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Current trends in MXene research: properties and applications

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A new class of two-dimensional (2D) materials known as MXene became one of the most promising candidates under investigation after the discovery of the first member of this group, $\text{Ti}_3\text{C}_2\text{T}_x$, in 2011. These layered transition metal nitrides, carbonitrides, and carbides have offered an attractive new area in inorganic 2D materials with their fascinating structural and chemical characteristics due to the versatility in elemental compositions and surface terminations. Significantly, the surface hydrophilicity of MXenes facilitates the easy composite formation with carbonaceous materials, polymers, and metal oxides that further opens up an efficient pathway for tuning the characteristics of MXenes for different applications. Despite exponentially increasing interest, MXenes lack proper systematic information. This article is focused on reviewing the most applicable aspects of MXenes including structural features with their relevant characteristics and applicability by describing both experimental and theoretical perspectives. A critical survey on current trends, status, and possibilities of MXenes and MXene-based materials have been represented for energy-related applications as well as electromagnetic interference (EMI) shielding, blends and composites, sensors, organic light-emitting diodes (OLED), and actuators and robotics associated with the limitations and future potentialities.

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1. Introduction

Two-dimensional (2D) materials are being immensely investigated for the past 16 years since the discovery of single-layered graphene with unique chemical and physical properties.¹ One striking thing

about graphene is that its properties are entirely different from the zero-dimensional (0D), one-dimensional (1D), and three-dimensional (3D) allotropes of carbon. The 2D characteristics are quite unique. However, it is required to explore the atypical chemical, physical and electronic properties because of electron caging in two dimensions. Graphene is the most efficient candidate among the carbon-based 2D materials, which have spectacular optical, electronic, thermal, and mechanical properties, quantum hall effect, high specific surface area, elevated carrier mobility, exceptional morphology, and tunable band gap.

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Graphene with these unique properties becomes suitable for diversified applications such as energy storage and conversion, sensing, electronics, optical devices, DNA sequencing, and hybrid materials.^{2–12} Inspired by the mammoth success of graphene research, scientists were further interested in exploring 2D materials beyond graphene. In this aspect, it is significant to notice that the layered metal oxides, transition metal dichalcogenides, layered double hydroxide, graphitic carbon nitride, hexagonal boron nitride, silicene, borophene, and phosphorene are graphene-like materials with multifunctional properties. The common characteristics of these layered 2D materials are the van der Waals interaction, which is involved between two adjacent sheets, as well as a strong covalent bond is also present in each sheet. This category of materials has tunable electronic structure starting from insulator to the semiconductor; even up to the range of metal, which enabled those to be used in versatile applications such as chemical sensor, catalyst, solar cell, supercapacitor, and optoelectronics.¹³

However, a few of these materials as mentioned above exist due to academic interest and a few of them suddenly gained interest due to their magnificent characteristics resulting in practical applications. Among the second type of materials, early group transition metal carbides, nitrides, or carbonitrides, typically called MXenes (uttered as 'maxenes') are a fast-developing class of 2D materials.¹⁴ These types of materials are generally synthesized by the delamination of their corresponding 3D MAX phases. Since its discovery, MXene has exhibited unique but diverse properties. For example, it shows analogous conductivity with that of few-layered graphene.¹⁵ In this aspect, it is essential to note that Khazaei *et al.* reported that, at lower temperatures, semiconducting MXenes can reach very high Seebeck coefficients.¹⁶ According to the density functional theory (DFT) calculation, the in-plane elastic

constant of MXene is above 500 GPa, which means MXene sheets are comparatively stiff.¹⁷ Due to its magnificent properties, MXene has attained enormous attention for its application in various fields such as an efficient electrode material for energy storage¹⁸ and supporting material for metal nanoparticles used as a catalyst in fuel cell.¹⁹ As another example, Wang *et al.* observed that MXene has good enzyme immobilization capability. It is also biocompatible with redox protein, which makes it a potential candidate as an electrochemical biosensor.²⁰ In a word, currently, MXenes are considered one of the hot topics for material scientists worldwide.

This review article focuses on recent developments on MXene and related compounds with different synthesis techniques, properties, and characterization techniques covering both theoretical aspects and experimental studies. We also briefly discuss the applications of MXene and MXene-based composites in various fields, including supercapacitor, secondary batteries, hydrogen storage, fuel cell, solar cell, electromagnetic interference (EMI) shielding, energy harvesting, blends and composites, electro-catalysis, sensors, organic light-emitting diodes (OLED), actuators, and robotics (briefly illustrated in Fig. 1). Besides, the obstacles and future research prospects are also provided for further exploration of this fascinating material.

2. Introduction of MXene

MXene, a novel category of 2D materials with metallic property is prepared by selective elimination of the 'A' layer from the MAX phase using selective etching reagent. MAX phase is stoichiometrically denoted by the formula $M_{n+1}AX_n$, ($n = 1-3$) where 'M' is the prior transition metals including Ti, Sc, V, Zr, Hf, Nb, Mo, Cr, *etc.*, 'A' is the sp elements of 12 to 16 group



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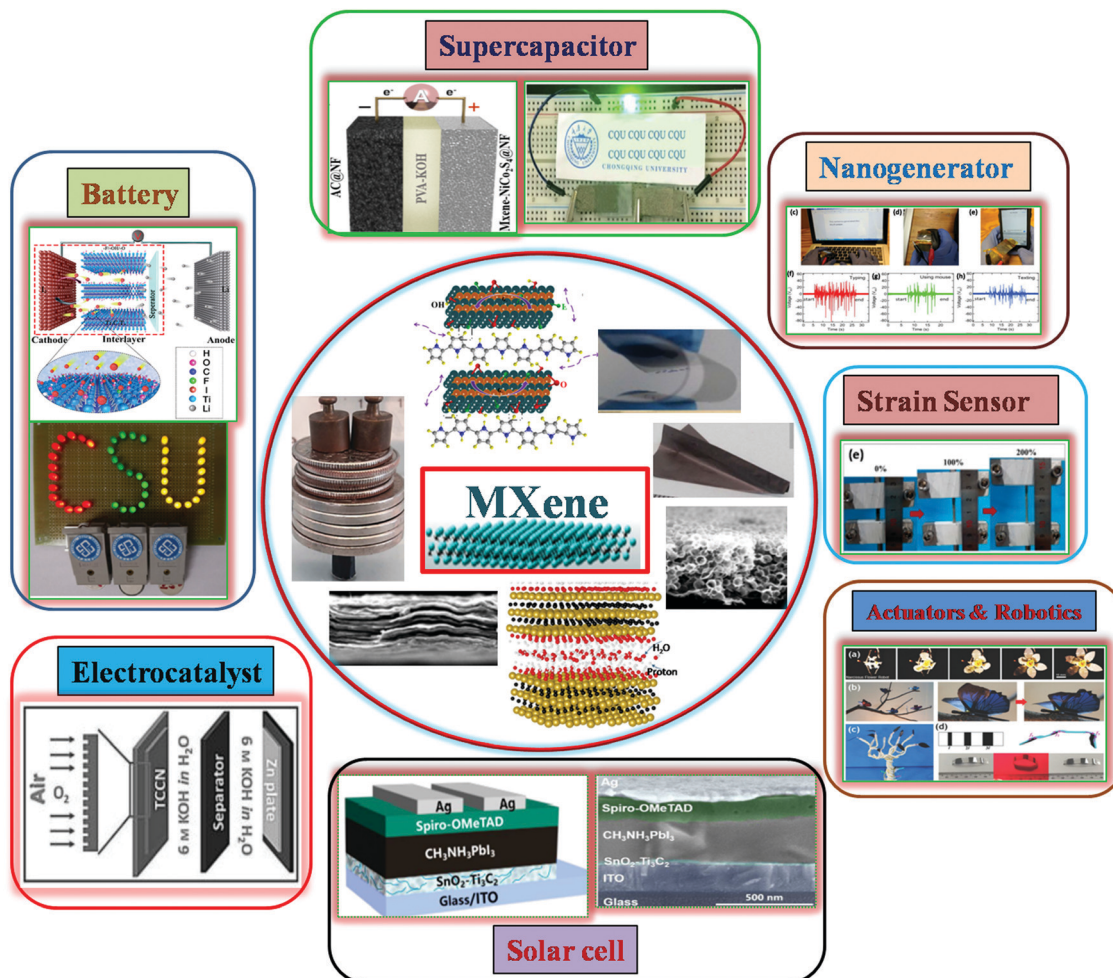


Fig. 1 Schematics representing the progress of the applications of MXene in different fields. Reused with consent from ref. 21–34.

elements such as Al, Ga, Si, P, *etc.*, and 'X' is C, N or both as presented in Fig. 2.^{21,35–38}

MAX phases are constructed with a hexagonal lattice structure with a space group of $P6_3/mmc$, where 'A' atoms are sandwiched between two MX layers. Herein, it is vital to know the crystal structure of MAX phases to explore its distinctive properties. Fig. 3 depicts the crystal structure of MAX phases with n values 1 to 3.²² In general, during the etching method, the 'A' atoms are wiped out from the MAX phase, resulting in a multi-layered MXene, which can be converted to a monolayer by ultrasonication. MXene has a general representation $M_{n+1}X_nT_x$, where T_x is the surface terminal groups including $-OH$, $-F$, or $-O$, from the etching process.³⁹ It is necessary to remember that the 2D MXene layers also have hexagonal structures inherited from the MAX phase. Due to such similarity with graphene, it has been named as MXene.⁴⁰

2.1 Historical development of MXenes and related compounds

In the past two years, MXene-based research work has been remarkably expanded, and over 750 institutes from 50 countries are studying MXene and articles are frequently published in

peer-reviewed journals.³⁸ In 2011, MXene was first synthesized by Gogotsi *et al.* at Drexel University, USA, without any previous prediction about its stability.¹⁴ Till then, above 30 MXene compositions have been established experimentally, as shown in Fig. 4 (labeled in blue). Moreover, dozens of them have also been explored theoretically (labeled in grey in Fig. 4). An exclusive feature of MXenes was discovered when two transition metals were fused in the MXene structure. Also, during the formation of solid solutions such as $(Ti,Nb)CT_x$ (labelled in green in Fig. 4), transition metals can generate an orderly structure in a 2D, a single flake of MXene either by in-plane (for $n = 1$) arranged structure formation such as $(Mo_{2/3}Y_{1/3})_2CT_x$, or atomic sandwich formation of transition metal planes (for $n \geq 2$) such as $Mo_2TiC_2T_x$. Though ordered MXenes were fabricated in 2014, various new MXene subfamily compositions have been developed (labeled in red in Fig. 4).⁴¹ Due to the rush in preparing new ordered MAX phases, around 30 new, 2D double transition metal, ordered MAX phases were reported since 2017, and their magnetic properties were also explored.^{42–44} In Fig. 2(b), the transition metals labeled in blue strips are only reported for the synthesis of MAX phases. Since the last three years, around 100 plausible stoichiometry of MXenes and their precursors have been

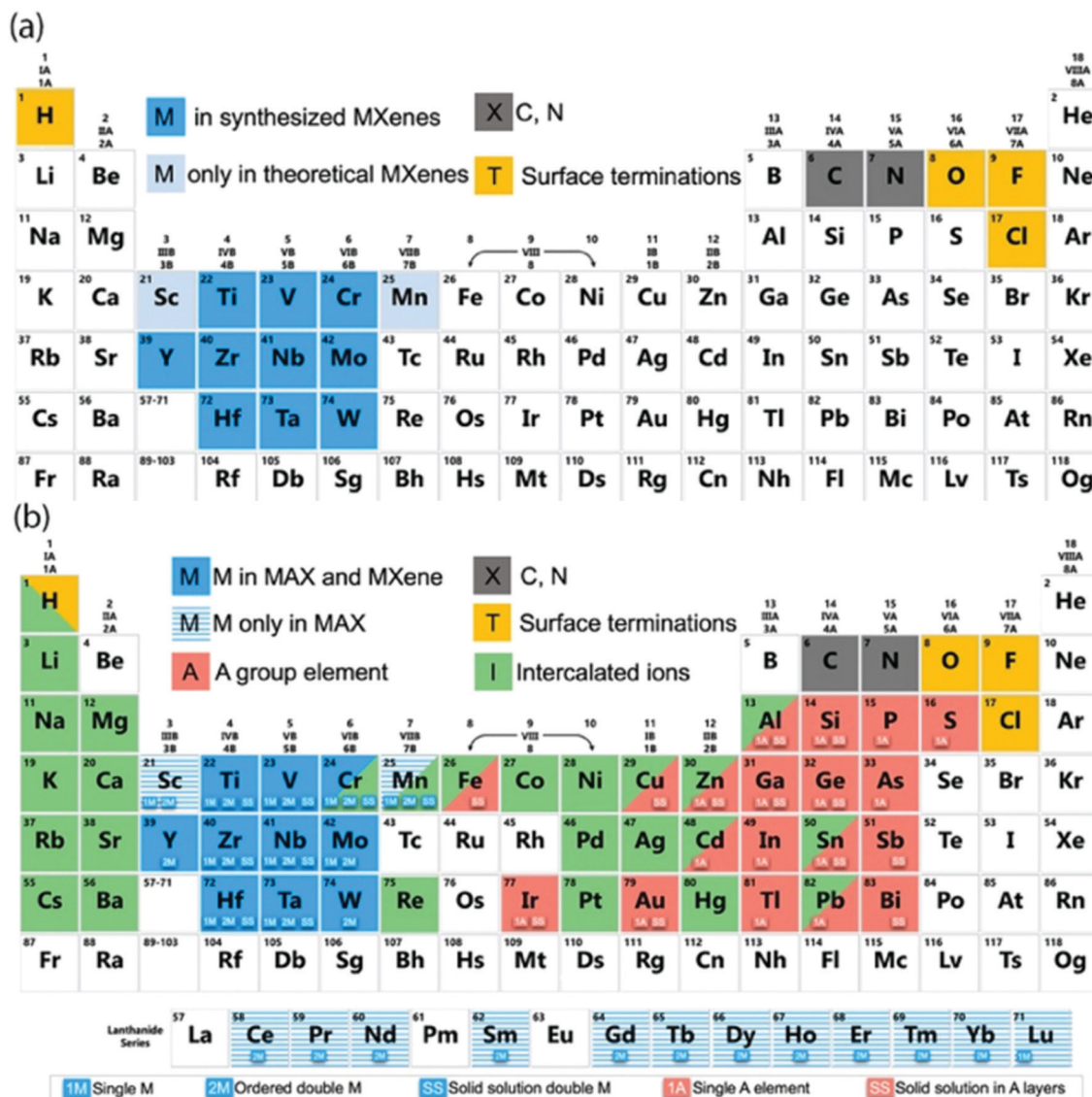


Fig. 2 In periodic table (a) elements utilized for MXene synthesis (experimentally and theoretically), (b) elements employed for MAX phase and MXene synthesis with different variations. Reused with consent from ref. 38. Copyright (2019) American Chemical Society.

established by computational studies.^{44–48} The preparation of solid solution on M or/and X, provides further opportunity to fabricate a huge number of non-stoichiometric MXenes and

accurately tune the features by mixing appropriate transition metals or even developing carbonitrides.

Another critical development observed in the past year is the fluoride-free fabrication of MXene. It is noteworthy that, in most of the initially reported fabrication processes, researchers employed fluoride-containing materials in both aqueous and molten salts for the synthesis of MXenes.²² An electrochemical route for such fluoride-free synthesis of Ti_2CT_x MXene in dilute hydrochloric acid was reported.⁴⁹ On the other hand, Huang *et al.* utilized ZnCl_2 salt to manufacture new MAX phase and fluorine-free MXene in the year 2019.⁵⁰ This method remarkably widens the synthesis process of MXenes, and now researchers can avoid fluoride-containing hazardous chemicals for the fabrication of MXenes. To date, above 70% of the MXene related researches have been aimed at $\text{Ti}_3\text{C}_2\text{T}_x$, which is the foremost discovered MXene.³⁸

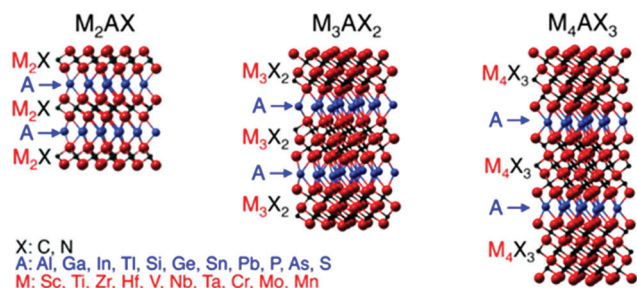


Fig. 3 Crystal structures of M_2AX , M_3AX_2 and M_4AX_3 . Reused with consent from ref. 22.

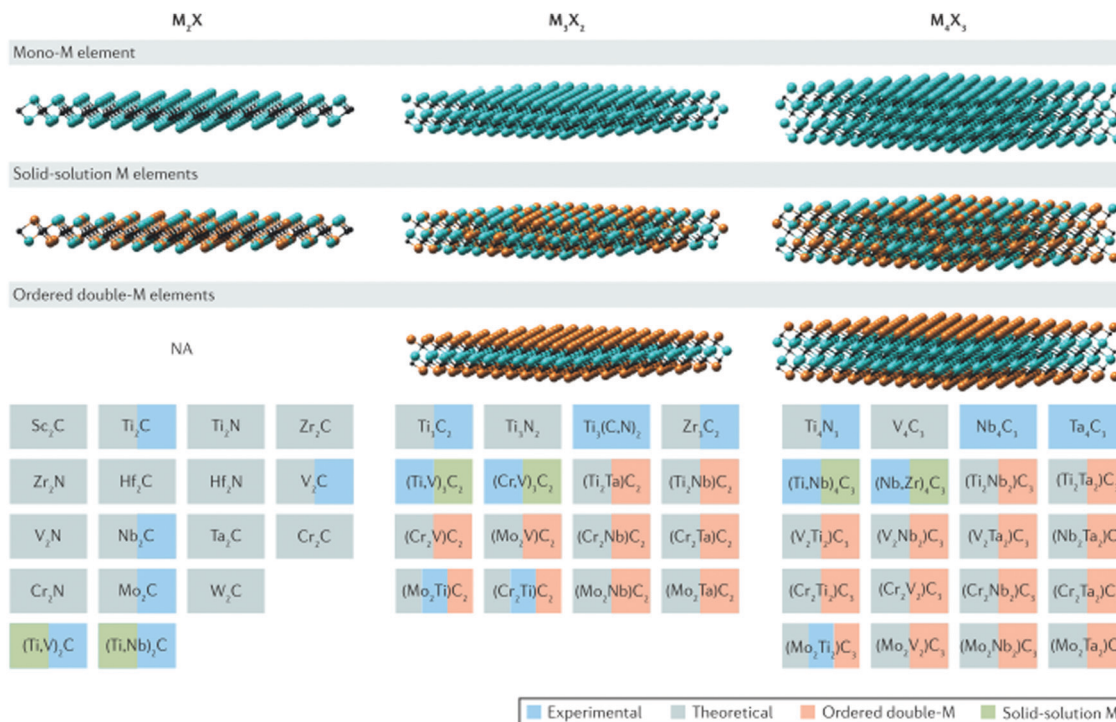


Fig. 4 Crystal structures with examples of three different MXenes: M_2X , M_3X_2 and M_4X_3 in three different conformations: mono M elements, solid solution M elements and ordered double-M elements. (NA – not applicable). Reused with permission from ref. 22.

2.2 Importance of MXenes

MXenes have a unique fusion of properties like high mechanical strength and excellent electrical conductivity of transition metal carbides, nitrides, or carbonitrides. Moreover, the surface functionalization makes MXene sheets hydrophilic and offers easy bond formation with different materials leading to the formation of a stable colloidal solution with water due to high negative zeta potential and capability of outstanding absorption of electromagnetic radiation leading to several applications for MXene. In Fig. 5, different applications of MXenes are represented as a pie chart.³⁸ The year of the first paper publication of each application is exhibited in the second circle of Fig. 5 to understand the recent trend of MXene research. The first reported use of MXene was in energy applications. Even a vast portion of MXene application is based on the energy storage field. However, for the past two years, the biomedical application of MXenes has become an attractive topic, including biosensors, theranostics, photothermal therapy of cancer, neural electrodes, and dialysis.^{38,51} Another hottest topic of MXene research is electromagnetic applications such as printable antennas and electromagnetic interference shielding.⁵² Like structural and electronics applications, most of the reported works are based on theoretical studies rather than a few experimental works. There are some predicted properties like topological insulators and ferromagnetism that are yet to be established experimentally.

