Experimental Section

Materials

Acrylic acid (AA) was purchased from Aladdin Chemistry Co., Ltd. 2-Hydroxy-1-[4-(hydroxyethoxy) phenyl]-2-methyl-1-propanone (photoinitiator 2959), potassium persulfate (KPS), N,N-methylenebis(acrylamide) (MBA), and protocatechuic acid (PCA) were obtained from Shanghai Energy Chemical Co., Ltd. Polyamidoamine-epichlorohydrin (PAE, 12.5% aqueous solution, Mw 25000) was provided by Shandong Tiancheng Chemical Co Ltd (China).Co., Ltd. Deionized water was used in all experiments. All the reagents were used as received unless otherwise stated.

Synthesis of PAA-PAE-PCA hydrogel

PAA-PAE-PCA hydrogels were prepared by a simple one-pot method. AA was mixed with 16 ml deionized water at 20% (w/v) of AA. The photoinitiator 2959, thermal initiator KPS and cross-linker MBA were added to the AA solution and stirred for 3 mins, followed by the addition of PCA. The mass ratios of AA to PCA were 1:0.02, 1:0.06, and 1:0.10, respectively. Then, PAE was added and the mass ratio of PAE to PCA was fixed at 1:1.25. The solution was then injected into a reaction cell, which consisted of two pieces of glass separated by a 2 mm silica spacer, and photopolymerized under 365 nm UV light for 1.5 h. Thereafter, the prepared hydrogels were heated at 75 °C for 5 h. Finally, the gels were washed with water for 2 hours with solution exchanged every 30 minutes to remove unreacted monomers or PCA. The samples were named 2%, 6%, and 10% PCA according to the mass ratio of PCA to AA. PAA and PAA-PAE hydrogels were prepared using the same procedure without the addition of PCA/PAE and PCA.

General characterization

The chemical structure of the hydrogels was determined by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Thermo iS10) with a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1} at room temperature.

Rheological measurements

Viscosity measurements were carried out on Thermo HAAKE MARS 60 rheometer using a cone-and-plate-geometry, with a cone angle of 2° and a diameter of 35 mm for high viscosity liquids (viscosity≥50 mPa·s), and module with a double-slit rotor and a dual slit cylinder with a diameter of 27 mm for low viscosity liquid phase (viscosity<50 mPa·s).

Swelling behavior

The swelling ratio of hydrogels was tested using a 14 mm sample disk. The sample was immersed in 50 mL of water at 25 °C, and the sample weights before (w_0) and after (w_n) immersion were used to calculate the swelling ratio ($SR=(w_n- w_0)/w_0$).

Mechanical measurements

The mechanical properties of hydrogels were carried out on an electronic universal testing machine (Suns) equipped with a 50 N tension sensor. All tests were carried out at room temperature (25 ℃, 60% RH). Measurements were repeated three times and were averaged for a given sample. The tensile tests of hydrogels were performed with rectangular samples with a size of 50 mm × 10 mm × 2 mm. The tensile strength and elongation at break were obtained at 10 mm min^{-1}. The compression tests of hydrogels were performed with cylindrical samples with a height of 10 mm and a diameter of 15 mm. They were compressed to 70% strain at a speed of 5 mm min^{-1}.

Adhesion measurement

To evaluate the adhesion ability of hydrogels, lap shear test, 90-degree peeling test, and 180-degree peeling test were used. An electronic universal testing machine (Suns) equipped with a 50 N tension sensor was used. For the lap shear test, the hydrogel was sandwiched with a size of 15 (w) × 15 (l) mm^2 between two glass slides, followed by an immediate test (10 seconds contact). The adhesion strength of hydrogel to porcine skin was measured by the same procedure. The adhesive shear strength was determined by dividing the max force by the contact aera of the sample. The interfacial toughness was obtained by 90-degree and 180-degree peeling tests. For 90-degree peeling test, the hydrogel was cut into a size of 50 mm × 10 mm × 2 mm, and was initially glued to a non-woven fabric to minimize its elongation along the peeling direction. Then, the hydrogel was attached to the surface of glass or porcine skin with a weight of 100 g for 10 seconds before peeling tests. The

interfacial toughness was calculated by dividing the max force by the width of the sample. For 180-degree peeling test, the hydrogel was cut into a size of 50 mm × 10 mm × 2 mm, sandwiched between two pieces of porcine skin, and lightly pressed with a 100 g weight for 10 seconds before peeling tests. The interfacial toughness was determined by dividing two times of the max force by the width of the sample. All tests were conducted with a constant peeling speed of 50 mm min^{-1}.

