

Supplementary Materials

Fabrication of Thermo-Responsive Controllable Shape-Changing Hydrogel

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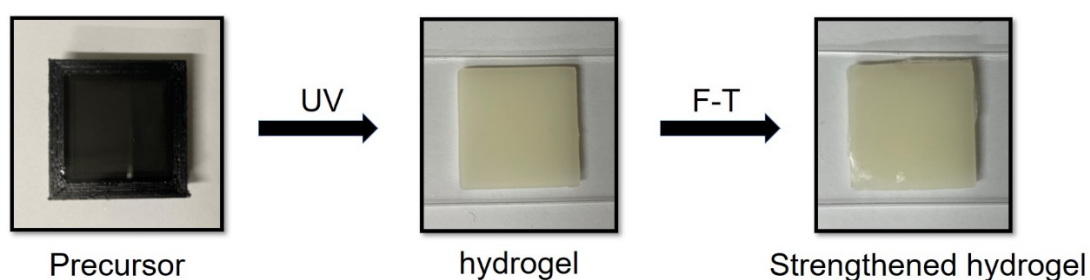


Figure S1. Photos of the hydrogel in each fabrication progress.

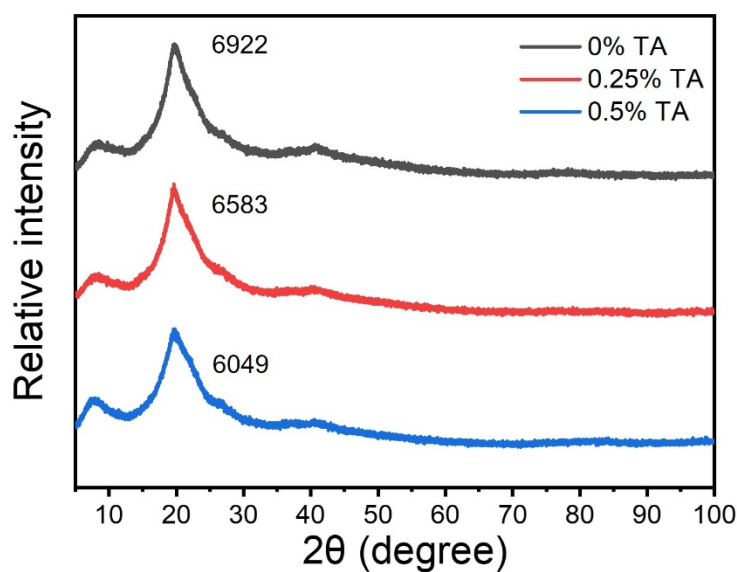


Figure S2. XRD spectra of the hydrogel without TA (black), with 0.25 wt.% TA (red) and 0.5 wt.% TA (blue).

