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Nacre-Mimetic, Mechanically Flexible, and Electrically Conductive Silk Fibroin-MXene Composite Foams as Piezoresistive Pressure Sensors

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ABSTRACT: The hierarchical nacre-like three-dimensional (3D) assembly of porous and lightweight materials is in high demand for applications such as sensors, flexible energy storage and harvesting devices, electromagnetic interference shielding, and biomedical applications. However, designing such a biomimetic hierarchical architecture is highly challenging due to the lack of experimental approaches to achieve the necessary control over the materials' microstructure on the multilength scale. Aerogels and foam-based materials have recently been developed as attractive candidates for pressure-sensing applications. However, despite recent progress, the bottleneck for these materials to achieve electrical conductivity combined with high mechanical flexibility and fast strain recovery remains. In this study, for the first time, inspired by the multiscale architecture of nacre, we fabricated a series of ultra-lightweight, flexible, electrically conductive, and relatively high-strength composite foams through hybridizing the cross-linked silk fibroin (SF) biopolymer, extracted from *Bombyx mori* silkworm cocoon, reinforced with two-dimensional graphene oxide (GO) and Ti_3C_2 MXene nanosheets. Nacre is a naturally porous material with a lightweight, mechanically robust network structure, thanks to its 3D interconnected lamella-bridge micromorphology. Inspired by this material, we assemble a cross-linked SF fibrous solution with MXene and GO nanosheets into nacre-like architecture using a bidirectional freeze-casting technique. Subsequent freeze-drying and gas-phase hydrophobization resulted in composite foams with 3D hierarchical porous architectures with a unique combination of mechanical resilience, electrical conductance, and ultra-lightness. The developed composite presented excellent performances as piezoresistive pressure-sensing devices and sorbents for oil/water separation, which indicated great potential in mechanically switchable electronics.

KEYWORDS: bio-inspired foams, silk fibroin, MXene, nacre, hybrid, piezoresistive wearable pressure sensor

1. INTRODUCTION

With the rapid development of artificial intelligence, a new set of materials for smart sensing and biomimetic robot technology are highly demanded.¹ A pressure sensor system, which can transduce strain and its variation into resistance, electrical potential, and capacitor, recently attracted significant attention for the development of wearable functional electronics.² Piezoresistive sensors transduce pressure stimuli into the changes in the resistance. The combination of mechanical compliance, i.e., high flexibility and fast strain relaxation after deformation, and appropriate electrical performance is crucial for creating highly sensitive flexible pressure sensors.^{2,3}

Recently, controlled assembly of porous macrostructures using renewable resources and functional nanofillers with a large specific surface area and outstanding mechanical, electrical, or thermal properties has drawn significant attention for some applications, including flexible devices,^{4,5} catalysts,⁶ sensors,⁷ energy storage,⁸ and electromagnetic interference

shielding materials.^{9,10} In this regard, lightweight foams based on sustainable precursors with cellular microarchitecture have demonstrated enormous potential for processing advanced structural and functional materials.¹¹

Our previous studies have shown the potential of novel silk fibroin (SF)-based aerogels, denoted *AeroSF*,¹² and their composite counterparts^{13,14} for diverse advanced applications, such as thermal insulation, water/oil separation, and as scaffolds for bone repair.^{15,16} SF, a biopolymer extracted from *Bombyx mori* silkworm cocoon, is a biocompatible and biodegradable fibrous protein. Thanks to its promising features such as processability, abundant surface functional groups, and

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Figure 1. Fabrication procedure of nacre-mimetic X-SF-MXene-GO hybrid foams through a bidirectional freeze-casting approach and gas-phase hydrophobization. (a) Extraction process of SF and the SEM micrograph, which indicates the fibrous nature of pristine-extracted SF. (b) Synthesis process of GO (foam) and (c) MXene nanosheets with their SEM micrographs prior to engaging them in the hybridization process and 3D cryo-assembly. (d) The surface modification of extracted SF with APTES and subsequent cross-linking with GA. (e) Incorporation of nanosheets into the X-SF solution to obtain a highly dispersed solution of X-SF-MXene-GO. (f) Bidirectional freeze-casting of the stable solution of X-SF-MXene-GO, freeze-drying of the obtained frozen samples, and a piece of ultralight X-SF-MXene9-GO foam that can easily sit on the leaf. (g) Gas-phase hydrophobization of the composite X-SF-MXene9-GO foams.

mechanical strength, it has been recently used to develop various functional (bio)materials.¹⁷ However, the SF aerogel by itself is not able to show enough elasticity or fast elastic deformation upon compression or deformation. Additionally, it is electrically nonconductive. Thus, for applications such as pressure sensing, it is required to improve the SF aerogel mechanical resilience and electrical conductivity by the incorporation of active components to add both properties to the composite. Our previous studies have demonstrated that hybridization of SF with various organosilanes at a molecular scale through self-assembly of SF peptides inside the sol-gel-processed silica^{12,14} and silsesquioxane gel¹³ network could improve the compression flexibility of pristine silica and could provide a high compression/bending strength to the pristine silsesquioxane aerogels.

In this study, we incorporated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and graphene oxide (GO) nanosheets into the SF network as functional nanoadditives to solve its conductivity and elasticity limitations. With their excellent physicochemical and mechanical properties, GO and reduced GO^{18,19} have shown great potential as functional nanoadditives for polymeric architec-

tures and aerogels, endowing them with high mechanical resilience and electrical conductivity.^{20,21} MXene nanosheets,^{22,23} recently emerged two-dimensional (2D) transition metal carbides (in this study, titanium carbide, $\text{Ti}_3\text{C}_2\text{T}_x$, T_x : —OH, —F, and =O), have also shown many impressive material properties, including large specific surface area, high electrical conductivity (up to $20\,000\text{ S cm}^{-1}$),²⁴ and high mechanical stiffness ($330 \pm 30\text{ GPa}$)^{25,26} for various advanced applications.²⁷ MXene composite aerogels combined with cellulose and GO have been previously reported by Bi et al.²⁸ and Ma et al.²⁹ for wearable pressure-sensing applications. However, there are no systematic studies to combine the intriguing biocompatibility and processability of SF with electrical conductivity of MXene nanosheets to develop three-dimensional (3D) synergistic foams.

