

ACCEPTED PAPER · MAIN TEXT

Multifunctional PCL/MXene ultrafine fiber scaffolds with tunable topology and photothermal response

Paper version: Accepted Paper

Accepted Papers are manuscripts accepted for publication, encompassing all changes made following the peer review process, along with a standard cover page indicating the paper version and an “Accepted Paper” watermark, but excluding any other editing, typesetting or other changes made by AccScience Publishing and/or authors post-acceptance.

Article ID: IJB026300324

Citation: Zou Z, Huang X, Shen Z, *et al.* Multifunctional PCL/MXene ultrafine fiber scaffolds with tunable topology and photothermal response. *Int J Bioprint*. 2026. doi: 10.36922/IJB026300324

Copyright: © 2026 Author(s). This is an Open Access article distributed under the terms of the Creative Commons Attribution License, permitting distribution, and reproduction in any medium, provided the original work is properly cited.

Publisher’s Note: AccScience Publishing remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

AccScience Publishing

ORIGINAL RESEARCH ARTICLE

Volume X Issue X (2026)

doi: 10.36922/IJB026300324

Multifunctional PCL/MXene ultrafine fiber scaffolds with tunable topology and photothermal response

Running title: PCL/MXene photothermal fiber scaffold

Zhongfei Zou^{1,2}, Xingke Huang^{1,3}, Zhen Shen⁴, Fangtao Shi⁴, Xianhui Cai⁴, Sen Yuan², Yuewei Chen^{2,4*}, and Yong He^{2*}

¹ School of Mechanical Engineering, Guizhou Institute of Technology, Guiyang, 550025, China

² State Key Laboratory of Fluid Power and Mechatronic Systems & Liangzhu Laboratory, School of Mechanical Engineering, Zhejiang University, Hangzhou, 310027, China

³ School of Mechanical and Electrical Engineering, Guizhou Normal University, Guiyang, 550025, China

⁴ School of Mechanical Engineering, Guizhou University, Guiyang, 550025, China

*** Corresponding authors:**

Yong He (yongqin@zju.edu.cn)

Yuewei Chen (ywchen3@gzu.edu.cn)

Citation: Zou Z, Huang X, Shen Z, *et al.* Multifunctional PCL/MXene ultrafine fiber scaffolds with tunable topology and photothermal response. *Int J Bioprint.* 2026. doi: 10.36922/IJB026300324

Received: July 26, 2026

Revised: August 24, 2026

Accepted: September 1, 2026

Published online: September 1, 2026

Copyright: © 2026 Author(s). This is an Open Access article distributed under the terms of the Creative Commons Attribution License, permitting distribution, and reproduction in any medium, provided the original work is properly cited.

Publisher's Note: AccScience Publishing remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

ACCEPTED PAPER

Abstract

Traditional tissue engineering scaffolds often serve primarily as passive extracellular matrix (ECM) mimics, lacking the capacity to actively regulate cellular behavior and dynamically engage in complex tissue repair processes. Inspired by the concept of thermal therapy, this study designed and fabricated a photothermal-responsive biomimetic ultrafine fiber scaffold that integrates micro/nano topological structures with localized thermal fields. Using high-precision melt electrowriting, PCL/MXene ultrafine fiber network scaffolds were fabricated with controllable architectures that mimic ECM alignment and may provide topographical cues for cells. Leveraging the photothermal conversion properties of MXene, the scaffold exhibits rapid and stable heating upon near-infrared (NIR) irradiation. Among the tested formulations, the 4 wt% MXene scaffold achieved a favorable balance between printability and photothermal performance, with a photothermal conversion efficiency of $59.4 \pm 2.1\%$ and stable temperature control within the mild hyperthermia range (37–42 °C) under cell culture conditions. The scaffold also exhibited concentration-dependent antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* (with the 4 wt% scaffold achieving ~99% bacterial reduction), which is consistent with the contact-mediated antibacterial mechanism commonly attributed to MXene nanosheets. In vitro L929 fibroblast studies revealed that under NIR irradiation, the 4 wt% scaffold enhanced cell viability and metabolic activity, suggesting that mild photothermal stimulation promotes cell proliferation. This scaffold design strategy, integrating biomimetic topological cues with dynamic thermal responsiveness, provides insights into the development of photothermal-responsive fibrous scaffolds for tissue engineering applications.

Keywords: PCL/MXene composite scaffolds; Photothermal responsive; Melt electrowriting; Topographical cues; Antibacterial activity

1 Introduction

The clinical translation of synthetic tissue engineering scaffolds is frequently hampered by the biological inertness of conventional biodegradable polymers.^[1, 2] Polycaprolactone (PCL), despite its FDA-approved status and favorable processability, lacks both intrinsic antibacterial defense and spatiotemporally responsive functionalities—two essential attributes for combating infection and guiding dynamic tissue regeneration in complex wound environments.^[3-7] Functional nano-reinforcement has emerged as a promising strategy to overcome these limitations, yet achieving a balanced integration that preserves scaffold printability while imparting robust bioactivity remains a persistent challenge.

Two-dimensional MXene nanosheets ($\text{Ti}_3\text{C}_2\text{T}_x$) present an attractive solution to this dilemma. Beyond their well-documented near-infrared (NIR) photothermal conversion efficiency (30–57%) and abundant surface terminations ($-\text{OH}$, $-\text{O}$, $-\text{F}$) that ensure colloidal stability, MXenes possess antibacterial activity attributed to the sharp-edged nanosheets physically disrupting bacterial membranes, while photothermal activation has been reported to synergistically compromise membrane integrity under NIR irradiation in other material systems.^[8-13] These attributes position MXene as an ideal functional filler to confer PCL scaffolds with photothermal responsiveness and contact-dependent antibacterial capability.^[14, 15] However, the translation of MXene's laboratory-scale advantages into a processable, high-fidelity composite ink for additive manufacturing introduces previously unanticipated complexities.

Melt electrowriting (MEW) offers a compelling fabrication route for PCL-based scaffolds due to its ability to deposit micrometer-scale fibers with precise architectural control.^[16-18] Nevertheless, incorporating MXene into a PCL melt matrix presents a classical "printability-functionality" trade-off that remains poorly understood. Hydrophilic MXene nanosheets are intrinsically incompatible with hydrophobic PCL, leading to aggregation at elevated loadings, which dramatically alters melt rheology and jeopardizes jet stability.^[19-21] While low MXene concentrations (<1 wt%) preserve printability, they fail to achieve the photothermal threshold required for effective antibacterial therapy.^[22, 23] Conversely, higher loadings that could deliver sufficient photothermal output tend to induce nozzle clogging, fiber breakage, and scaffold defects^[24]—a bottleneck that has thus far constrained the practical utility of MXene/PCL composites.

A recent pioneering study by Zahrabi et al.^[19] demonstrated the feasibility of MEW-printing MXene/PCL scaffolds at loadings of 0.1–1 wt%, confirming basic cytocompatibility with a fiber diameter of approximately 100 μm and a pore size of approximately 700 μm . Compared with this prior work, the present study extends the MXene loading range up to 10 wt% and systematically maps the upper printability limit, identifying 0–4 wt% as a stable printing window with target fiber diameters of 30–100 μm . Furthermore, while Zahrabi et al. focused primarily on printability and cytocompatibility at low loadings, the present work provides a more comprehensive structure–processing–function analysis, including rheological

characterization, photothermal conversion efficiency (44.5% at 1 wt% vs. 59.4% at 4 wt%), cycling stability, antibacterial evaluation against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*), and in vitro L929 fibroblast responses with and without NIR stimulation. Distinct from earlier surface-coated MXene PCL scaffolds, this study adopts bulk solution blending to achieve uniform MXene dispersion, and constructs four biomimetic topologies (auxetic, gradient, 60°/90° grids) to decouple topological guidance and photothermal stimulation. The core novelty lies in establishing a quantitative structure-process-function map for high-loading MEW PCL/MXene ink, rather than low-concentration cytocompatibility verification. However, the aforementioned work focused on lower concentration regimes, leaving two critical questions unresolved: (i) What is the upper printability limit of MXene/PCL composites, and how does nanosheet aggregation dictate the rheological transition from stable jetting to printing failure? (ii) How does MXene loading quantitatively regulate the photothermal response, temperature control accuracy, and cyclic stability under physiologically relevant conditions, particularly considering the susceptibility of MXene to oxidative degradation during high-temperature melt processing? Beyond these, existing reports predominantly focus on MXene-coated PCL surfaces, whereas systematic investigations of bulk-composited, MEW-dedicated inks are notably absent, and the structure-property relationships governing printing fidelity, photothermal performance, and cellular responses remain largely uncharted.^[15, 25, 26]

The broader tissue engineering literature has explored diverse strategies for promoting tissue regeneration and antibacterial performance, including osteogenic/antibacterial Mg-alloy coatings with polydopamine carriers^[27], scalable fabrication strategies for craniofacial bone regeneration^[28], macrophage polarization modulation by scaffold physicochemical characteristics^[29], anti-senescent biomaterials for intervertebral disc regeneration^[30], and decellularized ECM platforms for functional tissue reconstruction^[31]. These studies underscore the importance of integrating antibacterial functionality with biomimetic structural design in scaffold development. Herein, we address these challenges through a comprehensive material-process-performance investigation (in **Figure 1**).

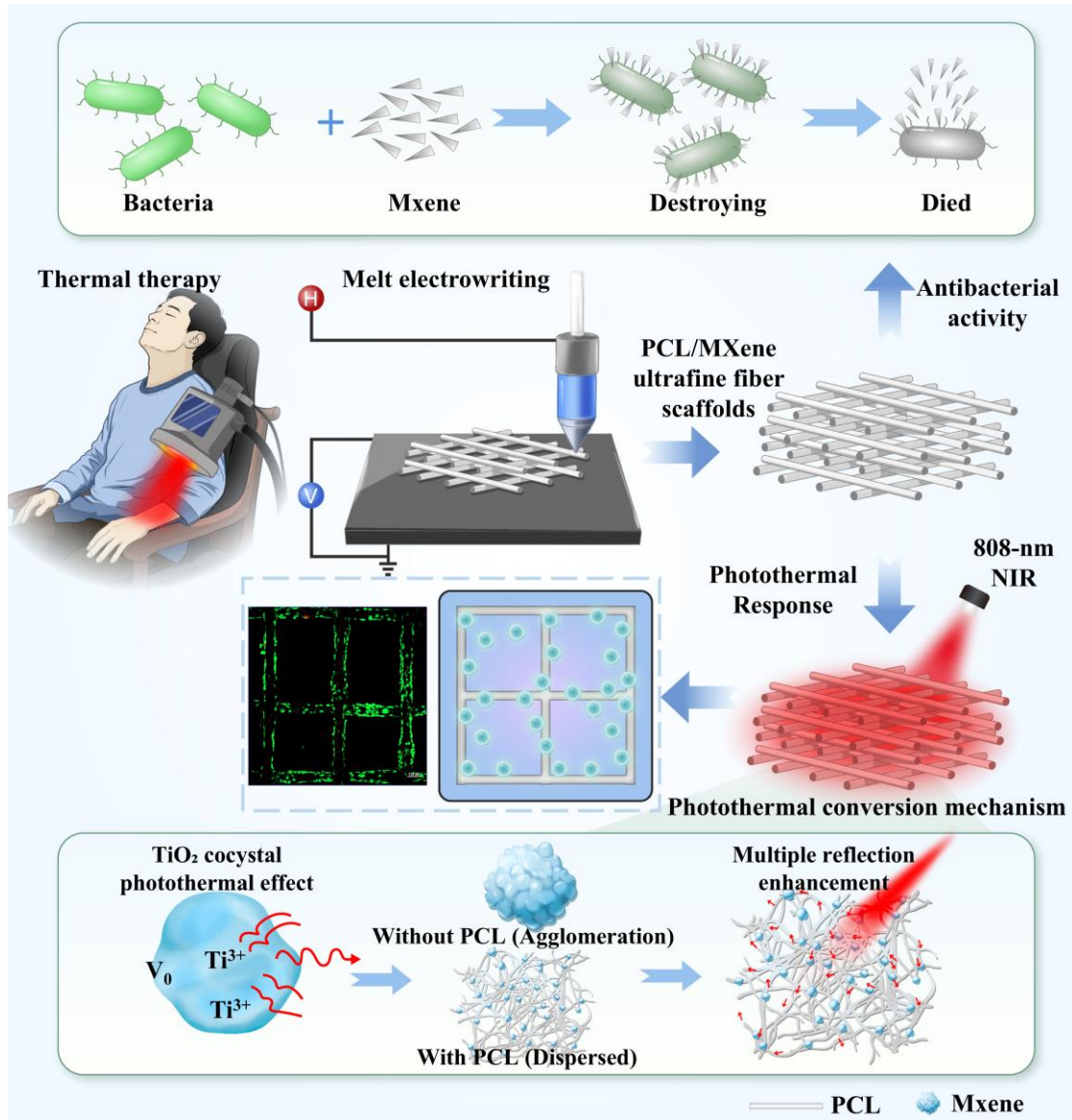


Figure 1. Schematics of PCL/MXene ultrafine fiber scaffold.

