



MXenes: Synthesis, properties, and applications for sustainable energy and environment

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ABSTRACT

MXenes, the largest and most diverse group of emerging two-dimensional materials, have potentials across multiple applications. The increasing attention is driven by the fascinating tunable surface properties, and synergetic chemistry facilitated by the presence of multiple chemical bonds dominated by covalent and metallic bonds between transition metals (M) and non-metals, X (such as carbon, nitrogen, or both). Although the various available synthesis approaches offer opportunities for tuning MXenes for specific applications, their inherent environmental and toxicity risks as well as poor scale-up potential are currently hampering research and commercialization progress. Therefore, ongoing efforts are focused on developing less hazardous, scalable methodologies to limit the barriers. This review comprehensively surveys the literature from the seminal MXene paper to the present, offering insights into the factors, latest advancements, limitations, trends, and existing gaps in MXene synthesis, properties, and applications in the areas of environment and energy storage. Special emphasis is placed on the need to address environmental concerns associated with fluoride-based synthesis while an overview of safer, non-fluoride alternatives is provided. Furthermore, the most recent breakthroughs in scalable top-down dry selective etching (DSE), bottom-up solid-state direct synthesis, and structural editing protocol using chemical scissors are presented. In particular, this review critically examines the current state of knowledge and identifies key research progresses and areas that deserve intensive attention to facilitate safe and industrial-scale synthesis and application of MXenes for catalysis, environmental remediation, and energy storage. Addressing the identified gaps will accelerate the transformation of MXenes and their composites into the components of our everyday appliances.

1. Introduction

The discovery of graphene [1] and its widespread applications in various fields resulted in the expansion of research interests into other 2-dimensional materials. In 2011, Professors Michel Barsoum, Yury Gogotsi, and other researchers at Drexel University used the term “MXene” in their published work [2] to describe the 2D titanium carbide (Ti₃C₂T_x) with the accordion-like morphological structure. Since then, the definition of MXenes has been generalized to refer to a new class of 2D carbides, carbonitrides and nitrides of transition metals with the general formula shown below.

$$M_{n+1}X_nT_x \quad (1)$$

Where *M* = one or combinations of certain transition metals,

X = carbon, nitrogen, or both

T_x = termination group which could be -OH, -O, -F, -Cl or their combinations while *x* represents the number of the functional terminations.

Currently, MXenes from the transition metals titanium (Ti), vanadium (V), chromium (Cr) [3], zirconium (Zr) [4], niobium (Nb) [5], molybdenum (Mo) [6], hafnium (Hf) [7], tantalum (Ta) [8] and tungsten (W) [9] have been experimentally confirmed. However, it is still

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impractical to experimentally synthesize MXenes from other transition elements such as scandium (Sc), lutetium (Lu) and manganese (Mn) [10]. Nonetheless, the feasibility of obtaining MXenes from these elements has been proven by first-principle theoretical calculations [11]. Furthermore, the synthesis of Lu_2SnC , a MAX phase, has been reported [12]. Also, the number of surface functionalities (x) is currently difficult to determine. Considering the large number of possible elemental combinations in MXenes, several types of MXenes could be synthesized. For instance, in the formula, $\text{M}_{n+1}\text{X}_n\text{T}_x$, n varies from 1 to 4, and M could be a single element or a combination of the elements listed above in various proportions. The same applies to X and the surface terminations can similarly be varied in terms of type and number. Although the method of determining the x in T_x is still intricate.

Nonetheless, MXenes are traditionally synthesized from 3D MAX phase. MAX phase materials have the general formula $\text{M}_{n+1}\text{AX}_n$ where A represents one of the elements Al, Si, P, Ga, Ge, As, In, Sn, and Pb. The element (A) is etched away during MXene synthesis leaving behind only M and X which are the main components of MXenes. The etching can be achieved in various ways contributing to the diversity of MXene types, properties and functionalities. This etching approach constitutes MAX-based top-down synthesis. In other non-MAX based top-down approaches, A -element containing X elements are etched rather than only A . In recent reports, bottom-up approaches and structural editing protocols are novel methods for cheaper, purer and scalable MXene synthesis [13–15]. In all cases, the combination of transition metals, and carbon or nitride and the presence of active termination groups impact several unique properties such as high metallic conductivity, low diffusion barrier, high ion transport properties, hydrophilic property, good surface areas and tunable surface chemistry. Another uniqueness of MXene is its chemistry which involves most of the elements in the periodic table either as the main component or intercalant. All these contribute to wide applications in various fields including energy storage [16–18], wastewater treatment [19–21], catalysis [22–24], hydrogen storage [25–27] and others. The application growth appears to be linked with progress in synthesis since it was first reported in 2011 till date (Fig. 1).

This review comprehensively assesses the established and novel synthesis methods and critically evaluates the links between the synthesis, properties and applications in energy storage, wastewater treatment, catalysis and hydrogen storage. Indeed, there have been well-

written reviews in some of these aspects [24,28–30]. However, the study of MXenes like that of other 2D materials is a fast-growing research area with notable discoveries being reported so fast that it is often difficult to catch up. For instance, within the space of just three months in 2023, two independent teams of researchers reported two ground-breaking, scalable, and direct methods for synthesizing MXenes. The pioneering approaches are: the top-down dry selective extraction (DSE) [31] and the bottom-up chemical vapor deposition (CVD) [14]. Such rapid advancements signify a pivotal moment in MXene research. For these reasons, this review aims to bring researchers up to speed with recent advancements and to critically examine the interplay between the diverse application domains, traditional and novel synthesis approaches as well as inherent MXene properties in line with recent publications. In this work, the important factors of focus that influence specific properties for specific applications were exhaustively highlighted, right from MAX synthesis to final MXenes. Furthermore, newer bottom-up and non-MAX synthesis protocols and their potential to enhance scalability and applicability were highlighted in a way to show the direction future research should beam light on. The discussion presents a compelling case for the transformative potentials of MXenes and further focuses on applications in catalysis, environmental remediation and energy storage. The existing and evolving gaps to modifying surface properties, and to amend or sever terminal chemical species on MXenes for specific applications were also discussed.

2. MXene synthesis

Traditionally, MXenes are synthesized by an approach of a top-down wet chemical method of etching out the A -layers in MAX phases. Nowadays, synthesis methods can be categorized broadly into top-down, bottom-up and up-bottom approaches. Fig. 2 presents a map summarizing the connections between the broad methods of synthesis. This section gives a concise overview of these approaches and then describes in detail the latest but notable progress reported recently.

2.1. Top-down approaches

Top-down methods, as described above, involve the etching away of the ' A ' elements (usually, Al, Si or Ga) from MAX phase or $(A-X)_m$ from non-MAX phase precursors of MXenes. Top-down approaches can be

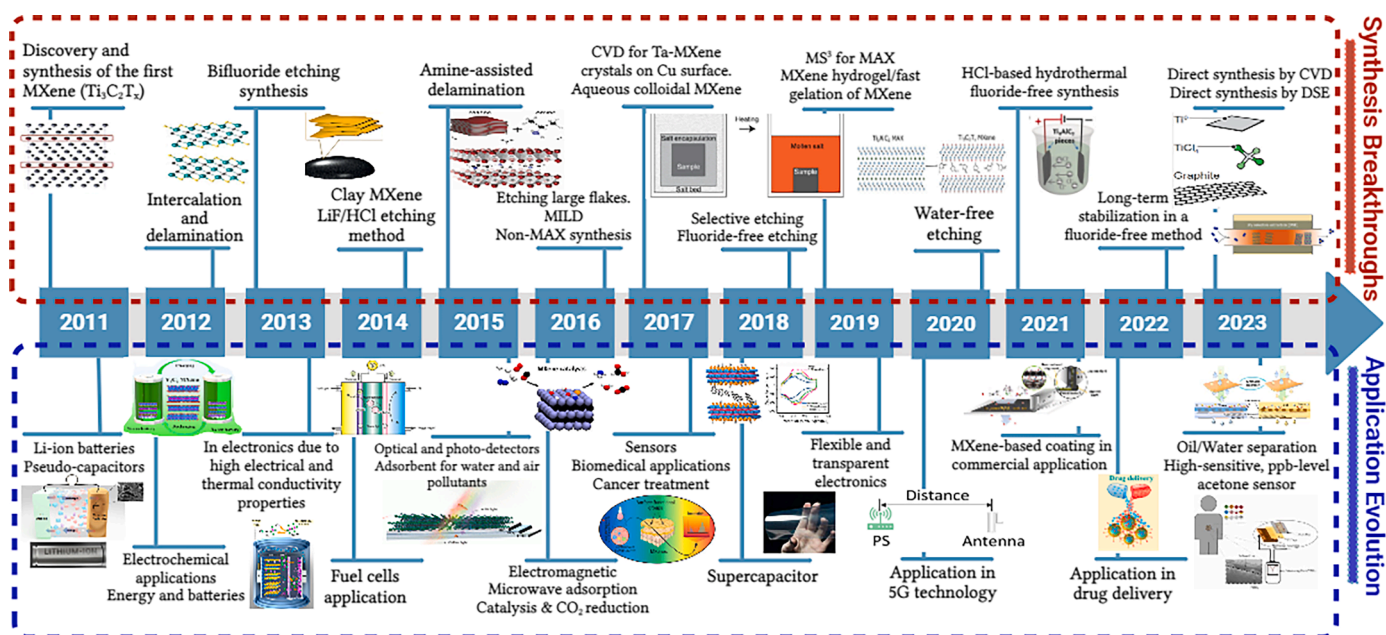


Fig. 1. Timeline of synthesis breakthroughs and application evolution from discovery in 2011 till date.

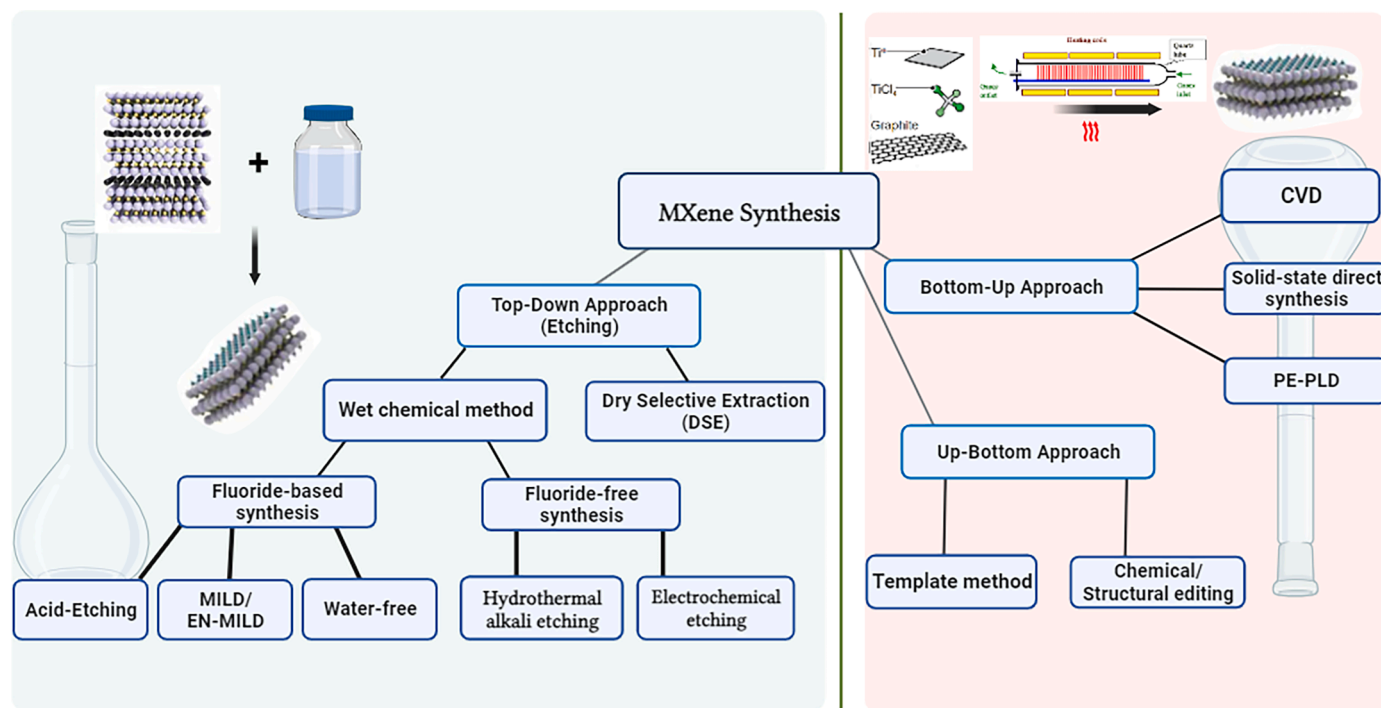


Fig. 2. MXene synthesis approaches broken down into top-down, bottom-up and up-bottom approaches.

subdivided broadly into wet chemical method and a more recent dry selective extraction (DSE) [31] method.

2.1.1. Dry selective extraction

DSE is a novel computationally guided fluoride-free halogen etching approach [32] involving the use of iodine vapor to etch out 'A' from MAX phase. Experimentally, the process is a bit similar to chemical vapor deposition (CVD) in that the reaction takes place in a borosilicate glass ampoule placed in a tube furnace. The ampoule is filled with a measured mass of MAX phase and iodine vapor is flowed through at an elevated temperature to act as the etchant Fig 3A. It is important to optimize the temperature, and it is determined to be 350 °C for $\text{Ti}_3\text{C}_2\text{I}_x$ synthesized using iodine. At a lower temperature, either the reaction would not occur, or gaseous product would not evolve. Whereas higher temperature, greater than 400 °C leads to over-etching [31]

2.1.2. Wet chemical methods

Wet chemical methods involve the use of strong chemicals, electrochemical exfoliation, and mechanical/hydrothermal methods to selectively remove the interlayer 'A' element(s). These are popular and among the well-researched synthesis approaches. For example, the famous and seminal $\text{Ti}_3\text{C}_2\text{T}_x$ was produced by etching aluminum from Ti_3AlC_2 using 50 wt% HF [2]. Typically, chemical exfoliation is followed by intercalation using cations or organic molecules [33]. Intercalation eases delamination, that is, the separation of the synthesized MXene into 2D layers [19]. While other etchant solutions are now in use, fluoride-containing acids such as HF and NH_4F are commonly used in chemical etching due to the strong ionizing nature of F. However, for safety and environmental concerns, fluoride-free etchants are lately gaining popularity. Based on this, wet chemical methods can further be subdivided into fluoride-based and fluoride-free etching.

2.1.2.1. Fluoride-based etching. The use of HF alone or in combination with HCl [34] was the traditional acid etching method to synthesis MXenes. Since the first MXene synthesis [2] where concentrated HF (50%) was used, various lower concentrations (5 to 40%) of HF have been tried [33,35]. While lower concentrations (5 to 10%) assure better

safety and lesser environmental impacts, the process is slow and may involve raising the synthesis temperature to ≥ 50 °C. Depending on MAX composition, the synthesis time can be up to 30 h or more [36]. For example, the synthesis of niobium, vanadium-, molybdenum-based and some other ternary MXenes requires a long time of stirring in etchant solutions and could take up to 7 days [37]. Whereas 2 h or less could be sufficient for $\text{Ti}_3\text{C}_2\text{T}_x$ synthesis especially if the concentration of the HF is above 40 wt%. HF remains the most effective etching agent for MXene. A review by Wyatt et al. [36] provided more scientific insights using atomic chemistry of the transition metals to explain the recalcitrant nature of some MAX phases requiring aggressive acids. Nonetheless, the concern for safety and the environment remains an issue.

In-situ synthesis of HF using fluoride salts (such as NaF, LiF, or NaBF_4) with a milder acid, HCl, was introduced as an alternative to limit exposure to HF [38]. This method was called minimally intensive layer delamination (MILD) by Alhabet et al. [33] to indicate that the approach was a relatively safer method compared to using direct HF. Notably, MILD was originally coined by Shahzad et al. [39] to explain a method to delaminate MXenes synthesized using LiF/HCl. A gentle shaking rather than aggressive sonication delaminates the MXenes into single layers. In the approach, the whole steps of HF synthesis, etching and intercalation take place as a single step in the same pot.

In a recent study, Shayesteh Zeraati et al. [40] proposed an improved MILD synthesis approach called "Evaporated-Nitrogen MILD" wherein dry nitrogen is purged into the etching pot to limit oxidation by eliminating dissolved oxygen. This increases acid concentrations by enhancing the dissolution of LiF. Although generally, MXenes synthesized via MILD are characterized by fewer defects, larger lateral dimensions and higher conductivity when compared with those synthesized via the direct HF method [40], EN-MILD method resulted in an improved yield of better quality MXene with significantly high electrical conductivity ($24,000 \text{ S cm}^{-1}$ as opposed to 5300 S cm^{-1} obtained from regular MILD method).

