Applications of MXene-based composite fibers in smart textiles

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Abstract. MXenes, a new family of early transition metal carbides or carbonitrides, have shown much promise over other 2D materials, due to the excellent conductivity, high power density, reliable cycling life and multifunctional applications. In general, the rich tunable surface terminations and chemical hydrophilicity of MXenes make them as attractive candidates in terms of energy-storage, sensors and shielding applications, especially in portable, wearable and flexible smart textiles. This review presents a brief phylogeny, synthesis, structural characteristics of MXene, and main applications of MXene-based composite in smart textiles, representing the tuning of properties for applications including fiber-based supercapacitors, sensors and electromagnetic shielding. Finally, the challenges and future perspectives of MXene in textiles are also considered.

1. Introduction

MXene was discovered by Y. Gogotsi, a professor of materials science at Drexel University in 2011 [1] presenting a graphene-like two-dimensional crystal structure. In addition to the performance of traditional two-dimensional materials, MXene also reveals good conductivity, hydrophilicity, light transmittance and magnetism [2-6], which is a promising candidate to be applied in smart textiles. The MXene-based textiles are explored in the fields of flexible supercapacitors, wearable sensors and electromagnetic shields etc., which can be further developed as physiological monitoring [7], human-computer interaction [8], temperature and humidity sensing [9], EMI shielding [10], energy storage [11] and other intelligent functions of wearable electronics in the future.

Smart fibers provide the possibility of improving the comfortability and flexibility of wearable electronic devices as shown in figure1. MXene shows a larger volume specific capacitance, more excellent hydrophilicity, higher metallic conductivity (up to 9880 S/cm) and more stable layered structure than those of carbon-based 2D materials like graphene. During the process of synthesis, some terminating groups (such as -OH, -F, -O, etc.) are introduced on the surface of MXene, which are easily to be modified. Different modification methods lead to different properties of MXene. There are a series of MXene-based composites: composites obtained by combining MXene with commercial fabrics showing excellent light-weight, heat and temperature sensitivity, which can be used to prepare self-heated textiles; composites obtained by combining MXene with conductive cloths presenting outstanding stability with high volume density and power density as wearable energy storage devices [12]. The “accordion-like” MXene structure also provides an interface for microwave absorption, which is an ideal choice of electromagnetic absorbers, and has great potential applications in protective...
clothing for pregnant women, electronics industry and military. With the development of spinning methods, MXene-based fibers that are directly or indirectly fabricated provide the possibility for the realization of wearable smart textile.

Figure 1. Illustration of the development of fibers from natural, regenerated, and synthetic sources to functional fibers to be enabled in smart garments [13].

2. Synthesis and structural characteristics of MXene
In 2011, Naguib et al. [14] firstly obtained a graphene-like material by etching the Ti$_3$AlC$_2$ precursor in an HF solution (50% concentration) at room temperature, which was so called as MXene. The Al element in the Ti$_3$AlC$_2$ phase was extracted to obtain the Ti$_3$C$_2$ MXene with an “accordion-like” structure. Using the same etching principle, more than 20 different MXenes have been obtained [15]. Because there are certainly great danger about using HF, people have developed a mild etching method with a mixed solution of HCl and LiF to etch the MAX phase, as well as NH$_4$NF$_2$ etching, chemical vapor deposition (CVD), template method, and other synthetic methods. Different synthetic methods cause different structures and graft demanded surface groups, but the hydrophilic surface of MXene is basically unaffected.

MXene has a large surface area, which provides high energy density and more active spots. MXene is easily oxidized when exposed in the air due to the large number of -O and -OH groups on the surface. In addition, the physical size of MXene sheets is quite small (less than 1 μm), and the interaction force between the sheets is weak which increase the difficulty of preparing pure MXene fiber. The terminal groups on the MXene surface combined with the functional groups on the fiber surface to increase adhesion, thereby realizing the fabrication of continuous fiber and also improving the mechanical properties of the composite fiber.

