

Electronic Supplementary Information

Autonomous self-healing of poly(acrylic acid) hydrogels induced by the migration of ferric ions

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1. Methodology and materials.

Materials: acrylic acid (AA, Sigma), N,N'-methylene-bis(acrylamide) (MBAA, Sigma), ferric chloride hexahydrate (FeCl₃·6H₂O, Baker), ammonium persulfate (APS, Sigma), sodium citrate (Sigma), Hydrogen dioxide (Fisher Scientific), Rhodamine B, Tetramethylethylenediamine (TEMED) were used as received. A stock solution of APS was prepared by dissolving APS in distilled water to a concentration of 0.5g/mL.

Hydrogel synthesis. A typical hydrogel was prepared by free radical polymerization of an aqueous solution containing 1.39 mol/L of AA, 1.25% FeCl₃ (mol/mol AA) and 0.1% MBA (mol/mol AA). The solution was degassed by purging with argon gas. A 5% (wt% compared with AA) of APS stock solution was then added to initiate the reaction. The solutions were sealed and left undisturbed for 16 hours at 25°C. Hydrogels with different physical cross-linking densities were produced by varying the concentrations of FeCl₃ between 0%, 0.5%, 1.25% and 2.5% (mol/mol, compared with AA). Hydrogels with different chemical cross-linker content were synthesized by using MBAA with a concentration of 0%, 0.1%, 0.5% and 1% (mol/mol AA). The details of the hydrogel recipe were listed in table 1. In order to precisely study the self-healing behavior, all experimental hydrogel samples were fabricated in cylindrical shapes with a diameter of 1 cm. The polymerization reactions for the experimental hydrogels were carried out as described above.

2. Stretching property test of hydrogel.

We studied the self-healing behavior of the hydrogel by mechanically stretching the hydrogel. We define the Maximum strain (ϵ) as $\epsilon = L/L_0 \times 100\%$, where L is the stretched length at the breaking point and L_0 is the original length (un-stretched length). The healing efficiency of a hydrogel (f) is defined as $f = \epsilon'/\epsilon$, where ϵ' is the modulus of the healed hydrogel and ϵ is the strength of the original hydrogel (uncut hydrogel). The value of f was used to assess the self-healing property of this hydrogel.

(Details were listed in Figure 4a, b, c)

Each hydrogel sample was fabricated in a cylindrical shape with a diameter of 1 cm. Each test required (In Figure 4 a, b), two samples, one sample was used to obtain the properties of the original sample, while the other sample was cut and left in contact to fuse. Finally, we manually stretched the sample and recorded the maximum strain (ϵ'). For each point in Figure 4 c, seven samples were tested and averaged. All of the samples were tested at different healing times (1h, 2h, 3.5h, 6h, 12h, 18h and 24h).

3. Spectroscopic Analyses.

Fourier transformed infrared attenuated total reflection (FTIR-ATR) of the samples were tested on Thermo Nicolet NEXUS 670 FTIR. The Raman test was formed on Raman Microscopy (Horiba Yvon LabRam ARAMIS). The sample used here was Entry 3 (In table 1) and the hydrogel samples were directly tested without any dispose.

4. Rheology test.

Steady and dynamic rheological experiments were performed to obtain strain sweep spectra (frequency 1rad/s), frequency sweep spectra (strain 5%) and time sweep (frequency 1rad/s, strain 5%) spectra of the hydrogel (Entry 3 in table 1) using an AR2000 stress controlled rheometer (TA Instruments). Measurements were performed on plate geometry (20 mm diameter) equipped with Peltier-based temperature control. All the measurements were conducted at $25 \pm 0.1^\circ\text{C}$. A solvent trap was also used to minimize the evaporation of solvent. A continuous step strain of this hydrogel (Entry 3 in table 1) measurement was also tested using this instrument. Briefly, gel Entry 3 was subjected to 400% strain first, then to 5% strain, and this process was cycled twice. A scanning frequency of 1 rad/s was used.

5. Sol-Gel reversible experiment.

In order to further confirm the physical cross-linking function of Fe^{3+} in the formation of hydrogel, a redox Sol-Gel reversible experiment was set up. In Figure S4, the PAA hydrogel was prepared following the same method, but this sample (Entry 6) does not contain any chemical cross-linker (MBAA). We can clearly see that Fe^{3+} could crosslink the PAA hydrogel (Figure S4a). Next, we added a small amount of sodium citrate solution and heated this sample in a water bath. We observed that this hydrogel changed to a Sol (Figure S4b) with a color change from brown to light yellow due to the reduction of Fe^{3+} to Fe^{2+} which cannot crosslink PAA chains¹⁹. Finally, we added H_2O_2 and HCl solutions into this Sol system. We observed that the Sol reverted to its original hydrogel state due to the oxidation of Fe^{2+} to Fe^{3+} ions by H_2O_2 (Figure S4c).

