Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Hierarchically reversible crosslinking polymeric hydrogels with highly efficient self-healing, robust mechanical property, double-driven shape memory behavior

Shishan Xue,[a, e] Yuanpeng Wu,*[a, b] Guanfei Liu,[a] Meiling Guo,[a] Yuhan Liu,[a] Tao Zhang*[c] and Zhanhua Wang*[d]

[a.] *The Center of Functional Materials for Working Fluids of Oil and Gas Field, School of New Energy and Materials, Southwest Petroleum University, Chengdu 610500, Sichuan, China. E-mail: ypwu@swpu.edu.cn*
[b.] *State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, Sichuan, China.*
[c.] *College of Textile and Clothing Engineering, Soochow University, Suzhou 215123, China. E-mail: zhang.tao@suda.edu.cn*
[d.] *State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute, Sichuan University, Chengdu 610065, China. E-mail: zhwangpoly@scu.edu.cn*
[e.] *School of Chemistry and Chemical Engineering, Mianyang Normal University, Mianyang 62100, China*

Table S1 The parameters of S_xC_y-hydrogel

Name of samples	The mass fraction of the P(ATU-*co*-AM)	Times of freezing-thawing cycles
S_0C_0-hydrogel	0	0
$S_{0.5}C_0$-hydrogel	0.5%	0
$S_{1.0}C_0$-hydrogel	1.0%	0
$S_{2.0}C_0$-hydrogel	2.0%	0
S_0C_1-hydrogel	0	1
$S_{0.5}C_1$-hydrogel	0.5%	1
$S_{1.0}C_1$-hydrogel	1.0%	1
$S_{2.0}C_1$-hydrogel	2.0%	1
S_0C_2-hydrogel	0	2
$S_{0.5}C_2$-hydrogel	0.5%	2
$S_{1.0}C_2$-hydrogel	1.0%	2
$S_{2.0}C_2$-hydrogel	2.0%	2
S_0C_3-hydrogel	0	3
$S_{0.5}C_3$-hydrogel	0.5%	3
$S_{1.0}C_3$-hydrogel	1.0%	3
$S_{2.0}C_3$-hydrogel	2.0%	3

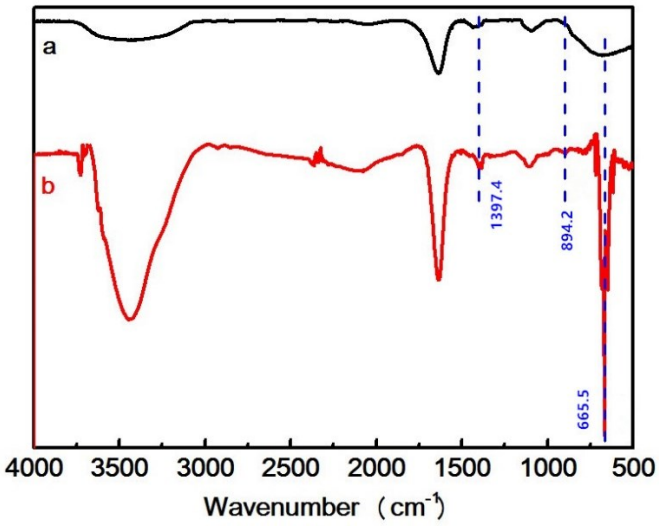

Fig. S1 FT-IR spectra of PVA-borax hydrogel immersing in (a) acid solution and (b) alkaline solution

