Review article

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MXenes: focus on optical and electronic properties and corresponding applications

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Abstract: The discovery of graphene, the first two-dimensional (2D) material, has caused an upsurge, as this kind of material revealed a tremendous potential of application in areas such as energy storage, electronics, and gas separation. MXenes are referred to as a family of 2D transition metal carbides, carbonitrides, and nitrides. After the synthesis of Ti_3C_2 from Ti_3AlC_2 in 2011, about 30 new compositions have been reported. These materials have been widely discussed, synthesized, and investigated by many research groups, as they have many advantages over traditional 2D materials. This review covers the structures of MXenes, discusses various synthesis routines, analyzes the properties, especially optical and electronic properties, and summarizes their applications and potential, which may give readers an overview of these popular materials.

Keywords: MXenes; optical properties; energy storage; 2D materials; optoelectronics.

1 Introduction

Dimensionality has a strong influence on the property of materials [1]. Two-dimensional (2D) materials have received much attention since the first graphene was successfully prepared in 2004 [2], as it has high potential to be implemented in areas such as energy storage, catalysis, and electronics. This is mostly due to their scarce and exceptional properties. For instance, the unusual Fermi surface of graphene, named as Dirac cone, provides high electron mobility for it. Combined with its in-plane stiffness, graphene is expected to be a possible material for next-generation electron devices [3]. Another kind of 2D materials, classified as 2D carbides, carbonitrides, and nitrides (a.k.a. MXenes), has drawn great attention since the first synthesis of separated single-layer Ti_3C_2 [4]. Nearly 30 structures were experimentally synthesized since then [4–14]. Unlike graphene, surface terminations such as -OH will be generated during the preparation, which endue their hydrophilicity but would not adversely impact the electron mobility of those structures [4]. These combinational properties revealed the high potential of MXenes in energy storage [15, 16], optics [17], electromagnetic interference shielding [18, 19], water purification [20], biomedical applications [21, 22], and so on.

MXenes are named as such because the first and majority of them were obtained by selectively removing the “A-layers (mostly Al)” in MAX phases or similar precursors. MAX are a series of materials with layered hexagonal structures, where M and X stand for the same meaning as they are for MXenes and A stands for the A-group element. An atom occupies the places between M and X, and the weak connection makes it easy to be selectively etched.

The general formula of MXenes can be written as $\text{M}_{n+1}\text{X}_n\text{T}_z$ ($z=1, 2, 3$) or $\text{M}_{1.33}\text{XT}_z$, where M represents early transition metals such as Ti, Sc, and so on, X stands for carbon and/or nitrogen, and T_x is for the surface terminations, including -O, -OH, and/or -F. Typical examples include $\text{Ti}_3\text{C}_2\text{T}_x$ [4] and Ti_2CT_x [23]. In MXenes, n-layers of X are covered by n+1 layers of M, forming an $[\text{MX}]_n\text{M}$ arrangement [22]. Figure 1 presents all the bare structures of $\text{M}_{1.33}\text{X}$, M_2X , M_3X_2 , and M_4X_3 which have been

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Figure 1: Overview of all experimentally synthesized MXenes, grouped by their structures. M_{1.33}X has ordered or random vacancies in M layers. Two, three, and four layers of M elements are interleaved by X elements for M₂X, M₃X₂, and M₄X₃, respectively. Note that this figure does not represent surface groups T. Detailed information and some examples of MXene phases are in Figure 2.

experimentally synthesized, together with their examples. Apart from the proportion of M and X elements, MXenes can also be sorted according to their crystal structure types, including mono M-element type, solid solution M-element type, ordered double M-element type, and vacancy ordering type (Table 1) [24, 34, 35]. Moreover, in real cases, all functionalized MXenes have surface termination groups that make them stable than bare MXenes. The properties of MXenes are strongly correlated with M

elements and T surface functional groups, as they jointly influence most of the electronic and optic properties. In the following sections, we will first discuss the typical synthesis methods of MXenes, then conclude their properties derived by both theoretical and experimental approaches as well as their applications in many different fields, and predict future research focuses. Optical properties of MXenes are mainly discussed. With this work, we hope to present the overall picture of the state-of-the-art

Table 1: Examples of MXenes in different structures, one or some etching methods, and corresponding references.

MXene type	Crystal structure type	Examples	Etching methods	Refs.
M _{1.33} X	Double M, ordered	Mo _{1.33} CT _z	HF	[24, 25]
	Double M, no order	Nb _{1.33} CT _z	HF	[26]
M ₂ X	Mono M	Ti ₂ CT _z	HF/HCl + LiF, etc.	[23, 27]
	Double M, ordered	(Mo _{0.67} Y _{0.33}) ₂ CT _z	HF	[25]
	Double M, no order	(Ti _{0.5} V _{0.5}) ₂ CT _z	HF	[23, 28]
	Precursor not MAX	Mo ₂ CT _z	HF/HCl + LiF	[29]
M ₃ X ₂	Mono M	Ti ₃ C ₂ T _z	HF/NH ₄ F ₂ , HCl + LiF, etc.	[4, 6, 8, 30]
	Double M, out-of-plane ordered	(Cr _{0.67} Ti _{0.33}) ₃ C ₂ T _z	HCl + LiF	[31]
	Double M, no order	(Ti _{0.5} V _{0.5}) ₃ C ₂ T _z	HF	[28]
	Precursor not MAX	Zr ₃ C ₂ T _z	HF	[32]
M ₄ X ₃	Mono M	Ti ₄ N ₃ T _z	LiF, NaF, KF molten salts	[9]
	Double M, out-of-plane ordered	(Nb _{0.8} Ti _{0.2}) ₄ C ₃ T _z	HF	[33]
	Double M, no order	(Mo _{0.5} Ti _{0.5}) ₄ C ₃ T _z	HF	[31]

research and applications of MXenes to any reader who is interested.

2 Synthesis

Two main methods have been reported to synthesize 2D materials, including one bottom-up approach and one top-down approach. One example of the bottom-up approach is chemical vapor deposition (CVD), which has been widely used to obtain graphene [36]. However, it is not popular in making MXenes because only multi-layer films can be synthesized through experiments. For instance, the production of Mo_2C films through CVD could only result in at least six layers instead of single-layer MXenes. More researches could be done in implementing this method to produce MXenes, as many successful examples have been reported in obtaining other 2D structures, including MoS_2 [37].

As indicated in Figure 2, the top-down approach can be further divided into mechanical and chemical exfoliation. The first separation of graphene using adhesive tapes was a typical mechanical exfoliation [2]. However, although relatively weaker than M-X bonds, the bonds between M and A (mostly Al) are mostly strong covalent or even metallic, which make the selective removal by forces extremely difficult [39] and even unreachable [38]. Chemical exfoliation instead is mostly used in obtaining MXenes from its precursors – MAX phases. The key point of this approach is to weaken the relatively strong interlayer

bonds by etching, which will be discussed in detail in the following part together with the selection of precursors and the following exfoliation into single flakes.

