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Bioinspired and biomimetic MXene-based structures with fascinating properties: recent advances

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Scientists have always been inspired by nature to design complex nanostructures and architectures with special features and functions. Latest among these is the construction of bioinspired MXenes and MXenebased structures with unique features such as high flexibility, strong electrical conductivity, high stability/ biocompatibility, lower toxicity, and special mechanical properties. There are important challenges ahead though, including the design of MXenes for single-purpose uses with high specificity and targeting properties or multi-purpose applications with special therapeutic and functional capabilities with improved toxicity and biosafety profile, environmental stability under diverse conditions, and industrialization/ optimization of the production process. The use of suitable manufacturing techniques with ecofriendly features and retracting the deployment of toxic and harmful substances is one of the leading challenges in the production of MXenes or MXene-centered composites. Inspired by biological systems, MXene-based entities or MXenes can be created for use in functional devices with special therapeutic and diagnostic capabilities; novel methods with sustainable and environmentally benign attributes ought to be realized for materials with unique designs (well-designed heterostructures and organic-inorganic hybrid materials) and desirable functions. Herein, recent advances pertaining to bioinspired and biomimetic MXenes and MXenecentered structures are discussed, focusing on important outcomes and future directions.

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1. Introduction

Biological structures with interesting functionalities have always attracted researchers to develop various novel nanoarchitectures and materials inspired by natural patterns. Recent advancements in engineering and materials science facilitate the creation of bioinspired (nano)structures with suitable multifunctionality, besides the improved properties. By learning from nature to produce biomimetics and bioinspired materials, various structures with unique physicochemical properties have been designed.¹ MXenes and MXene-based composites with their fascinating properties have been widely explored for diverse applications such as gene/drug delivery, biological imaging/ sensing, water desalination/treatment, tissue engineering, regenerative medicine, and cancer theranostics.²⁻⁷ These materials with diverse structural designs can be applied in various fields of electromagnetic interference (EMI) shielding, supercapacitors, electromagnetic wave absorption, solar cells, and wireless communication.8-11 As an example, EMI shielding with high performance was synthesized using MXenes (Ti₃C₂T_r) via a simple electrophoretic deposition technique.¹² In terms of the biomedical value of these compounds, Yin et al. 13 reported the synthesis of Nb₂C MXene-integrated three-dimensional (3D)-printing scaffolds against osteosarcoma, promoting osteo-conduction, -genesis, and -induction, as well as pushing the vascularization for bone regeneration.13

MXenes is one of the largest families of two-dimensional (2D) materials with adjustable structures, elastic mechanical strength, large surface area, high electronic conductivity, and environmental stability. 10,14 They have been broadly constructed by chemical vapor deposition, 15 electrochemical synthesis, 16 hydrothermal synthesis, 17 urea glass technique, 18 and various etching techniques, including electrochemical-, alkali-, molten salt-, and in situ hydrofluoric acid-forming etching approaches; 19-21 the selection of synthesis methods for MXenes significantly depends on their MAX precursor. Barsoum et al. 22 have reviewed the fabrication methods for MXenes and other ultrathin 2D transition metal carbides and nitrides. Besides, Gogotsi et al. 23 have discussed about the synthesis/processing of MXenes in addition to their structures, electronic/optical properties, and surface chemistry. Furthermore, in this direction, improving the performance and stability aspects, creating special properties and structure, reducing the toxicity, increasing the biocompatibility/biodegradability, and transforming laboratory scale generation into industry level production can be named as leading challenges.²⁴⁻²⁹

The construction of new micro and nanostructures with unique features, especially those inspired by nature, has always garnered the attention of scientists; assorted nature-enthused structures with high activity have been explored comprising bioinspired polymeric woods, lotus-leaf-like super-hydrophobic surfaces, and nacre-like structures. 30-33 The development of bioinspired and biomimetic (nano)structures embrace various fields of application such as drug/gene delivery, healing biological systems, textile industries (e.g., bioinspired fur from the polar bear), and waterproof effect (lotus leaf). 34,35 These materials have shown suitable advantages of cost-effectiveness and

