Om Prakash Pandey
Piyush Sharma *Editors*

MXenes: Emerging 2D Materials

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Editors
Om Prakash Pandey
Department of Physics and Materials Science (DPMS)
Thapar Institute of Engineering and Technology
Patiala, Punjab, India

Piyush Sharma
Division of Research and Development
Lovely Professional University
Phagwara, Punjab, India

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Preface

The development of technologies depends upon the availability of suitable materials. The innovation in materials has brought revolutionary change in modern civilization. The emergence of two-dimensional (2D) materials has been nothing short of revolutionary change of this era. These ultrathin sheets, often consisting of just a single layer of atoms, exhibit a plethora of extraordinary properties that defy the conventions of classical bulk materials. In recent years, the exploration of '(2D)' materials has become one of the most dynamic and transformative fields in materials science and nanotechnology. Among the diverse array of 2D materials, MXenes have rapidly emerged as one of the most promising and intriguing families.

Gogotsi and colleagues at Drexel University first discovered the MXenes family of 2D transition metal carbides, nitrides, and carbonitrides in 2011. Since then, MXenes have garnered immense attention due to their unique combination of properties, including high electrical conductivity, excellent mechanical strength, and exceptional chemical stability. Over the 14 years that have passed since the discovery of MXenes, there have been more than 1500 papers published by scientists all around the world on this topic. Moreover, MXenes exhibit tunable surface chemistry, making them highly versatile for a wide range of applications spanning from energy storage and conversion to electronics, catalysis, sensing, and beyond.

This book delves into the fascinating realm of 2D MXenes, exploring their synthesis, properties, and diverse applications. It brings together contributions from leading researchers in the field, providing a detailed and up-to-date overview of this rapidly evolving area of study. The book presents the various methods for synthesizing MXenes, ranging from selective etching of MAX phases to various exfoliation strategies and highlights the key factors influencing their structural and morphological properties. Furthermore, the book addresses the rich variety of properties exhibited by MXene materials, including their electronic, optical, mechanical, and electrochemical behaviors. Understanding these properties is critical for harnessing MXen'es full potential in practical applications and tailoring their properties to meet specific technological requirements.

One of the most exciting aspects of MXene research is the broad spectrum of applications of these materials that enable to open new applications every day.

Throughout this book, detailed insights into the cutting-edge applications of MXenes across different fields are provided, including energy storage devices such as batteries and supercapacitors, electrocatalysis for water splitting and pollutant degradation, electromagnetic interference shielding, flexible electronics, biosensing, and many others.

As researchers around the globe unravel the mysteries of MXenes and uncover new functionalities, it becomes increasingly evident that these materials hold the key to addressing some of the most pressing challenges of our time. Whether it is enabling next-generation batteries with enhanced energy density, designing ultra-efficient catalysts for sustainable chemical transformations, or revolutionizing flexible electronics for wearable devices, MXenes offer boundless opportunities for innovation and progress.

In this volume, leading experts in the field present a comprehensive overview of the latest developments in MXene research, offering insights into both fundamental science and practical applications. Each chapter provides a detailed examination of specific aspects of MXene materials, ranging from synthesis techniques, structural characterization, and advanced applications. By bringing together diverse perspectives and expertise, this book aims to serve as a valuable resource for researchers, students, and professionals interested in exploring the vast potential of 2D MXene materials.

We hope that this book will inspire readers to embark on their own journeys into the captivating world of MXenes, fostering collaboration and driving further advancements that will shape the future of materials science and technology.

Patiala, India
Dr. Om Prakash Pandey
Senior Professor
oppandey@thapar.edu

Phagwara, India
Dr. Piyush Sharma
piyushsharma0135@gmail.com

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Chapter 1
Wave of 2D MXene

Gurwinder Kaur, Piyush Sharma, and Om Prakash Pandey

1.1 Introduction

In the twentieth century, the refractory binary transition metal carbides and nitrides have emerged as a crucial industrial material [1]. These binary compounds are commonly named as MX phases, in which M refers to transition metals and X refers to C or N. The MX phases possess high elastic moduli, good mechanical properties, high oxidation, and corrosion resistance. These phases have shown great potential in a variety of industrial applications such as cutting and grinding tools, bearings, textile-machinery components, semiconductors, oxidation-resistant gas burners, etc. [2]. The discovery of their catalytic behavior in the 1970s sparked initial exploration of their applications in energy conversion and storage [3]. Later, various nanostructure designs were proposed to improve the surface properties and performance of transition metal carbides or nitrides [4, 5]. In addition, MX phases have limited thermal and electrical conductivity, are difficult to process, have little damage tolerance, and are exceedingly brittle, despite their many uses. To get around these drawbacks, MX phases with metallic characteristics are being developed as an alternative. Consequently, MAX phases (where A stands for metals) consisting of nano-laminated carbides and nitrides are discovered [6, 7]. Ti_3SiC_2 MAX phase was prepared by Barsoum and El-Raghy [8, 9], who sparked renewed attention to MAX phases. They investigated the material's mechanical, electrical, and thermal properties. The MAX phase was identified by this research team as a class of thermodynamically stable layered nanolaminate compounds. Subsequently, MAX phases captured the

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G. Kaur · O. P. Pandey (✉)
Department of Physics and Materials Science, Thapar Institute of Engineering & Technology, Patiala 147004, India
e-mail: oppandey@thapar.edu

P. Sharma
Division of Research and Development, Lovely Professional University, Phagwara 144411, India
e-mail: piyushsharma0135@gmail.com

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attention of the scientific community because of the exceptional blending of metal and ceramic characteristics [10]. These phases have excellent machinability, strong thermal shock and oxidation resistance, low weight, and good stiffness. Due to their unique combination of properties, MAX phases have a wide variety of potential applications in fields as diverse as high-temperature structural applications, protective coatings, sensors, low-friction surfaces, electrical connections, and many others [11–14].

In 2011, MAX phases were used as precursors for the synthesis of 2D MXenes. The first 2D titanium carbide ($Ti_3C_2T_x$) was discovered, which paved the way for the discovery of a new class of 2D transition metal carbides or nitrides called MXenes [15, 16]. MXenes are derived through etching of A layer from MAX phases, where A stands for metal (Al, Si, Ga, Ge, In, Sn). The hydrophilic nature of hydroxyl or oxygen-terminated surfaces and the properties of transition metal carbides make MXenes a particularly interesting material. The MXenes have shown tremendous potential in the field of energy, sensing, wastewater treatment, EMI shielding and biomedical. Nowadays, MXenes is one of the rapidly expanding families of 2D materials. The general formula for MXenes is $M_{n+1}X_nT_x$, where M stands for early transition metal, X for carbon or nitrogen, n is an integer and T_x stands for surface termination group ($=$ O, $-$F, and $-$OH) [8]. As of now, MAX phases have been synthesized by using approximately 14 M elements, 16 A elements, and 2 X elements [9]. In this way, different MAX phases can be synthesized by trying out different combinations. The scope also widened with the substitution or doping and with the discovery of quaternary MAX phases. The chemical diversity of MAX phases plays an important role in the development of novel MXenes. In the present chapter, the fundamental aspects related to its basic structure and synthesis of MXenes have been discussed. The chapter aims to provide insight into chemical diversity of MXenes. Finally, the properties and the potential applications of MXenes have been addressed.

