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# Two-Dimensional MXene Based Materials for Micro-Supercapacitors

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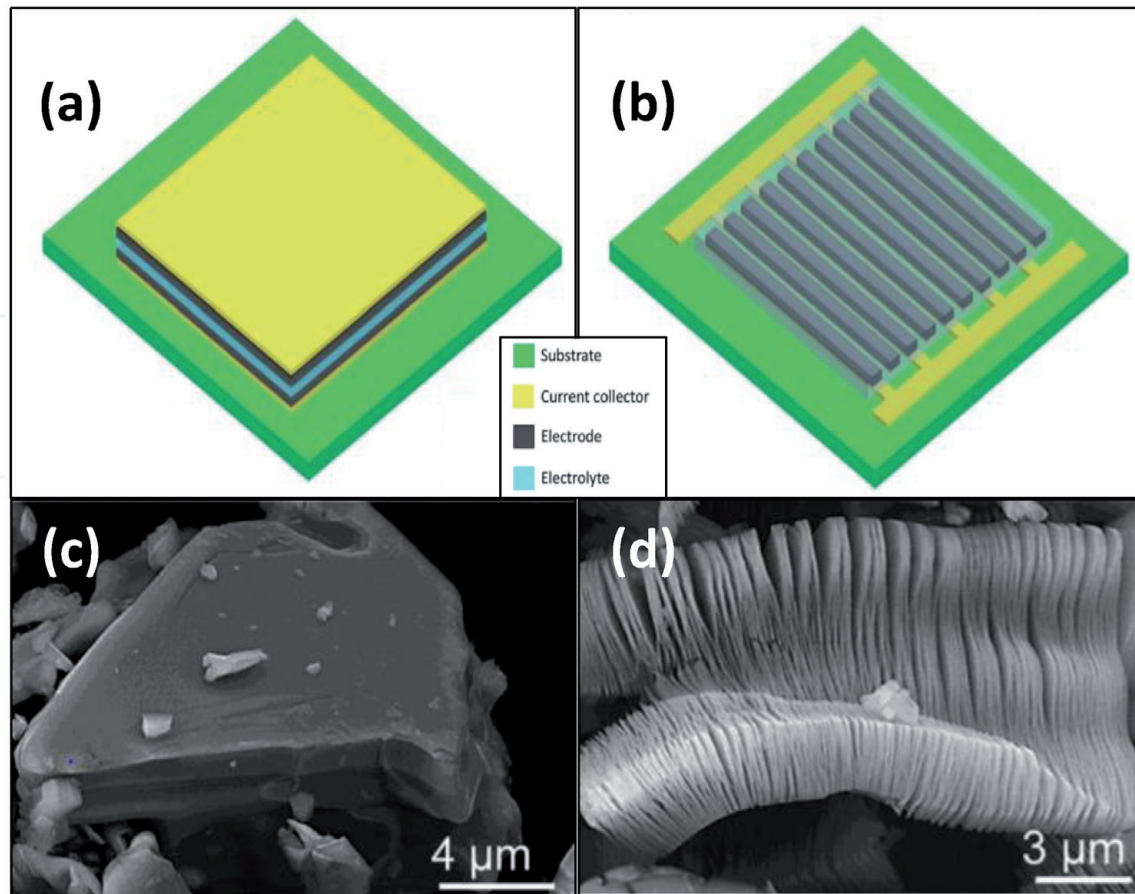
## Abstract

With the boom in the development of micro-electronics for wearable and flexible electronics, there is a growing demand for micro-batteries and micro-supercapacitors (MSCs). Micro-supercapacitors have garnered a considerable attention for the evolution of these energy storage micro-systems. The choice of electrode material plays a pivotal role in the fabrication and development of MSCs. Recently, a new emerging family of two-dimensional transition metal (M) carbides or nitrides (X) cited as 2D MXene has emerged as a novel material. Due to its exceptionally high electronic conductivity  $\sim 10,000 \text{ S cm}^{-1}$ , high charge storage capacity and easy processing capability helps to use MXene as the promising candidate for micro-supercapacitors electrodes. Taking the advantage of such exceptional properties, MXenes have been explored enormously in stacked as well as in interdigital architecture for on-chip micro-supercapacitors (MSCs). This book chapter includes a recent advancement of MXene based MSCs, with a brief overview of synthesis and fabrication techniques.

**Keywords:** 2D MXene, Micro-supercapacitor, Wearable and flexible electronics, Energy storage, Micropattern

## 1. Introduction

There is an increase in demand for flexible and solid-state on chip micro-electronics for smart wearable micro-devices for energy, environmental, biological, medical and various other applications which can be either wireless or integrated with solar or piezoelectric energy harvesters. Great efforts have been made by the scientists to design and develop smart as well as portable microsystems, primarily for self-powered and on-chip integrated power systems. To cope with the increasing demand of micro-electronics, there is an abrupt rise in the demand of micro-energy storage devices. However, micro-batteries are restricted due to their limited life and power density. Micro-supercapacitors (MSCs) hold the best alternate to the micro-batteries, despite the lower energy density. In contrast, MSCs can demonstrate superior cycle life, faster charge/discharge rates, high power density as well as overall stable performance which is promising [1]. Presently, MSCs have two types of architecture, one with the conventional sandwich type and others are in-plane interdigital pattern type as shown in **Figure 1(a, b)**, [2]. Generally, the interdigitated coplanar design offers better performance due to the short ion diffusion distance which gives the enormous surface area. Thus, exhibiting an excellent rate capability, high-power density and ease of integration with micro-devices [1, 4, 5].



**Figure 1.**

*Architecture of micro-supercapacitors: (a) sandwich type micro-supercapacitor, (b) interdigital patterned micro-supercapacitor. [2] (c) SEM image of  $Ti_3AlC_2$  (MAX) phase, (d) SEM image of etched  $Ti_3C_2T_x$  (MXene) phase [3].*

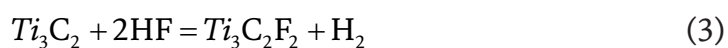
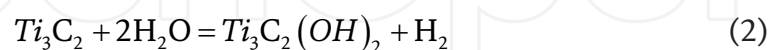
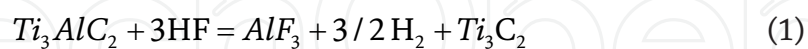
Two-dimensional (2D) materials like graphene, h-BN, Transition metal dichalcogenides (TMDCs), black phosphorus (BP), MXenes and 2D metal oxides and hydroxides etc. are most widely used in energy storage applications due to their outstanding electronic, mechanical, optical and physio-chemical properties [6]. Carbon based materials including Carbon [7], carbide derived carbon [8], onion-like carbon [9], graphene [10], Carbon nano tubes (CNT) [11], laser scribed graphene [12] displays high electronic conductivity and relatively large surface area but due to electric double layer formation, they lack high energy density. Similarly, pseudocapacitive materials such as transition metal oxides like  $MnO_2$  [13],  $MoO_3$  [14], conductive polymers [15] as well as TMDs [16] which suffer from low electronic conductivity with reasonable power and cycling performance has been already explored in Micro-supercapacitor devices applications. But, MXenes have garnered great attention from the scientific community all over the world since their discovery in 2011, by Naguib and group [17]. A large family of two-dimensional early carbides, nitrides and carbon nitrides produced by selective etching of A layer (typically Al and Ga) from the precursor layered ternary carbides/nitrides (MAX phases). Their general formula is  $M_{n+1}X_nT_x$  ( $n = 1, 2, 3$ ), where M represents a Transition metal, X is carbon and/or nitrogen, T stands for surface termination groups (-F, -OH, -O etc.) [18]. In particular, the dual nature of MXenes that is superior ion transport due to inner transition metal carbide layer as well as property to exhibit fast redox reaction because of large active sites [18, 19]. MXenes combine high electronic conductivity of MAX phases as well as hydrophilic nature due to the surface terminations such properties make them a considerable candidate for a host of applications.  $Ti_3C_2T_x$  is one of the most studied member of

MXene family, exhibiting a high electronic conductivity up to  $2.4 \times 10^4$  S/cm and volumetric capacitance  $1500 \text{ F/cm}^3$  with good rate capability of 10 V/s in acidic electrolyte [5]. Hence there is plenty of room to design and develop MXene based Micro-supercapacitor devices [20]. The 2D nature, excellent mechanical stability and exceptionally tunable physio-chemical properties makes MXenes, the best candidate for MSC device. This book chapter includes various direct–indirect techniques to fabricate MXene based MSC device.