We first synthesize high-quality monolayer MXene via a mixed-acid etching protocol and formulate a series of PCL/MXene composite inks with systematically varied loadings. By correlating rheological behavior with MEW processing parameters, we establish the critical printing window and successfully fabricate three-dimensional scaffolds with controlled porosity. We then rigorously evaluate the photothermal response and cycling stability in both air and culture media, and interpret the observed photothermal enhancement through a defect-engineering framework. Finally, we validate the dual functionality of the scaffolds via in vitro antibacterial assays against *S. aureus* and *E. coli*, alongside L929 fibroblast culture studies. This work establishes a processing roadmap for MXene/PCL MEW inks and provides insights into the design of photothermal-responsive fibrous scaffolds for tissue engineering applications.

2 Materials and methods

2.1 Materials

Titanium aluminum carbide (Ti_3AlC_2 , 400 mesh) was purchased from Yiyi Technology Co., Ltd. Hydrofluoric acid (HF, 49 wt%), hydrochloric acid (HCl), and methanol ($\geq 99.9\%$) were obtained from Shanghai Yi'en Chemical Technology Co., Ltd., Chongqing Chuandong Chemical Co., Ltd., and Shanghai Macklin Biochemical Co., Ltd., respectively. LiF ($\geq 99.9\%$) and LiCl were acquired from Shandong Xiya Reagent Co., Ltd. and Shanghai Macklin Biochemical Co., Ltd., respectively. PCL (CAPATM 6800, $M_n = 80,000 \text{ g mol}^{-1}$) was supplied by Perstorp AB. Prior to use, PCL pellets were dried in a vacuum oven at 60°C for 12 h to remove moisture.

Escherichia coli (*E. coli*, ATCC 25922) and *Staphylococcus aureus* (*S. aureus*, ATCC 25923) were obtained from Bozhou Wanjun Biotechnology Co., Ltd. Mouse fibroblasts (L929, ATCC CCL-1) were procured from Procell Life Science & Technology Co., Ltd. High-glucose Dulbecco's Modified Eagle Medium (DMEM) and the CCK-8 were purchased from Beijing Solarbio Science & Technology Co., Ltd.

2.2 Synthesis of monolayer MXene

MXene was synthesized via a mixed acid etching method combined with LiCl assisted intercalation. First, 20 mL of HF (49 wt%) was slowly added dropwise to a mixed solution of 20 mL HCl and 10 mL deionized water in a fume hood. Subsequently, 2 g of Ti_3AlC_2 powder was introduced, and the mixture was magnetically stirred at 400 rpm for 10 h at room temperature. After the reaction, the product was separated by centrifugation, and the precipitate was washed repeatedly with deionized water until the pH reached 6–7, yielding a black multilayered MXene precipitate.

For intercalation and exfoliation, 2 g of LiCl was dissolved in 40 mL deionized water and added to the precipitate, followed by manual mixing. The mixture was transferred to a stirring cup and stirred for an additional 10 h to facilitate Li^+ intercalation. After intercalation, the dispersion was concentrated by low speed centrifugation, the supernatant was discarded, and the swollen precipitate was collected. A small volume of deionized water was added for preliminary dispersion, followed by probe sonication in an ice water bath for 20 min to achieve monolayer exfoliation. Finally, the dispersion was centrifuged for 16 min, and the dark green supernatant was collected and subjected to vacuum freeze drying to obtain monolayer MXene powder.

The morphology and chemical structure of the product were characterized by scanning electron microscopy (SEM, Gemini 300, Zeiss, Germany), X ray photoelectron spectroscopy (XPS, 250XI, Thermo Fisher Scientific, USA), and Fourier transform infrared spectroscopy (FTIR, Nexus 670, Thermo Fisher Scientific, USA).

2.3 Preparation and characterization of PCL/MXene composites

2.3.1 Preparation of PCL/MXene composites

PCL/MXene composites were prepared via a solution blending method. First, MXene was dispersed in methanol under continuous stirring at 32°C for 12 h. Subsequently, pre-weighed PCL pellets were added to the dispersion, and the mixture was stirred in an oil bath at 65°C until the solvent was completely evaporated. The resulting product was transferred to a vacuum oven and

dried at 70 °C for 24 h to remove residual solvent, yielding the PCL/MXene composites. The preparation process was illustrated in **Figure 2(a)**.

2.3.2 Rheological properties

Rheological measurements were performed using a rotational rheometer (ARES G2, TA Instruments) with a parallel-plate geometry (25 mm diameter, 1.0 mm gap). Steady-shear tests were conducted at a constant shear rate of 5 s⁻¹ over 50–130 °C at a heating rate of 5 °C min⁻¹ under nitrogen atmosphere. The apparent (shear) viscosity was reported.

Because the measurements were performed under steady-shear conditions at a fixed shear rate, the measured quantity is reported as apparent (shear) viscosity rather than complex viscosity. All measurements were performed under a nitrogen atmosphere to prevent thermal degradation. It should be noted that the present rheological characterization is limited to temperature-dependent apparent viscosity at a single shear rate; shear-rate sweeps and oscillatory measurements would be required to fully characterize shear-thinning behavior and the flow behavior index (n), which are critical for correlating rheological properties with MEW printability. These analyses are planned as part of our ongoing work.

2.3.3 Mechanical properties

Tensile tests were performed on solution-cast PCL/MXene films using a universal testing machine (ETM2023A, WANCE) with a 100 N load cell at a crosshead speed of 5 mm min⁻¹ and 20 °C. Specimens were prepared using a custom mold according to ASTM D638 Type V (gauge length: 10 mm, gauge width: 2 mm, thickness: 1 mm). At least five specimens were tested per composition (0, 1, 4, and 7 wt% MXene). It should be emphasized that these solution-cast bulk specimens do not represent the mechanical behavior of the highly porous MEW-printed scaffolds (porosity > 70%), as the latter are additionally influenced by fiber diameter, fiber orientation, porosity, interlayer bonding, and scaffold topology. The data presented in this section reflect the intrinsic material properties of PCL/MXene composites as a function of MXene loading, rather than the load-bearing capacity of the printed fiber networks.

2.3.4 Photothermal response of bulk composites

An 808 nm near-infrared (NIR) laser was used as the excitation source. The power density was calibrated at the sample plane to 0.5 W cm⁻² using a thermopile power meter (PM16-121, Thorlabs, USA) at a fixed irradiation distance of 30 cm. Disc-shaped samples (diameter: 10 mm, thickness: 1 mm) of PCL/MXene composites with different MXene contents (1, 4, 7 wt%) were tested at an ambient temperature of 20 ± 1 °C. The surface temperature was recorded in real time using an infrared thermal camera (FLIR E8 Pro, FLIR Systems, USA) at a sampling frequency of 1 Hz. The camera was calibrated against a blackbody reference source prior to each measurement session, and the sample emissivity was set to 0.95. Spatial thermal maps were acquired at 5 s intervals to confirm temperature uniformity. Each group was tested in triplicate.

2.3.5 Differential scanning calorimetry

Thermal properties of PCL/MXene composites (0, 1, and 4 wt% MXene) were analyzed by differential scanning calorimetry (DSC25, Waters) under N₂ (50 mL min⁻¹). Samples (5–8 mg) were

sealed in aluminum pans and subjected to a heating–cooling–heating protocol: 20 → 120 °C at 10 °C min⁻¹, held for 3 min, cooled to 20 °C at 10 °C min⁻¹, and reheated to 120 °C at 10 °C min⁻¹. The melting temperature (T_m) and melting enthalpy (ΔH_m) were determined from the second heating scan. The degree of crystallinity (X_c) was calculated as

$$X_c = \frac{\Delta H_m}{\Delta H_{m0} \times w_{PCL}} \times 100\% \quad (1)$$

where $\Delta H_{m0} = 136 \text{ J g}^{-1}$ is the melting enthalpy of 100% crystalline PCL and w_{PCL} is the mass fraction of PCL in the composite.

2.4 Melt electrowriting of fiber scaffolds

Printability was a critical criterion for evaluating MEW inks, determining the structural precision and functional performance of the scaffolds. Different MXene concentrations (0, 1, 4, 7, 10 wt%) were investigated to systematically study the effects of MXene content and key process parameters on fiber formation. The 10 wt% formulation was included solely to determine the upper printability limit and is not further characterized in subsequent experiments. All fibers were fabricated using a bioprinter (BP6601, Yongqinquan Intelligent Equipment Co., Ltd., Suzhou, China) controlled by proprietary EFL_PotatoE software.

2.5 Photothermal response of PCL/MXene fiber scaffolds

Neat PCL (control group), 1 wt% PCL/MXene, and 4 wt% PCL/MXene fiber scaffolds were fabricated via MEW technology. The scaffold dimensions were 10 mm × 10 mm, with a fiber spacing of 500 μm and a fiber diameter of 50 μm.

2.5.1 Photothermal response in air and cycling stability

Photothermal performance was evaluated using an 808 nm NIR laser at 0.5 W cm⁻². Three irradiation distances (15, 30, and 45 cm) were screened, with the power density verified at the sample plane using a calibrated power meter. The beam diameter was approximately 12 mm at 15 cm and 17 mm at 30 cm, fully covering the 10 mm × 10 mm scaffold area. The laser was directed perpendicularly onto the sample surface at an ambient temperature of 20 ± 1 °C. An infrared thermal camera recorded the surface temperature at 0.5 Hz until thermal equilibrium was reached (temperature variation < 0.5 °C over 30 s). Heating curves of neat PCL, 1 wt%, and 4 wt% scaffolds were measured at all three distances. Cycling stability was evaluated under dry-state conditions using five consecutive on–off cycles (5 s irradiation / 5 s cooling, 10 s per cycle).

2.5.2 Photothermal response in culture medium

The photothermal behavior under cell culture conditions was evaluated with the same laser parameters (808 nm, 0.5 W cm⁻², 15 cm). Scaffolds were placed in a 24-well plate with 0.5 mL DMEM added per well. The initial medium temperature was 37 °C (pre-equilibrated in an incubator). Temperature changes on the medium surface were recorded in real time. For cycling in culture medium (simulating cell culture conditions), four consecutive cycles were performed with temperature feedback control (37 °C → 42 °C → 37 °C per cycle), and the heating/cooling times were recorded individually. The 45 cm distance was excluded because the peak temperature (~30 °C) was too close to ambient for reliable cycle-to-cycle discrimination.

2.5.3 Photothermal conversion efficiency calculation

Photothermal conversion efficiency (η) was calculated via the classic Roper method^[32]:

$$\eta = \frac{hS\Delta T_{max}}{I(1-10^{-A_{808}})} \quad (1)$$

where h is the heat-transfer coefficient; S is the surface area of the sample; $\Delta T_{max} = T_{max} - T_{amb}$ is the difference between the maximum steady-state temperature and the ambient temperature; I is the laser power; A_{808} is the absorbance of the sample at 808 nm.

According to Newton's Law of Cooling:

$$t = -\frac{\sum m_i C_{p,i}}{hS} \ln \theta \quad (2)$$

where the calculation formulas for the initial formula θ and C_p are shown in Equations (3) and (4):

$$\theta = \frac{T - T_{max}}{T_{max} - T_{amb}} \quad (3)$$

$$C_p = \frac{\frac{dQ}{dt}}{\frac{dT}{dt}} \quad (4)$$

where m is the mass of the tested sample; C_p is the specific heat capacity, dQ/dt is the heat-flow power per unit mass, dT/dt is the heating rate, which are obtained via DSC measurement; T denotes the real-time temperature. By performing linear fitting on $\ln \theta$ versus time t , the slope $k = -hS/(\sum m_i C_p)$ can be acquired, and then hS is calculated to obtain η . All parameters were averaged from 3 parallel samples, results expressed as mean $\pm$ standard deviation. Full calculation raw data are listed in **Table S5**.

