Electronic Supplementary Information

A lamellibranchia-inspired epidermal electrode for electrophysiology

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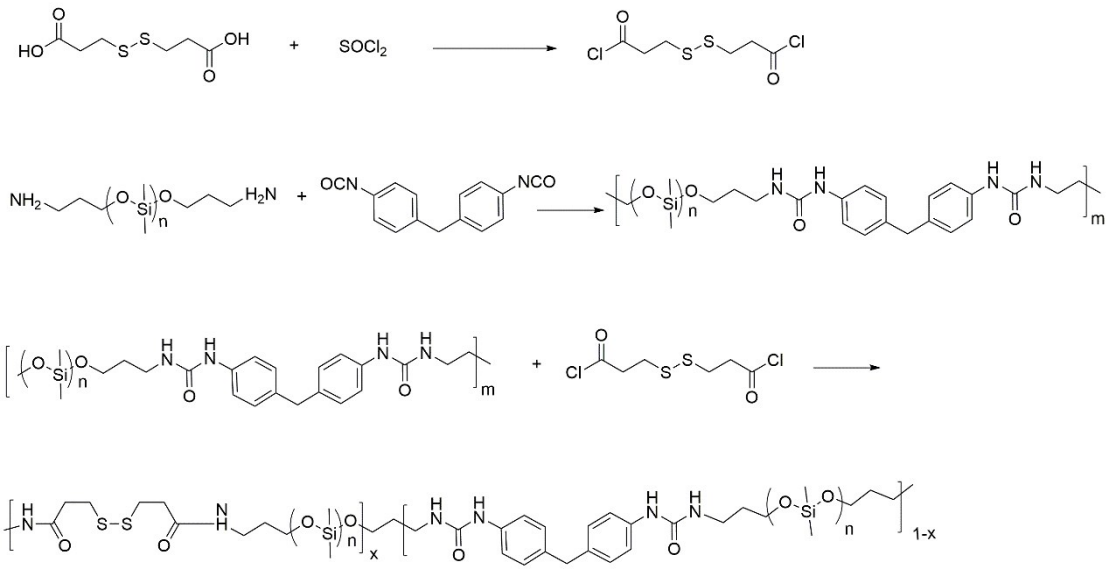

Fig. S1. Synthetic route of SS_x-PDMS-MPI_{1-x}.

Synthesis of PDMS-MPI. Bis(3-aminopropyl)-terminated poly(dimethylsiloxane) (H_2N-PDMS-NH_2, M_n = 5000-7000, 20.0 g, ~1eq) and triethylamine (2 mL) were stirred in anhydrous chloroform (100 mL) at 0 ºC under nitrogen atmosphere for 1 h. Subsequently, a solution of 4,4'-methylenebis(phenyl isocyanate) (1.0 g, 1eq) in anhydrous chloroform (30 mL) was added dropwise for 30min. The resulting mixture was stirred at room temperature for 3 days followed by evaporating the solvent to form viscous liquid. Then methanol (30 mL) was poured into it to form precipitate-like viscous liquid. The upper clear solution was decanted after settled for 30 minutes. The precipitate-like liquid was dissolved in chloroform and washed with methanol (30 mL) for 3 times to obtain purified PDMS-MPI. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.16-7.19 (m), 6.91-7.06 (m), 6.68-6.89 (m), 3.80-3.89 (m), 0.04 (b). Molecular weight according to GPC: Mw = 81,893; Mn = 48,921 (Đ = 1.67).

Synthesis of $SS_{0.1}$-PDMS-$MPI_{0.9}$. 3,3'-disulfanediyldipropanoic acid (1.0 g) was stirred in thionyl chloride (60 mL) at room temperature for 4 h. The white suspension gradually turned into a light yellow solution. Then the solvent was evaporated under vacuum to obtain yellow liquid 3,3'-disulfanediyldipropanoyl chloride (1.1 g). Secondly, H_2N-PDMS-NH_2 (20.0 g, ~1eq) and triethylamine (2 mL) were stirred in

anhydrous $CHCl_3$ (100 mL) at 0 ºC under nitrogen atmosphere for 1 h. Subsequently, a solution of 4,4'-methylenebis(phenyl isocyanate) (0.9 g, ~0.9 eq) in anhydrous chloroform was added dropwise for 30 min. The mixture was then allowed to stir at room temperature for 1 days. After that, a solution of 3,3'-disulfanediyldipropanoyl chloride (0.1 g, ~0.1 eq) was added dropwise. The mixture was again stirred at room temperature for 3 days. The same purified procedure as PDMS-MPI was used to obtain purified $SS_{0.1}$-PDMS-$MPI_{0.9}$. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.15 (s), 7.03-7.12 (m), 6.81-6.93 (m), 6.70 (s), 3.81-3.93 (m), 2.51-2.58 (m), 0.05 (b). Molecular weight according to GPC: Mw = 94,987; Mn = 49,580 (Đ = 1.92).

