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2019

Yu, H., Wang, Y., Jing, Y., Ma, J., Du, C.-F., & Yan, Q. (2019). Surface modified MXene-based nanocomposites for electrochemical energy conversion and storage. *Small*, 15(25), 1901503-. doi:10.1002/sml.201901503

<https://hdl.handle.net/10356/139681>

<https://doi.org/10.1002/sml.201901503>

This is the peer reviewed version of the following article: Yu, H., Wang, Y., Jing, Y., Ma, J., Du, C.-F., & Yan, Q. (2019). Surface modified MXene-based nanocomposites for electrochemical energy conversion and storage. *Small*, 15(25), 1901503-. doi:10.1002/sml.201901503, which has been published in final form at <https://doi.org/10.1002/sml.201901503>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions.

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DOI: 10.1002/ ((please add manuscript number))

Article type: Review

Surface modified MXene-based nanocomposites for electrochemical energy conversion and storage

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((Optional Dedication))

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Keywords: MXene, nanocomposites, surface chemistry, electrochemical, energy conversion and storage

Abstract: In recent year, the rapidly growing attention on MXenes makes the material a rising star in 2D materials family. However, most researches interests are still focused on the properties of bare MXenes, few attention has been paid on the surface chemistry of MXenes and MXene-based nanocomposites. To this end, this review offers a comprehensive discussion on the surface modified MXene-based nanocomposites for energy conversion and storage (ECS) applications. Based on the structure and reaction mechanism, the related synthesis methods towards MXenes are briefly summarized in the first part. After the discussion of existing surface modification techniques, the surface modified MXene-based nanocomposites and their inherent chemical principles are presented. Finally, the application

of these surface modified nanocomposites for supercapacitors (SCs), lithium/sodium-ion batteries (LIBs/SIBs), and electrocatalytic water splitting are discussed. The challenges and prospects of MXene-based nanocomposites for future ECS application are also presented.

1. Introduction

With the ever-growing green energy demands of modern society, many efforts have been paid on the development of novel materials for high efficient energy conversion and storage (ECS) applications. Base on the operating principle of electrochemical ECS, the surface and interface play critical roles in the ion intercalation, physical/chemical adsorption, and chemical reaction process.^[1] Therefore, the two-dimensional (2D) materials, represented by graphene and MoS₂ with extremely large specific surface areas and high electrical conductivities, are regarded as superior candidates for electrochemical ECS in recent decades.^[1d, 2] For the electrochemical energy conversion applications such as rechargeable lithium-ion batteries (LIBs) and electrocatalytic water splitting, the 2D materials have presented several advantages over others: i) the crystalline nature offers a low energy barrier for fast electron transportation within the atomic layer; ii) the layered structure generates abundant ion diffusion pathways, which facilitates the diffusion process; iii) the 2D structure can simultaneously buffer the volume changes during reaction and maintain a good connection between each nanosheet.^[2-3]

Beyond these well-known materials, recently a novel 2D metal carbide/nitride with unique surface chemistry, adjustable composition and physiochemical properties has aroused increasing attention in the field of ECS, that is, MXene. Since the first report of Ti₃C₂T_m MXene in 2011, this novel material family produced *via* the selective etching of MAX compounds has represented a promising electrode material in the supercapacitors (SCs).^[4] Likewise, owing to their unique oxygen/fluorine functionalized surface, a great potential of

MXene in the application of LIBs, sodium-ion batteries (SIBs), lithium-sulfur batteries (LSBs) and, electrocatalytic water splitting was predicted in the following years.^[5] However, most of the recent studies are still restricted to the performance of as-exfoliated MXene materials that without surface modification (denoted as “bare MXene”). As experienced by other 2D analogs, the MXene compounds with such an active surface should also possess a much better prospect in the construction of heterostructures and hybrid materials. However, although there have been plenty of reports on the bare MXene, few attention has been paid on the underlying scientific principle of their surface chemistry, let alone the controllable design and synthesis of MXene-based functional materials. Therefore, with a view to the application of MXene-based hybrids in ECS, there is an urgent need to summarize the recent progress and milestones of these novel material family in ECS applications.

In recent years, there have been some comprehensive reviews on these rapidly developing materials.^[1a, 3, 4b, 5a, 5c] However, even the MXene-based hybrids have shown their great potentials, previous reviews are mainly focused on the bare MXenes and the application of them for specific fields such as SCs or LIBs/SIBs.^[3, 5a, 5c, 6] Few attention has been paid on the surface properties of MXenes and the correlation between the surface modification species and MXene backbone. In this regard, we aim to provide a brief summary of recent works towards the surface modified MXene-based nanocomposites, offering an overview of new aspect of this promising material system. In the first section, the structure and preparation methods of MXenes and their associated surface characters are summarized. In the second section, combined with the recent-developed surface modification techniques, progress in the preparation of MXene-based nanocomposites is briefly summarized. The applications of MXene-based nanocomposites for electrochemical ECS are then discussed. Finally, the challenges and the prospect of MXene-based nanocomposites for future electrochemical ECS application are presented.

2. The structure and preparation methods of MXenes

Typically, the MXene can be regarded as the extraction of M_nX_{n-1} ($n = 2, 3, 4$) layer from the metal-ceramic phase (MAX, in which M = early transition metals; A = group IIIA or IVA elements; X = C, N) by removing the interlayered A atoms.^[7] As shown in **Figure 1**, the M and X atoms in MAX phase are stacked in a hexagonal lattice with the X atoms occupying the center of edge-shared M octahedral cages. Therefore, after removing the A atoms, the M_nX_{n-1} layer can still maintain the hexagonal lattice rather than the cubic structure of MX. With the alternative stacking of M_nX_{n-1} layers and planar A atomic sheets along the c axis, the MAX already reveals a pseudolaminar structure. Generally, the M–X bond shows multiple features of covalent, metallic, and ionic characters, which presents much stronger binding energy than the metallic M–A bond. This weak M–A bond endows the A atoms higher chemical reactivity thus the possibility of M_nX_{n-1} layer extraction.^[3]

The removal of interlayered A atoms will result in the dangling bond on the surface M atoms. Varied by the etching process, different terminal groups can bond to M atoms in order to fulfill their coordination sphere and reduce the surface Gibbs free energy (G_{sur}). Therefore, the surface characters of MXene nanosheets highly depend on the preparation methods. In this part, before the discussion of surface modification and application, we will first focus on and classify the preparation methods of MXene materials, illustrating the relationship between the preparation methods and the surface character of MXene materials.

2.1. Hydrofluoric acid (HF) etching method

The hydrofluoric acid (HF) etching method was first introduced by Gogotsi and Barsoum in 2011 in order to delaminate the Ti_3AlC_2 MAX.^[4a] In MAX phase, the M_nX_{n-1} layers are stacked in a hexagonal lattice, and each M_nX_{n-1} layer was divided by A atoms. Although the escape of A atoms from the MAX phase can occur under certain circumstances (carbothermic reduction, vacuum heating, et al), the remaining M_nX_{n-1} layer will undergo a phase transformation simultaneously, which results in the

cubic MX phase. However, in Gogotsi and Barsoum's studies, the HF can directly extract Al atoms from Ti_3AlC_2 through a simple displacement reaction, releasing H_2 . At the same time, H_2O and HF molecules will also react with generated Ti_3C_2 , producing $\text{Ti}_3\text{C}_2\text{T}_m$ ($\text{T} = \text{OH}$, F , and O) and releasing H_2 . The reaction process can be expressed as follows:

Later, a series of MAX compounds including Ti_2AlC , Ta_4AlC_3 , $(\text{Ti}_{0.5}\text{Nb}_{0.5})_2\text{AlC}$, $(\text{V}_{0.5}\text{Cr}_{0.5})_3\text{AlC}_2$, Ti_3AlCN , Nb_2AlC , Ti_3SiC_2 , $\text{Mo}_2\text{Ga}_2\text{C}$, and $\text{Zr}_3\text{Al}_3\text{C}_5$ were successfully exfoliated into MXene by the HF etching method.^[8] It should be pointed out that the $\text{Mo}_2\text{Ga}_2\text{C}$ and $\text{Zr}_3\text{Al}_3\text{C}_5$ are not traditional MAX material. However, the HF etching can still produce their respective MXene products. In addition, the HF etching temperature, etching time, and the HF concentration are all important parameters for high-quality MXene nanosheets. Proven by previous works, with the increase of n number, the longer etching time, higher etching temperature and lower pH value are required for the etching process.^[5c] However, it should be noted that the stronger acidic etching might also result in more surface defects or even reduce the yield of MXene.^[9] Up to now, the HF etching method is still one of the most versatile and widely adopted synthesis method towards MXene materials. Confirmed by Gogotsi et al., the $\text{Ti}_3\text{C}_2\text{T}_m$ etched by concentrated HF can deliver a well-exfoliated accordion-like morphology, which is hard to access via other etching methods.^[10] Through the HF etching method, the generated M_nX_{n-1} MXene has shown its original surface character with functional groups of $-\text{F}$, $-\text{OH}$ and $-\text{O}$. Cook et al. had carefully studied the surface

terminal groups of MXene via high-resolution X-ray photoelectron spectroscopy (XPS) analysis.^[11] A series of observations have been summarized including that the surface –F groups are the predominant species in fresh prepared MXene, –OH groups tend to adsorb H₂O molecules, and the fraction of –O groups increase after aging or Ar sputtering, which are in accord with the theoretical simulations.^[12] Moreover, the dispersity of HF-etched Ti₃C₂T_m in various organic solvents was evaluated to be closely related to the surface functional groups and the solvent polarity (**Figure 2**).^[13] These pioneering studies provide a comprehensive database for the development of surface chemistry regarding MXene.

