

## Supporting Information

### **Ca<sup>2+</sup>, Redox, Thermoresponse Supramolecular Hydrogel with Programmed Quadruple Shape Memory Effect**

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### **Experimental**

#### **1. Materials**

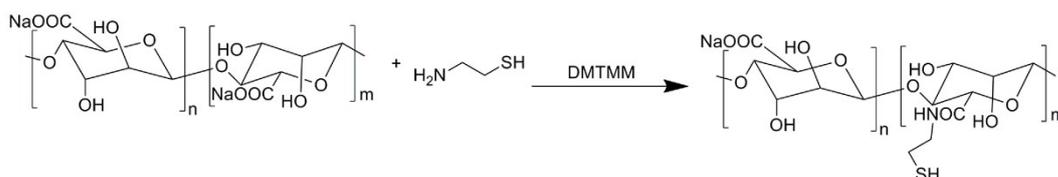
Sodium alginate(SA), Poly(vinyl alcohol) (PVA, average MW 145000), Cysteamine Hydrochloride, Ethylenediaminetetraacetic acid disodium salt (EDTA.2Na) were obtained from Aladdin. DL-1,4-Dithiothreitol (DTT) were received from Energy Chemical. 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM) were purchased from Yuanye Co., Ltd. Calcium chloride anhydrous (CaCl<sub>2</sub>) and Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) were purchased from Guangzhou Huada Chemical Co., Ltd. All the chemicals were used without further purification.

#### **2. Instruments**

The rheological measurements were performed on a stress-controlled rheometer AR-G2 (TA). Microscopic structure of the hydrogels were observed by SU8220 (Hitachi) Scanning electron microscope (SEM). Fourier transform infrared (FTIR) spectra were recorded on a VERTEX 70 Fourier transform IR spectrophotometer. Raman spectra were obtained from a FT-Raman spectrometer (Nicolet NXR9650).

### 3. Preparation of cysteamine grafted Sodium alginate (SA-SH)

SA-SH was prepared by grafting cysteamine in the presence of 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM). Sodium alginate (1.5 g, 7 mmol on monomer unit) was dissolved in 150 mL deionized water and stirred for 4 hours at room temperature, then DMTMM (1.93 g, 7 mmol) was added to the solution. After stirring at room temperature for 1h, the Cysteamine Hydrochloride (0.53 g, 4.67 mmol) was added, shielded from light, protected with the N<sub>2</sub> atmosphere, stirring at room temperature for 24 hours. The reaction mixture was poured in 500 mL of ethanol. Thiolated sodium alginate so obtained after being washed three times with ethanol and dried at room temperature. The IR spectra of sodium alginate (SA) and SA-SH are shown in Fig. S1, the peaks at 1645 and 1555 cm<sup>-1</sup> correspond to the amide I, C=O stretching vibrations, and amide II band, N-H bending vibrations, respectively, indicating cysteamine was successfully grafted on Sodium alginate.<sup>1</sup>



Scheme S1 The synthetic route of SA-SH

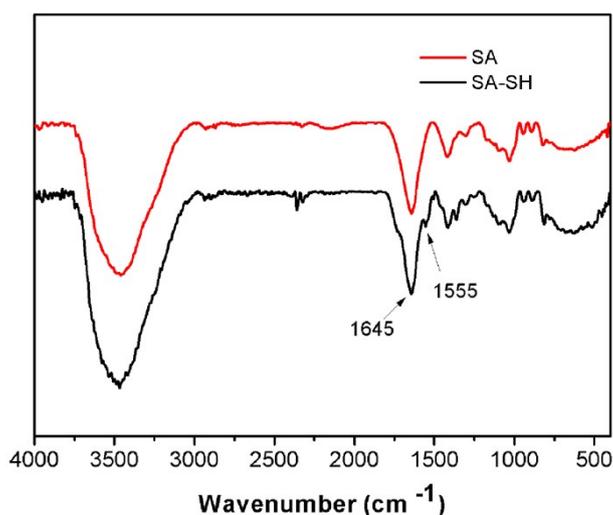


Fig. S1 IR spectra of SA and SA-SH.