Recently, Gentile et al. [41] proposed another fluoride-containing route. In the report, HBF_4 was used as the etchant, and the synthesized $\text{Ti}_3\text{C}_2\text{T}_x$ was compared with those from other *in-situ* approaches and 5% HF in terms of purity (measured as yield%) and properties. It

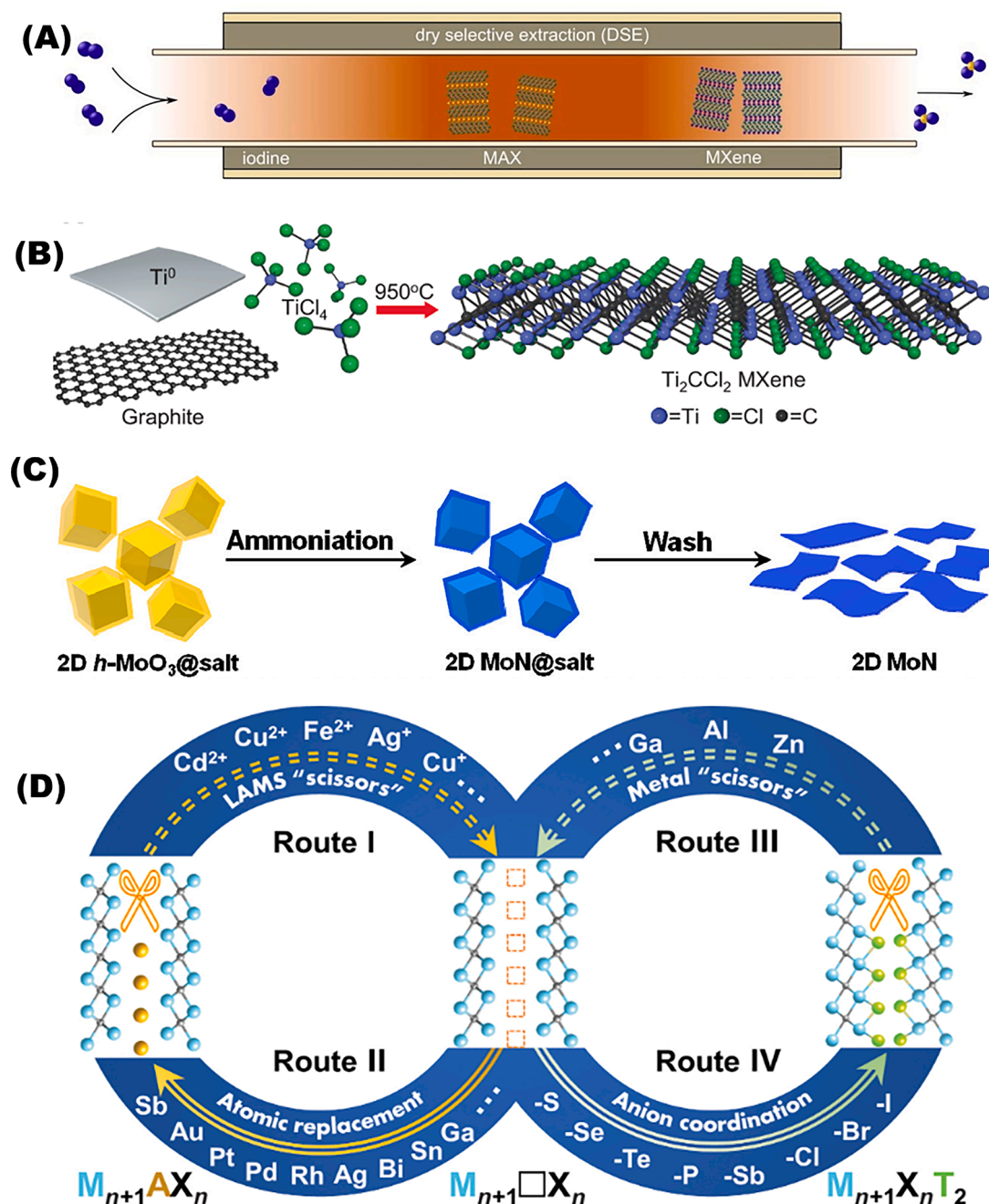


Fig. 3. Schematic diagrams of: (A) DSE showing molecules of iodine vapor flowing in and the MAX phase (in reality, placed in ampoule). The etched MAX becomes MXene, and A-I_2 vapor evolves [31]. (B) synthesis of Ti_2CCl_2 MXene by direct synthesis [14]. (C) MoN synthesis by salt-template method [46]. (D) structural editing protocol showing the four editing routes and some of the possible atomic replacement and anion coordination options [13].

was found that the $\text{Ti}_3\text{C}_2\text{T}_x$ synthesized using NaF/HCl and NH_4HF_2 have the best yields (at 94% and 90% respectively) and are comparable with that of 5% HF (95%). On the other hand, the yields from HBF_4 and NaBF_4 in HCl were low (71% and 65% respectively). In terms of properties, however, the differences are not so significant. Importantly, synthesis routes in which HF is used directly or synthesized remain the quickest and most effective synthesis approach. However, there is intensive ongoing research to design safer, cheaper, and more effective methods.

2.1.2.2. Water-free etching. Another relatively newer fluoride-free synthesis is the use of water-free etchants. In some MXene applications, the

presence of water is not acceptable. For such cases, the water-free etching method recently proposed [42] is suitable. Instead of water, propylene carbonate is used as a replacement. Incredibly, the synthesized MXene has only $-\text{F}$ as the termination species. However, for purity, it is required that the synthesis is done in Argon-filled glove box and with NH_4HF_2 solutions. Although the synthesis is quite slow as the etching step alone takes 8 days of stirring and is costly, the resulting MXene showed enhanced performance in Na-ion battery. There is a need to improve the method by trying other organic solvents. Future research is also needed to investigate the performance of MXene synthesis using water-free etchants in other applications. Nevertheless, there are organic-based etchants that are water-free and fluoride-free. This is

discussed in the next section under fluoride-free methods.

2.1.2.3. Fluoride-free etching. Fluoride free method is a recent synthesis route to circumvent the application of the toxic HF [43–45]. Natsu et al. [42] revealed that it is possible to etch the MAX phase in solutions other than widely used water. This was achieved by exploring polar organic solvent with ammonium dihydrogen fluoride to produce an F-terminated MXene as shown in Fig. 4A. The micrographs and selected area diffraction revealed an accordion-like morphology typical of $\text{Ti}_3\text{C}_2\text{T}_x$ affirming the possibility of synthesizing multi-layered $\text{Ti}_3\text{C}_2\text{T}_x$ in other solvents. Nonetheless, the procedure is time-consuming and studies on its optimization are needed before scale-up. Efforts to shorten the procedure by adopting anodic corrosion of Ti_3AlC_2 are possible but are not yet established for large-scale production. Therefore, further studies are needed on the fabrication of an environmentally friendly synthesis route for attaining MXenes with large surface area and robust features.

The search for fluoride-free alternative synthesis is intense among the concerned scientists and researchers. The outcomes of the efforts, so far, can be broadly categorized into 3:

(a) Hydrothermal alkali treatment and (b) acid treatment and (c) Electrochemical method

2.1.2.4. Hydrothermal alkali etching. This hydrothermal synthesis involves the use of a concentrated alkali solution to etch MAX into MXene. In this method proposed by Li et al. [47], a concentrated NaOH is prepared in argon-deaerated water (to reduce dissolved oxygen for possible oxidation). Powdered MAX is dissolved into the solution, sealed and

autoclaved for 12 h. The resulting MXene suspension can then be vacuum-dried. The Al in Ti_3AlC_2 reacts with the OH in solution due to Al affinity for OH. Unlike MILD method, the layers form are tightly packed and intercalation using dimethyl sulfoxide and sonication is essential to improve delamination. The method is much safer and less intrusive when compared to fluoride-based methods.

2.1.2.5. Acid treatment. The first fluoride-free synthesis attempt was reported in 2017 by Sun et al. [48]. The electrochemical method involved the use of low-concentration HCl as an electrolyte and Ti_2AlC as electrodes. The resulting Ti_2CT_x had no –F in the termination group. Four years after, a hydrothermal alternative involving the use of HCl was reported [49] for the synthesis of Mo_2C MXene following DFT theoretical prediction of the process.

2.1.2.6. Acid-free electrochemical method. In this fluoride-free electrochemical synthesis, the electrolyte comprises 1 M NH_4Cl and 0.2 M TMAOH while the electrodes are Ti_3AlC_2 [50]. The Al in Ti_3AlC_2 anode is etched off 5 h after the supply of 5 V of electricity. It is noteworthy that the OH concentration should be maintained around 0.2 M because higher concentrations etch off everything leaving amorphous carbon behind, while lower concentrations take too long time to complete the etching process. Although MXene yield is generally low with fluoride-free methods, the yield in acid-free electrochemical synthesis is significantly low and is usually about 40%. Jun Yao Wong et al. [51] wrote an excellent review on fluoride-free synthesis. Readers are encouraged to read the article for more information. Fig 4B summarizes

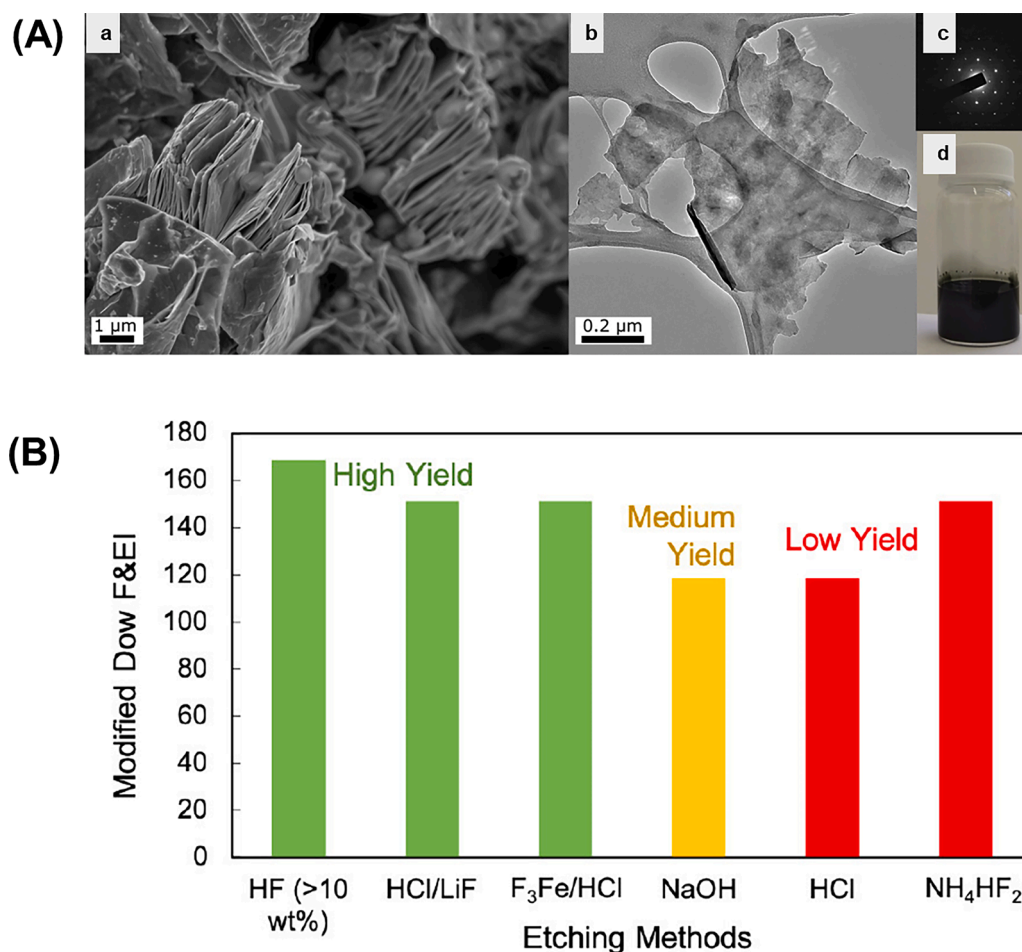


Fig. 4. (A) (a) SEM micrograph. (b) TEM micrograph (c) selected area diffraction (SAED) pattern obtained from flakes shown in (b) and (d) a photograph of $\text{Ti}_3\text{C}_2\text{T}_x$ suspension [42]. (B) Yield and relative hazards of different etching methods (Green bars= high yield, >55%; Red bars = low yield; Yellow bar = medium yield) [52].

and compares the yield and hazard potentials of the different synthesis methods. It is obvious that fluoride-based top-down syntheses retain the best position in MXene yield from etching.

2.2. Bottom-up synthesis approaches

While the use of bulk precursors offers scalability advantages, scientists prefer making a material ground-up from its elemental composition. This is because, bottom-up synthesis permits meticulous control over material chemistry, enabling tailored customization of material designs. Notable bottom-up approaches for MXene synthesis include chemical vapor deposition (CVD), plasma-enhanced pulsed layer deposition (PE-PLD) and solid-state direct synthesis.

2.2.1. Chemical vapour deposition (CVD)

In CVD, a film of MXene is deposited on a metal surface when gaseous precursors flow over the heated substrate. In 2017, Wang et al. [53] reported the synthesis of ultrathin crystal layers of tantalum carbide, nitride and boride on heated copper-tantalum surface when C_2H_2 , NH_3 and B-powder were used as precursors respectively. Remarkably, MXenes obtained from CVD has no surface terminations. The CVD process was not applicable to most transition metals (including Ti) and, the process was not scalable. These challenges have been addressed in a newly published research study [14].

In the study, Ti-based MXenes were synthesized for the first time via CVD [14]. The synthesis involves reacting methane or N_2 gas with $TiCl_4$ on titanium metal surface to yield chlorine terminated Ti_2CCl_2 or Ti_2NCl_2 respectively. The MXene sheets grow perpendicularly to the metal surface and then drop off exposing the metal surface for further reaction. This suggests that large amount of MXene sheets could be produced as far as the precursors' amount is sufficient. The proposed CVD design offers an opportunity to scale-up production of MXenes in commercial quantity. It also opens a prospect to explore and access new MXenes phases and morphologies. For example, the Ti_2NCl_2 synthesized was the first Cl-terminated nitride MXene ever reported [15].

2.2.2. Plasma-Enhanced pulsed-layer deposition (PE-PLD)

Plasma enhancement was originally integrated to conventional high-temperature CVD process to enable reduced temperature synthesis, in what is called PE-CVD [54]. PE-PLD combines the advantages PE-CVD and pulsed-layer deposition (a thin film deposition method) to facilitate continuous growth of single crystal films. This approach has been used as a non-MAX-based bottom-up method to generate up to 25 nm thick Mo_2C films [55] when 248 nm laser beam was focused on Mo target for 20 min [55]. At present, it is still more of a proof of concept than anything. Nonetheless, the Mo_2C films could be used as a catalyst on the surface of materials and possibly in optoelectronic devices.

2.2.3. Solid-state direct synthesis

Like the improved CVD proposed by Wang et al. [14], direct MXenes synthesis involves combining the constituents but in their original states (not in gaseous forms unlike in CVD) through high-temperature solid-state reaction. This approach was first reported in 2019 wherein YF_3 salt and graphite powder were heated to 1240 °C and held for 3 days to produce 3D ordered Y_2CF_2 crystals [56]. Exceptionally, the layered and crystalline Y_2CF_2 is structurally similar to 2D MXenes but the layers are connected via ionic bonds to uniquely characterize as 3D structures. It thus behaves electronically like a typical 2D material because the terminal F does not contribute to the valency or the conduction band.

Recently, 2D carbides and nitrides were produced at a lower temperature and shorter time via solid-state direct synthesis for the first time [14]. Titanium metal and graphite grounded together as the powder was combined with a desired amount of $TiCl_4$ and then placed in a sealed quartz ampoule. The ampoule was placed in a tube furnace and heated to 950 °C for 2 h (Fig. 3B). Direct synthesis was used this way to produce Ti-based and Zr-based MXenes. The potential to precisely control the

termination group based on the choice of precursors is an important benefit of this method.

2.3. Up-Bottom synthesis

This approach lies primarily within the realm of bottom-up methodology but incorporates elements of the top-down approach, positioning it between the two methods. The methods under this are the template method and the novel structural/chemical editing protocols.

2.3.1. Template method

Salt-templated synthesis was first reported in 2017 for the synthesis of molybdenum nitride (MoN) [46]. The synthesis involved 4 main steps (Fig. 3C):

- 2D-template preparation: using the Mo precursor to synthesis MoO_3 .
- Template coating with salt: by annealing the MoO_3 with NaCl in Ar atmosphere
- Ammoniation: MoN synthesis from 2D MoO_3 -coated NaCl heated to 650 °C in NH_3 atmosphere.
- Template removal: using deionized water to wash off the salt.

Notably, 2D MoN is synthesized from 2D non-layered MoO_3 . This account for categorizing the method into up-bottom approach rather than bottom-up. A variant of template method has been used to assemble 2D MXene layers into 3D MXenes to enable full utilization of their surface areas for electrochemical applications in batteries and supercapacitors [57]. In such construction into 3D MXenes, the template was aqueous MXene solution coated with a suitable polymer such as polystyrene which can later be removed by heating to 450 °C under inert atmosphere. Importantly, 2D metal carbide is merely being reconstructed into 3D MXene.

2.3.2. Structural editing protocol

The editing protocol uses chemical scissors to ease the precise control of MXene synthesis and structural manipulation. This groundbreaking method recently reported by Ding et al. [13] consists of 4 different routes which are: (Fig. 3D)

- Non-van der Waals gap opening in MAX phases using chemical scissors
- Atomic replacement via diffusion of metal ion intercalants into the interlayer vacancies
- Termination removal with chemical scissors
- Stitching up the 2D nanosheets having intercalating atom within to form either unique MAX phases or MXene with unique termination species.

The routes are not necessarily serial and can be terminated at any stage depending on choice. For example, it is possible to stop after termination removal in route III. MXenes (especially Zr-based MXenes) without terminations have stronger tensile strength [58]. Similarly, proceeding to route IV unveils exciting prospects for reconstructing novel MAX phases and broadens the range of intercalating and termination species.

The various types and examples of experimentally synthesized MXenes discussed above were reported over the years. Their synthesis routes and the year they were reported, from 2011 till date are shown in Fig. 5.

3. Properties of MXenes

The large number of elements that can combine to form MXenes and the wide range of possible stoichiometric combinations (M_2X , M_3X_2 , M_4X_3 , etc. [30]) suggest MXenes have extensive properties. Nonetheless, the co-occurrence of multiple bond types within metal carbides

layers of MXene (Ta_2C) coating in a plasmonic fiber as a refractive index sensor. Critically however, some important MXene optical properties such as emission colours, luminescence and other non-linear properties are yet to receive deserving attention [63]. When MXene is combined with other materials, the overall optical properties of the resulting heterostructure change, and this is being intensely investigated. For the current state of research on this aspect, readers are encouraged to read the excellent review article by Purbayanto et al. [74].

4. MXene application in catalysis and water treatment

4.1. Application as catalysts

Since its discovery, MXenes have found soaring attention in the field of catalysts development [75]. This is due to their inherent properties suitable for their application in catalysis such as large surface area to volume, tunable band gap, hydrophobicity, thermal, chemical, and mechanical stability, electrical conductivity, relative abundance of components, potential for intercalation of foreign molecules, tailored surface oxygenated terminations and extensive laboratory activities [76,75]. In addition, the unique and tunable 2-D structure of MXenes with an accompanied flexibility of their surface chemistry also contributed to their applications in a range of heterogeneous photochemical, electrochemical, and thermochemical reactions [77]. According to a bibliographical survey conducted by Saravanan et al. [78], the focus of global MXene applications since its discovery is more towards catalysis and sensing applications.

As an emerging member of the 2-D family with established properties, their favourable metallic and electronic properties coupled with minimal mass transfer limitations at the electrode-electrolyte interface buttressed their suitability as electrocatalysts [79]. Outstanding thermal conductivity, thermal degradation resistance, high mechanical strength and flexibility make MXenes strong candidates in industrial scale heterogeneous thermal reactions [76]. In photocatalysis, MXenes aid a rapid separation of photogenerated charge carriers and possess abundant surface functional groups for light harvesting [80]. Extensive research has been conducted to investigate the prospects of MXenes and

their derivatives as catalysts with results showing high activity and prolonged stability under harsh reaction conditions. However, in-depth understanding of the overall reaction mechanism involving the interplay of transitional metallic elements with carbon, nitrogen, and different surface terminations and how they modulate the catalytic activity of MXenes is still very much desired [75,79]. State-of-the-art experimental and theoretical studies are currently being conducted to further understand the nature of MXene catalysts and their mechanism of influencing reactions in areas of water splitting [81,82]; water pollutant degradation [21,83]; N_2 fixation [84]; CO_2 reduction [85,86]. These highlighted reactions have been the focus of catalytic MXene applications in the last five years. In these reactions, MXene and its derivatives in the field of catalysis acted either as pristine active phase, co-catalyst, support, defect sites, semiconductor or as sonocatalyst.

