Zhang, Chuanfang (John); Cui, Linfan; Abdolhosseinzadeh, Sina; Heier, Jakob

Two-dimensional MXenes for lithium-sulfur batteries

Published in:
InfoMat

DOI:
10.1002/inf2.12080

Published: 01/07/2020

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
CC BY

Please cite the original version:
Zhang, C., Cui, L., Abdolhosseinzadeh, S., & Heier, J. (2020). Two-dimensional MXenes for lithium-sulfur batteries. InfoMat, 2(4), 613-638. https://doi.org/10.1002/inf2.12080

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
Two-dimensional MXenes for lithium-sulfur batteries

Chuanfang (John) Zhang | Linfan Cui | Sina Abdolhosseinzadeh | Jakob Heier

1Laboratory for Functional Polymers, Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland
2Department of Electronics and Nanoengineering, Aalto University, Aalto, Finland
3Institute of Materials Science and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

Correspondence
Chuanfang (John) Zhang, Laboratory for Functional Polymers, Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland.
Email: chuanfang.zhang@empa.ch

Abstract
Rechargeable lithium-sulfur (Li-S) batteries have attracted significant research attention due to their high capacity and energy density. However, their commercial applications are still hindered by challenges such as the shuttle effect of soluble lithium sulfide species, the insulating nature of sulfur, and the fast capacity decay of the electrodes. Various efforts are devoted to address these problems through questing more conductive hosts with abundant polysulfide chemisorption sites, as well as modifying the separators to physically/chemically retard the polysulfides migration. Two dimensional transition metal carbides, carbonitrides and nitrides, so-called MXenes, are ideal for confining the polysulfides shuttling effects due to their high conductivity, layered structure as well as rich surface terminations. As such, MXenes have thus been widely studied in Li-S batteries, focusing on the conductive sulfur hosts, polysulfides interfaces, and separators. Therefore, in this review, we summarize the significant progresses regarding the design of multifunctional MXene-based Li-S batteries and discuss the solutions for improving electrochemical performances in detail. In addition, challenges and perspectives of MXenes for Li-S batteries are also outlined.

KEYWORDS
flexible electronics, Li-S battery, MXene, polysulfides, shuttling, two dimensional materials

1 | INTRODUCTION

The great demands for portable electronics and the emergence of electric vehicles have significantly stimulated the developments of energy-storage devices.1-4 Comparing to Li-ion batteries and other metal-sulfur batteries, lithium-sulfur (Li-S) battery is considered as one of the promising electrical energy storage systems owing to the natural abundance of sulfur, high theoretical specific capacity (1675 mA h g⁻¹) and energy density (~2670 W h kg⁻¹),5-8 as shown in Figure 1A. However, the soluble long chain lithium polysulfides (Li₂Sn, 4 ≤ n ≤ 8) produced in the discharge process disassociate into electrolyte and shuttle between cathode and anode (Figure 1B), typically known as the shuttling effect.6,7 This effect results in active material loss, causing rapid capacity decay, low cyclic performance and Coulombic efficiency. The Li₂Sn also reacts with the Li anode and forms an insulating layer, leading to serious polarization. In the meanwhile, the insulating nature of sulfur greatly lowers down the redox reaction
kinetics, thus reducing the rate capabilities and sulfur utilization. All of these abovementioned issues urgently require effective conductive hosts or separators to suppress the polysulfide migration process. In general, methods can be classified as physically confinements and chemically adsorption of the Li$_2$Sn.$^7$ For instance, carbon materials with high specific surface area and rich porosity provide effective physical confinements of Li$_2$Sn, leading to dramatically improved long-term cycling.$^9$-12 A conductive polymer matrix can also help to encapsulate sulfur in the cathode and achieve good capacity and cycling performance.$^{12,13}$ Graphene oxides with abundant surface functional groups, as well as the hydrophilic metal oxides on the other hand, trap the polysulfide diffusion through a chemical adsorption mechanism.$^{14,15}$ Since the discovery of Ti$_3$C$_2$Tx in 2011,$^{16}$ transition metal carbides and nitrides, so-called MXenes, have attracted extensive attention and exhibited excellent performances in energy, catalysis, optoelectronics, biomedical, environment, sensors, electromagnetic fields and so on (Figure 1C).$^{17}$ MXenes with formula M$_{n+1}$X$_n$Tx ($n = 1$-$3$) are usually derived from the parental MAX phases by selectively etching the A layer (where M represents a transition metal, A represents the group 13 or 14 elements in the periodic table and X represents carbon or nitrogen, T$_x$ stands for the surface terminations).$^{15,16,18,19}$ Thus, the obtained MXenes possess a unique layered structure. After etching, the surface of MXenes is terminated with various functional groups such as hydroxyl (—OH), oxygen (—O), chlorine (—Cl) and fluorine (—F), leading to a good hydrophilicity in MXenes which is in sharp contrast with hydrophobic graphene nanosheets.$^{18,20}$ Beyond the excellent electronic conductivity, MXenes have also exhibited impressive performances in many areas, especially in energy storage. Thus, the past few years have witnessed the rise of MXenes, best evidenced by the ever-increasing number of publications on this new class of two-dimensional (2D) wonder materials (Figure 1D). Particular attention should be paid to the application of MXenes in Li-S batteries. The surface groups on MXenes (especially hydroxyl groups) are highly affinitive to polysulfides and can spontaneously attract them without additional surface modifications. Moreover, the highly conductive core (Ti—C—Ti bonds) can greatly facilitate the charge transfer kinetics, allowing great enhancement of sulfur utilization and cell rate handling as a result.$^{22,23}$ Said otherwise, using MXenes as sulfur conductive host and/or modified

![Figure 1](image-url)

**FIGURE 1**  A, Comparison of energy densities of various metal-sulfur batteries. B, Schematic illustration of working mechanism of Li-S batteries. C, Explored applications of MXenes. Images are from the internet. D, The number of publications on MXene and E, MXene-based Li-S batteries (Source: Web of Science)
separator can dramatically boost the long-term cycling and capacity of the assembled Li-S cells.

As a matter of fact, publications on the MXenes for Li-S batteries also increase apparently, suggesting this field gets more and more research attention (Figure 1E). As such, it is important to summarize the significant progresses covering the topics like conductive hosts, high sulfur loading, modified separators, as well as the theoretical simulations and calculations, and so forth. Herein, we review the recent progresses of MXenes for Li-S batteries. We especially focus on the structural design of the MXene-S electrode, as well as solutions for boosting the electrode/device performances. We also revisit the theoretical calculations based on density-functional theories (DFT) to simulate the interactions between MXenes and polysulfides. Finally, we present the challenge of MXenes for the Li-S batteries and outlook the future possible solutions to these challenges.

2 | MXENE: SYNTHESIS AND PROPERTIES

2.1 | Synthesis of MXenes

As the first discovered MXene, Ti$_3$C$_2$Tx is produced by a wet-chemical etching process from MAX phase (Figure 2A).\textsuperscript{16,18,19,21,24,25} In this method, the etchant, typically aqueous hydrofluoric acid (HF), selectively etches away the A atomic layer from the MAX precursor as the M-A bond is more chemically active than the M-X bond. After etching, the solids are repeatedly washed with deionized water followed by centrifugation till the pH of the supernatant reaches 4-6, and multilayered (m-) Ti$_3$C$_2$Tx MXene is obtained. Similarly, by adjusting the HF etching conditions such as HF concentration, etching time and temperature, other types of MXenes, such as Ti$_2$CTx, Ti$_3$CNTx, Nb$_2$CTx and V$_2$CTx have also been synthesized.\textsuperscript{16,26,27}

In order to obtain individual 2D MXene nanosheets, delamination of the m-Ti$_3$C$_2$Tx is necessary. This can be done by intercalating polar organic molecules such as hydrazine, urea, dimethyl sulfoxide (DMSO) and isopropylamine into the m-Ti$_3$C$_2$Tx, followed by sonication to delaminate the sheets.\textsuperscript{28,29} In order to increase the yield of delaminated nanosheets, organic intercalants with large cation size, such as tetrabutylammonium hydroxide (TBAOH), choline hydroxide or n-butylamine, are used to give large amounts of delaminated nanosheet solutions, as shown in Figure 2B,C.\textsuperscript{30} After mechanical vibration or sonication in water, single or few-layer MXene solutions can be collected.

Unlike the HF acid etching, using lithium fluoride (LiF) and hydrochloric acid (HCl) mixture to produce HF in-situ can effectively etch away the A layer and result in Ti$_3$C$_2$Tx MXene with Li ion (Li$^+$) pre-intercalated in the layered solids. Consequently, by repeated ion exchanging (through DI-water washing) and manual shaking/sonication, delaminated nanosheets, with predominantly mono-layered flakes enriched in the solution, can be effectively

![Figure 2](image)

**Figure 2** A, Schematic illustration of MXene sheet synthesis process. Reproduced with permission.\textsuperscript{31} Copyright 2019, The Royal Society of Chemistry. B, Schematic of MXene delamination process via isopropylamine intercalation. Reproduced with permission.\textsuperscript{29} Copyright 2018, Wiley-VCH. C, Schematic for MXene delamination process by reacting MXenes with an organic base. Reproduced with permission.\textsuperscript{30} Copyright 2015, The Royal Society of Chemistry
Compared to the nanosheets produced via direct HF etching, the flakes prepared from the LiF-HCl route possess a cleaner surface with much less defects, and thus termed as minimally intensive layer delamination (MILD) route. Similarly, using molten salts, that is, KF, LiF, NaF is another route to effectively etch away the A layer and produce good quality MXenes.

Nevertheless, the abovementioned etching-delamination routes produce Ti$_3$C$_2$Tx nanosheet solutions at a low yield, typically <20%. To boost the yield of nanosheets, other novel methods such as electro-chemical etching and microwave-assisted delamination strategies have been developed. During the electro-chemical etching process, Ti$_3$AlC$_2$ can be etched in the Cl$^-$ containing electrolyte under a low potential as Cl$^-$ has a strong binding capability with Al. The microwave-assisted delamination strategy utilizes an agitation-intercalation-exfoliation process with organic solvent/ionic liquid media to break the interactions among the Ti$_3$C$_2$Tx nanosheets.

In particular, through employing a hydrothermal-assisted interaction strategy, the yield of Ti$_3$C$_2$Tx sheets can achieve 74% (Figure 3A). In this process, the intercalation process is facilitated under the hydrothermal conditions, thus promoting the delamination yield. On the other side, as the HF acid is highly corrosive, other safer strategies, such as alkali-etching method has also been emerged to obtain Ti$_3$C$_2$Tx (Figure 3B).

While the wet-chemistry method is able to efficiently synthesize carbide MXenes, it is quite challenging to prepare nitride MXenes using this method. Instead, nitride MXenes can be fabricated by high temperature etching of the MAX phase. A typical example is the synthesis of Ti$_4$N$_3$Tx, which was obtained by etching the Ti$_4$AlN$_3$ MAX phase in a molten fluoride salt mixture under 550°C in argon atmosphere (Figure 3C). By ammonization of the carbide MXene (ie, Mo$_2$CTx and V$_2$CTx) at 600°C, corresponding Mo$_2$NTx and V$_2$NTx (mixed with cubic VN) MXenes can be effectively prepared. Nevertheless, the production yield of nitride MXenes is low based on the ammonization of carbide MXene route. Said otherwise, more efficient routes to the nitride MXene synthesis are greatly in need to continuously expand the MXene family.