Synthesis of $SS_{0.2}$-PDMS-$MPI_{0.8}$ and $SS_{0.3}$-PDMS-$MPI_{0.7}$. $SS_{0.2}$-PDMS-$MPI_{0.8}$ and $SS_{0.3}$-PDMS-$MPI_{0.7}$ were synthesized by using different mixing molar ratio of 4,4'-methylenebis(phenyl isocyanate) and 3,3'-disulfanediyldipropanoyl chloride according to the same procedure as that used for $SS_{0.1}$-PDMS-$MPI_{0.9}$. ^1H NMR (400 MHz, $CDCl_3$, δ) for $SS_{0.2}$-PDMS-$MPI_{0.8}$: 7.17 (s), 7.02-7.11 (m), 6.83-6.95 (m), 6.74 (s), 3.82-3.93 (m), 2.52-2.57 (m), 0.05 (b). Molecular weight according to GPC: Mw = 71,724; Mn = 33,881 (Đ = 2.21). ^1H NMR (400 MHz, $CDCl_3$, δ) for $SS_{0.3}$-PDMS-$MPI_{0.7}$: 7.20 (s), 7.02-7.11 (m), 6.84-6.99 (m), 6.77 (s), 3.79-3.88 (m), 2.52-2.60 (m), 0.05 (b). Molecular weight according to GPC: Mw = 72,120; Mn = 36,533 (Đ = 1.97).

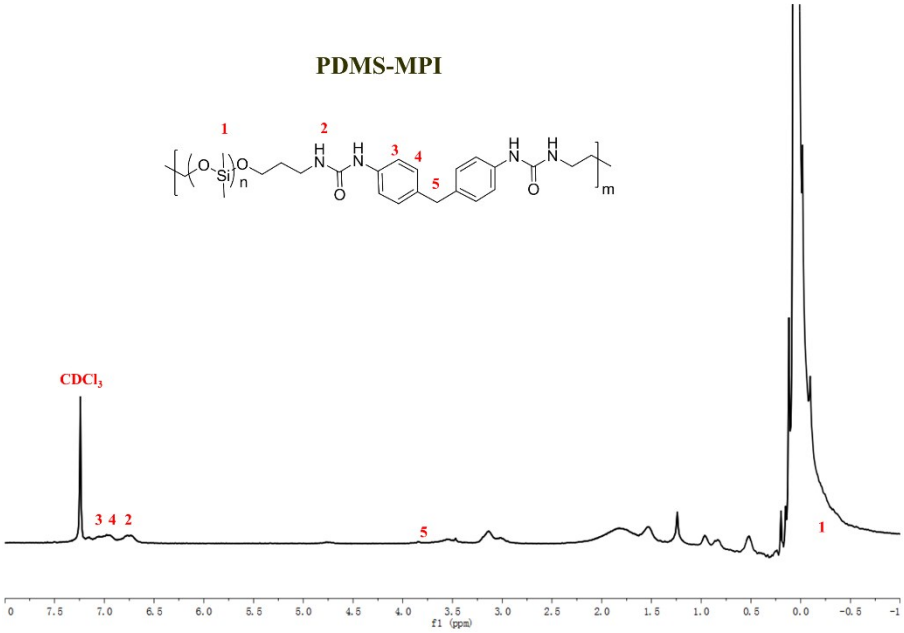

Fig. S2. ^{1}H NMR spectrum of PDMS-MPI in $CDCl_3$ at room temperature.

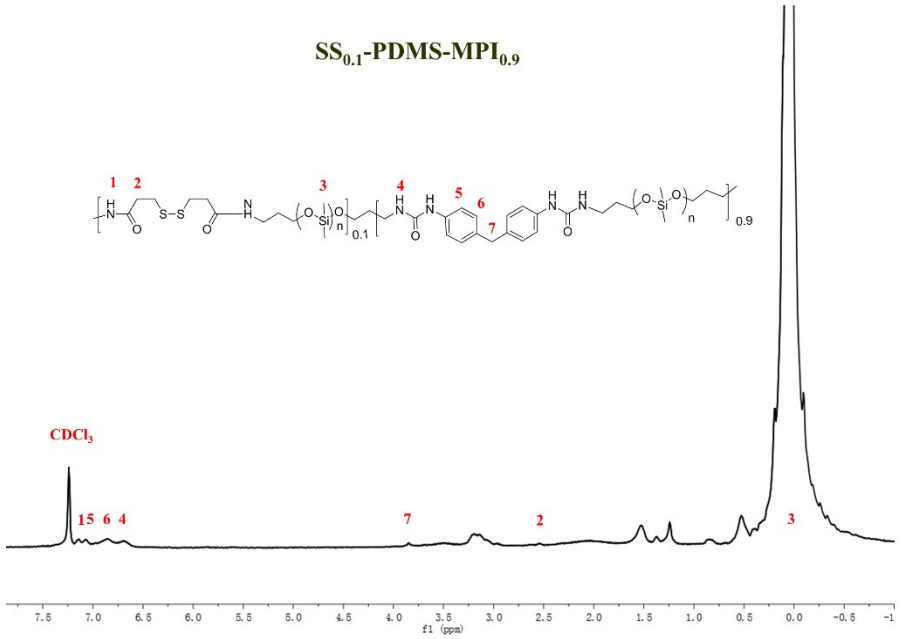

Fig. S3. ^{1}H NMR spectrum of $SS_{0.1}$-PDMS-$MPI_{0.9}$ in $CDCl_3$.