### 4. Preparation of SA-SH/PVA hydrogel

The SA-SH solution was obtained by dissolving 0.5 g SA-SH and 1g PVA in 10 mL deionized water. Subsequently, the mixture was subjected to the freezing/thawing treatment, during which the SA-SH/PVA hydrogel was cooled to  $-18^{\circ}\text{C}$  for 11 hours and then thawed at room temperature for 1 hour. This procedure repeated for 6 cycles.

## 5. IR Characterization of hydrogels

IR characterization of SA-SH/PVA hydrogels immersed in 0.2 M  $\text{CaCl}_2$  solution for various time (0 h, 3 h, 9h) were showed in Fig. S2. The asymmetric stretch and the symmetric stretch vibration of  $\text{COO}^-$  groups peaked at 1602 and 1412  $\text{cm}^{-1}$ , respectively.<sup>2</sup> With the increasing time immersed in calcium chloride solution, the

$\text{COO}^-$  symmetrical stretch peak shift from 1412  $\text{cm}^{-1}$  to 1420  $\text{cm}^{-1}$ , which proved the interactions between calcium ions and  $\text{COO}^-$  of alginate.

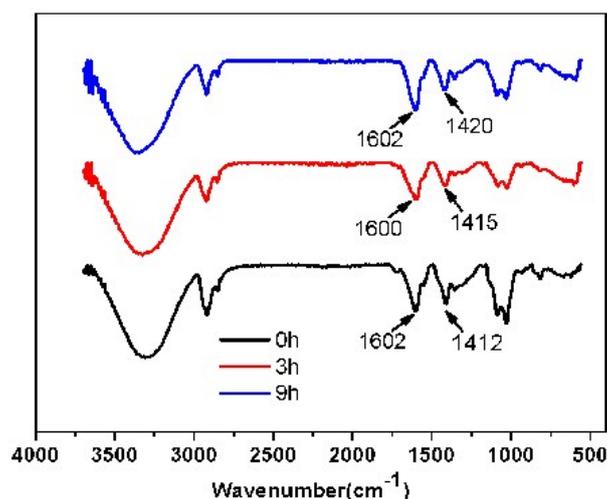


Fig. S2 IR spectra of SA-SH/PVA hydrogel immersed in 0.2 M  $\text{CaCl}_2$  solution for various time (0 h, 3 h, 9h).

## 6. FT-Raman Characterization of hydrogel

The FT-Raman spectrum of SA-SH/PVA hydrogel immersed in  $H_2O_2$  solution was shown in Fig. S3, The disulfide bond at  $512\text{ cm}^{-1}$  appeared, while there was no thiol peak at  $2570\text{ cm}^{-1}$ . It proved the thiol groups in hydrogel were oxidized to disulfide

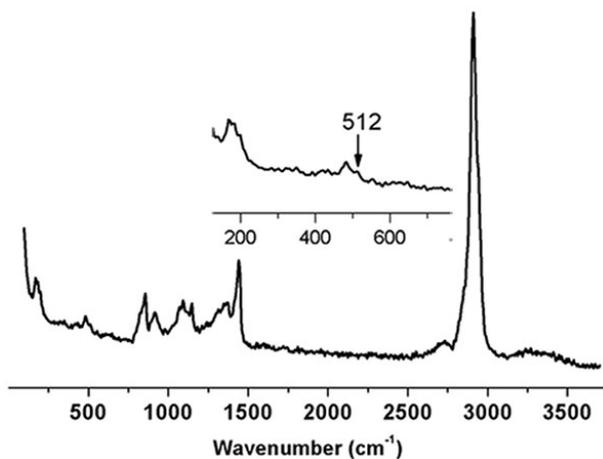


Fig. S3 FT-Raman spectrum of SA-SH/PVA hydrogel immersed in  $H_2O_2$  solution.

bonds by  $H_2O_2$  .