Evaluation of antioxidant, antibacterial, and anti-UV properties

The antioxidant ability of hydrogels was evaluated via DPPH (nitrogen-free radicals) and PTIO (oxygen-free radicals) radical scavenging assay. First, the standard curves of DPPH ethanol solution and PTIO aqueous solution were measured with UV–vis spectrometer (Thermo Scientific). For the DPPH assay, 500 mg hydrogels were added into 30 mL of DPPH ethanol solution (59 μg mL^{-1}). After incubating for 30 mins, 60 mins and 90 mins, the absorbance at 517 nm of supernatants was detected. Similarly, for the PTIO assay, 30 mL PTIO aqueous solution (200 μg mL^{-1}) was prepared, and 500 mg hydrogel and PCA (12 mg mL^{-1}) were added into different tubes for 6 hours at 37 ℃. The absorbance at 560 nm of supernatant was detected.

The antibacterial performance of the hydrogels was evaluated by the bacteriostatic circle method using Staphylococcus aureus (ATCC29213) as the model. Pure PAA hydrogels were used as controls. The hydrogels (10 mm in diameter and 2 mm in thickness) were sterilized after 30 minutes of irradiation under UV light. Subsequently, 100 μL of bacterial suspension (10^6 CFU mL^{-1}) was evenly spread on Luria-Bertani solid medium, and the hydrogels were placed on the surface of the medium with sterile forceps and pressed gently to make complete contact between the hydrogels and the medium, which were incubated at 37 ℃ for 24 hours. After the incubation, the samples were photographed, and the bacteriostatic circle size was measured. Each test group was repeated three times to obtain the average result.

To evaluate the anti-UV ability of hydrogels, hydrogels with 2 mm thickness were prepared. The UV–vis transmission spectra of hydrogels with different PCA content were measured using a UV–vis spectrometer (Thermo Scientific).

In vitro cytotoxicity test

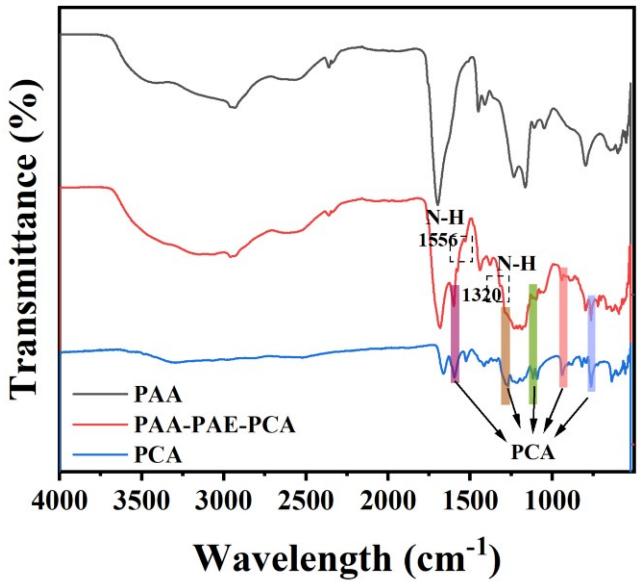
The hydrogels were immersed in 5.0 mL culture medium, which were placed at 37 °C for 24 hours to obtain the extract of the hydrogel and were sterilized under UV radiation at the same time. The extracts were diluted with culture medium and a series of extract dilutions (100.0, 50.0, 25.0, 12.5 mg mL^{-1}) were collected to evaluate the cytotoxicity using L929 cells with a Cell Counting Kit-8 (CCK-8) at 24 and 48 hours. The group with normal culture medium was used as the control group. The absorbance value (OD) at 450 nm was measured by microcoder. Survival rate (SR%) of cells was calculated using following Eq, $SR\%=(OD_b-OD_{blank})/(OD_0-OD_{blank}) \times 100\%$, where OD_0 is the OD450 of the control and OD_b is the OD450 of experimental groups.

