Supporting Information

Antifreezing Heat-Resistant Hollow Hydrogel Tubes

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Supplementary Figures

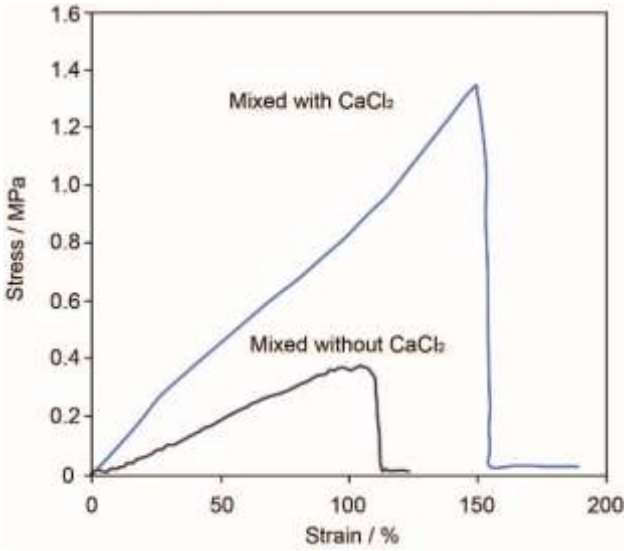

Figure S1. Stress-strain profiles displaying the crosslinking function of calcium ions for enhanced mechanical properties of SA hydrogel tubes. The crosslinking function was capable of avoiding dissolution of SA film strips upon immersion in the aqueous reaction solution.

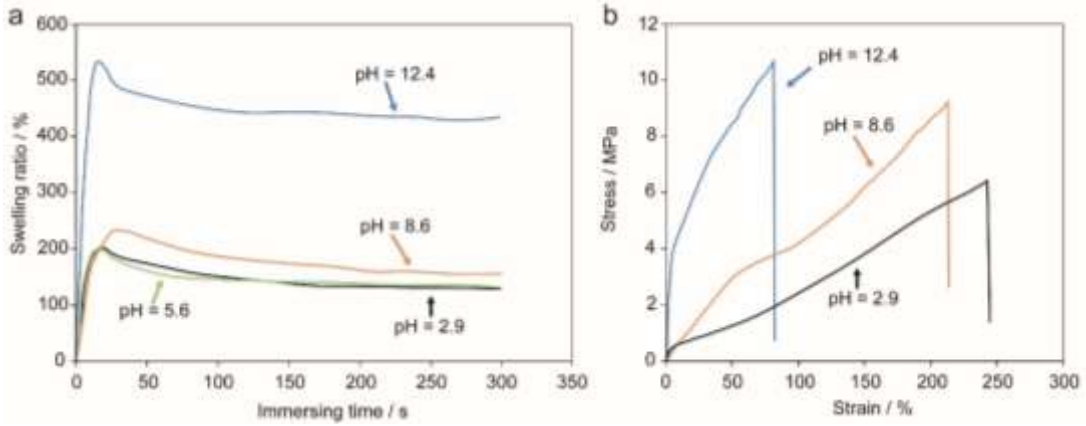

Figure S2. pH effects on the swelling capability of SA strips. We examined pH effects on the swelling ratio of SA strips by respectively immersing them into 1.0 mol/L $CaCl_2$ aqueous solutions with different pH values (pH: 2.9, 5.6, 8.6, 12.4). The initial weight of the dry strip was determined as w_0. After the first-time immersion in water for 30 s, its weight was recorded as w_1, and then the strip was again immersed for another 30 s with the weight being recorded as w_2. This process was repeated many times until a total swelling time of 300 s in water. The weight was given as w_1, w_2……w_t, respectively. The swelling ratios of the strip in different-pH aqueous solutions were calculated as $(w_t - w_0)$ x100%/w_0. (a) SA strips were swelled in the aqueous solution with different pH values. (b) We also examined the mechanical properties of SA strips after immersing them in 1.0 mol/L $CaCl_2$ aqueous solution with different pH values for 20 min.

