

Supplementary Information

Hierarchically structuralized hydrogels with ligament-like mechanical performance

Diwei Shi^{1,†}, Donghwan Ji^{2,3,†}, Jinhye Bae^{1,2,3*}

¹ Materials Science and Engineering Program, University of California San Diego, La Jolla, CA 92093, United States

² Aiiso Yufeng Li Family Department of Chemical and Nano Engineering, University of California San Diego, La Jolla, CA 92093, United States

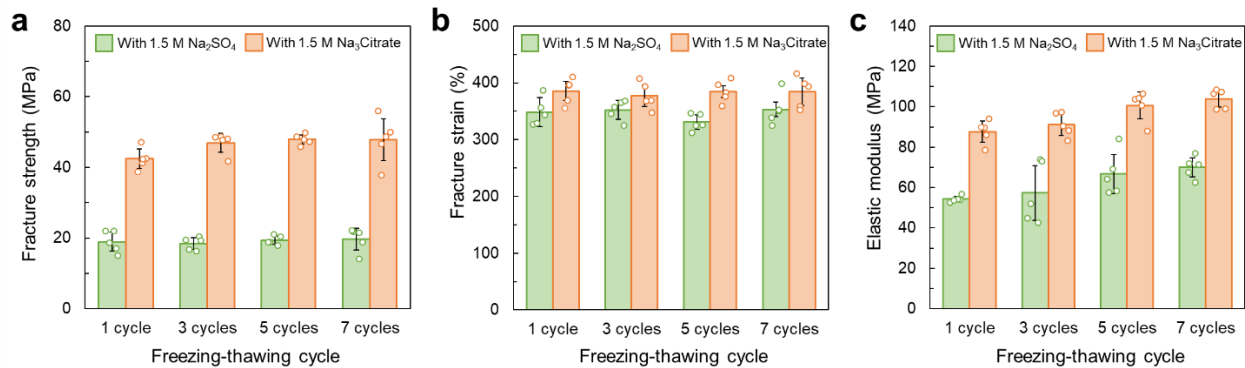
³ Department of Chemical Engineering, Chung-Ang University, 84 Heukseok-ro, Dongjak-gu, Seoul 06974 Republic of Korea

†These authors contributed equally.

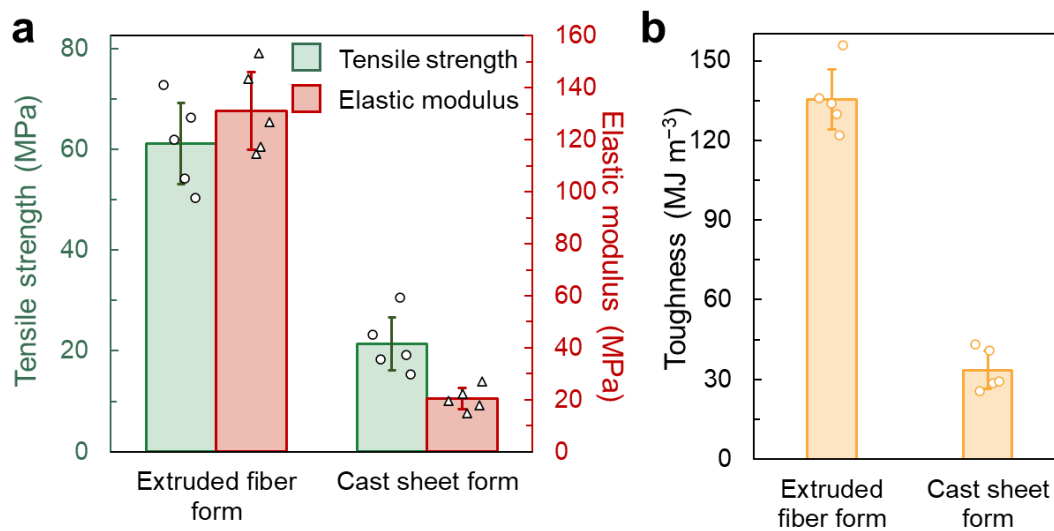
*Corresponding authors: *J. Bae* (jbae@cau.ac.kr)