2.3 Different types of MAX phases and MXenes

Since the discovery of MXene, over 70 MAX phases are established experimentally. Among them, V_2AlC , Ti_2AlC ,

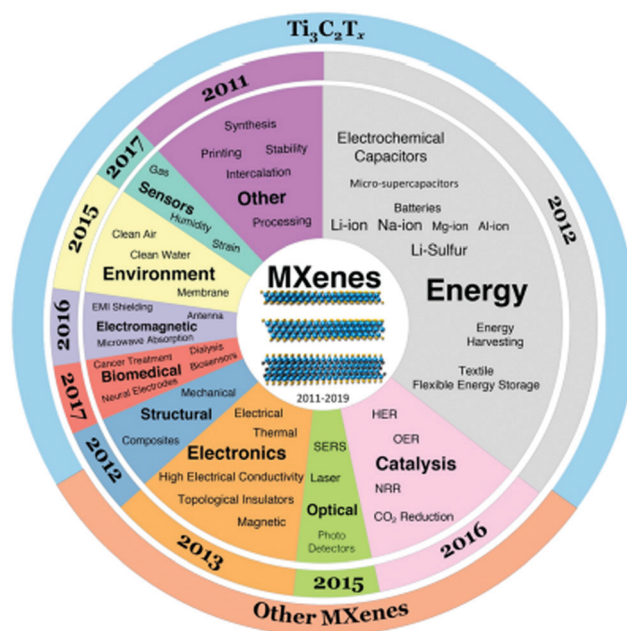


Fig. 5 Pie chart of the previously studied properties and applications of MXene (up to the year of 2017). Reused with permission from ref. 38. Copyright (2019) American Chemical Society.

Nb_2AlC , Ti_2AlN , Ti_3AlC_2 , Zr_3AlC_2 , Ti_3SiC_2 , V_4AlC_3 , Ti_4AlC_3 , Ta_4AlC_3 and Nb_4AlC_3 have been already etched into V_2C , Ti_2C , Nb_2C , Ti_2N , Ti_3C_2 , Zr_3C_2 , V_4C_3 , Ti_4C_3 , Ta_4C_3 and Nb_4C_3 MXenes.^{15,53–59} It is experimentally observed that the solution

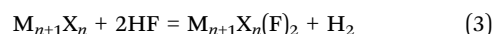
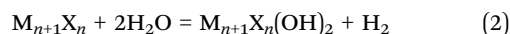
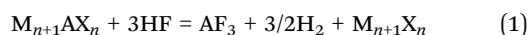
of two transition metals (M' and M'') or 'A' components (A' and A'') or 'X' elements (C and N) leads to the generation of MAX phase alloys and subsequently the formation of different MXene alloys. In this context, it is necessary to mention that the $(\text{Ti}_{0.5}\text{Nb}_{0.5})_2\text{C}$, TiNbC , Ti_3CN , $(\text{V}_{0.5}\text{Cr}_{0.5})_3\text{C}_2$, $(\text{Nb}_{0.8}\text{Zr}_{0.2})_4\text{C}_3$, and $(\text{Nb}_{0.8}\text{Ti}_{0.2})_4\text{C}_3$ alloy MXenes have already been developed experimentally.^{15,60} It has recently been observed that, by choosing proper stoichiometry of M, A, and X elements, two kinds of ordered MAX phases consisting of double transition metals can be prepared, known as iMAX and oMAX phases. The iMAX phases $(M'_{2/3}M''_{1/3})_2\text{AX}$, consist of in-plane ordered double transition metals. In contrast to the oMAX phases and conventional MAX phases, iMAX phases consist of both M' and M'' in every layer of transition metals, as shown in Fig. 6(a–c).⁴⁰ After exfoliation of iMAX phases, the derived MXenes are also called iMXenes, which also consist of two different transition metals in each layer of transition metals (Fig. 6(f)). Among the experimentally synthesized phases, $(M'_{2/3}M''_{1/3})_2\text{AX}$ (where, $M' = \text{Mo}, \text{Cr}, \text{W}$; $M'' = \text{Y}, \text{Sc}$), and $(M'_{2/3}\text{Zr}_{1/3})_2\text{AlC}$ (where, $M' = \text{Cr}, \text{V}$) have been already exfoliated.^{61,62}

Conversely, oMAX phases $(M'_2M''_2)\text{AX}_3$ and $(M'_2M''_2)\text{AX}_2$ are consisting of ordered out-of-plane double transition metals. Fig. 6(b) and (e) show the lattice configuration of $M'_2M''_2\text{AX}_2$ and its corresponding MXene $M'_2M''_2\text{X}_2$ and MXenes consisting of the transition metal M' in the outer layer and M'' in the inner layer.⁴⁰ Among the experimentally prepared oMAX phases, $\text{Cr}_2\text{TiAlC}_2$, $\text{Mo}_2\text{TiAlC}_2$, $\text{Mo}_2\text{ScAlC}_2$ and $\text{Mo}_2\text{Ti}_2\text{AlC}_3$ have already

been exfoliated into Cr_2TiC_2 , Mo_2TiC_2 , Mo_2ScC_2 and $\text{Mo}_2\text{Ti}_2\text{C}_3$ MXenes.^{41,63,64}

2.4 Techniques for MXenes synthesis

The bond strength mainly differentiates the M–X and M–A bonds. In fact, the M–X bond is stronger than the M–A bond.⁶⁵ Thus, the synthesis process of MXenes is based on the removal of weakly bonded 'A' atom layers. Due to this elimination of 'A' layers from MAX phases, this category of 2D carbides, nitrides, and carbonitrides are called MXenes. The pioneering synthesis process used hydrofluoric acid (HF, aq.) to etch $M_{n+1}\text{AX}_n$ (MAX phase) under constant agitation, and the 'A' atoms are replaced by surface terminal groups fluorine (–F), hydroxyl (–OH), oxygen (–O) as depicted in following equations,¹⁵



Herein, eqn (1) shows the removal of 'A' atoms, and eqn (2) and (3) represent the surface terminations with hydroxyl and fluorine, respectively. Later, the presence of oxygen functionalities was also confirmed for MXene.⁶⁶ Precisely, the M–A bonds are replaced by M–OH, M–F, and M–O bonds, and the synthesized MXene consist of multilayered sheets, weakly stacked by the van

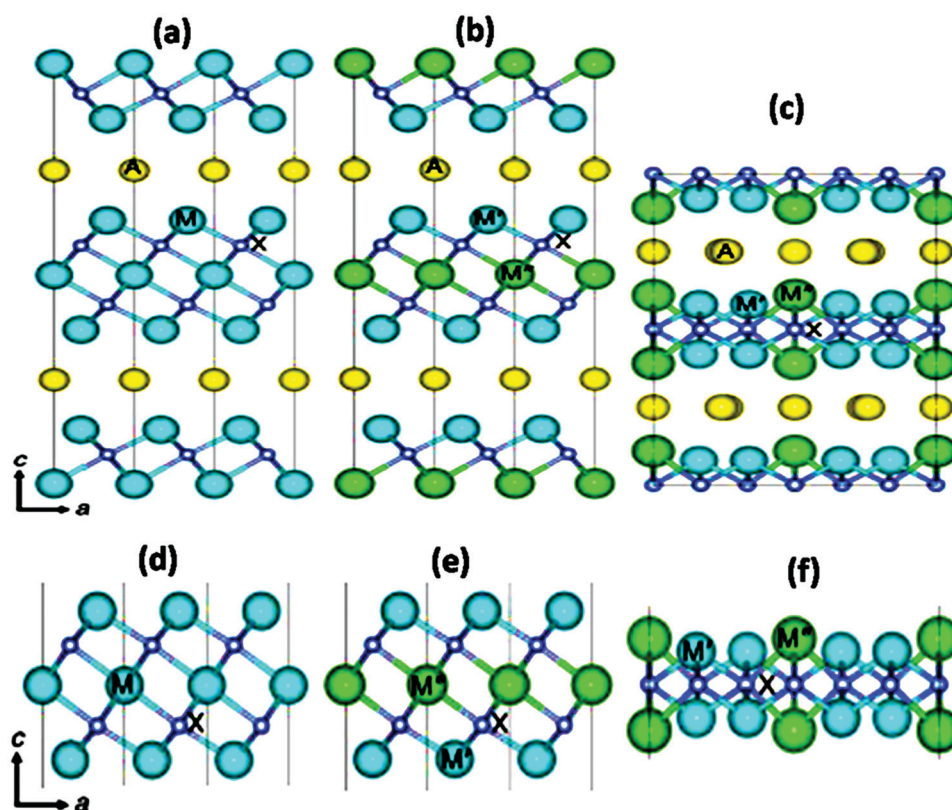


Fig. 6 Crystal structures of (a) $M_3\text{AX}_2$, (b) ordered out of plane double transition metal $M'_2M''_2\text{AX}_2$, (c) double transition metal in the plane $(M'_{2/3}M''_{1/3})_2\text{AX}$, (d) $M_3\text{X}_2$, (e) ordered out of plane double transition metal $M'_2M''_2\text{X}_2$ and (f) double transition metal in the plane $(M'_{2/3}M''_{1/3})_2\text{X}$. Solid lines designate the boundary of unit cells. Reused with permission from ref. 40.

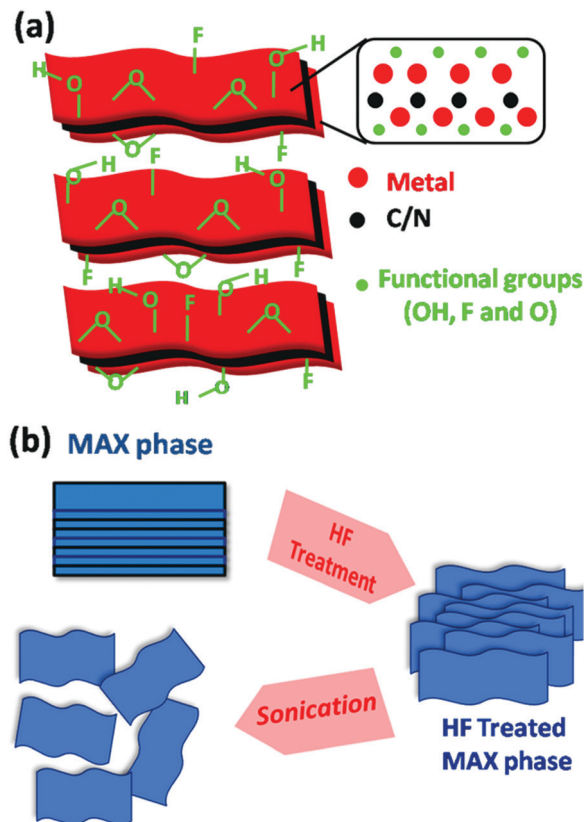


Fig. 7 (a) Surface functionalized MXene and (b) synthesis of MXene from MAX phase.

der Waals force of attraction and can be delaminated into single sheets through ultrasonication,^{67,68} as shown in Fig. 7(b).

According to the experimental observations, with the rising atomic number of M, stronger etching conditions and longer time are required due to the strength of the M–Al bond.³⁹ The XRD patterns before and after the etching of Ti_3AlC_2 with HF are exhibited in Fig. 8(a).

After exfoliation and etching, the terminated MXene has higher thermodynamic stability than its pristine counterpart, and these functional groups mostly affect the physicochemical characteristics of MXene.^{69,70} In recent years, another alternative route for MXene synthesis has also been reported, in which HF is formed *in situ* by using LiF, NaF, or KF along with HCl.³⁶ In this method, the MAX phase is mixed in the solution of fluoride salt and HCl, which leads to the formation of a clay-like product after repeated washing. Finally, this clay-like product can be converted into desired morphologies using different post-processing methods. This method also indicates that fluoride formation is vital for the synthesis of MXene. During fluoride salts' reaction with HCl, the metal ions (Li^+ , Na^+ or K^+) get inserted between the MXene layers and therefore enhance the interlayer distance. This type of metal ion intercalation is not possible when HF is directly used to prepare MXene. Hope *et al.* observed that the LiF–HCl route reduces the defect content of MXene.⁶⁶ Changing the molar ratio from 1.0 Ti_3AlC_2 : 5.0 LiF: 11.7 HCl to 1.0 Ti_3AlC_2 : 7.5 LiF: 23.4 HCl leads to a lesser toxic pathway (known as minimally intensive layer delamination (MILD) process) that was effectively employed for the synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_3CNT_x .^{71,72} Additionally, ammonium fluoride (NH_4F) and ammonium hydrogen bifluoride (NH_4HF_2) have also been efficiently utilized for the fabrication of $\text{Ti}_3\text{C}_2\text{T}_x$ from Ti_3AlC_2 .⁷³

MXene can also be synthesized from non-MAX phase materials. The first reported MXene, which is prepared from

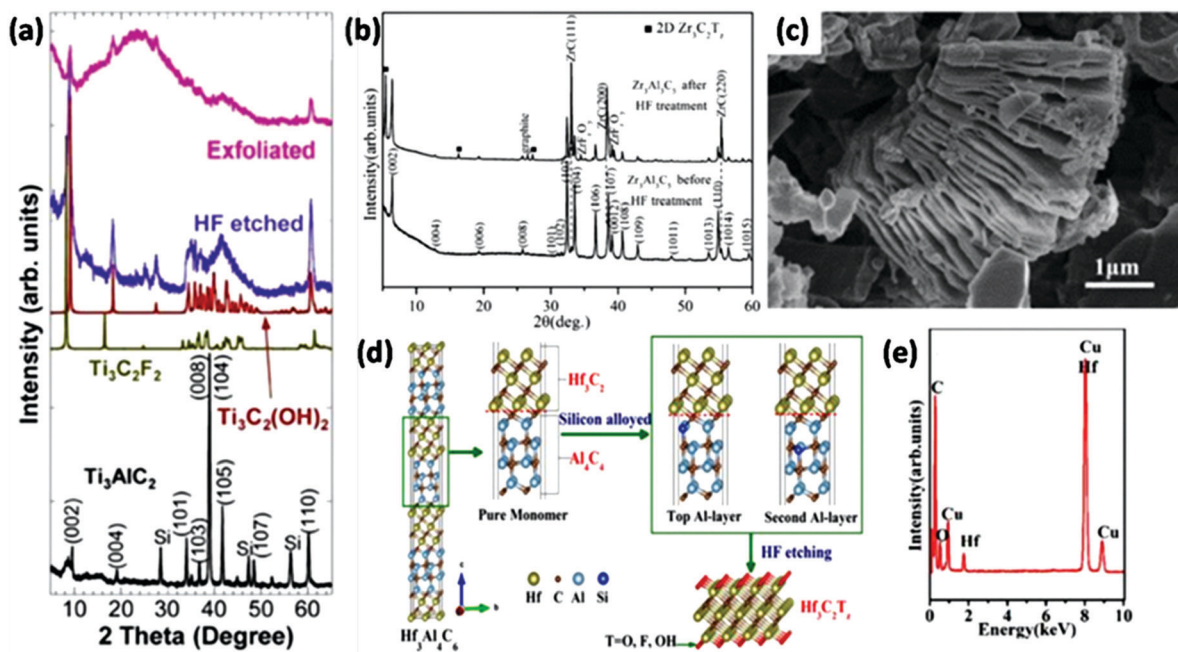


Fig. 8 XRD patterns before and after HF etching of (a) Ti_3AlC_2 and (b) Zr_3AlC_5 , (c) An SEM image of Zr_3AlC_5 after HF etching, (d) diagrammatic representation of $\text{Hf}_3\text{C}_2\text{T}_x$ preparation method, (e) EDS analysis of HF treated $\text{Hf}_3\text{Al}(\text{Si})_4\text{C}_6$. (a) Reused with permission from ref.,¹⁴ (b and c) reused with permission from ref. 55 and (d and e) adapted with permission from ref. 75. Copyright (2017) American Chemical Society.

non-MAX phase precursor $\text{Mo}_2\text{Ga}_2\text{C}$ by removing the Ga layer, is Mo_2CT_x .⁷⁴ Although having similarity with the MAX phase, this material has two 'A' atoms (Ga) layers between the carbide layers. Zhou *et al.* reported recent types of layered compounds $\text{Zr}_3\text{Al}_3\text{C}_5$ and $\text{Hf}_3[\text{Al}(\text{Si})]_4\text{C}_6$, which can be used as the precursor for $\text{Zr}_3\text{C}_2\text{T}_x$ and $\text{Hf}_3\text{C}_2\text{T}_x$ MXenes by eliminating aluminum carbide (Al_3C_3) and $[\text{Al}(\text{Si})\text{C}]_4$ rather than just A layers (Fig. 8b–e).^{55,75}

Another possible method of MXene synthesis is a bottom-up synthesis process like chemical vapor deposition (CVD).⁷⁶ In 2015, ultrathin 2D orthorhombic $\alpha\text{-Mo}_2\text{C}$ crystals having lateral sizes up to 100 μm , were fabricated from methane on a bilayer substrate of a Cu foil kept on a Mo foil by CVD. MXenes prepared using this method are associated with large surface areas and fewer defects.

Currently, a solvothermal method was reported for the fabrication of Nb_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ with a five times larger surface area than that by the HF-method.⁷⁷ As HF and LiF–HCl methods are unsuccessful in synthesizing nitride-based MXene, MAX phase precursor was reacted with molten salt at high temperature to fabricate the first nitride-based MXene in 2016.⁵⁶ Then, a salt-template method was employed by reducing the oxide precursors in ammonia to prepare V_2NT_x and W_2NT_x .⁷⁸ Most recently, Yang *et al.* reported a fluoride-free electrochemical synthesis of Ti_3C_2 MXene using NH_4Cl and tetramethylammonium hydroxide (TMAOH).⁷⁹ Few newly synthesized MXenes are summarized in Table 1.

As multilayered MXene has 2 to 6 fold interlayer interaction, which is stronger than that of MoS_2 and graphite, typical mechanical exfoliation results in the low yield of single layers. Generally, multilayered MXene can be delaminated into single

layers through intercalation with different polar organic molecules like urea, hydrazine, isopropylamine, dimethyl sulphoxide (DMSO), and bigger organic base molecules such as chlorine hydroxide, tetrabutylammonium hydroxide (TBAOH), *n*-butylamine.²²

2.5 Structural features of MXenes

2.5.1 Structural property of MXene sheets. Similar to the MAX phase precursors, 'X' atoms in MXene occupy an octahedral interstitial position, and 'M' atoms are in a closely packed structure. MXenes also has a hexagonal close-packed crystal structure. Fig. 9 shows three possible crystal structures of MXenes: $\text{B}\alpha\text{C}\beta\text{A}\gamma\text{B}-\text{B}\gamma\text{A}\beta\text{C}\alpha\text{B}$ ($\text{M}_4\text{X}_3-\text{M}_4\text{X}_3$), $\text{B}\gamma\text{A}\beta\text{C}-\text{C}\beta\text{A}\gamma\text{B}$ ($\text{M}_3\text{X}_2-\text{M}_3\text{X}_2$), and $\text{B}\gamma\text{A}-\text{A}\gamma\text{B}$ ($\text{M}_2\text{X}-\text{M}_2\text{X}$), where capital Roman and Greek letters represent positions of M and X elements. As a whole, MXene is associated with a hexagonal close-packed crystal structure. The arrangement of the 'M' atom changes from M_2X to M_3X_2 to M_4X_3 . In M_3X_2 and M_4X_3 , M atoms follow the ABCABC arrangement, which is a face-centered cubic stacking, whereas M atoms in M_2X follow the ABABAB arrangement, which is a hexagonal close-packed stacking.

