Supporting Information

Tough, self-healable and tissue adhesive hydrogel with tunable multifunctionality

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Preparation of hydrogels.

The PDA-PAM hydrogels were synthesized by the following procedures. (1) dopamine (DA) molecules went through an alkali-induced pre-polymerization process to form PDA chains by dissolving DA powder in a beaker containing NaOH aqueous solution (pH=11), and then allowing the DA to self-polymerize for 20 min in air atmosphere under stirring. (2) Acrylamide (AM), ammonium persulphate (APS), and N, N-methylenebisacrylamide (BIS) were mixed with the solution of PDA chains in an ice bath under stirring. After 10 min of mixing, the ice bath and stirrer were removed, and the AM was polymerized to form PDA-PAM hydrogels. Hydrogels with different weight ratios of DA/AM were synthesized to investigate the effects of DA on the properties of the hydrogels. The contents of those hydrogels are listed in Table S1. Note that more APS was needed when DA existed, because DA also consumed APS. In addition, PDA-PAM hydrogel cannot form when the weight ratio of DA/AM was higher than 8 wt. % (Figure S1), because the reductive DA molecules affected the activity of the initiator (APS) and thus retard the polymerization of AM monomers.

![Figure S1](image)

**Figure S1.** Suitable DA contents (DA/AM ≤ 8 wt.%) resulted in solid hydrogels. Higher DA contents (DA/AM=10 wt. %, and 12 wt.%) resulted in viscous solution.
The self-healable multi-functional hydrogels were also synthesized by the same polymerization process as that of PDA-PAM hydrogels. Before polymerization, the functional nanoparticles (Fe$_3$O$_4$ NPs and carbon black NPs) were added into DA solution to allow DA polymerizing on NP surfaces.
| Hydrogels | DA/AM (wt. %) | AM (g) | APS/AM (wt. %) | BIS/AM (wt. %) | TMEDA (μl) | Water (wt. %) |
|-----------|---------------|--------|----------------|----------------|------------|--------------|
| Pure AM   | 0             | 2.5    | 2              | 1.2            | 20         | 80           |
|           | 2             | 2.5    | 10             | 1.2            | 20         | 80           |
|           | 4             | 2.5    | 10             | 1.2            | 20         | 80           |
|           | 8             | 2.5    | 10             | 1.2            | 20         | 80           |

* Materials used: dopamine (DA, Sigma); acrylamide (AM, Sigma); ammonium persulphate (APS, Sigma); N, N’-Methylene bisacrylamide (BIS, Sigma); tetramethylethylenediamine (TMEDA, Sigma)
TOF-SIMS analysis.

**Experimental:** Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used to demonstrate the existence of PDA in the hydrogel and possible interaction between PAM and PDA. Static TOF-SIMS spectra of PDA, PAM and the PDA-PAM hydrogel (DA/AM 5 wt.%) were obtained from a TOF-SIMS V spectrometer (ION-TOF GmbH, Münster, Germany). Before measurement, the samples were washed three times in deionized water and ethanol to eliminate reactant residues from the samples, and dried in vacuum chamber at 40 °C for 2 days. The samples were bombarded with Bi$_3^+$ primary ions, which were accelerated at 25 kV with an average pulsed current of 0.3 pA. The raster area was 200 μm × 200 μm, and the acquisition time for each spectrum was 40 s, corresponding to an ion dose of < 4x10$^{11}$ ion cm$^{-2}$. Three positive and negative spectra were recorded for each specimen at different locations. The spectra were calibrated before the extraction of ion intensity data using SurfaceLab 6 software.

**Presence of PDA and PAM by spectral analysis:** The TOF-SIMS ion spectra clearly demonstrated the presence of both PAM and PDA in the PDA-PAM hydrogel. The positive spectrum of PAM (Figure S2A-1) revealed several intense peaks at $m/z$ 44 (CH$_2$NO$^+$), 55 (C$_3$H$_3$O$^+$), and 72 (C$_3$H$_6$NO$, repeat unit ion), which validated the PAM structure. The positive spectrum of PDA (Figure S2A-2) showed an apparent peak at $m/z$ 149 corresponding to an intact 5,6-dihydroxyindole (DHI) unit, which has been demonstrated to be an important building block of PDA $^1$. In the positive spectrum of PDA-PAM hydrogel (Figure S2A-3), the observation of the peaks at $m/z$ 44, 55, 72 indicated the presence of both PAM, while $m/z$ 149 belongs to PDA in the hydrogel.

In line with the positive spectra, the negative spectra of PAM, PDA and PDA-PAM hydrogel (Figure S2B) also confirmed the presence of both PAM and PDA in the hydrogel. In fact, the characteristic fragments of PAM and PDA were found in the PDA-PAM hydrogel. For example, the fragments that are characteristic of the cyclic nitrogen in PDA (C$_3$N$^-$, and C$_5$N$^-$)
were all present in the hydrogel. In addition, the relative intensity of CN⁻/CNO⁻ of the hydrogel was remarkably higher than that of PAM, which resulted from the addition of PDA.

**Chemical Mapping of PDA-PAM hydrogel:** In order to check whether PDA is uniformly distributed in the hydrogel, a cross section of the hydrogel was imaged using TOF-SIMS. The secondary ions, C₃H₆NO⁺ (m/z 72) and C₈H₇NO₂⁺ (m/z 149), were chosen to represent the PAM and PDA, respectively. As can be seen from Fig. 2a, these two ions were uniformly distributed across over the whole cross section area, suggesting the uniform distribution of PAM and PDA components in the hydrogel.