1.2 Fundamentals of MXenes

MXenes are a class of two-dimensional inorganic compounds. These materials consist of few atoms of thick layers of transition metal carbides, nitrides, or carbonitrides [10, 11]. These materials possess unique combination of properties of transition metal carbides and hydrophilic nature hydroxyl or oxygen-terminated surfaces [12]. The general formula of MXene is "$M_{n+1}X_nT_x$", here "M" represents early transition metal, "X" is carbon and/or nitrogen and "T_x" is the functional group attached with "M" element. The elements considered as "M", "X", and "T_x" in MXenes are shown in Fig. 1.1.

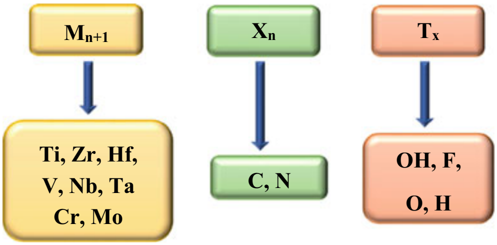

Fig. 1.1 The elements considered as “M”, “X”, and “T_x” in MXenes

1.2.1 Structure of MXenes

In general, MXenes surfaces are terminated with functional groups, which are obtained through etching of MAX phases. Figure 1.2 shows crystal structure of (M_3AX_2) MAX phase and their corresponding ($M_3X_2T_x$) MXene.

The general formula for MAX phases is “$M_{n+1}AX_n$”, where “M” is the transition metal carbide, “A” is the metal, and “X” is carbon and/or nitrogen. MAX phases possess layered hexagonal crystal structures with two formula units per unit cell, for structures n equal to 1 to 3. The unit cell consist of M_6X octahedra with the X-atoms filling the octahedral sites between the M-atoms, which are identical to those found in the rock salt structure of the MX binaries. The octahedra alternates with layers of pure A-elements located at the centers of trigonal prisms that are slightly larger, and

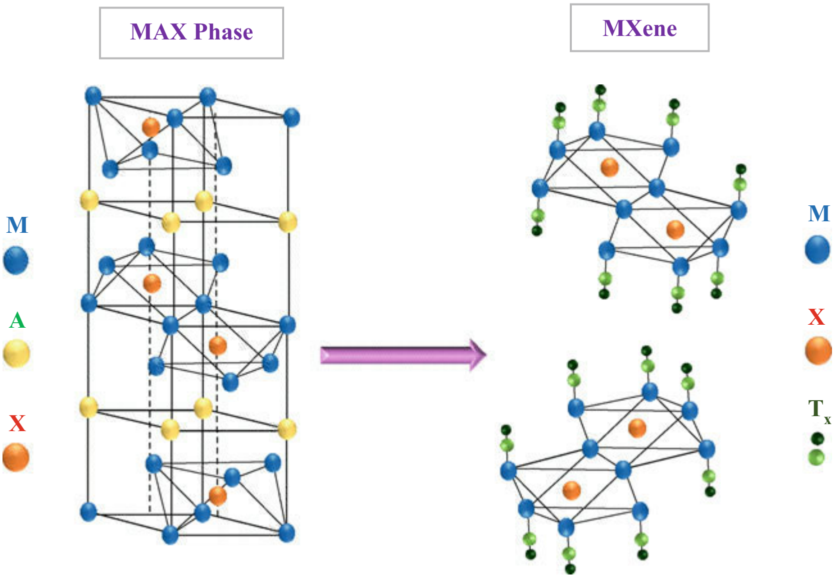

Fig. 1.2 Crystal structure of (M_3AX_2) MAX phase and their corresponding ($M_3X_2T_x$) MXene

thus more accommodating of the larger A-atoms. MXenes adopt three structures, as inherited from the parent MAX Phases: M_2C, M_3C_2, M_4C_3 [13].

1.2.2 Synthesis of MXenes

MXenes are synthesized by the following three different steps, i.e., (i) synthesis of MAX phase, (ii) exfoliation of "A" layer from MAX phase, and (iii) intercalation/delamination of MXenes layer, which will be discussed in Chap. 2. The schematic representation of the synthesis of MXenes is presented in Fig. 1.3. The brief description of the above steps for the synthesis of MXenes is as follows:

(i) *Synthesis of MAX Phases*

Several methods are reported for the synthesis of the MAX phases. Numerous researchers follow different sintering techniques such as conventional sintering, spark plasma sintering (SPS), hot isostatic pressing (HIP), and hot pressing (HP) to obtain highly pure nanolaminated MAX phases. In the conventional sintering process, no external mechanical pressure is employed on the material during heat treatment. In HIP and HP sintering techniques, the external mechanical pressure is induced [14]. Furthermore, electric field is applied to give heat treatment in SPS technique [17]. All the sintering processes are performed in the presence of argon environment to avoid the oxidation of the MAX phase. In SPS technique, a direct electric current is applied to heat up the electrically conductive devices in a graphite die [18].

(ii) *Exfoliation of "A" Layer from MAX Phase*

Exfoliation is the process in which "A" element can be etched from MAX phase, to separate the stacked layers into single flakes. The MAX is immersed and stirred or sonicated in acidic solution to obtain MXenes. After acidic treatment, the obtained

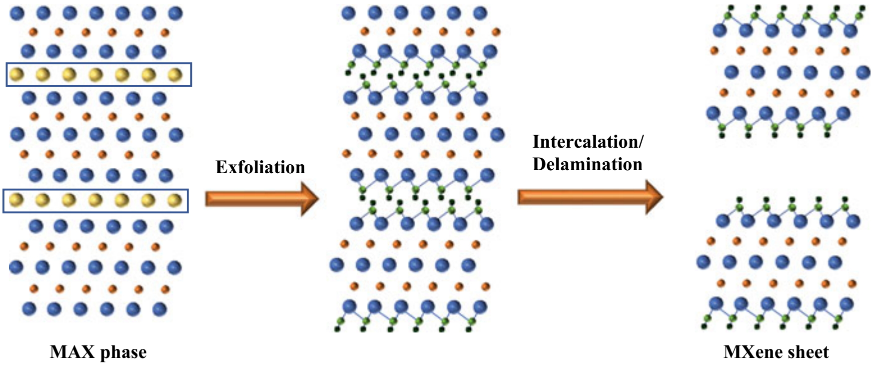

Fig. 1.3 The schematic representation of the synthesis of MXenes from 312 MAX phase

sample is washed several times in the centrifuge tube, to normalize the pH = 7. In this process, MXene layers are obtained but there is weak bonding between function group and transition metal. Hence, intercalation and delamination of exfoliated MAX phase should be done to obtain a single MXene layer or flake.

