Supplementary Information

Salt-Mediated Triple Shape-Memory Ionic Conductive Polyampholyte Hydrogel for Wearable Flexible Electronics

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1. Materials and methods

1.1 Characterization of 2-ureidoethyl methacrylate (UM)

FTIR spectrum (KBr; cm^{-1}): ν = 3456 (N-H), 3405, 3343 (N-H), 2958 (C-H), 2888 (C-H), 1718 (C=O), 1655 (C=O), 1574 (N-H). ^1H NMR (D_2O, ppm, 10 mg/mL): δ=1.94 (CH_3-C=CH_2), 3.46 (-C-CH_2-N-), 4.20 (-O-CH_2-CH_2-), 5.58 (CH_2=C-), 6.12 (CH_2=C-).

1.2. Synthesis of N-acryloyl glycinamide (NAGA)

The method of NAGA synthesis references to the work of Liu etal.[1] The details are as follows: 6.3g glycinamide hydrochloride, 6 mL cold deionized water, 33.6 mL of 2.0 mol/L cool potassium carbonate and 18 mL cold diethyl ether were added into a three-necked flask which was placed in an ice bath. Subsequently, a solution of 5.70 g of acryloyl chloride in 24 mL diethyl ether was slowly dropwised into three-necked flask. Then the mixture was further stirred for 4 hours at room temperature. After that, the pH of the solution was adjusted to 2 by using 6 mol/L HCl. Next, 150 mL of diethyl ether was used to wash the mixture to remove the organic phase and the remaining diethyl ether was evaporated under vacuum. Again, 2.0 mol/L NaOH was added into the mixture to adjust pH to neutral, and the mixture was freeze-dried. The raw product was washed three times with 150 mL of ethanol/methanol mixture (4/1, V/V). Then the ethanol and methanol were removed by rotary evaporation and the mixture left was recrystallized at 0 ºC to obtain the resultant NAGA which was dried in vacuum.

Characterization of NAGA. FTIR spectrum (KBr; cm^{-1}): ν = 3387, 3314 and 3191 (N-H), 1662, 1627 (C=O). ^1H NMR (D_2O, ppm, 10 mg/mL): δ=3.82 (CH_2-C=O), 5.57, 5.64 (H-C*H*=CH-), 6.06, 6.10 (*H*-CH=CH-), 6.13, 6.16, 6.18 and 6.20 (CH_2=C*H*-C-). The ^1H NMR and FTIR spectra of the polymers are shown in Fig. S2 and Fig. S3, respectively.

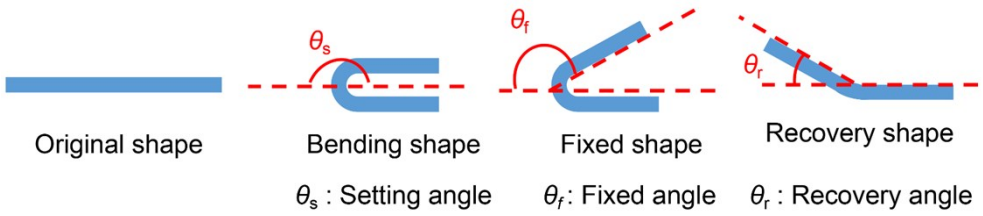

Fig. S1 Schematics of fixation and recovery progresses of P(NaSS-*co*-DMAEA-Q-*co*-UM) hydrogel. θ_s and θ_f represent the angles of original angle settled by external force and initial angle in the temporary shape, respectively. θ_r represents the angle of final angle of the recovered shape.

