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Electronic Supporting Information

Transparent Glycerol-Hydrogel with Stimuli-Responsive Actuation Induced Unexpectedly at Subzero Temperatures

This file includes:

1. Materials and Methods

1.1. Materials

Poly(2-(methacryloyloxy)ethyltrimethylammonium chloride) (PDMC) functionalized boron nitride nanosheets (f-BNNSs) were prepared and characterized according to the previous reports.[1,2] Poly(vinyl alcohol) (PVA, degree of polymerization = 1700, degree of hydrolysis = 99%), carboxymethyl cellulose (CMC, 99%), borax (99.0%), and ascorbic acid (99.0%) were purchased from Sigma-Aldrich. Glycerol (99.0%) and ferric chloride ($FeCl_3$, 99.0%), were purchased from Aladdin Industrial Corporation.

1.2. Preparation of Hydrogels

The f-BNNSs were first dispersed in deionized water and sonicated for 30 min to fabricate a homogeneously and steadily distributed f-BNNS dispersion. Subsequently, glycerol, PVA, and CMC were dissolved in the suspension by stirring at 100 °C for 5 h. And the as-prepared solution was transferred to the corresponding molds. Then, the mold was frozen at -60 °C for 12 h and thawed at room temperature for 6 h. The specific quantity of each component was listed in Tables S1 and S2.

1.3. Characterization

Fourier transform infrared (FTIR) spectra of the samples were recorded using a Thermo Fisher Nicolet Is10 spectrophotometer in attenuated total reflection (ATR) mode within the range 400-4000 cm^{-1}. The PVA/CMC/f-BNNS hydrogel and PVA/CMC/f-BNNS glycerol-hydrogel were investigated for their freezing temperature using a differential scanning calorimeter (DSC, TA Instruments Q20). The cooling cycle was performed from 10 °C to -70 °C at a rate of 5 °C/min. Transmittance spectra of the glycerol-hydrogels were obtained by using a UV-vis spectrophotometer (UV 2600, Shimadzu, Japan) in the visible light range (400-800 nm).

1.4. Dehydration Resistance

To demonstrate the long-term anti-dehydration, samples PVA/CMC/f-BNNS hydrogel and PVA/CMC/f-BNNS glycerol-hydrogel were placed at 25 °C and 50% relative humidity (RH, control by purging with dry airflow.) or 60 °C and 50% RH for 24 h. The anti-dehydration was characterized by the ratio of the initial weight of the hydrogels (W_0) to the weight of hydrogel after different durations of storage (W_t).

1.5. Mechanical Test

The tensile testing was carried out using a universal mechanical testing machine (Instron 2360) with a 200 N load cell under a loading rate of 50 mm/min at room temperature. The hydrogel samples were prepared into a dumbbell shape (GB/T 528-2009, 2 mm in inner width and 12 mm in gauge length).

1.6. Evaluation of Shape Memory Behaviors

The experiments were conducted at 25 and -45 °C, respectively. The glycerol-hydrogel specimens were cut into straight stripes with dimensions of 20 mm×1 mm×0.5 mm. The stripes were deformed into a temporary "V" shape by external force and then were immersed into 2.0 M $FeCl_3$ glycerol-water solution or 1.0 M borax glycerol-water solution for 10 min. To quantitatively describe the shape memory behaviours, the shape fixity ratio (R_f) was obtained by the following equation:

$$R_f=\theta_t/\theta_g\times100\% \qquad (3)$$

where θ_g is the given angle, θ_t is the fixed angle.

The recovery process was performed in 1.0 M ascorbic acid glycerol-water solution. The shape recovery ratio (R_r) was evaluated by the following equation:

$$R_r=(\theta_g-\theta_f)/\theta_g\times100\% \qquad (4)$$

where θ_f is the final angle.

1.7. Information Recording/Erasing

The experiments were conducted at -45 °C. The glycerol-hydrogel samples were prepared flat with a thickness of 1 mm. Then filter papers cut into different patterns were soaked in a 2.0 M $FeCl_3$ glycerol-water solution for 5 min and the patterns as mask information were placed on the glycerol-hydrogel surfaces under -45 °C. The patterns could be erased by dipping ascorbic acid glycerol-water solution with a brush pen.