(iii) *Intercalation and Delamination of MXenes*

Exfoliated MXene layers are intercalated to increase the distance between two adjacent layers. In this process, MXene layers are intercalated with different polar organic molecules and metal ions (mono and multivalent cations such as Li^+, Na^+, K^+, NH^{4+}, and Mg^{2+}). After intercalation, a single layer of 2D MXene is obtained. Furthermore, MXene layers are treated with organic solvents for the delamination of MXene.

1.3 Chemical Diversity

The chemical diversity of MAX phases allows for a wide variety of possible MXenes configurations [9]. Substitution or doping in MAX phases further opens the door to novel MXenes. It was observed that the MAX phase becomes magnetic in nature after the doping of Mn or Fe at M site [19]. In such a way, the properties of resulting MXenes can also be tuned, which is discussed in Chap. 3. It is worth noting that the MAX phase solid solution provides several opportunities for novel MXenes. The potential for expansion of the family of 2D MXenes has also been sparked by the discovery of in-plane and out-of-plane ordered MAX phases. Figure 1.4 shows the periodic table highlighting the elements used for the synthesis of MXenes and MAX phases [20].

In MAX phases, M elements (highlighted in blue) are sandwiched between a single layer of A element (highlighted in red), with X (highlighted in grey) occupying the interlayer octahedral sites. In MXenes, the layer of M elements is interleaved with n layers of X elements having T_x (highlighted with orange) surface terminations. Over a hundred different stoichiometric MXene compositions and an infinite number of solid solutions provide not only novel property combinations but also offer possibility to tune properties by varying ratio of M or/and X elements. The cations that have so far been intercalated into MXenes are visible on the green backdrop in Fig. 1.4. The legend at the bottom of the figure, 1M and 1A are related to the formation possibility of a single M and A element MAX phase and/or MXene, respectively. SS stands for the solid solutions of MAX phases and MXenes. 2M indicates the presence of two transition metals to form an ordered MAX phase and/or MXene. The figure demonstrated how the elements can be used as building blocks to create a wide range of nanomaterials, with MXenes, their precursor MAX phases, and intercalated metal ions in MXenes as embodiments of the fundamental principles of chemistry.

In addition, MXene-based composites are also developed to overcome the issue of restacking of MXene layers resulting in oxidation and decrease in electrical conductivity. Several researchers are involved in developing MXene-based composite

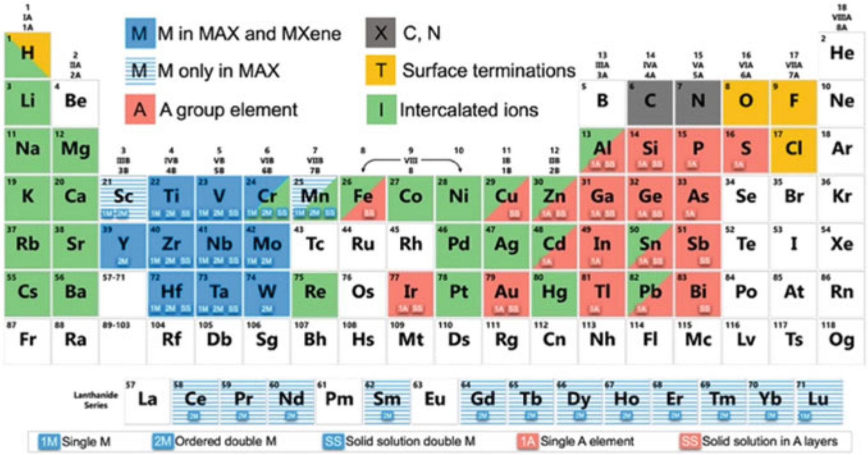

Fig. 1.4 The periodic table presents the elemental compositions of MXenes and MAX phases. Adapted with permission from [20]. Babak Anasori et al., Graphene and 2D Materials, MXenes: trends, growth, and future directions, 7, 75–79, 2022, Copyright (2022), Copyright the Authors, some rights reserved; exclusive licensee [Springer]

with a variety of materials including polymers, metals, and carbon-based materials. The resulting composites have shown improvement in their properties. A detailed discussion of MXene-based composites is presented in Chap. 4.

1.4 Properties of MXenes

MXenes have remarkable properties such as high Young's modulus, thermal conductivity, electrical conductivity, and the adjustable band gap [21]. The properties of MXenes are dependent on composition that includes solid solution formation and different transition metals "M" and "X" elements. In addition, MXene's properties also rely on thermal and chemical treatments, which are responsible for surface functionalization and variation in morphology [16]. The leading properties of MXene family exhibit very different properties as given here.

(i) *Electronic and Electrical Properties*

The two foremost interesting properties of MXenes are electronic and electric properties that can be modified by alteration of functional groups, stoichiometry, and solid solution formation. It has been observed that the experimental value of electrical conductivities of MXenes is similar to multi-layered graphene while higher than carbon nanotube materials. Moreover, it was witnessed that resistivity values increase with the rise in the number of layers and the presence of functional groups

[22], due to which the simulated conductivities have generally larger values than the one's observed experimental values [23].

The electrical conductivities of MXene are reported to vary due to changes in defect concentration, surface functional groups, delamination yield, d spacing between MXenes flakes and lateral sizes. The formation of MXenes with fewer defects and larger lateral sizes provides higher electrical conductivity because of lesser HF concentrations and etching time [24]. In case of electronic sensing materials [25], their conductivities are influenced from environmental humidity [24]. A useful way to enhance conductivity and electrical properties is surface modification via various treatments such as by altering the functional groups and intercalating the molecules.