**Interactions between PDA chains and PAM network:** A peak at m/z 261 was observed in the positive spectrum of PDA-PAM hydrogel, but it neither showed up on PAM spectrum nor on PDA spectrum. This suggests that the peak at m/z 261 may originate from the interaction between PAM and PDA molecules. It has been suggested that the catechol/quinone groups on the PDA could cross-link with the nucleophilic amine groups *via* a Schiff base reaction²⁻⁴. Agreed with this notion, a tentative assignment of the peak at m/z 261 was C₁₃H₁₄N₂O₄⁺ (see the inset of Fig. 2b), which results from the possible interaction between the amine groups of PAM and the catechol groups of PDA. This interaction connects the PDA chains on the PAM networks, which leads to non-covalent bonds between chains well dispersed in PAM network.
Figure S2A. Positive TOF-SIMS ion spectra of (1) PAM, (2) PDA, and (3) PDA-PAM hydrogel. The ions marked in red color in (2) were due to impurities (Na and K) and surface contamination (silicone).
Figure S2B. Negative TOF-SIMS ion spectra of (1) PAM, (2) PDA, and (3) PDA-PAM hydrogel.
Fourier transform infrared (FT-IR) analysis.

The FT-IR spectra of pure PAM, pure PDA and PDA-PAM hydrogel (5 wt.% DA/AM) were analyzed to search for possible crosslinks between PDA and PAM. The spectra were recorded between 4000 and 500 cm\(^{-1}\) using a FT-IR spectrometer (Nicolet 5700, Germany). Before measurement, the samples were washed three times in deionized water and ethanol to eliminate reactant residues from the samples, and dried in vacuum chamber at 40 °C for 2 days.

As shown in FT-IR spectra (Figure S3), the PAM hydrogel exhibited bands between 3000 cm\(^{-1}\) and 3500 cm\(^{-1}\), corresponding to a stretching vibration of N-H, and at 1650 cm\(^{-1}\) for C=O stretching. The bands at 1620 cm\(^{-1}\) (N-H deformation for primary amine), 1450 cm\(^{-1}\) (CH\(_2\) in-plane scissoring), 1420 cm\(^{-1}\) (C-N stretching for primary amide), 1350 cm\(^{-1}\) (C-H deformation), and 1120 cm\(^{-1}\) (NH\(_2\) in-plane rocking) were also detected. The PDA showed a band near 1500 cm\(^{-1}\) for aromatic rings. The band at 3400 cm\(^{-1}\) resulted from the overlapping of hydroxyls and water adsorbed in PDA polymer and amine groups of PDA.

In comparison with pure PAM and PDA, the spectrum of the PDA-PAM hydrogel showed a new peak at 1258 cm\(^{-1}\), corresponding to the C-N stretching in phenyl amines. The presence of this band indicates the interaction between -NH\(_2\) groups of PAM and catechol groups of PDA, as shown in the black square in Fig. 1b-(1). Furthermore, the intensity of C-N of aliphatic amine (1197 cm\(^{-1}\)) decreased, which also suggested the reaction of C-NH\(_2\) with catechol groups of PDA.
Figure S3. The FT-IR spectra of PAM, PDA and PDA-PAM (5 wt.% DA/AM) hydrogels.
**1H NMR spectroscopy analysis.**

**Experiments:** The 1H NMR spectra of DA, AM, and DA-AM were analyzed to investigate interactions between DA and AM. The 1H-NMR spectra were recorded in dimethyl sulfoxide (DMSO) and deuterium oxide (D2O) with a Bruker AM 400 spectrometer (400 MHz).

**Results:** The spectrum of DA in DMSO (Figure S4a-i) is the same as that of the standard spectrum listed in Biological Magnetic Resonance Data Bank database*. The characteristic resonance signals are phenyl protons (6.79 and 6.62 ppm), and methylene protons (3.4 and 2.6 ppm). By the method of heavy water exchange, we obtained two active hydrogens. The peak at 8.87 ppm belongs to the proton chemical shift of catechol groups (Figure S4a) ⁵. However, we could not assign the peak at 7.99 ppm to specific proton because they might belong to either catechol group or amino groups in DA.

The spectrum of AM in DMSO (Figure S4bii) showed the characteristic resonance signals of methylene protons at 5.71 and 6.23 ppm. By the method of heavy water exchange, we obtained active hydrogen at 7.1 and 7.54 ppm, which might belong to the proton chemical shift of NH₂ group in AM (Figure S4b).

After AM was mixed with the DA to form AM-DA complexation (Figure S4c), the broad band of catechol groups in DA (8.87 ppm) split into two sharp peaks (8.85 ppm and 8.88 ppm). In addition, the active hydrogen in DA shifted from 7.99 ppm to 7.8 ppm (Figure S4d). These results demonstrated that there were interactions between the oligomers of DA and AM (Figure S4d).

*Website of Biological Magnetic Resonance Data Bank database:*

http://bmrbr.wisc.edu/metabolomics/mol_summary/show_data.php?molName=dopamine&id=bmse000933
Figure S4. (a) (i) Overview of $^1$H NMR spectra of DA in D$_2$O, (ii) DA in DMSO, the red dotted box shows the active hydrogen in DA. (b) (i) Overview of $^1$H NMR spectra of AM in D$_2$O, (ii) AM in DMSO, the brown dotted box shows the active hydrogen in AM. (c) (i) Overview of $^1$H NMR spectra of DA-AM in DMSO, (ii) DA in DMSO. (d) The magnified view of the area marked by green dotted box in (c), and possible structure of DA-AM complexation.
**X-ray photoelectron spectrometer (XPS) analysis.**

**Experimental:** The surface chemical compositions of the PDA, PAM, PDA-PAM hydrogels were measured using XPS (Kratos, Axis Ultra DLD, UK). A monochromatic Al Kα X-ray was used as an excitation source ($h\nu = 1486.6$ eV) running at 15 kV and 150 W. The neutral C 1s peak (C-C (H), set at 285.0 eV) was used as a reference for charge correction.

To analyze the functional groups of the various samples, the high-resolution spectra of C 1s were curve-fitted (Figure S5). The basic feature of acrylamide, as revealed by C-C(H) at 285.0 eV and NH$_2$-C=O at 288.2 eV, was well reproduced in the PAM (Figure S5A). The C 1s of the PDA consisted of four components (Figure S5B), as follows C-C (H) at 285.0 eV, C-OH/C-N at 286.4 eV, C=O at 288.0 eV, O-C=O at 289.1 eV, which is consistent with our previous study $^1$. The C 1s of the PAM-PDA hydrogel (Figure S5C) displayed a similar shape to that of PAM, suggesting the major contribution of the PAM to the chemical composition of the PDA-PAM hydrogel. Compared with the PAM, however, a new peak at 286.4 eV in the C 1s spectrum of the PDA-PAM hydrogel was detected. This peak was due to the C-OH/C-N groups present in the PDA, which further confirmed the presence of the PDA in the PDA-PAM hydrogel. This peak was also one piece of evidence of free catechol groups in the hydrogel.
Figure S5. High-resolution XPS spectra of C 1s region for the (A) PAM, (b) PDA and (c) PDA-PAM hydrogel.
SEM morphology of the hydrogels.