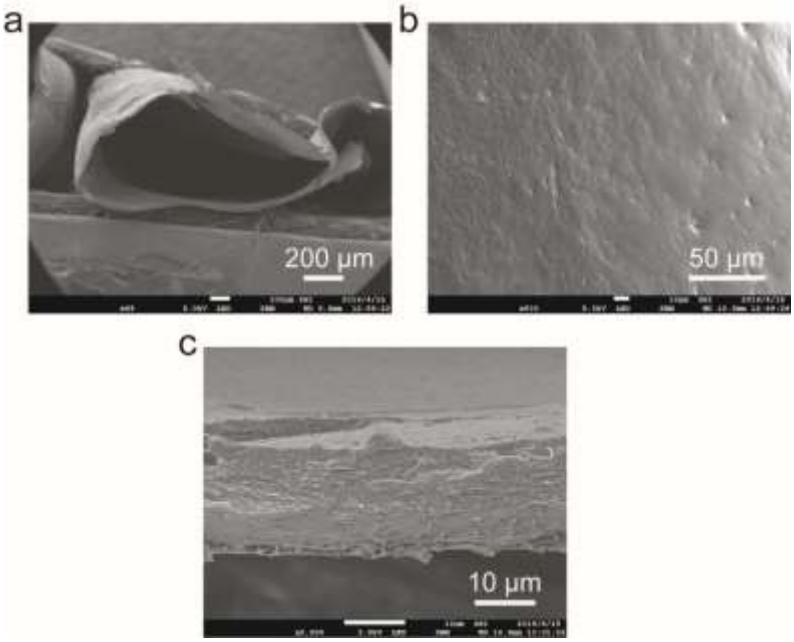

Figure S3. SEM images of H_2O@SA hollow hydrogel tube. The tube was first frozen by liquid nitrogen and lyophilized prior to the SEM observation. (a) Cross section of the tube showing the tubular structure. (b) Morphology of inner surface of the tube. (c) The tube was broken off and its cross section was observed, displaying a rough textile structure.

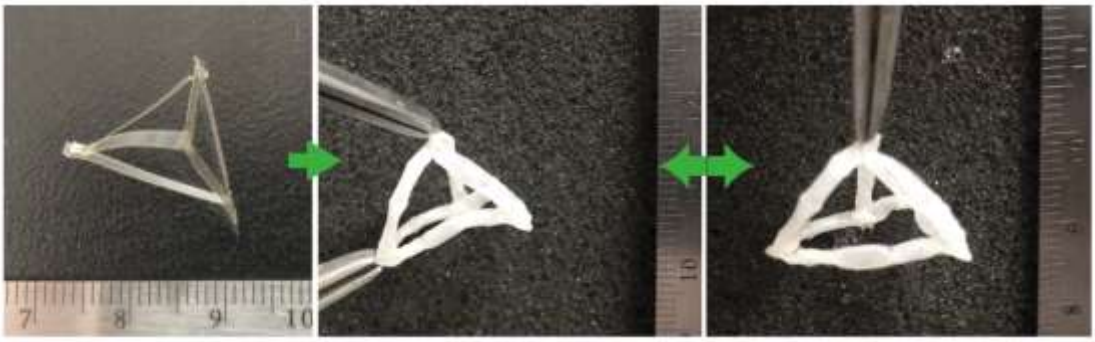

Figure S4. As a 3D shape that was composed of SA strips, was immersed in the reaction solution containing $CaCO_3$, $CaCl_2$, $NaHCO_3$ and HCl elements, a similar tubular 3D geometry could be prepared. This operation indicated that the method for the formation of SA hollow hydrogel tubes is universal for preparation of more complex shapes such as 3D structures.

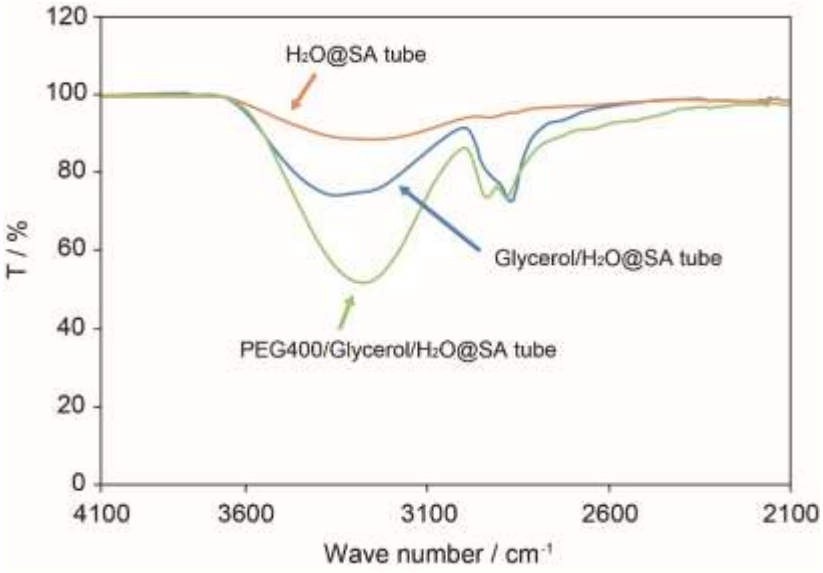

Figure S5. Attenuated total reflection flourier transformed infrared (ATR-FTIR) spectroscopy of H_2O@SA, Glycerol/H_2O@SA and PEG 400/H_2O@SA. The samples were dried in a vacuum oven at 40 °C for 48 h prior to the characterization. The PEG400/Glycerol/H_2O@SA was selected as a representative sample in all PEG-based tubes. After molecular displacement with Glycerol, produced Glycerol/H_2O@SA demonstrated an enhanced intensity of the peak at 3300 cm^{-1}. By further displacement in PEG400, the intensity was further increased. It can be concluded that the water-molecular displacement by glycerol and PEG proceeded successfully, confirmed by the intensity of hydroxyl peaks of Glycerol/H_2O@SA and PEG400/Glycerol/H_2O@SA that were increased greatly in comparison to that of H_2O@SA.