6. Hybrid hydrogel.

We evaluated the effect of the concentration of MBAA and Fe^{3+} on the mechanical properties of these hydrogels. For this purposes, we prepared a hybrid hydrogel (See Figure S5a). The transparent part consists of the pure Chemical Gel

(Entry 10, AA 10 wt%, water 90 wt%, MBAA 1 mol%), and the red portion consists of the composite Gel (Entry 7, AA 10 wt%, water 90 wt%, MBAA 0.25 mol%, Fe³⁺ 1.25 mol%, Rhodamine B). Upon stretching, the two hydrogels showed different moduli and elastic properties (Figure S5b). The hybrid gel was prepared as follows: firstly, a precursor of pure chemical hydrogel (recipe Entry 10) was filled into a glass tube with diameter 1cm. After the polymerization, a precursor of composite hydrogel (recipe Entry 7) and rhodamine B were filled into the top half of the tube. The hybrid hydrogel was obtained after the gelation of the second portion.

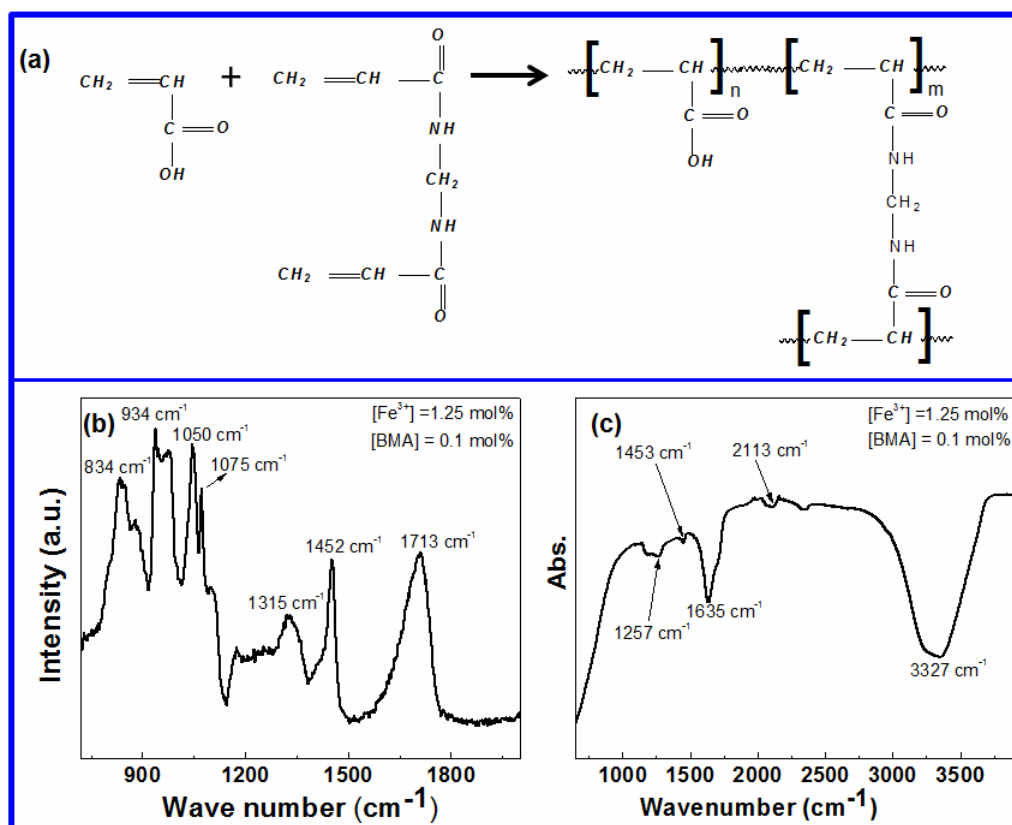


Figure S1. Reaction scheme and spectral analysis of the self-healing hydrogel. (a) Reaction scheme for the synthesis of hydrogels. (b) Raman spectral analysis. (c) FTIR spectral analysis. The sample used here is Entry 3.

The hydrogel was characterized by Raman spectroscopy and Fourier transform infrared spectroscopy (FT-IR). Raman spectra revealed a peak at 1713 cm⁻¹ that originated from carboxylate groups of PAA, and a band at 1452 cm⁻¹ due to the bend vibration of CH₂ in the polymer backbones (Figure S1b). The FT-IR spectra of this hydrogel has peaks at 1713 cm⁻¹ and 1453 cm⁻¹, which are also attributed to carboxylate groups of PAA and bend vibration of CH₂ in the polymer. The peak at 1635 cm⁻¹ is attributed to the C=O, C-N from polymer backbones. FTIR peak at 3327 cm⁻¹ is attributed to the -OH stretch of water or N-H stretch from polymers (Figure S1c).