4.1.1. MXenes for CO_2 reduction

Photochemical and electrochemical carbon dioxide reduction (CR) for production of value-added chemicals such as CO , CH_4 , HCHO , HCOOH and CH_3OH is a technology that succeeded CO_2 capture and sequestration in the quest for global warming mitigation and sustainable energy [87]. MXenes have shown remarkable potential for CO_2 reduction due to their ability for uptake and activation of inherently stable CO_2 molecules on their surfaces, and secondly is the provision of electrons for conversion of CO_2 to valuable hydrocarbons [88]. The spontaneity of CO_2 reduction of Mo_2C and M_2C catalysts for each elementary reaction step are described in Fig. 6A and 6B. They have also been found useful in photocatalytic CO_2 reduction by improving charge separation efficiency of cocatalysts, which is necessary for increasing CO_2 reduction activity [89]. This technology has not reached maturity as research are mostly conducted from first principles using DFT studies.

According to DFT studies, 2-D M_2C MXenes ($\text{M} = \text{Ti}, \text{W}, \text{Zr}, \text{Mo}, \text{Hf}, \text{Ta}, \text{V}, \text{Nb}$) at 0001 phases are predicted as more efficient for CO_2 adsorption, storage and reduction compared to their 3-D counterparts [90]. This is attributed to higher adsorption energy, efficient MXene to CO_2 charge transfer and activation of CO_2 to anionic $\text{CO}_2\delta^-$ species with extended $\delta(\text{CO})$ bonds formation. Handoko et al., (2018) discovered via DFT that W_2CO_2 and Ti_2CO_2 are the most promising among M_2XO_2

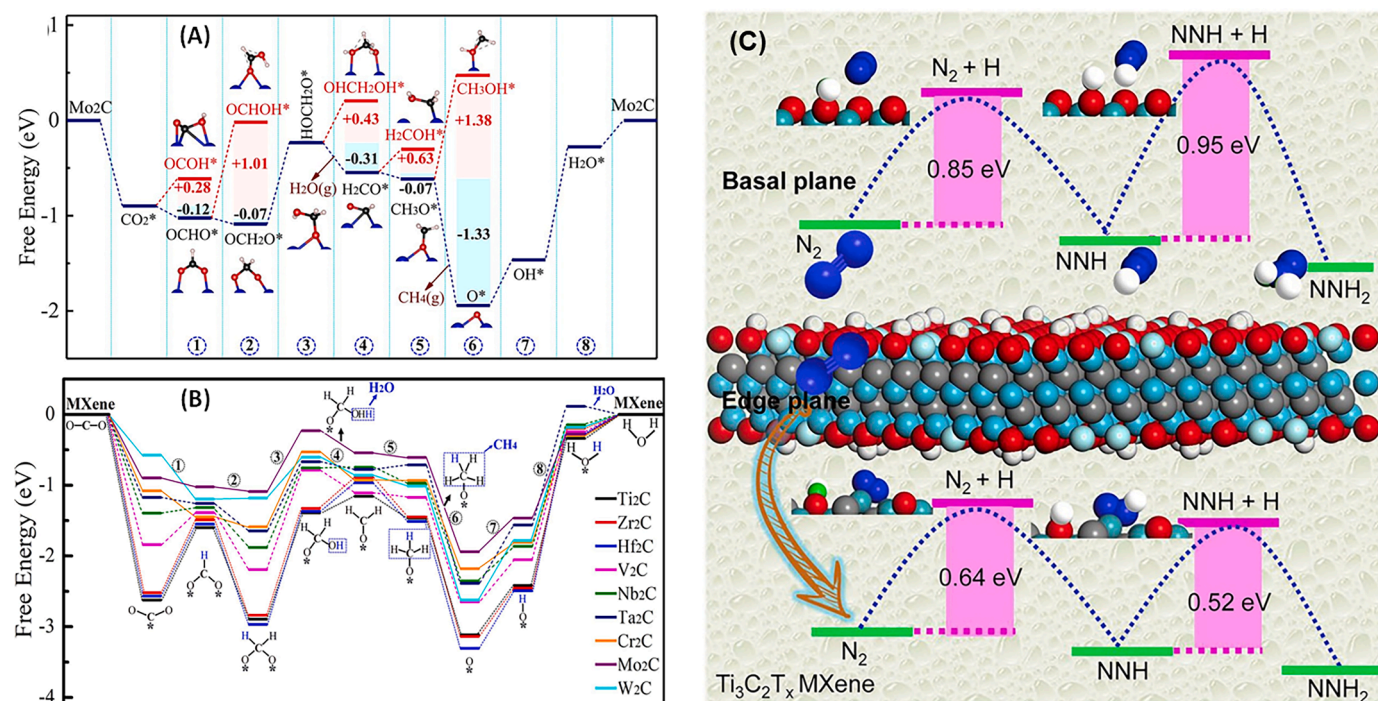


Fig. 6. Gibbs free energy of elementary steps for CO_2 reduction to produce CH_4 on (A) Mo_2C MXene and (B) different M_2C MXene catalysts [88]. (C) Reaction pathway of electrochemical N_2 reduction on $\text{Ti}_3\text{C}_2\text{T}_x$ MXene supported catalyst [96].

MXenes for electrocatalytic CO₂ reduction at low overpotential and high product selectivity. Pt supported on Ti_{3-x}C₂T_y single-atom catalyst (SAC) compared to Pt nanoparticles produced a better catalytic performance due to enhancement in atomic dispersion and partial positive charges which facilitate the reduction in adsorption and activation energies of CO₂ [91]. Based on DFT and ab-initio molecular simulations of single metal atoms on Mo₂CS₂ surface. Mo₂CS₂ supported Ru, Co and Fe SACs are selective for CH₄ production with Ru@Mo₂CS₂ having the lowest overpotential of 0.2 V. However, Ni@Mo₂CS₂ selectively produce HCOOH with 0.37 V overpotential [87]. Cheng et al., (2022) [92] investigated performance analysis of pristine and doped Nb₂CO₂ for electrochemical CR. It was notably discovered that pristine Nb₂CO₂ is least suitable for CR. Surface metal doped Nb₂CO₂ reduce limiting potential (U_L) for CR and affects the selectivity of reaction products. Doping of Nb₂CO₂ with nonmetals also possessed reduced potential limiting but there is no change in products formed. As indicated by electronic structure and charge transfer analysis, there is a strong interaction between surface metal and Nb₂CO₂. Thus, *COOH intermediates receives electrons from doped metals d-orbitals rather than from protons which then affects the types of products formed.

4.1.2. MXenes for nitrogen fixation

Electrochemical nitrogen reduction reaction (NRR) also known as nitrogen fixation reaction (NFR) has shown to be the most attractive alternative to the Haber-Bosch process for sustainable NH₃ production. However, the stability of N≡N bond and low adsorption potential of N₂ are the bottleneck of this technology leading to low Faradaic efficiency, NH₃ yield and selectivity [93]. The prospects of MXene-based catalysts have been explored to a reasonable degree of success for this application. Titanium-based MXene catalysts have been the most widely reported and the need for the study of other metal-based MXenes such as Mo, Cr, Nb, V, W have been emphasized [79]. Ti₃C₂T_x MXene nanosheets with attachments to vertically aligned metallic hosts achieved a performance of high Faradic efficiency of 5.78%, with a low potential for electrochemical NH₃ production as depicted in Fig. 6C, [94]. MXenes application improves the selectivity of electrocatalysts towards NH₃ production because of their tendency to invoke the Mars-van Krevelen (MvK) reaction mechanism over the dissociative and associative NRR mechanisms [95]. The MvK route aids selectivity by reducing the competition of NRR with H₂ evolution reaction (HER) on the active sites for NH₃ generation. With the drastic reduction or elimination of adsorption and dissociation processes on catalyst sites, selectivity of NH₃ is improved significantly.

Theoretical studies using DFT calculations and predictions have been comprehensively conducted to further investigate the potential and role of pristine and hybrid MXene catalysts towards dissociation of N≡N bond. Adsorption of N₂ on MXene occur exothermically at large adsorption energies at a range of -1.11 eV to -3.45 eV, leading to about 20% elongation of the N₂ bond length which aids the dissociation [84]. According to DFT, single atom anchoring of metals on MXenes significantly enhance their activity and selectivity for NRR at low limiting potential. Ru on MXene serves as an electron back-donation sites for N₂ adsorption and activation resulting to high Faraday efficiency and NH₃ [93,97]. These catalysts also lower the thermodynamic activation barrier for the first hydrogenation step. Synergy of highly porous ZIF-67 metal-organic framework (MOF) and hyperconductivity of Ti₃C₂ MXene produced an excellent yield of NH₃ higher than individual Ti₃C₂ and ZIF-67 at a good Faraday efficiency of 20.2% and -0.4 V versus reversible hydrogen electrode (RHE) potential [98]. Johnson et al., (2020) [99] also studied the potentials of 65 varieties of functionalized and unfunctionalized MXenes as electrocatalysts selective for NRR and antagonistic for the parasitic HER.

4.1.3. MXenes for water splitting

Splitting of water molecules for hydrogen production occurs mainly via photocatalytic and electrocatalytic reactions. Water splitting by

photocatalysis is completed through four fundamental steps namely: 1) absorption of incident light rays, 2) formation of electron-hole pairs on the photocatalyst, 3) Separation of charges and subsequent transfer to the photocatalyst surface, 4. increase in water molecules by generated electrons for hydrogen production and thus, oxidized at the vacant holes to produce oxygen to complete the water splitting. From the listed mechanistic steps, charge separation and transfer are the rate-determining step of the photocatalytic reaction [100]. Water splitting by electrocatalytic reaction is conducted via two half-cell reactions namely: 1) hydrogen evolution reaction (HER) taking place at the cathode, and 2) oxygen evolution reaction (OER) at the anode [101, 100]. The development of a highly active, stable, and conductive MXene-based catalyst as a replacement or support for the exorbitant precious metal catalysts by water splitting is an exceedingly important step towards the much-anticipated clean and sustainable hydrogen economy.

Since its discovery, Ti₃C₂T_x and Mo₂CT_x types of MXene were the first candidates reported for their potential for electrocatalytic water splitting for OER and HER reactions for selective oxygen and hydrogen production respectively [102]. Ever since, various strategies have been made to improve the electrocatalytic activity and stability of MXenes. These include tuning of surface functional groups of pristine and hybrid MXenes, engineering of their defect sites, doping of heteroatoms, design of hybrid nano structures [101]. The type of transition metals on MXenes determines its conductivity, surface terminal groups present induce their hydrophilicity and their layered structure is responsible for the large surface area [103]. Despite the potential exhibited by pristine MXenes for water splitting, the associated high overpotentials and strong transition metal – H bond are still monumental toward impeding their catalytic performance to produce the desired result. Fig. 7 shows the performance of different MXene catalysts for HER reaction based on their overpotentials. Therefore, concerted efforts have been made to enhance their electrocatalytic performances. Most notable ones are via introduction of cocatalysts such as Ni-Fe layered-double-hydroxides [85]; NiP [81]; NiFe₂O₄ spinel [104]; noble metals intercalation and immobilization [105,106]; 1T/2H phase MoSe₂ [107]; core-shell configuration with carbon nanodots [108]. Introduction of cocatalysts facilitates a synergistic interaction with the parent MXenes towards overall electrocatalytic performance. Theoretical studies have also been conducted for advanced understanding of interaction and reaction mechanism of MXenes, cocatalysts and reactants during water splitting. Density functional theory (DFT) simulations have been employed to theoretically study behaviours of novel catalysts at atomic and molecular level such as the: optimum nitrogen doped on Ti₂C MXene [82]; stability and activity of Mo₂C MXene functionalized with other metals [109]; decoration of NiFeO₄ nanoparticles on Ti₂C MXene sheets [104]; potential of ordered and O-terminated double transition-metal carbonitrides, M'₂M''CNO₂-MXene [110] and to study different MXene polymorphs [111].

Application of MXenes have recorded profound successes also in photocatalytic water splitting, but mostly as a cocatalyst. This is due to the outstanding success story of TiO₂ catalyst in terms of its overall effectiveness, excellent resistance to light corrosion, low cost and eco-friendliness over other semiconductors [112]. However, studies have shown from ab initio calculations that HF₂CO₂ and Zr₂CO₂ among the 2-D MXene family are strong candidates as single photocatalysts for water splitting. Their elevated and directional anisotropic charge carrier mobility and effective separation of photogenerated electrons and holes are responsible towards achieving high efficiency of performance [113]. MXenes possess outstanding electronic conductivity suitable for easier transfer of charge carrier from the parent TiO₂ or other potential semiconductors to the MXene surface. Accumulation of charges on MXenes results to a negative shift/alignment of Fermi level for improved photocatalytic activity [114]. Reduction of Ti₃C₂T_x with H₂/Ar gas led to a rapid formation of oxygen vacant sites on its surface. The Ti₃C₂T_x MXene enriched oxygen vacancies enhanced the electronic conductivity, light

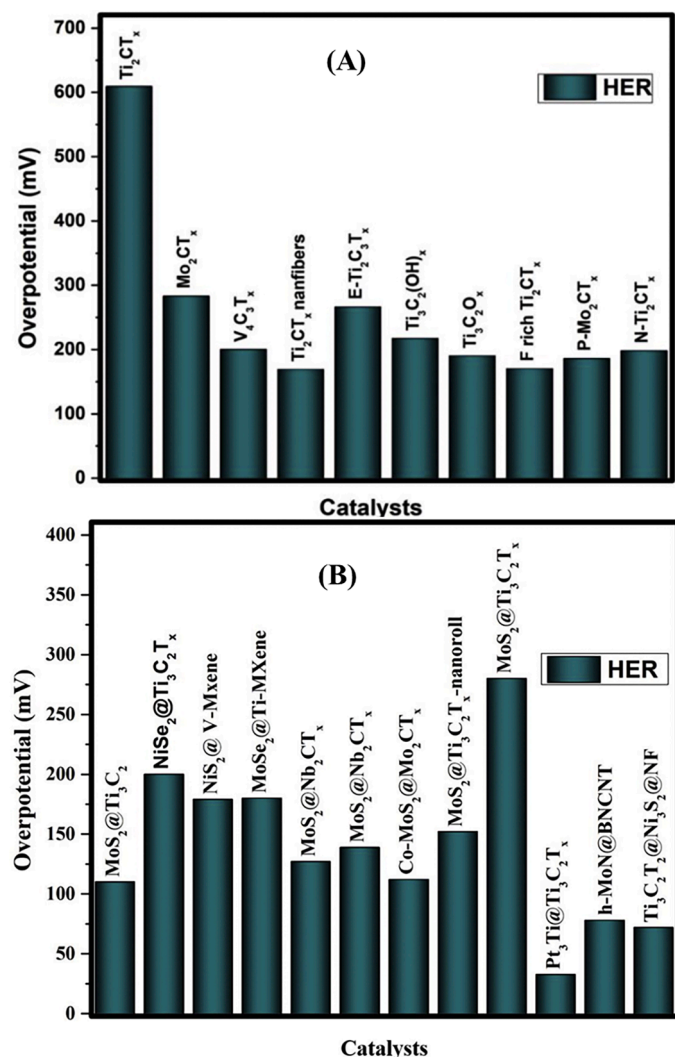


Fig. 7. Performance comparison of different MXene-based catalysts as (A) monocatalysts and (B) cocatalysts, for HER reaction [103].

harvesting efficiency and charge transfer capacity of the hybrid Cu₂O photocathode [115]. The position of MXenes cocatalyst at the interface with the parent catalyst has been found to significantly influence carrier charge generation and separation as discovered in the work of Sreedhar and Noh, (2021) [116]. There is an apparent difference in interfacial interaction between flake-like ZnO and monolayer Ti₃C₂, where the position of both ZnO and Ti₃C₂ are swapped based on which is deposited on the other. From the result obtained, Ti₃C₂ deposited interfacially on ZnO (ZnO/Ti₃C₂) produced superior performance in terms of light harvesting capacity, narrower bandgap, and effective charge carrier separation in comparison to ZnO anchored on Ti₃C₂ (Ti₃C₂/ZnO). Quantum dots interspersed Ti₃C₂ MXene nanosheet decorated with plasmonic Au nanorods by seed growth method produce a remarkable stable and high gas production rate that is thrice higher than the pristine MXene for photoelectrochemical (PEC) water splitting [85]. The high performance is attributed to the generation of strong plasmon induced electrons from Au nanorods and injection into the MXenes and efficient charge separation and transfer at their interface.

4.2. Application in water treatment

4.2.1. MXenes in photocatalytic degradation of water pollutants

MXenes have attracted increasing attention in the field of photocatalytic degradation of organic pollutants in the environment owing to

their tunable bandgap and low toxicity among other semiconductors [117]. Hybrid binary or ternary nanocomposites are also necessary for effective development of photocatalytic systems using MXenes to overcome the limitations of singular catalysts. Addition of ZnO to Ti₃C₂ MXene led to the formation of Schottky junction between Ti₃C₂ and ZnO, which is responsible for facilitating separation of photogenerated electrons and holes and preventing the photogenerated electrons from returning back to the ZnO [118]. Thus, the reason for an improved photocatalytic activity of ZnO@Ti₃C₂ over single ZnO and Ti₃C₂ catalysts for degradation of methylene blue (MB). Tahir et al., (2022) [119] also found out that Gd doped V₂O₅/MXene binary composite produced an enhanced activity and reusability for MB degradation. Gd-V₂O₅ increased the activity of V₂O₅ to 71%, while on addition MXene the activity increased further to 92% within a reaction time of 120 min. Gd³⁺ improved the photocatalyst optical properties by narrowing its bandgap to 2.33 eV. Simultaneous degradation of MB, Rhodamine B (RB), and tetracycline hydrochloride (TH) on hybrid Bi₂WO₆/Nb₂CT_x MXene nanosheets under visible light was reported [120]. Nb₂CT_x nanosheet enhances activity of Bi₂WO₆ by more than twice owing to its improved separation efficiency for photogenerated carriers. Some of the contemporary applications of MXenes for photocatalytic organic pollutant degradation are shown in Table 1. The best catalyst configuration was considered in each of the literature reported.

