

Supplementary Information

A novel strategy to construct hydrogels with anti-swelling and water-retention abilities by covalent surface modification

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Experimental Section

Materials

Sodium alginate (SA), dimethylaminoethyl methacrylate (DMAEMA), 2,2-Diethoxyacetophenone (DEPO) and polyethyleneimine (PEI) were purchased from Shanghai Macklin Biochemical Co., Ltd. N, N-methylenebis acrylamide (MBA) and 3-methacryloxypropyltrimethoxysilane (MPS) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Ammonia was purchased from Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd. All the reagents were used without further purification. Ultrapure water (the resistance is 18.25 M Ω ·cm) was used throughout.

Preparation of PSG hydrogels

2.5 g of SA were dissolved in 19 mL of ultrapure water to form a homogeneous aqueous SA solution. Subsequently, 2.4 g of DMAEMA, 0.08 g of MBA, and 26 μ L of DEPO were sequentially added to 1 mL of water under vigorous stirring. Then, the obtained mixture was slowly added to the SA solution under stirring at room temperature to obtain the hydrogel precursor solution. The prepared precursor solution was then poured into a mold and irradiated under ultraviolet light ($\lambda = 365$ nm) for 30 min to construct a hydrogel. The synthesized PSG hydrogel was sealed and stored for future use.

Modification of PSG hydrogels

The as-prepared PSG hydrogel was in PEI aqueous solution with a mass fraction of 20 wt% for 1 hour. After wiping the water on the hydrogel surface with filter paper, the PSPG hydrogel was soaked in MPS for 3 h to synthesize PSPMG hydrogel.

Measurements of FTIR

Fourier transform infrared (FTIR) spectroscopy (Nicolet 5700, USA) was used to monitor the modification process of PSG hydrogel. The spectra were recorded over a wavenumber range of 400 to 4000 cm^{-1} with a resolution of 1 cm^{-1} . The PSG, PSPG, and PSPMG hydrogels were freeze-dried for observation.

Characterization of SEM

The surface and internal morphology, as well as the elemental mapping of the PSG and PSPMG hydrogels, were observed using scanning electron microscopy and energy dispersive

spectroscopy (SEM-EDS, Sirion 200, Netherlands). The PSG and PSPMG hydrogel were freeze-dried, and followed by an Au film spraying on the cross-section and the surface of the hydrogel samples.

Surface wettability

The surface wettability of the hydrogel surface during the modification process was analyzed via a contact angle measuring instrument (JC500D2, China). The average water contact angle (WCA) values were determined by conducting measurements at three different locations on the same sample (10 mm×10 mm×4 mm).

Anti-swelling and water-retention behaviors

The swelling processes of PSG and PSPMG hydrogels were conducted by immersing the hydrogels in water at room temperature. The anti-swelling behaviors were monitored by calculating the swelling ratio of hydrogels through weight-measuring method. the swelling ratio is calculated using Eq. (1).

$$\text{Swelling ratio} = \frac{W_t - W_0}{W_0} \times 100\% \quad (1)$$

where W_t and W_0 represent the weight of the hydrogel at time t and 0, respectively.

The dehydration processes of PSG and PSPMG hydrogels were conducted by placing the hydrogels in air with 36 RH% at 25 °C. The water-retention behaviors were monitored by calculating the water loss ratio of hydrogels through weight-measuring method. The water loss ratio is calculated according to Eq. (2).

$$\text{Water loss ratio} = \frac{W_0 - W_t}{W_0} \times 100\% \quad (2)$$

where W_t and W_0 represent the weight of the hydrogel at time t and 0, respectively.

The calculation of the change ratio of absolute water content is shown in Eq. (3).

$$\text{Change ratio of absolute water content} = \frac{(W_t - W_n) - W_i}{W_i} \times 100\% \quad (3)$$

where W_n represents the absolute weight of the hydrogel network, and W_i represents the weight of water hosted in hydrogel at initial state.

In this experiment, the size of the tested sample is 10 mm × 10 mm × 4 mm. The experiments were conducted in triplicate independently.