As the fluoride-containing acidic solution is used for MXene synthesis, the MXene surface is functionalized with $-\text{OH}$, $-\text{O}$, and $-\text{F}$ groups. However, the most stable and effective surface termination of such functionalities has not been well-established yet, and it depends on different synthesis pathways and corresponding MAX phases. According to the theoretical study, in some MXenes such as M_2CT_x (where M = Ti, Zr and Hf),⁸⁹ $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{Ti}_4\text{N}_3\text{T}_x$,⁵⁶ $\text{Nb}_4\text{C}_3\text{T}_x$,⁹⁰ the surface functionalization stability follows the trend $-\text{O} > -\text{F} > -\text{OH}$. The $-\text{OH}$ functional group having the lowest stability is due to the substitution of

Table 1 Different synthesis conditions are summarised for the preparation of different MXenes from their precursor MAX phases

MXenes	MAX phase precursors	Etchants	Time (h)	Temperature ($^{\circ}\text{C}$)	Ref.
Ti_2CT_x	Ti_2AlC	10% HF	10	RT	80
$\text{Ti}_3\text{C}_2\text{T}_x$	Ti_3AlC_2	50% HF	2	RT	14
Ti_2NT_x	Ti_2AlN	5% HF	24	RT	57
Ti_3CNT_x	Ti_3AlCN	30% HF	18	RT	15
V_2CT_x	V_2AlC	50% HF	90	RT	81
$(\text{V}_{0.5}\text{Cr}_{0.5})_3\text{C}_2\text{T}_x$	$(\text{V}_{0.5}\text{Cr}_{0.5})_3\text{AlC}_2$	50% HF	69	RT	15
$\text{V}_4\text{C}_3\text{T}_x$	V_4AlC_3	40% HF	165	RT	59
Nb_2AlC	Nb_2CT_x	50% HF	90	RT	53
$\text{Nb}_4\text{C}_3\text{T}_x$	Nb_4AlC_3	50% HF	96	RT	82
$\text{Nb}_{4/3}\text{CT}_x$	$(\text{Nb}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$	48% HF	30	RT	83
$(\text{Ti}_{0.5}\text{Nb}_{0.5})_2\text{CT}_x$	$(\text{Ti}_{0.5}\text{Nb}_{0.5})_2\text{AlC}$	51% HF	28	RT	15
$\text{Mo}_2\text{TiC}_2\text{T}_x$	$\text{Mo}_2\text{TiAlC}_2$	50% HF	48	RT	41
$\text{Mo}_{4/3}\text{CT}_x$	$(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlC}$	48% HF	60	RT	61
$\text{Zr}_3\text{C}_2\text{T}_x$	$\text{Zr}_3\text{Al}_3\text{C}_5$	50% HF	60	RT	55
$\text{W}_{4/3}\text{CT}_x$	$(\text{W}_{2/3}\text{Sc}_{1/3})_2\text{AlC}$	48% HF	30	RT	84
$\text{Hf}_3\text{C}_2\text{T}_x$	$\text{Hf}_3[\text{Al}(\text{Si})]_4\text{C}_6$	35% HF	60	RT	75
Ti_2CT_x	Ti_2AlC	0.9 M LiF + 6 M HCl	15	40	85
$\text{Ti}_3\text{C}_2\text{T}_x$	Ti_3AlC_2	1 M NH_4HF_2	12	80	86
Ti_3CNT_x	Ti_3AlCN	0.66 g LiF + 6 M HCl	12	35	71
$\text{Ti}_3\text{C}_2\text{T}_x$	Ti_3AlC_2	NH_3F	150	24	73
V_2CT_x	V_2AlC	2 g LiF + 40 M HCl	48	90	87
$\text{Ti}_4\text{N}_3\text{T}_x$	Ti_4AlN_3	59% KF + 29% LiF + 12% NaF	0.5	550	58
Mo_2CT_x	$\text{Mo}_2\text{Ga}_2\text{C}$	3 M LiF + 12 M HCl	384	35	88
$\text{Cr}_2\text{TiC}_2\text{T}_x$	$\text{Cr}_2\text{TiAlC}_2$	5 M LiF + 6 M HCl	42	55	42
$(\text{Nb}_{0.8}\text{Zr}_{0.2})_4\text{C}_3\text{T}_x$	$(\text{Nb}_{0.8}\text{Zr}_{0.2})_4\text{AlC}_3$	LiF + 12 M HCl	168	50	60

RT–Room temperature.

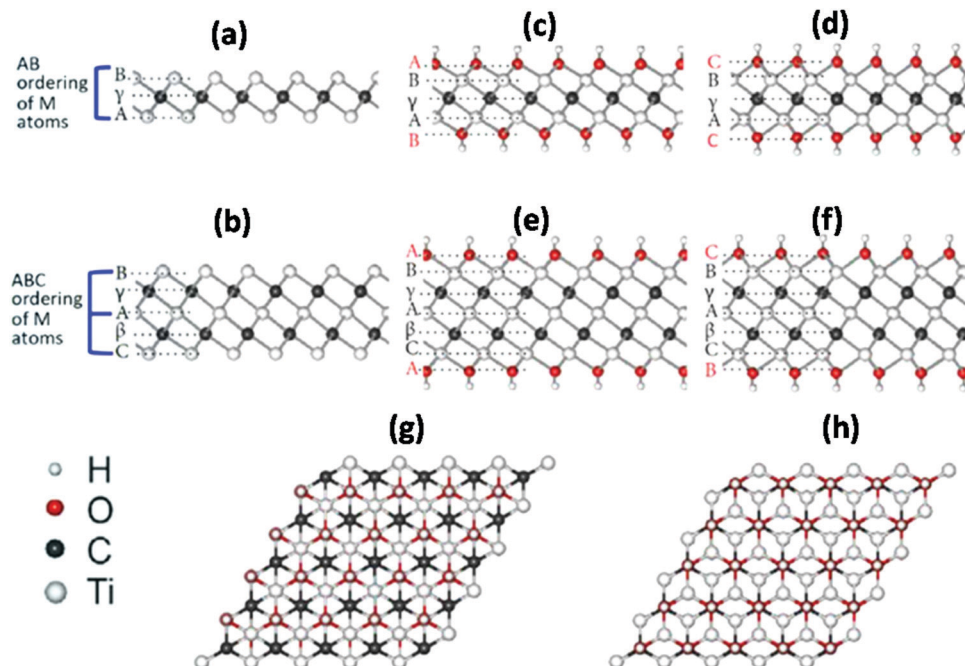


Fig. 9 Atomic structures of freestanding (a) Ti_2C , (b) Ti_3C_2 , (c and d) $\text{Ti}_2\text{C}(\text{OH})_2$ and (e and f) $\text{Ti}_3\text{C}_2(\text{OH})_2$. (c, e and g) $-\text{OH}$ groups remain at the hollow position between three neighbouring carbon atoms and (d, f and h) OH groups remain at the top position of the carbon atoms. (g and h) are top view. Reproduced with permission from ref. 22.

H-atoms by transition or alkali metals, and even at a higher temperature, it is converted to $-\text{O}$ group.⁹¹ According to the experimental report, for HF treatment, the functional group stability order is $-\text{F} > -\text{O} > -\text{OH}$, and for the thermal or LiF-HCl method, the stability order is $-\text{O} > -\text{F} > -\text{OH}$.^{66,92} According to a recent study, the surface terminations of $\text{Ti}_3\text{C}_2\text{T}_x$ and V_2CT_x are randomly distributed on the MXene surface without forming any particular region for a specific functional group.⁶⁶ From the neutron scattering study, it was observed that the interaction between two MXene layers is due to the hydrogen bonding between F/O atoms of one sheet with OH of another sheet of $\text{Ti}_3\text{C}_2\text{T}_x$ and the van der Waals interaction between O and F atoms present in opposite sheets.⁹³

2.5.2 Physical properties. Generally, bare MXenes like $\text{Ti}_{n+1}\text{X}_n$ are metallic in nature. But the metallic property decreases with increasing ' n ' value due to the addition of Ti-N bonds.⁹⁴ On the other hand, metallic property changes upon varying the 'X' atoms. For example, titanium carbide has lower metallic properties than titanium nitride because nitrogen is associated with more electrons than carbon. However, functionalized MXene sheets are metals or narrow band gap semiconductors, based on the type and inclination of the surface groups.^{95,96} Some functionalized MXenes possessing band gaps are Zr_2CO_2 , Sc_2CO_2 , Ti_2CO_2 , Hf_2CO_2 , Sc_2CF_2 , and $\text{Sc}_2\text{C}(\text{OH})_2$. A comparative diagram of predicted band gaps of $-\text{O}$ functionalized MXenes and the effect of the different termination groups on bandgap *via* DFT using HSE06 hybrid functional is shown in Fig. 10.⁹⁷

In recent studies, it was observed that the bandgap of MXene also depends on the material doping⁹⁸ and modulation strain.⁹⁹ For example, the band gap of Sc_2CO_2 decreases from

2.0 to 1.8 eV after doping with niobium atoms. Moreover, under 3% uniaxial strain, the bandgap can be further reduced to 1.4 eV. Additionally, few MXenes are topological insulators such as $\text{Sc}_2\text{C}(\text{OH})_2$, which can be transformed under an applied electric field from trivial to the topological insulator to metal.¹⁰⁰ Also, by changing the C/N ratio, MXene band gaps can be tuned, which was confirmed with $\text{Sc}_3(\text{CN})\text{F}_2$ carbonitride.¹⁰¹

Additionally, the sample synthesis process also affects the electrical conductivity of MXenes. Usually, higher conductivity

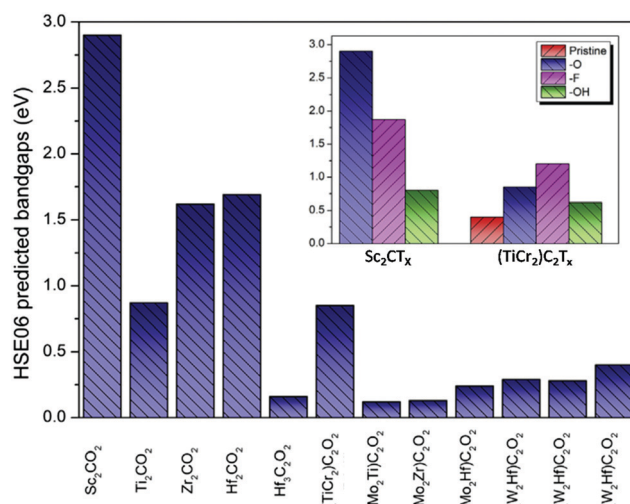


Fig. 10 A comparison of band gaps of oxygen functionalized MXenes. In the inset, the influence of different functional groups on specific compounds. Reused with permission from ref. 97.

is associated with large flake size and low defect concentration, which can be obtained with proper contact between each flake through coplanar alignment,²³ milder etching conditions and sonication-free delaminations,¹⁰² and elimination of the intercalated species between the layers by drying.¹⁰³ For example, the conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ is less than 1000 S cm^{-1} for cold-pressed disks consisting of HF-etched highly defective products.¹⁰³ However, for spin-cast films²³ and milder etched, delaminated vacuum-filtered products,¹⁰² the conductivity reaches 6500 and 4600 S cm^{-1} , respectively. Most interestingly, such electrical conductivity values of $\text{Ti}_3\text{C}_2\text{T}_x$ exceed graphene, too.¹⁰⁴

While estimating the magnetic properties, ferromagnetism and anti-ferromagnetism have been estimated for a few functionalization-free MXenes.^{16,97,105} Among all MXenes, only Cr_2NT_x and Cr_2CT_x have been estimated to have magnetic moments, despite having surface functionalization.^{16,106} Functionalized Cr-MXenes were assumed to be ferromagnetic; on the other hand, Cr_2NT_x and Cr_2CT_x were predicted to be anti-ferromagnetic. However, their magnetic properties are not precise and yet to be characterized.

In general, thin films of MXene and hybrid composites are transparent. More specifically, per nanometer thickness, Ti_3C_2 MXene transmits >97% of visible light²³ (Fig. 11(e and f)), and the optoelectronic characteristics can be monitored by electrochemical or chemical cation intercalation.

Applying the theoretical calculations, the mechanical properties of MXene were investigated considering its composition, layer thickness, and surface functionalization. Fig. 11a and b shows in-plane stiffness and out-of-plane rigidity

of different MXenes with different surface terminations describing their flexibility and elasticity.¹⁰⁷ The flexibility of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene paper was also demonstrated by folding in the shape of the airplane (Fig. 11c). Fig. 11d shows a cylinder of $\text{Ti}_3\text{C}_2\text{T}_x$ paper with thickness $5 \mu\text{m}$, which is capable of supporting ~ 4000 times its own weight.^{22,108} Researchers further strengthened these MXene papers by incorporating 10 wt% polyvinyl alcohol (PVA) with $\text{Ti}_3\text{C}_2\text{T}_x$ to hold ~ 15000 times its weight.

2.5.3 Stability. Individual MXene sheets are not adequately durable in the atmosphere containing oxygen and water.¹⁰⁹ However, MXene flakes are relatively steady in dry air or degassed oxygen-free water. Additionally, the oxidation of colloidal MXene solution gets accelerated in the presence of light. Thus, it is suggested to store MXene in a dark, oxygen-free environment under refrigeration. Usually, the oxidation of MXene flakes initiated from the edges results in nanocrystals of metal oxide (for example, TiO_2) at the flake edges initially and then by nucleation and growth, they developed throughout the entire surface of MXene.^{110–112}

The stability of MXene at high temperatures is based on the composition and environment. The phase stability of MXene can be predicted from the phase diagrams of non-stoichiometric transition metal carbides and nitrides.¹¹³ Currently, it has been observed that in Ar atmosphere, $\text{Ti}_3\text{C}_2\text{T}_x$ is quite stable at 500°C but, few TiO_2 nanocrystals generate on edges.¹¹⁰ Under Ar atmosphere, Ti_3C_2 structure remains intact even at 1200°C , and annealing defect generated. Under He atmosphere, a considerable weight loss of $\text{Ti}_3\text{C}_2\text{T}_x$ over 800°C is observed from mass spectroscopy with temperature-programmed

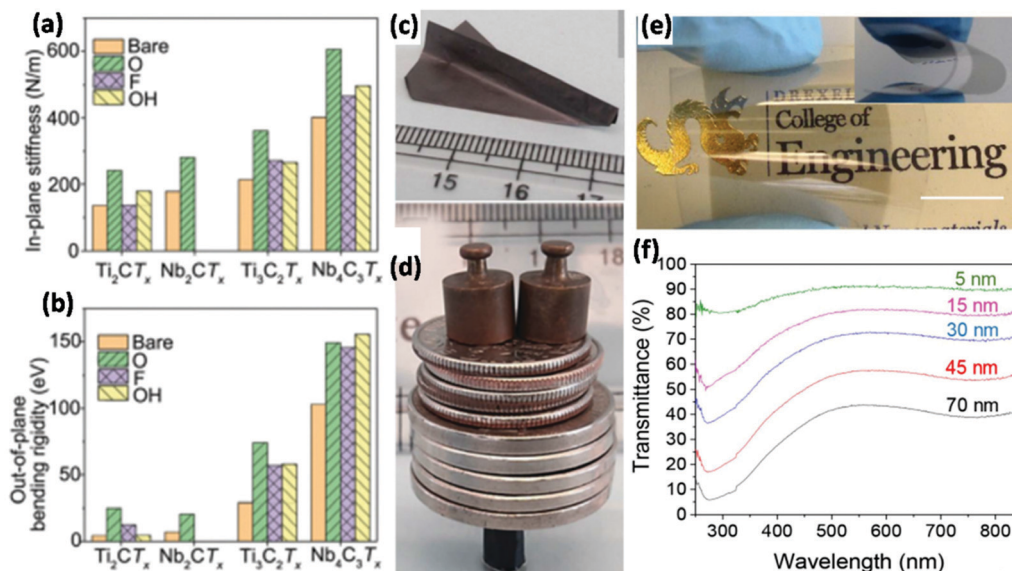


Fig. 11 (a) The in-plane stiffness and (b) the out-of-plane rigidity of different MXenes with different surface terminations, (c) a paper airplane made up by folding a $\text{Ti}_3\text{C}_2\text{T}_x$ film to illustrate its flexibility, (d) a $3.9 \mu\text{m}$ -thick strip of $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVA}$ composite (90 wt%) was folded into a hollow cylinder, which can tolerate about 15000 times its own weight. The loads used were 2.0 g weights, dimes (2.27 g) and nickels (5 g), (e) photograph of $\text{Ti}_3\text{C}_2\text{T}_x$ film, spray-coated on a flexible polyester substrate and the inset exhibits the bending capacity of a $\text{Ti}_3\text{C}_2\text{T}_x$ film on the flexible substrate. The scale bar is 1 cm. (f) UV-visible spectra of spray-coated $\text{Ti}_3\text{C}_2\text{T}_x$ films with changing thicknesses. (a and b) reproduced with permission from ref.,¹⁰⁷ (c and d) reused with permission from ref. 22 and (e and f) reproduced with permission from ref. 23.

desorption.¹¹⁴ It was confirmed from another study that under a different inert atmosphere, Ti_2CT_x is stable at 250 °C.¹¹² In Ar or H_2 atmosphere, Ti_2CT_x was observed to be quite stable at 1100 °C.¹¹⁵ In contrast to $\text{Ti}_3\text{C}_2\text{T}_x$ that converts to cubic carbide at high temperature, $\text{Zr}_3\text{C}_2\text{T}_x$ exhibited sufficient thermal stability and preserved its 2D nature even at 1000 °C temperature. The superior thermal stability of $\text{Zr}_3\text{C}_2\text{T}_x$ can be attributed to its structure, which is energetically more beneficial than bulk ZrC. On the other hand, $\text{Ti}_3\text{C}_2\text{T}_x$ is metastable compared with the bulk cubic TiC.

