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Supporting information *for*

Self-healable macro-/microscopic shape memory hydrogels based on supramolecular interaction

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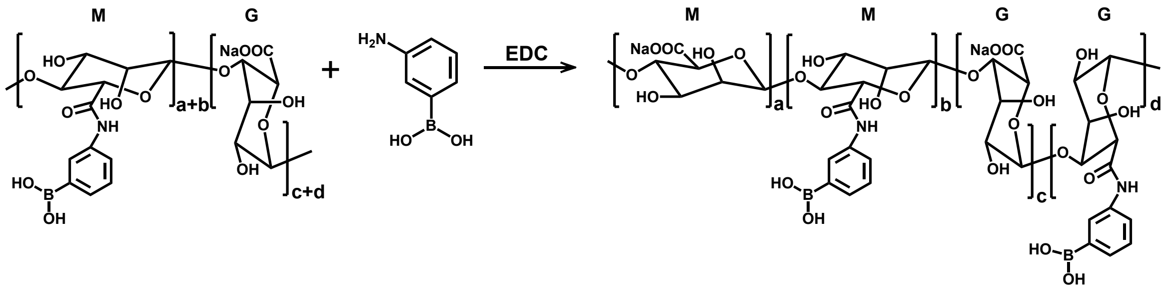
Materials: 3-Aminophenylboronic acid, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide Hydrochloride (EDC·HCl), calcium chloride ($CaCl_2$), ethylenediaminetetraacetic acid disodium salt (EDTA·2Na), Erioglaucine disodium salt (blue dye) and Rhodamine B (red dye) were obtained from Aladdin. Sodium alginate (Alg), poly(vinyl alcohol) (PVA, 98~99% hydrolyzed, average M_w 105600~110000), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), D-fructose and D-(+)-glucosewere purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used without further purification.

Instruments: ^{1}H NMRspectrumwas obtained on a Bruker AVANCE III spectrometer operating at 400 MHz for protons.The rheological measurements were performed on a stress-controlled rheometer (Haake Mars) equipped with a geometry of 35mm parallel plates. Optical microscopy images were taken on Nikon AZ100. Atom force microscopy (AFM) images were performed on a

CSPM 5500 scanning probe microscope system in the tapping mode. Fourier transform infrared (FTIR) spectra were performed on a Varian Scimitar1000 Fourier transform IR spectrophotometer.

Preparation of Alg-PBA: Alg-PBA was prepared by grafting 3-aminophenylboronic acidonto alginate in the presence of 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide Hydrochloride (EDC·HCl). Sodium alginate (2.0 g, 10 mmol on monomer unit), EDC·HCl (1.92 g, 10 mmol) and 3-aminophenylboronic acid (0.78 g, 5 mmol), were dissolved in deionized water (200 mL).The mixture was stirred at room temperature (about 10 ^{o}C) for 24 h and then dialyzed against distilled water for 1 week (M_w cut off = 3500 Da).The signal of phenyl groups was observed in the ^{1}H NMR spectrum of Alg-PBA, indicating 3-aminophenylboronic acid was successfully grafted onto alginate.The content of phenylboronic acid groups in the polymer was calculated to be 28 %.



Scheme S1 The synthetic route of Alg-PBA.