2.6 Antibacterial activity assay

The antibacterial performance of PCL/MXene composite scaffolds against *E. coli* and *S. aureus* was evaluated according to the modified JIS Z 2801 standard method.^[33, 34] Revived strains were inoculated in nutrient broth and cultured at 37 °C with shaking for 16–20 h. After centrifugation (200rpm, 1min), bacterial pellets were collected, washed twice with PBS (pH 7.4), and resuspended in fresh medium to a concentration of 1.5×10^6 CFU mL⁻¹. Scaffold samples (10mm×10mm×2mm, a fiber spacing of 0.5 mm and a fiber diameter of 50 μ m) were sterilized by UV irradiation for 1 h and placed in sterile 24-well plates. Then, 1 mL of bacterial suspension was inoculated onto each sample surface, ensuring complete coverage. Samples were incubated at 37 °C and 90% relative humidity for 24 h.

Adherent bacteria were recovered by vortexing (2000 rpm, 1 min) and sonication (40 kHz, 3 min) in PBS. Recovery efficiency was validated on sterile scaffolds ($\geq 80\%$ accepted). Serial ten-fold dilutions were plated on nutrient agar in triplicate and incubated at 37 °C for 24 h for colony counting. The antibacterial rate was calculated as:

$$\text{Antibacterial rate (\%)} = \left[\frac{(CFU_{control} - CFU_{sample})}{CFU_{control}} \right] \times 100\% \quad (5)$$

where $CFU_{control}$ is the viable count from the neat PCL group. The detection limit was 10 CFU

mL⁻¹. Three independent biological replicates were performed per group (n = 3), with three technical replicates (agar plates) per biological replicate. No inhibition-zone assay was performed in this study.

2.7 Live/dead cell staining

Cell viability on different scaffold surfaces was evaluated by live/dead staining. NIR groups received irradiation (808 nm, 0.5 W cm⁻², 10 min, once daily). The temperature of the medium was monitored in real time using a digital thermometer with a micro-thermocouple probe. To ensure mild photothermal stimulation without causing thermal damage, we adopted a feedback-controlled cycling protocol: the laser was automatically turned on when the medium cooled to 37 °C and switched off upon reaching 42 °C. Scaffolds were sterilized by UV irradiation for 1 h and placed in 24-well plates. L929 mouse fibroblasts (passages 3–6) were seeded onto the scaffold surfaces at a density of 1 × 10⁴ cells cm⁻², with five replicates per group (n = 5). Cells were cultured at 37 °C with 5% CO₂ for 1, 3, and 5 days. At each time point, the medium was discarded, and samples were washed three times with PBS. Calcein-AM/PI working solution (diluted 1:1000 in PBS) was added, and samples were incubated at 37 °C in the dark for 20 min. After incubation, samples were washed with PBS and observed under a fluorescence microscope (Calcein-AM: Ex/Em 494/517 nm, green; PI: Ex/Em 535/617 nm, red). Fluorescence images were analyzed using ImageJ, and green and red areas were quantified. Cell viability was calculated as:

$$Viability (\%) = [green\ area / (green + red\ area)] \times 100\% \quad (6)$$

2.8 CCK-8 cell proliferation assay

Cell proliferation activity was evaluated using the CCK-8 assay. NIR-treated groups received daily irradiation (808 nm, 0.5 W cm⁻², 10 min). Five replicates were prepared per group at each time point (n = 5). L929 cells (passages 3–6) were seeded at 1 × 10⁴ cells cm⁻² and cultured at 37 °C with 5% CO₂ for 1, 3, and 5 days. At each time point, the medium was discarded, and 250 µL of CCK-8 working solution (medium: CCK-8 = 10:1) was added to each well, followed by incubation at 37 °C in the dark for 3 h. After incubation, 100 µL of the reaction supernatant was carefully transferred to a fresh 96-well plate, ensuring that no scaffold material was carried over, and absorbance at 450 nm was measured using a microplate reader. Results were expressed as mean ± standard deviation.

2.9 Statistical analysis

All quantitative data are expressed as mean ± standard deviation (SD). The number of independent biological replicates (n) is specified in each subsection. Statistical analyses were performed using GraphPad Prism 9 (GraphPad Software, USA). Data normality and homogeneity of variance were assessed prior to parametric analysis. For comparisons among multiple groups, one-way analysis of variance (ANOVA) was performed, followed by Tukey's honestly significant difference (HSD) post hoc test for pairwise comparisons. For comparisons between two groups, an unpaired two-tailed Student's t-test was used. A *p*-value < 0.05 was considered statistically significant. Significance levels are denoted as *p* < 0.05, **p* < 0.01, ***p* < 0.001, and ****p* < 0.0001.

3 Results and discussion

3.1 Characterization of MXene and PCL/MXene composites

3.1.1 Morphological and Structural Characterization of MXene

The morphological evolution of MXene during etching and exfoliation was examined by SEM (**Figure S1**). After HF/HCl etching, the multilayered product exhibited a compact stacking morphology (**Figure S1(a)**), consistent with the mild etching behavior reported by Downes et al.^[35] Upon LiCl-assisted intercalation and sonication, the compact layers were successfully delaminated into large-area, ultrathin nanosheets (**Figure S1(b)**), with lateral dimensions ranging from 2 to 5 μm . No significant aggregation was observed in the exfoliated state.

3.1.2 Chemical Composition and Surface Chemistry of MXene

The chemical composition and bonding states of the exfoliated MXene were characterized by XPS (**Figure S1(c–e)**). The survey spectrum (**Figure S1(d)**) revealed characteristic Ti 2p, C 1s, and O 1s peaks at ~ 455 eV, ~ 285 eV, and ~ 530 eV, respectively, with no detectable impurity signals, confirming complete removal of the Al layers during etching. The high-resolution Ti 2p spectrum (**Figure S1(e)**) was deconvoluted into components corresponding to Ti–C and Ti–O bonding environments (461.3 eV and 457.3 eV), consistent with the formation of $\text{Ti}_3\text{C}_2\text{T}_x$ with surface terminations.^[36] The O 1s spectrum (**Figure S1(c)**) exhibited two distinct components at 530.0 eV (Ti–O) and 531.8 eV (C–O/–OH), further confirming the presence of oxygen-containing surface groups.^[37] This result further confirms the abundant functional group modification on the MXene surface.

The surface functionality was further probed by FTIR (**Figure S1(f)**). The broad band at 3458.9 cm^{-1} corresponds to the stretching vibration of surface –OH groups, and the peak at 1643.8 cm^{-1} is attributed to the H–O–H bending vibration of interlayer water molecules. In the fingerprint region, the characteristic absorption peak at 630.1 cm^{-1} is assigned to the stretching vibration of Ti–C bonds, confirming the integrity of the MXene crystal structure, which is in agreement with previous reports.^[38] The FTIR and XPS results together confirm the successful preparation of high-purity, functionalized $\text{Ti}_3\text{C}_2\text{T}_x$ MXene.

3.1.3 Dispersion State of MXene in PCL Matrix

The PCL/MXene composites were prepared via the blending procedure described in Section 2.3.1 (**Figure 2(a)**). The distribution of MXene within the PCL matrix was assessed by EDS elemental mapping for the 4 wt% PCL/MXene composite as a representative formulation. Ti (green, **Figure 2(b-i)**), O (blue, **Figure 2(b-ii)**), and C (red, **Figure 2(b-iii)**) were uniformly distributed across the entire sampled area, with no detectable Ti-rich clusters at the micrometer scale. These EDS mapping results suggest that MXene is relatively well dispersed in the PCL matrix at the loading investigated, achieved via the solution blending method. It should be noted that EDS mapping at this resolution cannot fully exclude nanoscale aggregation or assess dispersion homogeneity across different MXene loadings; complementary techniques such as TEM or rheological percolation analysis would be required for a more comprehensive evaluation. This relatively uniform distribution is expected to be beneficial for achieving consistent photothermal

and mechanical performance in the subsequent MEW-printed scaffolds.

3.2 Rheological, mechanical, and photothermal response properties of PCL/MXene composites

3.2.1 Rheological properties of PCL/MXene composites

As shown in **Figure 2(c)**, the apparent (shear) viscosity decreases significantly with increasing temperature for all the samples, demonstrating that the PCL matrix as well as its composites possess typical thermoplastic behavior. At 100 °C, the viscosity of pure PCL is ~41 Pa·s, increasing to 49 Pa·s, 65 Pa·s, and 117 Pa·s for 1, 4, and 7 wt% MXene composites, respectively. Over the MEW processing range (90–130 °C), the viscosities of the 0–4 wt% inks fall within a printable window that enables stable fiber formation: lower viscosity at elevated temperatures facilitates clog-free extrusion, while higher viscosity at lower temperatures ensures post-deposition solidification. The 7 wt% ink, however, exceeds this printable range (117 Pa·s at 100 °C, with further increases at lower temperatures), consistent with its poor printability observed in preliminary trials.

The viscosity increase with MXene loading is attributed to hydrodynamic interactions and the physical constraint effect of high-aspect-ratio nanosheets, which form an interconnected network that hinders polymer chain movement. Notably, the 4 wt% and 7 wt% composites exhibit a steeper viscosity decrease over 50–80 °C than pure PCL and 1 wt%, suggesting higher temperature sensitivity in the low-temperature interval. This rapid drop indicates that the shear-thinning network may undergo partial destruction with increasing temperature, yet the high-MXene-loading samples still maintain substantially higher viscosity than low-loading samples up to 110 °C.

It should be noted that the rheological data are limited to steady-shear measurements at a single shear rate (5 s^{-1}); therefore, the discussion of "rheological transition" and implications for jet stability during MEW printing should be considered preliminary. Shear-rate sweeps and oscillatory measurements are needed to fully characterize shear-thinning behavior, the flow index n , and rheological percolation, which we plan to pursue in future work.

