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MXetronics: Electronic and Photonic Applications of MXenes

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Abstract

MXenes, a large family of two-dimensional transition metal carbides and nitrides, have been attracting great interest since the discovery of Ti$_3$C$_2$Tx in 2011. The unique combination of metallic conductivity and hydrophilicity in Ti$_3$C$_2$Tx resulted in outstanding performances in electrochemical applications. The surface of MXene is highly chemically active after selective chemical etching of their precursor phases and always forms surface terminations such as hydroxyl, oxygen, or fluorine. Those surface functional groups not only affect their hydrophilic behavior and electrochemical properties such as ion adsorption and diffusion, but also affect their electronic structure, conductivity, work function, and hence their electronic properties. In this review, the emerging electronic and photonic applications of MXenes (henceforth referred to as MXetronics) are discussed. This is a fast-emerging field of MXene research with huge potential.
1. Introduction

MXene is a large family of two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides that can be derived from 40+ layered $\text{M}_{n+1}\text{AX}_n$ (MAX) phases or similar precursors by selective removal of the ‘A-layers’. The ‘M’ represents early transition metals, the ‘A’ stands for A-group elements in the periodic table (mostly group 13 and 14), the ‘X’ is carbon and/or nitrogen, and $n=1$-$3$.\cite{1} MXenes with a general chemical formula of $\text{M}_{n+1}\text{X}_n\text{T}_x$ can be obtained by several chemical routes including hydrofluoric acid (HF),\cite{2} F-containing acidic solutions (typically a mixture of hydrochloric acid and lithium fluoride),\cite{3} or base solutions such as potassium hydroxide for fluorine-free products.\cite{4} Acid mixture of sulfuric acid and hydrofluoric acid has been reported to minimize etch byproducts such as AlF$_x$.\cite{5} The electrochemical route has been recently explored using binary aqueous electrolyte for high-yield and fluorine-free synthesis of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene.\cite{6} The detailed guideline for synthesis and process protocols can be found elsewhere.\cite{7} These etching solutions attack the metallic M-A bonds more rapidly than covalent M-X bonds, hence result in few-atomic-layer-thick MXene nanosheets. While the A-element is etched, the surface of MXene layer becomes chemically active and thermodynamically prefer to create surface functional groups (represented as T$_x$), such as $=\text{O}$, $-\text{OH}$, and/or minor $-\text{F}$.\cite{8-10}

So far, over 20 different MXenes have been experimentally synthesized and characterized,\cite{1, 11-14} and more are under investigation. Figure 1 summarizes the diverse electronic properties of functionalized MXenes. The large family of MXenes can be first sorted by their crystal structure (single metal type, double metal type – solid solutions or ordered structure, and vacancy ordering type [11-13]) including the number of atomic layers. In addition, the species of transition metal element and surface functional groups are directly related to the electronic properties of MXenes. Although most MXenes are metallic, some semiconducting MXenes are predicted, which are in $\text{M}_2\text{CT}_x$ formula with oxygen termination and ordered structure. The surface functional groups, interlayer spacing, band structure, and
work function of MXenes are discussed in the following sections. MXenes have shown promises in electrochemical energy storage,[1] electromagnetic interference shielding,[15] biomedical applications,[16] and catalysis.[17, 18] In this review, recent advances in the electronic and photonic applications of MXenes (MXetronics) are discussed, and future promising research directions are outlined.
Figure 1. Schematic diagram presenting the diverse electronic properties of MXene family: structure, element of transition metal, and the type of functional groups are considered to sort the electronic properties of MXenes. Semiconductor MXenes are highlighted with colors upon appropriate surface functional groups: blue, violet, and sky-blue colors represent oxygen, fluorine, and hydroxyl group, respectively, while the metallic MXenes with any terminal groups are marked in grey color. The topological insulator/semimetals are shown with slash/horizontal line filled backgrounds, respectively. Mo$_{1.33}$C is semiconductor with mixed termination of O$_{0.67}$F$_{0.33}$.
2. Basic Properties of MXenes

2.1. Surface Functional groups

The presence of the surface termination groups renders the surfaces of MXenes hydrophilic (water contact angle of 21.5–35°). [3, 19, 20] Furthermore, most MXenes are highly conducting (~10^4 S cm^-1 for the most well-studied Ti_3C_2Tx).[21, 22] This unique combination of hydrophilicity and metallic conductivity is one of the advantages over graphene and its derivatives. In addition, the large surface area inherited from their 2D structure makes MXenes promising in electrochemical energy storage applications. The surface of functionalized MXenes is negatively charged due to the large electronegativity of O or F atoms in terminal groups, thus restacked MXene can allow reversible electrochemical intercalation of cations including Na^+,[23, 24] as well as multi-valence Mg^{2+} and Al^{3+} by strong Coulombic interaction between MXene and cations.[25] The surface groups also play an important role in pseudocapacitive redox reaction where oxygen groups can be converted to hydroxyl groups while accommodating both proton and electron in H_2SO_4 electrolyte.[26] The stable dispersion behavior of MXenes in polar solvents such as water, ethanol, acetone, acetonitrile, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), and propylene carbonate (PC) can allow facile integration with a variety of solvent-sensitive materials.[27] Ti_3C_2Tx MXene electrodes in supercapacitors with macroporous, hydrogel, and vertically aligned liquid crystal structures have been reported showing excellent electrochemical performance including ultrafast operating rate at 100 V s^-1,[28] ultrahigh volumetric capacitance of 1500 F cm^-3,[28] and thickness independent capacitance,[29] respectively.

The surface functional groups of MXenes affect not only their electrochemical performance, but also electronic properties (including band structure, work function), and optical properties. Although the method to precisely control the surface functional group
species is yet to be discovered, those surface functional groups are highly dependent on the synthesis route and post-synthesis treatments. $^1$H and $^{19}$F nuclear magnetic resonance (NMR) spectroscopy study has successfully quantified Ti$_3$C$_2$Tx MXenes prepared by HF route and HCl-LiF route.[30] Figure 2 (a) and (b) show the different morphology of multilayer Ti$_3$C$_2$Tx MXene prepared by volatile HF route and milder HCl-LiF route, respectively. The surface functional groups of Ti$_3$C$_2$Tx MXene has been experimentally observed as shown in Figure 2 (c) and (d), with the schematic illustration in Figure 2 (e). The larger-sized MXene nanosheet ~10 µm can be obtained by the milder method (Figure 2 (f)).

Treatment with tetrabutylammonium hydroxide (TBAOH) has been reported to reduce the fluorine content and increase oxygen content, in the case of Mo$_2$TiC$_2$Tx and Mo$_2$Ti$_2$C$_3$Tx MXenes.[31] Such cationic organic molecules can be readily intercalated between the negatively charged surfaces of multilayer MXene that allows effective delamination of 2D flakes. Alkalization of MXene using base solution is reported to transform F-groups into OH-groups in Ti$_3$C$_2$Tx.[32] Hydrazine treatment of Ti$_3$C$_2$Tx MXene has been reported to decrease the water contents and OH group, which was beneficial for enhanced volumetric capacitance.[33]
Figure 2. a-b) Scanning electron microscopy (SEM) images of HF route Ti$_3$C$_2$T$_x$ with accordion-like structure (a) and HCl-LiF route Ti$_3$C$_2$T$_x$ with a more compact structure (b). Reproduced with permission.[30] Copyright 2016, PCCP Owner Societies. c) high-angle annular dark-field (HAADF) image of multilayer Ti$_3$C$_2$T$_x$, showing ABAB stacking of adjacent two Ti$_3$C$_2$T$_x$ monolayers as inherited from the parent Ti$_3$AlC$_2$ MAX phase. d) Annular bright-field (ABF) image combined to HAADF, revealing the surface functional groups of Ti$_3$C$_2$T$_x$. e) Schematic description of the proposed atomic structure of Ti$_3$C$_2$T$_x$, where the surface functional groups locate the hollow site of three neighbor carbon atoms, creating ABCABC stacking of atomic layers. Reproduced with permission.[34] Copyright 2015, American Chemical Society. f) Annular dark-field scanning transmission electron microscopy (ADF STEM) image of delaminated Ti$_3$C$_2$T$_x$ nanosheet. Reproduced with permission.[21] Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
2.2. Tunable interlayer spacing

MXenes also have tunable interlayer spacing by controlling intercalated species between the nanosheets. Once cation species are intercalated, Ti$_3$C$_2$Tx MXene shows hygroscopic property and reversible humidity dependent behavior with interlayer spacing of 12.5-15.5 Å (including one or two intercalated water layers).[35] Organic molecules can also be intercalated between MXene nanosheets. For instance, Ti$_3$C$_2$Tx with pillared structure has been reported using cetyltrimethylammonium bromide (CTAB) or stearyltrimethylammonium bromide (STAB) with interlayer spacing of 22.3 or 27.1 Å, respectively.[36] A series of Alkylammonium cations have been intercalated and demonstrated tunable interlayer spacing between 14.7-38.0 Å.[37] Tetrabutylammonium cation (TBA$^+$) intercalated in Mo$_2$CT$_x$ is reported to have interlayer spacing of 16.9~18.9 Å depending on the degree of wetness.[38, 39] Such tunable interlayer spacing can be useful for gas sensing and gas separation applications.