In recent times, degradation of organic pollutants by ultrasonication (US) has gained increased popularity based on its safety, efficiency, simplicity of practice and low cost due to operability at ambient conditions [121]. Despite these glaring potentials, the technology has not been fully exploited, as such a broad research gap exists in the area. The US system involves the usage of ultrasound wave to destroy organic pollutant in water at frequencies in the range of 20 – 1000 kHz using a principle of acoustic cavitation. The mechanism of acoustic cavitation involves the nucleation, growth and subsequent collapse of micro-cavitation bubbles at a critical ultrasonic frequency [121]. MXenes are also integrated with other potential semiconductors to produce high performing materials with improved sonocatalytic activity for pollutant degradation [122]. Potential of MXene as a sonocatalyst was further proven in the work of Jun et al., (2020)[123] where the effects of sonication parameters such as US frequency, power density, solution temperature and pH were studied for MB and acid blue 80 degradation. The results depicted that the synergistic indices of catalyst components towards dye removal were higher than 1.0, which is an indicator of MXenes efficiency as a co-sonocatalyst for dye degradation. MXenes have thus been recently tested for sono-degradation of other important pollutants such as diclofenac and verapamil [124], paraquat pesticide [125]. For more discussion on the application of MXenes and other 2D materials for the treatment of pharmaceuticals from wastewater, readers are encouraged to read the critical review by Gonzalez-Poggini et al. [126]

4.2.2. Application for oil/water separation

The production of oil and gas for energy generates significant amount of oily wastewater also referred to as produced water [135]. Due to issues of greenhouse gas emission and climate change, strict regulations have been put in place regarding discharge of oily wastewater into water bodies. They require separation and treatment prior to discharge [136]. Hence, oil-water separation has received enormous attention in recent times. Previously, conventional techniques such as demulsification, adsorption, ion-exchange, skimming, biodegradation, sonication, amongst others, are used for oil-water separation processes. However, the use of this techniques has numerous limitations such as high cost, low efficiency, use of hazardous chemicals, and large equipment requirement [137]. Recently, membrane technology with higher efficiency and lower operating cost has evolved as a novel, cost-effective and efficient means of oil-water separation [138,139]. The characteristics of membranes which makes them efficient and desirable for separation of oily wastewater is their anti-fouling properties, excellent

Table 1

Bibliographic summary of contemporary MXene-based catalysts for Water Pollutant Degradation.

Catalyst	Pollutant	Experimental Conditions	Catalyst Loading (mg)	Degradation Efficiency (%)	Degradation Time (mins)	Performance Mechanism	Refs.
Ti ₃ C ₂ /Co ₃ O ₄	Methylene Blue	C ₀ = 12.5 mg/L, V = 100 mL, UV lamp, T= RT	10	92.4	240	Dispersion of Co ₃ O ₄ nanoparticles on the surface and inner layer of Ti ₃ C ₂ nanosheets	[94]
ZnO@Ti ₃ C ₂	Rhodamine B Methylene Blue	C ₀ = 5.0 mg/L C ₀ = 10 mg/L, V = 100 mL, UV lamp, T = 70 °C, 500 W Xe lamp	163	94.8	80 180	Formation of Schottky junction between ZnO and Ti ₃ C ₂ MXene	[118]
α-Fe ₂ O ₃ /Ti ₃ C ₂ T _x	Rhodamine B	C ₀ = 10 mg/L, V = 100 mL, UV lamp, T = 70 °C, 500 W Xe lamp	20	98.0	30	Formation of heterostructure interfaces for enhanced absorption of visible light and charge separation efficiency	[127]
Ti ₃ C ₂ T _x @CNTs	Rhodamine B	C ₀ = 0.1 mol/L, V = 100 mL, UV lamp, T = 70 °C,	100	75.0	15	Presence of 2D layered MXene material with direct growth 1D-CNTs for increased surface area and conductivity.	[128]
Bi ₂ WO ₆ /Nb ₂ CT _x	Methylene Blue Rhodamine B tetracycline hydrochloride	C ₀ = 15 mg/L, V = 100 mL, UV lamp	50	92.7 99.8 83.1	90	Introduction of Nb ₂ CT _x nanosheets significantly enhanced the separation efficiency of photogenerated carriers, and photocatalytic activity of Bi ₂ WO ₆	[120]
α-Fe ₂ O ₃ /Ti ₃ C ₂ T _x	Salicylic acid	C ₀ = 20 mg/L, V = 100 mL, UV lamp, T= RT,	20	97.0	120	Generation of OH [•] and SO ₄ ²⁻ radicals on photocatalyst	[129]
Fe ₃ O ₄ /Ti ₃ C ₂ T _x	Diclofenac	C ₀ = 10 mg/L, V = 200 mL, UV lamp, T= RT, pH=7	120	100.0	30	Higher adsorption capacity coupled with improved rate of electron transfer	[130]
CuFe ₂ O ₄ /Ti ₃ C ₂	Sulfonamides	C ₀ = 40 mg/L, UV lamp, T= RT	25	59.4	60	Extension of the lifetime of photoinduced carriers, minimizing electron-hole recombination	[131]
Fe ₂ CoTi ₃ O ₁₀ /Ti ₃ C ₂ T _x	2,4-dichlorophenoxyacetic acid	C ₀ = 20 mg/L, V = 100 mL, T= RT, pH = 7	20	98	15	Synergy among the three active sites of Ti, Co and Fe on the MXene catalyst surface	[132]
Co ₃ O ₄ /Ti ₃ C ₂ T _x	Bisphenol A	C ₀ = 20 mg/L, V = 100 mL, T= RT	10	95.0	7	Presence of OH [•] and SO ₄ ²⁻ radicals	[83]
PBA@Ti ₃ C ₂ MXene	Coumarin	pH = 10, V = 100 mL, UV lamp, T= RT (25 °C)	20	70.9	20	Unsaturated Ti-C-O lewis acid sites and terminal F-Ti on the PBA@MXene catalyst surface.	[133]
NF/MXene-Co ₃ O ₄	Refractory organic matter	pH=2.7,	9.55	99.3	3	Formation of excessive oxygen vacancies from Ti doped on Co ₃ O ₄ crystals	[134]

permeation rates, and highly effective wetting performance [140]. The mechanism of membrane application for separation of oily wastewater is that it creates a selective barrier between the hydrophilic aqueous phase and hydrophobic oleic phase which is majorly controlled by temperature/concentration/pressure differences [141]. Despite the efficiency of membrane filtration process, instability, contamination, and swelling of membranes reduce their efficiency during treatment processes [142]. To optimize the efficiency of membranes treatment processes, recent advancement and new research involves the introduction of nanomaterials to improve the stability and surface activity of membranes [143].

Like other 2D materials, MXenes have received prodigious attention for the enhancement of membrane separation process efficiency [144]. The incorporation of MXene as a functionality to improve membrane performance is due to their high specific surface area, adjustable nanochannels, high hydrophilicity, excellent chemical stability, activated metallic hydroxide sites, and high adsorption-reduction capacity, and other exemplary physicochemical properties [141]. The surface activity of the MXene based membrane depends on the synthesis method. The commonly used methods for synthesizing MXene-based membranes are majorly categorized into three namely, vacuum-assisted filtration method, phase-inversion method, and extrusion and molding method. Depending on the synthesis method, the intercalation of other nanomaterials can be added to formulate MXene composite membrane [145].

The application of MXene-based membrane for oil-water separation process owes to their remarkable hydrophilicity, good oleophobicity in water, and its characteristic rough surface structure which enables it to

trap water molecule on its surface and reject the oil. Moreover, the MXene-based membrane has nanoscale slit channels which encourages water permeation while inhibiting oil flux. When salt is present in the oil-water emulsion, MXene-based membrane demonstrates improve separation by contracting its interlayer spacing to give an enhanced oil rejection performance [141].

The important parameters that dictate the permeation rate of MXene-based membrane are MXene loading, membrane thickness, and wettability of the surface. High MXene loading is desired during oil-water separation because it causes the selective layer to be compact and denser. Resultantly, this lowers the flux and increases the quality of the permeate. Saththasivam et al. [146] synthesized a scalable Ti₃C₂T_x (MXene) membrane and investigated the effect of MXene loading on oil-water separation efficiency. They observed that increasing the MXene loading from 0.1 mg to 0.8 mg resulted in a five-fold reduction in the flux from 1019.1 L/m².hr.bar to 203.8 L/m².hr.bar of MXene composite membrane (Fig. 8A). Similarly, Feng et al. [147] synthesized a MXene based composite membrane using vacuum filtration method by intercalation of titanium oxide (TiO₂) nanoparticles and poly(arylene ether nitrile) (PEN) to form MXene/TiO₂/PEN composite membrane for oil-water separation. They noted that increasing the MXene loading of the composite membrane causes dense stacking of the MXene layer and reduction in porosity. Consequently, the water flux reduced from 1764 L.m⁻².h⁻¹ to 215 L.m⁻².h⁻¹ and oil rejection efficiency increased from 82.45% to 99.56%.

The surface wettability of MXene-based membrane and its impacts on oil-water separation efficiency have also been investigated. This property of membrane affects the antifouling and water permeation

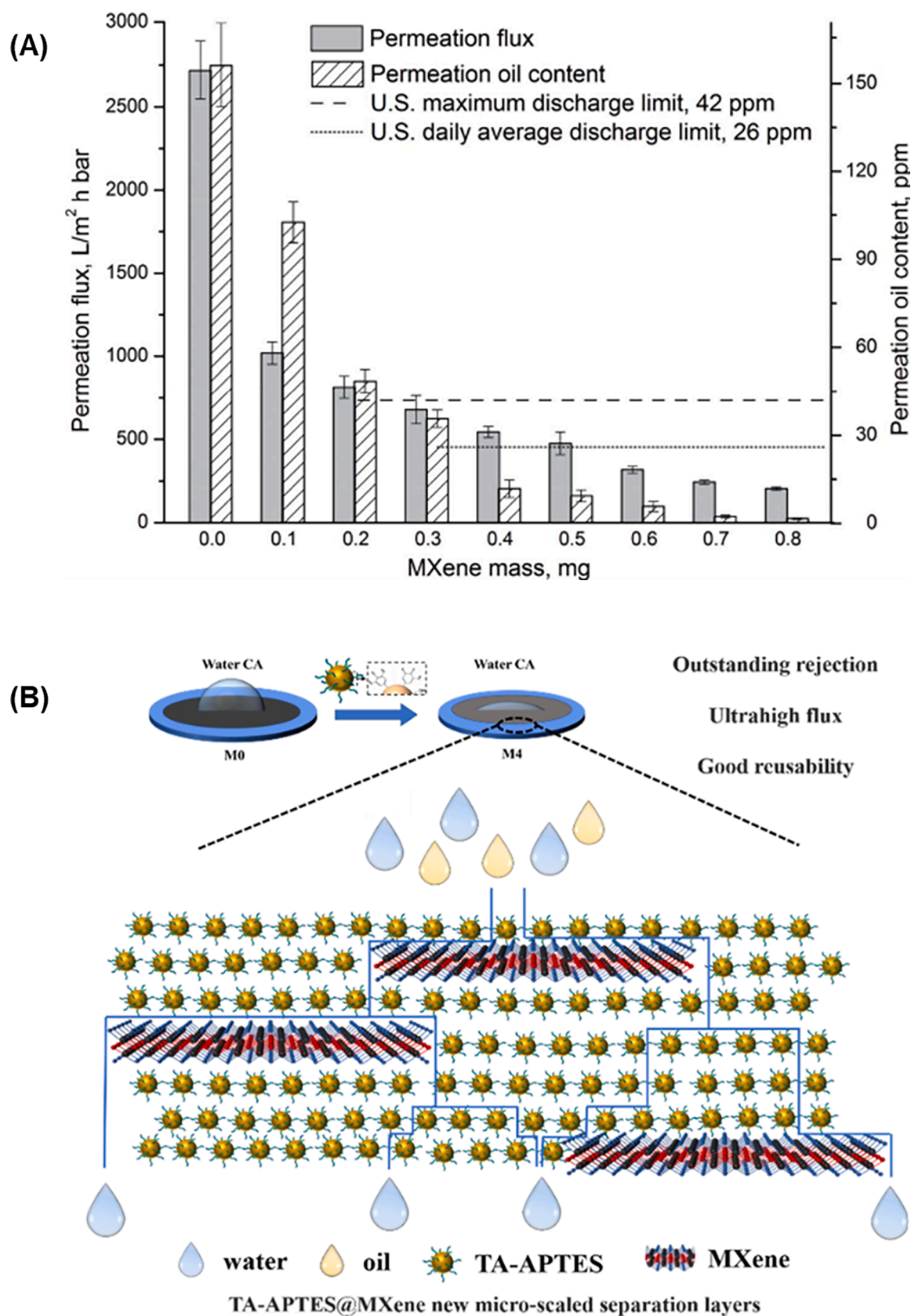


Fig. 8. (A) Effect of different MXene loading on permeation flux during oil-water separation [146]. (B) Schematics of oil rejection by MXene composite membrane [150].

performance. Contact angle is used to measure the wetting property and depends on the roughness and morphology of the membrane surface. For oil-water separation, moderate contact angle is desired. A lower water contact angle implies lower repulsion of oil droplets while high contact angle signifies inadequate flow rate through the membrane. Huang et al. [148] synthesized mixed cellulose-MXene membrane for oil-water separation and compared the wettability and oil rejection to that of mixed cellulose (MCE) membrane. They confirmed that the under-water oil contact angle for MCE-MXene and MCE is 111° and 62°, respectively. This indicates that the MXene-based membrane exhibits anti-oil droplet adhesion property. The hydroxyl group on the surface of MXene confers a high functionality and enhanced hydrophilicity on its membrane.

Furthermore, the greater the thickness of MXene membrane, the higher the permeability resistance and the better the membrane reduces the water flux. This can be adduced to extending the permeation pathway which lead to more residence time, thereby improving the efficiency of the membrane for removing pollutants. Zeng et al. [149]

developed a composite membrane of MXene, Zeolite imidazolium framework (ZIF-8) and tannic acid (TA) nanoparticles and investigated its efficiency for oil-water separation. The microstructural analysis shows that the introduction of TA-ZIF-8 nanoparticles to the MXene nanosheet increased the thickness from 5 μm to 12 μm . Consequently, water molecules encountered large resistance to flow through the transport channels. Similarly, Liu et al. [150] modified the surface of MXene-based membrane with TA and aminopropyltriethoxysilane (APTES) which caused increased thickness and enlargement of the separation layer to micro-scale from nano-scale. The modified MXene-based membrane exemplified high efficiency for oil-water separation with a water flux of 5990.11 $\text{L.m}^{-2}.\text{h}^{-1}$ and a 98% removal ratio for oil-water emulsions.

Several mechanisms have been postulated to explain the efficiency of MXene-based membrane for oil-water separation. These include electrostatic interaction, sieving, and the aggregation of oil on the membrane surface [141,151]. The most common mechanism is electrostatic

Table 2

Oil-Water separation efficiency of MXene-based membranes.

Refs.	MXene-based membrane	Oleic phase	Oil-water (v/v)	Operating pressure	Wettability Water CA	Water Separation flux ($\text{L.m}^{-2}.\text{h}^{-1}$)	Separation efficiency	Reusability
[155]	Mxene-rGO-PPS	Dichloromethane Kerosene Toluene Soybean oil	10:1		145°	11,502 7156 9087 1499.5	99.98% 99.99% 99.99% 99.97%	–
[156]	PM-COOH	Toluene Petroleum ether n-hexane	1:99		~150°	9378 9085 10,034	98.7%	10 cycles
[157]	MXene-UIO-66-(COOH) ₂	Toluene	–	0.09 MPa	158.77°	713.37	99.54%	10 cycles
[158]	rGO/PD/MXene	Lubricating oil Dodecane Petroleum ether	1:100	0.1 MPa	137.9°	174.16	>97%	6 cycles
[159]	Mxene@CS/TA-FeOOH	Isooctane n-Hexane Dichloromethane Toluene Petroleum ether 1,3,5 trimethylbenzene	1:99	0.08 MPa	160.87° 157.55° 156.3° 151.18° 154.33° 152.24°	788.6 582.9 525.21 1022.7 966.8 500.38	99.63% 99.72% 99.47% 99.32% 99.51% 99.58%	–
[160]	APTES/MXene-ACNT/CA	Lubricating oil Vegetable oil	1:100	0.1 MPa	54.8° (hydrophilic)	2892.8	99.6% 99%	7 cycles
[161]	Hal@MXene-PDA	Petroleum ether Lubricating oil	1:100	1 bar	14.5° (hydrophilic)	5036.2	99.99% 99.8%	3 cycles
[162]	coPA-MXene	Vegetable oil	10 ppm, 1000 ppm, 1000 ppm of oil	0.5 bar	124°	–	99.5%	–
[163]	MXene/O-MWCNT@PAN	Lubricating oil	1:100	0.1 MPa	155°	293	>95%	–
[164]	N-Bi ₂ O ₂ CO ₃ @MXene	Lubricating oil Vegetable oil	1:100	0.1 MPa	52° (hydrophilic)	815.3	99.1% 99.8%	5 cycles
[165]	Ag@MXene/PEN	Petroleum ether n-Hexane 1,3,5-trimethylbenzene Isooctane n-heptane	–	0.04 MPa	18° (hydrophilic)	4401 4519 4783 4210 4337	98.95% 99.09% 98.62 99.13% 99.11%	–

rGO – reduced graphene oxide.

PPS – Polyphenylene sulfide.

PM-COOH – Porous carboxyl functionalized MXene.

CS – Chitosan.

FeOOH – Iron hydroxide.

TA – Tannic acid.

CA – Cellulose acetate.

APTES – Amino propyl triethoxysilane.

PD - Polydopamine.

Bi₂O₂CO₃ – Bismuth semi-conductor.

coPA – copolyamide.

PEN – Poly(arylene ether nitrile).

ACNT – Amine functionalized carbon nanotubes.

interaction. The surface of MXene is characterized with OH^- and F^- . Hence, negatively charged ions are rejected due to the electronegative surface charge of the MXene membrane. For oil-water emulsions, electrostatic interaction between the electronegative charge of MXene and the hydrogen bond of the water molecule occurs on the membrane surface. Resultantly, a hydration layer is formed at the interface of water and membrane that causes strong repulsion to oleic phase (Fig. 8B). Moreover, enhanced interlayer spacing of the MXene is witnessed with the decoration of its functional layer with surface active materials which results in better separation efficiency.

