## Basics, properties, fabrication, and potential applications of MXenes

## Rupendra Kumar, Manoj Kumar Banjare\*

## *MATS School of Sciences (Chemistry), MATS University, Pagaria Complex, Pandri, Raipur, C.G. 492004, India*

**Abstract**

Researchers are attracted to 2D layered materials due to their unusual physical, chemical, and electrical properties. As a result, they can be used in energy storage, sensors, catalysis, and electronics. Over the years, intense research on new 2D materials has been conducted, fueled by graphene's exceptional characteristics. MXenes, which are compounds formed from the chemical delamination of ternary/quaternary layered carbides or nitrides, are one of the most promising groups of 2D materials under development. Among the distinguishing features of the MXene family are its complex bonding, atomic stacking, synthesis pathways, and surface terminal groups. MXenes remain an understudied class of materials despite their increased interest. In the current work, we go into great depth on the characteristics of MXene and assess its potential for the creation of wearable biosensors. A summary of recent advancements in this quickly evolving topic is given, along with recommendations for potential future study routes.

**I. Introduction**

MXenes are the fastest-growing class of two-dimensional materials with distinct characteristics and scalable synthesis techniques. They have gained great scientific interest [1-2]. Since the discovery of stable 2D atomic carbon sheet graphene, its advantages over bulk equivalents have prompted research advancements in various fields. Nanotechnology experts believe that 2D materials like graphene, layered double hydroxides, transition metal dichalcogenides, covalent organic frameworks, and black phosphorus have significant potential for use in various industries such as optoelectronics, energy storage, and biomedicine due to their unique optical, electrical, and mechanical properties. These materials have been extensively studied for the past decade for their potential in various applications [3-7]. MXenes have variable surface chemistry, metallic conductivity, and a redox potential similar to graphene. MXenes can be utilized for environmental applications since they often contain non-toxic elements like Ti, Si, and N. At Drexel University, titanium carbide (Ti3C2) MXene was first discovered [8].

In addition, recently, MXenes have found diverse applications such as electronics, biosensing, environmental remediation, water desalination, quantum dots, sensors, electrodes, and optical devices [9-10]. The focus of the most promising applications is on electrochemical energy storage technologies such as metal-ion batteries and electrochemical capacitors (ECs). MXene has enabled significant advancements in understanding charge-storage processes and creating innovative, ultra-high capacitance MXene electrodes [11]. MXenes have gained interest across scientific fields such as chemistry, physics, materials science, environmental science, and nanotechnology.

In the 2D domain, MXenes are among the most recent transition metal carbides, nitrides, and carbonitrides to appear [12-15]. The formula for these materials is Mn+1XnTx (n = 1-3), where M, X, and Tx represent early transition metals, nitrogen, and carbon, respectively. A few examples of these metals are Ti, V, Ta, Cr, Sc, Zr, Mo, and Hf. In the same way, we do with surface terminals Tx (such as hydroxyl, oxygen, or fluorine). There are three common structures for MXenes (M2X, M3X2, and M4X3). MXenes exist in over 200 different stable phases, including Ti3C2Tx, Ti2CTx, Nb2CTx, Mo2CTx, Ti4N3Tx, Ta4C3Tx, Cr2TiC2Tx, V2CTx, and Zr3C2Tx. In addition, MXene has excellent surface hydrophilicity and electrical conductivity in addition to its 2D layered structure. It is also possible for MXene to sandwich a variety of cations between its layers. These outstanding characteristics have drawn considerable attention in field such as electrochemical energy storage, gas adsorption, catalysis, gas sensing, etc [16-18]. In this chapter, we will investigate the fundamentals, properties, fabrication, and potential applications of MXenes through several research findings. In addition, we will focus on different spectroscopic characterization techniques such as UV-visible spectroscopy, Fourier transform infrared (FTIR) spectroscopy, dynamic light scattering (DLS), scanning electron microscope (SEM), and x-ray diffraction (XRD).