2.2 Modified acid etching method

In consideration of the high toxicity of HF, the transportation and operation of HF need to be extremely careful. Therefore, researchers attempt to explore other ways towards the extraction of A atoms from MAX phase avoiding direct usage of HF. The first developed method is a modified HF method or known as “*in-situ* HF method”, in which HF was replaced by the combination of fluoride salts (LiF, NaF, KF, and FeF₃) and HCl.^[14] During the etching, the HCl offers the H⁺ while the F[–] was released from the fluorides. Interestingly, except the extraction of A atoms and the generation of the surface functioned M_nX_{n-1}T_m layers, the modified method also allows the intercalation of metal ions into the interlayered space and thus weakens the interlayered interaction.

A recent work has also demonstrated that through the modified acid etching method, –Cl groups can be introduced as the surface terminal groups.^[15] Following, ammonium bifluoride (NH₄HF₂) was demonstrated as another available etchant as well.^[16] In previous report, the interlayer space of M_nX_{n-1}T_m is able to accommodate various cations including Li⁺, Na⁺, K⁺, NH₄⁺, Mg²⁺, Al³⁺, tetrabutylammonium (TBA), tetramethylammonium (TMA) and even neutral organic molecules like hydrazine monohydrate N₂H₄·H₂O (HM), N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), which in turn facilitates the delamination process.^[17] In 2017,

Gogotsi et al. summarized the etching and exfoliation of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene, offering the general guidelines for the preparation of these novel 2D materials.^[10]

2.3 Molten fluoride salt etching method

Compared with carbide MXenes, the nitride MXenes were rarely reported. When taking $\text{Ti}_n\text{AlN}_{n-1}$ as a model system, the $\text{Ti}_n\text{N}_{n-1}$ shows lower stability than $\text{Ti}_n\text{C}_{n-1}$ and the bonding of Al atoms in the $\text{Ti}_n\text{AlN}_{n-1}$ system is stronger. Most importantly, the $\text{Ti}_n\text{N}_{n-1}$ may dissolve in HF solution during the etching process.

To overcome the aforementioned challenge, Gogotsi et al. introduced ternary eutectic molten fluoride salt ($\text{LiF}:\text{NaF}:\text{KF} = 29:12:59$ in weight ratio) as the etchant to synthesize $\text{Ti}_4\text{N}_3\text{T}_m$ MXene.^[18] The mixture of Ti_4AlN_3 and fluoride salts were annealed at 550°C under Ar protection and the etching process was finished in 30 min. However, after etching, extra washing step (with H_2SO_4 and deionized (DI) water) and further delamination (in tetrabutylammonium hydroxide (TBAOH) solution) were still required. From the X-ray diffraction (XRD) spectra, the delaminated $\text{Ti}_4\text{N}_3\text{T}_m$ presented inferior crystallinity when compared with the other HF-etched titanium carbide MXenes like $\text{Ti}_3\text{C}_2\text{T}_m$.^[10] This might suggest that there are still some intricate issues in the synthesis of nitride MXenes *via* molten fluoride salt etching method. Generally, the wet chemistry processes are still the most qualified choice towards the synthesis of MXene materials.

2.4 Fluoride-free etching method

Although the modified acid etching method avoids the direct usage of HF, the existence of H^+ and F^- in the solution can still cause the release of HF. In regards to the amphotericity of interlayered A atoms, recently some fluoride-free etching methods were proposed. Zhang and Gu had designed an alkaline etching method by utilizing a NaOH solution as the corrosive medium (**Figure 3**).^[19] Generally, the Ti_3C_2 skeleton is unstable in the alkaline condition, in which the corrosion of Ti_3C_2 skeleton will happen

simultaneously during the removal of Al atoms. Therefore, keeping Ti_3C_2 layer intact while the selective etching of Al atom from Ti_3AlC_2 , is still a challenge. In this case, a high temperature (270 °C), high alkaline concentrate (27.5 M) condition was applied in order to prevent the damage of Ti_3C_2 skeleton, which was known as Bayer process. The authors claimed that the high temperature can facilitate the transformation of $\text{Al}(\text{OH})_3$ and $\text{AlO}(\text{OH})$ into the dissolvable $\text{Al}(\text{OH})_4^-$; while the high alkaline concentration, with low water containment, can prevent the oxidation of Ti species. By this fluoride-free etching process, the surface of Ti_3C_2 layer was covered by $-\text{OH}$ and $-\text{O}$ group.

However, the above-mentioned concentrated NaOH solution needs to be heated under a high temperature and pressure hydrothermal condition, which may also have safety concerns. Therefore, Cheng and Geng recently developed a moderate organic base etching method towards the delamination of Ti_3AlC_2 , in which the tetramethylammonium hydroxide (TMAOH) was chosen as the etchant (**Figure 4**).^[20] Commercially, TMAOH is an efficient Al etching ingredient. In the Ti_3AlC_2 delamination process, the generated $\text{Al}(\text{OH})_4^-$ anions bonded to the surface Ti atoms and the TMA^+ cation intercalated into the interlamellar space simultaneously. From this point of view, different surface characters of the TMAOH-etched Ti_3C_2 can be expected from the ones by HF and NaOH etching process.

Electrochemical etching is an alternative approach for the selective etching process. However, the electrochemical etching of Ti_3AlC_2 in dilute NaCl, HCl, and HF solution will lead to the corrosion of the whole material. In addition, the electrochemical etching of Ti_3AlC_2 in moderate concentration cannot proceed. Therefore, the careful selection of electrolyte is a critical factor for the electrochemical synthesis of MXene materials. Recently, Feng's group report the selective electrochemical etching of Al atoms from Ti_3AlC_2 (**Figure 5**).^[21] On account of the strong binding capability of Cl^-

with Al, an aqueous solution consisting of 1.0 M ammonium chloride (NH₄Cl) and 0.2 M TMAOH with a pH value >9 was chosen as the electrolyte. During the electrochemical etching process, the Al atoms were extracted by Cl⁻ anions and the intercalation of NH₄⁺ cations took place. The etching of Al atoms during the electrochemical process can be expressed as follows:

It is obvious that reactions (4) and (5) are similar to reactions (1) and (2), merely replacing reaction (3) with (6) in the electrolysis condition. Interestingly, the authors did not take the Al(OH)₄⁻ anions into consideration, which was claimed to be the terminal groups in Cheng and Geng's work.^[20]

Finally, the SEM images of powder morphology obtained by different etching methods were shown in **Figure 6**. Meanwhile, the comparison of the four exfoliation techniques and the resulting surface functional groups is presented in **Table 1**. The etching reagents and applicable MAX species are also given. As summarized in Table 1, the Ti₃C₂T_m presents the most widely studied MXene species and can be accessed *via* almost all etching method. In addition, the comparison of the four etching methods clearly showed the difference of surface functional groups between each strategy.

2.5 Other non-etching method

Beyond the traditional HF etching processes and the modified etching methods, there were also efforts on the development of non-etching methods in recent years. Exemplified by Kang and Ren,^[22] the chemical vapor deposition (CVD) strategy had shown great potential in the preparation of ultrathin α -Mo₂C MXene, which presents the large-area, high-quality and clean surface. However, although plenty works claim the successful synthesis of MXene *via* CVD and pyrolysis methods, the “MXene-like” layered metal carbides/nitrides still belong to the cubic structure of MX, which needs to be carefully identified.

3. Surface modification methods for MXenes

To date, MXene without surface termination groups has not yet been found. In most of the computational studies of MXene, surface functional groups were found to have dramatic impacts on their stabilities, electronic structures and other physicochemical properties.^[12, 23] However, the post-synthesis processing for a certain specific surface functional group was rarely reported.^[24] Efforts were made on the understanding of the configuration and interactions between each surface functional groups.^[25] Commonly, the mixed surface functional groups were randomly distributed on MXene surface. Neutron scattering on Ti₃C₂T_m suggests the existence of hydrogen bonding between –F or –O and the neighboring –OH groups; whereas the binding between –F and –O was the Van der Waal's interaction.^[25a] In addition, the intercalated water molecules seemed to show a favorable hydrogen bonding with surface –O and –OH groups.^[25b, 25c]

Therefore, a careful classification of MXene-based nanocomposites according to their surface modification methods is important and will contribute to the better understanding of their surface characters and reaction rules. In this section, four major

surface modification methods towards MXene-based nanocomposites are summarized and the reaction mechanisms are discussed in detail, which will offer an overview of the surface modification of MXene-based nanocomposites.

3.1 Direct oxidation induced surface reformation

In 2014, Barsoum and co-workers started to focus on various oxidation process of $\text{Ti}_3\text{C}_2\text{T}_m$ and Nb_2CT_m , i.e. under rapid heating in air, annealing in CO_2 and treated under hydrothermal environment.^[26] They have first studied the flash oxidation of $\text{Ti}_3\text{C}_2\text{T}_m$ powders in the air, which was heated to 1150 °C within 5s and kept at this temperature for 30s. After this flash oxidation process, the $\text{Ti}_3\text{C}_2\text{T}_m$ transformed to anatase TiO_2 nanocrystals decorated carbon sheets. Additionally, the TiO_2 nanocrystals were located at the edges and interlayered space, indicating the migration of Ti atoms from innermost layers to the surface. The $\text{Ti}_3\text{C}_2\text{T}_m$ annealed in CO_2 or treated under hydrothermal environment also showed similar results, but with much more moderate reaction temperatures. In their following works, Nb_2O_5 nanoparticles modified $\text{Nb}_4\text{C}_3\text{T}_m$ MXene was also obtained through the CO_2 annealing process (**Figure 7a-b**).^[27] These results pioneered a facile route towards controllable oxidation of MXene and guidelines for synthesis of metal oxide decorated MXene hybrids. At the same year, Taheri's group systematically studied the transformation mechanism of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene during oxidation in air through *in-situ* transmission electron microscopy (TEM) techniques.^[28] Based on the *in-situ* TEM images and Raman spectra, two oxidation mechanisms of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene under high-temperature flash heating and low-temperature annealing were proposed. During high-temperature flash heating, the surface Ti layers are first oxidized into planar anatase thin film. Then the innermost Ti atoms migrated to the surface, giving rise to the Ostwald ripening and growth of vertical 3D particles. On the contrary, the low-temperature annealing of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene only leads to the direct formation of a rutile **nanosheets** on the surface without anatase intermediate (**Figure 7c-d**). As commonly accepted that the initial crystallization of TiO_2 is in the form of anatase phase,^[29]

the oxidation mechanisms of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene reported here has offered a predictable method on the preparation of TiO_2 -based hybrids from MXene materials.

