MXene-based nanomaterials for supercapacitor applications: New pathways for the future

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ABSTRACT
MXenes have captivated investigators in methodical and technical areas towards different implementations, such as energy storage appliances, supercapacitors (SCs) and elastic batteries. The utilization of pristine MXenes and their nanomaterial in multiple types of SCs is cumulative due to their outstanding automatic, physicochemical, optical, electric, and electrochemical effects. Due to their exceptional electric performance, better mechanical strength, different practical clusters, and ample interlayer space, MXene-based nanomaterials (NMs) have demonstrated binding energy-storage capacity. In this review article, we have shown the timelines and progress in the synthesis methods over time and applications of MXene-based nanomaterials (NMs) in supercapacitors (SC). Lastly, we have concluded the theme with the future outlook in this field.

1. Introduction
The energy problem is the main principal of the utmost desirable issues for human beings. With the vast feasting of fossil fuels and the ever-rising energy needs in current decades, renewable energy has been broadly used to reduce ecological corrosion and energy lack (Mishra et al., 2022; Samarjeet Singh Siwal et al., 2022; Song & Zhou, 2013). Therefore, electrochemical energy storage devices (EESDs) are immediately required to restore and keep renewable energy towards electrochemical energy-overwhelming utilizations owing to the erratic nature of endurable power (Chu et al., 2017; Luo et al., 2015; Samarjeet Singh Siwal et al., 2019).

With the advancement of essentials in different functions and alleviation classes, elastic electronic devices support severe cases for power designs with high electrochemical performance and outstanding flexibility (Tyagi et al., 2020; Tyagi et al., 2019). Then, producing high-quality adaptable energy storage appliances is at the core of scheduling wearable client electronics (Karamveer et al., 2022; S. Samarjeet Siwal et al., 2020; Wang et al., 2014). ESDs, such as SCs and batteries, have transferred tremendous evolution within an electrochemical performance, benefiting from the in-depth understanding of the electrochemical device and the widespread adoption of nanotechnology (Tyagi et al., 2019; Tyagi et al., 2019). SCs, also named electrochemical capacitors, have been drawing
awareness owing to their high-power densities and long cycle life span, while batteries commonly show high energy densities with reasonably low power densities (Simon & Gogotsi, 2009; Samarjeet Singh Siwal & Zhang, 2022). The advancements in electrodes and electrolytes have offered an outstanding solution to the trade-off between power and energy densities (Li et al., 2016; Samarjeet Singh Siwal et al., 2022; Wang et al., 2012).

Many reviews on MXenes have been issued recently, but only some may concentrate on supercapacitors. The current review outcomes focus on implementing MXene supercapacitors that need a routine conversation, including the tool, fabrication, optimization, and practical application and are incapable of meeting the explosive direction in this area (Chen et al., 2022). The energy storage mechanisms of MXene supercapacitors are also presented, such as cation embolism, surface protonation reaction, and diverse behaviors among electrolytes.

Here, in this review article, we have demonstrated the timelines and progress in the synthesis methods over time and applications of MXene-based nanomaterials (NMs) in supercapacitors. Lastly, we have concluded the theme with the future outlook in this field. It will open the way for new researchers in this field to design their work accordingly.

2. Progress in the synthesis process

The efficient synthesis method is the basis for widening the application areas of MXene substances. Meanwhile, their finding in 2011, the preparation of MXenes utilizing different organic and physical systems has been precisely studied. Other synthesis methods have been designed to etch the MAX stage to reach rich formations and exceptional features of MXenes (Gogotsi & Anasori, 2019; Xiu et al., 2020). The M-X binds in the MAX segment are predominantly covalent and ionic interactions with increased binding power. In distinction, M-A interactions are mostly metallic bindings with relatively scrawny critical power. Therefore, it is feasible to selectively etch the “A” films from the MAX phases utilizing suitable etchants. Khazaei et al. (2018) estimated the force coefficients and static flaking energies of many MAX phases to indicate their etching and exfoliating option.

Fig. 1 illustrates the different synthesis methods offered to get MXenes. In the initial phase, the particular etchants were overwhelmed through fluorine-comprising complexes, for example, HF, LiF + HCl, bifluoride salinities, and fluorine-comprising molten salt, demarcated as the MXenes with three primary exterior endings, i.e., −F, −OH, and −O. In 2017, it briefed fluorine-free etching techniques such as electrochemical etching and robust alkaline hydrothermal etching.
to construct fluorine-free MXenes. Previously, it expressed a nonaqueous molten salt etching path utilizing Lewis acidic salts as the etchants to create accordion-similar MXenes with controllable surface endings. Single-film nanofilms may be acquired from accordion-like MXenes through fitting delamination processes, and the problem of the delamination method is instantly associated with the arrangement of surface-functional clusters.

