A thermo-responsive dual-crosslinked hydrogel with ultrahigh mechanical strength

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Experimental

Materials

Acrylic acid (AA), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ammonium persulfate (APS), N, N'-methylenebis-acrylamide (BIS) were purchased from Sinopharm Chemical Reagent, China. N-isopropylacrylamide (NIPAM), N, N, N', N'-tetramethyldiamine (TEMED) was purchased from Acros. All the reagents were used as received.

Preparation of double-crosslinked hydrogels

The hydrogels were prepared by a two-step method: First, 1.7 g NIPAM was dissolved in deionized water. Then different molar ratios of acrylic acid (5%, 15%, 25%, 30%, molar ratio of AA/NIPAM), 0.04 % (molar ratio of AA and NIPAM) chemical cross-linker BIS, 4 wt% initiator APS were added in the solution. The mixture solution was de-aired for 10 min with Ar. After that, 25 μL accelerator TEMED was added in the solution. Then the solution was transferred into the tube. The radical polymerization reacted at room temperature for 48 hours to form a covalently cross-linked hydrogel. Afterwards, 4.05 g $FeCl_3 \cdot 6H_2O$ was dissolved in 250 mL deionized water to form a homogeneous solution. The covalently hydrogel was immersed in the Fe^{3+} solution for 16 hours at room temperature to form a homogeneous transition state double-crosslinked hydrogel. After that, transition state double-crosslinked hydrogel was immersed in deionized water for 48 hours to remove superfluous Fe^{3+}. The feed compositions of the hydrogels are shown in Table 1. In this paper, hydrogels are expressed as C-hydrogel X or D-hydrogel X, where C refers to chemical crosslinking, D refers to dual cross-linking and X refers to the molar ratio of AA to NIPAM.

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Table 1 The feed compositions of the hydrogels.

Sample	NIPAM (g)	AA (g)	APS (g)	BIS (mg)	TEMED (μL)
C-hydrogel 5	1.70	0.0540	0.0717	0.92	25
C-hydrogel 15	1.70	0.191	0.0748	1.06	25
C-hydrogel 25	1.70	0.362	0.0845	1.16	25
C-hydrogel 30	1.70	0.465	0.0953	1.24	25

Characterization

The samples for SEM analysis were pretreated by freeze-drying technique. The morphology of specimens was observed on a QUANTA FEG 250 scanning electron microscope (SEM).The images were obtained under an accelerating power of 10 kV. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on an iN10MX spectrometer. The mechanical tests of the hydrogel were measured by an electrical universal material testing machine with a 100 N load cell (MTS Industrial Systems (China), CO., LTD.). The samples were cut into long strips with length 40 mm, width 5 mm and height of ~2 mm. The crosshead velocity was kept at 50 $mm \cdot min^{-1}$. All the measurements were conducted at room temperature. For the compressive tests, the hydrogel samples (column, with a diameter of 12 mm and height of 10 mm) were placed between the self-leveling plates. The samples were compressed at a rate of 20 mm min^{-1} until the compression ratio reached 80%.

Measurement of swelling ratio

Before the swelling experiment, the hydrogels were cut into small pieces and dried by lyophilization: Firstly, the hydrogels were set in the chamber at -56°C for 12 hours for pre-freezing. Afterwards, the frozen hydrogels were vacuum dried for 48 hours to a constant weight. The swelling ratios of hydrogel samples were measured in distilled water at various temperatures (20-60 °C) using a gravimetric method. The dried hydrogels were immersed in water until their weight became constant. The hydrogels were then removed from the water and their surfaces were blotted with filter paper

before weighed. The swelling ratio was calculated with the following equation:

$$Swelling\ ratio = \frac{W_s - W_d}{W_d} \quad (1)$$

where W_d and W_s represent the weights of the dried hydrogel and the hydrogel at swelling equilibrium state, respectively. All the experiments were carried out in triplicate, and the average values were reported.