## 2. MXenes: brief review

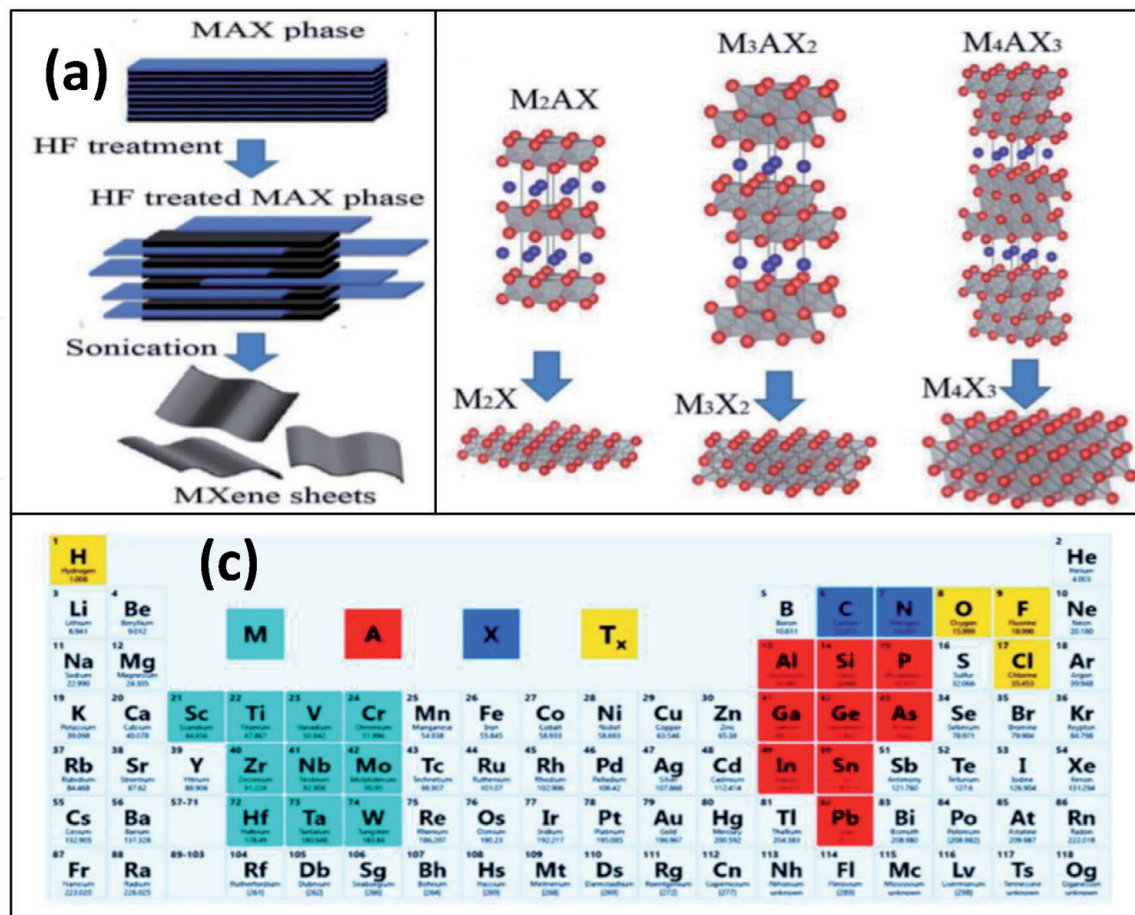
### 2.1 Synthesis

There are generally two methods to synthesize MXene i.e., (1) top-down approach which includes selective etching or exfoliation of metal layer and (2) bottom-up approach including chemical vapor deposition (CVD), template assisted growth method. Wet chemical etching i.e., fluoride based acids are most commonly reported methods to etch “A” element, generally group IIIA and IVA group (Al or Si) elements from MAX phases (one or several atomic layers) which are replaced by functional groups, where M is termed as early transition metals, from group IIIB to IVB, and X is carbide/nitride by using different wt % of fluoride containing acid such as HF or mixture of LiF-HCl acid [17, 20, 21]. The first ever report to synthesis MXene by eliminating the aluminium layer from  $\text{Ti}_3\text{AlC}_2$  (MAX) by using hydrogen fluoride (HF) in the range of 10 to 50 % concentration of etchant [17]. The exfoliated 2D  $\text{Ti}_3\text{C}_2\text{T}_x$  possess excellent 2D sheets like morphology almost similar to graphene sheets as shown in **Figure 1(c,d)** [3]. To avoid highly acidic HF acid, various other methods have been developed to produce in-situ HF salts comparatively less hazardous than HF. Recently, a new approach to etch with molten salts allows to dissolve A-element at high temperature [21]. This method demonstrated the complete removal of Fluorine ions and found to be much purer MXene than one etched with only HF. The presence of surface functional groups like -OH, -F and -O etc. improves the hydrophilic character of MXenes which further enhances the stability. The reaction mechanism of firstly synthesized  $\text{Ti}_3\text{C}_2\text{T}_x$  (MXene) by etching Al layers from  $\text{Ti}_3\text{AlC}_2$  (MAX phase) with HF is given in **Figure 2(a)** [22].



Reaction (2) and (3) gives rise to the surface terminations like -O, -OH, -F etc., respectively [17, 24]. MXenes have three possible structures with different layers of stacking as shown in **Figure 2(b)**, [22] The tentative elements of MXene precursor in the periodic table predicted till now presented in **Figure 2(c)** [23].

The timeline of synthesis of MXene in different year is given in **Figure 3(a)**. [25] Choice of synthesis and processing method including precursors etchant, intercalant, reaction sonication time etc. strongly influence the properties of resultant MXene. Mild alkali etchants like NaOH [26] and  $\text{NaBF}_4$  [27] were also proposed to synthesis  $\text{Ti}_3\text{C}_2$  by high temperature hydrothermal etching of Al layer from  $\text{Ti}_3\text{AlC}_2$ . This method extended to other MXenes such as  $\text{Nb}_2\text{C}$  [27]. Similarly, molten  $\text{ZnCl}_2$  were



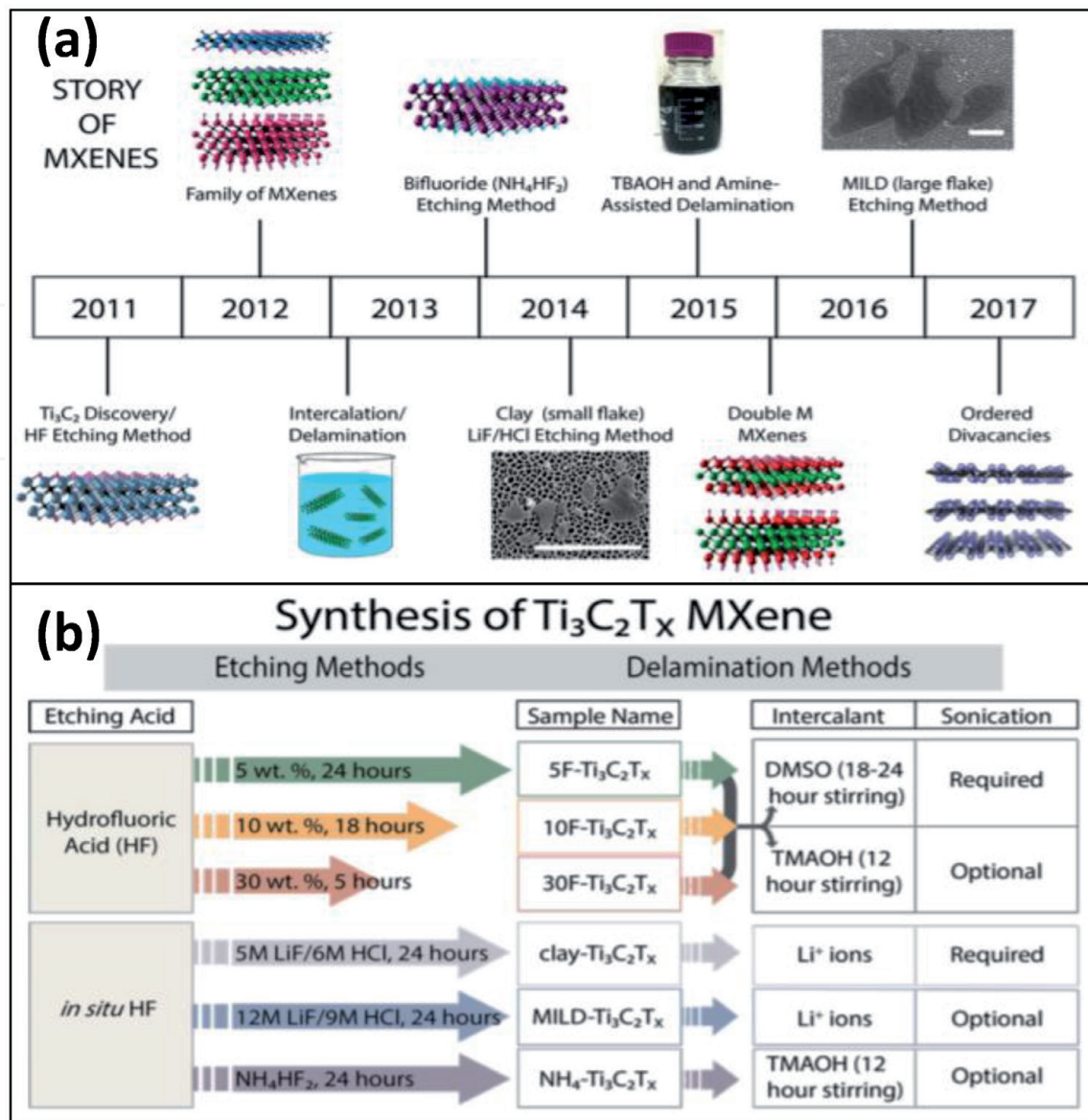
**Figure 2.** (a) Schematic showing the synthesis of MXene from MAX by HF treatment, (b) synthesis mechanism of different order of MXenes by MAX phases. [22] and (c) compositions of MXene elements in periodic table (Reprinted from [23] with permission from, copyright@2020, MDPI).

used for different MAX phases like  $\text{Ti}_3\text{AlC}_2$ ,  $\text{Ti}_2\text{ZnN}$ ,  $\text{Ti}_2\text{AlC}$  and  $\text{V}_2\text{AlC}$  to substitute  $\text{Zn}^{2+}$  ions [28]. Another report suggested a fluoride free-electrochemical etching at room temperature synthesis of  $\text{Ti}_2\text{C}$  and  $\text{Ti}_3\text{C}_2$  in dilute  $\text{HCl}$  [29] and  $\text{NH}_4\text{Cl}/\text{TMAOH}$  [30]. Also, a naturally delaminated MXenes with better electronic conductivity can be produced using minimally intensive layer delamination (MILD) without the use of further handshaking or sonication of MXenes [25]. More than 20 different types of MXenes have been synthesized experimentally [18]. **Figure 3(b)** represents the different etching methods that are used to synthesis different MXene products [25].