Later, more and more research groups started to concern about the surface reformation of MXene.^[24, 30] Hwang and Lee reported the modification of surface functional groups on Ti_2CT_m MXene by post thermal processing.^[24] The gradual loss of H and F atoms under an Ar/ H_2 protective atmosphere can be described as follow:

Alshareef's group compared the effect of post-etch annealing ambient (Ar, N_2 , N_2/H_2 , and air) on the structural and electrochemical properties of Ti_2CT_m MXene.^[30b] Except the already-known air treatment, annealing in the reductive N_2/H_2 atmosphere appears to have the best enhancement on the electrochemical properties. This can be attributed to the enlargement of interlayered space and specific surface area, increase in the carbon content and decrease in the surface fluorine content.

According to the abovementioned works, the controlled oxidation of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene could be a promising method to prepare functional TiO_2 @MXene hybrids. As expected, Yin *et al.* recently have first realized the surface TiO_2 modification of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene for microwave absorbing and shielding *via* annealing $\text{Ti}_3\text{C}_2\text{T}_m$ MXene in an argon atmosphere.^[30c] When annealed in absence of oxygen, the surface oxidation will be interrupted before further extraction of the innermost Ti atoms. Therefore, the $\text{Ti}_3\text{C}_2\text{T}_m$ MXene was partially transformed to TiO_2 and amorphous carbon, which formed a sandwich structure with MXene matrix. **Importantly, the formation of TiO_2 nanocrystals and carbon could generate capacitor-like structures, which optimizes the impedance match with free space and shows great potential for absorbing and shielding of electromagnetic wave.** Zhu and

Liu grew the TiO_2 quantum dots (QDs) on $\text{Ti}_3\text{C}_2\text{T}_m$ MXene by applying a cetyltrimethylammonium bromide (CTAB) assisted solvothermal treatment.^[30d] The CTAB can prevent the oxidation of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene and stabilize the water-in-oil emulsion on $\text{Ti}_3\text{C}_2\text{T}_m$ MXene surface, in which the TiO_2 QDs nucleated and grew. Recently, the oxidative reagents like H_2O_2 ,^[31] NaOH ,^[30g, 32] KOH ,^[30h, 32b, 33] FeCl_3 ,^[30n] and CuSO_4 were also introduced to oxidize the MXene surface.^[34]

3.2 Reactive surface reformation

Upon the direct surface oxidation and reformation studies of MXene, the reactivity of these surface atomic layers had opened a new door to the preparation of MXene-based hybrids. However, the controllable reaction of these surface atoms is still a huge challenge. According to Yang and Chen's DFT calculations, five surface sulfur-functioned MXenes out of twenty calculated types are dynamically stable, indicating the possibility of experimentally synthesis of sulfur-functioned MXene.^[23q] Additionally, as presented by Gogotsi et al, the metal atom distributions in double-transition metal MXenes could be predicted.^[35] Particularly, Mo atoms prefer to occupy the surface layers in a Mo-rich MXene and the ordered arrangement of Mo and Ti atoms in $\text{Mo}_2\text{TiC}_2\text{T}_m$ MXene was experimentally confirmed.^[35a, 36] Motivated by these discoveries, the $\text{Mo}_2\text{TiC}_2\text{T}_m$ MXene was chosen as a model compound for the selective surface sulfur reformation research.^[37] As reported by Miao and Gogotsi, the sulfur particles were first incorporated with $\text{Mo}_2\text{TiC}_2\text{T}_m$ MXene flakes *via* a liquid mixing process. The following thermal treatment of the mixture in an inert atmosphere triggered the reaction between sulfur and surface Mo–O species. As a result, a thin layer of MoS_2 was *in-situ* generated on the surface of $\text{Mo}_2\text{TiC}_2\text{T}_m$ MXene (**Figure 8**). Similar to the previous controlled oxidation studies, the *in-situ* sulfidation of surface Mo–O moieties was accompanied by the evaporation of sulfur. Therefore, the reaction terminated when sulfur was depleted. For this reason, the composition and morphology

of this hybrid could be easily controlled by adjusting the ratio of reagents, reaction time and temperature.

Zhang, Huang, and Zhi had reported another reactive surface reformation path towards the $\text{NaTi}_2(\text{PO}_4)_3$ (NTP) and $\text{Ti}_3\text{C}_2\text{T}_m$ MXene hybrids.^[38] They introduced an oxidation step to obtain TiO_2 @MXene structure prior to the *in-situ* transformation of TiO_2 into NTP. After solvothermal transformation, cube-like crystals of NTP were formed on the MXene surface. Even after high-temperature calcination, the NTP can still inherit the topological structure. In a recent work, the same compound can also be prepared by $\text{NH}_3\cdot\text{H}_2\text{O}$ treatment and hydrothermal reaction with $\text{NH}_3\text{H}_2\text{PO}_4$ and Na_2CO_3 ,^[39] indicating the universality of this reactive surface reformation strategy.

3.3 Bottom-up growth of heterostructures

In the conventional HF-etched $\text{Ti}_3\text{C}_2\text{T}_m$ MXene, the high proportion of surface exposed Ti atoms and the Ti–OH/F/O binding nature endow it with high surface activity and poor oxygen resistance. Other than the removal methods including consumption of the surface –F, –OH and –O groups and metal atoms, the surface modification also can be realized *via* an additive route. In order to distinguish the bottom-up growth method from the surface reformation ways, the bottom-up growth mentioned here refers to the preparation of heterogeneous phase which does not contain ingredients from MXene skeleton.

Traditionally, the bottom-up growth techniques involve physical or chemical deposition methods and wet chemistry methods. Alshareef et al. recently modified the $\text{Ti}_3\text{C}_2\text{T}_m$ MXene by SnO_2 and HfO_2 *via* a simple atomic layer deposition (ALD) route.^[40] During the ALD preparation, low temperature (150~200 °C) was applied and the thickness of the deposited layer can be adjusted by control the reaction time and deposition cycles.

Since the surface of MXene presents a poor oxygen resistance, their surface reducibility has aroused researchers' interest. Zhang and Peng recently prepared an Ag nanoparticles decorated MXene composite, which they try to confirm the surface reducibility of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene.^[41] They speculated that the reduction of Ag was related to the low valenced Ti. However, though Mahmoud reported a similar work in this year, the origination of the reducibility in $\text{Ti}_3\text{C}_2\text{T}_m$ MXene was still unclear.^[42] Zhang and He deposited bimetallic oxide alloy nanoparticles (PtO_aPdO_b) on the $\text{Ti}_3\text{C}_2\text{T}_m$ MXene surface *via* a solution plasma treatment.^[43] Qiu and Wang tried to stabilize the $\text{Ti}_3\text{C}_2\text{T}_m$ MXene nanosheets *via* a surface carbon nanoplating method.^[44] The carbon nanoplating was carried out by hydrothermal carbonization of glucose on the surface of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene. The hydrothermal carbonization resulted in a thin carbon layer on the surface of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene. In fact, the products could be regarded as the 2D titanium carbide nanosheets. In addition, the surface active moieties could be potentially utilized as nucleation sites for the growth of heterostructures. Also presented by Qiu and Wang, Ni/Fe layered double hydroxide (LDH) was successfully grown on the surface of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene.^[45] The LDH nanoplates were deposited on the $\text{Ti}_3\text{C}_2\text{T}_m$ *via* refluxing the $\text{Ti}_3\text{C}_2\text{T}_m$ with other reagents under an Ar atmosphere. Interestingly, although the LDHs possessed a 2D nature, they tended to grow perpendicularly on $\text{Ti}_3\text{C}_2\text{T}_m$ surface in this work. Further research showed the possibility of direct growth of In_2S_3 , Ni-LDHs and ternary NiFeCo-LDH on $\text{Ti}_3\text{C}_2\text{T}_m$ MXene *via* the hydro/solvothermal process.^[46] It should be noted that the anatase TiO_2 nanoparticles were clearly observed on these mentioned products. In consideration of the reagents, the surface oxidation might occur due to the existence of dissolved air, whereas the TiO_2 observed in Huang's work might be originated from the oxidation by Fe^{3+} rather than the dissolved air.^[46c] The hydrothermal was also available for the direct growth of other secondary phases such as SiO_2 , SnO_2 , MoS_2 , and ZnIn_2S_5 on $\text{Ti}_3\text{C}_2\text{T}_m$ surface.^[47]

In Gao and Ran's work, the $\text{Ti}_3\text{C}_2\text{T}_m$ MXene was cut into nanoparticles and integrated on the surface of CdS *via* a hydrothermal strategy.^[48] It was worth to note that the surface $-\text{F}$ on $\text{Ti}_3\text{C}_2\text{T}_m$ nanoparticles can be replaced by $-\text{O}$ and $-\text{OH}$ groups during hydrothermal condition, meanwhile, the nucleation of CdS nanoparticles on $\text{Ti}_3\text{C}_2\text{T}_m$ nanoparticles also occurred. The heterogeneous nucleation can be ascribed to the adsorption of Cd^{2+} cations on these oxygen-containing groups (**Figure 9**). Further growth and aggregation of CdS nanoparticles led to the cauliflower-structured CdS@ Ti_3C_2 sub-microsphere (SMS), on which the $\text{Ti}_3\text{C}_2\text{T}_m$ nanoparticles were intimately coupled. Due to the more negative Fermi level of CdS than $\text{Ti}_3\text{C}_2\text{T}_m$, the heterogeneous junction of CdS on $\text{Ti}_3\text{C}_2\text{T}_m$ leads to the rapid charge separation and migration from CdS to $\text{Ti}_3\text{C}_2\text{T}_m$, which contributes to the high photocatalytic activity.