**II. MAX phases: the precursors of MXenes**

In the first decades of the 1960s, the MAX phases were found [19]. According to fig. 1 [1], MAX phases are hexagonal carbides and nitrides with the formula Mn+1AXn (n=1, 2, 3). Generally, "M" indicates transition metals (such as Ti, Sr, V, Cr, Ta, Nb, Zr, Mo), while "A" indicates major group elements (primarily Al, Ga, In, Ti, Si, Ge, Sn, and Pb), and "X" indicates carbon or nitrogen. In the Max phase, M-X bonds are stronger than M-A bonds. It is easier to etch away the more chemically reactive A layers to obtain Mn+1Xnlayers, which are typically formed by -F, -OH, and -O groups due to their high surface energy [20].These ceramic-metal hybrids exhibit distinctive properties resulting from their uncommon combination of characteristics [21].

A MAX phase has high thermal and electrical conductivities, excellent machinability, and no corrosion resistance, in contrast to a conventional ceramic which have a low density, a high hardness, and no corrosion resistance [22-24]. A MAX step have three parts, according to fig. 2 [25], 211 for n=1, 312 for n=2, and 413 for n=3). There is a large number of MAX phases in the space group D46h-P63/mmc, which is a two-unit unit space group. These unit cells consist of layers of A elements (such as Si or Ge) sandwiched between layers of MX6 octahedral layers, with X atoms occupying the octahedral spaces between the M atoms [25].



## Figure 1: Constituent elements of MAX, MXenes and their intercalation ion. Reproduced with permission [1]. Copyright 2019, ACS Nano.



**Figure 2: Crystal phases of 211 (n=1), 312 (n=2), and 413 (n=3) MAX phases. Reproduced with permission [25]. Copyright 2017, Elsevier.**

**III. Properties of MXenes**

It is important to note that the kind of MXene precursor used, the etching process, the intercalation method, and the sonication frequency all affect MXenes optical, electrical, thermal, mechanical, and magnetic properties shown in fig. 3. There are numerous and adaptable interactions on the MXene surface due to the electrons linked to transition metal atoms.

**Figure 3: Properties of MXenes.**

**A. Optical properties**

Gogotsi Y. et al. [26] pointed out that there is little research on the optical characteristics of MXenes. The researchers demonstrated a transmittance of 91.2% for the 5 nm thick Ti3C2Tx film, and it can absorb light in the UV-Vis range from 300 to 500 nm [26]. Zhang C. et al. [27] studied that the MXenes concentration in solution determines how much of it is absorbed, whether as a colloidal form or as a thin film. It is the thickness of MXene thin films that causes an increase in absorption when it comes to thin films. At 550 nm, Ti3C2Tx MXenes in pure and intercalated forms have transmittances of 77% and 90%, respectively [27]. Wang et al. [28] investigated the presence of the functional groups (F, OH, and O) on the surface affects the optical characteristics of MXenes. Ti3C2 MXenes can function from infrared to ultraviolet light because F and OH have low in-plane absorption coefficients. The in-plane absorption coefficients are greater for naked and O functionalized MXenes. MXenes are promising candidates for flexible transparent electrode applications considering their optical transparency and metallic conductivity in the visible region, but their strong reflective properties in the ultraviolet area suggest anti-ultraviolet coatings. Lastly, it demonstrated high light-to-heat conversion efficiency (100%), which is helpful for biological applications [28].

**B. Thermal properties**

For storage and use in solutions and thin films, it is essential to comprehend the thermal stability of MXene. The thermal stability of MXenes was discovered to be substantially influenced by both their chemical makeup and the environment by combining thermogravimetric and mass spectrometry analyses. According to a Toulouseian research, although having a hexagonal structure, Ti3C2Tx (Tx = F or OH) is still stable at 800 °C, and its hexagonal structure in the Ar structure is still there even at 500 °C. Thermogravimetric investigations show that Ti3C2Tx, which turns into TiC in an argon (Ar) atmosphere, has a substantial weight rise at temperatures exceeding 800 °C. Ti3C2Tx MXene is partly annealed in an anatase TiO2 atmosphere at 200°C and fully annealed in a rutile TiO2 atmosphere at 1000°C. It is possible to create TiO2 with a variety of crystal structures and morphologies by adjusting the annealing temperature, the pace at which MXene is heated, and the length of the oxidation process. The end result is a wide range of MXene-based hybrids and derivatives. Due to their high surface energy and usual thermodynamic metastability, MXenes with exposed metal atoms on their surface frequently spontaneously oxidise in air [30–31].