Publications	Elastic modulus (MPa)	Fracture tensile strength (MPa)	Fracture elongation (%)	Work-of-fracture (MJ m ⁻³)
This work	131	61.5	430	135
Anisotropically Fatigue-Resistant Hydrogels, Advanced Materials (2021)	1	2.5	430	
Strong fatigue-resistant nanofibrous hydrogels inspired by lobster underbelly, Matter (2021)	5	3.5	340	
Poly(vinyl alcohol) Hydrogels with Broad-Range Tunable Mechanical Properties via the Hofmeister Effect, Advanced Materials (2021)	2.5	15	2100	153
Strong tough hydrogels via the synergy of freeze-casting and salting out, Nature (2021)	25	23.5	1400	210
Hierarchical Multiscale Hydrogels with Identical Compositions Yet Disparate Properties via Tunable Phase Separation, Advanced Functional Materials (2022)	1.1	7	1600	
Super-Strong, Nonswellable, and Biocompatible Hydrogels Inspired by Human Tendons, ACS Applied Materials & Interfaces (2022)	35.6	19.3	300	32.1
Strong Tough Conductive Hydrogels via the Synergy of Ion-Induced Cross-Linking and Salting-Out, Advanced Functional Materials (2022)	3.7	15	770	56
Bioinspired 2D Isotropically Fatigue-Resistant Hydrogels, Advanced Materials (2022)	18	9	250	
Coordinatively Stiffen and Toughen Hydrogels with Adaptable Crystal-Domain Cross-Linking, Advanced Materials (2023)	52.3	28	1200	199
Solvent-Exchange-Assisted Wet Annealing A New Strategy for Superstrong, Tough, Stretchable, and Anti-Fatigue Hydrogels, Advanced Materials (2023)	2.7	11.2	1360	82.9
Reinforcing Hydrogel by Nonsolvent-Quenching-Facilitated In Situ Nanofibrosis, Advanced Materials (2023)	0.6	2.7	700	10.4
Toughening Double-Network Hydrogels by Polyelectrolytes, Advanced Materials (2023)	0.5	1.5	750	5.4
ABiomimetic "Salting Out—Alignment—Locking" Tactic to Design Strong and Tough Hydrogel, Advanced Materials (2024)	7.5	20	600	70.7
Tough Supramolecular Hydrogels Crafted via Lignin-Induced Self-Assembly, Advanced Materials (2024)	14	20	500	50
Bioinspired structural hydrogels with highly ordered hierarchical orientations by flow-induced alignment of nanofibrils, Nature Communications (2024)	5	14	1700	154
3D printable strong and tough composite organo-hydrogels inspired by natural hierarchical composite design principles, Nature Communications (2024)	20.3	6.9	350	17.5
Spider-silk-inspired strong and tough hydrogel fibers with anti-freezing and water retention properties, Nature Communications (2024)	36.8	24.4	850	162
Control nucleation for strong and tough crystalline hydrogels with high water content, Nature Communications (2024)	1.9	7.4	1350	
Bamboo-inspired ultra-strong nanofiber-reinforced composite hydrogels, Nature Communications (2025)	35	48	470	122.4
Hierarchically aligned heterogeneous core-sheath hydrogels, Nature Communications (2025)	6.8	55.3	3300	1031
Cartilage-bioinspired tenacious concrete-like hydrogel verified via in-situ testing, Nature Communications (2025)	3.78	10.5	260	6.8
Robust super-structured porous hydrogel enables bioadaptive repair of dynamic soft tissue, Nature Communications (2025)	32.4	22.2	400	61.9
Thermoplastic Elastomer-Reinforced Hydrogels with Excellent Mechanical Properties, Swelling Resistance, and Biocompatibility, Advanced Science (2025)	2.8	11.2	1030	62.7
Muscle-Inspired Self-Growing Anisotropic Hydrogels with Mechanical Training-Promoting Mechanical Properties Advanced Materials (2025)	2.85	14.1	5700	465