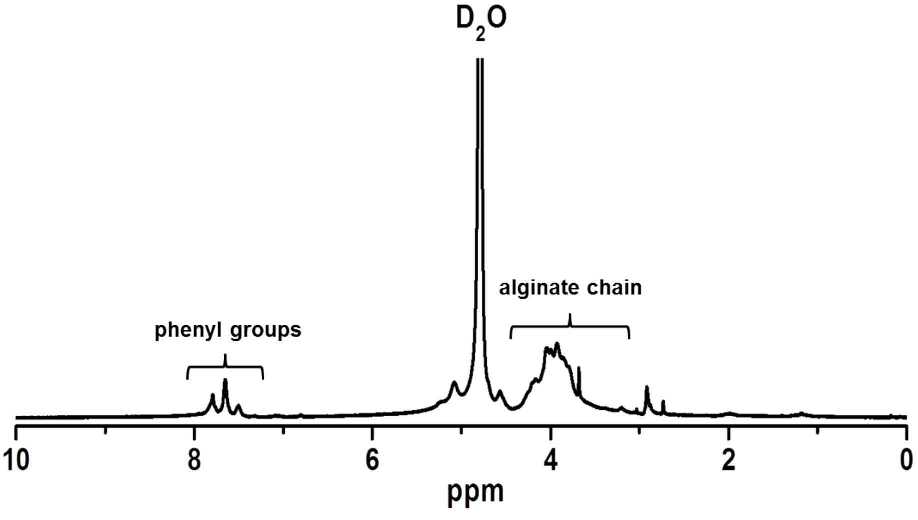
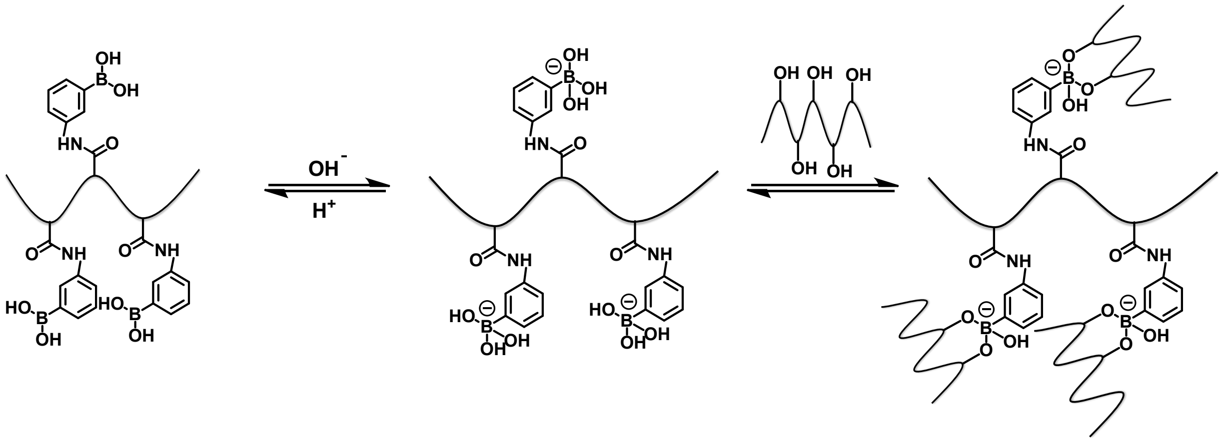


Fig.S1^{1}H NMR (D_2O) spectrum of Alg-PBA.

Preparation of Alg-PBA-PVAhydrogels: Alg-PBA-PVA hydrogel was prepared by mixing the solution of Alg-PBA and 10 % PVA (Alg-PBA : PVA= 6:1 w:w), then 100 μL of 0.1 M NaOH aqueous solution was added, and hydrogel was formed immediately after stirring.

When the pH values of the aqueous medium is higher than the pKa of phenylboronic acid groups (pKa≈8.5), the phenylboronic acid groups of Alg-PBA will shift from an uncharged to a charged form, and the charged phenylborates could form dynamic covalent PBA-diol ester bonds with PVA. Therefore, when base was added to the aqueous solution of Alg-PBA and PVA, supramolecular hydrogel will form immediately after stirring. Because of the pH-responsiveness of the dynamic PBA-diol ester bonds, when acid was added to the hydrogel, the PBA-diol ester bonds will be destructed, and leading to the disassociation of the supramolecular hydrogels (Scheme S2). The interaction between phenylboronic acid groups and monosaccharides such as fructose and glucose are stronger than that between phenylboronic acid groups and PVA, therefore when fructose or glucose was added to the supramolecular hydrogel, the dynamic PBA-diol ester bonds between Alg-PBA and PVA will be destroyed and lead to the broke of the hydrogel network (Fig.S2).



Scheme S2 Formation of supramolecular hydrogels.