3. Synthesis of MXene-based fiber
As the name implies, MXene-based fiber is a fiber spun from MXene or mixture of MXene and other materials. Coating or deposition technology has been widely utilized to fabricate composite fiber, which is simple and easy as long as MXene is applied to the fiber substrate. Hu et al. [16] designed a set-up to pass the cotton yarn or nylon multifilament through the MXene dispersion at a certain rate to obtain MXene coated yarn or fiber. Mixing MXene with organic solvent or polymer as a spinning dope is commonly used to manufacture MXene-based composite fiber only when each component is evenly dispersed and independent in dispersion. The comment methods of spinning fiber are wet spinning, electrostatic spinning and melt spinning [17]. The obtained composite fibers are broadly applied like MXene/carbon fiber supercapacitor, MXene/silver coated nylon fabric sensor and so on [18].

4. MXene-based composite fibers in smart textiles
Wearable, portable, and foldable electronic devices have been developed rapidly over the last decade and may further dominate life in the future. The popularity of these electronic devices such as smart backpacks and intelligent watches has renewed interest in MXene-based fiber accessories: [19] the scope
of application involves wearable energy storage [20], pressure sensor [21], strain sensor [22] and electromagnetic shield [23] etc.

4.1. Fiber-based supercapacitor

Among a wide variety of energy-storage devices, supercapacitors are very attractive alternative, owing to many promising features such as high power density, stable cycle life and operating temperature range. As an important basis of smart textiles, fiber supercapacitors can meet the energy needs of vulnerable groups in medical monitoring, military personnel communication conditions, and electronic production.

A series of MXene-based composite materials with excellent electrochemical performance have been reported in recent years, showing in figure 2. Pure MXene fibers can be obtained by wet spinning technology according to the mechanism of liquid crystal phase without additives, binders or stabilizers [24]. The homogeneously dispersed 2D MXene spinning dope successfully produced flexible meter-long continuous MXene fibers with an ultrahigh electrical conductivity of 7750 S/cm. Entirely pure 1D MXene fibers with high electrical conductivity shows a high volumetric capacitance of about 1265 F/cm³ at 10mV/s, which is equivalent to the independent MXene film electrode [25]. These data indicate that such free-standing and highly conductive pure MXene fiber is suitable for smart textile applications, especially supercapacitors. However, fabricating the pure MXene fiber is still a challenge because of the small size and the weaker interaction force between the sheets.

In addition, integrating MXene materials into fibers is one of the effective strategies to obtain flexible electrodes with high capacitance on account of the larger surface area of 1D fiber-shape. Yang et al. reported a wet-spinning assembly strategy for the continuous fabrication of MXene-based fibers through a synergistic effect between graphene oxides liquid crystals and MXene sheets. An excellent overall fiber electrical conductivity (2.9 × 10⁴ S/m) and superior volumetric capacitance (586.4 F/cm³) of the integrated fiber-constructed supercapacitor exceeding neat reduced graphene fibers were achieved and shown in figure 2 (a) and (b). Although the volume of device can be reduced by adding pseudo-capacitance materials to improve charge transfer, the introduce of pseudo-capacitance materials will affect the cyclical and mechanical properties of fiber [26].

On the contrary, the higher structural density obtained by adding Mxene can enhance the mechanical properties of the fiber, but its flexibility is relatively low [27]. Shao et al. [28] discussed the nanofibers
coated yarn concept which involved facile self-winding of electroactive nanofibers of MXene onto polyester (PET) yarn substrate via templated electrospinning. The resultant yarn self-possesses excellent required properties of flexibility, strength and high-power density owing to the highly electroactive MXene nanofibers and PET employed. Such modified yarns can perfectly fit in wearable storage applications for the anticipated drive of the next generation devices. Among these composite fibers, MXene provides excellent electrical conductivity and demonstrates outstanding flexibility and wearability as shown in figure 2 (d) and (e) [29-30]. These MXene-based fiber supercapacitors also show outstanding device stability when exposed to various deformations and cycle life testing, suggesting the potential use of MXene for the development of fiber supercapacitor as energy storage device for powering portable and wearable electronics.