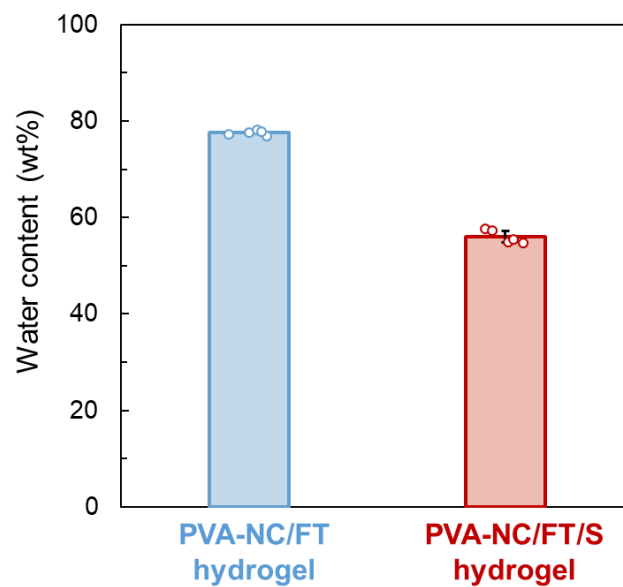
Supplementary Table 1. Summary of elastic modulus, fracture tensile strength, fracture strain, and work-of-fracture (toughness) of previously reported mechanically reinforced PVA-based hydrogels. Bright blue square: published in 2021; brown rhombus-shape diamond: published in 2022; green circle: published in 2023; purple triangle: published in 2024; Dark blue circle: published in 2025. The strength and elastic modulus of natural ligaments were displayed in a range based on literature, but the toughness value was not easy to be specifically displayed.



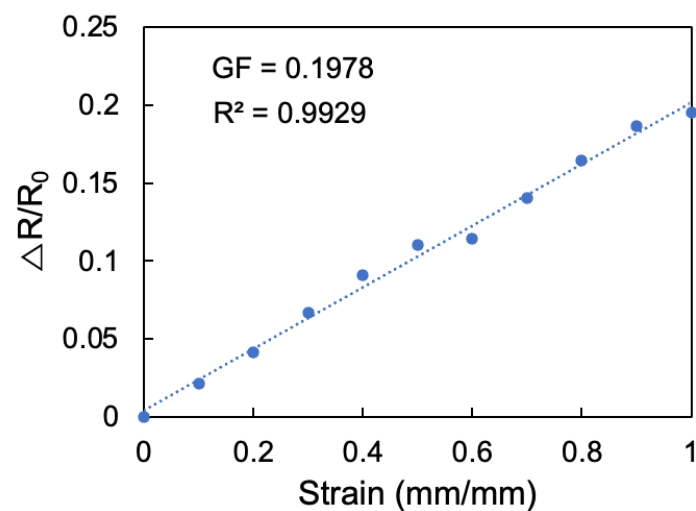
Supplementary Fig. 1. (a) Fracture strength, (b) fracture strain, and (c) elastic modulus of PVA-NC hydrogel fibers prepared by varying freezing-thawing cycles and treatment with 1.5 M Na₂SO₄ and 1.5 M Na₃Citrate, respectively. Data are presented as mean $\pm$ standard deviation ($n = 5$).