2.1 Precursors and corresponding product MXenes

Among nearly 30 MXenes that have been successfully synthesized, most are synthesized by etching away MAX phases that contain Al layers. In short, MAX phases are early transition metal carbides and nitrides that form layered and hexagonal structure and represent both metallic and ceramic properties. They are usually categorized by the number of M layers between A layers into mostly “211” (M_2AX), “312” (M_3AX_2), and “413” (M_4AX_3) [40]. Currently, MAX have grown as a large group of more than 130 different structures, and the majority are crystallized in space group of $\text{P6}_3/\text{mmc}$ and its derivation [38].

However, some exceptions have also been reported. In 2016 and 2017, Zhou et al. [32, 41] had reported two successful syntheses of $\text{Zr}_3\text{C}_2\text{T}_z$ and $\text{Hf}_3\text{C}_2\text{T}_z$ by etching Al_3C_3 and $[\text{Al}(\text{Si})]_4$ from $\text{Zr}_3\text{Al}_3\text{C}_5$ and $\text{Hf}_3[\text{Al}(\text{Si})]_4\text{C}_6$, respectively. In these two cases, the precursors are typical members of the layered ternary and quaternary transition metal carbides instead of MAX phases. Moreover, the precursor of Mo_2CT_z , $\text{Mo}_2\text{Ga}_2\text{C}$, has a similar structure to M_2AX . There is only a slight difference in the interlayer structure, as there are two Ga layers between MoC_6 layers instead of one. $\text{Mo}_2\text{Ga}_2\text{C}$ is also an example that the etched layer is

Figure 2: Synthesis pathway of 2D MXene flakes.

First, selective etching is performed to MXenes, and the product is then exfoliated to form single flakes, where (A), (B), and (C) are SEM micrographs of Ti_3AlC_2 , multilayer $\text{Ti}_3\text{C}_2\text{T}_z$, and overlapping single-layer $\text{Ti}_3\text{C}_2\text{T}_z$, respectively. Adapted with permission from [38], Elsevier B.V.

not formed by Al but another A-group element, Ga [42]. Similarly, Si instead of Al was etched during the synthesis of $\text{Ti}_3\text{C}_2\text{T}_z$ from Ti_3SiC_2 [5].

The order of precursors will determine the order of produced MXenes. Up to now, there are three MAX phase solid solutions known regarding M element. The first one is random solid solution, which was the only one known until 2014 [43]. This phase contains all “211”, “312”, and “413” layer structure phases. Examples include $(\text{Ti}_x\text{Nb}_{1-x})_2\text{AlC}$, $(\text{Ti}_x\text{Cr}_{1-x})_2\text{AlC}$ (211), $(\text{Ti}_{1/2}\text{V}_{1/2})_3\text{AlC}_2$ (312), and $(\text{Cr}_{5/8}\text{Ti}_{3/8})_4\text{AlC}_3$ (413) [43–45]. In 2014, with the discovery of $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$ and $(\text{Cr}_{5/8}\text{Ti}_{3/8})_4\text{AlC}_3$, out-of-plane ordered (o-MAX) quaternary MAX phase was discovered, which contains “312” and “413” structural phases [45]. Later in 2017, the in-plane order MAX phases (i-MAX), including only “211” phases, were first reported [24].

2.2 Etching

As the most important step in synthesizing MXenes, etching will always replace the A-group element layer by space termination groups, including -OH, -O, and -F. This step will produce a solution containing loosely connected $\text{M}_{n+1}\text{X}_n\text{T}_z$ multilayer structure held together by hydrogen and/or van der Waals bonds. In this section, different etching methods will be introduced and compared.

The most widely used method to etch the A layers from MAX phases involves the use of aqueous fluoride-containing acidic solutions [22]. Hydrofluoric acid (HF; 50 wt.%) was first used to obtain $\text{Ti}_3\text{C}_2\text{T}_z$ from Ti_3AlC_2 [4]. The etching conditions such as the HF concentration and time vary depending on the chemistry and structure of the parent material. For example, 50 wt.% HF will dissolve Ti_2AlC completely, whereas 10 wt.% HF yields Ti_2CT_z [23]. Moreover, it usually takes longer for the complete synthesis of MXenes with a larger n [31, 46].

Due to the threat of HF to human health, an alternative way to synthesize MXenes is to produce HF *in situ* by mixing a strong acid and a fluoride salt [6, 30, 46]. Ghidui et al. first used a mixture of hydrochloric acid (HCl) and lithium fluoride (LiF) to etch Ti_3AlC_2 [6] and found that the presence of metal halide is necessary for MXene “clay” formation [47]. In addition, other salts such as NaF, KF, and NH_4F [7, 48] and different HCl concentrations have proven to be successful etchants [49].

There are also other methods to avoid the use of HF. The most prospective one is likely to be the electrochemical synthesis [50], where the parent phases are processed in HCl, or ammonium chloride or tetramethylammonium hydroxide (TMAOH) electrolytes to remove Al. Yang et al.

reported a high yield of more than 90% of monolayers and bilayers of $\text{Ti}_3\text{C}_2\text{T}_x$ from Ti_3AlC_2 using a binary aqueous electrolyte [13]. Other methods include the hydrothermal synthesis to produce $\text{Ti}_3\text{C}_2\text{T}_z$ [10] and the synthesis of the first nitride MXene $\text{Ti}_4\text{N}_3\text{T}_z$ in molten salts of LiF, NaF, and KF [9]. Recently, Li et al. first synthesized fully Cl-terminated $\text{Ti}_3\text{C}_2\text{Cl}_2$ and Ti_2CCl_2 MXenes in the ZnCl_2 Lewis acidic molten salt [14].

The methods mentioned above generally work only on carbide MXenes, except for the synthesis of $\text{Ti}_4\text{N}_3\text{T}_z$ [50]. The ammoniation of carbides can yield nitride MXenes. For example, V_2NT_z [51, 52] and Mo_2NT_z [52] have been obtained from V_2CT_z and Mo_2CT_z , respectively, at 600°C. Wet chemical etching has only been used to produce nitride MXene Ti_2NT_z successfully up until now [53].

The methods using acidic fluoride-containing solutions are usually performed at temperatures below 60°C [38], as the gaseous halides will lead to the formation of carbide-derived carbon [54, 55]. However, it is still possible to obtain MXenes at higher temperatures. Apart from the V_2NT_z and Mo_2NT_z examples (600°C) mentioned above, $\text{Ti}_4\text{N}_3\text{T}_z$ was synthesized at 550°C in molten salts [9]. At 270°C, $\text{Ti}_3\text{C}_2\text{T}_z$ was produced by hydrothermal method using NaOH [10].

2.3 Exfoliation

Etching will produce MXene multilayers that should be exfoliated or delaminated to obtain colloidal suspensions containing single or few MXene layers. Before exfoliation, the multilayers should be washed by water or acidic solutions such as HCl or sulfuric acid (H_2SO_4) to rinse off salts produced by etching [9, 47]. In this part, different exfoliation methods and their suitable conditions as well as different processing methods will be introduced.