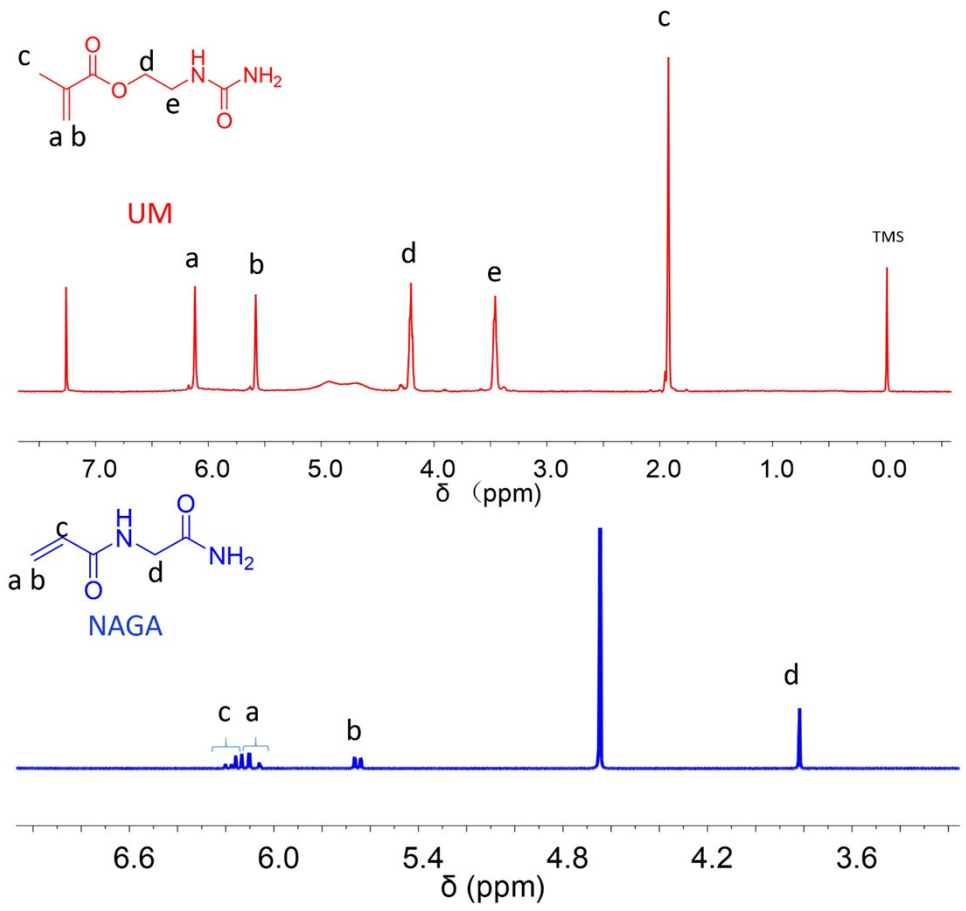

Fig. S2 ^{1}H NMR spectra of the monomers of UM and NAGA.

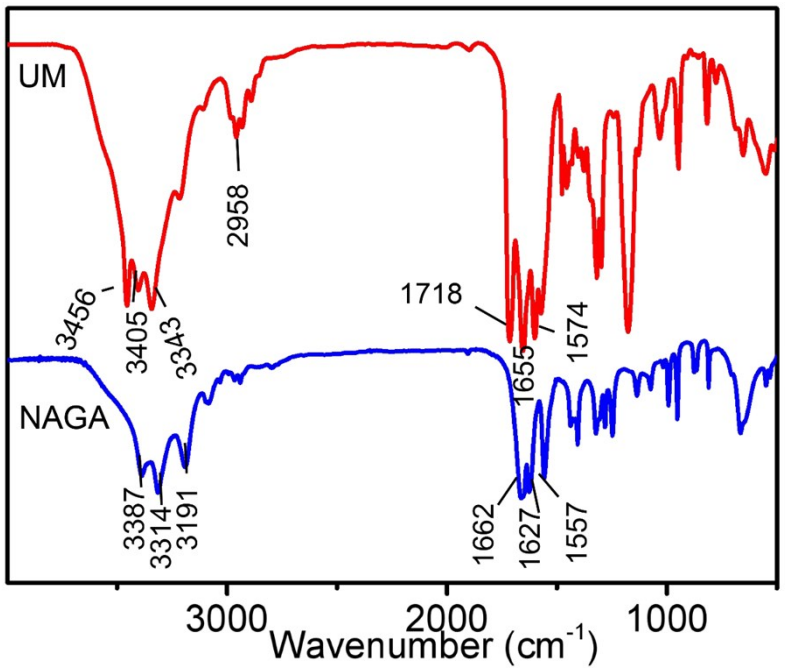

Fig. S3 FTIR spectra of the monomers of UM and NAGA.