Despite the impressive development of optimized building units with porous architectures in pressure sensing, most of the structures reported so far possess isotropic or randomly oriented cross-linked cellular networks due to the difficulty in controlling the pore shape and morphology.^{30,31} Recently, we developed anisotropic silica-SF biopolymer aerogels^{15,16} with a

Table 1. Different Formulations of X-SF-MXeneY-GO Composite Foams Prepared in this Study with Their Bulk Density Values

samples	X-SF (mg)	MXene (mg)	GO (mg)	[MXene]/[X-SF]	bulk density (ρ_b , g cm ⁻³)
X-SF-MXene0.01-GO	25	0.3	1	0.01	0.066
X-SF-MXene0.05-GO	6	0.3	1	0.05	0.025
X-SF-MXene0.33-GO	6	2	1	0.33	0.029
X-SF-MXene9-GO	1	9	1	9	0.01
X-SF-MXene5-GO	1	5	1	5	0.006

microhoneycomb-like microstructure and anisotropic mechanical behavior through unidirectional freeze-casting of the as-prepared silica-SF hydrogels followed by the supercritical drying approach. In this regard, we demonstrated that by carefully controlling the microstructure and pore morphology with freeze-casting parameters, the aerogels' final mechanical properties could be significantly controlled (maximum compression strength ~ 20 MPa with elasticity up to 80% of the strain).¹⁶

In the present study, ultralight and compressible multi-component foam-based pressure sensors with biomimetic microstructures were fabricated through compositing glutaraldehyde (GA)-cross-linked SF (called X-SF hereafter), GO, and Ti₃C₂T_x MXene, followed by processing the obtained hybrid sol through a versatile and well-studied bioinspired processing approach of bidirectional freeze-casting. In bidirectional freeze-casting, lamellar ice crystals are used to assemble ceramics, polymers, and composite particles/building blocks into a highly aligned biomimetic 3D porous network structure.^{32–36}

Since nacre has a hierarchical microarchitecture with an excellent combination of strength and toughness, it served as a source of inspiration in this study for foam microstructuration and network formation using the bidirectional freeze-casting approach.^{37,38} The developed dispersion has undergone the thermal gradient in two different directions, allowing the cryo-assembling of the network constituents into nacre-mimetic “brick-and-mortar” or lamella-bridge micromorphologies. It is demonstrated that the synergistic combination of SF with MXene and GO nanosheets endows the sensor with desirable ultralow density, high electrical conductivity, reversible compressibility, and durable stability. While stable and homogeneous dispersion of the MXene nanosheet in the X-SF matrix makes it electrically conductive, incorporation of GO into the matrix endows the overall final composite foams with extra compressibility and resilience.

Final gas-phase hydrophobization of the pore surface confers an extra feature of oleophilicity and hydrophobicity to the final composite foams. To the best of our knowledge, there is no report on the synergistic 3D assembly of SF biopolymers with MXene and GO to prepare composite foams that combine both high elasticity and hydrophobicity properties. The fabricated foam can act as a highly sensitive pressure sensor and sorbent for the separation of oils and organic solvents from water.

2. EXPERIMENTAL SECTION

B. mori cocoons were purchased from Treenway Silks, USA. Aminopropyltriethoxysilane (APTES, 99%), ethanol (99.9%, EtOH), calcium chloride (99.99%, CaCl₂), sodium carbonate (Na₂CO₃), and GA (50% in water) were purchased from Sigma Aldrich. SnakeSkin dialysis tubing with a molecular weight cutoff of 3.5 kDa was purchased from Thermo Fisher Scientific. Titanium aluminum carbide powder (Ti₃AlC₂, 99%) was purchased from

Nanosheel. Lithium fluoride (LiF, 98%) was purchased from Alfa Aesar.

2.1. SF Extraction. SF was extracted from *B. mori* silkworm cocoons by a modified procedure based on the protocols of Rockwood et al.¹⁷ and Zheng et al.³⁹ First, worm-free *B. mori* cocoons (5 g) were cut into dime-size pieces and boiled in an aqueous sodium carbonate solution (0.02 M, 2 L) for 30 min to remove sericin. The dried and degummed SF fibers (4 g) were dissolved in 20 mL of Ajisawa's reagent (calcium chloride/ethanol/water: 1:2:8 (molar ratio)) at 80 °C for 3 h and dialyzed against distilled water for 48 h in dialysis bags (9 cm) while changing the water every 3 h. After removing worm debris and globular silk aggregates via centrifugation (2 × 9000 rpm), concentrated SF solution (0.04 g mL⁻¹) was stored at 4 °C for future use (Figure 1a).

2.2. Synthesis of GO. GO was prepared based on improved Hummers' method.^{40,41} A 9:1 mixture of concentrated H₂SO₄/H₃PO₄ (360:40 mL) was added to a mixture of graphite flakes (3.0 g) and KMnO₄ (18.0 g). The resulting mixture was heated to 50 °C and stirred for 12 h. After cooling to ambient temperature, the reaction mixture was poured on ice (400 mL) with 30% H₂O₂. The brownish mixture was centrifuged (4500 rpm, 15 min) and washed with water, 30% HCl, and ethanol (Figure 1b). After filtration, the obtained solid was dried in a vacuum oven at ambient temperature. The concentration of GO solution was quantified by drying and weighing the GO film.

2.3. Synthesis of Ti₃C₂T_x MXene. Ti₃C₂T_x MXene 2D nanosheets were synthesized by the selective etching method from its Ti₃AlC₂ precursor, which is reported elsewhere.⁴² Lithium fluoride powder (1 g) (LiF, Alfa Aesar, 98+%) was slowly added into 20 mL of 9 M hydrochloric acid (HCl, Fisher, technical grade, 35–38%) and stirred for 30 min. Then, MAX phase Ti₃AlC₂ powder (1 g) was slowly added into the mixture solution to etch the Al layer at 35 °C for 24 h. The acidic supernatant was removed by a repeated centrifugation process at 9000 rpm (approximately 8–10 times) to finally obtain a stable dark green supernatant of Ti₃C₂T_x with a pH of ~ 6 (Figure 1c). The concentration of Ti₃C₂T_x MXene solution was quantified by drying and weighing the MXene film. We will refer to Ti₃C₂T_x MXene as MXene in the rest of this study for the sake of simplicity.

2.4. Cross-Linking of SF with GA (X-SF). First, the extracted SF (4 mL, 40 mg/mL) solution was modified with APTES to prepare silylated SF (SiSF) with amino functionalities through the addition of APTES (0.12 mL, 0.51 mmol) at room temperature for 30 min. Then, the obtained SiSF solution was dialyzed against distilled water to wash the unreacted APTES from the SiSF solution for 2 h at room temperature. Next, 4 mL of purified SiSF solution was added to the reaction with a GA cross-linker (25 v/v%, 6.12 mmol, 0.24 mL). The color of the solution turned dark orange in 2 min (Figure 1d).

2.5. Propylene Mold with a PDMS Wedge. According to Yang et al.,³⁸ 1 mL of polydimethylsiloxane (PDMS) solution (Sylgard 184, Dow Corning) was added into a cylindrical propylene mold (1 cm), and the mold was tilted to an angle of 20°. After curing in an oven at 80 °C for 2 h, the PDMS wedge was obtained.

2.6. Synthesis of X-SF-MXeneY-GO. First, 2 mL of mixed colloidal solution of GO (1.2 mg/mL)-MXene with varying concentrations of MXene was ultrasonicated for 1 h under argon (Ar) and then was added to 4.24 mL of the above-mentioned X-SF solution with varying concentrations shown in Table 1. The Y values defined as the MXene/X-SF mass ratio were adjusted to 0.01, 0.05,

Figure 2. (a–c) Multiscale SEM micrographs of the porous microstructures of X-SF-MXene9-GO; (d) the proposed schematic view from the bridges and lamellae in the composites; (e and f) the hierarchical structure of the lamellae with an intertwined structure of all network building blocks; (g) microstructural scheme of nacre and 3D reconstructions of the porous structure of X-SF-MXene9-GO derived from X-ray microcomputed tomography, which shows the alignment of the porous structure along the ice growth direction (image of abalone in lower left reprinted with permission from ref 46. Copyright 2021 Academic Press/Elsevier);⁴⁶ and (h) and (i) X-ray nanotomography images showing the nacre-mimetic bridge and lamella microstructural morphology.