Newly, Xiaodan et al. (2021) prepared MXene by selectively etching the “A” microscopic coating from the prototype MAX segment. “M” denotes a premature transition metal, “A” is commonly an IIIA or IVA group element, and “X” is carbon or/and nitrogen (Fig. 2(a)). Furthermore, till the day, a sequence of many-M solid-solution MXene has been studied (Fig. 2(b)), arrangements framing continued solid solutions upon M-position. Typically, the M-X bond supplies metallic, ionic, and covalent surfaces, showing higher pressing energy than the M-A bond. Therefore, the M-A bond into MAX may be more readily damaged than M-X bond. The molten salt etching process has been used towards etching MAX phases without HF solutions that may eradicate excessive oxidation or hydrolysis. Gogotsi and his colleagues employed ternary molten fluoride salts as an etchant to design the Ti$_3$N$_x$ through heat remedy at 550 °C in Ar circumstances. Further, a cadmium chloride (CaCl$_2$) or cadmium bromide (CaBr$_2$) molten salt as an etchant to design the Cl/Br-ended MXene (Fig. 2(c)).

3. Applications of MXene-based nanomaterials in supercapacitor

MXenes have complex chemical arrangements and compositions, so their energy storage tool in various electrolytes is still obscure. The structural, mechanical and electrical features of the parent arrangements of MXenes, i.e., MAX stages, are shortly examined. The structure, typical features, and species of multilayer MXenes, which differentiate their electrochemical behavior and SCs activity, are also discussed. The energy storage process and the parameters that affect electrochemical behavior are then drafted to assist developers in creating MXene-based NMs with improved electrochemical activity soon. Additionally, several kinds of MXene-based SCs highlight the importance of MXenes in appliance building.

Due to the exceptional blend of hydrophilicity and metallic conduction within MXene’s 2D configuration, the application of different kinds of MXenes towards energy storage, significantly as the probe substances towards batteries and SCs or as the conductive platform for sustaining the functional substances, has been exceptionally rising (Shin et al., 2021). New MXene-based NMs deliver ultrahigh volumetric capacitor,
pseudocapacitive behavior, favorable cycle resilience and a high-frequency capacity.

The assembly of hybrid NMs provides assortments of different functional effects, which cannot obtain from the traditional (single) material (Gogotsi & Huang, 2021; Kaur et al., 2022). Other MXene-based NMs have been manufactured by incorporating electroactive constituents, like metal blends, carbonaceous, and conducting polymers (CPs) (Siwal et al., 2019; Siwal et al., 2019) by MXenes. It achieved a combined development, where MXenes deliver excellent electronic performance ascribing to the quick electron transmission, improving the functional exterior area, and steadying the catalyst’s design. Furthermore, these resources work as the spacer and broaden the interlayer arrangement, averting the MXene nanosheets’ restacking. Thus, ion conveyance happens quickly, and ion convenience improves. Consequently, MXene-based NMs have shown enhanced electrochemical activity approximated to pristine MXene and that of active substances. Fig. 3 shows different types of MXene-based NMs and their standards for EEDs (Forouzandeh & Pillai, 2021).

![Figure 3](image.png)

Figure 3. The graphic exhibition of MXene-based NMs as electrode constituents towards EEDs. Reprinted with permission from Forouzandeh & Pillai (2021).

The SCs are helpful in day-to-day life due to their high energy density, speedy charging and discharging, and extended cycle vigor (Zhou et al., 2013). In contrast, metal ions within an aqueous media may interact with water molecules to develop an electric double-layer arrangement upon the surface of MXenes. Another side, oxidation-reduction can happen on the surface of MXenes, which significantly donates to the capacitance of MXene-based SCs (Levi et al., 2015; Okubo et al., 2018). Potential discrepancies upon the exterior of MXene into non-aqueous media show the double-layer structure to deteriorate slowly. Consequently, the capacitance is produced mainly through the chemical performance of the MXene surface. MXenes, because of their layered construction, will have ions redeposit during cyclic charge/discharge. Nevertheless, their energy density can be determined by controlling their usage in SCs. Insert material is continually presented within the MXene film to manage the issue of making an MXene-based NM. This impressive separator material can contain one of two materials: those with electric double-layer effects or pseudo-capacitance. The electric double-layer precursor can contain carbonaceous material, like carbon...
nanotubes (CNTs) (Siwal et al., 2018; Samarjeet Singh Siwal et al., 2021).

MXene film is the anode that widens the voltage range and enhances the volumetric energy density of MXene-based symmetrical SCs, as publicized in Fig. 4(a). Fig. 4(b) shows the potential scope of the MXene terminal (-0.6 to 0.3 V) and PANI$_{0.7}$/MXene cathode (-0.2 to 0.8 V) on a similar scan speed of 10 mV s$^{-1}$ which displays an alike digit of charges are kept upon each electrode. The total capacitance is mainly consequent from the redox pseudo capacitance that may also be illustrated through the GCD curves (Fig. 4(c)). As demonstrated in Fig. 4(d), it can retain the form of CV curves consistent at an elevated scan speed of 100 mV s$^{-1}$ that is accredited to the better electric performance and quick ion distribution the MXene and PANI$_{0.7}$/MXene in anode and cathode, respectively. The specific capacitance of the asymmetric appliance as a part of the scan speeds was schemed into Fig. 4(e), conferring to the entire dynamic catalyst mass load. Helping from the high volumetric activity and extended operational potential range, the asymmetric appliance produces an extreme energy density of 65.6 Wh L$^{-1}$ upon a power density of 1687.3 W L$^{-1}$ (Fig. 4(f)). During various bending state tests, as illustrated within Fig. 4(g), the CV curves of the asymmetric appliance nearly coincided at diverse angles of 0, 45, 90, and 180°, showing the excellent mechanical suppleness and strength of the constructed appliance. After 5000 successive charge/discharge (CD) processes (Fig. 4(h)) on