Besides the *in-situ* surface functional groups replacement during the reaction process, the substitution of surface functional groups on MXene and further heterostructures growth can also be performed individually. Huang and his co-workers recently reported the substitution of surface $-\text{F}$, $-\text{O}$ and $-\text{OH}$ groups on $\text{Ti}_3\text{C}_2\text{T}_m$ MXene by 1,4-benzenedicarboxylic acid (1,4-BDC) during the HF etching process.^[49] It was inferred that the successful substitution was due to the stronger coordination ability of carboxyl group with Ti than $-\text{OH}$ group. However, the authors did not provide further discussion on this aspect. The 1,4-BDC modified $\text{Ti}_3\text{C}_2\text{T}_m$ MXene then could act as heterogeneous nucleation substrate, forming the metal-organic frameworks (MOFs) hybridized MXene nanosheets through a diffusion-mediated method. Instead of the coordination of Ti atom by the Ti–OOC bonding, the $-\text{COOH}$ and *p*-phenyl- SO_3H groups grafted on multilayered $\text{Ti}_3\text{C}_2\text{T}_m$ (Ti– COOH and Ti–phenyl- SO_3H) were also realized *via* the reaction of $\text{Ti}_3\text{C}_2\text{T}_m$ with chloroacetic acid or sulfanilic acid diazonium salts, respectively.^[50] Interestingly, the surface grafted functional groups

will facilitate the delamination of MXene, which can be further applied for the aggregation process of dyes.^[50a, 51]

In consideration of the crystallization techniques, the bottom-up growth of secondary phase on MXene mainly relied on the increase of oversaturation. Recently, Wu et al. loaded Pt nanoparticles on Nb₂CT_m MXene by an incipient-wetness impregnation (IWI) method.^[52] The repeatedly instilment and desiccation process produced precipitation of Pt precursor on the surface of Nb₂CT_m MXene. Further reduction in 25% H₂/Ar atmosphere resulted in the crystallization of Pt nanoparticles and removal of the surface functional –F, –O and –OH groups on Nb₂CT_m MXene. In addition, the removal of surface functional groups also exposed new terminal Nb sites, leading to the formation of Pt/Nb bimetallic structures through the reactive metal-support interaction. Importantly, these findings emphasize the significant role that the reducibility of MXenes plays during the surface modification. Similarly, nanocomposites such as Co₃O₄@Ti₃C₂T_m,^[53] Co/PVP@Ti₃C₂T_m,^[54] Co/N-CNTs@Ti₃C₂T_m,^[55] Ammonium tetrathiomolybdate (ATM)@Ti₃C₂T_m,^[56] ZIF-67@Ti₃C₂T_m, TiO₂@Ti₃C₂T_m,^[30] and NiCoS@Ti₃C₂T_m can also be obtained through this route.^[57]

Other than the oversaturation, in Wang and the coworkers' work, the modification process was driven by the applied potential. During the reaction, electrochemical exfoliation of Mo₂TiC₂T_m and simultaneous Pt atom immobilization at Mo vacancy sites were realized (Figure 10).^[58] Through the strategy, the bottom-up process was stopped at the nuclear step, configuring a heteroatom modified MXene with a smooth surface in atomic level.

3.4 Surface self-assembly modification

The abovementioned surface modification methods are all based on the chemical reaction approaches, for which complicated operations and fine control of reaction

conditions are required. In addition, during the chemical reaction, surface functional groups are usually consumed and even along with the damage of MXene skeleton.

Recently, Yang et al. have reported a liquid-solid-phase assembly approach, which can easily produce the nanocomposite consisting of black phosphorus quantum dots (BPQDs) and HF-etched $\text{Ti}_3\text{C}_2\text{T}_m$ MXene.^[59] Verified by a series of characterizations and DFT calculation, the authors pointed out that the high affinity of BPQDs for oxygen would result in the strong covalent P–O–Ti interaction, which might contribute to the assembly of BPQDs on the surface of HF-etched $\text{Ti}_3\text{C}_2\text{T}_m$ MXene.

Beyond the strong chemical binding like covalent and ionic bonds, the weak intermolecular interaction or known as secondary binding is also important in synthetic chemistry. Especially, hydrogen bond and Van der Waal's interactions are the major contributors to the self-assembly process in supramolecular chemistry. In 2016, Wang et al. resolved the surface structure of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene by using the atomic pair distribution function.^[25a] It was confirmed that the strong interlayered correlations between two adjacent $\text{Ti}_3\text{C}_2\text{T}_m$ layers were originated from the $\text{F}\cdots\text{H}-\text{O}$ hydrogen bonding, suggesting that the hydrogen bond and Van der Waal's interactions could be the possible driven force for the surface modification of MXene.

Yan et al. have proposed a self-assembly modification method based on surface hydrogen bonding between transition metal LDHs and $\text{Ti}_3\text{C}_2\text{T}_m$ MXene.^[60] The self-assembly process was driven by the interaction between the –OH groups on transition metal LDHs and the –F groups on HF-etched $\text{Ti}_3\text{C}_2\text{T}_m$ MXene nanosheets (Figure 11). In addition, the excess amount of LDHs can cover the surface of $\text{Ti}_3\text{C}_2\text{T}_m$ nanosheets thus prevent the $\text{Ti}_3\text{C}_2\text{T}_m$ nanosheets from stacking together. With this facile and efficient process, the self-assembled nanohybrids were possible to be produced on a large scale. The authors have also demonstrated that these self-assembled nanohybrids could be a versatile precursor towards MXene-based alloy, metal sulfide and

trichalcogenidophosphate heterostructures. Then, the method was applied to the assembly of NiCoAl-LDH and $\text{Ti}_3\text{C}_2\text{T}_m$ MXene by Wang and Yin.^[61] The difference is, the electrostatic attraction was considered to be the driven force for the assembly of negatively charged $\text{Ti}_3\text{C}_2\text{T}_m$ and positively charged NiCoAl-LDH nanosheets.

Xu and Gogotsi also realized the self-assembly of TiO_2 nanorods and SnO_2 nanowires on the surface of HF-etched $\text{Ti}_3\text{C}_2\text{T}_m$ MXene nanosheets.^[62] The authors utilized THF as a poor solvent for MXene to increase its surface energy and aggregation tendency, therefore facilitating the assembly of surfactant-stabilized TiO_2 and SnO_2 nanostructures on MXene surface. Similarly, the nanoflakes of Co_3O_4 and NiCo_2O_4 can be assembled with $\text{Ti}_3\text{C}_2\text{T}_m$ MXene *via* the filtration method.^[63] While the freeze-dried $\text{TiO}_2@ \text{Ti}_3\text{C}_2\text{T}_m$ MXene reported by Chen and Li might belong to IWI products rather than assembly.^[30] Guo, Mai, and Chen recently obtained the iron phthalocyanine (FePc)@ $\text{Ti}_3\text{C}_2\text{T}_m$ MXene hybrids by self-assembled the FePc with $\text{Ti}_3\text{C}_2\text{T}_m$ MXene.^[64] As the FePc molecular possesses a conjugate rigid plane structure, the driven force for the complex assembly may mainly originate from the Van der Waal's interactions, while not ruling out the existence of other secondary bindings.

Recently, a capillary-forced assembling strategy was also proposed to processing $\text{Ti}_3\text{C}_2\text{T}_m$ MXene-based hybrids.^[65] The hierarchical 3D $\text{Ti}_3\text{C}_2\text{T}_m$ architectures with high aggregation resistance were obtained *via* spray drying the aerosol droplet of MXene-containing colloids. During the drying process, the inward capillary force generated by fast evaporation of the solvent led to the isotropic compression and assembly of $\text{Ti}_3\text{C}_2\text{T}_m$ nanosheets. In addition, various electrochemical active materials such as Co_3O_4 , CoP , SnO_2 , MnTiO_3 , Pt , Ag , and S also could be loaded on the $\text{Ti}_3\text{C}_2\text{T}_m$ 3D architectures. Therefore, a series of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene-based hybrids with hierarchical 3D architectures and broad functionalities were obtained.

Obviously, the heterogeneous phases obtained by self-assembly modification method are prefabricated or transformed from the assembled species. In the case of the self-assembly modification, also no additional metal source is required.

4. MXene-based nanocomposites for the electrochemical ECS applications

4.1 MXene-based nanocomposites for electrochemical capacitors

As one of the major energy storage devices, the electrochemical capacitors have got wide attention due to their fast charge/discharge capabilities, long cycle life, and high power densities. Since the first report of MXene species $\text{Ti}_3\text{C}_2\text{T}_m$ in 2011, the intrinsic high electrical conductivity of MXene makes them a promising candidate for the electrochemical capacitors. In previous reports, the single-layer $\text{Ti}_3\text{C}_2\text{T}_m$ reveals a conductivity of around $6.76 \times 10^5 \text{ S m}^{-1}$,^[9] which is comparable to graphene that prepared by the CVD method ($6 \times 10^6 \text{ S m}^{-1}$) and about two orders of magnitude higher than the 1T MoS_2 ($8 \times 10^3 \text{ S m}^{-1}$).^[66] Despite of the surface functional groups and the metal composition, the carrier mobility of Ti_2CO_m ($1.03 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), Sc_2COH_2 ($2.1 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and Hf_2CO_2 ($1.76 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) are all higher than the pristine graphene ($0.3\sim 1.2 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).^[24, 67] What is worth mentioning, the surface functional groups also have a dramatic impact on the capacitive performance: with the modified acid etching method (LiF-HCl), $\text{Ti}_3\text{C}_2\text{T}_m$ MXene with $-\text{O}$ as dominating surface functional group is able to reach a volumetric capacitance more than 900 F cm^{-3} or 245 F g^{-1} in $1 \text{ M H}_2\text{SO}_4$.^[14a] However, although there are numerous works on the electrochemical capacitive of bare MXenes, rare studies are focused on the MXene-based nanocomposites until recently.