0.33, 5, and 9. After 5 min of stirring at room temperature, the stable mixed colloidal solution was transferred into the sample containers covered with the PDMS wedge, sealed, and then brought into contact with a cold copper block immersed in a liquid nitrogen (LN_2) bath for bidirectional freeze-casting of the mixed solution by applying a dual temperature gradient to the solution. The samples were finally freeze-dried at 60 °C for 24 h (Figure 1e,f).

2.7. Gas-Phase Hydrophobization of X-SF-MXene9-GO Composite Foams. The dried monoliths were modified with methyl groups on the surface by placing the cylindrical porous foams with dimensions of $1.5 \times 1 \text{ cm}^2$ inside the desiccator that was filled with hexamethyldisilazane (HMDS, 10 mL) under an argon atmosphere and heated for 70 °C for 24 h.^{43,44} Afterward, the desiccator was degassed, and the treated porous network surface was monitored by measuring the water contact angle (WCA) (Figure 1g).

3. RESULTS AND DISCUSSION

Figure 1a–g illustrates the fabrication route for X-SF-MXene9-GO hybrid composite foams. First, SF had undergone cross-linking with GA (the product is called cross-linked SF or X-SF) through prior surface modification with APTES to enhance the surface amino groups for cross-linking.

An aqueous suspension of highly dispersed X-SF, MXene, and GO was frozen by a bidirectional freezing technique (Figure 1f). Upon freezing, the thermally insulating PDMS wedge (placed between the suspension and the cooling stage) generated dual temperature gradients in both vertical (ΔT_V) and horizontal (ΔT_H) directions.³² The temperature gradient in both directions governed the ice crystal nucleation and growth inside the mixture slurries into a long-range lamellar pattern.³⁴ In the bidirectional freezing technique, the ice lamella acts as a hard template for the final structures of biomimetic X-SF-MXene-GO foams after sublimation. The ice

crystal nucleation and growth pattern and subsequent final microarchitectures, such as porosity and anisotropy, were tuned by parameters such as suspension concentration/viscosity, the slope angle of the PDMS wedge, and the cooling rate.^{33,38,45} The bidirectional freezing technique is known as a simple, generic, and green (in the majority) method to fabricate highly ordered cellular materials with different constituents, namely, ceramics, polymers, and their composites.³⁴ The technique has also been frequently used for generating the bridge-and-lamella or brick-and-mortar nacre-mimetic structures from ceramic/carbon and polymer slurries.^{34–36}

MXene with a layered “clay” structure (cf. scanning electron microscopy (SEM) image in Figure 1c) was produced by an established method reported by Gogotsi et al.^{22,23} through selective etching of the Al layer from the MAX (Ti_3AlC_2) phase. The combination of high electrical conductivity and electrophilic nature of the hydroxyl- and oxygen-terminated surface in MXene enables it to become an exciting nanofiller candidate for SF-based composite foams of this study.

During freezing, MXene, GO, and X-SF were expelled and assembled to replicate the ice micromorphology. Finally, the X-SF-MXene-GO composite was obtained by freeze-drying the frozen samples. Due to the presence of abundant available –OH surface groups, composites were subjected to surface treatment in the gas phase by HMDS to functionalize the methyl groups to increase the surface hydrophobicity.

3.1. Physical, Microstructural, and Mechanical Properties. As shown in Table 1, we fabricated a series of composites with mass fractions of MXene to X-SF of 0.01, 0.05, 0.33, 5, and 9. We used different mass fractions to identify an optimum ratio to achieve a balance of the

Figure 3. Compressive behavior of the X-SF-MXene0.05-GO sample under the cyclic compression test with an increasing strain of 10%, 20%, and 30% (a), five repeated cycles at 30% (b), and the stress–strain curve until sample’s failure (c). Compressive behavior of the X-SF-MXene5-GO samples under the cyclic compression test with an increasing strain of 10%, 20%, and 30% (d), five repeated cycles at 30% (e), and the representative stress–strain curve until sample’s failure (f). Compressive behavior of the X-SF-MXene9-GO samples under the cyclic compression test for an increasing strain of 10%, 20%, and 30% (g), five repeated cycles at 30% (h), and stress–strain curve until sample’s failure (i). Strain relaxation of X-SF-MXene0.05, 5, and 9-GO samples up to $\epsilon = 30\%$ and slow relaxation to plastic deformation at $\epsilon > 30\%$ (j).

mechanical and electrical behavior in the final composites. The densities of the composites were measured in a very low range of $\rho_b = 0.006\text{--}0.066\text{ g cm}^{-3}$. The highest density was measured for the composite with the maximum SF and MXene contents. The lowest bulk density was obtained for the sample X-SF-MXene5-GO (0.006 g cm^{-3}), which is considerably lower than that of the previously developed SF-based aerogel composite of $\sim 0.1\text{ g cm}^{-3}$.¹⁴

The SEM images in Figure 2a–c demonstrate the long-range and hierarchically aligned nacre-mimetic brick-and-mortar or lamella-bridge network structures. In such nacre-mimetic structures, GO and MXene 2D nanosheet building blocks were well-dispersed and intertwined together with the cross-linked SF biopolymer and constituted the bridge structures (Figure 2d–f). Additionally, a part of X-SF is located as a spring or mortar between the bricks or lamellae in the composite structure (Figure 2c), which increases the network stability and resilience. The brick-and-mortar microstructural arrangement of the sample was also evident from the micro-

nano-CT analysis, as shown in Figure 2g–i. The recorded nano-CT in Figure 2i reveals that the anisotropic pore channel alignment was in the parallel direction to the ice crystal growth and created cross-bridges between the lamellae at lower length scales.

We then measured the elastic modulus, cyclic stress–strain, and failure strength under compression for three sets of compositions, X-SF-MXene0.05-GO, X-SF-MXene5-GO, and X-SF-MXene9-GO (Figure 3). While pristine SF¹² and MXene²⁹ foams/aerogels without additives deformed at relatively lower strain (10%), X-SF-MXene-GO composite foams, thanks to their unique microstructural assembly, could be compressed under cyclic compression and decompression at 10%, 20%, and 30% of strains (ϵ) without collapsing or failure (cf. Figure 3a,d,g). The elastic modulus (E) was measured from the most linear part of the first compression cycle of the stress–strain curves for all samples. The E values of the composites were measured to be 0.052 kPa (X-SF-MXene9-GO), 0.11 kPa (X-SF-MXene0.05-GO), and 0.047

Figure 4. (a) Liquid-state ^1H NMR spectra of SF and SiSF; (b) ATR-FTIR spectra of X-SF and X-SF-MXene9-GO; (c) solid-state mass ^1H NMR spectrum of X-SF-MXene9-GO; (d) XRD patterns of as-prepared MXene and X-SF-MXene9-GO; (e) XPS survey spectra and (f) XPS C 1s high-resolution spectra of X-SF-MXene9; and (g) Raman spectra of MXene, GO, and X-SF-MXene9-GO composite foams.

