Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

Self-healing conductive hydrogels based on alginate, gelatin and polypyrrole serve as a repairable circuit and a mechanical sensor

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1. The oxidation degree of oxidized sodium alginate

It can be seen from the comparison of the infrared spectra that a weak peak appears at 1735 cm^{-1} in red line, corresponding to aldehyde group in oxidized sodium alginate. Another characteristic peak of the aldehyde group is at 2820 cm^{-1}, which is masked by the alkyl peak.

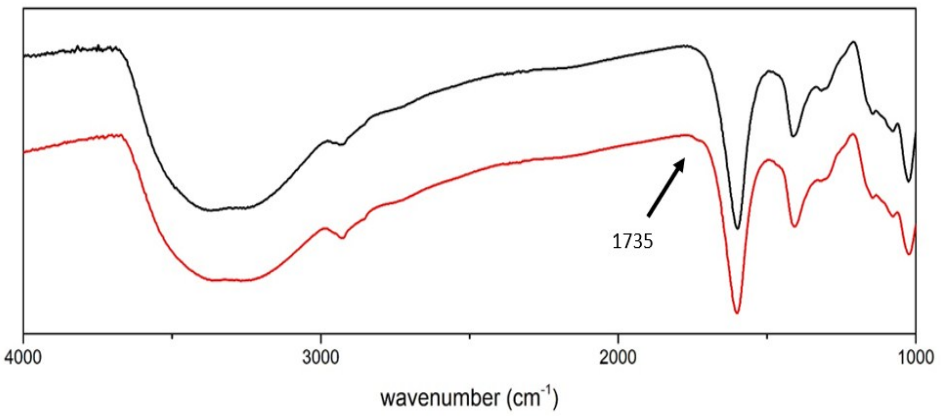

Fig. S1 FTIR spectra of sodium alginate (black line) and oxidized sodium alginate (red line)

The oxidation degree of oxidized sodium alginate is defined as the mole percent of

oxidized aldehyde to the sodium alginate uronic acid. The degree of oxidation can be determined by hydroxylamino hydrochloride titration. The procedure is embedded in detail.

(1) Preparation of hydroxylamino hydrochloride solution

Hydroxylamino hydrochloride was dissolved in deionized water, sodium hydroxide (NaOH) ethanol solution and 0.455% bromophenol blue solution were added into the solution. The solution was stirred and placed overnight. We took the supernatant for further detection.

(2) Preparation and calibration of hydrochloric acid solution

0.1 mol/L hydrochloric acid solution was prepared as a titration solution. 0.1 mol/L sodium hydroxide solution is accurately prepared, 0.1 mol/L sodium hydroxide solution is accurately prepared for calibrating hydrochloric acid solution. Two drops of phenolphthalein were added into hydrochloric acid and titrate it with NaOH solution, after that, we can get the exact concentration of hydrochloric acid solution.

(3) Titration of aldehyde group content

The sample was added to the hydroxylamino hydrochloride solution and titrated with a hydrochloric acid solution, and the consumption of the hydrochloric acid solution was recorded.

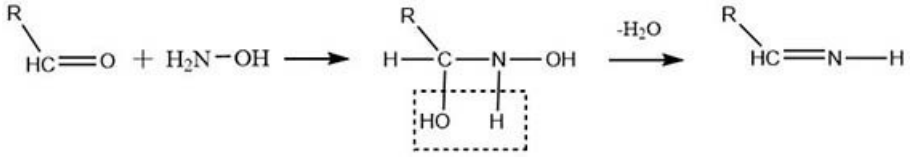

Fig S2. Hydroxylamino hydrochloride reaction mechanism

$$\text{oxidation degree} = \frac{198 \times N \times (V_2 - V_1)}{W} \times 0.5 \times 100\%$$

where N is the concentration of hydrochloric acid, V_1 is the amount of hydrochloric acid in experiment, V_2 is the amount of hydrochloric acid in blank test and W is the sample weight. In this experiment, the concentration of hydrochloric acid was 0.11 mol/L, V_1 was measured as 16.5 mL, V_2 was measured as 21.5 mL, W was measured as 0.1 g. After calculation, the oxidation degree is 54.45%.

2. The amino concentration of gelatin

It can be seen from the comparison of the infrared spectrum that the intensity of the peaks at 3307, 1645, and 1547cm^{-1} is obviously enhanced, which indicates that the concentration of the amino group increases after the reaction.