The structures of the bulk PAM hydrogel and PDA-PAM hydrogel (DA/AM 8 wt.%) were examined using a scanning electron microscope (SEM, JSM 6390, JEOL, Japan). Before examination, the hydrogels were freeze-dried. Then the dried hydrogels were cut to expose their inner structure, and the cross-section was observed.

Results:

![SEM morphology of dried PAM (left) and PDA-PAM (right) hydrogels.](image)

**Figure S6.** SEM morphology of dried PAM (left) and PDA-PAM (right) hydrogels.

SEM images revealed porous structure of dried hydrogels (Figure S6). The pure PAM hydrogel had smooth surfaces. The PDA-PAM hydrogel had microfibril structures. The microfibrils in the hydrogel may be caused by the complexion of PDA and PAM chains, which interweaved three-dimensional structures through π-π interaction and hydrogen bonds. The microfibrils in the PDA-PAM hydrogel might play as a bridge between two broken pieces to facilitate the broken hydrogel to self-heal. The microfibrils assisted healing process is similar to self-recovery of human skin upon damage with the aid of blood vascularization\(^6\).
Tensile tests.

The tensile tests were performed on a universal test machine (Instron, 5567, USA). The loading rate was 100 mm/min. The specimens had the width of 25 mm and the thickness of 3 mm. The gauge length between the clamps was 5 mm. The nominal stress ($\sigma$) was calculated as

$$\sigma = \frac{F}{A}$$

where $F$ is the tensile load and $A$ is the cross-sectional area.

The extension ratio ($\lambda$) was defined as the deformed length ($l$) relative to the original length $l_0$

$$\lambda = \frac{l}{l_0}.$$  

**Figure S7.** Tensile strength of the hydrogels with various DA/AM ratios. The strength decreased with the increase of DA content.
Tensile-recover test.

The PDA-PAM hydrogel (8 wt.% DA/AM) recovered its original length after it was pulled to an extension ratio of 20 and stored for a period of time (Figure S8).

Supplementary Figure S8. Tensile-recover testing. (a) The original length of the specimen was 5 mm. (b) The specimen was pulled to 100 mm. (c) The length of the specimen was 15 mm immediately after tension. (d) The length of the specimen was 8 mm after stored for 5 min. (e) The specimen recovered its original length (5 mm) after stored for 10 min.
**Time-dependent recoverability: tensile-recover-tensile test.**

A tensile-recover-tensile test was conducted to characterize the time-dependent recoverability of the hydrogel. First, the specimens were pulled to achieve an extension ratio of 6, and then unloaded. After stored at different time intervals (10 sec, 10 min, 20 min, 30 min and 1 day), the specimens were pulled to 6 times of its initial length again. The tensile stress during the tensile-recover-tensile cycles is shown in Figure S9.

The pure PAM hydrogel ruptured at the second tensile test, which suggested that it was intrinsically brittle and could not recover its damaged internal structure caused by tension (Figure S9a).

The PDA-PAM hydrogel was slightly weaker if the second loading was applied immediately (10 sec). However, the hydrogel recovered somewhat if the second loading was applied after it was stored a period of time, and can fully recover after a sufficient storage duration (1 day). These results indicate that the internal damage of the hydrogel can be healed after the addition of DA, although the recovering process took a period of time (Figure S9b).
Figure S9. Tensile-recover-tensile test of the hydrogels. (a) pure PAM. (b) PDA-PAM (8 wt.% DA/AM).
Determination of the fracture energy (Gc)

Fracture energy was determined by the classical single edge notch test on the universal test machine (Instron 5567). The speed of the crosshead was 2 mm/sec. The specimen was fixed between clamps with the gauge length of \(l_0 = 5 \text{ mm}\) (Figure S10a). The thickness and the width of the specimen were 3 mm and 25 mm, respectively. During the testing, a pair of specimens was pulled: one specimen was un-notched and the other was notched (Figure S10b). The unnotched specimen was pulled to obtain the stress-strain curve, whereas the notched specimen was used to determine the critical extension ratio \((\lambda_c)\), at which cracks expanded. As for the notched specimen, a notch with the length of 5 mm was made in the middle of the specimens (Figure S10a). The fracture energy \((G_c, \text{ J m}^{-2})\) is calculated using the Equation (1) proposed by Greensmith for elastomers \(^7\).

\[
G_c = \frac{1}{B} \left[ \frac{\partial (\Delta U)}{\partial a} \right] = 2 \frac{\pi}{\sqrt{\lambda_c}} a W_0 \quad \text{(Equation 1)}
\]

where, \(a\) is the length of the crack; \(\lambda_c\) is the extension ratio at which cracks expand in the single edge notch tests. In the present study, the crack expands slowly and it is not easy to record the point at which notches turn into a running crack. Thus, the \(\lambda_c\) is determined when the force reaches maximum during the pulling of the notched specimen. \(W_0\) is the strain energy density, which is calculated by integration of the stress versus engineering strain of un-notched samples, until \(\lambda_c (\lambda_c = \varepsilon_c + 1)\).

The method for \(G_c\) calculation is well established, and has been widely used to test fracture energy for elastomers \(^7\). According to the calculation, the fracture energy of pure PAM hydrogel is 579 J/m\(^2\), which is at the same level of that reported in previous study (250 J/m\(^2\))\(^8\). The consistence between our data and previous study proves that the calculation method and the data are reliable.
Figure S10. Single edge notch test to determine the fracture energy. (a) Geometry of notched specimen for single edge notch test. (b) Stress-strain curves of the unnotched (black) and notched (red) specimens. Stress-strain curve of notched (red) specimen was used to determine the critical extension ratio $\lambda_c$ ($\lambda_c = \varepsilon_c + 1$). Stress-strain curve of unnotched (black) specimen was used to calculate $W_0$. 
Rheological experiments.