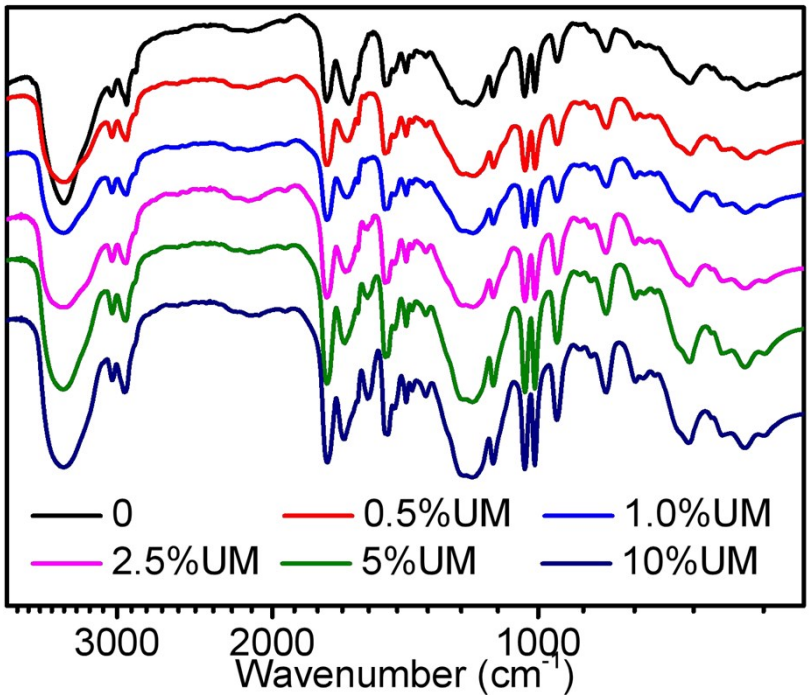

Fig. S4 FTIR spectra of P(NaSS-*co*-DMAEA-Q-*co*-UM) with different physical cross-linker monomer UM concentrations at 25°C.

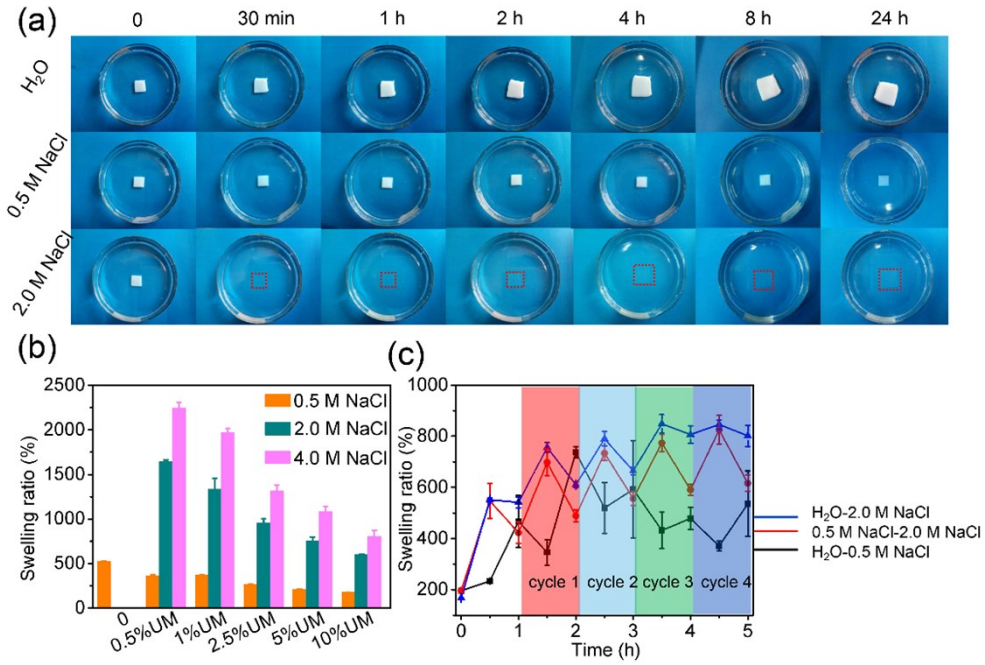

Fig. S5 (a) Photographs illustrate the swelling behavior of the polyampholyte hydrogel P(NaSS-*co*-DMAEA-Q-*co*-UM$_{1\%}$) in deionized water, 0.5 M NaCl solution and 2.0 M NaCl solution. (b) Swelling ratio of the polyampholyte hydrogel with different components of UM. (c) Swelling property of the P(NaSS-*co*-DMAEA-Q-*co*-UM$_{1\%}$) hydrogel in 4 cycles of immersing in alternant solutions.

