

Review

Insight on Electronic and Thermal Behaviors of Conductive MXene- $Ti_3C_2T_x$ -Based Polymeric Hybrid Material and Their Capacitive Energy Storage Applications: A Review

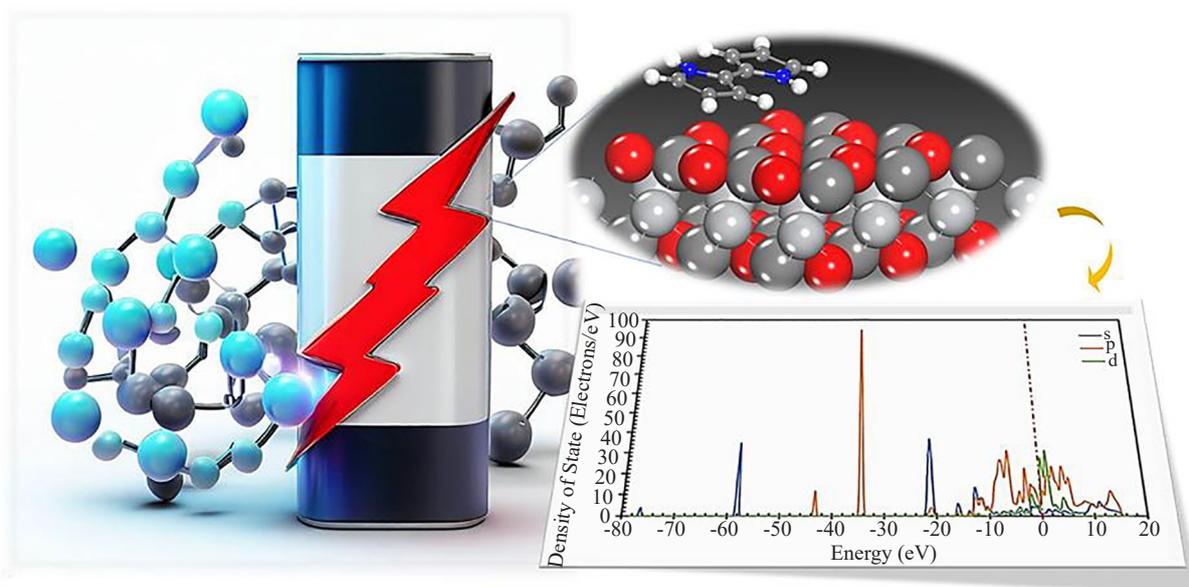
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Graphical Abstract



Abstract: The increasing research focus on two-dimensional carbides known as MXenes has garnered significant attention due to their effective capacitive properties, leading to their application in energy storage devices. Recently, the emerging technique of incorporating MXene into polymer matrices to form hybrid nanoclusters has significantly

contributed to modern nanoarchitectonics. However, there is no available review that elaborately discusses the thermal and electrical behaviors of these hybrid nanoclusters. This paper provides detailed insights into the thermal and electrical properties of conductive MXene-Ti₃C₂T_x-based polymeric hybrid nanoclusters. Further elucidation is given to their applications in energy storage devices, with a special interest in MXene-polypyrrole, MXene-polyaniline, and MXene-poly (3, 4 ethylenedioxythiophene) polystyrene sulfonate nanoclusters. Additionally, to address the challenges associated with electron transport within the atoms of the nanoclusters, we concluded by offering suggestions on a potential approach to alleviate these challenges and enhance their electrical performance for future applications.

Keywords: thermal properties, electrical properties, MXene-polymeric hybrids, nanoclusters, energy storage applications

1. Introduction

The attempt to solve the energy crisis has led to research on energy storage devices with attention given to the use of 2-D materials such as borophene, graphene nanosheets, exfoliated graphene, phosphorene, and silicene [1]. This is due to their low weight, high electron mobility, chemical stability, thermal and electrical conductivity, and flexibility [2]. Recently, a 2-D material known as MXene-Ti₃C₂T_x was produced by the exfoliation of Ti₃AlC₂ [3]. Generally, MXene is fabricated from the transition metallic nitrides, carbides, and carbonitrides known as MAX-phases with the formula M_{n+1}AX_n, (where n = 1, 2, 3 or 4; X represents carbon, nitride, or carbon nitride; M represents a transition metal, and A represents the periodic group 13 or 14 elements). MXene is synthesized through the etching of A elements [3] with surface terminations Tx, to give the general formula M_{n+1}AX_nT_x, (where T represents the functional group (-Cl, -O, -F, or -OH), x is the small part of the functional group). For energy storage applications, MXene presents so many advantages over other energy storage materials [4]. The surface chemistry of MXene, significantly contributes to its oxidative property, allowing the formation of composites with other capacitive materials. Like the other 2-D materials, MXene can be loaded into several materials to achieve the desired properties for targeted applications [5]. Among these materials are polymers that form MXene-polymer composites [5].

Generally, polymers are studied to have high electrical and thermal resistance, hence they are perceived to be insulators [6-10]. The inclusion of conductive nanofillers such as MXene-Ti₃C₂T_x into the polymer matrix has a significant change in the thermal and electrical conductivity of the resulting MXene-polymer nanocomposites (PNC) [11-15]. Several properties of MXene have been reported to improve by the addition of polymers. Such properties involve flame retardancy, stretchability, toughness, thermal stability, electron mobility, and chemical resistance [16-19]. Nowadays, MXene-polymer composites have been utilized as an engineering material for many applications ranging from biomedical, energy storage, electronic, and electromagnetic shielding, to photovoltaic applications [5, 17, 20-22].

On the other hand, several polymers have an inherent conductive nature, hence they are called conductive polymers [23-27]. Among these polymers are conductive polypyrrole (PPy), polyaniline (PANI), and poly (3, 4 ethylene dioxythiophene) polystyrene sulfonate (PEDOT:PSS) which have alternating double and single bonds at the backbone chain (Figure 1) with their overlapping p-orbitals forming a system of delocalized π -electron, which induces electron transfer. Hence, they are also referred to as conjugate polymers [28]. Conductive polymers, intrinsically, exhibit the ability to conduct electricity. They are positioned beyond insulators while showcasing metallic behavior, otherwise, classified as synthetic metals. This results in their useful inherent electronic properties, and their applications in both energy storage and thermoelectric devices [29-39].

The hybrids of MXene and conductive polymers have showcased innumerable advantages in the design of electrodes for energy storage devices (ESDs) [40, 41], hence, the study of their thermal and electrical behavior is paramount as regards energy storage. ESDs when in use, ranging from supercapacitors to batteries, generally, are subjected to temperatures between -40 °C to 60 °C [42, 43]. At this temperature range, the electrode is expected to deliver optimum performance with suitable thermal stability and thermal conductivity, without any degradation. Generally, the incorporation of nanofillers (MXene) into a polymer matrix will cause an obvious enhancement in properties which of course includes thermal stability/conductivity [44]. MXenes have a high surface area, hence a very large interfacial area and bonding sites, when adequately incorporated into a polymer matrix. MXene tends to alter the properties of the polymer in those interfacial areas, and as such, a larger area of modified properties will be achieved even at lower MXene content. This will result in a pronounced change in the macroscopic thermal property of the

MXene-polymer nanocluster [45]. The mechanism of thermal stability of MXene nanoclusters can be likened to that of graphite with a similar structure of layered nano thickness of approximately 10 nm. Following the highly anisometric structure of the fundamental particles of layered MXene, and its inherent thermal resistance, heat, and gas diffusion are likely to be prevented by forming physical barriers, thereby delaying the mass loss of polymer during degradation [45]. Moreover, the surface functional groups that exist on MXene nanosheets, which form strong bonds with the polymer, suggest enhanced thermal properties in MXene-based polymer nanocomposites [46].

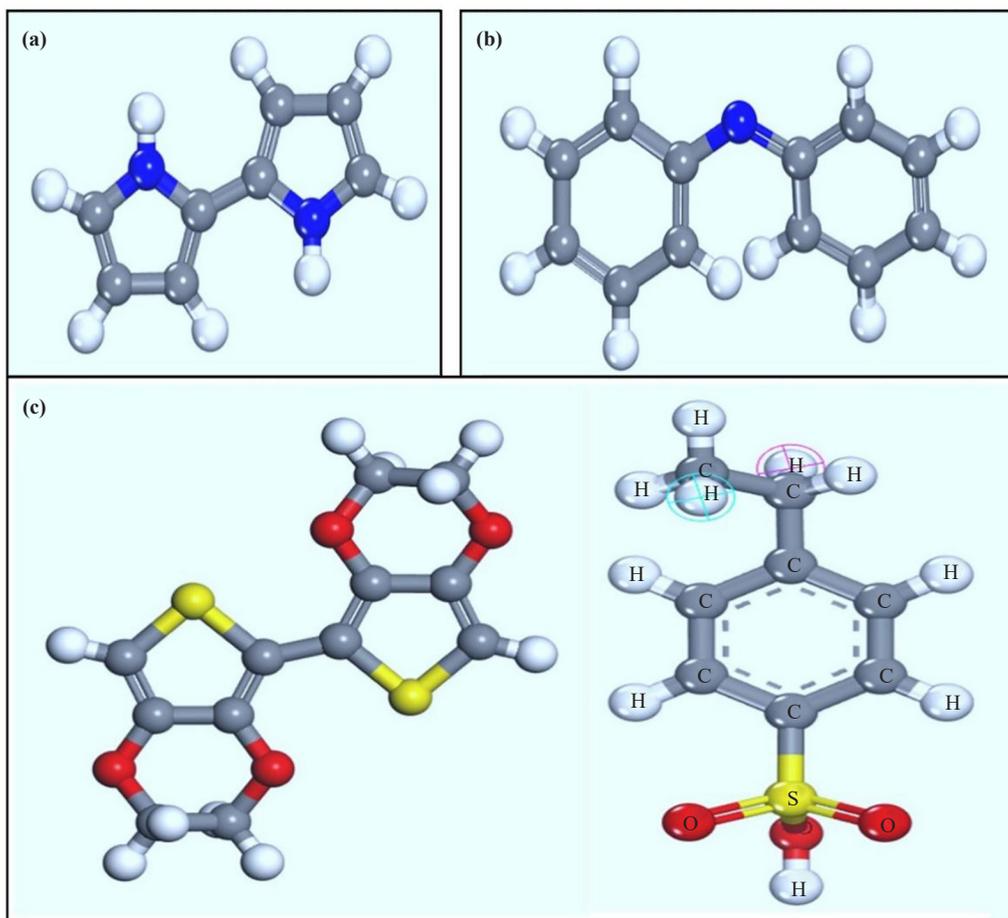


Figure 1. The 3D chain structure of the dimer of (a) PPy; (b) PANI; (c) PEDOT:PSS

The contribution of polymer to the thermal stability of MXene-polymeric nanoclusters has been reported [47]. In the thermogravimetric analysis (TGA) of MXene ($Ti_3C_2T_x$) and MXene-Poly vinyl alcohol (MXene-PVA) in both nitrogen and oxygen environments, pure MXene decomposed at the temperature of 785 °C, and MXene-PVA composite decomposed at the temperature of 823 °C, both in a nitrogen atmosphere. This implies that the MXene-PVA has better thermal stability than pure MXene in a nitrogen atmosphere. Again, in an oxygen atmosphere, pure MXene decomposed at the temperature of 729 °C, while MXene-PVA decomposed at the temperature of 811 °C. This suggests that the addition of polymer to MXene enhanced the thermal stability of MXene in both nitrogen and oxygen atmospheres. Hence, polymer encapsulation protects MXene from environmental oxidation in the presence of atmospheric air [48]. Also, the degree of dispersion of MXene layered sheets inside the polymer matrix contributes to the effective bonding of the composite, as this will create evenly distributed bonding sites, thereby allowing MXene nanosheets to protect more polymer particles against thermal degradation, hence the overall electrode is made thermally stable. It has been reported that the degree of nanofiller dispersion and its percentage loading affect the thermal properties of the polymer

nanocomposites [49, 50]. Dipika et al. reported the effect of MXene and its percentage loading on the weight loss of MXene polymeric nanocomposites for flexible energy storage materials [51]. The overall thermal behavior of MXene-based conducting polymer hybrid nanoclusters can also be attributed to the percentage loading and the degree of dispersion of MXene in the conducting polymers.

On the other hand, the electrical performance of the electrode also contributes to the overall performance of the supercapacitors and batteries. The electron transport ability of an electrode strongly depends on the material molecules of the electrode and its chemical/electrochemical environment. This is most effective when the probability of electron transmission through the molecules of the electrode material is near 100% [52]. Again, the molecular length, the connection means, the presence of alternating single and double bonds, and the inclusions of possible carbon clusters (carbon derivatives) within the molecular network of the electrode material have a significant effect on the electrical conductivity of the electrode [52]. This electron transport behavior in nanoclusters is significantly important in the design of electrodes for device applications, most especially in energy storage applications, where the balance in ions storage and electron transport must be maintained for efficient electrochemical performance. Figure 2 shows the various electron transport through different molecular chains. Benzene depicts the simplest type of electron transport in a single molecule with a large energy gap between the conduction and valence bands, and as such, has lesser conductance (see Figure 2a). The electron transport in graphene with little or no energy gaps, following the clustering of the benzene ring, is without restriction. Hence, a high conductance is seen in graphene molecules. The nano-clustering of MXene and conducting polymers utilizes the idea of bridging the gap between the conduction and valence bands, with the polymer molecules creating a pathway for efficient electron transport as revealed using the density functional theory (DFT). Figure 3 shows the intercalation/clustering of PPy in between the MXene layers, creating a pathway for efficient electron transport.

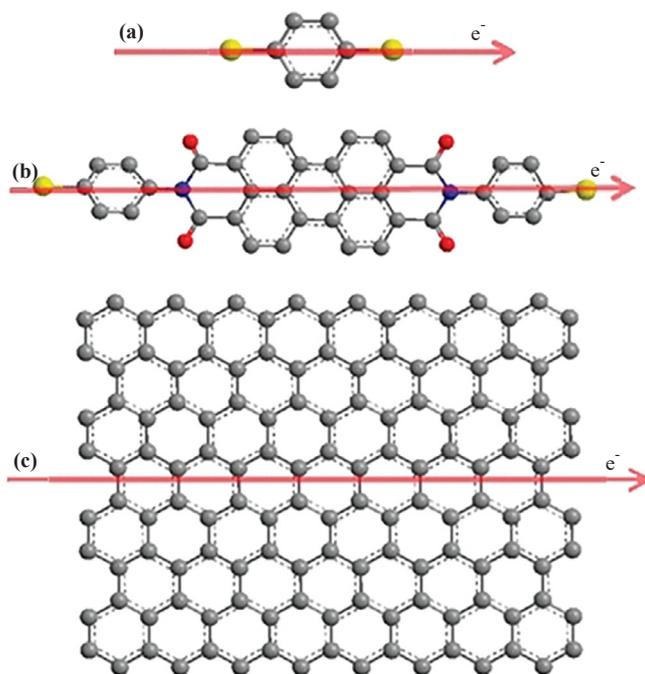


Figure 2. Electron transport in various molecular chains (a) electron transport in a single benzene molecule; (b) electron transport in a compound with fewer molecular chains; (c) electron transport in graphene. Reproduced with permission from Ref. [52]

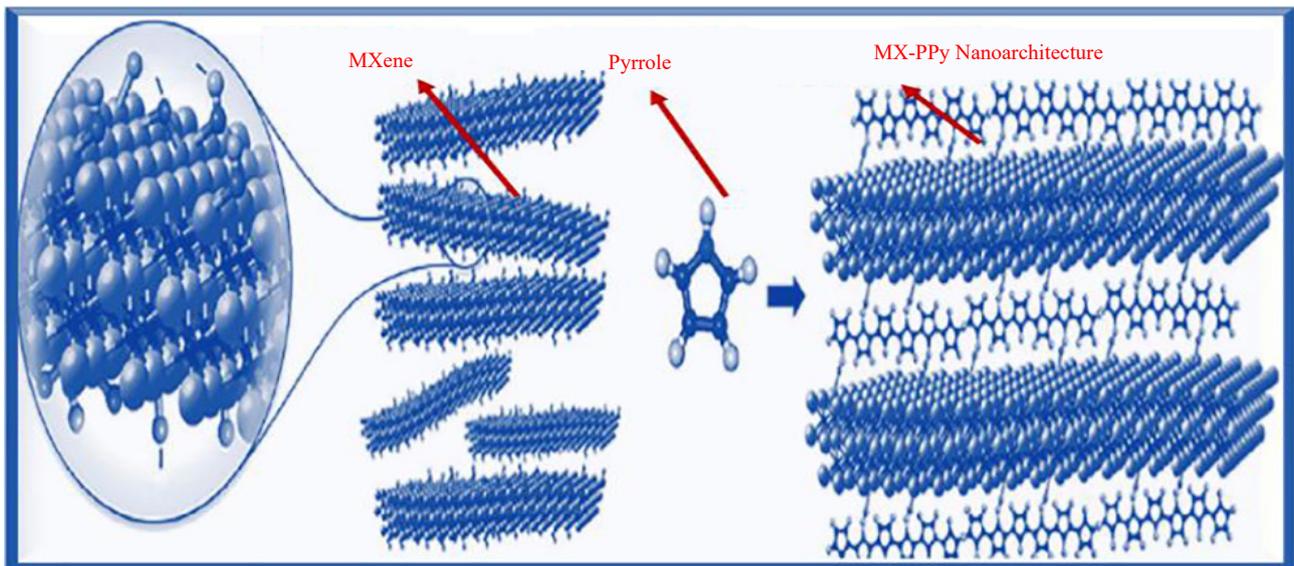


Figure 3. The intercalation of PPy in-between MXene nanolayers to form nanoclusters for efficient electron transport. Reproduced with permission from Taylor and Francis [40]

The study of the electron transport and photon emission of MXene-polymeric hybrid nanoclusters, not only answers the basic questions about the electrical conductivity and thermal conductivity of the conductive nanoclusters but also contributes to the ongoing pursuit of molecular-scale electronic devices. This paper focuses on elucidating the thermal and electrical behaviors of conductive MXene- $\text{Ti}_3\text{C}_2\text{T}_x$ -based polymeric hybrid nanoclusters. It discusses their potential applications in capacitive energy storage, particularly about MXene-conjugate polymers, which include MXene-PPy, MXene-PANI, and MXene-PEDOT:PSS. Also, insights are provided on the approach to remedy the insufficient charge carriers, which is a challenge for the use of MXene-based polymeric hybrid nanoclusters for energy storage applications.