Imsong and Purkayastha [152] synthesized MXene-PAN membrane for oil-water separation. The MXene-based membrane demonstrated remarkable efficiency for oil-water separation owing to its inherent hydrophilicity and anti-fouling properties. Moreover, the membrane exemplified good chemical stability and adsorb the organic contaminants present in the oily effluent. Zhang et al. [153] evaluated the use of MXene-based sodium bentonite composite membrane for oil-water separation. The presence of sodium bentonite nanoparticle enlarges the interlayer spacing of the MXene nanosheet and enhanced the permeability. The MXene composite membrane demonstrated sterling separation efficiency with the rejection ratio of 96%. Sun et al. [154] investigated the efficiency of MXene-TA-Zinc oxide (ZO)-PAN composite membrane for oil-water separation. The intercalation of ZnO nanoparticle tuned the interlayer spacing of the MXene nanosheet and significantly improved the membrane permeation flux. The composite membrane achieved > 99.4% separation efficiency in high-temperature and high salinity conditions. Table 2 summarizes the outcomes of other studies on MXene-based membrane for oil-water separation.

Overall, the incorporation of MXene in membranes for oil-water separation significantly improves the efficiency of the membranes and confers a higher functionality and anti-fouling property on the membrane. Due to its high efficiency and low oil-adhesion property, MXene-based membrane has been utilized for the separation of oil-water emulsions of light and heavy oil with high degree of success. However, most works on the application of MXene-based membrane for ultrafiltration of oil has been on the laboratory scale. Future research should focus on the scale-up of this technology to pilot and full-scale application for beneficial use.

The industrial revolution has prompted serious damage of the ecological environment due to incessant emission of multiple water pollutants such as textile dyes, organic, nuclear and heavy metal ions [166,167]. Despite several technological breakthroughs achieved over

the years, treatment of water pollutants remains a hurdle. Out of the various treatment methods, adsorption remains the popular method owing to its flexibility, ease of operation and cost effectiveness [168–170]. Adsorbents such as MXenes were reported to outperform conventional materials due to their excellent attributes, for example large surface area, unique electronic structure, hydrophilicity, high chemical inertness and good mechanical strength [170–172]. The present section aims to discuss the research progress in development of novel MXene derivatives for water treatment.

Generally, the adsorption of pollutants onto adsorbent surface is achieved by transport of pollutants from aqueous solution onto adsorbent surface, adsorption on adsorbent surface and subsequent transport within adsorbent particle [166,169,173]. The charged adsorbent attracts opposite charge pollutants because of electrostatic force of attraction. Water pollutants such as metal ions have high affinity for surface functional groups such as oxygen containing group ($-\text{O}$) and hydroxyl group ($-\text{OH}$). The adsorption process is categorized as chemisorption and physical, where the former forms covalent or ionic bonds via chemical reaction, and the latter forms adsorbate surface and adsorbent binding [174,175]. The efficacy of adsorbent is governed by concentration, pH, temperature, ionic strength and stirring duration. More so, properties of adsorbent (nature of functional groups and topology) as well adsorbate properties (functionality, polarity and size) dictate the adsorption capacity [176–178]. In Fig. 9, we summarize the desirable properties of an ideal adsorbent for removal of water pollutants. Hence, adsorbents with high adsorption capacity are desirable for effective removal of targeted water pollutants.

The adsorptive properties of MXene materials have led to their exploration in wastewater treatment via adsorption process. From Table 3, it is evident that MXene is an effective adsorbent for several metal ion pollutants. Novel synthesis techniques were pivotal to enhancement of surface binding sites, surface area and interlayer distances. The synthesis techniques dictate the architecture of carrier material which eventually controls the interaction that transpires. It was observed that reaction conditions such as high temperature and near neutral solution pH enhance adsorption of heavy metal ions. However, most researchers concentrate only on contaminants of interest, without considering nature of heavy metal ions which are complex and variable. Therefore, it is necessary for future studies on treatment of multiple or selective pollutants from complex wastewaters using MXene materials.

The need for milder and less dangerous etchants than the commonly used hydrogen fluoride cannot be over emphasized. As stated earlier in

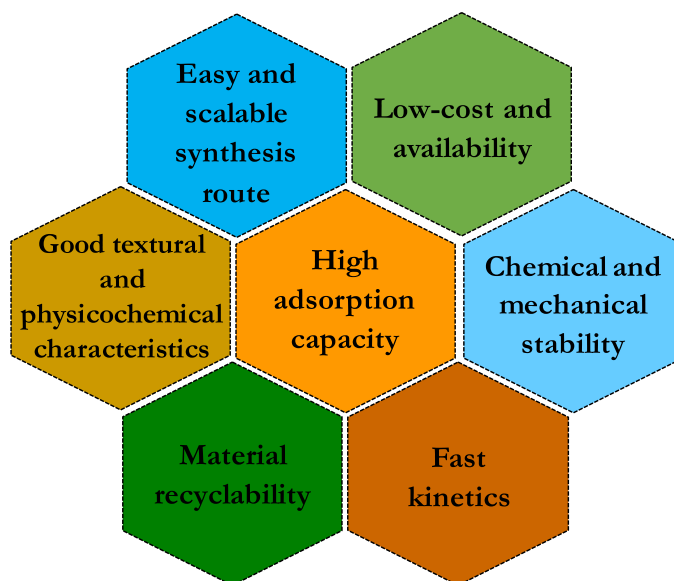


Fig. 9. Schematic representation of crucial properties of robust adsorbent for removal of water pollutants.

Table 3

Summary of research outputs on MXenes based materials for adsorptive removal of water pollutants.

Preparation method	Pollutant/s	Reaction conditions	Adsorption capacity (mg/g)	Refs.
Hydrofluoric acid treatment at 45 °C exfoliation temperature for 24 h.	Pd	^a 0.05 g/100 mL, 20 °C	184.6	[186]
Hydrofluoric acid treatment at 35 °C for 18 h.	Urea	^a 0.15 g/6 mL, 60 min	21.7	[168]
Regular functionalization by cross-linking with sodium alginate.	Cu	^b 6, 60 °C	234.3	[187]
Controlled hydrothermal method using sodium hydroxide.	Cd	^a 0.005 g/50 mL, 5.5, 25 °C	326	[188]
Functionalization with levodopa under magnetic stirring and pH of 8.5.	Cu	^a 0.0003 g/mL, 1–1.5 h	65	[189]
Hydrofluoric acid treatment at 40 °C for 18 h followed by ultrasonic dispersion.	Pb	^b 2–9, 25 °C	147	[190]
Mechanical stirring followed by sodium hydroxide treatment.	Ni	^a 0.01 g/50 mL, 60 min, 30 °C	222.7	[191]
Intercalation and exfoliation using hydrofluoric acid.	Ba	^a 0.05 g/100 mL, 50 min	9.3	[192]
Hydro-chloric acid treatment at 25 °C for 48 h.	Hg	^a 0.005 –0.1 g/20 mL, 120 min, ^b 3–9, 25 °C	1057.3	[193]
Hydrothermal method.	Pb	^a 0.01 g/20 mL, 200 min	140	[194]
Amino-functionalization using <i>in situ</i> polymerization.	Cr	^b 1–6, 10–30 °C	107.4	[167]
Exfoliation and alkalization-intercalation method.	Pb	^a 0.002 g/40 mL, 2 h	140	[195]
Etching followed by delamination using intensive layer delamination method.	Cr	^b 6, 20 °C	540.5	[196]
Sonication method at frequency of 28 kHz.	Amitriptyline	^a 0.02 g/30 mL, 2 h	241	[197]
Hydrothermal method.	Cr	^b 2.5, 20 °C	103.6	[198]
LiOH functionalization followed by magnetic stirring.	Methylene blue	^a 0.1 g/50 mL, 40 min, 30 °C	121	[199]
Functionalization with sodium alginate followed by magnetic stirrer for 6 h.	Pb	^a 0.1 g/200 mL, 3 h	382.7	[200]
Hydrothermal treatment followed by <i>in-situ</i> hybrid composite method.	Cr	^b 7–7.2, 25 °C	353.87	[201]
Hydrofluoric acid treatment followed by ultrasonic delamination.	Cr	15 min, 20–65 °C	250	[202]
Functionalization with poly diallyldimethylammonium chloride.	Re	^a 0.01 g/10 mL, 30 min, ^b 3	363	[172]
Layer-by-layer strategy followed by carboxyl functionalization.	Methylene blue	^a 0.8 g/50 mL, X min	71	[203]
		^b 5, 25 °C		
		^a 0.008 g/20 mL, 6 h		
		^b 1–10, 30 °C		
		^a 10 mg/200 mL, 60 min, 25 °C		

^a Dosage.^b pH.

Section 3.2, basically the synthesis methods could be categorized as milder fluoride salts, fluoride-free and hydrothermal processes. The milder fluoride salts (for example fluorides of Ca, Cs, K, Li and Na) are applied to synthesize etchant solution with the acidic media (sulfuric acid or hydrochloric acid). The materials produced in contrast to conventional HF etching MXene possess multi-layered metal carbides comprising of various topology and compositions, for example defect-free Ti₃C₂T_x MXene [179–181]. Similarly, Halim et al. [182] found that controlled application of milder etchant solution like ammonium bifluoride (NH₄HF₂) can improve adsorption capacity due to formed -NH₄⁺ interlayers which easily degrade negatively charged water contaminants. On another perspective, application of hydrothermal process could boost contact with the toxic HF vapors. Gu et al. [183] revealed that NH₄F etchant can form Ti₃C₂T_x MXene via hydrothermally etching of Ti₃AlC₂ sheets. Similarly, the use of toxic HF was avoided for preparation MXenes (Nb₂C and Ti₃C₂) through NaBF₄ etching using hydrochloric acid [181,184]. Findings revealed high adsorption capability (160 mg/g) of MXene intercalated dimethyl sulfoxide for adsorption of U(VI) was due to large surface and interlayer distances [178,185].

In recent times, diverse approaches for fabrication of stable MXene materials could pave way for its practical application in industrial wastewater treatment. Functionalization of MXenes by hydrothermal method led to development of adsorbents with abundant functional groups and enlarged interlayer spacing. Fast kinetics was reported for levodopa functionalized MXene materials [189]. The excellent removal performance was attributed to the catechol and carboxyl groups of

levodopa. A nanostructured magnetic MXene material produced good removal capacity for Hg(II) pollutants [21]. This is in accord with report of Shahzad et al. [188], where sodium alginate modified MXene produced 932.84 mg/g adsorption capacity. Molybdenum disulphide/MXene also led to excellent adsorption performance [204]. The synergistic effects of sodium alginate/molybdenum disulphides and oxygenated groups of MXene are beneficial for efficient adsorption of water pollutants. Application of surfactants such as bio based enzymatic hydrolysis lignin could also modify adsorption properties of MXene for better removal capacity [205]. Attempts to enhance removal of water pollutants have been made through delamination of MXene. Shahzad et al. [206] produced a delaminated MXene with high selectivity for Cu (II) pollutants and 80% adsorption rate within the first minute of reaction. Delaminated Ti₃C₂T_x flake was fabricated by placing MXene in H₂O to react amino acids where TiO₂ rutile phase are produced on the surface [207].

Coupling MXene with composite materials as presented in Fig. 10A could provide a unique handle to tune adsorption capability. Gong et al. [166] exemplified that electrostatic self-assembly synthesized MXene/-composite material had high permeability and stability. The outstanding performance was attributed to the multi-layered architecture containing both mesopores and micropores. Wan et al. [208] have exemplified such approach to design MXene/chitosan using solution synthesis method. The produced adsorbent combined the structural stability of MXene with abundant surface hydroxyl and amino groups on chitosan for efficient treatment of Cr(VI) contaminated water. Li et al. [203] revealed via

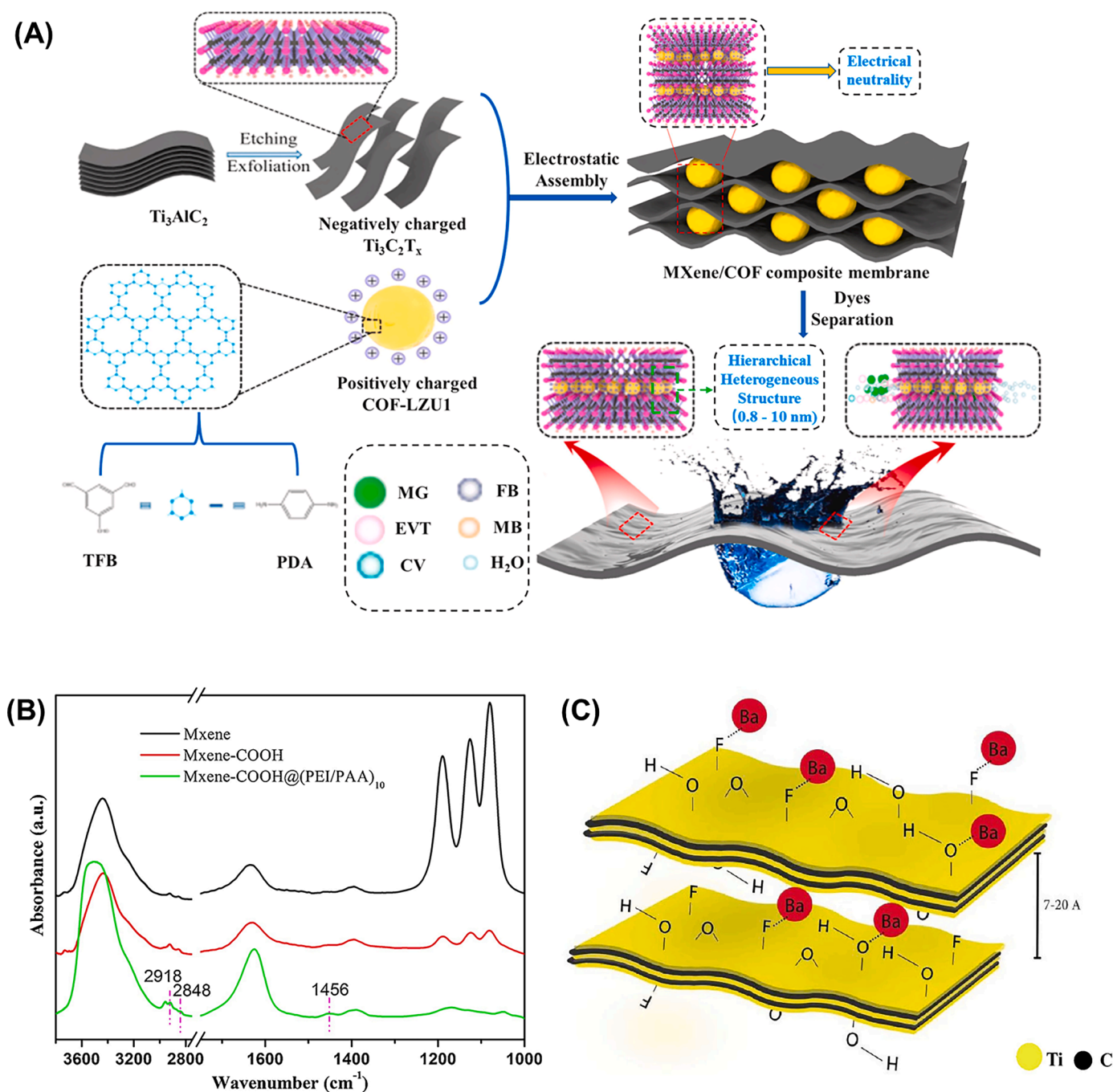


Fig. 10. (A) Schematic representation of MXene/composite material synthesis [166]. (B) Infrared spectra of MXene/COOH/polymer composites [203]. (C) Schematic representation of reaction mechanism for adsorption barium ion on $\text{Ti}_3\text{C}_2\text{T}_x$ MXene [192].

Fourier infrared spectroscopy experiments the presence of OH, C=O and C—O affirming carboxyl group modifications on MXene. The FT-IR spectra in Fig. 10B further affirmed polymeric shell formation with polyethylene polyimide (PEI) and poly acrylic acid (PAA). MXene/COOH/polymer composites produced excellent adsorption capacity and reusability due to the mesoporous structure and abundant reaction sites. Similarly, Khan et al. [201] found that *in-situ* hybrid synthesized MXene composite produced around 29% increase in adsorption capacity in contrast to pristine MXene. The BET surface area of the *in-situ* hybrid composite and pristine MXene are 129.25 m^2/g and 42.9 m^2/g . The key factors that contribute to the remarkable Cr capture are majorly larger surface area and plentiful polar groups (-OH, -O and -F).

Engineering MXenes with larger interlayer spacing and functional

charge by covalent cross-linking with amino propyl triethoxysilane, silane coupling agent and *in situ* polymerization are effective strategies to enhance reusability and selectivity. According to the findings of Kong et al. [167], the nanostructured $\text{NH}_2\text{-Ti}_3\text{C}_2\text{T}_x$ produced effectively removed Cr(VI) pollutants where oxidation of Ti(II) to Ti(VI) and -NH_2^+ to NO_3^- also occurred. Typically, simple regulation of MXene with silane coupling agent facilitate removal of Pb(II) pollutants [190]. The hydrophobic and hydrophilic groups of the silane enhance Pb(II)-adsorption sites interaction. The good performance of silane modified MXene was in good agreement with the findings by Zhang et al. [209]. Modified MXene was obtained in the presence of poly phenylenediamine and *in situ* polymerization, which led to the enhanced Cr(VI) removal in contrast to unmodified MXene [196]. Surface area analysis of

Ti₃C₂T_x/poly phenylenediamine revealed increase in interlayer spacing from 14.6 to 17.6 Å. These phenomena were attributed to intercalation of polymer modified Ti₃C₂T_x and monomers enrichment via electrostatic interaction and hydrogen bonding. Therefore, to achieve excellent pollutant removal, it is important to employ appropriate composite material that promote reduction and chelation interaction.

4.2.3. Adsorption mechanism of water pollutants on surface of MXene

Literature reported that adsorption mechanisms for removal of heavy metal ions over adsorbent materials are through: (1) synergistic effect of physical adsorption (2) electrostatic interaction (3) van der Waals forces and (4) hydrogen bonding [192,194,206]. Among novel adsorbents like graphene oxide and carbon nanotubes, MXene possess higher adsorption capabilities ascribed to its interlayer spacing, functional charge and faster kinetics [176,178,195,210]. The process of adsorptive removal of water pollutants is material species dependent as a result of the nature of defects and surface functional groups. The physicochemical properties of heavy metal ions for example ionic radius and solubility dictates the reaction mechanism [194]. However, the interplay between properties, synthesis materials and protocol with adsorption capacity remains unclear.