The choice of exfoliation method depends on the etching conditions. One of the advantages of using HCl/HF etchants is that the lithium cations and water intercalate the MXene layers, which increases their space and weakens their interactions [22]. The multilayers exfoliate spontaneously when washed to a pH value of about 6 [6]. With simple shaking or sonication, the yields can be increased [6]. For other etchants applied, exfoliation by the intercalation of cations or organic molecules is usually used as the yields of direct sonication are low [4]. These molecules will enlarge the space between the interlayers and decrease their interactions. Then, shaking or sonication can be applied.

The choice of exfoliation method also depends on the MXene compositions. The dimethyl sulfoxide

molecule cannot exfoliate MXenes other than $\text{Ti}_3\text{C}_2\text{T}_z$ [56] and $(\text{Mo}_{2/3}\text{Ti}_{1/3})\text{C}_2\text{T}_z$ [31]. Tetrabutylammonium hydroxide can be used on many MXenes, such as V_2CT_z and Ti_3CNT_z [57], $(\text{Mo}_{2/3}\text{Ti}_{1/3})\text{C}_2\text{T}_z$ and $(\text{Mo}_{1/2}\text{Ti}_{1/2})\text{C}_3\text{T}_z$ [46], $\text{Ti}_4\text{N}_3\text{T}_z$ [9], and Mo_2CT_z [29], but does not work for $\text{Ti}_3\text{C}_2\text{T}_z$. TMAOH can be used instead [49].

After exfoliation, a colloidal suspension of single and few MXene layers will be obtained by centrifugation. If the product is not in immediate use, it should be preserved near neutral pH [58, 59]. Otherwise, the ultrathin sheets can be processed by various ways: vacuum filtration [56], spin coating [27, 60], acid or base crumpling [58], and electrophoretic deposition [61].

3 Properties and corresponding applications

3.1 Stability and surface groups

Due to the synthesis process of MXenes in aqueous solutions, prepared MXenes are always attached by surface termination groups, including -F, -OH, and -O groups. The type of surface groups mostly depends on the synthesis route, to be specific, the reagent used in etching. While storing in the water, -F groups tend to be replaced by -OH groups, resulting in less stable -F-terminated MXene compared to -O- and/or -OH-terminated ones. In the same work, it has also been reported that high temperature and/or metal absorption can cause the transformation from -OH groups to -O groups [62]. Further studies revealed that metal contact, such as Mg, Ca, and Al, can further decompose -O group-terminated (functional) MXenes into bare (pristine) MXenes [63]. Bare MXenes are reported to be reactive in most of the cases. Oxidation is easy to happen for bare MXenes in environments with oxygen and water. This process will form metal oxide nanocrystals, which usually starts from the edge of flakes, and will finally grow to the entire flake. It is also reported that oxidation can be accelerated when exposed to light. Therefore, storing bare MXenes in an oxygen-free, dry, and dark space is mostly recommended [64]. Due to its instability, MXenes are functionalized by surface groups in most of the applications.

To further understand the structure of MXenes, it is important to analyze the location of surface groups. Building up a precise structure could help with that [65]. It was predicted that the possible location of the surface groups is between the three neighboring C atoms above the hollow sites [66]. This model was proven to be too simple, as later

researches reported that both locations and orientations of terminations should be more complicated [67]. The final properties of surface termination groups are jointly influenced by both their species and the component elements of MXenes. In most cases, the structures of MXenes are simplified as uniform terminating species, which cannot fit the real situation. Therefore, other more precise models need to be invented to represent this complicated system, as different surface groups can coexist, and random absorption happens jointly in many cases. Moreover, multilayer stacking is reported to exist in reality, which reveals the importance of analyzing the interlayer interactions, including hydrogen bonding and van der Waals forces [68].

Additionally, the surface groups of MXenes not only influence their stability but also affect nearly all the other properties, including electronic and optical properties, which will be further discussed [69].

3.2 Electronic properties

Theoretically, many researches have been done to make a thorough inquiry on the band structures, density of states (DOS), and many other electronic properties. Thus far, both first-principle calculation and experimental results revealed that most of the (functionalized) MXenes should be metallic or semimetallic, whereas MXenes that are semiconductors only take a small number. Early theoretical investigation reported several examples as shown in Figure 3A, including Sc_2CT_2 ($\text{T}=\text{OH}, \text{F}, \text{O}$), Ti_2CO_2 , Zr_2CO_2 , and Hf_2CO_2 with band gap between 0.24 and 1.8 eV [67]. In particular, $\text{Sc}_2\text{C}(\text{OH})_2$, Sc_2CF_2 , and Sc_2CF_2 are reported to have band gaps of 0.45, 1.03, and 1.8 eV, respectively, which reflect the influence of surface groups on the electronic properties of MXenes. Moreover, the band structures of $\text{Sc}_2\text{C}(\text{OH})_2$ and Sc_2CF_2 are more similar compared to Sc_2CO_2 . This is because both F and OH groups demand receiving one more electron to be stabilized, whereas O is capable of receiving two more. Analyzed by their band structures, five of six structures are predicted to have indirect band gap, except $\text{Sc}_2\text{C}(\text{OH})_2$. To further understand the mechanism that caused some MXenes to be semiconducting after functionalization, researchers have investigated the electronic structures of both bare and functionalized MXenes [67]. The result shows that, similar to MAX phases, bare MXenes are all metallic, as the Fermi energy is all contributed by *d* orbital of M element (Figure 4A–C) [67, 70]. The *p* band of X element is located slightly below the *d* band with a tiny band gap. Figure 4D and E reflects the condition after functionalization by F or O surface groups. To be specific, F

Figure 3: The density of states for bare Ti_2C , Ti and C atoms, Ti_2CF_2 , and Ti_2CO_2 . (A) DOS of bare Ti_2C . (B and C) PDOS on atomic orbitals of Ti and C atoms, respectively. (D and E) DOS of Ti_2CF_2 and Ti_2CO_2 , respectively. Fermi energy is at zero and is shifted to the center of the gap for semiconductors. Adapted with permission from [67], Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

functionalization caused the downward shifting of Fermi energy, as each F gained one electron from the system. In contrast, O functionalization caused a further downward shifting, which finally made Ti_2CO_2 a semiconductor. Projected DOS (PDOS) of Ti_2C , Ti_2CF_2 , and Ti_2CO_2 in Figure 5 could make this mechanism clearer. Further studies also reported that strain [71, 72] or an external electric field [73, 74] could strongly influence the band gap of Ti_2CO_2 and Sc_2CO_2 . In addition, the similarity of M element will also reveal some similar electronic properties. Typical examples are Ti, Zr, and Hf. As they are in the same group, they have the same outermost electron number and configuration ($4s^2$, $5s^2$, and $6s^2$, respectively). This makes them reflect similar transition trend from metallic to semiconducting characteristic [67]. For M_2CO_2 (M=Ti, Zr, Hf accordingly) MXenes, the band gap

keeps increasing with the period of M metal as the metallicity decreases [75]. However, as for $\text{Ti}_3\text{C}_2\text{O}_2$ and $\text{Ti}_4\text{C}_3\text{O}_2$ MXenes, the increasing number of Ti (M) element counteracts the function of the 2p orbital of O. Hence, these MXenes are back to be metallic [76].