**D. Mechanical properties**

Regarding the MXenes mechanical characteristics, Section The study is mostly concerned with mathematical computations. There have been several theoretical research on graphene and other 2D materials that resemble graphene, but some of these works are theoretical and experimental investigations on the mechanical properties of MXene material [32].

U. Yorulmaz et al. [33] investigated the dynamical and mechanical stability of the selected MXene phases for both pristine and fully surface-terminated forms. They have found that all the carbides and nitrides of Sc, Ti, Zr, Mo, and Hf pristine systems except for Mo2N and stable systems demonstrate metallic behavior. On the other hand, while the vast majority of the fully terminated structures of carbide-based MXenes are dynamically and mechanically abiding, this is not the case for nitride-based MXenes. In addition, Raman active modes of several MXene phases for the first time, which are crucial for the identification of MXene phases experimentally. They have demonstrated electronic band opening in some MXenes depending on the type of the system (carbide or nitride) and type of functional elements. It has been shown that MXenes phases show long variations in electronic and mechanical properties with respect to the type of early transition metal, type of X atom, and type of the surface functional group used [33].

**E. Magnetic Properties**

Among the MXene phases, Cr2CTx and Cr2NTx exhibit good magnetic order over long distances compared with Tan+1Cn, which shows significant long-range ferromagnetism. Magnetic properties of MXene are reduced or eliminated by the activated functional groups. In the MXene family, two-dimensional layers exhibit a wide range of magnetic properties. MXenes 2D Ti3C2 and Ti3N2 are predicted to be antiferromagnets, while 2D Cr2C, Cr2N, Ta3C2, and Cr3C2 are predicted to be ferromagnets that may dissociate from their MAX phases [34]. Because MXenes phases are possible to have different magnetic characteristics than MAX phases, studies made it possible to assess their magnetic characteristics more widely. Several antiquity-related substances have been predicted to possess magnetic moments, including Ti4C3, Ti3CN, Fe2C, Cr2C, Ti3N2, Ti2N, Zr2C, and Zr3C2. Finally, a unique analysis should be conducted for each MXenes and functionality group. The magnetic properties of Ti3CNTx and Ti4C3Tx are lost when functional groups are added, whereas Cr2CTx and Cr2NTx with OH and F groups maintain their magnetic properties at ambient temperatures, and Mn2NTx is magnetic regardless of surface termination. The reported magnetic moments have yet to be confirmed by experiments; they are based on computer forecasts. This is explained by the poor control of surface chemistry and the insufficient production of MXene molecules [35-38].

**IV. Fabrication of Mxenes**

Materials science and nanotechnology have been greatly impacted by MXene since its discovery in 2011. Theoretical calculations predict more than 100 different MXene compositions and more than 40 MXene structures have already been created in the laboratory from top-down approach or bottom-up approaches. To enhance the biocompatibility of MXenes for various biomedical applications, different surface functionalizations have been proposed. One can refer to some excellent reviews for a comprehensive summary of the related achievements of MXene synthesis and modification [39-40]. Preparation of MXenes are given below in fig. 4 [40]



**Figure 4: Preparation of MXenes by intercalation method. Reproduced with permission [40]. Copyright 2021, Springer.**

**A. Top-down Strategy**

A top-down MXene is produced by selectively removing the A atomic layer from the precursor while leaving the Mn + 1Xn layers intact. Due to the nominal oxidation state of the A atom in MAX (for example, Al0 in Ti3AlC2), the etching process involves oxidizing it to another state, such as Al3+ or Si4+. The strength of the M-A bond in comparison to the M-X bond, as well as other factors such as the Gibbs free energy of by-product formation, affect the etching reaction's Gibbs free energy, which determines the ability to remove the A element in the case of HF etching of Al-based MAX phases. In general, exfoliation involves oxidation of the A element, followed by conversion into soluble by-products via ligation [41]. The most traditional and popular top-down approach to making MXene is HF etching. There are two distinct steps in the interaction between MAX and HF during the etching process. Using Ti3AlC2 MAX as an example, Ti3AlC2 is fully devoid of Al atoms after being submerged in a 50% (w/v) HF solution for two hours at room temperature. As a result, Ti3C2 is produced [42]. The reaction between hydrofluoric acid solution and Ti3AlC2 is as follows:

