Super Tough Multifunctional MXene/PAA-CS Double Network Hydrogels with High Mechanical Sensing Properties and Excellent EMI Shielding Performance

Lin Mei, Wenchong Ouyang,* Limin Xu, Yuanlong Huang, Qi Liu, Yu Bai, Quanming Lu, Tianzhi Luo,* and Zhengwei Wu*

Hydrogels present significant potential in flexible materials designed for electromagnetic interference (EMI) shielding, attributed to their soft, stretchable mechanical properties and water-rich porous structures. Unfortunately, EMI shielding hydrogels commonly suffer from low mechanical properties, deficient fracture energy, and low strength, which limit the serviceability of these materials in complex mechanical environments. In this study, the double network strategy is successfully utilized along with the Hofmeister effect to create MXene/PAA (polyacrylic acid)-CS (chitosan) hydrogels and further strengthen and toughen the gel with $(NH_4)_2SO_4$ solution. The gel exhibits enhanced functionalities such as outstanding stretchability, excellent strain sensitivity (11.66), and super fracture energy $(\geq 9 \text{ kJ m}^{-2})$. Notably, it demonstrates outstanding shielding effectiveness of 73.8 dB in the terahertz (THz) range, and the shielding properties can be effectively tuned by varying the MXene content, the $(NH_4)_2SO_4$ concentration, and the thickness of the hydrogel. Additionally, the gel shows robust and superior shielding effectiveness after repeated stretching and long-term dehydration. The MXene/PAA-CS double-network (DN) hydrogels would be an excellent candidate for EMI shielding materials in advanced flexible electronic equipment and soft robots.

1. Introduction

Compared to the traditional gigahertz (GHz) frequency band, the terahertz (THz)frequency band offers several distinct advantages, including broader bandwidth, stronger penetration, lower energy, higher resolution, and unique spectral response characteristics. These features have driven its rapid development and widespread application in various areas such as 6G communication, medical imaging, security screening, biosensing, and atmospheric remote sensing.^[1-3] Consequently, there is an urgent demand for electromagnetic interference (EMI) shielding materials capable of addressing terahertz radiation to mitigate potential risks to human health, interference, and loss of communication equipment and electronic devices caused by terahertz radiation.^[4-6] Traditionally, various forms of EMI shielding materials, including sheets, films, foams, and aerogels, have garnered considerable attention

L. Mei, Z. Wu School of Nuclear Science and Technology University of Science and Technology of China Hefei 230026, China E-mail: wuzw@ustc.edu.cn L. Mei, T. Luo CAS Key Laboratory of Mechanical Behavior and Design of Materials Department of Modern Mechanics University of Science and Technology of China Hefei 230026, China E-mail: tzluo@ustc.edu.cn W. Ouyang, Q. Lu Deep Space Exploration Laboratory School of Earth and Space Sciences University of Science and Technology of China

Hefei 230026, China E-mail: oywc13978384979@mail.ustc.edu.cn

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/smll.202410687

DOI: 10.1002/smll.202410687

W. Ouyang, Z. Wu Joint Laboratory of Plasma Application Technology Institute of Advanced Technology University of Science and Technology of China Hefei 230031, China L. Xu, Y. Huang Advanced Institute of Photonics Technology School of Information Engineering Guangdong University of Technology Guangzhou 510006, China Q. Liu School of Engineering Yunnan University Kunming 650091, China Y. Ba Experimental Center of Engineering and Materials Sciences University of Science and Technology of China Hefei 230026, China T. Luo State Key Laboratory of Fire Science University of Science and Technology of China Hefei 230026, China

and application due to their high electrical conductivity and excellent EMI shielding capabilities.^[5–9] However, these conventional materials tend to be brittle, with limited stretchability and low fracture toughness, significantly restricting their suitability for advanced deformable and flexible electronic equipment.^[4] Therefore, the industry has an increasing demand for EMI shielding materials with excellent stretchability, flexibility, and electrical properties.

Conductive hydrogels have been increasingly employed in emerging areas, including but not limited to soft robots, foldable smartphones, and human-computer interaction, due to their remarkable characteristics, including flexibility, stretchability, and strain sensing.^[10,11] They are considered potential candidates for advanced, intelligent, flexible EMI shielding materials.^[12] The abundant water molecules in hydrogels can induce strong absorption attenuation, polarization, and dielectric loss when exposed to electromagnetic signals in the gigahertz and terahertz frequency bands. Hydrogels exhibit distinct advantages in highperformance EMI shielding applications due to their porous structure.^[13,14] Recently, several approaches have been developed to incorporate conductive fillers into hydrogel matrices, such as metal-based fillers, carbon nanotubes or nanofibers (CNT/CNF), and two-dimensional nanomaterials MXenes, to enhance their EMI shielding performance significantly.^[15–17] The results have shown that the combination of conductive fillers such as MXene, CNT, and silver nanowires (AgNWs) with different hydrogel network structures can effectively improve the EMI shielding effectiveness (EMI SE), which is manifested as 10-30 dB EMI SE improvement.^[17-21] This results in high-performance EMI shielding of over 50 dB in the X to Ka frequency band,^[22-24] with peak values reaching 90 dB.^[23] However, current research on conductive hydrogel EMI shielding materials has primarily focused on the gigahertz band, with limited attention paid to the challenges EMI shielding poses in the rapidly evolving terahertz band. To date, only a few studies have reported on the EMI shielding performance in the terahertz band. For example, MXene-PAA-ACC hydrogels and MXene/PEDOT: PSS organohydrogels based on conductive fillers such as MXene and PEDOT: PSS, have achieved EMI SE of 35-62 dB in the terahertz band.^[25,26] Nonetheless, the enhancement of shielding properties in the terahertz band remains constrained by the saturation limits of conductive fillers and their interactions with the hydrogel matrix, restricting further improvements in shielding performance.

More importantly, the reported EMI hydrogel shielding materials in the gigahertz and terahertz bands generally have weak mechanical properties and low conductivity,^[23] which limits their application to flexible electronic equipment and EMI shielding. Recently, typical strategies such as double-network (DN),^[4,27] directional freezing,^[23] nanocomposite,^[18] and salting out (molecular entanglement, Hofmeister effect),^[23] were applied to strengthen the EMI shielding hydrogels and the strength of the gels achieve 0.15–0.4 MPa. Wang et al.^[27] applied the DN and the nanocomposite strategies to form the PVA/CS/MXene/Fe₃O₄ hydrogels with a strength of 0.32 MPa. Yang et al.^[23,28] strength the PVA matrix through unidirectional freezing and salting-out to obtain the EMI shielding gels with a strength of 0.15 MPa. Conductive hydrogels have significant mechanical disadvantages compared to conventional film, Foam, and aerogel EMI shielding materials, particularly in their relatively low strength and durability. Moreover, even less research pays attention to the fracture energy of the EMI shielding hydrogel, and it is clear that the gel with high fracture toughness could perform better in the application under high and complex mechanical loads.^[29–31] Liu et al.^[30] used a protein crystallization-mediated self-strengthening strategy to obtain the PCOHs hydrogels and achieved a strength of 1.5 MPa and a fracture energy of 3.2 kJ m^{-2} , which is the highest strength and highest fracture toughness among the reported EMI shielding hydrogels. In general, the strength and fracture toughness of the tough EMI shield hydrogels remain low, and the stretchability of the gels also needs further improvement. Therefore, it remains a crucial problem and challenge in the current research and development of hydrogel electromagnetic shielding materials to achieve excellent mechanical properties while maintaining high-efficiency EMI shielding performance.

