Supporting information

Mussel-inspired Injectable Supramolecular and Covalent Bonds Crosslinked Hydrogels with Rapid Self-healing and Recovery via a Facile Approach Under Metal-free Conditions

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1. Experimental detail

1.1 Materials

Dopamine hydrochloride (purity 98%) was purchased from J&K. Gelatin (Catalog number: G7041, gelatin from cold water fish skin, type A, Mn=60kDa, heavy metals⩽20 ppm, gelatin solution is in liquid state at 10 ^{o}C hindering the test of bloom number of the gelatin), NaOH, dextran (Mn=35-45KDa) and sodium periodate ($NaIO_4$) were purchased from Sigma-Aldrich. Phosphate-buffered saline (PBS) was purchased from Gibco. All the other reagents are used as received.

1.2 Hydrogel preparation

The gelatin was dissolved in PBS (0.01 M, pH 7.4) at 60 ^{o}C then cooled to room temperature to prepare gelatin solution. After that, a designed amount of dopamine and NaOH solution (10 M) was added into the gelatin solution. The NaOH was used to adjust the pH of the gelatin/dopamine/$NaIO_4$ mixture back to 7.0 after the introduction of $NaIO_4$. After adding the desired amount of $NaIO_4$ solution into the above mixture, the mixture was vortex-mixed for 10 seconds and placed at 37 ^{o}C for gelation. The hydrogel components were shown in Table S1 and Table S2. The dextran (M_n=35000-45000 g/mol)/dopamine/$NaIO_4$ mixture (sol state) was prepared as the same as the above description. The concentrations of dextran and dopamine were 20wt% and 3wt%, respectively, and the molar ratio of $NaIO_4$ to dopamine was 1:1. Then, the dextran/dopamine/$NaIO_4$ mixture was placed at 37 ^{o}C for 12 hours to observe the state of the mixture. The hydrogels (GT150-DA30-SP0.5) with different initial pH values of 1 and 4 were prepared using a similar procedure as above

described except for adding 8μL and 1μL of concentrated hydrochloric acid into 1mL of GT150/DA30/SP0.5 mixtures, respectively.

1.3 Characterizations

The FT-IR spectra of gelatin, and dried gelatin/dopamine hydrogels (with dopamine: $NaIO_4$ molar ratios of 1:1 and 1:0.5, respectively) were recorded by a Nicolet 6700 FT-IR spectrometer (Thermo Scientific Instrument) in the range of 4000-600 cm^{-1}. The dried hydrogels for FT-IR spectra measurements were prepared by drying the hydrogel under 37 ^oC for 48 hours. The dried hydrogels were ground into powder and mixed with KBr for FTIR investigation.

The UV-vis spectra of dopamine in deionized water，$NaIO_4$ oxidized dopamine (with dopamine : $NaIO_4$ ratios of 1:1 and 1:0.5, respectively), gelatin/dopamine in deionized water and $NaIO_4$ oxidized gelatin/dopamine in deionized water (with dopamine : $NaIO_4$ ratios of 1:1 and 1:0.5, respectively) were recorded from 800 nm to 250 nm by employing a UV-vis spectrophotometer (PerkinElmer Lambda 35) at 0 h, 12 h and 24 h, respectively. The concentration of gelatin and dopamine was 0.5 mg/mL and 0.025 mg/mL, respectively. Spectra of $NaIO_4$ oxidized gelatin/dopamine in deionized water (with dopamine : $NaIO_4$ ratios of 1:0.5) at 37 ^oC for 12 h were recorded from 800 nm to 250 nm at 25 ^oC and 60 ^oC, respectively.

For the observation of the morphologies of the hydrogels, the hydrogels were prepared as previously described and then lyophilized. The surface of the hydrogels was sprayed with a gold layer, and a field emission scanning electron microscope (FE-SEM, SU-8000, Hitachi, Japan) was employed to perform the measurement.

Gelation time of the hydrogels was determined by using the inverting test tube method employing a 4 mL vial test tube (10 mm diameter) at 37 °C. The gelation time was determined as the time when no visual flow was observed within 30 s by inverting the vial. Each group was repeated three times.

1.4 Swelling test

The hydrogels were prepared in 2 mL tubes. After complete gel formation, the hydrogels were put into vials with 20 mL PBS (0.01 M, pH 7.4) and then the vials were placed at 37 °C for 24 h. After that, the hydrogels were brought out from the vials and the superficial water on the hydrogels was absorbed using a filter paper. The swelling ratio (SR) was calculated using the following equation: $SR= (W_t-W_i) / W_i$, in which W_i and W_t represent the initial weight and the weight of the swollen hydrogels in PBS, respectively. Each group was repeated three times.

1.5 Rheological measurements

The rheological measurements of the hydrogels were performed by employing a TA rheometer (DHR-2) using different methods. (1) A time sweep test with 1% constant strain and a constant frequency of 10 rad/s at 37 ^oC was used to evaluate the stiffness of the hydrogels. Before the collection of the data, 350 μL of the gelatin/dopamine/$NaIO_4$ mixture (mixing the gelatin, dopamine and $NaIO_4$ and then vibrating the mixture for 10 seconds using a vortex mixer) was placed between 20 mm parallel plates with a gap of 1000 μM and the periphery was sealed by silicone oil to prevent the evaporation of water. (2) The completely crosslinked hydrogel disk with a 20 mm diameter and a thickness of 1000 μM was prepared using a silicone

mould. The disk was placed between parallel plates with a 20 mm diameter and a gap of 1000 μM. Then the strain amplitude sweep test (γ=0.1%-500%) with constant frequency of 1 rad/s at 25 °C was performed. (3) Completely gelled hydrogel disc with a 20 mm diameter and a thickness of 1000 μM was placed between 20 mm parallel plates with a gap of 1000 μM at 25 °C. Then, the alternate step strain sweep test was performed at a fixed angular frequency (1 rad/s) at 25 °C. Amplitude oscillatory strains were switched from small strain (γ=1.0%) to subsequent large strain (γ=500%) with 100 s for every strain interval[1]. The self-healing efficiency of the hydrogel was calculated as following equation: self-healing efficiency %= G_2'/G_1', where G_1' was the original storage modulus and G_2' was the storage modulus after suffering the break strain.

1.6 Macroscopic self-healing experiments

Hydrogel discs (GT150-DA30-SP0.5, 20 mm in diameter and 10 mm in height) were prepared as previously described. The hydrogels were firstly cut into two pieces and then put them together to view that whether they could rapidly self-heal together. A short movie was used to show the cutting and adhesion processes of the hydrogels (see Movie S1). Besides, the hydrogel (GT150-DA30-SP0.5) was firstly cut into pieces, and then the hydrogel pieces were put into a syringe to form self-healed hydrogel line by injection with or without syringe needle. Movie S2 and Movie S3 recorded the processes.

1.7 Compression test to evaluate the self-healing efficiency of the hydrogel

Hydrogel was prepared into cylindrical hydrogel using a mode with an inner diameter

of 15 mm and height of 10 mm. Then, the cylindrical hydrogel was used to perform the compression strain test employing a TA rheometer with a compression speed of 100 μm/s. After the compression test, the broken hydrogel was cut into pieces and reshaped into cylindrical hydrogel using a mode with an inner diameter of 15 mm and height of 10 mm. After allowing the reshaped cylindrical hydrogel self-healing for 24 hours at room temperature, the self-healed cylindrical hydrogel was used to perform the compression strain test to obtain the stress at break. The self-healing efficiency was calculated using the following the equation: self-healing efficiency %= $S_{original}/S_{healed}$, where $S_{original}$ was the original hydrogel compression stress at break and S_{healed} was the self-healed hydrogel compression stress at break.