## 2.2 Properties

### 2.2.1 Electrical conductivity

MXenes have been extensively investigated by computational methods [31, 32], MXenes can be categorized into three types i.e., metallic, semi-metallic and semi-conducting [33]. Generally, bare MXenes have very high electronic conductivity with high density of states (DOS) at the fermi level. Electronic properties of MXenes are strongly influenced by the surface, morphology and stacking behavior of MXene sheets. Delaminated MXenes flakes show ultra-high electronic conductivity of upto  $9880 \text{ Scm}^{-1}$ , which can be further tuned by modifying the surface-terminations [34]. In addition to this, MXenes strongly depends on synthesis procedure which can be achieved by varying the synthesis conditions. HF etched highly defective MXene exhibits electronic conductivity of  $1,000 \text{ Scm}^{-1}$ . Whereas it improved to  $4600 \text{ Scm}^{-1}$  for powder and further enhanced to  $6500 \text{ Scm}^{-1}$  for



**Figure 3.** (a) Timeline of synthesis of MXenes, (b) different protocols to synthesis different kind of MXenes (Source: Reprinted from [25] with permission from, copyright@2017, ACS).

delaminated MXene thick films by simply varying the etching and sonication conditions [35]. Although, Theoretical investigations shows the high electronic conductivity in MXenes. But there is still lack of knowledge and experimental expeditions to synthesize such exceptional MXene with control over surface chemistry.

### 2.2.2 Surface morphology

MXenes are synthesized by MAX precursors where M atoms are close packed and X atoms at interstitial sites [36]. Generally, MXenes have hexagonal close-packed structure with different order of M atoms in which  $\text{M}_2\text{X}$  follows ABABAB type order with hexagonal-stacked packing while  $\text{M}_3\text{X}_2$  and  $\text{M}_4\text{X}_3$  follows ABCABC type order with face-centered cubic stacking [22]. A study published by wang et al., Surface moieties play a key role in altering the properties of MXenes. The orientation and interaction between the terminal groups like -OH, -O, -F etc. strongly enhances interlayer hydrogen bonds which further improves the quality of MXenes. [37]. Also, the hydrogen bonding in MXene is highly influenced by surface terminations and interlayer spacing. Depending upon the occupancy of a functional group like -OH, -F and -O etc. the properties can be tuned for the respective application.

Intercalating the MXenes with ions, further gives a chance to mitigate the restacking behavior of MXene sheets for better performance, leading to display clay-like-behavior [38]. There is a lot to study and prepare pure MXenes for future energy applications.

### 2.2.3 Mechanical properties

MXenes exhibit peculiar physical and chemical properties which directly contribute to their mechanical behavior such as young's modulus, stiffness, defect generation, surface and elastic properties. Defect-rich MXenes with different terminal groups has strong covalent bonding with transition metal ion. Overall, there are various parameters which can be tunable to produce high performance MXenes. There are several theoretical studies on the mechanical, electronic as well as thermal properties of different types of MXenes [31, 39–43]. Experimentally the young's modulus of  $\text{Ti}_3\text{C}_2\text{O}_2$  and  $\text{Ti}_3\text{CO}_2$  was found to be 466 GPA and 983 GPA [44], these values were almost closer to the value predicted by theoretical simulations of 502 GPA [45]. Theoretical studies claims that  $\text{M}_2\text{X}$  exhibit much stronger in contrast to  $\text{M}_3\text{X}_2$  and  $\text{M}_4\text{X}_3$ . But there is no experimental evidence to prove. However, in a study [46], A 5  $\mu\text{m}$  thick paper film of  $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVA}$  composite was able to hold ~15,000 times its weight, which is evident to its strong wear and tear resistance property. Based on the surface terminations, there is a chance to modify surface properties of MXenes. Further investigations are needed to tune and enhance its nature.

## 3. Micro-fabrication techniques

### 3.1 Photolithography

Photolithography is a most promising technique at industrial scale which enables on-chip fabrication of high-resolution interdigital patterns of microelectrochemical systems (MEMS), Integrated Circuits (ICs), and complementary metal-oxide-semiconductors (CMOS) devices on various substrates with the help of computer-generated photomasks and photoresist designs. Recently, Jiang *et al.* fabricated all MXene based microsupercapacitors (MSCs) by spray coating on  $\text{O}_2$  plasma treated predefined photoresists patterns prepared by direct photolithography on silicon substrates [47]. The thickness of the MXene coating was varied to get superior electrical conductivity. Device showed an ultra-high scan rate stability upto 300 V/s. Similarly, Kim and group fabricated a high performance MXene/CNT based hybrid on-chip MSCs by using Focused-ion beam (FIB) lithography technique [48]. They were able to fabricate the sub~500 nm gap between the fingers ( $W_g$ ) reducing the active electrode foot print ( $W_e$ ) of the device. Increasing the ratio,  $W_e/W_g$  by decreasing the gap between the electrode, which further shortens the ohmic losses. Hence improves the on-chip MXene based areal capacitance upto  $317 \text{ mFcm}^{-2}$  at  $50 \text{ mVs}^{-1}$ . The capacitance retention of 32.8% was achieved even at higher scan rate of  $100 \text{ Vs}^{-1}$ . Due to imperfect resolution and ultra-narrow interelectrode gap. There are potential risks of degradation and a short circuit between the electrodes [49]. But, due to lack of electrode materials and stability issues, photo-lithography is not been used at its threshold. Xue and co-workers successfully demonstrated the electrophoretic deposition (EPD) of MXenes on the pre-patterned current collector in acetone solvent. EPD method is also grabbing attention in the scientific community [50]. There is a big room to do research. Since, photolithography technique comes out to be a challenging yet rewarding in terms of industrial fabrication and scalability for micro-supercapacitor applications.

### 3.2 Inkjet printing

Inkjet printing is a very popular technique for fabricating MSCs with excellent precision of designed pattern on various non conducting substrates. Nowadays, inkjet printing is gaining momentum in the scientific community. One can get desired thickness of printed layer to meet the certain applications. As name suggests inkjet printing is solely depends upon the prepared liquid ink.

There are three basic parameters which defines the behavior of the liquid inks:

1. Reynolds No. ( $R_e$ )

$$R_e = \frac{v\rho_a}{\eta}$$

2. Weber ( $W_e$ )

$$W_e = \frac{v^2\rho_a}{\gamma}$$

3. Ohnesorge ( $O_h$ )

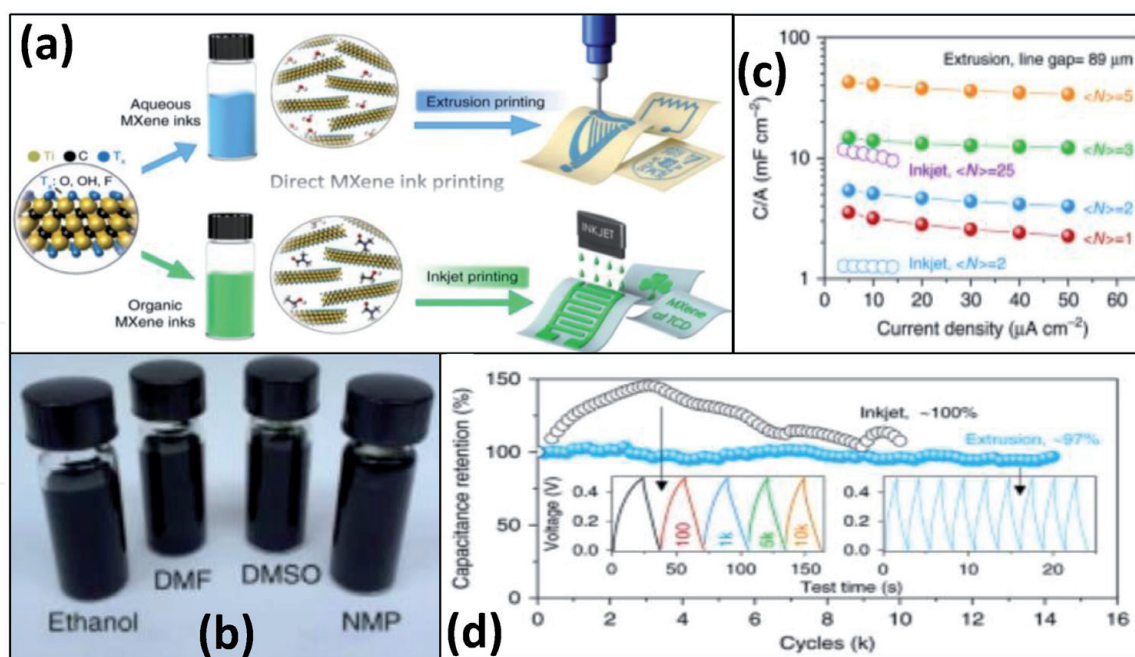
$$O_h = \frac{\sqrt{W_e}}{R_e}$$

Where  $\rho$  is the density ( $\text{Kg/m}^3$ ),  $\eta$  is the dynamic viscosity ( $\text{N.S/m}^2$ ),  $\gamma$  is the surface tension ( $\text{N/m}$ ),  $v$  is the velocity ( $\text{m/s}$ ),  $a$  is the nozzle diameter ( $\text{m}$ ) [5]. To generate, stable ink droplets, numerical simulations have demonstrated that the rheology behavior of the ink should be in the range of  $1 < Z < 10$  for better results. Also, to predict the rheological characteristics of a drop of ink, the inverse Ohnesorge number  $Z$  is used i.e.,  $Z = 1/O_h$ . [51]. As increase in demand of self-charged and wearable devices, highly functionalized conductive  $\text{Ti}_3\text{C}_2\text{T}_x$  (MXene) has attracted attention to directly prepare a highly stable conductive ink in various organic solvents. Inkjet printing is the cheapest and most viable technique to fabricate MXene based MSCs. Recently, Zhang et al. fabricated additive-free MXene ink based MSCs on flexible substrate shown in **Figure 4(a)**, N-Methyl-2-pyrrolidone (NMP) based MXene ink shows excellent volumetric capacitance of  $562 \text{ F/cm}^3$  by inkjet printing. Demonstrating stable ink formulation in different organic solvents displayed in **Figure 4(b)**. The extrusion printed patterns exhibits power density as high as  $11.4 \mu\text{Wcm}^{-2}$ . Also, by adjusting the printing pass, the authors were able to reduce the sheet resistance upto  $35 \Omega/\text{sq}$ . from  $445 \Omega/\text{sq}$ . the areal capacitance and cycling stability of inkjet and extrusion printed MSC is given in **Figure 4(c,d)**. This study opens a new technique to fabricate low cost MXene ink-based MSC devices [52]. MXene aqueous ink with excellent oxidation resistance power were directly printed on paper substrate. The hybrid MXene suspension capped with sodium ascorbate (SA) displays the superior stability of upto 20 days. Due to its oxidation resistance nature and large interlayer spacing the conductivity of SA MXene improves to  $119 \text{ Scm}^{-1}$  this shows that there is still big room to develop MXene ink based printable devices for MSC Application [53].