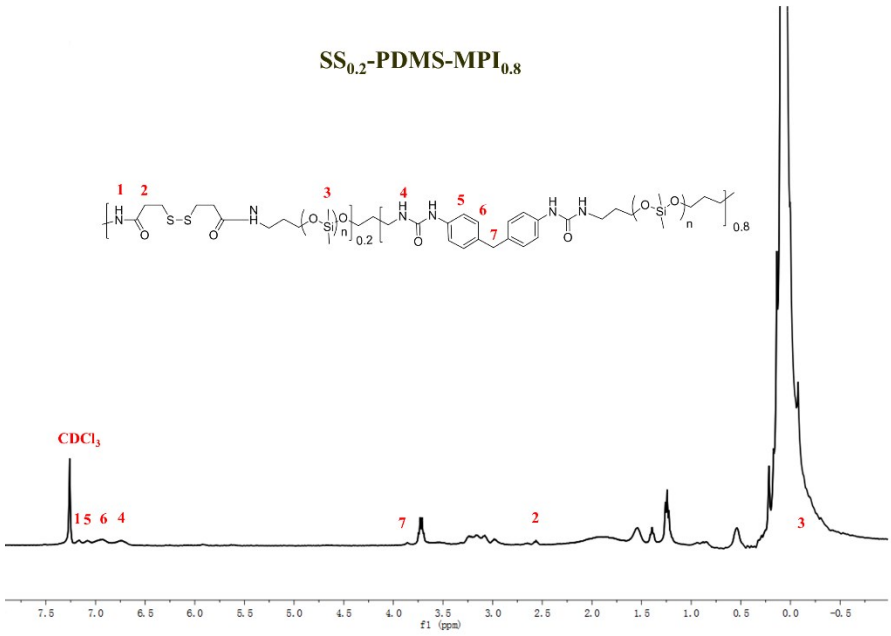

Fig. S4. ^{1}H NMR spectrum of $SS_{0.2}$-PDMS-$MPI_{0.8}$ in $CDCl_3$.

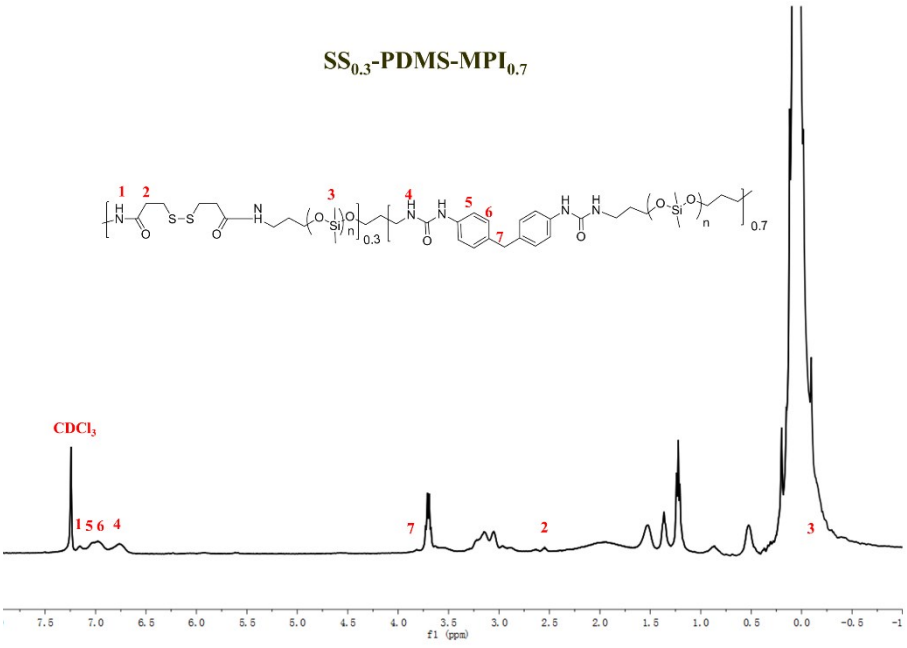

Fig. S5. ^{1}H NMR spectrum of $SS_{0.3}$-PDMS-$MPI_{0.7}$ in $CDCl_3$.