The direct surface oxidation induced $\text{TiO}_2@\text{Ti}_2\text{CT}_m$ nanocomposites were evaluated as electrodes for electrochemical capacitor by Alshareef et al. in 2015.^[30b] The post-annealing resulted in surface TiO_2 nanoparticles, which can increase the surface area and the interplanar distance. However, even the $\text{TiO}_2@\text{Ti}_2\text{CT}_m$ nanocomposites

obtained by N₂/H₂ annealing showed the best performance among all the tested samples in KOH electrolyte, the specific capacitance was only 51 F g⁻¹ at 1 A g⁻¹. There is still a big discrepancy with the bare MXene discussed above of 245 F g⁻¹. One of the reasons is that proton is the smallest cation and is in favor of fast surface redox. The other speculation of this inferior capacity is the incomplete etching and delamination of MAX compounds.

In order to control the morphologies of TiO₂ species, Zhu and the coworkers introduced NaOH as an alternative room temperature oxidizer.^[30g] When NaOH was introduced, the generated TiO₂ tended to grow in **nanowires**, while without NaOH, only TiO₂ **nanoparticles** can be obtained. In this work, the TiO₂-**nanowires**@Ti₃C₂T_m showed higher specific capacitance than the TiO₂-**nanoparticles**@Ti₃C₂T_m at a low current density (e.g. 60 and 50 F g⁻¹ at 0.5 A g⁻¹ for TiO₂-**nanowires**@Ti₃C₂T_m and TiO₂-**nanoparticles**@Ti₃C₂T_m, respectively), which could be due to the enlarged surface area of TiO₂-**nanowires**. However, also caused by a larger resistance of TiO₂-**nanowires** than TiO₂-**nanoparticles**, when the current density increased, the TiO₂-**nanowires**@Ti₃C₂T_m presented a deteriorated rate performance.

Besides the TiO₂-based modified nanocomposites, the TiO₂/C-Ti₃C₂T_m-MXene/NiO nanocomposite and NiCoAl-LDH@Ti₃C₂T_m compounds were also synthesized for high-performance electrochemical capacitor applications.^[46b, 61] As for the TiO₂/C-Ti₃C₂T_m-MXene/NiO nanocomposites, the reported equivalent series resistance (*R_s*) and charge-transfer resistance (*R_{ct}*) are 0.960 and 0.383 Ω, respectively, which are lower than the N₂/H₂ annealed sample and close to the TiO₂-**nanoparticles**@Ti₃C₂T_m one.^[30b, 30g] By contrast, the NiCoAl-LDH@Ti₃C₂T_m compounds reported by Wang and Yin showed a similar high conductivity, but much better electrochemical capacitance performance.^[61] After 10000 cycles in 1 M KOH solution at a current density of 2 A g⁻¹, the NiCoAl-LDH@Ti₃C₂T_m exhibited an outstanding specific

capacitance of 589.4 F g^{-1} , which was more than twice as much as the bare $\text{Ti}_3\text{C}_2\text{T}_m$ in H_2SO_4 .^[14a] The authors ascribed this excellent performance to the unique alternatively stacked molecular-level nanosheets, which provided the shortest ion diffusion pathway, highest electron transfer, and the full usage of the active sites.

Obviously, the surface modified MXene-based nanocomposites have great potential in future electrochemical capacitors. But it is important to point out that the modified species are not only required to have a large specific area and high electron conductivity, the sufficient contact between them and MXene substrate and stabilities in certain electrolyte are also critical for the material design.

4.2 MXene-based nanocomposites for metal-ion batteries

As discussed in Section 3, the stabilities, electronic structures and other physicochemical properties of MXene are affected intensively by their surface species and structure. When turned to the LIBs and SIBs, the thermodynamics and kinetics of metal-ion intercalation and diffusion in the interlamellar space of MXene have attracted the great interests. With the combination of the theoretical calculation and experimental studies, there are still various opinions on the understanding of different metal-ion storage mechanism, the optimal metal/MXene ratio and the suitable surface functional groups.^[6, 68] However, with Li as an example, the specific capacity of MXene species is around $200\sim 400 \text{ mAh g}^{-1}$ either from theoretical calculation or experimental studies, which is far less than the state-of-the-art electrode materials.^[69] Furthermore, following the general intercalation mechanism (**Equation 11**, still took Li as the example),^[68d, 70] no observable plateau is found on the galvanostatic charge-discharge profiles of MXenes.

Therefore, the surface modified MXene-based nanocomposites that integrated both advantages of conductive MXene substrate and electrochemical active materials were considered to be good candidates towards LIBs and SIBs with a high specific capacity.

Given the relatively high potential vs. Li and fewer side reactions with electrolytes, although the TiO_2 polymorphs show a theoretical capacity of 330 mA h g^{-1} that slightly lower than the graphite (372 mA h g^{-1}), they have long been studied in LIBs application.^[71] When the MXene surface was modified by TiO_2 , usually an enhancement of the specific capacity and rate capability was observed.^[30h, 30i, 30k, 31-32] The hydrothermally oxidized TiO_2 -nanoparticles@ $\text{Ti}_3\text{C}_2\text{T}_m$ showed a specific capacity of 291 mA h g^{-1} for LIBs at a current density of 100 mA g^{-1} , and 202 mA h g^{-1} at 2000 mA g^{-1} after 2000 cycles.^[30k] Whereas the TiO_2 -nanowires@ $\text{Ti}_3\text{C}_2\text{T}_m$ composite presents only 216 mA h g^{-1} at the same current density after 200 cycles.^[30n] The mixture of TiO_2 nanoparticles (4 nm in diameter) and $\text{Ti}_3\text{C}_2\text{T}_m$ delivered a lithium storage capacity of 132 mA h g^{-1} at the current density of 500 mA g^{-1} after 200 cycles, which was higher than the pure TiO_2 nanoparticles (60 mA g^{-1} under the same condition). With the decrease of M number, the TiO_2 -nanoparticles@ Ti_2CT_m revealed a reversible capacity of 389 mA h g^{-1} for LIBs at a current density of 100 mA g^{-1} after 50 cycles, and 280 mA h g^{-1} at 1 A g^{-1} during the 1000th cycle.^[31] In comparison, the self-assembled TiO_2 nanorods@ $\text{Ti}_3\text{C}_2\text{T}_m$ composite delivered a reversible capacity of 209 mA h g^{-1} for LIBs at a current density of 500 mA g^{-1} during the 200th cycles.^[62] Yu and Yang recently reported a NaOH oxidized $\text{Na}_{0.23}\text{TiO}_2$ nanobelt@ $\text{Ti}_3\text{C}_2\text{T}_m$ composite, in which the $\text{Na}_{0.23}\text{TiO}_2$ nanobelts offered a fast ion transfer path and $\text{Ti}_3\text{C}_2\text{T}_m$ layers ensured the electron transfer.^[32a] As a result, the composite presented a high reversible capacity of 220 mA g^{-1} at a current density of 2 A g^{-1} after 400 cycles and can reach a capacity of 142 mA g^{-1} at 5 A g^{-1} . For the SIBs, the hydrothermally oxidized TiO_2 -nanoparticles@ $\text{Ti}_3\text{C}_2\text{T}_m$ delivered a specific capacity of 156 mA h g^{-1} at

a current density of 50 mA g^{-1} after 500 cycles.^[30k] While the $\text{Na}_{0.23}\text{TiO}_2$ nanobelt@ $\text{Ti}_3\text{C}_2\text{T}_m$ composite can also reveal a superior Na-ion storage performance: 138 mA h g^{-1} at the current density of 100 mA g^{-1} , and 56 mA h g^{-1} at the current density of 3 A g^{-1} during the 4000th cycle, with nearly 100% capacity retention.^[32a] The enhancement of the specific capacity and rate capability were also observed on the surface oxidized Nb_2CT_m and $\text{Nb}_4\text{C}_3\text{T}_m$, which showed reversible capacities of 179 mA h g^{-1} and 208 mA h g^{-1} at the current density of 50 mA g^{-1} , respectively.^[27] Whereas the fresh Nb_2CT_m and $\text{Nb}_4\text{C}_3\text{T}_m$ only showed 92 mA h g^{-1} and about 75 mA h g^{-1} on the same condition, respectively.