1.8 Adhesive performance evaluation

A lap shear testing was used to test the bulk adhesive strength of the hydrogels. As reference [2] described, the actual pigskin tissues surfaces were used. The skin tissue surfaces were cut into 10 mm × 30 mm rectangle. Then, 40 μL of gelatin/dopamine/$NaIO_4$ mixture was applied to the surface of the fresh skin tissue epidermis and another skin tissue epidermis was placed on top of the previous skin tissue, the contact area of the two skin tissues was kept 10 mm × 10 mm. After that, the samples were placed at room temperature for three hours for gelation before the lab shear test. The samples were lap shear-tested to failure on an Instron Materials Test system (MTS Criterion 43, MTS Criterion) equipped with a 50 N load cell by using a cross-head speed of 5 mm/min under ambient conditions. All measurements were triplicate.

1.9 *In vitro* biocompatibility tests of the hydrogel

The cytotoxicity of the leachable fraction from the hydrogel was evaluated as reference [3] described. In brief, 2 mL hydrogel in 3 mL cell culture medium was incubated for 24 hours to obtain the 1 X hydrogel extract. Then the 1/5 X hydrogel extract was obtained by 5 times dilution of 1X hydrogel extract. L929 fibroblasts were seeded in 96-well plate (Costar) at a density of 10^4 cells/well. After cultured for 24 hours, the culture medium was removed and 100 μL of hydrogel extract was added into the plate and then cultured for another 24 hours in a humidified incubator containing 5% CO_2 at 37 °C. After that, the medium was removed and 10 μL of alamarBlue® reagent in 100 μL complete growth medium was then added into each well. The plate was incubated for 4 h. Then, 100 μL of the medium in each well was transferred into a 96-well black plate (Costar). Fluorescence was read using 530 nm as the excitation wavelength and 600 nm as the emission wavelength using a microplate reader (Molecular Devices) according to the manufacturer's instructions. Blank culture medium was used as control group. Tests were repeated four times for each group. The viability of the cells was also evaluated by LIVE/DEAD® Viability/Cytotoxicity Kit assay. Cells cultured on TCPS plate was used as positive control. Cell adhesion and proliferation were observed under an inverted fluorescence microscope (IX53, Olympus).

1.10 Reformability evaluation of the hydrogel

The hydrogel (GT150-DA30-SP0.5) was prepared as the hydrogel preparation part described. Then, on one hand, the hydrogel was cut up into pieces, and then the

hydrogel pieces were fabricated into hydrogel homogenate by a homogenizer. After that, the flowable hydrogel homogenate was introduced into a silica gel model containing four different shapes to reshape the hydrogel. After self-healing at room temperature for 12 hours, the flowable hydrogel homogenate transformed into non-liquid hydrogel. On the other hand, the hydrogel pieces were put into syringe to form self-healed hydrogel line by injection with syringe needle and then the hydrogel line could be reshaped into a whole hydrogel by rolling. Movie S4 recorded the processes.

1.11 Recovery evaluation of the hydrogel

The recovery of the hydrogels (GT150-DA30-SP0.5 and GT150-DA30-SP1.0) was preliminary evaluated using rheometer by a uniaxial compression test with compression speed of 500 μm/s. Also, the movies recording the process was provided (Movie S5 and Movie S6). Besides, we qualitatively evaluated the recovery and withstanding deformation property of the hydrogel under physiological condition. The female Sprague–Dawley rats with body weight of 240 g were used. All animal procedures were conducted in accordance with the Institutional Animal Ethics Committee of the University. Firstly, the animal was anaesthetized by injecting 10% chloral hydrate. When the rat had been anaesthetized, 1mL of mixture was subcutaneously injected into the rat using a syringe with a 25 gauge needle. After 1, 2 and 3 days, the hydrogel was removed from the rat's skin and the recovery and withstanding property was qualitatively determined by pressure and release. All the shapes of the hydrogels under pressure and after release were taken photographs.

1.12 Stability evaluation of hydrogels

Hydrogel GT150-DA30-SP0.5 and GT150-DA30-SP1.0 prepared without NaOH were immersed in 5 M urea solution and water, respectively at room temperature for different time. The morphology of the hydrogel was observed and photographed.

1.13 Biodegradation test of the hydrogel in vivo

For the in vivo biodegradation assay, female Sprague–Dawley rats with body weight of 240 g were used. All animal procedures were conducted in accordance with the Institutional Animal Ethics Committee of the University. Firstly, the animal was anaesthetized by injecting 10% chloral hydrate. When the rat had been anaesthetized, 100 μL of mixture was subcutaneously injected into the rat's skin using a syringe with a 25 gauge needle to allow gelation. After 0, 1, 2 and 3 weeks, the rats were sacrificed by cervical dislocation and the remaining hydrogels were peeled from the rats' skin. The wet hydrogels were weighed. All measurements were triplicate. The mass loss percentage was calculated from: (Wi- Wr) / Wi, where Wi and Wr were the initial weight and the residual weight of the hydrogels.

1.14 Determination of released dopamine/polydopamine in the hydrogel extratcs

2 mL hydrogel in 3 mL PBS was incubated for 24 hours at 37^{o}C with a 100 rpm shaking speed to obtain the hydrogel extract. Then the hydrogel extract was taken photographs after diluted three times. Besides, the UV-vis spectra of the hydrogel extracts were performed from 700 nm to 250 nm. The deeper color of extract means more dopamine/polydopamine content in the extract. The higher absorption value at about 280 nm means more dopamine/polydopamine.

1.15 Statistic analysis

The experimental data in this study were analyzed by Student's *t* test. $P < 0.05$ was considered as statistical significance. The results were expressed as mean ± standard deviation (SD).

2. Results and discussions

Table S1 The components of the hydrogels with 0.5 : 1 and 1:1 molar ratio of $NaIO_4$ to dopamine, respectively. GT, DA and SP represented gelatin, dopamine and sodium periodate, respectively. The number after GT and DA means the weight (mg) in per milliliter hydrogel, and the number after SP means the molar ratio of sodium periodate to dopamine.

Samples	Gelatin (mg)	DA (mg)	NaOH (mg)	$NaIO_4$ (mg)	Solvent (mL)	Gelation
GT100-DA5-SP0.5	100	5	0.8	2.82	1	NO
GT100-DA10-SP0.5	100	10	1.6	5.64	1	NO
GT100-DA20-SP0.5	100	20	3.2	11.28	1	YES
GT100-DA30-SP0.5	100	30	4.8	16.92	1	YES
GT100-DA40-SP0.5	100	40	6.4	22.56	1	YES
GT150-DA5-SP0.5	150	5	0.8	2.82	1	NO
GT150-DA10-SP0.5	150	10	1.6	5.64	1	NO
GT150-DA20-SP0.5	150	20	3.2	11.28	1	YES
GT150-DA30-SP0.5	150	30	4.8	16.92	1	YES
GT150-DA40-SP0.5	150	40	6.4	22.56	1	YES
GT200-DA5-SP0.5	200	5	0.8	2.82	1	NO
GT200-DA10-SP0.5	200	10	1.6	5.64	1	NO
GT200-DA20-SP0.5	200	20	3.2	11.28	1	YES
GT200-DA30-SP0.5	200	30	4.8	16.92	1	YES
GT200-DA40-SP0.5	200	40	6.4	22.56	1	YES
GT100-DA5-SP1.0	100	5	1.6	5.64	1	NO
GT100-DA10- SP1.0	100	10	3.2	11.28	1	YES
GT100-DA20-SP1.0	100	20	4.8	16.92	1	YES
GT100-DA30-SP1.0	100	30	6.4	22.56	1	YES
GT100-DA40-SP1.0	100	40	12.8	45.12	1	YES
GT150-DA5-SP1.0	150	5	1.6	5.64	1	NO
GT150-DA10-SP1.0	150	10	3.2	11.28	1	YES
GT150-DA20-SP1.0	150	20	4.8	16.92	1	YES
GT150-DA30-SP1.0	150	30	6.4	22.56	1	YES
GT150-DA40-SP1.0	150	40	12.8	45.12	1	YES
GT200-DA5-SP1.0	200	5	1.6	5.64	1	NO
GT200-DA10-SP1.0	200	10	3.2	11.28	1	YES
GT200-DA20-SP1.0	200	20	4.8	16.92	1	YES
GT200-DA30-SP1.0	200	30	6.4	22.56	1	YES
GT200-DA40-SP1.0	200	40	12.8	45.12	1	YES

Table S2 The components of the hydrogels. GT, DA and SP represented gelatin, dopamine and sodium periodate, respectively. The number after GT and DA means that the weight (mg) in per milliliter hydrogel, and the number after SP means that the molar ratio of sodium periodate to dopamine.