In vivo wound healing evaluation

The *in vivo* wound healing performance of the hydrogels was investigated using a mouse full-thickness skin defect model. Six-week-old male Kunming mice were randomly divided into three groups, including 3M Tegaderm group, suture group and 6% PCA hydrogel group. Mice were anesthetized by isoflurane inhalation and a full-thickness wound of 10 mm in length was created on their shaved back. Wound repairment was evaluated by monitoring the wound area on day 3, 6, and 12. Hematoxylin-Eosin (H&E) staining was carried out on day 3, 6, and 12 to detect the inflammation. Masson staining was carried out on day 12 to evaluate collagen fibers regenerated during wound healing.

In vivo Biosafety evaluation

Important organs and tissues in the 6% PCA hydrogel group, including liver, lung, heart, kidney, spleen and mussle were collected on day 12 to detecte the inflammation and damage alterations. They were fixed in 10% formalin, processed and embedded in paraffin. Organ sections were stained with H&E for biosafety evaluation.



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118 **Figure S1**. FTIR spectrum of PAA, PCA and PAA-PAE-PCA.

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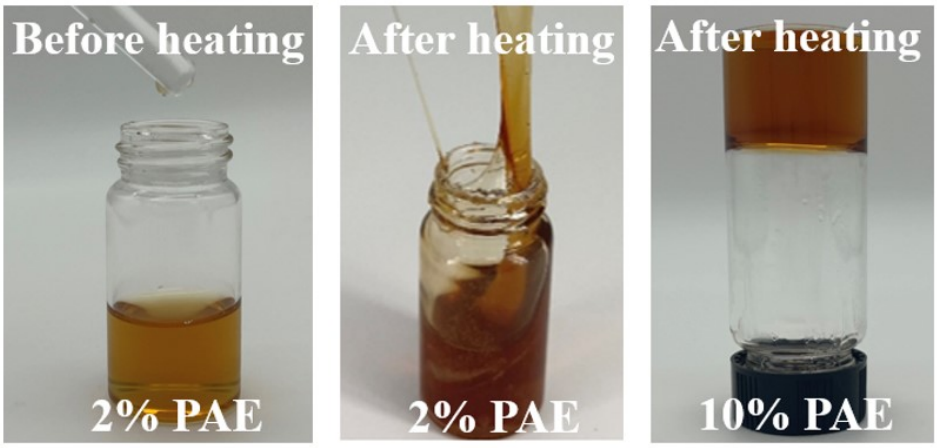
A



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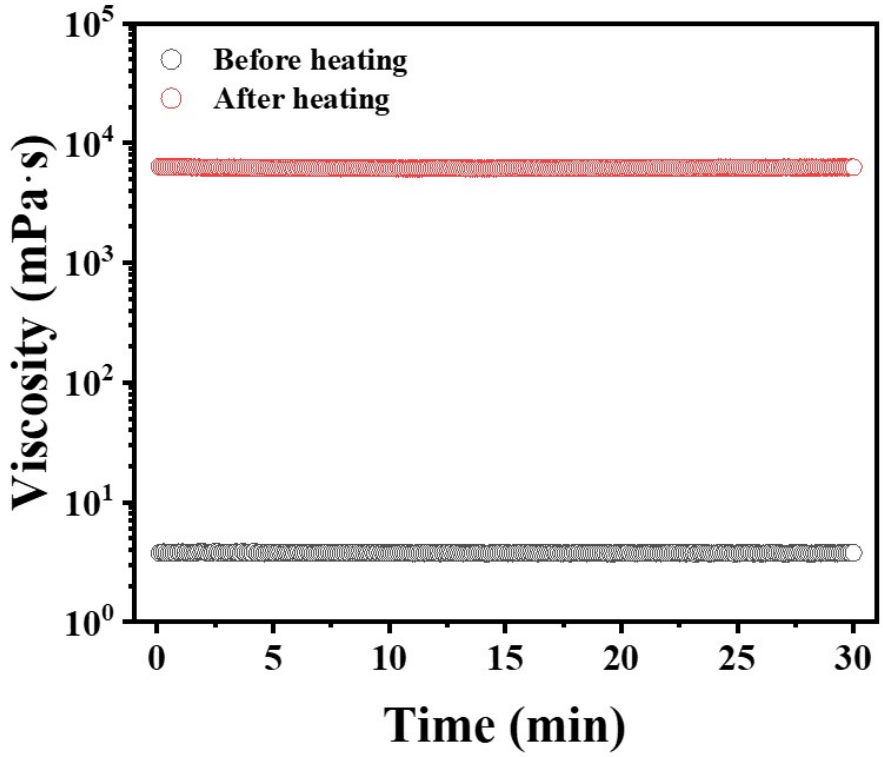