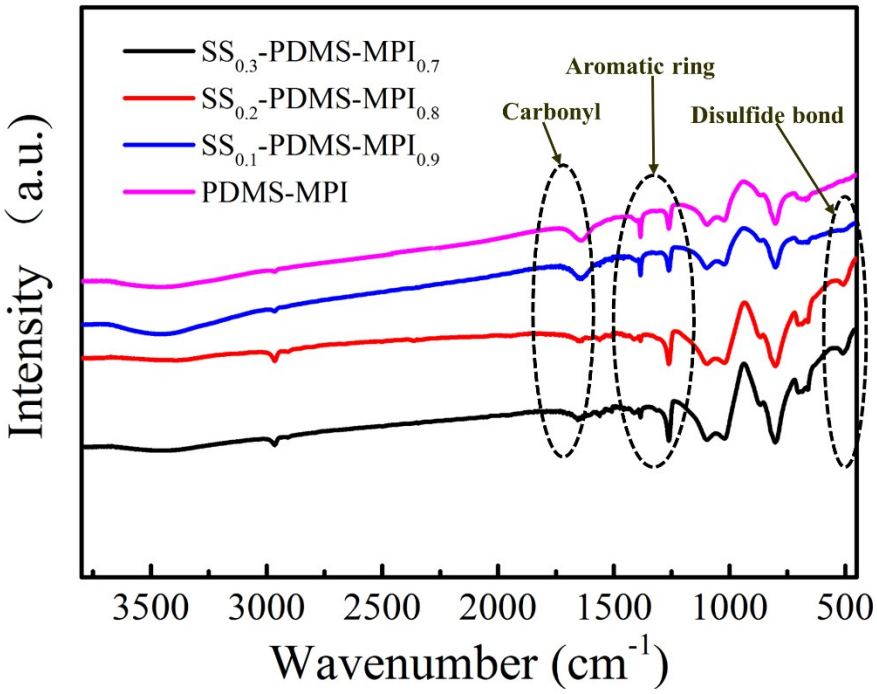

Fig. S6. FT-IR spectra of SS_x-PDMS-MPI_{1-x} (x=0, 0.1, 0.2, 0.3).

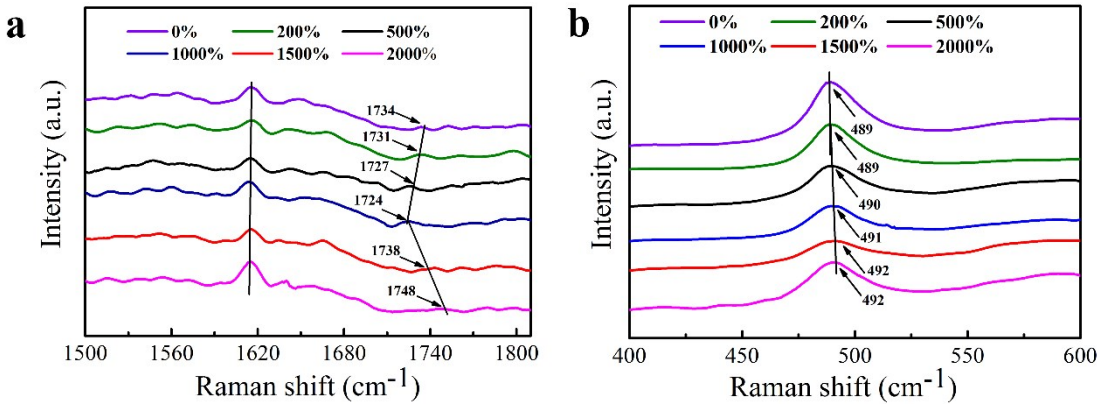

Fig. S7. Raman spectra of $SS_{0.1}$-PDMS-$MPI_{0.9}$ to demonstrate the changes of hydrogen bonds and (g) disulfide bonds under different strains.

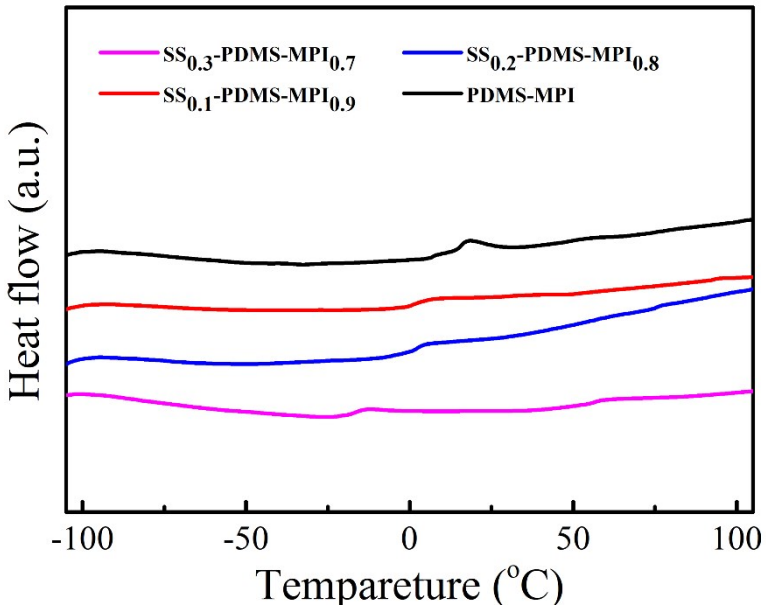

Fig. S8. Differential scanning calorimetry (DSC) thermal analysis of PDMS-MPI, $SS_{0.1}$-PDMS-$MPI_{0.9}$, $SS_{0.2}$-PDMS-$MPI_{0.8}$, and $SS_{0.3}$-PDMS-$MPI_{0.7}$.