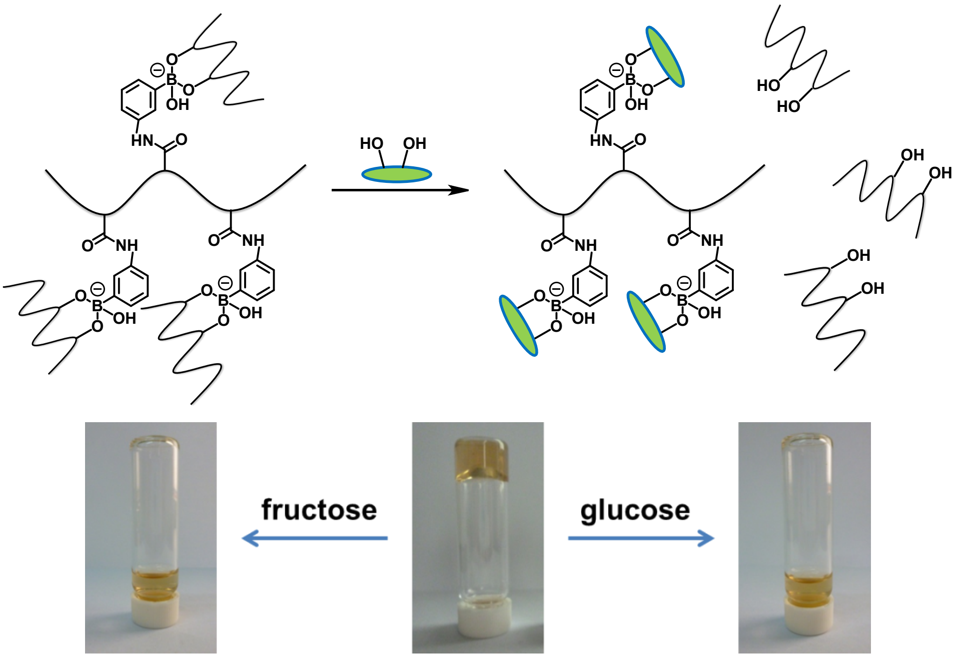


Fig. S2 The fructose and glucose responsiveness of Alg-PBA/PVA supramolecular hydrogel.

The formation of PBA-diol ester bonds was also characterized by Fourier transform infrared (FTIR) spectroscopy. As shown in the following figure, after modification of phenylboronic acid (PBA) groups,a new peak at 1341 cm^{-1}is observed, which can be assigned to B-Ostretching,[1,2] indicating PBA groups were successfully attached to sodium alginate. In the spectrum of Alg-PBA/PVA, the B-O stretching modes around 1341 cm^{-1}was not observed, suggestive of PVA binding to the PBA groups of Alg-PBA.[1]

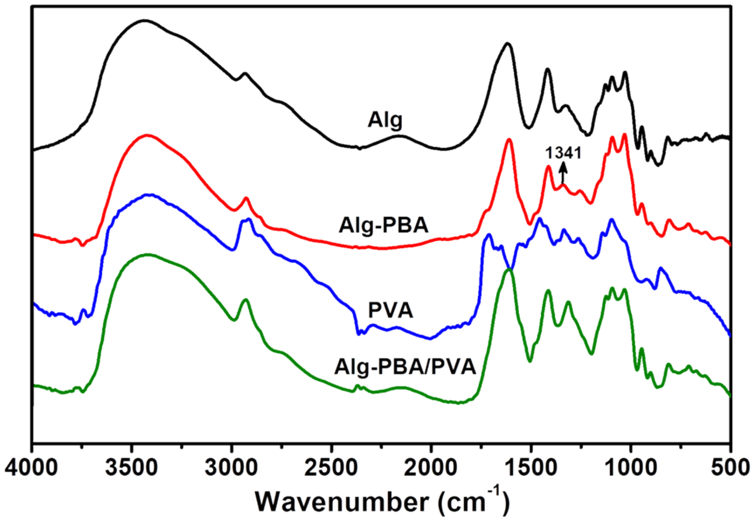


Fig. S3 FTIR spectra of Alg, Alg-PBA, PVA and Alg-PBA/PVA.

Rheological Experiments of Alg-PBA-PVA hydrogels: Stress sweep and frequency sweep experiments were used to investigate the viscoelastic properties of Alg-PBA-PVA hydrogel. The storage modulus (G') and loss modulus (G'') were measured as a function of time within a linear range of viscoelasticity at 25 ^{o}C. The gel samples in the form of sheets (35 mm) were subjected to the rheological measurements before and after self-healing process.The recovery property of the hydrogels in response to applied shear forceswereperformed as the following procedure: 20% (300 s) →150% (100 s) →20% (300 s) →150% (100 s) →20% (300 s).