### 3.3 Laser scribing

Laser engraving is another emerging cost-effective technique for the fabrication of MSCs on various customized substrates. Precise resolution with fast scanning speed makes this technique a superior approach in the field. But with all above benefits, there are few difficulties faced during the optimization of wavelength,





**Figure 4.**

(a) Schematic of direct printing of aqueous MXene inks used for extrusion printing and organic MXene inks used for inkjet printing on various substrates, (b) plot showing the areal capacitance of inkjet and extrusion printed MSC with various printing passes  $\langle N \rangle = 2$  and 25, (c) picture of different MXene organic inks, (d) cycling stability of inkjet and extrusion at current densities of 14 and  $200 \mu\text{A cm}^{-2}$ . (Source: Reprinted from [52], permission from, copyright @2019, Nature).

resolution and accurate speed suitable for the fabrication of MSCs on different substrates. Tang and co-group demonstrated the direct laser writing of  $\text{Ti}_3\text{C}_2\text{T}_x$  interdigital electrodes by tuning the direction of laser scanning and rate. Interlayer spacing of restacked MXene was increased due to high photothermal oxidation effect of direct laser writing which enhanced the ion transport nature of the films [54]. Wang et al., fabricated double sided flexible asymmetric MSCs on thin nickel sheet by using spray coating technique followed by cutting of interdigital patterns by UV laser. By increasing the mass of active material, the maximum capacitance improved to  $34 \text{ mF cm}^{-2}$  approximately double as compared to the previous one. The fabricated double-sided device displayed considerable energy density of  $2.62 \mu\text{Wh cm}^{-2}$  at  $2 \text{ mA cm}^{-2}$  [55]. Further, Kurra and co-members reported a high areal capacitance based on clay-like MXene MSCs fabricated directly on paper by using a  $\text{CO}_2$  laser. Clay-like MXene shows superior power density of  $46.6 \text{ mW cm}^{-2}$  at energy density of  $0.77 \mu\text{Wh cm}^{-2}$ , opening a new method to fabricate on-paper MSC devices [56].

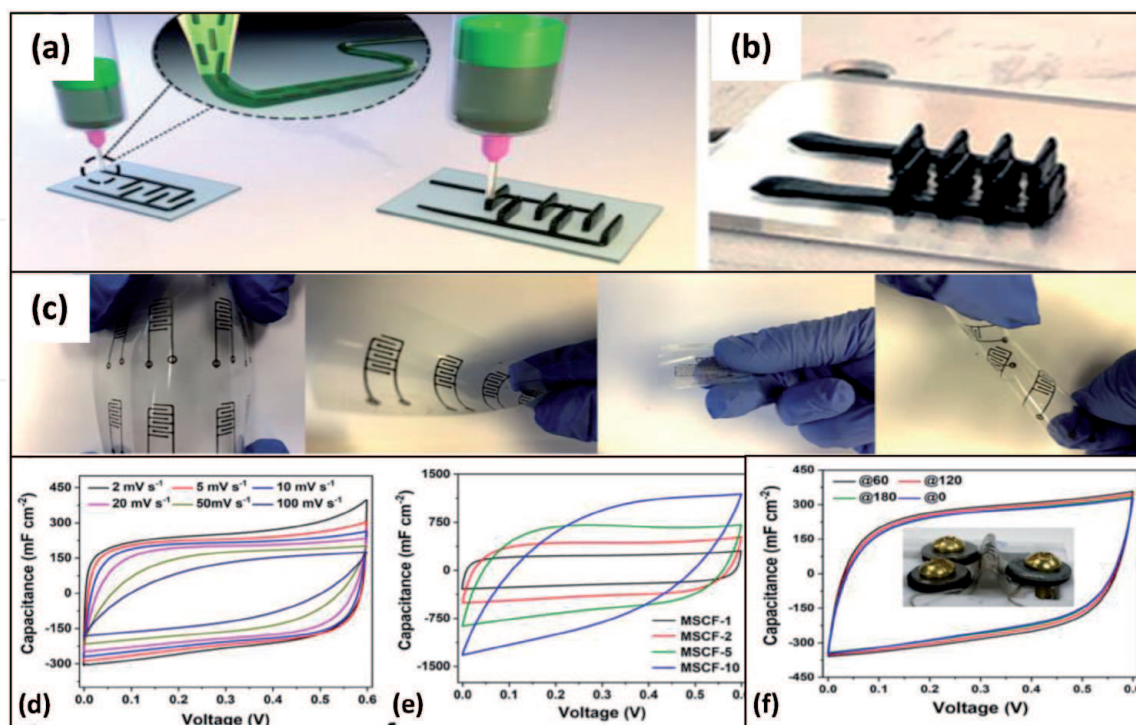
### 3.4 Screen printing

Screen printing technology is one of the popular traditional technique to transfer pre-designed ink patterns of active materials on various substrates. Important features of this technique are its scalability, reproducibility and repeatability. The screen printing technique is simple with high efficiency unlike other printing techniques, showing the enormous opportunity to explore. This inexpensive method can be used manually or even by automated machines. Generally, the setup includes the mesh screen with little gap between the substrate. With the help of squeegee, the ink is flooded over the screen mesh to print on the substrate [57]. Screen printing gained considerable attention to directly print MXene ink-based electrodes directly on a target substrate. Screen printing solely depends on rheological properties of ink which should be highly viscous and show a good shear thinning behavior. Additionally, the size and resolution of electrodes depends on mesh size. Recently,

screen printed MSCs were fabricated on paper by using homogeneous ink of MXene sediments. The perfectly tuned thickness of MSCs reduced the sheet resistance upto  $2.2 \Omega \text{ sq}^{-1}$  and gives excellent electrical conductivity of upto  $450 \text{ Scm}^{-1}$ . The energy density reached to  $158 \text{ mFcm}^{-2}$  which is highest of its kind [58]. A two-step screen printing technique is employed to fabricate asymmetric MSC with interdigital pattern on paper as well as PET substrate. High energy density of  $8.8 \mu\text{Whcm}^{-2}$  in PVA-KOH was observed, far superior than many of other reports [59]. There are advantages of the technique to get high mechanical stability on different substrates which definitely enhances the electronic conductivity of the fabricated devices.

### 3.5 3D printing

3D printing technology has attracted lot of attention for scalable fabrication of 3D architectures for the development of small and portable electronics. Recently a new trend has been introduced to fabricate 3D MSCs. This method is less complex and easy to handle compared to other lithography techniques. MXenes are the emerging material to be introduced by this technique for the fabrication of gel-type ink-based 3D MSC device to enhance its areal and volumetric capacitance. Recently, Orangi et al., fabricated an ultra-stable gel-type MXene ink based MSC given in **Figure 5(a)** by modifying its viscoelastic behavior in universal water solvent. The as fabricated device **Figure 5(b)** displays a maximum energy density of  $51.7 \mu\text{Whcm}^{-2}$ . Further optimizations of active material layer have been done to further enhance the areal capacitance. Good adhesion & no change of electrochemical performance, even on applying stress and strain on the device given in **Figure 5(c, f)**. The cyclic voltametric curves of all MSCFs and the best performing MSCF-10 as shown in **Figure 5(d, e)** [60]. Similarly, Free standing  $\text{Ti}_3\text{C}_2\text{T}_x$  (MXene) ink-based 3D MSCs were fabricated followed by freeze drying for shape retention. To increase the



**Figure 5.** (a) Demonstration of 3D interdigital MSC by 3D printing technique, (b) As printed MSC on glass substrate, (c) picture showing the strong adhesion of printed pattern on plastic substrate with great flexibility during repeated bending cycles, (d) CV curves of MSCF-1 at different scan rates from  $2 \text{ mVs}^{-1}$  to  $100 \text{ mVs}^{-1}$ , (e) CV curves of various MSCFs at scan rate of  $5 \text{ mVs}^{-1}$ , (f) CV curves of MSCF-10 at scan rate of  $10 \text{ mVs}^{-1}$  at different bending angles (Source: Reprinted from [60] with permission from, copyright@2020, ACS).

stability and electrical conductivity, optimizing the mass loading to get the better viscoelastic behavior are the key parameters to obtain high areal capacitance. The maximum areal capacitance of  $2.1 \text{ Fcm}^{-2}$  at  $1.7 \text{ mAcm}^{-2}$  was achieved by a single MSC device. This unique technique has a wide base to explore micro-supercapacitor applications just by playing with the rheological properties of inks [61].