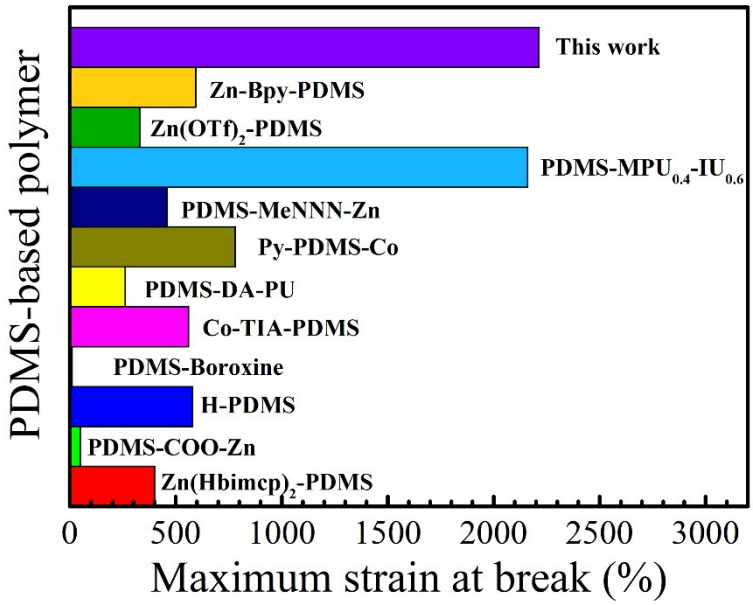

Fig. S9. The maximum strain at break of STAR and other recently reported self-healing PDMS-based polymers.

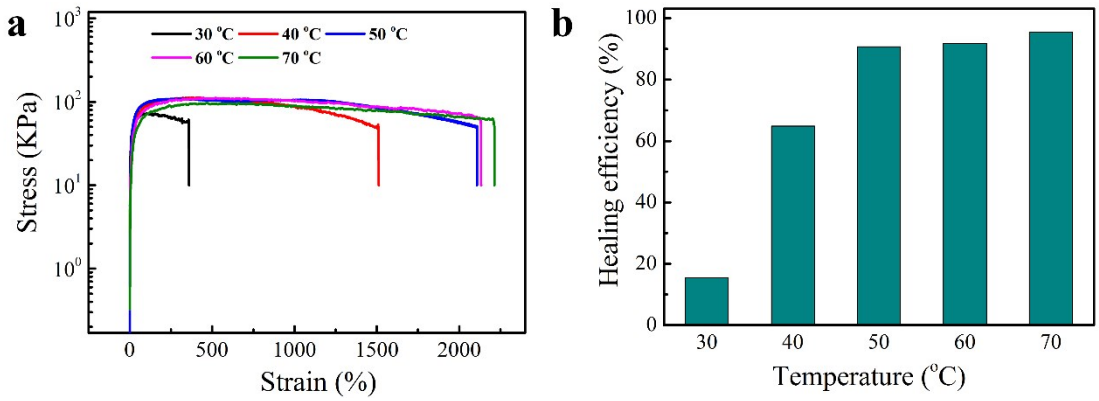

Fig. S10. (a) Stress-strain curves of STAR under different heating temperature for 10 min. (b) The healing efficiency of STAR under different heating temperature.