2.3. Band Structure

A number of theoretical studies have been conducted to identify the electronic band structures and interesting properties of MXenes from their large family.[40] Most of the functionalized MXenes are predicted to have metallic/semi-metallic band structures, while a few MXene systems are expected to be semiconducting. Sc$_2$CT$_x$ (T = O, OH, F), Ti$_2$CO$_2$, Zr$_2$CO$_2$, Hf$_2$CO$_2$ are reported to have band gaps between 0.24 to 1.8 eV.[8] The reported band structure and band gaps are shown in Figure 3 and Table 1, respectively. Only Sc$_2$C(OH)$_2$ is expected to have direct band gap while the others are predicted to have indirect band gaps among those 6 MXenes. Interestingly, the indirect to direct band gap transition can be induced by the presence of biaxial strain of 4, 10, and 14% for Ti$_2$CO$_2$, Zr$_2$CO$_2$, and Hf$_2$CO$_2$, respectively.[41] The transition from bare MXenes (metallic) to functionalized MXenes is
accompanied by a band gap opening due to newly created states below the Fermi level by strong band hybridization between M 3d orbital and C 2p or O 2p orbitals.[42] This can be explained by the lower electronegativity of transition metals compared to the functional groups and carbon atoms. The OH and F groups can receive one electron, while the O group can receive two electrons from the transition metal atoms. In addition, Ti, Zr, and Hf locate at the same column in the periodic table with the same outer-shell electronic configuration (two electrons in s- and d-orbitals), hence similar metallic to semiconducting character transition trends have been discovered in the corresponding M2C MXene forms after O group functionalization. The band gap of M2CO2 (M = Ti, Zr, Hf) MXenes increase following the metal (M) atomic number, due to the weakening in the metal electronegativity.[43] For the Ti_{n+1}CnO2 (n≥2) MXenes, the contribution of O 2p orbital diminishes as n increases and such MXenes are no longer semiconducting.[44] Mo2C and Cr2C are reported as semiconductors with OH, F, and Cl functional groups, while several double transition metal MXenes are semiconductors upon O termination. (See Table 1)

The experimental realization of thin-film transistor (TFT) using MXene as semiconducting channel is yet to be achieved, however, metallic MXenes can be used as contact materials where their hydrophilic nature can allow easy integration with various semiconducting materials including oxides, polymers, 2D transition metal dichalcogenides (TMDs), and quantum dots.

Few MXene systems with two different metal atoms together can create an ordered structure instead of randomly distributed solid-solution. These are categorized as ordered double transition metal MXenes, with the general formula of M’2M”C2 and M’2M”2C3, where M’ forms the outer surfaces and M” form the central layers of the structure.[45] For example, Mo2TiC2Tx has Mo atoms at the surface layers while Ti atoms are located in the central layers. Such ordered structure is known to affect the electronic properties of MXenes. For example,
Ti$_3$C$_2$Tx is metallic while Mo$_2$TiC$_2$Tx is semiconducting.[31] Moreover, several oxygen-terminated double transition metal MXenes, $M'_2M''C_2$O$_2$ and $M'_2M''_2C_3$O$_2$ ($M' = Mo, W$; $M'' = Ti, Zr, Hf$), have been predicted to be 2D topological insulators and topological semimetals, respectively.[46] A sizable topological gaps of 0.1-0.2 eV has been reported in Mo$_2$M''C$_2$O$_2$ ($M'' = Ti, Zr, Hf$) system, which is even large enough to realize quantum spin Hall effect at room temperature.[47] The energetically preferred oxygen-terminated surface can protect MXenes from oxidation under air ambient. Besides, $M_2$CO$_2$ ($M = W, Mo, Cr$) MXenes are also topological insulators.[48] Some of those topologically non-trivial MXenes have already been experimentally synthesized, hence these MXenes can be good candidate materials for electronic, spintronic devices, and topological superconductivity research.
Figure 3. Band structure of semiconducting $M_2CT_2$ MXene systems. The Fermi energy is at zero. The transition metal element and surface functional groups significantly affect the electronic band structure of MXenes. Reproduced with permission.[8] Copyright 2013, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
Table 1. Calculated band gaps [eV] of functionalized semiconducting MXenes based on conventional (PBE) and hybrid (HSE06) functionals. The latter is more accurate in band gap prediction. Direct band gap MXenes are marked, unless otherwise indirect band gap. Specified properties are remarked such as antiferromagnetic (AFM), ferromagnetic (FM), and topological insulator (TI).