Figure S2. **A**) Photographs of polymer solution without MBA before and after heat treatment. **B**) Viscosity of solution containing 2% PAE before and after heat treatment.

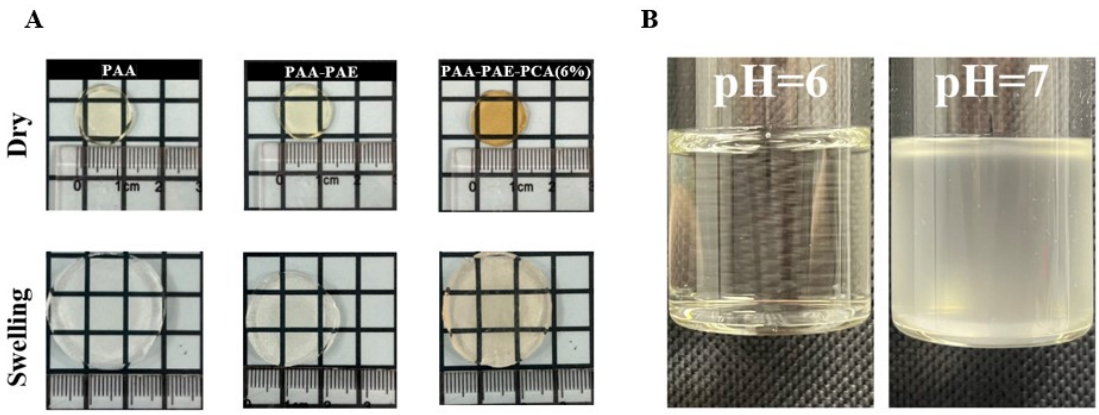


Figure S3. **A**) Photographs of dry hydrogels and hydrogels swelled in water for ~48 hours. **B**) Photographs of PAE aqueous solution (6.25 wt%) at different pH. Under neutral pH, the solution became turbid, indicating the relative hydrophobicity of PAE backbone.