In this work, we present novel EMI shielding double network (DN) hydrogels with high strength exceeding 3.3 MPa, a fracture energy of over 9 kJ m^{-2} (approximately three times higher than the published data), toughness exceeding 4.5 MJ m⁻³, and an EMI SE of >70 dB in the THz band. The matrix comprises short chitosan (CS) chains and flexible long polyacrylic acid (PAA) chains. MXene nanosheets were added into the gels to provide the essential electromagnetic shielding capability. The intermediate product was soaked in an ammonium sulfate solution to form a rigid CS ionic network, creating the PAA-CS DN. Additionally, the salting-out procedure not only activates the Hofmeister effect, leading to molecular entanglement of CS, which effectively toughens and strengthens the gels, but also provides mobile NH_4^+ and SO_4^{2-} ions which could elevate the conductivity of the gels and further improve the EMI shielding performance of the gel. More importantly, the gels could maintain stable shielding effectiveness after repeated stretching and dehydration. It is also worth pointing out that the gels have an outstanding strain sensitivity with a GF over 11, making the gel valuable for flexible sensors. In general, the MXene/PAA-CS DN hydrogels are poised to not only function as next-generation, stable materials for electromagnetic interference (EMI) shielding but also demonstrate remarkable functionality and sufficient fracture toughness^[32] (≈10 kJm⁻²) suitable for advanced applications in flexible electronic devices and soft robotics.

2. Experimental Section

2.1. Fabrication of MXene/PAA-CS DN Hydrogel

All reagents in this work were used as received without purification. Acrylic acid (AA, 99%, contains 200 ppm MEHQ as inhibitor), and 2,2'-azobis(2-methyl-propionamidine) dihydrochloride (V-50,97%), Ammonium sulfate ((NH₄)₂SO₄, 99%), were purchased from Aladdin Reagent Co., Ltd., China. N, Nmethylenebis(acrylamide) (MBAA, 99%) was purchased from Sigma Aldrich. Short-chain chitosan (CS, degree of deacetylation >90%, viscosity 45 mPa·s for 1% (w/v) solution) was purchased from Jinhu Company, China. Ti₃C₂ MXene dispersion (20 mg/mL) was obtained from 11 Technology Co., Ltd., Jilin, China.

The MXene/PAA-CS double network (DN) hydrogels were synthesized following the steps below. Firstly, 3 g of AA, an appropriate amount (0, 0.2, 0.4, 0.6 g) of CS, 2.5 mg of MBAA,



75 µL 0.8 M V-50 solution, and an appropriate volume (0, 1.5, 3.0, 4.5 mL) of 20 mg mL⁻¹ MXene dispersion were mixed, and ultrapure water (UP) water were added to under ice bath by a SCIENTZ-IID ultrasonic homogenizer (Scientz Biotechnology Co., Ltd Ningbo) under 240 W for 20 min to disperse MXene in the mixture evenly. The precursor would be further degassed by a TMV-200T Vacuum Mixer (Smida Intelligent Equipment Co., Ltd Shenzhen) with 1.5 kPa 1000 rpm for 3 min. Afterward, the mixture was injected into a mold comprised of two glass plates separated by a silicone rubber spacer. The polymerization of the PAA was activated under 50 °C for 12 h while MBAA served as the cross-linker and V-50 was used as the thermal initiator. Thus, the MXene/PAA-CS composite gels were obtained. Finally, the MXene/PAA-CS composite gels were immersed in (NH₄)₂SO₄ solution for 72 hours. The solution with proper $(NH_4)_2SO_4$ concentration could form the CS ionic network and triggering the Hofmeister effect which would form the molecular entanglement of CS chains.

2.2. Characterization

The FT-IR spectra of the hydrogels in the range of 4000–400 cm⁻¹ were obtained by a Nicolet 8700 IR spectrophotometer. The scanning electron microscopy (SEM) images of the hydrogels were captured by a Gemini SEM 500 (ZEISS, Germany) under an accelerating voltage of 3 kV while the same equipment carried out the energy dispersive spectroscopy (EDS) under an accelerating voltage of 20 kV. To avoid the impact of (NH₄)₂SO₄ precipitated during freeze drying on SEM observation (Figure S1, Supporting Information), all samples were immersed in deionized water for 30 min to remove an appropriate amount of $(NH_4)_2 SO_4$ before being frozen by liquid nitrogen. The transmission electron microscopy (TEM) images of the Ti₃C₂ MXene nanosheets were obtained by an HT7700 Exalens (HITACHI, Japan) under an accelerating voltage of 100 kV. The Raman spectra of the hydrogels in the range of 100-1500 cm⁻¹ were obtained by a Raman Spectrometer-LabRAM HR Evolution (Horiba, Japan). The X-ray diffraction (XRD) results of the hydrogels were carried out by a Theta/Theta Rotating anode X-ray Diffractometer (TTR III, Japan). The X-ray Photoelectron spectra (XPS) results of the gels were captured by an ESCALAB 250Xi (Thermo Scientific, the United States).

2.3. Mechanical Tests

The tensile tests and the pure sheer tests were performed by a Criterion C43 testing machine (MTS Co., LTD, China). For the tensile tests, the hydrogel sheets were stamped into a dumbbell shape with 2 mm inner width, 20 mm gauge length and the tensile rate was set to 50 mm min⁻¹ to reduce the influence of dehydration. The stress σ was obtained by $\sigma = F/A_0$ (F: loading force, A_0 : cross-sectional area). The strain ϵ was calculated by $\epsilon = (l - l_0)/l_0(l$: final length, l_0 : original length of the sample). The elastic modulus was calculated from the slope at strain in the range 0–50% of the stress–strain curves. The toughness was calculated by the area enclosed by the stress–strain curve of the dumbbell sample.

Furthermore, the fracture energy (also known as fracture toughness) Γ could be obtained by the pure shear tests.^[33,34] First, the rectangular samples with 30 mm width, 6 mm height, 1–2 mm thickness, and 12 mm crack (if notched) were prepared for fracture test. Subsequently, the tensile behaviors of the notched and unnotched rectangular samples were measured. Afterward, the fracture energy was calculated by the formula $\Gamma = HW(\epsilon_c)$. Here, *H* is the height of the unnotched sample. $W(\epsilon_c)$ was calculated by the area enclosed by the stress–strain curve of the unnotched samples, the strain axis, and $\epsilon = \epsilon_c$ (ϵ_c : the critical strain of a notched sample, in brief the strain of the notched sample at maximum strain^[31]).