### 3.6 Other techniques

Unconventional methods have also been employed to fabricate the MXene based MSCs. A group reported the direct writing of highly concentrated MXene-in-water inks of upto  $30 \text{ mg/mL}$  in water on different substrates by using commercial roller ball pen. Interdigital electrodes were designed to fabricate Micro-supercapacitors. Areal capacitance of single MXene MSC was  $5 \text{ mFcm}^{-2}$  and by joining four MSC devices in series, the potential window reached upto  $2.4 \text{ V}$  which is evident for the development of flexible MSC devices [62]. Zhang *et al.* used a novel stamping technique to fabricate interdigital MSC on various substrates by using  $\text{Ti}_3\text{CNT}_x$  (MXene) inks. They observed an areal capacitance upto  $61 \text{ mFcm}^{-2}$  at  $25 \mu\text{Acm}^{-2}$  which outperforms many of previous reports. The device also exhibits high coulombic efficiency of 100% even after 10,000 cycles. This novel approach opens a new exciting method to fabricate MSC in easy and facile way [63]. Hue *et al.* demonstrated a facile two-step laser jet vacuum assisted filtration approach to fabricate all-solid-state MXene based symmetric microsupercapacitors followed by gold sputtering on regular A4 paper. The device exhibits high energy density in the range of  $5.48\text{--}6.1 \text{ mWhcm}^{-2}$  depending upon the deposited thickness of the electrode. The maximum areal capacitance of  $27.29 \text{ mFcm}^{-2}$  was achieved. This

Techniques	Method	Merits	Demerits
Photolithography	Direct	Wafer-scale manufacturing, uniform & high-resolution patterning [47, 48].	Multi-step process, template assisted, time consuming method [48].
Inkjet and Extrusion Printing	Indirect	Scalable production, customized design, less wastage of material [52, 62].	Uncontrollable procedure of ink synthesis, Low resolution, nozzle jamming is one of the main disadvantages of this technique [52].
Laser Scribing	Direct	Cost effective, fast simple, high controllability [54, 55].	Confined to very few types of materials [6].
Screen Printing	Indirect	Highly scalable and fast process [59].	Relatively low-resolution power
3D Printing	Indirect	Controllable design of patterns, versatile thickness control [61].	Limited to few materials, complex processibility [61].
Electrophoretic Deposition	Direct	Economically viable, facile procedure [50].	Limited applicability.
Vacuum-assisted-filtration	Indirect	Easy process, controlled thickness [67].	Low resolution, size and shape limited.

**Table 1.**  
Merits and demerits of various fabrication techniques of MSCs.

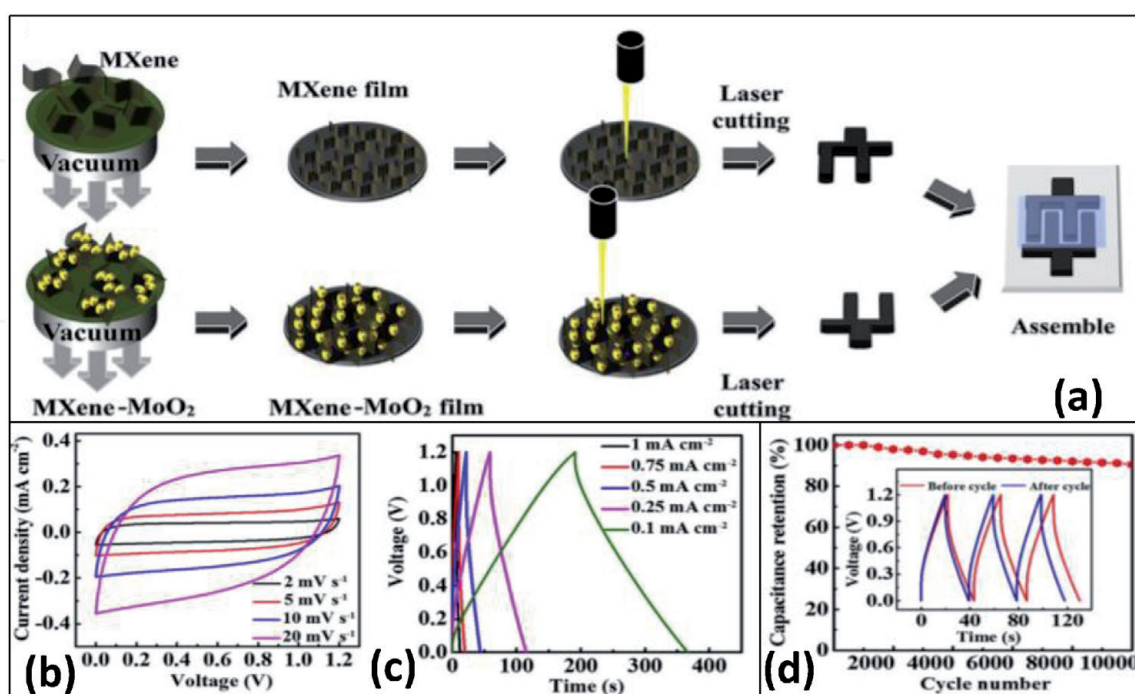
simple strategy of laser jet printed mask-assisted technique exhibits the potential for low cost fabrication method without compromising with device performance [64]. Li and co-workers proposed a simple scratch method to fabricate  $\text{Ti}_3\text{C}_2\text{T}_x/\text{EG}$  (MXene/exfoliated graphene) based MSC. A common syringe was employed with custom made X/Y axis instrument to fabricate the interdigital patterns. The device was able to display electrochemical stability upto 5000 charge/discharge cycles with around 90% retention of capacitance. This new approach shows promising results with almost negligible cost of fabrication at large scale [65]. Similarly, another group used automated scalpel technique to carve semi-transparent PEDOT/ $\text{Ti}_3\text{C}_2\text{T}_x$  heterostructures micro-supercapacitors. Device exhibit considerably high capacitance of  $2.4 \text{ mFcm}^{-2}$  at  $10 \text{ mVs}^{-1}$  shown by  $100 \text{ nm}$  device with almost 58% of capacitance retention at scan rate of  $1000 \text{ mV/s}$ . Further changes in color were observed on applying voltage  $0.6$  to  $0 \text{ V}$  and  $-0.6$  to  $0 \text{ V}$  while discharging which displays good electrochromic behavior PEDOT/ $\text{Ti}_3\text{C}_2\text{T}_x$  MSCs [66]. Advantages and disadvantages of various fabrication techniques of MSCs can be seen in **Table 1**.

## 4. MXene and its 2D hybrids for micro-supercapacitors

### 4.1 MXene based materials

In the past few years, MXenes have shown promising results for micro-supercapacitor applications. Due to their unique morphology, high metallic conductivity  $\sim 10,000 \text{ Scm}^{-1}$  and excellent intercalation behavior. Kurra *et al.* reported all MXene based low cost and highly scalable coplanar microsupercapacitors on paper substrates, the clay like MXenes based MSC displays the electrical conductivity of  $128 \text{ Scm}^{-1}$  and areal capacitance of  $25 \text{ mFcm}^{-2}$  in PVA- $\text{H}_2\text{SO}_4$  gel electrolyte. This study suggests the thickness of the active material plays a key role in the enhancement of the areal capacitance [56]. Similarly, Jiang and co-workers reported a wafer scale approach to fabricate an on-chip MXene based MSC device. The typical procedure includes photolithography of interdigital patterns followed by spray coating. The optimized  $\text{Ti}_3\text{C}_2\text{T}_x - 0.3 \mu\text{m}$  exhibits more capacitive behavior. The fabricated device was able to convert constant output positive peak voltage of  $0.6 \text{ V}$  into  $0.56 \text{ V}$  which is comparable with commercially available capacitor ( $4\text{mF}$ ). Demonstrating the advancements of MXene based MSCs for better alternative than bulky electrolytic capacitors in circuits [47]. Peng *et al.* fabricated interdigital patterned device by spray coating of  $\text{Ti}_3\text{C}_2\text{T}_x$  flakes directly on glass substrates which shows considerable areal capacitance of  $19.6 \text{ mFcm}^{-2}$  at  $20 \text{ mVs}^{-1}$  with ultra-high volumetric capacitance of  $356.8 \text{ Fcm}^{-3}$  at  $0.2 \text{ mAcm}^{-2}$  which is better than many of the carbon materials reported in the literature. But, the significant increase of areal capacitance  $27.3 \text{ mFcm}^{-2}$  at  $20 \text{ mVs}^{-1}$  can be seen by introducing the platinum current collectors [68]. Recently, A new strategy has been employed to pattern semi-transparent film of MXene based hybrid device on glass substrate without using any mask. An automated scalpel tool was used to produce micropatterns at various levels of transparency. On the increase of transparency from 38–88%, areal capacitance from  $19$  to  $283 \mu\text{Fcm}^{-2}$  can be evidently seen to be increased because of thick layers of MXenes. In contrast, With the increase of coating cycle, the resistance also increases from  $0.8$  to  $2 \text{ k}\Omega$ . The device demonstrated excellent capacitive behavior, offers variety of tunable approach by which one can enhance its physiochemical properties [69]. Li *et al.*, reported the fabrication of a double sided MSCs (DSMSCs) based on MXene ink with high working potential window of  $7.2 \text{ V}$  connected in different series and parallel configurations. With the decrease of interspace between MXene electrodes, the steep rise of capacitance can be seen.

Hence, DSMSC with 10  $\mu\text{m}$  interelectrode gap displays the highest volumetric capacitance of 308  $\text{Fcm}^{-3}$  at 5  $\text{mVs}^{-1}$  with ultra-high coulombic efficiency of 96.4% even after 10,000 cycles [70]. Quain and group reported direct writing with pen using additive-free MXene ink on flexible paper and non-paper substrates. The ink suspension displays good polydispersity index of 0.549 which consists of both small and large flakes of MXene at 30  $\text{mg mL}^{-1}$ . This single step fabrication technique is used to write on various flexible substrates. High potential window upto 2.4 V was also achieved by connecting four MSCs in series [62]. A facile Freeze-and -Thaw-assisted method (FAT) was used to produce two-atom thin layers of MXene with extra ordinary strength and flexibility. FAT-MXene exhibits an Areal capacitance of 23.6  $\text{mFcm}^{-2}$  with high volumetric capacitance. 591  $\text{Fcm}^{-3}$  at 20  $\text{mVs}^{-1}$  [71]. Zhang and group-fabricated a flexible asymmetric microsupercapacitors comprising MXene and MXene-MoO<sub>2</sub> films as negative and positive electrodes. The fabrication process includes vacuum filtration of the films followed by laser cutting of the interdigital patterns as given in the schematic **Figure 6(a)**. The asymmetric device exhibits large potential window of 1.2 V which is almost double of symmetric device. The device delivers volumetric capacitance of 63.3  $\text{Fcm}^{-3}$  and the CV and GCD curves shown in **Figure 6(b, c)** with excellent capacitance retention of 88% after 10,000 cycles **Figure 6(d)** [72]. Huang *et al.* reported a facile strategy to produce free standing-thick MXene sheets by vacuum filtration. The films exhibit an ultra-high conductivity upto  $1.25 \times 10^5 \text{ Sm}^{-1}$  for flexible-MSC. Further efforts has been done to fabricate an interdigital patterned MSC device which displays an considerable areal capacitance of 340  $\text{mFcm}^{-2}$  with volumetric capacitance of 183  $\text{Fcm}^{-3}$  and the corresponding energy density and power density are 12.4  $\text{mWhcm}^{-3}$  and 218  $\text{mWcm}^{-3}$  [73]. Another group demonstrated a highly conductive paper based MXene electrodes possessing a reasonable areal capacitance of 23.4  $\text{mFcm}^{-2}$  at 0.05  $\text{mAcm}^{-2}$ . One step process fabrication of electrodes in series as well as parallel to further get the desired capacitance [74].