As indicated previously, in most situations, MXenes that have two different transition metals have randomly distributed solid solution structures. There exist some special cases where these two M elements are ordered instead. These structures can be represented by general forms $\text{M}'_2\text{M}''\text{C}_2\text{T}_n$ and $\text{M}'_2\text{M}''\text{C}_3\text{T}_n$, as M' only takes the place of surface layers and M'' forms the central layers [31]. A typical example is $\text{Mo}_2\text{TiC}_2\text{T}_n$, as Mo locates at the surface, whereas Ti locates in the center. Compared to randomly distributed or monolayer structures, this ordered double transition metal (ordered double M) structure MXenes reveal different electronic properties. For example, $\text{Mo}_2\text{TiC}_2\text{T}_n$, which has a similar structure to $\text{Ti}_3\text{C}_2\text{T}_n$, is semiconducting instead of metallic [46]. Further researches speculated that certain ordered double M MXenes with oxygen terminations, $\text{M}'_2\text{M}''\text{C}_2\text{O}_2$ and $\text{M}'_2\text{M}''\text{C}_3\text{O}_2$ (where M' = Mo, W and M'' = Ti, Zr, Hf) in specific, are 2D topological insulators and topological semimetals, respectively [77]. In addition, not only ordered double M MXenes but also mono M ones can be topological insulators, as examples include W_2CO_2 , Mo_2CO_2 , and Cr_2CO_2 [78]. Theoretically, some $\text{Mo}_2\text{M}''\text{C}_2\text{O}_2$ (M'' = Ti, Zr, Hf) MXenes are even predicted to have spin Hall effect at room temperature, as they have considerable large topological gaps (0.1–0.2 eV) [79]. Although the synthesis of topologically nontrivial MXenes is still difficult, these MXenes have high application potential, especially in superconductivity areas.

Figure 3B shows the projected band structure of $\text{Sc}_2\text{C}(\text{OH})_2$, $\text{Hf}_2\text{C}(\text{OH})_2$, Hf_2CF_2 , Hf_2CO_2 , graphene, BN, graphene, and MoS_2 [77]. The color and size of dots represent the projected weight of the wave function onto different composed elements. The Fermi energy level is set at 0 eV. As will be shown later, these states are mainly located in vacuum region outside of the hydrogen atoms. They have near free electron (NFE) characteristics with parabolic energy dispersions concerning the crystal wave vector. The lowest energy of NFE states of OH-terminated MXenes is unoccupied and located above and near Fermi level, which is lower than that of graphene, BN, graphene, and MoS_2 . The reason is that positively charged hydrogen atoms exist at the surface of OH-terminated MXenes [77]. With this surface-charged hydrogen atom, the OH-terminated MXenes may have potential application to purify the heavy metal as Pb and Hg. As a result, it indicated that OH-terminated MXenes would be accessible more easily than in other 2D materials [77].

Figure 4: The band structures for six MXenes and for the constituent atoms in the systems in [42].

(A) Band structure of six semiconducting MXenes with M_2CT_2 structures. The Fermi energy is at zero. This image revealed the significant influence of M element and T surface group to the band structure of MXenes. Adapted with permission from [67], Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (B) Projected band structures on each constituent atoms for eight different systems indicated in the figures. The position of the lowest NFE near the Fermi energy at the G point is indicated by an arrow. The Fermi energy is located at zero energy. Adapted with permission from [70], The Royal Society of Chemistry.

Figure 5: PDOSs and projected band structures for (A) Ti_2C , (B) Ti_2CF_2 , and (C) Ti_2CO_2 .

The Fermi energy is located at zero energy. Adapted with permission from [70], The Royal Society of Chemistry.

Compared to OH-terminated MXenes, F- and O-terminated MXenes also show trend of NFE states while located at high energy. In this figure, Hf_2CF_2 , Hf_2CO_2 have the lowest energy NFE states at 3 and 5 eV above the Fermi energy. Such higher energy is the main limitation for the application of F- and O-terminated MXenes [77].

The partially occupied NFE states near the Fermi energy are sensitive to the variation of environment. The

states decline when applying enormous large pressure, adsorbing gas molecules, or doping the MXenes with graphene, BN, or graphene [77].

3.3 Optical properties

Theoretically, many of the optical properties, including absorption, reflection, and transmittance, can be analyzed

through the calculation of the imaginary part of dielectric function tensor, which can be treated as a function of photon wavelength. Approximations such as HSE06 are implemented to calculate desired properties above [80, 81]. In this way, the reflectivity, energy loss function, and absorption spectrum of bare Ti_2C , Ti_2N , Ti_3C_2 , and Ti_3N_2 have been investigated and reported [70, 82, 83]. These works derived plasmon energies of these four structures above to be 10.00, 11.62, 10.81, and 11.38 eV, respectively. It also reported in conditions that, when energies are less than 1 eV, the reflectivity could be 100% or less than 50% for systems with electric field parallel or perpendicular to the surface, respectively, which infers the capability of transmitting electromagnetic waves [82]. Apart from bare structures, the optical properties of functionalized Ti_2C and Ti_3C with surface terminations to be -F, -OH, and -O have also been theoretically investigated [83]. This work shows that, in range of infrared to ultraviolet (UV) light, -F and -OH functionalized MXenes (Ti_2C and Ti_3C in this work) have lower in-plane absorption coefficients than bare and O functionalized ones. In complement, it also indicates that -F- and -OH-terminated Ti_2CT_2 and Ti_3CT_2 should exhibit white color [83].

Generally, MXenes reveal a low photoluminescence (PL) response in aqueous solution. To enlarge its application potential, especially in biological and optical fields, forming quantum dots (QDs) will be a considerable way. This is because quantum confinement and edge effects could be emerged when QDs are made atomically thin

[84–87]. Unlike nanosheets, which are thin but large in flat, QDs are extremely small and have luminescence. Apart from QDs derived from traditional materials [86, 88, 89], a few MXene-based QDs (MQDs) with desired PL properties have also been reported thus far, including Ti_3C_2 and V_2C MQDs [87, 90], among which the former one is most widely researched. It was reported that MQDs can be synthesized by cutting the bulk layered Ti_3C_2 MXene using hydrothermal method with quantum yields up to 10%. By controlling the reaction temperature, colloidal MQDs with different morphologies could be yielded, namely, MQD-100, MQD-120, and MQD150 (Figure 6A). The UV-vis spectra, PL excitation (PLE) and PL spectra were tested and reported in Figure 6B–D. All products were proven to be able to achieve luminescence emission, whereas MQD-150 had a higher cytotoxicity than MQD-100 and MQD-120, which indicated that it was not suitable for bioapplication. The comparison between bright-field images and excited at 406, 488, and 543 nm images of RAW264.7 cells is presented in Figure 7, which indicates its potential application as multicolor cellular imaging reagents. Apart from this, other synthesis pathways result in higher quantum yield [91], and possible applications of PL in other fields have also been reported [92, 93].