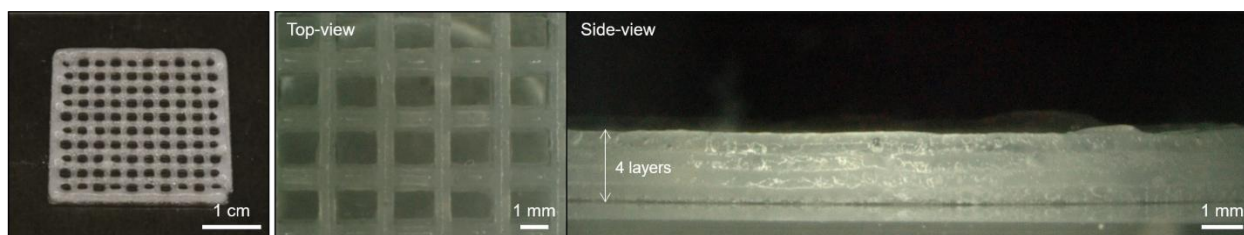
Supplementary Fig. 2. (a) Fracture tensile strength and elastic modulus, and (b) toughness of PVA-NC/FT/S hydrogels in extruded fiber form and cast sheet form, respectively. The hydrogels were processed by a single FT cycle and treated with 2.8 M Na₃Citrate solution. Data are presented as mean $\pm$ standard deviation (n = 5).



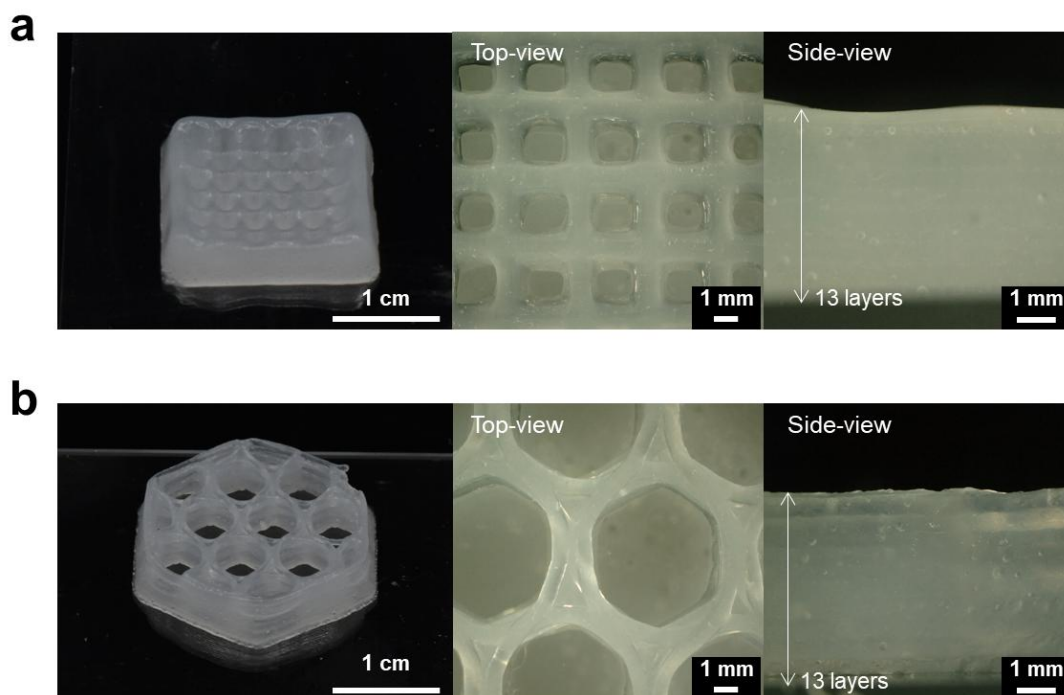
Supplementary Fig. 3. Water content of two different hydrogels. Data are presented as mean $\pm$ standard deviation (n = 5).