 Ti3 AlC2 +3HF = AlF3 +3/2H +Ti3C2 (i)

 Ti3C2+2H2O = Ti3C2 (OH)2+H2 (ii)

 or

 Ti3C2 +2HF = Ti3C2F2 + H2 (iii)

The same etching technique is used to prepare more MXenes, including Ti2CTx, V2CTx, and Mo2CTx. Handling and disposal of HF are hazardous because of its great toxicity and capacity to infiltrate through skin, tissue, and even bones. The usage of HF has been greatly reduced or eliminated through the development of numerous ways to improve the etching process. According to Alhabeb et al., there is a risk of creating hazardous HF when using the in situ approach to create Ti3C2Tx over a 24-hour etching time [43]. It was found that as little as 5 wt% HF can still be used to manufacture Ti3C2Tx. In 2014, Ghidiu et al. etched the conductive "clay" (Ti3C2Tx) by replacing the highly corrosive HF with fluoride salts such as NaF, KF, and LiF. To achieve delamination, large organic compounds dissolved in tetramethylammonium hydroxide (TMAOH) or dimethyl sulfoxide (DMSO) are utilized alongside NH4HF2 or HF, followed by sonication. The amount of LiF and HCl used determines whether delamination of Ti3C2Tx intercalated with Li+ using HCl-LiF can be done with or without sonication. The in situ technique offers the advantage of creating a larger interlayer space between water, which reduces their interaction with MXene compared to direct HF etching [44].

**B. Bottom-up Strategy**

Instead of starting with bulk material, bottom-up methods use molecular material as a starting point. Halim et al. [45] studied that transparent MXene films were created by selectively removing the A-element in the first bottom-up synthesis of MAX film. In this first work, they used DC magnetron sputtering to deposit thin films of Ti3AlC2 onto a TiC layer (which served as an incubation layer) while maintaining an ultrahigh vacuum and a temperature of 780 °C. Transparent, conductive Ti3C2Tx epitaxial films with well-maintained metallic conductivity down to 100 K were produced after the aluminum layer was removed using HF or NH4HF2. [45].

This approach can be used to create Mxene-derived quantum dots (MQDs) from microscopic precursors of organic and inorganic compounds. Bottom-up methods have several benefits, including better control over the structure and characteristics of quantum dots (QDs), increased atomic use, and faster functionalization. Previous investigations have provided a solid foundation for preparing bottom-up MXene. However, for large-scale fabrication, simple, highly efficient precursors with low toxicity, gentle reaction conditions, excellent crystallinity, monodispersity, and high yields must be addressed. Meanwhile, because of their relatively simple operating conditions compared to the top-down methods, one-pot bottom-up methodologies will likely be employed to prepare MXene in the future to fulfill the incremental application requirements. As there is little research on the bottom-up methodologies for MQD fabrication, the study is promising, and great stress should be given to these strategies [46].

**VI. Applications of Mxenes**

**A. Energy Storage**

Due to the depletion of fossil fuels and the increased consumption of energy, there has been a growing interest in renewable energy sources, as well as storage and conversion systems such as batteries and supercapacitors [47]. Even though energy storage was the earliest and most investigated application for MXenes, MXenes have shown significant potential in a variety of other applications. Anasori et al. [47] present a detailed assessment of the majority of MXenes energy- and non-energy-related applications researched thus far. First-principles calculations are an important tool in the search for prospective applications due to their cost and time efficiency compared to experimental efforts. MXenes are 2D layers that can contain ions of varying sizes and are useful for non-lithium-ion batteries (NLiBs), as electrode material choices are currently limited. Some oxygen-terminated MXenes have theoretical capabilities in Na, K, Mg, Ca, and Al-ion batteries. It's worth noting that Na+ and other ions are predicted to create an extra metal layer, doubling the capacity. Furthermore, different MXenes can produce a range of working potentials due to their chemical and structural variety, as well as surface chemistry tunability, making some of them suitable as anodes and others as cathodes. [48].