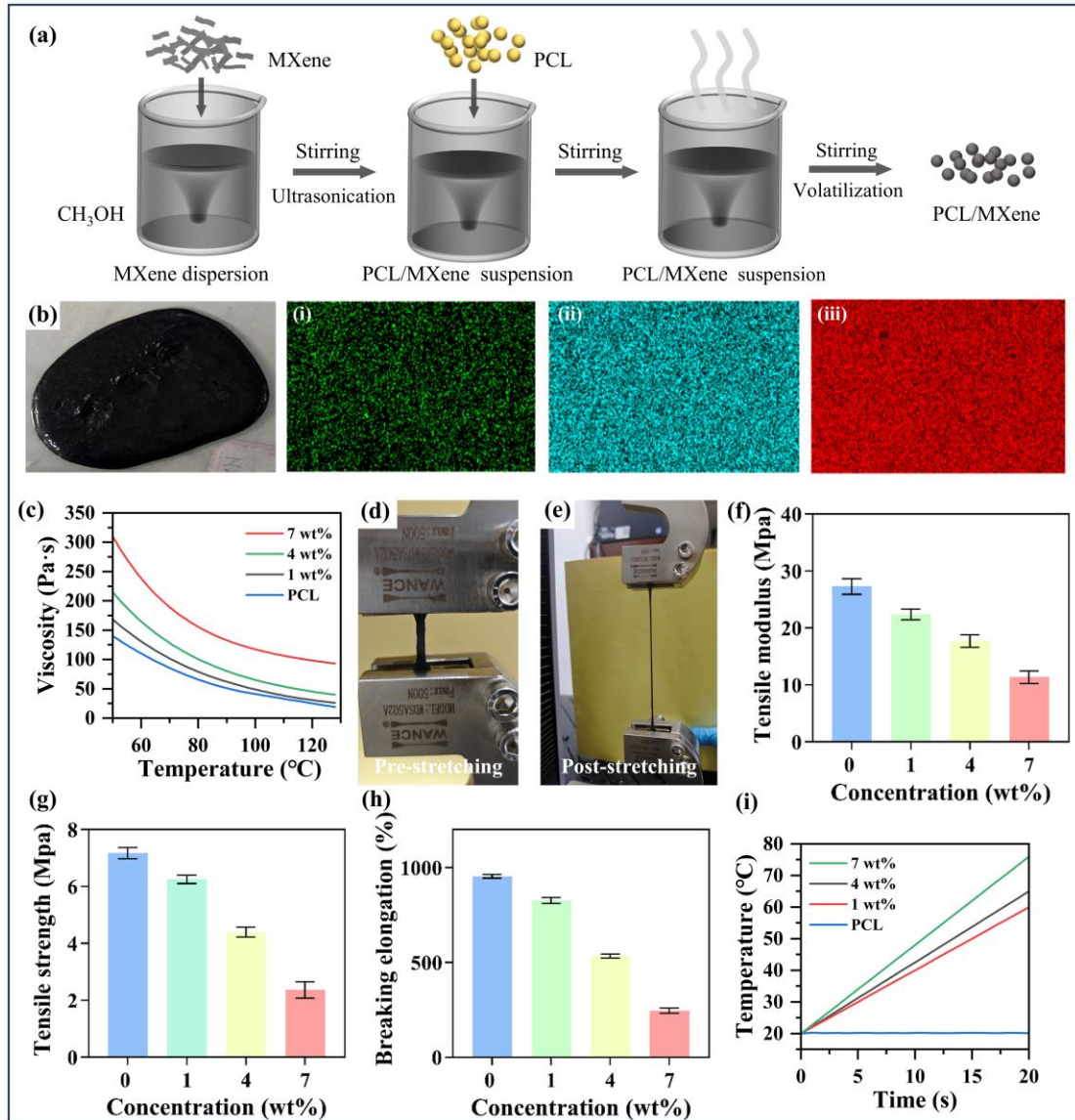


Figure 2. (a) Preparation process of PCL/MXene composites; (b) EDS elemental mappings of PCL/MXene composites: (i) Ti element mapping, (ii) O element mapping, (iii) C element mapping; (c) Temperature-dependent viscosity of PCL/MXene composites with different MXene concentrations; (d) Specimen before tensile testing; (e) Specimen after tensile testing; (f–h) Tensile modulus, tensile strength, and elongation at break of PCL/MXene composites with different MXene concentrations, respectively; (i) Photothermal temperature–time response curves of PCL/MXene composites with different MXene concentrations.

3.2.2 Mechanical properties of PCL/MXene composites

The mechanical properties of solution-cast PCL/MXene composite films were evaluated by tensile testing, with the corresponding tensile modulus, tensile strength, and elongation at break presented in **Figure 2(d–h)**. As the MXene loading increases from 0 to 7 wt%, the tensile modulus, tensile strength, and elongation at break all exhibit a monotonic and concentration-dependent decline. Taking the highest loading as an example, the tensile modulus decreases from 27.29 ± 1.35 MPa (neat PCL) to 11.38 ± 1.12 MPa, the tensile strength drops from 7.17 ± 0.19 MPa to $2.37 \pm$

0.28 MPa, and the elongation at break is reduced from $953.69 \pm 9.18\%$ to $245.53 \pm 13.32\%$, representing reductions of approximately 58%, 67%, and 74%, respectively.

This concurrent deterioration in strength, stiffness, and ductility is attributed to MXene-induced microstructural changes. Nanosheet aggregation at elevated concentrations introduces stress concentration sites and weakens filler–matrix adhesion, reducing modulus and tensile strength, while physical confinement restricts chain mobility and orientation during stretching, accounting for the loss of extensibility. These combined effects embrittle the composite. It should be re-emphasized that these data were obtained from solution-cast bulk specimens and reflect intrinsic material properties, not the mechanical behavior of the highly porous MEW-printed scaffolds. These findings are consistent with previous studies on PCL/MXene composites. For example, Diedkova et al.^[15] reported that MXene incorporation in electrospun PCL nanofibers led to reduced mechanical performance at higher loadings due to aggregation and poor interfacial adhesion. Similarly, Zhao et al.^[4] observed that excessive MXene loading in PCL/chitosan scaffolds compromised mechanical integrity.

The marked variation in mechanical performance across different formulations suggests that processing parameters, particularly extrusion temperature and printing speed, should be individually optimized for each MXene loading in subsequent printability assessments. It should also be noted that these data were obtained from solution-cast bulk specimens and reflect intrinsic material properties rather than the mechanical behavior of the highly porous MEW-printed scaffolds, whose performance is additionally influenced by fiber diameter, porosity, interlayer bonding, and topology. Nevertheless, the printed scaffolds maintained structural integrity during handling and NIR cycling (Section 3.4), confirming adequate robustness for in vitro use, and future work will include systematic compressive testing of different topological designs to further optimize mechanical performance.

3.2.3 Photothermal response of PCL/MXene composites

The composites were also tested with an NIR laser at different concentrations to observe their photothermal responses, as displayed in **Figure 2(i)**. Neat PCL exhibited a low temperature change, which confirmed that PCL did not have photothermal effects. By contrast, all MXene-loaded samples presented a distinct and concentration-dependent temperature increase. After 20 s of irradiation, the surface temperature increased from $\sim 60^\circ\text{C}$ (1 wt%) to $\sim 78^\circ\text{C}$ (7 wt%). These samples displayed higher heating rates and plateau temperatures with increasing MXene content. These results showed that the PCL composites have excellent photothermal conversion efficiency that could be modulated by simply adjusting the content of MXene.

3.3 MEW process and fiber network structure

3.3.1 Effect of MXene concentration on printability

The printability of PCL/MXene composite inks was systematically evaluated by MEW (**Figure 3(a)**), with a target fiber diameter of 50 μm as a representative case. Based on preliminary experiments, this study mainly focuses on process optimization for the 4 wt% formulation. To establish a quantitative basis for printability assessment, single-factor experiments were first

conducted to investigate the effects of printing temperature, pneumatic pressure, and printing speed on fiber diameter and morphological stability (detailed data in **Tables S1–S3**). The results identified the following suitable ranges for achieving stable 50- μm fiber deposition: temperature 100–120 $^{\circ}\text{C}$, pressure 50–70 kPa, and speed 1000–1400 mm/min. Within these ranges, the fiber diameter coefficient of variation ($\text{CV} = \text{SD}/\text{mean} \times 100\%$) remained below 7%. Subsequently, an $L_9(3^3)$ orthogonal array design was employed to determine the optimal parameter combination for the 50- μm target diameter, yielding: temperature 120 $^{\circ}\text{C}$, pressure 60 kPa, and speed 1400 mm/min (**Table S4**). Following the same optimization protocol, the optimal parameters for 30, 75, and 100 μm target diameters were established (**Table 1**), demonstrating that the 4 wt% ink offers a wide and tunable processing window.

Table 1. Optimized MEW parameters for 4 wt% PCL/MXene ink at different target fiber diameters.

Target diameter (μm)	Temperature ($^{\circ}\text{C}$)	Pressure (kPa)	Printing speed (mm/min)
30	95	45	1250
50	120	60	1400
75	120	85	1200
100	130	120	1100

Effect of MXene concentration. Based on the optimized parameters for each concentration, the printability of PCL/MXene inks with varying MXene loadings was quantitatively compared at the 50- μm target diameter. As summarized in **Table 2**, the 1 wt% and 4 wt% formulations produced uniform fibers with CV values of 5.2% and 4.8%, respectively, confirming excellent diameter control. In contrast, the 7 wt% ink exhibited a markedly increased CV of 18.5% with pronounced bead-on-string structures (**Figure S2**), and the 10 wt% formulation failed to produce continuous fibers due to severe nozzle clogging (inner diameter: 350 μm). These quantitative metrics provide the basis for classifying the printability into three distinct regimes: stable printing zone (0–4 wt%), characterized by $\text{CV} < 7\%$ and smooth surfaces; critical zone (7 wt%), where continuous fibers are still achievable but with $\text{CV} > 15\%$ and pronounced non-uniformity; and non-printable zone (≥ 10 wt%), where agglomeration and rheological failure preclude stable fiber formation.

Table 2. Quantitative printability comparison of PCL/MXene inks at 50 μm target diameter.

MXene concentration (wt%)	Fiber diameter (μm)	CV (%)	Fiber continuity	Printability classification
1	49.6 ± 2.6	5.2	Continuous, uniform	Stable
4	50.2 ± 2.4	4.8	Continuous, uniform	Stable
7	51.8 ± 9.6	18.5	Continuous but beaded	Critical

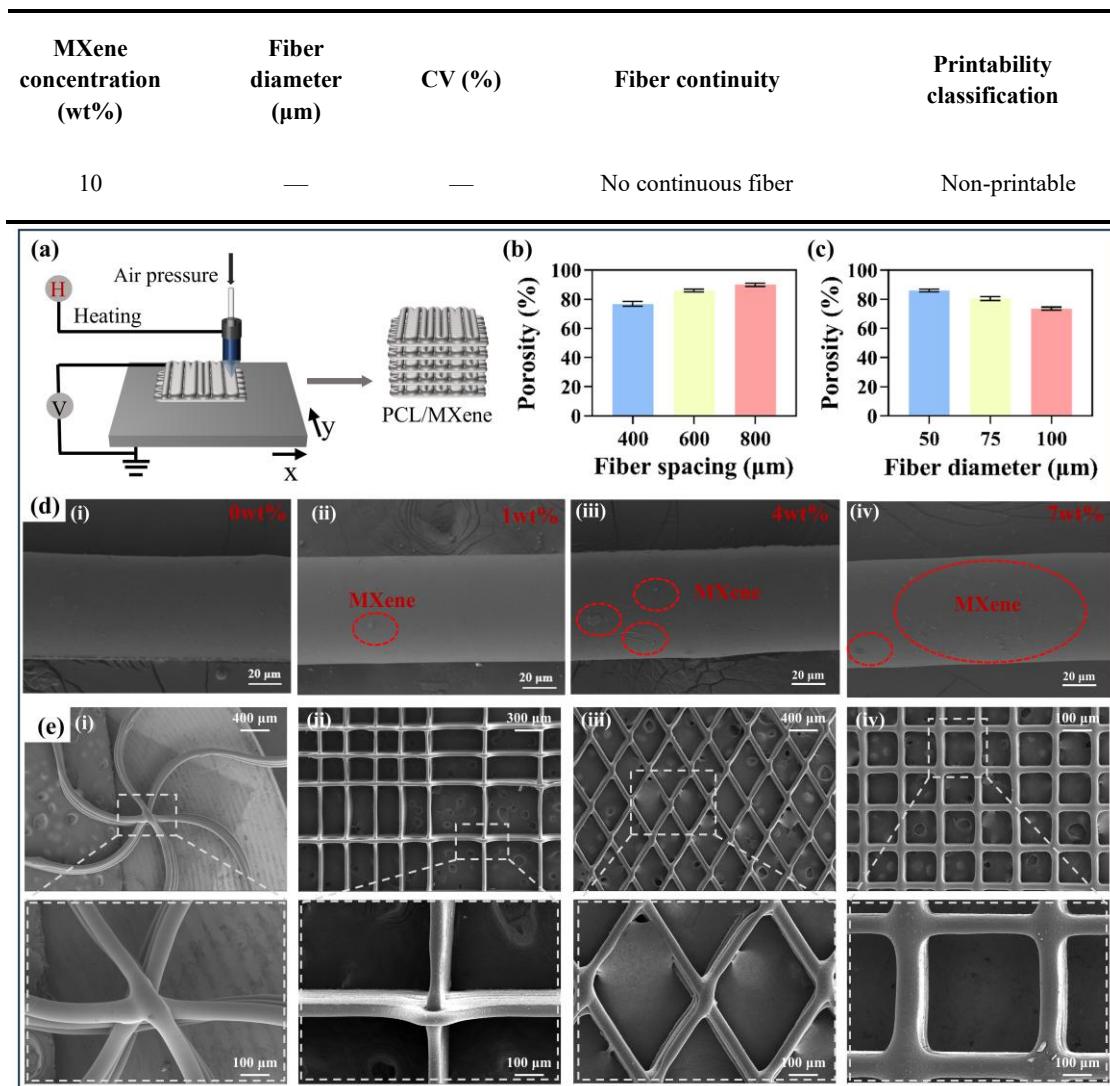


Figure 3. (a) MEW printing platform; (b) Porosity at different fiber spacings; (c) Porosity at different fiber diameters; (d) SEM images of monofilament fiber surfaces: (i) PCL, (ii) 1 wt% PCL/MXene, (iii) 4 wt% PCL/MXene, (iv) 7 wt% PCL/MXene; (e) Different PCL/MXene fiber network scaffold structures: (i) auxetic structure and magnified view, (ii) gradient structure and magnified view, (iii) 60° cross-hatched grid and magnified view, (iv) 90° orthogonal grid and magnified view.