2.4. Conductivity Test

The sample for the conductivity test was 5–8 mm in width, 1–2 mm in thickness, and had a gauge length of 10–50 mm. The resistance of the sample of hydrogels was captured by a TH2832 inductance, capacitance, and resistance (LCR) meter (Tonghui Electronic Co., Ltd. Changzhou). The conductivity *s* was calculated by the equation: s = L/RA. Here, *L* is the length of the sample, *R* is the resistance of the sample and *A* is the cross-sectional area of the sample.

2.5. Strain-Sensing Test

The sample for the strain-sensing test was 6 mm in width, 1–2 mm in thickness, and had a gauge length of 30–40 mm. The gauge factor $GF = \Delta R/R_0 \epsilon$ was used to quantify the strain sensitivity of the hydrogels. Here, R_0 is the initial resistance of the sample, ΔR is the resistance change of the sample and ϵ is the strain of the sample. The resistance change of the sample at different strains was measured by a TH2832 LCR meter while the sample was loaded and unloaded by an HY-0350 testing machine (HengYi Instrument Co., Ltd, Shanghai). To reduce the effect of dehydration on hydrogels, the loading-unloading rate for strain cycles of 0–25%, 0–50%, 0–75%, 0–100%, 0–200%, and 0–300% was 1 mm s⁻¹.

2.6. EMI SE Test

The specific testing and calculation details of EMI SE performance of the MXene/PAA-CS DN hydrogels can be found in Note S1 (Supporting Information).

3. Results

3.1. Synthesis and Structural Analysis of MXene/PAA-CS DN Hydrogels

The synthesis of MXene/PAA-CS double-network (DN) hydrogels was carried out according to the method shown in **Figure 1a**. Initially, a combination of AA, CS, MBAA, V-50, a proper volume of ultrapure water, and an appropriate volume of Ti_3C_2 MXene suspension was subjected to sonication at 240 W, followed by degassing using a vacuum mixer at 1000 rpm and 1.5 kPa such that

CIENCE NEWS



Figure 1. a) The manufacturing process of MXene/PAA-CS DN hydrogel. b) The SEM images of hydrogels with 0%, 15%, and 43% $(NH_4)_2SO_4$ (scale bar: 2 μ m). c) The TEM result of MXene (scale bar: 100 nm). d) EDS mapping of the C, O, S, and Ti elements in MXene/PAA-CS DN hydrogel with 9 mg mL⁻¹ MXene content (scale bar: 20 μ m).

a homogeneous precursor was obtained. Afterward, polyacrylic acid (PAA) networks were created utilizing MBAA as the crosslinker and initiated by V-50 at 50 °C for 12 hours. Finally, the intermediate product was soaked in a concentrated $(NH_4)_2 SO_4$ solution (the process known as salting out) for 72 hours, leading to the formation of a rigid CS network and activating the Hofmeister effect, which promotes the molecular entanglement of the DN.^[35] The SEM images demonstrate the micro structure of the gels, it could be found that the $(NH_4)_2SO_4$ solution would cause the form of the CS network and the shrinkage of the network pore size (Figure 1b; Figure S2, Supporting Information). The TEM image (Figure 1c) shows that the MXene nanosheets have a size \approx 500 nm, and the EDS mapping results (Figure 1d; Figure S3, Supporting Information) indicate that MXene was evenly distributed within the matrix after ultrasonic treatment and vacuum stirring.

The successful synthesis of MXene/PAA-CS double network (DN) hydrogels could also be confirmed through XRD, Raman spectroscopy, FTIR, and XPS characterization experiments (**Figure 2**), and the interactions between MXene, PAA chains, CS chains, and $(NH_4)_2SO_4$ were further revealed. In the XRD spectrum, the characteristic peak of MXene shifted from 6.54° to 6.48° in the MXene/PAA-CS DN hydrogel, confirming the successful incorporation of MXene sheets into the hydrogel structure,^[26] and similar peaks (17.00°, 20.50°, 22.86°, 28.42°, 29.28°, 29.82°, 35.60°, 38.84°, etc.) in PAA-CS DN and MXene/PAA-CS DN hydrogel peaks (17.00°, 20.50°,

drogels were mainly due to the impact of $(NH_4)_2SO_4$ contain in these two gels (Figure 2a; Figure S4, Supporting Information). The Raman spectroscopy results showed that the MXene/PAA-CS DN hydrogel displayed peak features comparable to MXene, including A_{1g} (Ti, C, O), A_{1g} (C), and E_g peak. A peak at \approx 505 cm⁻¹ similar to that of the PAA-CS DN hydrogel was also observed, indirectly confirming the synthesis of the MXene/PAA-CS DN hydrogel. Compared with MXene, the $A_{1o}(C)$ peak of MXene/PAA-CS DN shifted to the right from 728 to 731 cm⁻¹ (Figure 2b), revealing a potential interaction between MXene and the PAA and CS chains.^[36] In the FTIR spectrum, the -OH peak of MXene/PAA-CS DN hydrogel (3195.47 cm⁻¹) shifted to a higher wavenumber compared to the PAA-CS DN hydrogel (3192.58 cm⁻¹), indicating that the Ti-rich surface groups of MXene may have enhanced hydrogen bond formation (Figure 2c). Compared with PAA-CS DN hydrogel, the C=O peak of MXene/PAA-CS DN hydrogel also shifted to the right, which may be due to the interaction between MXene and PAA chains and CS chains. It was also observed that MXene/PAA-CS DN hydrogel had similar peak morphologies to PAA-CS DN and PAA-CS hydrogels at \approx 1401 and 1050 cm⁻¹, respectively.

In the spectral results of MXene/PAA-CS DN hydrogel, the coexistence of Ti 2p, C 1s, O 1s, N 1s, and S 2p was observed. Meanwhile, Ti 2p was detected in MXene with no observation of S 2p, while S 2p was detected in the PAA-CS DN hydrogels with no observation of Ti 2p (Figure 2d). In addition, Ti 2p and S 2p were

SCIENCE NEWS



Figure 2. a) XRD spectrum, b) Raman spectra, c) FT-IR of MXene/PAA-CS DN hydrogels along with reference samples. d) XPS comparison among MXene/PAA-CS DN hydrogels and reference samples, e–i) high-resolution spectra of (e) C 1s, (f) O 1s, (g) S 2p, (h) Ti 2p, and (i) N 1s for MXene/PAA-CS DN hydrogels.