Macroscopic shape memory behavior: The shape memory behavior of the Alg-PBA-PVA hydrogel was evaluated at room temperature according to previous reports. A straight strip of hydrogel (30 mm × 4 mm × 1 mm, water contents of hydrogel is about 88%) was bent into a U-form shape and immersed in 1% $CaCl_2$ aqueous solution for 30 s, then the U-shape hydrogel was transferred into 0.2 M Na_2CO_3 aqueous solution or 0.2 M EDTA·2Na aqueous solution to remove Ca^{2+} from the gel.They both can recover almost 100% of the deformation.

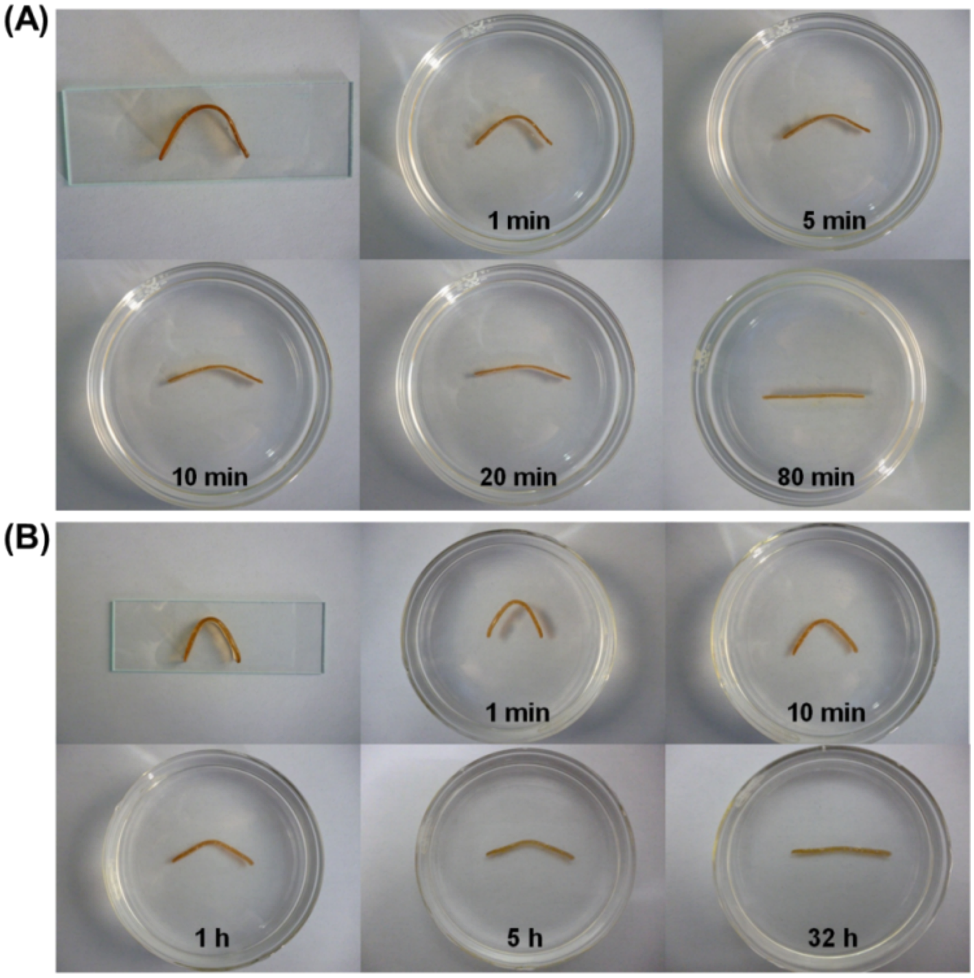


Fig.S4 Photographs that demonstrate the macroscopic shape-memory behavior of Alg-PBA-PVA hydrogel. Transition from temporary shape to original shape in (A) 0.2 M Na_2CO_3 solution and (B) 0.2 M EDTA·2Na solution.

Shape memory cycle: The quantitative shape memory cycle was determined according to the reported method.[3~5] The shape fixity ratio (θ_f) and shape recovery ratio (θ_r) were defined by the following equation:

$\theta_f = \theta_t/\theta_d \times 100\%$

$\theta_r = (\theta_d - \theta_f) / \theta_d \times 100\%$

Where θ_d is the deformed angle, θ_t is the temporarily fixed angle and$\theta_f$is the final angle. As shown in **Fig. S5**, the shape memory effect can be cycled at least 3 times.

