International Journal of Enhanced Research in Science, Technology & Engineering
ISSN: 2319-7463, Vol. 8 Issue 7, July -2019, Impact Factor: 4.059

A Brief Overview of 2D MXene: Exfoliation, Energy Applications and Recent Trends

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ABSTRACT

MXenes are a new family of 2D layered transition metal carbides and carbonitrides and have garnered significant attention recently due to their multi-faceted advantageous properties: large surface areas, high electrical and thermal conductivity, mechanical strength, etc. MXenes also show combined features of good electronic conductivity, flexibility and hydrophilicity, which are rare in 2D materials. MXene have shown applications in energy conversion and storage devices like supercapacitors, lithium-ion batteries and solar cell, catalysis, sensors, water purification and also in biomedical fields. In this brief note, the information about the steps involved in the synthesis of MXene by the etching process is explained. The main applications of MXene are highlighted with continued and new important trends related to the synthesis and applications of MXene are briefly explained by referring to the literature.

Keywords: Two-dimensional materials, MXene, exfoliation, Etching, etc.

HOW TO CITE THIS ARTICLE

Sachin J. Pawar, Rutuja A. Chavan, "A Brief Overview of 2D MXene: Exfoliation, Energy Applications and Recent Trends", International Journal of Enhanced Research in Science, Technology & Engineering, ISSN: 2319-7463, Vol. 8 Issue 7, July-2019.

1. Introduction

Layered materials composed of two or more elements offer huge opportunities for a myriad of applications, arising from their compositional diversity and structural flexibility. A new family of 2D early transition metal carbides, nitrides, and carbonitrides, usually referred to as MXenes, has recently been discovered [1]. A continued increasing interest in MXene-related research is observed as reflected by the stats shown in fig. 1. The 2D layers of those carbides are labeled as "MXene" because it is produced by etching a layer from MAX phases and the suffix "ene" to emphasize their similarity to graphene. Two-dimensional (2D) nanomaterials MXenes have attracted great interest in recent times due to their extraordinary physicochemical properties. They belong to a unique material family with a thickness of a single or several atomic layers. This unique ultra-thin nature gives a large specific area for charge storage. Also, the simple 2D sheet structure with a large aspect ratio endows them with direct incorporation with other nanomaterials creating new compositions for higher performance; and a self-assembly process for 3D structures with high mechanical integrity and flexibility originating from the large overlapping areas [2]. MXenes adopt three structures, as inherited from the parent MAX phases: M_2C, M_3C_2, and M_4C_3. Recently, it has been shown that by using a combination of chemical exfoliation and sonication, the synthesis and mass production of 2D materials from three-dimensional (3D) layered compounds with chemical bonding between the layers is also feasible [3].

Producing an MXene by etching a MAX phase occurs mainly by using strong etching solutions that contain a fluoride ion (F^-) such as hydrofluoric acid (HF) [3], ammonium bifluoride (NH_4HF_2) [4], and a mixture of hydrochloric acid (HCl) and lithium fluoride (LiF) [5]. During exfoliation, depending on the type of chemical environment, a mixture of F, O, or OH groups terminates the surface of MXenes [6]. Most experimental investigations have mainly focused on the excellent electrochemical behavior of MXenes for energy storage as ion batteries, gas storage, and various catalysis applications because of their large exposed surface area, hydrophilic nature, adsorption ability, and surface activities. The latest applications and developments of MXenes have been summarized in the recent review article [7-8].

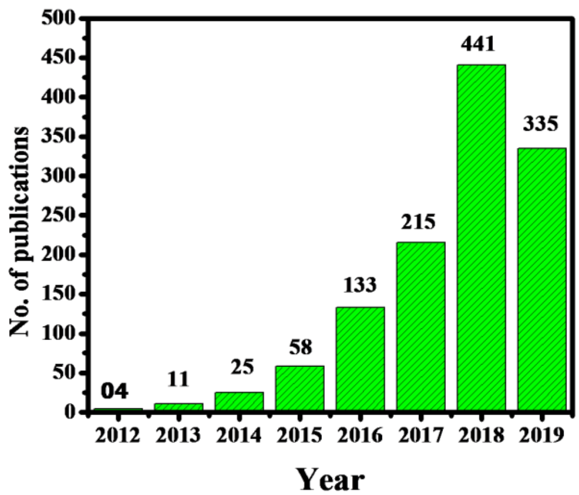


Figure 1. **The number of research papers per year on MXene.**
(Source: Scopus database "MXene" articles shown up to April 2019 only).