<table>
<thead>
<tr>
<th>MXene</th>
<th>Termination</th>
<th>PBE</th>
<th>HSE06</th>
<th>Remark</th>
</tr>
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<tbody>
<tr>
<td>Sc$_2$C</td>
<td>O</td>
<td>1.84[49], 1.86[50]</td>
<td>2.90[51], 2.91[52], 3.01[50]</td>
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</tr>
<tr>
<td></td>
<td>F</td>
<td>1.0[50, 53], 1.03[49], 1.05[54]</td>
<td>1.64[54], 1.84[51], 1.88[50]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>OH</td>
<td>0.34[50], 0.44[49], 0.45[8], 0.71[53]</td>
<td>0.71[50], 0.74[51]</td>
<td>Direct band gap</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.88[51]</td>
<td>1.64[51]</td>
<td></td>
</tr>
<tr>
<td>Ti$_2$C</td>
<td>O</td>
<td>0.17[53], 0.24[8, 44], 0.33[43]</td>
<td>0.78[55], 0.88[44], 0.92[56]</td>
<td></td>
</tr>
<tr>
<td>Zr$_2$C</td>
<td>O</td>
<td>0.66[53], 0.88[8], 0.96[43]</td>
<td>1.54[56]</td>
<td></td>
</tr>
<tr>
<td>Hf$_2$C</td>
<td>O</td>
<td>0.8[53], 1.00[8, 43]</td>
<td>1.65[57], 1.75[56]</td>
<td></td>
</tr>
<tr>
<td>V$_2$C</td>
<td>F</td>
<td>0.56[58]</td>
<td></td>
<td>AFM</td>
</tr>
<tr>
<td></td>
<td>OH</td>
<td>0.44[58]</td>
<td></td>
<td>AFM</td>
</tr>
<tr>
<td>Cr$_2$C</td>
<td>O</td>
<td></td>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>0.22[53]</td>
<td>3.15[59], 3.49[60]</td>
<td>AFM</td>
</tr>
<tr>
<td></td>
<td>OH</td>
<td>0.03[53]</td>
<td>1.39[59], 1.76[60]</td>
<td>AFM</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.15[53]</td>
<td>2.56[60]</td>
<td>AFM</td>
</tr>
<tr>
<td>Mo$_2$C</td>
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<td></td>
<td>Ti</td>
</tr>
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<td></td>
<td>F</td>
<td>0.25[53]</td>
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<td></td>
<td>OH</td>
<td>0.1[53]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>0.15[53]</td>
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<td></td>
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<tr>
<td>W$_2$C</td>
<td>O</td>
<td>0.194[48]</td>
<td>0.472[48]</td>
<td>Ti</td>
</tr>
<tr>
<td>(Mo$<em>{2/3}$Sc$</em>{1/3}$)$_2$C</td>
<td>O</td>
<td>0.04[61]</td>
<td>0.58[61]</td>
<td>Piezoelectric</td>
</tr>
<tr>
<td>(Mo$<em>{2/3}$Y$</em>{1/3}$)$_2$C</td>
<td>O</td>
<td>0.45[61]</td>
<td>1.23[61]</td>
<td>Piezoelectric</td>
</tr>
<tr>
<td>(W$<em>{2/3}$Sc$</em>{1/3}$)$_2$C</td>
<td>O</td>
<td>0.675[61]</td>
<td>1.3[61]</td>
<td>Piezoelectric</td>
</tr>
<tr>
<td>(W$<em>{2/3}$Y$</em>{1/3}$)$_2$C</td>
<td>O</td>
<td>0.625[61]</td>
<td>1.3[61]</td>
<td>Piezoelectric</td>
</tr>
<tr>
<td>Mo$_{1/3}$C</td>
<td>O$<em>{2/3}$F$</em>{1/3}$</td>
<td>0.5[62]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hf$_2$C</td>
<td>O</td>
<td>0.155[63]</td>
<td></td>
<td></td>
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<tr>
<td>Hf$_2$MnC$_2$</td>
<td>O</td>
<td>0.238[64]</td>
<td></td>
<td>FM</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>1.027[64]</td>
<td></td>
<td>AFM</td>
</tr>
<tr>
<td>Hf$_2$VC$_2$</td>
<td>F</td>
<td>0.4[65]</td>
<td>0.9[65]</td>
<td>Multiferroic (type-II)</td>
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<td>Compound</td>
<td>Symbol</td>
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<td>Parameter 2</td>
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<td>-------------</td>
</tr>
<tr>
<td>Mo$_2$TiC$_2$</td>
<td>O</td>
<td>0.041[46], 0.052[47]</td>
<td>0.119[46], 0.125[47]</td>
<td>TI</td>
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<td>Mo$_2$ZrC$_2$</td>
<td>O</td>
<td>0.069[46], 0.087[47]</td>
<td>0.125[46], 0.147[47]</td>
<td>TI</td>
</tr>
<tr>
<td>Mo$_2$HfC$_2$</td>
<td>O</td>
<td>0.153[46], 0.213[47]</td>
<td>0.238[46], 0.301[47]</td>
<td>TI</td>
</tr>
<tr>
<td>W$_2$TiC$_2$</td>
<td>O</td>
<td>0.136[46]</td>
<td>0.290[46]</td>
<td>TI</td>
</tr>
<tr>
<td>W$_2$ZrC$_2$</td>
<td>O</td>
<td>0.170[46]</td>
<td>0.280[46]</td>
<td>TI</td>
</tr>
<tr>
<td>W$_2$HfC$_2$</td>
<td>O</td>
<td>0.285[46]</td>
<td>0.409[46]</td>
<td>TI</td>
</tr>
<tr>
<td>Cr$_2$TiC$_2$</td>
<td>F</td>
<td>1.35[59]</td>
<td>AFM</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td></td>
<td>0.85[59]</td>
<td>AFM, Direct Band gap</td>
<td></td>
</tr>
</tbody>
</table>
2.4. Work Function

Locating at the surface of MXenes, the functional groups are directly related to the work function, which is critical for electronic device applications. Khazaei et al. have reported OH-terminated MXenes tend to have ultralow work functions while other functional groups always induce large work function.[66] The theoretical studies discovered a sufficient wide work function range for the functionalized MXenes, between ca. 1.6 and ca. 8.0 eV from Sc$_2$C(OH)$_2$ and Cr$_2$CO$_2$, respectively.[66, 67] (Figure 4(a)). Such work function range is even wider than conventional metals (dashed lines in Figure 4(a)), which suggests the promise of functionalized MXenes as contact materials in electronic devices. There is an interesting negative correlation between the work function of O-terminated MXene and OH-terminated MXene (Figure 4(b)), where the extremely large modulation of work function can be utilized in novel electronic/sensing devices. Surface terminations not only draw electrons from MXene core but also change the surface dipole moment, hence affect the work function of the host MXenes.[66, 68] (Figure 4(c)) Substitutionally doped MXene with alkali and/or alkali earth metals can further reduce their work functions down to ca. 1.2 eV.[68] Moreover, OH-terminated MXenes have been reported to have nearly free electron (NFE) states which are partially occupied and located near Fermi level.[69] (Figure 4(d) and (e)) This implies that the electron transport in OH-terminated MXenes can be free of nuclear scattering, hence it can be useful for electrical applications. The NFE states, however, disappear upon heterojunction formation with other 2D materials.

Liu et al. have proposed MXenes as Schottky barrier-free contact materials for semiconducting TMDs.[67] For example, O-terminated MXenes are suitable for Schottky-barrier-free hole injection for p-type WSe$_2$. The proposed concept is not only based on the high work function of O-terminated MXenes but also the weak van der Waals interaction at metal-semiconductor interface, which can release the Fermi-level pinning effect.[70]
Similarly, the OH-terminated MXenes with low work functions are suitable contact for n-type MoS$_2$.

In metal-semiconductor junctions, the Mott-Schottky rule is generally used to predict or explain the contact conditions. Depending on the difference between the work function (metal) and electron affinity or ionization energy (semiconductors), either Ohmic contact or Schottky junctions with certain barrier height can be achieved. However, the experimental results often deviate from the fundamental theory, which is mainly due to the interfacial defects and Fermi-level pinning effect. For example, high-energy metal deposition methods such as e-beam evaporation can damage underlying material and create gap states. Recently, it has been demonstrated that transferred metal electrodes can realize van der Waals metal-semiconductor junctions following the Mott-Schottky rule.[71] In their work, the MoS$_2$ transistors with various transferred metal electrodes have shown completely different transistor operating behaviors from the cases using the common high-energy deposited metals contacts. Therefore, the low-energy metal deposition method is important, and the solution processed MXenes can be one of the practical options.
Figure 4. a) Calculated work functions of bare and terminated MXenes in comparison with Sc and Pt. b) Work functions of OH- and F- functionalized MXenes as a function of O-functionalized MXenes. Reproduced with permission.[67] Copyright 2016, American
Chemical Society. e) Surface functionalization induced changes in work function of MXenes with respect to the surface dipole moment. Reproduced with permission.[68] Copyright 2017, The Royal Society of Chemistry. d) Electron localization function (ELF) contour plot of Hf₂C(OH)₂ showing the NFE states outside of MXene. e) The relative energy position of the lowest NFE state with respect to the Fermi level (Eᵋ) as a function of work function for functionalized MXenes in comparison with graphene, MoS₂, and BN. The solid line is the vacuum level. Reproduced with permission.[69] Copyright 2015, American Physical Society.
3. General Electronic Applications

As discussed earlier, MXenes are promising candidate materials for electronic applications based on their metallic conductivity, hydrophilic surface, tunable work function, and interlayer spacing. A thin film consisting of MXene nanosheets can be suitable for electronic devices. For Ti$_3$C$_2$Tx, the well-studied metallic MXene, the reported experimentally measured work functions values are 4.37 eV (measured by ultraviolet photoelectron spectroscopy (UPS) under vacuum),[72] 4.60 eV (by photoelectron spectroscopy in air (PESA)),[22] and 5.28 eV (by Kelvin Prove atomic force microscope (KPFM) under air ambient).[73] Such large modulation of work function (ca. 1 eV) in these cases could be attributed to the difference in both surface functional groups composition and the measurement ambient/technique. Further systematic studies are required. Similarly, monolayer MoS$_2$ has been reported to show different work function values of 4.36, 4.04, and 4.47 eV under air, ultrahigh vacuum, and oxygen ambient, respectively.[74] The surface adsorption can induce charge transfer between MXene and the adsorbate, which can be useful to build a novel gas sensor based on Schottky diode.