kPa (X-SF-MXene5-GO). It is evident that by increasing the content of X-SF and MXene in the composite foams, the elastic modulus and the maximum strength were enhanced. The covalent cross-linking of SF in the composite and further incorporation of GO and MXene nanosheets not only reinforced the highly porous structure of the resultant foams but also enhanced the elasticity. A strain relaxation was also observed during five loading and unloading compression cycles for all samples at 30% of the strain (Figure 3b,e,h). Besides, repeated compression by hand further substantiated the high compressibility and elasticity of the developed foams at the strain values mentioned above (cf. Video S1). Figure 3j shows the schematic hierarchical structure of the composite foams during the cyclic compression–decompression for $\varepsilon < 30\%$. For the same samples, increasing the compressive loads, for $\varepsilon > 30\%$, the sample decompression was very slow and at $\varepsilon = 80\%$, the samples were entirely deformed.

3.2. Chemical and Crystal Structures. The surface amino functional groups in the SF molecular structure are scarce; for example, lysine amino acid comprises only $\sim 2 \text{ mg g}_{\text{SF}}^{-1}$. Therefore, for cross-linking of SF with GA, surface chemistry of SF was first modified with amino-functionalized silane, APTES, through condensation of the dangling hydroxyl side chain of SF with the ethoxy group in APTES to modify the surface with more amino functionalities. The amino-modified SF was called SiSF in this study. The incorporation of the amino functionalities into SiSF is evident from ^1H NMR spectra shown for plain SF and SiSF in Figure 4a. Besides the characteristic peaks belonging to SF,⁴⁷ the SiSF was accompanied by extra chemical shifts at 0.5 (2H, t), 1.08 (2H, Q), 1.68 (2H, Q), and 3.54 ppm (2H, Q) due to the incorporation of APTES. The cross-linking with GA was substantiated with solid-state mass ^1H NMR and the ATR-FTIR spectroscopies shown in Figure 4b,c, respectively. As shown in Figure 4b, the composite structures were further confirmed with the presence of characteristic bands of ν_{as}

($-\text{Si}-\text{O}-\text{C}-$), ν_{as} ($-\text{Si}-\text{O}-\text{Si}-$), and ν_{as} ($-\text{Ti}-\text{O}-$) at 1052, 1102, and 662 cm^{-1} , respectively. In addition, in all composites, the X-SF was characterized by amide I (ν_{as} ($\text{C}=\text{O}$), 1618–1640 cm^{-1}), amide II (δ_{s} ($\text{N}-\text{H}$) deformations/bending 1512–1544 cm^{-1}), and amide III (ν_{as} ($\text{C}-\text{N}$), 1230 cm^{-1}) vibrations.¹² With cross-linking of SiSF with GA, two different double bonds appear in the structure of SiSF-GA, i.e., $-\text{C}=\text{C}-$ bonds from GA and $-\text{C}=\text{N}-$ from the cross-linking reaction between the amine groups in SiSF and aldehyde groups in GA. These double bonds form a conjugated planar structure in the X-SF, which enabled it to become autofluorescent. The peak at 1585 cm^{-1} is associated with the $-\text{C}=\text{C}-$ bonds, and the peak at 1658 cm^{-1} is attributed to the imine bonds ($-\text{C}=\text{N}-$), which is also designated as peak 5 at 7.6 ppm in the solid-state ^1H NMR mass spectrum in Figure 4c.

The surface termination groups in MXene (T_x : $-\text{OH}$, $-\text{O}$, and $-\text{F}$) not only enabled its nanodispersibility inside the X-SF aqueous solution but also resulted in its further dipole–dipole interactions and hydrogen bondings with the $-\text{COOH}$ surface termination of GO and the $-\text{OH}$ side chain of X-SF and its subsequent homogeneous mixing at the nanoscale before freeze-casting.

According to the XRD patterns in Figure 4d, MXene nanosheets were detected in the foam matrix through their characteristic peaks of (002) at 5.9° .⁴⁸ For the as-synthesized MXene, the typical diffraction peak (002) appeared at around $2\theta = 7.01^\circ$, indicating that the interlayer distance of MXene was about 1.3 nm according to the Bragg equation: $2d\sin\theta = n\lambda$. After incorporation of MXene into the foam, this peak shifted to a lower angle around $2\theta = 5.9^\circ$, indicating that interlayer spacings expanded to about 1.5 nm. This was also confirmed with the XPS survey spectra in Figure 4e, indicating the elemental compositions of C, N, Ti, O, and F and the valence states of the elements of MXene and X-SF in the composite matrix. The Ti 2p high-resolution spectrum in Figure S1a exhibits binding energies of 455.3 and 461.4 eV

Figure 5. The pressure-sensing performance of the X-SF-MXene-GO. (a) Electrical resistance vs pressure. (b) Electrical resistance vs compressive strain. (c) $R-T$ curves of the X-SF-MXene-GO foam with two different ratios of MXene/X-SF (5:1 and 9:1) under five various external forces. (d) Relative current changes with respect to the applied pressure, where the two curves represent the different ratios of MXene:X-SF (9:1 and 5:1). (e) $I-V$ curves of X-SF-MXene9-GO and (f) X-SF-MXene5-GO under varying pressures. (g) Proposed mechanism of strain (or pressure) sensitive conductivity. (h) Effect of compression and decompression of X-SF-MXene-GO on the brightness of an LED. (i) and (j) The scheme and the device installation for evaluation of X-SF-MXene9-GO performance under varying voltages and external pressures and reporting $I-V$ curves. (k) Assembling the electrode for muscle movement and (l) resistance response of a piece of foam by attaching the sensor to the human cheek for evaluation of the sensing performance of the foam sensor for the human muscle movement.

corresponding to Ti 2p (3/2) and Ti 2p (1/2) of the Ti—C bonds. Moreover, the peaks located at 456.3 and 459.3 eV correspond to Ti 2p (3/2) of Ti—O and Ti—F. As shown in Figure 4f, the C 1s peaks at 282.1 and 284.8 eV correspond to the Ti—C and C—C bonds of X-SF, confirming the presence of the carbon and carbonated species of the X-SF-MXene9 composite.⁴⁹ The O 1s peaks located at 530.1, 531, and 532.5 eV correspond to O 1s in Ti—O—, carbonyl, and hydroxyl groups in the composite (cf. Figure S1b). In addition, the F 1s intense peak at 685.5 eV is attributed to Ti_3C_2F .⁵⁰ The Raman spectrum of MXene (Figure 4g) can be separated into three

active Raman modes/regions corresponding to A_{1g} (Ti, C, and O), at 201 cm^{-1} , and E_g (Ti, C, and O) peaks at $230\text{--}470\text{ cm}^{-1}$, which are in-plane and out-of-plane vibrations of Ti in the outer layer and carbon and surface groups, respectively. In-plane E_g vibrations at $230\text{--}470\text{ cm}^{-1}$ also represent the surface functional groups (T_x) attached to the Ti atoms. This region is usually used for probing the surface chemistry and the type of functional groups on MXene. The region between 591 and 731 cm^{-1} is assigned to the carbon vibrations in both E_g and A_{1g} modes.⁵¹ All of these vibrational modes could also be detected in the composite X-SF-MXene9-GO, with additional