environment-friendliness as compared to other available ones. In the field of drug delivery, they have exhibited improved biocompatibility, biodegradability, and targeting properties compared to other conventional materials;³⁶ in cancer therapy, they have exhibited reduced side effects by improved targeting properties. By the combination of biological and synthetic systems, innovative drug or gene carrier systems can be developed. Such delivery systems have demonstrated important benefits of improved biocompatibility, low toxicity, and lesser immunogenicity.37 In addition, bioinspired sensors systems present attractive features such as ultra-sensitivity, low-power consumption, and self-adaptability.³⁸ In one study, the production of spider web-inspired graphene skeleton was reported with appealing potentials in battery thermal management.³⁹ In addition, a mussel-inspired tactic was described for designing conductive polymeric nanoparticles with high biocompatibility; the prepared hydrogels with long-term adhesiveness from these nanoparticles have been employed in implantable bioelectronics and tissue regeneration applications. 40 By innovatively designing bioinspired MXene-based structures, a new path for the improvement of their properties such as adsorption performance, flexibility, photothermal conductivity, electric conductivity, and mechanical features has opened up. 41-43 However, the efforts still need extensive and focused exploration to uncover simple, inexpensive, and up-scalable techniques for designing bioinspired MXene-based structures with high performance and improved features. 44-47 Furthermore, by applying suitable functionalization/modification procedures, vital criteria of bioinspired MXene-based structures such as multifunctionality, stability, and biosafety can be better adjusted and improved. 41-43 Biomimetic and bioinspired MXenes with special features will soon find their distinctive position on research platforms focusing on the biomedicine and nanomedicine arena. They can be applied for developing next-generation smart nanosystems with clinical and biomedical potentials. 3,48-50 The shift toward the clinical use of MXenes and their derivatives with detailed assessments is warranted so that these substances, similar to many recognized materials, do not remain just at the laboratory level of biomedical curiosity without clinical uses; this necessitates detailed and long-term studies to find existing gaps and accurate evidences. Herein, the recent advances pertaining to bioinspired MXenes and MXene-based composites are highlighted, in view of their importance with an outlook on the future developments.

2. Bioinspired and biomimetic synthesis of nanomaterials

A variety of bioinspired and biomimetic synthesis strategies have been introduced to obtain nanostructures with unique morphologies and architectures. 35,51 In particular, the abundance/ availability of biomass and facile fabrication processes make these synthesis strategies very promising for the up-scalable fabrication of nanomaterials;52 however, biomass templates may exhibit some degree of inflexibility. Typically, biomimetic techniques can be divided into high-level biomimetic synthesis through

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soft/hard-combined membranes (e.g., artificial-active-membrane, eggshell-membrane, and commercial-polymer-film), intelligent biomimetic fabrication through liquid membranes with carriers (e.g., emulsion liquid membrane, supported liquid membrane systems, and reverse-micelle/microemulsion biomimetic techniques), living-organism biomimetic fabrication techniques (plants or microorganisms), and bioinspired fabrication through biomacromolecule regulation (e.g., protein-, nucleic-acid-, and polysaccharide-based templates). For instance, soft templates such as reverse micelles, liquid crystals, and microemulsion, in addition to hard templates such as anodic aluminum oxide and carbon nanotubes, can provide attractive tools for manufacturing nanostructures via their template-inducing effects and confinement abilities, respectively. 35,53 Nanomaterials prepared by applying hard templates have some advantages of uniformity and predictability, together with some limitations of inflexibility or difficulty to obtain complicated architectures. On the other hand, by applying soft template techniques, unique nanostructures can be obtained. However, they have the disadvantage of difficult control of the size/uniformity of the nanostructures, signifying the importance of optimization conditions.34-37

Bioinspired and biomimetic MXene structures

There is a vital need to design simple, low-cost, safer, and environmentally-benign methods with reliability for manufacturing MXenes. In this context, nature-inspired techniques have been rarely studied for synthesizing MXenes and their derivatives (Table 1).⁵⁴ MXene-integrated photonic crystal arrays have been constructed inspired by the wettability structure of Stenocara beetle and the adhesion capability of mussel; these arrays were employed for multichannel bioinformation coding.55 The designed MXenes were further integrated on the photonic crystal array's substrate mimicking the adhesion capacity of mussel-inspired dopamine. Because of their fluorescence resonance energy transfer influence, these MXene nanosheets could quench the fluorescence signals of quantum dot-altered DNA probes unless the corresponding targets exist. Also, these nanosheets could improve the contrast of structural color.⁵⁵ Flexible bioinspired MXene (Ti₃C₂T_r)-based films constructed from cellulose nanofibers, MXenes, and silver nanoparticles via a vacuum-assisted filtration technique exhibited high thermal conductivity; this was mainly because of the bridging effect of

Table 1 Some selected examples of bioinspired/biomimetic MXenes with their applications and advantages