3. Applications of MXene materials

The versatility of MXene-based materials has gained huge attention in several fields of applications. Their tunable surface properties, electrical conductivity, and high Young's modulus are attractive to composites, and on the other hand, in ion intercalation, tunable bandgap, and chemical stability indicates energy storage and catalysis applications like fuel cell, supercapacitors, batteries, sensing, EMI shielding, OLED, and hydrogen storage.^{22,39,116,117} Among these fields, MXenes have attracted maximum attention in supercapacitor and battery applications. In some of these applications, the performance of MXene is similar or even better than other available materials, such as energy storage

systems^{36,117} and EMI shielding in electronic components and aerospace.^{101,118}

3.1 Supercapacitor

Supercapacitors (SCs) are an alternative to batteries as an energy storage device with a high charging/discharging rate and longer cyclic stability. As per the energy storage mechanism, SCs are categorized into two groups, one is electrical double-layer capacitors (EDLCs), and the other is pseudocapacitors. EDLCs store energy through the generation of an electrical double layer on the electrode surface. Pseudocapacitors reserve energy through redox reactions that take place at or near the electrode surface by specific materials. MXenes, having unique geometry and electronic properties have gained sufficient attention as electrode material for supercapacitors.^{119,120}

3.1.1 Elemental MXene. Recently, Gogotsi *et al.* fabricated two different $\text{Ti}_3\text{C}_2\text{T}_x$ architectures, one is macroporous $\text{Ti}_3\text{C}_2\text{T}_x$, and the other is hydrogel $\text{Ti}_3\text{C}_2\text{T}_x$ for SC applications using H_2SO_4 electrolyte.²⁴ The schematic representation of MXene for electrochemical energy storage application is shown in Fig. 12a, in which a 2D structure with pre-intercalated water ensures quick ion transfer, a conducting transition metal carbide layer enables quick electron transport, and a transition metal oxide-type surface provides a redox activity. The hydrogel $\text{Ti}_3\text{C}_2\text{T}_x$ film (Fig. 12b), having a thickness of 13 μm , provided a volumetric capacitance of 1500 F cm^{-3} at 2 mV s^{-1} (Fig. 12d),

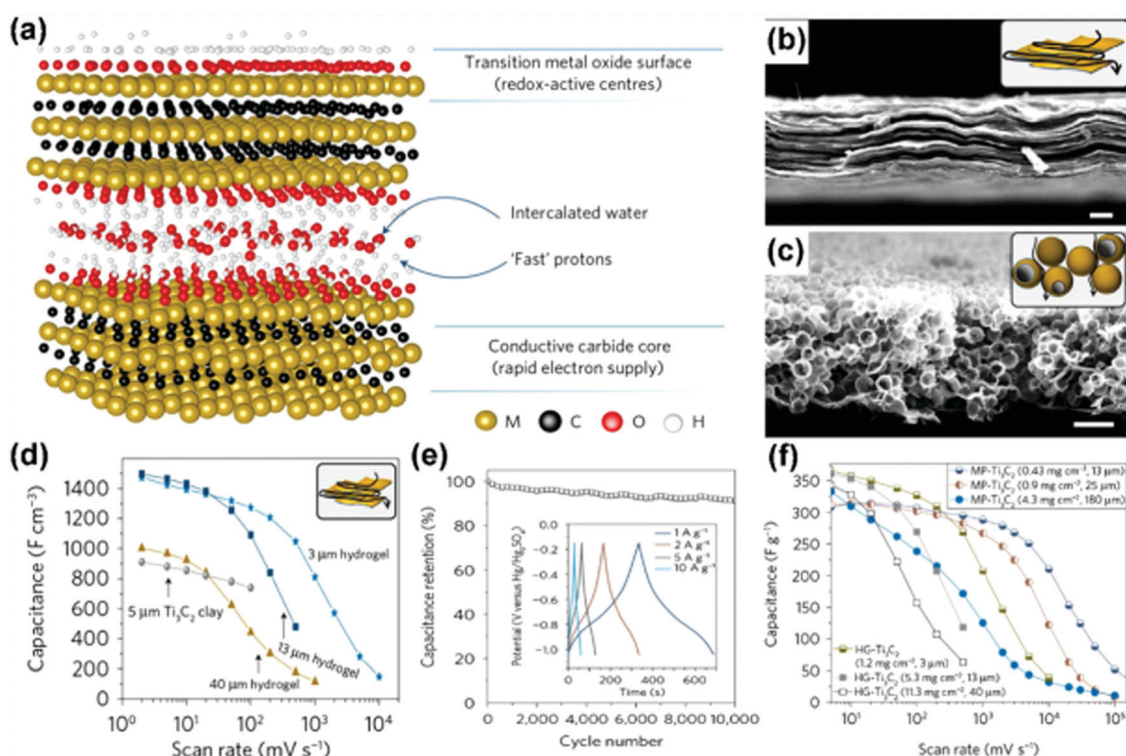


Fig. 12 (a) Diagrammatic representation of MXene configuration, (b) and (c) SEM images of $\text{Ti}_3\text{C}_2\text{T}_x$ hydrogel and macroporous $\text{Ti}_3\text{C}_2\text{T}_x$. Scale bars 5 μm , (d) volumetric capacitance of 3 μm -thick, 13 μm -thick and 40 μm -thick hydrogel film electrode in 3 M H_2SO_4 (mass loadings of 1.2 mg cm^{-2} , 5.3 mg cm^{-2} and 11.3 mg cm^{-2} respectively) comparing the efficiency with the reference of 5 μm -thick 'clay' electrode in 1 M H_2SO_4 , (e) cycling behaviour of a 13 μm hydrogel film at 10 A g^{-1} and (f) rate capability of MXene films varying the synthesis processes and mass loadings. Reused with permission from ref. 24.

with outstanding capacitance retention of 90% after 10 000 cycles (Fig. 12e). Additionally, the macroporous $\text{Ti}_3\text{C}_2\text{T}_x$ film (Fig. 12c) displayed a gravimetric capacitance of 210 F g^{-1} at 10 V s^{-1} (Fig. 12f), surpassing the best-reported carbon material for SCs. It is also important to mention that the capacitive mechanism of MXene is dependent on the choice of the electrolyte. For instance, in acidic electrolytes such as H_2SO_4 , MXene stores the charge *via* surface redox behaviour.²⁴ In organic or aqueous electrolytes, it stores charge *via* the cation (such as Na^+ , K^+ , Li^+ , NH_4^+ , Al^{3+} , Mg^{2+}) intercalation reaction.^{36,121,122}

A 2D V_2CT_x MXene was fabricated as an electrode material for a supercapacitor and its performance was studied in seawater electrolytes. The V_2CT_x MXene electrode delivered a good specific volumetric capacitance of 317.8 F cm^{-3} and gravimetric capacitance of 181.1 F g^{-1} with excellent capacitance retention of 89.1% after 5000 cycles.¹²³ The electrochemical behavior of the V_2CT_x MXene electrode is shown in Fig. 13.

2D tantalum carbide (Ta_4C_3) MXene was prepared by Syamsai *et al.*, which allowed the path for electrolyte ions inside the electrode leading to the enhancement in the electrochemical performance.¹²⁰ In 0.1 M H_2SO_4 electrolyte, the fabricated electrode exhibited a specific capacitance of 481 F g^{-1} at 5 mV s^{-1} with capacitance retention of 89% after 2000 cycles.

3.1.2 MXene composited with carbon materials. Though MXene is associated with several advantages, the self-restacking of MXene sheets limits its electrochemical utilization ratio.¹²⁴

To successfully prevent self-restacking and enhance the electrochemical performance, different materials such as carbonaceous materials, polymers and metal oxides have been used to form a hybrid composite with MXene.^{125,126} Gogotsi *et al.* fabricated a flexible SC electrode with MXene/RGO composite in which nanosheets of RGO were inserted into MXene layers through electrostatic interaction.¹²⁵ The limitation of self-restacking was effectively prevented, leading to a higher number of electrochemical active positions. The flexible freestanding MXene/RGO-5 wt% electrode displayed a volumetric capacitance of 1040 F cm^{-3} at 2 mV s^{-1} . Additionally, in aqueous electrolytes, the assembled symmetric SC showed an outstanding energy density of 32.6 W h L^{-1} , and that was the largest reported value of MXene and carbon materials.

The electrochemical performance of Nb_2CT_x was studied for the first time in an aqueous electrolyte, and after incorporation of CNTs as conducting material, the rate performance of the composite electrode enhanced significantly.²⁴ The asymmetric supercapacitor fabricated with activated carbon as a positive electrode and Nb_2CT_x -CNT as a negative electrode delivered the highest energy and power density of $154.1 \mu\text{W h cm}^{-2}$ and $74843.1 \mu\text{W cm}^{-2}$, respectively. In a three-electrode electrochemical setup, Nb_2CT_x -CNT provided a specific capacitance of 202 F g^{-1} , in an aqueous electrolyte, while in another study, $\text{Ti}_3\text{C}_2\text{T}_x$ -CNT showed capacitance of 245 F cm^{-3} , in an organic electrolyte.¹²⁶ In a recent study, a stretchable supercapacitor electrode was fabricated with $\text{Ti}_3\text{C}_2\text{T}_x$ -reduced graphene oxide

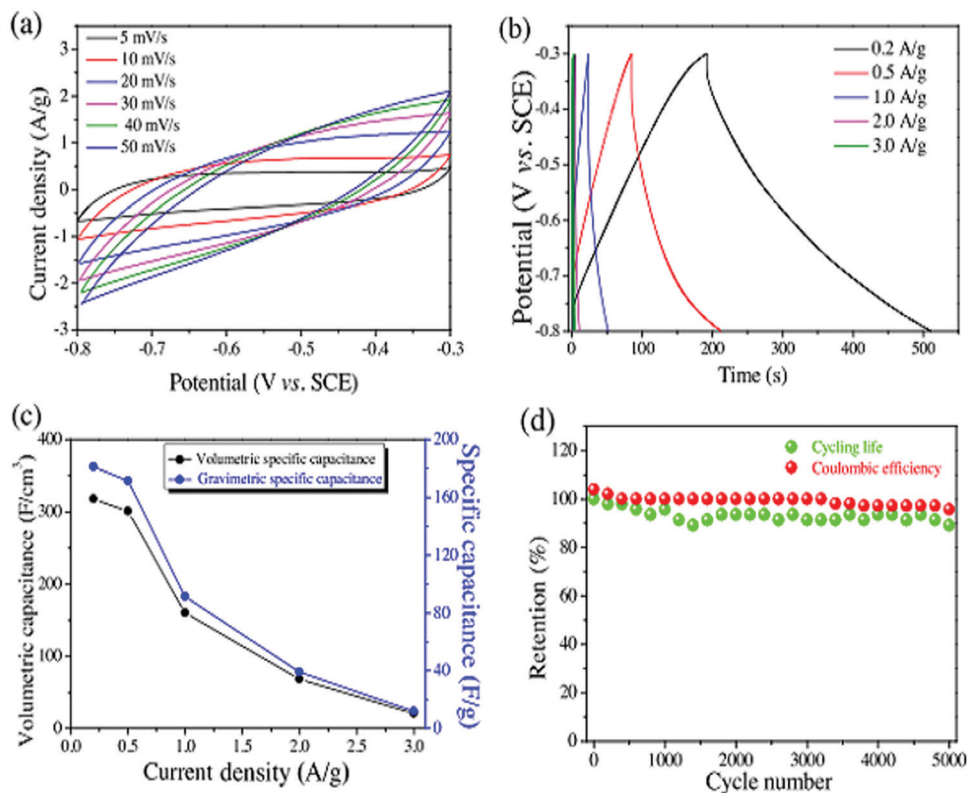


Fig. 13 Electrochemical performance of V_2CT_x electrode (a) cyclic voltammetry, (b) gravimetric charging-discharging, (c) a comparison of specific volumetric and gravimetric capacitance and (d) coulombic efficiency and cyclic stability at 2 A g^{-1} . Reproduced with permission from ref. 123.

nanocomposite and the assembled symmetric supercapacitor device delivered a specific capacitance of 18.6 mF cm^{-2} as well as up to 300% stretchability.¹²⁷

3.1.3 MXene composited with polymers. To increase the efficiency of MXene, polymers, including polyaniline (PANI) or polypyrrole (PPy) have also been incorporated. A freestanding hybrid $\text{Ti}_3\text{C}_2\text{T}_x/\text{PANI}$ electrode displayed an enhanced pseudo-capacitive behaviour than pristine $\text{Ti}_3\text{C}_2\text{T}_x$ with a large specific capacitance of 503 F g^{-1} .¹²⁸ In another study, Wu *et al.* revealed that the insertion of PPy chains inside the Ti_3C_2 MXene layers increases interlayer spacing and facilitates the diffusion for electrolyte ions and the charge transfer, resulting in an enhancement in specific capacitance.²⁵ The electrochemical performance of a novel organ-like $\text{Ti}_3\text{C}_2/\text{PPy}$ composite electrode with different mass ratios of Ti_3C_2 and PPy is illustrated in Fig. 14. The highest specific capacitance of 184.36 F g^{-1} was delivered by the nanocomposite electrode at a 2 mV s^{-1} scan rate with 83.33% retention of specific capacitance after 4000 cycles at 1 A g^{-1} .

3.1.4 MXene composited with metal oxides. The hybrid composites of MXene with mixed metal sulfide²⁶ and layered double hydroxide (LDH)²⁷ provided excellent performance as supercapacitor electrode materials. A homogeneous deposition of NiCo_2S_4 over the $\text{Ti}_3\text{C}_2\text{T}_x$ sheets on nickel foam was fabricated as a binder-free electrode material for a supercapacitor and delivered around six times enhancement of the specific capacity from 106.34 C g^{-1} to 596.69 C g^{-1} at 1 A g^{-1} than NiCo_2S_4 nanoflakes.²⁶ Fig. 15(a) shows the schematic diagram of the

assembled asymmetric supercapacitor (ASC) device, and Fig. 15(b–e) shows the ASC cell lighting up a red LED. In another study, porous 3D NiFe-LDH/MXene electrode delivered enhanced specific capacitance of 720.2 F g^{-1} than NiFe-LDH nanosheets (465 F g^{-1}).²⁷ At different current densities, the specific capacitances of 60 mg loaded NiFe-LDH/MXene ASC device are exhibited in Fig. 15(f), and the digital photograph of powering up a green LED by the ASC device is shown in Fig. 15(g). A few applications of MXene-based materials for supercapacitor are summarized in Table 2.

3.2 Secondary batteries

3.2.1 Li-ion battery. Li-ion batteries (LIBs) have been extensively utilized in transportable electronic gadgets because of their large energy density and sufficient cyclic life. For advanced development in efficiency, it is crucial to introduce the latest and efficient electrode materials for LIBs.

3.2.1.1 Elemental MXene. After the discovery of MXene, it was first studied as an anode material in LIBs. For example, the theoretical capacity of Li intercalated bare Ti_3C_2 was predicted as 320 mA h g^{-1} by Xie *et al.*¹³⁸ But, the existence of $-\text{F}$ or $-\text{OH}$ surface terminations reduces the Li-ion storage capability. Tang *et al.* had shown the capacity for $\text{Ti}_3\text{C}_2(\text{OH})_2$ was only 67 mA h g^{-1} and for $\text{Ti}_3\text{C}_2\text{F}_2$ was 130 mA h g^{-1} .⁹⁵ A novel, H_2O_2 assisted, oxidized V_2CT_x was studied as an anode material for Li-ion batteries, and the oxidized V_2CT_x displayed enhanced electrochemical behavior with 125 mA h g^{-1} at 1000 mA g^{-1}

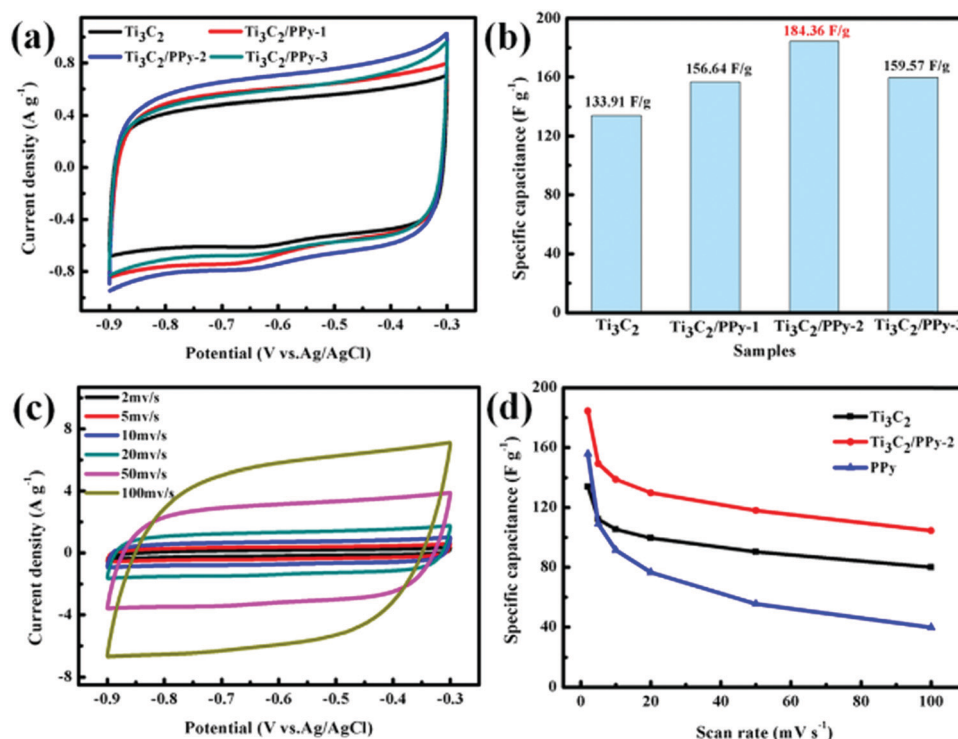


Fig. 14 (a) Cyclic voltammogram curves of Ti_3C_2 and $\text{Ti}_3\text{C}_2/\text{PPy}$ composites were compared at 10 mV s^{-1} scan rate, (b) specific capacitance of Ti_3C_2 and $\text{Ti}_3\text{C}_2/\text{PPy}$ composites were compared at 2 mV s^{-1} scan rate, (c) CV curves of $\text{Ti}_3\text{C}_2/\text{PPy-2}$ composite electrode with varying scan rates and (d) specific capacitance of Ti_3C_2 , $\text{Ti}_3\text{C}_2/\text{PPy-2}$ and PPy electrode at scan rates from 2–100 mV s^{-1} . Reused with permission from ref. 25.

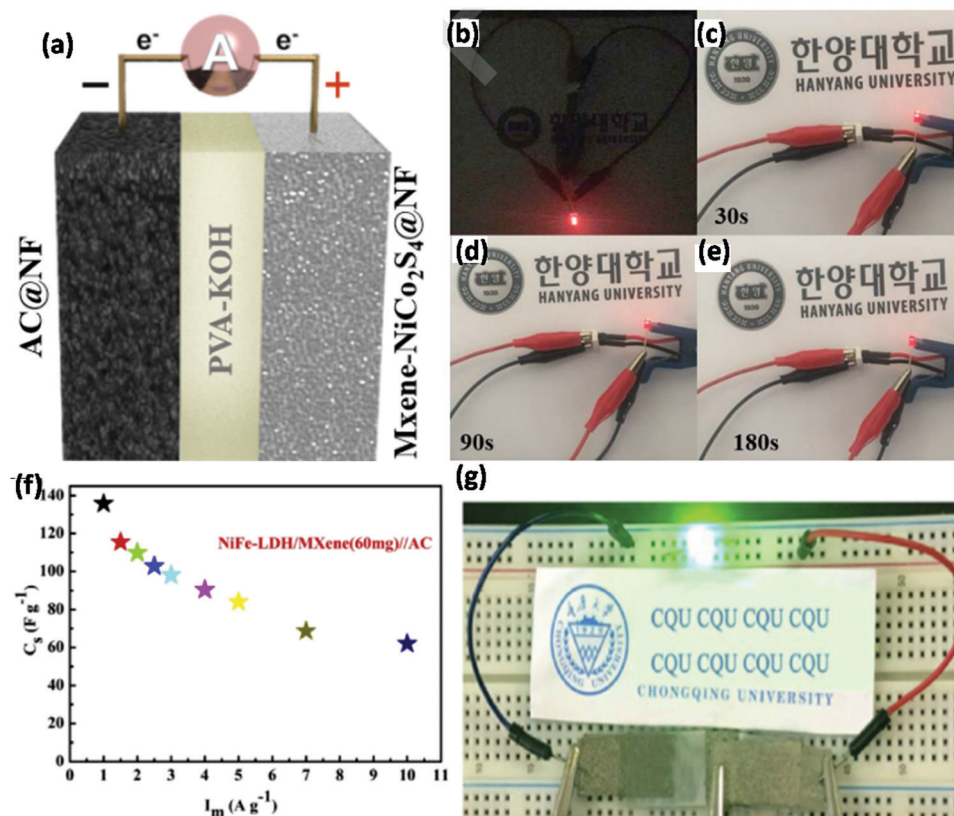


Fig. 15 Asymmetric device performance of $\text{Ti}_3\text{C}_2\text{T}_x\text{-NiCo}_2\text{S}_4\text{@NF}$ (a) schematic representation of the assembled asymmetric device, (b–e) digital photograph of the cell lighting up a red LED. Asymmetric device performance of NiFe–LDH/MXene (f) at various current densities the specific capacitance of the assembled device and (g) photograph of lighting up a green LED by the device. (a–e) reused with permission from ref. 26 and (f and g) reused with permission from ref. 27.

after 1000 cycles and 318 mA h g^{-1} at 100 mA g^{-1} after 100 cycles with a superior rate performance as well as excellent cyclic stability.¹³⁹

Other types of MXene materials, in addition to the most studied titanium carbides, have also shown promising performances in LIBs. Yu *et al.* used a complex MXene Ta_xC_y ($x = 2$ and $y = 1$, or $x = 1$ and $y = 1\text{--}4$) as an anode material in LIBs and also explored their stabilities and frameworks.¹⁴⁰ A new type of nitrogen-incorporated Nb_2CT_x MXene was prepared by Liu *et al.* as an efficient anode material for Li-ion batteries through the hydrothermal treatment with urea (Fig. 16a), leading to the increment in the d-spacing in Nb_2CT_x MXene.¹⁴¹ The N-doped Nb_2CT_x displayed excellent cyclic stability of 288 mA h g^{-1} at 0.5 C after 1500 cycles and a much higher reversible capacity of 360 mA h g^{-1} at 0.2 C than Nb_2CT_x without doping (Fig. 16b and c). Another type of MXene $\text{Hf}_3\text{C}_2\text{T}_x$ used for LIBs, which was fabricated from $\text{Hf}_3[\text{Al}(\text{Si})_4\text{C}_6]$ showed an excellent reversible volumetric capacity of $1567 \text{ mA h cm}^{-3}$ at 200 mA g^{-1} after 200 cycles.⁷⁵

3.2.1.2 MXene composited with carbon materials. A systematic study of the electrochemical characteristics of Ti_2CT_x /graphene heterostructure using first-principles theory revealed that the incorporation of graphene eliminates the restacking problems of MXene as well as increases the Li adsorption capability,

electrical conductivity and mechanical strength.¹⁴² It was proposed that Ti_2CO_2 /graphene composite could be the most favorable member with excellent performance for future MXene based materials. Later, Li *et al.* experimentally fabricated a 3D spring-roll like Ti_3C_2 /carbon wrapped Fe_3O_4 hybrid composite for Li-ion batteries as the anode material to achieve a long cyclic performance of Fe_3O_4 and get rid of intrinsic limits.¹⁴³ The hybrid composite provided 997 mA h g^{-1} reversible capacity at 1 A g^{-1} after 2000 cycles and the capacity retention was 543 mA h g^{-1} at 5 A g^{-1} .