Figure 6. (a) Variation of the WCA values vs time for the composite foams with three different formulations. (b) Oil and organic absorption performance of the composite foams based on the composites' weight gain. (c) Separation of a three-component *n*-hexane–Oil-red O–water mixture with X-SF-MXene0.05-GO through the absorption–squeezing technique. (d) Schematic of the mechanism of separation of the three components of *n*-hexane–Oil-red O–water with absorption and separation of the mixture.

vibration modes for GO at 1600 cm⁻¹ (G band) and 1355 cm⁻¹ (D band). The D and G bands explain the structural defect (disorder-induced mode) and first-order scattering from the sp² carbon bonding, respectively. The ratios of the D band to the G band intensity (I_D/I_G) values in GO and X-SF-MXene9-GO are 0.88 and 0.74, respectively, which indicated that the X-SF and MXene increased the local defects and disorder of GO.

3.3. Pressure-Sensing Properties. MXene incorporation into the foam due to its metallic electrical conductivity is very pivotal. Various MXene-to-X-SF ratios in composite foams caused different electrical responses and pressure sensitivity. For the formulation in which the MXene/X-SF ratio was less than 0.33, the organic part in the composite was the dominated phase in the composites, and therefore, the electrical response was also relatively compromised. The synergistic combination of electrical conductivity and mechanical resilience was only obtained for samples with higher MXene/X-SF ratios of 5:1 and 9:1. As shown in Figure 5a,b, the electrical resistance of the X-SF-MXene9-GO foam decreased with an increase of compressive strain in a strain range of 0–30% and the pressure up to 1.43 kPa. This experiment was performed by a gradual increase in the stress/load on the composite foams and monitoring the resistance changes upon applying the pressure and decreasing the resistance. For the X-SF-MXene9-GO sample, the percentage decreases of electrical resistances were 73.16%, 91.7%, 95.1%, and 98.7% at the compressive strain values of 1%, 5%, 20%, and 30%, respectively. Also, the elastic skeleton springs back after decompression, which made the electrical resistance of X-SF-MXene9-GO foams recoverable. The diverse low pressures of 71 Pa, 143 Pa, 358 Pa, 716 Pa, and 1.43 kPa can be detected with fast responses, indicating a high and linear sensitivity for pressure detection (cf. Figure 5c,d). A gentle touch usually relates to 1–10 kPa. According to Figure 5c, the electrical resistance also recovered fast (~3 s) during the decompression process up to 10 cycles. The linear

relationship between $\Delta I/I_0$ and pressure determines the sensor output and sensitivity. The sensitivity (S) is defined as eq 1

$$S = (\Delta I/I_0)/\Delta P \quad (1)$$

where ΔI is the change in the current under an applied pressure, I_0 is the initial current without applied pressure, and ΔP is the applied pressure change.

Despite most of the reported carbon-based pressure-sensing materials, such as the carbon aerogel,^{52–54} flexible substrate-loaded carbon,^{55,56} and carbon film,^{57–59} the present foams could maintain a better linear sensitivity, which are 14.23 and 12.53 kPa⁻¹ under 1.4 kPa for X-SF-MXene9-GO and X-SF-MXene5-GO, respectively. The reported sensitivity values were also higher than the values obtained from the MXene/GO composite foams reported by Ma et al.²⁹ ($S = 4.05$ kPa⁻¹ at pressure ~1 kPa). At a constant concentration of GO and X-SF, with an increased ratio of MXene to X-SF from 5 to 9, more MXene nanosheets were connected; therefore, the sensitivity of the hybrid foam increased due to the increase of the conductive path. This is due to the fact that the pore walls (brick and mortar) of the X-SF-MXene5,9-GO were made up of MXene and GO, which are intertwined together with the X-SF matrix as glue and support the overall network compressibility.

Due to the hierarchical and homogeneous distribution of MXene single sheets in the foam structure, once the foam is compressed, the contact area of MXene nanosheets is increased, leading to a decrease in the resistance and consequently an increase in the current. In addition, the sensor could sense the continuous increase of the applied force or pressure and respond to it as a steady increase in the current density. The almost linear relation of the I – V curves (Figure 5e,f) upon varying the voltage values from 0.5 to 5 V (Figure 5i,j) suggested that ohmic contacts between X-SF-MXene9-GO and copper electrodes were formed, and the sensor performance was according to Ohm's law. With the increase of

the pressure, the slope of I – V curves increased, indicating the continuous decrease of the sensor's resistance. As presented in Figure 5g, more contacts among conductive MXene nanosheets in X-SF-MXene9-GO foams were produced upon compression, which subsequently decreased the electrical resistance.

To better visualize the effect of compression on the foam resistance, we connected an X-SF-MXene9-GO composite foam to a light-emitting diode (LED) and a battery circuit. The brightness of the LED increased upon compression and decreased upon decompression of the foam, which further confirmed the pressure-sensitive conductivity (cf. Figure 5h and Video S2).

To evaluate the performance of sensors for real-time sensing of human movements, a thin cylindrical foam was fixed between two flexible copper-based electrodes and attached to the human cheek. As it is evident from Figure 5k,l, the X-SF-MXene9-GO foam sensors also showed competence in detecting the body's small motion and biosignals. For example, they can distinctly sense the human face expression upon blowing the cheek muscles and show it as changes in the output resistance signals. This sensing performance is particularly important to diagnose some diseases and substantiate the potential of foams for various wearable applications.

3.4. Hydrophobicity and Oil/Water Separation Performance. The hydrophobicity was also effectively improved by a simple chemical vapor hydrophobization of the developed composite foams with HMDS in a closed chamber at a high temperature for 24 h (see Figure 1g). The saturated vapor of HMDS diffused into the open and interconnected porous structure of the composites and reacted with free surface hydroxyl groups of the pore surface, which originated from the MXene nanosheets and SF functionalities. The vapor phase modification of the final dried samples developed from directional freeze-casting of the precursors' solution without having the gel phase is particularly advantageous as it minimizes the utilization of the organic solvent upon surface treatment. In contrast to the untreated composite foams, in which the water droplet immediately diffused into the porous structure and wetted the composites, the hydrophobized samples with various MXene/X-SF ratios indicated a better hydrophobicity as well as oleophilic properties. This is evident from the WCA values shown in Figure 6a. The WCAs of the composite foams with three different MXene/X-SF ratios of 0.01, 0.05, and 0.33 were 124.8°, 121.8°, and 123.3°, respectively. The higher the X-SF content in the composite, the larger the WCA values due to the greater extent of available hydroxyl groups treated with trimethylsilyl moieties. This was also the same with the higher MXene content in the composite, which can provide more available hydroxyl groups for hydrophobization; for example, MXene/X-SF ratios of 0.05 and 0.33 had the same X-SF and GO but different MXene contents. With a higher concentration of X-SF (e.g., MXene/X-SF: 0.01) in the composite, the porous structure was denser ($\rho_b = 0.06 \text{ g cm}^{-3}$); therefore, the dispensed water droplet was also more stable after 5 min of placing on the composite surface without diffusing into the monolith. The composite with a low X-SF concentration (MXene/X-SF: 0.05 and 0.33) had a low bulk density (0.025 and 0.029 g cm^{-3}) with a more open porous structure and larger pore channels; therefore, despite hydrophobicity of the pore surface, the water droplet

gradually diffused into the pore channels, and the WCA decreased to $\sim 116^\circ$.