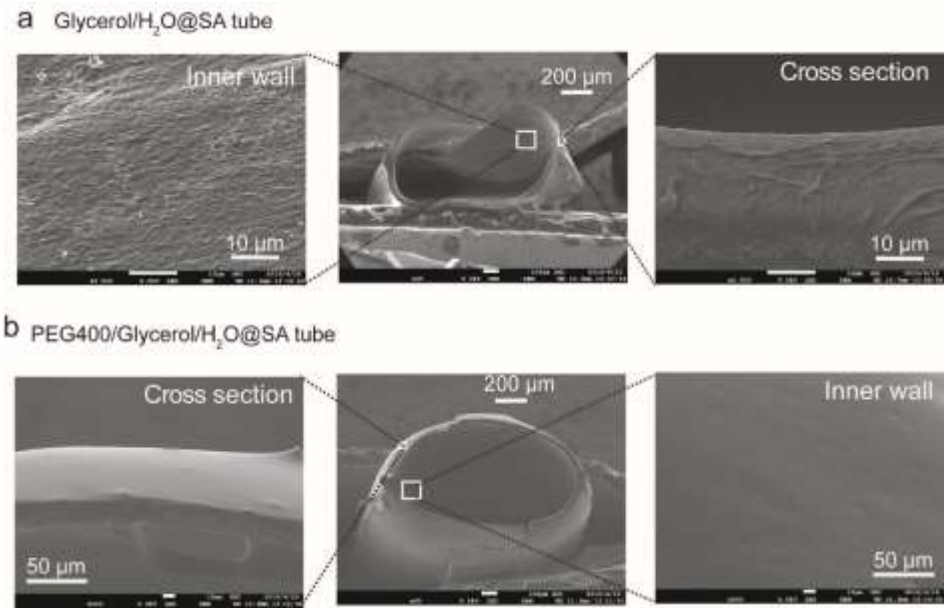

Figure S6. SEM images of hollow hydrogel tubes showing their morphologies and structures of the inner wall and the cross section. (a) Glycerol/H_2O@SA tube. (b) PEG 400/Glycerol/H_2O@SA tube.

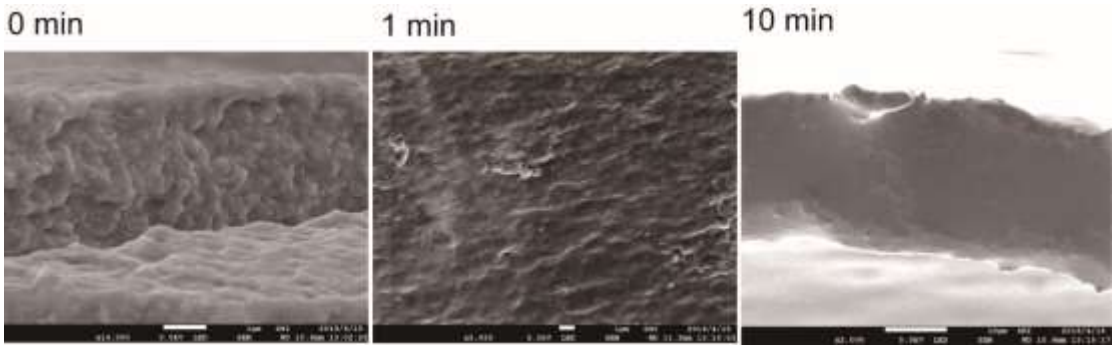

Figure S7. Immersion time-dependent structure variation of SA hollow hydrogel tubes in PEG400. After immersion in PEG400 for different periods, the H_2O@SA tubes were lyophilized, and their cross section were observed by SEM, respectively. The neat H_2O@SA tube displayed a rough cross section. By the molecular displacement in PEG400 for 1 min, the roughness at its cross section was obviously decreased. After this immersion time was extended to 10 min, most of water molecules could be replaced by PEG, and its cross section became smooth.