not observed in PAA-CS hydrogel, which validated the successful incorporation of MXene, PAA, CS, and $(NH_4)_2SO_4$ into the DN gel. At the same time, the C 1s, N 1s, O 1s, and Ti 2p peaks in MXene/PAA-CS DN hydrogel were post-processed by deconvolution to explore the interactions in the DN hydrogel system (Figure 2e–i). In the peak analysis results of C 1s, peaks were observed at 282.2 eV (C-Ti-O), 284.8 eV (C-O/C-N), 286.4 eV (C-C), and 288.9 eV(C=O)^[37] (Figure 2e). The O 1s result shows three peaks at 530.8 eV (C-Ti-O), 531.5 eV (Ti-O), and 533.1 eV (O-H)^[38] (Figure 2f). The S 2p result shows that there are four pairs of S $2p_{3/2}$ and Ti $2p_{1/2}$ doublets at 163.7/164.8 eV (C-S), 168.7/169.7 eV (SO₄^{2–}) (Figure 2g). Meanwhile, the Ti 2p result shows that there are four pairs of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ doublets at 455.0/461.2 eV (Ti-C), 456.4/462.2 eV (Ti²⁺), 457.25/463.45 eV (Ti³⁺) and 458.9/465.1 eV (Ti-O)^[36,37] (Figure 2h). The appearance of the corresponding peaks of C-Ti-O, Ti-O, Ti-C, O-H well proved the interaction between MXene and PAA chains and CS chains. In addition, the peaks corresponding to -NH- (399.5 eV), -NH₂ (401.6 eV), and NH₄⁺ (401.9 eV) were observed in the N Is peak separation results (Figure 2i).^[37] Under acidic conditions, the -NH₂ groups in CS are protonated to form -NH₃⁺,^[39] which can subsequently form ionic bonds with the -COO⁻ groups on the PAA chains.^[40] These ionic bonds, established through Coulombic interactions between oppositely charged groups both within and between polymer chains, along with the molecular entanglement of CS chains driven by the Hofmeister effect of (NH₄)₂SO₄, markedly enhance the mechanical strength of the hydrogel.

NANO . MICRO

www.small-journal.com

NANO . MICRO



Figure 3. a) Various types of stretching and b) weight-lifting capability, c) stress–strain curves of MXene/PAA-CS DN hydrogels with 0–43% $(NH_4)_2SO_4$ concentration, d) strength and modulus of hydrogels with 0–43% $(NH_4)_2SO_4$ concentration, e) maximum strain and toughness of hydrogels with 0–43% $(NH_4)_2SO_4$ concentration, e) maximum strain and toughness of hydrogels with 0–43% $(NH_4)_2SO_4$ concentration, e) maximum strain and toughness of hydrogels with 0–43% $(NH_4)_2SO_4$ concentration, e) maximum strain and toughness of hydrogels with 0–43% $(NH_4)_2SO_4$ concentration, e) maximum strain and toughness of hydrogels with 0–43% $(NH_4)_2SO_4$ concentration, e) maximum strain and toughness of hydrogels with 0–43% $(NH_4)_2SO_4$ concentration, e) maximum strain and toughness of hydrogels with 0–43% $(NH_4)_2SO_4$ concentration, h) fracture energy (fracture toughness) Γ of gels with 0–43% $(NH_4)_2SO_4$ concentration.

3.2. Mechanical Properties

MXene/PAA-CS DN hydrogels are capable of enduring different types of deformations (**Figure 3**a). Moreover, the gel could withstand over 1000 times its own weight (Figure 3b). These observations indicate that MXene/PAA-CS DN hydrogels possess excellent mechanical properties.

To explore the influence of $(NH_4)_2SO_4$ concentration on the mechanical properties of hydrogels, tensile tests were conducted on hydrogels containing 0.06 g mL⁻¹ CS, 0.3 g mL⁻¹ PAA, 9 mg mL⁻¹ MXene, and varying concentrations of $(NH_4)_2SO_4$. As the concentration of $(NH_4)_2SO_4$ increased from 0% to 43%, the strength of MXene/PAA-CS DN hydrogels rose from 0.08 \pm 0.01 MPa to 1.62 \pm 0.05 MPa. Concurrently, the max strain of the samples improved from 500 \pm 35% to 620 \pm 14%, and the modulus of the samples increased from 81.48 \pm 4.98 kPa to 0.44 \pm 0.02 MPa. The toughness of the gels also experienced

a significant rise, from 1.05 ± 0.18 MJ m⁻³ to 4.64 ± 0.19 MJ m⁻³ (Figure 3c–e). To assess the impact of $(NH_4)_2SO_4$ on fracture energy (Γ), pure shear tests^[33,41] were conducted. Results (Figure 3f–h) revealed that the Γ of the gels increased substantially from 0.19 \pm 0.03 to 9.22 \pm 1.29 kJ m⁻² with higher concentrations of $(NH_4)_2SO_4$ solution. It is worth pointing that the gels fabricated in this study exhibited the highest fracture energy reported among all existing EMI shielding gels.

The data suggests that increasing the concentration of $(NH_4)_2SO_4$ can significantly enhance various mechanical properties of the hydrogels. This improvement likely arises from three primary effects:^[42] 1) an increase in the density of ionic bonds, thereby reinforcing the chitosan (CS) first network; 2) a heightened Hofmeister effect, which promotes greater molecular entanglement, strengthening both the entanglement within the first network and that between the first and second networks; 3) Densifying the DN by dehydrating the gel (Figure 1b). While the sample was stretched, the above effects would cause: 1) more strain energy is required to reach the same strain and 2) the delay of crack generation in the matrix. Thus, the strength, modulus, toughness and max strain would be improved. Similarly, the DN structure and the molecular entanglement may restrict the local propagation of cracks during the tear test, causing a higher fracture energy.

To examine how chitosan affects mechanical properties, gels formulated with 43% $(NH_4)_2SO_4$, 9 mg mL⁻¹ MXene, 0.3 g mL⁻¹ PAA, and CS concentrations ranging from 0.00 to 0.06 g mL⁻¹ were subjected to testing during synthesis. The results revealed that as CS content increased, the strength of the samples rose from 181 ± 4.1 kPa to 1.62 ± 0.05 MPa. Initially, the max strain of the samples increased from $600 \pm 69\%$ to $746 \pm 22\%$ before decreasing to $620 \pm 14\%$. The modulus of the gels climbed from 84 ± 12 kPa to 0.44 ± 0.02 MPa, and the toughness exhibited a significant rise from 0.56 \pm 0.15 MJ m⁻³ to 4.64 \pm 0.19 MJ m⁻³ (Figure 4a-c). Moreover, the pure sheer tests (Figure 4d-f) indicate that the Γ of the hydrogels would significantly rise from 2.41 \pm 0.26 kJ m⁻² to 9.22 \pm 1.29 kJ m⁻² with the CS contents elevated. With increasing CS content, gels' strength, modulus, and toughness also show remarkable improvement. As is well known, a double-network matrix typically consists of a rigid first network (which contributes sacrificial bonds) and a flexible second network (which offers hidden length).^[43,44] In this work, the CS short chain constitutes the first network, and the PAA long chain provides the second network. The first network could be densified with the rise in CS concentration (Figure S5, Supporting Information), allowing the matrix to absorb more energy during the same stretching process and inhibit crack propagation. Consequently, the strength, modulus, toughness, and Γ of the DN gels are significantly improved.