(ii) *Mechanical Properties*

Mechanical properties of MXenes are highly interesting because of its strong bonding between atoms. An elastic constant (c11) of MXene is two times greater than MAX phases and other 2D materials along with high bending stiffness, which is good towards their use as reinforcements in composites [26, 27]. Apart from this, MXenes have functional groups due to which they interact better with polymeric matrixes than graphene for composite applications [23, 27]. With an increase in the number of layers of MXenes, Young Modulus of both MXene carbides and nitrides decreases but nitride-based compounds possess higher values than carbides [28]. The growth of critical deformations increases as the value of c11 decreases due to the occurrence of terminations. More importantly, these values of MXenes are higher as compared to graphene which possess the feature of flexibility in electronics. Although several methods for mechanical testing of bulk materials exist, the evaluation of mechanical properties of 2D is still challenging. Most of the time, mechanical properties of 2D nanomaterials were calculated by nanoindentation technique, in which an AFM tip applies force at the center of a 2D material film [29]. All in all, complete theoretical and experimental evaluations of mechanical properties with the different functionalization groups are still to be performed.

(iii) *Thermal Properties*

Thermal properties of MXenes are important particularly in electronic devices, which require faster heat dissipation. It plays an important role in electronics and energy-related heat dissipation devices due to their non-stop reduction in size [30]. Some studies suggested that MXenes have high thermal conductivities and low thermal expansion as compared to phosphorene and MoS_2 monolayer. Apart from this, it is observed that thermal conductivities of Ti_2CO_2, Zr_2CO_2, Hf_2CO_2, and Sc_2CF_2 vary from 22 to 472 $Wm^{-1}\ K^{-1}$ at room temperature. Interestingly, the thermal conductivity is dependent on length of MXenes as the thermal conductivity of Sc_2CF_2 increases from 298 to 722 $Wm^{-1}\ K^{-1}$ when the flake lengths vary from 1 to 50 μm [31]. Regarding the oxygen–terminated compounds, it was found that their thermal conductivities increase with the metal "M" atomic number. Overall, the synthesis procedure adopted and the resultant morphology are both substantial for thermal conductivity.

(iv) *Magnetic*

Several studies reported the variation in magnetic properties of MXenes using different theoretical calculations. In many compounds of MXenes, viz., Ti_4C_3, Ti_3CN, Fe_2C, Cr_2C, Ti_3N_2, Ti_2N, Zr_2C and Zr_3C_2 MXenes demonstrate retention in magnetic moments. Depending upon the surface terminations and functional groups, Ti_3CNT_x and $Ti_4C_3T_x$ turn into non-magnetic behavior, whereas Cr_2CT_x and Cr_2NT_x stay ferromagnetic at room temperature [32, 33]. In addition, Mn_2NT_x behaves as ferromagnetic irrespective of the surface terminations [34]. Due to limited synthesis and control on surface chemistry of MXene compounds, magnetic moments are calculated theoretically and have not observed experimentally yet.

(v) *Optical*

The absorption of visible and UV light is vital for transparent conductive electrode devices, photocatalytic, photovoltaic, and optoelectronic. In case of $Ti_3C_2T_x$ MXenes, it could absorb light in the UV region from 300 to 500 nm whereas 5 nm thickness film exhibited transmittance up to 91.2% [35]. Depending on the film thicknesses, it may present a strong and broad absorption band at around 700–800 nm which plays an important role in photothermal therapy (PTT) applications [36]. More importantly, with change in thickness and ion intercalation of MXene, the value of transmittance could be optimized. During the synthesis process, the value of transmittance decreases when hydrazine and DMSO are used as reducing agent whereas tetramethylammonium hydroxide (NMe_4OH) increased it from 74.9 to 92.0%. Apart from this, the presence of functional groups also influences the optical properties of these 2D compounds. For instance, –F and –OH terminations decrease absorption and reflectivity in the visible range whereas all terminations enhance the reflectivity in the UV region. MXenes are potential candidates for flexible transparent electrode applications as they have optical transparency in the visible region. Finally, it has the outstanding capability to convert light into heat which is further useful for biomedical and water evaporation applications [37].

1.5 Applications of MXenes

1.5.1 MXenes for Energy Conversion and Storage

Graphene-like materials such as TMCs, MXenes, and TMNs with better carrier mobility and an intrinsic layered structure have shown promise as a replacement for expensive noble metal electrocatalysts. TMCs and TMNs are intriguing because these materials share the same electronic structure as noble metals like Pt, making them a possible replacement for Pt and IrO_2/RuO_2 noble [3, 38]. The 2D MXenes have gained interest as a means of improving the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) activity as well as stability of TMCs and

TMNs electrocatalyst because of their remarkable inherent and extrinsic features. The enhanced water-splitting ability of MXene can be attributed to their similar band structure to Pt (caused by carbon inclusion in a metal lattice), their larger number of edge sites, and their improved active sites due to connected functional groups on the surface. Electrocatalyst for HER and OER has been developed using various TM-based MXene species (Ti, Mo, and V). MXene-based electrocatalysts are also used for other energy conversion reactions such as oxygen reduction reaction (ORR), methanol oxidation, nitrogen reduction reaction (NRR). It is worth noting that the electrochemical performance of MXenes can be tuned with the change in the functional group attached. Moreover, Bare MXene and most functionalized derivatives exhibit metallic or narrow band gap semiconducting characters, offering MXene inherent advantages in terms of electronic conductivity [39, 40]. This makes them suitable candidate for energy storage applications. Figure 1.5 shows the schematic representation of MXenes for the energy conversion and storage applications.

Among various MXenes, Ti_3C_2 is a promising candidate for lithium-ion battery (LIB) anodes with low operating voltage and diffusion barrier. Delaminating multilayer MXene into paper-like structure can effectively improve the electrochemical performance [41]. The pillared MXene with proper interlayer spacing can accommodate the ions of electrolytes, facilitate the adsorption and intercalation of electrolytes, and then improve the electrochemical performance. Due to the intrinsic

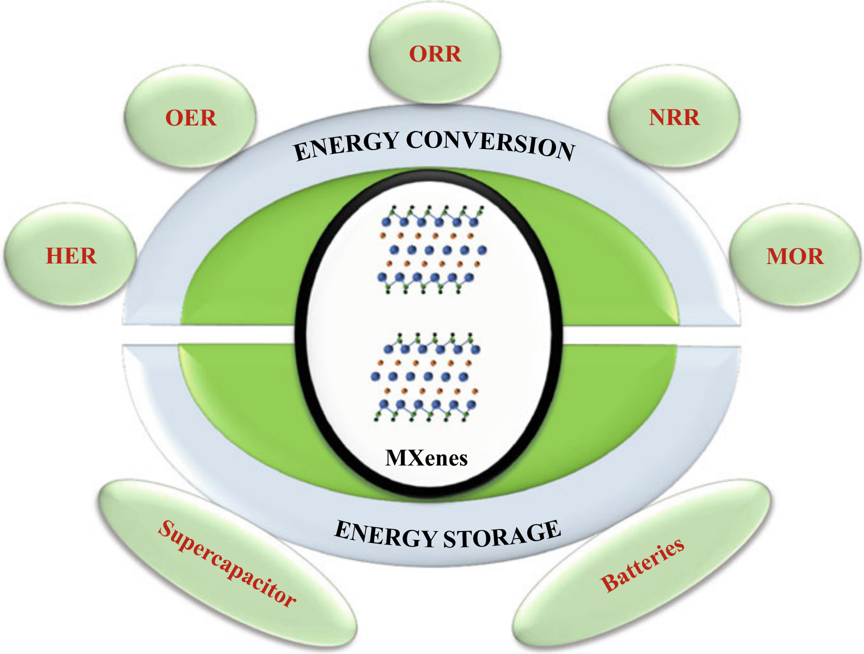

Fig. 1.5 Schematic representation of MXenes for the energy conversion and storage applications