 Due to their high metallic conductivity, MXenes, particularly Ti3C2Tx, are frequently utilized in supercapacitor applications to facilitate rapid electron transfer. It has been discovered that MXene, a 2D material, can store energy through electrochemical or spontaneous interconnection by metal ions [49]. Ions diffuse to shallow and deep adsorption sites in MXenes. Initially, they are accommodated at low adsorption sites at the particle's edges, and then at deep sites in the particle's center. This results in high ion adsorption activation. Show off your energy. Ions rapidly adsorb at low absorption locations with MXenes, making them the best alternative for precise charge storage quantification and improved rate performance. Additionally, cation intercalation can affect the interlayer water content in MXene nanosheets. These nanosheets precipitate in a partially hydrated form with kosmotropic ions such as Mg2+, Li+, and Al3+. On the other hand, chaotropic ions like TEA+ and Cs+ can successfully dehydrate MXenes. During the process of extracting and inserting ions from aqueous media, there are frequent changes in C-value. It has been observed that the deformation behavior generated by different ions in MXene is different from that of interlayer gap extension in graphite. The interlayer gap between Ti3C2Tx MXene nanosheets can be minimized by using cations with high charge and short ionic radius for interpolation while using cations with low charge and large ionic radius will lead to interlayer expansion of MXene [50].

**B. Biosensors**

Electrochemical sensors are the most commonly used biosensors for analysis. This type of sensor offers various advantages for application in biomaterial detection due to its ability to measure observable electrochemical properties based on the properties of the target material that preferentially react with bio-receptors [51]. Biosensing has gained much interest as a good tool for analyzing specific biomolecules in a variety of applications. The study of direct electron transfer (DET) between enzymes and electrodes is crucial for making mediator-free electrochemical biosensors [52-53]. The DET between enzymes and electrodes is limited, however, due to the fact that proteins' electroactive centers are buried deep within their protein structures, and the electrode's electrolytes often kill electrode surface proteins. Nanomaterials have been used to immobilize enzymes on electrode surfaces to overcome this problem. Due to their outstanding electrical characteristics, large surface area, and high biocompatibility, MXene-based materials have shown promise as biosensing nanomaterials [54].

**C. Energy harvesting**

Solar energy is considered a promising option to meet our energy needs in the future because of its exceptional characteristics. It is ecologically friendly, unlimited, and safe. Therefore, technologies that can directly convert solar energy into electrical energy are receiving a lot of attention. MXene, a two-dimensional material, has the potential to be used in solar cells. It can be used in three categories: electrode materials, electron/hole transport layer materials, and other materials [55]. Due to its unique physicochemical features such as outstanding electrical conductivity, high transmittance, and appropriate flexibility, Ti3C2Tx, as a representative member of the emerging group of MXenes, has proven significant potential as solar cell electrodes. This section discusses the use of Ti3C2Tx electrodes in sequencing solar cells made of silicon, perovskite, organic, and dye-sensitized materials. MXenes can serve not only as bulk materials for electrodes or ETL/HTL but also as additives in solar cell components, such as active layers, ETL/HTL, to modify their physicochemical properties. Guo et al. were the pioneers to incorporate Ti3C2Tx nanosheets into a perovskite precursor to alter the perovskite layer [56].

**VII. Future scope**

**Figure 5: Future directions of MXenes research.**

**VIII. Conclusion**

MXenes are a brand-new member of the 2D material family with a lot of promise for applications in sensors and energies. 2D transition metal carbides and nitrides have sparked intense research interest in biomedical technology, environmental science, energy storage and conversion, and catalysis. The creation of colloidal solutions devoid of surfactants enables diversity in device manufacture, including a range of printing methods. By using additive manufacturing, the rheological properties can be adjusted to create sensors. MXenes' capacity to create free-standing films offers versatility in design. MXenes have demonstrated exceptional performance in energy storage, supercapacitors, and sensors, indicating that this new class of 2D materials has promising applications for next-generation energy storage and conversion devices

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