Nonlinear optics focuses on handling light-matter interaction for materials that respond nonlinearly to electromagnetic field (nonlinear-optical media) [94]. This phenomenon is the base of many optical communication systems, sensing, lasers, and photonic devices. The

Figure 6: The preparation diagram of MQDs and the intensities over UV-vis spectra, PLE, and PL spectra for MODs in aqueous solutions at different temperatures.

(A) Schematic diagram of preparation of MQDs. (B–D) UV-vis spectra (solid line), PLE (dashed line), and PL spectra (solid line, Ex = 320 nm) of MQD-100, MQD-120, and MQD-150 in aqueous solutions, respectively. (Photos inside are MQD-100, MQD-120, and MQD-150 solution under visible light and 365 nm UV lamp.) Adapted with permission from [87], Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 7: Bright-field imaging of RAW264.7 cells and the confocal imaging of the cells incubated in MQD-100 and MQD-120. (A and E) Bright-field imaging of RAW264.7 cells. Confocal imaging (405, 488, and 543 nm) of RAW264.7 cells incubated with (B–D) MQD-100 and (F–H) MQD-120. Adapted with permission from [87], Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

nonlinear optical properties of MXenes did not draw much attention at first, but since 2017, a series of researches have been reported [17, 49, 95–100]. The broadband nonlinear optical response of $\text{Ti}_3\text{C}_2\text{T}_x$ was the first property to be investigated. This work revealed the industrial application possibility for implementing $\text{Ti}_3\text{C}_2\text{T}_x$ as femtosecond laser generator. Compared to graphene, the lower linear absorption losses of $\text{Ti}_3\text{C}_2\text{T}_x$ also reflect its better photonic application. Other works focusing on Z-scan measurements (Figure 8A–C) show that the light absorption of $\text{Ti}_3\text{C}_2\text{T}_x$ tends to be nonlinear, which is also known as saturable absorption [95]. When illuminating intensity increases, as shown in Figure 8D, absorption coefficient will decrease before reaching a threshold intensity (I_{th}) and turn up after I_{th} [17]. Moreover, the saturable absorption could be found for all the testing wavelengths from 800 to 1800 nm. Both facts above suggest a possibility that the nonlinear absorption behavior of $\text{Ti}_3\text{C}_2\text{T}_x$ is contributed by more than one mechanism. Researchers then indicated that, at low illuminating intensity, the one-photon saturable absorption process dominates, whereas the multiple-photon process occurs at higher illuminating intensity. In addition, the other nonlinear absorption processes become the dominant processes when the illuminating intensity rises above the I_{th} threshold.

Many properties of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes are beneficial to industrial applications. First, the saturable absorption of MXenes makes it suitable for ultrafast laser applications, where it could be used as a spectral filter to induce

mode-locked laser pulses, as illustrated in Figure 8E. As an example in Figure 8F and G, a stable mode-locked laser pulses with a period of 65 ns and a temporal width of 660 fs is produced by Ti_3CNT_x [96]. In addition, $\text{Ti}_3\text{C}_2\text{T}_x$ was also reported to reach similar performance. It is even able to produce a broadband wavelength ranging from 1550 to 1620 nm, which includes the essential telecommunication band, C-band. This property indicates its prospect in signal and communication area [17]. The effective nonlinear absorption coefficient is tested to be about $-10^{-21} \text{ m}^2/\text{V}^2$, which points out its high potential in optical switching areas [17, 95].

In comparison to other traditional 2D materials, including graphene and black phosphorus, the nonlinear optical performance of MXenes could reach a similar performance [17]. Moreover, it was shown that $\text{Ti}_3\text{C}_2\text{T}_x$ with a thickness of 5 nm is more resilient at high laser energy than other 2D materials [95]. Further experimental studies proved that an optical diode could be formed by coupling $\text{Ti}_3\text{C}_2\text{T}_x$ with a reverse saturable absorption material, C_{60} [95]. This could be implemented as a filter for high rectification ratio optical signal. Lastly, it is also reported that, when dispersing $\text{Ti}_3\text{C}_2\text{T}_x$ in rhodamine 101 solution, a metamaterial is formed as random lasing can be observed [101].

Recently, attention has been paid to the plasmonic properties that have been observed and implemented in some electronic devices. As defined in [102], plasmons are collective electron oscillations formed by high matter

Figure 8: Selected nonlinear optical properties.

(A) Illustration of an MXene thin film Z-scan measurement experiment. (B and C) Saturable absorption property of Ti₃C₂T_x MXene film is tested. (D) Relationship between absorption coefficient and laser intensity of MXene at 1064 nm. (E) Illustration of a Ti₃CNT_x-based mode-locked implemented ring-cavity erbium-doped fiber laser. (F) This can generate femtosecond laser pulses. (G) Autocorrelation trace measured in (E). (A–C) Adapted with permission from [95]. (D) Adapted with permission from [17]. (E–G) Adapted with permission from [96], Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

interaction. According to the material, it has been investigated as surface plasmon (SP) and bulk plasmon (BP). BPs are electron oscillations formed deep within the body of a free carrier, whereas SPs exist at a metal-dielectric interface at the surface of the metal. Excitation of plasmons may cause an energy loss to the interaction of the fast-moving electron through a solid [103].

Among all the MXenes, Ti₃C₂ is the most studied one for nearly all properties, including optical. In the early research about plasmons of Ti₃C₂, theoretical and experimental methods were both applied to measure the electron energy loss (EEL), as the energy loss is related to the plasmons [104]. In Figure 9, SPs of MXene systems were measured experimentally by the high-resolution EEL spectra in the energy range from 0.2 to 30 eV with *ab initio* calculated theoretical simulation for different thickness. The peaks of interband transition 1 to 3 indicate that the

calculation method choice is reasonable. The peaks of SPs are observed at very low energy range, so the detailed views from 0.2 to 2.0 eV are provided.

In Figure 9, as the thickness of multilayer MXenes decreased, reduction in BP intensity is observed. In contrast, the intensity of SP shows an increasing trend with the decrease of thickness. This result can be explained as the contribution of surface terms at low thickness, as the influence of surface terms is negligible in BP. The position of BP peaks shows independently of the variation of thickness and the number of layers, which can be explained by weak inter-layer coupling between neighbor layers in Ti₃C₂T₂. For other 2D materials, it is the opposite of Ti₃C₂T₂. The BP peak shifts with the variation of thickness, such as graphene, hexagonal boron nitride, and transition metal dichalcogenides [105].