2. MXene as a capacitive material for energy storage applications

MXenes are a wide family of 2-D materials (Figure 4b), which can be selectively etched from several atomic layers of MAX-phases (Figure 4a). These ternary transitional metals of carbides/nitrides are composed of layers of group 13 and 14 elements “A”, closely packed atoms of “M”, and X atoms which occupy the octahedral sites. So far, more than 70 different MAX-phases have been discovered [53], which includes the obvious pure MAX-phases. Following the difference in the bonding strength between M-X and M-A, the elemental layer “A” can be etched selectively with proper temperature and etchant to give a 2-D layered structure of MXene. Several etchants have been employed to fabricate MXene from MAX phases while preserving its 2D structure.

The obvious use of MXene as a capacitive material for energy storage applications is renowned [54-58]. This is due to its likely properties with graphene which include the interlayer spacing of its molecules, which is majorly explored for energy storage in the form of ions/charges in an electrochemical setup for later discharge, resulting in the release of the energy in the form of electron movement [59, 60]. The clustering architecture of a single MXene sheet (Ti_3C_2) as shown in Figure 4a is extracted from its metallic carbide lattice. This MXene single sheet is readily oxidized which contributes to its thermal instability when compared with the metallic carbide MAX-phase [61-64].

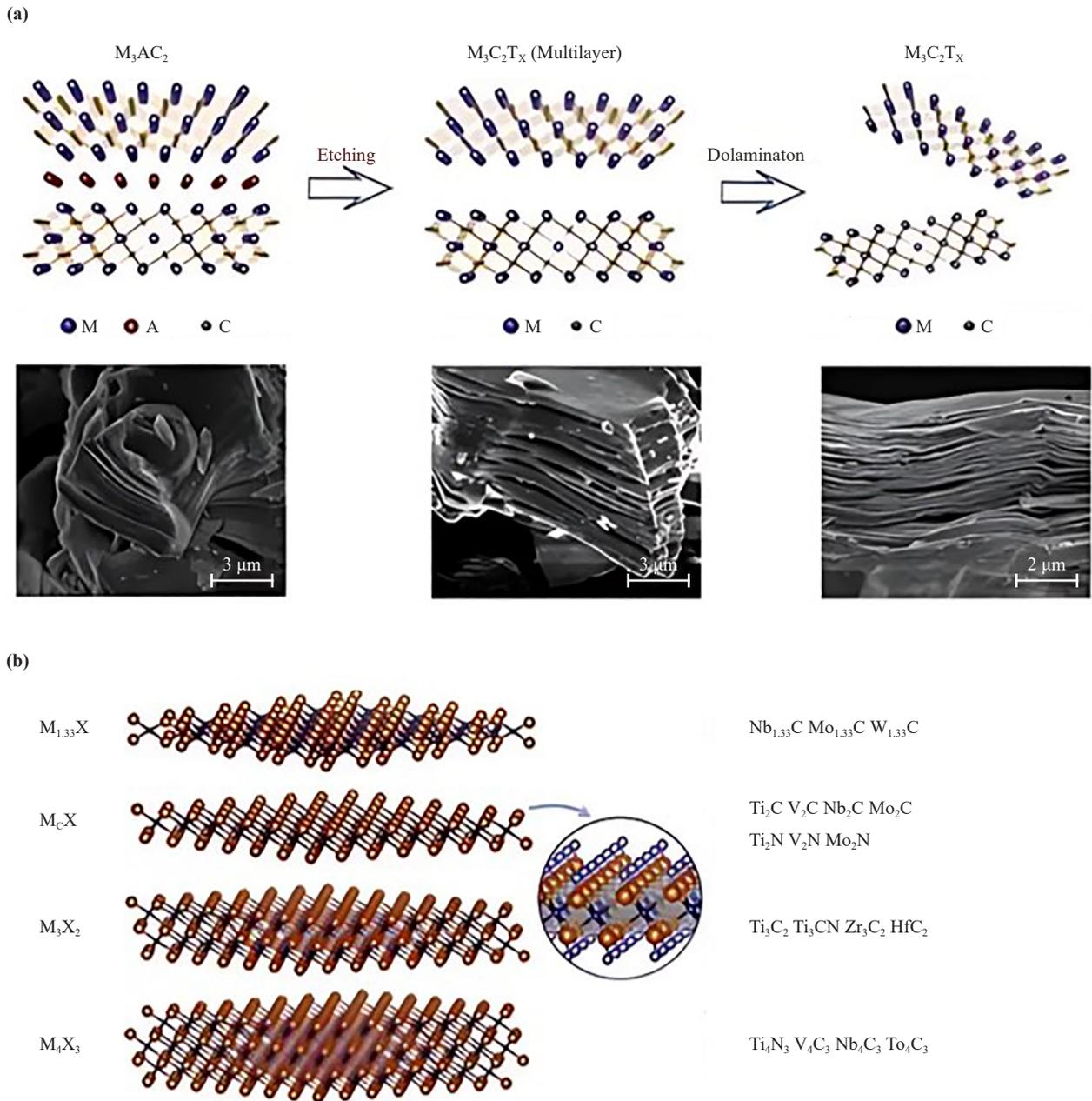


Figure 4. (a) Schematic illustration, and the SEM images of the fabrication process of MXene from the MAX phases. b) Different MXenes synthesized experimentally so far. Reproduced with permission from Elsevier [65]

2.1 Synthesis of MXene ($Ti_3C_2T_x$)

The top-down etching method remains the most common technique for synthesizing MXene, by etching “A” from the MAX phase (Ti_3AlC_2), where A is aluminum; M represents the transition metals, which in this case is Titanium; whereas X is the carbide group [66, 67]. Generally, the bond that exists in the MAX phases is both metallic and covalent [68], which requires an etchant to weaken the bond and allow the removal of aluminum from the MAX phase [69]. Till now, research has been ongoing in the quest to discover the best etchant for the complete removal of aluminum without the leaching of M or X, which will result in achieving a higher mass deposit of MXene. Several etchants have been employed in the etching of aluminum from MAX phases, ranging from acidic medium (HF, LiF, HCl) [70-75] to

alkaline medium (NH_3OH) [76-78]. The synthetic metal carbide is similar to graphene which belongs to the class of 2D materials, it is commonly known as MXene [79]. Following the initial awareness of MXene in 2011, this material was originally fabricated through the HF etching of its precursor, the MAX phase as shown in Figure 4a.

The top-down pathway involves the etching and delamination of the MXene into nanosheets [80, 81]. The HF etching of Aluminum leaves the MXene surface with terminations of -O, -OH, and -F [82-84], this initiates intercalation of the cations which assists in MXene delamination into mono or bi-layered MXene-nano sheets.

Additionally, MXenes synthesized via HF are characterized by tiny hole voids, this allows Titanium ions to react with air by oxidation which results in the formation of Titanium oxide [85-87]. When compared to the Li-HCL etching route, $\text{Ti}_3\text{AlC}_2 + 3\text{H}^+ + 3\text{F}^- = \text{AlF}_3 + 3/2\text{H}_2 + \text{Ti}_3\text{C}_2$, known as the clay approach, following the clay-prone formation of $\text{LiF-HCl-Ti}_3\text{C}_2\text{T}_x$. $\text{LiF-HCl-Ti}_3\text{C}_2\text{T}_x$ is hydrophilic due to the presence of OH molecules. As the etching proceeds, there is twice an increase in volume, due to the wetting of the intercalated lithium [88].

Furthermore, the etching detection follows LiF and HCL constituents, as intercalation of Li-ion characterizes the former, while the degree of etching showcases the latter. Again, when compared with the HF-etching route, the Li-HCL etching route is more yielding, as the etching system shows high interface and surface quality and enhanced mechanical stability. This was observed from the dimensions of the MXene sheets, which are larger without sonication.

Again, the use of dilute HCl through electrochemical etching was employed to remove aluminum from its MAX-phase (Ti_3AlC_2) to obtain a porous and layered sheet of MXene. The surface terminations on these MXenes were found to be Cl, -O, -OH groups [75]. In another research, Zhang et al. [88] utilized a binary aqueous salt comprising 1M ammonium chloride and 0.2 M tetramethylammonium hydroxide for the removal of aluminum from Ti_3AlC_2 through an electrochemical technique. This route provides MXene with a large lateral dimension and a high yield of bilayer or mono-layer MXene nanosheet. Also, an organic base etchant (TMAOH) was utilized to remove aluminum from the multi-layer of Ti_3AlC_2 [89]. This method involves the hydrolysis of aluminum by TMAOH to form Ti_3C_2 . MXene with intercalated TMA^+ .

Nevertheless, the geometry of the synthesized MXene is affected by the etching temperature, etching duration, and etching route [67, 90]. The surface chemistry, induced by the etching process, which involves the terminations of -OH, -F, and so on, inhibits the further etching of aluminum. Hence, increasing the etching temperature increases the degree and rate of etching [91]. The performance of MXene for energy storage can be optimized and harnessed by the introduction of a porous structure [92]. Due to the force of attraction that exists between MXene interlayers, MXene lacks the desired porosity for energy storage applications. Bu et al. [93] suggest that adding other materials into MXene, and freeze-drying MXene after exfoliating, can result in porous MXene for capacitive energy storage applications.

2.2 Capacitive properties of conductive MXene for energy storage applications

Density functional theory (DFT)/molecular dynamics (MD) models revealed that the atomic composition of MXene has 2-D geometry compared to that of graphene [94-96]. When compared to other carbon materials, MXene has high density as well as surface functional groups, as a result of metallic constituents present in its chain [83, 97]. The inherently high density of MXene, when compared with other carbon-oriented substrates, has resulted in its high volumetric capacitance [98]. Also, MXene shows metallic conductivity and hydrophilicity, this assists in fast electron transport in addition to the wetting of the electrolyte.

The modifiable surface functional groups that exist on MXene, result in its exceptional attributes. For instance, the -O entity, on the MXene surface, provides bonding sites for redox reactions [99, 100]. Moreover, the negative functional groups on the MXene surface contribute to the negative nature of MXene surface charges, and bonding between MXene and water via hydrogen bonding, hence the even dispersion nature of MXene in a solvent [99]. Due to the MXene architecture and geometry, it addresses the defects associated with electrodes made from other carbon-oriented materials for capacitive energy storage applications [101] as shown in Figure 5.

MXene shows a range of capacitive behaviors, depending on the architecture, functional groups, and the dimensions of the electrolyte cations [59, 80, 102]. Inherently, the MXene surface contains termination functional groups of -OH, -F, and -O. During the movement of electrolyte cations, around and within the layers of MXene, an electrostatic attraction occurs between the two unlike charges [103, 104]. This will cause the minute electrolyte cations to penetrate and diffuse into the MXene layers which will result in the altering of the electrode molecular structure, and as such, a pseudo-capacitance is said to have occurred. However, during the penetration of the electrolyte cations,

the bigger cations are restricted from diffusion due to the electrostatic repulsion which maintains high cycle stability through electrochemical adsorption [105]. Finally, MXenes are used as fillers to modify and improve the capacitance, thermal, and electrical properties of various materials including polymers [17, 41, 106-113].

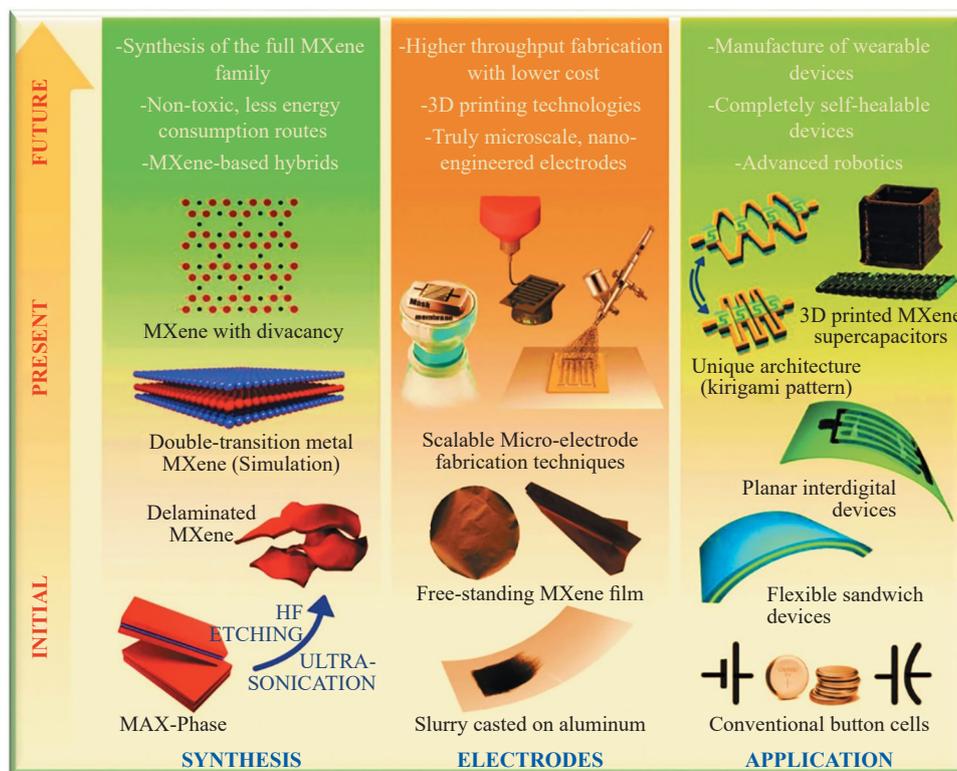


Figure 5. (Left) synthesis of MXene through HF MAX etching, under sonication to form a delaminated single nanosheet, presently a 2-D double transition metal MXene realized through simulation, and in the future, less energy consumption routes for MXene and MXene-hybrids will be achieved. (Middle) evolution of the application of MXene in electrode design, from slurry cast on aluminum to free-standing MXene film, scalable micro-electrodes, and in the future a higher throughput fabrication with lower cost via 3-D printing. (Right) capacitive MXene-designed batteries and supercapacitors to wearable energy storage devices. Reproduced with permission from Taylor and Francis [4, 40]

3. Fabrication techniques of conductive MXene-based polymeric hybrid nano-clusters

To achieve improved MXene-polymeric nanocluster properties, even and effective dispersion of exfoliated MXene layers into the polymer matrix is of utmost importance. Even so, it is paramount to demonstrate that reinforcement with monolayers might not necessarily improve the mechanical properties, as revealed by using graphene-reinforced polymer hybrids [114]. There, it was shown that the hybrids' optimum modulus was achieved with a mono sheet of tri-layered graphene of 1 nm thickness. Therefore, considering the numerous advantages associated with scalability, MXene with multi-layer may be a practicable option for reinforcing polymeric nanoclusters, this will necessitate the need for MXene delamination.