In addition, carbides with double or triple A layers have also been selected as precursors to synthesize MXenes. Mo$_2$CTx can be prepared from Mo$_2$Ga$_2$C by etching two A-element layers while Zr$_3$C$_2$Tx is synthesized from Zr$_3$Al$_3$C$_5$ by etching Al$_3$C$_3$. On the other hand, molybdenum carbide with large lateral size and less defects can also be prepared through a chemical vapor deposition (CVD) method. As shown in Figure 3D, ultra-thin α-Mo$_2$C has been produced through CVD on a copper foil which was placed on a molybdenum foil. During the
reaction, the Mo atoms diffuse to the top Cu surface and combine with the decomposed carbon atoms, forming \( \alpha \)-Mo\(_2\)C nuclei which grow continuously along the epitaxial direction. As a result, the \( \alpha \)-Mo\(_2\)C flakes are of high quality, allowing the investigation of their intrinsic properties such as electrical, mechanical and optoelectronic properties.41,45

2.2 | Properties of MXenes

MXene crystals possess a hexagonal close-packed stacking structure where M atoms are closely packed and X atoms fill the octahedral interstitial sites.21 The MXene family usually has three packing configurations, that is, M\(_2\)X, M\(_3\)X\(_2\) and M\(_4\)X\(_3\) with the corresponding single sheets of 3, 5, 7 layers, rendering the great diversity of the MXene family (Figure 4A). Recently, Anasori et al reported the ordered double transition metal MXenes, where one (or two) transition metal layer(s) is (are) sandwiched between the second transition metal layers (as shown in Figure 4B).25 Such an atomic structure is totally different from the solid-state solutions MXenes, where the different metal atoms are distributed randomly. The discovery of the ordered double transition metal MXenes have greatly enriched the MXene family, opening up new possibilities in tuning the band gap, work function, and optoelectronic properties of MXenes.

Typically, MXenes synthesized via HF or HF-containing solution possess abundant hydrophilic surface functional groups (—OH, —O, and —F). In order to modify the surface groups, especially to produce MXenes with reduced surface functionalities, annealing MXenes under argon (Ar) has been proved to be quite effective.46 For example, by annealing the Ti\(_3\)C\(_2\)Tx MXene in Ar at 500°C, most of the surface groups can be removed. It is quite challenging to produce MXenes with one specific surface group. Nevertheless, many studies assume that MXene possess only one type of surface groups, which greatly simplify the simulation process. For instance, one can predict the locations of the hydroxyl groups by assuming Ti\(_3\)C\(_2\)Tx MXene is terminated with —OH groups only. As shown in Figure 4C, three possible configurations are predicted to exist according to the principle of energetically favorable termination orientations.47 In configuration X, —OH groups are positioned above the hallow sites between the neighboring C atoms. In configuration Y, —OH groups are located above the C atoms toward both sides of the Ti\(_3\)C\(_2\) layers. Configuration Z is defined as one side of the Ti\(_3\)C\(_2\) is in configuration X and the other side is in configuration Y. Other possible configurations are unstable and tend to transform into these three configurations.48

**FIGURE 4** A, Structure of MAX phases and the corresponding MXenes. Reproduced with permission.18 Copyright 2018, Wiley-VCH. B, Schematic of MXene structures with more than one M atom. Reproduced with permission.25 Copyright 2015, American Chemical Society. C, Optimized atomic structures of (I) free-standing Ti\(_3\)C\(_2\) layer and (II-IV) its hydroxylated forms, Ti\(_3\)C\(_2\)(OH)\(_2\). The first row is the side view, the second row is the top view. Reproduced with permission.47 Copyright 2012, Elsevier
configuration X is found to have the lowest energy, suggesting the highest structure stability. In other words, the –OH groups are more likely to arrange in configuration X in Ti$_3$C$_2$Tx MXene.

In practice, MXene is terminated with mixed types of groups (OH, O, and F terminations), rendering the DFT calculations much more complex. Furthermore, water molecules are typically trapped among the layers, which for sure have a great influence on the stability, conductivity and capacitance in the energy storage device. In other words, understanding the surface groups (including distribution and arrangement of surface terminations) as well as the trapped water (and the water removal if needed) are useful for both theoretical studies and the resultant MXene properties. This is especially true for some applications that require MXenes with specific properties, which are typically obtained by engineering the surface functionalities and interlayer chemistries.

Unlike 2D graphene material, delaminated MXenes with single or few layer flakes are hydrophilic, and thus can form a stable dispersion in aqueous media without the addition of surfactant. In addition, due to the match of the Hansen solubility parameters, MXene nanosheets can be dispersed in a range of organic solvents, forming stable MXene organic solutions without the necessity of a binary solvent. We note this is a great advantage over graphene, allowing facile solution processing of MXene dispersions into any items or composites, and opening up great opportunities in thin-film coating, inkjet/extrusion printing, and many other applications. When dispersed in aqueous media, MXene nanosheets are vulnerable to oxidation by dissolved oxygen and water, highlighting the proper storage of the delaminated nanosheets solution. Zhang et al revealed that by isolating the solution from the dissolved oxygen through Ar-filling hematric bottles, which were placed in a low-temperature environment, the shelf-life of Ti$_3$C$_2$Tx and Ti$_3$CTx aqueous solutions were greatly extended. Recently, Mochalin et al suggested that water is more pronounced in oxidizing MXene nanosheets; the solution's stability was much improved when dispersing the nanosheets in isopropanol. Actually, by dispersing Ti$_3$C$_2$Tx nanosheets in organic solvents like N-Methyl-2-Pyrrolidone (NMP), dimethyl sulfoxide (DMSO), dimethylformamid (DMF), the dispersions are stable over 12 months, showcasing the long-term stability.

According to DFT calculations, the electronic properties of Ti$_3$C$_2$Tx layers are surface functionalities dependent. The theoretical calculations shows that bare Ti$_3$C$_2$ is a metallic conductor, which switches to a semiconductor as the surface is terminated by –OH or –F (bandgaps are 0.05 eV and 0.1 eV for Ti$_3$C$_2$(OH)$_2$ and Ti$_3$C$_2$F$_2$, respectively), as shown in Figure 5A. Some

**FIGURE 5** A. Calculated band structure of single-layer MXene with –OH and –F surface terminations and no termination (Ti$_3$C$_2$). Reproduced with permission. Copyright 2011, Wiley-VCH. B. Band structures near the Fermi level for (I) X-Ti$_3$C$_2$F$_2$, (II) Y-Ti$_3$C$_2$F$_2$, (III) Z-Ti$_3$C$_2$F$_2$, (IV) X-Ti$_3$C$_2$(OH)$_2$, (V) Y-Ti$_3$C$_2$(OH)$_2$, (VI) Z-Ti$_3$C$_2$(OH)$_2$. Reproduced with permission. Copyright 2012, American Chemical Society. C. Optical images of Ti$_3$C$_2$Tx films on glass (I) and polyester (II) substrates, respectively (scale bars are 1 cm). (III) UV-vis spectra of Ti$_3$C$_2$Tx films with different thicknesses. Reproduced with permission. Copyright 2016, Wiley-VCH.
O-terminated MXenes are also predicted to be semiconducting. Thus, the electronic properties of MXenes such as the bandgaps can be tuned by varying surface functional groups. The locations of surface functionalities also influence the band gap structures of MXenes. For instance, Ti_3C_2F_2 and Ti_3C_2(OH)_2 in the configuration Y (Figure 4C) are predicted to be metallic. In contrast, Ti_3C_2F_2 and Ti_3C_2(OH)_2 in configuration X and Z are shown to be semiconductors with narrow bandgaps (X-Ti_3C_2F_2:0.04 eV, Z-Ti_3C_2F_2:0.03 eV, X-Ti_3C_2(OH)_2:0.05 eV, Z-Ti_3C_2(OH)_2:0.07 eV) (Figure 5B). There are also some MXene phases with heavier transition metals such as chromium, molybdenum and tungsten that are predicted to be topological insulators. MXene thin films are predicted to possess enhanced mechanical properties compared to their parental MAX phases. Moreover, M_2X MXenes are predicted to be stiffer and stronger than their M_3X_2 and M_4X_3 counterparts based on the DFT and molecular dynamics results. The elastic modulus of single-layer Ti_3C_2Tx exhibits an electronic conductivity up to 6760 S cm\(^{-1}\) while MILD-derived Ti_3C_2Tx thin films possess values up to 10 000 S cm\(^{-1}\). The electrical conductivity of Ti_3C_2Tx heavily depends on the preparation method. The sonicated, single-layer Ti_3C_2(OH)_2:0.05 eV, Z-Ti_3C_2(OH)_2:0.07 eV) (Figure 5B). Thanks to the strong M-X bonds, MXenes are predicted to possess enhanced mechanical properties compared to their parental MAX phases. Moreover, M_2X MXenes are predicted to be stiffer and stronger than their M_3X_2 and M_4X_3 counterparts based on the DFT and molecular dynamics results. The elastic modulus of single-layer Ti_3C_2Tx sheet terminated with -OH is calculated to be 3.1 | INTERACTIONS BETWEEN MXENES AND POLYSULFIDES

3.1 | Polysulfide anchoring behavior of MXenes

Considering the notorious polysulfide shuffling effect, an ideal sulfur host should be conductive and possesses a strong affinity to Li_2S_n so as to suppress the migration kinetics of the latter. 2D MXenes, especially titanium carbide MXenes, have demonstrated high electronic conductivity and strong polysulfide adsorption capabilities, thus have been received substantial research attention for Li-S application.

Nazar’s group reported Ti_2CT_x MXene as sulfur host for the first time to entrap polysulfides and achieved good capacity retention. Interaction and chemisorption mechanism of polysulfides with the active species (mainly Ti sites and OH surface groups) are postulated. As shown in Figure 6A, polysulfides are firstly chemisorbed on the MXene surface and undergo redox reactions with the OH terminations, forming thiosulfate groups. Those surface thiosulfate groups further react with the soluble polysulfides to form polythionates and eventually insoluble “lower” polysulfides. Such a polysulfide entrapping mechanism is similar to that of MnO_2 and graphene oxide. The cleavage of surface OH groups exposes Ti atoms with unoccupied orbitals, which greatly facilitate the chemisorption of electronnegative polysulfide ions and form Ti-S bonds with high binding energy via Lewis acid-base interaction. Thus, Ti-based MXenes with dual-mode entrapping behaviors have exhibited excellent performance in suppressing the polysulfides dissociation and migration back to the electrolyte, resulting in MXene-based Li-S batteries with stable cycling life.

In addition, an ideal host should possess a relatively mild adsorption strength with Li_2S_n intermediates so that the conversion kinetics to the low-order Li_2S_n is facilitated without apparent Li_2S_n intermediate dissolution. Otherwise, if the adsorption strength is too strong, the high-order Li_2S_n tends to decompose and then S atoms are easy to diffuse into electrolyte.

Taking Ti_2C as an example, when S atoms disperse on the surface of bare Ti_2C, the distance between S atoms and Ti atoms is short (i.e., close contact), thus the S-Ti bonds are so strong that the bare Ti atomic layer can further “grab” sulfur atoms by breaking the Li-S bonds in Li_2S_n and form Ti-S bonds. Once the Ti-S bonds are formed, sulfur atoms are unable to dissociate from the Ti-S bonds and form Li_2S_n again by combining with Li\(^+\) (Figure 6B). Although the interaction between Ti and S becomes weaker if the surface is terminated with functional groups, the surface functionalized groups also can interact with Li_2S_n intermediates and may help to strike a balance between the interaction strength and structural intactness of the Li_2S_n.

Most theoretical studies on Ti-based MXenes mainly focus on the interaction behavior of Li_2S_n and Ti_2CT_x with various surface functional groups. DFT calculations indicate that the OH-terminated Ti_2C (Ti_2C(OH)_2) distort the long chain Li_2S_n. By contrast, the Li_2S_n molecular configuration is maintained when it is absorbed on the surface of Ti_2CO_2 and Ti_2CF_2, indicating...
that OH-terminated Ti$_2$C possesses stronger attractions for Li$_2$Sn compared to that of Ti$_2$CO$_2$ and Ti$_2$CF$_2$. Actually, O and F functionalized Ti$_2$C MXenes show different suppressing mechanisms. On the O-functionalized surface, Li$_2$Sn tends to be oxidized to neutral S which exhibits slight solubility. For the F-functionalized Ti$_2$C, it exhibits strong interaction with Li$_2$Sn intermediates. Figure 6C(I) shows the binding energy of Li$_2$Sn on various functionalized Ti$_2$C MXene. The differences of the binding energy could be originated from the Coulomb interactions between Li$_2$Sn and MXenes (Figure 6CII). Bare MXenes possess strong Coulombic interactions and thus the induced Ti-S interactions are strong. When the Ti$_2$C surface is terminated with functional groups, Ti-S interactions will be reduced by the repulsive force from negatively charged atoms (O/F to S). Li atoms also play a role in the Li$_2$Sn binding. Although the interaction between Li and O/F could enhance the binding of Li$_2$Sn, these groups lead to a larger Ti-S distance and weaken the Li$_2$Sn binding effect. This is why the binding energy of Li$_2$Sn on bare MXenes is much stronger than that of functionalized MXenes. Since the O atoms in Ti$_2$C(OH)$_2$ are passivated with H atoms, the repulsive forces caused by negatively charged O atoms are reduced. The positively charged H atoms can enhance the attraction for S atoms. As a result, firm interactions between Li$_2$Sn and Ti$_2$C(OH)$_2$ are obtained.