Figure 9 highlights the dominance of SPs over bulk ones even for a 45-nm-thick sample. This observation is in

Figure 9: Comparison between experimental (A) and calculated OH-terminated (B) low-loss spectra recorded on $\text{Ti}_3\text{C}_2\text{T}_x$ for different thickness.

In (A), the right figure is the detailed view of the left one from 0 to 2 eV. In (B), the right figure is the detailed view of the left one. Adapted with permission from [104], American Physical Society.

contrast with other plasmonic metals, such as aluminum or gold [106]. The small value of the SP damping factor, weak interlayer coupling, and lower probability of low-energy SP decay lead to a reduction in BP probability and, in turn, an SP dominance system. This mechanism indicates that the SP resonances in MXenes can be tuned by altering the electronic structure while controlling the thickness. It also shows that the electronic structure of MXenes is modified by the surface functionalization from -OH and -F.

Although the studies of nonlinear optical properties of MXenes are in the early stage, they have shown a promising future for multiple applications of the materials. More investigations should be made on the photonic, optoelectronic, and plasmonic properties of various MXenes as well as their interaction with light.

4 Application

4.1 Energy storage

4.1.1 Batteries

As indicated above, 2D MXene sheets show a combination of high electrical conductivity and hydrophilicity and possess tuneable interlayer space, which may allow ions to be inserted into or extracted from the materials. As a result, it is a promising material for electrochemical ion batteries.

The conductivity of MXenes can vary from metallic-like to semiconducting or even insulating. It can be manipulated by changing the nature of its terminal functional groups and the M elements. Based on the previous

studies, Ti- and Mo-based MXenes, such as Ti_2CT_x , $\text{Ti}_3\text{C}_2\text{T}_x$, and so on, with less defects and good contact among the flakes, exhibit high conductivity [70]. In addition, the conductivity is also related to interlayer spacing [50]. In conclusion, single-layer MXenes or MXenes without terminations exhibit metallic conductivity theoretically, whereas the nature of the conductivity between layers determines the electronic behavior [70].

Compared to MAX, MXenes with large interlayer spacing facilitate the diffusion of ions between layers. With its high conductivity, it is a promising electrode material for secondary ion batteries, including Li-, Na-, K-, and Al-ion batteries. Li-ion batteries (LIB) are one of the most well-studied applications with MXene electrode. Monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ presents a capacity of about 150 mAh/g at 260 mA/g in LIBs, which is lower than that of carbon-based electrode (~380 mAh/g) [50, 107]. During the charge/discharge process, especially the first cycle, the MXene sheets will collapse or stack, leading to less active sites and more difficult diffusion between layers for inserted ions. Higher capacity is expected for delaminated or intercalated MXene flakes and hybrid MXenes with a stable interlayer structure. Ren's group reported an approach to prevent the restacking using porous $\text{Ti}_3\text{C}_2\text{T}_x$ flakes and carbon nanotube (CNT) spacer, which resulted in a capacity of four times of the original value in LIBs [108]. Another method is to intercalate between the MXene sheets with Sn^+ or other cations to stabilize the interlayer structure [58, 59]. To improve the performance, a lot of researchers explored the hybridization of MXenes and other materials as shown in the Table 2. The hybrid material $\text{MoS}_2/\text{Ti}_3\text{C}_2\text{MXene@C}$ exhibits a significantly high capacity of about 1200 mAh/g at 200 mA/g [110]. Besides LIBs, MXene-based

Table 2: Comparison of performance of batteries with MXene-based electrodes.

Batteries	Materials	First C.E.	Initial discharge/charge capacities (mAh/g)	Cyclability (mAh/g)	Ref.
LIB	MoS ₂ /Ti ₃ C ₂ -MXene@C	69.1%	1210/1750 @ 200 mA/g	1200 @ 100 mA/g after 3000 cycles	[89]
SIB	Ti ₂ C ₃ T _x nanodot-P composite	66%	600/909 @ 100 mA/g	400 @ 400 mA/g after 150 cycles	[59]
Li-S	S/L-Ti ₃ C ₂	99.8%	1288/1291 @ 200 mA/g	970 @ 200 mA/g after 100 cycles	[109]

hybrid electrodes in other ion batteries or Li-S batteries also have great potentials. More researchers are exploring in this field, as the theoretical capacity of these batteries could be even higher than that of graphene.

4.1.2 Supercapacitors

Supercapacitor is an energy storage device that can provide high-energy density with short charge/discharge time. Based on the energy storage mechanism, there are mainly two types of supercapacitors, namely electrical double-layer capacitor (EDLC) and pseudocapacitor. The EDLC stores electrostatic charges by forming electrical double layer on the surface of electrode. The pseudocapacitor stores Faradic charges through redox reactions on the electrode surfaces. In general, it stores more charges than that of EDLC with lower stability [111].

With 2D structure, high electrical conductivity, and large specific surface area, MXenes can be widely used as electrodes in supercapacitors. The MXene electrode stores charges predominately from the redox reaction, where the polar organic molecules or cations intercalate spontaneously [16]. In addition, the MXene electrode also exhibits appreciable capacitance at high scan rate, where the

Faradic charge transfer is a rate-limited step. This means that sufficient electrostatic charges can be stored on the MXene surface as well [112]. Compared to carbon-based materials, MXenes with a high density always shows high volumetric capacitance and high cyclability [95].

Ti₃C₂T_x is one of the most studied MXenes for supercapacitors. Its volumetric capacitance (free-standing paper electrode) in basic and neutral electrolyte reaches 300 to 400 F/cm³, which is comparable to the activated graphene-based electrodes (350 F/cm³) [113]. In the acidic electrolyte 1 M H₂SO₄, the volumetric capacitance was demonstrated to exceed 900 F/cm³ for rolled Ti₃C₂T_x clay electrode [96]. The reasons for this fascinating performance are as follows: (a) the intercalated Li⁺ ions during the synthesis process prevent the restacking of MXene sheets during redox reactions and (b) there are more accessible electrochemical active sites for the smallest cations [22]. In addition, Ti₃C₂T_x-based supercapacitors can sustain its capacitance after 10,000 cycles, showing excellent cyclability [6].

Besides the intercalation of cations to prevent the restacking, the performance of MXene-based supercapacitors can be affected by modification of the surface terminal groups. The capacitance will be increased significantly by eliminating the -F groups or replacing them with -O-containing groups. As reported, the modified Ti₃C₂T_x with

Figure 10: Comparison of rate performances of selected MXene electrodes. Note that both pristine and modified ones are included [6, 29, 114–117].

eliminated terminal groups contains more electrochemical active sites and exhibits a larger capacitance than that of pure $\text{Ti}_3\text{C}_2\text{T}_x$ by 211% [16, 114]. The HF-produced $\text{Ti}_3\text{C}_2\text{T}_x$ was treated to replace the -F with -OH groups, resulting in at least twice of the capacitance of the original one [97]. In the acidic electrolyte, the improvements can be as high as seven times of the original value. Other MXene materials, both solution-based pristine ones and modified structures (by polypyrrole and PEDOTS), such as $\text{Ti}_3\text{C}_2\text{T}_x$ and Mo_2CT_x , respectively, also have high volumetric capacitance as shown in Figure 10, indicating the great potential of MXene in supercapacitors [22].