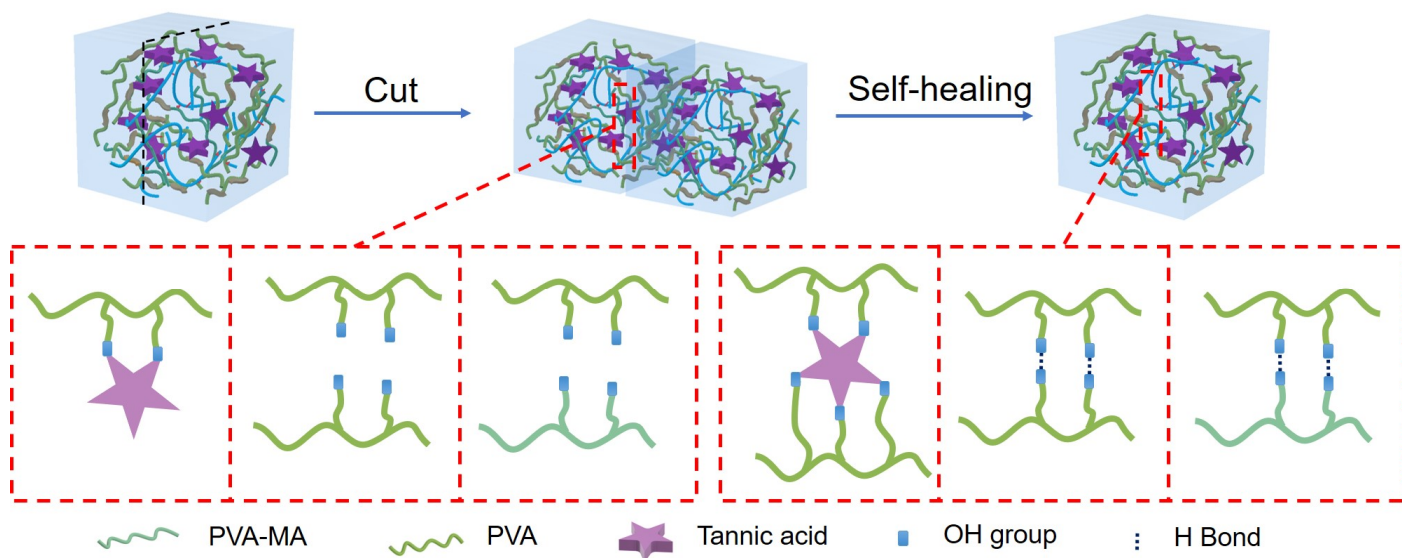


Figure S3. The mechanism of the self-healing.

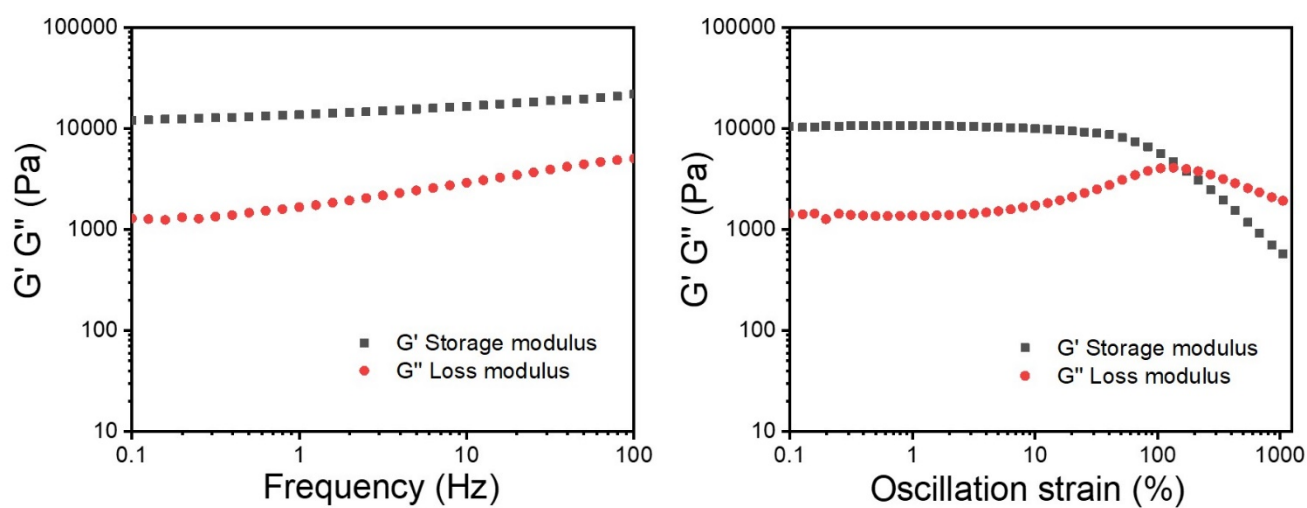


Figure S4. The rheological properties of hydrogels: the amplitude sweeps (a) and the frequency sweeps (b) of the hydrogels.

