| Heteroatoms (N,S)        | N-Ti$_3$C$_2$Tx | NH$_3$                       | Precursor intercalation and annealing (200°C) | 1.23                      | 0.27     | [71] |
|                          | CT-S@Ti$_3$C$_2$ | S                           | Precursor intercalation and annealing (450°C) | 1.37                      | 0.39     | [67] |
| Alkali metal ions        | Multilayer Ti$_3$C$_2$ | LiOH,NaOH, KOH,MgSO$_4$ | Liquid phase intercalation (RT) | 1.25                      | 0.23     | [60] |
| Metal ions (Sn$^{4+}$, Co$^{2+}$, Sn$^{2+}$) | PVP-Sn(IV)@Ti$_3$C$_2$ | SnCl$_4$                   | Liquid phase pre-pillaring and pillaring (RT) | 1.28                      | 0.30     | [63] |
|                          | V$_2$C@Co       | Co(CH$_3$COO)$_2$           | Liquid phase pre-pillaring and pillaring (RT) | 0.95                      | 0.21     | [65] |
|                          | CT-Sn(II)@Ti$_3$C$_2$ | SnCl$_2$                   | Liquid phase pre-pillaring and pillaring (40 °C) | 1.9                       | 0.92     | [66] |
| Polymers (PVA, PDDA, PPy) | Ti$_3$C$_2$Tx/PDDA | PDDA                        | Liquid phase self-assembly (RT) | 1.84                      | 0.48     | [69] |
|                          | Ti$_3$C$_2$Tx/PVA | PVA                         | Liquid phase self-assembly (RT) | 2.25                      | 0.89     | [69] |
|                          | PPy-Ti$_3$C$_2$Tx | PPy                         | Precursor intercalation and in-situ polymerization | 2.4                       | 1.02     | [70] |
|                          | PPy/l-Ti$_3$C$_2$ | PPy                         | Electrochemical polymerization | 0.96                      | 0.02     | [68] |
| Large cations (CTA$^+$, STA$^+$, DDA$^+$, amine ions) | CTAB@Ti$_3$C$_2$ | CTAB                        | Liquid phase pillaring (40 °C) | 2.23                      | 1.25     | [55] |
|                          | STAB@Ti$_3$C$_2$ | STAB                        | Liquid phase pillaring (50°C) | 2.71                      | 1.73     | [55] |
|                          | DDAC@Ti$_3$C$_2$ | DDAC                        | Liquid phase pillaring (70°C) | 2.10                      | 1.12     | [55] |
|                          | Nb$_5$CTx + i-PrA | (CH$_3$)$_2$CHNH$_2$        | Liquid phase intercalation (RT) | 2.27                      | 1.23     | [49] |
| 1D/2D nanomaterials      | Ti$_3$C$_2$Tx/MWCNT | MWCNT                     | Lay-by-layer assembly (RT) | 1.42                      | 0.21     | [72] |
|                          | MXene-rGO       | rGO                         | Electrostatic self-assembly (RT) | 1.67                      | 0.36     | [73] |
|                          | MoS$_2$-in-Ti$_3$C$_2$ | MoS$_2$                  | Precursor mixing and annealing (500°C) | 1.22                      | 0.26     | [91] |
decrease of surface area and the deterioration of ionic and electronic transport in electrode materials, resulting in the performance degradation of MXene-based electrodes for energy storage. Meanwhile, the aggregation of MXene nanosheets restricts the accessibility and ion exchange at the electrode-electrolyte-gas triple-phase interface, impeding the development and application of MXene-based materials for electrocatalysis. Besides the introduction of intercalants, designing MXene with hierarchical structures by nanosheets-assembly, including MXene aerogel, 3D macroporous spheres, and crumpled nanosheets have also been proposed to solve the above-mentioned issues. Therefore, in this section, representative examples about the hierarchical MXene structure design are discussed, and the relationship between MXene hierarchical structures and their electrochemical performance are analyzed in detail.