In addition, the transformation of TiO_2 to other metal-ion host is also possible to integrate the advantages of both active materials and MXene substrate. Exemplified by $\text{NaTi}_2(\text{PO}_4)_3$ (NTP), the active anode material for Na-ion storage with a theoretical capacity of 133 mA h g^{-1} , which can be easily transformed from TiO_2 species on $\text{Ti}_3\text{C}_2\text{T}_m$ surface. As reported by Zhang, Huang and Zhi,^[38] the *in-situ* formed NTP@ $\text{Ti}_3\text{C}_2\text{T}_m$ composite consisting of NTP cubes and $\text{Ti}_3\text{C}_2\text{T}_m$ nanosheets, presented a dual-mode capacity of capacitance-type and battery-type contribution. Benefiting by the high capacitance contribution, the composite presented an excellent rate performance with 208 mA h g^{-1} at the current density of 0.1 A g^{-1} , and about a 50% capacity retention after the current density increase to 10 A g^{-1} . The composite also delivered an excellent cycling stability, which did not show apparent decay of capacity underwent 10000 cycles at 5 A g^{-1} . But in another work reported by Zhang and Yuan, a similar composite only delivered a capacity of about 120 mA h g^{-1} at a current density of 0.1 A g^{-1} .^[39]

As one of the typical 2D TMD materials, MoS_2 has been widely studied as a host for Li and Na-ion due to its high carrier mobility and a theoretical capacity of 670 mA h g^{-1} based on the conversion mechanism.^[72] When integrated with MXene, the MoS_2 @MXene nanocomposites exhibited a significant improvement in the specific

capacity and rate performance. Wang et al. synthesized a $\text{MoS}_2@\text{Ti}_3\text{C}_2\text{T}_m$ MXene nanocomposite *via* the IWI method.^[56] However, the obtained $\text{Ti}_3\text{C}_2\text{T}_m$ nanosheets were not well isolated with the MoS_2 randomly stacking on $\text{Ti}_3\text{C}_2\text{T}_m$ surface. As a result, the capacity of this nanocomposite was only around $131.6 \text{ mA h g}^{-1}$ at a current density of 1000 mA g^{-1} for 200 cycles. Guo et al. increased the weight content of MoS_2 to 20% *via* the hydrothermal growth process.^[47b] In this work, the MoS_2 nanosheets were observed perpendicularly grown on the $\text{Ti}_3\text{C}_2\text{T}_m$ MXene. With this configuration, a fast and stable Li-ion intercalation kinetics can be achieved, in which the discharge capacity can reach 656 mA h g^{-1} and 153 mA h g^{-1} at the current densities of 50 mA g^{-1} and 3 A g^{-1} , respectively. In contrast, the *in-situ* formed $\text{MoS}_2@\text{Mo}_2\text{TiC}_2\text{T}_m$ heterostructure revealed a discharge capacity of 646 mA h g^{-1} at a current density of 100 mA g^{-1} , and 315 mA h g^{-1} at a current density of 1 A g^{-1} , which has not much improvement.^[37] However, theoretical calculations were carried out in this work to further understand this $\text{MoS}_2@\text{Mo}_2\text{TiC}_2\text{T}_m$ heterostructure for Li-ion storage. The influence of $\text{Mo}_2\text{TiC}_2\text{T}_m$ MXene can be explained from two steps: (1). The oxygen surface at the interface between MoS_2 and $\text{Mo}_2\text{TiC}_2\text{T}_m$ showed electrons accumulation, which led to the stronger Li adsorption on the top of Mo atom in MoS_2 ; (2). The oxygen surface in $\text{Mo}_2\text{TiC}_2\text{O}_2$ also showed stronger adsorption towards Li, Li_2S , and Li_2S_2 , which prevented the polysulfide shuttling and contributed to the enhanced Li-ion storage performance.

Recently, Jiang and Li also prepared the MoS_2 -in- $\text{Ti}_3\text{C}_2\text{T}_m$ hybrids *via* the IWI method (**Figure 12a**).^[73] Surprisingly, the addition of ATM is around 20-times higher than Wang et al, but the MoS_2 nanocrystals can still uniformly grow on the $\text{Ti}_3\text{C}_2\text{T}_m$ surface perpendicularly. What's more, the hybrids revealed a Li-ion storage capacity of 340 mA h g^{-1} at 20 A g^{-1} after 1000 cycles, which is 3-times higher than the bulk MoS_2 (**Figure 12b-c**). And for Na-ion storage, the specific capacity can also reach 310

mA g⁻¹ at 1 A g⁻¹ after 1600 cycles (**Figure 12d**). The authors attributed this outstanding performance to the large interface capacitance from the highly exposed surface and rich edges of the MoS₂ nanocrystals. Recently, the Mg-ion storage performance of the Ti₃C₂T_m-supported MoS₂ has also drawn the investigative attention,^[47c] and the reported capacity was comparable with the recently developed N-CNFs@MoS₂ hybrids.^[74]

Besides, materials that based on the alloying reaction is another important system for the LIBs/SIBs. For instance, tin-based materials represented by SnO₂ has a high theoretical capacity of 1494 mA h g⁻¹ (712 mA h g⁻¹ based on the conversion reaction and 782 mA h g⁻¹ based on the reversible alloying reaction). However, the huge volume change during alloying/dealloying processes usually results in poor cycle stability. Therefore, composite SnO₂ with other conductive porous skeletons could be a promising way towards high capacity Li/Na-ions storage. Wang et al. grew SnO₂ nanoparticles on Ti₃C₂T_m surface via a simple hydrothermal method.^[84] However, the SnO₂-nanoparticles@Ti₃C₂T_m only delivered a reversible specific capacity of 360 mA h g⁻¹ at a current density of 100 mA g⁻¹ after 200 cycles. This low capacity might be due to the poor exfoliated morphology and surface oxidization of MXene nanosheets. Gogotsi and Xu recently reported the SnO₂ nanowires@Ti₃C₂T_m self-assembled composite for Li-ion storage, which presented a high reversible capacity of 720 mA h g⁻¹ at a current density of 100 mA g⁻¹ and 530 mA h g⁻¹ at 1 A g⁻¹ after 500 cycles (**Figure 13**).^[62] In this work, the well-exfoliated MXene nanosheets contributed the critical factor for the high capacity. Alshareef et al. prepared the 10 nm SnO₂ layer modified Ti₃C₂T_m via the ALD technique.^[40] In order to enhance the cycling stability, thin passivation layer of HfO₂ was also deposited on the composite. The HfO₂/SnO₂/Ti₃C₂T_m electrode delivered a specific capacity of 843 mA h g⁻¹ at a current density of 500 mA g⁻¹ after 50 cycles.

Other metal (Ag nanoparticles) or metal oxides (Co_3O_4 , NiCo_2O_4) modified MXene nanocomposites were also prepared for Li-ion storage.^[41, 63] For the Ag nanoparticles@ $\text{Ti}_3\text{C}_2\text{T}_m$ composite, the addition of Ag was confirmed to improve the electronic conductivity of the whole composite. However, the authors did not give further explanation of the dramatically capacity improve by Ag modification.

4.3 MXene-based nanocomposites for electrocatalytic water splitting

Recent studies have shown that the irreversible electrochemically oxidation of $\text{Ti}_3\text{C}_2\text{T}_m$ MXene might present a stable window for electrochemical applications.^[75] However, the bare MXene materials show less active for either HER or OER. Exemplified by the $\text{Ti}_3\text{C}_2\text{T}_m$ and $\text{W}_{1.33}\text{CT}_m$, the fresh $\text{Ti}_3\text{C}_2\text{T}_m$ and $\text{W}_{1.33}\text{CT}_m$ MXene all presents an overpotential (η) of more than 550 mV to reach a current density of 10 mA cm^{-2} .^[60b, 76] Even after annealed in H_2/Ar , the $\text{W}_{1.33}\text{CT}_m$ MXene still needed a η of 320 mV.^[76] This might mainly be attributed to the inapposite surface bonding strength between MXene and catalytic intermedia species. Therefore, the adjustment of the surface electronic structure via introducing a secondary phase was developed for the preparation of MXene-based high active electrocatalyst for water splitting.

Zhao et al. studied the HER activity of N-doped graphene supported by the M_2CT_m ($\text{M} = \text{Ti}, \text{V}, \text{Nb}, \text{or Mo}$) MXene monolayer by first-principles calculations.^[77] Due to the strong electronic coupling between the graphene and MXene monolayer, the graphene band profile and band center were pushed to the Fermi level. For the N-doped graphene/ V_2CT_m heterostructure, the Gibbs free energy of hydrogen adsorption (ΔG_{H}) was estimated to be $-0.04 \sim 0.17 \text{ eV}$, which was competitive to that of Pt (-0.10 eV).

However, in practical HER application, the noble-metal-based electrocatalysts (such as Pt) still represent the best performance. As reported by Zhang and He, the PtO_aPdO_b bimetallic oxide alloy nanoparticles were deposited on $\text{Ti}_3\text{C}_2\text{T}_m$ MXene surface, which

showed enhanced HER performance comparing to pristine $\text{Ti}_3\text{C}_2\text{T}_m$ MXene.^[43] The PtO_aPdO_b nanoparticles@ $\text{Ti}_3\text{C}_2\text{T}_m$ required η of 26.5 and 57 mV to reach a current density of 10 mA cm^{-2} in 0.5 M H_2SO_4 and 1 M KOH solutions, respectively. Nonetheless, even the surface PtO_aPdO_b nanoparticles hybridization presented excellent HER activity, the inevitable usage of noble-metal made the work less creative.

Instead of the heterostructure, recently a heteroatom (Pt) modified $\text{Mo}_2\text{TiC}_2\text{T}_m$ MXene with a smooth surface in atomic level was designed for HER application.^[58] As shown in **Figure 14**, the $\text{Mo}_2\text{TiC}_2\text{T}_m\text{-Pt}_{\text{SA}}$ catalyst presented an extraordinary catalytic ability with a low overpotential of 30 mV to achieve the current density of 10 mA cm^{-2} in 0.5 M H_2SO_4 , which was significantly lower than the pristine $\text{Mo}_2\text{TiC}_2\text{T}_m$ (around 300 mV) and even lower than the commercial Pt/C catalyst. According to the DFT calculation, the Pt single atom occupied at Mo vacancy was able to reduce the charge density around the Pt atom, showing higher occupied states than the bare MXene near the Fermi level. The results indicated an accelerated electron transfer and improved electron environment for HER. The calculated hydrogen adsorption free energy (ΔG_{H^*}) also confirmed the conclusion, in which the ΔG_{H^*} for Pt site on $\text{Mo}_2\text{TiC}_2\text{T}_m\text{-Pt}_{\text{SA}}$ was only about -0.08 eV , even lower than the commercial Pt catalyst (-0.10 eV).

