Supporting information

Mussel-inspired multifunctional supramolecular hydrogels with self-healing, shape memory and adhesive properties

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Materials: Dopamine hydrochloride, 3-aminophenyboronic acid, 1-(3-dimethylaminopropy)-3-ethylcarbodiimide hydrochloride (EDC·HCl), glycine (Gly), sodium alginate (Alg), Erioglaucine disodium salt (blue dye) and Rhodamine B (red dye) were obtained from Aladdin. Calcium chloride ($CaCl_2$) and sodium hydroxide (NaOH) were purchased from Sinopharm Chemical Reagent Co, ltd. All the chemicals were used without further purification.

Instruments: ^{1}H NMR spectrum was obtained on a Bruker AVANCE Ⅲ spectrometer operating at 400 MHz for protons. UV-vis spectra were recorded on a TU-1810 spectrophotometer from Beijing Purkinje General Instrument Co. Ltd. The rheological measurements were performed on rheometer (Haak Mars) equipped with a geometry of 35 mm parallel plates.

Synthesis of alginate-dopamine (Alg-DA) and alginate-phenylboronic (Alg-PBA): Alg (1.00 g, 4.63 mmol in the terms of repeating unit), EDC·HCl (0.96 g, 4.63 mmol) and DA (0.44 g, 2.32 mmol) were dissolved in 100 mL of deionized water. The reaction mixture was stirred at room temperature under N_2 atmosphere for 24 h, and then was dialyzed against distilled water for 5 days (cutoff : 3500 Da). The content of catechol groups in the polymer was calculated to be 17 % based on ^{1}H NMR (D_2O) spectrum. Alg-PBA was synthesized from Alg (1.00 g) and PBA (0.39 g) in the same procedure, the content of phenyboronic acid groups in the polymer was calculated to be 21 % on the basis of ^{1}H NMR (D_2O) result (Fig. S2). Compared to the pristine DA, Alg-DA exhibits the same absorption peak at ~300 nm in its UV-vis absorption spectrum (Fig. S3). Both NMR and UV results indicate DA and PBA groups are successfully grafted on the alginate chain.

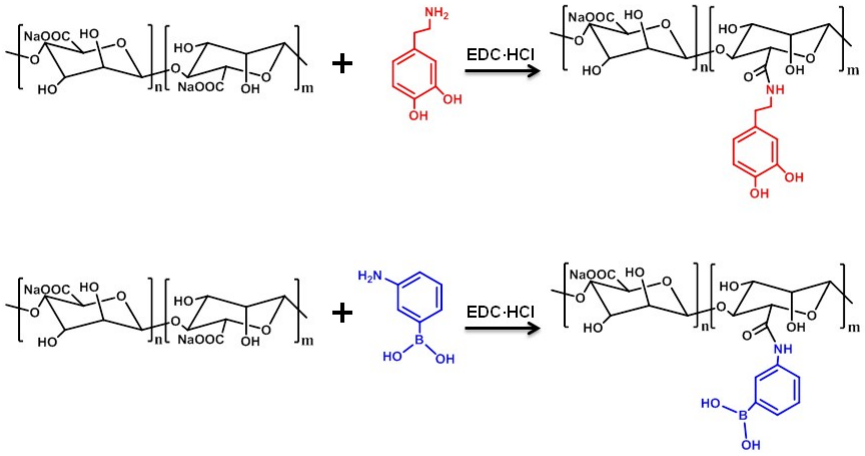

Fig. S1 The synthetic routes of Alg-DA and Alg-PBA.