To explore the effect of MXene concentration on mechanical properties, gels containing 0.3 g mL⁻¹ AA, 0.06 g mL⁻¹ CS, 43% $(NH_4)_2$ SO₄, and varying content of Mxene nano-sheets were subjected to tensile testing. The data indicates that as the MXene concentration increased, the strength of the samples diminished from 3.31 ± 0.08 to 1.62 ± 0.05 MPa. Additionally, the max strain of the gels decreased from 720 \pm 17% to 620 \pm 14%, while the modulus remained ≈ 0.45 MPa. The toughness of the gels also dropped from 10.65 \pm 0.37 to 4.64 \pm 0.19 MJ m⁻³. Furthermore, with the increase of MXene contents, the Γ decreased from 11.16 \pm 0.93 to 9.22 \pm 1.29 kJ m⁻² (Figure 4j–l). Combing the experiments above, we believe that the introduction of MXene leads to larger network pore size and might influence the molecular entanglement of CS (Figure S6, Supporting Information), thus reducing the mechanical properties of hydrogels. However, it is essential to note that the DN and the Hoffmeister effect can actually improve the overall properties of hydrogels and the gels were rigid and tough enough for the application in a complex mechanical environment.[30,32]

3.3. EMI Shielding Performances and Mechanism

Hydrogels have potential applications in EMI shielding thanks to their porous structure, substantial water content, and high conductivity, especially in the terahertz band. The EMI SE of the MXene/PAA-CS double-network (DN) hydrogel, and the ef______SIIIQII www.small-journal.com

ANO . MICRO

fects of varying component concentrations were evaluated using terahertz time-domain spectroscopy (THz-TDS). The introduction of MXene significantly enhanced the EMI SE of the hydrogel. The EMI SE of 9 mg mL⁻¹ MXene content at 1 mm thickness increased by 22.4 dB compared with 0 mg mL⁻¹ EMI SE (Figure 5a), which is well matched with our previous work.^[36] Notably, in this work, by increasing the MXene content to a critical concentration (9 mg mL⁻¹), the MXene/PAA-CS hydrogel achieved an EMI SE of 48.9 dB in the terahertz range, significantly surpassing the commercial requirement of at least 20 dB for EMI SE.^[45] The increase in MXene content led to a notable enhancement of the conductivity of the gels, and additionally facilitated the forming of MXene conductive networks, elevating the energy dissipation of electromagnetic waves.^[46] The EMI SE was also measured at varying CS contents to explore its regulation ability. The EMI SE values for CS contents of 0.02–0.06 g mL⁻¹ did not show significant differences. Still, they were significantly higher than that of 0 g mL⁻¹ CS (\approx 3 dB) (Figure 5b). The main contribution of CS to the composite hydrogel is to ensure the uniformity of MXene dispersion (Figure S7, Supporting Information) and the improvement of mechanical properties.^[43] The absence of CS will cause a decrease in the uniformity of MXene in the hydrogel, resulting in lower EMI SE. The MXene/PAA-CS DN hydrogel treated with (NH₄)₂SO₄ significantly increased the mechanical properties and observed its positive contribution to EMI SE. As the $(NH_4)_2SO_4$ concentration rose from 0% to 30%, the EMI SE of MXene/PAA-CS DN hydrogel increased from 48.9 to 63.8 dB. However, as the concentration of $(NH_4)_2SO_4$ continued to rise toward saturation, the EMI SE subsequently declined to 59.4 dB. (Figure 5c). This enhancement in EMI SE is likely attributed to the substantial rise in conductivity induced by the $(NH_4)_2$ SO₄ treatment. In addition to the influence of the above component content, the hydrogel thickness can also effectively regulate EMI SE. As the samples became thicker (from 0.5 mm to 2.0 mm), the EMI SE in the terahertz band rose by \approx 17.8 dB (Figure 5d). The increased thickness extended the transmission path of terahertz waves, promoting multilayer reflection and absorption of electromagnetic waves within the hydrogel's porous structure, thereby achieving a higher EMI SE. Consequently, the MXene/PAA-CS DN hydrogel with a thickness of 2 mm, 9 mg mL⁻¹ MXene, and 30% (NH₄)₂SO₄ can exhibit a maximum EMI SE of 73.8 dB (Figure 5e,f), which exceeds most of the current terahertz shielding materials [S1-S24] (Table S1, Supporting Information). In order to better compare the shielding effects of MXene/PAA-CS DN hydrogel with different terahertz shielding materials, the shielding effectiveness ratio is defined by the ratio of EMI SE to thickness, and the shielding effectiveness ratios of different terahertz materials are further compared (Figure S8, Supporting Information). Obviously, Film material has a significantly higher shielding effectiveness ratio due to its ultra-thin property, but its tensile, strain, and sensor performance are generally poor [S1-S6] (Figure S8, Supporting Information), which limits its application in flexible electronic devices. Among flexible terahertz shielding materials such as foam, aerogel, and hydrogel, the shielding performance ratio of our MXene/PAA-CS DN hydrogel ranks among the best (Figure S8, Supporting Information).

In addition to achieving active regulation of high EMI SE, hydrogel shielding materials' practical application effect and ADVANCED SCIENCE NEWS ______

www.small-journal.com

NANO . MICR



Figure 4. a) Stress–strain curves of MXene/PAA-CS DN hydrogels with $0\sim0.06$ g mL⁻¹ CS content, b) strength and modulus, c) max strain and toughness of samples with varying CS concentration, tensile curve of d) unnotched and e) notched samples with varying CS content, f) fracture energy (fracture toughness) Γ of gels with varying CS content. g) Stress–strain curves of MXene/PAA-CS DN hydrogels with varying content of MXene, h) strength and modulus, i) max strain and toughness of hydrogels with varying content of MXene, the tensile curve of j) unnotched and k) notched samples with varying content of MXene, l) fracture energy Γ of gels with varying content of MXene.

stability are also crucial. The EMI SE of MXene/PAA-CS DN hydrogel after thousands of repeated stretching is unaffected (Figure 5g), which may be attributed to its excellent flexibility and tensile deformation performance of more than 6 times its own (Figure 3a,c). Although a significant decrease in EMI SE was observed after a week of water evaporation, the hy-

drogel still maintained a terahertz shielding performance of 36.4 dB (Figure 5h), which exceeded MXene/PAA-CS hydrogel and other traditional hydrogels.^[15] Additionally, the practical application effect of MXene/PAA-CS DN hydrogel in power supply and electronic product radiation was visually demonstrated. When there is no shielding between the radiation source and the