The surface morphology of printed fibers at same optimal processing parameters was further examined by SEM (**Figure 3(d)**). Neat PCL fibers display a smooth and defect-free surface, while the 1 wt% and 4 wt% composites show relatively flat surfaces with MXene nanosheets uniformly dispersed within the PCL matrix, without evident protrusions or agglomerates. This indicates favorable filler dispersion and good fiber-forming quality in the 0–4 wt% range. At 7 wt%, however, the fiber surface becomes noticeably rougher, with localized protrusions of approximately 5–10 μm in size. These features are attributed to the stretching and deformation of MXene agglomerates during melt extrusion, which ultimately deteriorate surface quality and diameter uniformity.

Two aspects explain the deterioration of printability of PCL/MXene ink with increasing concentration. First, the high-aspect-ratio MXene nanosheets form an interconnected network

within the PCL melt, substantially elevating the viscosity and compromising extrusion stability, particularly at 7 wt% and above. Second, the increased filler content intensifies nanosheet agglomeration, which disrupts melt flow uniformity and induces localized surface defects during fiber solidification. These combined effects ultimately restrict the printable concentration window to ≤ 4 wt% for high-quality fiber deposition. Accordingly, the 1 wt% and 4 wt% formulations were selected as representative compositions for subsequent investigations. The printability of the PCL/MXene inks with different target fiber diameters is summarized in the **Tables 3 and 4** below.

Table 3. Printing windows of PCL/MXene inks with different concentrations.

Material	Voltage (kV)	Printing temperature (°C)	Air pressure (kPa)	Printing speed (mm/min)
PCL	3.5~4.55	90~95	35~100	800~1100
1 wt%	3.7~4.6	100~115	35~100	800~1200
4 wt%	4.0~5.25	95~130	45~120	1100~1400

Table 4. Process parameters of PCL/MXene inks for different target fiber diameters.

Material	Fiber diameter (μm)	Voltage (kV)	Printing temperature (°C)	Air pressure (kPa)	Printing speed (mm/min)
PCL	30	3.5	90	35	1100
	50	3.8	90	55	1000
	75	4.2	90	80	1000
	100	4.55	95	100	800
1 wt%	30	3.7	100	35	1200
	50	3.9	105	60	1100
	75	4.2	115	70	1100
	100	4.6	115	100	800
4 wt%	30	4.0	95	45	1250
	50	4.3	120	60	1400
	75	4.7	120	85	1200
	100	5.25	130	120	1100

3.3.2 Microstructure of fiber networks

In addition, four distinct topological structures, i.e., auxetic, gradient, 60° cross hatched and 90° orthogonal grids, were MEW-printed using optimized printing parameters, as shown in **Figure 3(e)**. These four topological designs—auxetic, gradient, 60° cross-hatched, and 90° orthogonal—demonstrate the manufacturing versatility of MEW for PCL/MXene inks. Each offers distinct features: negative Poisson's ratio (auxetic), porosity gradients (gradient), and varying pore geometries (60°/90°). While these architectures may differentially affect cellular responses, systematic comparison of their porosity, mechanics, and cell behavior is beyond the present scope and awaits future investigation. As can be observed, uniform fibers were obtained on topologically structured scaffolds and were accurately deposited along the designed paths, indicating a robust printing of the composite inks. As an example, porosity analysis was performed on the 90° orthogonal scaffold to elucidate its impact on structure characteristics. The results showed that porosity increased with increasing inter fiber spacing and decreasing fiber diameter, resulting in a range of 73.56 to 90% porosity for these PCL/MXene composites (**Figure 3(b-c)**). This wide range of porosity provides ample flexibility in designing these 3D scaffolds for future biological testing.

3.4 Factors affecting the photothermal response of composite scaffolds

3.4.1 Effects of irradiation distance and MXene concentration

Figure 4(a-b) illustrates the photothermal profiles of PCL/MXene composite scaffolds containing 1 wt% and 4 wt% MXene, respectively, irradiated at varying distances of 15, 30, and 45 cm. Because the laser output power was adjusted at each distance to maintain a constant sample-plane power density, the beam diameter increased with distance (from 12 mm at 15 cm to 17 mm at 30 cm), resulting in a larger irradiated area at 30 cm. The observed distance dependence therefore reflects changes in beam geometry and heat dissipation, rather than attenuation of irradiance. In all groups, the scaffold temperature rose rapidly within 10 s, followed by a gradual plateau at near constant temperatures after around 30 s, indicating that the photothermal heating reached equilibrium. The equilibrium temperature decreased with increasing irradiation distance, independent of the MXene content, indicating that distance-dependent reduction in photothermal performance. It is important to note that the temperature drop of the composite scaffolds from 15 to 30 cm was greater than that from 30 to 45 cm, meaning that the effect of distance-dependent attenuation on the photothermal performance was nonlinear. The composite scaffold with 4 wt% MXene exhibited a higher temperature than that with 1 wt% at the three irradiation distances, indicating that increasing the concentration of the MXene in the scaffold was an effective strategy to overcome the effects of attenuation due to a greater irradiation distance.

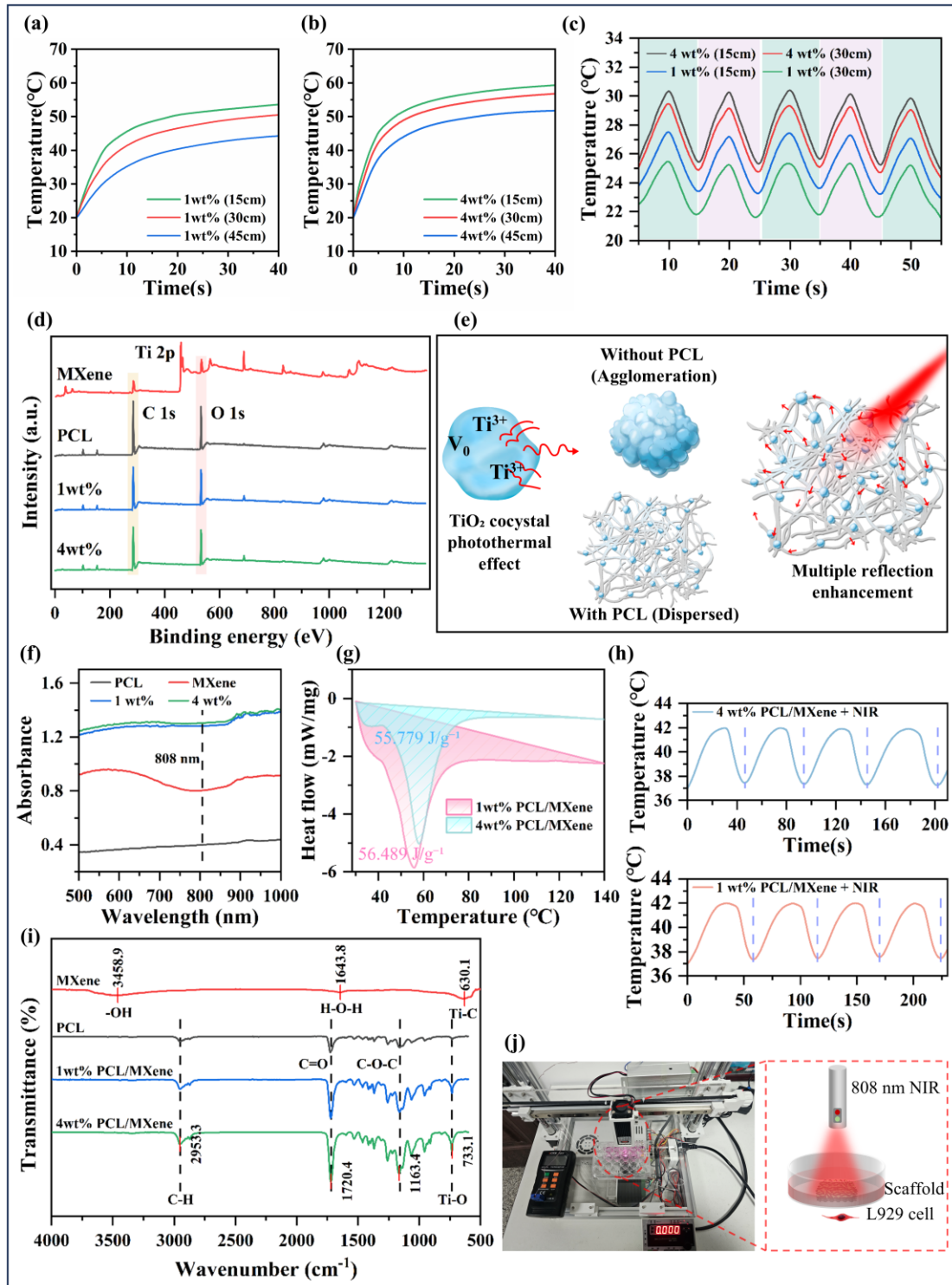


Figure 4. (a–b) Heating curves of fiber network scaffolds with 1 wt% and 4 wt% MXene contents under different irradiation distances; (c) Photothermal cycling heating curves of PCL/MXene fiber network scaffolds; (d) XPS spectra of MXene, PCL, and PCL/MXene composites with different concentrations; (e) Photothermal response mechanism of PCL/MXene composites; (f) UV-vis-NIR absorption spectra of MXene, PCL, and PCL/MXene composites with different concentrations; (g) DSC curves of PCL/MXene composites; (h) Cyclic temperature rise curves of fiber networks under NIR laser irradiation; (i) FTIR spectra of MXene, PCL, and PCL/MXene composites with different concentrations; (j) NIR irradiation of PCL/MXene fiber networks in culture medium.

3.4.2 Photothermal cycling stability

Long-term stability of photothermal performance was investigated through consecutive cycles ($n = 5$) of heating and cooling at two typical irradiation distances, i.e., 15 and 30 cm, and the cycling test at 45 cm was excluded because of the very weak photothermal signal ($\sim 30^\circ\text{C}$) that may make stable measurement impossible (**Figure 4(c)**). It is obvious that almost all the photothermal curves of samples for different cycles nearly overlap and there is no apparent drop in peak temperature. The heating rate and maximum temperature reached by scaffolds are 4 wt% (15 cm) > 4 wt% (30 cm) > 1 wt% (15 cm) > 1 wt% (30 cm), which confirms the higher MXene content and lower irradiation distance are both helpful for efficient photothermal performance of scaffolds.

Using the heating and cooling curves and the classic method by Roper,^[32] the photothermal conversion efficiency (η) for the scaffolds could be obtained by calculations. The calculated photothermal conversion efficiencies were $44.5 \pm 1.8\%$ and $59.4 \pm 2.1\%$ for the 1 wt% and 4 wt% scaffolds, respectively (mean $\pm$ SD, $n = 3$). This represents an absolute increase of 14.9 percentage points, corresponding to a relative increase of approximately 33.5% ($(59.4 - 44.5)/44.5 \times 100\% \approx 33.5\%$). The 14.9 percentage-point increase with MXene loading is attributed to the higher density of photothermally active sites and enhanced NIR absorption, consistent with the UV-vis-NIR results in **Figure 4(f)**. Uncertainty analysis: the combined standard uncertainty was propagated from temperature measurement ($\pm 0.5^\circ\text{C}$, $\pm 1.2\%$), power-meter calibration ($\pm 5\%$, $\pm 1.3\%$), absorbance (± 0.02 , $\pm 0.5\%$), and cooling-curve fit ($R^2 > 0.99$, $\pm 0.8\%$), giving $\eta = 59.4 \pm 2.1\%$ (4 wt%) and $44.5 \pm 1.8\%$ (1 wt%). This can be explained by the fact that the higher MXene content can provide more photothermally active sites for energy absorption to enhance overall photothermal performance.