Figure 4. The electrochemical activity of MXene/PANI NMs asymmetric SC within H$_2$SO$_4$ media, (a) technique of ASC, (b) CV arc on 10 mV s$^{-1}$, (c) GCD profile at distinct current densities, (d) CV arc on various scan speeds, (e) gravimetric and volumetric capacitance by variable scan speeds, (f) Ragone curve of the manufactured ASC approximated to additional ASC, (g) CV arcs on various bending positions at 20 mV s$^{-1}$, (h) coulombic efficacy and cycle resilience at 20 mA cm$^{-2}$ for 5000 scans. Reprinted with permission from Wang et al. (2021).
a current density of 20 mA cm\(^{-2}\), 87.5\% of its preliminary capacitance may be included within the broad potential window of 0-1.4 V, presenting better cycling resilience activity. Two asymmetric appliances correlated in sequence may cause a red light-emitting diode, as the actual utilization shows the appliance displayed in Fig. 4(h) inset. The results indicate that a sensible arrangement strategy may boost the potential window and execute a high-energy-density EED (Wang et al., 2021) (Table 1).

<table>
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<tr>
<th>MXene-based NMs</th>
<th>Electrochemical activity</th>
<th>Applications</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Nitrogen-doped-Ti(_3)C(_2)T(_x)</td>
<td>192 F g(^{-1}) in 1 M H(_2)SO(_4)</td>
<td>SC</td>
<td>(Wen et al., 2017)</td>
</tr>
<tr>
<td>Ti(_3)C(_2)</td>
<td>~350 F cm(^{-3}) after 10 K runs</td>
<td>SC</td>
<td>(Lukatskaya Maria et al., 2013)</td>
</tr>
<tr>
<td>Ti(_3)C(_2)T(_x)/PVA</td>
<td>~530 F cm(^{-3}) at 2 V s(^{-1})</td>
<td>SC</td>
<td>(Ling et al., 2014)</td>
</tr>
<tr>
<td>PPY-Ti(_3)C(_2)T(_x)</td>
<td>~1000 F cm(^{-3}) by capacitance retaining of 92% afterward 25 000 runs</td>
<td>SC</td>
<td>(Boota et al., 2016)</td>
</tr>
<tr>
<td>MXene/GO</td>
<td>165 F g(^{-1}) even on 1000 A g(^{-1})</td>
<td>SC</td>
<td>(Shang et al., 2019)</td>
</tr>
<tr>
<td>1D bacterial cellulose/MXene</td>
<td>416 F g(^{-1}) and 2084 mF cm(^{-2})</td>
<td>SC</td>
<td>(Y. Wang et al., 2019)</td>
</tr>
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Table 1. Overview of the interfacial network configuration of MXene and their supercapacitor applications.

4. Conclusions and future prospects

After a decade of their invention, MXene-based NMs with special electrochemical effects have attained incredible advancement in energy storage. This review article outlined the synthesis pathways and presented advances in MXene-based NMs for SC applications. Compared by the crucial innovations completed upon graphene into a general retail implementation, the MXene-based NMs are new but have superb possibilities for EED. Conspicuously, the governable incorporation of steady MXene with a specific description of film quantity, interlayer spacing, and active clusters is facilitative to quick reaction kinetics.

MXene-based SCs in aqueous media show a broad series of implementations owing to their excellent ionic conduction, easy synthesis processes, and low incorporation expense. Nevertheless, in a few cases, the outflow of aqueous electrolytes adversely affects the device’s electrochemical performance and imposes a significant security threat. Additionally, the liquified oxygen in an aqueous media decreases its activity through surface oxidation. Therefore, more studies must be done to enhance the electrochemical activity of MXene-based NMs SCs utilizing solid and non-aqueous electrolytes as replacements for the aqueous media. A more profound knowledge of the EED tool in MXene-based NMs SCs and the different characteristics (surface interaction, interlayer network, film restacking, etc.) affecting them may guide the incorporation of effective SCs.

In developing the possible incorporation of MXenes at industry-related ranges, protection, controllability, and other problems restraining large-scale production’s potential will require assessment. Current techniques based on bottom-up approaches need more critical investigation.

MXenes are advantageous pseudocapacitive electrodes established on two-dimensional systems and surface functional groups. This review will stimulate associations and contacts and help provide the utmost intent of retail supercapacitors for various applications that depend upon pure and renewable energy.

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