ADVANCED SCIENCE NEWS



Figure 5. EMI SE, power coefficient, stability and environmental resistance test, practical shielding test for electronic devices, and analysis of the shielding mechanisms in the MXene/PAA-CS DN hydrogels. SE_R , SE_A , and SE_T of MXene/PAA-CS DN hydrogels under different a) MXene concentration (1 mm, 0.06 g mL⁻¹ CS, 43% (NH₄)₂SO₄), b) CS concentration (1 mm, 9 mg mL⁻¹ MXene, 43% (NH₄)₂SO₄), c) (NH₄)₂SO₄ concentration (1 mm, 0.06 g mL⁻¹ CS, 9 mg mL⁻¹ MXene), and d) hydrogel thickness (0.06 g mL⁻¹ CS, 9 mg mL⁻¹ MXene, 30% (NH₄)₂SO₄), comparison of EMI SE under different e) component contents and f) hydrogel types, EMI SE shielding performance under g) repeated stretching and h) long-term dehydration for thousands of times, i) EMI shielding effect testing for practical applications of power and electronic product radiation, j) analysis of multiple mechanism of MXene/PAA-CS DN hydrogels for shielding.

www.small-journal.com

LICense

ADVANCED SCIENCE NEWS _____ www.advancedsciencenews.com

detector, the electric field radiation of the power supply and the radio frequency radiation of the computer reach 565 V m⁻¹ and 85.2 mW m⁻², respectively (Figure 5i). When shielded with white paper of the same size as the hydrogel, the radiation of the power supply and the laptop computer was slightly reduced, but still displayed a warning color. Interestingly, after shielding with MXene/PAA-CS DN hydrogel, the electromagnetic radiation of the power supply instantly dropped from 498 V m⁻¹ of white paper to 0 V m⁻¹, and the RF radiation of the laptop computer dropped significantly from 56.8 mW m⁻² of white paper to 7.5 mW m⁻² (Figure 5i). Manifestly, MXene/PAA-CS DN hydrogel shows good commercial feasibility and stability.

The shielding mechanism of MXene/PAA-CS DN hydrogel was further explored by comparing the power transmission, reflection, absorption coefficient, and EMI SE under different component contents. 1 mm PAA-CS hydrogel still maintains an EMI SE of 28.5 dB without introducing MXene and $(NH_4)_2SO_4$, which is attributed to the multi-layer reflection and absorption effect caused by its water-rich porous structure. Many theories and experiments have proved the strong absorption effect of water on terahertz waves.^[13] Furthermore, the hydrogel's porous structure contributes to an extended transmission distance for electromagnetic waves and facilitates multiple internal reflections, which significantly enhanced the internal dissipation of the electromagnetic energy.^[26] The introduction of MXene remarkably improved the conductivity of the MXene/PAA-CS hydrogel, promoting the formation of conductive MXene networks and strengthening the conductive loss of terahertz waves within the hydrogel.^[46] Moreover, increasing MXene content positively contributes to the interface polarization between MXene and the double network, further amplifying the polarization loss of terahertz waves.^[36] Further treatment with $(NH_4)_2SO_4$ also substantially enhanced the shielding effectiveness of the DN hydrogel. This improvement can be attributed to the substantial increase in conductivity (Figure S9a, Supporting Information), which in turn enhanced the contribution of conductive loss. However, the improvement of EMI SE by (NH₄)₂SO₄ was not as significant as that achieved with MXene. This difference in effectiveness may be attributed to the contribution of an appropriate level of conductivity to the optimal EMI SE. The conductivity of 15% $(NH_4)_2SO_4$ was much higher than that of 30% (NH₄)₂SO₄ (Figure S9b, Supporting Information) (which matched up with previous works^[42,47]), but it had lower EMI shielding performance (Figure 5e). Compared with (NH₄)₂SO₄, the interfacial polarization between MXene and the DN also contributed to the greater extent of influence. With MXene and $(NH_4)_2SO_4$ content increase, the power reflection coefficient SE_{R} increased with almost the same degree of response (Figures S10 and S11, Supporting Information), suggesting a higher impedance mismatch.^[4,48] At the same time, the observed power reflection coefficient (0.86-0.97) and power absorption coefficient (0.04-0.13) indicate that the EMI shielding contribution mechanism of MXene/PAA-CS DN hydrogel is mainly reflection and supplemented by absorption (Figures S10 and S11, Supporting Information). Combined with the above analysis, this EMI shielding mechanism illustrates the combined effects of multiple reflection and absorption facilitated by the water-rich and porous structures, the conductive loss caused by the significant increase in the conductivity of MXene and $(\rm NH_4)_2SO_4,$ and the interface polarization of MXene-PAA and MXene-CS.

3.4. Strain Sensing Properties

Commonly, conductivity hydrogels could serve as sensors to detect deformations.^[49,50] The GF (**Figure 6a**,b) was measured to assess the strain sensitivity of hydrogels with different $(NH_4)_2SO_4$ concentrations. The hydrogels with different $(NH_4)_2SO_4$ concentrations exhibit superior strain sensitivity, particularly in the higher strain range (300~500%). It is worth pointing out that the maximum GF of the gel could reach 11.66 \pm 0.93, surpassing that of most hydrogels reported in the literature.^[42,47]

The stability and repeatability of sensors are widely recognized as crucial factors. To evaluate these attributes, the resistance variations of the samples across different cycles of strain were measured. The results (Figure 6c,d) indicate that the samples displayed strong repeatability and good stability during varying strain cycles. To demonstrate the functional capability of the MXene/PAA-CS DN hydrogels as sensors, a gel sample was integrated into a circuit with an LED bubble. Theoretically, as the gel undergoes stretching, its resistance is expected to rise, decreasing the current passing through the LED. Experimental observations confirm that the brightness of the LED decreased as the gel was stretched which matched up with the theoretical predication (Figure S12, Supporting Information). As shown in Figure 6e-h, the hydrogel sensors could detect different angles of finger bending and different frequencies of wrist bending. The gel sensor could also detect the facial movement such as pumping and speaking the words "Alpha" and "Ni hao", as these movements produced significantly different resistance response behaviors. Additionally, the gel could monitor the balloon compression (Figure 6i). The fully recoverable and repeatable resistance signal indicates that the MXene/PAA-CS hydrogels could be good candidates for flexible sensors

To highlight the advantages of MXene/PAA-CS DN hydrogels in terahertz shielding applications, we comprehensively compared the mechanical properties and EMI SE with the typical terahertz shielding materials represented by film, foam, aerogel, and hydrogel (Figure 7; Table S1, Supporting Information). Observably, MXene/PAA-CS DN hydrogel has a high EMI SE in the terahertz band, ranking among the best among currently reported terahertz shielding materials (Figure 7a). Another advantage of MXene/PAA-CS DN hydrogel is its excellent mechanical and electrical properties represented by strength, stretchability, and sensor performance, which are crucial for harsh environments and stability in terahertz shielding applications (Figure 7b). Traditional film and foam materials both demonstrate high strength. However, their stretchability and strain sensitivity are limited, indicating a lack of good flexibility (Table S1, Supporting Information). Typically, aerogels and hydrogels have good tensile properties for flexible shielding materials, but their strength is low. In comparison, our MXene/PAA-CS DN hydrogel achieves a strength of 3.3 MPa and a high GF of 11.7 while exhibiting excellent stretchability of 746.2% (Figure 7c). The (NH₄)₂SO₄/MXene-treated MXene/PAA-CS DN hydrogel has achieved significant improvements in comprehensive properties

SCIENCE NEWS



Figure 6. a) Relative resistance-strain curves for gels with varying concentrations of $(NH_4)_2SO_4$, b) GF of gels with 0–43% $(NH_4)_2SO_4$ concentration in different range, real-time $\Delta R/R$ curves recorded during cycles of c) lower strain and d) higher strain, e–h) real time $\Delta R/R$ signal for e) finger bending at various angles, f) wrist shaking at different speed, facial movement of g) pumping and h) speaking, i) monitoring the inflation and deflation of a balloon.

such as EMI shielding and mechanical and electrical properties, which is expected to become the next generation of flexible electromagnetic shielding materials and multifunctional electronic devices.