Currently, Wu *et al.* used an east carbon nanoplate method to fabricate $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{-MXene@C}$ composite and this nanocomposite exhibited an enhanced discharge capacity of 1750 mA h g^{-1} at 0.2 A g^{-1} .¹⁴⁴ The $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{-MXene@C}$ composite showed adequate rate performance and reversible capacity of 1200 mA h g^{-1} at 1 A g^{-1} after 700 cycles. To enhance the battery potential, Gogotsi *et al.* introduced $\text{Ti}_3\text{C}_2\text{T}_x\text{-CNT}$ paper electrode as a cathode, dendrite-free Mg metal as an anode and a dual-salt electrolyte containing Mg^{2+} and Li^+ .¹⁴⁵ This flexible $\text{Ti}_3\text{C}_2\text{T}_x\text{-CNT}$ free-standing electrode displayed around 100 mA h g^{-1} at 0.1 C and around 50 mA h g^{-1} at 10 C .

3.2.1.3 MXene composited with metal or metal oxides. The fabrication of nanocomposites with interrelated characteristics

Table 2 Summary of the applications of MXene-based materials for supercapacitor applications

MXene-based electrode material	Specific capacitance	Electrolyte	Cyclic life	Device	Specific capacitance	Cyclic life	Energy density	Ref.
Nb ₂ CT _x /CNT	202 F g ⁻¹ at 2 mV s ⁻¹	1 M H ₂ SO ₄	80.3% after 5000 cycles	5000 AC/Nb ₂ CT _x /CNT	462.0 mF cm ⁻² at 2 mV s ⁻¹	73.3% after 2000 cycles	154.1 μW h cm ⁻²	124
Modified-Ti ₃ C ₂ T _x by annealing	442 F g ⁻¹ at 0.5 A g ⁻¹	1 M H ₂ SO ₄	95.4% after 5000 cycles	Modified-Ti ₃ C ₂ T _x //Modified-Ti ₃ C ₂ T _x	223 F g ⁻¹ at 0.5 A g ⁻¹		15.2 W h L ⁻¹	119
V ₄ C ₃	330 F g ⁻¹ at 5 mV s ⁻¹	1 M H ₂ SO ₄	90% after 3000 cycles					129
Ti ₃ C ₂ T _x -NiCo ₂ S ₄ @Nickel Foam	596.69 C g ⁻¹ at 1 A g ⁻¹	3 M KOH	80.4% after 3000 cycles	Ti ₃ C ₂ T _x -NiCo ₂ S ₄ @NF//AC@NF			27.24 W h kg ⁻¹	26
Ni _{1.5} Co _{1.5} S ₄ @Ti ₃ C ₂ NiFe-LDH/MXene	166 mA h g ⁻¹ at 1 A g ⁻¹ 720.2 F g ⁻¹ at 1 A g ⁻¹	2 M KOH 1 M KOH	86% after 1000 cycles	Ni _{1.5} Co _{1.5} S ₄ @Ti ₃ C//AC NiFe-LDH/MXene//AC	140 F g ⁻¹ at 1 A g ⁻¹ 135.7 F g ⁻¹ at 1 A g ⁻¹	90% after 8000 cycles	49.8 W h kg ⁻¹ 42.4 W h kg ⁻¹	130 27
Ti ₃ C ₂ T _x -RGO	140 F g ⁻¹ at 0.5 A g ⁻¹	1 M H ₂ SO ₄	-	Ti ₃ C ₂ T _x -RGO//Ti ₃ C ₂ T _x -RGO	29 F g ⁻¹ at 0.1 A g ⁻¹	85% after 10000 cycles		127
Ti ₃ C ₂ /CuS	169.5 C g ⁻¹ at 1 A g ⁻¹	1 M KOH	90.5% after 5000 cycles	Ti ₃ C ₂ /CuS//Ti ₃ C ₂	49.3 F g ⁻¹ at 1 A g ⁻¹	82.4% after 5000 cycles	15.4 W h kg ⁻¹	131
MXene/CoS ₂	1320 F g ⁻¹ at 1 A g ⁻¹	2 M KOH	78.4% after 3000 cycles	MXene/CoS ₂ //rGO	80.6 F g ⁻¹ at 1 A g ⁻¹	98% after 5000 cycles	28.8 W h kg ⁻¹	132
rGO/Ti ₃ C ₂ T _x	405 F g ⁻¹	60 M KOH		rGO/Ti ₃ C ₂ T _x //rGO/ Ti ₃ C ₂ T _x	148.5 F g ⁻¹ at 0.2 A g ⁻¹	100% after 10000 cycles	63 mW h cm ⁻³	133
Ti ₃ C ₂ T _x /PANI	503 F g ⁻¹ at 2 mV s ⁻¹	3 M H ₂ SO ₄	98.3% after 10000 cycles	Ti ₃ C ₂ T _x /PANI//Ti ₃ C ₂ T _x /PANI	575 F cm ⁻³ at 2 mV s ⁻¹		79.8 W h L ⁻¹	128
Ti ₃ C ₂ T _x /CF	401 F g ⁻¹ at 10 mV s ⁻¹	1 M H ₂ SO ₄	98% after 20000 cycles	RuO ₂ /CF//Ti ₃ C ₂ T _x /CF	93 F g ⁻¹ at 10 mV s ⁻¹	86% after 20000 cycles	29 W h kg ⁻¹	134
N-Ti ₃ C ₂ T _x	192 F g ⁻¹ at 1 mV s ⁻¹	1 M H ₂ SO ₄	92% after 10000 cycles					135
BiOCl/Ti ₃ C ₂ T _x	396.5 F cm ⁻³ at 1 A g ⁻¹	1 M KOH	95.2% after 5000 cycles	BiOCl/Ti ₃ C ₂ T _x //BiOCl/ Ti ₃ C ₂ T _x	64.3 F cm ⁻³ at 0.5 A g ⁻¹	85% after 5000 cycles	15.2 W h kg ⁻¹	136
NiO/derived-TiO ₂ /C-Ti ₃ C ₂ T _x	92.0 mA h cm ⁻³ at 1 A g ⁻¹	1 M KOH	70.4% after 5000 cycles	NiO/derived-TiO ₂ /C-Ti ₃ C ₂ T _x	4.7 mA h g ⁻¹ at 0.1 A g ⁻¹	72.1% after 5000 cycles	1.04 × 10 ⁻² W h cm ⁻³	137

AC-activated carbon; CNT-carbon nanotube; NF-nickel foam; rGO-reduced graphene oxide; PANI-polyaniline; CF-carbon fabric.

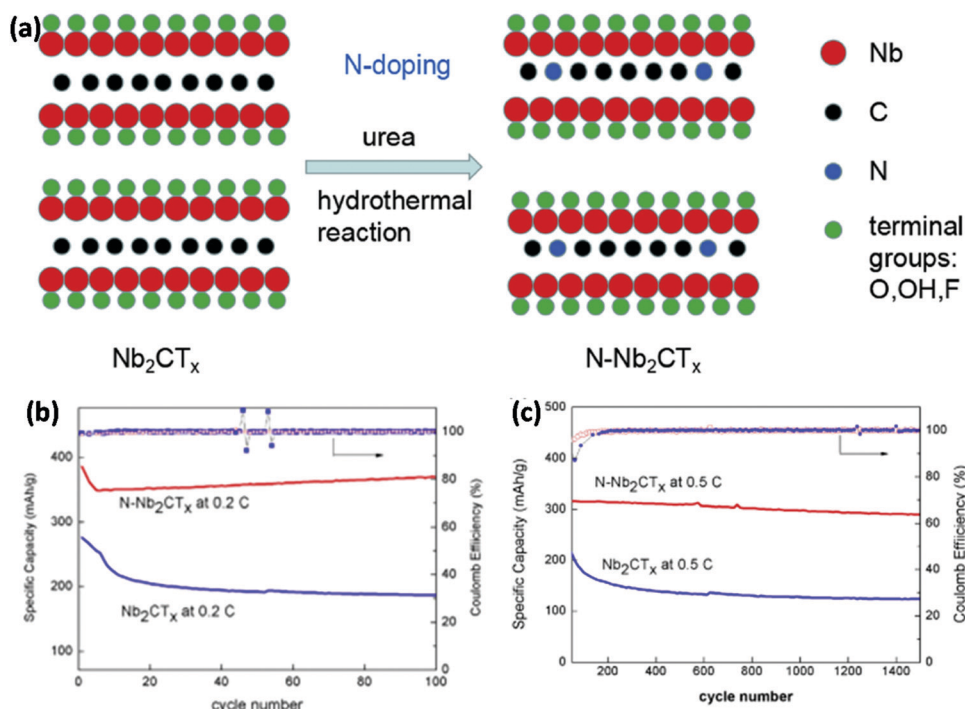


Fig. 16 (a) Diagrammatic representation of the synthesis of N-Nb₂CT_x by hydrothermal reaction, (b) cycling performance of Nb₂CT_x and N-Nb₂CT_x at 0.2 C up to 100 cycles and (c) cyclic stability of Nb₂CT_x and N-Nb₂CT_x electrodes at 0.5 C up to 1500 cycles. Reused with permission from ref. 141.

and well-fashioned conformation is a promising prospect to prepare multi-functional, efficient materials for LIBs. Sun *et al.* prepared SnO_x@Ti₃C₂ nanocomposite through the hydrothermal method in which ultrathin nanosheets of SnO_x were uniformly decorated over the Ti₃C₂ matrix leading to efficient lithium storage (Fig. 17a–c).¹⁴⁶ The metallic conductivity of Ti₃C₂, the huge capacity of SnO_x nanosheets, and strong interaction between Ti₃C₂ and SnO_x contributed to superb rate performance and prolonged cyclic life. The composite delivered a large reversible

capacitance of 540 mA h g^{−1} at 500 mA g^{−1} current density after 1000 cycles (Fig. 17d and e).

The incorporation of metal oxides with MXene results in high capacity with improved electrochemical performance. Ahmed *et al.* synthesized SnO₂/Ti₃C₂T_x composites for anode materials in LIBs *via* the atomic layer deposition method.¹⁴⁷ Further, the HfO₂ layer was coated on the surface of SnO₂ to enhance the electrochemical performance and the HfO₂ coated SnO₂/Ti₃C₂T_x composites showed a discharge-specific capacity

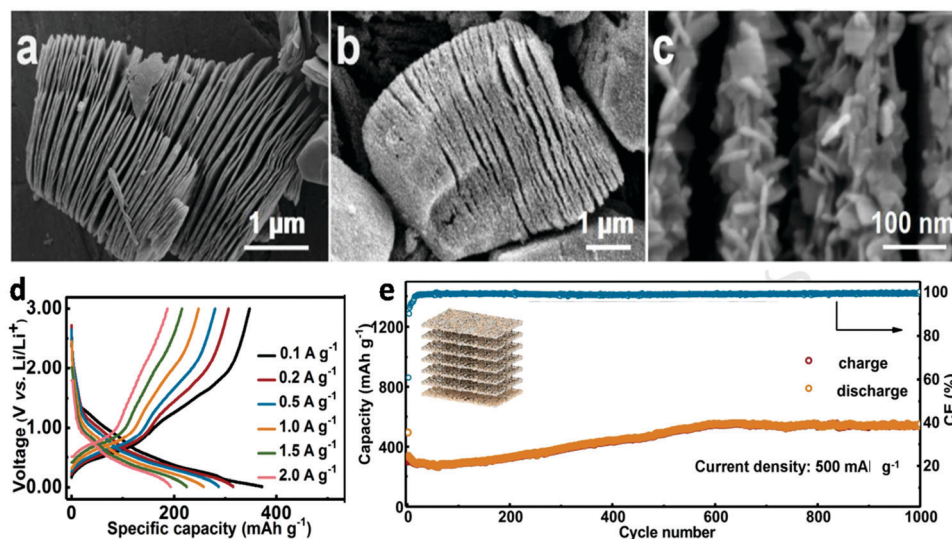


Fig. 17 FESEM images of (a) Ti₃C₂T_x, (b and c) SnO_x@Ti₃C₂, (d) charging–discharging curves of SnO_x@Ti₃C₂ anode at various current densities and (e) cyclic life and Coulombic efficiency (CE) of SnO_x@Ti₃C₂ at 500 mA g^{−1} current density. Reproduced with permission from ref. 146.

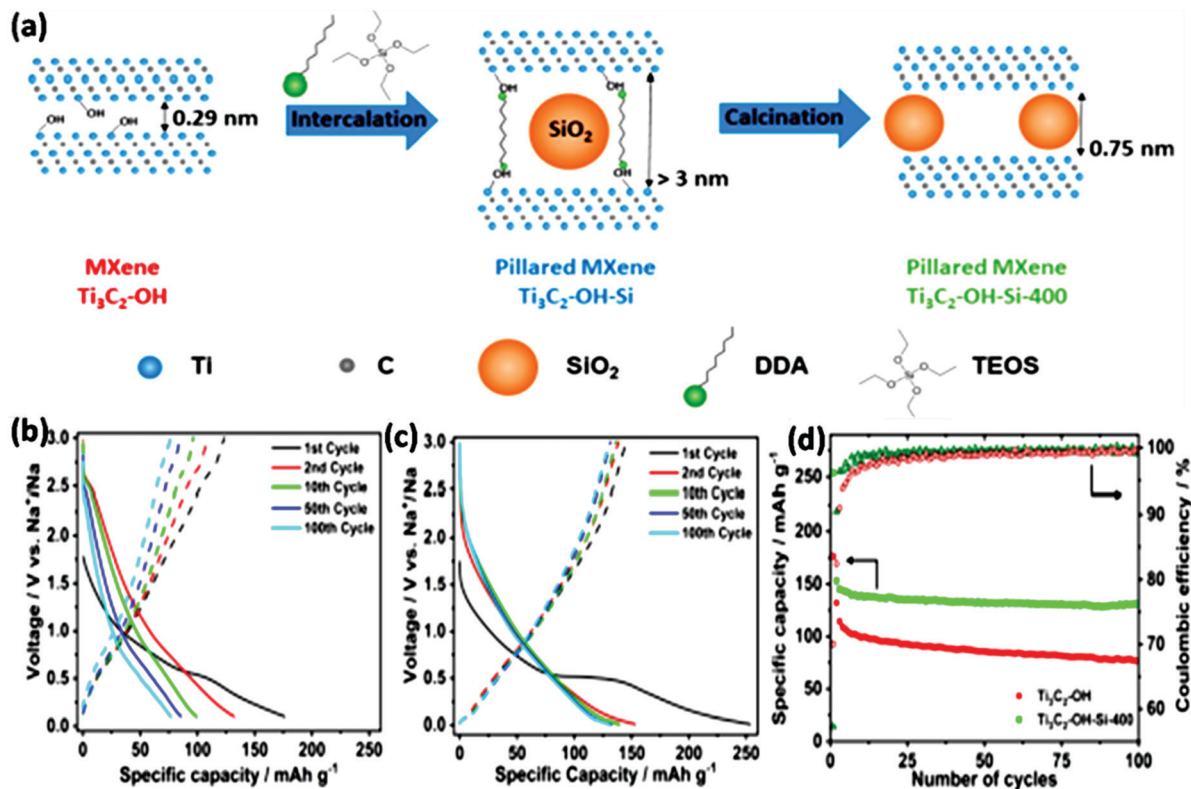


Fig. 18 (a) Diagrammatic representation of the pillaring method of MXene, galvanostatic charging–discharging curves of (b) $\text{Ti}_3\text{C}_2\text{-OH}$ and (c) $\text{Ti}_3\text{C}_2\text{-OH-Si}$, discharge capacities and Coulombic efficiency of $\text{Ti}_3\text{C}_2\text{-OH}$ and $\text{Ti}_3\text{C}_2\text{-OH-Si}$ over 100 cycles. Reused with permission from ref. 149. Copyright (2020) American Chemical Society.

of 843 mA h g⁻¹ at 500 mA g⁻¹ over 50 cycles. A unique $\text{Fe}_3\text{O}_4@\text{Ti}_3\text{C}_2$ composite with well-anchored Fe_3O_4 nanoparticles inside Ti_3C_2 layers was fabricated by Xu *et al.* and the charge polarization due to covalent Ti–O–Fe bonds effectively enhanced the electron transfer as well as lithium storage mechanism.¹⁴⁸ The hybrid composite exhibited an ultrahigh capacity of 1172 mA h g⁻¹ with 90% retention of capacity at 5 A g⁻¹ after 1000 cycles.

3.2.2 Na-ion battery. Though LIBs have been extensively used in various areas, the limited supply of lithium has failed to meet the increasing requirement of the global market. So, the evolution of new categories of batteries has become mandatory and in this context, sodium-ion batteries (NIBs) are associated with comparable working principles with LIBs. Also, sodium resources are very abundant on the earth. Thus, NIBs could be a better option for large-scale energy storage for wind and solar energy. MXenes were also studied widely as an electrode material for NIBs due to their unique structure and properties.

3.2.2.1 Elemental MXene. A new amine-supported pillaring method was effectively demonstrated using silica-based pillars intercalating inside the Ti_3C_2 layers (Fig. 18a) for NIB applications, which eliminated the difficulty in ion accessibility inside the closely stacked multilayered MXene sheets.¹⁴⁹ In this process, the interlayer distance of MXene can be adjusted by opting for specific amine and temperature of calcination and there was a huge increment in the surface area of 235 m² g⁻¹ that is six-fold

higher than the unpillared one. The porous MXene material exhibited excellent rate capability, specific capacity and superb cyclic stability than the unpillared MXene with 98.5% capacity retention between 50th and 100th cycles (Fig. 18b–d).

The charge storage mechanism of V_2CT_x was studied by Bak *et al.* during Na⁺ ion intercalation/deintercalation.¹⁵⁰ The XRD pattern of V_2CT_x showed the shifting of (002) diffraction peak from 9.3 to 8.1 during the initial sodiation process from open-circuit voltage to 0.1 V state corresponds to the increment of the c-lattice parameter from 19.0 to 21.8 Å. As well as Na⁺ adsorption on the surface of V_2CT_x , leading to double-layer storage, energy stored *via* Na⁺ intercalation in the interlayer spacing of V_2CT_x . This mechanism was similar to Ti_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene materials.^{39,151} Recently, Zhao *et al.* reported a template method to fabricate macroporous $\text{Ti}_3\text{C}_2\text{T}_x$ 3D film, which was used as a freestanding, flexible and highly conducting electrode.¹⁵² This macroporous 3D MXene film showed a reversible capacity of 330 mA h g⁻¹ at 0.25 C and after 1000 cycles, the $\text{Ti}_3\text{C}_2\text{T}_x$ 3D film exhibited a reversible capacity of 295 mA h g⁻¹ at 2.5 C.