Conductivity and Sensing performance

The conductivity and sensing performance of hydrogels after different treatments were measured using an intelligent digital meter (Keithley 2450, USA), with the voltage as 1 V. As for conductivity measurements, at least three tests were performed for each sample (10 mm×10 mm×4 mm), and the data were presented as mean values with mean absolute deviations. As for sensing performance, the hydrogel sample was connected to the electrical signal analyzer via a wire. The sensitivity of the hydrogel-based sensor was expressed by the relative resistance change ($\Delta R/R_0$) (Eq. (4)).

$$\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0} \times 100\% \quad (4)$$

where R_0 and R are the initial resistance and the real-time resistance, respectively.

Mechanical testing

Tensile tests were conducted using an electronic universal testing machine (WDW-5T, China). All tests were carried out in ambient air at room temperature. The tensile testing samples were prepared as a rectangular shape (75 mm×25 mm×4 mm), and the deformation velocity was set as 20 mm/min.

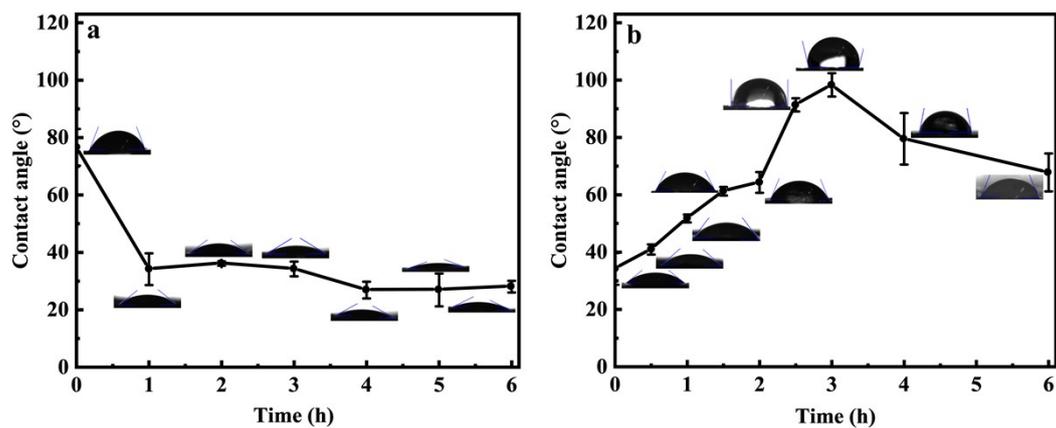


Fig. S1. The WCA of hydrogel immersed in PEI (a) and MPS (b) with time evolution.

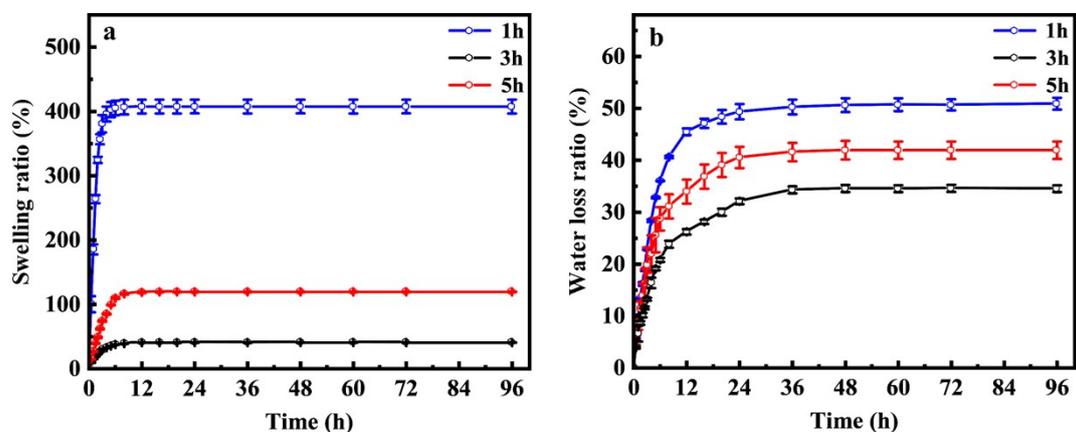


Fig. S2. The swelling ratio (a) and water loss ratio (b) of PSPMG hydrogels modified with MPS after different treatment.