Some functional groups such as S and Cl can also be modified on the MXene surface to further suppress Li$_2$Sn shuttling. S terminated Ti$_2$C is calculated to possess a higher efficiency to restrain the polysulfide shuttle as its binding energy is higher than that of O/F terminated.
Ti$_2$C. S terminated Ti$_3$C$_2$Tx also exhibits the highest adsorption strength when compared with pristine Ti$_3$C$_2$Tx (T$_x$ = OH, O, F) (Figure 6D).

The theoretical analysis performed by Zhao et al indicates that Ti$_3$C$_2$(OH)$_2$ becomes unstable after absorption of Li$_2$Sn species; H atoms spontaneously migrate to S atoms of the Li$_2$Sn while the remained O atoms interact with Li atoms, leading to the breakup of the Li$_2$Sn species eventually. While the F-functionalized Ti$_2$C showcases weak binding energy of Li$_2$Sn, the Ti$_2$CO$_2$ and Ti$_3$C$_2$O$_2$ MXenes exhibit similar binding energies for Li$_2$Sn compared to that between Li$_2$Sn and electrolyte. As a result, oxygen-terminated MXenes are more efficient in chemisorption of the polysulfides. Nevertheless, these DFT calculations were performed on the interactions between polysulfides and MXenes terminated with only one type of functional group, which is different from the real case where different types of functional groups may coexist on the MXenes, and may change the polysulfides suppression mechanism.

The interaction behavior between Li$_2$Sn and other MXenes has also been theoretically studied which may guide future rational selection of MXenes to act as sulfur hosts for Li-S batteries. Fan's group investigated the Li$_2$Sn anchoring behavior of five O-functionalized MXenes (M$_3$C$_2$O$_2$, M = Cr, V, Nb, Hf and Zr) through DFT calculations. The study suggests that all the selected MXenes possess higher binding energies with Li$_2$Sn than that with organic electrolytes (Figure 6E), among which Cr$_3$C$_2$O$_2$ MXene shows the strongest anchoring effect toward Li$_2$Sn based on a lattice constant-dependent anchoring effect. The interactions with Li$_2$Sn mainly originate from the Li-O covalent bonds (Figure 6EIII). When the lattice constant increases, the Li-O bond length extends and then structural distortion happens which weakens the interaction between Li$_2$Sn and M$_3$C$_2$O$_2$, reducing the binding energy.

Some transition metal nitrides have already proved to be good sulfur host materials. Titanium nitride based MXenes are also potential conductive sulfur hosts with quite promising performance. Specifically, the anchoring mechanism of O- and F-functionalized Ti$_2$N has been investigated. Based on the charge transfer analysis, chemical interactions are confirmed between Li$_2$Sn and Ti$_3$NO$_2$, leading to a large adsorption energy (Figure 6F). For the Ti$_3$NF$_2$, the contribution to interactions is mainly van der Waals (vdW) interaction with less charge transfer from Li$_2$Sn to Ti$_2$FO$_2$.

### 3.2 Catalytic behavior of MXenes in Li-S batteries

Apart from the Li$_2$Sn shuttling effect, the final discharged product Li$_2$S with high decomposition energy would also compromise the electrochemical performances such as high overpotential and low rate capability. To this end, materials with high catalytic capability can effectively reduce the overpotential, promote the charge transfer kinetics process and improve the rate performance as a result. The 2D MXenes with various surface terminations exhibit unique catalytic capabilities and thus can be employed to address these issues. Surface-terminated Ti$_3$C$_2$T$_x$ typically demonstrates strong interactions with Li$_2$S while possessing a low Li$_2$S decomposition barrier. Direct comparisons of Li$_2$S decomposition barriers on the different surface-terminated MXenes are shown in Figure 7A. Unlike Ti$_3$C$_2$N$_2$, Ti$_3$C$_2$F$_2$ and Ti$_3$C$_2$Cl$_2$, the Ti$_3$C$_2$S$_2$ and Ti$_3$C$_2$O$_2$ MXenes showcase much reduced Li$_2$S decomposition barriers, which facilitate the decomposition of Li$_2$S, shorten the Li$_2$Sn accumulation time in the cathode and further suppress the Li$_2$Sn dissolution. Ti$_3$C$_2$S$_2$ can also maintain good catalytic capability even at high sulfur loading (Figure 7B).

Appropriate functional group vacancies could promote the interactions with Li$_2$Sn species. For example, Ti$_3$C$_2$Cl$_2$ exhibits poor adsorption capability and electrode reaction kinetic as the vdW interaction with Li$_2$Sn species dominates the lithiation process. However, when Cl vacancies form on the Ti$_3$C$_2$Cl$_2$ surface, the chemical interactions with Li$_2$Sn could be increased, leading to improved Li$_2$Sn adsorption capacity and further lowering down the decomposition energy of Li$_2$S due to the presence of Cl vacancies (Figure 7C,D). Thus, surface modification is an efficient method to adjust the electrocatalysis behavior and to improve the electrode kinetics for boosting the electrochemical performances of Li-S batteries. Besides that, the total number of atomic layers of carbide-based MXenes also has an effect on catalytic ability.

As a crucial aspect for Li$_2$Sn nucleation and decomposition, fast Li$^+$ diffusivity can assist the electrochemical process as well. Calculations on Ti$_3$C$_2$T$_x$ demonstrate much lower Li$^+$ diffusion barriers than that for graphene (Figure 7DIII-DVII). V-based MXenes with different surface terminations have also been studied, revealing that V$_2$CS$_2$ has a lower energy barrier for Li$^+$ diffusion, facilitating the conversion of Li$_2$Sn into low order Li$_2$S (Figure 7E).

Even when the MXene surface is covered by the polysulfides, the band gap of MXenes remain unchanged and MXenes can maintain their metallic properties to provide free electrons. We note that the good preservation of metallic host even after chemisorption of Li$_2$Sn is beneficial for both the continuous redox reactions and the enhancement of active S utilization.

Based on the above discussions, MXenes possess substantial advantages in Li-S batteries due to their unique properties including surface chemistry, metallic conductivity and ultrathin nanosheet morphology, and so forth.
Understanding the $Li_2Sn$ anchoring and catalytic behaviors of MXenes are important for designing high-performance Li-S batteries, which will be discussed below.

### 4 | MXENE BASED LI-S BATTERIES

#### 4.1 | Design of MXenes-based sulfur host in Li-S cathode

Introducing functional additives and constructing advanced structures for sulfur hosts are desirable strategies to entrap $Li_2Sn$ in the cathode and suppress the shuttle problem. Thanks to the strong interaction with polysulfides, MXenes with excellent electronic conductivity have been developed as highly effective sulfur cathode host materials, achieving improved cycling performance.\(^ {23,80}\) Without optimization, low capacity decay rates (~0.05% per cycle) can be reached on the $Ti_3C_2T_x$ MXene/S composites, which are comparative to various reported sulfur hosts such as graphene oxide and titanium oxide, and so forth.\(^ {14,81-84}\) Beside the utilization as sulfur cathode, MXenes can also be used to fabricate $Ti_3C_2T_x/Li_2S$ cathodes to further improve the $Li_2Sn$ trapping ability.\(^ {85}\)

Delaminated MXene sheets are easily restacked due to the vdW interactions which may hinder the chemical interaction with polysulfides. To improve the MXene nanosheet utilization, one desirable strategy is to develop MXene based hybrids through introducing spacers among...
the MXene layers. Nazar’s group reported a porous and conductive Ti$_3$C$_2$T$_x$/carbon nanotube (CNT) structure as sulfur host. The CNTs dispersed among the MXene sheets effectively suppress the nanosheets restacking, and thus achieve a high surface area (MXene/CNT: 350 m$^2$ g$^{-1}$, exceeding the sum surface area of MXene and CNT) which is beneficial for both physically confinement of Li$_2$S$_n$, and enhanced utilization of chemisorptive MXene polar sites. Interconnecting CNTs in the MXene can maintain high electrical conductivity and facilitate the electron transport. Carbon fibers (CF) and reduced graphene oxide (rGO) are typically used to hybridize with MXenes so as to alleviate the MXene nanosheet restacking phenomenon (Figure 8A). The alternative strategy is to construct three-dimensional (3D) MXene architectures by introducing Ti$_3$C$_2$T$_x$ sheets into porous skeletons as polysulfide reservoir to improve the utilization of the Ti$_3$C$_2$T$_x$ sheets. For example, the Ti$_3$C$_2$T$_x$/mesoporous carbon matrix exhibits a higher surface area of 1531.9 m$^2$ g$^{-1}$ and pore volume of 0.577 cm$^3$ g$^{-1}$ than those of restacked Ti$_3$C$_2$T$_x$/mesoporous carbon mixtures, suggesting the important role of the 3D matrix. Besides the mesoporous carbon, MXene/graphene aerogel also provides large spaces for encapsulating sulfur and accommodating the volumetric expansion of the cathode. Utilizing conductive carbon materials as additives can effectively improve the electrochemical performances of MXene/S cathode. However, the weak affinity among different host materials increases the interfacial transfer resistance and slows down the reaction kinetics of sulfur species. To improve the affinity to sulfur, a crumpled nitrogen-doped Ti$_3$C$_2$T$_x$ (N-Ti$_3$C$_2$T$_x$) nanosheet with well-defined porous structure was developed by Wang’s group, as shown in Figure 9A(I). This optimized MXene structure possesses a 10 times enhanced surface area (385.4 m$^2$ g$^{-1}$) and large pore volume (0.342 cm$^3$ g$^{-1}$) compared with those of the mechanically mixed Ti$_3$C$_2$T$_x$ (surface area: 30 m$^2$ g$^{-1}$, pore volume: 0.0321 cm$^3$ g$^{-1}$, Figure 9A[II]). Such nitrogen-doped MXenes also showcase a greater capability to adsorb polysulfides than that of pure MXenes, demonstrating an improving reversible capacity of 950 mAh g$^{-1}$ after 200 cycles at 0.2C (Figure 9A[III]). Beyond nitrogen doping to promote the surface polarity, the redox reactivity of sodium polysulfides can also be enhanced by incorporating sulfur surface groups on MXenes to boost the performance of Na-S batteries. In another case, Ti$_3$C$_2$T$_x$ nanodots as spacer were integrated among the Ti$_3$C$_2$T$_x$ nanosheets (TCD-TCS), as shown in Figure 9B(I). Such a nanostructure exposes more surface terminations and provides large amounts of active sites to trap the Li$_2$S$_n$, thus boosting the overall performances of the electrode (Figure 9BII-IV).

Materials with polar sites such as TiO$_2$, polydopamine (PDA), MnO$_2$, and MoS$_2$ have also been composited with MXenes as sulfur hosts to increase the active polysulfide entrapping sites and to enhance the Li$_2$S$_n$ immobilization.