As discussed in the previous section, hybridization of MXenes with other materials has attracted more and more attention, as it combines the advantages of both materials. Polymers with polar functional groups, including polydiallyldimethylammonium chloride and polyvinyl alcohol, were investigated to intercalate into $\text{Ti}_3\text{C}_2\text{T}_x$ flakes [115]. These polymers show greatly enhanced mechanical and electrochemical properties. Conductive polymer polypyrrole was applied to hybridize with $\text{Ti}_3\text{C}_2\text{T}_x$, demonstrating significantly improved volumetric capacitance to 1000 F/cm^3 , as more charges were stored on the hybrid during the redox reactions [116].

To obtain MXene-based supercapacitors with high performance, the electrolyte and counterelectrode employed also play important roles. More work can be done to optimize the performance with well-modified MXenes and proper electrolytes and counterelectrodes.

4.2 Transparent conductive thin films in optoelectronics

The $\text{Ti}_3\text{C}_2\text{T}_x$ MXene thin film shows a combination of high transmittance and electrical conductivity, which could

be widely used in optoelectronics. The properties can be affected by the surface termination groups and its microstructures. Sprayed MXene film obtained from aqueous suspensions exhibits higher transmittance than the one fabricated through ethanol-based suspensions. Intercalation with TMAOH may dramatically improve more than 20% of the transmittance. Spin-coated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene thin film with thickness of 4 nm shows an excellent transmittance of 93% and high electrical conductivity of 5736 S/cm due to its horizontally orientated large flakes (Mxentoinc; Figure 11). The mechanism of the relationship between its transparency and microstructure requires further study.

Many properties of MXenes, including high electrical conductivity, relatively high transparency, 2D morphology, processability, and excellent mechanical properties, make them suitable to construct transparent conductive thin films [94]. A number of theoretical and experimental researches have been done on the optical properties of MXenes. In particular, a series of experimental studies about $\text{Ti}_3\text{C}_2\text{T}_x$ have been done to create MXene-based transparent thin films by depositing MXenes with different thickness on substrates such as glasses [27, 30, 60, 95, 118–123]. In 2014, the first transparent MXene film family, $\text{Ti}_3\text{C}_2\text{T}_x$ -IC film, was produced by etching magnetron-sputtered Ti_3AlC_2 precursor on sapphire substrate. Compared to normal film, the highly transparent $\text{Ti}_3\text{C}_2\text{T}_x$ -IC film intercalated $\text{Ti}_3\text{C}_2\text{T}_x$ with NH_4HF_2 , which could reach about 90% transmittance. In contrast, the thin film of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and Ti_3AlC_2 MAX precursor has only 70% and 30% transmittance, respectively (Figure 11A) [30]. The transmittance spectra also reveal the difference between MAX and MXenes; whereas the former one shows a flatter spectrum, the latter has an absorption peak of about 300 nm. This work also reported an observation that the thickness of $\text{Ti}_3\text{C}_2\text{T}_x$ and the intercalated films could linearly influence

Figure 11: The transmittance spectra and the light absorbance of several MXenes and the change of film's resistance upon bending. (A) Transmittance spectra with their corresponding images for Ti_3AlC_2 , $\text{Ti}_3\text{C}_2\text{T}_x$, and $\text{Ti}_3\text{C}_2\text{T}_x$ -IC. Adapted with permission from [30], Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (B) Light absorbance of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Ti}_3\text{C}_2\text{T}_x$ -IC with different thickness and (C) change of film's resistance upon bending. Adapted with permission from [118], Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

its absorbance (Figure 11B). Later, a solution processing method, named spin casting, was invented to make aqueous solution of MXenes into optical quantity nanometre thin films, which was reported to reach conductivity of 6600 S/cm with 97% transparency remaining [60]. In 2016, Mariano et al. reported that, for 550 nm wavelength visible light, $\text{Ti}_3\text{C}_2\text{T}_x$ has 77% transmittance. Moreover, this work reported that vacuum annealing of the films was able to remarkably improve the conductivity without largely defecting their transparency [119]. Therefore, to obtain films with better performance, a drying process (typically vacuum annealing) should be performed after deposition. Among all the films, Zhang et al. reported a film with the highest conductivity, 9880 S/cm, which was prepared by spin casting of d- $\text{Ti}_3\text{C}_2\text{T}_x$ (hand-shaken, nonsonicated) and vacuum annealing at 200°C [120]. In addition, compared to glass, the conductivity of flexible substrate will be slightly decreased when bended to small radius. For a set radius, however, the bend cycle will not significantly influence the conductivity (Figure 11C) [27, 120]. Compared to other two solution processing methods, including spray coating and dip coating, although the spin-casting method yielded the best performance film as mentioned above, high concentration d-MXene dispersion (usually >5 mg/ml) is needed [41, 124] to obtain considerably thick films. The substrate needs to be flat to obtain the best conductivity, whereas the size is also limited by spin chamber. Together, these restrictions limit the scale production of MXene films by the spin-casting method. For the other two methods, spray coating is a simple and controllable alternative of thin film deposition. In particular, spray coating only requires relatively low concentration (0.5–3 mg/ml) [66] of solution but is able to deposit in a large area. The thickness is also controllable, which will be able to fabricate film in a large range of thickness (nanometers to micrometers) by controlling the number of spraying. However, the resulting films usually tend to

have rough surface with granule boundaries, which is also difficult to be applied and industrialized [121].

4.3 Sensors

The above analysis shows that MXenes have very critical properties in optoelectronics and thermoelectrics. MXenes work as a kind of 2D material. It has similar applications to other 2D materials, such as MoS_2 and black phosphorus. Therefore, many research groups applied MXenes as a substitutional material to work as sensors.

Pressure sensor is one of the most important applications, as the conductivity cross-plane is highly related to its interlayer spacing on its unique structure [125, 126]. As reported by Ma et al., the interlayer spacing of MXenes can be altered by external pressure and mechanical strain, making it a great candidate for piezoresistive sensors [126]. $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits higher sensitivity to mechanical strains and pressure than carbon-based materials, metal wires, and MoS_2 . A porous 3D MXene sponge obtained from dip coating can detect mechanical pressure as low as 9 Pa [127]. Its sensitivity even makes it possible to build a pressure sensor for human-machine interfacing. Conductive MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) nanosheets were sandwiched between two polylactic acid sheets to achieve up to 30 kPa broad range [128]. When it is applied to human activity, for example, attached on muscle or joint with sealing a transparent tape, the monitor of motion provides continuous tracking for muscles and joints, which will be very helpful in medical rehabilitation [126].

Another kind of sensor is electrochemical biosensor that could be used to track volatile organic compounds, water vapor, label-free dopamine, disease biomarkers, environmental contaminants, and so on [69, 129–131]. Table 3 shows different kinds of sensor using different electrodes to detect different analytes and their detection parameters.