MXenes	Inspired structures	Applications	Advantages/properties	Ref.
Ti ₃ C ₂	Inspired by the wettability structure of <i>Stenocara</i> beetle and the adhesion ability of mussel	Multichannel bioinformation coding	– High throughput information – High stability	55
$Ti_3C_2T_x$	Nacre-like structures	Multifunctional thermal management film	 High flexibility and thermal conductivity Unique mechanical, photothermal, and light-to-heat performance 	56
$\mathrm{Ti}_{3}\mathrm{C}_{2}\mathrm{T}_{x}$	Inspired by black scales of Bitis rhinoceros	Solar steam formation and wearable thermal management	– High light-to-heat performance with broadband light absorption	6
Ti_3C_2	Inspired by the multisensory feature of biological skin	User-interactive electronic skin; next-generation flexible electronics	 Excellent electromechanical features Suitable Joule heating function Ultra-flexible and user-interactive 	57
$\mathrm{Ti}_{3}\mathrm{C}_{2}\mathrm{T}_{x}$	Nacre-like structure	High-power flexible devices	 High thermal conductivity Improved electrical insulation 	58
$\mathrm{Ti}_{3}\mathrm{C}_{2}\mathrm{T}_{x}$	Nacre-like structure	Electromagnetic interference (EMI) shielding	 High flexibility Suitable mechanical properties Superb electric conductivity Excellent EMI shielding features Ultra-small thickness 	59
${ m Ti}_3{ m C}_2{ m T}_x$	Mussel-inspired MXene films	Energy storage and EMI	 Highly aligned tight layer structures Enhanced tensile strength with a simultaneous increase of elongation Good stability High electrical conductivity 	60
$\mathrm{Ti}_{3}\mathrm{C}_{2}\mathrm{T}_{x}$	Inspired by natural nacre	EMI and thermal managements	– Excellent EMI shielding properties – Excellent mechanical properties – Exceptional tensile strength (198.80 \pm 5.35 MPa) – Large strain (15.30 \pm 1.01%) – Good flexibility – High EMI shielding effectiveness (\sim 13188.2 dB cm 2 g $^{-1}$) – Excellent Joule heating function	61
$Ti_3C_2T_x$	Feather-like microstructure	Practical solar-powered water desalination under natural	 High energy efficiency (~88.52%) Highly efficient solar-powered water evaporation 	62
$\mathrm{Ti}_{3}\mathrm{C}_{2}\mathrm{T}_{x}$	Soft robotic skin with cephalopod skin-inspired multifunctionality	sunlight; thermal managements MXene robotic skins with ther- mal/strain sensation potentials	 Tunable infrared emission (0.30-0.80) Intrinsic Seebeck effect Crack propagation behaviors High electrical conductivity 	63

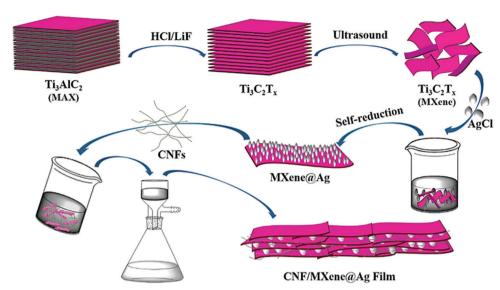


Fig. 1 Preparative process for cellulose nanofibers (CNF)/MXene@Aq multifunctional films with unique photothermal and mechanical features. Reproduced with permission from ref. 56 Copyright 2021 Elsevier

silver nanoparticles, which could greatly reduce the interface thermal resistance between MXene nanosheets in cellulose nanofibers matrix.56 The cellulose nanofibers/MXene film with a typical biomimetic nacre-like structure demonstrated suitable mechanical characteristics with a tensile strength of 71.4 \pm 2.8 MPa and a toughness of 1.0 \pm 0.06 MJ m⁻³, photothermal properties (the surface temperature of the film could reach \sim 48 °C after 210 s of 55 W light irradiation), and light-to-heat activity (Fig. 1); these structures can be applied for designing multifunctional thermal management film.⁵⁶ In addition, biomimetic MXene textures were constructed from MXenes (Ti₃C₂T_x), reduced graphene oxide, and MoS₂ (molybdenum disulfide) by applying a generalized technique through sequential thermal actuations to design biomimetic 2D-material nanocoatings. These structures exhibited improved light-to-heat activity with broadband light absorption (up to 93.2%);⁶ these bioinspired MXene nanocoatings should be further explored for designing next generation devices with stretchability and wearability features.⁶ This applied synthesis technique with simplicity ought to be further explored for designing innovative structures with multiple solar-thermal applications.

Wei et al. 64 described an innovative technique for the bioinspired functionalization of MXene-based materials wherein polymeric composites were constructed from Ti₃C₂T_x MXene and levodopa under mild reaction conditions. Levodopa adhered to the surface of MXenes via a self-polymerization technique; various carboxyl groups were involved during the polymerization process to produce poly-levodopa. These composites could be applied as adsorbents, providing significant adsorption capability for removing the heavy metal ions in comparison to pristine MXenes.⁶⁴ Moreover, such bioinspired functionalization methods may help to improve the biocompatibility and reduce the toxicity effects, thus promising new multifunctional structures for biomedical applications.⁶⁵ Shen et al.⁶⁶ reported biocompatible films composed of flexible silk fibroin@Ti3C2Tx MXenes with multifunctionality and biomimetic 3D cross-link structures, providing fascinating potentials for pressure sensing and human health monitoring; natural silk fibroin was utilized as a bridging agent for self-assembling nanosheets of MXenes into a continuous wave-shaped lamellar macrostructure (Fig. 2). It was assumed that hydrogen bonds could be formed between silk fibroin and MXenes due to the abundant surface functional groups (e.g., H, O, or F elements) on MXene sheets. These bonds strive to connect MXene nanosheets together to improve the mechanical strength and biocompatibility to meet the necessities for devices with flexibility and wearability. The designed films provided suitable sensitivity ($\sim 25.5 \text{ kPa}^{-1}$), good stability (~ 3500 cycles), rapid response/recovery time ($\sim 40/35$ ms), low elastic modulus (~1.22 MPa), and subtle pressure detection of limit (9.8 Pa).66 These biomimetic MXene-based composites are attractive candidates for next-generation personal healthcare wearable devices and artificial skins. 66 Shi et al. 67 have discussed the preparation and applications of MXenes in flexible devices, wherein wet chemical etching is still the common synthesis method for their preparation; however, some drawbacks such as contamination by pollutants during the synthesis process as well as efficient control during the etching steps are remaining challenges. Hence, there is a need for extensive research on newer assembly methods under mild conditions, low cost, up-scalable, and time-efficient features for manufacturing MXenes with high mechanical strength, flexibility, and electrical conductivity apt for flexible devices.⁶⁷