Samples	Gelatin (mg)	DA (mg)	NaOH (mg)	$NaIO_4$ (mg)	Solvent (mL)	Gelation
GT150-DA30-SP0	150	30	0	0	1	NO
GT150-DA30-SP0.25	150	30	0.45	8.46	1	NO
GT150-DA30- SP0.5	150	30	0.90	16.92	1	YES
GT150-DA30- SP0.625	150	30	0.96	21.15	1	YES
GT150-DA30-SP0.75	150	30	1.35	25.38	1	YES
GT150-DA30-SP1.00	150	30	1.8	33.84	1	YES

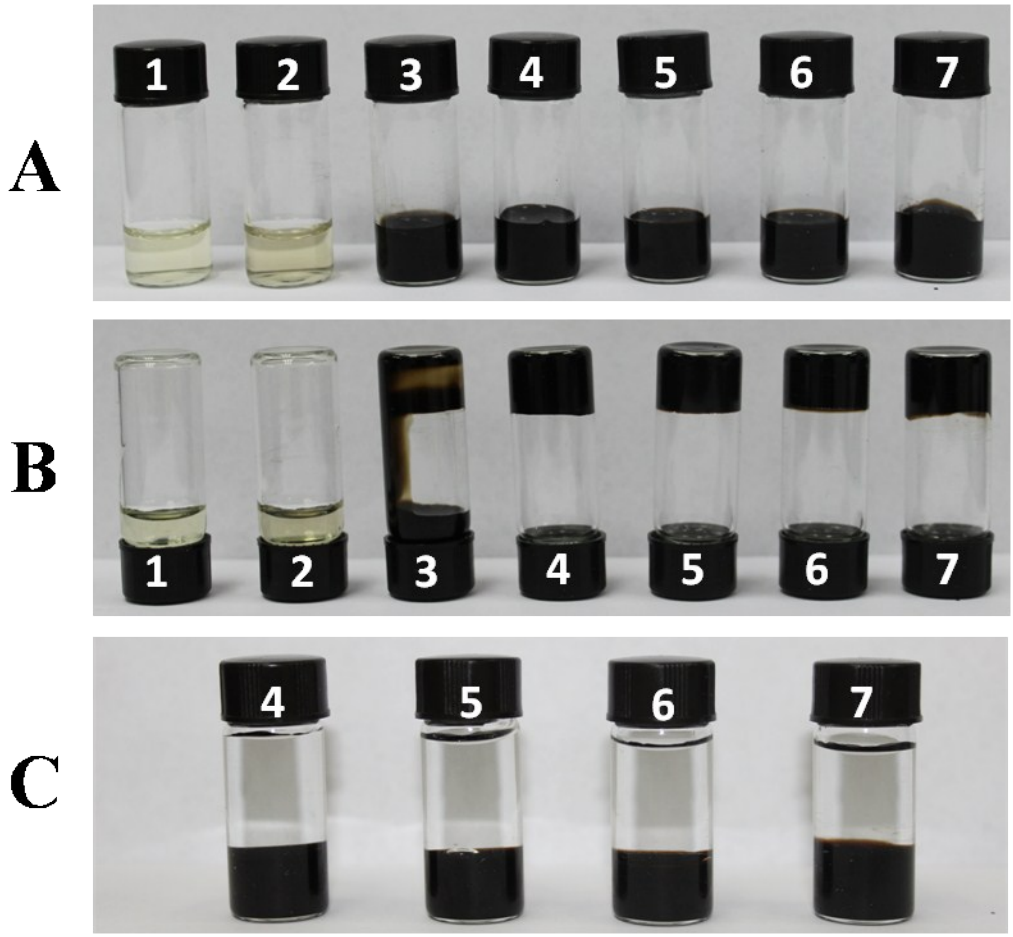


Figure S1. Photographs of gelatin (1), gelatin/dopamine mixture (2), and gelatin/dopamine mixture with 0.25 (3), 0.5 (4), 0.625 (5), 0.75 (6), and 1.0 (7) molar ratio of $NaIO_4$ to dopamine, respectively, at 37 ^oC for 12 hours. Row A is positive position of the bottles, Row B is inversion of the bottles, and Row C is the situation of hydrogels (4-7) soaked in water. The diameter of the bottles is 15 mm.

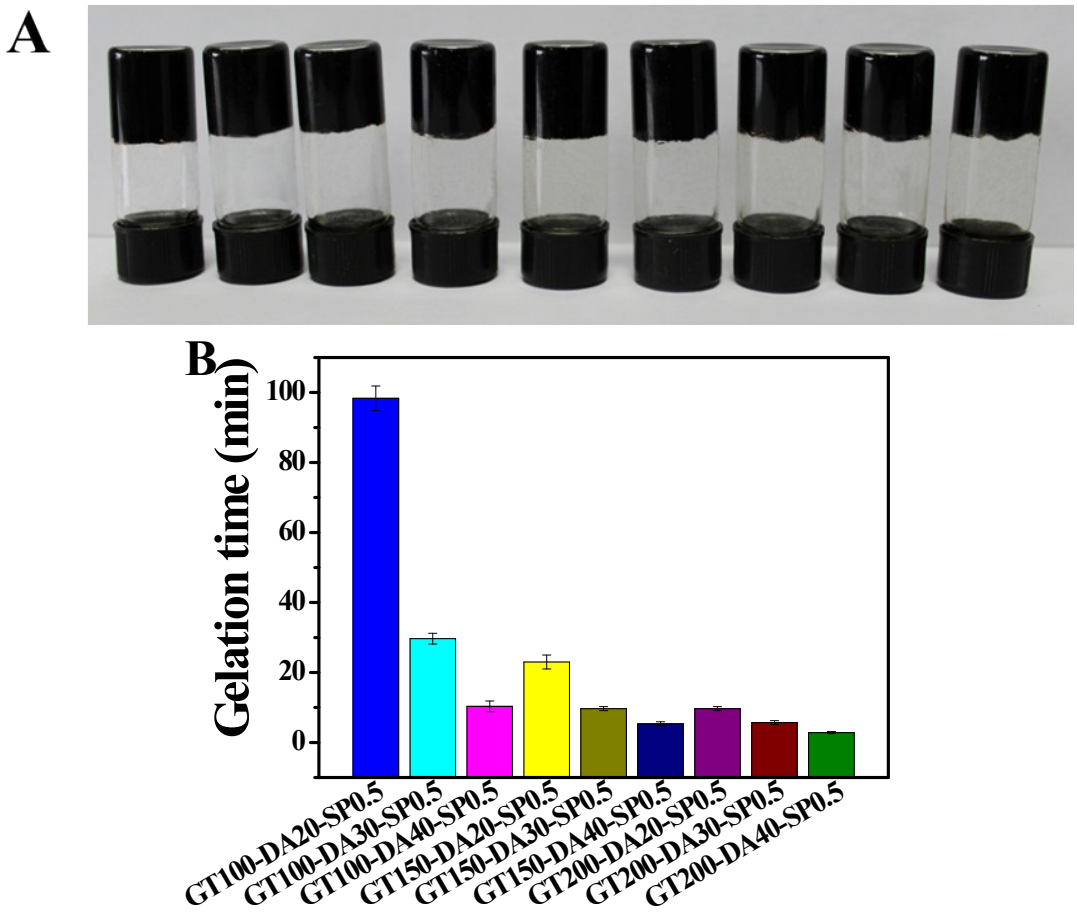


Figure S2. (A): photographs of hydrogels of GT100-DA20-SP0.5, GT100-DA30-SP0.5, GT100-DA40-SP0.5, GT150-DA20-SP0.5, GT150-DA30-SP0.5, GT150-DA40-SP0.5, GT200-DA20-SP0.5, GT200-DA30-SP0.5 and GT200-DA40-SP0.5 (from left to right); (B): gelation time of the hydrogels at 37 ^{o}C.