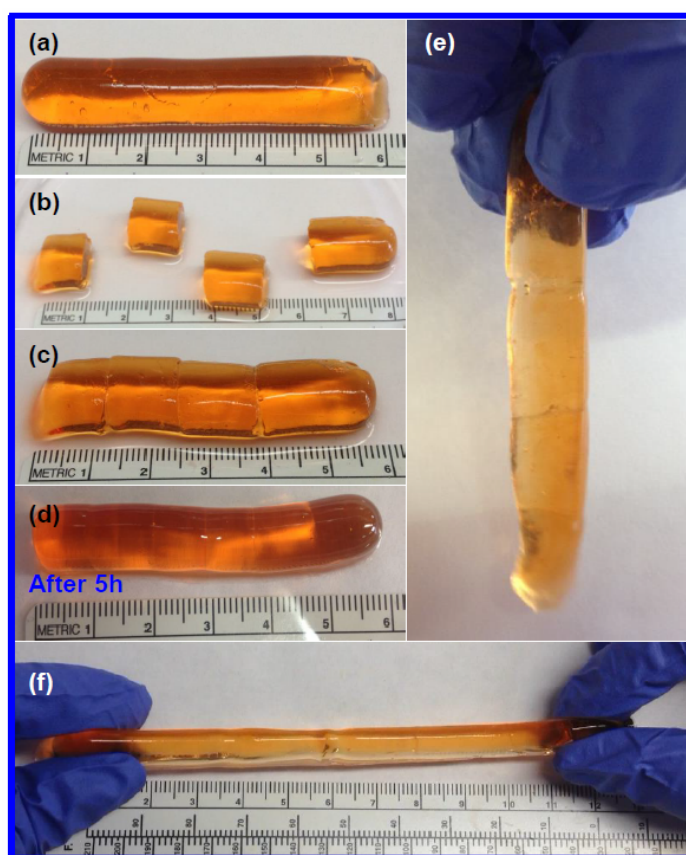


Figure S2. Self-healing hydrogel (Entry 3). (a) Original hydrogel. (b) The hydrogel was separated by cutting. (c) Hydrogel sections are left in contact to allow for self-healing. (d) Hydrogel after 5 hours of self-healing. (e) Healed hydrogel can support its own weight. (f) Hydrogel was stretched to test mechanical properties. It is shown that the hydrogel can be stretched to 200% original length even after healing.