4.2. Sensor

One of the challenges of strain sensing fabrics is that the addition of conductive fillers will decrease the spinnability or elasticity of fibers, so the conductive material cannot be assigned to elastomer polymer fibers. MXene sheets show excellent conductivity, hydrophilicity and rich terminal groups, which enhances their adhesion to the fiber and remains the elasticity of the composite fiber. MXene-based composite fiber can meet the basic requirements for the detection of physical deformation on electrical conductivity and stretchability. MXene-based sensor can be applied at wearable medical electronic products such as tracking human motion, motion guidance, rehabilitation training, remote health monitoring etc.

Seyedin et al. [22] reported a coaxial MXene/PU composite fiber with high electrical conductivity and stretchability in figure 3 (i) and (j). Compared with traditional composite fiber, MXene/PU fiber has better sensitive performance and mechanical performance. MXene/PU fibers were then integrated into an elbow sleeve by commercial-scale weaving. After wearing it, the computer successfully received the signal, proving that the MXene/PU textile can track various movements and achieve motion monitoring functions. Based on musculoskeletal disease (MSD), a sensor composed of AgNW/WPU-MXene multilayer sensing structure fiber was prepared by Pu et al. [31], which can monitor people's posture and correct bad body posture, thereby alleviating the prevalence of MSD (figure 3 (a-h)). The WPU particles and AgNW are physically cross-linked, which can improve the stability of the AgNW network in composite.

Figure 3 (a-h) Demonstration of monitoring, analysis and correction system of body posture in terms of head-forward, shoulder imbalance, kyphosis, fingers and the wrist [31], illustrations of (i) jersey textiles and (j) elbow sleeve knitted by using MXene/PU composite fibers [22].
4.3. Electronic shield

Nowadays, a large number of wireless signal transmissions will not only interfere with each other but also damage human health, especially for pregnant women and babies. The Po-Yen Chen team at the National University of Singapore prepared a stretchable conductor by depositing 2D Ti$_3$C$_2$T$_x$ MXene sheets and single-walled carbon nanotubes (SWNT) on pleated latex (Latex). It can be used to prepare high-performance wearable antennas and electronic shielding devices as demonstrated in figure 4 (b) [32]. MXene-SWNT/Latex (S-MXene/Latex) device can withstand up to 800% of the surface strain and exhibit strain-insensitive resistance characteristics in 500 continuous fatigue tests.

![Figure 4](image.png)

**Figure 4** (a) EMI shielding mechanism of MXene [34], and (b) digital photos of the scenarios fabricated by S-MXene shield's [32].

Wang et al. [23] introduced a stable ink by in-situ polymerizing polypyrrole (ppy) on the surface of MXene, coating silicone to increase the hydrophobicity and prevent the oxidation/degradation of MXene in a high humidity environment. The fabricated ppy/MXene composite was then deposited on the polyethylene terephthalate (PET) fabric to produce highly conductive and hydrophobic fabric with excellent electromagnetic interference (EMI) shielding efficiency and excellent Joule heating performance. Zhang et al. [33] deposited MXene in a plain-weave cotton fabric with vertical interweaving of warp and weft yarns by a spray coating method to form a vertically interconnected conductive network. The degree of conductive interconnection of the fibers can be determined by the operational cycles. The fabric decorated with MXene is not only breathable and flexible but also has excellent Joule heating, EMI and strain sensing performance. This versatile smart fiber is used to realize smart clothing [34].

5. Conclusion and Outlook

MXene, a novel and attractive two-dimensional material, is considered to be ideally applied in functional and flexible textiles due to the excellent inherent conductivity, adjustable surface chemistry and unique layered structure whether it is formed into filaments alone or composites with other fibers. This review shows the fibers fabricated by combining MXene with nanowires, conductive polymers, carbon-based materials and mixed conductive fillers, which proves that MXene has strong adaptability with other materials, further expanding the application range of MXene. This review mainly focuses on the application of MXene-based fibers in smart textiles like flexible supercapacitors, sensors and EMI electronic shielding. Although there are many breakthroughs in the electrochemical energy storage of MXene-based materials, further improvement of the performance of the MXene-based devices should be seriously considered.

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