3.1. Electrical Contacts

Despite the great potential of MXenes as electrical contact materials, the literature reports are limited to only three cases with oxides,[22] TMDs,[75] and polymer.[76] Wang et al. have demonstrated all-MXene-contacted oxide TFTs with n-type ZnO and p-type SnO channels. Spray-coated Ti$_3$C$_2$Tx MXene film was used as source, drain, and gate contacts.[22] (Figure 5) The Ti$_3$C$_2$Tx MXene showed Ohmic-like contacting characteristics with both ZnO and SnO channels, where negligible Schottky barrier heights of 0.03 and 0.02 eV were found, respectively. Based on the measured work functions and the Ohmic-like contacting characteristics, negligible Fermi pinning effects existed between Ti$_3$C$_2$Tx and these oxide
semiconductors. The spray-coated Ti$_3$C$_2$T$_x$ MXene film showed a root mean square roughness of 3.69 nm, and the hydrophilic surface allows facile atomic layer deposition (ALD) of high-k HfO$_2$ without any surface treatment. (Figure 5(b) and (c)) Finally, well-operating n- and p-type TFTs (Figure 5(d) and (e)), and complementary metal oxide semiconductor (CMOS) inverters with a high gain value of 80 were successfully fabricated. (Figure 5(f) and (g)) The ALD growth mechanism and low-limit of ALD high-k dielectric film thickness are interesting topics that should be discussed in the near future.
Figure 5. a) Schematic process flow for spray-coated Ti$_3$C$_2$T$_x$ MXene film and all-MXene contacted device fabrication. b-c) AFM images of spray-coated Ti$_3$C$_2$T$_x$ MXene film (b), and ALD HfO$_2$ film on the top of spray-coated Ti$_3$C$_2$T$_x$ MXene film (c). d-e) Transfer curves of p-type SnO TFT (d), and n-type ZnO TFT (e), using spray-coated Ti$_3$C$_2$T$_x$ film as source, drain, and gate electrodes. f) Voltage transfer curve of CMOS inverter with a gain value of 80 at a supply voltage of 10 V. g) Magnified dynamic response to 100 Hz square input waveform. Reproduced with permission.\textsuperscript{[22]} Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
Xu et al. have fabricated MoS$_2$ and WSe$_2$ field effect transistors (FETs) using mechanically exfoliated Ti$_2$CT$_x$ MXene as contacts.\cite{75} \textbf{(Figure 6(a)-(c))} The work function of prepared Ti$_2$CT$_x$ was measured as 4.98 eV by KPFM technique. The effective Schottky barrier heights were extracted to be 0.23 and 0.19 eV for Ti$_2$CT$_x$/WSe$_2$ and Ti$_2$CT$_x$/MoS$_2$ FETs, respectively. Considering the valence band edge of ca. 5.2 eV for WSe$_2$\cite{76}, Ti$_2$CT$_x$ MXene exhibited negligible Fermi-level pinning effect at the Ti$_2$CT$_x$/WSe$_2$ interface. On the other hand, the Schottky barrier at Ti$_2$CT$_x$/MoS$_2$ ca. 0.19 eV was smaller than expected from the conduction band edge of MoS$_2$ ca. 4.27 eV,\cite{77} suggesting the possible existence of Fermi level pinning. However, further studies are required to confirm the contact properties as the experimentally prepared Ti$_2$CT$_x$ has mixed surface terminal groups. OH-group dominated Ti$_2$CT$_x$ can be metallic that should form Schottky barrier-free contact with MoS$_2$;\cite{67} On the other hand, O-group dominated Ti$_2$CT$_x$ can be semiconductor with small band gap, \cite{8, 43, 49, 53, 56} which might bring an additional Schottky junction at the metal/Ti$_2$CT$_x$ interface into the whole circuit.

Lai et al. have fabricated Pentacene organic FET using Ti$_2$CT$_x$ flakes as source, drain contacts.\cite{76} \textbf{(Figure 6(d)-(f))} The Pentacene film was deposited by organic molecular beam deposition (OMBD) on the top of MXene, which resulted in the ‘stand-up’ structure growth of Pentacene molecules which is similar to the case of SiO$_2$/Si or rGO surface. The π–π interaction between Pentacene molecules is dominant for the film growth, and Ti$_2$CT$_x$ MXene has a relatively weak interaction with Pentacene molecules due to the presence of surface termination groups. In the case of metal contacts, for example, Pentacene adopts ‘lying-down’ structure on Au substrate due to metal-organic interaction. A small hole-injection barrier height of 0.17 eV was found for Ti$_2$CT$_x$/Pentacene junction, which is nearly one-third of Au/Pentacene (0.45 eV). As a result, record low contact resistance of 3 kΩ·cm was found. This work encourages further studies of MXenes for contacts with organics. The chemical
reaction between the organic molecules and surface terminations of MXenes can be another important topic to investigate.

**Figure 6.** a) SEM image of Ti₂CTₓ/WSe₂ FET. b-c) Transfer curves of Ti₂CTₓ/WSe₂ FET (b), and Ti₂CTₓ/MoS₂ FET (c). Black squares and grey circles are negative and positive V_DS bias, respectively. Reproduced with permission.[75] Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. d) Optical microscope image and e) transfer curve of Ti₂CTₓ MXene/Pentacene FET device. f) Effective barrier height at Ti₂CTₓ MXene/Pentacene contacts as a function of gate voltage, extracted from the Richardson plots. Inset shows energy band diagram corresponding to the flat band conditions. Reproduced with permission.[76] Copyright 2018, The Royal Society of Chemistry.
3.2. Conductive Filler

Tu et al. have shown that MXene sheets can be used as effective fillers in insulating polymers where significant enhancement in the dielectric constant was discovered.[78] (Figure 7) Specifically, an ultrahigh dielectric permittivity of $1.39 \times 10^5$ along with relatively small dielectric loss of 4.1 was achieved, with optimized MXene loading of 15.4 wt%, which is near their percolation limit. The dielectric permittivity was 2500 times larger than pristine polymer poly(vinylidene fluoride-trifluoro-ethylene-chlorofluoroehyle) (P[VDF-TrFE-CFE]), although the dielectric loss was 68 times larger than pristine polymer. The $\text{Ti}_3\text{C}_2\text{Tx}$ MXene can be homogeneously mixed into fluoropolymer matrix, due to hydrogen bonding interaction between the surface atoms of MXene (O, F) and the hydrogen atoms in PVDF molecules. Such microscopic dipoles can align along with an externally applied electric field, where the charge accumulation leads to enhanced dielectric constant. The work demonstrates that MXenes are not only hydrophilic but also fluorophilic. Therefore, the composites of MXenes and fluoropolymers used in flexible device applications (such as CYTOP) can be utilized to enhance the dielectric constant.
Figure 7. **a-b)** Schematic illustration of the polarization charges in pristine P(VDF-TrFE-CFE) MIM capacitor (a), and MXene/P(VDF-TrFE-CFE) MIM capacitor (b) under external electric field ($E_{\text{ext}}$). **c)** Dielectric permittivity and dielectric loss as a function of MXene loading in P(VDF-TrFE-CFE) at room temperature and 1 kHz. **d)** Comparison of the maximum dielectric permittivity and corresponding dielectric loss reported in the literature for other conductive fillers in P(VDF-TrFE-CFE) matrix. **e)** Raman and **f)** FT-IR spectra of MXene/P(VDF-TrFE-CFE) composites with different MXene concentration. Reproduced with permission.[78] Copyright 2018, American Chemical Society.
3.3. Energy harvesting

Kim et al. measured the thermoelectric properties of three molybdenum-based MXenes (Mo$_2$CT$_x$, Mo$_2$TiC$_2$T$_x$, and Mo$_2$Ti$_2$C$_3$T$_x$).[38] (Figure 8(a)-(f)) Mo$_2$CF$_2$ MXene have been theoretically predicted as the most promising thermoelectric candidate among 35 different M$_2$CT$_x$ MXenes.[53] The latter two MXenes have ordered double metal structure where Mo atoms are preferentially located on their surface, creating similar surface nature as Mo$_2$CT$_x$. These MXenes were processed into free-standing flexible papers by simple vacuum filtrated method. Cationic organic molecules (TBA$^+$) were found to be intercalated between MXene nanosheets, resulting in low electrical conductivity and Hall mobility due to the large interlayer spacing. Upon annealing at 500-600 K under Ar/H$_2$ ambient, the intercalated water and organic molecules could be removed from MXene papers, revealing their conductive nature. Among the three Mo-based MXenes, Mo$_2$TiC$_2$T$_x$ showed both high electrical conductivity of 1380 S cm$^{-1}$ and relatively large Seebeck coefficient of -47.3 $\mu$V K$^{-1}$ at 803 K, with the largest thermoelectric power factor of $3.09 \times 10^{-4}$ W m$^{-1}$ K$^{-2}$.