To achieve both efficient dispersion and exfoliation of MXene, the method through which the MXene nanosheets are introduced into the polymer matrices to form nanoclusters affects their clustering as well as their properties. Mainly, three nanocluster processing techniques are widespread and accepted, namely, in situ polymerization, solvent blending, and melt blending.

3.1 *In situ* polymerization approach

A significant effective approach for fabricating nanoclusters involves the polymerization of monomer in the presence of inclusions/fillers, hence, an in-situ polymerization [115-117] (Figure 6). This technique provides the formation of polymeric chains nearer to the inclusion surfaces. Intercalation of monomers in-between the layered materials such as MXene, through polymerization, results in spacing and exfoliation of MXene nanosheets.

Reports for in situ polymerizations of MXene polymeric hybrid nanoclusters [5, 19, 113, 118, 119] have shown that improved nanoclusters' properties can be attained through an in situ polymerization approach. This can be attributed to the proximity of the polymeric chain gradient to the entire surface area of the nanofillers. Where MXene is embedded in a material, maybe a resin, followed by the filling of the second material, this will prompt a polymerization reaction, as the unsaturated polymer will react with the surface-functionalized MXene to form nanoclusters. Alternatively, an aqueous medium can be utilized to facilitate an in-situ polymerization reaction, as shown by various polymers [120-125].

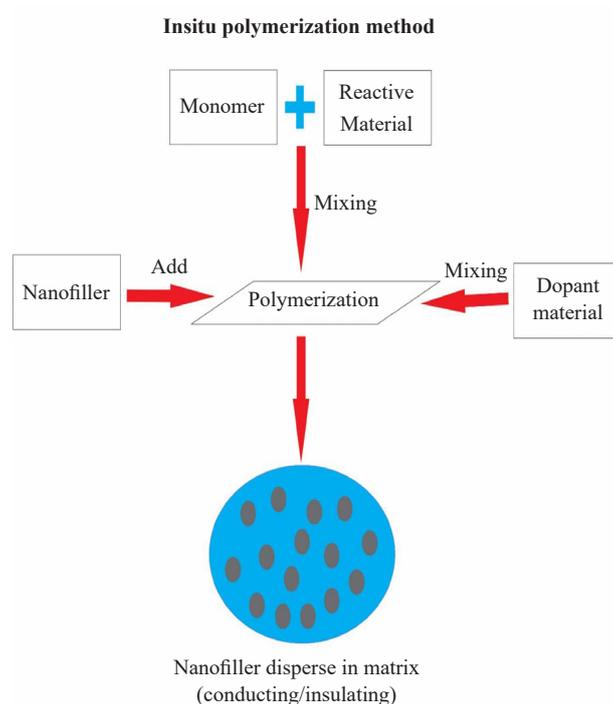


Figure 6. In situ polymerization approach of preparation for both insulating and conductive polymeric nanoclusters [126]

3.2 *Solvent blending* approach

Solvent blending, otherwise called solution mixing portrays the most common pathway for MX-polymeric nanoclusters preparation. The approach involves the usage of a solvent medium to disperse and include the MXene nanosheets into, and unto the polymer matrix through colloidal agitation [29] (Figure 7). However, the choice of solvent is of interest in the solvent blending technique, as it is limited to polar solvents. This is a result of MXene's inherent solubility in polar solvents, hence, its compatibility with solvents of similar solubility parameters [29]. However, various surface treatments can cause MXene solubility in non-polar solvent entities. On the other hand, polymer matrices are also limited to several solvents. To achieve an effective solvent blending of MXene and polymers, the colloidal solution system may be thermodynamically altered, with the solvent compatible with both MXene as well as the polymer [28].

Oftentimes, after blending, MXene-nanoclusters are realized from the solution through evaporation, vacuum filtration, or precipitation to achieve a zero-solvent state. Various MXene-nanoclusters have been prepared to utilize

water-compatible polymer matrices such as cellulose nanofibrils, polyallylamine hydrochloric, PA, PAA, polydopamine, PEO, PEDOT:PSS, polyether polyamide block co-polymer, and PVA [29].

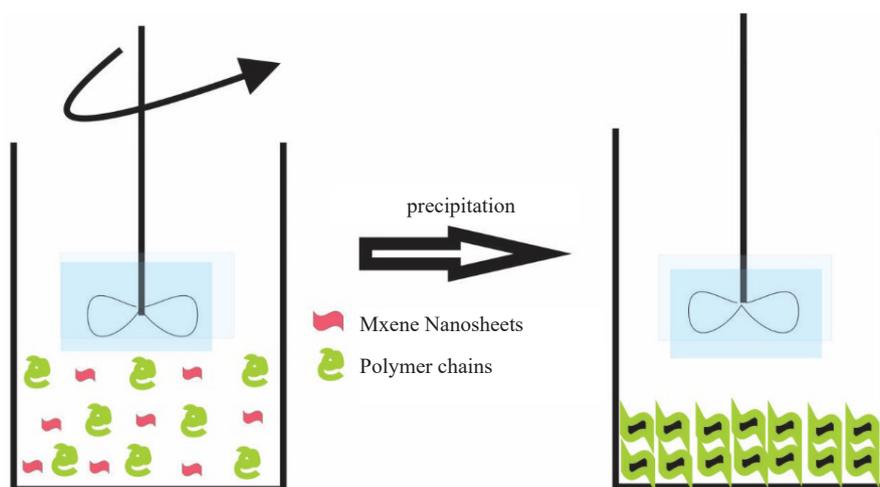


Figure 7. Solution blending of Polymers and MXene nanosheets to form nanoclusters

3.3 Melt blending process

In melt-blending, the incorporation of MXene into the polymer matrix is achieved above the polymer melting point. This is to allow the movement of the polymer chain to welcome the MXene nanosheets and possible grafting into the polymeric chain [63]. Melt blending involves processing techniques such as injection molding, extrusion, and sintering that can be employed to achieve MXene nanosheets even dispersion within and unto polymer matrices. These processes are mainly utilized for the blending of large-scale nanoclusters to achieve uniform clustering. However, most thermosetting polymers are not blended through this approach which is most likely employed for thermoplastic polymers. Also, high-temperature blending may cause oxidation of MXene as well as polymer chain deterioration. Notably, when compared with other 2-D materials relative to this blending technique, MXene has the advantage of high bulk density, which facilitates material transport through the hopper during the production process. Melt blending has been employed in the preparation of most MXene-thermoplastic-polymeric nanoclusters including MXene-PS, MXene-nylon 6, MXene-polyurethane, and MXene-phthalonitrile [28-29]. Surface treatment of MXene is often carried out to achieve good adhesion with the polymer matrix for optimum nanocluster properties, especially thermal properties.

3.4 Electrodeposition technique

The electrodeposition technique, conventionally called electroplating, is a vital technique employed for the fabrication of nano-clustered materials, which allows control over the properties, composition, and structure. The technique helps in the preparation of special materials with desirable enhanced properties which cannot be achieved through other techniques. The flexible low cost of the technology has given its use in the preparation of three- and two-dimensional materials which include films. The electrodeposition process is based on the principles of electrochemical occurrence related to the deposition or reduction of electroactive elements and compositional species on the cathode surface. This technique has been reported for the fabrication of MXene-polymeric nanocomposites, which involves the in-situ polymerization and deposition unto the desired material usually a glass electrode [19, 127, 128]. Hence, it is often employed for the coating of materials using polymer nanocomposites. However, controlling and designing of electrodeposition process involves many experimental factors for harnessed redox reaction during the process [129]. In the preparation of MXene-polymeric nanocomposites which involves conjugate polymers, over-oxidation of the conductive polymers affected by the presence of the MXene is probable [130-132]. This reduces the electrical

conductivity of the prepared nanocomposites as a result of the formation of the oxides [133].

4. Thermal properties of conductive MX-based polymeric hybrid nanoclusters

Thermal properties of polymer composite as illustrated by Zhang, Choi [134], [135], depend on the concentration, size, type, filler dispersion, and very crucially, the presence of a thermal barrier between polymer chains. MXene has good thermal stability as well as excellent thermal conductivity. MXene, when added to thermal insulators that are usually polymers, can transform them into conductive equivalents. In comparison to graphene-based nanoclusters, which have thermal conductivities of 0.14 to 0.41 W/(m·K) at a 2 wt% loading [136, 137]. MXene-based polymeric nanoclusters have shown better thermal properties of 0.5 W/(m·K) with lower filler loadings [138, 139]. To promote heat transfer kinetics, thermal conductivity necessitates strong connections between the inclusions and the polymer. When the concentration of MXene is high enough to create a network, its high inherent thermal conductivity greatly exceeds the inherent thermal resistivity of the polymeric matrix, resulting in uniform thermal conductivity, and increased thermal stability [140]. This section tends to analyze the thermal properties of conductive MXene-Ti₃C₂T_x-based polymeric hybrid nanoclusters.

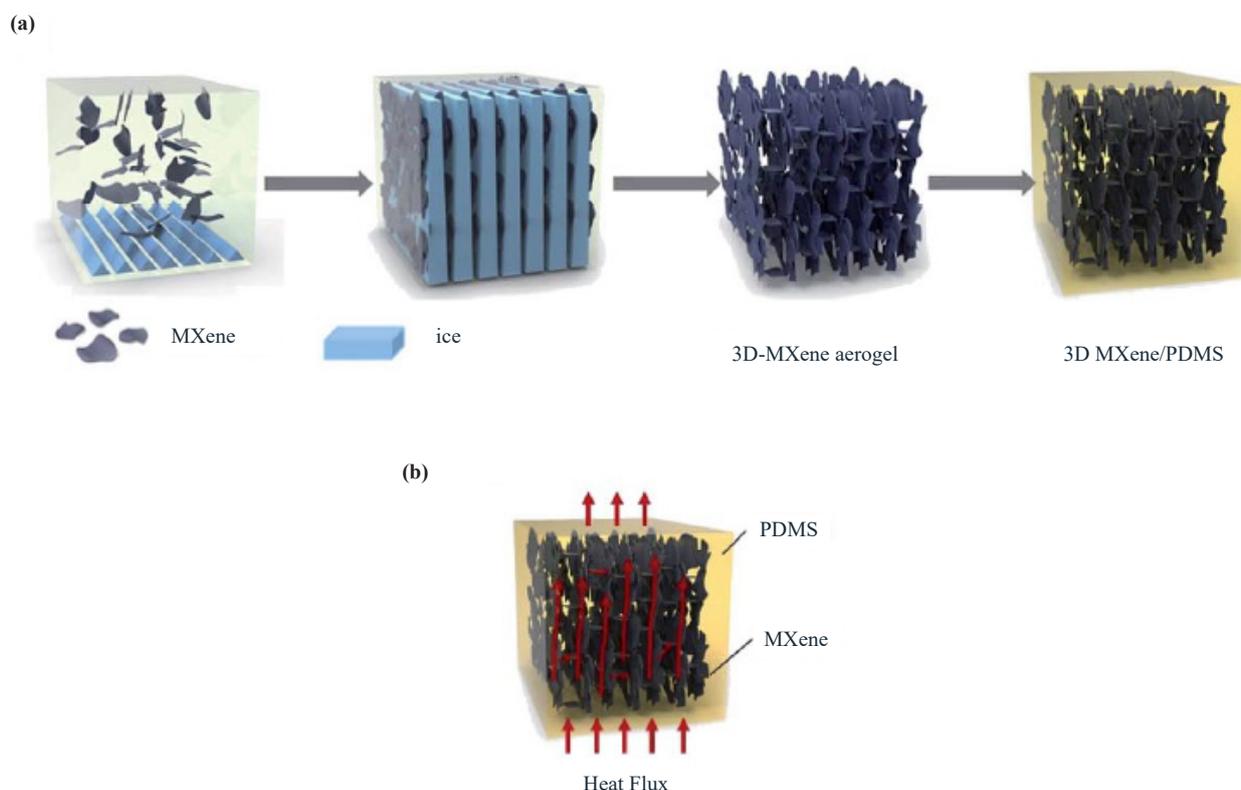


Figure 8. (a) the creation of a 3-dimensional MXene network through the freeze-drying approach, and inclusion in a PDMS matrix. (b) illustration of heat transfer pathways by MXene network in a PDMS matrix. Reproduced with permission from Ref. [11]

Based on theoretical calculations, the average MXenes' high thermal conductivities have been calculated to be 472, indicating its potential for usage in EMI shielding surfaces with excellent dissipation of heat [141]. However, regarding the macroscopic MXene-based nanoclusters for thermal conductive EMI shielding surfaces, fewer reports so far have been given. The easily-oxidized characteristics of MXene may contribute to its absence in thermal conductive EMI shielding film; taking example Ti₃C₂T_x MXene, the numerous active functional groups (-OH, = O, and -F) on the

nanosheet surface are readily oxidized into TiO_2 , especially in the high-temperature circumstances resulting in fast reduced electron and phonon transport efficiency on the MXene [142]. This will negatively impact thermal conductivity, making it unsuitable for use in EMI shielding devices [143].

Other researchers have looked into the thermal stability of MXene nanocomposite [144]. Creating a network between MXene sheets within the nanoclusters to build an MXene cluster is critical for developing an effective thermally conductive system. Percolation concentration is the concentration at which network creation occurs. Rather than randomly scattering MXene flakes, it is proposed to induce a 3-dimensional network of arranged MXene sheets within a polymer matrix to achieve low-concentration percolation as seen in Figure 8a.

As earlier said, the preparation of a one-directional, 3-dimensional porous MXene structure is probable by freeze-drying. As reported, the 3-D-oriented MXene structure inculcates excellent heat exchange pathways in a polymeric matrix (Figure 8b). The inclusion of just 0.7 wt% mono-layer Ti_3C_2 into the matrix of PDMS, a non-thermal conductive polymer, enhanced the thermal conductivity of the nanocluster by 220% and its thermal stability by 14 in arithmetic order of increase [145].