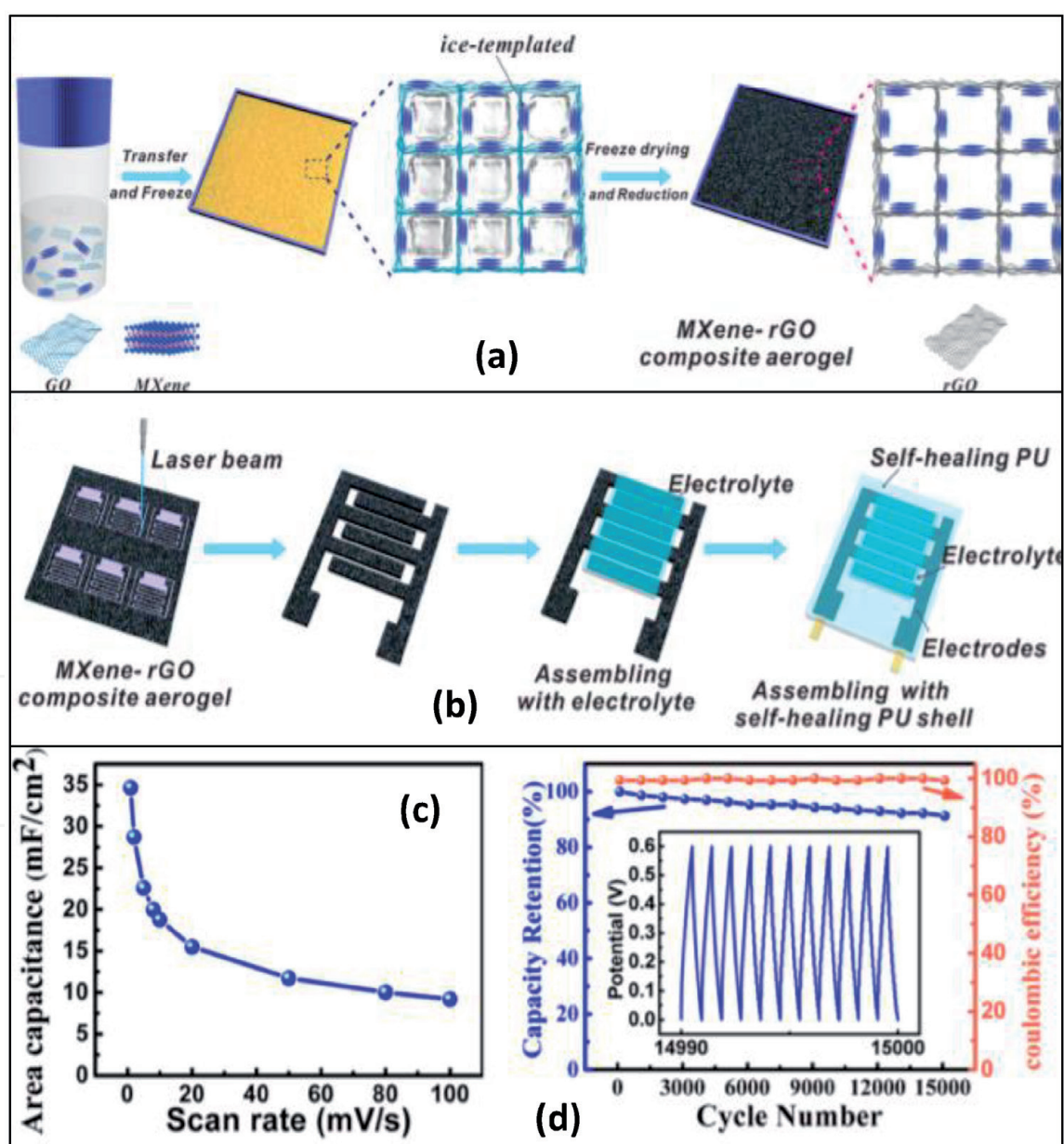


**Figure 6.**

(a) Fabrication procedure of MXene/MXene-MoO<sub>2</sub>-AMSCs asymmetric MSC, (b) cyclic voltametric curves at different scan rates from 2 to 20  $\text{mVs}^{-1}$ , (c) Galvanostatic charge-discharge at different current densities from 0.1 to 1  $\text{mAcm}^{-2}$ , (d) cyclic stability at current density of 0.5  $\text{mAcm}^{-2}$ . Inset shows the charge-discharge cycles after and before 10,000 cycles (source: Reprinted from [72] permission with Elsevier).

## 4.2 MXene and carbon materials

Recently, Kim et al., reported a scalable production of MXene/CNT based MSCs with a 500 nm gap between the interdigital fingers exhibiting fast ion diffusion for superior conductivity. High areal capacitance of  $317.3 \text{ mFcm}^{-2}$  was achieved at  $50 \text{ mVs}^{-1}$  by composite of S-DWCNT/MXene in PVA- $\text{H}_2\text{SO}_4$  gel electrolyte. It is also observed that by decreasing the electrodes gap  $10 \mu\text{m}$  to  $500 \text{ nm}$ , improves the ionic transfer rate, leading to increase in areal capacitance and energy density [48]. A 3D MXene/rGO self-healable aerogel MSC were reported by Yue and group. The fabrication process is shown in **Figure 7(a, b)** They employed new approach to fabricate highly stable device by keeping in focus to real time applications. Fabricated device was encapsulated into self-healing Polyurethane (PU) which enabled the device to adhere the external damage. The composite aerogel exhibited an exceptional recovery of electronic and mechanical properties even

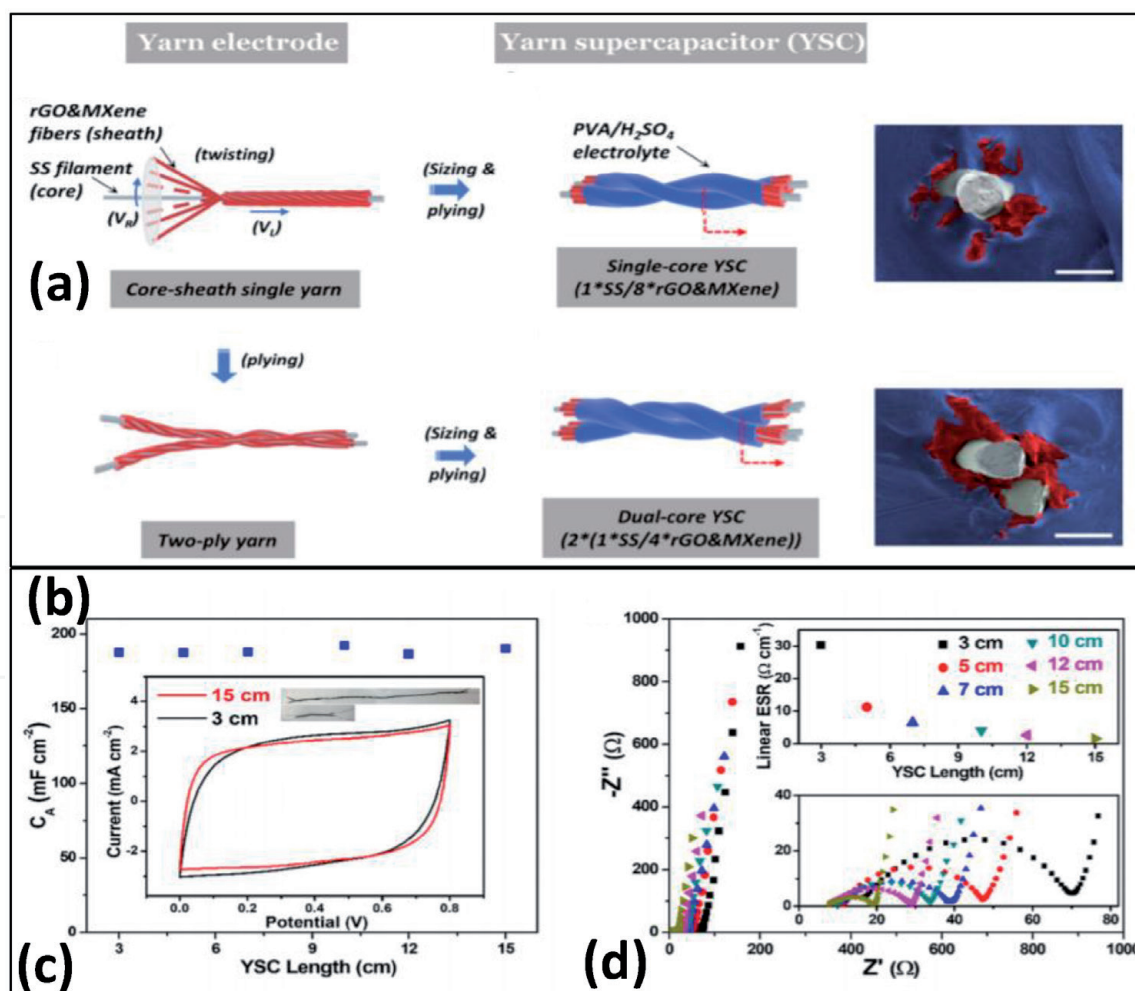


**Figure 7.** (a) Fabrication procedure of MXene-rGO composite aerogels, (b) laser cutting of interdigital pattern on MXene-rGO composite followed by assembling with self-healing PU, (c) graph showing the areal capacitance vs. scan rate MXene-rGO composite, (d) cycling stability of MXene-rGO composite aerogel MSC at  $2 \text{ mAcm}^{-2}$  (inset showing the GCD curves from 14990th to 15000th cycles (source: Reprinted from [75] with permission from, copyright@2018, ACS).