3.2.2.2 MXene-based composites. An easy solution-phase technique was employed to prepare $\text{Sb}_2\text{O}_3/\text{Ti}_3\text{C}_2\text{T}_x$ composites by Guo *et al.*, wherein, Sb_2O_3 nanoparticles were uniformly distributed over the 3D $\text{Ti}_3\text{C}_2\text{T}_x$ network.¹⁵³ The discharge capacity of this nanocomposite was 472 mA h g⁻¹ after 100 cycles at 100 mA g⁻¹ while used as the anode material for NIBs. The hybrid composite showed better rate performance than the

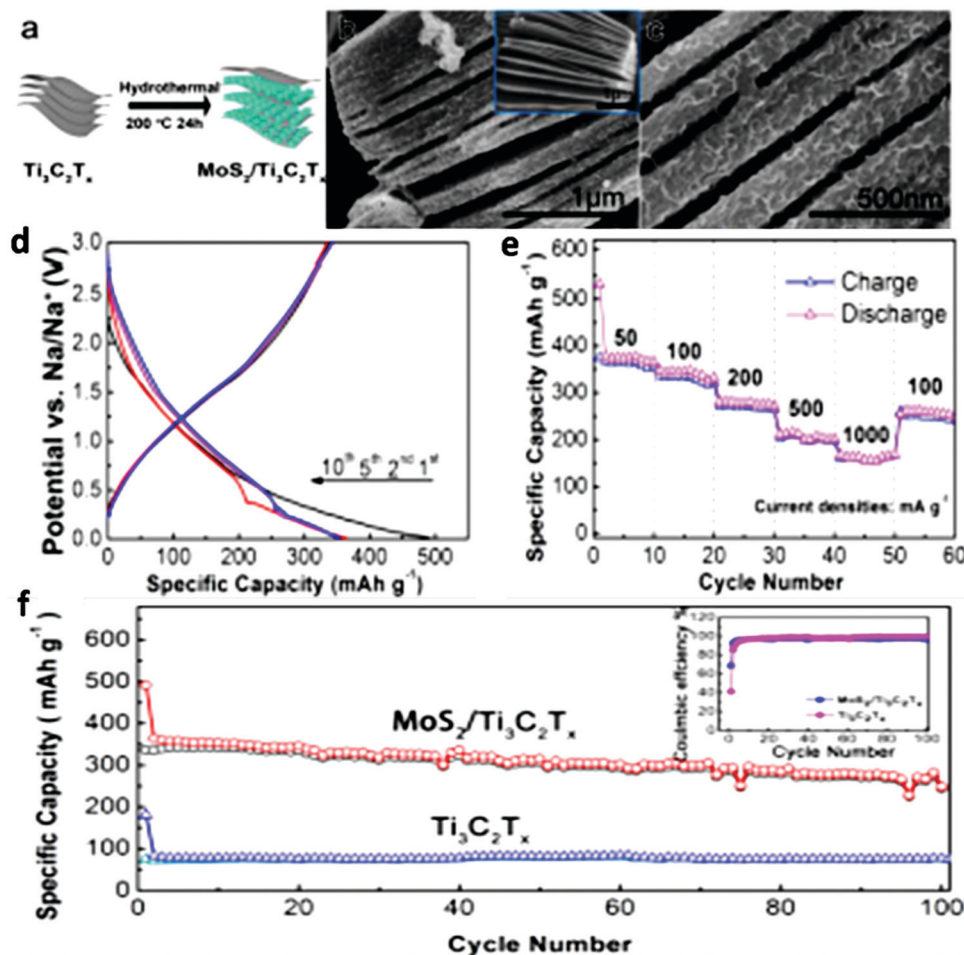


Fig. 19 (a) Schematic representation displaying the preparation of MoS₂/Ti₃C₂T_x composite hydrothermally, (b and c) SEM images of Ti₃C₂T_x (inset b) and MoS₂/Ti₃C₂T_x composite. The electrochemical properties of the MoS₂/Ti₃C₂T_x composite in a two-electrode sodium-ion cell with Na foil as the counter and reference electrode: (d) charge/discharge curve of MoS₂/Ti₃C₂T_x composite at 100 mA g⁻¹ in the voltage range of 0.01–3.0 V, (e) rate capability of MoS₂/Ti₃C₂T_x composite and (f) cycling performance of pure Ti₃C₂T_x and MoS₂/Ti₃C₂T_x composite at 100 mA g⁻¹, the Coulombic efficiencies of MoS₂/Ti₃C₂T_x composite and pure Ti₃C₂T_x are also shown. Reused with permission from ref. 154.

pure Sb₂O₃ anode and that can be ascribed to the distinctive structure and synergistic effects of Ti₃C₂T_x sheets and Sb₂O₃ nanoparticles. To enhance the ion accessibilities in MXene sheets, recently Wu *et al.* prepared MoS₂/Ti₃C₂T_x hybrid composite *via* the hydrothermal method, in which MoS₂ nanosheets remain intercalated between Ti₃C₂T_x layers (Fig. 19a–c).¹⁵⁴ This composite exhibited a discharge capacity of 250.9 mA h g⁻¹ at 100 mA g⁻¹ after 100 cycles with a reasonable rate performance of 162.7 mA h g⁻¹ at 1 A g⁻¹, while used as an anode for NIBs (Fig. 19d–f).

A high-performance MoSe₂/Ti₃C₂T_x heterostructure electrode as anode material for NIBs was fabricated through a facile hydrothermal reaction followed by annealing by Xu *et al.*¹⁵⁵ The van der Waals force of attraction between MoSe₂ and Ti₃C₂T_x prevented the volume change that occurs during sodium ion intercalation/deintercalation and enhanced the reaction kinetics resulting in a potential sodium storage application. The fabricated cells delivered an impressive reversible capacity of 490 mA h g⁻¹ at 1 A g⁻¹ current density and 250 mA h g⁻¹ at 10 A g⁻¹ current density with 99.8% Coulombic efficiency.

3.2.3 Li-S battery. Li-S batteries have gained considerable attention because of their vast energy density, but some issues limit their practical applications. The discharge products Li₂S and 'S', both are insulators. Additionally, the resultant intermediate groups get dissolved in many organic electrolytes and are transferred to the anode by the shuttle effect and react to form Li₂S, causing the reduction of the Coulombic efficiency and cyclic life. The multilayered Ti₃C₂T_x nanosheets were also utilized as a separator for Li-S batteries and Ti₃C₂T_x/CNT modified polypropylene (PP) separator maintained a capacity of 650 mA h g⁻¹ at 1 C after 200 cycles.²⁸ Fig. 20(a and b) shows the capacities obtained during self-discharge of Li-S batteries with different separators after 120 h rest and cyclic stability after the rest time of 120 h. Fig. 20(c) shows the digital photograph of the assembled Li-S batteries using Ti₃C₂T_x/CNT modified PP (10%) powering the LEDs.

A unique strategy of coupling MXene-based cathode with an antifouling separator to increase the rate performance and sulfur loading of Li-S batteries through an easy electrostatic self-assembly procedure was proposed by Guo *et al.*¹⁵⁶ MXene

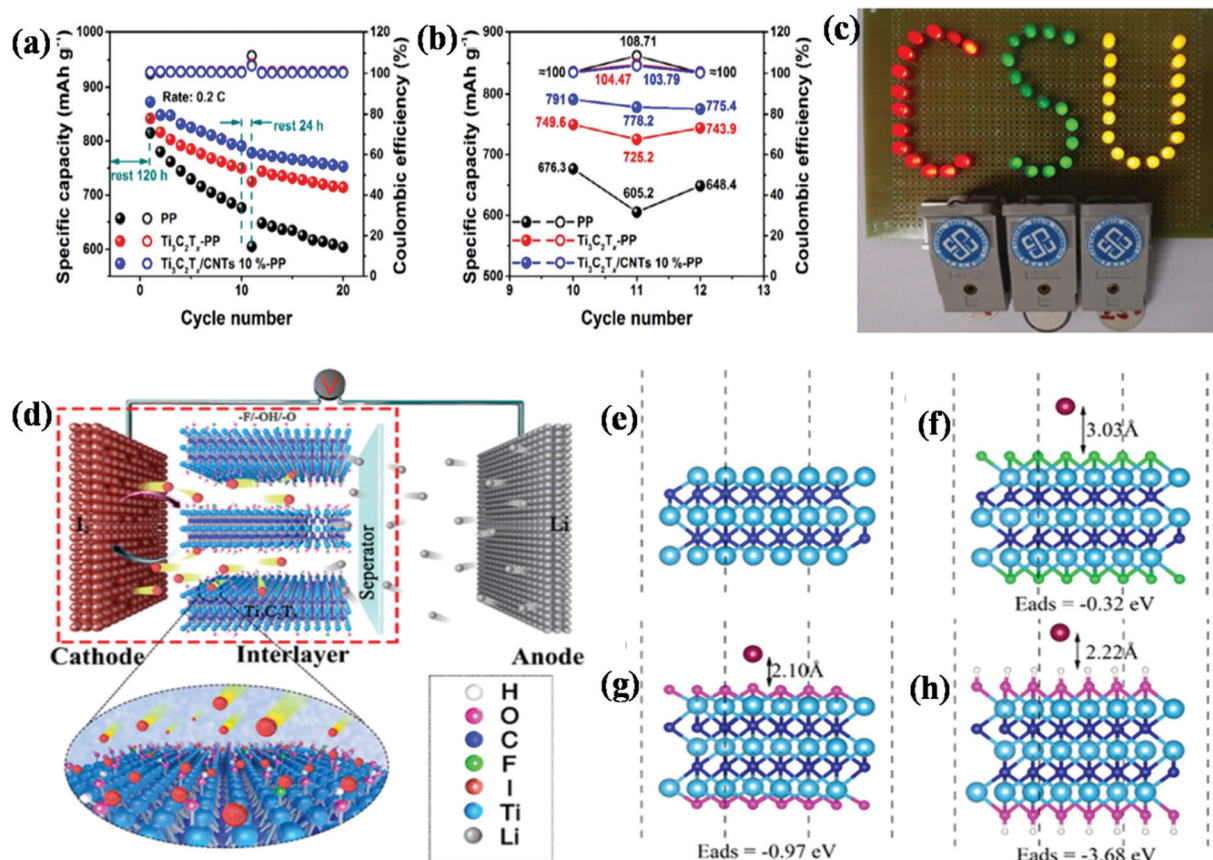


Fig. 20 (a) Self-discharge of Li-S batteries with different separators after 120 h rest, (b) cyclic stability after the rest time of 120 h, (c) photograph of Li-S battery using Ti₃C₂T_x/CNT modified PP (10%) powering up LEDs. (d) Schematic diagram of the reaction mechanism of lithium-iodine battery using MXene interface layer and molecular models of (e) Ti₃C₂, binding energies of iodine with (f) Ti₃C₂F_x, (g) Ti₃C₂O_x and (h) Ti₃C₂(OH)_x. (a–c) reused with permission from ref. 28 and (d–h) reproduced with permission from ref. 29. Copyright (2020) American Chemical Society.

composite with CNT-polyethyleneimine delivered an ultrahigh capacity of 980 mA h g⁻¹ at 5 mA cm⁻² after 500 cycles. Liang *et al.* investigated the surface-responsive nature of Ti₃C₂, Ti₃C₂ and Ti₃CN with polysulfide species through DFT calculations

and X-ray photoelectron spectroscopy (XPS) analysis.¹⁵⁷ For further improvement of conductivity and check the restacking of MXene sheets, CNTs were combined with MXenes and this S/CNT-MXene composite displayed excellent cyclic life up to 1200 cycles.

Table 3 Summary of the efficiency of MXene-based materials in battery applications

Material	Application	Current density	Reversible capacity//Cycle number	Ref.
Carbon coated Fe ₃ O ₄ /Ti ₃ C ₂	Li-ion battery	1 A g ⁻¹	997 mA h g ⁻¹ //2000	143
N-Nb ₂ CT _x	Li-ion battery	0.5 C	288 mA h g ⁻¹ //1500	141
Oxidized V ₂ CT _x	Li-ion battery	1000 mA g ⁻¹	125 mA h g ⁻¹ //1000	139
Fe ₃ O ₄ @Ti ₃ C ₂	Li-ion battery	1.6 mA cm ⁻²	592 mA h g ⁻¹ //500	148
SnO _x @Ti ₃ C ₂	Li-ion battery	500 mA g ⁻¹	~540 mA h g ⁻¹ //1000	146
Hf ₃ C ₂ T _x	Li-ion battery	200 mA g ⁻¹	1567 mA h cm ⁻³ //200	75
MoS ₂ /Ti ₃ C ₂ -MXene@C	Li-ion battery	1 A g ⁻¹	1200 mA h g ⁻¹ //700	144
HfO ₂ coated SnO ₂ /Ti ₃ C ₂ T _x	Li-ion battery	500 mA g ⁻¹	843 mA h g ⁻¹ //50	147
Macroporous 3D Ti ₃ C ₂ T _x film	Na-ion battery	0.25 C	330 mA h g ⁻¹ //1000	152
Sb ₂ O ₃ /Ti ₃ C ₂ T _x	Na-ion battery	100 mA g ⁻¹	472 mA h g ⁻¹ //100	153
MoS ₂ /Ti ₃ C ₂ T _x	Na-ion battery	100 mA g ⁻¹	250.9 mA h g ⁻¹ //100	154
MoSe ₂ /Ti ₃ C ₂ T _x	Na-ion battery	1 A g ⁻¹	434 mA h g ⁻¹ //200	155
Ti ₃ C ₂ T _x -CNT modified PP	Li-S battery	1 C	640 mA h g ⁻¹ //200	28
MXene/CNT-polyethyleneimine	Li-S battery	5 mA cm ⁻²	980 mA h g ⁻¹ //500	156
S/CNT-MXene	Li-S battery	C/2	~450 mA h g ⁻¹ //1200	157
Ti ₃ C ₂ T _x /rGO/S	Li-S battery	0.5 C	878.4 mA h g ⁻¹ //300	158
N-Ti ₃ C ₂ @CNT/S	Li-S battery	1 C	775 mA h g ⁻¹ //1000	160

CNT-Carbon nanotube; PP-Polypropylene; rGO-Reduced graphene oxide.

Bao *et al.* fabricated reduced graphene oxide (rGO)/Ti₃C₂T_x hybrid composite as a host material for Li-S batteries.¹⁵⁸ The Ti₃C₂T_x/rGO/S composite exhibited a large initial capacity of 1144 mA h g⁻¹ and after 300 cycles the capacity retention was 878 mA h g⁻¹ due to the effective interaction of sulfur and polysulphide with -OH decorated MXene phase. Recently, the capability of MXene as a host material for polysulphides in Li-S batteries was explored by DFT calculations and it was observed that both Ti₃C₂O₂ and Ti₂CO₂ single-layers could allow outstanding trapping with polysulphide species, preventing the shuttling effect.¹⁵⁹ In another study, N-Ti₃C₂@CNT microspheres were prepared as an efficient sulfur host, as well as allowed proper chemical immobilizations of polysulphides and capture them inside the porous microspheres.¹⁶⁰ The N-Ti₃C₂@CNT/S cathode exhibited an initial specific capacity of 927 mA h g⁻¹ at 1 C and 775 mA h g⁻¹ after 1000 cycles with only 0.016% degradation rate per cycle.

Recently, MXene was introduced as a potential material for lithium iodine batteries. A porous, 3D MXene foam was introduced as a cathode-electrolyte interface in lithium-iodine batteries, which provided long cyclic life and high rate performance.²⁹ Fig. 20d shows a schematic representation of the reaction mechanism of lithium-iodine batteries using the MXene interface layer and Fig. 20(e-h) shows the theoretical

model of Ti₃C₂ and the binding energies of iodine with MXenes. The electrochemical performance of some MXene-based materials in battery applications are summarized in Table 3.

3.3 Electrocatalyst for water splitting

Electrolytic/solar water splitting is a green and sustainable energy field, which includes oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Generally, expensive noble metal electrocatalysts have been used for water splitting reactions. The 2D MXene materials having excellent efficiency and stability have become a promising alternative to costly noble metals.

Wang *et al.* fabricated Ti₃C₂T_x MXene composited with TiO₂ and studied the effect of Ti₃C₂T_x loading on the catalytic performance of the composite (shown in Fig. 21a).¹⁶¹ The optimized TiO₂/Ti₃C₂T_x composite with 5 wt% Ti₃C₂T_x loading displayed an improvement of around 400% in photocatalytic HER reaction than that of pure TiO₂. The constructive decoration of TiO₂ over Ti₃C₂T_x sheets leads to adequate light absorption, which accelerates the effective charge transport from TiO₂ to Ti₃C₂T_x, developing a Schottky barrier at the interface of TiO₂-Ti₃C₂T_x (Fig. 21b) that indicates the superior photocatalytic activity. This research group also synthesized TiO₂/Ti₂CT_x and

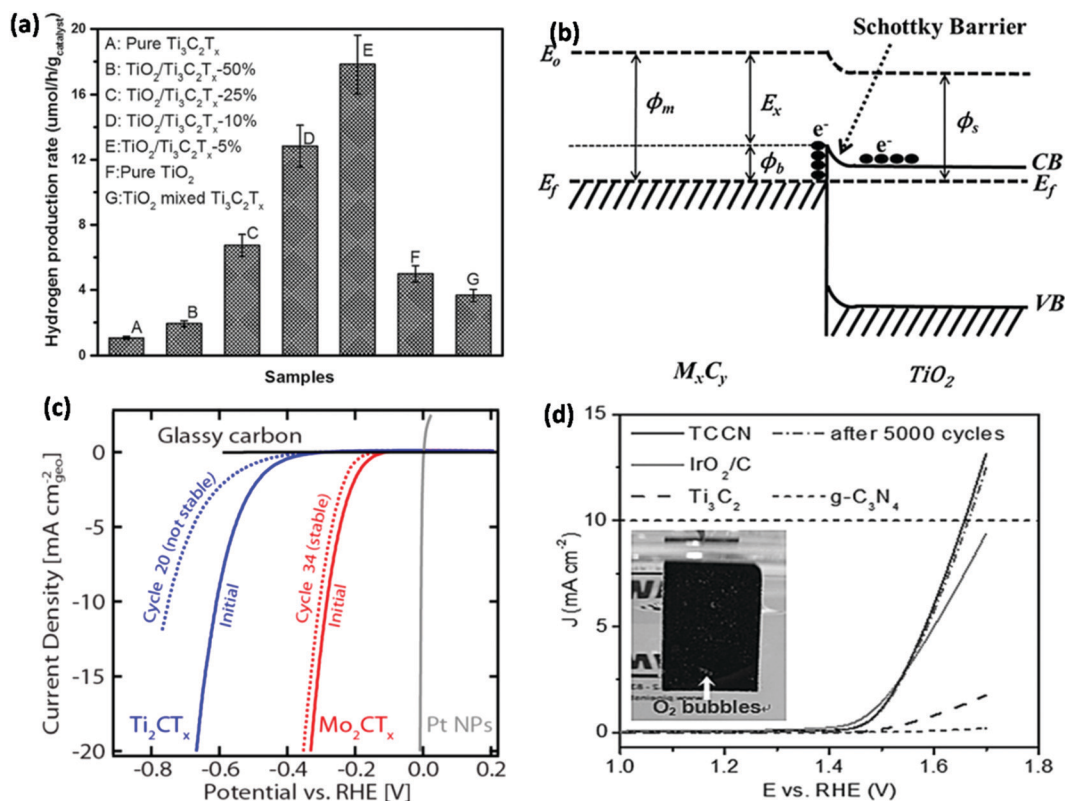


Fig. 21 (a) The effect of Ti₃C₂T_x loading on photocatalytic hydrogen production rates. (b) A schematic diagram of the Schottky barrier formation at TiO₂-Ti₃C₂T_x interface. (c) HER performance of MXene showing LSV of Mo₂CT_x and Ti₂CT_x with commercial Pt for comparison and (d) polarization curve, inset optical image of O₂ bubble generation on the electrode surface at 1.7 V using TCCN (Ti₃C₂ and g-C₃N₄ hybrid composite film) as OER electrode, dotted lines are polarization curve of samples after 5000 cycles at 100 mV s⁻¹ scan rate. (a and b) Reused with permission from ref.161 (c) reused with permission from ref. 35 (Copyright (2016) American Chemical Society) and (d) reused with permission from ref. 21.