1.8. Density Functional Theory (DFT) Study

1.8.1 Computational methods

To gain further insight into the molecular interactions of the glycerol-hydrogel, DFT calculations were carried out. The simulation was performed using the density functional theory program DMol^3 in Material Studio (Accelrys, San Diego, CA).[3] The physical wave function was treated by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) parameterization.[4] All-electron treatment and double numerical basis including d-and p-polarization function (DNP) were used.[5] The convergence criteria for the geometric optimization and energy calculation were set as follows: (i) an energy tolerance of 1.0×10^{-5} Ha/atom; (ii) a maximum force tolerance of 0.002 Ha/Å; (iii) a maximum displacement tolerance of 0.005 Å.

1.8.2 Model building

The water molecule interaction model (named W-W model) was built at first and then a glycerol molecule was placed on the water molecule model to investigate the interaction between water molecule and glycerol molecule (named G-W model). The models of PVA polymers were composed of 2 monomers. A glycerol molecule was placed on the polymer model to investigate the interaction between glycerol and PVA (named G-PVA model). In the next step, a water molecule was also added to investigate water effect on PVA (named W-

PVA model). Moreover, the interactions among PVA, glycerol and water (named G-W-PVA model) were investigated.

1.8.3 Interaction energy calculation

The intensity of the interaction between the components in the system could be described by the interaction energy (E_i) of the molecules, which was defined as the following equation:

$$E_i = E_t - \sum E_c \quad (6)$$

where E_i represents the total energy of the composite system, and E_c is the energy of each component in the system. A negative value of binding energy corresponds to a stable interaction between the components. More negative E_i indicates a stronger interaction in the system.

2. Supplementary Tables

Table S1. Composition of the prepared hydrogels and glycerol-hydrogels.

Sample	PVA (g)	CMC(g)	f-BNNS/CMC (wt %)	Glycerol (g)	H_2O (g)
PVA/CMC/hydrogel	0.12	0.04	0	0	3.00
PVA/CMC/f-BNNSs hydrogel	0.12	0.04	2	0	3.00
PVA/CMC/glycerol-hydrogel	0.12	0.04	0	2.00	1.00
PVA/CMC/f-BNNSs glycerol-hydrogel	0.12	0.04	2	2.00	1.00

Table S2. Interaction energy between PVA, water, and glycerol.

Model	Interaction energy (eV)
W-W model	-0.24
G-W model	-0.43
W-PVA model	-0.30
G-PVA model	-0.36
G-W-PVA model	-0.94

3. Supplementary Figures

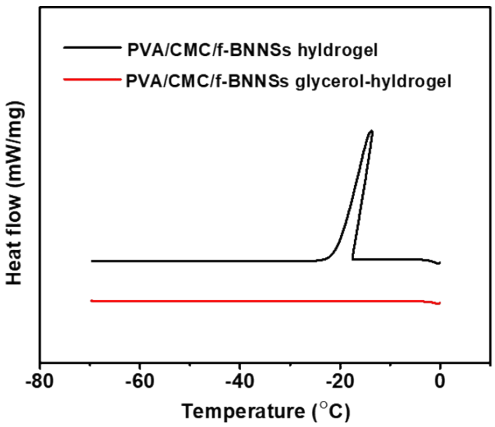

Fig. S1 DSC thermograms of PVA/CMC/f-BNNS hydrogel and PVA/CMC/f-BNNS glycerol-hydrogel.