Bioinspired user-interactive electronic-skin was designed using a mold-casting technique to obtain digital electrical response and optical visualization upon external mechanical stimulus.⁵⁷ This flexible electronic-skin prepared from carbon nanotubes, cellulose nanofibers, and MXene nanohybrid network displayed suitable electromechanical optical and sensing property to obtain visual motion monitoring; it comprised a stretchable elastomer layer prepared from silicone rubber and **Materials Advances** A Degummed SF@MXene aqueous solution Dialyzed SF aqueous solution Assembly Silkworm cocoon Vacuum filtrate Ti,C,T, MXene SF molecular structure lamellar macrostructure Flexible biocomposite film



PET substrate

thermochromic pigments. Notably, this conductive nanohybrid network with excellent Joule heating function could produce controllable thermal energy under voltage input, providing the dynamic coloration of silicone-based elastomer. Human activities could be monitored with high accuracy using this bioinspired electronic skin, offering great opportunities for designing nextgeneration flexible electronic devices.⁵⁷ The preparation of MXene-based materials with appropriate mechanical properties and high flexibility has engrossed researchers' attention lately, especially to design next-generation portable and wearable electronic gadgets. However, some lingering challenges such as the severe restacking in the system and the lack of robust interfaces in individual MXene nanosheets are still awaiting resolution.⁶⁸ In one study, MXene structures were prepared inspired by the brick and mortar structure of nacre through the layer-by-layer assembly technique (Fig. 3).68 The MXene nacre has unique mechanical toughness with geometrical elasticity; its photothermal conversion potential was improved and the restacking of MXene nanosheets could be effectively suppressed. The electrodes

O: H

В

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constructed from these multifunctional MXenes can be deployed as all-solid-state supercapacitors with photothermal activity for applications in structurally-flexible energy systems.⁶⁸

SF@MXene film

The fabrication of extremely conductive and transparent MXene electrodes for malleable photodetectors is an important challenge because of the interchange between resistance and transmittance. 69 For this purpose, bioinspired transparent and flexible MXene films with significant transmittance of \sim 90% and low sheet resistance worth of $\sim 3 \Omega \text{ sq}^{-1}$ were constructed. Using various etching procedures, the function of MXene electrode could be adjusted owing to the existence of different terminal groups on the surface.⁶⁹ In addition, bioinspired $Ti_3C_2T_x$ (MXene) composite films were designed with an interlocking "brick-andmortar" microstructures through a vacuum-assisted filtration procedure (Fig. 4).⁷⁰ The designed nacre-like composite films exhibited unique mechanical properties and high electrical conductivity, offering alluring electromagnetic-interference shielding materials that are suitable for various smart devices.⁷⁰ Jiao et al.58 developed composite films with high flexibility and

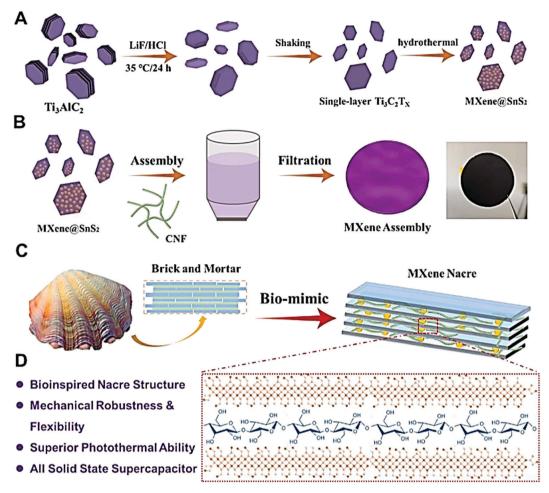


Fig. 3 Preparative process for bioinspired MXene-based structures constructed from $Ti_3C_2T_x$ nanosheets and SnS_2 nanoparticles. Reproduced with permission from ref. 68 Copyright 2021 Elsevier.