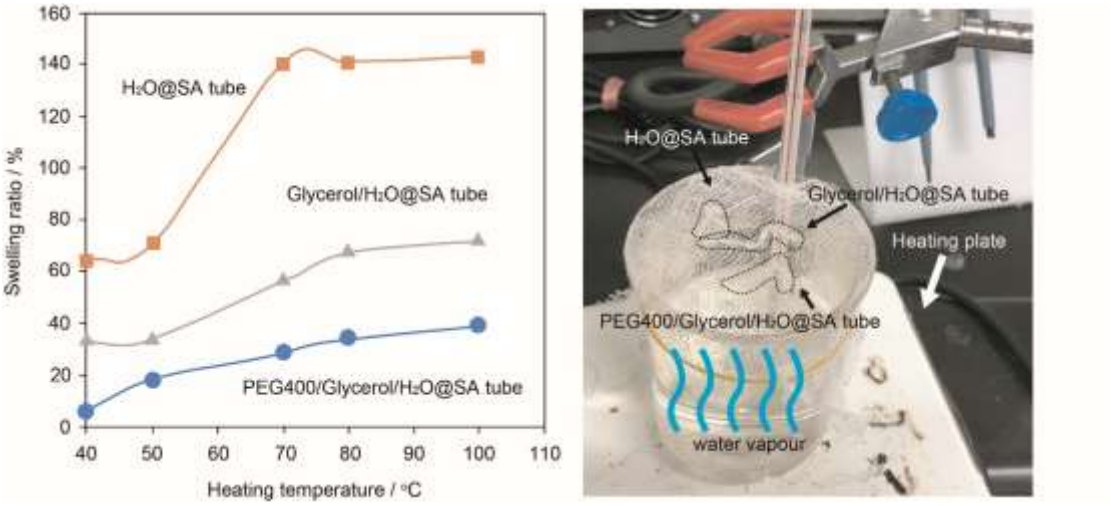

Figure S8. Temperature effects on the swelling ratios of the tubes of H_2O@SA, Glycerol/H_2O@SA and PEG400/Glycerol/H_2O@SA: We designed a simple device, where the tubular samples were hanged over the hot water. We heated the water to different temperatures to generate different concentration gradients of water vapor. The tubes adsorbed water vapors and increased in weights. The initial weights and their weights after vapor sorption were recorded respectively for the calculation of swellability of tubes at different heating temperatures. (a) The temperature-dependent swelling tests revealed that all the tubes increased their weights by the sorption of water vapors with increasing the temperature of water. However, the H_2O@SA tube swelled much more rapid than the tubes of Glycerol/H_2O@SA tube and PEG400/Glycerol/H_2O@SA. (b) A simple device for the swelling tests of various hydrogel tubes.

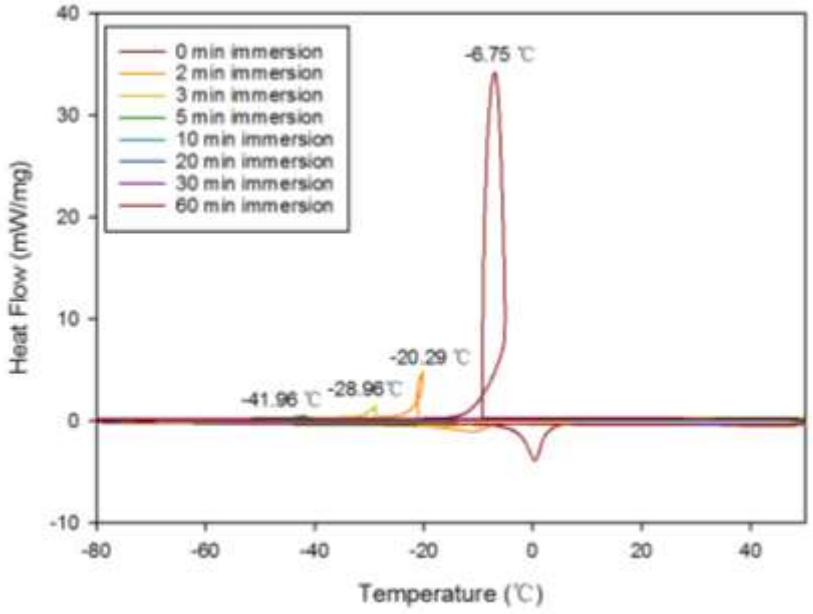

Figure S9. DSC thermograms of H_2O@SA and Glycerol/H_2O@SA hydrogel tubes. The tests indicate that water molecules have been displaced by glycerol, and remained water molecules inside SA tube can combine with glycerol to form "bonding water" that has lower freezing point and higher boiling point.