Table S1. Mechanical data of PVA/TA(0.5 wt.)/PVA-MA-g-PNIPAAm hydrogel at 25°C

| TA content (wt) | 0% | | 0.25% | | 0.50% | |
|-----------------------------|------------|-------------|-------------|-------------|-------------|-------------|
| | original | self-healed | original | self-healed | original | self-healed |
| Young's modulus (MPa) | 0.12 | 0.108 | 0.058 | 0.044 | 0.085 | 0.082 |
| elongation at break (mm/mm) | 2.76 | 1.24 | 7.05 | 5.87 | 8.82 | 8 |
| stress at break (MPa) | 0.4 (0.05) | 0.13 (0.08) | 0.69 (0.04) | 0.43 (0.03) | 1.39 (0.04) | 1.13 (0.02) |
| healing-efficiency HE (%) | 33 | | 62 | | 81 | |

Table S2. Rheological data of BIS-crosslinked PVA/TA (0.5 wt.)/PVA-MA-g-PNIPAAm and crosslinked PVA/TA(0.5 wt.)/PVA-MA-g-PNIPAAm.

| Time (s) | Oscillatory stress (Pa) | | G' (Pa) | | G'' (Pa) | |
|----------|-------------------------|------------------------|-----------------|------------------------|-----------------|------------------------|
| | BIS-crosslinked | Physically crosslinked | BIS-crosslinked | Physically crosslinked | BIS-crosslinked | Physically crosslinked |
| 6 | 89.36 | 11.61 | 24390 | 10510 | 3191 | 1307 |
| 13 | 241.1 | 95.44 | 23630 | 8930 | 3058 | 1344 |
| 19 | 237.2 | 88.87 | 23290 | 8862 | 3002 | 1453 |
| 26 | 235.3 | 88.46 | 23720 | 8812 | 3099 | 1467 |
| 39 | 237 | 88.01 | 23850 | 8771 | 2927 | 1534 |
| 45 | 238.3 | 87.94 | 23910 | 8755 | 3047 | 1520 |
| 58 | 236.3 | 87.62 | 23830 | 8703 | 2861 | 1550 |
| 70 | 235.4 | 87.36 | 23380 | 8714 | 2847 | 1551 |
| 77 | 236 | 87.33 | 23730 | 8660 | 2770 | 1574 |
| 90 | 237.2 | 87.17 | 23920 | 8684 | 2705 | 1595 |
| 106 | 9827 | 1334 | 1204 | 138.9 | 6363 | 649.8 |
| 113 | 11730 | 1379 | 1459 | 109.5 | 5846 | 524.2 |
| 119 | 12760 | 1389 | 1759 | 117.4 | 6074 | 548.9 |
| 126 | 13680 | 1458 | 1974 | 125.5 | 6008 | 576.1 |
| 139 | 14950 | 1584 | 2272 | 142.4 | 5962 | 621.9 |
| 145 | 15350 | 1595 | 2378 | 144.1 | 5973 | 623.3 |
| 158 | 15890 | 1663 | 2528 | 151 | 5892 | 650.9 |
| 170 | 16150 | 1685 | 2663 | 154.3 | 5959 | 659.2 |
| 177 | 16320 | 1727 | 2732 | 159 | 5998 | 672.3 |
| 190 | 16380 | 1770 | 2793 | 161.4 | 5953 | 690.1 |
| 206 | 87.08 | 11.93 | 22140 | 11800 | 3278 | 2313 |
| 213 | 221.6 | 102.6 | 21710 | 9081 | 3142 | 1888 |
| 219 | 219.9 | 91.94 | 22030 | 9174 | 3203 | 1831 |
| 226 | 222.1 | 92.06 | 22060 | 9127 | 3048 | 1773 |
| 239 | 223.5 | 91.33 | 22150 | 9054 | 3008 | 1740 |
| 245 | 223.4 | 90.99 | 22130 | 9033 | 2914 | 1712 |
| 258 | 223.9 | 90.2 | 22120 | 8937 | 3064 | 1700 |
| 270 | 224.7 | 89.56 | 22350 | 8884 | 3091 | 1676 |