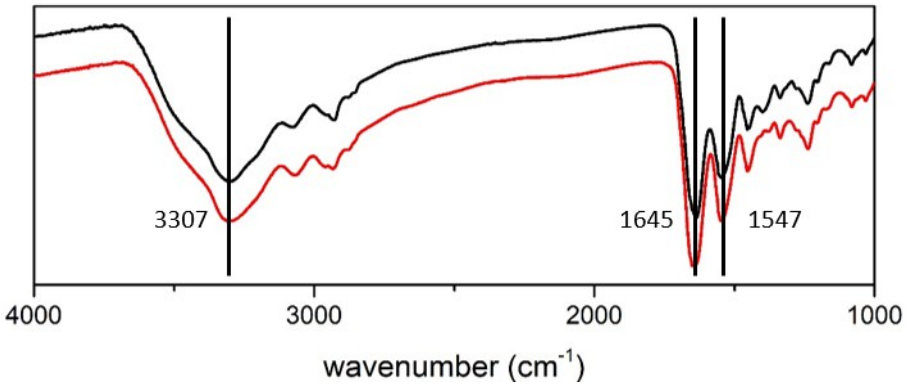

Fig S3. FTIR spectra of gelatin (black line) and aminated gelatin (red line).

The exact concentration of the amino group can be determined by comparing the absorbance values after staining the amino group with ninhydrin. The procedure is embedded in detail.

(1) Preparation of ninhydrin solution

Ninhydrin and stannous oxide are dissolved in water. The solution was stirred well and left in the dark for 24 hours.

(2) Determination of absorbance standard curve

Different concentrations of glutamic acid solution were prepared and a ninhydrin solution was added to the mixture, followed by heating in a water bath. After the solution was cooled, the absorbance at 570 nm under each concentration condition was recorded. The above operation was repeated by changing the initial gelatin to ammoniated gelatin.

(3) Determination of amino group concentration

A certain quality sample is dissolved in water to prepare a solution and a ninhydrin solution was added, followed by heating in a water bath. After the solution was cooled, the absorbance at 570 nm under each concentration condition was recorded. The determine the amino concentration of the sample according to the standard curve.

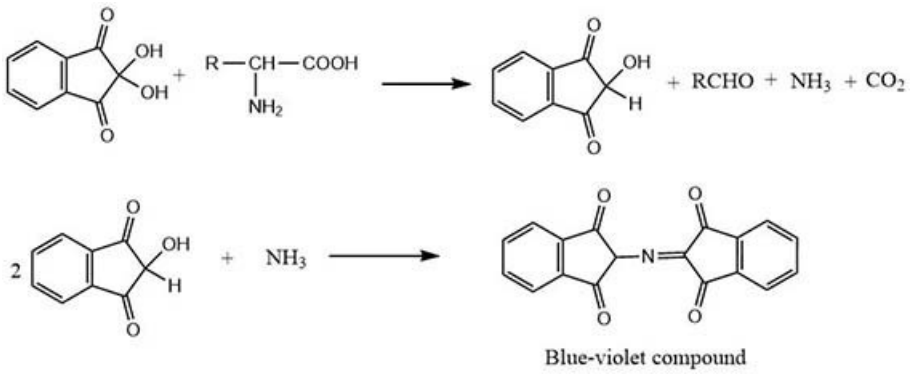

Fig. S4 Mechanism of ninhydrin colorimetry

After calculation, the curve variance was 0.98425. The absorbance of the initial gelatin solution was 0.26338, and the absorbance of the ammoniated gelatin solution was 0.91335. The amino concentration of initial gelatin was 0.513 mmol/g, and the amino concentration of ammonia gelatin was 1.507 mmol/g.

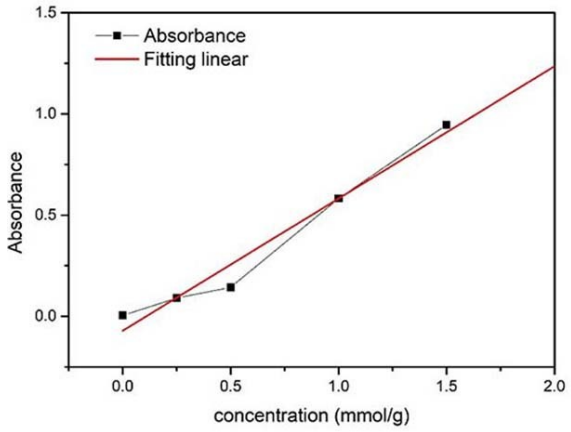

Fig. S5 Absorption standard curve measured by ninhydrin colorimetry at 570 nm in the spectrum.