metallic conductivity and the highly active 2D surface, MXene-based materials are expected to be promising hosts for Li–S batteries. Ti_2C MXene phase was effective as a cathode host material for Li–S batteries [42].

Due to the high power density, rapid charging/discharging rate, and long cycle life, MXene-based supercapacitors and pseudo-capacitors have attracted a lot of research interest [43]. Owing to their high power output, supercapacitors are always used in hybrid electric vehicles and fuel cell vehicles for start-stop control systems [43, 44]. Therefore, supercapacitors play a significant role in future energy storage systems. On the other side, pseudo-capacitors depend on fast and reversible Faradic processes. MXene-based pseudo-capacitors can store more energy at high charge/discharge rates and have attracted considerable attention [13]. The performance of pseudo-capacitive material mainly depends on the interaction between electrode materials and the electrolyte ions. However, the understanding of the interaction is still limited. A detailed discussion on energy conversion and storage is presented in Chap. 5.

1.5.2 MXenes for Wastewater Treatment

Water contamination has become a top problem for the industrialized world as a whole and a significant cause of worry for society and governmental agencies [45]. Water pollution happens when one or more pollutants are released into it that will negatively alter the water. These compounds may have negative effects on our environment and living organisms. Water contamination may be categorized in two ways depending on the main sources such as point and non-point. The first kind of pollution refers to contaminants that come from a single source, such as industrial water pollution, whereas the second type of pollution refers to contaminants that come from several sources [46]. There are several factors that contribute to water pollution, including energy consumption, radioactive waste, urban growth, sewage and wastewater management, industrial waste, mining operations, pesticides, and chemical fertilizers. Water pollution is inevitable simply because it is utilized for so many different purposes. Industrial, home, and agricultural operations all create wastewater that contains harmful contaminants. Water resources in this situation must be continuously protected.

In the developed nations, the regulation governing liquid industrial effluent is becoming harsher and now requires that all wastewater be treated before it is discharged into the environment [47]. As a result, the treatment of effluents has taken precedence in the industrial world. Numerous physical, chemical, and biological procedures, including flotation, precipitation, oxidation, solvent extraction, evaporation, carbon adsorption, ion exchange, membrane filtration, electrochemistry, biodegradation, and phytoremediation, have been documented during the last three decades. In general, physical, chemical, and biological methods are used to remove contaminants.

Recently, MXenes and MXene-based composites emerged as a potential catalyst for wastewater treatment. Various research groups are involved in the development of MXene-based catalyst for the removal of heavy metal ions, radionuclides, and organic pollutants (Fig. 1.6) [45]. Several factors (pH, dosage, oxidant concentration, temperature, and co-existing ions) are involved that govern the overall performance of MXenes for wastewater treatment. In addition, the chemical diversity of MXenes offers numerous possibilities to design and fabricate high-performance catalysts. A detailed discussion on the catalytic mechanisms of MXenes and MXene-based composites is presented in Chap. 6. Regarding their scalability for practical applications, the existing issues and future possibilities in wastewater treatment have also been presented in Chap. 6.

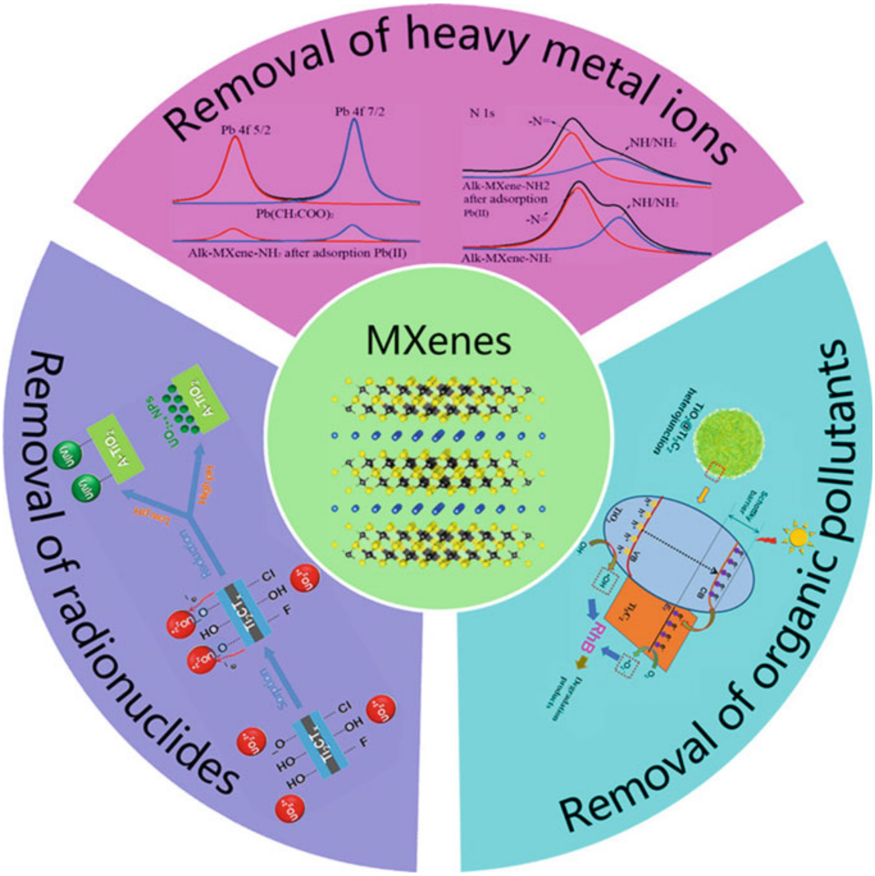

Fig. 1.6 MXenes for the removal of contaminants from the water. Adapted with permission from [45]. Copyright (2023), Copyright the Authors, some rights reserved; exclusive licensee [Elsevier]. Distributed under a Creative Commons Attribution License 4.0 (CC BY) https://creativecommons.org/licenses/by/4.0/

1.5.3 MXenes as Sensors

MXene materials have been proven as highly sensitive and selective detection platform for sensing applications in spite of their very short journey [48]. Morphology, extraordinary surface chemistry and excellent conducting properties, biocompatibility is among one of the most prominent features of MXenes which make them highly suitable matrix for fabrication of advance bio-sensing platforms [49]. MXene-based electrodes have been utilized as effective transducers for immobilization of biological receptors onto their surface and have shown considerable sensing characteristics. MXene biosensors enhance the catalytic performances of sensing matrix and help enzymes/protein to retain their bioactivity without altering the original native conformation.