MoS_2 is another wide studied and promising candidate for HER electrocatalyst. It is generally assumed that the active sites in MoS_2 are located on the edge and defect position. Therefore, a common strategy on designing MoS_2 catalysts is to reduce the thickness of MoS_2 nanosheets forming vertical arrays.^[1d, 78] Strongin et al. recently aligned the MoS_2 nanosheets vertically on the $\text{Ti}_3\text{C}_2\text{T}_m$ MXene surface for electrocatalytic HER, which showed a η of 110 mV in 0.5 M H_2SO_4 ($j=10 \text{ mA cm}^{-2}$) and a Tafel slope of 40 mV dec^{-1} .^[47d] However, compared to that of control MoS_2 ($\eta = 160 \text{ mV}$, Tafel 48 mV dec^{-1}), only inconspicuous enhancement was observed. Since the interaction between MoS_2 and $\text{Ti}_3\text{C}_2\text{T}_m$ substrate might

affect the electrocatalytic performance, the in-depth understanding is necessary for future studies. For other secondary phase modified $\text{Ti}_3\text{C}_2\text{T}_m$ as HER electrocatalyst, the $\text{CoP}@3\text{D Ti}_3\text{C}_2\text{T}_m$ delivered a η of 168 mV and a Tafel slope of 58 mV dec^{-1} in 1 M KOH (**Figure 15**),^[65] while the $\text{Ni}_{0.9}\text{Fe}_{0.1}\text{PS}_3@\text{Ti}_3\text{C}_2\text{T}_m$ nanohybrid showed a η of 198 mV and a Tafel slope of 114 mV dec^{-1} in 1 M KOH.^[60b] When the Nb-doping and surface Ni/Co alloying were synergistically introduced into $\text{Ti}_3\text{C}_2\text{T}_m$ MXene, the $\text{Ni}_{0.9}\text{Co}_{0.1}@\text{Nb-doped-Ti}_3\text{C}_2\text{T}_m$ nanohybrids can even present a η of 43.4 mV, which is comparable to the commercial 10% Pt/C catalyst (34.4 mV).^[60c] The difference between these MXene-based nanocomposites indicates that the surface modified secondary phases can have a great impact on the catalytic activity, and there is plenty of room for exploring on the design and synthesis of novel MXene-based electrocatalysts.

When turning to the OER, the most stable catalysts are the metal oxide and hydroxide species. However, as exemplified by the noble-metal-containing PtO_xPdO_y nanoparticles@ $\text{Ti}_3\text{C}_2\text{T}_m$ composites, a η of 310 mV was required in 0.1 M KOH, which was higher than the commercial RuO_2 catalyst ($\eta = 150$ mV).^[43] This result suggests that for the MXene-based OER catalysts, noble-metal-based modified species might not always be the best choice.

Recently, a $\text{FeNi-LDH}@\text{Ti}_3\text{C}_2\text{T}_m$ was reported as a good OER catalyst, delivering a η of 298 mV and a Tafel slope of 43 mV dec^{-1} in 1 M KOH.^[45] The FTIR and UV-vis spectra all suggested the strong electronic interaction between FeNi-LDH and $\text{Ti}_3\text{C}_2\text{T}_m$ MXene. Since the metal oxyhydroxide layers had been demonstrated to be the true active species for OER in many works, the authors introduced a Fe-doped NiOOH monolayer supported by $\text{Ti}_3\text{C}_2\text{O}_2$ structure for DFT calculation to further clarify the coupling between FeNi-LDH and MXene. It was found that in the composite, the electron was extracted from FeNi-LDH to $\text{Ti}_3\text{C}_2\text{T}_m$, which shifted the d-band center of the Ni and Fe atoms to higher energy, leaving the Ni and Fe atoms more positively

charged, and results in less occupied antibonding states between the FeNi-LDH and adsorbed O intermediates. Thereby, the FeNi-LDH@Ti₃C₂T_m composite presented an enhanced OER activity than either FeNi-LDH or bare Ti₃C₂T_m.

While for other species such as metal sulfides, phosphides, and trithiophosphates, the modified Ti₃C₂T_m nanocomposites show an enhanced OER activity than the pristine Ti₃C₂T_m in most situation. For instance, the NiCoS@Ti₃C₂T_m provided a η of 365 mV and a Tafel slope of 58.2 mV dec⁻¹ in 1 M KOH,^[57] while the CoP@3D Ti₃C₂T_m delivered a η of 298 mV and a Tafel slope of 51 mV dec⁻¹ in 1 M KOH.^[65] The Ni_{0.7}Fe_{0.3}PS₃@Ti₃C₂T_m nanohybrid showed an even lower η of 282 mV and a Tafel slope of 36.5 mV dec⁻¹ in 1 M KOH.^[60b] As a comparison, the Co/N-CNTs@Ti₃C₂T_m and CoBDC@Ti₃C₂T_m nanocomposites delivered larger OER η of 411 and >600 mV in the 0.1 M KOH,^[49, 55] suggesting lower activities of the two modified species. However, for the aforementioned species, a thin *in-situ* forming surface oxide layer (or known as metal oxyhydroxide) during the electrocatalytic process also need to be considered. Therefore, during the OER process, the interfacial interaction between modified species and MXene substrate and its impact on performance become even more complicated, which awaits for further investigation.

5. Conclusion

In summary, the adjustable metal/carbide/nitride composition, metallic skeleton, variable surface functional groups and the 2D nature of MXene, all of which make it an ideal material for ECS applications. To further extend its application, better understanding of the MXene materials is necessary. In this review, the attention is mainly focused on the surface chemistry and the hybrids of MXene. Particularly, the relationship between surface functional groups and the respective preparation conditions are summarized under four exfoliation categories. And recent works on the MXene-based hybrids are also summarized according to the four surface modification strategies. It should be pointed out that the surface characters are depended on the preparation method, and will also dramatically affect the final products.

To date, more and more research attention is paid on MXene-based hybrids, and it can be predicted that in the near future, MXene will become another versatile 2D substrate for multifunctional ECS applications. However, as mentioned in the introduction part, the underlying scientific issues for controllable design and synthesis of MXene-based functional materials are still to be addressed. The difficulties lie in the understanding of detailed bonding nature between surface species of bare MXene, the regulation rule between surface metal species and the surface functional groups, the interfacial interaction of MXene and hybrid phases, and so on.

There is no doubt that the hybrid elements need to be carefully selected based on the application requirements. However, not until the interaction between MXene and hybrid phase be clarified theoretically or experimentally before any implementation into practical usage can be done. Therefore, in consideration of the enormous potential of MXene-based hybrids in ECS, more efforts should be paid to the combination of theoretical prediction and experimental study in the future.

Acknowledgments

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No. 51802265), the Fundamental Research Funds for the Central Universities (No.31020195C001), and the China Postdoctoral Science Foundation Grant (No. 2018M631191). The authors also gratefully acknowledge Singapore MOE Tier 2 MOE2017-T2-2-069, MOE AcRF Tier 1 under grant Nos. RG113/15 and 2016-T1-002-065, Singapore EMA project EIRP 12/NRF2015EWT-EIRP002-008, and the NRF of Singapore (No. NRF2016NRF-NRFI001-22).

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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Figure 1. (left) The known MAX phases and elements of the periodic table that react to form them. (right) Atomic structures of M_2AX , M_3AX_2 , and M_4AX_3 phases, with emphasis on the edge-sharing nature of the XM_6 octahedra. Reproduced with permission.^[7] Copyright (2013), Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 2. (a) Schematic describing the synthesis of $\text{Ti}_3\text{C}_2\text{T}_m$ by 50% HF and dispersion in organic solvent X. (b) Dispersions of 50% HF-etched $\text{Ti}_3\text{C}_2\text{T}_m$ in the 12 solvents listed above. Time points of just after sonication (top), 24 h after sonication (middle), and 96 h after sonication (bottom) were used to monitor stability. Reproduced with permission.^[13] Copyright (2017), American Chemical Society.