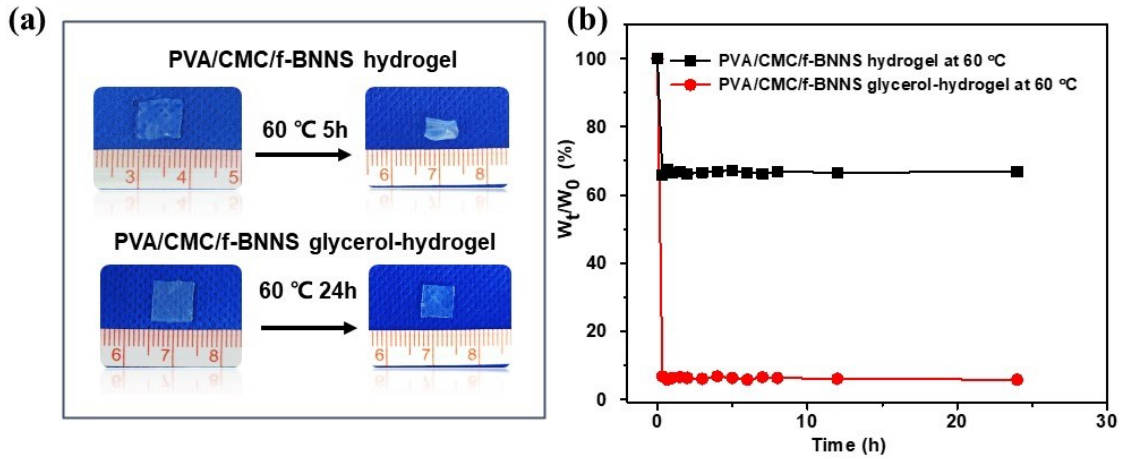

Fig. S2 (a) Comparison of the PVA/CMC/f-BNNS hydrogel and PVA/CMC/f-BNNS glycerol-hydrogel stored at 60 °C and 50% RH for 24 h. (b) Weight variation of the gels stored at 60 °C and 50% RH for 24 h.

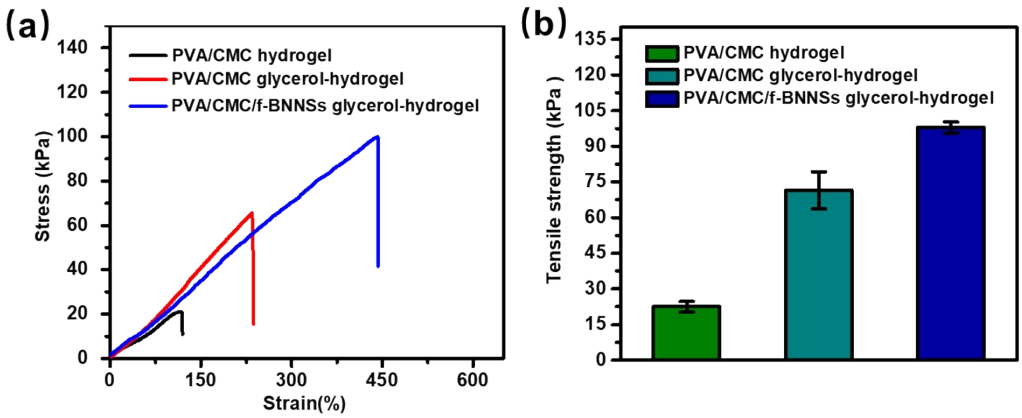

Fig. S3 (a) Stress-strain curves, and (b) tensile strength of different hydrogels.

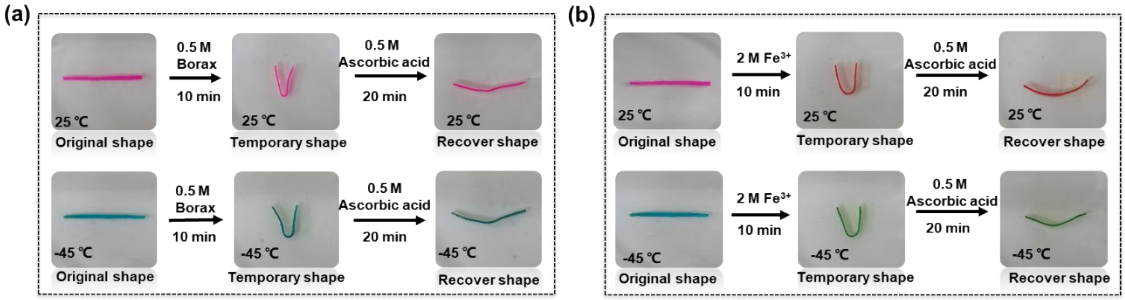

Fig. S4 (a) Shape memory and shape recovery process of PVA/CMC/f-BNNSs glycerol-hydrogel on the basis of reversible chemical bonding between PVA and borax at 25 and −45 °C. (b) Shape memory and shape recovery process of PVA/CMC/f-BNNSs glycerol-hydrogel on the basis of the reversible physical bonding between CMC and $FeCl_3$ at 25 and −45 °C.

