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Supporting Information

"Freezing", Morphing, and Folding of Stretchy Tough Hydrogels

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Experimental Section

Materials: Sodium alginate was purchased from Aladdin. Acrylamide and ammonium persulphate, $CaSO_4 \cdot 2H_2O$, and $FeCl_3 \cdot 6H_2O$ were purchased from Macklin. N,N'-methylenebisacrylamide and N,N,N',N'-tetramethylethylenediamine were purchased from Sigma-aldrich.

Synthesis of Ca-alginate/PAAm tough hydrogels: Sodium alginate (0.25 g) and acrylamide (2.00 g) were dissolved in 12.5 mL deionized water. After degassing for 2 hours, 60 μL 0.10 g/mL ammonium persulphate (APS) aqueous solution as photo-thermal-initiator, 96 μL 0.025 g/mLN,N'-methylenebisacrylamide (MBAA) aqueous solution as crosslinking agent, and 10 μL N,N,N',N'-tetramethylethylenediamine (TEMED) as crosslinking accelerator were added to the former solution. Subsequently, 4 mL calcium sulphate ($CaSO_4 \cdot 2H_2O$, 0.0221 g) aqueous slurry was added as ionic crosslinker for alginate. The resulting solution was poured into a plastic container, and cured with UV light at a wavelength of 254 nm (25 W, ZF-5, Shanghaijiapeng) at 55 ^oC for 1.5 h. Subsequently, the cured mixture was left in a humid box for several hours to stabilize the reactions.

Freezing, morphing and folding of the tough hydrogels: Pieces of Ca-alginate/PAAm hydrogels were soaked in $FeCl_3$ aqueous solutions at different concentration of 0.01 M, 0.10

M, 0.30 M, 0.60 M, 1.00 M at room temperature for 1 hour, leading to the formation of Fe^{3+}/Ca-alginate/PAAm tough hydrogels. To fabricate 3D structures, tough gels were first stretched or molded into different shapes, followed by soaking in a 1.00 M Fe^{3+} ion aqueous solution for 20 min. The "frozen" 3D structures were obtained and stored in a sealed petri dish. Patterning of Fe^{3+} ions on tough hydrogels were carried out by painting on either single or both sides with a cotton swab, which was soaked in the 1.00 M Fe^{3+} solution. Tough gels with spatially encoded high stiff structures were fabricated and subjected to various demonstrations in stretching and 3D-folding/unfolding.

Water content and swelling ratio measurements of the untreated and Fe^{3+} ion-treated tough hydrogels: To measure the water content, the weights (W_{wet}) of four peices of untreated tough hydrogels and Fe^{3+} ion-treated hydrogels were measured after preparation, respectively. Afterward, the hydrogels were dried overnight with a vacuum desiccator and the weights (W_{dry}) were measured. The water content of the hydrogel gel was calculated from equation of $(W_{wet}-W_{dry})/W_{wet}$. To determine the swelling ratio, the dried tough gels were imerged in dionized water which was replaced by fresh water every 4 hours until the hydrogels reached their swollen equilibrium strates. The swelling ratio of was calculated by from equation of $W_{swollen}/W_{dry}$.

Mechanical characterization: Tensile tests of the Fe^{3+}/Ca-alginate/PAAm hydrogels were carried out by using a tensile machine (CMT4204, SANS). The samples were cut into cuboid shape (length = 25 mm, width = 15 mm, thickness = 2 mm). The size of the hydrogel was measured using a Vernier caliper. Both ends of the sample were connected to the clamps with the lower clamp fixed. The upper clamp was pulled at a constant velocity of 10 mm/min at room temperature, by which the force-displacement curve was obtained. The force-length curve and stress-strain curve were obtained from the force-displacement curve. The elastic modulus was determined by the average slope over 0~10% of strain ratio from the stress-strain curve.The fracture energy was calculated from

$$\Gamma = \frac{U(L_c)}{a_0 b_0},$$

in which L_c was the distance between two clamps when the sample started to be fractured, $U(L_c)$ was the area beneath the force-length curve when the two clamps were pulled to the distance L_c, and a_0 and b_0 were the width and thickness of the sample.

Movie S1: The video shows that the repeatable stretching and release cycles of Fe^{3+} ion patterned tough gel. The patterned area is virtually constant upon stretching and releasing.

Movie S2: The video shows that the 3D-folding and unfolding of an "S" shaped structure, which was achieved by releasing and stretching of the asymmetrically patterned tough gel.