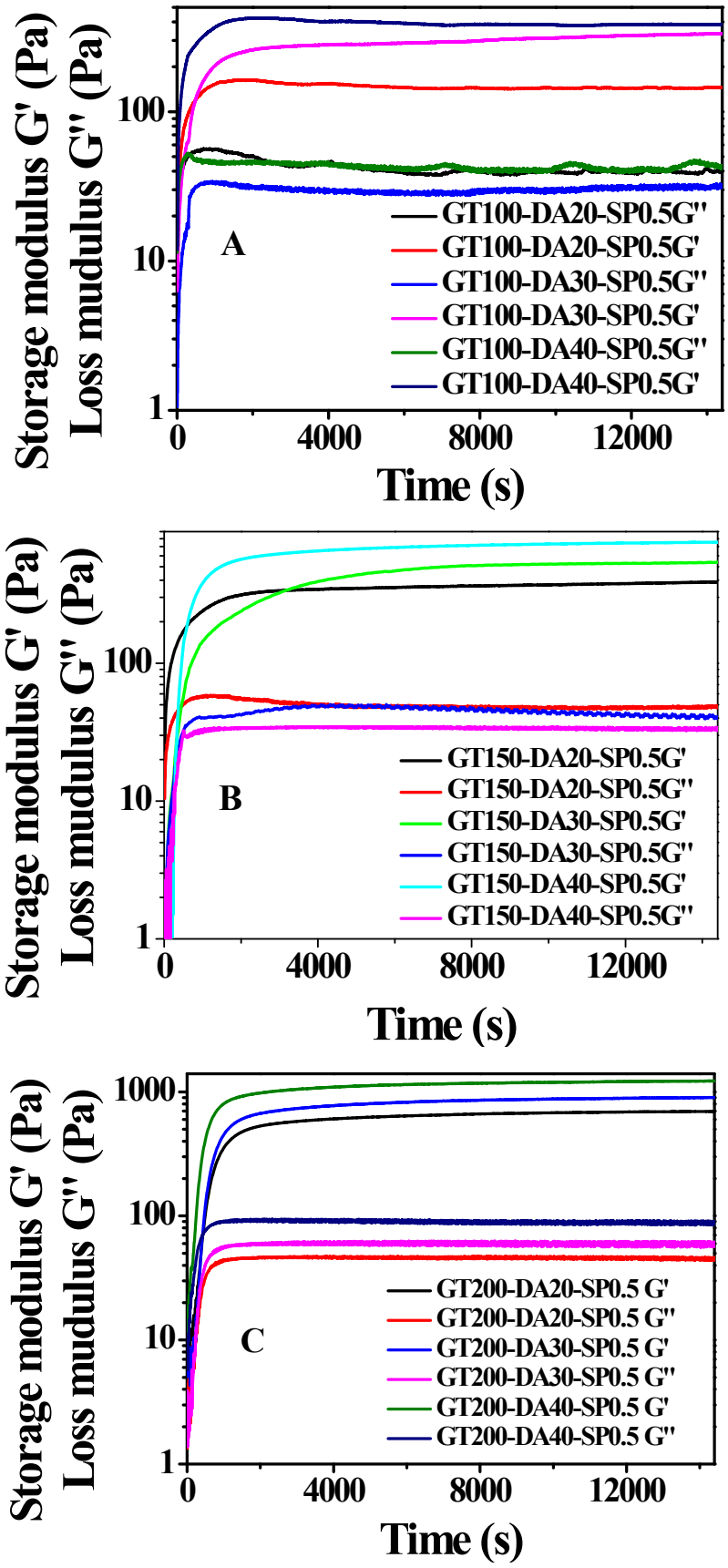


Figure S3. Time sweep test for mechanical strength test. A: GT100-DA20-SP0.5,

GT100-DA30-SP0.5, GT100-DA40-SP0.5; B: GT150-DA20-SP0.5, GT150-DA30-SP0.5, and GT150-DA40-SP0.5; C: GT200-DA20-SP0.5, GT200-DA30-SP0.5, and GT200-DA40-SP0.5.