Gogotsi and coworkers used polymethyl methacrylate (PMMA) as the template to create Ti$_3$C$_2$ MXene microspheres with open structure (Figure 5A). The wall thickness of MXene microspheres with 1-2 μm diameters and crumpled nanosheets have also been proposed to solve the above-mentioned issues. Therefore, in this section, representative examples about the hierarchical MXene structure design are discussed, and the relationship between MXene hierarchical structures and their electrochemical performance are analyzed in detail.

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is close to submicron level, hence greatly reducing the ion transport lengths (Figure 5B). Besides, TEM results confirm that each MXene microsphere is composed of a few monolayers with some flakes shares between each of them, which provide the mechanical robustness and good connection. As a supercapacitor electrode, the obtained macroporous MXene electrode enables prominent capacitance retention even at a high rate of 1 V s$^{-1}$ (210 F g$^{-1}$ at 10 V s$^{-1}$ and 100 F g$^{-1}$ at 40 V s$^{-1}$). It is worth mentioning that this result is more superior than the highest performance carbon materials reported to date. On the other hand, as a Na-ion storage anode, this 3D macroporous MXene (Ti$_3$C$_2$, V$_2$C, and Mo$_2$C) architectures exhibit greatly enhanced electrochemical performance compared to multilayer MXene and MXene/CNT hybrid electrode. All 3D macroporous MXene (Ti$_3$C$_2$, V$_2$C, and Mo$_2$C) electrodes are stable during the 1000 cycles at 2.5 C (1 C = 200 mA g$^{-1}$). After 1000 cycles, the capacity values retained by Ti$_3$C$_2$, V$_2$C, and Mo$_2$C film electrodes remain to be 295, 310, and 290 mAh g$^{-1}$, respectively. At a higher current density of 25 C, Ti$_3$C$_2$, V$_2$C, and Mo$_2$C electrodes can retain a capacity of 120, 170, and 125 mAh g$^{-1}$ after 1000 cycles, respectively (Figure 5C). On top of the above sacrificial template approach, a series of other strategies about easy and scalable production of MXene materials with favorable aggregation-resistant properties have been proposed recently. Wang et al. used a facile one-step strategy to synthesize crumpled N-doped Ti$_3$C$_2$ MXene (N-Ti$_3$C$_2$) nanosheets by thermal annealing of negatively charged Ti$_3$C$_2$ nanosheets and positively charged melamine (Figure 5D). Characterization on the microstructure confirms that the obtained crumpled MXene nanosheets have well-defined porous structure (Figure 5E), high surface area, and unique polysulfide absorption characteristic, which is an ideal scaffold to accommodate S cathode material for Li-S batteries. The crumpled N-Ti$_3$C$_2$ nanosheets/S cathode delivers a high reversible capacity of 1144 mAh g$^{-1}$ at 0.2 C (1 C = 1673 mA g$^{-1}$), and 770 mAh g$^{-1}$ at 2 C. The excellent electrochemical performance can be ascribed to the unique porous architecture along with physical confinement and chemical absorption of polysulfides, largely minimizing the polysulfide shuttle effect. Yang et al synthesized a 3D MXene hydrogel by a facile self-assembly method in the presence of GO and ethylenediamine (EDA) (Figure 5G). During the gelation, GO acts as a crosslinking agent and EDA acts as an initiator for inducing MXene flakes to form the hydrogel with unique 3D porous structure (Figure 5H). When used as an electrode for supercapacitors, 3D MXene hydrogel exhibits superb gravimetric capacitance and excellent rate performance (Figure 5I). The outstanding electrochemical performances can be attributed to the rapid electron transfer rate and fast ion transport toward the redox-active center in the 3D porous structure of MXene. In addition to the above method, Yang’s group reported the fast gelation of MXene in the presence of divalent metal ions initiator in an aqueous solution. During the gelation process, the divalent metal ions are strongly bonded to the -OH groups on MXene that destroys the electrostatic repulsive forces, and act as the linkers that cause the gelation of MXene nanosheets in aqueous solution. The MXene hydrogel obtained by this easy and facile gelation process shows excellent electrochemical performance (226 F g$^{-1}$ at 1 V s$^{-1}$) as an electrode for supercapacitors. Generally, the gelation of MXene is an easy and facile way to realize the 3D assembly of MXenes. Apart from the gelation, Qiu et al used isotropically capillary force to assemble MXene nanosheets into 3D architecture with hierarchical structure. The obtained 3D architectures by this method have many advantages, including large surface area, high robustness, 3D conductive framework, and good processability, which render them to be versatile hosts with hierarchical hybrid nanostructure for energy storage and conversion. For example, the CoP@3D Ti$_3$C$_2$ MXene hybrid architecture demonstrates high electrocatalytic activity toward oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) in KOH solution owing to enlarged active area, high conductivity, accelerative charge and mass transport at the reaction interface (Figure 5L).