3.5 Mechanism of near-infrared photothermal response of PCL/MXene

3.5.1 Chemical structure and surface chemical state

XPS and FTIR were used to characterize the chemical structure and surface chemistry of the PCL/MXene composites. The XPS survey spectra (**Figure 4(d)**) showed characteristic peaks of neat PCL (C 1s, O 1s) and MXene (Ti 2p at ~ 455 eV, O 1s at ~ 530 eV, C 1s at ~ 285 eV), with no impurity peaks detected. In the composite spectra, however, the Ti 2p signal was not clearly resolved, likely because the relatively low MXene loading (≤ 4 wt%) resulted in the PCL C 1s and O 1s signals dominating the spectrum. This observation, together with the EDS elemental mapping results, confirms that MXene was successfully incorporated into the PCL matrix.

The FTIR spectra (**Figure 4(i)**) provided complementary information. For MXene, the peak at 3458.9 cm^{-1} corresponds to O-H stretching of surface hydroxyl groups and adsorbed water, 1643 cm^{-1} to H-O-H bending, and 630.1 cm^{-1} to Ti-C lattice vibrations. For neat PCL, characteristic absorptions appear at 2953.3 cm^{-1} (C-H stretching), 1720.4 cm^{-1} (C=O stretching), and 1163.4 cm^{-1} (C-O-C stretching). In the composite spectra, all PCL characteristic peaks remained observable without any shift in position or emergence of new peaks associated with covalent bond formation, indicating that no chemical reaction occurred between MXene and PCL and that the composites were formed via physical mixing. The relative intensities of PCL peaks decreased slightly with

increasing MXene loading, consistent with dilution of the polymer matrix by the MXene filler. Notably, an additional band appeared at 733.1 cm^{-1} in the composite spectra, with intensity increasing from 1 wt% to 4 wt% MXene; this band is tentatively assigned to Ti–O vibrations, suggesting the presence of oxidized surface species on the MXene nanosheets, which may provide additional photothermal active sites. In addition, a slight broadening of the PCL C=O peak at 1720.4 cm^{-1} was observed, which may suggest possible hydrogen-bonding interactions between the carbonyl groups of PCL and the surface functional groups (–OH, –O) of MXene. However, given the absence of a clear peak shift, this FTIR evidence alone is not sufficient to conclusively demonstrate hydrogen-bond formation; it should be interpreted as suggestive rather than definitive. Complementary techniques such as XPS deconvolution of the O 1s region or solid-state NMR would be required to confirm interfacial hydrogen bonding. Overall, the FTIR results confirm the successful fabrication of the composite systems and suggest the presence of MXene-derived surface species that may contribute to the photothermal response of the PCL/MXene scaffolds.

3.5.2 Photothermal response and thermal performance analysis

UV-vis-NIR spectroscopy was used to evaluate the light absorbance of the composites over 500–1000 nm, with particular focus on the 808 nm wavelength (**Figure 4(f)**). Neat PCL showed low absorbance (~ 0.4 at 808 nm), confirming its NIR transparency. Pristine MXene exhibited broad absorbance (~ 0.8 at 808 nm). Upon incorporation into the PCL matrix, the 1 wt% and 4 wt% composites showed significantly higher absorbance values of 1.28 and 1.30, respectively, which can be attributed to the intrinsic absorbance of MXene and multiple scattering at polymer–filler interfaces that increases the effective optical path length. Notably, the absorbance reached near-saturation at 1 wt% MXene, with only a marginal increase at 4 wt%, suggesting that the enhanced photothermal efficiency at higher loadings (44.5% at 1 wt% vs 59.4% at 4 wt%) is not solely governed by absorbance but also influenced by thermal conductivity and heat management within the composite. Based on these results, the 808 nm wavelength was selected for subsequent NIR irradiation experiments.

DSC analysis (**Figure 4(g)**) revealed a single melting transition centered at 55–65 °C for all samples, indicating that the crystal structure of PCL was not altered by MXene incorporation. The melting temperature increased slightly from $\sim 55\text{ °C}$ to $\sim 60\text{ °C}$ with increasing MXene content (1–4 wt%), which may reflect confinement effects or enhanced nucleation density at the polymer–filler interface. The melting enthalpy remained nearly constant ($\sim 56\text{ J}\cdot\text{g}^{-1}$) regardless of filler content, suggesting that MXene did not significantly change the crystallinity of PCL. These thermal characteristics confirm that the composites are processable via melt-based fabrication methods such as MEW.

The enhanced photothermal response of the PCL/MXene composites can be rationalized by three synergistic factors operating at different levels: (1) the intrinsic photothermal activity of MXene and its surface derivatives, (2) the dispersion and stabilization provided by the PCL matrix, and (3) light scattering enhancement within the composite microstructure (**Figure 4(e)**).

First, intrinsic photothermal activity of MXene. The predominant contribution arises from the

intrinsic photothermal effect of MXene. Due to its metallic conductivity and surface functional groups, MXene absorbs NIR light through interband transitions and efficiently converts photons to heat. FTIR analysis (Section 3.5.1) revealed the appearance of a Ti–O band at 733.1 cm^{-1} , suggesting partial surface oxidation of MXene during composite preparation. Such oxidized surface species have been reported to introduce additional defect states that enhance NIR absorption,^[39,40] thereby contributing to the overall photothermal performance.

Second, dispersion and stabilization by the PCL matrix. During solution blending, PCL chains intercalate between MXene layers, preventing nanosheet restacking through physical interactions. SEM and EDS mapping confirmed uniform dispersion of MXene within the PCL matrix, which maximizes the number of photothermally active sites and ensures homogeneous temperature distribution. Furthermore, the slight broadening of the PCL C=O peak in the FTIR spectra may indicate possible hydrogen-bonding interactions between PCL carbonyl groups and MXene surface groups (–OH, –O), suggesting improved interfacial compatibility and dispersion stability, although this interpretation remains tentative pending further characterization.

Third, light scattering enhancement. The refractive index mismatch between MXene and the PCL matrix introduces scattering at polymer–filler interfaces, leading to multiple reflection and dispersion of incident light. This extends the effective optical path length within the composite, increasing the probability of NIR photon absorption by photothermally active species. This scattering enhancement is consistent with the observed absorbance increase in the composites compared to neat PCL, and similar behavior has been reported by Luo et al.^[41]

In summary, the photothermal performance of the PCL/MXene composites arises from the combination of MXene's intrinsic NIR absorption and surface oxidation states, the stabilizing role of the PCL matrix in ensuring uniform filler dispersion, and scattering-induced optical path extension within the composite microstructure. These three factors collectively enable the enhanced and tunable photothermal response demonstrated in this study.

3.5.3 Photothermal response performance of fiber networks in culture medium

The photothermal performance of the composite scaffolds in culture medium (**Figure 4(j)**) was evaluated within the therapeutic temperature window of $37\text{--}42\text{ }^{\circ}\text{C}$ (**Figure 4(h)**). Both the 1 wt% and 4 wt% scaffolds exhibit rapid and controllable photothermal conversion. The higher-loading group displays an accelerated heating rate, reaching $42\text{ }^{\circ}\text{C}$ from $37\text{ }^{\circ}\text{C}$ in $30 \pm 2\text{ s}$, versus $40 \pm 2\text{ s}$ for the 1 wt% group, while both show similar cooling kinetics ($\sim 10 \pm 2\text{ s}$). Temperature fluctuations are confined within $\pm 0.5\text{ }^{\circ}\text{C}$ throughout the cycles. For culture-medium cycling, the 1 wt% and 4 wt% groups showed no significant attenuation after four cycles, with peak temperature fluctuations remaining within $\pm 0.5\text{ }^{\circ}\text{C}$, further confirming the excellent photothermal reliability under cell-relevant conditions.

3.6 Evaluation of antibacterial performance

To assess the antibacterial effect of PCL/MXene scaffolds against *E. coli* and *S. aureus*, bacterial counting experiments were conducted (**Figure 5**). It should be emphasized that the antibacterial assays in this study were performed without NIR irradiation; therefore, the results

reflect contact-dependent antibacterial activity only and do not demonstrate photothermally enhanced or on-demand photothermal antibacterial effects. **Figure 5(b)** indicates that the neat PCL film was unable to inhibit bacterial growth, and the addition of 1 wt% MXene only exhibited a certain degree of antibacterial activity in *E. coli* (72.7%) and *S. aureus* (96.9%), probably due to the lack of a lipopolysaccharide outer membrane for Gram positive *S. aureus*.^[42] When the MXene content was 4 wt%, an antibacterial rate of ~99% was observed for both bacterial species. Bacteria count results also reveal almost negligible counts of viable bacteria after 24 h of co culture with 4 wt% PCL/MXene (**Figure 5(c-e)**). These results demonstrate that the PCL/MXene scaffolds exert concentration-dependent and effective broad-spectrum antibacterial activity under the tested conditions.

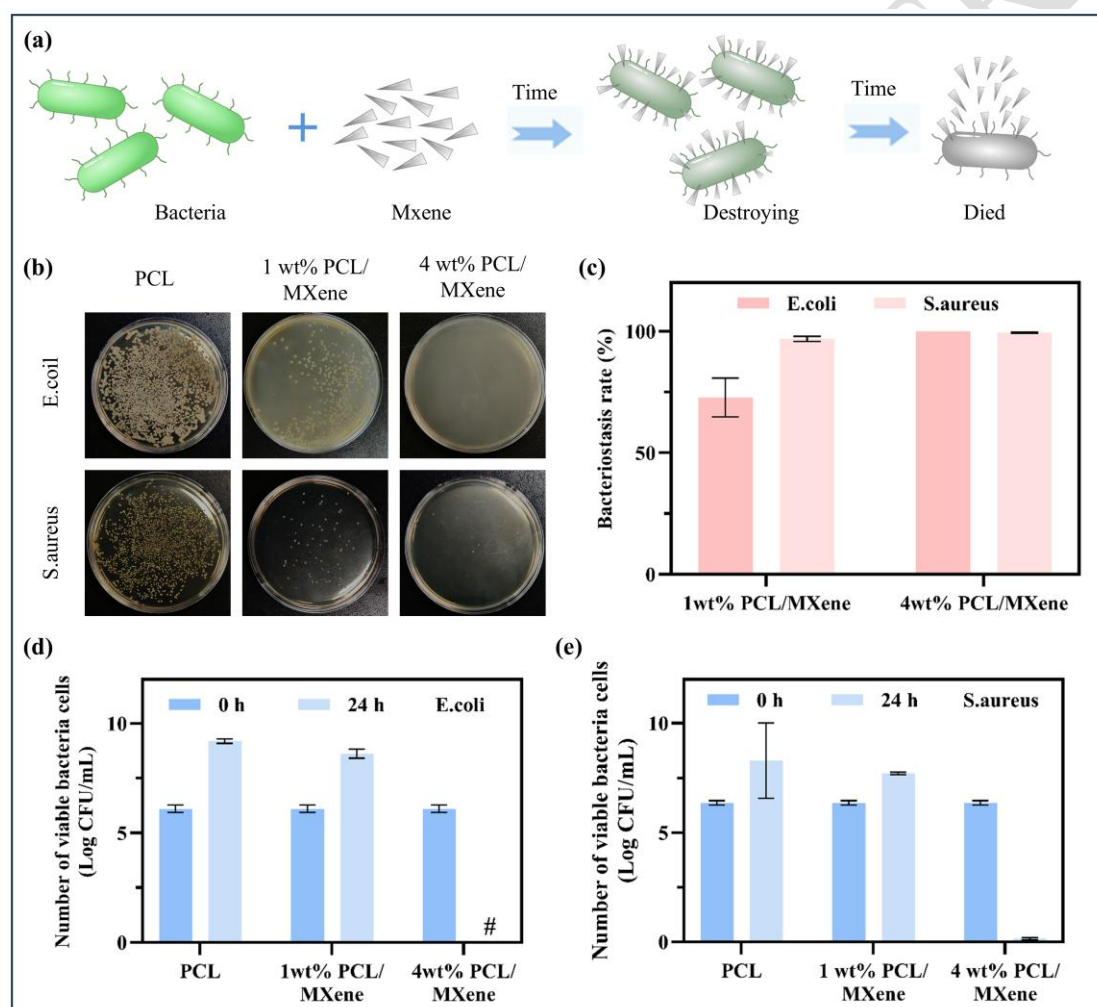


Figure 5. (a) Antibacterial mechanism of PCL/MXene; (b) Agar plate images of *E. coli* and *S. aureus* after 24 h incubation on PCL, 1 wt% PCL/MXene, and 4 wt% PCL/MXene scaffolds; (c) Antibacterial rates of 1 wt% and 4 wt% PCL/MXene scaffolds against *E. coli* and *S. aureus*; (d) Number of *E. coli* after 24 h incubation on PCL, 1 wt% PCL/MXene, and 4 wt% PCL/MXene scaffolds (symbol “#” indicates no viable bacteria); (e) Number of *S. aureus* after 24 h incubation on PCL, 1 wt% PCL/MXene, and 4 wt% PCL/MXene scaffolds.