Thanks to the highly open porous structure with ultralow density, hydrophobicity, and high compressibility, the X-SF-MXene-GO foams exhibited an excellent absorption performance for organic liquids and oils. As shown in Figure 6b, the resulting foams possessed high absorption capacities for organic solvents and oils such as chloroform, which can be absorbed in the composite foams. The weight gains of X-SF-MXene0.01-GO ($\rho_b = 0.06 \text{ g cm}^{-3}$), X-SF-MXene0.05-GO ($\rho_b = 0.025 \text{ g cm}^{-3}$), and X-SF-MXene0.33-GO ($\rho_b = 0.029 \text{ g cm}^{-3}$) after absorbing chloroform, *n*-hexane, and mineral oil were in the ranges of 20–60, 39–120, and 24–58 g g^{-1} , respectively. The obtained absorption capacities of the composites were in the absorption range of previously reported aerogels in the literature.^{13,15,31} In addition, X-SF-MXene0.05-GO could effectively separate dye, oil, and water (such as *n*-hexane, Oil-red O, and water) from the three-component oil–dye–water mixtures in a single absorption step (Figure 6d).

4. CONCLUSIONS

In summary, we have successfully fabricated SF-MXene-GO composite foams with hierarchical architectures mimicking the nacre microstructure using a well-established and versatile bioinspired bidirectional freeze-casting approach. The fabricated bioinspired architectures were composed of lamellae and interconnected bridges, which can confer exceptional strength and resilience to the composite foam. This structural complexity, together with improved mechanical resilience, is usually hard to achieve for porous materials processed by conventional synthesis and fabrication techniques such as sol–gel and hard templating approaches. The composite foams developed in this study exhibited a tunable and highly porous structure composed of inter-cross-linked SF chains, which were also intertwined with MXene and GO nanosheets. The X-SF-MXene foams combined an ultralow density (6–60 mg cm^{-3}), hydrophobicity (WCA up to 124°), compressibility (reversible compressibility up to 30% without failure and ultimate compression more than 80%), high absorption capacity for organic liquids (up to $\sim 120 \text{ g g}^{-1}$), efficient multicomponent oil/dye/organic solvent separation, and pressure-sensing capability. Besides, the strain/pressure sensors based on X-SF-MXene-GO are highly sensitive and can be used for high-performance flexible sensing arrays for the detection of strain (up to 50%) and pressure ($\sim 1 \text{ Pa}$ to 2 kPa) distributions.

Finally, the present study provides the essential concepts to translate the natural porous architectures into synthetic foams to improve their mechanical properties and functions with a high level of control on the microarchitecture. The fabricated flexible multifunctional porous nanocomposites show promising applications in flexible pressure sensors/electronic skins, pollutant separation, and other high-performance applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.1c09675>.

High-resolution XPS spectra of O 1s (a) and Ti 2p (b) and explanation about used characterization methods (PDF, MP4, and MP4)

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Notes

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REFERENCES

(1) Lee, S.; Shin, S.; Lee, S.; Seo, J.; Lee, J.; Son, S.; Cho, H. J.; Algadi, H.; Al-Sayari, S.; Kim, D. E.; Lee, T. Ag Nanowire Reinforced Highly Stretchable Conductive Fibers for Wearable Electronics. *Adv. Funct. Mater.* **2015**, *25*, 3114–3121.

(2) Li, J.; Bao, R.; Tao, J.; Peng, Y.; Pan, C. Recent Progress in Flexible Pressure Sensor Arrays: From Design to Applications. *J. Mater. Chem. C* **2018**, *6*, 11878–11892.

(3) Zang, Y.; Zhang, F.; Di, C.; Zhu, D. Advances of Flexible Pressure Sensors toward Artificial Intelligence and Health Care Applications. *Mater. Horiz.* **2015**, *2*, 140–156.

(4) Nyström, G.; Roder, L.; Fernández-Ronco, M. P.; Mezzenga, R. Amyloid Templated Organic–Inorganic Hybrid Aerogels. *Adv. Funct. Mater.* **2018**, *28*, No. 1703609.

(5) Hamed, M.; Karabulut, E.; Marais, A.; Herland, A.; Nyström, G.; Wågberg, L. Nanocellulose Aerogels Functionalized by Rapid Layer-by-Layer Assembly for High Charge Storage and Beyond. *Angew. Chem., Int. Ed.* **2013**, *52*, 12038–12042.

(6) Carlsson, D. O.; Nyström, G.; Zhou, Q.; Berglund, L. A.; Nyholm, L.; Strømme, M. Electroactive Nanofibrillated Cellulose Aerogel Composites with Tunable Structural and Electrochemical Properties. *J. Mater. Chem.* **2012**, *22*, 19014–19024.

(7) Zhuo, H.; Hu, Y.; Tong, X.; Chen, Z.; Zhong, L.; Lai, H.; Liu, L.; Jing, S.; Liu, Q.; Liu, C.; Peng, X.; Sun, R. A. Supercompressible, Elastic, and Bendable Carbon Aerogel with Ultrasensitive Detection Limits for Compression Strain, Pressure, and Bending Angle. *Adv. Mater.* **2018**, *30*, No. 1706705.

(8) Xu, X.; Zhou, J.; Nagaraju, D. H.; Jiang, L.; Marinov, V. R.; Lubineau, G.; Alshareef, H. N.; Oh, M. Flexible, Highly Graphitized Carbon Aerogels Based on Bacterial Cellulose/Lignin: Catalyst-Free Synthesis and Its Application in Energy Storage Devices. *Adv. Funct. Mater.* **2015**, *25*, 3193–3202.

(9) Hu, D.; Huang, X.; Li, S.; Jiang, P. Flexible and Durable Cellulose/MXene Nanocomposite Paper for Efficient Electromagnetic Interference Shielding. *Compos. Sci. Technol.* **2020**, *188*, No. 107995.

(10) Cao, W.-T.; Chen, F.-F.; Zhu, Y.-J.; Zhang, Y.-G.; Jiang, Y.-Y.; Ma, M.-G.; Chen, F. Binary Strengthening and Toughening of MXene/Cellulose Nanofiber Composite Paper with Nacre-Inspired Structure and Superior Electromagnetic Interference Shielding Properties. *ACS Nano* **2018**, *12*, 4583–4593.

(11) Zeng, Z.; Wu, T.; Han, D.; Ren, Q.; Siqueira, G.; Nyström, G. Ultralight, Flexible, and Biomimetic Nanocellulose/Silver Nanowire Aerogels for Electromagnetic Interference Shielding. *ACS Nano* **2020**, *14*, 2927–2938.