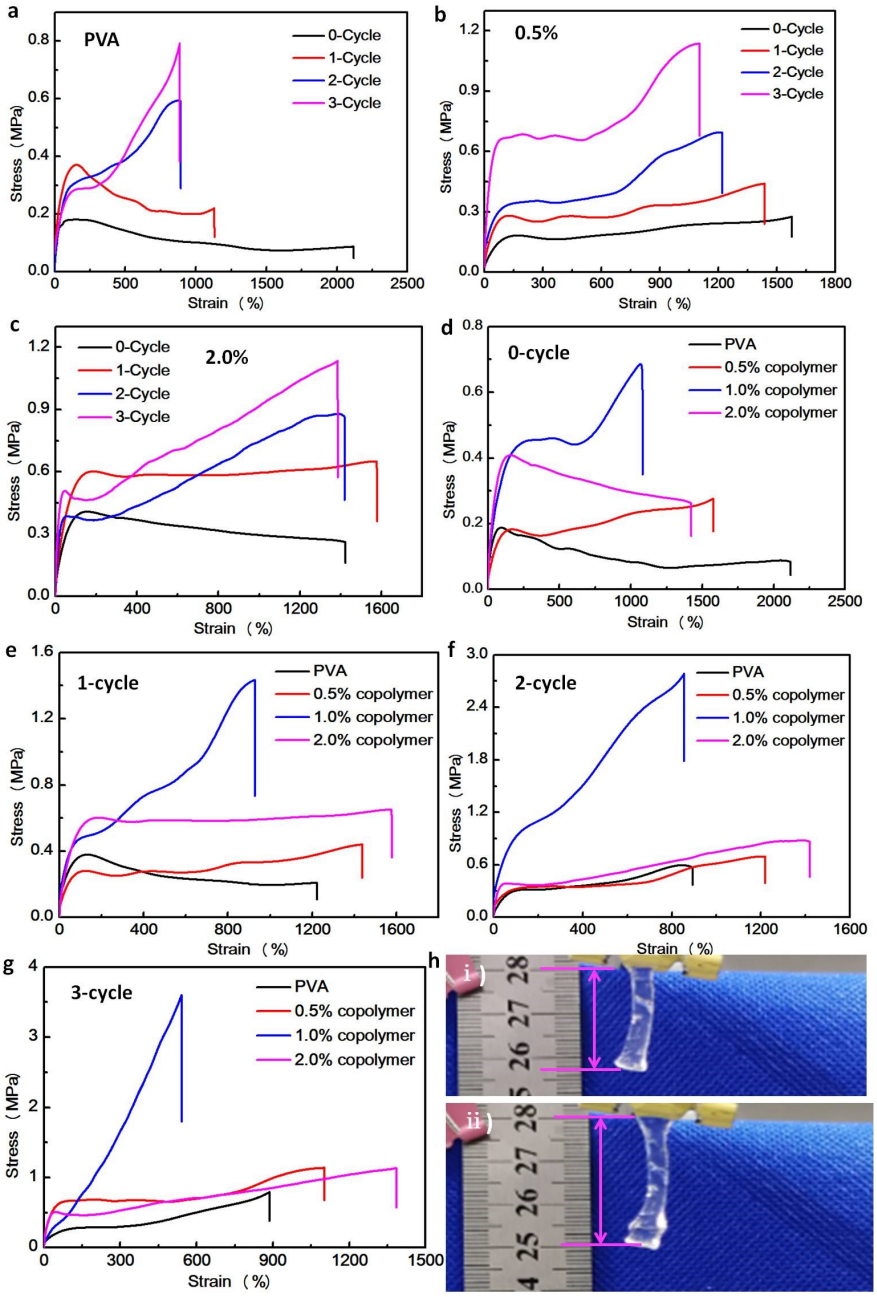

Fig. S2 Stress-strain curves of (a) S_0C_y-hydrogel (b) $S_{0.5}C_y$-hydrogel and (c) $S_{2.0}C_y$-hydrogel subjected to different freezing-thawing cycles and (d) S_xC_0-hydrogel (e) S_xC_1-hydrogel (f) S_xC_2-hydrogel (g) S_xC_3-hydrogel with different concentration of copolymer (h) the picture of the $S_{1.0}C_3$-hydrogel before (i) and (ii) after stretching.