Dong et al. demonstrated metallic MXenes for flexible triboelectric nanogenerators (TENG) that converted mechanical energy into electric power.[79] (Figure 8(g)-(h)) Ti$_3$C$_2$T$_x$ MXene was reported to be more negative than polytetrafluoroethylene (PTFE or Teflon) in the triboelectric series. The negative side triboelectric materials are mostly insulating and are difficult to make conducting composite or metallic coating on them due to their low surface energy. The larger difference between two materials in the triboelectric series can produce the larger output, however, these insulating electronegative materials often limit their triboelectric applications into the single-electrode mode. The high electrical conductivity and the negative surface of Ti$_3$C$_2$T$_x$ MXene solved this limitation, where Ti$_3$C$_2$T$_x$ MXene showed a comparable $V_{oc}$ to PTFE in a triboelectric device coupled with polyethylene terephthalate (PET) in single electrode mode. A large $V_{oc}$ output of ca. 650 V with peak power of ca. 0.65
mW was observed for $5 \times 2.5 \text{ cm}^2$ sized TENG device under a vertical compressive force of 15 N at 2 Hz. Flexible MXene TENG was also demonstrated for energy harvesting from daily human motions with excellent stability (50,000 cycles of bending angle up to 30°).

Figure 8. a) Digital photograph of $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ paper showing flexibility. b-c) Cross-sectional SEM images of $\text{Mo}_2\text{TiC}_2\text{T}_x$ paper before (b) and after annealing (c). d-f) Temperature-dependent thermoelectric properties of Mo-based MXene papers: Electrical conductivity (d), Seebeck coefficient (e), and thermoelectric power factor (d). Reproduced with permission.[38] Copyright 2017, American Chemical Society g) Open circuit voltage output of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene/glass TENG coupled with PET/ITO under the vertical compressive force of 15 N at 2 Hz, and h) magnified view of the panel (g). i) Open circuit voltage output of flexible MXene TENG for human thumbs movement. Reproduced with permission.[79] Copyright 2017, Elsevier Ltd.
4. Photonic applications

4.1 Optoelectronics

Kang et al. have investigated the MXene-silicon van der Waals heterostructure as a self-powered photodetector.[72] (Figure 9) The Schottky junction was constructed by drop-casting Ti$_3$C$_2$Tx MXene film (with work function of 4.37 eV) on n-type silicon (n-Si) substrate. The built-in electric field is responsible for the effective separation of light-induced electron-hole pairs in the semiconductor. Balanced transparency and sheet resistance are required from the MXene film for such applications. The thicker film lacks transmittance, while the thinner film shorts in conductivity, which the latter expedites recombination of carriers at the interface. The thickness of drop-casted MXene film was controlled by modulating the concentration of the MXene suspension, where the deposited volume of solution is fixed. Such transparent and conductive MXene thin films can also be prepared by several methods such as spin-coating,[21, 73, 80] spray-coating,[22] and dip-coating,[81] with DC to optical conductivity ratio ($\sigma_{DC}/\sigma_{op}$) up to 15.

The photovoltaic performances of Ti$_3$C$_2$T$_x$/n-Si heterostructure were found to decrease with hydrophilic treatment due to the formation of Si-OH groups. The Ti$_3$C$_2$T$_x$/n-Si heterostructure device annealed at 200°C for 2 hours showed improved Schottky junction properties for photo-detecting, where the ideal factor of 3.10 decreased to 2.53 and Schottky barrier of 0.48 eV increased to 0.53 eV. This suggests that annealing not only removes the defects at the interface but also affects the surface functional groups of Ti$_3$C$_2$T$_x$ MXene. The optimum Ti$_3$C$_2$T$_x$/n-Si heterostructure photodetector device showed on-off ratio of $\sim$10$^5$, responsivity of 26.95 mA W$^{-1}$, under an incident laser power density of 15.17 mW cm$^{-2}$ (excitation laser wave length was 405 nm).
Figure 9. a) UV-Vis transmittance curve of drop-casted Ti$_3$C$_2$Tx films. b) I-V curve at different temperatures and c) Energy band diagram and of Ti$_3$C$_2$Tx/n-Si Schottky junction in dark. d) J-V curve of Ti$_3$C$_2$Tx/n-Si devices fabricated by different concentration of colloidal MXene solution under illumination. e) J-V curve of Ti$_3$C$_2$Tx/n-Si device under different energy density illumination. f) Photoresponse of Ti$_3$C$_2$Tx/n-Si heterostructure under 15.17 mW cm$^{-2}$ laser (405 nm) irradiation. Reproduced with permission.[72] Copyright, 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
Hantanasirisakul et al. have demonstrated transparent conducting Ti$_3$C$_2$T$_x$ films with tunable film thickness by simple spray-coating method.[82] (Figure 10(a)-(c)) Homogeneous MXene films were deposited on various substrates over large area. The Ti$_3$C$_2$T$_x$ film prepared by aqueous suspension shows a better optical figure of merit ($\sigma_{DC}/\sigma_{op}$) over ethanol-based suspension. This can be due to the exchange of surface functional group of MXene flakes, and/or the different drying dynamics leading to microstructural differences in the final films. MXene films deposited on flexible substrates exhibit stable electromechanical behavior up to the bending radius of 8 mm. The optical properties of MXene film can also be modulated by chemical intercalants. For example, a significant increase in the transmittance from 74.9 % to 92.0 % was found after intercalating tetramethylammonium hydroxide (TMAOH, or NMe$_4$OH) molecules, while the interlayer spacing between MXene nanosheets increased only 3 Å. The improved transparency showed no dependence on the interlayer spacing, and this relationship requires further study.

Zhang et al. have reported the state-of-the-art transparent, flexible, and conductive Ti$_3$C$_2$T$_x$ MXene films by spin-coating for supercapacitors applications, which showed enhanced optical figure of merit ca. 15.[21] (Figure 10(d)-(f)) The MXene films with transmittance of 93 ~ 29 % (thickness 4 ~ 88 nm) exhibited high electrical conductivity of 5736 ~ 9880 S cm$^{-1}$, due to the large flake size and horizontally-aligned arrangement which avoided percolation issues. Such films can be used as transparent electrodes in optoelectronic applications.
Figure 10. a) Optical images of spray-coated Ti$_3$C$_2$T$_x$ films on a glass (top) and a flexible polyester (bottom) substrate. The inset shows high flexibility. b) XRD patterns of Ti$_3$C$_2$T$_x$ films with different intercalants. c) Changes in transmittance of Ti$_3$C$_2$T$_x$ films due to chemical intercalation. (Positive change means increase in transmittance). Reproduced with permission.[82] Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. d) Photographs of flexible, transparent Ti$_3$C$_2$T$_x$ film on PET substrate (top) and sandwiched solid-state supercapacitor with gel electrolyte (bottom). e) UV-Vis transmittance curve of spin-coated Ti$_3$C$_2$T$_x$ films. f) Transmittance plot as a function of sheet resistance, in comparison rGO, graphene, CNT/polymer composite, and PEDOT:PSS. Reproduced with permission.[21] Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
4.2 Plasmonics

