Electronic Supplementary Information

**Designed Fabrication of Super-Stiff Hybrid Hydrogel via Linear Remodeling of Polymer Networks and Subsequent Crosslinking**

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**Experimental**

**Materials:** Alginic acid sodium salt from brown algae (Sigma), acrylamide (Sigma), ammonium persulphate (Sigma-Aldrich), N,N-methylenbisacrylamide; MBAA (Sigma), N,N,N',N'-tetramethylethylenediamine (TMEDA, Sigma), calcium sulphate (Samchun), calcium chloride dihydrate (≥99%, Sigma-Aldrich), barium chloride dihydrate (>99.0%, Kanto), aluminum chloride hexahydrate (Fluka), and iron nitrate nonahydrate (Sigma-Aldrich) were purchased and used without further purifications.

**Preparation of alginate/PAM hydrogel:** Alginate/PAM hybrid hydrogels were synthesized following a previously published method.\(^1\) First, appropriate amounts of alginate and acrylamide were dissolved in deionized water to obtain a homogeneous and transparent solution. Ammonium persulphate (4 wt% of acrylamide) as a photo-initiator, MBAA (6 wt% of acrylamide) as a cross-linker, TMEDA (0.25 wt% of acrylamide) as a cross-linking accelerator, and a calcium sulphate slurry (13.28 wt% of alginate) as an ionic cross-linker were mixed with the as-prepared solution. The final concentration of the solution was fixed
as 2 wt% alginate/12 wt% acrylamide. The resulting solution was poured on a glass plate and covered with another glass plate to set the appropriate gel thickness, which corresponds to the space between two glass plates. The solution was cured by irradiating ultraviolet light (254 nm, 6 W) for 1 hour, resulting in the alginate/PAM hybrid hydrogel. The resulting hydrogel was cut into a rectangular shape (50 × 5.0 × 3.0 mm) for further experiments.

**Linear remodeling and subsequent cross-linking of alginate/PAM hydrogels.** As-synthesized Ca-alginate/PAM hydrogels were stretched to 150 (1.5×), 200 (2×), or 300% (3×) of their initial length in one direction. The stretched hydrogels were soaked in a 100 mM aqueous solution of divalent or trivalent cations (Ba\(^{2+}\), Al\(^{3+}\), Fe\(^{3+}\)) at room temperature in their stretched state during 5 min. After secondary ionic cross-linking, the hydrogels were removed from the cross-linking solution.

**Mechanical testing.** The samples for the tensile test were cut into rectangular shapes (length 50 mm, width 5 mm, and thickness 3 mm). Tensile test of the hydrogels was performed in air at room temperature using a 10-kgf load cell (Cometech, QC-508E). The samples were connected to the grips with a fixed lower grip. The upper grip was pulled by the load cell at a constant velocity of 60 mm/min at room temperature. The stress-strain curves were measured and analyzed using QC-tech software. The modulus was determined by looking at the average slope in the linear portion of the elastic region.

**Reference**

**Fig. S1.** SEM images of linear transformation of hybrid hydrogel networks via the RsC process. Ba-alginate/PAM hybrid hydrogel prepared (a) without a stretching step and (b) with stretching to 300% of its initial length.

**Fig. S2.** The water contents of the RsC hydrogels prepared with different degrees of stretch.
**Fig. S3.** Enlarged version of Fig. 4a, stress-strain curves of $2 \times$ /Ba-alginate/PAM hydrogels with various polymer ratio with a fixed total polymer concentration of 14 wt%.

**Fig. S4.** The effects of different crosslinking ions on the elastic modulus of RsC hybrid hydrogels obtained from different degrees of stretch. The control corresponds to the Ca-alginate/PAM hydrogel.