The dynamic rheological tests of PDA-PAM hydrogels were characterized at room temperature using a Rheometric Scientific HAAKE (MARS, German) strain-controlled rheometer equipped with 20 mm parallel plates. The hydrogels were loaded into a 0.5 mm gap between the plates and allowed to relax until the normal force was zero. Water was applied to the outer edges of the gel to prevent drying. Strain amplitude sweeps (0.01-100%) were first performed to determine the linear viscoelasticity region. Dynamic frequency sweeps were performed at angular velocities ranging from 0.01 to 10 Hz at 1.0% strain amplitude (liner region). All rheological measurements were performed in triplicate.

The storage modulus ($G'$) and the loss tangent (ratio of loss modulus $G''$ to storage modulus $G'$) of the hydrogel were determined as the frequency changes. The loss tangent indicated relative degree of the viscosity to elasticity of the hydrogels (Figure S11). The results showed that the $G'$ of PDA-PAM hydrogel was lower than that of pure PAM hydrogel, revealing that the DA addition led to the decrease of elasticity of the hydrogel. The loss tangent of PDA-PAM hydrogel was higher than that of pure PAM hydrogel, which showed that DA addition resulted in the increase of the viscosity of the hydrogel. Although DA addition might limit the ability of these hydrogels to bear loads, the high viscosity also allowed the PDA-PAM hydrogels to self-healing during torn.

![Figure S11. Viscoelasticity of PDA-PAM hydrogels with different DA/AM ratios. (a) Storage modulus ($G'$) and (b) loss tangent ($G''/G'$) of the hydrogels.](image-url)
Effects of crosslinker (BIS) contents on the properties of PDA-PAM hydrogels.
The maximum extension ratio (ER) of PDA-PAM hydrogels decreased with the BIS content, which indicated that the hydrogels become brittle when the BIS content increased (Table S2), while the tensile strength of both PAM and PDA-PAM hydrogels increased with the BIS content (Table S3).

Table S2. The effects of crosslinker (BIS) on ER of hydrogels

| BIS /AM ratio (wt.%o) | 1.2 | 2.4 | 3.6 | 6  |
|-----------------------|-----|-----|-----|----|
| PAM hydrogel          | 12  | 11  | 5   | 1  |
| PDA-PAM hydrogel      | 25  | 18  | 10  | 5  |

(8 wt.% DA/AM)

Table S3. The effects of crosslinker (BIS) on tensile strength of hydrogels (unit: KPa)

| BIS /AM ratio (wt.%o) | 1.2 | 2.4 | 3.6 | 6  |
|-----------------------|-----|-----|-----|----|
| PAM hydrogel          | 24  | 45  | 50  | 55.2|
| PDA-PAM hydrogel      | 16  | 21  | 22  | 29  |

(8 wt.% DA/AM)
Self-healing ability tests.

Tensile-heal-tensile test.
The self-healing ability of hydrogel was quantitatively evaluated tensile-heal-tensile test (Fig. 4b, c). The hydrogel was stretched to break on the universal test machine (Instron 5567) and the crosshead was moved back to make the two broken pieces into contact; the two pieces of hydrogels were self-healed after 2 hours; the healed specimen was stretched to break again.

(3) Dynamic rheological tests
The self-healing ability was also confirmed by dynamic rheological tests using the two-step procedure of Krosggaard et al 10. Firstly, the hydrogels were broken by applying a 100% strain through a strain amplitude sweep, which caused their G’-values to diminish drastically (Figure S12). The healing of the hydrogels was then monitored over time by continuing to oscillate the hydrogels at a low strain (0.01%) amplitude and low frequency (f =1 Hz) that allowed the hydrogels to recover. The PDA-PAM hydrogel nearly recovered its initial storage modulus G’-value (2707 Pa) within 30 sec after stopping large strain (Figure S12a), while the pure PAM hydrogel did not recover its initial G’-value (Figure S12b). The recovered storage modulus of PDA-PAM hydrogel was close to the initial value (2869 Pa), thereby confirming that the reversible nature of the non-covalent bonds between PDA chains could re-form after breakage and therefore impart the self-healing properties to the PDA-PAM hydrogel. The high reactive catechol groups in PDA also contributed to the self-healing property.
Figure S12. (a) PDA-PAM hydrogel (8 wt.% DA/AM). (b) pure PAM hydrogel. (c) Photographs of the self-healing experiment of two uncut hydrogel.
Adhesion tests.

Tensile adhesion testing was performed to measure the adhesive strength of PDA-PAM hydrogels to porcine skin. The hydrogels were applied to the surface of the specimens with a bonded area of 25 mm × 20 mm. The samples were pulled to failure by a universal testing machine (Instron 5567) with a cross-head speed of 5 mm/min under the ambient conditions. Adhesion-strip cyclic tests were also conducted to evaluate the multiple-time adhesion strength of the hydrogels. The adhesion strength was calculated by the measured maximum load divided by the bonded area.

Figure S13. The effect of crosslinker (BIS) on the adhesive properties of PDA-PAM hydrogels.

The results indicated that the increase of BIS content severely affected the adhesion strength of the PDA-PAM hydrogels (Figure S13), which is because the increase of crosslinking density of the hydrogel restricts the mobility of polymer chains \[^8\]. Consequently, the viscosity of the hydrogel decreased and the polymer chain was not easy to diffuse into the tissue surface and form intimate contact with tissue surfaces. Thus, increasing BIS content resulted in the decrease of adhesiveness of the hydrogel.
Gas chromatography for quantification the residual amount of acrylamide monomers

Before cell culture and in vivo implantation, the PDA-PAM hydrogel was purified and the residual amount of acrylamide monomers in the hydrogel was quantified by gas chromatography (GC)\textsuperscript{11}.