**FIGURE 8** Various designs to prevent MXenes from restacking. A, Schematic illustration of Ti$_3$C$_2$T$_x$/rGO fabrication. Reproduced with permission. Copyright 2017, Wiley-VCH. B, Synthesis procedure of the Ti$_3$C$_2$T$_x$/mesoporous carbon (Meso-C) composites. Reproduced with permission. Copyright 2016, Wiley-VCH. C, Preparation process of the Ti$_3$C$_2$T$_x$/rGO aerogel electrodes. Reproduced with permission. Copyright 2019, The Royal Society of Chemistry
Figure 9. A. (I) Schematic illustration of synthesis process of the crumpled N-Ti₃C₂Tx/S electrodes. (II) N₂ adsorption-desorption isotherm curves of crumpled N-Ti₃C₂Tx nanosheets. (III) Cycling performances of crumpled N-Ti₃C₂Tx/S electrode and mixed-Ti₃C₂Tx/S electrodes. Reproduced with permission. 91 Copyright 2018, Wiley-VCH. B. (I) Schematic illustration for the preparation of TCD-TCS/S composites. (II-IV) Electrochemical performances of TCD-TCS/S electrodes. Reproduced with permission. 93 Copyright 2019, American Chemical Society

capability, respectively. 94-99 Figure 10 summarizes the detailed materials synthesis strategies, including oxide loading, freeze-drying, polymer coating, pumping, solvothermal and hydrothermal, and so forth. The as-obtained Ti₃C₂Tx based heterostructures well preserve the 2D layered geometry and alleviate the nanosheet restacking, greatly opening up more polysulfide entrapping sites.

For instance, MXene decorated with TiO₂ quantum dots (QDs) as sulfur host showcases quite promising performance for achieving fast and stable Li-S batteries. 98 Compared with a MXene/S cathode which displayed 308 mAh g⁻¹, TiO₂ QDs@ MXene/S delivered a much higher capacity of 680 mAh g⁻¹ at 2C (1C = 1675 mA g⁻¹) after 500 cycles (Figure 11A), due to the stronger adsorption ability of Li₂Sn species in the latter. 98 Similarly, another polar hybrid sulfur host was achieved by confining conductive MXenes into 1T-2H MoS₂-nitrogen-doped carbon (Ti₃C₂Tx/1T-2H MoS₂-C) composites, demonstrating a higher initial capacity of 1194.7 mAh g⁻¹ at 0.1C than that of MXene/S electrode (845.1mAh g⁻¹) (Figure 11B). After cycling, the black surface of Ti₃C₂Tx/1T-2H MoS₂-C cathode without obvious sulfur spots, coupled with the flat, shining Li metal surface, suggests that the Li₂Sn shuttling has been effectively suppressed and the smooth deposition of Li during upon repeated charge-discharge processes. 99

While titanium carbides have been widely studied as sulfur host, other types of MXenes, with different
electronic conductivity, surface chemistry and other properties, certainly deserve to be explored for the Li-S battery applications. For instance, Mo$_2$CT$_x$ MXene was confirmed with good capability in immobilizing polysulfides due to the Lewis acid-base interaction from the Mo atoms with Li$_2$Sn. By interweaving with CNTs, a highly conductive Mo$_2$CT$_x$/CNT hybrid was developed as sulfur host, as shown in Figure 12A. The Mo$_2$CT$_x$/CNTs electrode delivered excellent electrochemical performances in terms of high capacity, good rate capability and high initial reversible capacity at various sulfur loading (1314 mAh g$^{-1}$ at 1.8 mg cm$^{-2}$ sulfur loading, 959 mAh g$^{-1}$ at 5.6 mg cm$^{-2}$ sulfur loading) (Figure 12A). Composites based on hybridizing Mo$_2$C with CNF (Mo$_2$C/CNFs, Figure 12B) and a porous carbon matrix (Mo$_2$C/C, Figure 12C), respectively were also reported as sulfur hosts to facilitate electron transport and lithium ion diffusion, showcasing good Li$_2$Sn immobilization capability. We note that metal carbides play important roles in enhancing the polysulfide anchoring, improving the electrocatalytic kinetics and accelerating the polysulfide conversion into lower-order Li$_2$S (Figure 12D). Similarly, tungsten carbide (W$_2$C) was reported as an efficient sulfur host with stable cycling for Li-S batteries, which could be ascribed to the enhanced adsorption and catalytic sites on W$_2$C. For example, decorating W$_2$C nanoparticles on the
CNF (W_2C NPs/CNFs) and loading W_2C nanoclusters on the nitrogen-phosphorous co-doped carbon matrix (W_2C/N/P-rGO) (Figure 12EI) resulted in composites with enhanced polysulfides interaction and improved electrochemical kinetics. The W_2C/N/P-rGO composites delivered high reversible capacities under different sulfur loadings (Figure 12EII,III).

4.2 | MXene as separator in Li-S battery

Another important aspect of MXenes in Li-S battery is the employment as separator. As we know, Li_2Sn diffusion not only causes active mass loss, but also results in unfavorable reactions with the Li anode, causing significant polarization. In addition to develop advanced sulfur hosts, adding an Li_2Sn absorptive interlayer or fabricating functional separators can further improve the electrochemical performances of Li-S batteries. For example, when inserting a CNT freestanding interlayer between MXene/S cathode and separator, the separator almost remained its original color after cycling and achieved better electrochemical performances compared to the cell without CNT interlayer (the color of the separator changed to a light yellowish color after cycling), indicating the inserted CNT membrane efficiently block the migration of Li_2Sn.

Inspired by this design, Wang et al modified the separator by coating a MXene thin film onto the battery.
Celgard separator, in which the coated conductive MXene film acts as a second current collector to reduce the electron transfer resistance as well as suppresses the polysulfide shuttling effects,110 as shown in Figure 13A. Consequently, Li-S batteries with a Ti3C2Tx-modified separator exhibit better cycling retention and reversibility than that of the pristine battery.110 Based on the preliminary research on the MXene for modifying separators, extensive studies have been devoted to optimizing the structures such as Ti3C2Tx/GF,111 Ti3C2Tx/eggshell membrane (ESM),112 Ti3C2Tx/CNT,113 N-Ti3C2Tx/C114 and Ti3C2Tx/Nafion115 (Figure 13B-E). MXene-modified separators also facilitate good areal capacity under high sulfur loading. For a Ti3C2Tx/Nafion modified polypropylene (PP) separator, the Li-S cell achieved a reversible areal capacity of 5 mAh cm−2 with sulfur loading of 6.0 mg cm−2.115 When loading an impressively high amount of sulfur (10 mg cm−2), very high areal capacity of 6.3 mAh cm−2 was achieved with the N-Ti3C2Tx/C coated PP separator.114

It should be noted that the coated MXene-based composites usually have a dense laminar structure which may hinder the effective infiltration of electrolyte. Meanwhile, insulating Li2S/Li2S2 products keep accumulating on the separator, leading to increased interfacial charge transfer resistance and sluggish ion transport kinetics. As a result, serious polarization and capacity decay especially under high sulfur loading or at high rate may occur. In addition, the MXene nanosheets stacking behavior (ordered vs random) is also important for
achieving high Li-S performances. In any case, the modified layer partially suppresses the diffusion of Li$_2$Sn species and inhibits Li$^+$ mobility to some extent, highlighting the importance of optimization on the MXene membrane thickness.  

4.3 | Comprehensive Li-S cell design based on MXenes

To further improve the Li-S battery performance, some strategies are proposed by comprehensively designing MXene-based cathodes and separators. For instance, Wu et al reported the employment of Ti$_3$C$_2$Tx MXene for hosting sulfur and modifying the separator.  

By using 3D alkalized Ti$_3$C$_2$Tx MXene nanoribbon as sulfur host, as well as a 2D Ti$_3$C$_2$Tx nanosheet coated on the separator, a high S loading coupled with high reversible capacity (1062 mAh g$^{-1}$ at 0.2C) and energy density (833 Wh kg$^{-1}$) were achieved, as shown in Figure 14A. Very recently, an antifouling separator of self-assembled Ti$_3$C$_2$Tx/CNT-polyethylenimine (Ti$_3$C$_2$Tx/CNT-P) composite was reported (Figure 14B). The nanohybrid based separator possesses well-developed 3D conductive channels and good affinity to polysulfides. These advantages from the hybrid membrane allow rapid electrolyte transport as well as fully utilization of active species. As a result of the comprehensive cell design, the pouch cell demonstrated excellent rate performance (1110, 1035 and 950 mAh g$^{-1}$ at 0.5C, 1C and 2.5C, respectively) and stable cycling performance under high sulfur loading of 5.8 mg cm$^{-2}$ (Figure 14BII,BIII).  

Combining the advantages of Li$_2$Sn immobilization and high electrocatalytic properties, a multifunctional Ti$_3$C$_2$Tx/TiO$_2$ heterostructure was prepared by a controlled oxidation process of MXenes. The in-situ formation of Ti$_3$C$_2$Tx/TiO$_2$ heterostructure with stronger Li$_2$Sn chemisorption capability ensures smooth Li$_2$Sn diffusion to the MXene and then accelerate the conversion to low-order Li$_2$S$_{1-2}$ (Figure 14CI). The Ti$_3$C$_2$Tx/TiO$_2$ could also act as interlayer for the Li-S pouch cell with stable cycling, ultralow capacity decay rate (0.028% per cycle over 1000 cycles at 2C) and excellent capacity retention (93% after 200 cycles) even at a high sulfur loading of 5.1 mg cm$^{-2}$ (Figure 14CII).  

Another important aspect for achieving high-performance Li-S batteries is to fabricate electrodes with a high sulfur loading amount. Therefore, utilizing a highly conductive host is quite necessary so as to maintain good electron transport paths after loading a large amount of insulating sulfur. Constructing 3D microporous channels to form MXene foam, as well as increasing
interlayer spacing by pillaring the nanosheets in order to increase surface area, are promising routes for achieving high sulfur loading electrodes.\textsuperscript{23,86,89,93,99,114,115,118} For example, the self-supported Ti$_3$C$_2$Tx foam was able to uniformly accommodate a large amount of sulfur due to the well-defined porous structure. Consequently, the cell still maintained 689.7 mAh g$^{-1}$ after 1000 cycles with sulfur loading of 5.1 mg cm$^{-2}$ (Figure 15A).\textsuperscript{123}

Recently, Wang et al designed a flower-like porous Ti$_3$C$_2$Tx nanomesh, in which well-aligned conductive Ti$_3$C$_2$Tx nanosheets provide abundant active sites to entrap polysulfides, allowing rapid electron/ion transport and electrolyte penetration for fast redox reactions (Figure 15B).\textsuperscript{124} Based on this structure, the sulfur mass loading was improved to 10.5 mg cm$^{-2}$, resulting in high areal and volumetric capacities (10.04 mAh cm$^{-2}$ and 2009 mAh cm$^{-3}$) (Figure 15C). The abovementioned Ti$_3$C$_2$Tx nanodots in nanosheets electrode configuration (TCD-TCS) demonstrated the highest sulfur loading (13.8 mg cm$^{-2}$) among the reports, leading to an areal capacity of 13.7 mAh cm$^{-2}$ that is three times higher than that of commercialized Li-ion batteries (~4 mAh cm$^{-2}$, Figure 15D).\textsuperscript{93} Table 1 summarizes the areal capacities of MXene-based Li-S batteries with high sulfur loadings.