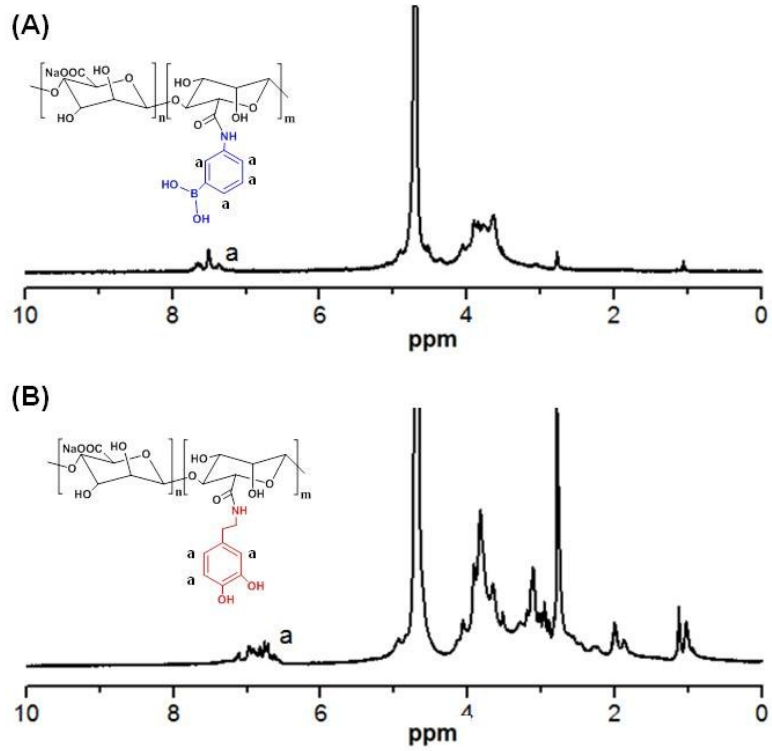

Fig. S2 ^{1}H NMR (D_2O) spectra of (A) Alg-PBA, (B) Alg-DA.

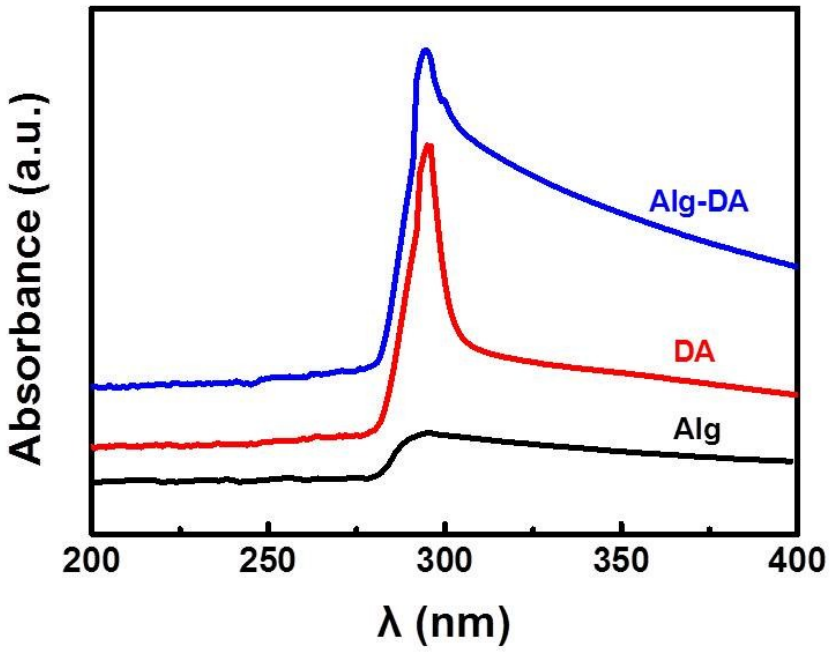

Fig. S3 UV-vis spectra of Alg-DA, DA and Alg.

Preparation of PBA-DA hydrogels: PBA-DA hydrogel was prepared by mixing 2 mL Alg-DA (2 wt%) solution and 0.05 g Alg-PBA, then 100 μL of 0.1 M NaOH aqueous solution was added, and hydrogel was formed immediately after stirring.

Rheological Experiments of PBA-DA hydrogels: Stress sweep and frequency sweep experiments were used to investigate the viscoelastic properties of PBA-DA hydrogel. The storage modulus (G') and loss modulus (G'') were measured as a function of time within a linear range of viscoelasticity at 25 °C. The gel samples in the form of sheets (35 mm) were subjected to the rheological measurements before and after self-healing process. The amplitude sweep indicated the hydrogels transform to quasi-liquid state beyond 200% strain (frequency=1.0 Hz). The recovery property of the hydrogels in response to applied shear forces were performed as the following procedure: 20% (300 s) →400% (100 s) →20% (300 s) →400% (100 s) →20% (300 s).