after full breakdown and shows the areal capacitance of  $34.6 \text{ mF cm}^{-2}$  at  $1 \text{ mVs}^{-1}$ , the areal capacitance and Cycling stability is shown in **Figure 7(c, d)**. [75] Couly *et al.* fabricated a high performing asymmetric flexible micro-supercapacitor based on MXene as negative and rGO as positive in both sandwich as well as interdigital configurations by using simple spray-coating of active material on PET substrates. The working potential window increased to 1 V for asymmetric device even with no. of bending and folding cycles, the maximum areal capacitance of  $2.4 \text{ mFcm}^{-2}$  at  $2 \text{ mV/s}$  was achieved. This study shows MXene as a promising material for negative electrode in asymmetric configuration with good stability and robust performance [76]. There is still wide room for further exploitation of carbon-based materials for micro-supercapacitor applications. A new emerging trend to produce nanofibers based on yarn type super capacitors for self-charged and wearable energy storage devices. MXenes have shown great potential to produce textile-based energy storage devices due to its robust stability as well as extraordinarily tunable properties. Yu and group, reported a helical shape MXene/CNT scaffold hybrid structure with reasonable volumetric capacitance of  $19.1 \text{ Fcm}^{-3}$  at  $1.0 \text{ Acm}^{-3}$  in 6 M of aqueous LiCl electrolyte. The MXene/CNT fiber exhibit good Energy density of 2.55 to  $1.15 \text{ mWhcm}^{-3}$  at power density of  $0.046$  to  $1.82 \text{ W cm}^{-3}$  in LiCl gel electrolyte. The best performing device displays the capacitance retention of  $19.5 \text{ Fcm}^{-3}$  (84%) at current density of  $1.0 \text{ Acm}^{-3}$  [77]. MXene/rGO hybrid fiber supercapacitors were fabricated by wet-spinning assembly strategy with extremely high volumetric capacitance of  $586.4 \text{ Fcm}^{-3}$  at  $10 \text{ mV/s}$ . The composite fibers display an ultra-high electrical conductivity of  $2.9 \times 10^4 \text{ S cm}^{-1}$ . They observed that the flexibility of the fiber can be increased by adjusting the concentration of graphene [78].

In another report by chen and group, MXene-MoS<sub>2</sub> based free standing MSCs were fabricated by simple and low-cost vacuum filtration method followed by carving of interdigital patterns with laser source. By introducing the MoS<sub>2</sub> into MXenes which further enhances the electrochemical performance with almost 60% increase as compared to pristine MXene. i.e., the fabricated device displays a high specific capacitance of  $173.6 \text{ F/cm}^3$  at the scan rate of  $1 \text{ mV/s}$ , MSC shows around 98% of capacitance retention with 89% of coulombic efficiency even after 6000 cycles along with several bending angle of device upto  $150^\circ$ . The above study demonstrated huge potential of TMDs which can be introduced with MXenes to make high performing MSC devices [67]. Li *et al.* demonstrated a strategy to mitigate the self-restacking of MXene layers by introducing RuO<sub>2</sub> nanoparticles by simple wet chemical phase reaction to improve the ion exchange rate. Also integrating with conductive Ag nanowires into the MXene further decrease the surface resistance of electrodes. The optimized MSC device achieved an ultrahigh volumetric capacitance of  $864.2 \text{ Fcm}^{-2}$  at  $1 \text{ mV/s}$  with 90% of capacitance retention even after 10,000 cycles [79]. For the first time, Wang *et al.* reported PANI/MXene based film electrodes with an exceptionally high volumetric capacitance of  $1167 \text{ Fcm}^{-3}$ . The asymmetric device by taking MXene as a negative electrode exhibit a maximum energy density of  $65.6 \text{ WhL}^{-1}$  which overshadows many of the previous reported MXene based Micro-supercapacitors [80]. A new kind of stretchable micro-supercapacitors based on MXene/Bacterial Cellulose (MXene/BC) composite free-standing paper were fabricated showing an exceptionally high young's modulus of 15–35 GPa with tensile strength of upto 200–300 GPa. Here BC acts as a spacer intercalated between the MXene sheets to prevent the re-stacking of MXene flakes. A conventional laser cutting tool used to fabricate stretchable micro-supercapacitor device was prepared which displays the high areal capacitance of  $111.5 \text{ mF cm}^{-2}$  in parallel device configuration with reasonable energy density of  $0.00552 \text{ mWhcm}^{-2}$  [81]. Shao *et al.* synthesized MXene-polymer composite nanofibers as flexible

yarn electrodes by simple electrospinning the active material on PET sheets. The symmetric device displays high areal capacitance of upto  $18.39 \text{ mFcm}^{-2}$  at scan rate of  $50 \text{ mVs}^{-1}$  which is better than many other carbon based yarn fiber supercapacitors [82]. Another group of researchers fabricated MXene/PEDOT-PSS based yarn supercapacitors (YSCs). A 3 cm flexible fiber shows extraordinarily high length capacitance of  $131.7 \text{ mF cm}^{-1}$  at  $0.2 \text{ mAcm}^{-1}$  with capacitive retention of 95% even after 10,000 cycles. They observed the reasonable contribution of conductive-polymer PEDOT-PSS in improving the device performance, suggesting a potential candidate in flexible yarn supercapacitor in portable electronics [83]. A new strategy has been employed to fabricate dual-core yarn supercapacitor (YSC), fabrication process shown in **Figure 8(a, b)** consist of rGO and MXene hybrid fibers encapsulated with PVA- $\text{H}_2\text{SO}_4$ . The average diameter of YSC is  $500 \mu\text{m}$  showing the superior linear capacitance  $43.6 \text{ mFcm}^{-1}$  at  $20 \text{ mVs}^{-1}$ . The areal capacitance was maintained above  $175 \text{ mFcm}^{-2}$  with respect to increasing length. They observed the charge transfer resistance ( $R_{ct}$ ) ESR of YSCs decreases gradually with increase in length such as  $30.3 \Omega\text{cm}^{-1}$  at 3 cm,  $3.9 \Omega\text{cm}^{-1}$  at 10 cm to  $1.6 \Omega\text{cm}^{-1}$  at 15 cm the graphs are shown in **Figure 8(c, d)**. The YSC device of 15 cm displayed areal density of  $54.5 \mu\text{Whcm}^{-2}$  at a power density of



**Figure 8.** Schematic illustrations of fabrication process of (a)  $1^*SS/S^*rGO\&MXene$  YSC single core YSC cross-sectional SEM image (scale bar -100 μm), (b)  $2^*(1^*SS/4^*rGO\&MXene)$  dual-core YSC cross-sectional SEM image (scale bar -100 μm), (c) areal capacitance of dual-core YSC inset: CV curves at  $20\text{mVs}^{-1}$  in 3 and 15 cm, (d) comparison of Nyquist plots of dual-core YSCs from 1 MHz to 0.01 Hz in different length inset: Linear ESR as a function of YSC length (top), zoom in image of Myquist plots (bottom) (source: Reprinted from [84] with permission from, copyright@2020, ACS).



Material	Method	Electrolyte	Potential Window	Device Performance		Specific Capacitance		Capacitance Retention	References
				Energy Density	Power Density	Areal	Volumetric		
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> (100 nm-25 μm)	Photo-lithography		0 to 0.6	_____	PVA-H <sub>3</sub> PO <sub>4</sub>	0.5 mFcm <sup>-2</sup> @120 Hz	30 Fcm <sup>-3</sup> @120 Hz	_____	[47]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> /CNT <sub>500nm</sub>	FIB Lithography	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	_____	_____	317 mFcm <sup>-2</sup> @ 50mVs <sup>-1</sup>	_____	_____	[48]
Ti <sub>3</sub> C <sub>2</sub> T <sub>xN=25</sub> Ti <sub>3</sub> C <sub>2</sub> T <sub>xN=5</sub>	Inkjet Extrusion	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.5	_____	_____	12 mFcm <sup>-2</sup> _____	562 Fcm <sup>-3</sup> _____	100% (10,000) 97% (15,000)	[52]
SA- Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> P-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Inkjet Inkjet	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 1	100.2 mWhcm <sup>-3</sup> _____	1.9 Wcm <sup>-3</sup> _____	108.1 mF cm <sup>-2</sup> @1 Ag <sup>-1</sup> 48.4 mFcm <sup>-2</sup> at 1Ag <sup>-1</sup>	720.7 Fcm <sup>-3</sup> @1 Ag <sup>-1</sup> _____	94.7% (4,000) 72.4% (4,000)	[53]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Laser Writing	3 M H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	0.25 μWhcm <sup>-2</sup>	2.94 mWcm <sup>-2</sup>	15.03 mFcm <sup>-2</sup>	_____	105% (10,000)	[54]
Double sided Zn//MXene (Asymmetric) Carbon//MXene (Asymmetric)	Laser writing Laser writing	PVA- Zn (CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> PVA-LiCl	0 to 1.1 0 to 0.8	_____	_____	66.5 mFcm <sup>-2</sup> 52.3 mFcm <sup>-2</sup> @2mAc <sup>-2</sup>	_____	86% (5,000) _____	[55]
Clay like Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Laser Writing	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	0.77 μWhcm <sup>-2</sup>	46.6 mWcm <sup>-2</sup>	25 mFcm <sup>-2</sup>	_____	92% (10,000)	[56]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> Sediments	Screen Printing	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	1.32 μWhcm <sup>-2</sup>	778.33 μWcm <sup>-2</sup>	158 mFcm <sup>-2</sup>	_____	95.8% (16,000)	[58]
MXene//Co-Al layered double hydroxide (Asymmetric) MXene	Screen Printing Screen Printing	PVA-KOH PVA-KOH	0.4 to 1.45 0 to 0.6	8.84 μWhcm <sup>-2</sup> 3.38 μWhcm <sup>-2</sup>	0.23 mWcm <sup>-2</sup> _____	40.0 mF cm <sup>-2</sup> @0.75bmAc <sup>-2</sup> 25 mFcm <sup>-2</sup>	_____	92% (10,000) _____	[59]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	3D Printing	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	8.4 μWhcm <sup>-2</sup>	3.7 mWcm <sup>-2</sup>	168.1 mFcm <sup>-2</sup>	_____	_____	[60]