3. Biotoxicity test of hydrogel

(1) Preparation of hydrogel film

HP_0 and HP_1 hydrogels were prepared and filmed, soaked with deionized water, and changed twice a day. The treated film was cut into a sample with 1 cm in diameter. The sample was sterilized by using ethanol and ultraviolet radiation and lyophilized.

(2) MTT experiment

The hydrogel sample was immersed in the culture medium to obtain the hydrogel extracts for use. The MC3T3 cell suspension was inoculated into the culture plate. The blank control, the positive control, the HP_0 and the HP_1 group were set for the comparison. The plate was cultured for 24 hours, and the original culture solution was discarded to obtain the cells. The blank control group was added with fresh cell-culture medium; the positive control group was added with DMSO solution. The other groups were separately added with extracts of different groups of materials and cultured for 24 hours. Then, MTT solution was added to the well. After 4 hours of incubation, the liquid in the plate was discarded, DMSO was added, and waited for 10 min. The absorbance

was measured at a wavelength of 630 nm and averaged, and the amount of cell proliferation was characterized by absorbance.

$RGD=A/A_0*100\%$

（RGD is the relative proliferation degree, A is the material absorbance, and A_0 is the blank control absorbance.）

We found that the negative control group was more toxic, the proliferation rate was 21.82%; the relative proliferation rates of HP_0 and HP_1 were 53.18% and 64.08%, respectively, and the toxicity was smaller than that of 1% DMSO, and the toxicity was mild.

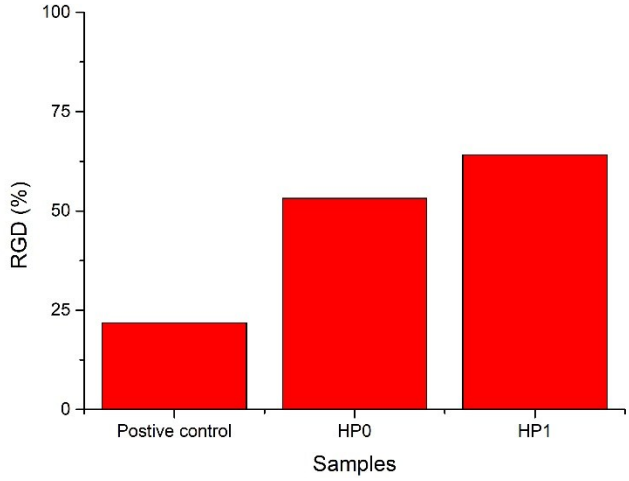

Fig. S6 Cytotoxicity results of samples

4. TEM test of hydrogel

We performed a TEM test by diluting the precursor solution and dropping onto a copper mesh. The images show void size at 1-5 μm, similar to the results of SEM (Figure 3). Also, there exist some rigid particles that adhere to the hydrogel network. Result demonstrates the growing of Ppy is nearby the hydrogel network with sodium alginate serving as the structural templating agent, ensuring the conductive property of

the hydrogel.

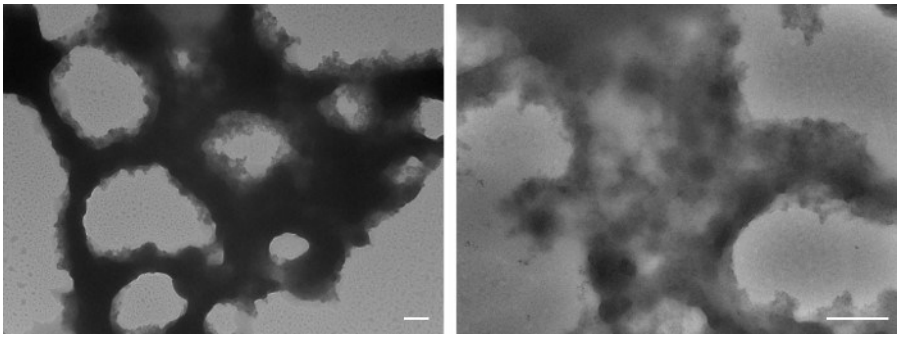

Fig.S7 TEM photograph of HP_1. The scale bars are 500 nm.

5. Mechanical strength of LTH with different polypyrrole contents

As shown in Figure S8, the mechanical property of HP_5 is better than other ratios. A small amount of polypyrrole could increase the mechanical strength of the hydrogels, but when the amount went too much, it could affect the formation of the hydrogel network, resulting in difficulty on forming the hydrogel network and reduction of its mechanical properties. When the content of polypyrrole reaches 15 wt%, the internal structure of the hydrogel was dominated by rigid polypyrrole particles, which causes the hydrogels breaking at lower strain.