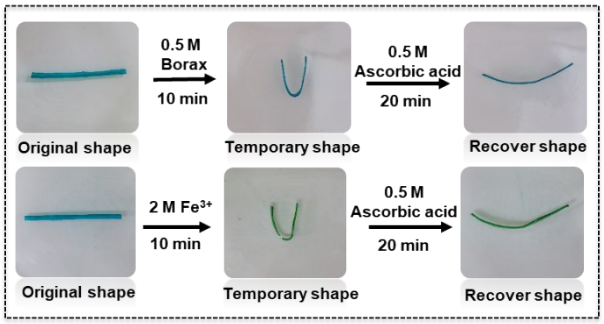

Fig. S5 Shape memory and shape recovery process of PVA/CMC/glycerol-hydrogel on the basis of reversible chemical bonding at −45 °C.

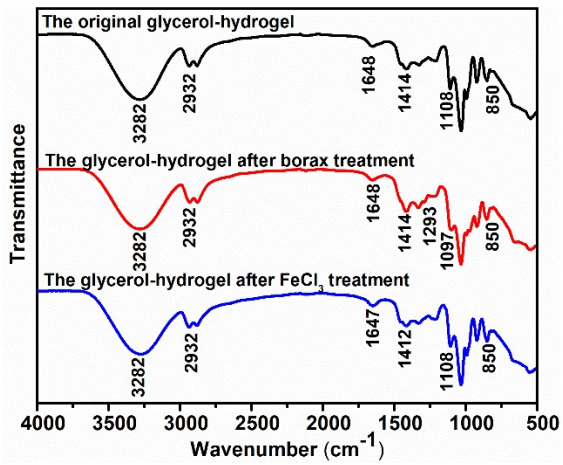

Fig. S6 ATR-FTIR spectra of the original PVA/CMC/f-BNNS glycerol-hydrogel, the glycerol-hydrogel after borax treatment, and the glycerol-hydrogel after $FeCl_3$ treatment.

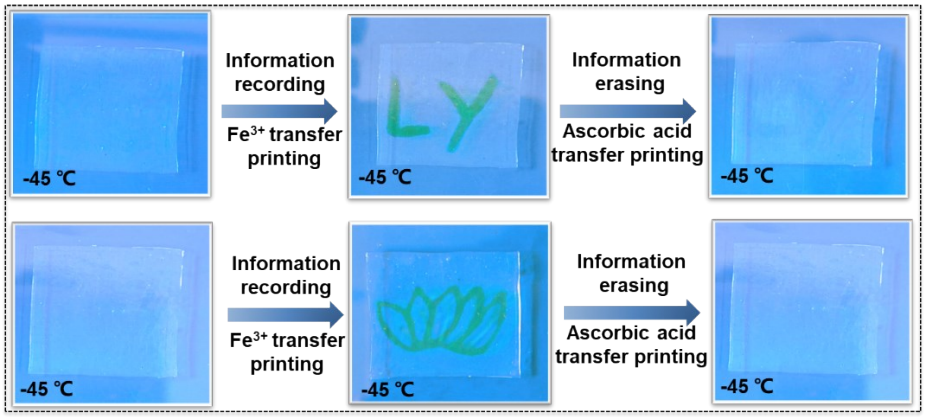

Fig. S7 Simple information recording and erasing process of the glycerol-hydrogel at -45 °C.

4. Supplementary Videos S1-S2

Video S1. Programmable shape memory of the hydrogel designed by kirigami. The movie is played at 8× normal speed.

Video S2. Programmable shape recovery of the hydrogel designed by kirigami. The movie is played at 8× normal speed.

References

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