4.4 | Novel design for MXene-based Li-S battery

To match the trends of the fast-growing portable and wearable devices, power sources should also be flexible and robust enough. This requires the sulfur electrodes to be highly resilient while exhibiting excellent capacities upon bending or twisting. To address these challenging issues, a general strategy is to embed sulfur into a conductive matrix with impressive mechanical properties.\textsuperscript{125} As detailed previously, 2D Ti$_3$C$_2$Tx MXenes possess metallic conductivity and the nanosheets showcase an ultrahigh
FIGURE 15  A, Schematic illustration of Ti$_3$C$_2$Tx foam/S in the charge/discharge process. Reproduced with permission. Copyright 2018, The Royal Society of Chemistry. B, Schematic illustration of synthesizing flower-like Ti$_3$C$_2$Tx and the formation mechanism of the nanomeshes in the Ti$_3$C$_2$Tx nanosheet. C, Areal and volumetric capacities at 1/30C for the flower-like Ti$_3$C$_2$Tx electrode under various sulfur loadings. Reproduced with permission. Copyright 2019, American Chemical Society. D, (I) Schematic of Ti$_3$C$_2$Tx TCD-TCS/S composites, (II) cycling performance of Ti$_3$C$_2$Tx TCD-TCS electrodes under sulfur loading of 13.8 mg cm$^{-2}$ at 0.05C. Reproduced with permission. Copyright 2019, American Chemical Society

| Materials          | Application     | Sulfur loading (mg cm$^{-2}$) | Areal capacity (mAh cm$^{-2}$) | Ref. |
|-------------------|-----------------|------------------------------|-------------------------------|-----|
| Mo$_2$CT$_x$/C    | Cathode host    | 4.2                          | 1.1/1C                        | 102 |
| Ti$_3$C$_2$Tx/CF$^a$ | Cathode host    | 5                            | 3.2/1 mA/cm$^{-2}$            | 86  |
| Crumpled N-Ti$_3$C$_2$Tx | Cathode host | 5.1                          | 4.2/0.2C                      | 91  |
| Ti$_3$C$_2$Tx/CNT$^b$ | Cathode host    | 5.5                          | 5/0.05C                       | 23  |
| Mo$_2$CT$_x$/CNT  | Cathode host    | 5.6                          | 5.3/0.1C                      | 100 |
| Ti$_3$C$_2$Tx/CNT-P$^c$ | Separator      | 5.8                          | 7.1/0.25C                     | 118 |
| Ti$_3$C$_2$Tx/Nafion | Separator      | 6                            | 5/0.2C                        | 114 |
| Ti$_3$C$_2$Tx/rGO aerogel | Cathode host | 6                            | 5.27/0.1C                     | 89  |
| Ti$_3$C$_2$Tx/graphene/Li$_2$S | Cathode host | 9                            | 5.04/0.2C                     | 90  |
| N-Ti$_3$C$_2$Tx/C | Separator      | 10                           | 6.3/0.1C                      | 115 |
| Flower-like Ti$_3$C$_2$Tx | Cathode host | 10.5                         | 10.04/0.03C                   | 124 |
| Ti$_3$C$_2$Tx (TCD-TCS)$^d$ | Cathode host | 13.8                         | 13.7/0.05C                    | 93  |

$^a$Carbon fiber (CF).
$^b$Carbon nanotube (CNT).
$^c$Polyethyleneimine (P).
$^d$Ti$_3$C$_2$Tx nanodots/nanosheets (TCD-TCS).
The tensile strength of 300 MGa.\textsuperscript{126} Thus, delaminated Ti$_3$C$_2$Tx MXene nanosheets can be used as conductive binder and backbone for flexible sulfur cathode. For example, a free-standing Ti$_3$C$_2$Tx electrode with ultramicroporous channels was employed to encapsulate small sulfur molecules (Ti$_3$C$_2$Tx-UMC/S$_2$4), achieving both excellent flexibility and high charge-storage performances.\textsuperscript{127} The MXene/1T-2H MoS$_2$-C electrode also showcases excellent mechanical properties, which can withstand repeated bending without compromising the electrochemical performances, demonstrating its potential applications in the flexible Li-S punch cell.\textsuperscript{98}

To further improve the electrical, mechanical and electrochemical performances of MXene-S electrodes, Zhang

**FIGURE 16** A, (I-III) Images of Ti$_3$C$_2$Tx/S ink with high viscosity which can be written on Celgard membrane and coated on Al foil. (IV) Cycling performance and (V) Coulombic efficiency of Ti$_3$C$_2$Tx/S electrode at 0.2C. (VI) Schematic demonstration of Ti$_3$C$_2$Tx entrapping the polysulfides by forming a sulfate complex protective barrier. Reproduced with permission.\textsuperscript{128} Copyright 2018, Wiley-VCH. B, (I) Schematic fabrication process of the Ti$_3$C$_2$Tx/S paper. (II, III) Galvanostatic charge-discharge profiles and (IV) application of the pouch cells (Ti$_3$C$_2$Tx/S paper//Li foil) under flat and bent states. Reproduced with permission.\textsuperscript{130} Copyright 2019, Wiley-VCH
et al reported an aqueous Ti$_3$C$_2$Tx MXene-S composite ink, by which electrodes with high S content (70%) were quickly fabricated through a commercialized slurry casting technique.\textsuperscript{128} Thanks to the high concentration and viscosity from the composite ink, the as-formed Ti$_3$C$_2$Tx-S freestanding electrodes were highly conductive and flexible that was achieved in the absence of additional conductive agents and polymeric binders (Figure 16AI-III). The architecture based on the highly conductive network ensures intimate contact between sulfur species and Ti$_3$C$_2$Tx. In addition, a complex sulfate layer can be in situ formed through the interactions between the OH surface groups and Li$_2$Sn species. Combined with Lewis acid-base interaction between Ti atoms and Li$_2$Sn, the Li-S batteries exhibited excellent electrochemical performances including high capacity of 1244 to 1350 mAh g$^{-1}$ and impressive cycling stability (0.035-0.048% capacity loss per cycle), showing great promise for applications in wearable device (Figure 16AIV-VI).\textsuperscript{128} Very recently, Zhang et al further extended the applications of the viscous MXene aqueous inks, including constructing high capacity MXene-silicon anodes\textsuperscript{129} and additive-free printing of micro-supercapacitor.\textsuperscript{54}

Furthermore, Zhang et al prepared MXene/S conductive paper as electrodes by filtration the viscous MXene ink, followed by S impregnation, as demonstrated in Figure 16BI.\textsuperscript{130} Such robust electrodes showcased excellent long-term cycling performance with a capacity decay rate of 0.014% per cycle, which has greatly surpassed all other MXene-S electrodes in terms of cycling stability,\textsuperscript{130} as shown in Table 2. A prototype full cell based on MXene/S paper and lithium foil is demonstrated in Figure 16BII-BIV, implying the promising applications in next-generation wearable, portable electronics.

### 5 | SUMMARY AND OUTLOOK

In this work, we summarize the applications of MXenes for Li-S batteries. Due to their exotic properties, such as abundant surface terminated groups, excellent electronic conductivity and mechanical strength, and so

---

**TABLE 2** Summary of electrochemical performances of MXene-based Li-S batteries

| Materials           | Application          | Sulfur content/sulfur loading | Specific capacity (mAh g$^{-1}$) | Cycle life (cycles) | Capacity decay rate (% per cycle) | Ref. |
|---------------------|----------------------|------------------------------|---------------------------------|---------------------|----------------------------------|------|
| Ti$_3$C$_2$Tx         | Cathode host         | 70 wt%                       | 1090/0.5C                       | 650/0.5C            | 0.05                             | 22   |
| Ti$_3$C$_2$Tx/CNT     | Cathode host         | 83 wt%/1.5 mg cm$^{-2}$      | 1240/0.05C                      | 1200/0.5C           | 0.043                            | 23   |
| Ti$_3$C$_2$Tx/CNT     | Cathode host         | 83 wt%/1.5 mg cm$^{-2}$      | 1216/0.05C                      | 1263/0.05C          |                                  |      |
| Ti$_3$C$_2$Tx         | Cathode host         | 57.6 wt%                     | 1291/200 mA g$^{-1}$            | 100/200 mA g$^{-1}$ | 0.25                             | 80   |
| Ti$_3$C$_2$Tx/Li$_2$S | Cathode host         | 0.8 mg cm$^{-2}$             | 630/0.2C                        | 100/0.2C            | 0.2857                           | 85   |
| Ti$_3$C$_2$Tx/CNT     | Cathode host         | 1.2 mg cm$^{-2}$             | 1380/0.1C                       | 1000/1C             | 0.044                            | 86   |
| Ti$_3$C$_2$Tx/rGO     | Cathode host         | 70.4 wt%                     | 1144.2/0.5C                     | 300/0.5C            | 0.0774                           | 87   |
| Ti$_3$C$_2$Tx/Meso-C$^a$ | Cathode host     | 72.88 wt%/2.0 mg cm$^{-2}$   | 1225.8/0.5C                     | 300/0.5C            | 0.142                            | 88   |
| Ti$_3$C$_2$Tx/rGO aerogel | Cathode host | 45 wt%/1.57 mg cm$^{-2}$ 6 mg cm$^{-2}$ | 1270/0.1C 879/0.1C | 500/1C | 0.07                             | 89   |
| Ti$_3$C$_2$Tx/graphene/Li$_2$S | Cathode host | 62 wt%/3 mg cm$^{-2}$ 6 mg cm$^{-2}$ 9 mg cm$^{-2}$ | 710/0.2C 590/0.2C 545/0.2C | 100/0.2C | 0.133                            | 90   |
| Crumpled N-Ti$_3$C$_2$Tx | Cathode host | 73.65 wt%/1.5 mg cm$^{-2}$ 5.1 mg cm$^{-2}$ | 1609/0.05C 765/0.2C | 1000/2C 500/0.2C | 0.026 0.046 | 91   |
| Ti$_3$C$_2$Tx (TCD-TCS) | Cathode host | 67.6 wt%/1.8 mg cm$^{-2}$ | 1609/0.05C                       | 400/2C              | 0.057                            | 93   |
| Ti$_3$C$_2$Tx/TiO$_2$ | Cathode host         | 60 wt%                       | 1417/1C                         | 1000/1C             | 0.053                            | 94   |
| Ti$_3$C$_2$Tx/MnO$_2$ | Cathode host         | 70 wt%/1.2 mg cm$^{-2}$      | 1140/0.05C                       | 500/1C              | 0.06                             | 95   |
| Ti$_3$C$_2$Tx/PDA$^b$ | Cathode host         | 78.3 wt%/5 mg cm$^{-2}$      | 1001/0.2C                       | 1000/0.2C           | 0.035                            | 96   |
| Ti$_3$C$_2$Tx/TiO$_2$ | Cathode host         | 78.4 wt%/1.8-2.0 mg cm$^{-2}$ | 1408.6/0.2C 200/2C | 200/2C | 0.2036                           | 97   |
| Ti$_3$C$_2$Tx/TiO$_2$ QD$^c$ | Cathode host | 80 wt%/1.5 mg cm$^{-2}$ | 1158/0.2C                       | 500/2C              | 0.04                             | 98   |

(Continues)
| Materials          | Application | Sulfur content/sulfur loading | Specific capacity (mAh g$^{-1}$) | Cycle life (cycles) | Capacity decay rate (% per cycle) | Ref. |
|-------------------|-------------|-------------------------------|----------------------------------|---------------------|-----------------------------------|------|
| Ti$_3$C$_2$Tx/1T-2H MoS$_2$-C | Cathode host | 79.6 wt%/1 mg cm$^{-2}$ | 1194.7/0.1C | 300/0.5C | 0.07 | 99 |
| Mo$_2$CT$_x$/CNT | Cathode host | 87.1 wt%/0.8 mg cm$^{-2}$ | 1438/0.1C | 250/0.1C | 0.1 | 100 |
| Mo$_2$C/CNFs | Cathode host | 1.5 mg cm$^{-2}$ | 1017/0.1C | 50/0.1C | 0.4916 | 101 |
| Mo$_2$C NPs/CNFs | Cathode host | 2.5 mg cm$^{-2}$ | 1085/0.2C | 200/0.2C | 0.136 | 102 |
| W$_2$C/N/P-rGO | Cathode host | 63 wt%/1.5 mg cm$^{-2}$ | 914/1C | 400/1C | 0.0777 | 104 |
| Ti$_3$C$_2$Tx | Separator | 50 wt%/1.0-1.2 mg cm$^{-2}$ | 1458/0.1 A g$^{-1}$ | 1500/0.8 A g$^{-1}$ | 0.04 | 109 |
| Ti$_3$C$_2$Tx | Separator | 68 wt%/1.2 mg cm$^{-2}$ | 1046.9/0.2C | 500/0.5C | 0.062 | 110 |
| Ti$_3$C$_2$Tx/GF | Separator | 70 wt%/1.9 mg cm$^{-2}$ | 1462/0.1 A g$^{-1}$ | 100/0.5 A g$^{-1}$ | 0.22 | 109 |
| Ti$_3$C$_2$Tx/ESM$_4$ | Separator | 67 wt%/2.07 mg cm$^{-2}$ | 1003/0.5C | 250/0.5C | 0.104 | 112 |
| Ti$_3$C$_2$Tx/CNT | Separator | 70 wt%/0.8 mg cm$^{-2}$ | 1415/0.1C | 600/1C | 0.06 | 113 |
| N-Ti$_3$C$_2$Tx/C | Separator | 79 wt%/3.4 mg cm$^{-2}$ | 1332/0.1C | 500/0.5C | 0.07 | 114 |
| Ti$_3$C$_2$Tx/Nafion | Separator | 74.1 wt%/2 mg cm$^{-2}$ | 1234/0.2C | 1000/1C | 0.03 | 115 |
| Ti$_3$C$_2$Tx/MNR | Cathode host | 68 wt%/0.7-1 mg cm$^{-2}$ | 1062/0.2C | 200/0.5C | 0.2615 | 117 |
| Ti$_3$C$_2$Tx/CNT-P | Cathode host | 70.2 wt%/2.6 mg cm$^{-2}$ | 1110 0.5C | 500/1C | 0.021 | 118 |
| Ti$_3$C$_2$Tx/TiO$_2$ | Separator | 75 wt%/1.2 mg cm$^{-2}$ | 800/2C | 1000/2C | 0.028 | 119 |
| Ti$_3$C$_2$Tx/ESM$_4$ | Separator | 70 wt%/2.07 mg cm$^{-2}$ | 1003/0.5C | 250/0.5C | 0.104 | 112 |
| Flower-like Ti$_3$C$_2$Tx | Cathode host | 71.1 wt%/1.5 mg cm$^{-2}$ | 1226.4/0.2C | 1000/1C | 0.05 | 123 |
| Ti$_3$C$_2$Tx/S$_2$-4-UMC | Cathode host | 37.2 wt% | 1029.7/0.1C | 200/0.1C | 0.0405 | 127 |
| Ti$_3$C$_2$Tx/S film | Cathode host | 70 wt% | 1244/0.1C | 800/0.2C | 0.048 | 128 |
| Ti$_3$C$_2$Tx/S paper | Cathode host | 30 wt% | 1383/0.1C | 150/1C | 0.014 | 130 |