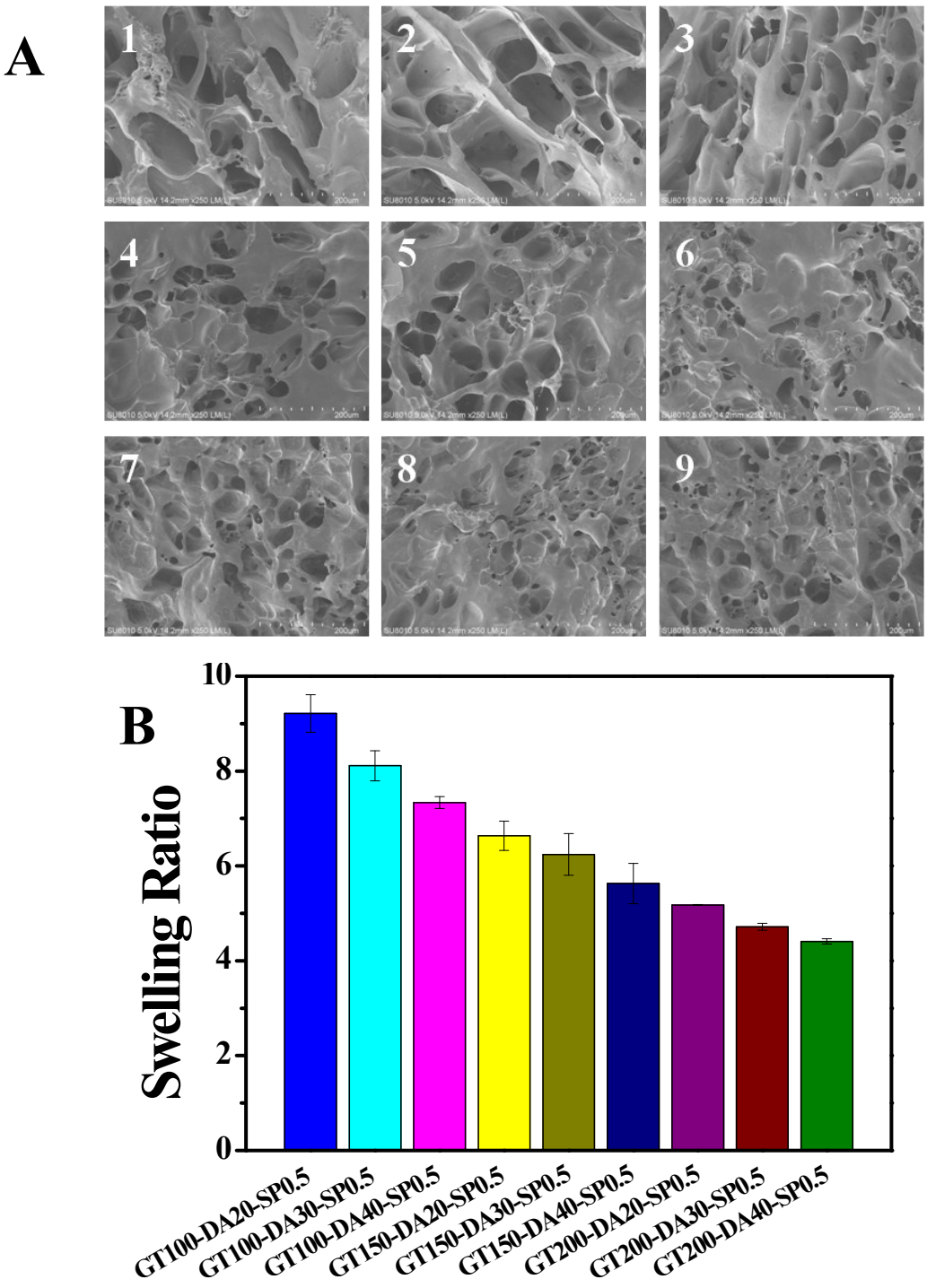


Figure S4. A: SEM of the hydrogels: GT100-DA20-SP0.5 (1), GT100-DA30-SP0.5

(2), GT100-DA40-SP0.5 (3), GT150-DA20-SP0.5 (4), GT150-DA30-SP0.5 (5), GT150-DA40-SP0.5 (6), GT200-DA20-SP0.5 (7), GT200-DA30-SP0.5 (8) and GT200-DA40-SP0.5 (9); B: Swelling ratios of the hydrogels.

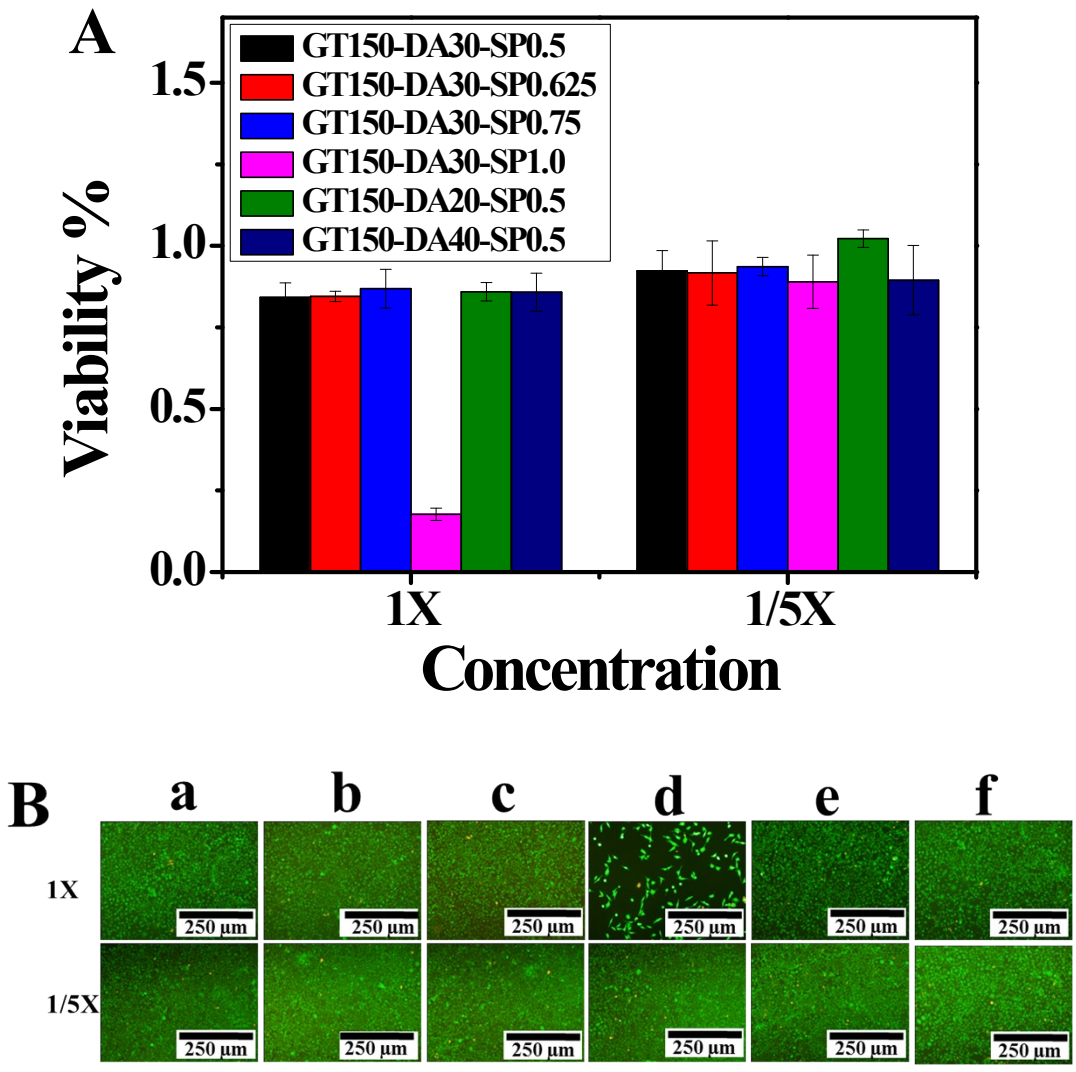


Figure S5. Cytotoxicity of hydrogel extracts for 24 hours. A: cell viability measured by Alamarblue assay; B: Live/Dead staining of cell. 1x represented 2 mL hydrogel in 3 mL culture medium, and 1/5x represented the five times dilution of the 1x extracts. Scale Bar 250 μm. a-f: GT150-DA30-SP0.5, GT150-DA30-SP0.625, GT150-DA30-

SP0.75, GT150-DA30-SP1.0, GT150-DA20-SP0.5, and GT150-DA40-SP0.5.