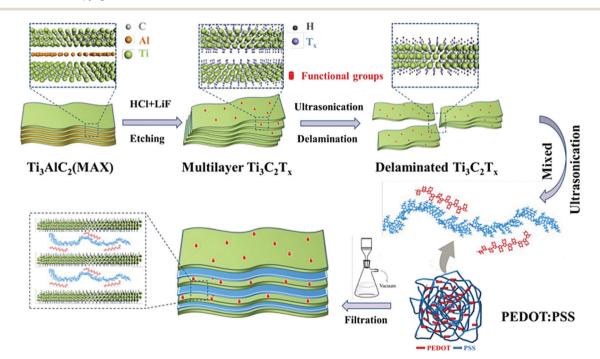


Fig. 4 The fabrication process for the bioinspired flexible composite films from $Ti_3C_2T_x$ and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) materials. Reproduced with permission from ref. 70 Copyright 2018 American Chemical Society.

typical nacre-like structures using cellulose nanofibers, nanodiamond, and MXenes (Ti₃C₂T_x) via a simple vacuum-assisted filtration technique. These composite films exhibited improved electrical insulation (1.63 \times 10⁶ Ω cm), and also significant thermal conductivity ($\sim 17.43 \text{ W m}^{-1} \text{ K}^{-1}$) owing to the bridging effect of nanodiamonds and MXene nanosheets. Notably, nacrelike structures and robust hydrogen bonding between the MXene nanosheets and cellulose nanofibers provided suitable mechanical features (89.14 \pm 3.61 MPa). These MXene-based composites are promising candidates for high-power flexible devices.58

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MXenes nanosheets demonstrated high conductivity with abundant surface functional groups, which are suitable for wave absorption and EMI shielding. To improve the fire safety and mechanical features of thermoplastic polyurethane, nanocomposites of MXenes (Ti₃C₂T_x)@strontium hydroxystannate (SrSn(OH)₆) nanorods were engineered inspired by leaf veins using a biomimetic method, providing promising options for portable devices. As a result, the toughness and tensile robustness of the nanocomposites was improved by 126% and 46%, respectively.71 These nanocomposites performed leaf veininspired hierarchical structure during the stretching behavior, causing 55% enhancement of elongation at break. After the fire safety evaluations, it was indicated that the peak heat release rate decreased by 37.31%. The hazardous pyrolysis products of thermoplastic polyurethane during the combustion were significantly reduced, in particular, the formation of carbon oxide and carbon dioxide were reduced by 96.04% and 89.85%, respectively, while the addition of MXene nanosheets was only 2 wt%. Consequently, ternary catalytic influence and labyrinth structure could improve the safety of thermoplastic polyurethane in electronic devices/products, showing superior toughness and reinforced fire safety advantages.⁷¹ In another study, silver nanowires with high flexibility and conductivity were doped on MXene (Ti₃C₂T_x)/cellulose nanofibrils films via the construction of biomimetic leaf-vein scaffolds using a facile vacuum-assisted filtration, thus providing significant electrical conductivity and high EMI shielding effectiveness value (Fig. 5); the ultrathin composite films were obtained with strengthened mechanical flexibility and robustness because of the "brick-andmortar" structures. 72 Also, these films exhibited fast response, high stability and precision, and ultralow voltage supply (1-3 V), offering promising applications such as wearable devices, thermotherapy, and smart garments.⁷² Yu et al.⁷³ prepared textiles endowed with high EMI shielding activities, flexibility, hydrophobicity, and remarkably sensitive humidity response by the deployment of the vacuum-assisted layer-by-layer assembly method. The leaf-like nanostructures were assembled from MXene nanosheets (the lamina) and silver nanowires (highly conductive skeleton, vein), offering promising potentials for humidity sensors, EMI shielding, and smart garments.⁷³

Bioinspired platforms have been designed from MXene (Ti₃C₂T_x) nanostructures, silver nanowires (brick), and poly(dopamine)/Ni²⁺ (mortar) as sensitive and highly stretchable strain sensors with potential use in human health and motion analyses.⁷⁴ In addition, polyurethane/MXene nanocomposites with nacre-like "brick and

mortar" architectures were constructed,59 which displayed high flexibility, promising EMI shielding characteristics, and unique mechanical features. Their thickness was ultrasmall (less than 10 μ m) and electric conductivity was superb (~2897.4 S cm⁻¹).⁵⁹ It appears that by further optimization and suitable selection of the polymer matrix, these bioinspired nanocomposites can find their equitable place in bio- and nanomedicine. Impressively, biomimetic MXene (Ti₃C₂T_r)-based structures were designed inspired by the overlap architecture of the placoid scale to significantly improve the mechanical features, flame retardancy of the epoxy resin, and interfacial compatibility. As a consequence, the prepared hybrid epoxy resin nanocomposites demonstrated high tensile strength and the fire hazard of these composites was greatly cut down.⁷⁵ Besides, cellulose nanofibers were compounded with MXenes to produce nacre-like and loofah-like carbonized membranes with biomimetic structures via a vacuum-assisted filtration technique (Fig. 6); these membranes exhibited high microwave (MW) absorption activity as well as tunable absorption bands.⁷⁶ Nacre-like composites displayed layer-by-layer structures, but loofah-like composites had porous-layered structures. It was revealed that some parameters such as dipole polarization, multiple reflections, conductive loss, capacitorlike structures, and interfacial polarization with synergistic effects promoted the attenuation of electromagnetic wave, providing the improvement of the MW-absorbing activity.⁷⁶