| | | | | | | |
|-----|-------|-------|-------|--------|------|-------|
| 277 | 224.9 | 89.1 | 22340 | 8825 | 3003 | 1659 |
| 290 | 225.7 | 88.59 | 22470 | 8800 | 3060 | 1663 |
| 306 | 12910 | 1517 | 3238 | 185.5 | 6048 | 781.5 |
| 313 | 16430 | 1557 | 2421 | 129.2 | 5601 | 583 |
| 319 | 15470 | 1630 | 2745 | 149.9 | 5803 | 649.8 |
| 326 | 15940 | 1636 | 2709 | 147.2 | 5757 | 636.9 |
| 339 | 15870 | 1715 | 2774 | 159.3 | 5738 | 674.1 |
| 345 | 15860 | 1782 | 2794 | 168.3 | 5723 | 699 |
| 358 | 15760 | 1814 | 2801 | 172.3 | 5658 | 706.5 |
| 370 | 15590 | 1834 | 2797 | 175.5 | 5587 | 715.6 |
| 377 | 15490 | 1844 | 2778 | 177.1 | 5531 | 718.9 |
| 390 | 15230 | 1915 | 2760 | 185.1 | 5455 | 745.9 |
| 406 | 83.46 | 11.73 | 19850 | 12150 | 3084 | 2567 |
| 413 | 198.1 | 106 | 19270 | 9308 | 2790 | 2182 |
| 419 | 195.7 | 95.37 | 19660 | 9489 | 3002 | 2183 |
| 426 | 198.1 | 95.73 | 19640 | 9439 | 2849 | 2106 |
| 439 | 199.7 | 94.88 | 19880 | 9366 | 2838 | 2056 |
| 445 | 199.8 | 94.31 | 19780 | 9308 | 2654 | 2005 |
| 458 | 199.9 | 93.51 | 19680 | 9248 | 2808 | 1987 |
| 470 | 200.2 | 92.66 | 19980 | 9177 | 2945 | 1945 |
| 477 | 201.4 | 92.44 | 19970 | 9121 | 2911 | 1945 |
| 490 | 203.1 | 91.49 | 20240 | 9054 | 2994 | 1908 |
| 506 | 12160 | 1613 | 3151 | 190.8 | 5537 | 757.2 |
| 513 | 15230 | 1697 | 2360 | 153.3 | 5142 | 601.6 |
| 519 | 14270 | 1708 | 2613 | 175.2 | 5269 | 657.6 |
| 526 | 14570 | 1795 | 2554 | 182.8 | 5213 | 677.4 |
| 539 | 14470 | 1811 | 2582 | 175.45 | 5189 | 694.1 |
| 545 | 14390 | 1860 | 2578 | 178.75 | 5156 | 689.9 |
| 558 | 14220 | 1868 | 2578 | 191.2 | 5085 | 698.6 |
| 570 | 14160 | 1874 | 2577 | 199.25 | 5054 | 744.9 |
| 577 | 14120 | 1916 | 2607 | 205.8 | 5038 | 748.2 |
| 590 | 14110 | 2070 | 2624 | 212.3 | 5016 | 764.4 |

Table S3. Length (L), final length change (LC), and its linear rate constant (R_{LC}) of PVA/TA(0.5 wt%)/PVA-MA-g-PNIPAAm while cycling in 30 min intervals between 25 °C and 50 °C in deionized water.

| operation | L (%) | LC (%) | R_{LC} (%/min) |
|-----------|-------|--------|------------------|
| heat 1 | 83.63 | 16.37 | 16.37 |
| cool 1 | 85.34 | 14.37 | 17.18 |
| heat 2 | 82.40 | 17.25 | 17.60 |
| cool 2 | 83.99 | 15.40 | 19.07 |
| heat 3 | 82.23 | 17.20 | 17.77 |
| cool 3 | 82.93 | 16.16 | 20.21 |
| heat 4 | 82.03 | 17.16 | 17.97 |
| cool 4 | 82.35 | 16.78 | 21.43 |
| heat 5 | 81.79 | 17.31 | 18.21 |
| cool 5 | 82.27 | 16.76 | 21.55 |