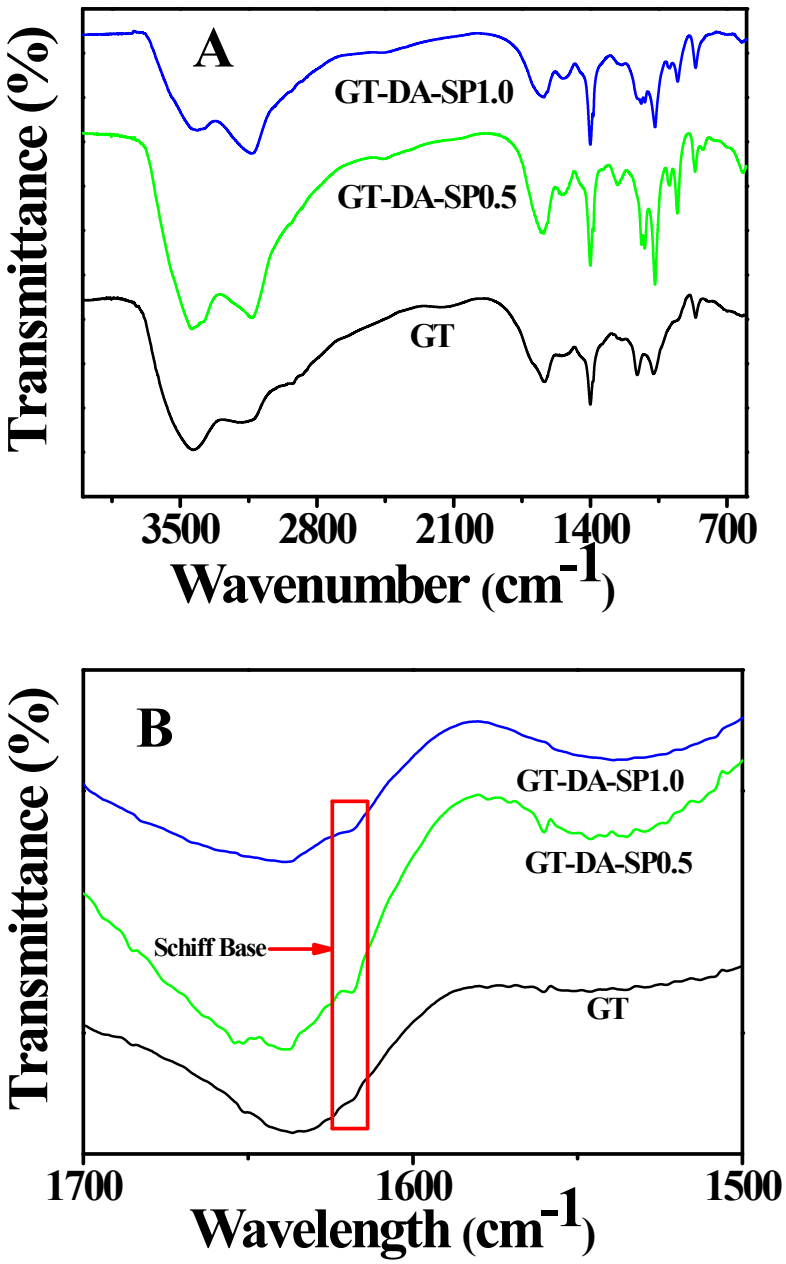
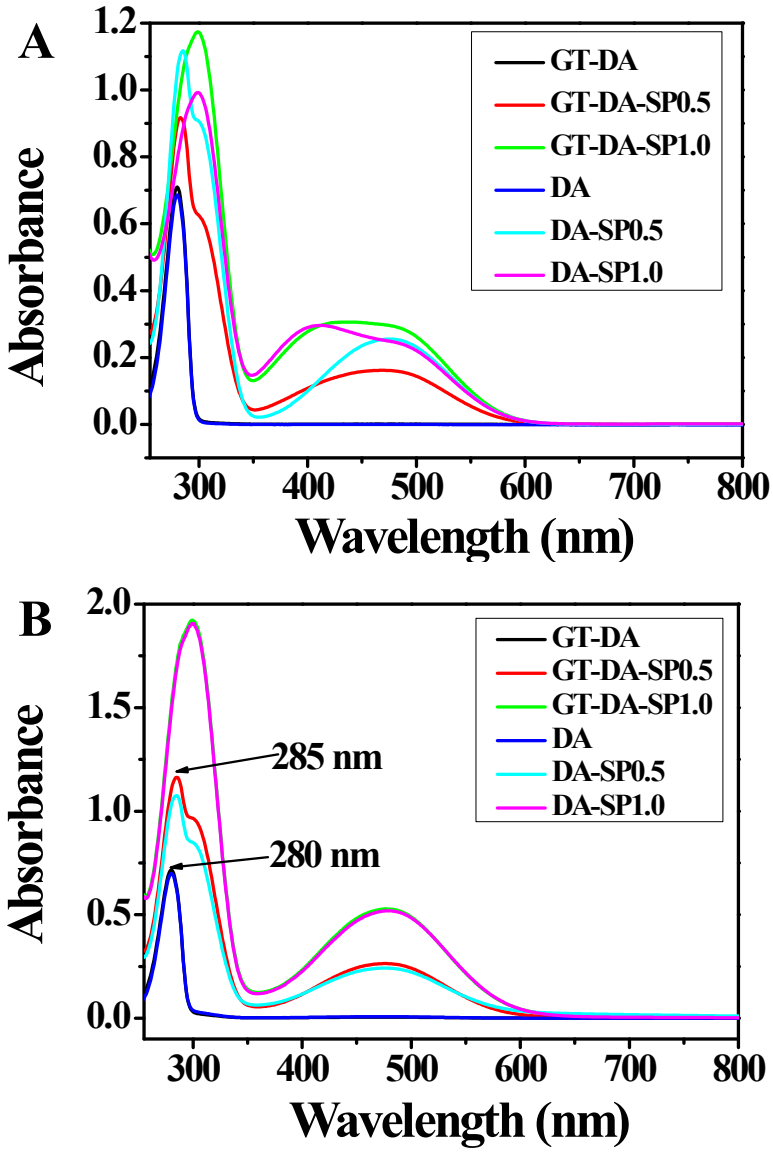


Figure S6. FTIR spectra of the dried hydrogels (GT150-DA30-SP0.5, and GT150-DA30-SP1.0), and gelatin (A), and a magnification of the spectrum from 1700 cm^{-1} to 1500 cm^{-1} (B).

The characteristic peaks of polydopamine could be found from the FTIR spectra

(Figure S6A) of hydrogels. Absorption at about 1637 cm^{-1} corresponding to the stretching vibration of aromatic ring and bending vibration of N-H [4], the catechol-OH groups at around 3420 cm^{-1} [5], the phenolic C-O-H bending vibration at 1400 cm^{-1}, and C-O vibration at 1120 cm^{-1} [4] were all observed.



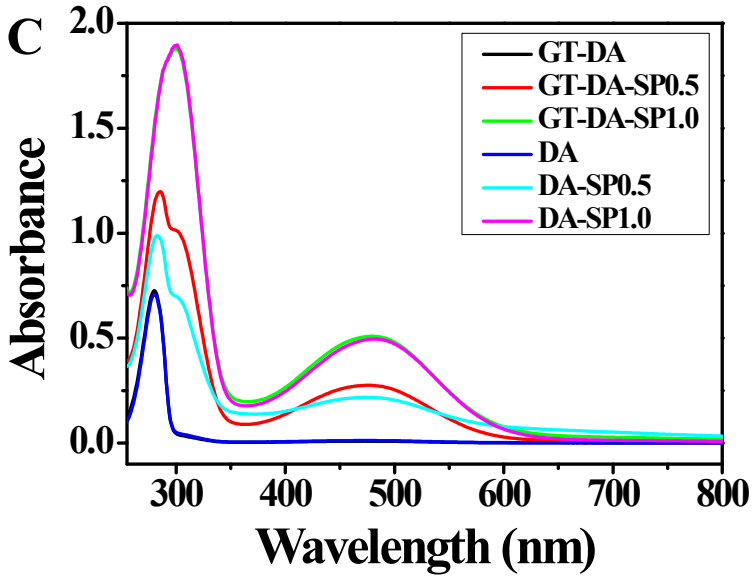


Figure S7. UV-vis spectra of dopamine, dopamine oxidized by 0.5 and 1.0 molar ratio of $NaIO_4$, gelatin/dopamine, gelatin/dopamine oxidized by 0.5 and 1.0 molar ratio of $NaIO_4$, at 0 hour (A), 12 hours (B) and 24 hours (C), respectively, in deionized water. GT, DA and SP represented the gelatin, dopamine and $NaIO_4$, respectively.

As shown in Figure S7A, the spectra of DA and GT/DA (0.5 mg/mL GT and 0.025mg/mL DA) presented the characteristic absorption peak at 280 nm corresponding to unoxidized catechol groups [6]. After the introduction of half molar ratio of $NaIO_4$ into pure DA solution and GT/DA solution, in addition to the unoxidized catechol groups absorption peaks, two new features appeared in the spectra at 300 nm and 476 nm (Figure S7B), which is associated with aminochrome [7]. However, when adding equal molar ratio of $NaIO_4$ into the pure DA solution and GT/DA solution, the catechol group absorption peak disappeared, and a characteristic peak for dopaquinone at about 400 nm appeared (Figure S7A) and gradually replaced

by the absorption peaks of aminochrome at 300 nm and 476 nm.