2. Preparation of MXene.

In the past several years, an elegant exfoliation approach has been used to successfully create a new family of 2D transition metal carbides, nitrides, and carbonitrides, termed MXene, from layered MAX phases, which also require different etching conditions.

MAX phase as Precursors

MAX phases are a family of solids with layered hexagonal structures and a space group symmetry of P63/mmc (No.194), whose chemical compositions are traditionally known by the chemical formula $M_{(n+1)}AX_n$, where n = 1, 2, or 3, "M" is an early transition metal (Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, or Mo), "A" is an element from groups III-VI in the periodic table (Al, Ga, In, Tl, Si, Ge, Sn, Pb, P, As, Bi, S, or Te), and "X" is carbon and/or nitrogen [9]. Till date, more than 72 MAX phases have been reported. According to the value of n, different MAX phase stoichiometries are usually referred to as M_2AX or 211 phases, M_3AX_2 or 312 phases, and M_4AX_3 or 413 phases. The basic difference in the crystal structure of these three groups is the number of M layers separating A layers. There are two, three, and four M layers in between two A layers in 211, 312, and 413 phases, respectively. MXenes are synthesized by selective etching of A elements from the MAX phase using strong acids and exfoliation as shown in fig. 2.

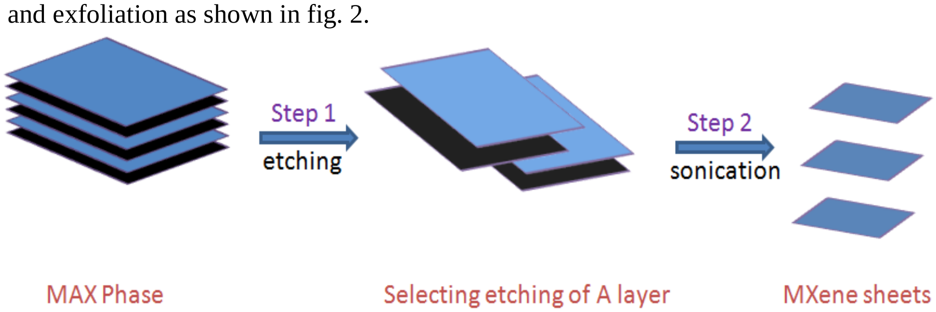


Figure 2. **Schematic diagram showing the preparation of MXene**

2.1 Exfoliation/Etching of MAX phases to MXene by HF

Ti_3C_2Tx (T = OH, and F) is obtained by extracting the weakly bonded Al layers from the Ti_3AlC_2 phase [3]. The reactions of the HF solutions with Ti_3AlC_2 include:

$Ti_3AlC_2 + 3HF = AlF_3 + 3/2H_2 + Ti_3C_2$, (1)

$Ti_3C_2 + 2H_2O = Ti_3C_2 (OH)_2 + H_2$, (2)

$Ti_3C_2 + 2HF = Ti_3C_2F_2 + H_2$. (3)

Reactions (2) and (3) result in OH and F terminations, respectively. Centrifugation is performed to separate the solids, which are then washed with deionized water. Without delamination, MXenes possess multilayered structures. To obtain single- or few-layer MXenes, sonication is performed and later replaced by intercalation of dimethyl sulfoxide (DMSO), which proved to be more efficient [10]. This strategy is applied to prepare almost all other MXene sheets from Al-containing MAX phases. Notably, the etching conditions (time and HF concentration) are necessary to convert a given MAX phase vary widely, depending on the particle size and temperature. For example, reducing the MAX phase particle size by attrition or ball milling can effectively reduce the necessary etching time and/or HF concentration [11]. In addition, discrepancies in M-Al bond energies for different MAX phases also require different etching conditions. For example, the larger Ti-Al bond energy in Ti_2AlC compared with the Nb-Al bond energy in Nb_2AlC results in extended etching time and increased HF concentration [12]. Hence, appropriate etching conditions are necessary to achieve high yields and complete the conversion of MAX phases into MXenes.

2.2 Exfoliation/Etching of MAX phases to MXenes by NH_4HF_2

Recently, Halim et al. reported the use of ammonium bifluoride, NH_4HF_2, as an etchant in instead of the hazardous HF [4]. Its milder nature and concomitant intercalation of cations during the etching process render it more suitable for preparing delaminated MXenes. As the etching and intercalation processes occur simultaneously, it is reasonable to conclude that the following reactions exist:

$Ti_3AlC_2 + 3NH_4HF_2 = (NH_4)_3AlF_6 + 3/2H_2 + Ti_3C_2$ (4)

$Ti_3C_2 + aNH_4HF_2 + bH_2O = (NH_3)c(NH_4)dTi_3C_2(OH)_xF_y$ (5)

Because of slower and less vigorous reaction processes, and the intercalation of both NH_3 and $NH^{+\ 4}$, the atomic layers in $Ti_3C_2T_x$ are more uniformly spaced and appear to be glued together.