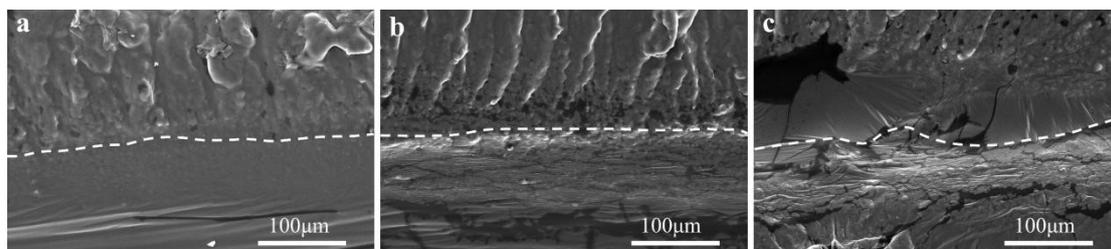


Fig. S3. SEM images of cross section of PSPMG hydrogel after different treatments. (a) Initial state. (b) Dehydration state after three swelling/dehydration cycles. (c) Swollen state after three dehydration/swelling cycles.

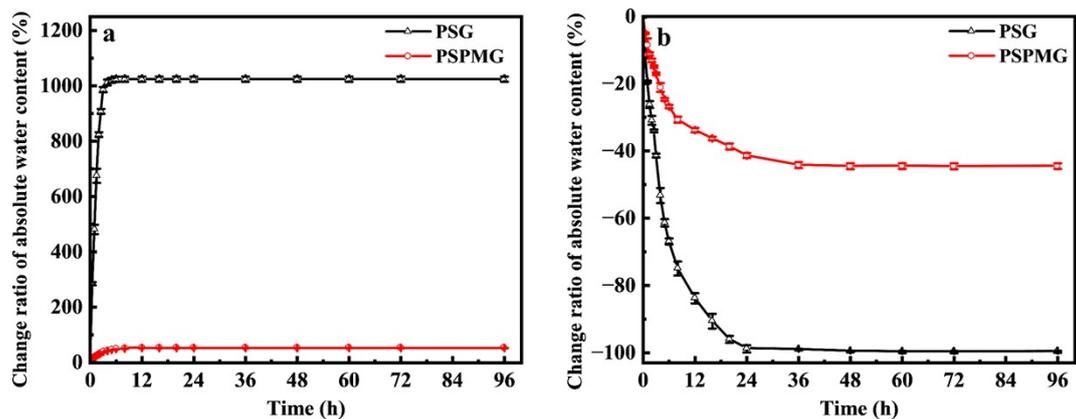


Fig. S4. The change ratio of absolute water content of PSG and PSPMG during swelling (a) and dehydration process (b) with time evolution.

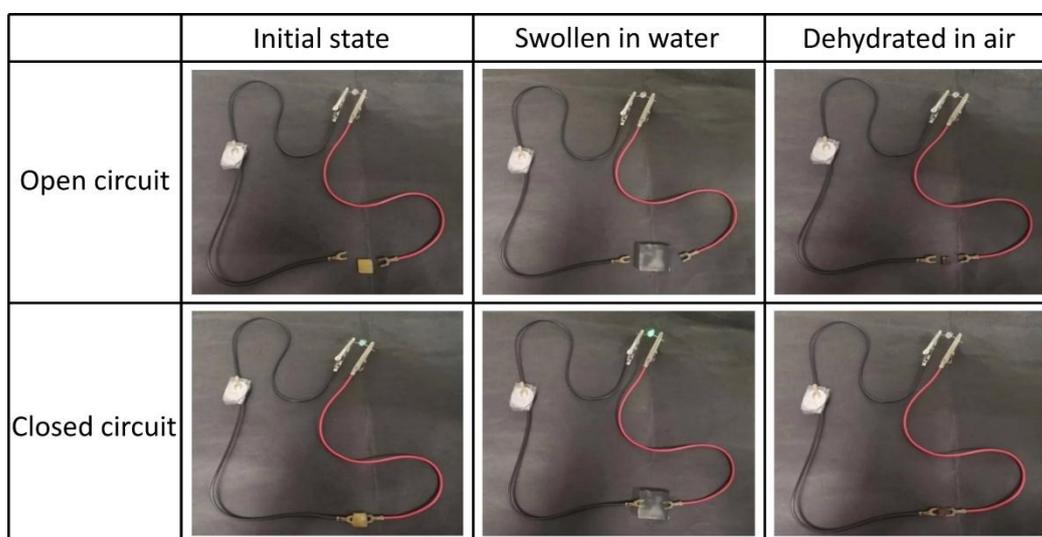


Fig. S5. Images of PSG hydrogels as conductors in the circuits of light-emitting diode indicators after different treatments.