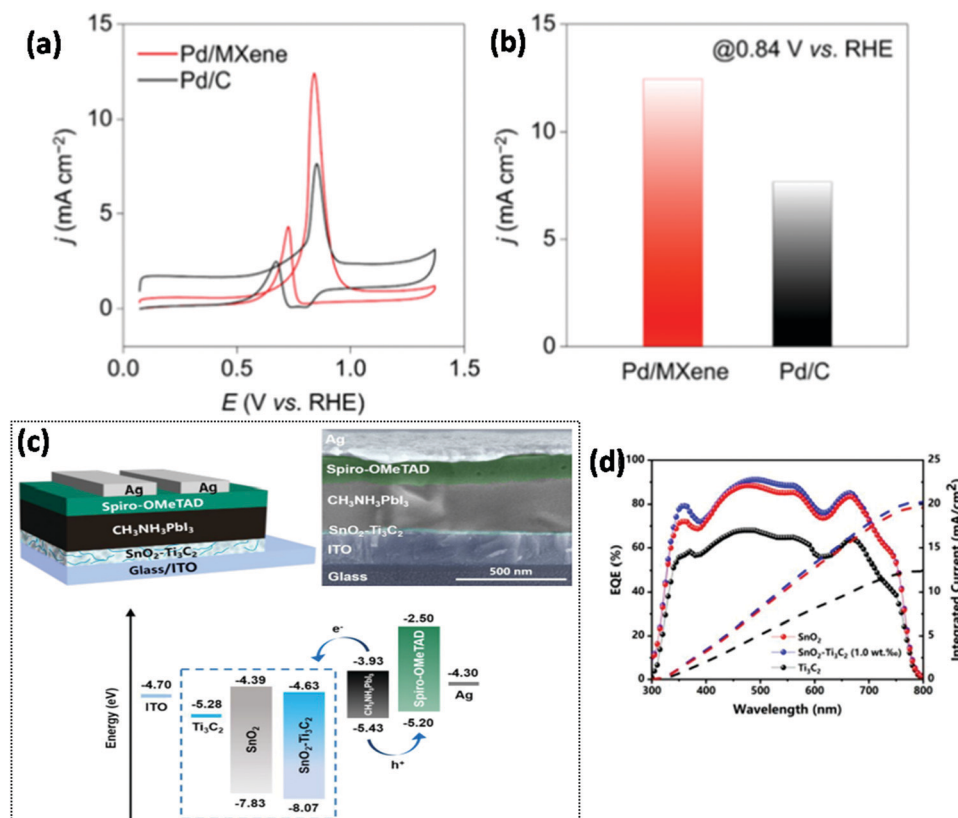


Fig. 22 Fuel cell performance (a) CV plots of Pd/MXene and Pd/C in 1 M KOH and 1 M methanol solution mixture and (b) comparison of current densities of Pd/MXene and Pd/C at 0.84 V vs. RHE. (c) Schematic diagram and SEM image of cross-sectional PSC device assembly and energy diagram of individual PSC layers. (d) external quantum efficiency (EQE) and integrated current of the fabricated PSC device with SnO₂, SnO₂-Ti₃C₂ (1.0 wt%) and Ti₃C₂. (a and b) redrawn with permission from ref. 162 (Copyright (2020) American Chemical Society.) and (c and d) reused with permission from ref. 30.

TiO₂/Nb₂CT_x composite with 5 wt% MXene packing and TiO₂/Nb₂CT_x exhibited the best HER performance.

A combination of theoretical and experimental investigation of Mo₂CT_x and Ti₂CT_x as electrocatalysts for HER was reported by Seh *et al.*³⁵ From the computational study, they confirmed that Mo₂CT_x is a better HER catalyst than Ti₂CT_x because of the catalytically active basal planes of Mo₂CT_x towards HER. According to the experimental study, the HER activity of Mo₂CT_x after 30 cycles remained almost stable, attaining a current density of 10 mA cm_{geo}⁻² with 305 mV overpotential (Fig. 21c). On the other hand, Ti₂CT_x exhibited a deteriorated cyclic life and attained 10 mA cm_{geo}⁻² current density at 609 mV overpotential.

A freestanding Ti₃C₂T_x MXene film composited with graphitic C₃N₄ (g-C₃N₄) was studied by Ma *et al.* as electroactive material for OER.²¹ The hybrid composite displayed an onset potential of 1.44 V vs. RHE (reversible hydrogen electrode) and a lesser operating potential of 1.65 V in 0.1 M KOH to attain 10 mA cm⁻² current density (Fig. 21d). They also fabricated a rechargeable Zn-air battery using MXene composite as an efficient cathode.

3.4 Fuel cell

In fuel cells, the cathode reaction, known as the oxygen reduction reaction (ORR) generally requires costly Pt group metals as a catalyst. MXenes having interesting characteristics

emerged as a useful replacement of noble metals as a catalyst in fuel cells.

Lang *et al.* used 2D Ti₃C₂T_x MXene as a productive catalyst for methanol oxidation reaction and attained above 60% performance improvement over conventional Pd catalyst.¹⁶² Here, MXene was used as support for Pd catalyst and the Pd/MXene catalyst exhibited a superior current density of 12.4 mA cm⁻² for methanol oxidation reaction than that shown by a conventionally used Pd/C catalyst, which displayed a current density of 7.6 mA cm⁻² (Fig. 22a and b). In another study, Ti₃C₂T_x was used as a support material for the Pt catalyst used in proton exchange membrane fuel cell.¹⁹ The introduction of Ti₃C₂T_x enhances the homogeneous dispersion and proper attachment of Pt nanoparticles due to the existence of surface terminal groups (-OH, -F, -O) in Ti₃C₂T_x and this superior Ti₃C₂T_x-Pt interaction led to reduced oxidation and degradation of the catalyst.

An urchin-like bimetallic nanowire composite of Ti₃C₂/Ag/Ag_{0.9}Ti_{0.1} was prepared by Zhang *et al.* by combining alkali (NaOH) treated Ti₃C₂T_x, AgNO₃ and PVP.¹⁶³ The hybrid composite displayed an outstanding efficiency towards ORR with and V half-wave potential and onset potential, respectively. Ti doping on Ag nanowire expanded the defect concentration leading to avail increased oxygen adsorption sites and conductive Ti₃C₂T_x layers facilitated the electron transfer from Ti to Ag

or different oxygen adsorption sites. Ti_3C_2 was used in a microbial fuel cell as an efficient anode material by Liu *et al.* after being inoculated with the bacterial mixture for 1 day.¹⁶⁴ The 2D Ti_3C_2 MXene provided an output voltage of around 640 ± 8 mV and external resistance of 1000Ω with the highest power density of 3.74 W m^{-2} that was better than that of commercial carbon cloth, which exhibited an output voltage of 550 ± 8 and power density of 2.05 W m^{-2} .

3.5 Solar cell

Due to the novel fusion of metallic conductivity and hydrophilicity, MXene materials have been explored in different types of solar cells. Yang *et al.* fabricated $\text{SnO}_2/\text{Ti}_3\text{C}_2$ hybrid composites with varying Ti_3C_2 concentrations for low-temperature working planar perovskite solar cells (PSC) as electron transport layers (ETLs).³⁰ The fabricated PSC device was assembled as indium tin oxide (ITO)/ETL/ $\text{CH}_3\text{NH}_3\text{PbI}_3/2,2',7,7'$ -tetrakis-(*N,N*-di-*p*-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMe TAD)/Ag (Fig. 22c). Ti_3C_2 (1 wt%) was composited with SnO_2 and provided the best result with power conversion efficiency (PCE) of 18.34%, while pure showed PCE of 5.28% (Fig. 22d). Layered MXene sheets facilitate electron mobility and electron extraction, allow charge transfer by decreasing resistance at the interface and lead to superior photocurrents.

A flexible, transparent $\text{Ti}_3\text{C}_2\text{T}_x/\text{Ag}$ nanowire conductive hybrid nanocomposite film was prepared by Tang *et al.*, which exhibited an excellent figure of merit of 162.49.¹⁶⁵ The assembled organic photovoltaics resulted in PCE of 8.30% with 84.65% retention of initial PCE after 1000 cycles of bending/unbending to a bending radius of 5 mm. Ti_3C_2 nanosheets were utilized as an electrode material for dye-sensitized solar cells after converting into porous TiO_2 through oxidization.¹⁶⁶ The influence of oxidation time and temperature on the device efficiency with varying thickness was studied. The best device performance with PCE of 2.66% was obtained at 450°C temperature with a 30 min duration time and $6.4 \mu\text{m}$ film thickness.

3.6 EMI shielding

$\text{Ti}_3\text{C}_2\text{T}_x$ was first studied by Qing *et al.* as fillers with epoxy composites having a thickness of 1.4 mm and the surface terminal groups and defects present in the MXene sheets facilitate polarization and influence the dielectric loss.¹⁶⁷ They achieved a superb microwave absorption efficiency (above 92%) with less reflection loss of -11 decibels (dB) at the frequency region of 12.4–18 GHz. In another study, a composite was prepared with varying Ti_3C_2 concentrations over the frequency region of 2.0 to 18.0 GHz.¹¹⁸ It was observed that EMI shielding effectiveness was enhanced with increasing Ti_3C_2 concentration and the best result (39.1 dB) was achieved at 60 wt% of Ti_3C_2 with a thickness of 2.0 mm (shown in Fig. 23a and b).

A $\text{Ti}_3\text{C}_2\text{T}_x\text{-ZnO}$ composite having urchin-like morphology was fabricated by Qian *et al.* via a co-precipitation method for the application of electromagnetic absorber due to the generation of wider interface and novel semiconductive networks.¹⁶⁸

The synthesized composite provided a superior electromagnetic absorbing efficiency with much less reflection loss (-26.30 dB) than pure pristine $\text{Ti}_3\text{C}_2\text{T}_x$ (-6.70 dB). They studied that by varying the formation time of ZnO, the absorption performance of the nanocomposite was significantly influenced within the region of 14.0–18.0 bands. In another report, delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ composited with sodium alginate (10 wt%) provided superb EMI shielding performance of 92 dB with $45 \mu\text{m}$ thickness and 57 dB with $8 \mu\text{m}$ thickness.¹⁰² It is evident that EMI shielding and absorption application of MXenes are limited with only $\text{Ti}_3\text{C}_2\text{T}_x$ by varying the synthesis pathway or composite formation.

3.7 Energy harvesting

Electrically conductive MXene ($\text{Ti}_3\text{C}_2\text{T}_x$), which is triboelectrically much negative compared with Teflon or polytetrafluorethylene, was used as a triboelectric nanogenerator, which transforms the useless mechanical energy that comes from human motion into electrical energy.³¹ The flexible $\text{Ti}_3\text{C}_2\text{T}_x$ nanogenerator can assist large open-circuit voltage within the region of 500–600 V as well as power-up instantly ~ 0.5 to 0.65 mW, which would light up above 60 light-emitting diodes (LEDs) or $1 \mu\text{F}$ capacitor could be instantly charged up to 50 V. Additionally, this powerful MXene nanogenerator can generate electrical energy from general body movements like texting or typing and become attractive for wearable electronics (Fig. 23c–h).

Hong *et al.* reported $\text{Ti}_3\text{C}_2\text{T}_x$ lamellar membranes with ion-selective nanochannels for osmotic power generation.¹⁶⁹ In the presence of a salinity gradient, the $\text{Ti}_3\text{C}_2\text{T}_x$ membranes allow a cation-selective pathway with the help of surface terminal groups. Under a 1000-fold salinity gradient, a very high power density of 21.0 W m^{-2} and power conversion efficiency of 40.6% was achieved at room temperature. It was observed that a very high thermal increment at 331 K was obtained due to thermal control of ionic mobility and surface charges, leading to the enhancement of power density up to 54 W m^{-2} .

3.8 Sensors: biosensors and electrochemical sensors

The use of MXenes in the field of sensing attract interest due to their biocompatibility, metallic conductivity, a huge number of absorption sites and homogeneous dispersion in the aqueous medium, resulting in high signal, lower detection limit as well as lower electrical noise, which are prominent criteria for efficient sensors.^{170,171} MXenes were introduced as sensors in a variety of applications in biomedical, electrochemical and environmental detection like enzymes, NH_3 ,^{172,173} N_2 gases,¹⁷⁴ humidity,^{175,176} encapsulating haemoglobin,²⁰ phenol,¹⁷⁰ SO_2 ,¹⁷² cancer biomarkers,¹⁷⁷ adrenalin,¹⁷⁸ macromolecules and cell adsorption.¹⁷⁹

According to the theoretical calculation, V_2CO_2 and Mo_2CO_2 exhibited superior selectivity towards NO; on the other hand, Ti_2CO_2 and Nb_2CO_2 showed selectivity towards NH_3 .^{172,173} It was also confirmed that MXenes have efficient characteristics for the selective adsorption or storage of methane,¹⁸⁰ hydrogen,¹⁸¹ CO_2 ¹⁸² at environmental conditions. Theoretical as well as experimental studies displayed that CO_2 uptakes

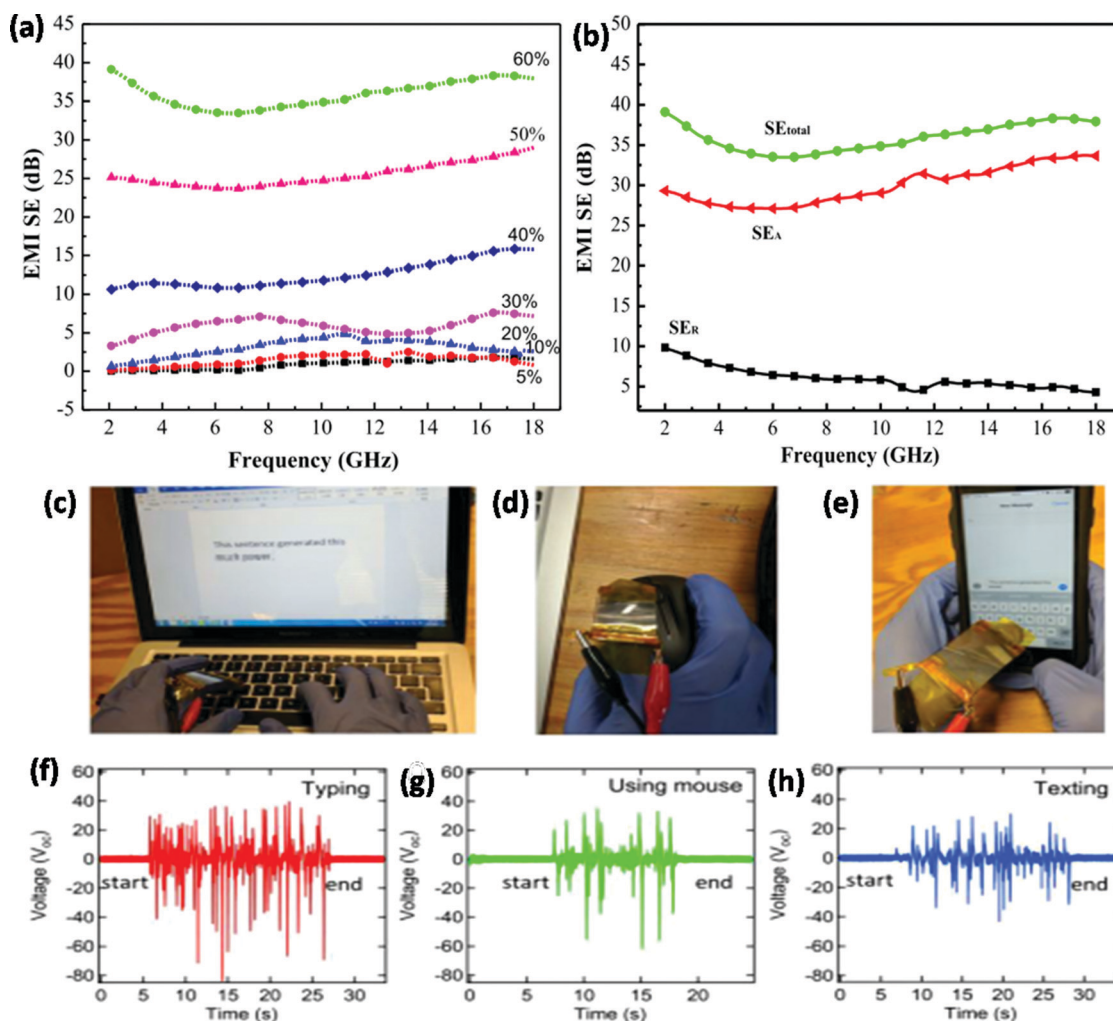


Fig. 23 (a) EMI shielding (EMI SE) of the nanocomposite with varying Ti₃C₂ loading (5–60 wt%) within the frequency window of 2.0–18.0 GHz with 2.0 mm thickness, (b) comparison of SE_{total}, SE_A and SE_R of the Ti₃C₂/paraffin composite at 60 wt% Ti₃C₂ loading (SE_{total} is the sum of absorption SE_A and reflection SE_R contributions). A flexible nanogenerator assembled with Ti₃C₂x/polyethylene terephthalate (PET)-indium tin oxide (ITO): PET-ITO triboelectric nanogenerator mounted on the index finger harvesting waste mechanical energy from the human body motion (c) typing, (d) clicking a mouse, (e) texting, (f–h) voltage produced due to the actions in (a–c) respectively. (a and b) Reused with permission from ref. 118 and (c–h) reused with permission ref. 31.

using MXene materials were up to around 12 mol CO₂/kg,¹⁸³ which is much better than recently studied materials in this field. Junkaew *et al.* reported that oxygen functionalized MXene materials provide more efficient gas sensing than bare MXenes.¹⁷²

Currently, MXene materials used as strain sensors like piezoresistive¹⁸⁴ and hydrogel¹⁸⁵ provide superior efficiency than the earlier reported MoS₂ or hydrogels. While incorporated in electronic skin and wearable devices, MXene materials displayed superb sensitivity, superior stability, quick response and impressive accuracy with delicate human movement detection, such as handwriting, throat swallowing, or eye blinking.^{32,184,185} In anti-counterfeiting applications, they could be used and allowed the possibility of the vocally damaged people to hear. For example, strain sensors consisting Ti₃C₂T_x/CNT composite provided a sensing region of 30 to 130% and a gauge factor of 4.4 to 772.6 (Fig. 24a), which is far more superior than the conventional semiconductor or metal-based strain sensors.³²

Fig. 24b shows a digital photograph of this Ti₃C₂T_x/CNT sensor before and after stretching up to 200%. It is important to mention that multilayered MXenes exhibited more sensitivity compared with partly exfoliated MXenes.