Basically, high surface area as well as plentiful surface binding sites are responsible for superior efficiency of removal of heavy metal ions over adsorbent materials [21,166,191,201,205]. More so, factors such as temperature, background ions and pH dictate rate of efficiency of contaminants' removal. Recently, research efforts have been put into the enhancement of surface area and surface binding sites for increased sorption of water pollutants on MXene based materials. Quest for larger interlayer distances is still ongoing in the field of treatment of complex water pollutants using MXene. Fig. 10C revealed chemical adsorption of Ba²⁺ by surface functional groups on Ti₃C₂T_x MXene surface. The functional groups (-OH, -F, -O) serve as adsorption sites for Ba²⁺ to be adsorbed, where barium hydroxide and barium fluoride are formed [192]. The authors further elaborated that aside physisorption on the Ti₃C₂T_x surface, chemisorption process occurs via chemical bonding between Ba²⁺ and the functional groups. The Ba-O and Ba-F bond formed was responsible for the adsorption process. Peng et al. [195] also reported that the strong bond formed between Pb²⁺ pollutants with surface hydroxyl on MXene led to high adsorption capacity (140 mg/g).

The adsorption mechanism for Cu²⁺ uptake on Ti₃C₂T_x MXene is via ion exchange between surface functional groups and Cu²⁺ and subsequent oxidation–reduction reaction [206]. From the work of Jun et al. [194], improved sorption of metal ion pollutants was attributed to interlayer space and high surface area. Uranium containing water follow the electrostatic interaction for adsorptive removal of heavy metal ions [194,197]. Hydrogen bonding have pivotal role in sorption of organic water pollutants such as methylene blue [180]. The influence of hydrogen bonding adsorption mechanism was reported in the work of Zhang et al. [211]. For further understanding on the role of hydrogen bonding in uptake of heavy metal pollutants, more studies are required.

The surface of MXene adsorbent and its hydrophilic property facilitate entrapment of molecular and ionic species through mechanisms comprising of electrostatic interaction, complexes formation and ion exchange reactions. Therefore, maximization of interaction between MXene layers and surface hydroxyl groups is a prerequisite for remarkable adsorption capacity. The ion exchange mechanism seems the dominant for removal of heavy metal ion pollutants on MXene based materials [178,180,195,212]. The Freundlich adsorption isotherm as well as Langmuir maximum adsorption capacity represents the widely adopted parameters for interpreting metal ions adsorption unto several adsorbent materials [166,213]. Since numerous criteria are adopted to report findings on adsorption of water pollutants on surface of MXene, design of a versatile kinetic model to unravel the individual impact of pollutant concentration and adsorbent loading could be beneficial.

4.2.4. Regeneration of spent MXene adsorbents

The process of adsorption is adjudged as reversible when accompanied by a desorption process. It is therefore imperative to develop adsorbent materials that can easily be regenerated for long term application. The recycling ability of MXene adsorbent is an added advantage for industrial water treatment application [178]. Regeneration and reuse of MXenes can be achieved through washing with deionized/distilled water and subsequent treatment with solutions such as nitric acid [180,206], sodium hydroxide [196], calcium nitrate [195], and ethanol [203]. From the findings of Wang et al. [214], near 90% removal efficiency was recorded after several cycles using 0.2 M nitric acid as regenerant. This is in accord with the report on hydrochloric acid treated MXene adsorbents [188]. Interestingly, Peng et al. [195] recorded optimal recovery of pollutants using a combination of nitric acid and calcium nitrate regenerant. However, less than 80% recovery of methylene blue pollutant was obtained using ethanol regenerant [180]. This suggests moderate recovery capability of organic based regenerant. Regeneration by acid solution remains the popular approach, due to high recovery of active sites without deterioration/modification of porosity or composition of MXene adsorbents. Future works using single or multiple regenerant is necessary for optimum recovery of water pollutants over MXene materials.

5. MXene applications in energy storage systems

5.1. MXene-based composites and batteries

MXene-based composites have attracted significant attention due to their unique properties and potential applications in various fields, including energy storage [16–18]. MXenes have several attractive properties, such as high surface area, good electrical conductivity, and good chemical stability, which make them potential materials for use in energy storage devices, such as batteries [215–217]. One of the main advantages of MXene-based composites is their high capacity for adsorption, which can be exploited in various applications [218]. For example, MXene-based composites have been shown to possess good electrochemical performance, high specific capacitance, good rate performance, high energy density and good cycling stability, making them promising materials for use in lithium-ion batteries [219–221]. The competitiveness of MXene with other 2D materials is justified by their extensive variety, chemically and structurally [222,223]. This allows theoretical studies to be useful in identifying the ideal candidate for energy storage applications. Nb₂C, Sc₂C, Ti₂C and V₂C, having low formula weight according to their theoretical gravimetric capacities (amount of storable per gram of the material) are the ideal candidates [224]. As a result, electrodes made from MXene-based materials with formula weight, M₂X are expected to show better gravimetric capacities than the MXenes with M₃X₂ and M₄X₃ formula weights. An example is Ti₂C and Ti₃C₂ with the same surface chemistry but different gravimetric capacitance with Ti₂C having a theoretically and experimentally proven to have higher (50%) gravimetric capacitances due to an inactive TiC layer present in Ti₃C₂. It is logical to assume that the ions only penetrate the interstices between the layers of MXene since the bonds between M and X are too strong to be easily broken. All available experimental evidence confirms this [225]. The ratio of covalent, metallic and ionic chemical bonds in contributes to this observation as explained in details under Section 3 of this review.

Despite the potential of MXene-based composites, there are still a number of challenges that must be addressed in order to fully realize their potential in energy storage and other applications. One of the main challenges is the scalability and stability of MXene-based composites, as they are still a relatively new class of materials and there is much that is not known about their properties and behavior. There is also a need for further research to better understand the fundamental properties of MXene-based composites and to optimize their use in various applications [226–228]. Generally, MXene-based composites are a promising

class of materials with a wide range of potential applications in energy storage and other fields. Further research is needed to understand the properties and potential of MXene-based composites fully and to overcome the challenges currently hindering their widespread adoption [229,230].

MXenes (exfoliated transition metal carbides and nitrides) have been proposed as promising electrode materials for batteries due to their high theoretical capacity, good electronic conductivity, and good stability in aqueous and non-aqueous electrolytes [231]. MXenes have shown promising results as anode materials in lithium-ion batteries. For example, Nb₂C-based MXene electrodes have been reported to have a reversible capacity of 170 mAh/g in lithium-ion cells. V₂C-based MXene electrodes have also demonstrated a reversible capacity of 260 mAh/g in lithium-ion cells [231,232]. There has been a lot of research on Li-based batteries, but they have not yet been successfully commercialized due to ongoing challenges. The cathode, which is the part of the battery through which oxygen travels and where the products of the cycling process are deposited and decomposed, is a key factor in the performance of these batteries. TiC MXenes, a type of material, have the potential to address some of the limitations of various cathodes by providing a range of properties [233]. In addition to lithium-ion batteries, MXenes have also been investigated as cathode materials in other types of batteries, such as sodium-ion batteries [234], lithium-sulfur batteries [235] lithium-air batteries [236], etc.

5.1.1. Lithium- and sodium-sulfur batteries

MXenes composites have attracted significant attention as electrode materials in lithium-ion and sodium-ion batteries due to their high conductivity, large surface area, and good electrochemical stability. In recent years, several studies have investigated the use of MXene-based materials as electrodes in lithium-sulfur and sodium-sulfur batteries [237–240]. According to the some studies conducted, it was found that electrode composed of MXene composite and sulfur showed good cycling stability and high capacity when used in a lithium-sulfur battery. They reported that lithium-sulfur batteries have high theoretical energy density (2567 Wh kg⁻¹) and specific capacity (1675 mAh g⁻¹) due to the multi-electron chemistry between sulfur and lithium [241–243]. Sulfur is also a cost-effective, abundant, and environmentally friendly material. However, Li-S batteries have low conductivity and are prone to side reactions between intermediate polysulfides (Li₂S_n, 3 ≤ n ≤ 8) and the lithium anode, leading to low specific capacity, rapid capacity decay, and poor performance at high rates of discharge. In addition, there is a large volume expansion during the conversion of sulfur to Li₂S, further impacting their performance [244]. To facilitate the kinetics between the Li and S to lead to high reversible capacity and long cycle life for the Li-S batteries, elaborate sulfur hosts design, the use of an interlayer between the cathode and separator and tailored surface chemistry were extensively studied [245].

Prior to MXene use in electrode fabrication, an all-graphene structure for the sulfur-cathode was fabricated with highly porous graphene as hosts for sulfur, highly conductive graphene to collect current and partially oxygenated graphene as adsorption layer for polysulfide [246]. This was built on the reliability of flexible Li-S batteries, where it interacts strongly with lithium polysulfides and alleviates the shuffle effect and collects internal current to aid transport of continuous electrons. The properties make MXenes attractive for various energy-related applications, including Lithium-Sulphur (Li-S) batteries. Li-S batteries are considered as a promising next-generation energy storage technology due to their high theoretical energy density, low cost, and environmental friendliness. However, their practical application is limited by several challenges, such as low electrical conductivity of the sulfur cathode, the formation of a solid electrolyte interphase (SEI) on the cathode [247–249], and the shuttle effect of lithium polysulfides [250, 251].

Recent efforts have focused on the design of flexible and integratable electrodes for Li-S batteries with premium requirement for

flexibility and conductivity to eliminate collection of metal current [252–254]. For internal current collector, highly conductive graphene coated on polypropylene have been employed due to its excellent mechanical and electrical properties as carbon-based nanomaterial in lieu of Al foil for instance to support sulfur cathode. Other materials like carbon nanotubes, nano fibrillated cellulose, hollow carbon fiber foam, etc. have also been used in the structure of sulfur-based flexible cathodes [255–257]. MXenes, have unique properties that make them useful in lithium-sulfur (Li-S) batteries. These materials have high conductivity in their core and functional groups like OH, F, and O on their surface. The functional groups on the surface of MXenes can easily bond with lithium polysulfides through a chemical interaction called Lewis's acid-base interaction. This helps to improve the stability of Li-S batteries by forming a strong bond between the MXenes and the lithium polysulfides [258–260].

Sodium-sulfur batteries have the potential to become a widely used and affordable alternative to current battery technology due to the abundance and low cost of their constituent elements, sodium and sulfur. However, research is needed to improve the sulfur host materials used in sodium-sulfur batteries to achieve the same level of capacity and cyclability as lithium-ion batteries [261]. An ideal sulfur host material for sodium-sulfur batteries will have high electrical conductivity and adsorption capabilities, both of which are necessary for improving cycling stability and making the technology practical for large-scale use [262]. For example, the layered-like structure of TiO₂-Ti₃C₂ MXene material prepared by simple hydrothermal method possesses a better optimal structure with evenly dispersed TiO₂ on the Ti₃C₂. Impregnating the MXene material with sulfur, led to a significant specific capacity of 255.196 mA h/g after 1500 cycles at a 1 C-rate with a low-capacity decay, making TiO₂-Ti₃C₂ MXene a propitious cathode material for sodium-sulfur batteries [262]. In a similar strategy, sulfur was introduced to MXene nanosheets using the vacuum freeze-drying method to create tailor-made wrinkled sulfur-doped MXene (S-Ti₃C₂T_x) nanosheets. These nanosheets were used as the electrode host material in the sodium-sulfur batteries. The authors found that the high polarity of the S-Ti₃C₂T_x matrix with sodium polysulfides restricted the diffusion of these substances. The resulting electrode had a high sulfur loading of 4.5 mg cm⁻² and showed a reversible capacity of 577 mAh g⁻¹ at 2 C after 500 cycles, indicating good electrochemical performance [261].

From the reviewed literature, it is clear that the use of nano-structured materials for the sulfur host is one area of study that has significant potential. It is conceivable to enhance the surface area accessible for the electrochemical processes and boost performance by reducing the sulfur particle size and incorporating it into a nano-structured matrix. The issue of polysulfide shuttle, which may cause capacity decline in traditional sulfur batteries, have also been addressed with the use of nanostructured materials. In other studies, the sulfur host material was modified or added to in order to enhance its electrochemical capabilities. For instance, some investigations have indicated that the electrical conductivity of the sulfur host can be enhanced by the inclusion of conductive elements like MXenes composites.

5.1.2. Lithium and sodium metal batteries

Lithium metal has long been considered a promising anode material for rechargeable batteries due to its high specific capacity, low density, and low electrochemical potential [263]. However, the challenges of dendritic lithium growth and low Coulombic efficiency during lithium deposition and stripping have hindered the practical implementation of these batteries. Also, the increasing overpotential during cycling can lead to capacity fading, and a deeper understanding of interfacial chemistries and lithium deposition behavior, which is challenging have been the core of many research over the years [264–266]. The successful operation of lithium metal anodes is essential for the advancement of post-lithium-ion battery technologies, such as lithium-air, lithium-sulfur, and lithium metal batteries with intercalation compound cathodes [263,267]. Lithium metal batteries are a type of battery that

uses lithium metal as the anode, and have the potential to achieve high energy density (greater than 500 Wh kg⁻¹) and reduce costs. Because of this, they have attracted attention and investment from automotive companies looking to develop them. LMBs have a high energy density due to the high theoretical specific capacity of lithium (~3860 mA h g⁻¹) and its low electrochemical potential (-3.04 V vs. standard hydrogen electrode). These properties make LMBs a promising technology for various applications [267].

Sodium metal has great potential as a next-generation energy storage material, but it faces similar challenges as lithium metal in terms of dendrite and "dead" sodium formation. This can result in reduced Coulombic efficiency, shortened lifespan, and safety issues. The uncontrolled deposition of sodium without proper nucleation site regulation is the main cause of these problems. As a result, it is important to carefully control the nucleation and early growth stages of sodium to ensure a desirable final morphology [268–270].

The practical implementation of lithium metal batteries is hampered by safety issues and low Coulombic efficiencies, which result from the non-uniform and irreversible growth of Li dendrites on their anodes [271]. Metal dendrite growth as a major hinderance to aqueous and non aqueous metal batteries have been addressed via different materials such as MXene composites, graphene oxide, etc., to serve as hosts/scaffolds [271–273]. For example [273], in a nonaqueous lithium metal battery, a mechanically flexible, highly conductive, hydrophilic, and lithiophilic Ti₃C₂T_x MXene@Zn paper was developed to serve as both a zinc and lithium metal anode host. The growth mechanism of Zn metal on both a standard Zn foil and on a Ti₃C₂T_x MXene@Zn composite was also studied. After comparative study with Zn foil, the Ti₃C₂T_x MXene@Zn paper was able to effectively inhibit the dendrites' growth on the Zn surface, enabling rapid and reversible plating and stripping of the metal in an aqueous electrolyte. Additionally, the Ti₃C₂T_x MXene@Zn paper also functioned as a 3D host for a lithium metal anode, using Zn as a nucleation agent to prevent the growth of Li dendrites. The freestanding Ti₃C₂T_x MXene@Zn@Li anode showed excellent reversibility with a high Coulombic efficiency of 97.69% over 600 cycles at a current density of 1.0 mA/cm² and low polarization compared to a Cu@Li anode.

In a similar study to inhibit dendrite growth during lithium plating/stripping, MXene aerogels with a three-dimensional porous structure are proposed as hosts for high-rate lithium metal anodes, using Ti₃C₂ as an example. These scaffolds have high metallic electron conductivity, fast lithium-ion transport capability, and many sites for lithium nucleation, which could provide high cycling stability and low over-potential at current densities up to 10 mA/cm² [274].

Like lithium metal in batteries, sodium metal is not free from the challenges of dendrite growth and low Coulombic efficiencies. Efforts like electrolytic formula optimization, surface modification of metallic electrode, etc., have been made to address the issues. While these strategies have helped to stabilize the sodium metal anode to some extent, the unrestricted growth of dendrites and uncontrolled volumetric changes of the sodium metal have not been effectively solved [234,268,275]. Two-dimensional lightweight materials with desired characteristics including high mechanical strength, extensive surface chemistry, ultra-thin thickness, and huge specific surface area, such graphene and MXene, have the potential to stabilize the sodium-metal anode.

5.1.3. Sodium-ion batteries

In large-scale renewable energy storage systems, sodium-ion storage has the potential to replace lithium-ion storage because of their similar physical and chemical properties, larger elemental abundance, and lower price compared to lithium. However, due to a few variables, sodium is less effective for usage in storage devices. More specifically, compared to lithium, they a lower electronegativity, a higher standard reduction potential, and a larger ion radius, which causes slower sorption and insertion rates as well as greater volume expansion in products like sodium-ion batteries, sodium-sulfur batteries, and sodium-ion capacitors [276,277]. These elements contribute to these devices' poor

cycle stability and low reversible capacity to increase the effectiveness of sodium storage [278–280]. To increase the effectiveness of sodium storage, novel chemical structures and architectural designs of materials that can accommodate sodium are to be created. MXenes have been viewed as attractive possibilities because of their exceptional metallic conductivity, adjustable surface chemistry, and 2D layered structure. MXenes have been viewed as attractive possibilities because of their exceptional metallic conductivity, adjustable surface chemistry, and 2D layered structure [281].

In addition to their use in lithium-ion batteries, MXenes have also been explored as potential materials for sodium and potassium ion batteries [282–284]. These types of batteries are being developed as a potential alternative to lithium-ion batteries due to the abundance of sodium in the earth's crust, which makes them more readily available and potentially less expensive than lithium. Although, sodium is abundant and cheap, sodium-ion batteries has low reversible capacities and poor cycle stability because of their low open circuit voltages and wide ionic radii. This makes it challenging to find an appropriate host for these types of batteries [277,285]. MXenes have been shown to have good ion-hosting and ion-transport properties, and they have been used as both anode and cathode materials in sodium-ion batteries [286–288]. MXenes have been used in energy storage due to its high electrical conductivity, low resistance to ion movement, and unique structure. Though, with a history of stacking or aggregating and their low theoretical capacities, which impede the flow of charges across the electrodes and reduce their capacity. Several solutions have been put forth to address these issues, including employing single- or few-layer MXenes, widening the interlayer gap, and developing 3D porous architectures. These methods seek to enhance the electrochemical kinetics and boost electrode capacity [281].