4. Conclusion

This work fabricated a novel multifunctional flexible MXene/ PAA-CS DN hydrogel with high mechanical properties, good conductivity, excellent strain sensibility, and superior EMI shielding performance. The double network strategy and the molecular entanglement caused by Hofmeister Effect, markedly toughened and strengthened the hydrogel. The gels have a strength of over 3.3 MPa, a modulus of over 0.4 MPa, and a fracture energy of over 9 kJ m⁻², which could support its application in complex mechanical environments. Additionally, the water-rich and porous matrix, the conductivity of MXene and $(NH_4)_2SO_4$, and the interface polarization between MXene and the double network greatly benefit the EMI SE of the gels. Notably, the gels could achieve a remarkable shielding effectiveness of 73.8 dB in the 0.1–1 THz band. More importantly, the gels exhibit reliable and stable shielding performance even after 1000 stretching cycles and long-term dehydration. It is also worth pointing out that the gels have a high strain sensitivity with a GF exceeding 11. Generally, the gels exhibit stable and impressive EMI shielding effectiveness, outstanding mechanical properties, and elevated strain sensitivity, positioning them as a high-quality candidate for advanced flexible electronic equipment and soft robotics.





Figure 7. Comprehensive performance comparative analysis on EMI shielding, mechanical, electrical of MXene/PAA-CS DN hydrogels and traditional terahertz shielding materials. a) Comparison of EMI SE and material thickness. b) Comparison of strength, strain, and GF performances. c) Comparison of EMI SE, mechanical, and electrical comprehensive performances.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was financially supported by the China Postdoctoral Science Foundation under Grant No. 2024T170893 and No. 2023M743402, Postdoctoral Fellowship Program of CPSF under Grant No. GZC20232566, ITER Project of the Ministry of Science and Technology under Grant No. 2022YFE03080001, Joint Laboratory of Plasma Application Technology Funding, under Grant No. JL06120001H, the Fundamental Research Funds for the Central Universities (grant no. WK2480000006). The authors are grateful for the technical support from Prof. Xinglong Gong and Prof. Songlin Xu. This work was partially carried out at the Instruments Center for Physical Science, University of Science and Technology of China, and the authors are also grateful for the technical support from Prof. Chengming Wang.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

L.M. and W.O. wrote the original draft; visualized the idea for the study; performed the validation; designed the methodology; and performed the investigation and data curation. L.X., Y.H., Q.L., and Y.B. performed data curation. Q.L. wrote, reviewed, and edited the manuscript, and also performed supervision. T.L. wrote, reviewed, and edited the manuscript, and also performed supervision and project administration. Z.W. wrote, reviewed, and edited the manuscript, supervision, project administration, supervision, project administration, and data curation.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

electromagnetic interference (EMI) shielding, fracture energy, hydrogel, MXene, strain sensing

Received: November 11, 2024 Revised: December 7, 2024 Published online: December 26, 2024

- W. Wang, Y. J. Tan, T. C. Tan, A. Kumar, P. Pitchappa, P. Szriftgiser, G. Ducournau, R. Singh, *Nature* 2024, 632, 522.
- [2] K. Peng, D. Jevtics, F. Zhang, S. Sterzl, D. A. Damry, M. U. Rothmann, B. Guilhabert, M. J. Strain, H. H. Tan, L. M. Herz, L. Fu, M. D. Dawson, A. Hurtado, C. Jagadish, M. B. Johnston, *Science* **2020**, *368*, 510.
- [3] J. Li, X. Li, N. T. Yardimci, J. Hu, Y. Li, J. Chen, Y.-C. Hung, M. Jarrahi, A. Ozcan, Nat. Commun. 2023, 14, 6791.
- [4] P. Li, H. Wang, Z. Ju, Z. Jin, J. Ma, L. Yang, X. Zhao, H. Xu, Y. Liu, ACS Nano 2024, 18, 2906.
- [5] P. Liu, S. Gao, G. Zhang, Y. Huang, W. You, R. Che, Adv. Funct. Mater. 2021, 31, 2102812.
- [6] Y.-J. Wan, X.-Y. Wang, X.-M. Li, S.-Y. Liao, Z.-Q. Lin, Y.-G. Hu, T. Zhao, X.-L. Zeng, C.-H. Li, S.-H. Yu, P.-L. Zhu, R. Sun, C.-P. Wong, ACS Nano 2020, 14, 14134.
- [7] Q. Wei, S. Pei, X. Qian, H. Liu, Z. Liu, W. Zhang, T. Zhou, Z. Zhang, X. Zhang, H.-M. Cheng, W. Ren, Adv. Mater. 2020, 32, 1907411.
- [8] Y. Zhang, Y. Huang, T. Zhang, H. Chang, P. Xiao, H. Chen, Z. Huang, Y. Chen, Adv. Mater. 2015, 27, 2049.
- [9] L. Tian, H. Gu, Q. Zhang, X. You, M. Wang, J. Yang, S.-m. Dong, ACS Nano 2023, 17, 12673.
- [10] J. Cui, J. Chen, Z. Ni, W. Dong, M. Chen, D. Shi, ACS Appl. Mater. Interfaces 2022, 14, 47148.
- [11] M. Nie, Q. Zhao, X. Du, Nano Res. 2024, 17, 649.
- [12] H. Guo, Y. Shi, F. Pan, S. Zheng, X. Chai, Y. Yang, H. Jiang, X. Wang, L. Li, Z. Xiu, J. Wang, W. Lu, *Nano Energy* **2023**, *114*, 108678.
- [13] W.-L. Song, Y.-J. Zhang, K.-L. Zhang, K. Wang, L. Zhang, L.-L. Chen, Y. Huang, M. Chen, H. Lei, H. Chen, D. Fang, *Adv. Sci.* **2020**, *7*, 1902162.
- [14] D. C. Hogg, F. O. Guiraud, Nature 1979, 279, 408.