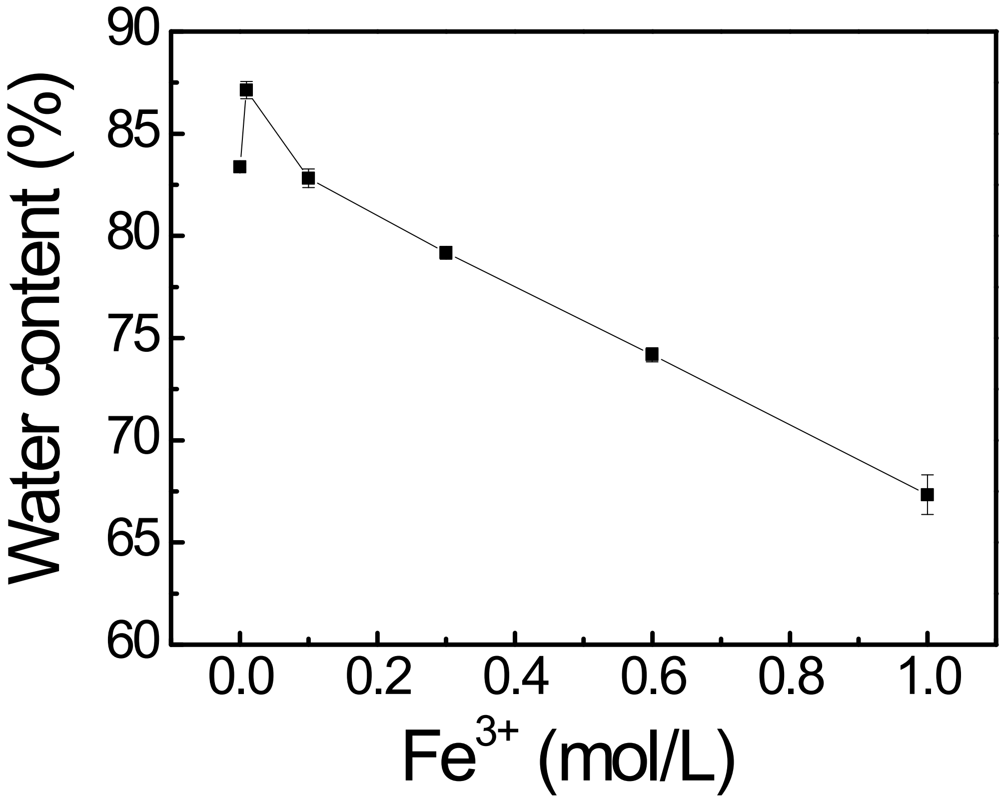

Figure S1. Water content of the untreated tough hydrogels and tough hydrogels treated with Fe 3+ ion aqueous solution of different concentrations. The water content of the untreated tough hydrogels was 83.4 ± 0.1%. By soaking in an Fe^{3+} ion solution (0.01M), the water content slightly increased to 87.1 ± 0.4%. For soaking in an Fe^{3+} ion solution with higher concentration increasing from 0.1 M to 1.0 M, the water content decreased from 82.8±0.5% to 67.3 ± 1.0%.