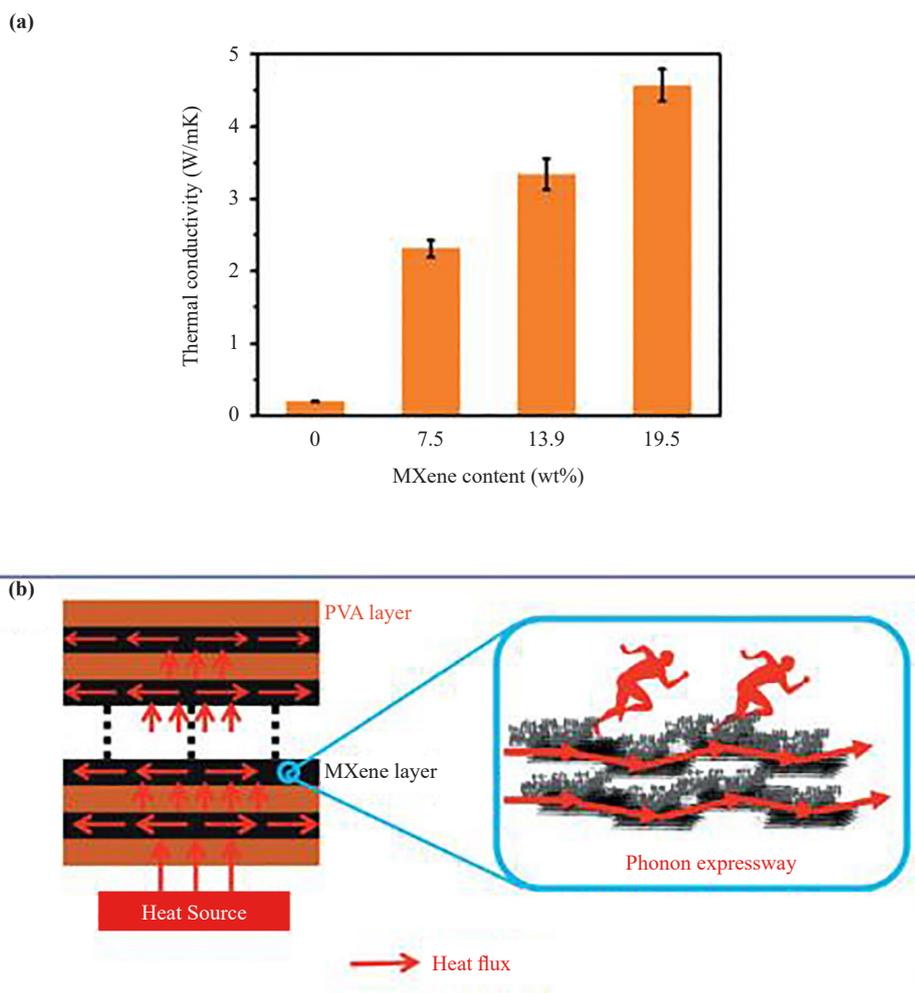


Figure 9. (a) plot of thermal conductivities of different MXene/PVA nanoclusters and pristine PVA; and (b) illustration of the thermal conductive pathways of MXene/PVA nanocluster. Reproduced with permission from Ref. [146]

Thermal conductivity and thermal conductivity mechanisms are shown in Figure 9. Relative to neat PVA, thermal conductivity was increased by 1,570%. The MXene forms a constant thermal conductive network throughout the matrix.

The heat flux was proficiently dissipated through the uninterrupted MXene layers [146].

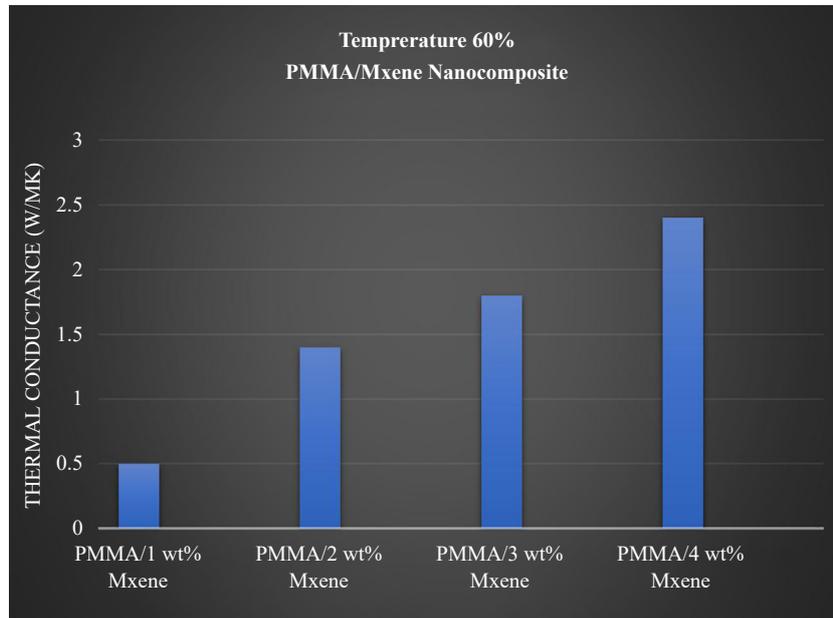


Figure 10. The effect of concentration of MXene on the thermal conductance of PMMA [148]

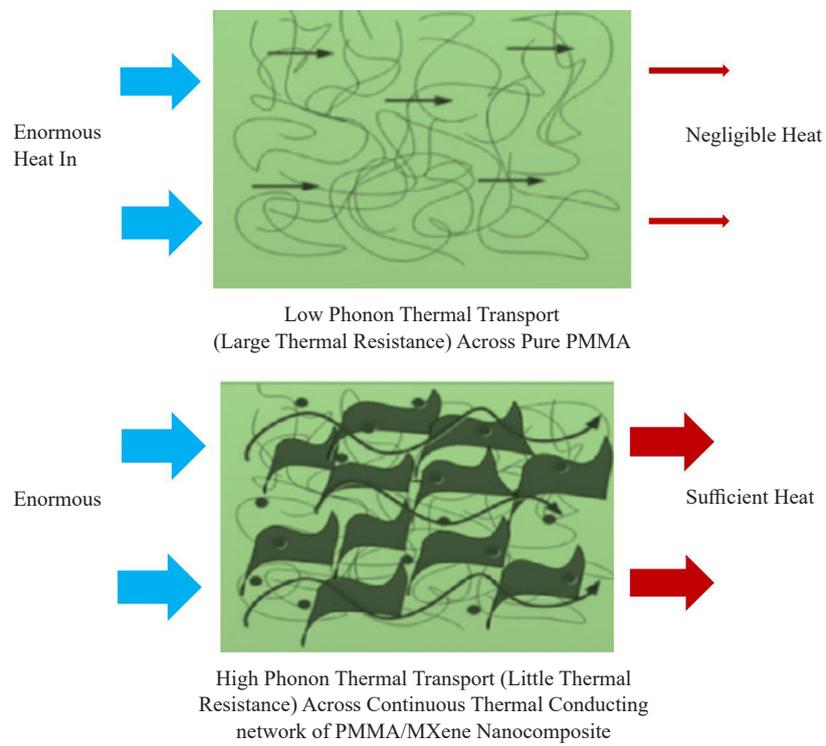


Figure 11. Illustration of thermal conductance of pure PMMA, and a composite of PMMA respectively [148]

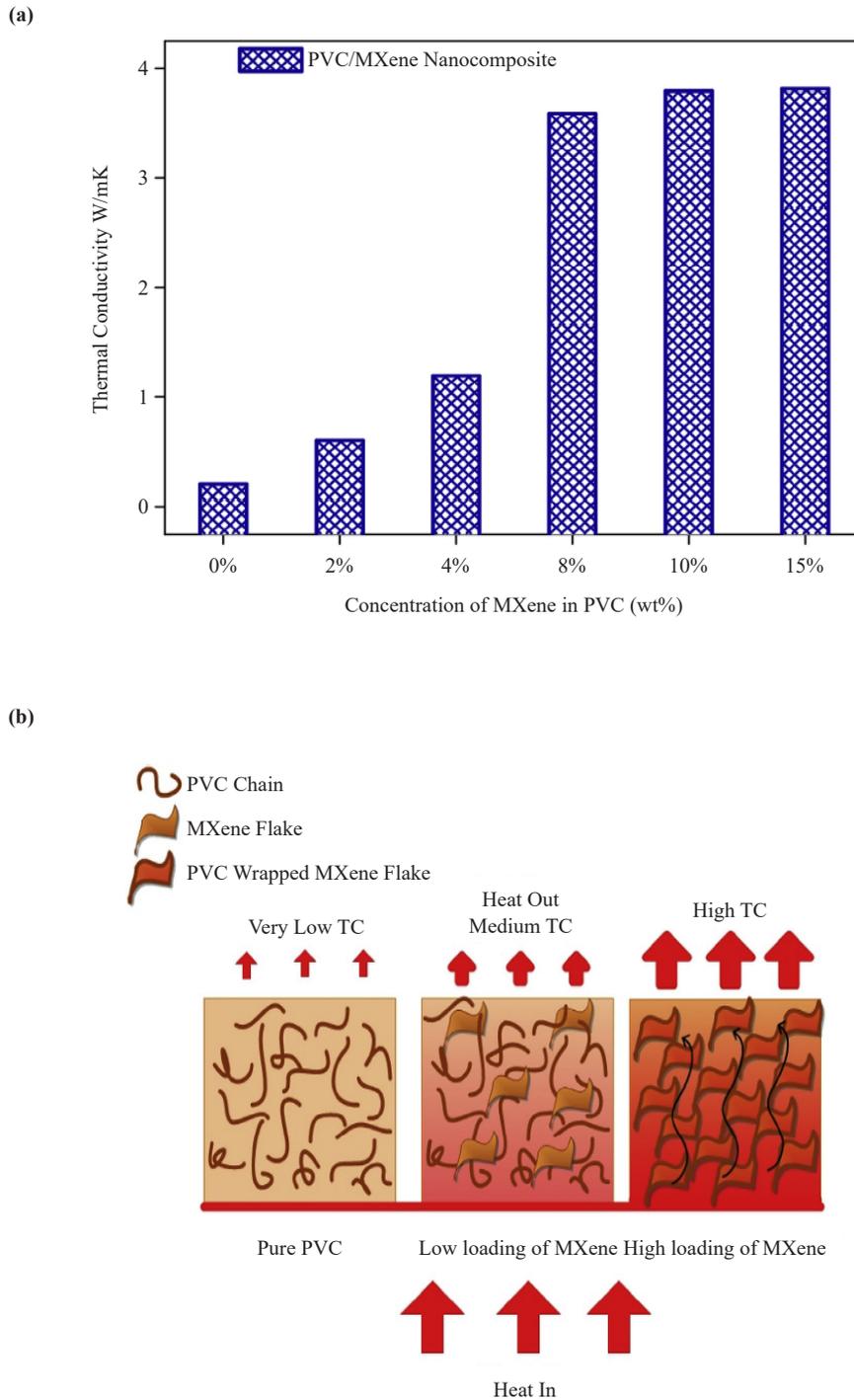


Figure 12. (a) Thermal conductivities of PVC/MXene nanoclusters Vs MXene loading, (b) diagram showing the thermal conductive network of PVC/MXene nanocluster. Reproduced with permission from Ref. [153]

The creation of a heat conduction network is one key mechanism responsible for the considerable improvement in the thermal conductance of PPMA. Because PMMA is an amorphous polymer with voids/spaces in its structure, increasing MXene content improves thermal conductivity by generating a heat conduction network [147]. However, the concentration of MXene significantly affects the conductivity of the polymer composite [134, 135]. MXene-

based nanocluster hybrid of PMMA/MXene was analyzed by Ul Haq, and Murtaza [148] using the common hot plate technique. A heat exchange contact that exists between the polymeric chain of PMMA is formed at a certain limit called the percolation threshold, here there's a high bridging ratio of MXene-MXene and the polymer chain [149]. Another reason for improved conductance according to Ul Haq, and Murtaza [148], is the distribution and compatibility of MXene within the polymer matrix. This results in strong surface and interfacial bonding of MXene sheets, which facilitates the transfer of heat by PMMA from one interface to another within the composite [150, 151]. Figure 10 shows the increasing heat transfer in the PMMA lactic structure due to the improving concentration of MXene. Another reason is the phonon scattering nature of MXene nanosheet which is due to the inherent high thermal conductivity, even distribution of MXene in the matrix, and high surface area reducing the interfacial performance of PMMA [141, 152]. An illustration of the thermal conductance of pure PMMA and a composite of PMMA is presented in Figure 11.

Mazhar and Qarni [153] investigated the thermal conductivity of the prepared PVC/MXene nanoclusters using the conventional hot plate method with varying concentrations of MXene monolayer nanosheets. Noticeably, there is a significant improvement in the thermal conductivity of PVC/MXene nanoclusters as shown in Figure 12 (a & b). As previously stated, the thermal conductivity of polymer composites is determined by a variety of characteristics, including size, concentration, type, filler dispersion, and, most importantly, the presence of a thermal barrier between polymer chains [134]. Consequently, Figure 12(a) implies that the increase in the concentration of MXene causes a significant increase in the thermal conductivity of the PVC. The thermal conductive network is the prominent factor among other factors, that explains the enhancement of thermal conductivity of MXene/PVC nanoclusters [147]. Hence the continuous increase in the concentration of MXene improves the thermal conductance of the composite by filling the voids in the Polyvinyl chloride matrix and establishing a connection across the MXene flakes/polymeric medium reaching a percolation threshold [149]. Figure 12(b) schematically explains the presence or absence of a thermal conductance network formed all over the polymer matrix in pure PVC and PVC/MXene nanocluster following a reduced and increased lodging of MXene respectively. The affinity of the MXene with PVC and the Phonon scattering behavior of MXene are significant reasons for the increased thermal conductivity of the polymer composite [141, 150].

Cao, Deng [147] used solution blending to examine the thermal conductance (TC) of a poly (vinylidene fluoride) (PVDF)/MXene composite (Figure 13). The investigation found that PVDF clusters with different concentrations of MXene (0-5wt%) had improved thermal conductivity as compared to pure PVDF. It is noteworthy that the PVDF composite with 5wt% MXene had the highest thermal improvement. This is due to some variables, the first of which is that MXene monolayer nanosheets are evenly scattered within the PVDF matrix, increasing the proximity ratio between them. Second, MXene in the matrix offers nucleation size for the PVDF medium, which is critical for enhancing composites' TCs. Finally, the stage interfacial compactivity between the MXene and PVDF matrix decreases the boundary thermal resistance because of the high surface area of the MXene nanosheets and hydrogen surficial bonding between the PVDF matrices.

High-thermal-conductivity and high thermal stability of MXene/PVA nanoclusters were prepared by Liu and Li [154]. The out-turn of the PVA matrix on MXene's heat characteristics is investigated. By providing strong Ti-O linkages and clinging to the surface of the MXene without a noticeable altering of the crystal structure, the polymer significantly improves the heat stability of the MXene. The TCs of pristine MXene and MXene/PVA composite are observed to be 55.8 and 47.6 W/(m·K), respectively, this is higher when compared with some metals and fewer 2-D materials.

Research on MXene-prepared conductive polymeric nanoclusters (MXCP) which include polyaniline (PANI), (poly(3,4-ethylene dioxythiophene): poly(styrene sulfonic acid)) (PEDOT:PSS), polypyrrole (PPy), with focus on personal thermal management (PTM), have been reported [155, 156]. The psychological perception of an individual regarding the degree of coldness and hotness of the environment is referred to as PTM [157, 158]. Thermal comfort must be balanced to sustain an individual's physiological and/or psychological well-being. Some reviews on MXCP composites focus on personal comfort devices, for example [145] lodged silicon onto Polypyrrole/MX-designed textile, prepared through in-situ polymerization, was employed for Joule heating. The prepared nanocluster textiles demonstrated an increased conductivity up to 1,000 (W/(m·K)) per 2.33 sq and retained a good conductivity after 1,000 cycles with thermal resistance ranging from 39 to 61 K/W. The high-quality thermally enhanced textile was used to create a self-heating fabric for personal heat management. It was observed that the MX-PPy-silicon decorated textile improved the joule heating property of the designed fabrics from 40 °C to 79 °C, which can be compared to the Joule

heater prepared with MXene functionalized montmorillonite [159]. Surprisingly, the constructed heater's durable effectiveness was ascertained when it showed a constant temperature of 57 °C for 3,600 seconds after attaining the saturation temperature. Such exceptional heating capability at such a low driving voltage could pave the way for the development of wearable and smart heating systems.

Not long ago, Jiang, Yuan [160], [161] fabricated PEDOT and MXene incorporated multi-task cotton garments, for personal heating applications. This was achieved through spray-coating and vapor phase polymerization techniques as illustrated in Figure 14. The surface temperature of the designed textile structure increased from 71 to 78 °C, when 9 V voltage was applied. Further increase in the voltage to 12V, results in a tremendous increase in surface temperature to 193 °C as shown in Figure 14 c.