Satheeshkumar et al. have fabricated hybrids of noble metal nanoparticles (Ag, Au, and Pd) and Ti$_3$C$_2$Tx MXene nanosheets by one-step solution processing for surface-enhanced Raman spectroscopy (SERS) application.[83] (Figure 11) The metal nanoparticles were successfully hybridized on the surface of MXene by sonication in diluted (0.1 mM) aqueous AgNO$_3$, HAuCl$_4$, and PdCl$_2$ salt solutions, respectively. According to the proposed hybridization mechanism for Ag@MXene hybrids, the intercalated DMSO molecules acted as reduction/nucleation sites and create [Ag$^+$-DMSO] complex monomers. The [Ag$^+$-DMSO] formed strong bond with the –OH groups on MXene surface, which involved charge transfer that immediately changed the color of solutions. The charge transfer initialized MXene-Ag DMSO dimerization, and further reduction of MXene-Ag dimeric complex formed stable Ag$^0$ nano clusters. The Ag, Au, and Pd nanoparticles were randomly distributed on the MXene hybrid surfaces, implying the random distribution of hydroxyl groups. Further surface engineering of MXene nanosheets was expected to modulate the distribution and density of embedded nanoparticles. The surface plasmon resonance (SPR) bands of spherically shaped Ag and Au@MXene hybrids appeared in visible range, at 440 and 558 nm, respectively. On the other hand, the SPR peak of disk-like shaped Pd@MXene was observed in UV range at 160 nm. The growth of metal particle on MXene surface with controllable shapes, orientations, and sizes can be an important topic to investigate for plasmonic devices, catalysis, etc. All three Ag@MXene, Au@MXene, and Pd@MXene hybrids successfully detected diluted (10$^{-6}$ M) methylene blue molecules by SERS with a calculated enhancement factor of ca. 10$^5$, using 35 mW He/Ne laser (632.8 nm). Sarycheva et al. later reported enhanced SERS performance of Ti$_3$C$_2$Tx MXene using HCl-LiF route, which can detect 10$^{-7}$ M of Rhodamine 6G, and 10$^{-6}$ M of methylene blue, crystal violet, and acid blue dyes without embedded nanoparticles.[84]
Figure 11. a) High-resolution TEM image of pristine MXene nanosheets, and low-resolution TEM images of Ag@MXene, Au@MXene, and Pd@MXene hybrid nanosheets. b) UV-Vis spectroscopy analysis of diluted Ti₃C₂Tx suspension with and without metal nanoparticles (Ag, Au, Pd), and c) corresponding surface enhanced Raman spectroscopy for diluted (10⁻⁶ M) methylene blue dye. The line colors are same as panel (b). Reproduced with permission.[83] Copyright 2016, Nature Publishing Group.
Owing to the high density of metal-like free electrons of Ti$_3$C$_2$T$_x$ MXene, some pioneer studies on the plasmonic properties of MXene flakes have been reported.[85, 86] High-resolution electron energy loss spectroscopy (EELS) with scanning transmission electron microscopy (STEM) was used to investigate the local surface plasmonic (SP) modes of Ti$_3$C$_2$T$_x$.[86] (Figure 12) The high spatial resolution of electron microscopy allows accurately excite and map both optically active and forbidden SP modes of single MXene flakes in nanoscale. The oscillation energy and spatial distribution of the longitudinal multipolar modes were correlated with the geometrical aspect of the specific MXene flakes, while the transversal SP mode and inter-band transition were invariant. Further, due to the weak interlay coupling, the independent polarizability of each Ti$_3$C$_2$T$_x$ monolayers is explicitly revealed, which might allow more detailed engineering on the future plasmonic applications. Moreover, the tunability of the SP energy of the longitudinal and transverse SP modes was revealed by changing the free electron density. Blue shifts were discovered with the increase of free electron density at MXene surface, which is concurrent with the desorption of the surface F group through in-situ vacuum annealing of the MXene flakes at elevated temperature. The selectivity and dynamic control of SP energies suggest Ti$_3$C$_2$T$_x$ holds great potential for a gamut of novel near-IR to MIR applications, relying on accurate excitation and detection of single SPs.
**Figure 12.** a) Zero-loss peak (ZLP) subtracted EELS spectra of a truncated triangular shaped Ti$_3$C$_2$Tx MXene flake (7.5 nm thick). The inset shows the most intensive positions of each colored modes. b) EELS intensity mapping images showing 6 different surface plasmon modes of Ti$_3$C$_2$Tx MXene; longitudinal dipole (0.44 eV), quadrupole (0.66 eV), breathing (0.8 eV), central (0.95 eV), transversal mode (1.7 eV), and interband transition (3.5 eV) at specific positions of MXene flake. c) Temperature-dependent core-loss EELS spectra of Ti$_3$C$_2$Tx MXene. d) Estimated [O]/[F] ratio at different temperatures. e) Carrier concentration ($N_e$, black triangles), dipole plasmon energy (red circles), and transverse plasmon energy (blue squares) as a function of [O]/[F] ratio. Reproduced with permission.[86] Copyright 2018, American Chemical Society.
Besides the SP mode studies of single flakes, nanoscale disk-like Ti$_3$C$_2$T$_x$ MXene flake assembly has been utilized to metasurface device for broad wavelength and effective absorbance applications.[87] The utility of Ti$_3$C$_2$T$_x$ in metamaterial absorber application is mainly based on two facts: a) the inherent larger optical loss due to the interband transition and bulk disorder-related scattering; b) the existence of the scattering enhancement from localized surface plasmon resonance (LSPR) in the nanostructures. The resonance frequency of Ti$_3$C$_2$T$_x$ MXene film was identified at ca. 280 THz (wavelength of ca. 1070 nm) for 30 nm thick film, where the real part of experimentally measured permittivity turns from positive to negative while the wavelength increases. The resonance frequency further decreases for the thicker MXene film, which agrees well with previous literature.[80] It is worth to note that the plasmonic behavior of metallic Ti$_3$C$_2$T$_x$ MXene does not need doping or bias voltage, which is a huge difference to graphene plasmonics. Such prototype plasmonic applications of MXene flake assembly exhibited a high-efficiency absorption (ca. 90%) for broad bandwidth illumination (550~2100 nm), covering a significant visible to near-IR spectral window.
5. Sensors

Several types of MXene-based sensors have been demonstrated for monitoring the mechanical strain,[88-92] gases,[93-96] and biomolecules.[97] Typical MXene films consist of nanosheets are electrically conductive and highly flexible.[98] The horizontally stacked structure is suitable to create a number of electrical pathways even under mechanical deformation, where the Coulombic charge interaction between negatively charged MXene surface and positive intercalants or dipolar water molecules can help maintain the structural integrity. These advantages make MXenes suitable for wearable sensor applications.

5.1. Mechanical Sensors

2D MXenes show anisotropic transport behavior,[99] where in-plane conduction is preferred and cross-plane transport is limited due to their anisotropic effective mass of carriers and layered structure. The larger spacing between MXene nanosheets can hinder the charge transport along c-direction. The interlayer spacing can be tuned as discussed in earlier section. Ma et al. have reported a highly flexible and sensitive piezoresistive sensor in which the interlayer spacing of MXene responds to external pressure and mechanical strain.[88] (Figure 13) The dynamic response of MXene’s interlayer spacing against external pressure was observed by in-situ TEM study. The current of MXene piezoresistive sensor increased monotonically with the applied pressure up to 13 kPa. Ti$_3$C$_2$Tx MXene exhibited superior sensitivity with Gauge Factor (GF, ($\Delta R/R_0$)/$\varepsilon$) of 180.1–94.8 (0.19–0.82% strain) and 94.8–45.9 (0.82–2.13% strain), which are higher than carbon materials, metal nanowires, and MoS$_2$. The piezoresistive sensor could detect full range human activities including eye blinking, throat swallowing, finger movement, etc. In a similar piezoresistive sensing approach, Yue et al. reported 3D porous MXene sponge prepared by simple dip-coating method.[92] As the
external pressure creates additional conduction paths, the Ti$_3$C$_2$T$_x$ MXene sponge exhibited high sensitivity with low detection limit of 9 Pa.