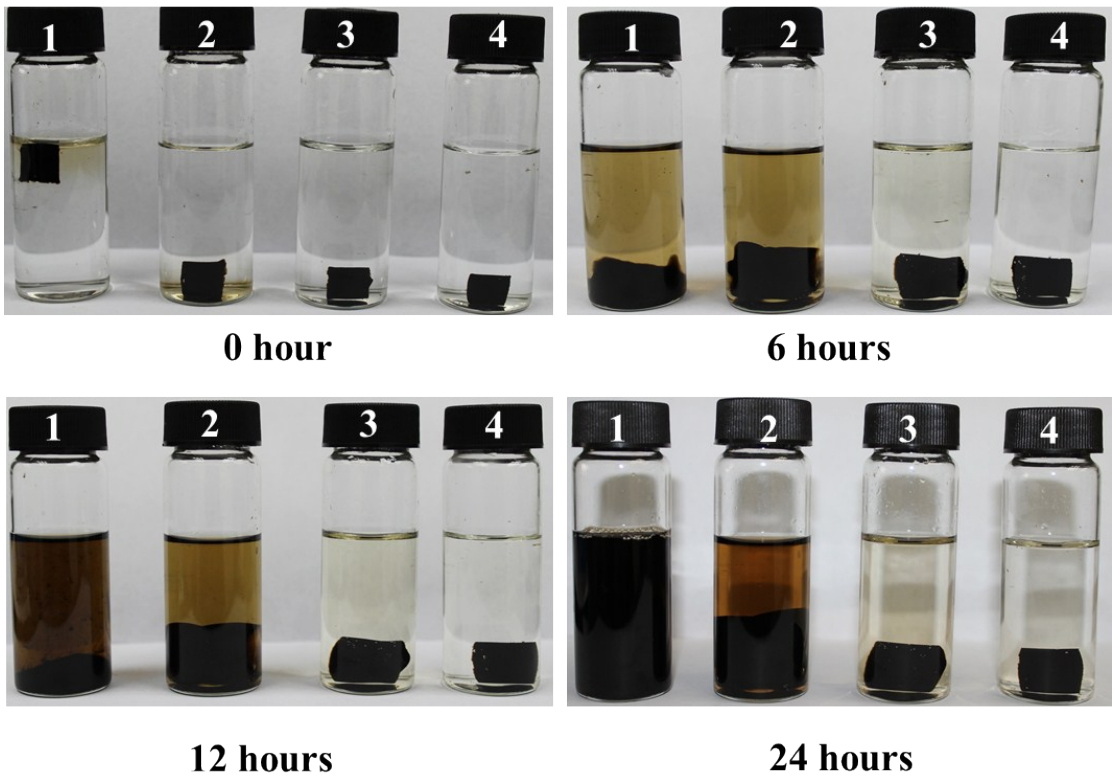


Figure S8. Stability test of hydrogels in 5 M urea solution and deionized water. (1). Hydrogel GT150-DA30-SP0.5 in 5 M urea solution; (2). Hydrogel GT150-DA30-SP0.5 in deionized water; (3). Hydrogel GT150-DA30-SP1.0 in 5 M urea solution; (4). Hydrogel GT150-DA30-SP1.0 in deionized water.

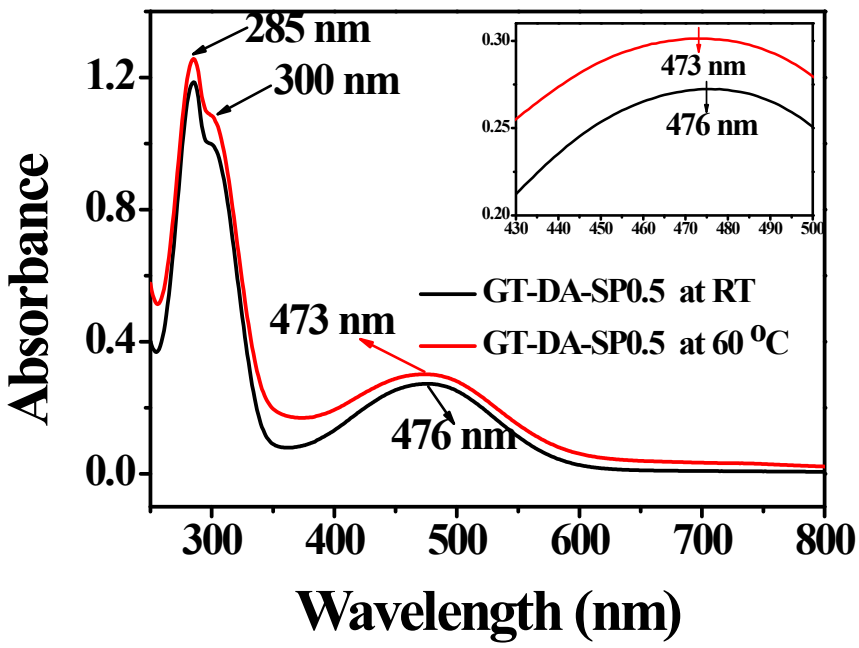


Figure S9. UV-vis spectra of GT-DA-SP0.5 cured at RT and 60°C, respectively.

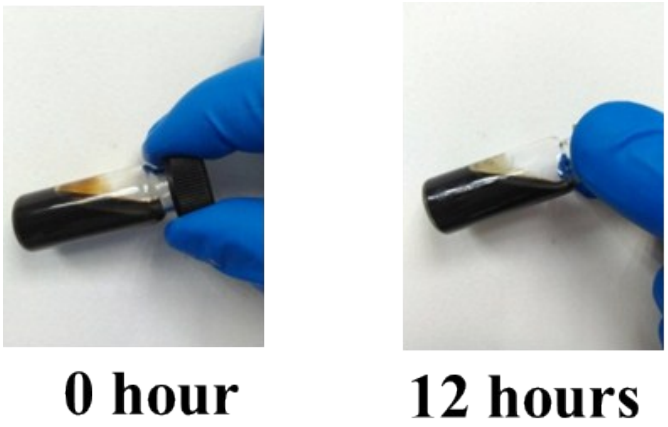


Figure S10. Photographs of 20wt% dextran with 3wt% dopamine oxidized by 1:1 molar ratio of $NaIO_4$ to dopamine at 37 °C for 0 hour and 12 hours, respectively.

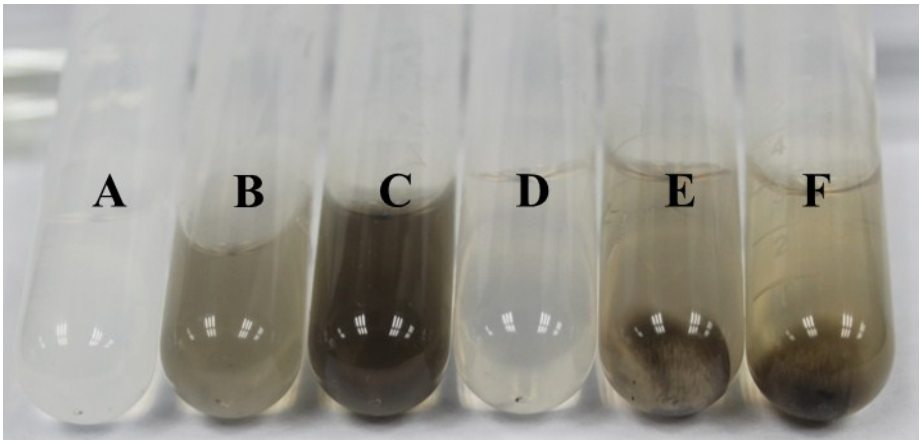


Figure S11. Photographs of gelatin/dopamine (A), gelatin/dopamine oxidized by 0.5 (B) and 1.0 (C) molar ratio of $NaIO_4$, dopamine (D), and dopamine oxidized by 0.5 (E) and 1.0 (F) molar ratio of $NaIO_4$, at room temperature for 10 days.