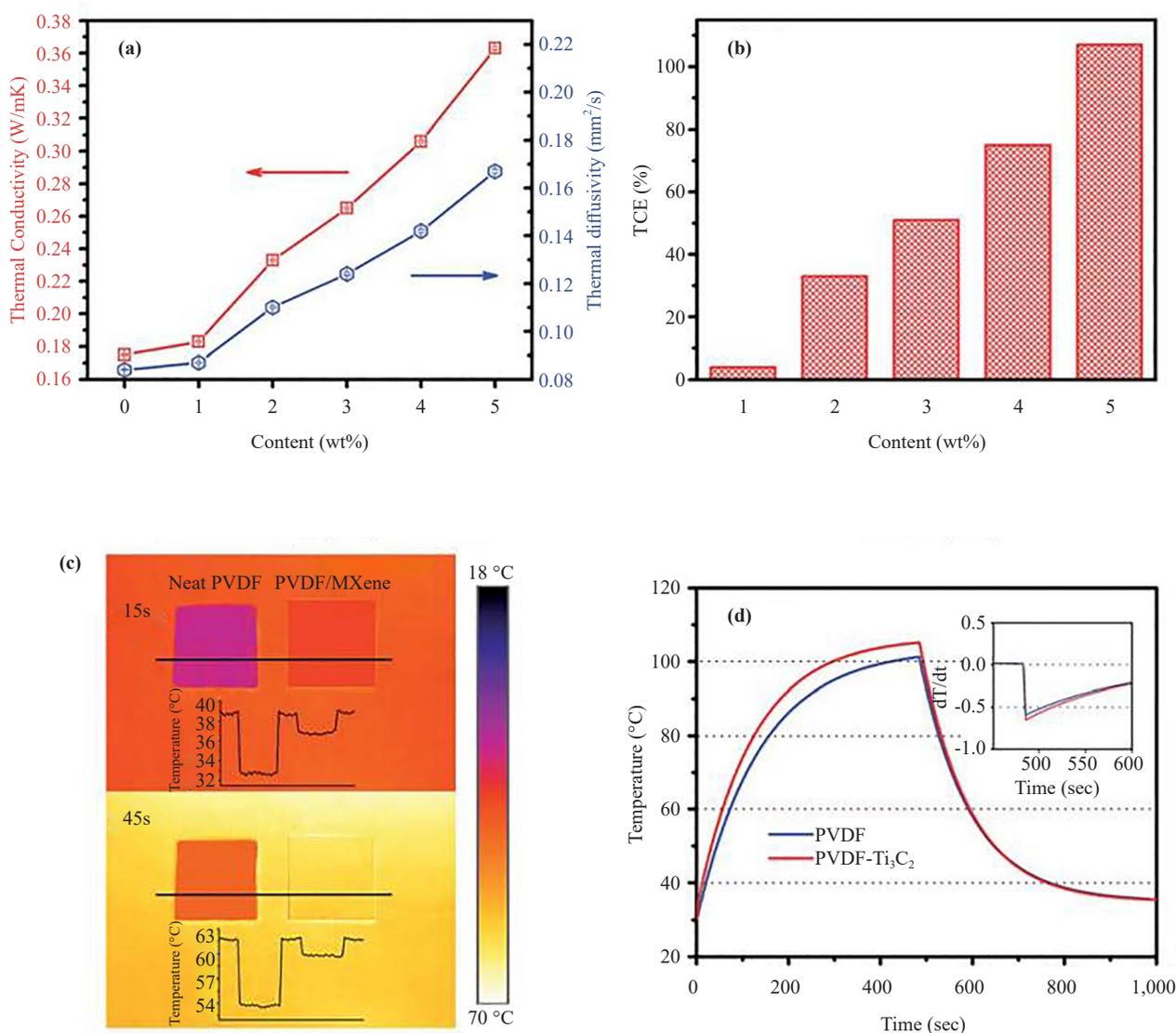


Figure 13. (a) effect of different fiber loading on the thermal diffusivity and thermal conductivity of PVDF composite (b) Thermal conductivity improvement of PVDF clusters compared to pristine PVDF. (c) Infrared images of pristine PVDF, and PVDF clusters with 5 wt% MXene, with 70 °C and 18 °C as the high and low temperatures respectively. (d) the varying surface temperature when heated and cooled, with 482 seconds as starting time. Reproduced with permission from Ref. [147]

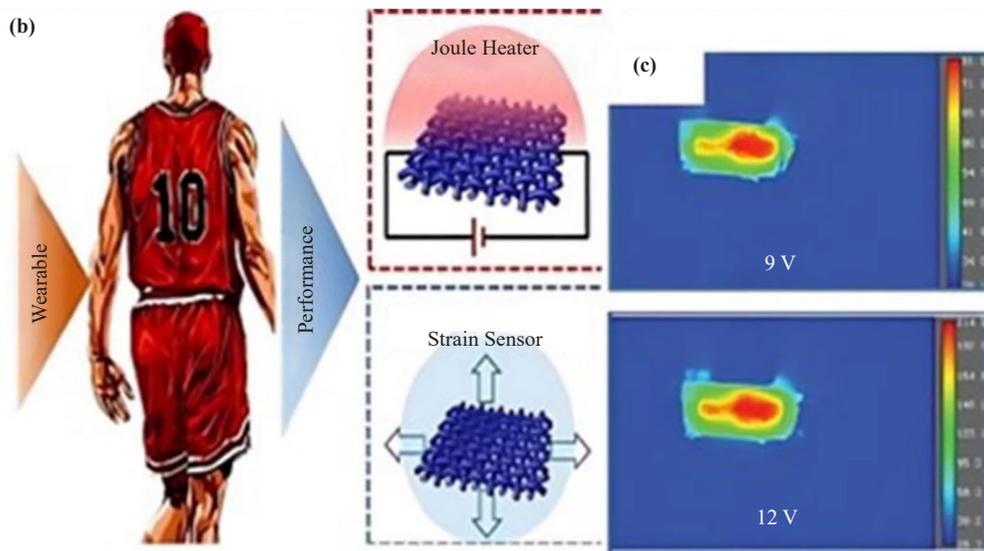
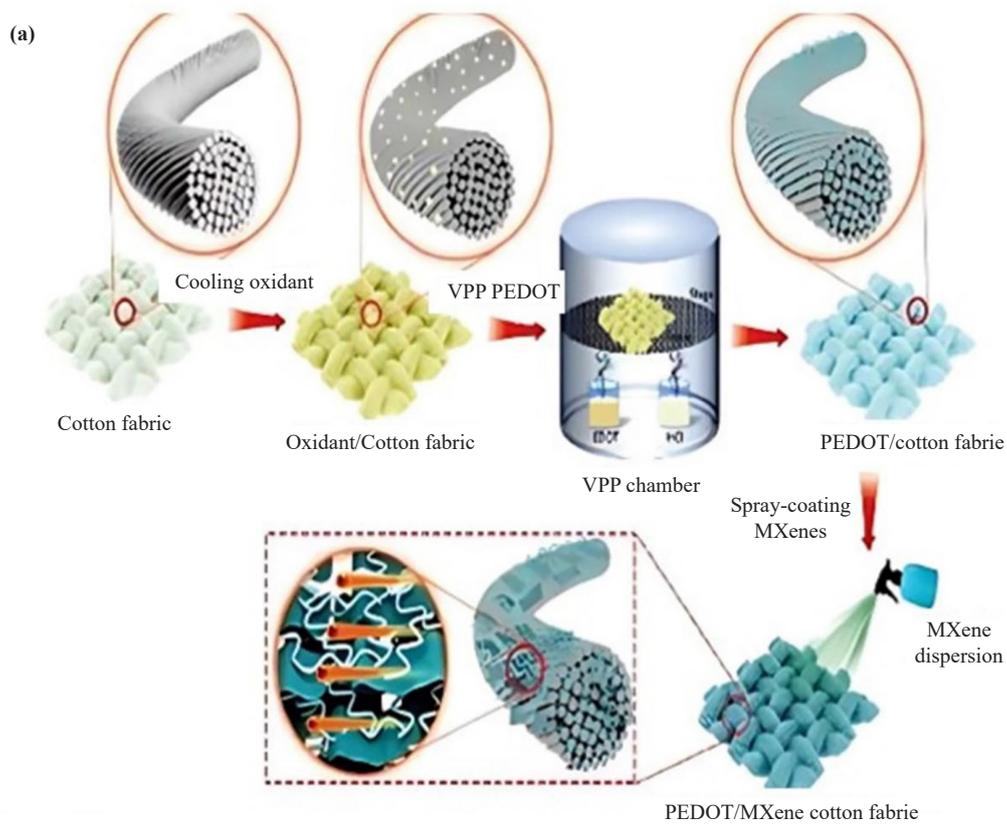


Figure 14 (a. and b.) Preparation and assembly of MXene-conductive polymer-coated multi-task fabrics, respectively [160]. (c) heating behavior of designed fabrics at varying inputted voltages [161].

5. Electrical properties of conductive MXene-polymeric hybrid nanoclusters

Regardless of the influence of surface groups, density functional theory demonstrates that pure MXenes have metal-like electrical conductivity [162]. Ascribable to the variability in the thickness, surface functionality, and layering tendency, MXenes have a variety of electronic characteristics which include metallic, energy storage, and semiconducting properties. The sorts of functional groups and their arrangement on the 2-D plane are related to the electrical structures of functionalized MXenes with -OH and -F exhibiting apparent semiconducting properties, according to theoretical simulations [162]. Depending on the synthesis and stacking procedure, MXenes have electrical conductivities ranging from $1 \text{ S}\cdot\text{cm}^{-1}$ to thousands of $\text{S}\cdot\text{cm}^{-1}$ [163]. Most studies on the electrical properties of MXene-polymeric nanoclusters are for electromagnetic interference shielding applications. $\text{Ti}_3\text{C}_2\text{T}_x$, the most widely researched MXene, has been integrated into many polymer matrices so far, because of their excellent layered structure and inherent electrical conductivity.

MXenes were deemed suitable nanosheets for creating multi-task and flexible fabrics [145]. Lodging in-situ polymerized PPy-loaded MXene flakes unto PET fabrics followed by a silicone coating resulting in a hydrophilic and highly electrically conductive textile. The resulting multifunctional fabric has an enhanced electrical conductivity of $\approx 1,000 \text{ S}\cdot\text{m}^{-1}$ when compared with pristine PPy-PET composite [123]. Following the strong quick-drying tendency of the fabric, the dependence of the composition of the polypyrrole/MXene hybrid in the textile and the electrical conductivity on the dip-coating cycle briskly increased with the dip-coating cycle number (Figure 15).

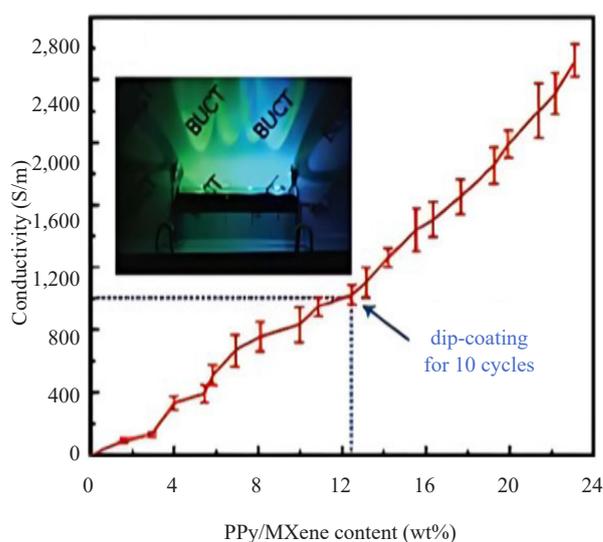


Figure 15. Plot of MXene-textile conductivity vs. Polypyrrole/MXene hybrid composition in textiles with varying dip-coating cycle numbers. Redrawn with permission from Ref. [145]

Utilizing a composite of $\text{Ti}_3\text{C}_2\text{T}_x$ -MXene nano-flakes and poly(3,4-ethylene dioxythiophene): polystyrene sulfonate, a one-step wet-spinning technique for fabricating highly conductive fibers was reported [7]. Fibers with a known electrical conductivity of $\approx 1,489 \text{ S}\cdot\text{cm}^{-1}$ were produced using this method. When MXene inclusion was raised to 30 wt%, the electrical conductivity of PEDOT:PSS fiber dropped to $548 \pm 62 \text{ S}\cdot\text{cm}^{-1}$. The conductivity rose when the MXene loading was raised further, reaching a maximum value. These findings imply that at lower loadings (30 wt. %) of MXene, the conductivity of PEDOT:PSS dominated the fiber conductivity and that the loading of MXene-flakes disrupted the orderly packing of PEDOT, decreasing the fiber conductivity. The conductivity of MXene becomes more prominent at high MXene loading due to improved charge transport between MXene sheets. In another study, an unattached, flexible, and ultra-thin MXene/poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) cluster film with a “stonework” structure was biomimetically designed and manufactured through a vacuum-assisted

filtering method [164]. The electrical conductivity of the polymeric cluster films fell dramatically as the PEDOT:PSS composition snowballed. The electrical conductivity of the pure MXene film was 1,000 S/cm, while the electrical conductivity of MXene to PEDOT:PSS was slowly reduced from 340.5 to 20.4 S/cm by reducing the MXene to PEDOT:PSS ratio from 7:1 to 3:1.

Following the fabrication of core-shell $\text{Fe}_3\text{O}_4@\text{PANI}$ composites, vacuum-assisted filtration was used to create a lightweight and flexible MXene/ $\text{Fe}_3\text{O}_4@\text{PANI}$ cluster film with a burger-like intercalation architecture [165]. With more MXene, the electrical conductivities of the ultrathin nanoclusters with MXene nanosheets are enhanced. Utilizing hydrochloric acid and dodecylbenzene sulfonic acid (DBSA), polyaniline (PANI) was co-doped, and a few-layered MXene was produced using ionic intercalation and a sonication-employed technique [166]. Vacuum-assisted filtering was used to create MXene/co-doped PANI cluster films. The electrical conductivity improved as the mass fraction of MXene increased. The thickness of MXene/c-PANI cluster film was only 40 μm when the mass ratio of MXene to c-PANI was 7:1, and the electrical conductivity was dramatically increased to 24.4 $\text{S}\cdot\text{cm}^{-1}$ as a result.

The Resistance (R), resistivity (ρ), length (L), sheet resistance (R_s), and cross-section ($A = wt$; where w is width and t is thickness) can all be used to compute electrical conductivity (s). The resistance ($R = (\rho L)/A$) of the material is calculated using the arithmetic multiplication of resistivity and length divided by cross-section. The result of multiplying the values of R_s and t is the ρ [167]. The conductivities of nanoclusters made from the MXene-PAT-poly(p-aminophenol)-polyaniline copolymer were investigated by Raagulan et al. [168]. The electric conductivity (EC) of the MXene-PAT-poly (p-aminophenol)-polyaniline copolymer cluster was 7.0 $\text{S}\cdot\text{cm}^{-1}$. The nanoclusters of polyaniline (PANI), poly para-aminophenol (PpAP), PANI-PpAP, polythiophene (PTH), and Polypyrrole (PPy) polymers were also examined [168]. The thickness of the clusters ranged from 0.4 to 1.6 mm. Surface resistance and resistivity ranged from 1.6-160,000 Ω and 0.128-256,000 Ωcm , respectively, in the composites. The composites had conductivities ranging from 3.906×10^{-5} to 7.0 $\text{S}\cdot\text{cm}^{-1}$. In comparison to other composites, the MXene-PAT-PPY had a much higher resistance and resistivity, as well as an extremely poor electrical conductivity of 3.906×10^{-5} $\text{S}\cdot\text{cm}^{-1}$.