The issues of the unavoidable stacking phenomena and low theoretical specific capacity obstructing the passage of ions must be resolved to allow for the practical and efficient usage of MXene in sodium-ion batteries. In addition, MXenes have shown poor cycling stability in sodium-ion batteries, with a significant drop in capacity observed after only a few cycles. This is likely due to the large volume changes that occur during the charging and discharging process, which can lead to structural degradation of the MXene electrode. To address these challenges, researchers are exploring various approaches such as modifying the surface chemistry of MXenes, using MXenes in composite electrodes with other materials, and developing new electrolyte formulations [289,290]. For example, Zang et al. [291] demonstrated that by synthesizing a type of nanocomposite composed of a bimetallic sulfide (Co_xFe_{1-x}S₂) and sulfur-doped Ti₃C₂ MXene (S-Ti₃C₂). This 3D structural material, Co_xFe_{1-x}S₂@S-Ti₃C₂, made up of interconnected MXene nanosheets, are able to effectively mitigate volume changes and improve charge transfer. Furthermore, the sulfur-doped MXene nanosheets provide a high number of active sites for sodium storage and prevent sulfur loss during charging/discharging, resulting in an increase in specific capacity and improved cycling stability of the anode material.

5.1.4. Non-lithium (K, Mg, Al and Ca) batteries

The extensive use of lithium-ion batteries for electrical energy storage is hindered by the unpredictability of limited lithium supply, high production costs, and security concerns. The limitations of lithium materials are becoming increasingly obvious in recent years as the usage of lithium-ion batteries has increased considerably. More and more focus has been placed on the study of sodium, potassium, magnesium, and aluminum-ion batteries due to the benefits of plentiful reserves and cheaper cost [292]. The development of new battery technologies is crucial for the future of advancements in sustainable power sources in order to meet these difficulties. Like those made of Na⁺, batteries made of K⁺, Mg²⁺, Ca²⁺, and Al³⁺ are being studied because they employ abundant materials, have large theoretical capacities, the right potential (negative redox), are comfortable to use, and are environmentally beneficial [293–303].

In comparison with Li- and other batteries, potassium-ion batteries (see Fig. 11A) also have some merits such as abundance, low cost and low (-2.92 V) standard potential (in comparison with SHE [(Standard Hydrogen Electrode)]), attracting wider attention from researchers. Specifically, potassium-ion batteries have the potential for higher operating voltage and higher energy density because the standard electrode potential of K/K^+ (-2.93 V, vs. SHE) is closer to that of Li/Li^+ (-3.04 V, vs. SHE), compared to the standard potential of Na/Na^+ (-2.71 V, vs. SHE) which is relatively low [304–306]. With a closer electrode potential than that of Li-ion batteries, this makes the K-ion batteries an ideal alternative with competitive performance. By successfully using commercial graphite anode in potassium-ion batteries, a foundation has been set for potassium-ion batteries to become a viable commercial option in the future.

The large size of potassium ions presents a significant challenge for researchers developing potassium storage electrode materials. Because of the large size of potassium ions ($d = 1.38$ Å), the insertion and de-insertion process in the active material causes severe damage to the internal structure, which results in poor performance with short cycle life. Therefore, the development of electrode materials with high stability and tolerance to large volume strain is crucial for the successful application of potassium-ion batteries. Carbon-based materials are of significant interest to researchers due to their abundance, low potential and cost, and have broad potential applications in potassium-ion batteries. However, the kinetics of potassium ions is slower than lithium ions, which leads to lower initial Coulombic efficiency and poor rate performance. Zhang et al. [307] developed a new type of Sb_2S_3 nanocomposite wrapped in MXene, called $Sb_2S_3@MXene$, was developed for use as an anode material in potassium-ion batteries. The MXene framework and strong Sb-O-Ti bonding at the interface of the $Sb_2S_3@MXene$ help to facilitate charge transfer, preventing the formation of aggregates of Sb_2S_3 nanoparticles, and mitigating volume expansion of Sb_2S_3 during potassium intercalation. These features make the $Sb_2S_3@MXene$ highly effective at storing potassium, as demonstrated by its high reversible capacity of 399.7 mAh g^{-1} at a current density of 100 mA g^{-1} , excellent cycling stability (retaining a capacity of 422.1 mAh g^{-1} after 100 cycles), and good rate capability (119.0 mAh g^{-1} at 2 A g^{-1}). These results show that $Sb_2S_3@MXene$ has great potential as an anode material for potassium-ion batteries.

Researchers working on potassium storage electrode materials face a lot of difficulties because of the size of potassium ions. The insertion and de-insertion processes in the active material severely degrade the internal structure due to the high size of potassium ions ($d = 1.38$), which leads to poor performance and a short cycle life. The effective use of potassium-ion batteries therefore depends on the development of electrode materials with high stability and tolerance to enormous volume strain. Researchers are particularly interested in carbon-based materials because of their availability, affordability, and wide range of possible uses in potassium-ion batteries. But potassium ions move more slowly over space than lithium ions do, which results in inferior initial Coulombic efficiency and subpar rate performance. To lower the potassium insertion barrier and enhance electrochemical performance, one approach to this problem is to increase the interlayer spacing of heterostructured composite materials. For this use, MXene is a promising material due to its high specific surface area, hydrophilicity, and flexible interlayer spacing. MXene stands out from other 2D layered materials due to its remarkable ionic and electronic conductivity and excellent cycle stability, despite self-stacking issues that lower its real capacity relative to its theoretical value.

The applications of MXenes in potassium-ion batteries have received less attention than those of MXenes for lithium-ion batteries, even though many of these publications are still in the theoretical research stage. MXenes use adsorption-desorption to store energy in secondary batteries [308]. Energy study shows that potassium ions are more likely to intercalate into layer space and be absorbed on the surface or interface of MXenes than to penetrate the core structure. It is helpful to

categorize MXenes into bare MXenes and terminated MXenes in order to better understand the mechanisms of potassium storage in MXene materials [309]. Bare MXenes has not been successfully synthesized so far, most of the relevant/primary studies have all been based on theoretical calculations [310,311]. For instance, Er et al. using DFT analysed possible potassium adsorption sites on Ti_3C_2 MXene as high-capacity electrode materials to assess its potassium storage performance. The effective ion radius of the metal ions that Ti_3C_2 MXene can adsorb has a strong correlation with its theoretical capacity for adsorption. Lithium (Li^+) and sodium (Na^+), which have tiny effective ion radii and may achieve theoretical capacities of 447.8 mAh g^{-1} and 351.8 mAh g^{-1} , respectively, have smaller effective ion radii than potassium (K^+), which results in a lower theoretical capacity (0.6) for Ti_3C_2 K_x [283]. This conclusion was consistent with another investigation that found that the Ti_2C , V_2C , Nb_2C , Ti_3C_2 bare MXenes had a maximum stable coverage of K of just $2/3$ [310]. The same study method was adopted in another work [312] to assess the performance of potassium storage of V_3C_2 MXene. Theoretical potassium adsorption capacity in V_3C_2 monolayer was determined to be 269.86 mAh g^{-1} by the authors', and the highest x value of corresponding could reach up to 1.78 , demonstrating that V_3C_2 had a better capacity for potassium storage than Ti_3C_2 . V_3C_2 has a theoretical capacity that was comparable to graphite's.

Aside bare MXenes, there are terminated MXenes with functionalized groups to aid in potassium adsorption to the MXene surfaces. The process of storing potassium ions in terminated MXenes, which have surfaces coated with OH, O, and F functional groups, is facilitated by the interactions between these functional groups on the surface and potassium. While potassium can be readily adsorbed by MXenes functionalized by other groups, MXenes terminated by OH group ($Ti_2C(OH)_2$, $Ti_3C_2(OH)_2$, $V_2C(OH)_2$ and $Nb_2C(OH)_2$) have relatively high negative or positive adsorption energies, which is an indication that potassium cannot easily adsorb by it. For instance, Ti_2CO_2 , V_2CO_2 , Nb_2CO_2 , and $Ti_3C_2O_2$ MXenes displayed greater negative adsorption energies for potassium when MXenes were ended by O, suggesting that O groups were more conducive to the adsorption of potassium. According to theoretical calculations, Ti_2CO_2 and V_2CO_2 have potassium storage capacities of up to 264 mAh g^{-1} , whereas Nb_2CO_2 and $Ti_3C_2O_2$ have capacities of less than 200 mAh g^{-1} .

Generally, researchers are working to improve the interlayer structure, build a 2D hierarchical heterostructure, lessen the self-stacking effect, and add more potassium storage sites in an effort to solve these difficulties. By making sure potassium ions can pass through the material fast, scientists intend to increase the reversible capacity and rate performance. PDPA-NPCN/ Ti_3C_2 is a brand-new heterostructure material that was recently reported on by a team of scientists lead by Zhao et al. [313]. The substance is made through face-to-face electrostatic contact between many layers of Ti_3C_2 MXene and N-rich porous carbon nanochips (NPCN). The resultant PDPA-NPCN/ Ti_3C_2 heterojunction has a multilayer structure and a significant amount of specific surface area, allowing for intimate interaction between Ti_3C_2 and NPCNS as well as the efficient use of two components and more accessible active sites. The performance of the PDPA-NPCN/ Ti_3C_2 heterojunction material as an anode in potassium-ion batteries was next examined by the researchers. The heterojunction material's reversible capacity was determined to be 358 mAh g^{-1} after 300 cycles at 0.1 A g^{-1} . The material also showed a reversible capacity of 252 mAh g^{-1} with a degradation rate of just 0.03% per cycle after 2000 cycles at 1.0 A g^{-1} . This shows that the substance has outstanding rate performance and cycle stability, which makes it a viable contender for use as an anode in potassium-ion batteries. In order to investigate the development of the structure, the researchers also performed an *ex-situ* XRD study of the electrode following the initial discharge/charge operation. The findings indicated that the interlayer gap of NPCNS increased from 4.08 to 5.37 following K^+ insertion, which helped to buffer the volume expansion of NPCNS, which reached 31.6% . After the whole discharge process, the final product (KC8) has a considerably greater potential platform than

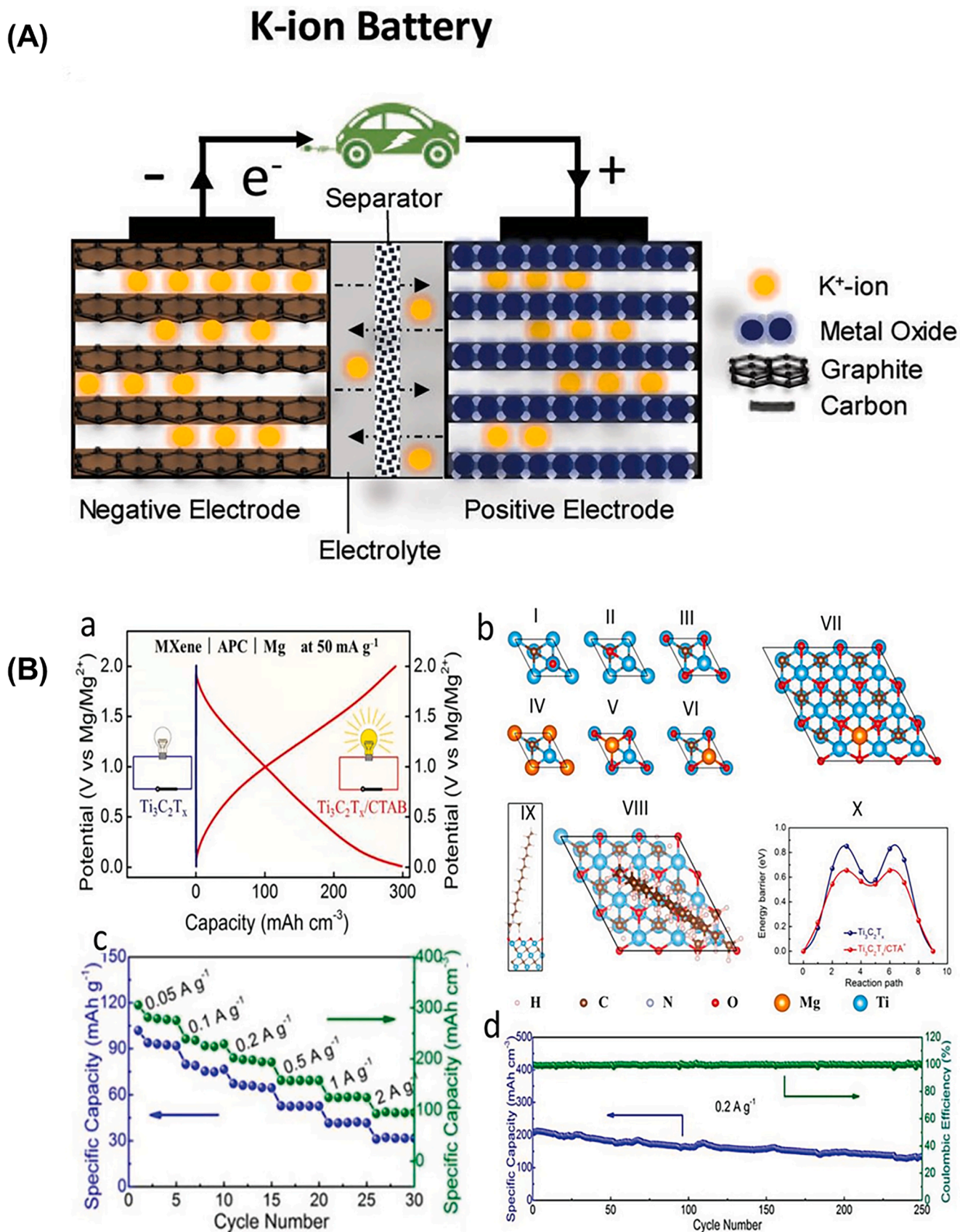


Fig. 11. (A) A typical illustration of rechargeable potassium ion batteries [321]. (B) (a) CT- $\text{Ti}_3\text{C}_2\text{T}_x$ at 50 mA g⁻¹ charge/discharge profiles (b) Calculated geometries of Ti_3C_2 for O- and Mg-atom adsorption on the surface (c) Rate performance of CT- $\text{Ti}_3\text{C}_2\text{T}_x$ (d) Cycling performance of CT- $\text{Ti}_3\text{C}_2\text{T}_x$ at 0.2 A g⁻¹ [320].

potassium metal, which lowers the chance of dendrite formation. As the interlayer gap increased from 19.2 to 24.6, indicating that K^+ intercalation into the PDDA-NPCN/ Ti_3C_2 anode, the diffraction peak (001) of Ti_3C_2 shifted to a lower angle. To increase the rate of ion/electron transport, the heterojunction hybrid material offers a wider interlayer gap and a special 3D connective conductive network. Summarily, the PDDA-NPCN/ Ti_3C_2 heterostructure material was reported to have exceptional performance as an anode in potassium-ion batteries due to its unique composition and high interlayer spacing. This material offers a significant capacity and excellent cycle performance, as well as rate performance and good rate capability for potassium-ion batteries. The research team proposed a new method for preparing high-performance MXene-based potassium-ion battery anodes using this material, which opens up new possibilities for the application of self-assembled heterojunction materials in the energy storage systems.

Potassium-ion batteries have higher potential than sodium-ion batteries and lithium-ion batteries in certain solutions, such as propylene carbonate (PC) [306]. The Stokes radius of K^+ is also bigger than that of Na^+ and Li^+ . Additionally, K^+ has a low charge density which reduces its solvation radius and Lewis's acidity. Because of these factors, potassium-ion batteries are expected to surpass lithium-ion batteries and become the next generation of high-performance metal ion batteries [283,305,314]. However, MXenes have complex effects on potassium adsorption because of the limitations in current preparation technologies. The mechanisms of MXenes in batteries are not yet fully understood, and more research is needed to better understand the potassium storage mechanisms of MXenes [283,315].

Like other non-lithium batteries, magnesium as battery materials is a promising alternative to lithium in the development of magnesium-ion batteries. Magnesium is a common and inexpensive metal, just like the other ions used to make batteries except lithium. Magnesium-ion batteries do not exhibit dendrite development, which is a major issue in lithium-ion batteries that can result in safety concerns and decreased battery performance. Additionally, under the same circumstances, magnesium's positive valence (Mg^{2+}) interacts with two electrons simultaneously to produce a capacity that is double (2205 mAh g^{-1}) that of lithium-ion batteries. A potential solution for eco-friendly energy storage systems, magnesium-ion batteries also offer a high theoretical capacity, a long lifespan, and a high volumetric energy density [316–318].

Inasmuch as magnesium-ion batteries have the potential to replace lithium-ion batteries and draw a blueprint for a bright future, they face some challenges, such as the strong electrostatic forces of divalent Mg^{2+} having strong interactions with the host material, resulting in very slow diffusion kinetics and inferior reversible capacity. Additionally, many host materials are not compatible with the electrolytes used in magnesium-ion batteries, which obstructs the development of new cathode materials for the batteries [318,319]. Due to their large volumetric capacity, superior conductivity, and use in supercapacitors, lithium-ion and sodium-ion batteries, 2D $Ti_3C_2T_x$ MXene materials have received a lot of interest. According to the theoretical results, Ti_3C_2 MXene without functional groups and terminations has excellent Mg-ion storage capabilities but has not yet been experimentally synthesized. As a result, it is essential to investigate suitable experimental techniques to enable MXene's storage performance. Previous research has demonstrated that $Ti_3C_2T_x$ does not allow for the reversible embedding of divalent Mg^{2+} ions, which leaves $Ti_3C_2T_x$ MXene with essentially negligible storage capacity [283].

$Ti_3C_2T_x$ MXene has recently been described by Xu et al. [320] as an effective cathode material for magnesium-ion batteries. The electrical properties of MXene were altered by the authors using a technique involving pre-embedded cationic (CTA^+) from cetyltrimethylammonium bromide (CTAB) surfactant, resulting in $Ti_3C_2T_x$ MXene with a high capacity for magnesium ions. The findings demonstrate that while the cationic surfactant can encourage MXene's Mg^{2+} storage, the surfactant may improve the interlayer gap of $Ti_3C_2T_x$

MXene. By lowering the diffusion barrier of Mg^{2+} on the surface of MXene, the embedded CTA^+ cations were discovered by XPS and DFT to greatly improve the reversible insertion/de-insertion performance of Mg^{2+} between MXene layers. Using MXene as the positively charged electrode, the magnesium-ion battery demonstrates high volumetric capacity (300 mAh cm^3 at a current density of 50 mA g^{-1}), great rate performance, excellent rate capability, and cycle stability, according to the electrochemical results (Fig. 11B). In addition to offering a new option for the choice of positive materials for MIBs, this work offers a novel concept for the use of MXene in the field of electrochemical energy storage. We believe that MXene with pre-expanded interlayer spacing has outstanding kinetic performance in the diffusion process of strongly electrostatic Mg^{2+} and can enhance the interlayer spacing by pre-inserting organic cations (for example, CTA^+) or Mg^{2+} ions. Additionally, neutral-surfaced MXenes could significantly lessen the strong electrostatic contact between Mg^{2+} and the surface terminals, which enhances the MXene dispersion dynamics.