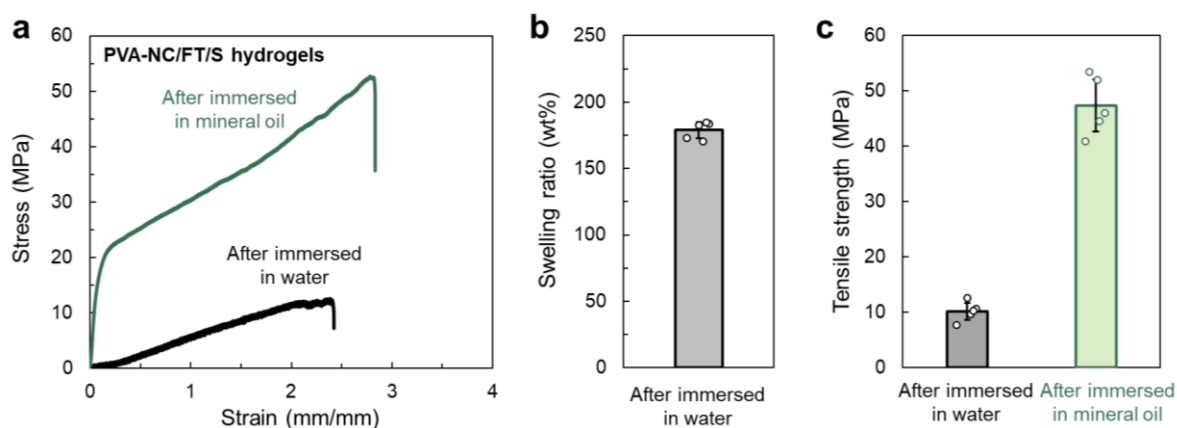
Supplementary Fig. 4. The relative resistance variation ($\Delta R/R_0$) of 8-fiber-braided hydrogel bundle over a strain region of 0–100%. The gauge factor (GF), which is defined as the slope of the $\Delta R/R_0$ versus applied strain, is 0.1978.



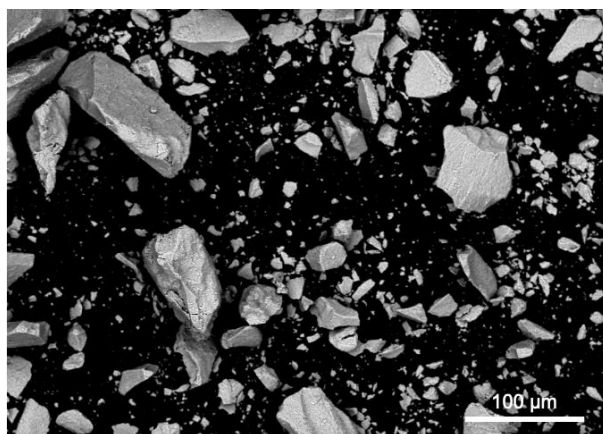
Supplementary Fig. 5. Photographs of the printed structure of PVA-NC/FT/S hydrogel.



Supplementary Fig. 6. Photographs of the printed structures of PVA-NC/FT/S hydrogel. (a) Square structure printed by a grid printing route. (b) Hexagon structure printed by a honeycomb printing route.



Supplementary Fig. 7. (a) Stress-strain curves of PVA-NC/FT/S hydrogel after immersed in mineral oil and in pure water, respectively. (b) Swelling ratio of the hydrogel in pure water. Data are presented as mean $\pm$ standard deviation ($n = 5$). (c) Tensile strength of two different hydrogels. Data are presented as mean $\pm$ standard deviation ($n = 5$).



Supplementary Fig. 8. SEM image of as-received dry NC powder.

Supplementary Movie 1. Loading (404.5g) test of individual PVA-NC hydrogel fiber treated with one freezing-thawing cycle and 2.8 M Na₃Citrate salting-out processes.

Supplementary Movie 2. Loading (404.5g) test of individual PVA-NC/FT/S, PVA-NC/S and PVA-NC/FT hydrogel fiber.

Supplementary Movie 3. Loading (13.6 kg) test of 50-fiber-braided hydrogel bundle.

Supplementary Movie 4. Real-time printing process of PVA-NC mixture.