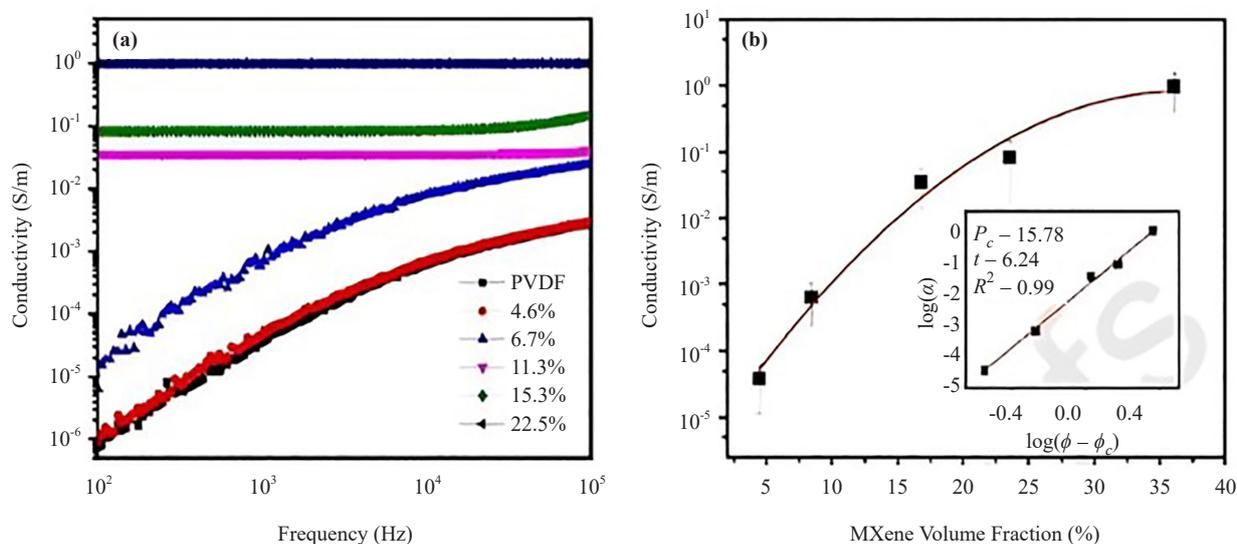


Figure 16. (a) electrical properties of MXene-polymer nanocomposites with varying volume fractions and frequency dependence. b) The effect of MXene filler loading on conductivity. Reproduced with permission from Elsevier [169]

The two-dimensional $\text{Ti}_3\text{C}_2\text{T}_x$ MXene/Polyvinylidene fluoride (PVDF) nanocomposites were tested for electrical conductivity [169]. The key challenge for effective electron transport in a non-conducting matrix is the arrangement of a well-connected conducting network with appropriate inclusion contents [170]. The AC electrical conductivity (σ_{AC}) of various concentrations of packed MXene lodged within the PVDF matrix was studied as a function of frequency (Figure 16a), and the elevated σ_{AC} after including different filler loading content was a result of the choosy localization of

MXene sheets in polymeric composite, whereas pristine PVDF demonstrates non-conductive behavior [171]. MXene-PVDF films' alternative current (AC) conductivity was measured as a function of frequency [172]. The AC electrical conductivity of every film enhanced in an almost transitional pattern as the frequency was increased. As expected, the highly conductive characteristic of MXene caused a rise in the AC conductivity of all uniform films when the MXene concentration was increased [173]. The increase in MXene volume fraction also increased the conductivity of the polymer nanocluster (Figure 16b).

Multilayered casting was used to create PVA/MXene films having an alternating multilayered structure [146]. The continual MXene sheet created a close network for electron conductivity. The PVA/MXene films with MXene contents of 7.5 wt%, 13.9 wt%, and 19.5 wt% exhibited electrical conductivities of 17, 379, and 716 $\text{S}\cdot\text{m}^{-1}$, respectively. The continual MXene sheet formed a connected conductive network, which contributed to the improvement of the electrical conductivity of the PVA/MXene multi-layered films. Furthermore, when the overall mass fraction of MXene grew, the thickness of the MXene sheet also increased. This allowed for the creation of a considerably effective conductive network throughout the film, resulting in increased electrical conductivity in the 13.9 and 19.5 wt% PVA/MXene films. Electrospinning was also used to successfully manufacture MXene-filled PVA nanofibers. The DC conductivity of PVA nanofibers containing 0.14 wt% MXene was 0.8 $\text{mS}\cdot\text{cm}^{-1}$ [174].

A simple freeze-drying process was used to create porous MXene/PVA cluster foams made of few-flaked MXene and PVA [175]. Due to the insulating holes being eliminated, the conductivity of the nanoclusters increased from 8.3×10^{-6} to $8.0 \times 10^{-4} \text{ S}\cdot\text{m}^{-1}$. Electrostatic coupling of positive polystyrene microspheres with negative MXene nanoflakes, followed by compression molding, was demonstrated as a method for producing improved conductive MXene-polystyrene nanoclusters [176]. The resulting nanoclusters have a low percolation threshold of 0.26 vol % and a phenomenal conductivity of 1,081 $\text{S}\cdot\text{m}^{-1}$ thanks to MXenes' high conductivity and very efficient conducting network within the polystyrene matrix. In a different study, MXene was combined with either a charged polydiallyl dimethylammonium chloride (PDDA) or an electrically neutral polyvinyl alcohol (PVA) [177]. The electrical conductivities of the MXene films were measured to be on the order of $2.4 \times 10^5 \text{ S}\cdot\text{m}^{-1}$ using a typical four-probe approach, which is greater than carbon nanotube or graphene [178]. The as-prepared clusters were flexible and had electrical conductivities of up to $2.2 \times 10^4 \text{ S}\cdot\text{m}^{-1}$ for the MXene/PVA cluster film, and the films comprising PDDA have a conductivity of up to 2,000 $\text{S}\cdot\text{m}^{-1}$. The inclusion of polymer chains between the $\text{Ti}_3\text{C}_2\text{T}_x$ sheets is thought to be the cause of the noticed decrease in conductivity when likened to pristine MXene films. Flexible polymer sheets, silicon, nylon fiber, stretchable poly (dimethyl siloxane), and glass were all effectively coated with MXene multilayers. MXene multilayer coatings that are conductive and conformal and can withstand bulk mechanical distortion while retaining a conductivity of up to 2,000 S/m have been reported [179].

Electrical conductivities of three-dimensional MXene/C hybrid foam/epoxy nanoclusters have been examined [180]. Ionic intercalation and sonication-assisted methods were employed to produce few-layered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, while sol-gel followed by thermal crushing was utilized to create porous three-dimensional MXene/C hybrid foam (MCF). Vacuum-enabled curing and impregnation methods were then employed to fabricate MCF/epoxy nanoclusters. The electrical conductivity of the nanocomposites was found to be highest at 184 $\text{S}\cdot\text{m}^{-1}$. Wang et al. looked into the electrical characteristics of heated MXene/Epoxy nanocomposites in another work [181]. Solution casting was used to create annealed MXene/epoxy nanoclusters. At lower concentrations, $\text{Ti}_3\text{C}_2\text{T}_x$ was randomly dispersed in the epoxy matrix, and MXene was frequently separated or enveloped by the epoxy matrix, hardly permitting them to come into touch with each other. As a result, forming efficient conductive networks was challenging, and electrical conductivities improved slowly. More contact with MXene could gradually create conductive networks as the mass fraction of MXene rose, resulting in enhanced electrical conductivities. The conductive networks of MXene-MXene became more efficient as the amount of MXene added increased, and the ability to conduct electrons increased as well, resulting in optimal electrical conductivity. The electrical conductivity of $\text{Ti}_3\text{C}_2\text{T}_x$ /epoxy nanocomposites reached a maximum of 38 $\text{S}\cdot\text{m}^{-1}$ when the mass fraction of MXene was 15 wt%. The electrical conductivities of heated MXene/epoxy nanoclusters changed similarly to MXene/epoxy nanocomposites but at a faster rate. It had a higher electrical conductivity and a slower percolation threshold (Figure 17). The electrical conductivity of annealed MXene/epoxy nanocomposites reached up to 105 $\text{S}\cdot\text{m}^{-1}$ when the mass fraction of heated MXene was 15 wt%.

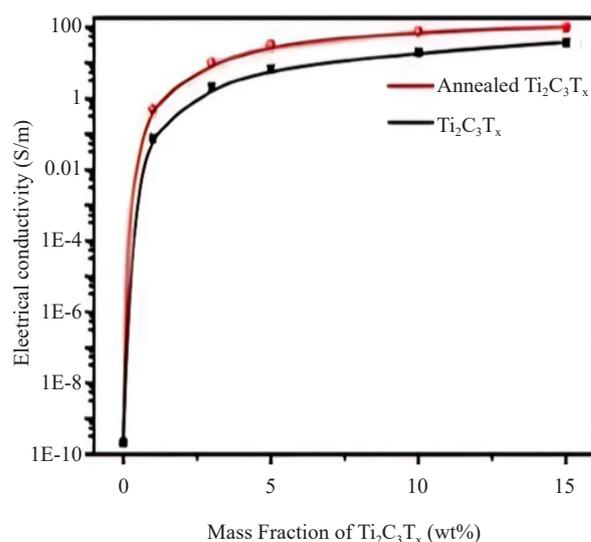


Figure 17. Electrical conductivities of the MXene/epoxy and heated MXene/epoxy nanocluster. Reproduced with permission from Elsevier [181]

Nanoclusters of graphene/MXene/epoxy (rGMH/epoxy) were developed [182]. To make the honeycomb structure rGO-MXene, an Al_2O_3 honeycomb was used as a template, and MXene was subsequently self-assembled on the rGH by electrostatic adsorption (rGMH). Through the addition of epoxy, rGMH/epoxy nanocomposites were successfully prepared. With the same MXene loading, the conductivity of rGMH/epoxy nanocomposites decreases as the honeycomb cell size grows. When using a cell size of 0.5 mm and 1.2 wt% rGO + 3.3 wt% MXene loading, much higher conductivity values ($387.1 \text{ S}\cdot\text{m}^{-1}$) were obtained.

Following their remarkable metallic nature and electrical conductivity, MXenes are deemed attractive close substitutes to graphene. The hydrophilicity of MXene films, on the other hand, may have an impact on their reliability and stability when used in hydrated conditions. By stacking MXene flakes into films and then using a hydrazine-induced foaming technique, an efficient and simple method for fabricating hydrophobic, flexible, and freestanding MXene foam with optimum strength has been reported [183]. Contradicting the common hydrophilic MX materials, the MXene foams unexpectedly have excellent water-resisting surfaces and durability. The electrical conductivity of the MXene sheet was up to $400,000 \text{ S}\cdot\text{m}^{-1}$. The samples' thickness grew after foaming, whereas their electrical conductivities dropped. This was due to the insulating holes that had been inserted. Additionally, because of the high aspect ratio, large specific surface area, and enough terminated OH groups, 2-D MXene was prepared and used as a common inclusion. To ascertain the role of MXene on membrane microstructure and proton conduction properties, it was introduced into a polymer matrix. Membrane matrixes were made up of phase-separated and non-phase-separated (basic chitosan) polymers [184]. The membranes' proton conduction properties were investigated. It is shown that MXene has a considerable promotion effect on the membrane proton conduction by enabling both Grotthuss-type proton transfer and vehicle-type, resulting in multiple higher proton conductivity under varied conditions for all polymeric cluster membranes.

By creating linked MXene networks in the NR matrix, Luo et al. [185] established an effective vacuum-assisted filtering technique for the manufacture of highly conductive and flexible MXene/natural rubber (NR) nanoclusters. High electrical conductivities of polymer nanoclusters with low MX concentration remained a challenge. There is an insulator-to-conductor transition as the MXene concentration increases, and the fitting results gave the nanoclusters one of the lowest percolation thresholds of 0.91 vol%. Furthermore, for 3.10 vol% and 6.71 vol%, excellent electrical conductivities of 500 and $1,400 \text{ S}\cdot\text{m}^{-1}$ were attained, respectively. The usual transitional ohmic property of their I-V curves, as well as the higher gradients with increasing concentration, corroborated the increased electrical characteristics of the MXene/NR nanoclusters. Mayer Berger and colleagues prepared and analyzed polymer-MXene composite nanofibers [186]. Delaminated MXene flakes were electrospun with alginate/PEO, poly (acrylic acid) (PAA), poly (vinyl

alcohol) (PVA), and polyethylene oxide (PEO). The structure and characteristics of nanofibers with minor amounts of delaminated MXene (1% w/w) were compared and examined to those of pristine polymer nanofibers. The inclusion of MX enhanced the electrical conductivity of most polymer solutions. The conductivity of the 1% (w/w) MXene/PEO solution increased by 73.6% when compared to the conductivity of PEO alone. In comparison to their basic polymer solutions, 1% (w/w) MXene/PEO/alginate and 1% (w/w) MXene/PVA showed a 34.6% and 6.2% improvement in conductivity, respectively. The conductivity of the MXene/PAA solution at 1% (w/w) was essentially unaffected, with only a 0.9% drop. The conductivity data support the 1% (w/w) MXene/PAA solutions, indicating weak bonding between the two constituents.

The preparation and characterization of MXene-Polyacrylamide (PAM) nanocluster films were evaluated [187]. Inter-layering of dimethyl sulfoxide between MXene layers resulted in complete delamination of the MXene layers, resulting in a homogeneous distribution of solvent-resistant MXene nanoflakes in wet PAM solutions. Polymeric cluster solutions containing almost 75% polymer were synthesized. The conductivity of the as-fabricated cluster samples was improved greatly to $3.3 \times 10^{-2} \text{ S} \cdot \text{m}^{-1}$ with only 6 wt% (1.7 vol%) MXene inclusion. Casting was used to create transparent, flexible, and electrically conductive thin nanocluster films based on a polyamide matrix functionalized with two-dimensional MXene nanoflakes [188]. The optimum reported electrical conductivity was $1.4 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ for the cluster loaded with 5 wt% MXene, while the percolation threshold of the MXene inclusion within the PAM matrix was found to be 0.05 vol%. The as-fabricated MXene has an electrical conductivity of $9.1 \text{ S} \cdot \text{cm}^{-1}$, while the MAX phase has a conductivity of $172 \text{ S} \cdot \text{cm}^{-1}$.

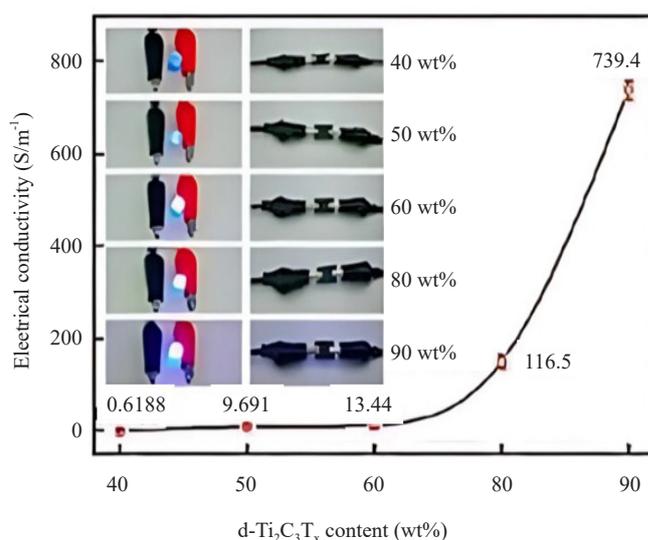


Figure 18. Plot of electrical conductivity versus d-Ti₃C₂T_x inclusion for the d-Ti₃C₂T_x/CNF cluster paper flakes with varied d-Ti₃C₂T_x inclusions. Reproduced with permission from Elsevier [170]

Conductive MXene/cellulose nanofiber (CNF) films were investigated by Zhan et al. [189]. By developing a well-established conductive channel, the composite paper's conductivity gradually rose as the MXene content grew. The electrical conductivity of the composite paper with 20 wt% MXene was $2.1 \text{ S} \cdot \text{m}^{-1}$. An increase in MXene content gives additional opportunity for MXene nanoflakes to overlap in MXene/CNF composite sheets, resulting in better conductivity. With 50 wt% MXene loadings, an optimum conductivity of $2,837 \text{ S} \cdot \text{m}^{-1}$ was achieved. The causes for the composite papers' ideal conductivity were explained because of the extraordinarily high MXene loadings, which provided composite papers with effective conduction pathways. Secondly, the orientated alignment of 2-D MXene nanoflakes resulted in a flawless connection and a larger overlap area. Finally, 1-D CNFs resulted in reduced re-stacking between MXene nanoflakes. Sequel to the fast-increasing usage of electrical communication equipment, a vacuum-filtration-induced self-assembly approach was used to create flexible and ultrathin MXene (d-Ti₃C₂T_x)/CNF cluster

paper with a nacre-like lamellar structure [190]. The electrical conductivity of the MXene/CNF cluster paper was $739.4 \text{ S}\cdot\text{m}^{-1}$ when the content of $\text{d-Ti}_3\text{C}_2\text{T}_x$ was 90 wt%, (Figure 18). The $\text{d-Ti}_3\text{C}_2\text{T}_x$ sample had an electrical conductivity of $1,142.5 \text{ S}\cdot\text{m}^{-1}$. The electrical conductivity of the $\text{d-Ti}_3\text{C}_2\text{T}_x/\text{CNF}$ cluster paper decreased when likened to the $\text{d-Ti}_3\text{C}_2\text{T}_x$ sample because CNFs are an insulating polymer. Fortunately, when compared with the conventional dielectric polymers, the CNFs have a unique 1-D nanofiber structure, resulting in low non-conductive interactions with 2-D conductive $\text{d-Ti}_3\text{C}_2\text{T}_x$ nanoflakes. Furthermore, the vector arrangement of the 2-D $\text{d-Ti}_3\text{C}_2\text{T}_x$ nanoflakes along the planar direction can produce a conductive network, which assures the sufficient linkage of $\text{d-Ti}_3\text{C}_2\text{T}_x$ nanoflakes, thanks to the cohesive action of CNFs.