**Figure 13.** **a)** Schematic illustration of MXene for piezoresistive sensor. The wider distance ($D_w$) shows the easier compressive deformation upon external pressure than the narrow distance ($D_n$). Inset is equivalent circuit diagram, where the total resistance decreases while the nanosheets get closer. **b)** TEM images showing in-situ dynamic process of multilayer Ti$_3$C$_2$T$_x$ MXene under an external pressure. **c-d)** $I$-$T$ plots of the MXene piezoresistive sensor for different external pressure ~13 kPa (c), and human eye blinking (d). Reproduced with permission.[88] Copyright 2017, Nature Publishing Group.
Zhang et al. have introduced Ti$_3$C$_2$T$_x$ MXene as conductive filler into commercially available poly (vinyl alcohol) (PVA)-based hydrogel.[89] (Figure 14) The MXene/PVA hydrogel showed extremely high stretchability of ca. 3400 %, 10 times enhanced GF, self-heal ability, and great adhesive properties. Interestingly, the MXene/PVA hydrogel exhibited higher sensitivity under compressive strain (GF~80) than tensile strain (GF~25). This asymmetrical strain sensitivity and viscoelastic nature of MXene/PVA hydrogel were utilized to demonstrate a new sensing capability of hydrogels, where increasing/decreasing resistance response was found upon surface contact motions to vertical/parallel direction versus the current pathway. The Ti$_3$C$_2$T$_x$ MXene/PVA hydrogel successfully distinguished the handwriting from different persons and even vocal sounds of similar phonetics, “B”, “D”, “E”, etc.

![Figure 14. a-b) Digital photographs of Ti$_3$C$_2$T$_x$ MXene/PVA hydrogel showing extremely high stretchability (a), and self-healing ability (b). c-d) Resistance responses of MXene/PVA hydrogel for surface motion directions of normal (c), and parallel to the current direction (d). e) Schematic for vocal sensing test of MXene/PVA hydrogel. f) Resistance response for similar sounds of “B”, “D”, and “E”. Reproduced with permission.[89] Copyright 2018, American Association for the Advancement of Science (AAAS).]
Cai et al. have fabricated Ti$_3$C$_2$T$_x$ MXene/carbon nanotube (CNT) composite film on flexible latex substrate by layer-by-layer (LbL) spray technique. The multilayer sandwich structured Ti$_3$C$_2$T$_x$/CNT film showed ultralow detection limit of 0.1% strain, high stretchability of ca. 130%, great sensitivity with GF ca. 772.6, and excellent stability >5000 cycles. The high sensitivity was demonstrated by vocal sound test with words “Carbon”, “Sensor”, “MXene”, as well as human leg movement.

An et al. have integrated the negatively charged Ti$_3$C$_2$T$_x$ MXene with positively charged polymer, poly(diallyldimethylammonium chloride) (PDAC), by LbL assembly in either dipping or spray. The multilayer Ti$_3$C$_2$T$_x$/PDAC was successfully deposited on various substrates including flexible polymers and nylon fiber. Due to the conformal deposition of alternating MXene and polymer, the film exhibited high conductivity ~ 2000 S/cm even after mechanical deformation, where the resistance response was recoverable up to 2.5mm of bending radius and 40% tensile strain. The Ti$_3$C$_2$T$_x$/PDAC film was successfully used for finger motion sensing and topographical scanning of moving object.

5.2. Gas Sensors

Lee et al. have reported gas-sensing behavior of Ti$_3$C$_2$T$_x$ MXene for volatile organic compounds (VOCs) such as ethanol, methanol, and acetone as well as ammonia. The gas sensor device was prepared by simple drop-casting of Ti$_3$C$_2$T$_x$ suspension solution on a flexible polyimide substrate with patterned Pt electrodes. The Ti$_3$C$_2$T$_x$ MXene channel showed a clear increasing resistance once exposed to 100 ppm (parts per million) gases at room temperature. The gas sensing mechanism is not fully understood yet; the adsorption and desorption of target molecules may take place at defect sites of MXene or the surface functional groups. Given the fact that all the tested gases have been reported as electron donor gas, the increasing resistance response was considered as p-type sensing
behavior, in a viewpoint of semiconductor concept based on a large baseline resistance >10 kΩ.

Kim et al. have conducted further systematic investigation for the sensing performance of Ti$_3$C$_2$T$_x$ with metallic channel approach.[94] (Figure 15(b) and (c)) With a small baseline resistance ~80 Ω, Ti$_3$C$_2$T$_x$ MXene sensor device showed great selective response to hydrogen bonding gases (ethanol, acetone, propanol, and ammonia) over acidic gases (NO$_2$, SO$_2$, and CO$_2$), suggesting the important role of surface functional groups. The metallic Ti$_3$C$_2$T$_x$ MXene sensor device showed extremely high signal-to-noise ratio (SNR), which are 2 orders of magnitude higher than all other 2D materials. In addition, MXene exhibited the lowest limit of detection (LOD) ~50 ppb (parts per billion) among all types of 2D material sensors. X-ray photoelectron spectroscopy (XPS) study revealed a significant amount of hydroxyl group, and the density functional theory (DFT) simulation predicted strongest binding energy of Ti$_3$C$_2$(OH)$_2$ for acetone and ammonia, among Ti$_3$C$_2$O$_2$, Ti$_3$C$_2$F$_2$, graphene, MoS$_2$, and black phosphorus.
Figure 15. a) Gas-sensing results of Ti$_3$C$_2$Tx gas sensor for 100 ppm of ethanol, methanol, acetone, and ammonia at room temperature. Reproduced with permission.[93] Copyright 2017, American Chemical Society. b) Gas response performances of Ti$_3$C$_2$Tx sensor for diluted (50-1000 ppb) acetone, ethanol, and ammonia. c) Electrical noise of Ti$_3$C$_2$Tx sensor under N$_2$ ambient in comparison with black phosphorus (BP), MoS$_2$, reduced graphene oxide (RGO). Reproduced with permission.[94] Copyright 2018, American Chemical Society.
Römer et al. have studied the humidity sensing behavior of Ti$_3$C$_2$T$_x$ MXene film, as well as plasma-assisted conductivity modulation by hydrogen- and oxygen-plasma.[95] A spin-coated Ti$_3$C$_2$T$_x$ MXene film showed large variation of resistance from 243 $\Omega$ in vacuum to 6340 $\Omega$ with relative humidity of 80 % while the dynamic response is comparable to the commercial humidity sensor. Hydrogen plasma reduced the oxidation state of titanium in Ti$_3$C$_2$T$_x$ MXene, hence resulting in higher electrical conductivity; oxygen plasma, in contrast, acted oppositely and created TiO$_2$ on the surface of MXene.

Muckley et al. have investigated the structural, electrical, and gravimetric response of ion-intercalated MXenes to water vapor.[96] K$^+$ or Mg$^{2+}$ ion intercalated Ti$_3$C$_2$T$_x$ MXene film showed monotonic response for 0.8-85.0 % relative humidity range. By utilizing quartz crystal microbalance (QCM), it has been discovered that the gravimetric response of MXene was 10 times faster than electrical response. The water molecules tend to induce swell/contraction of interlayer space between MXene nanosheets, and the trapped water molecules are responsible as charge-depleting dopants. Neutron scattering combined with ab initio calculation results revealed that average two/five water molecules per K$^+$/Mg$^{2+}$ ions cause increase in interlayer spacing by a pillaring effect.

5.3. Bio-Sensor

Xu et al. have utilized ultrathin Ti$_3$C$_2$T$_x$ MXene as channel material in solution-gated FET for label-free dopamine detection and real-time monitoring of neural activity.[97] (Figure 16) The ultrathin MXene micropatterns were prepared using aqueous MXene suspension solution and PDMS stamp by micro-contact printing method. Ti$_3$C$_2$T$_x$ MXene had been reported to have majority carrier of electrons and shown a linear relationship between $I_{DS}$ and $V_{GS}$ in a single-flake FET using SiO$_2$ dielectric layer on p$^{++}$ Si gate.[100, 101] In contrast, the solution-gated Ti$_3$C$_2$T$_x$ MXene FET showed an interesting V-shaped ambipolar
field-effect characteristic, where the device operated in n-type/p-type mode when gate voltage was above/below + 0.3V. The p-type operating MXene FET effectively detected the charge interaction between dopamine molecules and surface functional groups of MXene, where increases in the hole concentration resulted in enhancing electrical conductance. The device showed a highly linear current modulation for dopamine concentration range of 100 nM to 50 μM. Furthermore, the MXene FET device successfully monitored the spiking activity of primary hippocampal neurons in real-time. The measured current peaks not only well matched with simultaneously conducted calcium imaging but also included unique spikes.