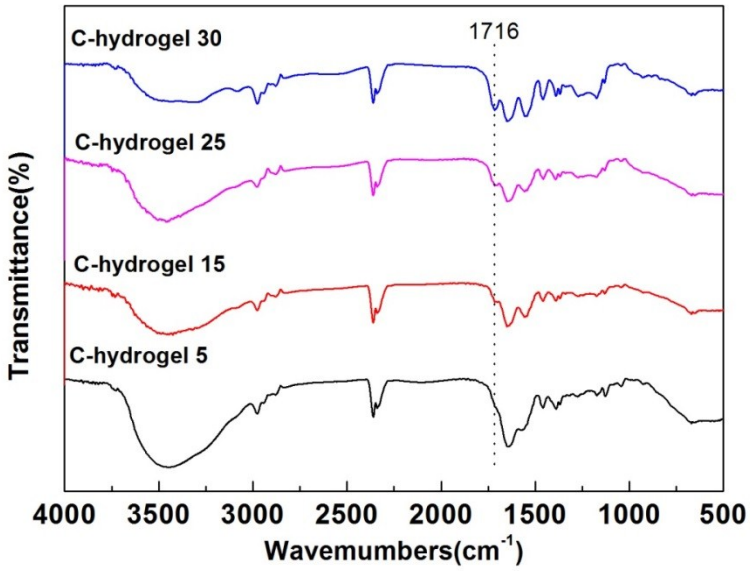

Fig. S1. FT-IR of C-hydrogels with the varying feed compositions.

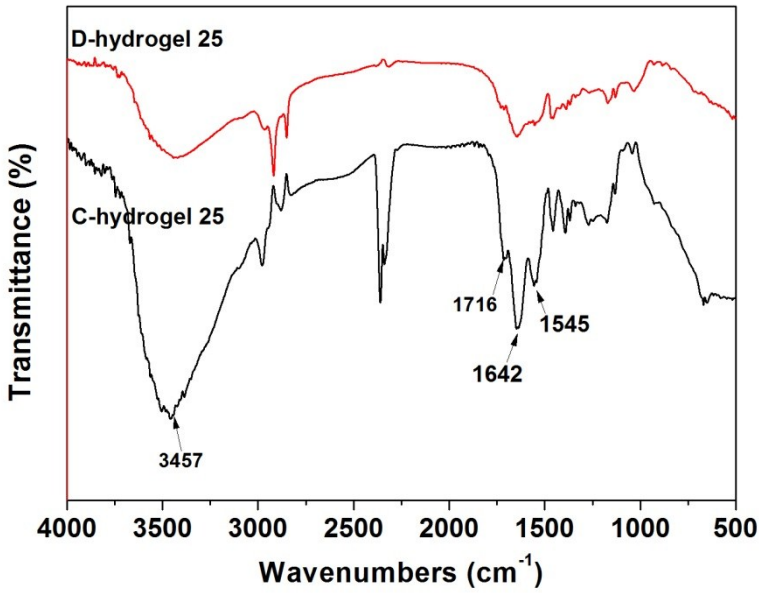

Fig. S2. FT-IR spectra of C-hydrogel 25 and D-hydrogel 25.

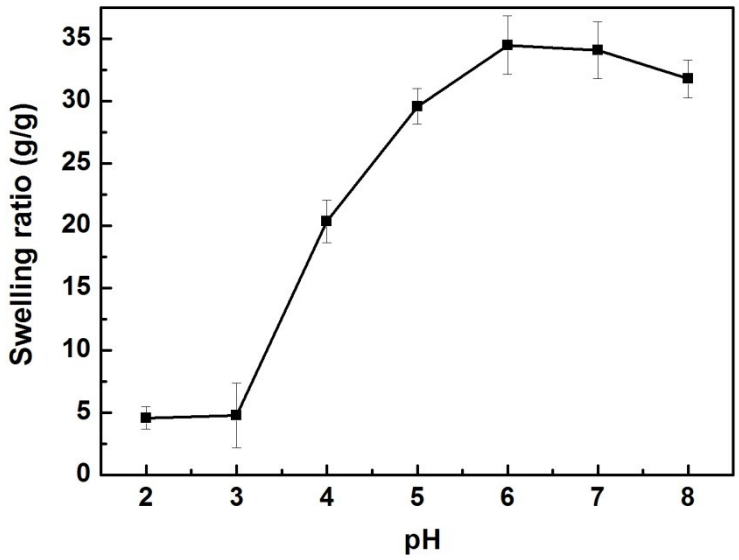

Fig. S3. The swelling ratio of C-hydrogel 15 as a function of pH.