Apart from electrochemical biosensors, MXenes have driven an impressive research in gas-sensing applications [48]. Determination of volatile organic compounds (VOCs) at ultra-trace level (ppb) for pollution analysis, detection of toxic gases, and therapeutic breath analysis for early identification of many diseases is highly crucial [44]. MXene materials have been considered as solid-state gas sensors with low electrical noise and well designed to detect these gaseous molecules with strong signal intensity, high manufacturing substrate flexibility and portability [50, 51]. Moreover, sensing approaches often include wearable nano-electronics, which have gained inexplicable attention for monitoring various health-related activities such as physical stimuli, weak pressure, and physiological signals [52]. MXenes are to be used as highly advanced platform for detection of phonations and substantial movements like walking, jumping, running or other human activities like coughing, joint bending [40].

In addition, MXenes are also used as a photoluminescence sensor. Photoluminescence is an effective technique that has often been employed in optical, biomedical, and cellular imaging areas [53]. However, recent advancements in materials sciences have made it possible to construct highly sensitive optical MXene-based quantum dots (MQDs) for bio-imaging applications [54]. In a recent study, an intracellular photoluminescent ratiometric pH sensor was developed using Ti_3C_2-MQDs for detection of cell metabolism [53]. A detailed description related to the MXene-based sensor is presented in Chap. 7.

1.5.4 MXenes in Biomedical Science

MXenes have many uses in the field of biomedical sciences. Optical and electrical signals of MXene-based sensor could be used for bioimaging, biosensing, therapy, drug delivery, etc. MXenes have become a known candidate for the development of extraordinary biosensors due to their high surface-to-volume ratio, unique electrical and optical properties, functional groups on the surface, and great hydrophilic behavior [55]. MXene-based sensor can detect hydrogen peroxide, nitride, glutathione, glucose, dopamine, epinephrine, organophosphate, and pesticides by sending electrical signals from a surface that has been changed by adding different analytes, which are made up of proteins and amino acids. MXenes are also used as optical sensors, in which signals can be picked up by two types: electrochemiluminescence (ECL) biosensors and surface plasmon resonance (SPR) biosensors. The ECL biosensors are used to detect proteins, enzymes, and DNA, while SPR biosensors are used to find and treat cancer cells by detecting carcinoembryonic antigen in human serum. Moreover, MXenes have superior electronic and mechanical properties that can change the way electrical signals behave in response to physical conditions like pressure and tension [56, 57]. Physical sensors, which are made with MXenes, are used to detect things like muscle strains and other physiological processes. A detailed insight related to the role of MXenes in biomedical science is presented in Chap. 8.

1.5.5 MXenes for Electromagnetic Shielding

The high electrical conductivity and distinctive multi-layer structure of MXene are primarily responsible for its remarkable EMI shielding capabilities. With a conductivity of roughly 0.3 S cm^{-1}, the Ti_2CT_x MXene has demonstrated the highest EMI SE over 70 dB when the thickness is 0.8 mm, exceeding most of the reported carbon- and metal-based materials [58]. The 2D structure and adequate functional groups on MXene's surface make them easily hybridized with other nanomaterials to accomplish the goal of tuning MXene's properties. It is difficult to get exceptional EMI shielding performance because of the homogeneous material. Therefore, the design of the material's structure and composition is crucial to address the need for MXene-based materials in EMI shielding. In Chap. 9, the use of MXenes for electromagnetic interference (EMI) shielding is discussed in depth.

1.5.6 MXenes in Biotechnology

The dielectric response of MXenes is greatly influenced by their metallic nature and interband transitions. It has been shown that the optical performance of MXenes is significantly influenced by surface functionalization (or functional groups) [59]. The MXene's absorption peaks are red-shifted due to the presence of functional group from the UV to the visible light spectrum by ~40% and depends on the location of the functional group. Further investigation based on thin film testing demonstrated the intrinsic electrochromic properties of titanium-based MXenes [60]. For the development of electroactive materials for biotechnological applications, controlling the band gap value is crucial. By inserting a metal atom, altering the material's surface terminals, or inducing hybridization, the band gap value of MXenes may be altered. The tunable band gap and exceptional electrical and transport properties are the promising prospects for their use as electroactive agents in biotechnology. The importance of MXenes to the biotechnology industry is discussed in Chap. 10.

1.5.7 MXenes for Separation Processes

Several materials with desirable properties have been studied to improve the separation efficiency. To fabricate high-performance membranes, which may be designed on a nanoscale or even sub-nanometer scale requires atomically thin 2D materials, which have been the subject of intense research. Hence, the trade-off constraint might potentially be overcome by lowering the transport resistance that will increase permeance and guarantee a clean separation process. According to the structure, 2D material-based membranes are often divided into two types: nanosheet membranes and lamellar membranes [61]. In the case of nanosheet membranes, solutes are carried through inherent or drilled holes in a membrane consisting of a single or few layers of nanosheets. It is predicted that the ultimate permeance and selectivity will be achieved by a nanosheet membrane with an atomic thickness. Nevertheless, it is still difficult to create nanopores with a consistent size and a high density. Graphene-based membranes have paved the way for this new class of membranes, which exhibit unprecedented permeance and selectivity. By using vacuum-assisted filtration (VAF), Li et al. [62] developed ultrathin graphene oxide (GO) membranes with thicknesses ranging from 1.8 to 20 nm. These membranes showed unprecedented separation performance toward hydrogen, with selectivities of H_2/CO_2 and H_2/N_2 pair gases reaching as high as 3400 and 900, respectively, and are quite stable across a wide range of temperatures. The separation performance surpasses that of reported polymeric membranes, hence dissolving the polymeric membranes' top bond. A wide range of 2D materials, beyond GO, have been explored for use in the fabrication of separation membranes. These include molybdenum disulfide, metal–organic frameworks (MOFs), covalent organic frameworks (COFs), and zeolites [61]. MXene, a relatively novel 2D material with unusual physical properties, has recently attracted considerable scientific interest. MXenes are well suited for separation application due to their hydrophilicity, remarkable flexibility, and abundance of surface groups. Separation applications such as gas separation, water treatment, organic solvent purification, nanofluidic ion transport, and osmotic energy conversion are discussed in detail in Chap. 11.