3.9 Blends and composites: mechanical properties

One of the chief benefits of MXene materials is their metallic conductivity with hydrophilicity that allows greater interaction with polymeric matrices, making them favorable in the field of blends and composite materials.^{108,186–188} Also, these composites can be prepared by a facile cost-effective process like solution mixing and a variety of shapes like fibers, 3D structures, films are obtained.^{189–191} Variety of polymer matrices composite with MXenes were reported, including polyvinyl alcohol (PVA),^{108,192,193} polyethylene,¹⁸⁸ polyacrylamide (PAM),¹⁹⁴ polydiallyl dimethylammonium chloride (PDDA),¹⁰⁸ polyurethane (PU),¹⁹⁵ epoxy,¹⁹⁶ polyfluorenes¹⁸⁷ and poly(vinylidene fluoride).¹⁹⁷

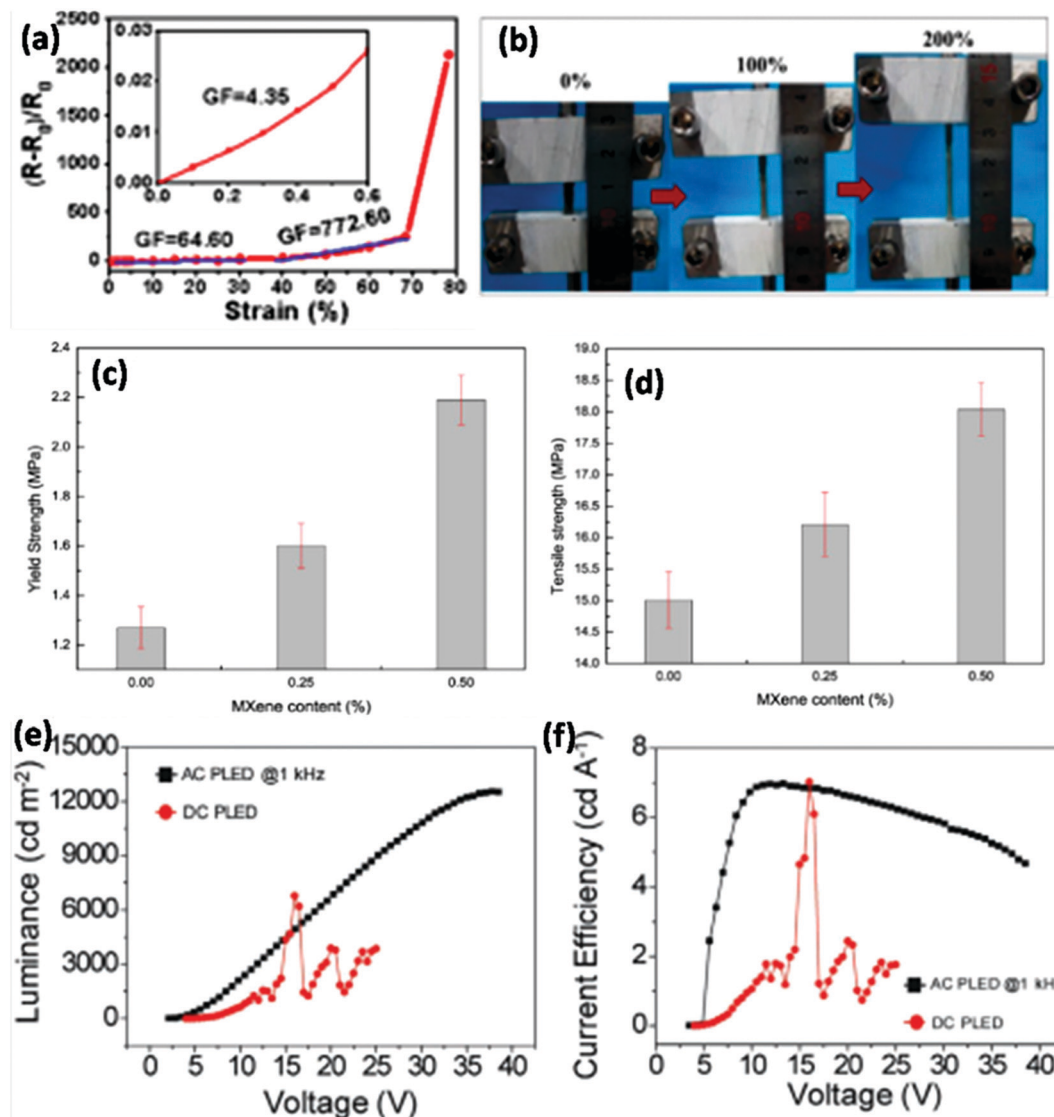


Fig. 24 (a) Relative resistance vs. the strain curve $\text{Ti}_3\text{C}_2\text{Tx}/\text{CNT}/\text{latex}$ strain sensor at the stretching rate $5\% \text{ min}^{-1}$. Inset is the curve at strain 0.6%, (b) digital photograph of a strain sensor before and after stretching up to 100% and 200%, (c) yield strength and (d) tensile strength of MXene/PU composite, (e) luminance vs. voltage plot and (f) current efficiency vs. voltage plot of AC MXene PLED under AC and DC condition at 1 kHz AC frequency. (a and b) Reused with permission from ref. 32 (Copyright (2018) American Chemical Society), (c and d) redrawn with permission from ref. 195 (e and f) reused with permission from ref. 200.

Actually, MXenes are introduced to enhance the mechanical properties as well as the electrical conductivity of polymer materials. The Ti_2CT_x -epoxy composite provided impact strength and storage modulus increments by 76% and 38%, respectively¹⁹⁶ and $\text{Ti}_3\text{C}_2\text{Tx}/\text{PVA}/\text{cellulose}$ nanocrystals (CNC) composite fibers enhanced the Young Modulus from 392 to 855 MPa.¹⁹² Further, the incorporation of $\text{Ti}_3\text{C}_2\text{Tx}$ (0.5 wt%) in the PU polymer matrix enhanced the stress yield by around 70%¹⁹⁵ (Fig. 24c and d). Regarding electrical conductivities, $\text{Ti}_3\text{C}_2\text{Tx}$ -PAM,¹⁶⁶ PVA, PDDA¹⁰⁸ composites showed superb electrical conductivity and V_2C -based polymer composites enhanced electrical conductivity by tenfold with increasing temperature from 15 to 45°C .¹⁸⁶

A recent experimental study on MXene-polyfluorenes with various functional groups, including polar, non-polar or

charged end alkyl chains, showed that the polymer intercalation inside the MXene ($\text{Ti}_3\text{C}_2\text{Tx}$) layer is favorable for the nitrogen-containing functional groups due to the polarity.¹⁸⁷

3.10 Organic light-emitting diodes (OLED)

MXene (Ti_3C_2) as a solution-processed electrode was used as OLED due to its huge work function of 5.1 eV, the large electrical conductivity of 11670 S cm^{-1} and excellent optical transmittance up to 85%.¹⁹⁸ A flexible transparent conducting electrode (TCE) of single-layered Ti_3C_2 was fabricated *via* a single-step spin-coating technique and to prevent damaging surface oxidation, as well as deterioration of electrode film; a hole-injection layer of conducting polymer was used. MXene TCE provided an external quantum efficiency of 28.5% ph/el and current efficiency of 102.0 cd A^{-1} ,

which was well in accordance with the theoretical highest values from optical simulations.

In another study, MXene was treated solvothermally in dimethylformamide (DMF) to prepare carbon-derived, amphiphilic, graphene quantum dots (GQDs), which showed promising performance as light-emitting composite and fluorescent ink due to its excellent photo-stability and tunable photoluminescence.¹⁹⁹ Recently, Lee *et al.* demonstrated transparent MXene electrodes as polymer light-emitting diodes (PLED) due to their superb electrical stability under alternating current (AC).²⁰⁰ The PLED using MXene electrode performed under AC at 1 kHz frequency, displayed current efficiency of 7 cd A⁻¹, the turn-on voltage of 2.1 V and brightness of 12 547 cd m⁻² (Fig. 24e and f).

3.11 Actuators and robotics

It was established from *in situ* atomic force microscopy, X-ray diffraction and morphology that different cations can be intercalated into the MXene layers electrochemically, leading to the volume change, which is beneficial for the actuators with electrical stimulants.^{33,123,201,202} The intercalation occurs due to the polar terminal groups and the negative surface of MXene.²⁰³ Fig. 25 shows the electroactive MXene-based actuators used as electroactive, photothermal and moisture actuators that were established as the best performer regarding actuation efficiency and promising application.²⁰⁴ Umrao *et al.* reported a flexible Ti₃C₂T_x/poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT:PSS) nanocomposite electrode in which PEDOT:PSS was intercalated inside Ti₃C₂T_x layers and displayed excellent conductivity and high capacitance leading to a potential member

for soft robotics.³³ The composite electrode displayed a huge volumetric capacitance of 932 F cm⁻³ with excellent durability and cyclic stability of 97% retention after constant actuation up to 18 000 cycles.

In another study, MXene/cellulose/polycarbonate (PC) composite was employed as photothermal actuators with high light to heat conversion ability and good repeatability. Under near-infrared (NIR) light irradiation at 80 mW cm⁻² intensity, the reported composite was capable of bending at an angle of 11° from flat 108° state to 169° within 6.5 s. Due to the presence of polar terminal groups and huge free spacing between layers, MXenes also became a potential humidity-responsive actuator.²⁰⁴ Depending on the relative humidity, the surface terminal groups absorb water molecules through H-bonding and the *d*-spacing of MXene sheets increases without changing the crystal structure. Cai *et al.* reported a humidity-responsive bilayer actuator using Ti₃C₂T_x/cellulose hygroscopic nanocomposite as an active part and PC as an inert layer.³⁴ At 70% relative humidity, the actuator was almost flat and with decreasing humidity at 10%, it became bent.

MXenes as electroactive ionic actuators have become promising candidates for soft-robotics such as a human hand, worm, lobsters, flower and fish due to their ability to self-sensing.²⁰⁴ MXene based soft ionic actuators are used to power up to three kinetic art pieces (shown in Fig. 26a–c).³³ In Fig. 26a, an artificial flower was prepared, which bloomed, and the petals were closed by changing the stimulation in two reverse directions. As shown in Fig. 26b, a tree branch was designed, which hosted many art butterflies. As shown in

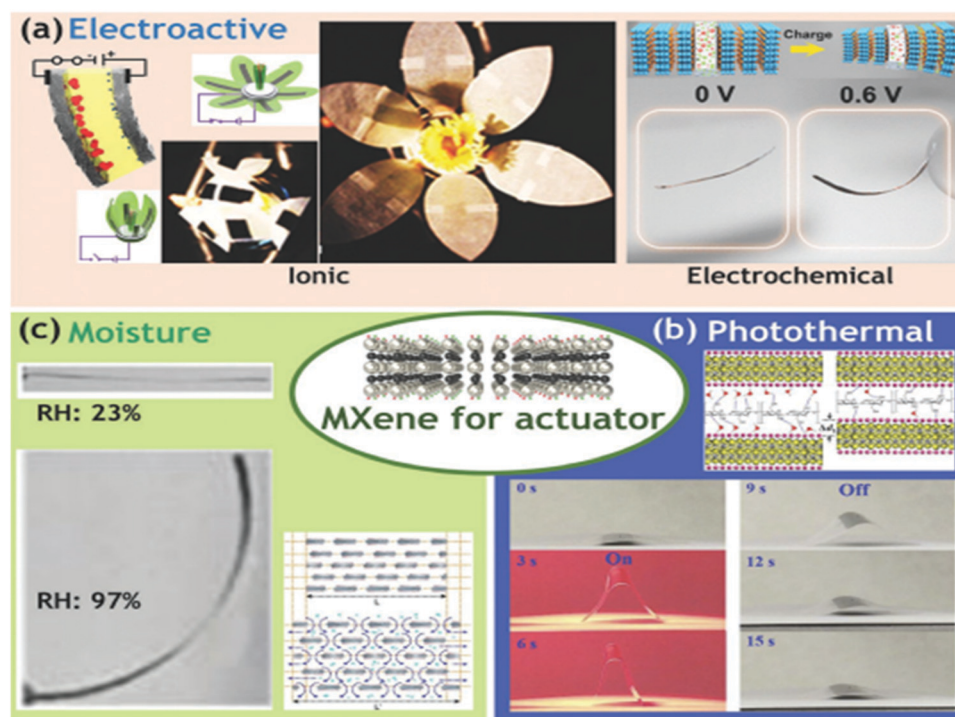


Fig. 25 MXene used in stimuli-responsive actuators (a) electroactive, (b) photothermal and (c) moisture-responsive actuators. Reused with permission from ref. 204.

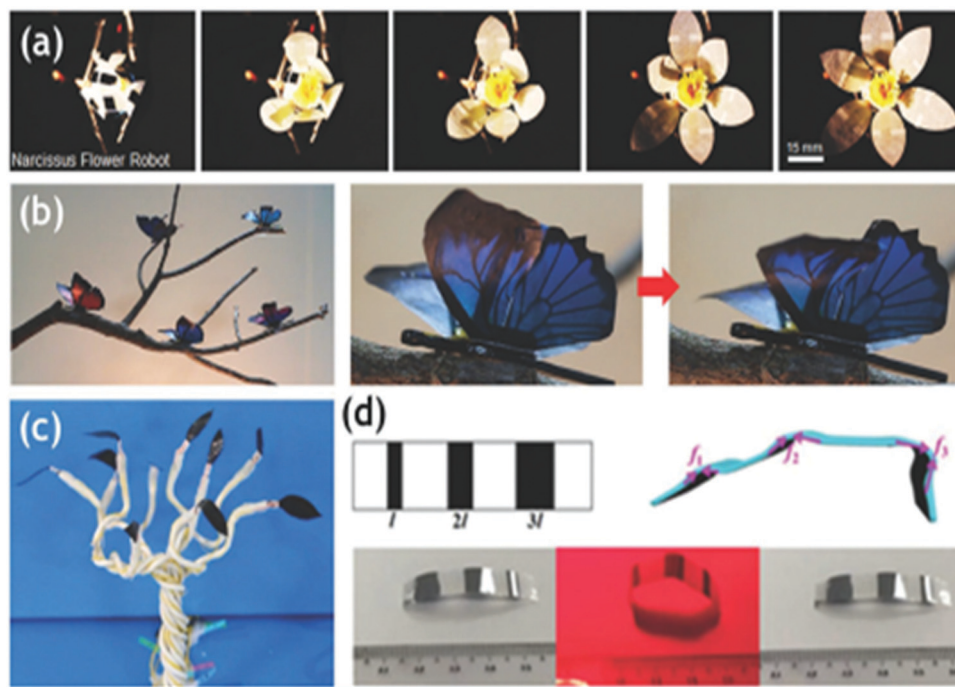


Fig. 26 MXene-based actuators used in soft robotics (a) narcissus flower robot, (b) butterflies on the tree branches, (c) leaves on the tree and (d) worm-like robot. (a–c) reused with permission from ref. 33 and (d) adapted with permission from ref. 34.

Table 4 Some other applications of MXene

Application	MXene based Material	Details	Ref.
Water purification	GO/MXene membrane	Rejection of organic dyes (MB, NR, CV, BB) and natural organic matter in raw water	205
	$\text{Ti}_3\text{C}_2(\text{OH})_2$	Heavy metal (lead) adsorption	206
	$\text{Ti}_3\text{C}_2\text{T}_x$ -Iron oxide	Phosphate sequestration	207
	$\text{Ti}_3\text{C}_2\text{T}_x$	Charge and size-selective rejection of molecules and ions.	208
	$\text{Ti}_3\text{C}_2\text{T}_x$ -rGO	Heavy metal adsorption (chromate and arsenic)	209
	$\text{Ti}_3\text{C}_2\text{T}_x$ /cellulose membrane	Solar driven interfacial water evaporation	210
	Phytic acid/MXene	Adsorption of MB	211
Dye adsorption	NaOH- $\text{Ti}_3\text{C}_2\text{T}_x$	Adsorption of MB	212
	MXene and Al-based metal-organic framework	Adsorption of MB and AB	213
	$\text{Ti}_3\text{C}_2\text{T}_x$	Adsorption and photocatalytic decomposition of AB and MB	109
Lubricant	$\text{Ti}_3\text{C}_2\text{T}_x$ -nanosheets	Solid lubricant in machine elements	214
	$\text{Ti}_3\text{C}_2\text{T}_x$ -nanoparticles	Solid lubricant under dry friction and reduced adhesive, abrasive and tribo-chemical wear	215
Antibacterial activity	Ti_3C_2	Antibacterial activity towards Gram-negative <i>Escherichia coli</i> bacteria	216
	$\text{Ti}_3\text{C}_2\text{T}_x$ -nanosheets	Resistance against <i>Escherichia coli</i> and <i>Bacillus subtilis</i> bacteria	217
Photothermal therapy	PEG-coated Ti_2C	Biocompatible, high photothermal conversion efficacy and NIR-induced capability for cancer cells' ablation	218
Nuclear waste management	Carboxyl functionalized $\text{Ti}_3\text{C}_2\text{T}_x$ MXene	Superior adsorption capacity of $\text{U}(\text{VI})$ and $\text{Eu}(\text{III})$	219

GO-graphene oxide; MB-methylene blue; NR-neutral red; CV-crystal violet; BB-Coomassie brilliant blue; HA-humic acid; BSA-bovine serum albumin; rGO-reduced graphene oxide; AB-acid blue; PEG-polyethylene glycol.

Fig. 26c, an artificial tree of thick wires was designed, and the wires were moved slowly in various directions by changing AC input stimulation. So also, kinetic artificial soft robots, as shown in Fig. 26d are made using a MXene-based photo-thermal actuator in the shape of a worm by arranging the MXene-cellulose composite on a PC membrane.³⁴ In the presence of NIR irradiation, the robot bent upward and shrunk.

Some other applications of MXene beyond the above-discussed topics are summarised in Table 4.

4. Conclusions

MXenes are 2D layered carbonitrides, carbides, or nitrides, which are generally prepared by selective etching and delamination of

layered hexagonal MAX phase precursors. During the synthesis process, the surface of MXene layers is functionalized with $-F$, $-OH$ and $-O$ groups that are responsible for the hydrophilic nature of MXenes. They can form a stable colloidal solution with an aqueous medium without any surfactant due to the surface-negative charge and hydrophilicity, leading to the easy formation of MXene film and paper electrodes.

Theoretical studies revealed the promising properties of MXene-like thermo-electronic, electronic, and optical properties. Specifically, in the existence of terminal groups and water intercalation inside the sheets, $Ti_3C_2T_x$ exhibits metallic conductivity. On the other hand, some MXenes (Mo_2CT_x and $Mo_2TiC_2T_x$) also exhibit semiconductor characteristics. Further, polymer composites with MXene and films of MXenes have excellent mechanical characteristics, and many theoretical predictions about properties are yet to be confirmed experimentally.

Additionally, MXenes allow the intercalation of a variety of cations, long polar organic molecules inside the layers that facilitate energy storage application as well as water purification, soft actuators, and robotics. The metallic conductivity and electronic properties make them potential candidates for solar cells, OLED, and electrochemical sensors. All these exceptional properties establish MXenes as one of the “hot topics” of modern science and technology.

5. Future prospects

After nine years of discovery, tremendous progress has been made on the fabrication methods, structural properties, and variety of applications, as well as continuous discovery of the latest types of MXenes. However, similar to other 2D materials, a range of limitations has to be overcome for further developments as well as further progress. Few drawbacks of this material are discussed below –

1. Regarding the extension of the MXene family, till now, only 1/8th portion of discovered MAX phases has been exfoliated experimentally, and another 37 are expected to be feasible.²²⁰ Among the 44 predicted MAX quaternary phases, only nine are prepared so far mainly because of the restricted production of nitride precursors, and MAX phase synthesis is mostly restricted with aluminum. The development of synthesis pathways to get proper control on surface termination groups, controlled morphology, lateral size, and design to tune the properties for a particular application are required to the explored.²²¹ It is also important to highlight that the characterization of surface terminal groups experimentally or their exact image viewing is still challenging.²²²

2. It has been observed that the theoretical studies are much higher in number than experimental confirmations. Finite element modeling and conventional molecular dynamics are still infrequent in the case of the MXene simulation survey. A few characteristics of MXenes are only described by theoretical calculations like mechanical and magnetic properties, which are not confirmed experimentally yet.²²³ In addition, some applications like EMI shielding, actuators and

robotics, OLED, and energy harvesting are only limited to $Ti_3C_2T_x$ and needed to explore with other MXenes.

3. Finally, for industrial applications, high cost and environmental stability are the two main factors that hinder the practical utilization of MXenes. The high cost of MXene is associated with costly MAX phase precursors (Y-Carbon, Ukraine, ~\$550 per 150 g MAX phase) as well as synthesis, delamination, and device manufacturing cost of MXene.²²⁴ So, a cheaper synthesis process, including the MAX phase and device manufacturing, is needed. Due to the oxidation tendency during the storage and degradation during the applications urge expansion of stability characterizations in various solvents and explore for different applications for interest. Future research should be directed to overcome such obstacles.

Overall, the current material MXene has been considered as one of the magical 2D materials of the current century. However, further research is required, mainly in the synthesis and application parts for the progress of the MXene family in order to make them commercially viable.

Conflicts of interest

There are no conflicts to declare.

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