The antibacterial mechanism of MXene-based materials involves multiple factors, including

the physical "nanoknife" effect (sharp edges piercing membranes),^[38] ROS-induced oxidative stress, and phospholipid extraction.^[8-10] Photothermal heating has also been reported as a contributing factor under NIR irradiation, but was not activated in our system as the assays were conducted without NIR exposure. Notably, direct mechanistic evidence (e.g., SEM/TEM, membrane permeability assays) is not provided, as such analyses require dedicated bacterial culture systems beyond the current scope. Therefore, the observed antibacterial activity should be interpreted as a concentration-dependent contact-mediated effect, and future studies incorporating membrane integrity assays and electron microscopy are needed to elucidate the precise mechanism.

3.7 Biocompatibility

All biological evaluations were performed using the 90° orthogonal scaffold architecture with 500 µm fiber spacing and a target fiber diameter of 50 µm. As shown in **Figure 6(a)**, cells adhered to and proliferated on all scaffold surfaces, with cell density increasing over time in all groups. At day 1, cells in the MXene-containing groups appeared more spread than those on neat PCL, and the cells exhibited a spindle-shaped morphology. By day 3, cells began to form intercellular connections, and differences among groups became more apparent: under the same MXene loading, NIR-irradiated groups showed higher cell densities than their non-irradiated counterparts; under NIR irradiation, the 4 wt% group showed higher cell density than the 1 wt% group. By day 5, the 4 wt% + NIR group exhibited the most extensive cell coverage, while the neat PCL and 1 wt% groups showed relatively modest proliferation. The overall trend of cell growth observed qualitatively was: 4 wt% + NIR > 4 wt% > 1 wt% + NIR > 1 wt% > PCL.

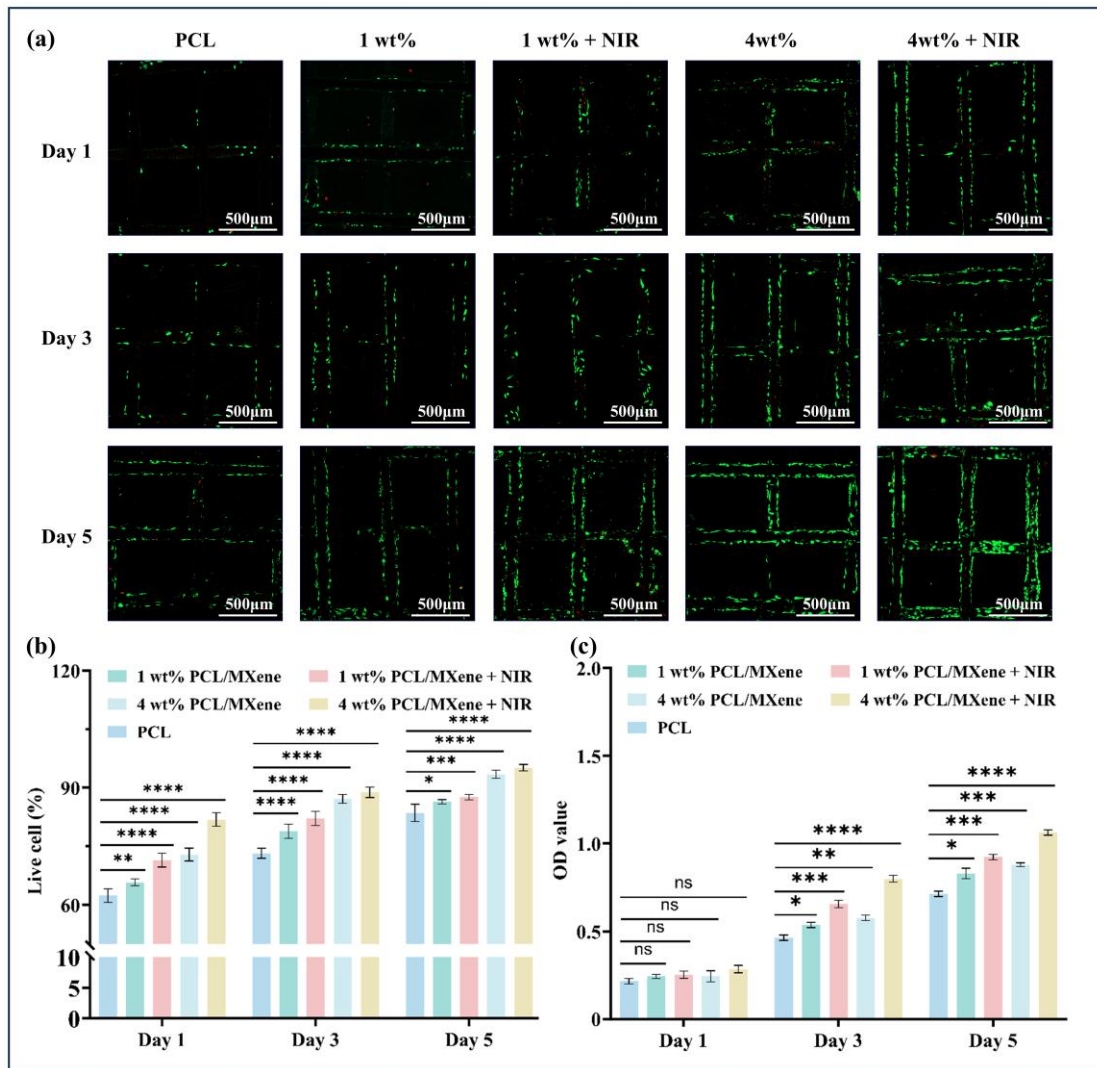


Figure 6. (a) Live/dead staining fluorescence images of cells cultured on different fiber networks at days 1, 3, and 5; (b) Cell viability of L-929 cells cultured on different fiber networks at days 1, 3, and 5 (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, **** $p < 0.0001$); (c) OD values of L-929 cells co-cultured with different scaffolds for 1, 3, and 5 days (ns: not significant, * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, **** $p < 0.0001$).

From the results of cell viability assay in **Figure 6(b)**, by day 5, the viability of all groups exceeded 80%, confirming the cytocompatibility of both PCL and PCL/MXene scaffolds. The 4 wt% + NIR group showed the highest viability, followed by the 4 wt% group, 1 wt% + NIR group, 1 wt% group, and PCL group, indicating a beneficial effect of MXene loading and NIR stimulation on L929 cell proliferation. At day 1, the 4 wt% + NIR group exhibited higher viability than the 4 wt% group without irradiation, suggesting that NIR stimulation promoted early-stage cell proliferation. The difference between NIR-irradiated and non-irradiated groups became less pronounced by day 5, which may be attributed to contact inhibition at higher cell confluence outweighing the proliferative effect of NIR stimulation. Live/Dead staining was used primarily for qualitative visualization of cell viability; the reported percentages are approximate estimates based on fluorescence area and should be interpreted with caution, as this method can be influenced by cell

spreading, density, scaffold geometry, and background. Quantitative assessment of cell proliferation was based on CCK-8 assays.

The CCK-8 OD values in **Figure 6(c)** showed a similar trend to the cell viability results. The OD values of all groups increased 3.4 to 5.0 times from day 1 to day 5. Consistent with the live/dead results, the 4 wt% + NIR group showed the highest CCK-8 OD value (1.02) on day 5. Of greater significance than the absolute OD values across different formulations is the comparison within the same MXene loading with and without NIR stimulation: the CCK-8 OD value of the 1 wt% + NIR group was significantly greater than that of the 1 wt% group (increasing by approximately 27%, $p < 0.01$), and the 4 wt% + NIR group was significantly greater than the 4 wt% group (increasing by approximately 48%, $p < 0.01$) on day 3, indicating that NIR irradiation promoted cell metabolic activity. It should be noted that acellular material controls were not included in the present study; therefore, the absolute OD values should be interpreted with caution. Future studies incorporating acellular controls are warranted to further validate the background-corrected metabolic activity. It is worth noting that the initial cell viability on day 1 was relatively modest across all groups (62–82%), which is a commonly observed phenomenon for cells seeded on 3D fibrous scaffolds. This lower initial viability may be attributed to: (i) the adaptation period required for cells to attach and spread on the fibrous surface compared with 2D tissue culture plastic; (ii) the hydrophobic nature of PCL, which may initially limit cell adhesion; and (iii) the porous 3D geometry, which can affect nutrient diffusion and cell distribution during the early seeding phase. Similar initial viability patterns have been reported in previous studies on PCL-based fibrous scaffolds.^[16, 18] The subsequent increase in viability from day 1 to day 5 across all groups confirms that the scaffolds support cell proliferation over time.

These results indicate that PCL/MXene scaffolds are cytocompatible and that higher MXene loading combined with NIR stimulation promotes L929 fibroblast proliferation in vitro. However, several limitations should be acknowledged. The biological evaluation is limited to short-term in vitro assays and does not include in vivo wound-healing models, histology, or angiogenesis analysis; thus, the results support cytocompatibility and pro-proliferative effects but do not directly demonstrate tissue repair or regeneration. In addition, no quantitative cell orientation analysis (e.g., F-actin/DAPI staining with angular distribution) was performed; future in vivo studies and quantitative orientation analyses are required to validate the tissue regeneration potential of these scaffolds.

4 Conclusion

In this study, we established a complete fabrication route for PCL/MXene ultrafine fiber scaffolds via melt electrowriting, covering composite ink formulation, rheological optimization, and topological design. The 0–4 wt% MXene loading range was identified as the stable printing window, beyond which severe agglomeration and viscosity surge preclude further processing. Among the tested formulations, the 4 wt% formulation achieved the most favorable balance between printability and photothermal performance. Within this window, the scaffolds achieved structural fidelity across multiple topologies (auxetic, gradient, 60° and 90° grids), primarily demonstrating the

manufacturing versatility of the MEW process, and exhibited dual functionality: stable and tunable photothermal heating under NIR irradiation, and concentration-dependent contact antibacterial activity potentially mediated by MXene nanosheets. Notably, the combination of 4 wt% MXene loading with mild NIR stimulation (37–42 °C) promoted early cell adhesion and proliferation in vitro, surpassing the performance of scaffolds without NIR stimulation. Despite these promising results, several limitations should be acknowledged: the lack of in vivo validation, the use of bulk specimens for mechanical testing, the absence of antibacterial mechanism characterization, and the need for quantitative printability and cell orientation analyses. The long-term stability of MXene also requires further study. Addressing these issues will be essential for future tissue engineering applications.

Funding

This work was supported by the National Natural Science Foundation of China (Grant Nos. 52465035, 52565030, 52325504), the Science and Technology Planning Project of Guizhou Province (Grant Nos. ZK[2024]510, [2026]YB356), the Open Foundation of the State Key Laboratory of Fluid Power and Mechatronic Systems (GZKF-202511, GZKF-202404), the High-level Talents Project of Guizhou Institute of Technology (2023GCC031, 2023GCC033), the Introduced Talents Research Project of Guizhou University (GDRJHZ-202416).

Conflict of Interest

The authors declare no conflicts of interest. No known competing financial interests or personal affiliations exist that could have unduly influenced the work presented in this paper.