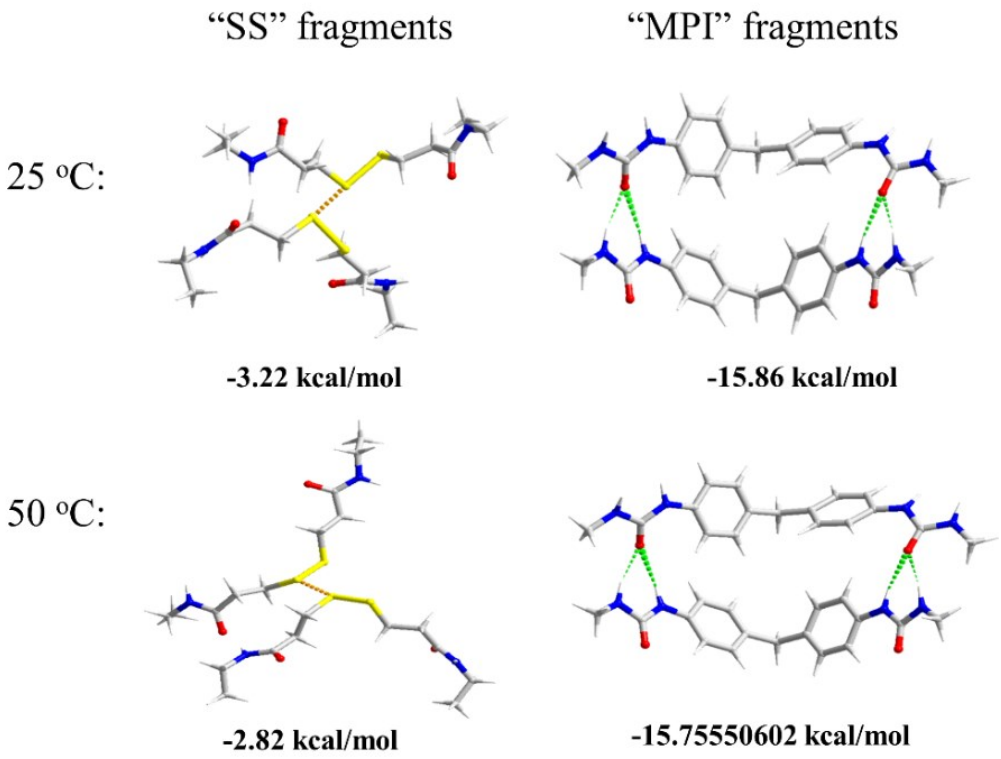

Fig. S11. Optimized configuration of bimolecular "SS" (A-A) and bimolecular "MPI" (B-B) fragments at 25 °C and 50 °C.

At 25 °C: $E_A = \varepsilon_0 + E_{tot}$ =Sum of electronic and thermal energies = -1449.11843 Ha

$E_{A\text{-}A} = \varepsilon_0 + E_{tot}$ = Sum of electronic and thermal Energies= -2898.241993 Ha

The energy of S-S bonds: $\Delta E_S = E_{2A} - 2E_A$=-3.22 kcal/mol

At 50 °C: $E_A = \varepsilon_0 + E_{tot}$ =Sum of electronic and thermal energies = -1449.115815 Ha

$E_{A\text{-}A} = \varepsilon_0 + E_{tot}$ = Sum of electronic and thermal Energies= -2898.236123 Ha

The energy of S-S bonds: $\Delta E_S = E_{2A} - 2E_A$= -2.82 kcal/mol

At 25 °C: $E_B = \varepsilon_0 + E_{tot}$ = Sum of electronic and thermal energies = -1028.981478 Ha

$E_{B\text{-}B} = \varepsilon_0 + E_{tot}$ = Sum of electronic and thermal Energies= -2057.988227 Ha

$\Delta E_H = E_{2B} - 2E_B$= -15.86 kcal/mol

At 50 °C: $E_B = \varepsilon_0 + E_{tot}$ = Sum of electronic and thermal energies = -1028.978006 Ha

$E_{B\text{-}B} = \varepsilon_0 + E_{tot}$ = Sum of electronic and thermal Energies= -2057.98112 Ha

$\Delta E_H = E_{2B} - 2E_B$= -15.75550602 kcal/mol

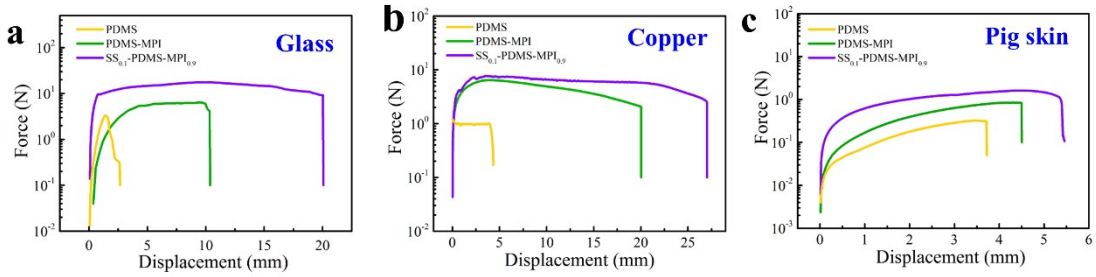

Fig. S12. Adhesion force-displacement curves of PDMS, PDMS-MPI, and STAR on (a) glass, (b) copper, and (c) pig skin.

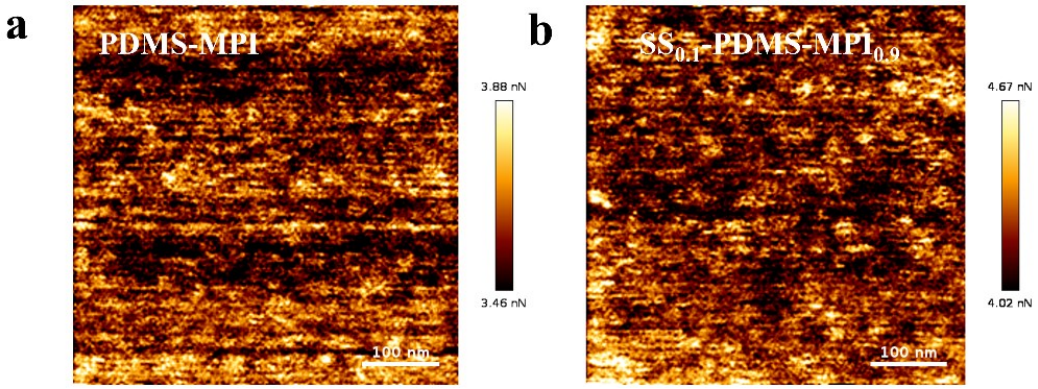

Fig. S13. AFM adhesion force images: (a) PDMS-MPI, (b) $SS_{0.1}$-PDMS-$MPI_{0.9}$.