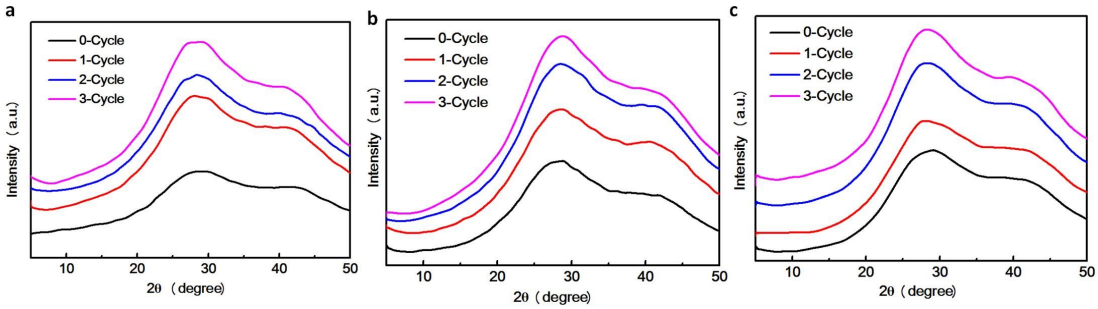

Fig. S3 X-ray diffraction patterns of (a) $S_{0.5}C_y$-hydrogels, (b) $S_{1.0}C_y$-hydrogels and (c) $S_{2.0}C_y$-hydrogels.

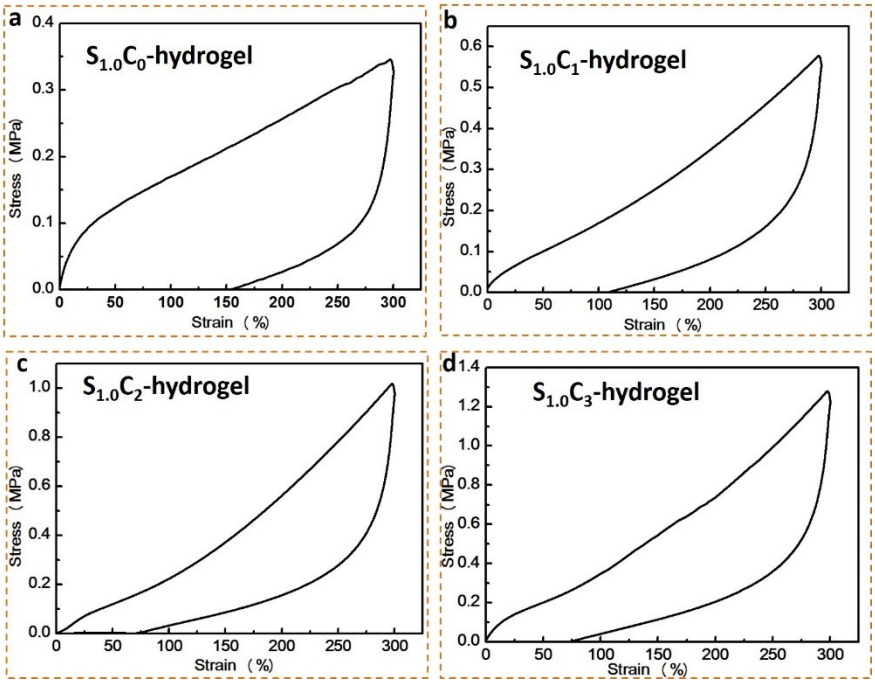

Fig. S4 Cyclic tensile of loading-unloading curves of (a) $S_{1.0}C_0$-hydrogel, (b) $S_{1.0}C_1$-hydrogel, (c) $S_{1.0}C_2$-hydrogel and (d) $S_{1.0}C_3$-hydrogel under the deformation rate of 50 mm min^{-1}