*Mesoporous carbon (Meso-C).
*Polydopamine (PDA).
*Quantum dots (QDs).
*Ti$_3$C$_2$Tx nanodots/nanosheets (TCD-TCS).
*MXene nanoribbon (MNR).
*Sulfur molecules (UMC).
forth, the laminated MXenes possess many unique advantages over other 2D materials and are quite promising for constructing high-performance electrodes. Specifically, (a) the unique layered structure endows MXene nanosheet with sufficient contact area for sulfur/sulfides, and provides good mechanical strength to withstand the stress induced by large volume expansion of sulfur; (b) the metallic conductivity facilitates the electron transport kinetics across the electrode/electrolyte interface, alleviates electrode polarizations and facilitates high rate responses even at a high sulfur loading; (c) MXenes can entrap the soluble Li$_2$Sn, though a strong Ti-S interaction to suppress the shuttling effect. Meanwhile, MXene surface functional groups also have a strong chemisorption to Li$_2$Sn, which efficiently reduces the active material loss and maintain high capacities after long-term cycling; (d) MXenes with specific surface groups and configurations show a low Li$_2$S decomposition energy barrier and fast Li$^+$ diffusivity, leading to good catalytic performance and facilitating the electrochemical redox reactions.

Based on these merits, MXenes have been devoted as both sulfur hosts and modified separators. The electrochemical performances of MXene-based Li-S batteries can be improved mainly through the materials and cell design. For instance, increasing the active interaction sites to strength Li$_2$Sn immobilization, introducing spacers to suppress the nanosheet restacking and constructing 3D frameworks to enhance sulfur loading, and so forth. We believe the electrochemical performance of MXene-based electrodes/devices can be further improved through the following categories.

First, the most common way to synthesize MXenes is by etching of the MAX phase. As a result, functional surface groups are inevitably terminated on the MXenes. According to the theoretical analysis, MXene surface groups play an important role in confining Li$_2$Sn. The interaction mode of Ti-S is influenced by the functional groups like —O, —OH, —F, —S, and so forth. On the one hand, reducing the amount of these terminations is beneficial to form strong Ti—S bonds. On the other side, Li$_2$Sn species are prefer to interact with MXenes terminated with a specific type of functional groups. Thus, engineering MXene surface chemistry is crucial in order to achieve electrodes with a good affinity to Li$_2$Sn species.

Second, although the electrochemical performances of Li-S batteries have been efficiently improved by introducing MXenes, some of the properties are achieved at a low sulfur loading or tap density. Thus, the areal and volumetric capacities are typically low at the current stage. Future studies should pay attention to the construction of high S loading electrodes with a high tap density. As such, MXene-based Li-S batteries with superior properties are expected.

Third, in line with the fast development of portable and wearable electronic devices, the power sources should also be lightweight and flexible enough (even foldable) without compromising their charge-storage performances. To this end, exploring facile and low-cost techniques to construct electrodes with robust structure and high mass loading are meaningful for new type MXene-based Li-S batteries and beyond.

Finally, as a new class of 2D wonder materials, MXenes are not just Ti$_3$C$_2$Tx. To date, more than 30 MXene phases have been reported with more predicted to exist. There are certainly enough incentives to explore other MXene members for high-performance Li-S batteries. Moreover, through tuning the physical and chemical properties of existing MXenes under the guide of theoretical simulations, there is certainly much room available for the reported MXene-S systems to further boost their electrochemical performances in Li-S batteries. We firmly believe that, through the collective efforts from all over the world, MXene-S based Li-S batteries will finally come to our daily life, just give it enough time.

ACKNOWLEDGMENTS
C.Z., S.A., and J.H. would like to thank the support from an Empa interal research grant.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

ORCID
Chuanfang (John) Zhang @ https://orcid.org/0000-0001-8663-3674

REFERENCES
1. Larcher D, Tarascon J-M. Towards greener and more sustainable batteries for electrical energy storage. Nat Chem. 2015;7 (1):19-29.
2. Dunn B, Kamath H, Tarascon J-M. Electrical energy storage for the grid: a battery of choices. Science. 2011;334(6058):928-935.
3. Goodenough JB, Manthiram A. A perspective on electrical double-layer and lithium-sulfur batteries. Nat Mater. 2012;11(1):19-29.
4. Yin YX, Xin S, Guo YG, Wan LJ. Lithium-sulfur batteries: electrochemistry, materials, and prospects. Angew Chem Int Ed. 2013;52(50):13186-13200.
5. Evers S, Nazar LF. New approaches for high energy density lithium-sulfur battery cathodes. Acc Chem Res. 2012;46(5):1135-1143.
6. Manthiram A, Fu Y, Chung S-H, Zu C, Su Y-S. Rechargeable lithium-sulfur batteries. Chem Rev. 2014;114(23):11751-11787.
10. He G, Ji X, Nazar L. High “C” rate Li-S cathodes: sulfur imbibed bimodal porous carbons. Energ Environ Sci. 2011;4(8):2878-2883.

11. Jayaprakash N, Shen J, Moganty SS, Corona A, Archer LA. Porous hollow carbon@sulfur composites for high-power lithium-sulfur batteries. Angew Chem Int Ed. 2011;50(26):5904-5908.

12. Zhou W, Yu Y, Chen H, DiSalvo FJ, Abraño HD. Yolk-shell structure of polyaniline-coated sulfur for lithium-sulfur batteries. J Am Chem Soc. 2013;135(44):16736-16743.

13. Fu Y, Manthiram A. Orthorhombic bipyrimalidial sulfur coated with polypyrrole nanolayers as a cathode material for lithium-sulfur batteries. J Phys Chem C. 2012;116(16):8910-8915.

14. Song M-K, Zhang Y, Kwok CY, Pang Q, Nazar LF. Interwoven nitrides (MXenes) for energy storage. Nat Commun. 2013;4:3255.

15. Ji X, Evers S, Black R, Nazar LF. Stabilizing lithium-sulphur cathodes using polysulphide reservoirs. Nat Commun. 2011;2:325.

16. Naguib M, Kurtoglu M, Presser V, et al. Two-dimensional nanocrystals produced by exfoliation of Ti$_3$AlC$_2$. Adv Mater. 2011;23(37):4248-4253.

17. Gogotsi Y, Anasori B. The rise of MXenes. ACS Nano. 2019;13:8491-8494.

18. Naguib M, Mochalin VN, Barsoum MW, Gogotsi Y. 25th anniversary article: MXenes: a new family of two-dimensional materials. Adv Mater. 2014;26(7):992-1005.

19. Naguib M, Gogotsi Y. Synthesis of two-dimensional materials by selective extraction. Acc Chem Res. 2014;48(1):128-135.

20. Okubo M, Sugahara A, Kajiyama S, Yamada A. MXene as a charge storage host. Acc Chem Res. 2018;51(3):591-599.

21. Anasori B, Lukatskaya MR, Gogotsi Y. 2D metal carbides and nitrides (MXenes) for energy storage. Nat Rev Mater. 2017;2(2):16098.

22. Liang X, Garsuch A, Nazar LF. Sulfur cathodes based on conductive MXene nanosheets for high-performance lithium-sulfur batteries. Angew Chem Int Ed. 2015;54(13):3907-3911.

23. Liang X, Rangom Y, Kwok CY, Pang Q, Nazar LF. Interwoven MXene nanosheet/carbon-nanotube composites as Li-S cathode hosts. Adv Mater. 2017;29(3):1603040.

24. Ghidiu M, Halim J, Kota S, Bish D, Gogotsi Y, Barsoum MW. Ion-exchange and cation solvation reactions in Ti$_3$C$_2$ MXene. Chem Mater. 2016;28(10):3507-3514.

25. Anasori B, Xie Y, Beidaghi M, et al. Two-dimensional, ordered, double transition metals carbides (MXenes). ACS Nano. 2015;9(10):9507-9516.

26. Naguib M, Mashtalir O, Carle J, et al. Two-dimensional transition metal carbides. ACS Nano. 2012;6(2):1322-1331.

27. Ghidiu M, Naguib M, Shi C, et al. Synthesis and characterization of two-dimensional Nb$_2$C$_3$ (MXene). Chem Commun. 2014;50(67):9517-9520.

28. Mashtalir O, Naguib M, Mochalin VN, et al. Intercalation and delamination of layered carbides and carbonitrides. Nat Commun. 2013;4:1716.

29. Mashtalir O, Lukatskaya MR, Zhao MQ, Barsoum MW, Gogotsi Y. Amine-assisted delamination of Nb$_2$C$_3$ MXene for Li-ion energy storage devices. Adv Mater. 2015;27(23):3501-3506.

30. Naguib M, Unocic RR, Armstrong BL, Nanda J. Large-scale delamination of multi-layers transition metal carbides and carbonitrides “MXenes”. Dalton Trans. 2015;44(20):9353-9358.

31. Bian RJ, He GL, Zhi WQ, Xiang SL, Wang TW, Cai DY. Ultra-light MXene-based aerogels with high electromagnetic interference shielding performance. J Mater Chem C. 2019;7(3):474-478.

32. Shahzad F, Alhabe M, Hatter CB, et al. Electromagnetic interference shielding with 2D transition metal carbides (MXenes). Science. 2016;353(6304):1137-1140.

33. Sang X, Xie Y, Lin M-W, et al. Atomic defects in monolayer titanium carbide (Ti$_3$C$_2$T$_x$) MXene. ACS Nano. 2016;10(10):9193-9200.

34. Lipatov A, Alhabe M, Lukatskaya MR, Boson A, Gogotsi Y, Sinitskii E. Effect of synthesis on quality, electronic properties and environmental stability of individual monolayer Ti$_3$C$_2$ MXene flakes. Adv Electron Mater. 2016;2(12):1600255.

35. Halim J, Lukatskaya MR, Cook KM, et al. Transparent conductive two-dimensional titanium carbide epitaxial thin films. Chem Mater. 2014;26(7):2374-2381.

36. Urbankowski P, Anasori B, Makaryan T, et al. Synthesis of two-dimensional titanium nitride Ti$_3$N$_2$ (MXene). Nanoscale. 2016;8(22):11385-11391.

37. Wu W, Xu J, Tang X, et al. Two-dimensional nanosheets by rapid and efficient microwave exfoliation of layered materials. Chem Mater. 2018;30(17):5932-5940.