2.2 Exfoliation/Etching of MAX phases to MXenes by LiF and HCl

Ghidiu et al. reported a new high-yield method for the simultaneous preparation of many MXene sheets [5]. In this method, Ti_3C_2Tx is prepared by dissolving Ti_3AlC_2 powders in LiF and HCl solutions, mixture was heaed at 40°C for 45 h, and finally washing the sediment to remove the product and increase the pH. A clay-like paste formed from this processing; was rolled to produce flexible, free-standing films with high volumetric capacitance The lack of defects reflects the milder nature of the LiF + HCl etchant compared with HF. Intriguingly, other combinations of fluoride salts and acids, such as NaF, KF, CsF, tetrabutylammonium fluoride [$(C_4H_9)4NF$], and CaF_2 with HCl or H_2SO_4, showed similar etching behaviors. This one-step etching procedure is desirable for future explorations.

3. Applications of MXene

MXene has shown applications in many technological fields. MXenes are highly conductive and extremely durable, they can block electromagnetic interference, sense chemicals in the air, remove salt from water, and capture hydrogen They've made a strong case to be involved in the future of energy storage, wireless communication and wearable technology. wearable electronics, energy storage and electromagnetic interference shielding are among those on the horizon as well as understanding how to make them stable in atmospheric conditions for extended periods. They also point the way toward creating magnetic MXenes that could be used for data storage devices. MXenes as transparent conductors [4,13], field-effect transistors [14], supercapacitors[13, 15], Li-ion batteries [12], electromagnetic interface shielders

[16], fillers in polymeric composites [17], hybrid nanocomposites [18], purifiers [19], dual-responsive surfaces [20], catalysts [21] and photocatalysts for hydrogen production. There is a worldwide contest to develop alternative clean energy resources in this regard, MXene is assumed a satisfactory material used in energy conversion and storage devices There is a great improvement in the properties of the materials with reinforcement by using various modified strategies. There is a wide range of applications of MXene and MXene reinforced materials. For brevity, here we discuss recently reported applications of MXene in the two main fields namely Lithium-ion batteries, and supercapacitors only.

3.1 Lithium-ion batteries

Researchers have been devoting numerous efforts to improving both cathodes and anodes to achieve LIBs with high capacity, short charge-discharge time and long cycle life. MXenes have been demonstrated to be satisfactory materials for anodes of LIBs. Some interesting recent reports about the use of MXene as anode materials for lithium-ion batteries. Electrochemical performance of Sn@V_2C MXene, the Coulombic efficiency is stable and higher than 96% even under high current densities, suggesting the excellent stability of Sn@V_2C electrode. Almost 100% reversible lithium storage capacity of 1262.9 mAh g^{-1} is still restored after 90 cycles at the current density of 0.1 Ag^{-1}, implying marvelous rate performance [22]. Facile construction of SnOx@Ti_3C_2 composites, where ultrathin SnOx nanosheets (NSs) of 5 nm in thickness are loaded uniformly on the interlayers and/or surfaces of Ti_3C_2 matrix, by hydrothermal method towards efficient lithium storage. The resulted SnOx@Ti_3C_2 composites exhibit long-duration cycling stability and superior rate behaviors. Competitively, a large reversible capacity of 540 mAh g^{-1} after 1000 cycles at a current rate of 500 mA g^{-1} [23]. The performance of MXenes (Ti_2CT_x) combined with electrolytic manganese dioxide (EMD) with the ratio of MXene: EMD = 80:20 was examined as anode material for Lithium-ion batteries exhibited 460 mAh g^{-1} capacity after 200 cycles at a current density of 100 mA g^{-1} [24].

Recent reports about the use of MXene as a promising cathode for lithium-ion batteries, facile, universal, and effective strategy to suppress the dissolution of manganese at 55 °C by encapsulating $LiMn_2O_4$ particles in crumpled $Ti_3C_2T_x$ nanosheets using an electrostatic self-assembly process The capacity retention ratio can be improved by 18.3% at 55 °C after 200 cycles at 2 C [25].

3.2 Supercapacitors

The recently reported applications of MXene related to supercapacitor includes the synthesis of tantalum carbide MXene sheets by etching the intermediate “aluminium” from the parental Ta_4AlC_3 MAX phase using hydrofluoric acid. The tantalum carbide MXene showed cyclic stability of 89% over 2000 cycles in the acidic electrolyte (0.1M H_2SO_4) and a high specific capacitance of 120 F g −1 [26].