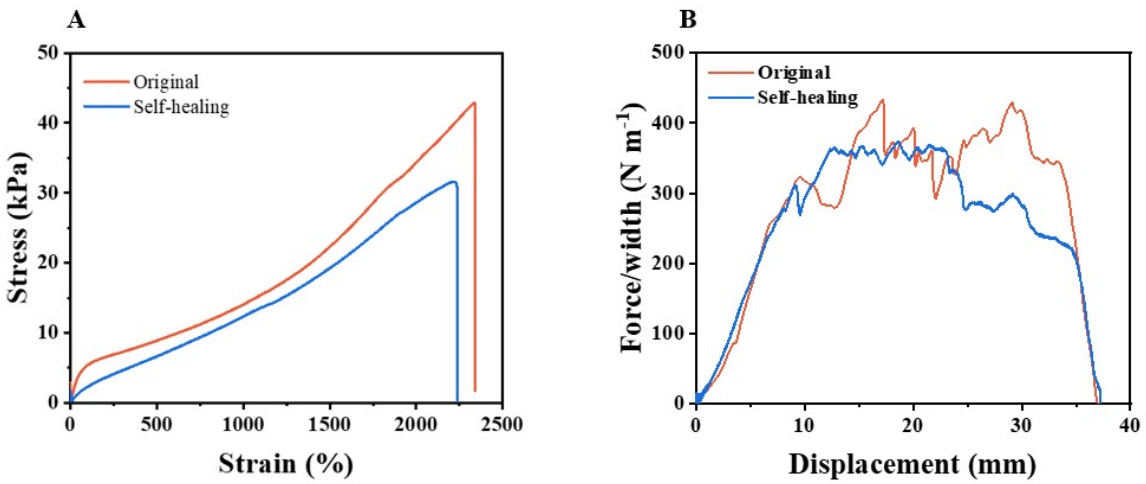
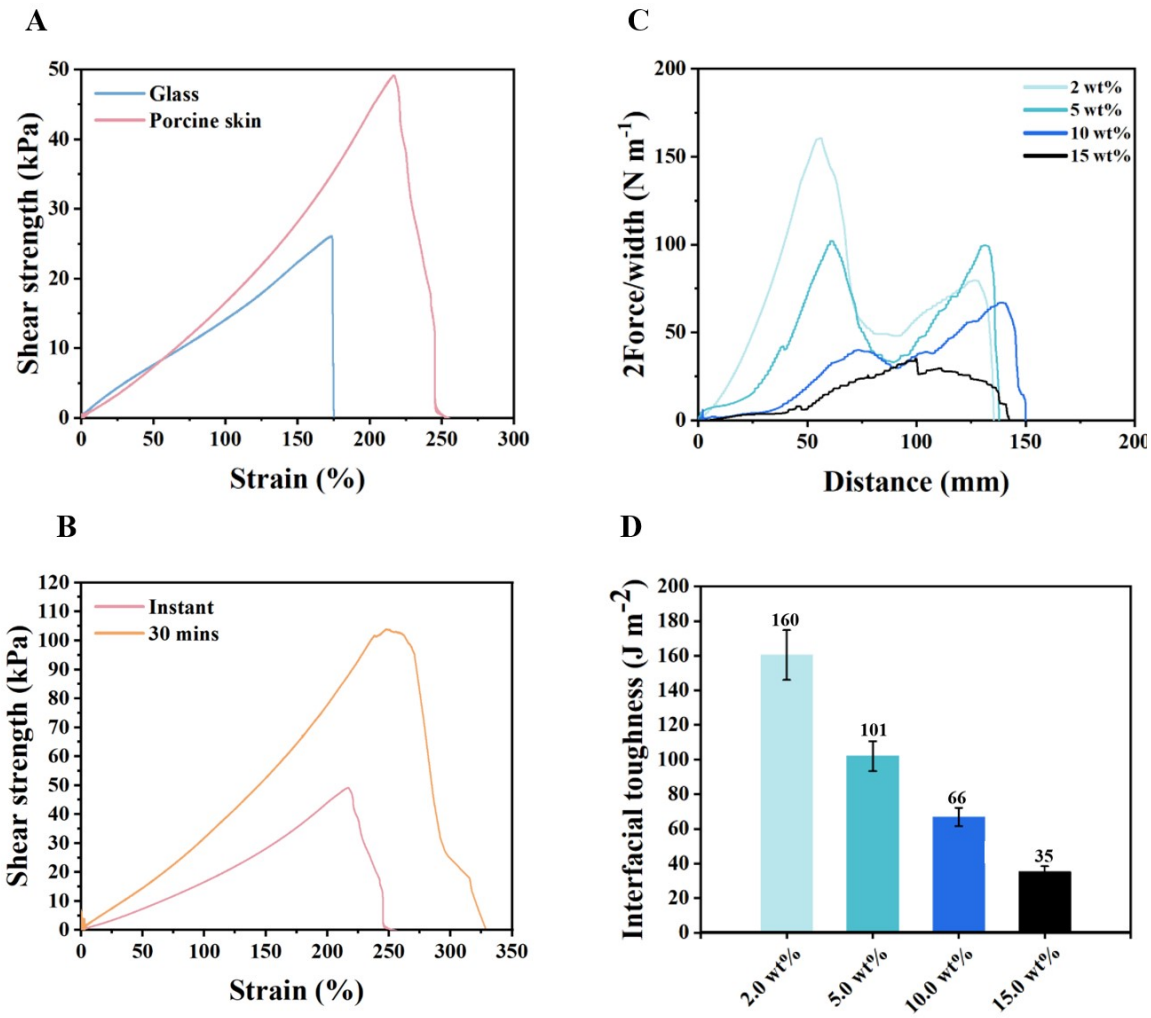


