Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Versatile controlled ion release for synthesis of recoverable hybrid hydrogels with high stretchability and notch-insensitivity

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Materials

Sodium alginate, glucono delta-lactone (GDL), $EDTANa_2$, acrylamide (AAm) monomer persulfate (KPS) and N, N'-methylenebisacrylamide (MBAA) were purchased from Aldrich. $CaCO_3$, $Co(OH)_2$, $Cu(OH)_2$, $La(OH)_3$ and $Ce(OH)_4$, which were also supplied from Aldrich, were used to react with $EDTANa_2$ to achieve ion/EDTA chelators.

Experimental section

Multivalent ion (i. e., Co^{2+}, Cu^{2+}, Ca^{2+}, La^{3+} and Ce^{4+}) /EDTA buffer solutions were first prepared. Taking Ca^{2+}/EDTA as an example, Ca^{2+}/EDTA buffer solution were first synthesized by mixing stoichiometry $EDTANa_2$ and $CaCO_3$ in DI water at 70 ºC for 4h. To synthesize the alginate/PAAm hybrid hydrogels, sodium alginate, AAm monomer and MBAA were added and mildly stirred under a water and Ca^{2+}/EDTA buffer mixture solution. After the sodium alginate powders were thoroughly dissolved, certain amount of KPS and GDL were dissolved into another 10ml Ca^{2+}/EDTA solution and mixed with the former mixture to form the hydrogel precursors. The hydrogel precursors were carefully poured into pairs of glass modes inserted with silicon spacers. They were stored at room temperature in a dark storage for 24 h to ensure the release of Ca^{2+} ions from EDTA cage. Then, the glass modes were heated in a water bath at 60 ^{o}C for another 10 h to polymerize the second PAAm network. For the first network, the sodium alginate content was kept at 4 wt % to the water weight with different amount of GDL addition. As for the soft second network, the AAm monomer content were kept constant with 1: 7 (wt%) to sodium alginate. The formulation of initiator KPS and crosslinker MBAA in the second PAAm network were both 0.01% to the mole ratio of AAM monomer.

Characterizations

Rheological investigation were conducted by using a Physical MCR-301 instrument (Anton Paar, Austria) under a constant strain amplitude (γ = 1%) and a fixed angular frequency (10 rad s^{-1}) at room temperature. The alginate/PAAm hybrid hydrogels were cut into dumbbell-shaped specimens (gauge width: 2mm, gauge length: 20mm, thickness: 3.5mm) for uniaxail tensile tests at a crosshead velocity of 100 mm min^{-1} until fracture. For tensile recovery tests, dumbbell-shaped samples (gauge width: 2 mm, gauge length: 20 mm, thickness: 2 ~ 2.5 mm) were pre-stretched to 700% strain and then immediately unloaded to their initial length. The as-prepared samples were covered with PP membrane and immersed into 80 °C hot oils. The immersed samples were picked out from the hot oil after certain time intervals, cooled at ambient temperature for 5 mins and then tested with another 700% strain loading-unloading process. Both the loading and unloading tests were conducted at the same crosshead speed of 100 mm min^{-1}. As for notch tests, film hydrogel samples (length: 30mm, gauge width: 20mm, gauge length: 10mm, thickness: 2.5mm) were prepared and artificially cut with notches in the centre and edge by a sharp knife. The notch samples were also stretched at a crosshead velocity of 100mm min^{-1} until fractured. All the mechanical tests were operated with an Instron 5567 machine (Instron Corporation, MA) and each test was repeated at least for three specimens. Swelling experiments of the hybrid hydrogels were conducted with fresh hydrogels. Typically, cylindrical fresh hydrogels （diameter = 9 mm， thickness = 3 ~ 4 mm） were immersed into 70ml DI water and the swollen hybrid hydrogels were weighted and recorded at certain time intervals until 830 min.

Results and discussion

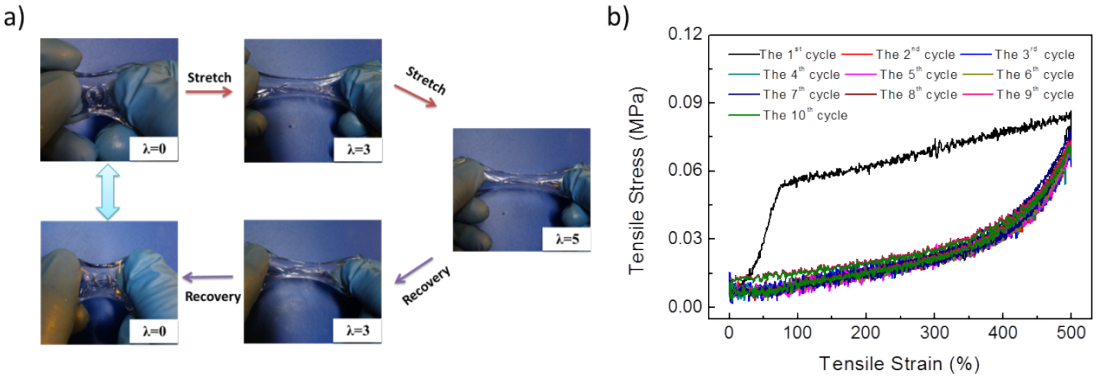

Figure S1. a) Indentation-notched hydrogel samples showed an immediate shape recovery with tensile loading-unloading cycles up to 500% strain. b) Representative cyclic loading-unloading curves of the hydrogels.