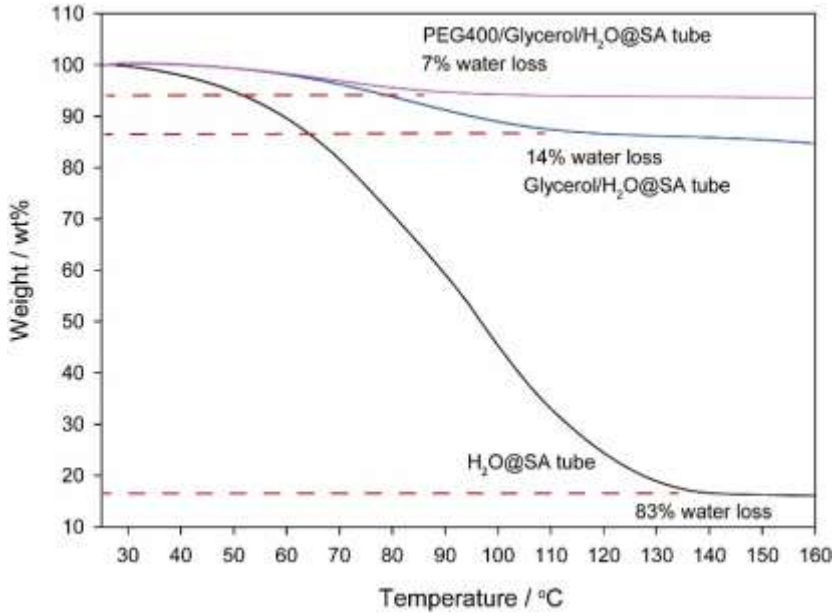

Figure S10. TGA profiles of un/treated SA hydrogel tubes. This test is to measure the water content inside the various tubes. The tubes were heated at a rate of 10 °C/min.

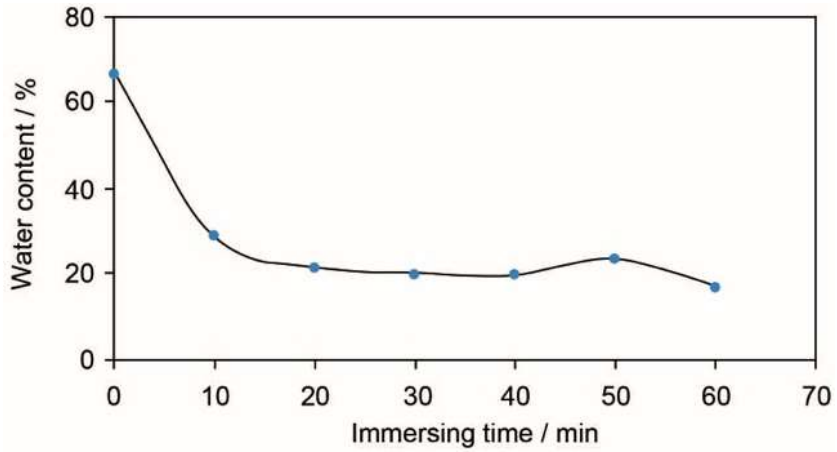

Figure S11. Glycerol effects on the water contents in Glycerol/H_2O@SA tubes. In order to determinate an optimal time for molecular displacement, H_2O@SA tubes were soaked in glycerol with different times and heated to 105 ℃ through thermogravimetric moisture meters. The results indicated that water content was decreased to 21.67% by immersion in glycerol for 20 min that did not have a significant decrease by extending the immersion time.

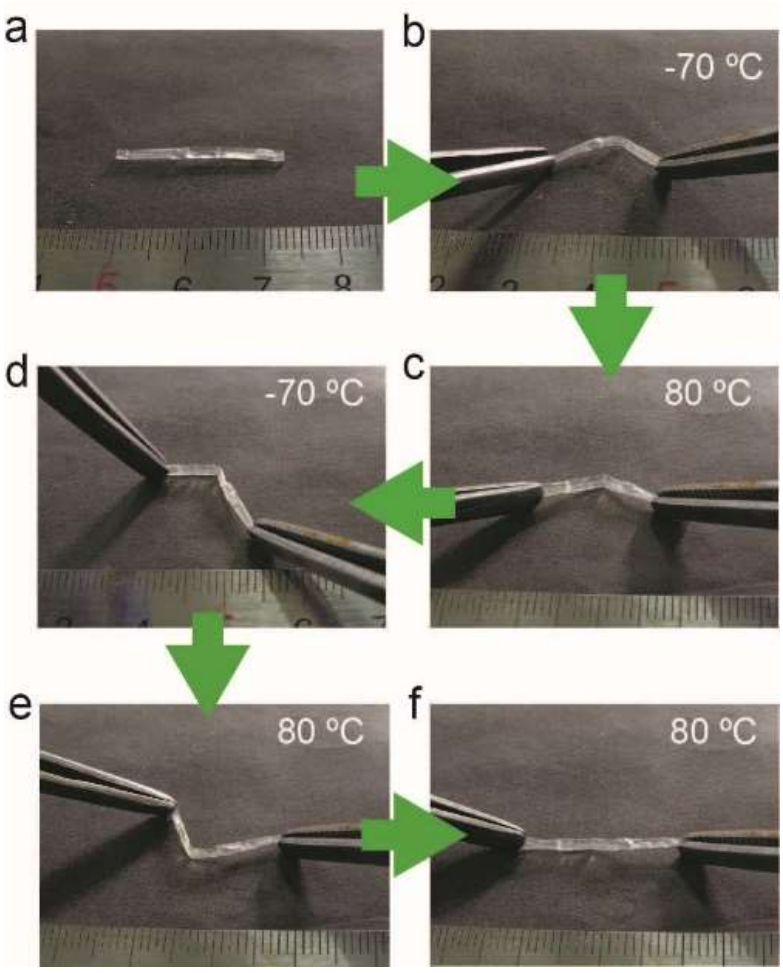

Figure S12. Freezing-heating cycles. (a) Image of Glycerol/H_2O@SA hydrogel tube. (b) After the tube was frozen for 1 h at -70 °C, it was flexible. (c) Such the tube was then heated at 80 °C for 1 h, and it was still flexible. (d,e,f) The tube was capable of keeping its flexibility and tubular structure with continuous heating/freezing tests.