Experiments:
GC condition: An A90 gas chromatograph (Echrom Technologies Co., Shanghai, China) equipped with a flame ionization detector (FID) was used for all analyses. The GC fitted with a capillary column (Agilent HP-5, 30 m × 0.32 mm × 0.50 μm) was used for sample separation and operated under following conditions: (1) the injector port was operated at split mode with a split ratio of 10 and kept at 240 °C, (2) constant current mode, (3) usage of high-purity nitrogen gas as the carrier gas (2.2 ml/min) and make-up gas (30 ml/min). Hydrogen and air were used as detector gases at 30 and 300 ml/min, respectively.

Analytical procedure: Before measurement, the PDA-PAM hydrogels were firstly purified by soaking the hydrogel in the deionized (DI) water for one day and the DI water was refreshed every day. The purification process was repeated three times. Then the hydrogel was freeze-dried and ground to powder. Finally, 0.1 g of accurately weighted powder of PDA-PAM hydrogels was added into a mixture solution (10 ml, DI water: methanol = 2:8) under vigorously vortex for 5 hours to extract residual AM monomers. Working solution of AM was prepared by diluting the stock solution with the concentration of 10 mg/ml to a series of graded concentrations, including 1 mg/ml, 0.4 mg/ml, 0.2 mg/ml, 0.1 mg/ml, and 0.04 mg/ml, which was used to determine the standard curves of AM.

Results: Figure S14 shows the standard curve of AM, which has good linearity over the range of 0.04 - 1 mg L\textsuperscript{-1}, the calibration equation is \(y = 287.64 x -5.479\) with \(R^2\) of 0.9987. The method detection limit (MDL) was 0.0023 mg/ml.
Figure S15 shows the FID chromatogram of the AM extracted from purified PDA-PAM hydrogel. A quite weak peak was observed at 2.733 minutes. The concentration of AM was below than MDL and could not be calculated, which demonstrated nearly no residual AM monomers in PDA-PAM hydrogel after three times of purification.

Figure S14. AM calibration curve.

Figure S15. Chromatogram of PDA-PAM hydrogel sample.
Cell affinity test.

The PDA-PAM hydrogels with various DA contents (0, 2 wt.‰, 4 wt.‰ and 8 wt.‰ to AM) were used to investigate the behaviors of cells. The hydrogels with a diameter of 7 mm and a thickness of 2.5 mm were sterilized by immersing them in 75% alcohol for 24 hours. Then the purified hydrogels were immersed in Dulbecco's modified eagle medium (DMEM) and swelled to the equilibrium state for 2 days in a CO₂ incubator at 37 °C. NIH-3T3 fibroblasts (Stem Cell Bank, Chinese Academy of Sciences, SCSP-515) were used to investigate the cell affinity of the hydrogel, by assaying the proliferation and morphology of the cells cultured on the hydrogels.

Cells in a growth phase were treated with trypsin and harvested, and then suspended in the culture medium to obtain a cell density of 1×10⁵ cells/ml counted by a hemocytometer. Cells were seeded on the hydrogels with a density of (5 × 10⁴ cells) in the wells of tissue culture plates and left undisturbed in an incubator for 3 hours to allow for cell attachment. Then an additional 1 ml of the DMEM supplemented with 10% FBS was added into each well. Cells were allowed to adhere and grow for 3 days and 7 days. After that, the morphologies of cells adhered on the hydrogel surfaces were observed by SEM (JSM 6390). Prior to SEM observation, the cells on the hydrogels were fixed with glutaraldehyde solution (2.5% w/v) for 4 hours. Following that, the cells were step-by-step dehydrated in graded series of ethanol/water solutions (30%, 70%, 90%, 100%, and 100%), 10 min each step. Then the cells went through critical point drying and then gold sputtering.

The biocompatibility of the hydrogel and cell proliferation is assessed by MTT assay. Briefly, after 3 and 7 days of culture, the culture medium was replaced with DMEM supplemented with 100 μl of 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT, 0.5 mg/ml) to each culture-well, and the resulting mixture was incubated 4 hours at 37 °C. After that, the MTT solution was removed and 400 μl of DMSO was added to dissolve the formazan crystals and incubated in a shaking incubator (37 °C, 100 rpm) for another 15 min.
The optical density (OD) of DMSO extracts was read at 570 nm using an ELISA reader (MQX200, BioTEK, USA). The behavior of cells cultured on epidermal growth factor (EGF)-loaded PDA-PAM hydrogels were also investigated to confirm the in vitro bioactivity of the released EGF from the hydrogels. For obtaining the EGF-loaded hydrogel, the hydrogel (30 mg) was first sterilized in 75% alcohol, and then EGF (Shanghai Primegene Bio-Tech Co., Ltd., China, 10 μg/sample) were adsorbed into the hydrogel.

Figure S16. Fibroblasts cultured on hydrogel surfaces after 3 days and 7 days. (a,b) PAM, (c,d) PDA-PAM, and (e,f) EGF-loaded PDA-PAM hydrogels. A large number of fibroblasts adhered and spread well on the surfaces of the PDA-PAM hydrogel, and the morphology of fibroblasts did not change in the culture period.
Characterizing the affinity of extracellular matrix proteins to hydrogels.

The affinity of extracellular matrix proteins to hydrogels was experimentally determined by evaluating the adsorption and release of fibronectin (Fn). Fn was selected as the representative protein because it widely exists in ECM and promotes cell adhesion\textsuperscript{12,13}. To quantify the adsorption of ECM proteins, PDA-PAM and PAM hydrogels were soaked in 1 ml of Fn in PBS (10 µg/ml)\textsuperscript{14}. After 24 h, the samples were washed three times using PBS to remove non-adsorbed protein. The quantities of the adsorbed protein were calculated by subtracting the amount of proteins left in the PBS solution from the initial amount. The adsorption rate of Fn was measured by the ELISA kit (Cloud-Clone Corp., USA), according to the manufacturer’s protocol.

The release kinetics of Fn from the hydrogels was characterized in vitro by the half-change method in the PBS solution (pH 7.4). Fn-loaded PDA-PAM and PAM hydrogels were immersed in the PBS solution (1 ml) and shaken (100 rpm) at 37 °C. At predetermined intervals (1 d, 3 d, 5 d, 10 d, 15 d), fifty percent of the release PBS was collected and replaced by fresh PBS. The amount of released Fn was measured by the ELISA kit (Cloud-Clone Corp), according to the manufacturer’s protocol. All of the tests were repeated three times.