To improve the mechanical and electrical properties of MXene-based composites, biomimetic core/shell fibers were constructed from graphene oxide (mechanical layer) and MXenes inspired by the structure of wood.⁷⁷ Graphene oxide layer was selected for assembling the MXene particles into macroscale structures and protecting them from the oxidation. These fibers exhibited remarkable tensile strength (~290 MPa) with high electrical conductivity (~2400 S m⁻¹), providing promising options for assorted fabric-based appliances.⁷⁷ Kim et al.⁶⁰ prepared MXene $(Ti_3C_2T_x)$ films by introducing mussel-inspired polydopamine to improve their mechanical and electrical properties (Fig. 7A). Furthermore, their environmental stability and electromagnetic-interference shielding properties were greatly improved; such MXene/polydopamine hybrids with synergistic effects can be considered as promising candidates for various multipurpose applications. The ensuing polydopamine nanobinders with uniform atomic-level thickness instigated MXene films to be ideally parallelly-stacked with high enhanced tensile strength and markedly improved oxidation resistance, without forgoing their primary significant electrical conductivity.60 It was revealed that the proteininspired self-healing flexible MXene-based composites constructed from Ti₃C₂ and rubber-based supramolecular elastomers had suitable potentials for smart sensing applications (Fig. 7B). The surface of MXenes was modified by serine using the esterification reaction, and the nanostructured MXene network could be designed in the form of a composite via a suitable latex assembly technique. Consequently, the MXenes/ polymer nanocomposites exhibited suitable mechanical properties, making them appropriate choice for manufacturing sensitive sensors for the accurate detection of external moisture

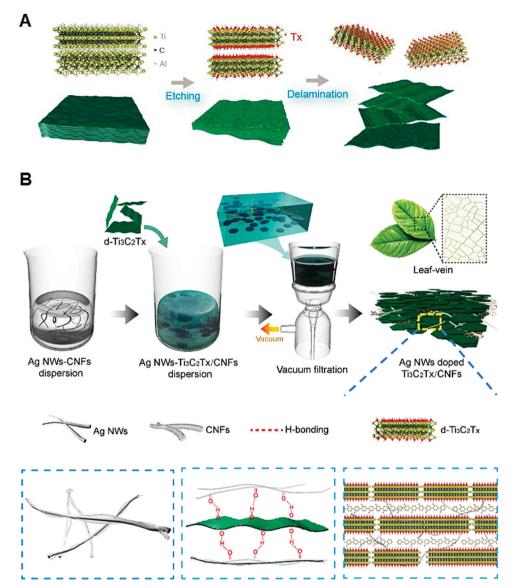


Fig. 5 (A) The preparative process for delaminated MXene nanosheets. (B) The production of the biomimetic silver (Ag) nanowires (NWs)-doped MXene (Ti₃C₂T_y)/cellulose nanofibrils (CNFs) films through a vacuum-assisted filtration technique. Reproduced with permission from ref. 72 Copyright 2021 Elsevier.

changes and human physiological motions; they can be applied for soft smart robotics and wearable electronic sensors.⁷⁸ Besides, for the catalytic application of biomimetic MXenebased structures, there have been still very limited explorations. However, in one study, mussel-inspired biomimetic technique was developed for fabricating MXene (Ti₃C₂)-based magnetic Fe₃O₄ composites via the self-polymerization of dopamine and the subsequent mild temperature pyrolysis process.⁷⁹ The ensuing composites were deployed for the catalytic degradation of organic dyes through the Fenton reaction with significant efficiency (more than 97%). They exhibited suitable recyclability (5 cycles) and functionality, offering highly efficient catalysts for advanced oxidation processes. Both radical *OH and O₂*were reported as the reactive species involved in the degradation process.⁷⁹

4. Challenges and future perspectives

MXenes have exhibited attractive physicochemical properties such as good hydrophilicity, metallic conductivity, high surface areas, outstanding chemical stability, and high strength/stiffness, which have encouraged scientists to initiate extensive research on their applications in various forms. However, there are still two major issues related to MXenes, one being the commercialization and another one is the involvement of inexpensive and eco-friendly manufacturing techniques that require comprehensive and systematic explorations. Thus, focusing on sustainable and nature-inspired green chemistry techniques can help reduce the toxicity and enhance the biocompatibility of MXenes and their derivatives. 45,80-84 As an example, the benignly synthesized Ti₃C₂T_x MXene nanosheets

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Ti₃AlC₂ Nacre-like structure Dried-CCM etching . Freeze-dried CCM hand shaking d-Ti₃C₂T₃ loofah-like structure Carbonization Dry in oven Nacre-like structure Vacuum assisted filtration Carbonization Freeze-drying loofah-like structure