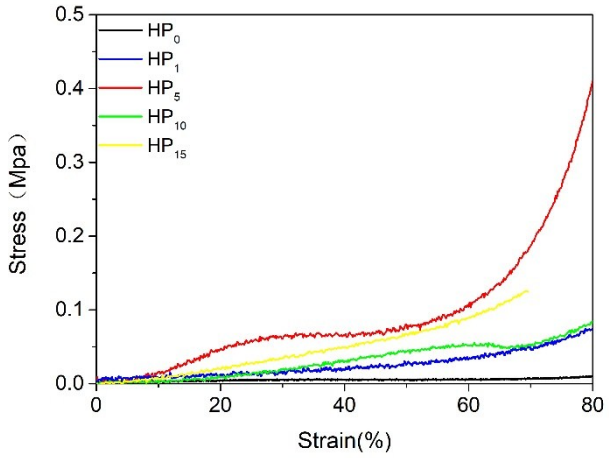

Fig. S8 Compressive stress-strain curve of HPx

6. Self-healing test of hydrogel

We have measured the rheological property of self-healing hydrogels (Figure 5b and 5c) that presents above 40% recovery of their original moduli in a short time after damage. To further verify the self-healing property, we measure the hydrogel without Schiff base structure (prepared from unoxidized sodium alginate and gelatin) that shows modulus recovery less than 10%.

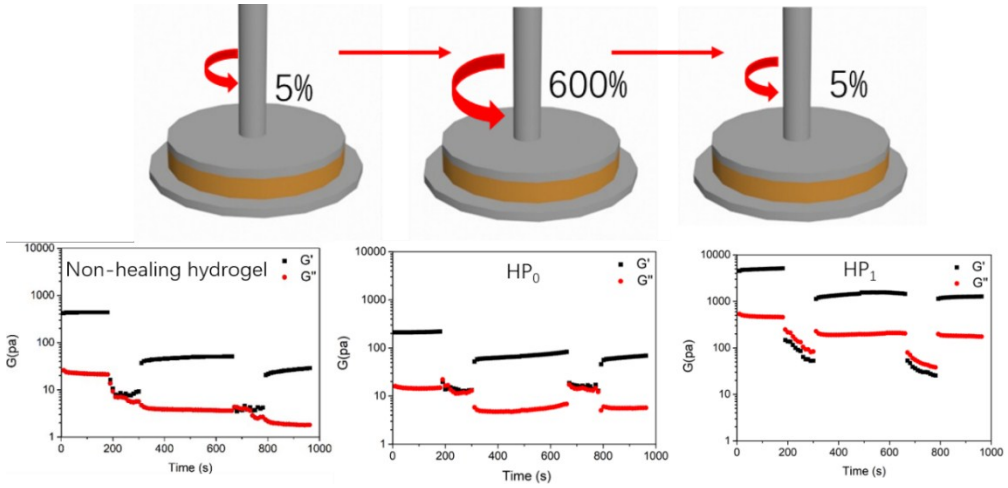

Fig.S9 Rheological tests comparison

7. Changes in electrical properties of hydrogels in different shapes and sizes

We tested the hydrogels of different shapes and sizes in the same way and found that although the initial resistance values were different, the resistance values changed similarly during the bending process. The initial resistance of cuboid (10mm × 40mm × 3mm), cuboid (10mm × 40mm × 6mm), and cylinder (12mm diameter × 30mm length) were 5.3KΩ,v3.75KΩ, and 1.56 KΩ, respectively.

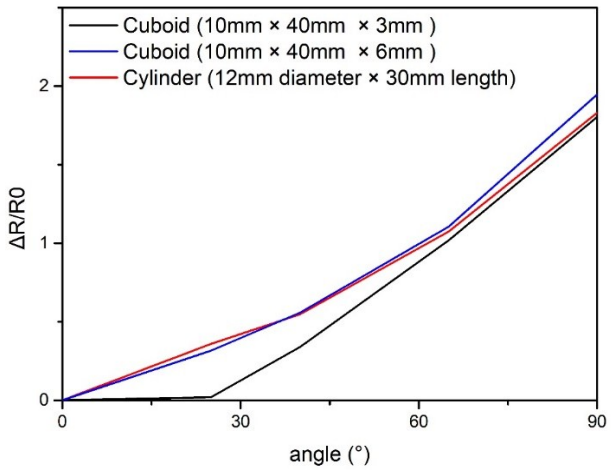

Fig. S10 Resistance curve of hydrogels in different shapes and sizes.