![Figure S17](image)

**Figure S17.** (a) Fn absorption ratio on pure PAM hydrogel and PDA-PAM hydrogel. (b) The release profiles of Fn from the hydrogels in PBS.

The results demonstrated that Fn was fully adsorbed by the PDA-PAM hydrogel. The release profiles also demonstrated that no burst release was detected in both two cases, and the release of Fn from PDA-PAM hydrogel was slower than that from pure PAM hydrogel and,
as shown in Figure S17. Both the adsorption and release results demonstrated that the PDA-PAM hydrogel has higher protein affinity than PAM hydrogel, which is because PDA endows the hydrogels with abundant binding sites for immobilization of ECM proteins.
Epidermal growth factor (EGF) release experiment.

EGF release experiment was conducted to investigate the stable immobilization of growth factors in the hydrogel. The release profiles of EGF from the hydrogels were characterized in vitro by the half-change method in the PBS solution (pH 7.4). EGF-loaded PDA-PAM (30 µg per sample) and PAM hydrogels were immersed in the PBS solution (1 ml) and shaken (100 rpm) at 37 °C. At predetermined intervals (1 d, 3 d, 5 d, 10 d, 15 d), fifty percent of the release PBS was collected and replaced by fresh PBS. The amount of released EGF was measured by the ELISA kit (Cloud-Clone Corp., USA), according to the manufacturer’s protocol. All of the tests were repeated three times.

![Figure S18. The release profiles of EGF from the hydrogels in PBS.](image)

EGF was sustained released during whole period, and no burst release was observed in the initial stage (Figure S18). The release of Fn from PDA-PAM hydrogel was slower than that from pure PAM hydrogel. These results indicated that EGF was stably immobilized in the hydrogel. The stable immobilization of growth factor was attributed to PDA in the hydrogel. PDA enabled the chemical conjugation of biomolecules containing primary amine or thiol groups via imine formation or Michael addition reaction as demonstrated by previous studies, and physically immobilized growth factors through non-covalent interaction [12-14]. Yoshihiro et al. [15] reported that PDA treated titanium and stainless steel surfaces effectively immobilized the epidermal growth factor and promoted cell growth efficiently. Shin et al. [16] also demonstrated that secondary ligation of VEGF via deposited polydopamine layer on the
surface of polymeric vascular graft materials accelerated endothelialization. In summary, the PDA in the hydrogel facilitated growth factor immobilization, which favored the potential application of the hydrogel in soft tissue repair.
In vivo wound healing.

Surgery

Full skin wounds were created on the dorsal area of rats and treated with the PDA-PAM hydrogels (8 wt.% DA/AM) and the epidermal growth factor (EGF)-loaded PDA-PAM hydrogels. The wounds treated by blank were used as a control.

Briefly, 5 male Sprague Dawley (SD) rats weighing 180-220 g were used. After being anesthetized with pentobarbital (2 wt.%, 2 ml/kg), the dorsal area of rats was totally depilated and 4 full-thickness circular wounds (5 mm in diameter) were created on the upper back of each mouse by a disposable 5 mm skin biopsy punch. On each rat, a blank wound without hydrogel was used as control. The PDA-PAM and EGF-loaded hydrogels (EGF, 30 µg/sample, Shanghai Primegene Bio-Tech Co., Ltd.) were implanted on other wound sites of the rats, as shown in the red cycles in Figure S19. Totally 5 parallel specimens of each type of hydrogels were tested. The hydrogels were placed directly on the wounds. The wounds were additionally covered with a 4 cm×10 cm piece of Tegaderm™ dressing (3 M, St. Paul, MN, USA) to keep the hydrogel in place and to protect them from infection, as shown in Figure S19. In the following 3 days, rats were injected with penicillin to reduce the risk of infection. The experiments were performed in accordance with protocols approved by the local ethical committee and laboratory animal administration rules of China.
Figure S19. In vivo implantation. Full-thickness cutaneous wounds (5 mm in diameter) were created on the depilated dorsal skin of a SD rat with a biopsy punch, and the samples were implanted in the wounds (as indicated by the red circles). The wounds were covered by a Tegaderm™ dressing (3 M, USA) to keep the hydrogel in place and to protect it from infection.

At day 0, 5 and 15 of post-wounding, photographs of the wound closure were taken for each wound with a digital camera, and percentages of wound closure was easily calculated. The rats showed no adverse reactions over the 15-day treatment period. All rats were sacrificed on day 15 and the wound site with surrounding skin was harvested. Central wound sections were fixed on glass slides and stained with hematoxylin and eosin (H&E) and Masson’s trichrome to evaluate the wound healing progress and investigate the skin tissue regeneration and collagen deposition.

Intuitive observation indicated that the PDA-PAM hydrogel accelerated the wound healing. After 15-day treatment, the regenerated skin tissue covered by the PDA-PAM hydrogel was comparable to that covered by the EGF-loaded hydrogel (Fig. 6e). The new skin tissue on both the PDA-PAM hydrogel and the EGF-loaded hydrogel covered the whole wound.

The size of the wound on each photograph was measured. The wound closure was quantitatively evaluated by the ratio of the area of the 15-day and 5-day to that of 0-day, which is shown in (Fig. 6d). The results demonstrated that the size of the wound tended to decline during the 15-day implantation. Both PDA-PAM hydrogels with and without EGF had a wound healing ratio of ~80%, higher than that of blank group (60 %).
**Histological examinations**

Histological examination further indicated that the PDA-PAM hydrogels accelerated skin tissue regeneration compared with that of blank groups after 15 day-treatment, as shown by the H&E and Masson’s trichrome staining images in Fig. 6f. The wound treated with PDA-PAM hydrogels were covered by a complete and thick epidermis (Fig. 6f-1). No inflammatory reaction appeared at the interface between new skin tissue and hydrogels), while the wound area generates a few microvessels (Fig. 6f-2). Masson’s trichrome staining images showed that the PDA-PAM hydrogels treated wound areas showed adequate collagen deposition (Fig. 6f-3). More organized aligned collagen fibers, and more mature fibers were found in the PDA-PAM hydrogel than those in the blank groups (Fig. 6f-9).