1.5.8 MXenes in Solution-Processed Optoelectronic Devices

New insights into the properties of 2D materials have shown an attractive platform for energy conversion and storage technologies of the future. Mechanical exfoliation of the bulk material revealed the unique characteristics of these materials as 2D systems. Recent developments in liquid phase exfoliation have provided a new avenue for research into these materials by allowing for the mass fabrication of solutions containing distributed nanosheets of 2D crystals [63]. Since these novel 2D materials may be applied in a liquid phase, it provides a new path to solution-process procedures, which can improve manufacturing efficiency and decrease production costs. Among various 2D materials, MXenes emerged as a suitable candidate for separation application. The optoelectronic properties of MXenes are tunable with the choice of intercalating agents. MXene-based films are the foundation of plasmonic application. MXenes (colloidal aggregate flakes) have an astonishing figure of merit (FOM) for their optoelectronic properties, which is twice as great as that of reduced graphene oxide. For high-performance solution-processed optoelectronic devices (organic/perovskite light-emitting diodes and solar cells), Chap. 12 highlights the many uses of MXenes in electrode, interface, and emitting/active layers.

1.5.9 Future Prospective and Research Avenues

There are several properties of MXene has been explored. However, considering its structural features which depends on the procedure adopted for preparation, many more applications needs to be explored. This has been highlighted in Chap. 13 of this book.

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Chapter 2
Strategies to Prepare 2D MXenes

Aydan Yeltik, Alp Yilmaz, Nihan Kosku Perkgoz, Feridun Ay,
and Sina Rouhi

2.1 Introduction

Since the synthesis of the first MXene in 2011, its demand has been increasing. MXenes have been used in various applications such as batteries, supercapacitors, hydrogen storage, and biosensors due to their high electrical conductivity, high volumetric electrochemical capacitance, adjustable band gap, high thermal conductivity, and high strength resistance [1, 2]. MXenes are characterized by the chemical formula $M_{n+1}X_nT_x$ (M = Ti, V, Mo, Hf, Cr, etc.; X = C, N; T = –OH, –O, –F, etc.) and can be synthesized using a variety of top-down and bottom-up methods. Presently, top-down methods are favored due to their low cost, ease of use, and scalability for large-scale 2D MXene synthesis. However, the quality of products synthesized using top-down methods is often lower, leading to the preference for bottom-up methods in producing high-quality 2D MXenes, albeit at a higher complexity, cost, and smaller-scale production [3]. In this chapter, 2D MXene preparation strategies are described under two sections as top-down methods and bottom-up methods.

A. Yeltik (✉) · A. Yilmaz
Department of Material Science and Nanotechnology Engineering, TOBB University of Economics and Technology, Ankara 06560, Turkey
e-mail: ayeltik@etu.edu.tr

N. K. Perkgoz · F. Ay · S. Rouhi
Department of Electrical and Electronics Engineering, Eskisehir Technical University, Eskisehir 26555, Turkey

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2.2 Top-Down Methods

Top-down methods stand out particularly in terms of being used in the industrial field, as they allow products to be synthesized on a larger scale and at lower cost. For the synthesis of 2D $M_{n+1}X_nT_x$ MXenes with these methods, the layers of A atoms are removed from the $M_{n+1}AX_n$ MAX phase (A = Al, Si, Zn, etc.) by selective etching. Top-down methods are presented here under the headings of wet-chemical synthesis of 2D MXene and other advanced top-down methods as well as fabrication of 2D MXene films, respectively. The wet-chemical synthesis part was examined under four subtitles, respectively, as fluorine-based acid etchants, fluorine-free base etchants, molten-salt etchants, and electrochemical etching.

2.2.1 Wet-Chemical Synthesis of 2D MXene

2.2.1.1 Fluorine-Based Acid Etchants

One of the frequently used methods for the synthesis of MXene from the MAX phase is the selective etching of A atoms using HF solvent as described in Fig. 2.1a. In 2011, Naguib et al. synthesized nanometer-thick Ti_3C_2 MXene crystal layers for the first time by removing Al from the Ti_3AlC_2 MAX phase [4]. The Al atoms in the MAX phase, which act as a bridge between the Ti_3C_2 layers and connect the layers with metallic bonds, were etched using HF solvent. Accordingly, it was observed that dangling bonds terminated with –OH or –F surface groups were formed in the synthesized 2D Ti_3C_2 layers. The chemical reactions occurring in the process are shown in Eqs. 2.1–2.3. After centrifugation, 2D layers were obtained by replacing stronger metallic bonds in the layered structure with weak van der Waals bonds.

$$Ti_3AlC_2 + 3HF \rightarrow AlF_3 + (3/2)H_2 + Ti_3C_2 \tag{2.1}$$

$$Ti_3C_2 + 2H_2O \rightarrow Ti_3C_2(OH)_2 + H_2 \tag{2.2}$$

$$Ti_3C_2 + 2HF \rightarrow Ti_3C_2F_2 + H_2 \tag{2.3}$$

As a further study to optimize the standard HF-based etching method and examine the underlying mechanism, Chang et al. observed the effect of HF treatment time on the etching process [5]. Accordingly, after 20 h of HF treatment, it was observed that the Ti_3AlC_2 MAX phase transformed into Ti_3C_2 MXene phase with a layered structure as a result of the selective etching of Al atoms, as shown in Fig. 2.1b–d. In addition, the synthesis of the MXene phase was proven with the mostly disappearance of the peaks of the Ti_3AlC_2 MAX phase after 20 h of treatment in the XRD pattern given in Fig. 2.1e. In another study, Liu et al. observed that the performance of the