(12) Maleki, H.; Montes, S.; Hayati-Roodbari, N.; Putz, F.; Huesing, N. Compressible, Thermally Insulating, and Fire Retardant Aerogels through Self-Assembling Silk Fibroin Biopolymers Inside a Silica Structure—An Approach towards 3D Printing of Aerogels. *ACS Appl. Mater. Interfaces* **2018**, *10*, 22718–22730.

(13) Maleki, H.; Whitmore, L.; Hüsing, N. Novel Multifunctional Polymethylsiloxane–Silk Fibroin Aerogel Hybrids for Environmental and Thermal Insulation Applications. *J. Mater. Chem. A* **2018**, *6*, 12598–12612.

(14) Maleki, H.; Huesing, N. Silica-Silk Fibroin Hybrid (Bio)-Aerogels: Two-Step versus One-Step Hybridization. *J. Sol-Gel Sci. Technol.* **2019**, *98*, 430–438.

(15) Bruder, V.; Ludwig, T.; Opitz, S.; Christoffels, R.; Fischer, T.; Maleki, H. Hierarchical Assembly of Surface Modified Silk Fibroin Biomass into Micro-, and Milli-Metric Hybrid Aerogels with Core-Shell, Janus, and Composite Configurations for Rapid Removal of Water Pollutants. *Adv. Mater. Interfaces* **2021**, *8*, No. 2001892.

(16) Maleki, H.; Shahbazi, M.-A.; Montes, S.; Hosseini, S. H.; Eskandari, M. R.; Zaunschirm, S.; Verwanger, T.; Mathur, S.; Milow, B.; Krammer, B.; Hüsing, N. Mechanically Strong Silica-Silk Fibroin Bioaerogel: A Hybrid Scaffold with Ordered Honeycomb Micro-morphology and Multiscale Porosity for Bone Regeneration. *ACS Appl. Mater. Interfaces* **2019**, *11*, 17256–17269.

(17) Rockwood, D. N.; Preda, R. C.; Yücel, T.; Wang, X.; Lovett, M. L.; Kaplan, D. L. Materials Fabrication from *Bombyx mori* Silk Fibroin. *Nat. Protoc.* **2011**, *6*, 1612–1631.

(18) Qin, Y.; Peng, Q.; Ding, Y.; Lin, Z.; Wang, C.; Li, Y.; Xu, F.; Li, J.; Yuan, Y.; He, X.; Li, Y. Lightweight, Superelastic, and Mechanically Flexible Graphene/Polyimide Nanocomposite Foam for Strain Sensor Application. *ACS Nano* **2015**, *9*, 8933–8941.