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [15] Y. Yu, P. Yi, W. Xu, X. Sun, G. Deng, X. Liu, J. Shui, R. Yu, Nanomicro Lett. 2022, 14, 77.
- [16] Q.-F. Guan, Z.-M. Han, K.-P. Yang, H.-B. Yang, Z.-C. Ling, C.-H. Yin, S.-H. Yu, *Nano Lett.* **2021**, *21*, 2532.
- [17] Q. Zhou, J. Lyu, G. Wang, M. Robertson, Z. Qiang, B. Sun, C. Ye, M. Zhu, Adv. Funct. Mater. 2021, 31, 2104536.
- [18] W. Yang, B. Shao, T. Liu, Y. Zhang, R. Huang, F. Chen, Q. Fu, ACS Appl. Mater. Interfaces 2018, 10, 8245.
- [19] M. Xiang, H. Niu, S. Qin, R. Yang, W. Lin, S. Zhou, Z. Yang, S. Dong, J. Mater. Sci. 2022, 57, 10983.
- [20] J.-M. Thomassin, C. Jérôme, T. Pardoen, C. Bailly, I. Huynen, C. Detrembleur, Mater. Sci. Eng., R 2013, 74, 211.
- [21] X. Huang, L. Wang, Z. Shen, J. Ren, G. Chen, Q. Li, Z. Zhou, Chem. Eng. J. 2022, 446, 137136.
- [22] C. Li, D. Li, M. Zhang, B. You, Z. Wu, Y. Tao, Y. Sun, L. Wu, X. Mo, ACS Appl. Mater. Interfaces 2024, 16, 12939.
- [23] Y. Yang, N. Wu, B. Li, W. Liu, F. Pan, Z. Zeng, J. Liu, ACS Nano 2022, 16, 15042.
- [24] G.-C. Xu, Y. Nie, H.-N. Li, W.-L. Li, W.-T. Lin, Y.-R. Xue, K. Li, Y. Fang, H.-Q. Liang, H.-C. Yang, H. Zhan, C. Zhang, C. Lü, Z.-K. Xu, *Adv. Mater.* 2024, *36*, 2400075.
- [25] H. Zou, P. Yi, W. Xu, H. Cai, J. He, X. Sun, X. Li, C. Chen, G. Deng, Y. Yuan, Z. Li, M. Fang, J. Shui, X. Liu, R. Yu, *Chem. Eng. J.* **2023**, 461, 141856.
- [26] Y. Zhu, J. Liu, T. Guo, J. J. Wang, X. Tang, V. Nicolosi, ACS Nano 2021, 15, 1465.
- [27] C. Wang, L. Xu, J. Zheng, Z. Zhu, Z. Huang, C. Hu, B. Liu, Int. J. Biol. Macromol. 2024, 278, 134354.
- [28] Y. Yang, B. Li, N. Wu, W. Liu, S. Zhao, C. J. Zhang, J. Liu, Z. Zeng, ACS Mater. Lett. 2022, 4, 2352.
- [29] X. Li, J. P. Gong, Nat. Rev. Mater. 2024, 9, 380.
- [30] J. Liu, B. Zhang, P. Zhang, K. Zhao, Z. Lu, H. Wei, Z. Zheng, R. Yang, Y. Yu, ACS Nano 2022, 16, 17998.
- [31] M. Hua, S. Wu, Y. Ma, Y. Zhao, Z. Chen, I. Frenkel, J. Strzalka, H. Zhou, X. Zhu, X. He, *Nature* **2021**, *590*, 594.
- [32] J. Tang, Z. Tong, Y. Xia, M. Liu, Z. Lv, Y. Gao, T. Lu, S. Xie, Y. Pei, D. Fang, T. J. Wang, J. Mater. Chem. B 2018, 6, 2713.

[33] J.-Y. Sun, X. Zhao, W. R. K. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak, Z. Suo, *Nature* **2012**, 489, 133.

- [34] J. Tang, J. Li, J. J. Vlassak, Z. Suo, Extreme. Mech. Lett. 2017, 10, 24.
- [35] Y. Yang, X. Wang, F. Yang, L. Wang, D. Wu, Adv. Mater. 2018, 30, 1707071.
- [36] W. Ouyang, L. Mei, Q. Liu, C. Ding, Y. Liu, C. Zhao, L. Xu, F. Lu, D. Luo, C. Miao, Y. Bai, Q. Lu, T. Luo, Z. Wu, *Chem. Eng. J.* 2024, 494, 153068.
- [37] Y. Li, R. Fu, Z. Duan, C. Zhu, D. Fan, ACS Nano 2022, 16, 7486.
- [38] P. Zhang, X.-J. Yang, P. Li, Y. Zhao, Q. J. Niu, Soft Matter 2020, 16, 162.
- [39] J. Yang, R. Bai, Z. Suo, Adv. Mater. 2018, 30, 1800671.
- [40] J. Chen, F. Liu, T. Abdiryim, H. Yin, X. Liu, Int. J. Biol. Macromol. 2024, 258, 128912.
- [41] J. Tang, Y. Qiao, Y. Chu, Z. Tong, Y. Zhou, W. Zhang, S. Xie, J. Hu, T. Wang, J. Mater. Chem. B 2019, 7, 1311.
- [42] J. Cong, Z. Fan, S. Pan, J. Tian, W. Lian, S. Li, S. Wang, D. Zheng, C. Miao, W. Ding, T. Sun, T. Luo, ACS Appl. Mater. Interfaces 2021, 13, 34942.
- [43] T. Matsuda, T. Nakajima, J. P. Gong, Chem. Mater. 2019, 31, 3766.
- [44] W. Zhang, X. Liu, J. Wang, J. Tang, J. Hu, T. Lu, Z. Suo, Eng. Fract. Mech. 2018, 187, 74.
- [45] J. Wei, L. Dai, P. He, M. Zhu, F. Jiang, Z. Zhou, G. Fei, T. Lei, J. Mater. Sci. Technol. 2024, 169, 199.
- [46] K. Mendez, W. Whyte, B. R. Freedman, Y. Fan, C. E. Varela, M. Singh, J. C. Cintron-Cruz, S. E. Rothenbücher, J. Li, D. J. Mooney, E. T. Roche, *Adv. Mater.* 2023, *36*, 2303301.
- [47] L. Mei, J. Cong, S. Li, T. Ren, Y. Bai, Q. Liu, C. Miao, W. Ding, T. Luo, Compos. Part A Appl. Sci. Manuf. 2023, 168, 107478.
- [48] Y. Liu, Y. Wang, N. Wu, M. Han, W. Liu, J. Liu, Z. Zeng, Nanomicro Lett. 2023, 15, 240.
- [49] L. Hu, P. L. Chee, S. Sugiarto, Y. Yu, C. Shi, R. Yan, Z. Yao, X. Shi, J. Zhi, D. Kai, H.-D. Yu, W. Huang, *Adv. Mater.* **2023**, *35*, 2205326.
- [50] H. Fu, B. Wang, J. Li, J. Xu, J. Li, J. Zeng, W. Gao, K. Chen, Mater. Horiz. 2022, 9, 1412.