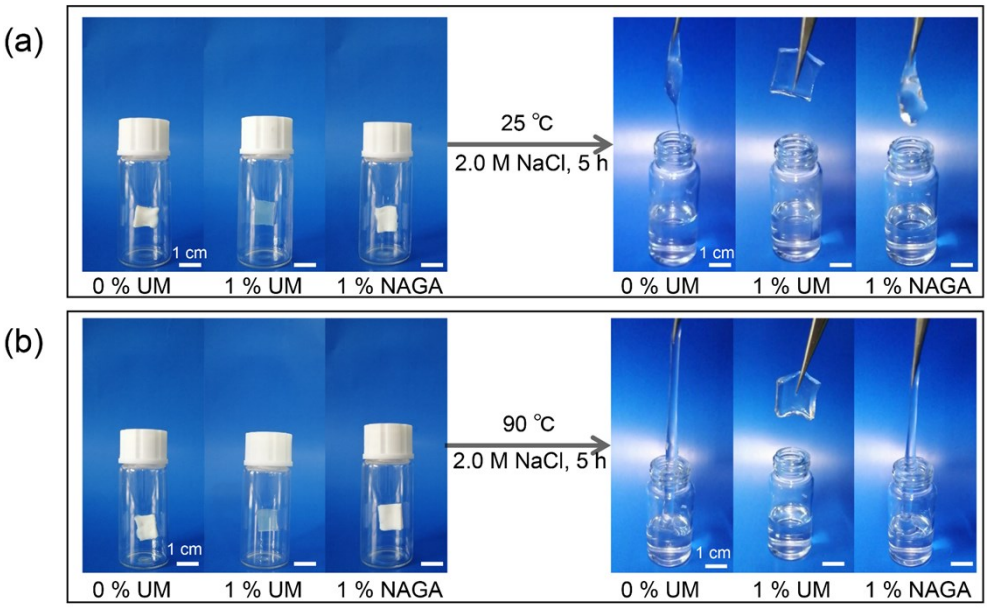

Fig. S6 Stability of the polyampholyte hydrogel in 2.0 M NaCl solution and high temperature.

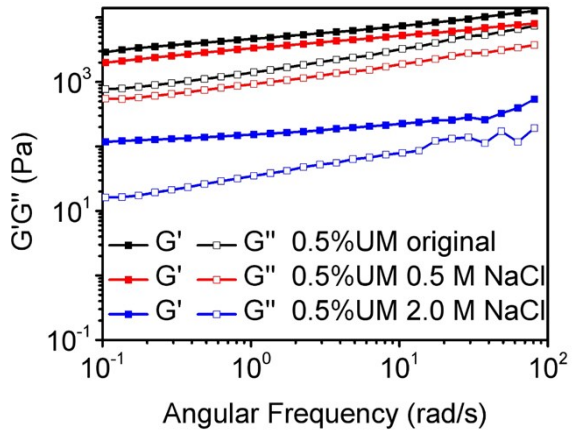

Fig. S7 Frequency dependence of storage modulus G′and loss modulus G″ at 1% strain measured by rheological measurements.