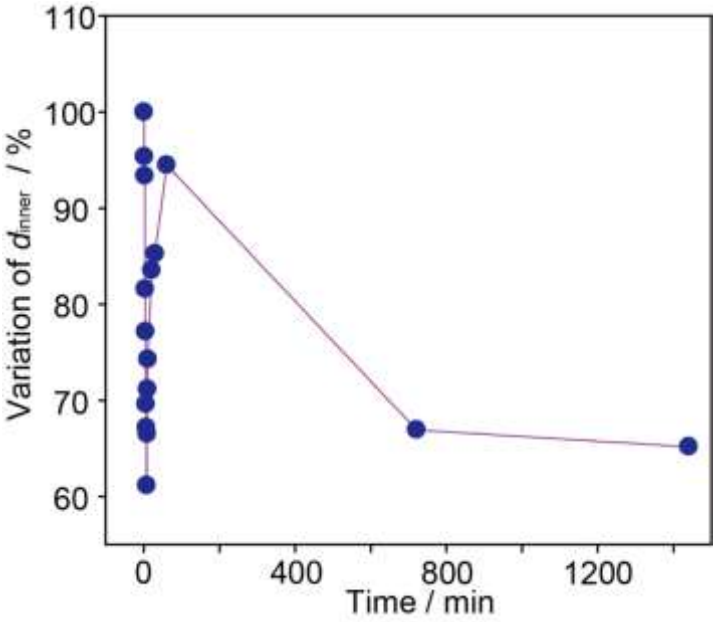

Figure S13. Effects of glycerol displacement on the inner diameter of H_2O@SA hydrogel tubes.

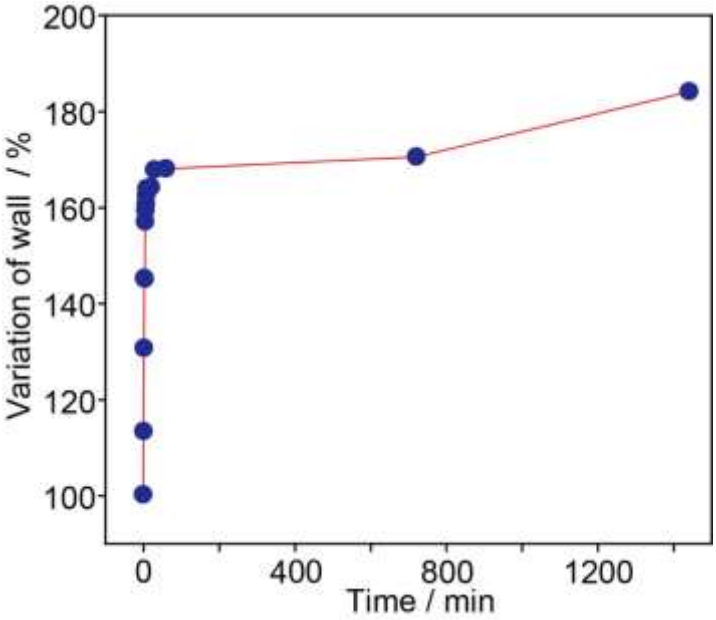

Figure S14. Effects of glycerol displacement on the wall thickness of H_2O@SA hydrogel tubes.