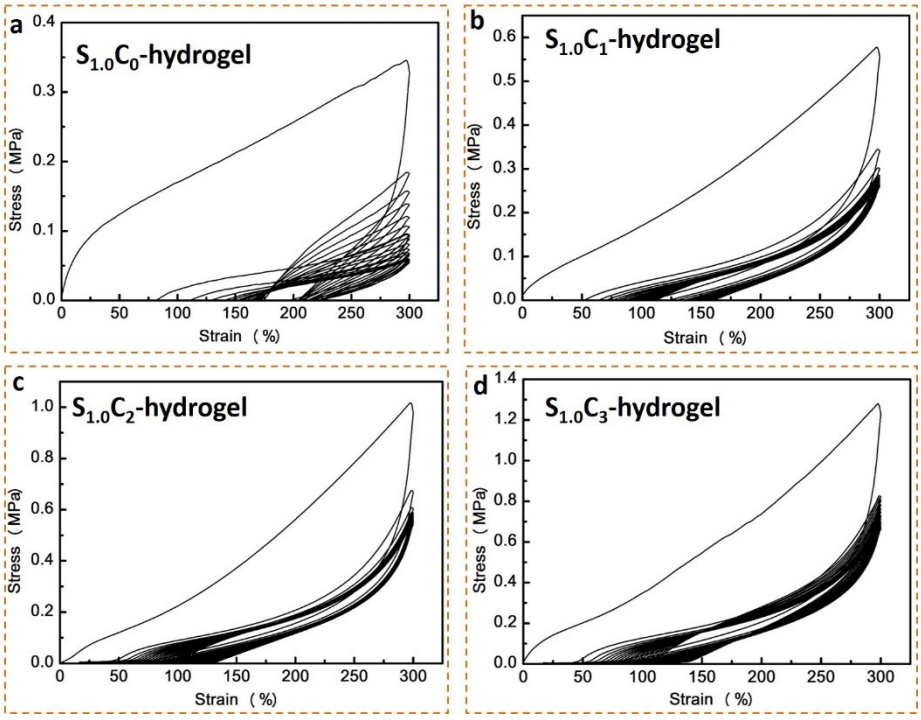

Fig. S5 Cyclic tensile loading−unloading curves of (a) $S_{1.0}C_0$-hydrogel, (b) $S_{1.0}C_1$-hydrogel, (c) $S_{1.0}C_2$-hydrogel and (d) $S_{1.0}C_3$-hydrogel at the strain of 300% for 20 times under the deformation rate of 50 mm min^{-1}

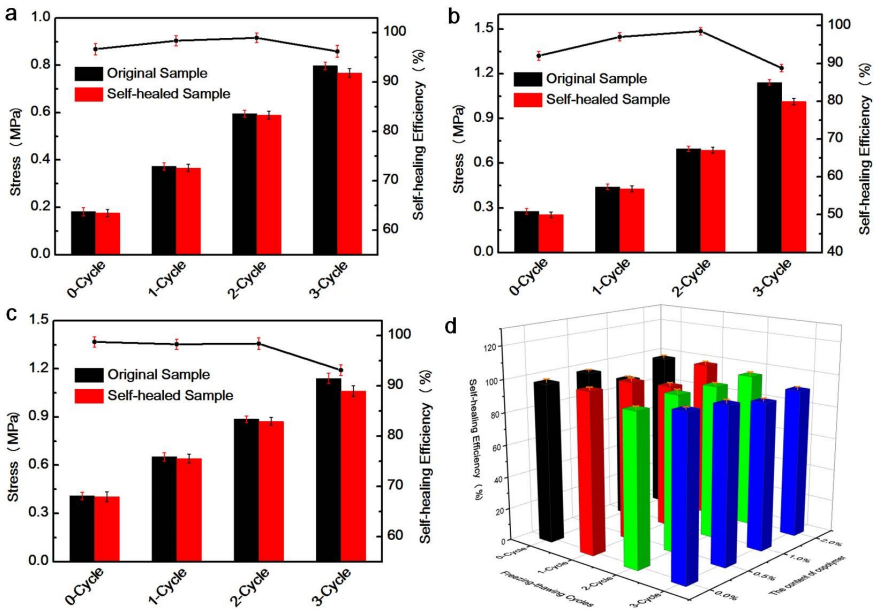

Fig. S6 (a) The tensile stress (original and self-healed samples) and self-healing efficiency of S_0C_y-hydrogels; (b) The tensile stress (original and self-healed samples) and self-healing efficiency of $S_{0.5}C_y$-hydrogels; (c) The tensile stress (original and self-healed samples) and self-healing efficiency of $S_{2.0}C_y$-hydrogels; (d) the self-healing efficiency of the elongation at break of hydrogels with different content of copolymer and different freezing-thawing cycles