When the hydrogel loaded with EGF, more mature tissue grew into the wound area as indicated by the mature glands grown from the glandular cavity (Fig. 6f-5). Masson’s trichrome staining showed that the collagen fibers grown in EGF-hydrogel treated wound were compact and aligned in order and parallel to the epidermis (Fig. 6f-6).

For blank group, a small amount of inflammatory reaction appeared, and the collagen fibers in the wound area were randomly arranged (Fig. 6f-7,8,9).

In summary, the EGF-free PDA-PAM hydrogel facilitated a quicker wound healing process than that of the blank groups. The good wound healing ability of the PDA-PAM hydrogel was attributed to four reasons. Firstly, the high tissue adhesiveness of PDA-PAM hydrogel guaranteed the hydrogel intact fixation with surrounding tissue and protects the wound sites from infection during the entire healing period. Secondly, the excellent cell affinity of the hydrogel facilitied cells adhesion, attachment and migration. Thirdly, the hydrogel had good affinity to ECM proteins (Figure S14), and the protein adsorption could further improve cell attachment, which established positive feedback loop and finally created suitable ECM microenvironments for cell adhesion\(^{14}\). Finally, the hydrogel stably immobilizes epidermal growth factor (EGF) that enhanced the migration of fibroblasts to the wound area and promoted complete skin regeneration for superior treatment of dermal wounds (Figure S15).
The excellent wound-healing performance of hydrogel led the hydrogel to the great potential clinic applications.
Self-healable, conductive hydrogels.

The PDA-PAM hydrogels could be tuned to conductive hydrogels by incorporating carbon black (CB) nanoparticles in the hydrogels (Figure S20a).

The conductive hydrogel was synthesized by the same polymerization process as that of PDA-PAM hydrogels. CB NPs were added into DA solution to allow DA to polymerize on nanoparticles surfaces. Thus, the PDA functionalized CB NPs can well disperse in the hydrogels (Fig. 7b-i). The CB NPs incorporated hydrogels with various CB NPs content (5 wt. % - 50 wt.% to AM) were finally obtained by the same polymerization process as that of PDA-PAM hydrogels (Table S4). CB NPs-PAM hydrogels without PDA grafting were also prepared as controls. The conductivity of hydrogels sample was measured by a two-probe method using a potential state (CHI 660, USA). The effect of water content on the conductivity was also studied. Three kinds of CB NPs-PDA-PAM hydrogels containing 70 wt.%, 75 wt.%, and 80 wt.% of water were prepared, as listed in Table S5. The CB NPs content in the hydrogels were kept at 20 wt.%.

**Table S4** The compositions of CB NPs-PDA-PAM hydrogels with different CB NPs content

| CB-NPs/AM (wt.%) | CB-NPs (g) | DA (g) | AM (g) | Water (ml) | APS (g) | BIS (g) | TMEDA (μl) |
|------------------|------------|--------|--------|------------|--------|--------|------------|
| 1                | 0          | 0      | 0.02   | 2.6        | 10     | 0.25   | 0.003      | 20         |
| 2                | 10         | 0.26   | 0.02   | 2.6        | 10     | 0.25   | 0.003      | 20         |
| 3                | 20         | 0.52   | 0.02   | 2.6        | 10     | 0.25   | 0.003      | 20         |
| 4                | 30         | 0.78   | 0.02   | 2.6        | 10     | 0.25   | 0.003      | 20         |
| 5                | 40         | 1.04   | 0.02   | 2.6        | 10     | 0.25   | 0.003      | 20         |
| 6                | 50         | 1.3    | 0.02   | 2.6        | 10     | 0.25   | 0.003      | 20         |

* In this table, CB NPs content increased while the contents of other components were fixed.
**Table S5** The compositions of CB NPs-PDA-PAM hydrogels with different water content

| CB-NPs/AM (wt.%) | DA (g) | AM (g) | Water (ml) | Water content in hydrogel (%) |
|------------------|--------|--------|------------|-----------------------------|
| 1                | 20     | 0.02   | 2.6        | 8                           | 70                           |
| 2                | 20     | 0.02   | 2.6        | 10                          | 75                           |
| 3                | 20     | 0.02   | 2.6        | 12                          | 80                           |

* In this table water content increased while the contents of other components were fixed.

**Results:**

The hydrogel incorporated with CB NPs displayed homogeneous morphology at the microscopic level using SEM (JSM 6390), which suggested that the CB NPs were well dispersed into the polymeric matrix and covered with PDA microfibrils (Figure S20b). The conductivity of PDA-PAM hydrogel was $10^{-7}$ S/cm, which was nearly insulated. After CB NPs were incorporated, the conductivity of the hydrogels significantly increased (Figure S20c). The inset of Figure S20c showed that increasing CB NPs contents led to the increase of the conductivity of CB NPs-PDA-PAM hydrogels. The conductivity of the hydrogels increased with water content (Figure S20d).

To investigate self-healing and stretchable ability, a battery-powered circuit with an LED was used (Fig. 7b-ii). (1) The CB NPs-PDA-PAM hydrogel with 20 wt.% of CB NPs was worked as a conductor to connect circuit, and the LED was bright; (2-3) the hydrogel was stretched, and the light of LED gradually became weak during the process; (4) the hydrogel was stretched until to break and the LED was off; (5) the fractured two parts of hydrogel were put into contact to heal for 2 hours and the LED was bright again; (6) the healed hydrogel was stretched again. These results showed that the conductive hydrogels still had self-healing and stretchability. The resistance of CB NPs-PDA-PAM hydrogel with 20 wt.% of CB NPs during stretching was measured. The hydrogel was embedded into two parallel titanium
electrodes and was connected into electrical loop. The electrical resistance was recorded when 2, 4, and 7 of extension ratio was applied. The relative electrical resistance change ($\Delta R/R_0$) was calculated by following Equation S2.

$$\Delta R/R_0 = (R - R_0)/R_0 \text{ (Equation S2)}$$

Where $R_0$ and $R$ denote the resistance without and with applied strain, respectively.