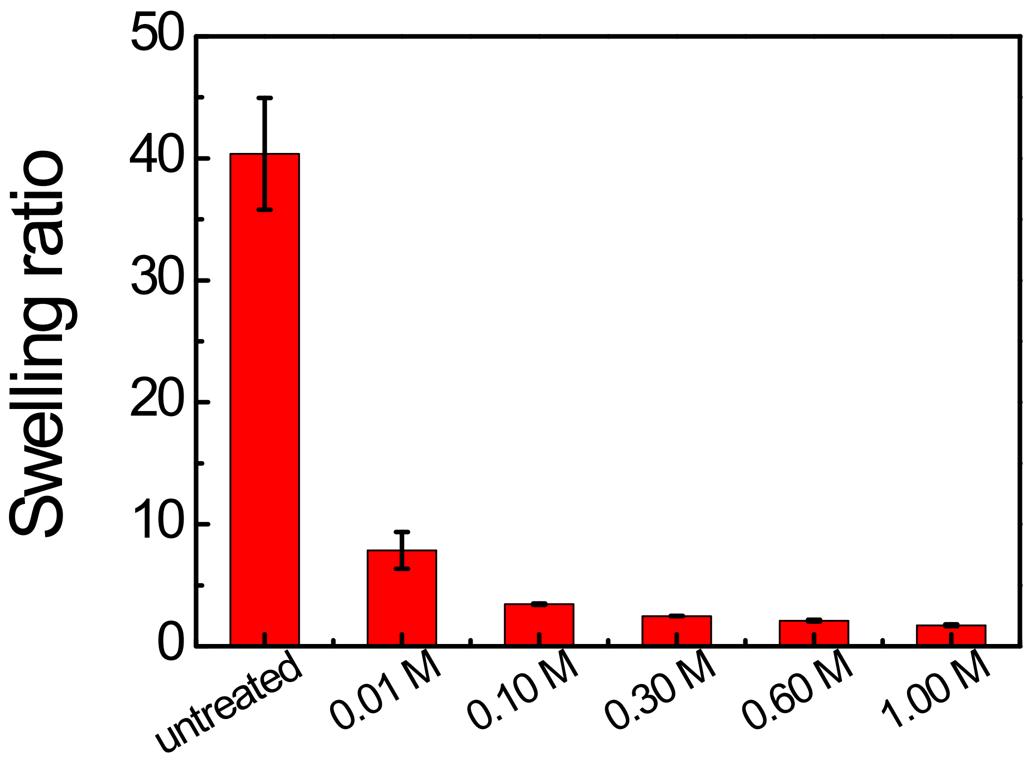

Figure S2. Swelling ratio of the untreated and Fe^{3+} ion-treated tough hydrogels at different concentrations increasing from 0.01 to 1.00 M. The swelling ratios of untreated and Fe^{3+} ion-treated hydrogels were 40.38 ± 4.59, 7.85±1.51, 3.45±0.06, 2.48±0.02, 2.10±0.07, and 1.72±0.07, respectively.

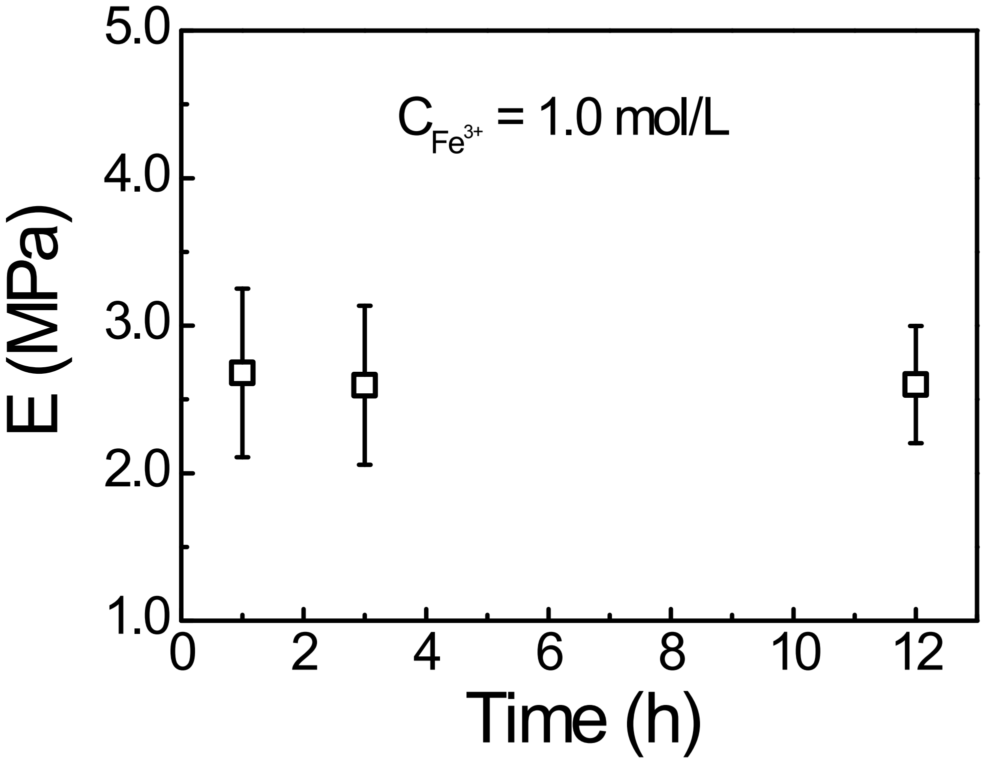

Figure S3. The elastic modulus (E) of the Fe^{3+} ion-treated tough hydrogels at different soaking durations. The E remains virtually constant within the examined soaking time.