## 7. Shape memory behavior

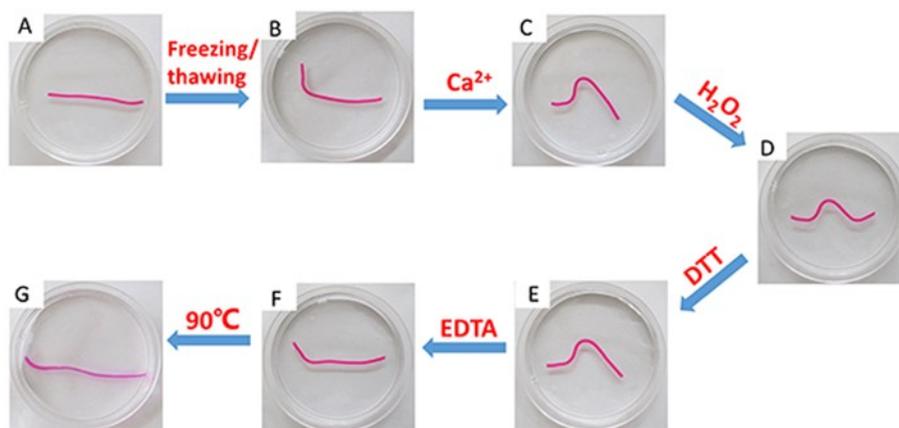


Fig. S4 Photographs of programmed quadruple shape memory performance of SA-SH/PVA hydrogel induced by thermal,  $Ca^{2+}$  and redox as the stimulus in sequence. A-D) programmed shape memory behaviour. D-G) programmed shape recovery behaviour.

## 8. Shape memory cycle

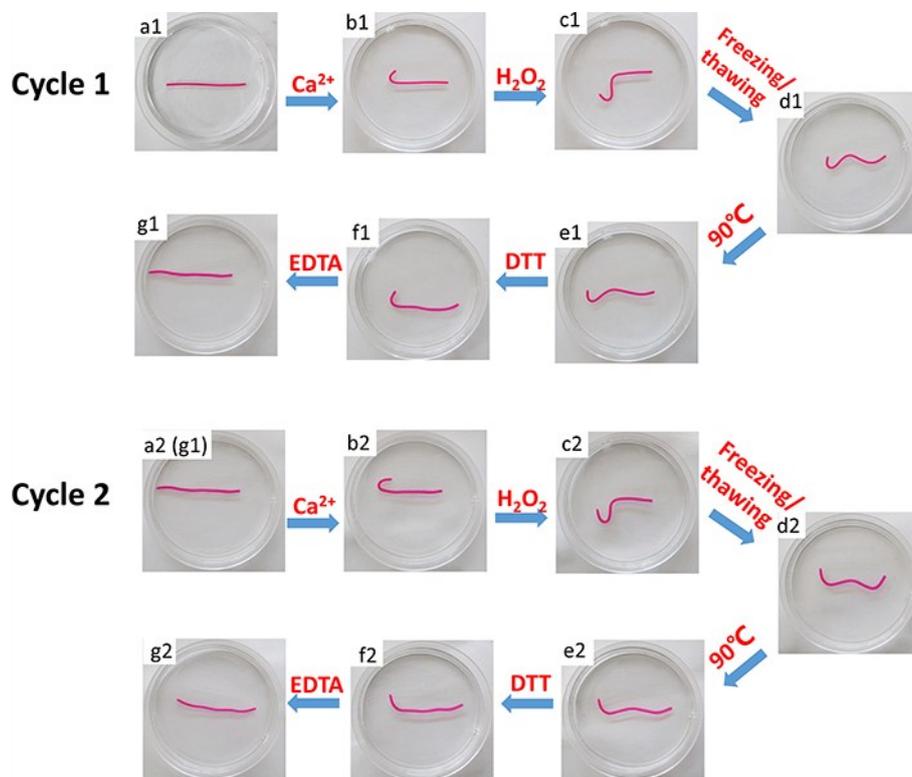


Fig. S5 Cycled programmed quadruple shape memory performance of SA-SH/PVA hydrogel induced by  $\text{Ca}^{2+}$ , redox and thermal as the stimulus in sequence. a1-d1) programmed shape memory behaviour in the first cycle. d1-g1) programmed shape recovery behaviour in the first cycle. a2-d2) programmed shape memory behaviour in the second cycle. d2-g2) programmed shape recovery behaviour in the second cycle.

### Reference

- 1 Y. Zhao, S. Gao, S. Zhao, Y. Li, L. Cheng, J. Li and Y. Yin, *Materials Science and Engineering: C*, 2012, **32**, 2153-2162.
- 2 C. Sartori, D. S. Finch, B. Ralph and K. Gilding, *Polymer*, 1997, **38**, 43-51.