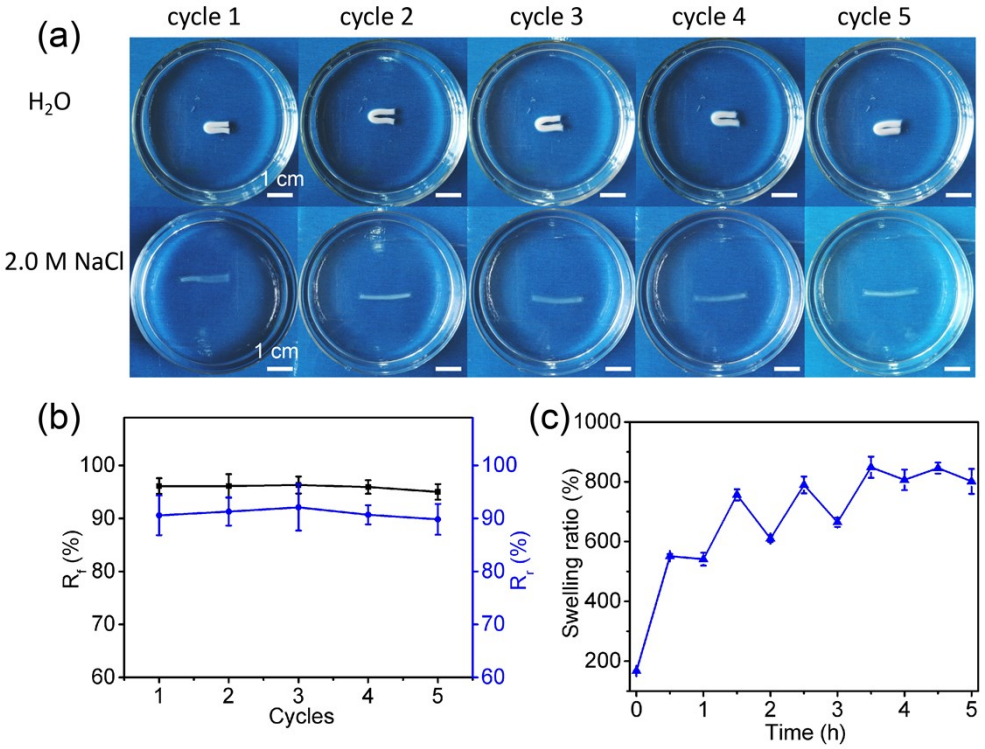

Fig. S8 (a) Photographs illustrate the 5 cyclic shape-memory performance of the P(NaSS-*co*-DMAEA-Q-*co*-$UM_{1\%}$) between 2.0 M NaCl solution and demonized water. (b) The fixed ratio and recovery ratio of the 5cyclic shape-memory process. (c) The swelling behaviour during the 5 cycles between 2.0 M NaCl solution and deionized water.

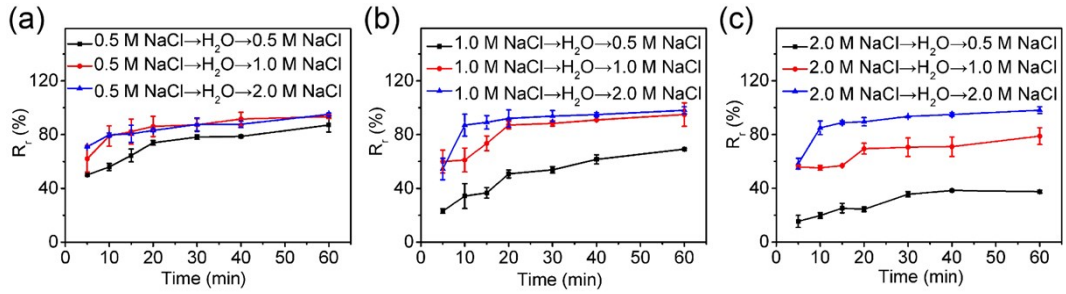

Fig. S9 The recovery time of P(NaSS-*co*-DMAEA-Q-*co*-$UM_{1\%}$) hydrogel with different concentrations of salt solutions. (a) Hydrogel was initially immersed in 0.5 M NaCl solution for 30 min，deformed and fixed in the H_2O, and recovered in 0.5 M NaCl, 1.0 M NaCl, and 2.0 M NaCl solution, respectively. (b) Hydrogel was initially immersed in 1.0 M NaCl solution for 30 min, and the R_r in different NaCl solutions was measured. (c) Hydrogel was initially immersed in 2.0 M NaCl solution for 30 min, and the R_r in different NaCl solutions was measured.