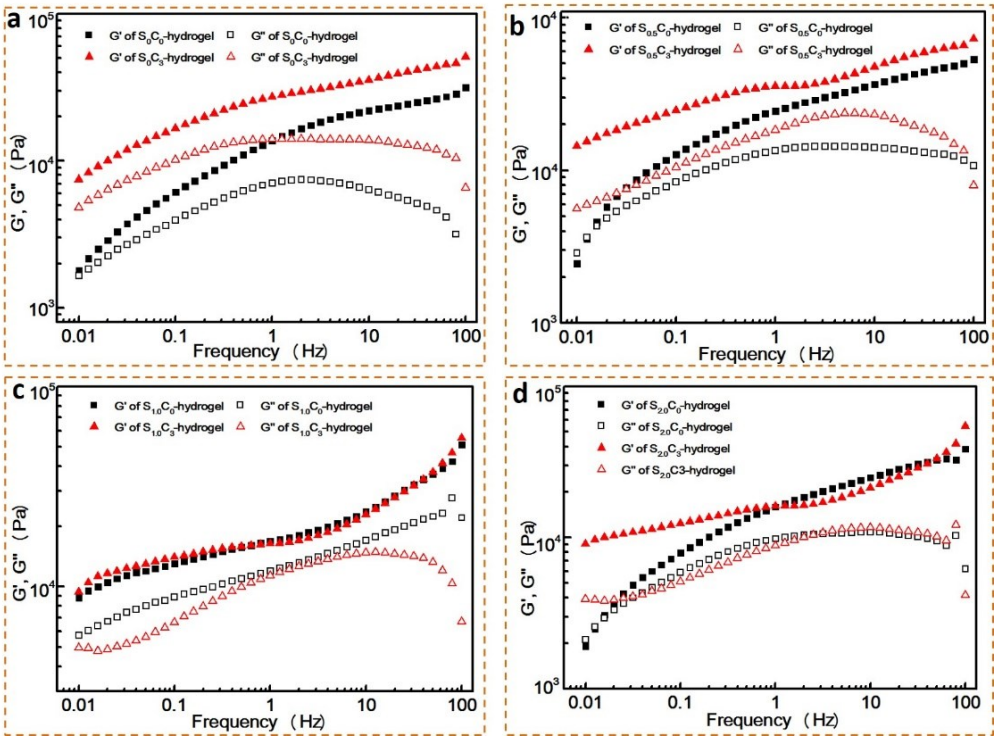

Fig. S7 Storage modulus (G') and loss modulus (G'') of (a) S_0C_0-hydrogel and S_0C_3-hydrogel, (b) $S_{0.5}C_0$-hydrogel and $S_{0.5}C_3$-hydrogel, (c) $S_{1.0}C_0$-hydrogel and $S_{1.0}C_3$-hydrogel and (d) $S_{2.0}C_0$-hydrogel and $S_{2.0}C_3$-hydrogel

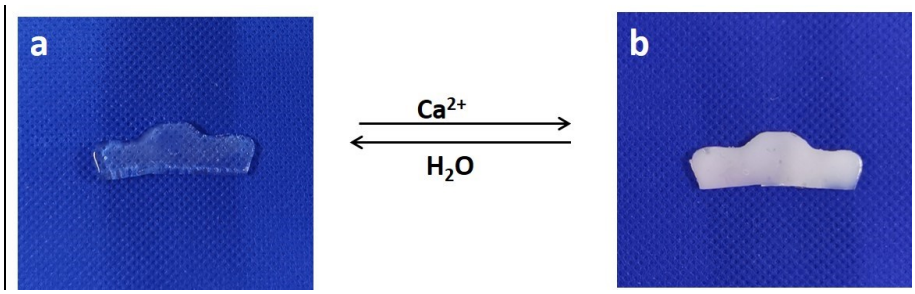

Fig. S8 The photos of PVA/P(ATU-*co*-AM) hydrogel with the "cloud" shape exhibited reversible Ca^{2+} responsiveness. (a) Before immersing in Ca^{2+} solution or after immersing in deionized water; (b) after immersing in Ca^{2+} solution.