Fig. 6 The preparative process for carbonized biomimetic membranes with nacre-like and loofah-like structures constructed from cellulose nanofibers (CNF) and MXenes. HF: hydrofluoric acid. Reproduced with permission from ref. 76 Copyright 2020 Elsevier

exhibited enhanced oxidation stability, conductivity, and surface-enhanced Raman scattering activity, and consequently, rendered them as suitable candidates for producing batteries/ supercapacitors, sensors, and photodetectors.⁵² In addition, the greener synthesis of MXenes based on the electrochemical technique has been described for extending their application in the field of aqueous energy storage without the deployment of dangerous acid/alkali etchants; the designed MXenes exhibited outstanding stability and battery performance. 85 Consequently, due to the need to implement nature-inspired techniques for both, the synthesis and surface functionalization of MXenes is increasingly felt to develop simple and low-cost methods based on the principles of green chemistry. However, these techniques can be employed for the up-scalable synthesis of MXenes only after optimization procedures, systematic analysis, and in vivo/in vitro assessments.86-89 Toxicology (nanotoxicology) studies as well as the environmental stability and surface chemistry of these materials should be specifically deliberated; MXenes may suffer from aggregation, which culminate in the degradation of their performance and decreasing the surface area. 90 Notably, various theoretical evaluations, such as discrete Fourier transform, can help to predict the specific characteristics of MXene-based structures. 91,92

Surface functionalization/modification can help to overcome some challenging concerns such as the stability and biocompatibility of MXenes. For instance, MXenes have been functionalized by various silylation reagents. As a consequence, the silvlation reaction could efficiently stabilize the MXenes and reduce their structural degradation because of spontaneous oxidation. Furthermore, the improvement of their surface properties was reported with controllable hydrophilicity after such functionalization.93 Important criteria such as dispersibility, optical features, environmental stability, multifunctionality, and electrical/thermal properties can be significantly amended through suitable functionalization procedures.94 It has been observed that the functionalization of MXene nanosheets with phenylsulfonic groups could enhance their dispersibility as well as their specific surface area. 94 On the other hand, by changing the surface terminal groups and the ratio of M or X elements, the properties of MXenes can be modified. By altering the lamellar spacing, number of layers, and the particle size in MXenes, different optical and electrical features can be realized; electrical conductivity could be reduced by lowering the number of layers in MXenes.95 In some cases such as V2CTx MXenes, there have been limited studies regarding their multilayered forms because of the instability of delaminated V2CTx MXenes

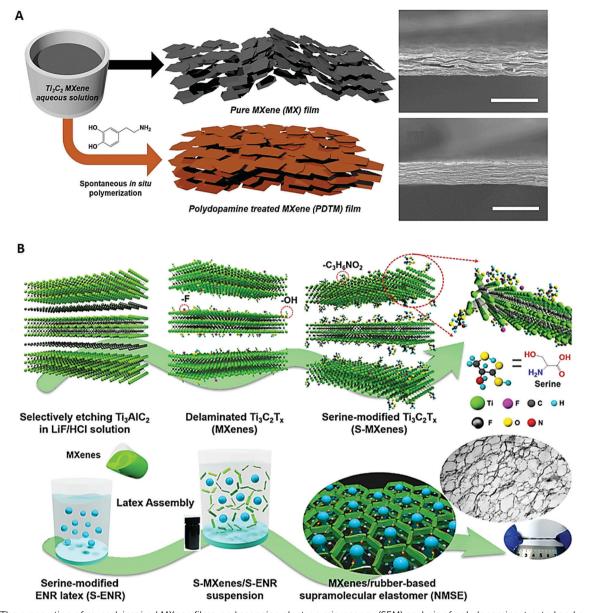


Fig. 7 (A) The preparation of mussel-inspired MXene films, and scanning electron microscopy (SEM) analysis of polydopamine-treated and pure MXene films. Reproduced with permission from ref. 60 Copyright 2020 American Chemical Society. (B) The fabrication process of self-healable MXene-based nanocomposites constructed from serine-modified MXene nanosheets. Reproduced with permission from ref. 78 Copyright 2020 American Chemical Society

in their colloidal state. However, Gogotsi et al. 96 reported V₂CT_x MXenes with unique optical and electronic properties prepared under mild conditions via an ion-exchange procedure coupled with flocculation, thus increasing their shelf-life in aqueous suspensions by approximately three orders of magnitude, from a few hours to several months.96

MXenes can be hybridized with low-dimensional materials (e.g., metals, metal oxides, and polymers nanomaterials) to improve their features or attain new properties and multiple functionalities. For instance, noble metal nanoparticles have been spontaneously grown on flexible biomimetic MXene papers, providing outperforming electrocatalytic performances with good stability, sensitive detection potential of superoxide

(O₂• −), and reproducibility; such MXene-based composites have promising applicability for high-performance energyrelated devices and flexible bioelectronics.97 In addition, ZnS nanodots/Ti₃C₂T_x MXene hybrids with high capacity, functionality, and cyclic stability were fabricated via the attachment of ZnS nanodots on MXenes by coordinating modulation between MXene and the metal-organic framework (MOF) precursor (ZIF-8), followed by sulfidation. The deployment of these hybrids have some important advantages such as improved interfacial electron transfer, low lithium diffusion energy barrier, and significant lithium adsorption potential. 98 Although the synthesis methods have shown promise for large-scale production, they may suffer from low production yield and requirements of

post-synthesis treatments. By applying some theoretical evaluations such as density functional theory (DFT) calculations, several modifications can be further proven and evaluated. In one study, Sharbirin et al. 99 reported the synthesis of watersoluble MXene (Ti_2N) quantum dots (~ 3.14 nm) with efficient photoluminescence and maximum quantum yield of $\sim 7.5\%$. Besides, Nb₂C quantum dots with good photostability and pH stability have been synthesized; these quantum dots exhibited green fluorescence and a quantum yield of up to 19%. 100 The sulfur and nitrogen doping on these MXene quantum dots was reportedly the main reason for the enhanced high quantum yield, which was further corroborated by DFT calculations. 100