Figure 3. The reaction between Ti_3AlC_2 and NaOH water solution under different conditions. a) Al (oxide) hydroxides block the Al extraction process under low temperatures. b) Some Al (oxide) hydroxides dissolve in NaOH under high temperatures but low NaOH concentrations. Here, the high water content leads to the oxidation of MXene and yields NTOs. c) According to the Bayer process, high temperatures and high NaOH concentrations will help dissolve the Al (oxide) hydroxides in NaOH.^[19] Copyright (2018), Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 4. Schematic illustration showing the intercalation and delamination process. The organic base, TMAOH, reacts with the Al atomic layer in the gallery to promote key processes, including cleavage of the Ti–Al bonds through Al hydrolysis, modification of the TC unit surface with $\text{Al}(\text{OH})_4^-$, and the intercalation of bulky TMA^+ into the gallery, in a single step. The cleavage of Ti–Al metallic bonds and bulky-ion intercalation facilitates the subsequent disassembly of the precursor layered crystals into their elementary layers.^[20] Copyright (2016), Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 5. Anodic etching of bulk Ti_3AlC_2 in a binary aqueous electrolyte. (a) Schematic of the etching and delamination process; (b) The configuration of electrochemical cell; (c) Optical image of the as-received bulk Ti_3AlC_2 ; (d) The aqueous dispersion of delaminated $\text{Ti}_3\text{C}_2\text{T}_m$ (0.15 mg mL^{-1}); (e) X-ray diffraction patterns of Ti_3AlC_2 , $\text{Ti}_3\text{C}_2\text{T}_m$, and $\text{Ti}_3\text{C}_2\text{T}_m$ film. Reproduced with permission.^[21] Copyright (2018), Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 6. SEM images of MAX and MXene powders obtained by different etching methods. (a) Ti_3AlC_2 powder and multilayered $\text{Ti}_3\text{C}_2\text{T}_m$ powder synthesized with (b) 30 wt %, (c) 10 wt %, and (d) 5 wt % HF. (e) Multilayered $\text{NH}_4\text{-Ti}_3\text{C}_2\text{T}_m$ powder synthesized with NH_4F and HCl and (f) $\text{MILD-Ti}_3\text{C}_2\text{T}_m$ powder etched with 10 M LiF in 9 M HCl . Reproduced with permission.^[10] Copyright (2017), American Chemical Society. (g) Molten salt treated Ti_4AlN_3 at 550 °C for 0.5 h under Ar flow. Reproduced with permission.^[18] Copyright (2016), Royal Society of Chemistry. (h) $\text{Ti}_3\text{C}_2\text{T}_m$ powder obtained using 27.5 m NaOH under 270 °C. Reproduced with permission.^[19] Copyright (2018), Wiley-VCH Verlag GmbH & Co. KGaA. (i) $\text{Ti}_3\text{C}_2\text{T}_m$ powder obtained using aqueous TMAOH. Reproduced with permission.^[20] Copyright (2016), Wiley-VCH Verlag GmbH & Co. KGaA. (j) The electrochemical etched $\text{Ti}_3\text{C}_2\text{T}_m$ powder. Reproduced with permission.^[21] Copyright (2018), Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 7. (a) Scanning electron microscopy (SEM) images of oxidized $\text{Nb}_4\text{C}_3\text{T}_m$ for 0.5 h. (b) Schematic of hierarchical $\text{Nb}_4\text{C}_3\text{T}_m$ structure before and after oxidation. Reproduced with permission.^[27] Copyright (2016), Wiley-VCH Verlag GmbH & Co. KGaA. (c) SEM image of $\text{Ti}_3\text{C}_2\text{T}_m$ after oxidation. Top left inset is another SEM image at a different location for the same sample. Reproduced with permission.^[26] Copyright (2016), Royal Society of Chemistry. (d) Schematic of the oxidation mechanisms under two oxidation regimes. Reproduced with permission.^[28] Copyright (2014), Royal Society of Chemistry.

Figure 8. (a) XRD patterns of Mo₂TiAlC₂ before (red) and after (green) HF treatment and after delamination (blue). (b) Schematics of Mo₂TiAlC₂ to Mo₂TiC₂T_m transformations; red, green, blue, and black circles represent Mo, Ti, Al, and C atoms, respectively. (c) HRSTEM of Mo₂TiAlC₂ and Mo₂TiC₂T_m, respectively. Atoms are shown with the same colors as (b). The lower magnification TEM image of Mo₂TiC₂T_m in (c, right) showing the layered structure throughout the sample. Reproduced with permission.^[35a] Copyright (2015), American Chemical Society. (d) Schematic illustration of the preparation of MoS₂@MXene hybrids. (e) Cross-sectional TEM images of MoS₂-on-MXene heterostructures: MoS₂@Mo₂TiC₂T_m-500 (left panel) and MoS₂@Mo₂TiC₂T_m-700 (right panel). Reproduced with permission.^[37] Copyright (2018), Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 9. Synthesis procedure of CdS/Ti₃C₂T_m cauliflower-structured submicrosphere (SMS). Reproduced with permission.^[48] Copyright (2017), Springer Nature Publishing AG.

Figure 10. Schematic of the electrochemical exfoliation process of MXene with immobilized single Pt atoms.^[58] Copyright (2018), Springer Nature Publishing AG. KGaA.

Figure 11. The HF etching and exfoliation of $\text{Ti}_3\text{C}_2\text{T}_m$ Nanosheets, and the schematic illustration of transition metal LDHs assemble on $\text{Ti}_3\text{C}_2\text{T}_m$ surface. The enlarged view indicating the hydrogen bond interaction between $-\text{F}$ groups on $\text{Ti}_3\text{C}_2\text{T}_m$ and $-\text{OH}$ groups from transition metal LDH.^[60b] Copyright (2018), Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 12. (a) Schematic illustration for the fabrication of the MoS₂-in-Ti₃C₂T_m hybrids. (b) The capacities retention of the MoS₂-in-Ti₃C₂T_m, the MoS₂-out-Ti₃C₂T_m, the MoS₂ bulks, and the Ti₃C₂T_m for LIBs at 0.1 to 20 A g⁻¹. (c) The cycling performance of the MoS₂-in-Ti₃C₂T_m hybrids for LIBs at 500 and 5000 mA g⁻¹ for 1000 cycles. (d) The capacities retention of the MoS₂-in-Ti₃C₂T_m, the MoS₂-out-Ti₃C₂T_m, and the Ti₃C₂T_m for SIBs at 0.05 to 3.0 A g⁻¹. Reproduced with permission.^[73] Copyright (2018), Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 13. (a) Schematic diagram for the simple self-assembly of TMO nanostructures, including TiO₂ Nanorods and SnO₂ Nanowires, on MXene Nanosheets in THF through van der Waals interactions. (b) Low-magnification TEM of SnO₂@MXene heterostructure. (c) Rate capabilities of SnO₂ Nanowires, MXene Nanosheets, and SnO₂@MXene heterostructure. Reproduced with permission.^[62] Copyright (2018), Wiley-VCH Verlag GmbH & Co. KGaA.

Figure 14. (a) HER polarization curves of carbon paper (CP), $\text{Mo}_2\text{TiC}_2\text{T}_m$, $\text{Mo}_2\text{TiC}_2\text{T}_m\text{-V}_{\text{Mo}}$, $\text{Mo}_2\text{TiC}_2\text{T}_m\text{-Pt}_{\text{SA}}$ and Pt/C (40%), acquired using graphite rod as the counter electrode in 0.5 M H_2SO_4 solution. (b) Corresponding Tafel slope derived from (a). (c) DFT calculation results. (c-d), Top view of the slab models used to describe $\text{Mo}_2\text{TiC}_2\text{O}_2$ (c) and $\text{Mo}_2\text{TiC}_2\text{O}_2\text{-Pt}_{\text{SA}}$ (d). Atoms in blue, purple, green, brown and red represent Ti, Mo, Pt, C and O, respectively. (e) Calculated charge density distribution differences between $\text{Mo}_2\text{TiC}_2\text{O}_2$ and $\text{Mo}_2\text{TiC}_2\text{O}_2\text{-Pt}_{\text{SA}}$. The isosurface value is $0.01 \text{ e \AA}^{-3}$ to better plot the differences. (f) Calculated PDOS of $\text{Mo}_2\text{TiC}_2\text{O}_2$ and $\text{Mo}_2\text{TiC}_2\text{O}_2\text{-Pt}_{\text{SA}}$, with aligned Fermi level. (g) Calculated free energy profiles of HER at the equilibrium potential for $\text{Mo}_2\text{TiC}_2\text{O}_2$, $\text{Mo}_2\text{TiC}_2\text{O}_2\text{-Pt}_{\text{SA}}$ and Pt/C. Reproduced with permission.^[58] Copyright (2018), Springer Nature Publishing AG.

Figure 15. (a) Capillary-forced assembly of MXene to 3D architecture and related hybrid systems by spray drying the aerosol droplet of MXene-containing colloids. (b) SEM images of CoP@3D $\text{Ti}_3\text{C}_2\text{T}_m$ -MXene architecture. (c) TEM image revealing the uniform dispersion of ultrafine CoP Nanoparticles on the surface of 3D MXene architecture. (d) HRTEM image of a CoP NP in CoP@3D $\text{Ti}_3\text{C}_2\text{T}_m$ -MXene architecture. (e) The iR -corrected polarization curves of CoP@3D $\text{Ti}_3\text{C}_2\text{T}_m$ -MXene, CoP@ $\text{Ti}_3\text{C}_2\text{T}_m$ -MXene, CoP, and Pt/C catalysts for HER at a scan rate of 10 mV s^{-1} in 1 M KOH at 1600 rpm. Reproduced with permission.^[65] Copyright (2018), American Chemical Society.

Table 1. Comparison of the four exfoliation techniques and the resulting surface functional groups.

Techniques	Reagents	Applicable	Surface Functional groups
HF etching	HF	Nearly all $M_nX_{n-1}T_m$	Dominated on fresh surface: -F, -OH Increase over time: -O
Modified acid etching	LiF/NaF/KF/ FeF_3 + HCl	$Ti_3C_2T_m$	-F, -OH, -O, -Cl
	NH_4HF_2	$Ti_3C_2T_m$	-F, -OH, -O
Molten fluoride salt etching	LiF + NaF + KF	$Ti_4N_3T_m$	-F, -O, -OH
Fluoride-free etching	NaOH	$Ti_3C_2T_m$	-OH, -O
	TMAOH	$Ti_3C_2T_m$	-OH, $-Al(OH)_4$
	NH_4Cl + TMAOH	$Ti_3C_2T_m$	-OH, -O

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The table of contents:

Recently, the MXenes have gained increasing attention in the fields of energy conversion and storage (ECS). Meanwhile, the unique surface chemistry of MXenes endows them great potential in the construction of 2D based nanocomposites. To this end, the present work try to offer a comprehensive summary of the surface modified MXene-based nanocomposites for ECS applications.

Keyword: MXene, nanocomposites, surface chemistry, electrochemical, energy conversion and storage

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Surface modified MXene-based nanocomposites for electrochemical energy conversion and storage

ToC figure ((Please choose one size: 55 mm broad $\times$ 50 mm high **or** 110 mm broad $\times$ 20 mm high. Please do not use any other dimensions))