Author contributions

Conceptualization: Zhongfei Zou, Yuewei Chen, Yong He

Data curation: Xianhui Cai, Zhen Shen, Fangtao Shi

Funding acquisition: Zhongfei Zou, Yuewei Chen

Investigation: Xianhui Cai, Zhen Shen, Fangtao Shi

Methodology: Zhongfei Zou, Yuewei Chen, Xianhui Cai

Project administration: Zhongfei Zou, Yuewei Chen, Yong He

Writing—original draft: Zhongfei Zou, Xingke Huang

Writing—review & editing: Zhongfei Zou, Xingke Huang

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

References

- [1] Talebian S, Mehrali M, Taebnia N, et al. Self-Healing Hydrogels: The Next Paradigm Shift in Tissue Engineering? [J]. *Advanced Science*, 2019, 6(16).<https://doi.org/10.1002/advs.201801664>
- [2] Eldeeb A E, Salah S, Elkasabgy N A. Biomaterials for Tissue Engineering Applications and Current Updates in the Field: A Comprehensive Review [J]. *AAPS PharmSciTech*, 2022, 23(7).<https://doi.org/10.1208/s12249-022-02419-1>
- [3] Kim S H, Lee S, Kim H-J, et al. 3D-printable, heat-resistant polycaprolactone-based polymer scaffold for sustained NO release in tissue engineering applications [J]. *Colloids and Surfaces B: Biointerfaces*, 2026, 261.<https://doi.org/10.1016/j.colsurfb.2026.115447>
- [4] Zhao H, Fu Q, Wang Z, et al. Fabrication and characterization of bifunctional PCL/chitosan scaffolds decorated with MXene nanoflakes for bone tissue engineering [J]. *Polymer*, 2024, 303.<https://doi.org/10.1016/j.polymer.2024.127111>
- [5] Wang C, Yang M, Chen L, et al. Polycaprolactone strengthening gelatin/nano-hydroxyapatite composite biomaterial inks for potential application in extrusion-based 3D printing bone scaffolds [J]. *Collagen and Leather*, 2024, 6(1).<https://doi.org/10.1186/s42825-024-00170-w>
- [6] Chen Z, Liu Y, Huang J, et al. Enhanced In Vitro Biocompatible Polycaprolactone/Nano-Hydroxyapatite Scaffolds with Near-Field Direct-Writing Melt Electrospinning Technology [J]. *Journal of Functional Biomaterials*, 2022, 13(4).<https://doi.org/10.3390/jfb13040161>
- [7] Yupanqui Mieses J, Vyas C, Daskalakis E, et al. Electrospun polyvinyl alcohol fibres incorporating an antimicrobial gel for enzymatically controlled reactive oxygen species release [J]. *Bio-Design and Manufacturing*, 2024, 7(6): 899–925.<https://doi.org/10.1007/s42242-024-00312-3>
- [8] Yadav S, Raghav S, Chavda V, et al. Recent computational insights into MXene and their composite materials for biomedical applications: Design strategies, key advances, and future directions [J]. *Materials Today Chemistry*, 2026, 54.<https://doi.org/10.1016/j.mtchem.2026.103659>
- [9] Tan Y, Sun H, Lan Y, et al. Study on 3D printed MXene-berberine-integrated scaffold for photo-activated antibacterial activity and bone regeneration [J]. *Journal of Materials Chemistry B*, 2024, 12(8): 2158–79.<https://doi.org/10.1039/d3tb02306k>
- [10] He X, Qian Y, Wu C, et al. Entropy-Mediated High-Entropy MXenes Nanotherapeutics NIR-II-Enhanced Intrinsic Oxidase Mimic Activity to Combat Methicillin-Resistant *Staphylococcus Aureus* Infection [J]. *Advanced Materials*, 2023. <https://doi.org/10.1002/adma.202211432>
- [11] Thakur A, Pathania A, Salvi A, et al. Biomedical Applications of 2D MXene Nanocomposites: A Review [J]. *ChemBioEng Reviews*, 2023, 10(6): 1050–72.<https://doi.org/10.1002/cben.202300029>
- [12] Hao S, Han H, Yang Z, et al. Recent Advancements on Photothermal Conversion and Antibacterial Applications over MXenes-Based Materials [J]. *Nano-Micro Letters*, 2022, 14(1).<https://doi.org/10.1007/s40820-022-00901-w>

- [13] Lee O-S, Madjet M E, Mahmoud K A. Antibacterial Mechanism of Multifunctional MXene Nanosheets: Domain Formation and Phase Transition in Lipid Bilayer [J]. *Nano Letters*, 2021, 21(19): 8510–7. <https://doi.org/10.1021/acs.nanolett.1c01986>
- [14] Ye S, Zhang H, Lai H, et al. MXene: A wonderful nanomaterial in antibacterial [J]. *Frontiers in Bioengineering and Biotechnology*, 2024, 12. <https://doi.org/10.3389/fbioe.2024.1338539>
- [15] Diedkova K, Pogrebnyak A D, Kyrylenko S, et al. Polycaprolactone–MXene Nanofibrous Scaffolds for Tissue Engineering [J]. *ACS Applied Materials & Interfaces*, 2023. <https://doi.org/10.1021/acsami.2c22780>
- [16] Jia J, Lei Q, Liu Z, et al. Advances in Melt-Electrowriting of Fibrous Bioscaffolds: A High-Resolution Manufacturing Strategy for Tissue Regeneration [J]. *Advanced Fiber Materials*, 2026. <https://doi.org/10.1007/s42765-025-00658-y>
- [17] Zhang Y, Zhao F, Qiao A, et al. Rational Design and Functionalization of Melt Electrowritten 4D Scaffolds for Biomedical Applications [J]. *Nano-Micro Letters*, 2026, 18(1). <https://doi.org/10.1007/s40820-025-01986-9>
- [18] Devlin B L, Allenby M C, Ren J, et al. Materials Design Innovations in Optimizing Cellular Behavior on Melt Electrowritten (MEW) Scaffolds [J]. *Advanced Functional Materials*, 2024, 34(18). <https://doi.org/10.1002/adfm.202313092>
- [19] Zahrabi M, Altunbek M, Çelik S, et al. 3D melt electrowritten MXene-reinforced scaffolds for tissue engineering applications [J]. *Biofabrication*, 2025, 17(4). <https://doi.org/10.1088/1758-5090/adf803>
- [20] Kade J C, Dalton P D. Polymers for Melt Electrowriting [J]. *Advanced Healthcare Materials*, 2020, 10(1). <https://doi.org/10.1002/adhm.202001232>
- [21] Mishra P, Badiyani V M, Singh A K, et al. Complexities and challenges associated with articular cartilage tissue defect reconstruction: an overview of bioprinting therapeutics [J]. *Bio-Design and Manufacturing*, 2025, 8(5): 877–908. <https://doi.org/10.1631/bdm.2400363>
- [22] Li Z, Xu D, Deng Z, et al. Single-Atom-Catalyzed MXene-Based nanoplatform with Photo-Enhanced Peroxidase-Like activity nanotherapeutics for *Staphylococcus aureus* infection [J]. *Chemical Engineering Journal*, 2023, 452. <https://doi.org/10.1016/j.cej.2022.139587>
- [23] Liu J, Yu S, Shen L, Qiao J, Zuo X, Peng Q. Albumin corona surrounding Ti3C2Tx MXene nanosheets weakens its antibacterial photothermal therapy. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 2026;747:140954. doi:10.1016/j.colsurfa.2026.140954
- [24] Jin J, Wu S, Wang J, et al. AgPd nanocages sandwiched between a MXene nanosheet and PDA layer for photothermally improved catalytic activity and antibacterial properties [J]. *Dalton Transactions*, 2023, 52(8): 2335–44. <https://doi.org/10.1039/d2dt03596k>
- [25] Zhang J, Cheng H, Jiao Y, et al. Photothermal driven shape memory polymer based on MXene-grafted-polycaprolactone with fast response and easy recyclability. *Polymer*. 2026;345:129554. doi:10.1016/j.polymer.2026.129554
- [26] Woods I, Spurling D, Sunil S, et al. 3D-Printing of Electroconductive MXene-Based Micro-Meshes in a Biomimetic Hyaluronic Acid-Based Scaffold Directs and Enhances Electrical Stimulation for Neural Repair Applications [J]. *Advanced Science*, 2025, 12(34). <https://doi.org/10.1002/advs.202503454>
- [27] Shen X, Zhang Z, Cheng C, et al. Bone regeneration and antibacterial properties of calcium-phosphorus coatings induced by gentamicin-loaded polydopamine on magnesium alloys [J]. *Biomedical Technology*, 2024, 5: 87–101. <https://doi.org/10.1016/j.bmt.2023.06.002>
- [28] Vignolo S M, Roth D M, Wu L, et al. Strategies for craniofacial tissue engineering: innovations for

- scalable bone regeneration [J]. *Plastic and Aesthetic Research*, 2025. <https://doi.org/10.20517/2347-9264.2025.09>
- [29] Jackson J, Samarah H, Palmer W, et al. The impact of biomaterial characteristics on macrophage phenotypes in tissue engineering: a review [J]. *Plastic and Aesthetic Research*, 2025. <https://doi.org/10.20517/2347-9264.2024.166>
- [30] Ding J-Y, Ge Y-S, Shen J, et al. Anti-Senescent Biomaterials for Breaking Intervertebral Disc Degeneration [J]. *Engineering*, 2025, 53: 259–85. <https://doi.org/10.1016/j.eng.2025.07.015>
- [31] Wang Z, Lin X, Shi Y, et al. Decellularized extracellular matrix: Advanced bioplatfroms for functional tissue restoration via innovative decellularization techniques [J]. *Biomedical Technology*, 2026, 13. <https://doi.org/10.1016/j.bmt.2025.100131>
- [32] Shin H, Jeong W, Han T H. Maximizing light-to-heat conversion of Ti₃C₂Tx MXene metamaterials with wrinkled surfaces for artificial actuators [J]. *Nature Communications*, 2024, 15(1). <https://doi.org/10.1038/s41467-024-54802-0>
- [33] Phatchayawat P P, Yodmuang S, Phisalaphong M. Bacterial Nanocellulose-Chitosan-Gelatin-Hydroxyapatite Scaffolds for Bone Tissue Engineering [J]. *Macromolecular Bioscience*, 2025, 25(11). <https://doi.org/10.1002/mabi.202500299>
- [34] Han J, Zhou Z, Yin R, Yang D, Nie J. Alginate–chitosan/hydroxyapatite polyelectrolyte complex porous scaffolds: Preparation and characterization. *International Journal of Biological Macromolecules*. 2010;46(2):199-205. doi:10.1016/j.ijbiomac.2009.11.004
- [35] Downes M, Shuck C E, McBride B, et al. Comprehensive synthesis of Ti₃C₂Tx from MAX phase to MXene [J]. *Nature Protocols*, 2024, 19(6): 1807–1834. <https://doi.org/10.1038/s41596-024-00969-1>
- [36] Yang Y, Zeng Z, Zeng G, et al. Ti₃C₂ MXene/porous g-C₃N₄ interfacial Schottky junction for boosting spatial charge separation in photocatalytic H₂O₂ production [J]. *Applied Catalysis B: Environmental*, 2019, 258. <https://doi.org/10.1016/j.apcatb.2019.117956>
- [37] Zhang S, Liao S, Qi F, et al. Direct deposition of two-dimensional MXene nanosheets on commercially available filter for fast and efficient dye removal [J]. *Journal of Hazardous Materials*, 2020, 384. <https://doi.org/10.1016/j.jhazmat.2019.121367>
- [38] Govindaraju R, Paul J, Kim J, et al. Iron and nitrogen co-doped MXene quantum dots: A novel dual-mode electrochemical and fluorescence sensor for dopamine detection [J]. *Journal of the Taiwan Institute of Chemical Engineers*, 2026, 179. <https://doi.org/10.1016/j.jtice.2025.106421>
- [39] Pan X, Yang M-Q, Fu X, et al. Defective TiO₂ with oxygen vacancies: synthesis, properties and photocatalytic applications [J]. *Nanoscale*, 2013, 5(9). <https://doi.org/10.1039/c3nr00476g>
- [40] Greiner M T, Chai L, Helander M G, et al. Transition Metal Oxide Work Functions: The Influence of Cation Oxidation State and Oxygen Vacancies [J]. *Advanced Functional Materials*, 2012, 22(21): 4557–68. <https://doi.org/10.1002/adfm.201200615>
- [41] Luo P, Zhao C, Luo Q, et al. Preparation and Application of Micron-Sized ZnS QDs@Polysiloxane Core–Shell Light-Diffusion Hybrid Microspheres. *Acta Materiae Compositae Sinica*. 2023;40(3):1438–1445. [In Chinese] doi:10.13801/j.cnki.fhclxb.20220516.005
- [42] Rasool K, Helal M, Ali A, et al. Antibacterial Activity of Ti₃C₂Tx MXene [J]. *ACS Nano*, 2016, 10(3): 3674–84. <https://doi.org/10.1021/acs.nano.6b00181>