- (19) Marcano, D. C.; Kosynkin, D. V.; Berlin, J. M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L. B.; Lu, W.; Tour, J. M. Improved Synthesis of Graphene Oxide. *ACS Nano* **2010**, *4*, 4806–4814.
- (20) Wicklein, B.; Kocjan, A.; Salazar-Alvarez, G.; Carosio, F.; Camino, G.; Antonietti, M.; Bergström, L. Thermally Insulating and Fire-Retardant Lightweight Anisotropic Foams Based on Nanocellulose and Graphene Oxide. *Nat. Nanotechnol.* **2015**, *10*, 277–283.
- (21) Wan, C.; Li, J. Graphene Oxide/Cellulose Aerogels Nanocomposite: Preparation, Pyrolysis, and Application for Electromagnetic Interference Shielding. *Carbohydr. Polym.* **2016**, *150*, 172–179.
- (22) Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-Dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2 . *Adv. Mater.* **2011**, *23*, 4248–4253.
- (23) Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y. 25th Anniversary Article: MXenes: A New Family of Two-Dimensional Materials. *Adv. Mater.* **2014**, *26*, 992–1005.
- (24) Mathis, T. S.; Maleski, K.; Goad, A.; Sarycheva, A.; Anayee, M.; Foucher, A. C.; Hantanasirisakul, K.; Shuck, C. E.; Stach, E. A.; Gogotsi, Y. Modified MAX Phase Synthesis for Environmentally Stable and Highly Conductive Ti_3C_2 MXene. *ACS Nano* **2021**, *15*, 6420–6429.
- (25) Lipatov, A.; Lu, H.; Alhabeb, M.; Anasori, B.; Gruverman, A.; Gogotsi, Y.; Sinitskii, A. Elastic Properties of 2D $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Monolayers and Bilayers. *Sci. Adv.* **2018**, *4*, No. eaat0491.
- (26) Wyatt, B. C.; Rosenkranz, A.; Anasori, B. 2D MXenes: Tunable Mechanical and Tribological Properties. *Adv. Mater.* **2021**, *33*, No. 2007973.
- (27) Gogotsi, Y.; Anasori, B. The Rise of MXenes. *ACS Nano* **2019**, *13*, 8491–8494.
- (28) Bi, L.; Yang, Z.; Chen, L.; Wu, Z.; Ye, C. Compressible AgNWs/ $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Aerogel-Based Highly Sensitive Piezoresistive Pressure Sensor as Versatile Electronic Skins. *J. Mater. Chem. A* **2020**, *8*, 20030–20036.
- (29) Ma, Y.; Yue, Y.; Zhang, H.; Cheng, F.; Zhao, W.; Rao, J.; Luo, S.; Wang, J.; Jiang, X.; Liu, Z.; Liu, N.; Gao, Y. 3D Synergistic MXene/Reduced Graphene Oxide Aerogel for a Piezoresistive Sensor. *ACS Nano* **2018**, *12*, 3209–3216.
- (30) Zu, G.; Kanamori, K.; Maeno, A.; Kaji, H.; Nakanishi, K.; Shen, J. Ambient-Dried Highly Flexible Copolymer Aerogels and Their Nanocomposites with Polypyrrole for Thermal Insulation, Separation, and Pressure Sensing. *Polym. Chem.* **2019**, *10*, 4980–4990.
- (31) Zu, G.; Kanamori, K.; Nakanishi, K.; Lu, X.; Yu, K.; Huang, J.; Sugimura, H. Superelastic Multifunctional Aminosilane-Crosslinked Graphene Aerogels for High Thermal Insulation, Three-Component Separation, and Strain/Pressure-Sensing Arrays. *ACS Appl. Mater. Interfaces* **2019**, *11*, 43533–43542.
- (32) Bai, H.; Chen, Y.; Delattre, B.; Tomsia, A. P. Bidirectional Freeze Casting for Fabricating Lamellar Structures. *US20170100857A1*. 2017.
- (33) Bai, H.; Chen, Y.; Delattre, B.; Tomsia, A. P.; Ritchie, R. O. Bioinspired Large-Scale Aligned Porous Materials Assembled with Dual Temperature Gradients. *Sci. Adv.* **2015**, *1*, No. e1500849.
- (34) Shao, G.; Hanaor, D. A. H.; Shen, X.; Gurlo, A. Freeze Casting: From Low-Dimensional Building Blocks to Aligned Porous Structures—A Review of Novel Materials, Methods, and Applications. *Adv. Mater.* **2020**, *32*, No. 1907176.
- (35) Deville, S. Freeze-Casting of Porous Ceramics: A Review of Current Achievements and Issues. *Adv. Eng. Mater.* **2008**, *10*, 155–169.
- (36) Shahbazi, M.-A.; Ghalkhani, M.; Maleki, H. Directional Freeze-Casting: A Bioinspired Method to Assemble Multifunctional Aligned Porous Structures for Advanced Applications. *Adv. Eng. Mater.* **2020**, *22*, No. 2000033.
- (37) Zhao, N.; Yang, M.; Zhao, Q.; Gao, W.; Xie, T.; Bai, H. Superstretchable Nacre-Mimetic Graphene/Poly(Vinyl Alcohol) Composite Film Based on Interfacial Architectural Engineering. *ACS Nano* **2017**, *11*, 4777–4784.
- (38) Yang, M.; Zhao, N.; Cui, Y.; Gao, W.; Zhao, Q.; Gao, C.; Bai, H.; Xie, T. Biomimetic Architected Graphene Aerogel with Exceptional Strength and Resilience. *ACS Nano* **2017**, *11*, 6817–6824.
- (39) Zheng, Z.; Guo, S.; Liu, Y.; Wu, J.; Li, G.; Liu, M.; Wang, X.; Kaplan, D. Lithium-Free Processing of Silk Fibroin. *J. Biomater. Appl.* **2016**, *31*, 450–463.
- (40) Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339–1339.
- (41) Chen, J.; Yao, B.; Li, C.; Shi, G. An Improved Hummers Method for Eco-Friendly Synthesis of Graphene Oxide. *Carbon* **2013**, *64*, 225–229.
- (42) Alhabeb, M.; Maleski, K.; Anasori, B.; Lelyukh, P.; Clark, L.; Sin, S.; Gogotsi, Y. Guidelines for Synthesis and Processing of Two-Dimensional Titanium Carbide ($\text{Ti}_3\text{C}_2\text{T}_x$ MXene). *Chem. Mater.* **2017**, *29*, 7633–7644.
- (43) David, G.; Gontard, N.; Guerin, D.; Heux, L.; Lecomte, J.; Molina-Boisseau, S.; Angellier-Coussy, H. Exploring the Potential of Gas-Phase Esterification to Hydrophobize the Surface of Micrometric Cellulose Particles. *Eur. Polym. J.* **2019**, *115*, 138–146.
- (44) Dianat, G.; Seidel, S.; De Luna, M. M.; Gupta, M. Vapor Phase Fabrication of Hydrophilic and Hydrophobic Asymmetric Polymer Membranes. *Macromol. Mater. Eng.* **2016**, *301*, 1037–1043.
- (45) Deville, S.; Saiz, E.; Nalla, R. K.; Tomsia, A. P. Freezing as a Path to Build Complex Composites. *Science* **2006**, *311*, 515–518.
- (46) Gilbert, P. *Physics in the Arts*, 3rd ed.; Academic Press/Elsevier, 2021.
- (47) Asakura, T.; Okushita, K.; Williamson, M. P. Analysis of the Structure of *Bombyx mori* Silk Fibroin by NMR. *Macromolecules* **2015**, *48*, 2345–2357.
- (48) Dong, Y.; Wu, Z.-S.; Zheng, S.; Wang, X.; Qin, J.; Wang, S.; Shi, X.; Bao, X. Ti_3C_2 MXene-Derived Sodium/Potassium Titanate Nanoribbons for High-Performance Sodium/Potassium Ion Batteries with Enhanced Capacities. *ACS Nano* **2017**, *11*, 4792–4800.
- (49) Wang, X.; Shen, X.; Gao, Y.; Wang, Z.; Yu, R.; Chen, L. Atomic-Scale Recognition of Surface Structure and Intercalation Mechanism of $\text{Ti}_3\text{C}_2\text{X}$. *J. Am. Chem. Soc.* **2015**, *137*, 2715–2721.
- (50) Shah, S. A.; Habib, T.; Gao, H.; Gao, P.; Sun, W.; Green, M. J.; Radovic, M. Template-Free 3D Titanium Carbide ($\text{Ti}_3\text{C}_2\text{T}_x$) MXene Particles Crumpled by Capillary Forces. *Chem. Commun.* **2017**, *53*, 400–403.
- (51) Sarycheva, A.; Gogotsi, Y. Raman Spectroscopy Analysis of the Structure and Surface Chemistry of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene. *Chem. Mater.* **2020**, *32*, 3480–3488.
- (52) Zhuo, H.; Hu, Y.; Chen, Z.; Peng, X.; Liu, L.; Luo, Q.; Yi, J.; Liu, C.; Zhong, L.; Carbon, A. Aerogel with Super Mechanical and Sensing Performances for Wearable Piezoresistive Sensors. *J. Mater. Chem. A* **2019**, *7*, 8092–8100.
- (53) Luo, Q.; Zheng, H.; Hu, Y.; Zhuo, H.; Chen, Z.; Peng, X.; Zhong, L. Carbon Nanotube/Chitosan-Based Elastic Carbon Aerogel for Pressure Sensing. *Ind. Eng. Chem. Res.* **2019**, *58*, 17768–17775.
- (54) Huang, J.; Zeng, J.; Liang, B.; Wu, J.; Li, T.; Li, Q.; Feng, F.; Feng, Q.; Rood, M. J.; Yan, Z. Multi-Arch-Structured All-Carbon Aerogels with Superelasticity and High Fatigue Resistance as Wearable Sensors. *ACS Appl. Mater. Interfaces* **2020**, *12*, 16822–16830.
- (55) Ali, A.; Khan, A.; Karimov, Kh. S.; Ali, A.; Daud Khan, A. Pressure Sensitive Sensors Based on Carbon Nanotubes, Graphene, and Its Composites. *J. Nanomater.* **2018**, *2018*, No. 9592610.
- (56) Lin, X.; Zhang, T.; Cao, J.; Wen, H.; Fei, T.; Liu, S.; Wang, R.; Ren, H.; Zhao, H. Flexible Piezoresistive Sensors Based on Conducting Polymer-Coated Fabric Applied to Human Physiological Signals Monitoring. *J. Bionic. Eng.* **2020**, *17*, 55–63.
- (57) Zhao, S.; Liu, R.; Fei, C.; Zia, A. W.; Jing, L. Flexible Sensor Matrix Film-Based Wearable Plantar Pressure Force Measurement and Analysis System. *PLoS One* **2020**, *15*, No. e0237090.
- (58) Li, Q.; Luo, S.; Wang, Q.-M. Piezoresistive Thin Film Pressure Sensor Based on Carbon Nanotube-Polyimide Nanocomposites. *Sens. Actuator, A* **2019**, *295*, 336–342.

(59) Gao, L.; Wang, Y.; Hu, X.; Zhou, W.; Cao, K.; Wang, Y.; Wang, W.; Lu, Y. Cellular Carbon-Film-Based Flexible Sensor and Waterproof Supercapacitors. *ACS Appl. Mater. Interfaces* **2019**, *11*, 26288–26297.