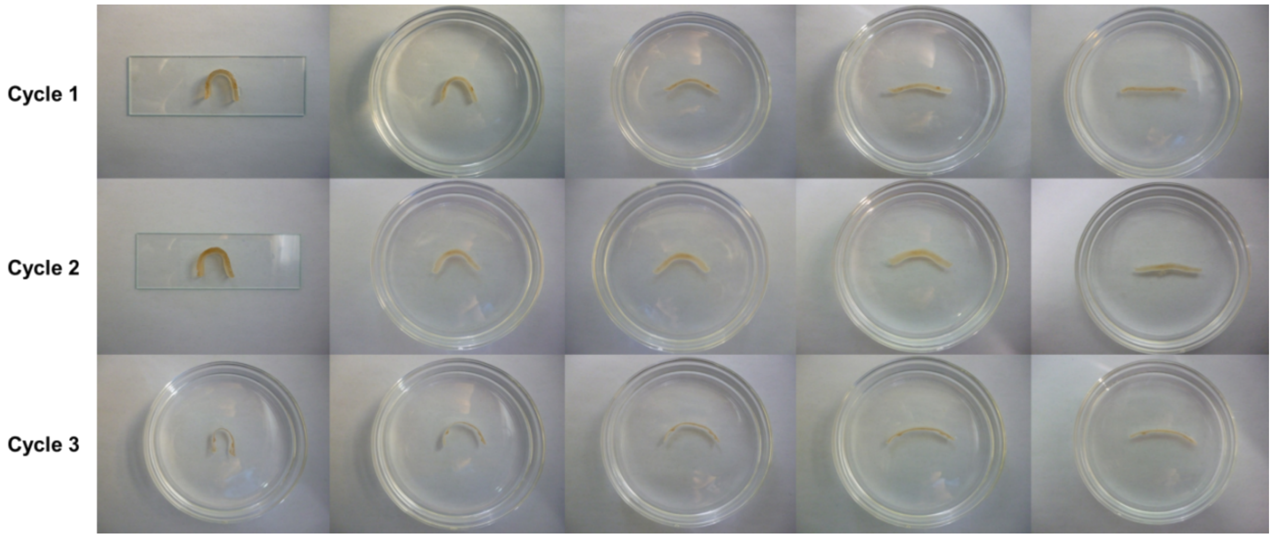


Fig. S5 Cycled shape memory performance of Alg-PBA/PVA hydrogel. Na_2CO_3 was applied to induce the shape recovery.

Microscopic shape memory behavior: A thin layer of hydrogel (100 μm) was deposited on glass substrate, and a structured polydimethylsiloxane(PDMS) stampwas brought contact with the hydrogel with gentle force to create micropatterns(10μm × 10 μm) in the surface by micro-contact printing method.Before removing the PDMS stamp, the hydrogel was soaked in 1% $CaCl_2$ solution for 10s to fix the micropatterns. By soaking the patterned hydrogel in 0.2 M EDTA·2Na solution, the microstructures on the surface can be removed.

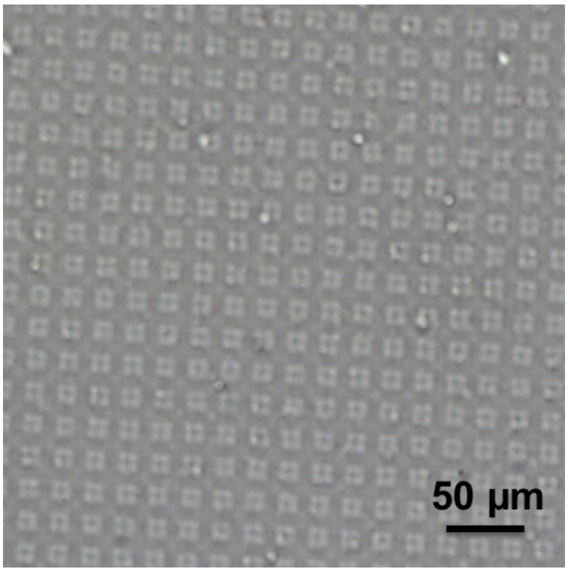


Fig. S6 Optical microscope imageof hydrogels with deformed micropatterns.

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