As shown in Figure S20e, The resistance of the hydrogel increased during tension. When the extension ratio was 2, the electrical resistance of the hydrogel increased 18%. When the extension ratio was 7, the electrical resistance of the hydrogel increased 86%.
Figure S20. Self-healable conductive hydrogel with carbon black (CB) NPs; (a) SEM images of CB NPs. (b) CB NPs were uniformly distributed in the hydrogel. (c) Bulk electrical conductivity of CB NPs-PDA-PAM hydrogels from a two-point probe measurement. The inset is the amplified image that shows the effects of CB NPs on the conductivity of CB NPs-PDA-PAM hydrogels. (d) Conductivity of CB NPs-PDA-PAM hydrogels with different water contents. (e) The resistance change of the hydrogel during stretching.
Self-healable, magnetic hydrogels.

The PDA-PAM hydrogels can be transformed to the magnetic hydrogels by incorporating Fe₃O₄ NPs in the hydrogels.

**Synthesis and Characterization of Fe₃O₄ nanoparticles:** Fe₃O₄ NPs were synthesized using a method reported previously. First, FeCl₂·4H₂O (5 mmol) and FeCl₃·6H₂O (10 mmol) were dissolved in distilled water (10 ml) containing HCl (0.06 mol/l) as precursor solution I; Secondly, an aqueous NaOH solution (50 ml, 1.5 mol/l) was used as precursor solution II. The precursor solution II was added into precursor solution I drop-wisely with strong stirring under the protection of nitrogen at 30 °C. Just after mixing the solutions, the color of the solution changed from brick to black, indicating the formation of Fe₃O₄ NPs. Then the mixture was allowed to crystallize completely for another 30 min under rapid stirring and stand for 10 min on a magnet for precipitating. The precipitated Fe₃O₄ NPs were washed by repeating the cycles of centrifugation and re-dispersion in distilled water, and dried in a vacuum oven at room temperature for 24 hours.

**Preparation of magnetic hydrogel:** The magnetic hydrogel was synthesized by the same polymerization process as that of PDA-PAM hydrogels. Fe₃O₄ NPs were added into DA solution to allow DA to polymerize on nanoparticles surfaces. Thus, the PDA functionalized Fe₃O₄ NPs well dispersed in the hydrogels. Fe₃O₄ NPs-PAM hydrogels without PDA grafting were also prepared as controls.

**Characterization of Magnetic nanoparticles and hydrogels:** The morphology of NPs and hydrogels was examined by SEM (JSM 6390). The magnetization (M) of dried magnetic hydrogels sample with various Fe₃O₄ NPs contents in the dried hydrogel state (0.5 wt. % - 8 wt.% to AM) was characterized by using a vibrating sample magnetometer (VSM, LakeShore, 7037, USA) as a function of the applied field (H) at 293 K.
Results:

After PDA grafting, Fe₃O₄ NPs were well dispersed in the PDA solution, whereas Fe₃O₄ NPs without PDA grafting settled at the bottom of water. When the PDA grafted Fe₃O₄ NPs were incorporated into the hydrogel, they were homogeneously distributed in the hydrogel (Figure S21 a, b). The magnetic curves had almost no hysteresis, which is typical for super paramagnetic materials; and the saturation magnetization (Ms) and coercivity (Hc) of the hydrogels increased with the content of Fe₃O₄ NPs in the hydrogel (Figure S21c). The Fe₃O₄ NPs incorporated hydrogel can be attracted by a magnet, and tightly adhere on the magnet, and then can be stretched 7 times of its initial length (Figure S21d). These results demonstrate that the hydrogel with Fe₃O₄ NPs incorporation still has adhesiveness, magnetism and stretchability. In order to prove the self-healing ability of the magnetic hydrogels, the hydrogel blocks with (black) and without (brown) Fe₃O₄ NPs were put into contact and self-healed to form a hydrogel rope. Then the hydrogel rope adhered on the nails and was bended by two magnets. These results showed that the Fe₃O₄ NPs incorporated hydrogels had self-healing and magnetic properties.

Figure S21. Self-healable magnetic hydrogel with Fe₃O₄ NPs. (a) SEM images of Fe₃O₄
NPs. (b) SEM image shows that $\text{Fe}_3\text{O}_4$ NPs were covered by PDA in the hydrogel. (c) The magnetization curves of the hydrogels with addition of 2.6 and 7.8 wt.% $\text{Fe}_3\text{O}_4$ NPs. The hydrogels showed paramagnetic behavior and no hysteresis was observed. (d) 1), the clamped hydrogel was hung without magnetic field; 2), hydrogel was attracted by external magnetic field; 3), the hydrogel strongly adhered to the magnet and was stretched to 7 times of its initial length.

**Figure S22.** (a, c) PDA grafting functional NPs uniformly distributed in the hydrogel. (b, d) The NPs distributed heterogeneously in the PAM hydrogel without PDA.
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Videos

1. Single-edge notch test of PAM hydrogel

This movie showed that pure PAM hydrogel performed a running crack quickly when a pre-crack was made in the middle of the hydrogel during tensile test. The crack length was 5 mm. The thickness of the hydrogel was 3 mm. The gauge length was 5 mm. The width was 25 mm. The tests were performed using the universal tensile machine (Instron 5567) with a 100-N load cell. The speed of the crosshead was 2 mm/sec.

2. Single-edge notch test of PDA-PAM hydrogel

This movie showed that PDA-PAM hydrogel was not sensitive to the notch. The hydrogel with a pre-crack could still bear large extension. The DA/AM ratio in the hydrogel was 8 wt.%o. The tests were performed using the same parameter as that of the PAM hydrogel.

3. Repeatable adhesion of PDA-PAM hydrogel to human skin

This movie showed that PDA-PAM hydrogel could adhere to human skin tightly. After six cycles of adhere-strip, the hydrogel still had good adhesiveness and stretchability. The human skin was not hurt during adhere-strip test. The DA/AM ratio in the hydrogel was 8 wt.%o.