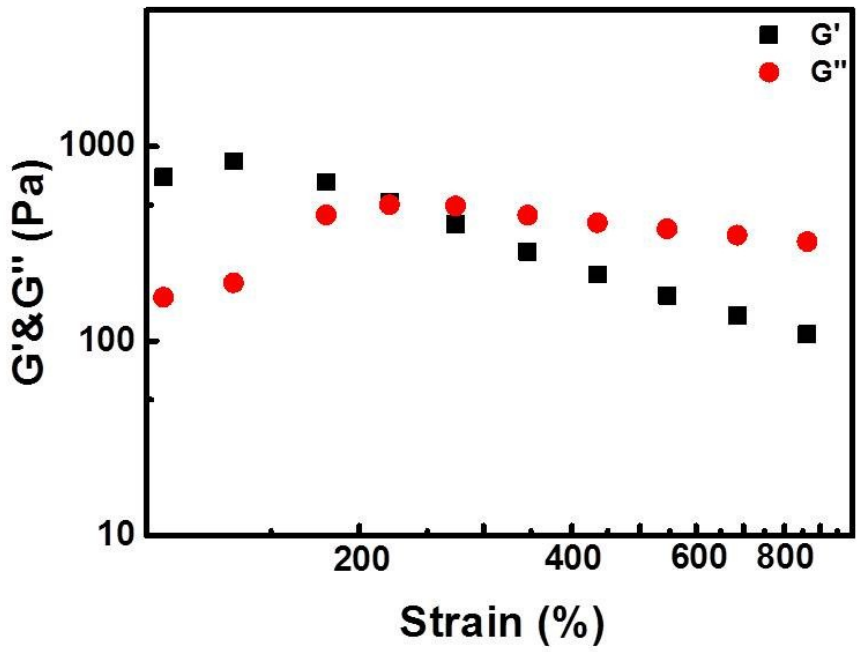

Fig. S4 Rheological profiles from the amplitude sweep of the hydrogels.

Self-healing in the presence of Alg-Ca^{2+} crosslinks: The hydrogel would still show self-healing property with the Alg-Ca^{2+} crosslinks (Fig. S5A), however, the interaction between alginate and Ca^{2+} is very strong,[1,2] the hydrogel needs a long time to heal the cracks, because the strong coordination between alginate chain and Ca^{2+} will hinder the movement of the polymer chain, and thus retard the self-healing process. The self-healing behavior in the presence of Alg-Ca^{2+} crosslinks was further evaluated by rheological measurements. As shown in Fig. S5B, under a 20% strain, G′ is much larger than G″, implying the formation of self-standing hydrogel. However, if a large-amplitude oscillatory (γ = 400%, Frequency = 1.0 Hz) was applied, G″ is much larger than G′, which suggests the hydrogel collapses to quasi-liquid state. G′ and G″ can recover to initial values by decreasing the amplitude (γ =20%, frequency = 1.0 Hz), which confirm the self-healing ability of the PBA-DA hydrogel with Alg-Ca^{2+} crosslinks. In addition, both G′ and G″ of PBA-DA hydrogel in the presence of Alg-Ca^{2+} crosslinks are larger than that of the PBA-DA hydrogel, which is easy to understand, because dual crosslinks are present in this hydrogel.

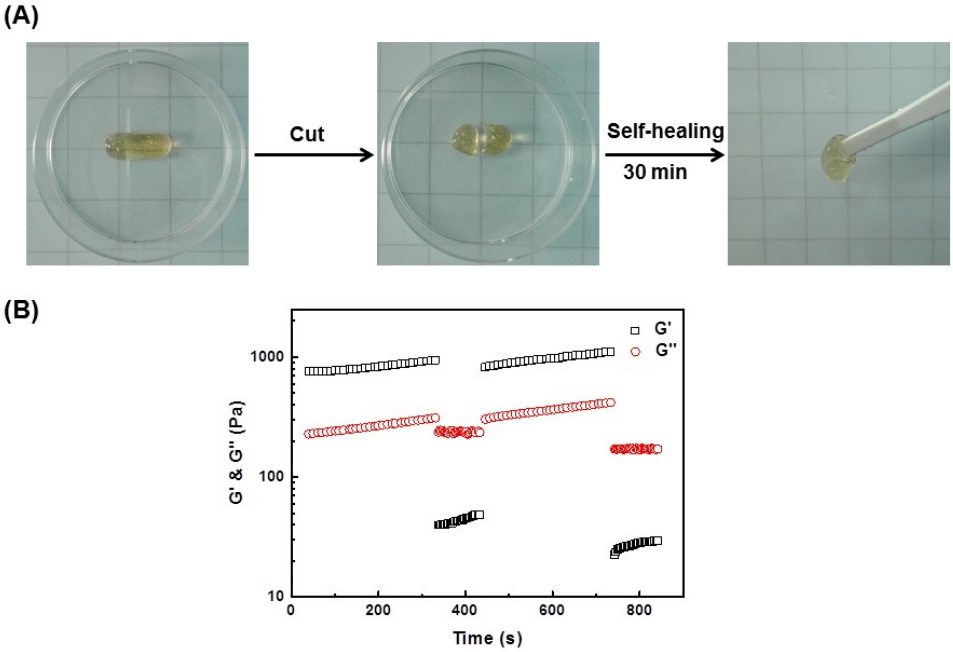

Fig. S5 (A) The self-healing process of the PBA-DA hydrogel with Alg-Ca^{2+} crosslinks. (B) Rheological analyses of the self-healing behavior of the PBA-DA hydrogel with Alg-Ca^{2+} crosslinks.

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 θ_f is the final angle.

Fig. S6 Cycled shape memory performance of PBA-DA hydrogel in Gly aqueous solution (pH 6.0).

Reference

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