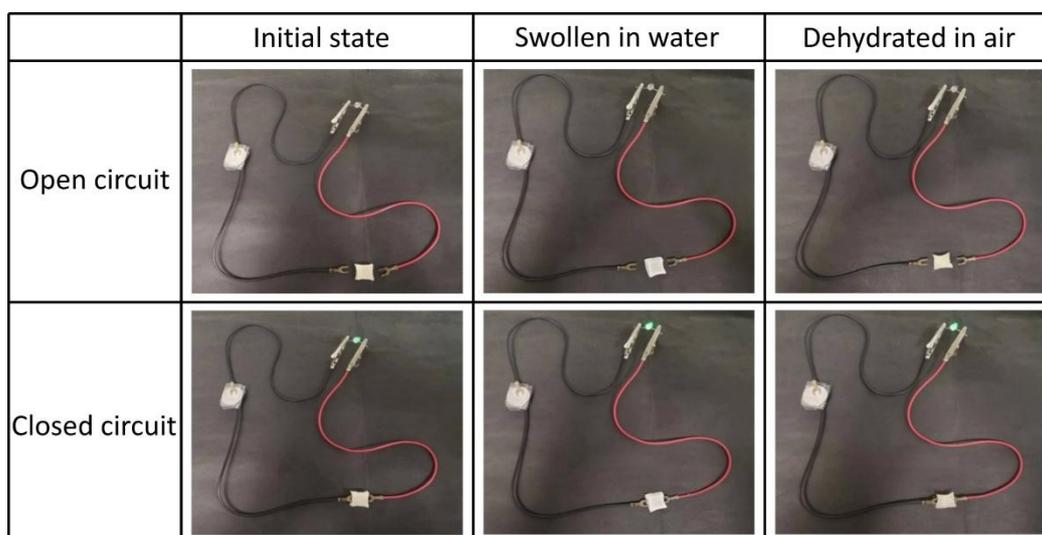


Fig. S6. Images of PSPMG hydrogels as conductors in the circuits of light-emitting diode indicators after different treatments.

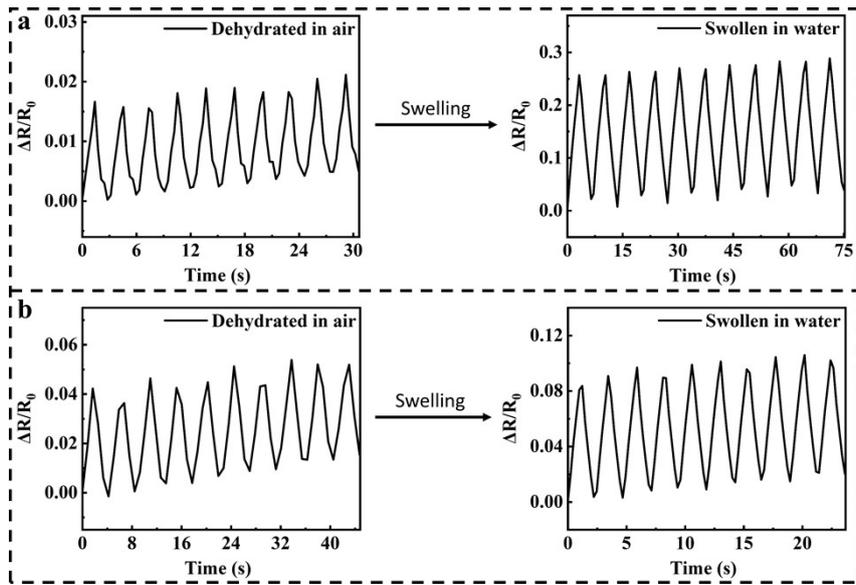


Fig. S7. The resistivity of (a) PSG and (b) PSPMG hydrogels after subsequent swelling of dehydrated sample.