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Wyatt et al. 101 have explained the effect of the synthesis conditions on the MXene properties and structures. The reaction conditions need to be optimized for increasing the production yield as well as improving the physicochemical features and functionality to move toward large-scale production 102 and entry in to clinical phases; 103 the commercialization and industrialization aspects for MXenes ought to be analytically studied. 104 The optimization is vital for avoiding the structural defects and heteroatom functional groups in MXenes; these imperfections can affect the multifunctionality, stability, and their properties. 105-107 The correlation among the different critical parameters and toxicity include the establishment of standards for synthesis tactics, morphology/size, and chemical structures. 108 Biomimetic/bioinspired synthesis strategies embodying feasibility, reproducibility, controllability, and up-scalability are still at their infancy, and more explorations are still warranted to obtain MXenes with targeted properties and high standards. Such biomimetic and bioinspired microand nanostructures comprising MXenes and their derivatives should be further explored for use in bio- and nanomedicine, especially for antiinflammatory/wound healing, tissue engineering, drug/gene delivery, pressure sensors, nanobiosensors, bioprinting, (photo)catalytic reactions, and development of bioinspired medical devices. 109-112 It appears that with the growing momentum of research in the field of MXenes, advanced methods with high efficiency and generation of lower pollution could safely produce structures with unique mechanical and tribological properties. 101 With the rapid development of industrial sectors, the need to use sustainable methods based on green chemistry and with low emission of pollutants is increasingly comprehended. Using bioinspired structures and biomimetic approaches, it is possible to create optimal and unique properties in MXenes-based structures as well as to use renewable, sustainable, and greener materials in their production. The demand for devices dealing with energy storage, environmental remediation/treatment, conversion, and sensing is increasing rapidly due to the variety of industrial procedures and high energy consumption rate in smart electrical applications. Notably, the deployment of advanced techniques based on bioinspired or biomimetic MXenes to fabricate devices such as electrochemical supercapacitors, lithium-ion batteries, and solar energy storage devices can be envisioned as sustainable alternatives to large energy requirements. 113,114

Conclusion and future outlooks

The development of bioinspired/biomimetic MXenes with multifunctionality is still in its infancy and more detailed studies are still required for marked improvements and optimization of procedures. More elaborative studies are essential for analyzing and adjusting the biocompatibility, biodegradability, long-term toxicity/cytotoxicity, fluorescence emission, pH- and photostability, and other important criteria. This new intriguing class of 2D transition metal carbides and/or carbonitrides has been broadly employed for environmental remediation, theranostics, and energy storage, benefitting from exceptional structural characteristics, including highly active sites, significant chemical stability, hydrophilicity, large interlayer spacing, high specific surface area, and superb sorption-reduction potential. Notably, MXene-based nanocomposites exhibit fascinating properties and diverse versatile applications such as catalysts, sensors, supercapacitors, battery electrodes, and electromagnetic-interference shielding. However, they suffer from some important drawbacks such as mechanical brittleness as well as exposure to oxidation/ aggregation, which can reduce their stability or cause their degradation. Natural polymers such as cellulose or chitosan nanofibers can be utilized in combination with MXene-based structures to improve their biocompatibility and functionality. The optimization of the reaction conditions, commercialization/ large-scale production criteria, surface chemistry analyses, nanotoxicological assessments, systematic biocompatibility evaluations (in vitro/in vivo), and pre-/clinical studies are some of the aspects that need to be comprehensively addressed.

Flexibility, environmental stability, biosafety, and multifunctionality are important elements for the future applications of these materials at the industrial and commercial scale. Instead, investigations have primarily focused on Ti₃C₂T_x MXenes because of their unique physicochemical properties such as high electrical conductivity even without extra thermochemical treatment. Future studies warrant more extensive research, especially on additional bioinspired/biomimetic MXenes and their derivatives, to discover newer properties and their multipurpose potentials. Extensive research to contrive procedures with inherent sustainability and environmentally-benign features as well as adequate adjustability, simplicity, and cost-effectiveness should be the focus of attention with incessant inspiration from nature. Although extensive and comprehensive research is still awaited on bioinspired/biomimetic MXenes, these structures with good biocompatibility, unique designs, high conductivity, selectivity/sensitivity features, and low toxicity will soon find their distinctive position on the research platform focusing on the bio- and nanomedicine arena.

Conflicts of interest

The author(s) declare no competing interest.

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