38. Yang S, Zhang P, Wang F, et al. Fluoride-free synthesis of two-dimensional titanium carbide (MXene) using a binary aqueous system. Angew Chem Int Ed. 2018;130(47):15717-15721.

39. Han F, Luo S, Xie L, et al. Boosting the yield of MXene 2D sheets via a facile hydrothermal-assisted intercalation. ACS Appl Mater Interfaces. 2019;11(8):8443-8452.

40. Li T, Yao L, Liu Q, et al. Fluorine-free synthesis of high-purity Ti$_3$C$_2$T$_x$ (T= OH, O) via alkali treatment. Angew Chem Int Ed. 2018;57(21):6115-6119.

41. Gogotsi Y. Chemical vapour deposition: transition metal carbides go 2D. Nat Mater. 2015;14(11):1079-1080.

42. Urbankowski P, Anasori B, Hantanaisirakul K, et al. 2D molybdenum and vanadium nitrides synthesized by ammoniation of 2D transition metal carbides (MXenes). Nanoscale. 2017;9(45):17722-17730.

43. Moshkian R, Näslund L-Å, Halim J, Lu J, Barsoum MW, Rosen J. Synthesis of two-dimensional molybdenum carbide, Mo$_2$C, from the gallium based atomic laminate Mo$_5$Ga$_3$C. Scr Mater. 2015;108:147-150.

44. Zhou J, Zha X, Chen FY, et al. A two-dimensional zirconium carbide by selective etching of Al$_2$C$_3$ from nanolaminated Zr$_3$Al$_2$C$_5$. Angew Chem Int Ed. 2016;55(16):5008-5013.

45. Xu C, Wang L, Liu Z, et al. Large-area high-quality 2D ultrathin Mo$_2$C superconducting crystals. Nat Mater. 2015;14(11):1135-1141.

46. Lai S, Jeon J, Kang SK, et al. Surface group modification and carrier transport properties of layered transition metal carbides (Ti$_x$CT$_{2x}$, T=—OH, —F and —O). Nanoscale. 2015;7(46):19390-19396.

47. Enyashin A, Ivanovskii A. Atomic structure, comparative stability and electronic properties of hydroxylated Ti$_3$C$_2$ and Ti$_3$C$_2$ nanotubes. Comput Theor Chem. 2012;989:27-32.

48. Tang Q, Zhou Z, Shen P. Are MXenes promising anode materials for Li ion batteries? Computational studies on electronic properties and Li storage capability of Ti$_3$C$_2$ and Ti$_3$C$_2$X$_2$ (X= F, OH) monolayer. J Am Chem Soc. 2012;134(40):16909-16916.
49. Naguib M, Halim J, Lu J, et al. New two-dimensional niobium and vanadium carbides as promising materials for Li-ion batteries. *J Am Chem Soc*. 2013;135(43):15966-15969.

50. Maleski K, Mochalin VN, Gogotsi Y. Dispersions of two-dimensional titanium carbide MXene in organic solvents. *Chem Mater*. 2017;29(4):1632-1640.

51. Allhabe M, Maleski K, Anasori B, et al. Guidelines for synthesis and processing of two-dimensional titanium carbide (Ti3C2Tx MXene). *Chem Mater*. 2017;29(18):7633-7644.

52. Zhang CJ, Pinilla S, McEvoy N, et al. Oxidation stability of colloidal two-dimensional titanium carbides (MXenes). *Chem Mater*. 2017;29(11):4848-4856.

53. Huang S, Mochalin VN. Hydrolysis of 2D transition-metal carbides (MXenes) in colloidal solutions. *Inorg Chem*. 2019;58(3):1958-1966.

54. Zhang CJ, McKeon L, Kremer MP, et al. Additive-free MXene inks and direct printing of micro-supercapacitors. *Nat Commun*. 2019;10(1):1795.

55. Khazaei M, Arai M, Sasaki T, et al. Novel electronic and magnetic properties of two-dimensional transition metal carbides and nitrides. *Adv Funct Mater*. 2013;23(17):2185-2192.

56. Anasori B, Shi C, Moon EJ, et al. Control of electronic properties of 2D carbides (MXenes) by manipulating their transition metal layers. *Nanoscale Horiz*. 2016;1(3):227-234.

57. Seh ZW, Fredrickson KD, Anasori B, et al. Two-dimensional molybdenum carbide (MXene) as an efficient electrocatalyst for hydrogen evolution. *ACS Energy Lett*. 2016;1(3):589-594.

58. Hu T, Hu M, Li Z, et al. Interlayer coupling in two-dimensional titanium carbide MXenes. *Phys Chem Chem Phys*. 2016;18(30):20256-20260.

59. Xu J, Shim J, Park JH, Lee S. MXene electrode for the integration of WSe2 and MoS2 field effect transistors. *Adv Funct Mater*. 2016;26(29):5328-5334.

60. Zhang C, Anasori B, Seral-Ascaso A, et al. Transparent, flexible, and conductive 2D titanium carbide (MXene) films with high volumetric capacitance. *Adv Mater*. 2017;29(36):1702678.

61. Wang H-W, Naguib M, Page K, Wesolowski DJ, Gogotsi Y. Resolving the structure of Ti3C2Tx MXenes through multilevel structural modeling of the atomic pair distribution function. *Chem Mater*. 2015;28(1):349-359.

62. Dillon AD, Ghidie MJ, Krick AL, et al. Highly conductive optical quality solution-processed films of 2D titanium carbide. *Adv Funct Mater*. 2016;26(23):4162-4168.

63. Hantanasirakul K, Zhao MQ, Urbankowski P, et al. Fabrication of Ti3C2Tx MXene transparent thin films with tunable optoelectronic properties. *Adv Electron Mater*. 2016;2(6):1600050.

64. Liang X, Hart C, Pang Q, Garsuch A, Weiss T, Nazar LF. A highly efficient polysulfide mediator for lithium-sulfur batteries. *Nat Commun*. 2015;6:5682.

65. Rao D, Zhang L, Wang Y, et al. Mechanism on the improved performance of lithium sulfur batteries with MXene-based additives. *J Phys Chem C*. 2017;121(21):11047-11054.

66. Wang D, Li F, Lian R, et al. A general atomic surface modification strategy for improving anchoring and electrocatalysis behavior of Ti3C2Tx MXene in lithium-sulfur batteries. *ACS Nano*. 2019;13(10):11078-11086. https://doi.org/10.1021/acsnano.9b03412

67. Li N, Meng Q, Zhu X, et al. Lattice constant-dependent anchoring effect of MXenes for lithium-sulfur (Li-S) batteries: a DFT study. *Nanoscale*. 2019;11(17):8485-8493.

68. Lin H, Yang D-D, Lou N, Zhu S-G, Li H-Z. Functionalized titanium nitride-based MXenes as promising host materials for lithium-sulfur batteries: a first principles study. *Ceram Int*. 2019;45(2):1588-1594.

69. Sim ES, Yi GS, Je M, Lee Y, Chung Y-C. Understanding the anchoring behavior of titanium carbide-based MXenes depending on the functional group in LiS batteries: a density functional theory study. *J Power Sources*. 2017;342:64-69.

70. Liu X, Shao X, Li F, Zhao M. Anchoring effects of S-terminated Ti3C MXene for lithium-sulfur batteries: a first-principles study. *Appl Surf Sci*. 2018;455:522-526.

71. Sim ES, Chung Y-C. Non-uniformly functionalized titanium carbide-based MXenes as an anchoring material for Li-S batteries: a first-principles calculation. *Appl Surf Sci*. 2018;435:210-215.

72. Zhao Y, Zhao J. Functional group-dependent anchoring effect of titanium carbide-based MXenes for lithium-sulfur batteries: a computational study. *Appl Surf Sci*. 2017;412:591-598.

73. Sun Z, Zhang J, Yin L, et al. Conductive porous vanadium nitride/graphene composite as chemical anchor of polysulfides for lithium-sulfur batteries. *Nat Commun*. 2017;8:14627.

74. Wang Y, Zhang R, Pang Y-C, et al. Carbon@ titanium nitride dual shell nanospheres as multi-functional hosts for lithium sulfur batteries. *Energy Storage Mater*. 2019;16:228-235.

75. Lim WG, Jo C, Cho A, et al. Approaching ultrastable high-rate Li-S batteries through hierarchically porous titanium nitride synthesized by multiscale phase separation. *Adv Mater*. 2019;31(3):1806547.

76. Xiao X, Wang H, Bao W, et al. Two-dimensional arrays of transition metal nitride nanocrystals. *Adv Mater*. 2019;31:1902393.

77. Zhou G, Tian H, Jin Y, et al. Catalytic oxidation of Li2S on the surface of metal sulfides for Li-S batteries. *Proc Natl Acad Sci USA*. 2017;114(5):840-845.

78. Wang Y, Shen J, Xu L-C, et al. Sulfur-functionalized vanadium carbide MXene (V2CS2) as a promising anchoring material for lithium-sulfur batteries. *Phys Chem Chem Phys*. 2019;21(34):18559-18568.

79. Lin H, Yang L, Jiang X, et al. Electrocatalysis of polysulfide conversion by sulfur-deficient MoS2 nanoflakes for lithium-sulfur batteries. *Energy Environ Sci*. 2017;10(6):1476-1486.

80. Zhao X, Liu M, Chen Y, et al. Fabrication of layered Ti3C2 with an accordion-like structure as a potential cathode material for high performance lithium-sulfur batteries. *J Mater Chem A*. 2015;3(15):7870-7876.

81. Qiu Y, Li W, Zhao W, et al. High-rate, ultralong cycle-life lithium/sulfur batteries enabled by nitrogen-doped graphene. *Nano Lett*. 2014;14(8):4821-4827.

82. Seh ZW, Li W, Cha JJ, et al. Sulphur-TiO2 yolk-shell nanorarchitecture with internal void space for long-cycle lithium-sulphur batteries. *Nat Commun*. 2013;4:1331.

83. Yao H, Zheng G, Hsu P-C, et al. Improving lithium-sulphur batteries through spatial control of sulphur species deposition on a hybrid electrode surface. *Nat Commun*. 2014;5:3943.

84. Pang Q, Kundu D, Cuisinier M, Nazar L. Surface-enhanced redox chemistry of polysulphides on a metallic and polar host for lithium-sulphur batteries. *Nat Commun*. 2014;5:4759.

85. Liang X, Yun J, Xu K, et al. A multi-layered Ti3C2/Li2S composite as cathode material for advanced lithium-sulfur batteries. *J Energy Chem*. 2019;39:176-181.
86. Jin Q, Li L, Wang H, Gao H, Zhu C, Zhang X. Dual effects of the carbon fibers/Ti$_3$C$_2$T$_x$ interlayer on retarding shuttle of polysulfides for stable lithium-sulfur batteries. *Electrochim Acta*. 2019;312:149-156.

87. Bao W, Xie X, Xu J, et al. Confined sulfur in 3D MXene/reduced graphene oxide hybrid nanosheets for lithium-sulfur batteries. *Chem Eur J*. 2017;23(51):12613-12619.

88. Bao W, Su D, Zhang W, Guo X, Wang G. 3D metal carbide@mesoporous carbon hybrid architecture as a new polysulfide reservoir for lithium-sulfur batteries. *Adv Funct Mater*. 2016;26(47):8746-8756.

89. Song J, Guo X, Zhang J, et al. Rational design of free-standing 3D porous MXene/rGO hybrid aerogels as polysulfide reservoirs for high-energy lithium-sulfur batteries. *J Mater Chem A*. 2019;7(11):6507-6517.

90. Wang Z, Zhang N, Yu M, Liu J, Wang S, Qiu J. Boosting redox activity on MXene-induced multifunctional collaborative interface in high Li$_2$S loading cathode for high-energy Li-S and metallic Li-free rechargeable batteries. *J Energy Chem*. 2019;37:183-191.

91. Bao W, Liu L, Wang C, Choi S, Wang D, Wang G. Facile synthesis of crumpled nitrogen-doped MXene nanosheets as a new sulfur host for lithium-sulfur batteries. *Adv Mater*. 2018;30(13):1702485.