According to the above examples, MXene nanosheet-assembled hierarchical structures can be obtained by several synthetic methods, including self-assembly and subsequent freeze-drying, capillary-forced assembly and subsequent spray drying, and sacrificial template approach. The 3D hierarchical structures can provide an ideal solution to the problem of poor electronic and ionic transport in electrode materials, and effectively inhibit the nanosheets aggregation, hence resulting in the high electrochemical performance. Besides, 3D MXene with hierarchical structures has the following advantages: (a) high surface area; (b) 3D conductive skeleton; (c) excellent mechanical properties, which renders them to be versatile skeletons for designing hierarchical hybrid nanostructures by coupling with other electrochemical active 0D/1D/2D nanomaterials for electrochemical energy storage and conversion.

### 3.3 MXene-based hybrid nanostructures

Owing to the high electronic conductivity, excellent mechanical flexibility, and versatile surface chemistry, MXenes are considered as ideal 2D substrates for energy
storage and conversion applications. MXene as a matrix not only enables rapid electron and ion transport, but also provides ample active sites for low dimensional nanomaterials bonding/loading and prevents them from aggregation during the electrochemical reaction process. In recent years, several studies are conducted to combine the MXene substrates with 0D nanomaterials (eg, Pt, P, Ag, TiO₂, SnO₂, Mn₃O₄, and Sb₂O₃), 1D nanomaterials (eg, CNTs, and bacterial cellulose), and 2D nanomaterials (eg, Layered double hydroxides (LDHs), Transition metal dichalcogenides (TMDs), and Metal-organic frameworks (MOFs)). Furthermore, their applications in the field of electrochemical energy storage and conversion are systematically investigated. Hence, in this section, representative examples about nanostructures designed by 0D/1D/2D and MXene matrix are analyzed, and their energy storage and electrocatalysis mechanisms are discussed in detail.

Recently, Yang et al constructed black phosphorus quantum dots (BPQDs) and Ti₃C₂ nanosheets...
nanocomposite by liquid phase self-assembly process (Figure 6A). The 0D BPDOs with size distribution from 1.6 to 6.5 nm are uniformly distributed on the Ti3C2 nanosheets by forming P-O-Ti interfacial bonds. Due to this unique structure, the nanocomposites exhibit an enhanced charge adsorption and efficient interfacial electron transfer. As an anode for lithium-ion storage, BPDOs/Ti3C2 nanocomposites show a novel battery-capacitive dual-model energy storage mechanism that delivers high capacity (910 mAh g\(^{-1}\)) at 0.1 A g\(^{-1}\) and long cycling stability (2400 cycles without capacity decay) (Figure 6C). Using the same method, Xu et al synthesized transition metal oxide/Ti3C2 MXene nanostructures. By a facile self-assembly process, TiO2 nanorods/Ti3C2 and SnO2 nanowires/Ti3C2 nanocomposites can be successfully constructed by van der Waals interactions (Figure 6D). TEM results indicate that the length of uniformly distributed SnO2 nanowires ranges from 70 to 100 nm, and the diameter is about 4 nm (Figure 6E). Ti3C2 MXene in the nanocomposites not only enables rapid electron and ion transport, but also prevents the transition metal oxides from aggregation during the cycling process. In turn, the transition metal oxides nanomaterials in the nanocomposites act as spacers to prevent Ti3C2 nanosheets from restacking. Therefore, the obtained TiO2/Ti3C2 and SnO2/Ti3C2 exhibit outstanding electrochemical performance due to the short Li\(^+\) diffusion pathways and incremental active sites (Figure 6F).