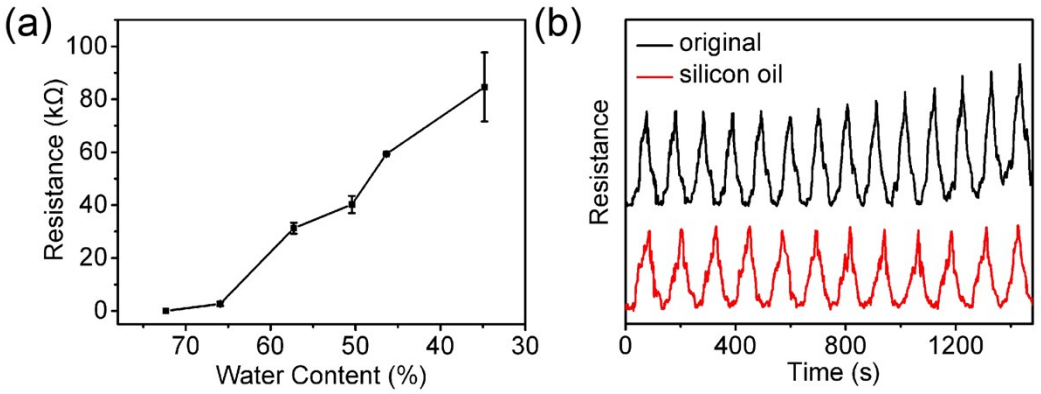

Fig. S10 (a) The resistance of the hydrogel with various water content. (b) Resistance changes of the polyampholyte hydrogels including original P(Nass-*co*-DMAEA-Q-*co*-$UM_{1\%}$) hydrogel and P(Nass-*co*-DMAEA-Q-*co*-$UM_{1\%}$) hydrogel with coating silicon oil during cyclic loading/unloading tests with strain varying between 0 and 300%.

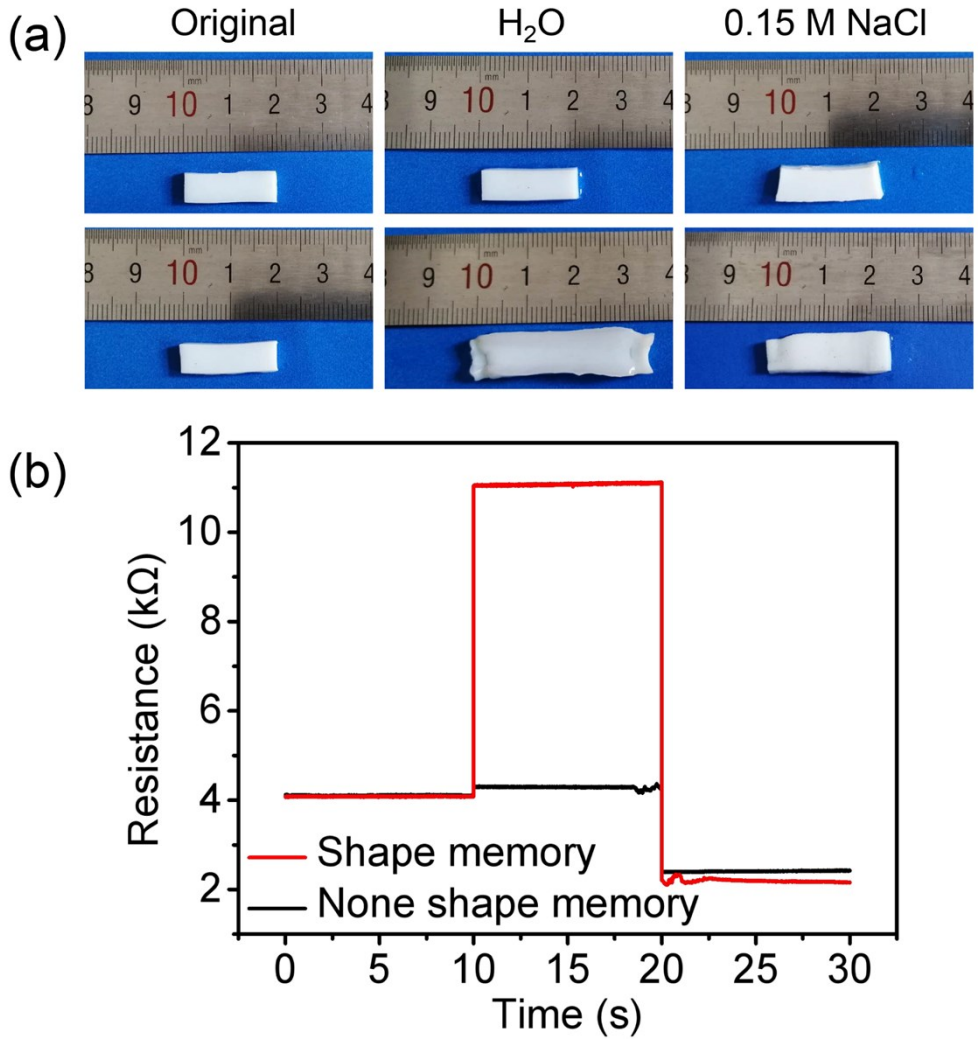

Fig. S11 (a) Signals from shape-memory progress of hydrogels (b) The effect of shape recovery on the resistance of P(NaSS-*co*-DMAEA-Q-*co*-$UM_{0.5\%}$).