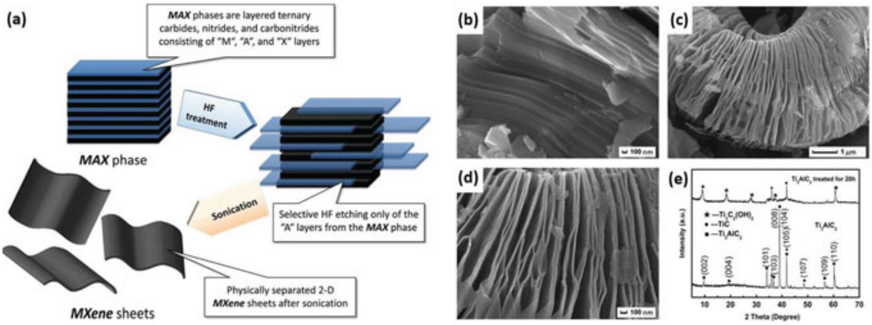

Fig. 2.1 **a** Schematic representation of MXene synthesis from the MAX phase using HF [7]. SEM images showing unetched and etched MAX phases; **b** before etching process, **c** after 20 h, and **d** high-resolution image of the etched sample, respectively. **e** XRD pattern of unetched and etched MAX phases. Adapted with permission from [5]. Copyright (2013), Copyright The Authors, some rights reserved; exclusive licensee [Elsevier]. Distributed under a Creative Commons Attribution License 4.0 (CC BY) https://creativecommons.org/licenses/by/4.0/

etching process increased due to the higher solubility of the HF solvent as a result of increasing the etching temperature [6]. In addition, it was observed that the number of bonds terminated with –OH and –F groups is higher in etching processes at higher temperatures, due to greater ion mobility.

As a variant of 2D MXene, $Hf_3C_2T_x$ (T_x; –OH, –O, –F groups), few-layered flakes with the 2–5 μm lateral dimensions were synthesized by Zhou et al. using HF from the $Hf_3(Al\text{-}Si)_4C_6$ MAX phase having the A layers doped with Si [8]. With this method different from the standard HF-based etching, the length of the bonds between the Hf-C atoms increased and weakened due to the doping of Si atoms, resulting in stronger bonds between the C-Al atoms with the adhesive energy decreasing at the etching interface which increased the efficiency of the etching process. As a result, $Hf_3C_2T_x$ MXene flakes were obtained by removing Al_4C_4 molecules from the structure.

In addition to using HF acid etchant directly, it can be formed as a product by using a mixture of HCl and LiF acid as shown in Eq. (2.4). In 2015, Anasori et al. examined the MXene structures of about 20 double transition metals carbides using density functional theory (DFT) calculations and synthesized Mo_2TiC_2Tx, $Mo_2Ti_2C_3T_x$, and $Cr_2TiC_xT_x$ double metal carbide 2D MXene flakes by etching with a mixture of HCl and LiF solvents followed by delamination including DMSO intercalation and sonication steps [9]. $Cr_2TiC_2T_x$ and $Mo_2Ti_2C_3T_x$ MXene flakes synthesized with this method were found to contain more contamination compared to $Mo_2TiC_2T_x$ MXene flakes.

$$\mathrm{LiF} + \mathrm{HCl} \rightarrow \mathrm{HF} + \mathrm{LiCl} \tag{2.4}$$

To investigate the electrochemical and heterogeneous electron transfer properties of MXenes, Nayak et al. synthesized few layer and multilayer 2D $Ti_3C_2T_x$ (T_x; –OH, –O, –F groups) MXene crystals using two methods named Clay and minimum intensive layer delamination (MILD), as depicted in Fig. 2.2a–b [10]. In the Clay method, the Ti_3AlC_2 MAX phase was etched using a mixture of LiF and HCl solvent to obtain the bulk $Ti_3C_2T_x$ phase, and then the ultrasonication method was used to break the weak bonds between the layers. The MILD method was carried out to synthesize few-layered MXene phases with simple shaking instead of sonification, using a mixture of LiF and HCl solvent with increased LiF ratio in the etching process. As a result, multilayer (10–13 layered) $Ti_3C_2T_x$ MXene flakes were obtained in the clay method, while few layer (1–2 layered) $Ti_3C_2T_x$ MXene flakes were obtained in the MILD method (Fig. 2.2c–f).

Furthermore, Shayesteh et al. developed the evaporated-nitrogen MILD (EN-MILD) process by adding dry nitrogen to the system to improve the MILD method and increase the stability, capacitance, and electrical conductivity of MXene flakes [11]. By using nitrogen environment in EN-MILD method, the acid concentration was increased by providing partial evaporation of the LiF and HCl solvent mixture used for etching, and hence, etching and delamination processes could be performed with higher efficiency. Moreover, by increasing the etching time, high-efficiency

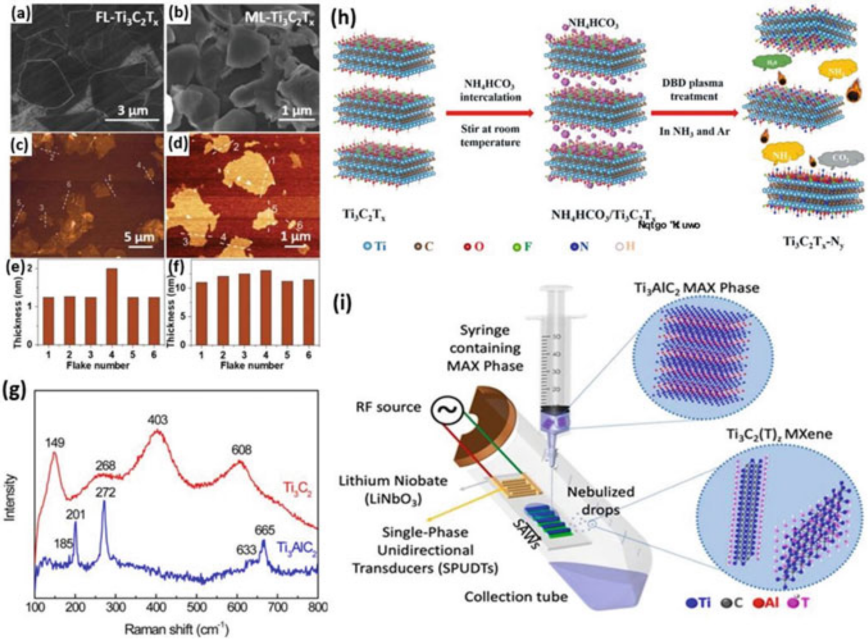

Fig. 2.2 SEM images of **a** few-layered and **b** multilayered MXene flakes of varying thickness, shown in **c**, **d** AFM images and **e**, **f** thickness distributions [10]. **g** Raman spectra of Ti_3AlC_2 and Ti_3C_2 after etching [13]. **h** Diagrams illustrating a plasma treatment-assisted DBD plasma system method used to obtain nitrogen-doped $Ti_3C_2T_x$, adapted with permission from [14]. Copyright (2021), Copyright: The Authors, some rights reserved; exclusive licensee [Elsevier]. Distributed under a Creative Commons Attribution License 4.0 (CC BY) https://creativecommons.org/licenses/by/4.0/, and **i** an etching process assisted by SAWs to synthesize $Ti_3C_2T_x$ MXene flakes [15]