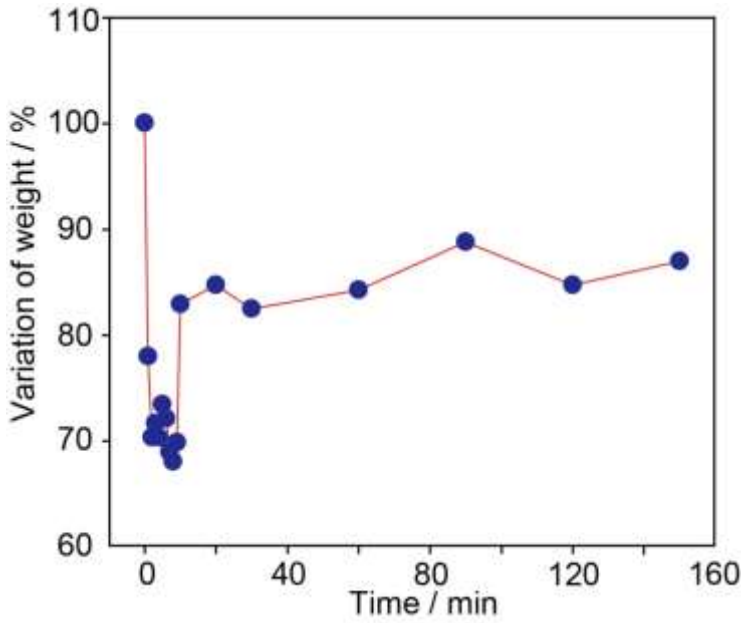

Figure S15. Effects of glycerol displacement on the weight of H_2O@SA hydrogel tubes.

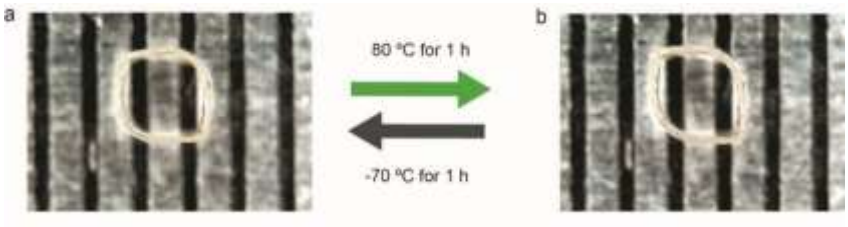

Figure S16. Stability test on the hollow structure of Glycerol/H_2O@SA hydrogel tube. To demonstrate the temperature effects on the hollow structure, the tube was cut into a section that was examined at low and high temperature. (a) Image of the section after it was frozen at -70 °C for 1 h. (b) Image of the same section after it was heated at 80 °C for 1 h. The result indicates that the geometric structure of Glycerol/H_2O@SA hydrogel tubular section was stable in response to extremely low and high temperatures.