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Table S1. The weight percentage of elements in polyampholyte hydrogel of P(NaSS-*co*-DMAEA-Q) through element analysis.

wt % (C)	*wt* % (H)	*wt* % (N)	*wt* % (S)	*f*
48.00	7.48	3.45	7.55	0.42

Table S2. Summary of mechanical properties of P(NaSS-*co*-DMAEA-Q-*co*-UM) hydrogels (measured at a stretching speed of 100 mm/min).

Sample	Elasticity modulus E (kPa)	Tensile strength σ_b (kPa)	Elongation at break ε_b (%)
P(NaSS-*co*-DMAEA-Q)	13.3±1.2	44.3±7.1	1505±344
P(NaSS-*co*-DMAEA-Q-*co*-$UM_{0.5\%}$)	29.2±4.6	58.5±9.2	806±97
P(NaSS-*co*-DMAEA-Q-*co*-$UM_{1\%}$)	48.6±4.5	99.7±9.2	1034±65
P(NaSS-*co*-DMAEA-Q-*co*-$UM_{2.5\%}$)	61.0±2.3	133.4±9.7	959±98
P(NaSS-*co*-DMAEA-Q-*co*-$UM_{5\%}$)	62.8±4.3	123.8±4.0	409±77
P(NaSS-*co*-DMAEA-Q-*co*-$UM_{10\%}$)	120±2.6	143.1±9.5	492±42
P(NaSS-*co*-DMAEA-Q-*co*-$UM_{1\%}$)/0.5 M NaCl	21.8±1.3	32.5±0.7	752±39
P(NaSS-*co*-DMAEA-Q-*co*-$UM_{1\%}$)/2.0 M NaCl	5.5±1.3	13.0±5.7	518±144
P(NaSS-*co*-DMAEA-Q-*co*-$NAGA_{1\%}$)	17.6±1.4	47.9±1.2	1131±157
P(NaSS-*co*-DMAEA-Q-*co*-$MBAA_{1\%}$)	123±4.2	81.1±20.9	157±20

Table S3. Summary of shape-memory properties of P(NaSS-*co*-DMAEA-Q-*co*-UM) hydrogels. (Including fixed ratio and recovery ratio during shape-memory process)

Sample	Fixed ratio R_f(%)			Recovery ratio R_r(%)		
	2.0 M NaCl ↕ H_2O	0.5 M NaCl ↕ H_2O	2.0 M NaCl ↕ 0.5M NaCl	2.0 M NaCl ↕ H_2O	0.5 M NaCl ↕ H_2O	2.0 M NaCl ↕ 0.5 M NaCl
P(NaSS-*co*-DMAEA-Q-*co*-$UM_{0.5\%}$)	94.8±1.2	82.8±8.6	54.1±9.7	90.0±5.8	80.8±2.4	85.0±3.2
P(NaSS-*co*-DMAEA-Q-*co*-$UM_{1\%}$)	90.7±3.4	66.5±6.5	69.4±5.6	91.6±0.9	81.9±8.0	89.2±6.3
P(NaSS-*co*-DMAEA-Q-*co*-$UM_{2.5\%}$)	81.5±4.5	61.7±5.5	39.4±7.1	86.3±3.8	80.4±3.4	82.1±8.0
P(NaSS-*co*-DMAEA-Q-*co*-$UM_{5\%}$)	43.9±8.4	44.4±1.9	6.9±2.1	95.1±2.6	80.4±3.4	79.5±8.8
P(NaSS-*co*-DMAEA-Q-*co*-$UM_{10\%}$)	47.0±2.5	53.2±2.3	11.7±3.1	87.4±1.2	73.2±8.2	73.3±3.8

Reference

1. Y. Zhang, H. Gao, H. Wang, Z. Xu, X. Chen, B. Liu, Y. Shi, Y. Lu, L. Wen, Y. Li, Z. Li, Y. Men, X. Feng and W. Liu, *Adv. Funct. Mater.*, 2018, **28**, 1705962.