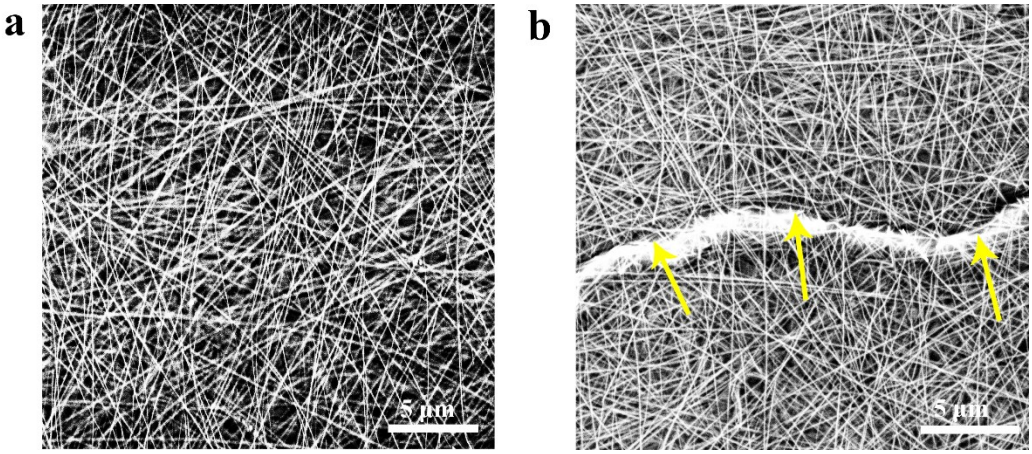

Fig. S14. SEM images of (a) STAR electrode and (b) healed STAR electrode. The yellow arrows mark the crack area.

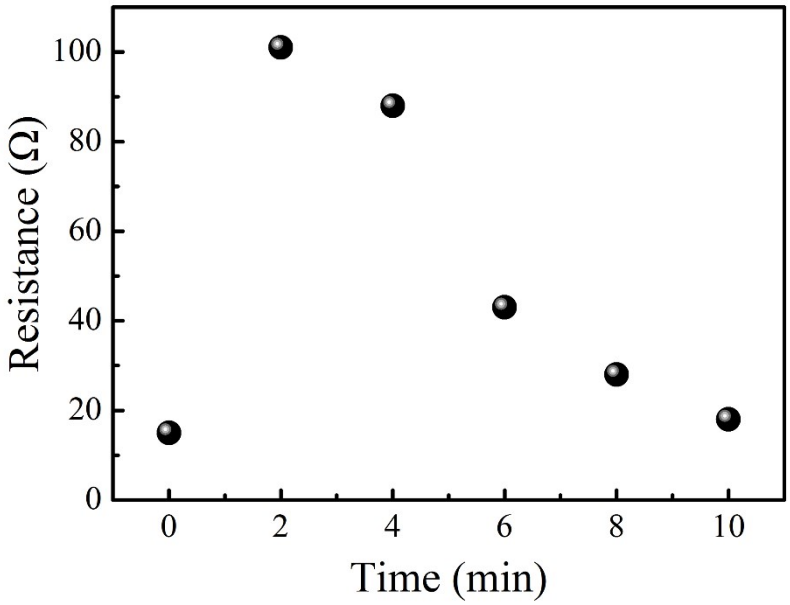

Fig. S15. The resistance of a STAR electrode as a function of time before cutting (0 min) and during the healing process at 50 °C.

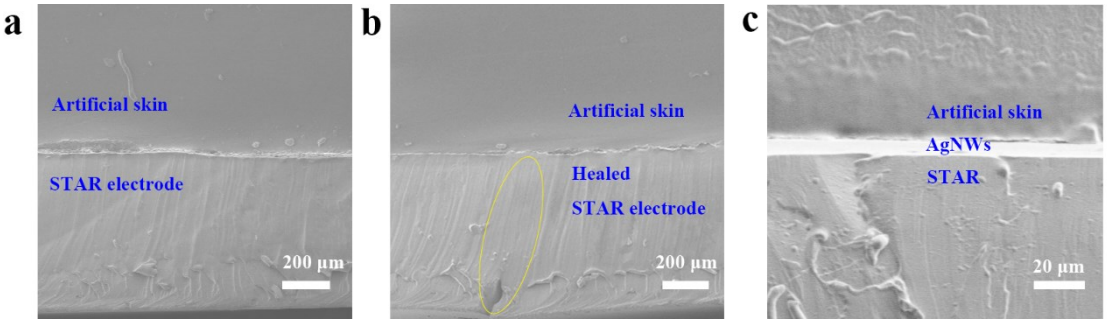

Fig. S16. SEM images of the cross-section view to investigate the thickness of (a) STAR electrode, (b) healed STAR electrode and (c) AgNWs conductor.