92. Bao W, Shuck CE, Zhang W, Guo X, Gogotsi Y, Wang G. Boosting performance of Na-S batteries using sulfur-doped Ti$_3$C$_2$T$_x$ MXene nanosheets with a strong affinity to sodium polysulfides. *ACS Nano*. 2019;13(10):11500-11509.

93. Xiao Z, Li Z, Li P, Meng X, Wang R. Ultrathin Ti$_3$C$_2$ MXene nanodots-impervious nanosheet for high-energy-density lithium-sulfur batteries. *ACS Nano*. 2019;13(3):3608-3617.

94. Pan H, Huang X, Zhang R, et al. Titanium oxide-Ti$_3$C$_2$ hybrids as sulfur hosts in lithium-sulfur battery: fast oxidation treatment and enhanced polysulfide adsorption ability. *Chem Eng J*. 2019;358:1253-1261.

95. Zhang H, Qi Q, Zhang P, et al. Self-assembled 3D MnO$_2$ nanosheets@delaminated-Ti$_3$C$_2$ aerogel as sulfur host for lithium-sulfur battery cathodes. *ACS Appl Energy Mater*. 2018;2(1):705-714.

96. Wang X, Yang C, Xiong X, et al. A robust sulfur host with dual lithium polysulfide immobilization mechanism for long cycle life and high capacity Li-S batteries. *Energy Storage Mater*. 2019;16:344-353.

97. Du C, Wu J, Yang P, Li S, Xu J, Song K. Embedding S@TiO$_2$ nanospheres into MXene layers as high rate cyclability cathodes for lithium-sulfur batteries. *Electrochim Acta*. 2019;295:1067-1074.

98. Gao XT, Xie Y, Zhu XD, et al. Ultrathin MXene nanosheets decorated with TiO$_2$ quantum dots as an efficient sulfur host toward fast and stable Li-S batteries. *Small*. 2018;14(41):1802443.

99. Zhang Y, Mu Z, Yang C, et al. Rational design of MXene/1T-2H MoS$_2$-C nanohybrids for high-performance lithium-sulfur battery. *Adv Funct Mater*. 2018;28(38):1707578.

100. Lv LP, Guo CF, Sun W, Wang Y. Strong surface-bonded sulfur in carbon nanotube bridged hierarchical Mo$_3$C-based MXene nanosheets for lithium-sulfur batteries. *Small*. 2019;15(3):1804338.

101. Zhuang R, Yao S, Shen X, Li T, Qin S, Yang J. Electrosyn $\beta$-Mo$_3$C/CNFs as an efficient sulfur host for rechargeable lithium sulfur battery. *J Mater Sci Mater Electron*. 2019;30(5):4626-4633.

102. Zhou F, Li Z, Luo X, et al. Low cost metal carbide nanocrystals as binding and electrocatalytic sites for high performance Li-S batteries. *Nano Lett*. 2018;18(2):1035-1043.

103. Chen G, Li Y, Zhong W, et al. MOFs-derived porous Mo$_3$C-C nano-octahedrons enable high-performance lithium-sulfur batteries. *Energy Storage Mater*. 2019; in press. https://doi.org/10.1016/j.ensm.2019.09.028.

104. Shi N, Xi B, Feng Z, et al. Strongly coupled W$_3$C atomic nanoclusters on N/P-codoped graphene for kinetically enhanced sulfur host. *Adv Mater Interfaces*. 2019;6(9):1802088.

105. Lei T, Chen W, Hu Y, et al. A nonflammable and thermostolerant separator suppresses polysulfide dissolution for safe and long-cycle lithium-sulfur batteries. *Adv Energy Mater*. 2018;8(32):1802441.

106. Lei T, Chen W, Lv W, et al. Inhibiting polysulfide shuttling with a graphene composite separator for highly robust lithium-sulfur batteries. *Joule*. 2018;2(10):2091-2104.

107. Zhang L, Liu D, Muhammad Z, et al. Single nickel atoms on nitrogen-doped graphene enabling enhanced kinetics of lithium-sulfur batteries. *Adv Mater*. 2019;31(40):1903955.

108. Zhang L, Chen X, Wan F, et al. Enhanced electrochemical kinetics and polysulfide traps of indium nitride for highly stable lithium-sulfur batteries. *ACS Nano*. 2019;12(9):9578-9586.

109. Jin Q, Zhang N, Zhu C, Gao H, Zhang X. Rationally designing S/Ti$_3$C$_2$T$_x$ as a cathode material with an interlayer for high-rate and long-cycle lithium-sulfur batteries. *Nanoscale*. 2018;10(35):16935-16942.

110. Song J, Su D, Xie X, et al. Immobilizing polysulfides with MXene-functionialized separators for stable lithium-sulfur batteries. *ACS Appl Mater Interfaces*. 2016;8(43):29427-29433.

111. Lin C, Zhang W, Wang L, et al. A few-layered Ti$_3$C$_2$ nanosheet/glass fiber composite separator as a lithium polysulfide reservoir for high-performance lithium-sulfur batteries. *J Mater Chem A*. 2016;4(16):5993-5998.

112. Yin L, Xu G, Nie P, Dou H, Zhang X. MXene debris modified eggshell membrane as separator for high-performance lithium-sulfur batteries. *Chem Eng J*. 2018;352:695-703.

113. Li N, Cao W, Liu Y, Ye H, Han K. Impeding polysulfide shuttling with a three-dimensional conductive carbon nanotubes/MXene framework modified separator for highly efficient lithium-sulfur batteries. *Colloids Surf A Physicochem Eng Asp*. 2019;573:128-136.

114. Jiang G, Zheng N, Chen X, et al. In-situ decoration of MOF-derived carbon on nitrogen-doped ultrathin MXene nanosheets to multifunctionalize separators for stable Li-S batteries. *Chem Eng J*. 2019;373:1309-1318.

115. Wang J, Zhai P, Zhao T, et al. Laminar MXene-nafion-modified separator with highly inhibited shuttle effect for long-life lithium-sulfur batteries. *Electrochim Acta*. 2019;320:134558.

116. Li N, Xie Y, Peng S, Xiong X, Han K. Ultra-lightweight Ti$_3$C$_2$T$_x$ MXene modified separator for Li-S batteries: thickness regulation enabled polysulfide inhibition and lithium ion transportation. *J Energy Chem*. 2020;42:116-125.

117. Dong Y, Zheng S, Qin J, et al. All-MXene-based integrated electrode constructed by Ti$_3$C$_2$ nanoribbon framework host and nanosheet interlayer for high-energy-density Li-S batteries. *ACS Nano*. 2018;12(3):2381-2388.

118. Guo D, Ming F, Su H, et al. MXene based self-assembled cathode and antifouling separator for high-rate and dendrite-inhibited Li-S battery. *Nano Energy*. 2019;61:478-485.
119. Jiao L, Zhang C, Geng C, et al. Capture and catalytic conversion of polysulfides by in situ built TiO$_2$-MXene heterostructures for lithium-sulfur batteries. *Adv Energy Mater.* 2019;9(19):1900219.

120. Zhao S, Fang R, Sun Z, et al. A 3D multifunctional architecture for lithium-sulfur batteries with high areal capacity. *Small Methods.* 2019;2(6):1800067.

121. Zeng S, Li X, Zhong H, Chen S, Mai Y. Layered electrodes based on 3D hierarchical porous carbon and conducting polymers for high-performance lithium-sulfur batteries. *Small Methods.* 2019;3(5):1900028.

122. Chen W, Lei T, Lv W, et al. Atomic interlamellar ion path in high sulfur content lithium-montmorillonite host enables high-rate and stable lithium-sulfur battery. *Adv Mater.* 2018;30(40):1804084.

123. Zhao T, Zhai P, Yang Z, et al. Self-supporting Ti$_3$C$_2$Tx foam/S cathodes with high sulfur loading for high-energy-density lithium-sulfur batteries. *Nanoscale.* 2018;10(48):22954-22962.

124. Xiao Z, Yang Z, Li Z, Li P, Wang R. Synchronous gains of areal and volumetric capacities in lithium-sulfur batteries promised by flower-like porous Ti$_3$C$_2$Tx matrix. *ACS Nano.* 2019;13(3):3404-3412.

125. Yao M, Wang R, Zhao Z, Liu Y, Niu Z, Chen J. A flexible all-in-one lithium-sulfur battery. *ACS Nano.* 2018;12(12):12503-12511.

126. Lipatov A, Lu H, Alhabeb M, et al. Elastic properties of 2D Ti$_3$C$_2$Tx MXene monolayers and bilayers. *Sci Adv.* 2018;4(6):eaat0491.

127. Zhao Q, Zhu Q, Miao J, Zhang P, Xu B. 2D MXene nanosheets enable small-sulfur electrodes to be flexible for lithium-sulfur batteries. *Nanoscale.* 2019;11(17):8442-8448.

128. Tang H, Li W, Pan L, et al. In situ formed protective barrier enabled by sulfur@titanium carbide (MXene) ink for achieving high-capacity, long lifetime Li-S batteries. *Adv Sci.* 2018;5(9):1800502.

129. Zhang CJ, Park S-H, Seral-Ascaso A, et al. High capacity silicon anodes enabled by MXene viscous aqueous ink. *Nat Commun.* 2019;10(1):849.

130. Tang H, Li W, Pan L, et al. A robust, freestanding MXene-sulfur conductive paper for long-lifetime Li-S batteries. *Adv Funct Mater.* 2019;29(30):1901907.

**AUTHOR BIOGRAPHIES**

**Chuanfang (John) Zhang** completed his PhD program in East China University of Science and Technology (Shanghai, China) and Drexel University (Philadelphia, PA) in 2015 under the joint supervision of Prof. Yury Gogotsi. In 2015, he joined Trinity College Dublin, Ireland as a research fellow. He joined Empa, ETH Domain in 2019 as a senior scientist, working on the additive manufacturing of printed electronics based on multifunctional two-dimensional crystal inks. He serves as a reviewer for 32 peer-review journals, such as *Nature Comm.*, *Joule*, *JACS*, *EES*, *AM*, *ACS Nano*, *AEnM*, *Small*, *EnSM*, *Nano Energy*, and so forth. He has published ~50 cutting-edge studies on top journals, including Springer Nature (book chapter), *Nature Energy*, *Nature Communications*, *Adv. Mater* (VIP), *Adv. Funct. Mater* (VIP), *ACS Nano*, *Nano Energy*, and so forth. His H-index is 29 with SCI citations >3300. He has given >70 invited talks in universities/major conferences/companies. He was shortlisted 2016 and 2018 Irish Lab Scientist of the Year, Lab Staff Member of the Year and Young Leader of the Year (Ireland). He is the recipient of “2019 Top 10 Chinese Leading Talents in Science and Technology in Europe.”

**Linfan Cui** received her PhD degree in Chemistry from Beijing Institute of Technology under the supervision of Prof. Liangti Qu, in 2019. In 2018, she studied as a visiting PhD in A.J. Drexel Nanomaterials Institute and Department of Materials Science and Engineering at Drexel University under the guidance of Prof. Yury Gogotsi. She is currently a postdoctoral researcher in the Department of Electronics and Nanoengineering (Prof. Harri Lipsanen group), Aalto University, Finland. Her research interests lie in the development of new methods and strategies to synthesize 2D functional materials for various applications.

**Jakob Heier** graduated in physics from Konstanz University (Germany) and received a Ph.D. in Materials Science and Engineering from Cornell University (NY) in 1999. Jakob Heier is group leader in the Laboratory for Functional Polymers at the Swiss Federal Laboratories for Materials Science and Technology (Empa). His research focuses around self-assembly phenomena related to thin film formation from solution. Along this line, he is heading the large-area wet coating and printing activities of Empa’s Coating Competence Center.

**How to cite this article:** Zhang C(J), Cui L, Abdolhossein zadeh S, Heier J. Two-dimensional MXenes for lithium-sulfur batteries. *InfoMat.* 2020; 2:613–638. [https://doi.org/10.1002/inf2.12080](https://doi.org/10.1002/inf2.12080)