6. Capacitive energy storage applications of conductive MXene-MXene-polymeric hybrid nanoclusters

The extensive and unique physicochemical, mechanical, optical, electrochemical, and electronic properties of MXene and conducting polymers have drawn the attention of researchers. They are keen on designing high-performance energy storage clusters using these materials to address the growing demand in the technology sector for instant power supply to wearable electronics [64]. The use of conducting polymers alone is a well-developed technology but there are concerns with it in terms of practicability, prompting researchers to look for necessary modifications to the architecture for optimal performance. On the heels of this research adventure, MXene-based conducting polymeric hybrid nanoclusters were developed to simultaneously maximize the individual advantages of the two materials while making up for their inherent functional deficiencies. In this section, the recently emerging progress in the applications of conductive MXene-based polymeric hybrid nanoclusters in energy storage systems is elucidated. The preparation techniques and the electrochemical performance of the nanoclusters are also described. The discussions are based on the three MX-polymeric nanoclusters (MX-PPY, MX-PANI, and MX-PEDOT:PSS). This presents insight and a technological path for preparing high-capacitive MXene-PPy, MXene-PANI, and MXene-PEDOT:PSS clusters for applications in energy storage systems.

6.1 Applications of MXene-Polyaniline (PANI) nanoclusters in energy storage devices

PANI is a conducting polymer with an organically connected semiconducting chain that belongs to the semi-flexibility rod-like polymeric class. It exhibits exceptional temperature inhibition characteristics, mechanical and electrochemical properties, solubility in various types of solvents, and eco-benign stability [191, 192]. PANI is also known as aniline black and comes in a variety of forms depending on the degree of oxidation. Pernigraniline base refers to completely oxidized PANI; emeraldine base refers to partially oxidized PANI; and leucoemeraldine base refers to completely reduced PANI [192, 193]. PANI is a good conducting polymer owing to its ease of synthesis, tunable characteristics, high polymerization yield, inexpensiveness, and environmental stability. PANI has potential uses in energy storage, electrodes, EMI shielding, sensors, solar cells, and nonlinear optics, among others [192].

The creation of PANI-nanoclusters with inorganic nano-reinforcement like MXene is a promising strategy to improve PANI's performance and characteristics. This results in a nanocomposite that demonstrates appreciable synergistic/complementary characteristics. The applications of these nanoclusters are found in energy storage, LEDs, electrochromic gadgets, electrostatic discharge systems, batteries, EMI shielding, chemically and biochemically manufactured sensors, etc. [194]. However, the focus of this section is on its application in energy storage gadgets.

The fabrication of high electrochemical performance supercapacitor electrodes using a graphene-encapsulated MXene/polyaniline (GMP) composite has been studied by Fu et al. [195]. The GMP electrode so developed has enhanced cycle stability and electrochemical performance. It has a high gravimetric capacitance value of $635 \text{ F}\cdot\text{g}^{-1}$, and a volumetric capacitance of $1,143 \text{ F}\cdot\text{cm}^{-3}$ with exceptional cycling stability of 97.54% after 10,000 cycles at a current density of $1 \text{ A}\cdot\text{g}^{-1}$. Besides, the pouch-type asymmetric supercapacitor produced utilizing GMP as a positive electrode and graphene as a negative electrode has a high energy density value of $42.3 \text{ Wh}\cdot\text{kg}^{-1}$ at a power density of $950 \text{ W}\cdot\text{kg}^{-1}$ and excellent cycle stability of 94.25% after 10,000 cycles at $10 \text{ A}\cdot\text{g}^{-1}$.

In another study, the significance of high energy density, as well as improved capability rate in supercapacitors

for flexible electronics, was especially highlighted. PANI-NTs/MXene nanoarchitecture was synthesized through a facile and self-alignment of 1-D PANI nanofibrous polymer and 2-D MXene nanosheets providing hyper-elevated rate capability, highly improved specific capacitance ($596.6 \text{ F}\cdot\text{g}^{-1}$ at $0.1 \text{ A}\cdot\text{g}^{-1}$), distinctive cyclability (94.7% after 5,000 cycles), optimum energy density ($25.6 \text{ Wh}\cdot\text{kg}^{-1}$ at $153.2 \text{ W}\cdot\text{kg}^{-1}$), power density ($1,610.8 \text{ W}\cdot\text{kg}^{-1}$ at $13.2 \text{ Wh}\cdot\text{kg}^{-1}$) and exceptional cycling stability (81.1% after 4,000 cycles) thus delivering valuable pathway for the design of energy storage gadgets that exhibit high power and energy densities [196].

Further, Layer-by-layer (LbL) coupling, which is based on the alternating adsorption of oppositely charged species to a surface to build a nanostructured electrode, has been identified by Yun, Echols [197] as a potential technique for developing ultrathin-film electrodes. Their work focused on the LbL formation of hybrid electrodes from positively charged polyaniline nanofibers (PNFs) and negatively charged 2-D MXene for thin-film energy storage gadgets. The coupling involved the deposition of PNFs and MXene in films of 49 nm/layer thickness. The content comprises 23 and 77 wt% of MXene and PNFs respectively. This resulted in a sandwich cell that gave an areal capacity of $17.6 \mu\text{A}\cdot\text{h}\cdot\text{cm}^{-2}$, an energy of $22.1 \mu\text{W}\cdot\text{h}\cdot\text{cm}^{-2}$, and a power of $1.5 \text{ mW}\cdot\text{cm}^{-2}$ for a 2 μm thickness of PNF/MXene multilayer. The work demonstrated that LbL PNF/MXene thin films could be employed as electrode materials in thin-film energy storage devices for wearable electronics. In another study by Zhou et al. [198], MXene/PANI composites were investigated as potential anode materials for sodium-ion batteries. The findings showed that the introduction of PANI effectively aided the suppression of the restacking as well as improved mechanical flexibility and electric conductivity. The introduction of PANI also aids in the preservation of high sodium adsorption strength and rapid sodium mobility, as well as the positive features associated with average open circuit voltage and maximum sodium content of MXenes. Based on these positive attributes, the authors suggested that MXene/PANI composites are potential anode choices for Na-ion batteries. Also, the utilization of MXene/PANI hybrid electrodes for the production of sophisticated supercapacitors through the hydrothermal reaction process has been reported by Li et al. [199]. With current densities ranging from 0.5 to $20 \text{ A}\cdot\text{g}^{-1}$, the 1:3 MXene/PANI electrode demonstrated high capacitance retention and specific capacity of 84.72% and $563 \text{ F}\cdot\text{g}^{-1}$ respectively. At the same MXene/PANI ratio of 1:3, it also exhibited a long usage cycle, with 95.15% capacitance retention after 10,000 cycles as well as energy and power densities of 22.67 Wh/kg and 0.217 kW/kg respectively.

In a different study, a novel nanocomposite of MXene/PANI decorated with graphene nanosheets has been fabricated by Wang et al. [200]. The fabricated nanocluster showed enhanced pseudocapacitive characteristics when utilized as a supercapacitor electrode, the graphene helps to inhibit the assemblage of the MXene single-layers and enables the uneven formation of PANI on the layered MXene structure. Besides, graphene helps to create more pathways for ions/electrons to flow between the electrodes and the electrolyte, acting as “conductive bridges.” The results showed that the fabricated nanoarchitecture has an exceptional electrochemical performance way better than the reported MXene-based devices.

6.2 Applications of MXene-Polypyrrole (PPy) nanoclusters in energy storage devices

Polypyrrole is a conducting polymer that has sparked a lot of interest because of its unusual biocompatibility, ease of synthesis, and inherent high conductivity [192, 201]. Polypyrrole is an organically linked polymeric matrix created by oxidative pyrrole polymerization. Because of its potential electrochemical inclination, PPy has garnered a lot of interest in supercapacitor electrodes, but its electrochemical output has been limited by its poor cycle stability and tightly packed architecture [202]. To overcome the shortcomings of sole conducting PPy, the blending of PPy with MXenes is an attractive technique to enhance its electrochemical performance and mechanical stability by complementing each other's advantages [203, 204].

An unsymmetrical supercapacitor device operating with a voltage of 1.7 V and a 0.5 M Na_2SO_4 electrolyte has been fabricated using MXene/PPy composites [205]. An increased capacitance of $1.37 \text{ F}\cdot\text{cm}^{-2}$ was reported from the cyclic voltammetry (CV) results while the galvanostatic charge-discharge (GCD) data gave $1.18 \text{ F}\cdot\text{cm}^{-2}$. A helpful technique for fabricating MXene/PPy composites was presented, allowing for their use in negative electrodes and enabling exceptional capacitive properties at an AML of $40 \text{ mg}\cdot\text{cm}^{-2}$. Upon the optimization of the negative electrode's composition and performance, an increased capacitance of $2.11 \text{ F}\cdot\text{cm}^{-2}$ and $2.49 \text{ F}\cdot\text{cm}^{-2}$ were obtained from the CV and GCD data, respectively while maintaining low electrode resistance.

Wei et al. [206] in their study demonstrated a simple technique to fabricate an MXene/PPy heterostructure nanocomposite as an improved electrode material for supercapacitors. 75 nm PPy nanospheres were attached to ultra-

thin MXene nanosheets through in situ polymerizations of PPy monomers at the input of MXene suspension. At a scan rate of $2 \text{ mV}\cdot\text{s}^{-1}$, the specific capacitance of the nanocomposite was $458 \text{ F}\cdot\text{g}^{-1}$, which was much higher than that of pure MXene ($132 \text{ F}\cdot\text{g}^{-1}$). Also, the optimal MXene/PPy nanocluster demonstrated outstanding cycle stability. At a power density of $499.94 \text{ W}\cdot\text{kg}^{-1}$, the MXene/PPy supercapacitor delivered an elevated energy density of $21.61 \text{ Wh}\cdot\text{kg}^{-1}$. An initial capacitance retention value of 73.68% was obtained at $1 \text{ A}\cdot\text{g}^{-1}$ after 4,000 charge and discharge tests. Generally, the novel nanocluster (MXene/PPy) demonstrated stable microstructure and exceptional energy storage attributes and has good prospects for practical application in energy storage devices.

In a different study, monomers of pyrrole were in-situ polymerized under low temperatures to form evenly distributed PPy nanoparticles on organ-like MXene/PPy nanoflakes, resulting in a unique organ-like MXene/PPy nanocomposite [207]. The electrochemical properties and microstructures of the MXene/PPy composites were studied at different mass ratios. The organ-like MXene/PPy nanocluster demonstrated an optimum specific capacitance value of $184.36 \text{ F}\cdot\text{g}^{-1}$ at $2 \text{ mV}\cdot\text{s}^{-1}$ with unique cycling stability of about 83.33% at $1 \text{ A}\cdot\text{g}^{-1}$ after 4,000 cycles. The organ-like MXene configuration inhibits PPy development, reduces PPy stacking, and improves MXene/PPy nanocomposite structural stability. Furthermore, the intercalation of identical Polypyrrole nanoparticles increased the interlayer spacing of MXenes, and the well-aligned PPy polymer chains provide additional paths for the diffusion of the ions of the electrolyte and charge transfer, resulting in increased specific capacitance and lower charge transfer resistance. Above all, it presented a convenient and low-cost method for large-scale fabrication of MXene/Polypyrrole nanoclusters which have amazing properties and look interesting as a supercapacitor electrode material. More so, a simple and effective technique to fabricate MXene/PPy 3-D carambola-like composite film electrodes was developed *via* a single-step co-electro-deposition by Jian, He [127]. The 3-D composite configuration aided ionic diffusion and electron transfer, hence the MXene/Polypyrrole cluster film electrodes demonstrated excellent electrochemical attributes with an outstanding gravimetric capacitance of $416 \text{ F}\cdot\text{g}^{-1}$ at $0.5 \text{ A}\cdot\text{g}^{-1}$ current density.

Mani Mahajan and co-workers [208] used a simple synthetic approach to synthesize polypyrrole-encapsulated polyoxomolybdate (PMo_{12}) embellished with MXene as a novel potential 2-D/3-D nanosheets for a high-performance lithium-ion battery for energy storage. Sequel to the inherent self-assembly and electrostatic repulsion attributes of PMo_{12} anions, they (PMo_{12} anions) are wrapped by the discrete PPy molecules and aid in effective inter-placing between the layers of MXene. As a consequence, the composite electrode demonstrates an outstanding lithium storage capacity of about $764 \text{ mAh}\cdot\text{g}^{-1}$ at $0.1 \text{ A}\cdot\text{g}^{-1}$ and elongated cycling stability of about 2,000 cycles at $3 \text{ A}\cdot\text{g}^{-1}$ as well as remarkable rate performance. Because of the synergistic impact between PPy-encapsulated PMo_{12} and MX, this distinctive 2D/3D design shows a hybrid battery-capacitive attribute. The reversible redox reactions of PMo_{12} are responsible for the battery component while PPy and MXene provide for the pseudocapacitive component.

To further demonstrate the benefits of incorporating conducting PPy on MXene in energy storage systems, Yan et al. [209] used MXene nanosheets following a facile “dipping and drying” technique to obtain conductive textile electrodes whose specific capacitance value ($182.70 \text{ F}\cdot\text{g}^{-1}$) was higher than the values reported for active carbon and carbon nanotubes. When conducting Polypyrrole was deposited (electrochemically) on the surface of MXene textiles, a Polypyrrole/MXene composite textile electrode with a specific capacitance value of $343.20 \text{ F}\cdot\text{g}^{-1}$ was obtained. Also, a symmetrical PPy-MXene textiles-based supercapacitor with an energy density of $1.30 \text{ mW}\cdot\text{h}\cdot\text{g}^{-1}$ (power density, $41.1 \text{ mW}\cdot\text{g}^{-1}$) was assembled. The work presented a novel MXene-based textile supercapacitor that is promising for utilization in the assembling of wearable energy storage devices.

6.3 Applications of MX-Poly (3, 4-ethylene dioxythiophene):Polystyrene Sulfonate (PEDOT:PSS) nanoclusters in energy storage devices

PEDOT:PSS is the product of the doping of poly(3,4-ethylene dioxythiophene) (PEDOT) with poly(styrene sulfonate) (PSS) [210]. It is a polymeric blending of dual ionomeric configurations [192, 211]. The fabrication of PEDOT:PSS is accomplished by mixing an aqueous solution of PSS with an EDOT monomeric unit, then adding a sodium persulfate and ferric sulfate solution to the resulting blend [212]. PEDOT:PSS finds its utilization in different areas of conductive organic thermoelectrical architectures such as in thermoelectrical generators, however, the majority of its applications are centered on transparent, conductive polymeric units with maximum ductility [192, 213]. In organic bioelectronics, PEDOT:PSS is the most widely utilized conducting polymer [210]. Nevertheless,

electrochemical capacitances surpassing what is currently provided by the existing conducting polymers are required for state-of-the-art electronic and energy storage devices. Also, there are concerns over the long-term durability of sole-conducting polymer films in aquatic environments during device operation and storage [210]. To this end, the blending of PEDOT:PSS with MXene to form a nanocluster that maximizes their unique advantages while complementing their shortfalls has recently received special attention from researchers.