Some other researchers (Liu et al., 2019) [322] used sandwich-structured MXene@carbon nanosphere composites as electrode for magnesium-ion storage. This heterostructure assembly was realized through the electrostatic interactions of 2D MXene nanosheets and positively charged 3D carbon nanospheres. To prevent restacking of MXene nanosheet, the approach effectively opens the interlayer to aid the electrolyte transport thus reducing the path for the ion diffusion. When $Ti_3C_2T_x@C$ is used as a cathode for magnesium-ion batteries, it achieves an excellent reversible specific capacity (at 10 mA g^{-1} , 198.7 mAh g^{-1}), exceptional rate capability (at 200 mA g^{-1} , 123.3 mAh g^{-1}) and better cycling stability (after 400 cycles, approx. 85% retained capacity). With the same sandwich-structure approach, the author concluded that other MXenes, such as V_2CT_x can be prepared with nice rate performance and cycle life. The use of a simple self-assembly approach to synthesize MXene@C nanospheres opens new and realistic paths for developing potential Mg-storage materials with high capacity and extended cycle life.

Aluminum-ion batteries have also piqued researchers' interest due to their high conductivity, good mechanical properties, and excellent stability, making them attractive candidates for use in battery electrodes.

The potential of MXenes to enhance the overall effectiveness of aluminum-ion batteries is one of their key benefits. High specific capacitance and good rate performance of MXene composites have been demonstrated, making them suitable for use in high-power applications. Furthermore, it has been discovered that MXene composites exhibit strong cycle stability, which is crucial for long-term battery performance. Additionally, it has been discovered that MXene composites work well to increase the energy density of lithium-ion batteries. MXene composites can aid in boosting the battery's total energy density by enhancing the electrode's capacity. For applications like electric cars, where high energy density is essential for reaching extended driving ranges, this is significant.

A study by Tan et al. in 2021 [323], reported that the MXene composite of $Ti_3C_2T_x$ and MoS_2 as cathode material for aluminum-ion batteries. Metal dichalcogenide cathodes are materials that can be used to increase the capacities of rechargeable aluminum-ion batteries. After an electrochemical performance test, the Al/ MoS_2 -MXene battery was shown to have a capacity of 224 mAh/g in the first cycle and retained 166 mAh/g after 60 cycles. These values are higher than the specific capacity of Al/ MoS_2 batteries of 88 mAh/g after 60 cycles. The higher charge density of trivalent metal cations (Al^{3+}) and the strong polarization effect on the host lattice, however, result in poor MoS_2 cycling performance. To address this issue, the researchers designed MoS_2 -MXene composites as a novel cathode to improve the performance of rechargeable aluminum-ion batteries. The authors used a facile solvothermal method to synthesize MoS_2 -MXene composites. The $Ti_3C_2T_x$ MXene was able to provide a conductive framework with exceptional mechanical integrity for MoS_2 , allowing it to maintain its shape and structure even when exposed to high levels of stress. The

electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) results showed that $\text{Ti}_3\text{C}_2\text{T}_x$ MXene can prevent pulverization and provide a conductive framework for MoS_2 , resulting in a strong structure. Furthermore, the electrochemical performance of MoS_2 can be significantly improved by compounding it with $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. This means that the combination of the two materials can increase the efficiency of the battery, allowing it to store more energy and last longer. This study showed that MoS_2 -MXene composites have great potential as cathode materials for aluminum-ion batteries.

Another study introduces a rechargeable Al-ion battery based on a two-dimensional (2D) vanadium carbide (V_2CT_x) MXene as a cathode material. The charge storage of the battery is no different, which is based on the reversible intercalation of Al^{3+} cations between the MXene layers. To improve the electrochemical performance can be significantly improved by converting multilayered V_2CT_x particles to few-layer sheets. With specific capacities of more than 300 mAh/g at high discharge rates and relatively high discharge potentials, V_2CT_x MXene electrodes showed one of the best performances among the reported cathode materials for Al batteries. By demonstrating the possibility of a vast variety of intercalation-type cathode materials based on MXenes, this study and others can lay the groundwork for the creation of rechargeable Al-ion batteries with high capacities and high energy densities. In essence, MXene composites have demonstrated tremendous promise for usage in lithium-ion batteries. They have been discovered to enhance the battery's overall performance, including boosting energy density and enhancing rate performance. Additionally, it has been discovered that MXene composites have strong cycle stability, which is crucial for long-term battery performance. Additional research is required to perfect the synthesis of MXene composites and to investigate their application in various kinds of batteries. Several synthetic strategies have been performed to control the morphology or modify the surface terminating groups of MXenes. In addition, due to the low theoretical capacity of MXene, hybridizing with different high theoretical capacity materials to form a composite material is a way to realize the synergistic effect between the two components and ultimately achieve excellent electrochemical performance [324].

5.1.5. MXene-based composites and supercapacitors

Supercapacitors, often referred to as electrolytic capacitors or ultracapacitors, are a brand-new category of energy storage technology based on fast electron transport or physical electrostatic adsorption on electrode surfaces [325]. They are energy storage devices that can store and release energy quickly, making them suitable for applications such as power electronics, electric vehicles, and portable electronics [326]. To accomplish quick energy storage, ions in the electrolyte can quickly adsorb and desorb on the surface of the supercapacitor electrodes under the influence of an electric field. Supercapacitors have greater capacitance than conventional capacitors, and they outperform conventional batteries in terms of power densities and cycle stability. Supercapacitors can be widely employed because to their benefits in sectors including consumer electronics, solar energy systems, smart grids, industrial energy recovery, and the electric vehicle industry [325,327,328].

The high specific surface area of MXene materials makes them ideal for use as the active material in supercapacitors, as it allows for a high capacitance. MXenes' distinctive layered structures offer transition metal active redox sites on the surface while simultaneously improving electrolyte ion transport. Due to these characteristics, MXenes are especially attractive as high-performance electrodes for electrolytic capacitors (supercapacitors) [329]. The combination of their unique properties such as high conductivity, large specific surface area, high chemical stability, and high mechanical strength gave MXene the attractiveness towards wide range of applications, including energy storage and conversion, water treatment, and sensing [19,326,330]. One of the most promising applications of MXene materials is in supercapacitors. Supercapacitors can be split into electrochemical double layer capacitors (EDLC), pseudocapacitors, and hybrid capacitors based on the actual energy storage method.

Supercapacitors, often referred to as electrochemical double-layer capacitors (EDLCs), are energy storage technologies that can swiftly store and release energy. By creating a second layer of charge at the interface of the electrodes and the electrolyte, EDLCs store energy. The electrode surface area and double layer thickness have a significant impact on the capacitance of EDLCs. Pseudocapacitors are energy storage devices as well, but they do it chemically rather than by accumulating two layers of charge. The quantity of charge that may be stored on the surface of the electrodes as well as their surface area influence the capacitance of pseudocapacitors. Although pseudocapacitors frequently have higher energy densities than EDLCs, their higher internal resistance restricts the speed at which energy may be stored and released. However, in hybrid capacitors, energy is stored using both the double-layer and pseudocapacitance mechanisms. They benefit from the high-power density of EDLCs and the high energy density of pseudocapacitors [329,331].

MXenes are an innovative class of transition metal carbide material [332], and their distinct architectures make them desirable for supercapacitors. For an EDLC, the interlayer gap between MXene single layers creates a natural conduit for ion transport. Rich redox sites are provided by the transition metal oxide-like outermost layers, enabling pseudocapacitive energy storage, while high electron conductivity is supported by the transition metal carbide interior layers [333]. MXenes have drawn a lot of attention and are now recognized as the next generation of useful materials for supercapacitors because of their distinct electronic configuration and chemical and physical characteristics. The graph presented in Fig. 12 clearly demonstrates the substantial advancements that have been made to date in utilizing MXene as an electrode material for supercapacitor applications, as evidenced by the high gravimetric capacitance it exhibits.

The performance of MXene-based supercapacitor is influenced by a combination of factors, including the specific MXene material used, the synthesis method, surface modification, electrode preparation, electrolyte choice, temperature, and humidity. For supercapacitors and flexible electronics, MXene-based electrodes, particularly the free-standing films created from MXenes, show considerable potential [335–337]. Binder-free $\text{Ti}_3\text{C}_2\text{T}_x$ paper in KOH electrolyte may reach a volumetric capacitance of 442 Fcm^{-3} at 2 mVs^{-1} and show nearly no deterioration after 10,000 cycles at 1 Ag^{-1} [338]. $\text{Ti}_3\text{C}_2\text{T}_x$ clay electrodes in H_2SO_4 electrolyte exhibit a volumetric capacitance of up to 900 Fcm^{-3} at 2 mVs^{-1} , and they remain stable after 10,000 cycles at 10 Ag^{-1} [339]. The Lukatskaya et al.-created MXene hydrogels might produce volumetric capacitance of about 1500 Fcm^{-3} [340]. The utilization and future of MXenes in supercapacitors are now more viable thanks to these outstanding achievements. Electrophoretic deposition (EPD) technology was used to create binder-free Ti_3C_2 MXene/carbon nanotubes ($\text{Ti}_3\text{C}_2/\text{CNTs}$) films onto graphite paper for supercapacitor electrodes and then studied for performance. Utilizing the synergistic effects of the hybrid, this straightforward yet efficient process creates a sturdy $\text{Ti}_3\text{C}_2/\text{CNTs}$ hybrid film. The $\text{Ti}_3\text{C}_2/\text{CNTs}$ electrode as made displays increased specific capacitance that is, respectively, 1.5 times and 2.6 times greater than that of pure Ti_3C_2 and CNTs films. $\text{Ti}_3\text{C}_2/\text{CNTs}$ electrodes impressively exhibit high cycling stability, with no capacitance decline after 10,000 cycles at 5 A/g . The addition of CNTs act as interlayer spacers for Ti_3C_2 in the hybrid film, providing a continuous charge transport channel and preventing the Ti_3C_2 nanosheets from restacking, both of which improve electrochemical performance. These findings imply that robust $\text{Ti}_3\text{C}_2/\text{CNTs}$ films may be made using a straightforward yet efficient EPD technique, which may be applied to various hybrid MXene systems [341].

Research on the application of MXene-based composites in supercapacitors has focused on various factors that can affect the performance of the supercapacitor, including the synthesis method, surface modification, electrode preparation, electrolyte choice, temperature, and humidity. Synthesis methods such as exfoliation and chemical vapor deposition (CVD) have been used to produce MXenes, with CVD being

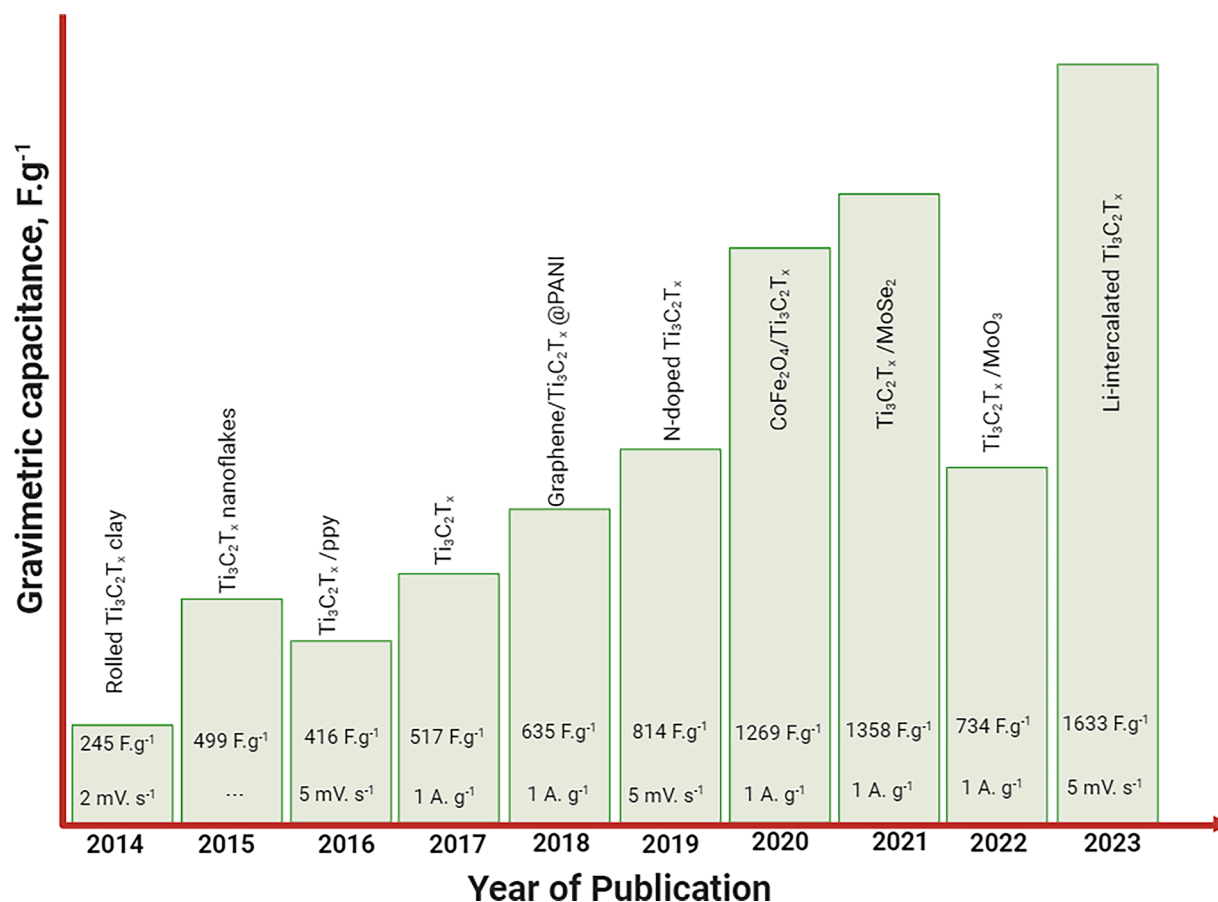


Fig. 12. Research on gravimetric capacitance of MXene-based composite electrodes from 2014 to 2023. Adapted from [334] and updated to the recent status.

considered more efficient and producing MXene with fewer defects [128,342]. Surface modification techniques, such as chemical doping, functionalization, and electrochemical doping, have been used to improve the electrochemical performance of MXenes by increasing their surface area, reducing defects, and increasing their stability [343–345]. The preparation of the MXene-based electrode, including factors such as the thickness and porosity of the electrode, the type of binder used, and the method of electrode fabrication, have been found to have a significant impact on the performance of the supercapacitor [346]. The choice of electrolyte can also affect the performance of MXene-based supercapacitors, with electrolytes that have higher ionic conductivity and electrochemical window being found to improve the rate capability and stability of the supercapacitor [347–349]. Temperature and humidity have also been found to affect the performance of MXene-based supercapacitors, with high-temperature operation improving the ionic conductivity and electrochemical performance but causing thermal deterioration of the materials and humidity leading to swelling of the electrodes [350–352]. In conclusion, studies on the use of MXene-based composites in supercapacitors have discovered that several variables, including the synthesis technique, surface modification, electrode preparation, electrolyte selection, temperature, and humidity, can impact the performance of the supercapacitor. To optimize these elements and raise the performance of MXene-based supercapacitors, more study is required.

6. Conclusions and future outlook

Herein, the current state-of-the-art on MXene synthesis, properties, and applications was reviewed. MXenes are a new class of 2D materials synthesized traditionally by etching away the 'A' element from the parent 3D MAX phases using any of the top-down synthesis methods

(chemical etching, electrochemical exfoliation, mechanical exfoliation, etc.). Although the existing bottom-up approaches offer better controls of the material structures and chemistry, scale-up potential generally limited. However, newer synthesis approaches particularly, DSE and solid-state direct synthesis, are scalable methods that can be designed and implemented at industrial scales. Furthermore, the enormous number of elements that may combine to produce MXenes, as well as the wide variety of conceivable stoichiometric combinations make MXenes have a wide range of characteristics. The most recent structural editing protocol using chemical scissors further extends the possible number of MXenes and MAX phases. It also offers a more precise control of the chemistry and structures of 2D and 3D carbides/nitrides as well as their properties and applications. Hence, MXene has emerged as a promising class of 2D materials with unique electronic, optical, and mechanical properties. More importantly, the sterling properties of MXenes have resulted in their wide range of applications ranging from energy storage to catalysis, and treatment of wastewater and oilfield produced water. Despite significant progress in understanding the synthesis, properties and behavior of MXenes, there are still many fundamental questions that need to be addressed. Thus, future research on MXene should prioritize the following to extend the frontier of knowledge:

- MXene research and commercial application are limited by the arduous, costly, low-scale and environmental unfriendly synthesis methods. These barriers could be removed by some of the newly proposed methods (such as DSE, solid-state direct synthesis and structural editing protocol). Since they do not involve the use of HF, no acid waste stream is generated, and thus they more environmentally friendly. Exploring these methods could facilitate the ease of synthesizing hitherto predicted-but-difficult-to-synthesis members of MXene family.

- The role of the functional groups of MXene on its properties needs to be probed further. For example, further theoretical and experimental work is needed to elucidate the nature of the electronic states in MXenes, especially the new members of MXene family. In addition, the chemical reactivity of MXenes is still an active area of research, and efforts are being made to understand their interactions with other materials, such as water or gasses. Adequate understanding of these fundamental research could lead to new discoveries and enable the development of new MXene-based materials with tailored properties.
- Currently, MXenes have already shown great potential in various environmental applications. Moreover, existing literature has shown the tremendous potential of MXene for CO₂ capture technologies. Future research should evaluate the feasibility of MXene-based materials and composites for the capture and removal of other gaseous pollutants such as SO_x, NO_x, and others.
- The doping and optimization of metals on the surface of MXene is an open area of research that could be explored for the creation of novel materials with sterling and fascinating properties.
- Finally, progress of research and developments have focused on properties and application of MXenes. However, very little is known about the toxicity associated with MXene based materials and composites. Further studies on the short-term, mid-term and long-term exposure to MXene materials on humans and environment are required.

CRedit authorship contribution statement

Tajudeen A. Oyehan: Conceptualization, Investigation, Methodology, Project administration, Visualization, Writing – original draft, Writing – review & editing. **Babatunde Abiodun Salami:** Investigation, Methodology, Project administration, Visualization, Writing – original draft, Writing – review & editing. **Abdulrahman A. Abdulrasheed:** Investigation, Methodology, Writing – original draft, Writing – review & editing. **Hambali Umar Hambali:** Investigation, Methodology, Writing – original draft, Writing – review & editing. **Afeez Gbadamosi:** Supervision, Conceptualization, Investigation, Methodology, Project administration, Writing – original draft, Writing – review & editing. **Eugenia Valsami-Jones:** Supervision. **Tawfik A. Saleh:** Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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