The self-assembly method not only can be applied in MXene with 0D nanomaterials, but also can be used with 1D nanomaterials. Yuan et al designed a 3D porous MXene/bacterial cellulose (BC) self-supporting film by the interaction between their surface oxygen-containing groups (Figure 6G). After vacuum-filtration and freeze-casting, the highly interconnected MXene/BC network with outstanding mechanical properties and high flexibility can be obtained. Due to the excellent electron and ion transport channel (Figure 6H), the 3D porous MXene/BC film delivers ultrahigh capacitance performance (416 F g\(^{-1}\), 2084 mF cm\(^{-2}\)) even with a high mass loading of 5 mg cm\(^{-2}\) (Figure 6I). Besides, Gogotsi et al fabricated porous Ti3C2 MXene/CNT composite paper electrodes by electrostatic attraction between MXene nanosheets and positively charged CNTs. The well-defined porous structure can facilitate electrolyte transport and ions utilization. Used as an electrode for Na-ion storage, the Ti3C2 MXene/CNT porous film shows a high volumetric capacity of 421 mAh cm\(^{-3}\) at 20 mA g\(^{-1}\), and good rate performance. In addition to the above self-assembly method, the ball-milling method can also be used for preparing MXene/CNT composites. Generally, the MXene/CNT composites have electron/ion transport channel and mechanical flexibility, which can be used as an excellent host for S and silicon electrodes.

Other than 0D and 1D nanomaterials, MXene-based hybrid nanostructures can also be built by the combination between MXene and other 2D nanomaterials. Huang et al designed a novel MXene-MOF composite via an interdiffusion reaction strategy (Figure 6J). By confining the reaction of metal ions and ligands in a mixed-solvent layer, the MOF layers are seamlessly coated on the surface of Ti3C2 nanosheets (Figure 6K). Hydrophilic Ti3C2 MXene nanosheets in the composite not only can support the porous structure MOF, but also facilitate the easy access of aqueous electrolyte to the catalytic activity center. Besides, the in-situ deposition MOF on Ti3C2 MXene with well-defined interface facilitates the charge transfer, achieving good electrocatalytic performance. As a catalyst for OER, the obtained MXene-MOF composite shows a lower potential (1.64 V vs reversible hydrogen electrode, RHE) as the current density reaches 10 mA cm\(^{-2}\) in 0.1 M KOH solution (Figure 6L). Similar structure can also be synthesized by electrochemical deposition. Qiu and his coworkers used electrochemical deposition to synthesize mesoporous NiFe layered double hydroxides (NiFe-LDHs) nanosheets on Ti3C2 MXene scaffolded by nickel foam (NF) (Ni-Fe-LDH/MXene/NF). The 3D MXene frame has high conductivity and hydrophilic property, which not only assists the mass/charge transport across the catalyst, but also enhances the OER and hydrogen evolution reaction (HER) kinetics. Used as a binder-free electrocatalytic electrode, the Ni-Fe-LDH/MXene/NF achieves high current density of 500 mA cm\(^{-2}\) at low overpotential for OER (300 mV) and HER (205 mV) in 1.0 M KOH. Moreover, stacking different 2D materials into heterostructures architectures can endow the constructed electrodes with the combined advantages of the individual building blocks while minimizing the associated shortcomings, which can greatly expand current energy storage technologies. Gogotsi et al synthesized 2D MoS2-on-MXene heterostructures by in-situ sulfuration of Mo2TiC2 MXene. Theoretical calculation results confirm that the obtained metallic MoS2-on-MXene heterostructures exhibit an enhanced adsorption towards Li and Li2S during the intercalation and conversion reactions. Used as anodes for Li-ion batteries, the as-prepared heterostructures shows a high reversible capacity and excellent cycling performance. Furthermore, Xu et al used first principle calculations to explore 16 different kind of heterostructures constructed by TMDs and MXenes (bare and O-terminated case), and studied their potential applications in Na-ion batteries and Na-O\(_2\) batteries. Among all these heterostructures, only VS2 with O-terminated MXenes structures can load five layers of Na ions, therefore a highly promising material for Na-ion...
batteries. Besides, VS₂/Ti₂CO₂ heterostructure also exhibits a great potential in Na-O₂ batteries. These simulations are important for future battery design.