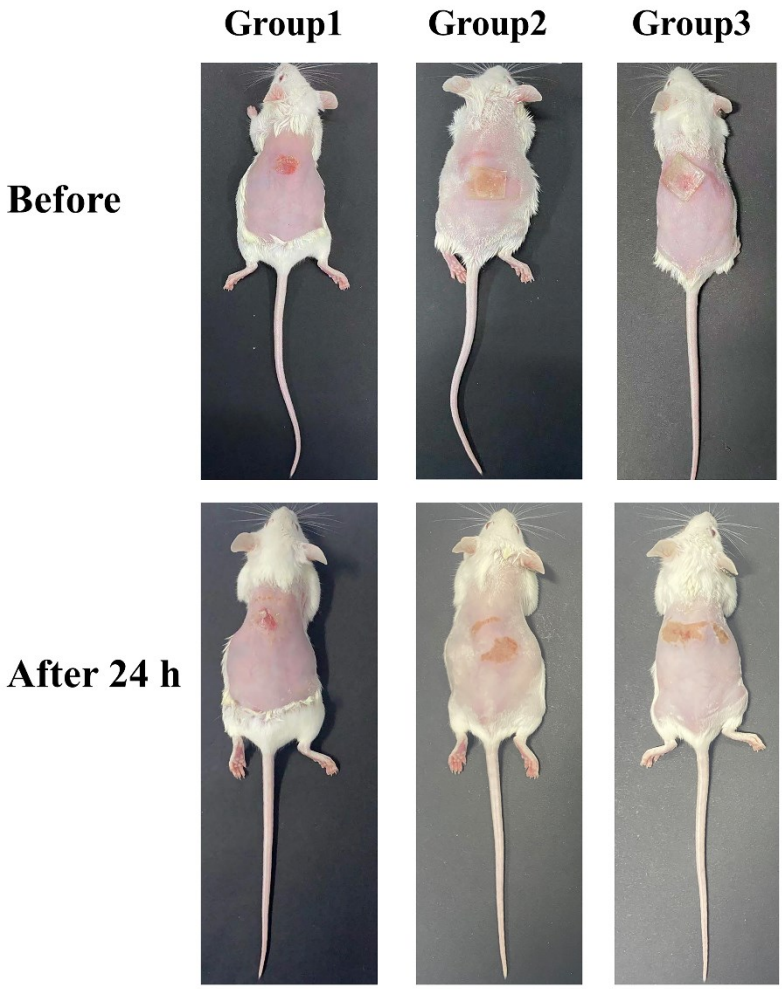

Fig. S17. Photos of in vivo experiments performed in mice: Group1(control group), Group2 (The wounded area was covered by STAR), and Group3 (The wounded area was covered by STAR electrodes).

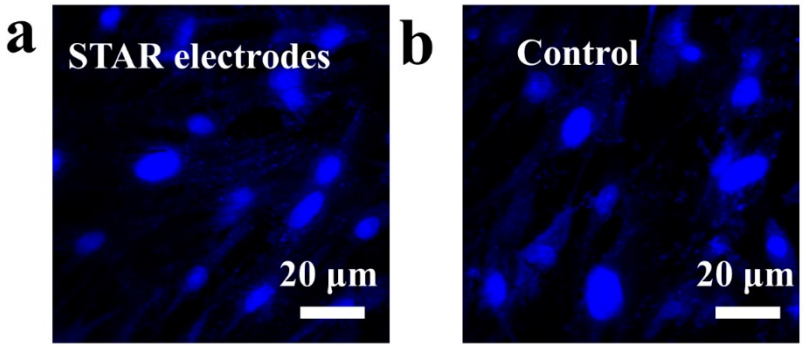

Fig. S18. Fluorescent images of CCC-HPF1 fibroblasts cells: (a) with STAR electrodes, (b) control (the environment in which cells grow under the best conditions).

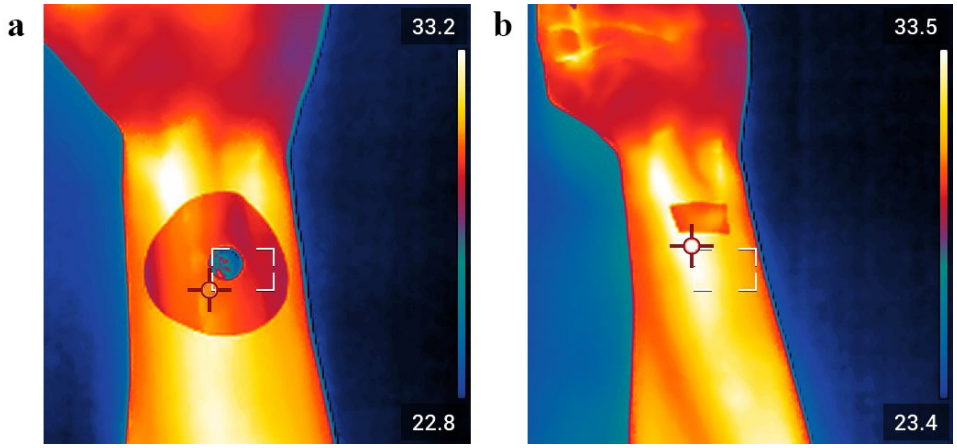

Fig. S19. Infrared images of the STAR electrodes and commercial electrodes on a volunteer's forearm.