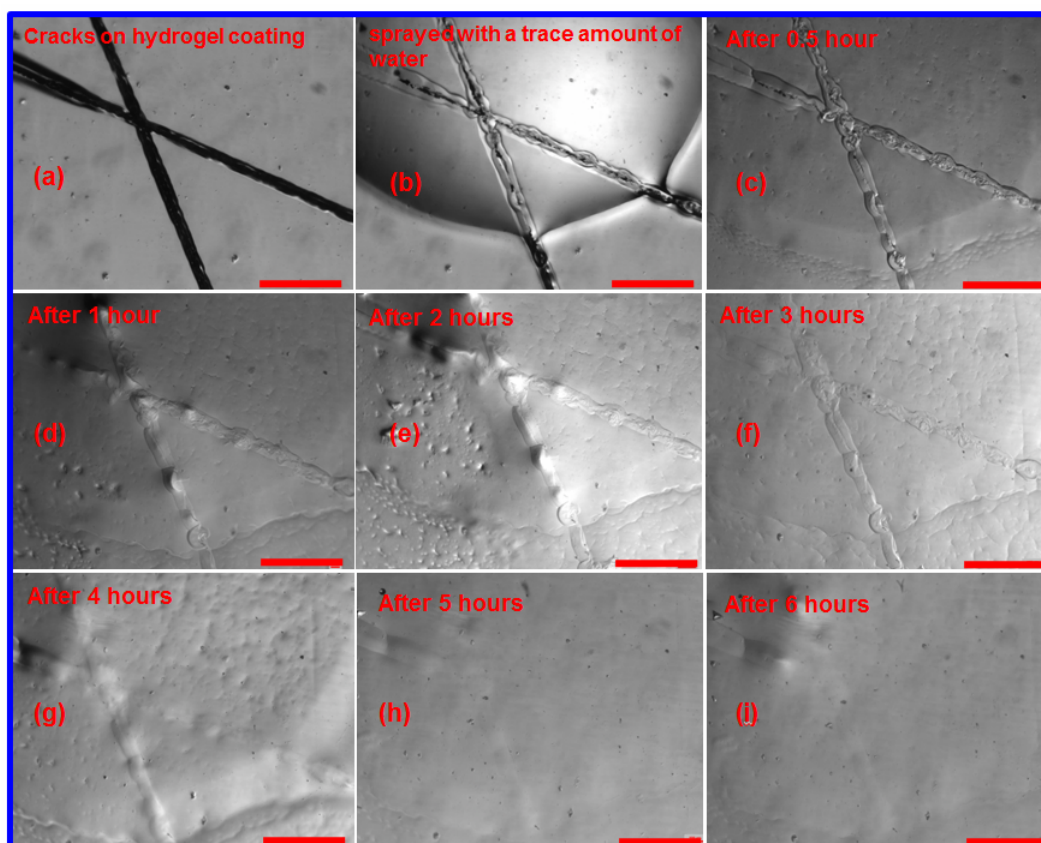


Figure S3. The use of dried PAA&Fe³⁺ self-healing hydrogel film as a protective coating. (a) Hydrogel with a crack of about 100μm in width on a glass surface. (b) The hydrogel was sprayed with a trace amount of water. (c-i) the hydrogel at different times in the process of self-healing. The hydrogel completely healed with no visible cracks after 6 hrs. Images were taken with an optical microscope (Nikon Eclipse Ti). The scale bar is 500 μm.

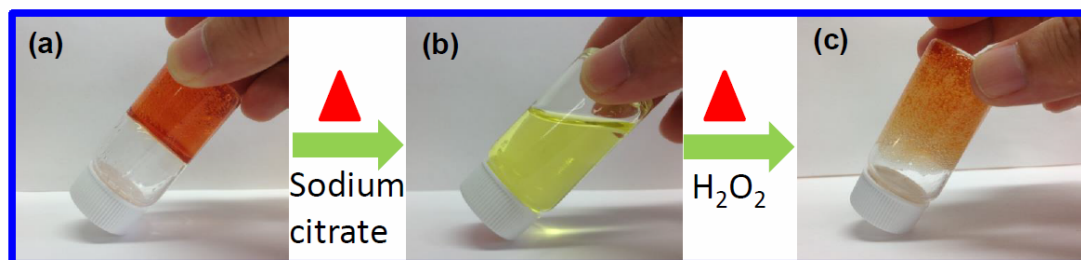


Figure S4. Switchable gel-sol-gel transition demonstrates the cross-linking function of Fe^{3+} . (a) Hydrogel synthesized in a vial followed the recipe of Entry 6. (b) A gel to sol transition was observed upon the addition of sodium citrate solution and followed by heating. (c) The gel recovered upon the addition of H_2O_2 . There are some bubbles (O_2) produced in the hydrogel due to the redox reaction of H_2O_2 .

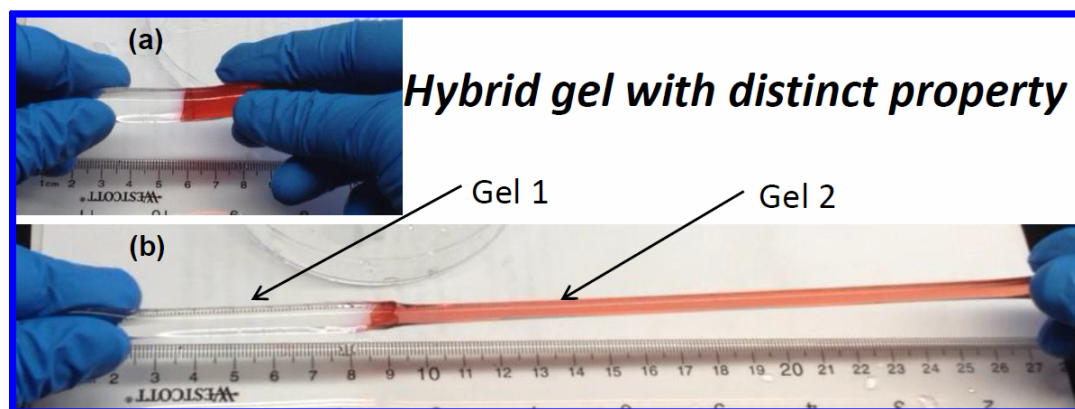


Figure S5. Hybrid hydrogel with different mechanical properties. (a) Hybrid hydrogel with transparent Gel₁ (followed the recipe Entry 10) and red Gel₂ (followed the recipe Entry 7) (b) The hybrid hydrogel was stretched.