Based on the above examples, MXene-based hybrid nanostructures can be obtained by several synthetic techniques, including ball milling, electrodeposition, liquid phase mixing or/and annealing, in-situ exfoliation and atom trapping, self-assembly, and liquid phase oxidation. MXene in the hybrid nanostructures can prevent 0D/1D/2D nanomaterials from aggregation. Besides, MXene can endow the nanomaterials with improved conductivity and relieved stress. When used as the electrodes for electrochemical energy storage and conversion, the hybrid structures have rapid charge and ion transfer ability.

4 CONCLUSIONS AND PERSPECTIVES

MXenes have attracted increasing research interests in the field of electrochemical energy storage and conversion due to their high electrical conductivity, large redox active surface area, exceptional mechanical properties, tunable structures, and rich surface chemistries. Specifically, over the last decade, there has been a rapid increase in the number of publications on the properties and potential applications of MXenes in electrochemical energy storage and conversion.

In this review, we first summarized the synthesis techniques of MXene, with a particular focus on the wet-chemistry etching synthesis approach. The synthesis techniques used to produce MXene directly influence the properties of the obtained MXenes and therefore dictating their electrochemical performance. The characteristics of techniques, reaction conditions, and the properties of the obtained MXene by different synthesis approaches are summarized and discussed in detail. In general, HF etching and modified fluoride-based acid etching are the most commonly used synthesis techniques. Compared to HF etching and the clay method (5 M LiF/6 M HCl), the MILD-LiF/HCl method provides the least defects, and higher electrical conductivity and larger flake size of MXene.

In the research process of electrochemical energy storage and conversion, a better understanding of the structure and surface chemistry of MXene materials is necessary, especially in terms of the relationship between

| Interfacial structure type | Electrode materials | Applications | Electrochemical performances | Refs |
|---------------------------|---------------------|--------------|-----------------------------|------|
| Layered structure with enlarged interlayer spacing | N-Ti₃C₂Tx | SCs | 192 F g⁻¹ in 1 M H₂SO₄ | [71] |
| | CT-S@Ti₃C₂ | SICs | 550 mAh g⁻¹ at 0.1 A g⁻¹ and ~120 mAh g⁻¹ at 15 A g⁻¹ | [67] |
| | Ti₃C₂ | SCs | ~350 F cm⁻³ after 10 K cycles | [60] |
| | PVP-Sn(IV)@Ti₃C₂ | LIBs | 1375 mAh cm⁻³ (635 mAh g⁻¹) at 0.1 A g⁻¹ | [63] |
| | CT-Sn(II)@Ti₃C₂ | SMBs | High Coulombic efficiency over 500 cycles (up to 10 mA cm⁻² and 5 mAh cm⁻²) | [66] |
| | Ti₃C₂Tx/PVA | SCs | ~530 F cm⁻³ at 2 V s⁻¹ | [69] |
| | PPy-Ti₃C₂Tx | SCs | ~1000 F cm⁻³ with capacitance retention of 92% after 25 000 cycles | [70] |
| Nanosheet-assembled hierarchical structures | CTAB-Sn(IV)@Ti₃C₂ | LICs | 765.6 mAh g⁻¹ at 0.1 A g⁻¹ | [55] |
| | 3D macroporous MXene film | SIBs | ~350 mAh g⁻¹ at 0.25 C | [58] |
| | Crumpled MXene nanosheets | LSBs | 610 mAh g⁻¹ at 2 C 1000 cycles | [79] |
| | MXene/GO hydrogel | SCs | 165 F g⁻¹ even at 1000 A g⁻¹ | [75] |
| | Fluffy CoP-3D MXene architecture | OER/HER | Overpotential of 168 mV (10 mA cm⁻²) for HER; Overpotential of 298 mV (10 mA cm⁻²) for OER | [74] |
| MXene-based hybrid nanostructures | Black P quantum dots/MXene | LIBs | 910 mAh g⁻¹ at 100 mA g⁻¹ | [80] |
| | TiO₂ nanorods /MXene | LIBs | 176 mA h g⁻¹ at 1 A g⁻¹ after 200 cycles | [57] |
| | 1D bacterial cellulose/MXene | SCs | 416 F g⁻¹ and 2084 mF cm⁻² | [87] |
| | 2D MOFs/MXene nanocomposites | OER | Lower potential (1.64 V vs RHE) at 10 mA cm⁻² | [90] |