Figure 16. a) Schematic illustration of MXene FET biosensor. b) SEM image of ultrathin MXene micropatterns. c) Merged image of bright-field and fluorescence images of neuron cells on patterned MXene stripes. d) Real-time monitoring of current in MXene FET while modulating the dopamine concentration. e) The linear and saturation behavior of MXene FET for dopamine detection. f) Real-time neuronal spiking activities recorded by the current in MXene FET (upper panel) and simultaneously conducted calcium imaging (lower panel). Reproduced with permission.[97] Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
6. Conclusions and Perspectives

The unique properties of two-dimensional transition metal carbides and nitrides (MXenes) as well as recent advances in their electronic and photonic applications (MXetronics) have been summarized. (Table S1, see supporting information) The initial applications in electronic, photonic, energy harvesting, and sensing fields are discussed, along with the fascinating tunable properties of MXenes that can be tuned by structure, transition metal elements, surface functional groups, and etching chemistry. These important parameters are related and directly impact the properties of MXenes as presented in Figure 17(a).

The large family of MXenes has a huge potential not only in the electrochemical field but also in a new area which is defined as MXetronics. The metallic MXenes show great potential serving as the electrical contact materials of electronic or optoelectronic devices, which generally require high conductivity, suitable work function, and less defective interface. First, the most well studied metallic Ti$_3$C$_2$T$_x$ MXene shows very high electrical conductivity (ca. $10^4$ S cm$^{-1}$). The hydrophilicity inherited from the surface functional groups allows further water-based materials growth process, for example, solution-processed materials or atomic layer deposition. Second, the large family of MXene indicates a wide range of work function distribution. The various functional groups bring more variety in work function of each MXene, which contributes to an even wider work function distribution over entire MXene family, even wider than conventional metals. Finally, the low-energy solution process of MXene electrodes can effectively avoid interfacial defects and/or additional states that unavoidably induced from conventional high-energy deposition (e-beam evaporation or magnetron sputtering). Although the presence of Fermi-level pinning effect at MXene/semiconductor junction still requires further study, the current evidence suggests that Ti$_3$C$_2$T$_x$ can from Ohmic-like contacts with oxide semiconductors (p-SnO and n-ZnO). In addition, Ti$_2$CT$_x$ have shown a low contact barrier and contact resistance with Pentacene. Furthermore, Ti$_2$CT$_x$ have also been integrated into FETs with TMD channel (MoS$_2$ and
WSe$_2$). The successful integrations of MXene contact in various material systems demonstrate the promising potential of MXetronics.

Besides the hydrophilicity, the presence of surface functional groups also brings strong negatively charged surface to MXene, which further expand the applications of MXene. For example, triboelectric nanogenerator and new layer-by-layer composites with positively charged nano-particles or polymers. The MXene flakes can be dispersed in several different solvents, which allows the co-solution-processing with other nanomaterials or solvent-sensitive materials. However, at the current stage, full control of the surface terminal groups has yet to be demonstrated. In fact, mixed terminal groups of =O, –OH, and –F (or other halogens) exist on the surface of MXenes. Although the -F can be avoided by base-etch route, the presence of =O and -OH are still beyond experimental control level. Thus, an easier method for identifying the surface terminal groups of MXene samples is desperately required to boost the research in multi-functional MXetronics. At the same time, despite the existence of mixed function groups, most theoretical studies are limited in the single type of functional groups cases, more realistic simulation results are desired with randomly mixed terminations.

The tunable interlayer spacing can be a great advantage of MXene, where the negative surface charge can cause spontaneous intercalation of positively charged molecules. The intercalation phenomenon itself can be adopted for sensor application. The interlayer spacing engineered MXene films can be useful for gas/ion sensing and sieving applications. The initial sensing applications for mechanical strains, volatile organic compounds, and biomolecules have shown promising results. The future MXene sensors can be built based on the tunable work function of functionalized MXene, the environment dependent change in the Schottky barrier height will boost the sensitivity of the MXene based junction into a new level. The MXene/organic composite is also expected to show promising sensing performance based on the difference between MXene-atmosphere interaction and MXene-polymer interaction. To fulfill these advanced applications, it is necessary to investigate the work function
modulation via accurate control of surface terminal groups, and also understand the chemical reaction between surface functional groups of MXenes and organic molecules.

The plasmonic applications of metallic Ti$_3$C$_2$Tx MXene is a novel study subject. The initial studies have demonstrated SERS applications using metal nanoparticle embedded MXene hybrid system. The surface plasmonic resonance frequency can be modulated by controlling the size and shape of the metal nanoparticles. The highly conductive Ti$_3$C$_2$Tx MXene prepared from an advanced etch recipe (HCl-LiF) was utilized as an excellent SERS substrate, a high enhancement factor of ca. $10^6$ was achieved. The detailed surface plasmon modes of MXene flakes have been identified by recent EELS study. The longitudinal surface plasmon energies depend on the thickness, size, shape, and surface functional groups of MXene flake, while transverse SP mode and interband transition were found at fixed wavelengths. The relatively weak interlayer coupling allows each MXene nanosheets retain their own SP energies, which can be engineered for novel devices. The layered structure of restacked MXenes with the hydrophilic surface can be attractive for plasmonic sensors or ruler. The rich surface of MXene can be engineered for accommodating certain target molecules, and charge interaction induced spontaneous intercalations of positively charged biomolecules can be utilized in bio-sensing or diagnosis applications. The distance between plasmonic particles is known to significantly affect their resonance frequency, hence the multilayer structure can be ideal where the signal can be further boosted by the numbers of the restacked layers. The patterned Ti$_3$C$_2$Tx MXene nanodisk array showed high-efficiency absorption (ca. 90%) for a wide range of incident light via their strong localized surface plasmon resonance at NIR range, suggesting possible light-harvesting applications in a near future.

More importantly, several semiconducting MXenes are expected to be utilized for novel device applications involving tunable electronic and magnetic properties. The current research of MXetronics is mostly based on metallic Ti$_3$C$_2$Tx. This can be partially attributed to
the difficulty in preparing parent MAX precursors since they can form several secondary carbide phases. In fact, the synthesis processes of MXenes other than Ti$_3$C$_2$T$_x$ suffers from issues where the A-layers are too difficult to be etched from the precursor MAX phases, or the prolonged etching time resulted in oxidation of MXene during the synthesis. The theoretically predicted semiconducting MXenes are awaiting experimental confirmation, hence the investigations for new MAX phases and similar layered precursor materials are important to overcome current synthesis challenges. The experimental demonstration of semiconducting MXene can be a good contribution to MXetronics research, especially direct band gap MXenes for light emitting devices. Semiconducting Ti$_2$CO$_2$ can be a good start as it has already been experimentally synthesized, but relatively more sensitive to oxidation during the synthesis process than Ti$_3$C$_2$T$_x$.

The diverse and tunable properties of MXenes make this material family attractive for numerous multi-functional electronic and photonic device applications as shown in a schematic illustration (Figure 17(b)). Double transition metal MXenes with ordered structure further diversify the MXene family and are promising for spintronics and data storage applications upon oxygen termination. The reversible electrochemical intercalation of multi-valence cations between MXene nanosheets suggests their potential applications in synaptic electronics. Given the excellent electrical and optical properties of MXenes, we anticipate that MXetronics research will flourish in the near future.
Figure 17. a) MXenes science tetrahedron: The four important parameters for tunable properties of MXenes. b) Schematic illustration of the applications in MXetronics.
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Conflict of Interest

The authors declare no conflict of interest.

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