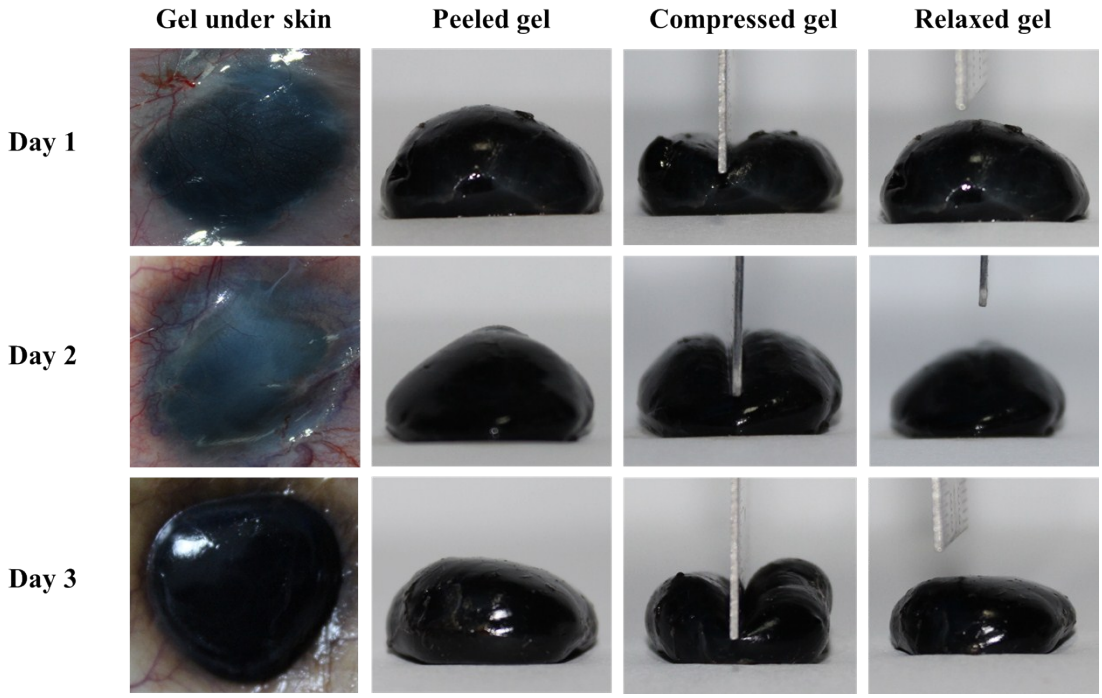


Figure S12. Hydrogel morphologies under the rat's skin for 1, 2 and 3 days, peeled from the skin, after compressed by steel rule, and relaxed state after experiencing compression.

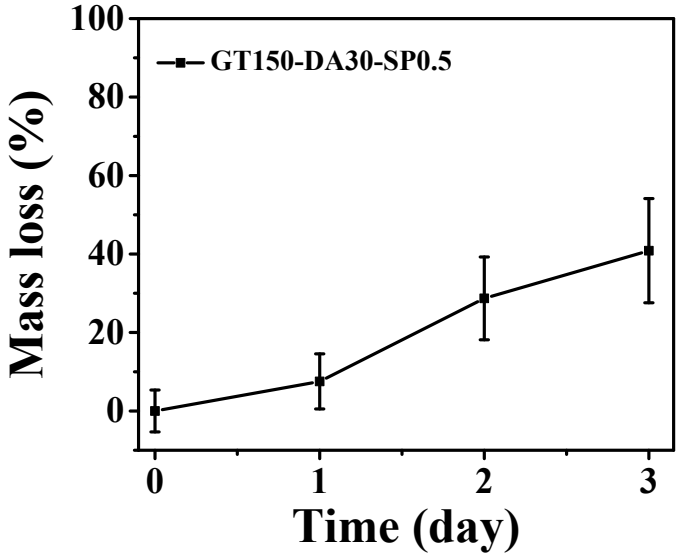


Figure S13. In vivo biodegradation profile of hydrogel GT150-DA30-SP0.5 under rat's skin.

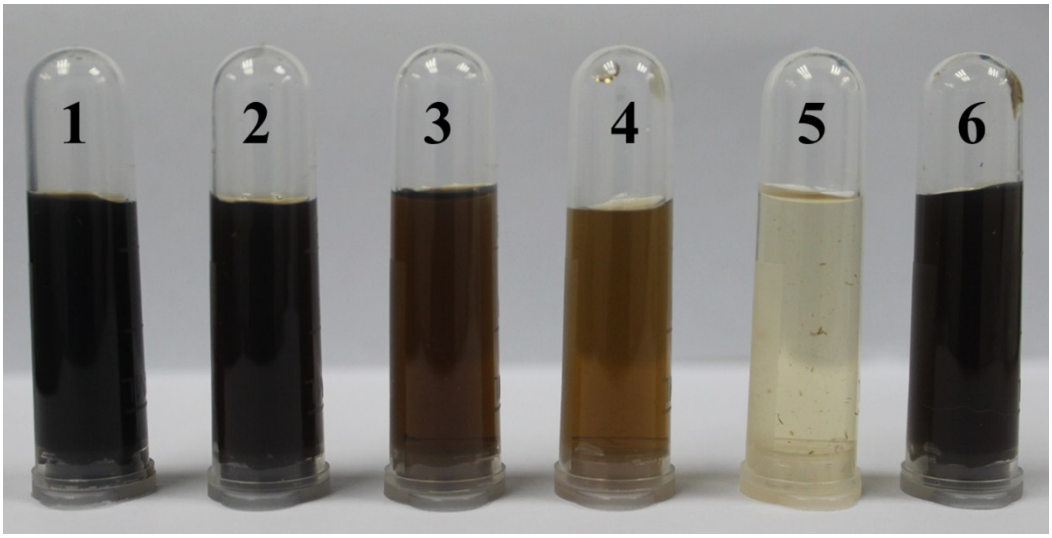


Figure S14. Photographs of hydrogel extracts after diluted 3 times. (1) GT150-DA20-SP0.5; (2) GT150-DA30-SP0.5; (3) GT150-DA30-SP0.625; (4) GT150-DA30-SP0.75; (5) GT150-DA30-SP1.0; (6) GT150-DA40-SP0.5.

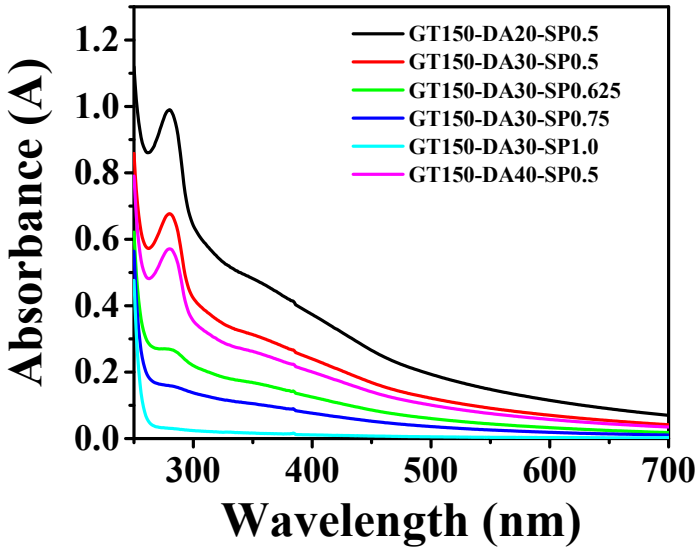


Figure S15. UV-vis spectra of hydrogel extracts.

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