Table 3: Comparison of different electrodes according to their types of analytes and detection parameters.

Electrode	Analyte	Detection method	Detection limit	Detection range	Ref.
$\text{Ti}_3\text{C}_2\text{T}_x$ -MXene	Carbendazim	DPV	103 nM	50 nM–100 μM	[132]
Hb/ $\text{Ti}_3\text{C}_2\text{eGO}$ /gold foil electrode	H_2O_2	Amperometry	1.95 mM	2 mM–1 mM	[133]
$\text{Ti}_3\text{C}_2\text{T}_x$ /GCE	H_2O_2	Chronoamperometry	0.7 nM	–	[134]
Anti-CEA/f- Ti_3C_2 /GCE	CEA	CV	18 fg/ml	100 fg/ml–2 μg /ml	[135]
MXenes/Apt2/exosomes/Apt1/PNIPAM-AuNPs/GCE	MCF-7 exosome	ECL	125 particles/ μl	5×10^2 – 5×10^6 particles/ μl	[136]
Urease/MB-MXene/SPE	UA, urea	SWV	5, 0.02 μM	30–500, 0.1–3.0 μM	[137]
Alke Ti_3C_2 /GCE	Cd(II), Pb(II), Cu(II), Hg(II)	SWASV	0.098, 0.041, 0.032, 0.130 μM	0.1–1.5 μM	[138]

In the application of environmental contaminants detection, delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene was used as an electrode modifier for the detection of fungicide carbendazim [132]. For heavy metallic ion detection, $\text{Ti}_3\text{C}_2/\text{GCE}$ is applied to measure Cd, Pb, Cu, and Hg content [138]. H_2O_2 is a common reactive oxygen species in living cells and plays an important role in biological systems because it is a by-product of several oxidase reactions. Detection of H_2O_2 is performed by either enzymatic or nonenzymatic way. Due to the high surface area and electronic properties, $\text{Ti}_3\text{C}_2\text{T}_x/\text{GCE}$ Hb/ $\text{Ti}_3\text{C}_2\text{eGO}$ /gold foil electrode MXene sensor shows the ability to analyze the direct electron transfer between enzyme and electrode, which indicates the concentration of H_2O_2 [133, 134]. Biomarker is a biological molecule found in blood, fluids, and tissues as a sign of abnormal biological process and diseases [139]. For example, anti-carcinoembryonic antigen (CEA)/ $\text{f-Ti}_3\text{C}_2/\text{GCE}$ is used to detect cancer biomarker CEA [135]. In another work, enhanced chemiluminescence (ECL) biosensor was reported using MXene aptamer composite for MCF-7 exosome detection [136]. MB-MXene is reported to detect urine and uric acid (UA) in blood [137]. However, some of the mechanisms are not clear yet. With deeper discoveries, the applications in biosensor could be extended.

4.4 Biomedical

MXenes also have a promising future in biomedical applications, such as biosensors, drug delivery, photothermal therapy (PTT) for cancer, bioimaging, etc., due to their hydrophilicity, large specific surface areas [140], excellent biocompatibility [141, 142], biodegradability [143], high absorption over the near-infrared (NIR) region [144], and high light-to-heat conversion efficiency [145]. MXenes have huge potential in multitudinous biomedical applications.

PTT uses the heat generated by NIR laser to ablate the cancer cells. MXenes can act as photothermal agents to convert light into heat due to its high absorption and photothermal conversion efficiency. Many researches have shown that MXenes are efficient in *in vitro* cell damage and *in vivo* tumor eradication [144, 146]. For example, Xie et al. reported that, combined with chemotherapy, tin sulfide nanosheet-based dual therapy nanoplatforms can efficiently kill the cancer cells without observable side effects on healthy tissues in mice [147].

MXenes can be used to deliver drugs for its hydrophilicity and large surface areas. For example, Han et al. first reported that Ti_3C_2 can be used to deliver drugs with a high drug loading capability of 211.8%, which can be applied to chemotherapy [148]. This means that MXenes can be used

to perform synergistic therapy, which combines PTT and chemotherapy.

Apart from fighting cancer, MXenes can be employed for other biomedical applications, such as biosensing, bioimaging, theranostics, and antibacterial activities.

The potential of MXenes can be further explored by surface modifications. For example, Ti_3C_2 can be PEGylated to improve its stability in physiological solutions, terminated by Al oxoanion to enhance its photothermal effect [149], and combined with MnO_x or GdW_{10} -based polyoxometalates or mesoporous silica nanoparticles for different purposes, such as concurrent therapeutics, diagnostic imaging, magnetic resonance, computed tomography, etc. [91, 150, 151].

The biocompatibility of MXenes has been tested to ensure their safety. For instance, Chen et al. determined the good cytocompatibility of Ti_3AlC_2 , Ti_3SiC_2 , and Ti_2AlN [142]. Han's group found that Ti_3C_2 can be easily excreted out of the test subjects via urine and feces [148]. Xie et al. demonstrated the photodegradability of tin sulfide nanosheets after long periods of exposure to laser irradiation [147]. Yu et al. used a fluorine-free method to prepare MXene QDs, which show great biocompatibility [144]. Despite various research, the toxicity and biocompatibility of MXenes, especially *in vivo*, still need to be further investigated before their biomedical applications.

In conclusion, MXenes have various biomedical applications, such as PTT, drug delivery nanoplatforms, biosensing, bioimaging, theranostics, and antibacterial activities. More research is still needed in its toxicity, and more exploration can be made into its surface modifications.

5 Conclusion and perspectives

Since its first successful synthesis in 2011, MXenes have been widely studied and analyzed. Most of them were synthesized through a two-step process, etching from MAX layers using mostly HF and then exfoliation into single 2D nanosheets. About 30 different MXene compounds have been successfully synthesized thus far. Functionalized MXenes are relatively stable with surface termination groups attached. Their unique and fascinating properties, especially optical properties, made MXenes a focus of worldwide researchers. High electrical conductivity and hydrophilicity together make MXenes perfect candidates for energy storage materials, whereas high transmittance makes it suitable for producing transparent conductive thin films. There are many other possible applications,

including supercapacitors and sensors, which might be commercialized in the future. Some MXene materials with good interlayer contact and less defects show even better performance when employed in LIB or supercapacitors than that of C-based materials such as graphene or CNTs. More possible applications have been explored in magnetic shielding, photocatalysis, lubrication fields, etc. However, the understanding of the inner and edge structure of MXenes should yet to be enhanced. Researchers still have several questions to be solved, for example, proposal for a convincing model to describe the mechanism of MXenes. The electrical conductivity and the electrochemical stability are also very important. For MXenes, these properties can be manipulated by the terminal groups and M elements. For broad biomedical applications of MXenes, more attention should be focused on surface modifications and the biocompatibility of MXenes. Although the foreground of MXenes seems to be bright and clear, researchers should still contribute a lot to push this material into industrial applications.

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