In another report, the fabrication of a flexible aerogel composed of reduced graphene oxide (rGO) and delaminated titanium carbide (Ti_3C_2) sheets prepared via room temperature interfacial gelation route and successive reduction of GO at Zn surface. The vacuum dried composite aerogel showed high areal capacitance of 171.4 mF cm^{-2} at a current density of 1 mA/cm^2, cyclic stability of 96% over 1500 cycles at a current density of 3 mA/cm^2 [27].

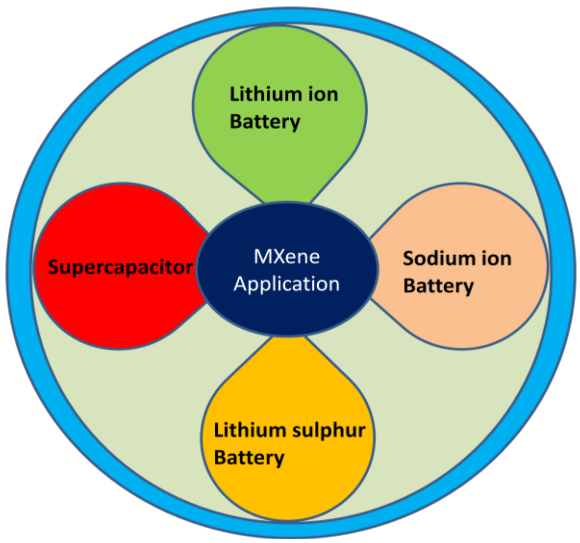
Guo et al. reported the preparation of a composite electrode made up of 2D delaminated Ti_3C_2 sheets (d-Ti_3C_2) and 3D Ni foam (NF) by electrostatic self-assembly. In this electrode, d- Ti_3C_2nanosheets are adsorbed on the surface of the 3D Ni foam skeleton structure, eliminating the need for insulative polymer binders. The self-assembly strategy endows d-Ti_3C_2/NF composites with a unique 2D/3D structure that possesses the merits of excellent conductivity, sufficient active sites, high charge transfer efficiency and short ions diffusion path. d-Ti_3C_2/NF composite electrode exhibits a high specific capacitance up to 654 F g^{-1} at 1 A g^{-1} and good cycling stability. An asymmetrical supercapacitor with d- Ti_3C_2/NF composite as a positive electrode, bulk Ti_3C_2 (b- Ti_3C_2) as a negative electrode, and 6 M KOH as an electrolyte exhibit a maximum energy density of 18.1 Wh kg −1 (at 397.8 W kg −1) and excellent cycling stability 80.6% after 5000 cycles [28].

In another recent study wang, et al. have provided the high rate performance and excellent cycling stability of V_4C_3 MXene electrodes mainly attributed to the high electronic conductivity (1137 Sm^{-1} at 300 K) They have prepared 2D multi-layered V_4C_3 MXene by selectively etching Al from V_4AlC_3 and it shows a high capacitance of 209 F g^{-1} at 2 mV s^{-1} scan rate, good rate performance, and stable long cyclic performance with a capacitance retention rate of 97.23% over 10,000 cycles at 10 A g^{-1} current density in 1 M H_2SO_4 electrolyte [29] .

4. Limitations of MXene

There is a need for a simple, low-cost, mild, hazard-free, synthesis route of MXene to be developed as a need of time for practical applications in various fields. Though Florine salts with mild acids combination are way milder than HF strong acid etching method, however, the results are not yet satisfactory as the morphology still shows defects that affect the charge storage capacity. The charge store mechanism between the MXene layer needs to be understood and requires more effort. The stability is an essential property of MXene that need to be investigated to utilize MXene in various applications Fields**.**

5. Recent trends



Although investigations on MXenes have just begun in the last decade, MXene materials have shown great potential to work as electrode candidates for effective energy storage. MXene is considered a satisfactory material used in energy conversion and storage devices like supercapacitors, lithium-ion batteries Sodium-ion batteries, lithium sulp and solar cells, catalysis, sensors, water purification and also in the biomedical field. For future applications, more efficient synthetic strategies are necessary while doping strategy showed the impressiiive The recent experimental achievements on MXene anodes are impressive, and we believe that more MXene materials can be realized shortly. Opportunities and challenges exist simultaneously. We hope that researchers will tackle the challenges and will explore these new and exciting materials in various fields.

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