Material	Method	Electrolyte	Potential Window	Device Performance		Specific Capacitance		Capacitance Retention	References
				Energy Density	Power Density	Areal	Volumetric		
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	3D Printing	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	0.0244 mWhcm <sup>-2</sup>	0.64 mWcm <sup>-2</sup> @ 4.3 mAcms <sup>-2</sup>	2.1 Fcm <sup>-2</sup> @1.7 mAcms <sup>-2</sup>	_____	90% (10,000)	[61]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Direct Writing	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	_____	_____	5mFcm <sup>-2</sup>	_____	_____	[62]
l-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Stamping Strategy	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	0.63 μWhcm <sup>-2</sup>	0.33 mWcm <sup>-2</sup>	56.8 mFcm <sup>-2</sup> @ 10mVs <sup>-1</sup>	_____	93.7% (10,000)	[63]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Laser jet Printing	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	6.1 mWhcm <sup>-3</sup>	_____	27.29 mFcm <sup>-2</sup> @0.25 mAcms <sup>-2</sup>	_____	_____	[64]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Scratch method	PVA-H <sub>3</sub> PO <sub>4</sub>	0 to 0.7	2.3 mWhcm <sup>-3</sup>	159.6 mWcm <sup>-3</sup>	25.5 mFcm <sup>-2</sup> @ 5mVs <sup>-1</sup>	_____	90% (5,000)	[65]
PEDOT/Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> 100nm	Spray Coating	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	_____	_____	2.4 mFcm <sup>-2</sup> @ 10mVs <sup>-1</sup>	_____	_____	[66]
Free-standing Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> – MoS <sub>2</sub>	Laser Engraving	Gelatin-ZnSO <sub>4</sub>	0 to 0.8	15.5 mWhcm <sup>-3</sup>	0.97 Wcm <sup>-3</sup>	_____	173.6 Fcm <sup>-3</sup> @1mVs <sup>-1</sup>	98% (6,000)	[67]
s-Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Spray coating + Laser engraving	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	11–18 mWhcm <sup>-3</sup>	0.7–15 W cm <sup>-3</sup>	27.3 mFcm <sup>-2</sup> @ 20mVs <sup>-1</sup>	356.8 Fcm <sup>-3</sup> @ 0.2 mAcms <sup>-2</sup>	100% (10,000)	[68]
90 nm Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> thin film	Dip Coating + Automated Scalpel patterning	PVA-H <sub>3</sub> PO <sub>4</sub>	0 to 0.6	_____	_____	_____	1500 Fcm <sup>-3</sup>	_____	[69]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -MSC 10 μm	Laser Etched	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	_____	_____	_____	308 Fcm <sup>-3</sup> @5mVs <sup>-1</sup>	93% (10,000)	[70]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Mask-assisted vacuum filtration	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	10.3 to 29.6 mWhcm <sup>-3</sup>	18.6 to 3.1 Wcm <sup>-3</sup>	23.6 mFcm <sup>-2</sup>	591 Fcm <sup>-3</sup>	97.8% (2,000)	[71]

Material	Method	Electrolyte	Potential Window	Device Performance		Specific Capacitance		Capacitance Retention	References
				Energy Density	Power Density	Areal	Volumetric		
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> //Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -MoO <sub>2</sub> -AMSCs (Asymmetric)	Vacuum filtration + Laser cutting	PVA- LiCl	0 to 1.2	9.7 mWhcm <sup>-3</sup>	0.198 Wcm <sup>-3</sup>	19 mFcm <sup>-2</sup>	63 Fcm <sup>-3</sup> @ 2mVs <sup>-1</sup>	88% (10,000)	[72]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Vacuum filtration + Laser cutting	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.7	43.5 mWhcm <sup>-2</sup> 12.4 mWhcm <sup>-3</sup>	87.5mWcm <sup>-2</sup> 218.8 mWcm <sup>-3</sup>	73–340 mFcm <sup>-2</sup>	183–162 Fcm <sup>-3</sup>	82.5% (5,000)	[73]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> on paper	Spray coating + Laser coating	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	1.48 mWhcm <sup>-3</sup>	189.9 mWcm <sup>-3</sup>	23.4 mFcm <sup>-2</sup> @0.05 mAcms <sup>-2</sup>	—	92.4% (5,000)	[74]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> -Graphene aerogel	Laser cutting	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	—	—	34.6 mFcm <sup>-2</sup> @ 1 mVs <sup>-1</sup>	—	91% (15,000)	[75]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> //rGO (Asymmetric)	Spray coating	PVA- H <sub>2</sub> SO <sub>4</sub>	0 to 1	8.6 mWhcm <sup>-3</sup>	0.2 Wcm <sup>-3</sup>	2.4 mFcm <sup>-2</sup> @2 mVs <sup>-1</sup>	80 Fcm <sup>-3</sup>	97% (10,000) - Interdigital	[76]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> /CNT (YSC)	—	PVA-LiCl	0 to 0.9	2.55mWhcm <sup>-3</sup>	45.9 mWcm <sup>-3</sup>	—	22.7 Fcm <sup>-3</sup> @ 0.1 Acms <sup>-3</sup>	99% (1,600)	[77]
Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> /rGO	—	PVA-H <sub>3</sub> PO <sub>4</sub>	0 to 0.8	13.03 mWhcm <sup>-3</sup>	0.59 Wcm <sup>-3</sup>	—	586.4 Fcm <sup>-3</sup> @ 10 mVs <sup>-1</sup>	—	[78]
RuO <sub>2</sub> /Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	Screen printing	PVA-KOH	0 to 0.6	13.5 mWcm <sup>-3</sup>	48.5 Wcm <sup>-3</sup>	—	864.2 Fcm <sup>-3</sup> @ 1mVs <sup>-1</sup>	90% (10,000)	[79]
PANI/MXene//MXene	—	1 M H <sub>2</sub> SO <sub>4</sub>	0 to 1.4	65.6 WhL <sup>-1</sup>	1687.3 WL <sup>-1</sup>	—	231.4 Fcm <sup>-3</sup> @ 10mVs <sup>-1</sup>	87.5% (5,000)	[80]
MXene/Bacterial Cellulose	Vacuum filtration + Laser cutting	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	0.0055 mWhcm <sup>-2</sup>	—	112.2 mFcm <sup>-2</sup>	—	—	[81]
Polyester @MXene	Electrospinning of fibers	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.6	0.38–0.67 μWhcm <sup>-2</sup>	0.09–0.39 mWcm <sup>-2</sup>	7.99 mFcm <sup>-2</sup> – 18.39 mFcm <sup>-2</sup>	~4.5 Fcm <sup>-3</sup> @5 mVs <sup>-1</sup>	98.2% (6,000)	[82]

Material	Method	Electrolyte	Potential Window	Device Performance		Specific Capacitance		Capacitance Retention	References
				Energy Density	Power Density	Areal	Volumetric		
MXene/ PEDOT-PSS	Fiber coating	Conductive binder PEDOT-PSS	0 to 0.5	—	—	131.7 mFcm <sup>-1</sup> @0.2 mAcm <sup>-1</sup>	—	90% (10,000)	[83]
rGO/MXene Hybrid	Wet-spinning	PVA-H <sub>2</sub> SO <sub>4</sub>	0 to 0.8	5.5 μWhcm <sup>-1</sup>	510.9 μWcm <sup>-1</sup> 2502.6 μWcm <sup>-2</sup>	77 mFcm <sup>-1</sup> 377.3 mFcm <sup>-2</sup>	23.2 Fcm <sup>-3</sup>	82% (10,000)	[84]

**Table 2.**  
Summary of recently reported MXene based micro-supercapacitors.

1251.5  $\mu\text{Wcm}^{-2}$  which directly outperforms the previous reported literatures [84]. The detailed summary of data is presented in the **Table 2**.

## 5. Future perspective and outlook

Since the discovery of MXenes in 2011 by Naguib et al. [17] MXenes have become a best choice for micro-electrodes to develop on-chip and self-charged MSC for wireless and wearable electronics applications. There is a significant increase in research on MXene based MSC due to its extraordinarily high electronic conductivity, good volumetric capacitance and excellent advancement in properties.

But, the development of MXene based MSC are still in early stage with necessity of optimization of electrode material, suitable electrolyte, substrates and many more. Right now, the focal point of researchers is on the enhancement of areal capacitance and power density of the fabricated MXene based MSC devices. However, there is an act of negligence over its property to self-discharged in open-circuit which needs to be resolved as soon as possible. One solution to this is to further integrate MSCs device with energy harvester like micro-piezoelectric or solar power cell component which will improve long term charge-storage property instead of self-discharging.

Also, the choice of electrolyte plays an important role to enhance the electrochemical performance of MSC device. Generally, polymer gel electrolyte. Particularly, PVA- $\text{H}_2\text{SO}_4$  is widely used ion exchange for MXene based electrodes for micro-devices. But due to low voltage window there is a call for an alternative which can help to increase the stability and voltage window. So that, there is an urgent requirement to study different electrolytes and polymers to achieve better performing MSC. In contrast to polymer matrix electrolyte, a new emerging class of quasi-solid electrolyte called as ionogel which is more mechanically and thermally stable than the regular gel electrolyte. All this demonstrates the possibility of ionogel to be a potential candidate for MSCs. To further expand potential window there is a requirement to make asymmetric devices which can further increase the voltage range above 3 V for real time applications.

Despite recent developments of  $\text{Ti}_3\text{C}_2\text{Ti}_x$  (MXene) based MSCs. There is still a big room to synthesis new MXene materials and explore their properties for the better understanding of charge storage mechanism which later can pave the way for future MSCs devices.

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## Conflict of interest

The authors declare no conflict of interest.

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