Figure S4. **A**) Tensile test of self-healed hydrogel (water content was ~47%). **B**) 90 degree peeling test of self-healed hydrogel on procine skin (water content was ~30%).



133 **Figure S5**. **A**) Shear strength of the hydrogel containing 6% PCA on glass and porcine skin. **B**)
134 Shear strength of the hydrogel containing 6% PCA on porcine skin after different contact time. **C,**
135 **D**) The 180-degree peeling test and interfacial toughness of hydrogels on porcine skin after soaking
136 in different concentration of NaCl solution.

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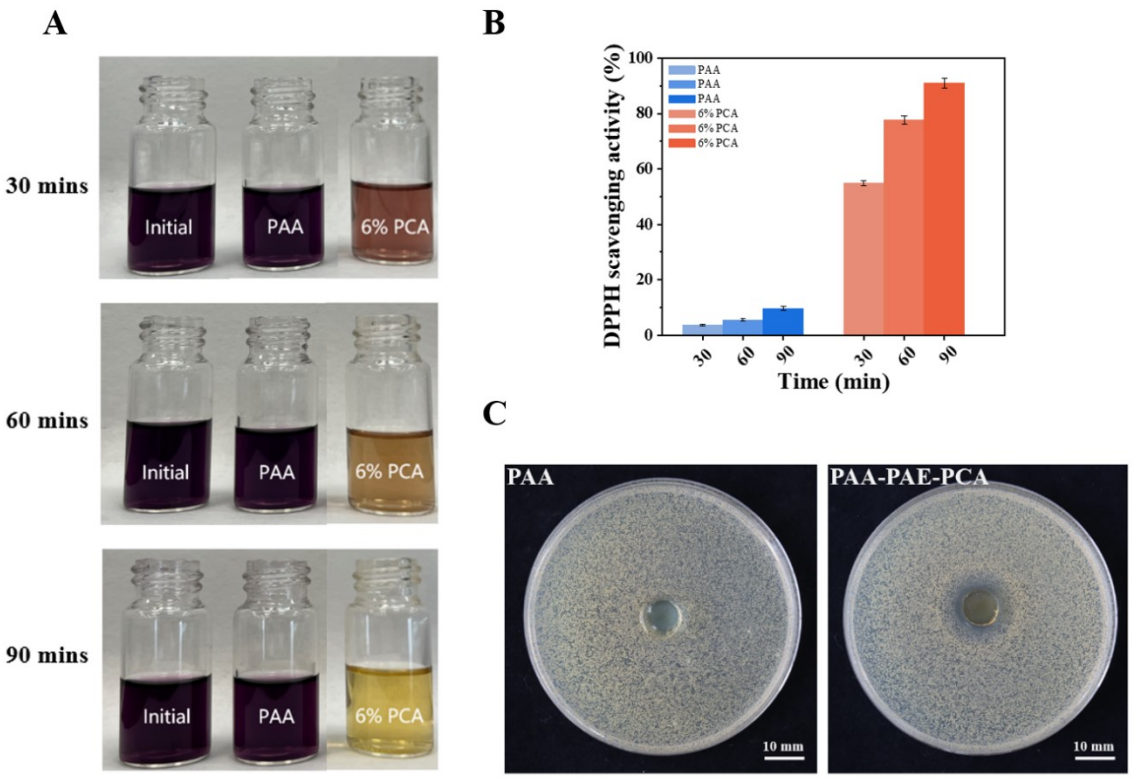

Figure S6. **A**) Photographs of DPPH solution treated by different samples at the specified time. **B**) DPPH scavenging activity of PAA and 6% PCA hydrogels after different contact time. **C**) Photographs of bacteriostatic circle.