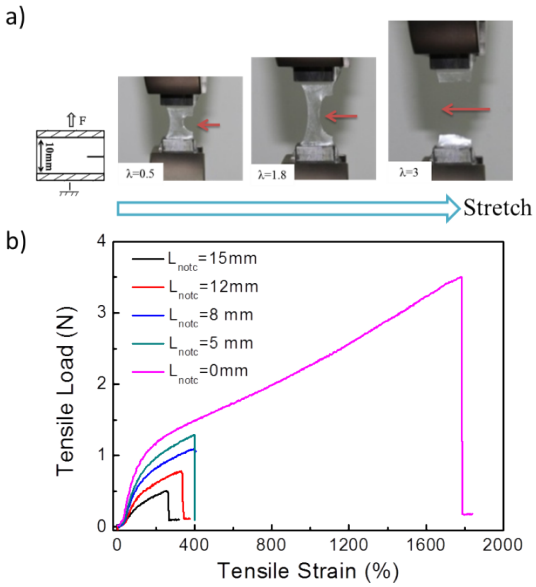

Figure S2. a) Photos of the PAAm hydrogel stretched with an 8 mm notch at the edge. b) Tensile load-strain curves of the PAAm hydrogel films with artificial notch of 0, 5, 8, 12 and 15 mm.

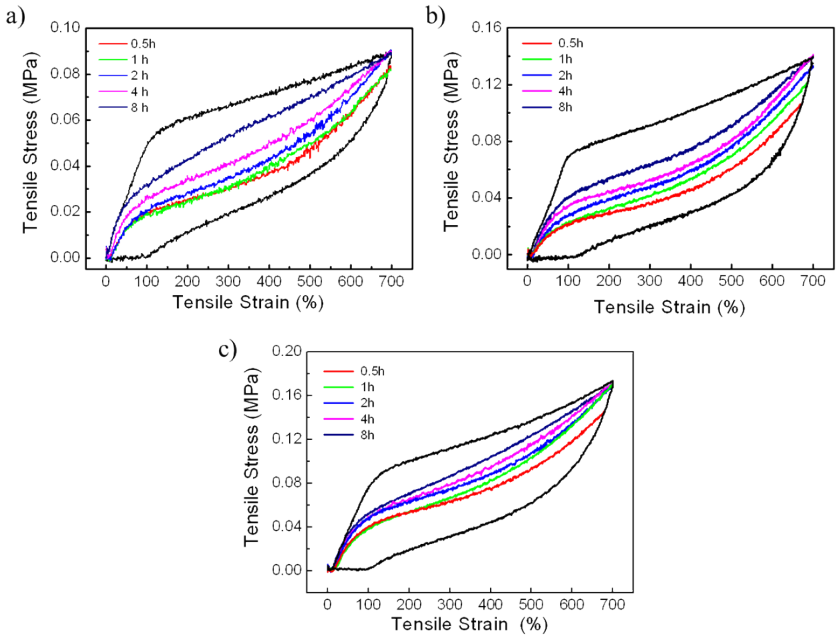

Figure S3. a-c) Tensile recovery curve of hGel-1(a), hGel-3(b) and hGel-5(c) hydrogels after immersed in oil for predefined time intervals at 80 °C.

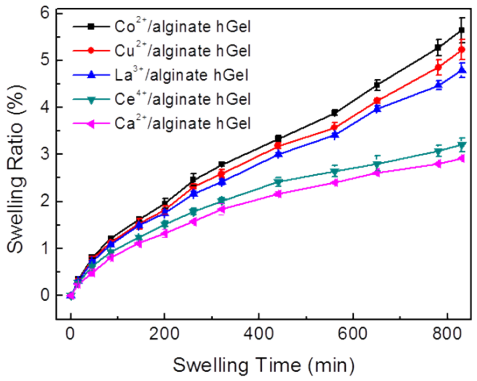

Figure S4. (a) Representative swelling curves of hybrid hydrogels crosslinked with multivalent ions (e.g., Co^{2+}, Cu^{2+}, Ca^{2+}, La^{3+} and Ce^{4+}) in DI water for 830min.