Abbreviations: HER, hydrogen evolution reaction; LIB, lithium-ion battery; LIC, lithium-ion capacitor; LSB, lithium-sulfur battery; OER, oxygen evolution reaction; SC, supercapacitor; SIB, sodium-ion battery; SIC, sodium-ion capacitor.
the interfacial structure and electrochemical performance. Therefore, we have proposed the interfacial structure design of MXene and their corresponding electrochemical energy storage and conversion applications. To date, the interfacial structure design according to different modification methods mainly include:

(a) Layered structure with enlarged interlayer spacing;
(b) Nanosheet-assembled hierarchical structures;
(c) MXene-based hybrid nanostructures. Generally, designing layered structure MXene with enlarged interlayer spacing, especially the controlled and fine-tuned interlayer spacing of MXenes (from 1 to 2.7 nm) based on the spontaneous intercalation of cationic surfactants can facilitate the adsorption/intercalation of charge carrying ions within the MXene host and maximize the electrochemical performance. Furthermore, the hierarchical structure design of MXene can prevent MXene nanosheet aggregation and provide the rapid ionic and electronic transport in electrode materials, hence resulting in the superior electrochemical performance. Besides, MXene as a matrix not only enables rapid electron and ion transport, but also provides abundant active sites for low dimensional nanomaterials bonding/loading, which can prevent them aggregation during the electrochemical reaction process, enhancing the overall electrochemical performance as a result. The interfacial structure design of MXene and their corresponding performances for electrochemical energy storage and conversion applications are summarized in Table 3.

Although MXene research for electrochemical energy storage and conversion applications has developed rapidly, some remaining challenges still need to be overcome for the practical utilization of MXene. For future research, the following points are of particular importance. (a) Achieving uniform and controllable terminations (eg, -OH, -F, -Cl) on the designated surface is necessary for different applications. (b) A comprehensive understanding and systematical investigation on the properties (stability, transport, and bonding environment) of intercalation agents (eg, ionic, molecular species) and their effects on the physiochemical and electrochemical properties of layered MXenes is necessary. (c) A fundamental understanding on the nature of active centers (terminations and interfacial transition metal layers) for ion dynamics and energy storage/electrocatalysis mechanism by the collaboration between experiment and theoretical calculation can lay solid foundations for the applications of MXenes in electrochemical energy storage and conversion.

ACKNOWLEDGMENTS

The authors greatly acknowledge the support from the start-up funds at Thayer School of Engineering, Dartmouth College, and support by the National Natural Science Foundation of China (Grant no. 51722210), the Natural Science Foundation of Zhejiang Province (Grant no. LD18E020003). The authors thank Prof. Jianwei Nai from Zhejiang University of Technology for valuable discussion.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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**How to cite this article:** Luo J, Matios E, Wang H, Tao X, Li W. Interfacial structure design of MXene-based nanomaterials for electrochemical energy storage and conversion. *InfoMat*. 2020;2:1057–1076. [https://doi.org/10.1002/inf2.12118](https://doi.org/10.1002/inf2.12118)