To demonstrate the practical application of MXene/PEDOT:PSS nanocluster in energy storage devices, a tartaric acid-treated, MXene/PEDOT:PSS composite was prepared and used as electrodes for ultra-fast supercapacitor as depicted in Figure 19. Among all other 2-D nanoclusters, the MXene/PEDOT:PSS-based supercapacitor offers outstanding performance in alternating current (AC) filtering applications [214].

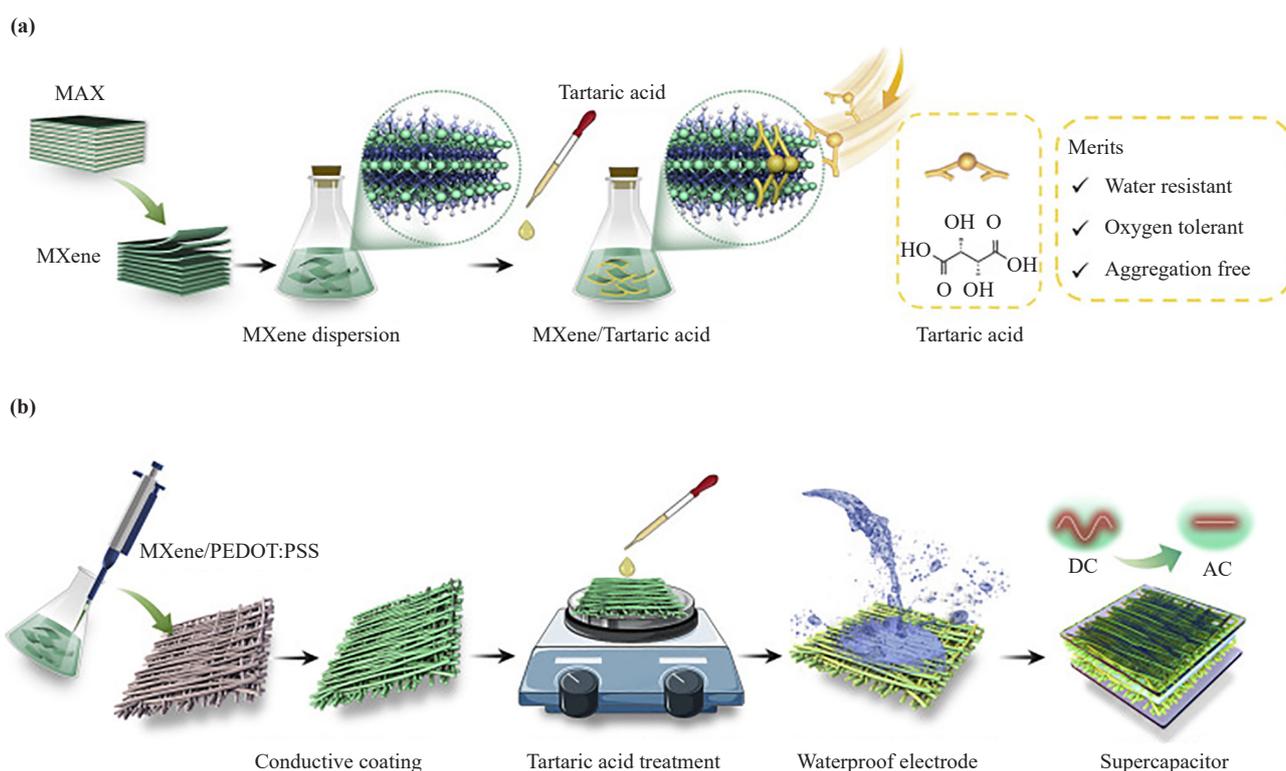


Figure 19. Schematics of the processing procedure of an ultrafast supercapacitor using a tartaric acid-treated, MXene/PEDOT:PSS composite. (a) chemically stabilized MXene aided by tartaric acid; (b) structurally stabilized MXene/PEDOT:PSS cluster coating for fabrication of supercapacitor. Reproduced with permission from Elsevier [214]

Further, the electrochemical synthesis of MXene/PEDOT:PSS composite has been reported by Wustoni, Saleh [210]. It was discovered that the incorporation of PEDOT:PSS in the MXene architecture results in films with unusually high stability (capacitance retention = $78.44 \pm 1.75\%$ over 500 cycles) and volumetric capacitance ($607.0 \pm 85.3 \text{ F}\cdot\text{cm}^{-3}$), better than sole PEDOT:PSS films fabricated under the same process conditions. In another study, Li, Zhang [215] introduced a facile and plausible technique to fabricate flexible MXene/PEDOT:PSS films with remarkable volumetric capacitance for unsymmetrical supercapacitors. The method involved filtering the MXene/Clevios compound inks, this was proceeded by sulphuric acid treatment. The acid treatment helps to eliminate the portion of the non-conducting PSS from the MXene/PEDOT:PSS composite film, leading to an important improvement in the conductivity of the cluster. Besides acting as a bridge between MXene sheets to expose further electroactive surfaces and minimize the pathways for ion diffusion, conductive PEDOT also served as a conductive network, forming thousands of dimensional electronic transport routes for speeding up the electrochemical interaction process. Consequently, the synthesized

MXene/PEDOT:PSS-100-H composite film demonstrated a 4.5-fold rise in the specific surface area with greater rate performance, as well as outstanding volumetric capacitance ($1,065 \text{ F}\cdot\text{cm}^{-3}$ at $2 \text{ mV}\cdot\text{s}^{-1}$). The composite film electrode showed significant potential for utilization as a robust power source for smart wearable electronic gadgets.

More so, a high-performance, very-thin, wearable supercapacitor was developed based on a layered structure of $\text{Mo}_{1.33}\text{C}$ MXene/PEDOT:PSS hybrid film with concentrated sulphuric acid posttreatment. The smart flexible supercapacitor offers an optimum capacitance ($568 \text{ F}\cdot\text{cm}^{-3}$), high energy density, and power density of $33.2 \text{ mWh}\cdot\text{cm}^{-3}$ and $19,470 \text{ mW}\cdot\text{cm}^{-3}$ respectively. When treated with H_2SO_4 , the prepared hybrid film demonstrated a decrease in resistance, increased capacitance ($1,310 \text{ F}\cdot\text{cm}^{-3}$), and enhanced rate abilities than the $\text{Mo}_{1.33}\text{C}$ MXene/PEDOT:PSS hybrid films that were not H_2SO_4 treated [216].

On the other hand, owing to their appreciable low cost, energy density, and environmental friendliness, lithium-sulfur (Li-S) batteries have generated a lot of interest. However, the severe shuttle effect associated with Li-S batteries remains an impediment to its practical application. An effective approach to remedy this challenge is to formulate a modified separator as the second collector using conductive and polar materials. To this end, Li et al. [217] fabricated an MXene/PEDOT:PSS composite for the modification of PP separators. The use of MXene/PEDOT:PSS makes MXene nano-sheets efficiently anchor polysulfide, thereby preventing the shuttle effect. Hence, Li-S batteries with MXene/PEDOT:PSS filled-separators show highly improved performances, such as low decay rate and elongated cycling stability (0.030% /cycle at 0.5 C) after 1,000 cycles, and high discharge capacity ($1,241.4 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at 0.2 C). In a further response to the need for future electrodes for wearable electronics, a new blend of the silver nanowire (AgNW) MXene/PEDOT:PSS (AgNW- MXene@PEDOT:PSS) was fabricated through a solution blending [218]. Bonding between MXene and PEDOT:PSS aids a high conductive AgNW- MXene@PEDOT:PSS realizes a sheet resistance and transmittance of $17 \Omega\cdot\text{sq}^{-1}$ and 97.6% respectively, as well as enhances stability and anti-corrosion attribute. It proposed an essential step toward the fabrication of nanoclusters for flexible smart electronics.

Table 1. Summary of MXene/conductive polymeric nanoclusters, application, and performance in energy storage

| Nanocomposite | Application | Performance | References |
|----------------------------------------|---------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| Graphene-encapsulated MXene/PANI (GMP) | Asymmetric Supercapacitor (ASC) | Gravimetric capacitance, $635 \text{ F}\cdot\text{g}^{-1}$; Volumetric capacitance, $1,143 \text{ F}\cdot\text{cm}^{-3}$ at $1 \text{ A}\cdot\text{g}^{-1}$; Cyclability, 97.54% after 10,000 cycles; Energy density, $42.3 \text{ Wh}\cdot\text{kg}^{-1}$; Power density, $950 \text{ W}\cdot\text{kg}^{-1}$. | [195] |
| MXene/PANI Nanotubes (PNTs) | Symmetric supercapacitors (SSC) | Specific capacitance, $596.6 \text{ F}\cdot\text{g}^{-1}$ at $0.1 \text{ A}\cdot\text{g}^{-1}$; Cyclability, 94.7% after 5,000 cycles; Energy density, $25.6 \text{ Wh}\cdot\text{kg}^{-1}$ at $153.2 \text{ W}\cdot\text{kg}^{-1}$; Power density, $1,610.8 \text{ W}\cdot\text{kg}^{-1}$ at $13.2 \text{ Wh}\cdot\text{kg}^{-1}$. | [196] |
| M MXene/PANI Nanofibers (PNFs) | Thin-film electrodes (microbatteries) | Areal capacity, $17.6 \mu\text{A}\cdot\text{h}\cdot\text{cm}^{-2}$; Energy, $22.1 \mu\text{W}\cdot\text{h}\cdot\text{cm}^{-2}$; Power, $1.5 \text{ mW}\cdot\text{cm}^{-2}$. | [197] |
| MXene/PANI | Sodium-ion batteries | NA | [198] |
| MXene/PANI | Asymmetric supercapacitors (ASC) | Specific capacity, $563 \text{ F}\cdot\text{g}^{-1}$ at $0.5 \text{ A}\cdot\text{g}^{-1}$; Cyclability, 95.15% after 10,000 cycles; Energy density, 22.67 Wh/kg ; Power density, 0.217 kW/kg . | [199] |
| Graphene-decorated MXene/PANI (GMP) | Asymmetric supercapacitor (ASC) | Gravimetric capacitance, $452 \text{ F}\cdot\text{g}^{-1}$; Volumetric capacitance, $606 \text{ F}\cdot\text{cm}^{-3}$; Rate capability, 79.6%; Cyclability, 80.4% after 5,000 cycles. | [200] |
| MXene/PANI | Supercapacitor (SC) | Gravimetric capacitance, $503 \text{ F}\cdot\text{g}^{-1}$; Volumetric capacitance, $1,682 \text{ F}\cdot\text{cm}^{-3}$; Cyclability, 98.3% after 10,000 cycles. | [219] |

Table 1. (cont.)

| Nanocomposite | Application | Performance | References |
|---------------------------------------------------------------|-----------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| MXene/PPy | Asymmetric supercapacitor (ASC) | Volumetric capacitance, $2.11 \text{ F}\cdot\text{cm}^{-3}$; Gravimetric capacitance, $49 \text{ F}\cdot\text{g}^{-1}$; Low electrode resistance. | [205] |
| MXene/PPy | Supercapacitor (SC) | Specific capacitance, $458 \text{ F}\cdot\text{g}^{-1}$; Power density, $499.94 \text{ W}\cdot\text{kg}^{-1}$; Energy density, $21.61 \text{ Wh}\cdot\text{kg}^{-1}$; Cyclability, 73.68% after 4,000 cycles. | [206] |
| MXene/PPy | A supercapacitor (SC) | Specific capacitance, $184.36 \text{ F}\cdot\text{g}^{-1}$; Cycling stability, 83.33% after 4,000 cycles. | [207] |
| MXene/PPy | Symmetric supercapacitors (SSC) | Gravimetric capacitance, $416 \text{ F}\cdot\text{g}^{-1}$; Cyclability, 86.4% after 5,000 cycles. | [127] |
| PPy-encapsulated polyoxomolybdate (PMo_{12})/MXene | Lithium-ion battery | Lithium storage capacity, $764 \text{ mAh}\cdot\text{g}^{-1}$; Cycling stability, 2,000 cycles at $3 \text{ A}\cdot\text{g}^{-1}$. | [208] |
| PPy/MXene | Symmetrical textiles-based supercapacitor | Specific capacitance, $343.20 \text{ F}\cdot\text{g}^{-1}$; Energy density, $1.30 \text{ mW}\cdot\text{h}\cdot\text{g}^{-1}$; Power density, $41.1 \text{ mW}\cdot\text{g}^{-1}$. | [209] |
| Tartaric acid-treated MXene/PEDOT:PSS | Ultrafast supercapacitor (UFSC) | Areal capacitance (C_A), $1,149 \mu\text{F}\cdot\text{cm}^{-2}$; Phase angle, 80° at 120 Hz. | [214] |
| MXene/PEDOT:PSS | Organic bioelectronics (neural electrodes) | Volumetric capacitance, $607.0 \pm 85.3 \text{ F}\cdot\text{cm}^{-3}$; Cyclability, $78.44 \pm 1.75\%$ after 500 cycles. | [210] |
| MXene/PEDOT:PSS | Asymmetric supercapacitor (ASC) | Volumetric capacitance, $1,065 \text{ F}\cdot\text{cm}^{-3}$; A 4.5-fold rise in the specific surface area. | [215] |
| $\text{Mo}_{1.33}\text{C}$ MXene/PEDOT:PSS | Ultrathin Flexible Solid-State Supercapacitor | Specific capacitance, $1,310 \text{ F}\cdot\text{cm}^{-3}$; Energy density $33.2 \text{ mWh}\cdot\text{cm}^{-3}$; Power density, $19,470 \text{ mW}\cdot\text{cm}^{-3}$. | [216] |
| MXene/PEDOT:PSS | Lithium-sulfur (Li-S) battery | Cycling stability and decay rate, 0.030% per cycle at 0.5 C after 1,000 cycles; Discharge capacity, $1,241.4 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at 0.2 C. | [217] |

7. Conclusion

The growing demand for smart and flexible electronics has driven researchers to seek necessary modifications to these architectures to enhance their performance. Due to the remarkable synergistic effects between materials in designed hierarchical structures, composite materials often exhibit enhanced physical and chemical properties. This underscores their potential for significant advancements in electrochemical attributes and high performance in wearable electronic devices. MXene/conducting polymeric hybrid nanoclusters were developed to simultaneously maximize the individual advantages of the two materials while making up for their inherent functional deficiencies. Herein, the electronic and thermal behaviors of conductive MXene- $\text{Ti}_3\text{C}_2\text{T}_x$ -based polymeric composites and their capacitive energy storage applications are presented (Table 1).

The thermal properties of the composites are influenced by various factors such as the size, concentration, type, dispersion of fillers, and the presence of a thermal barrier between polymer chains. This survey revealed that the concentration of MXene significantly impacts thermal conductivity. Higher MXene concentration in the polymer matrix enhances both the thermal conductance and stability of the polymer nanocomposite. This effect is attributed to MXene's ability to form a thermal conductive network by establishing hydrogen bonds with the polymer, facilitating smooth heat flow within the composite. Additionally, strong interfacial compatibility between MXene and the polymer matrix, along with the phonon scattering nature of MXene nanosheets, contribute to the improved thermal conductivity and stability of conductive MXene/polymer hybrid nanoclusters.

The electrical conductivity of MXene-polymer nanoclusters is highly dependent on the ability of MXene to form an effective conductive network within the polymeric nanoclusters. The more efficient the MX-MX conductive network becomes, the better the electron transport within the nanoclusters. Additionally, metal nanoparticles such as Ag and Fe on functionalized MXene have been beneficial to the electrical conductivity of nanoclusters. Conductivity has been found to increase with the addition of metal particles in MXene nanoclusters.

Conclusively, it is important to note that while the use of standalone 2-D MXene in energy storage devices is a growing trend, the application of conducting polymers is a well-established technology. The practical applications of MXene/PANI, MXene/PPy, and MXene/PEDOT:PSS in energy storage devices as well as the preparation techniques were extensively discussed in this review. The work also elucidated the routes for exploring the enormous potential of MXene/conducting polymeric nanocomposites as one of the most promising state-of-the-art energy storage materials for smart, wearable, and flexible electronic applications.

Conflict of interest

The authors declare no competing financial interest.

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