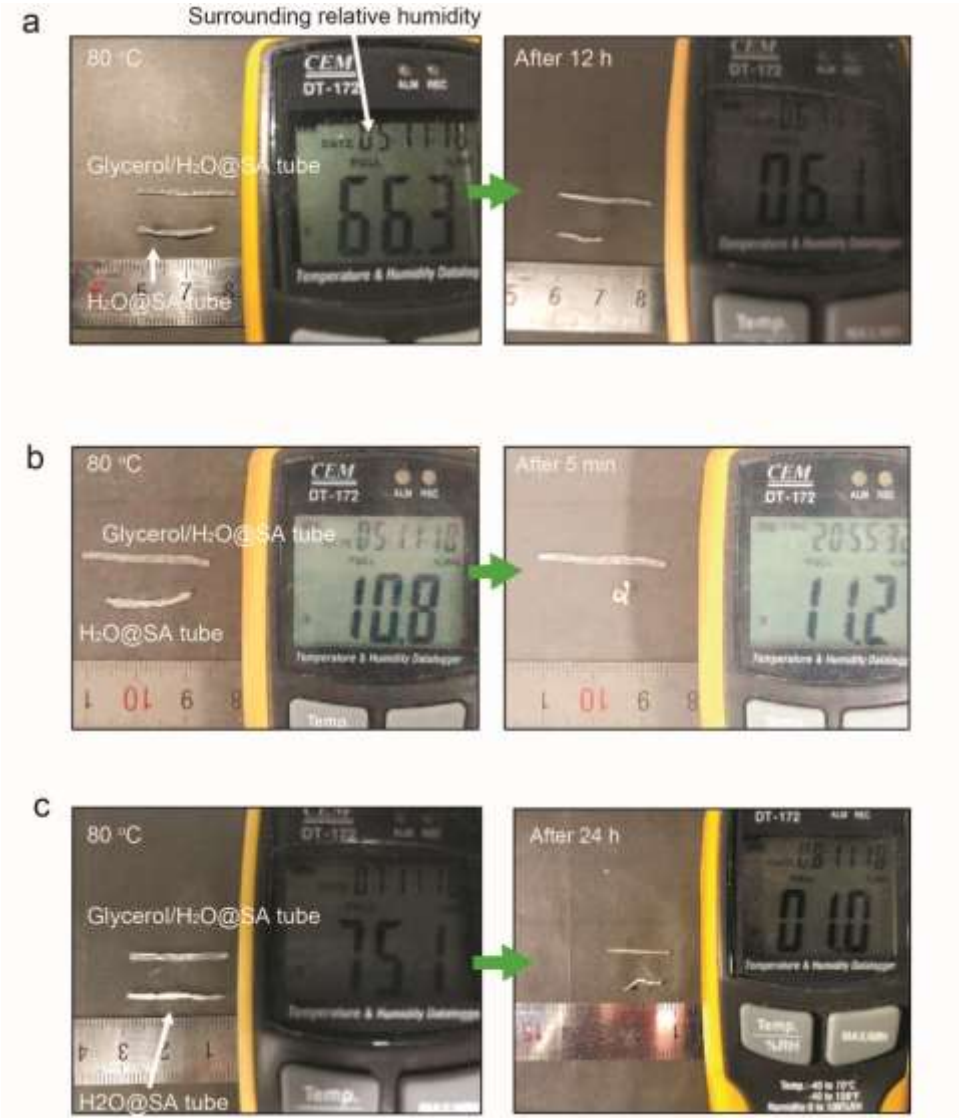

Figure S17. Humidity effects on the hollow hydrogel tubes during the heating treatment. When H_2O@SA hydrogel tube was heated at 80 °C, it always dehydrated quickly and shrank greatly. For Glycerol/H_2O@SA hydrogel tube, it did not show apparent shrinkage; however, its surface color could be affected by surrounding relative humidity (RH). (a) When the RH was decreased to 4.9%, the Glycerol/H_2O@SA tube was heat at 80 °C with the surface color changing to yellow. (b) We then increased the RH to 25.7%, and apparent surface color change was not caused at 80 °C. (c) As the RH was again decreased to 14.2%, the Glycerol/H_2O@SA tube was heated at 80 °C for 10 h without resulting in the surface color change. We thus conclude that if the Glycerol/H_2O@SA hydrogel tube was utilized at 80 °C, it's better to keep the surrounding RH at least higher than 14.2%.

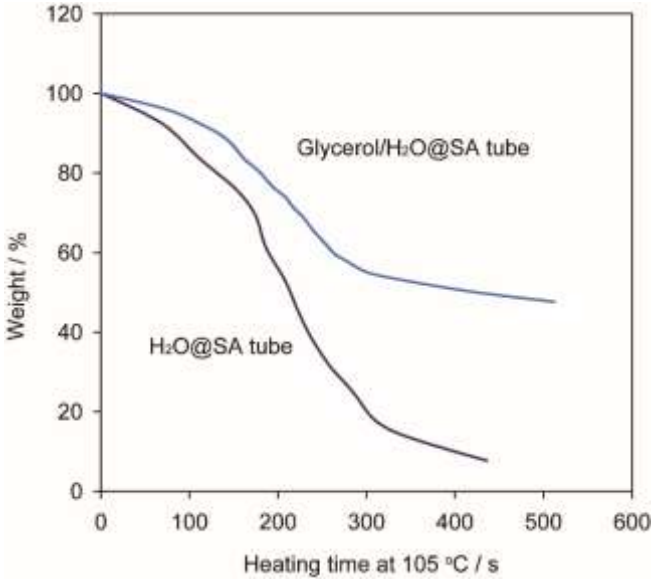

Figure S18. Water Holding Capacity of hydrogel tubes. The tubes were kept at 105 °C to record their dehydration process. The results show Glycerol/H_2O@SA hydrogel tube dehydrated much slower than H_2O@SA hydrogel tube at the same temperature.

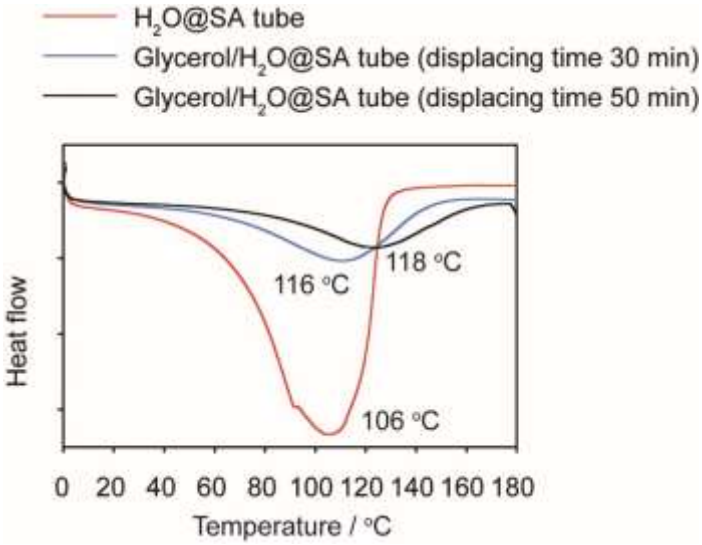

Figure S19. DSC profiles of H_2O@SA and Glycerol/H_2O@SA hydrogel tubes. Apparently, after displacement with glycerol, water content reduced greatly inside the hydrogel tube. On the other hand, replacement with glycerol molecules also resulted in increase of water boiling point.

Table S1. The effects of immersion times on the flexibility of H_2O@SA tube in Glycerol.

Immersion time of H_2O@SA tube in Glycerol	**Flexibility at -70 °C**
0 min	Fragile, inflexible
10 min	Bendable
20 min	Highly bendable
30 min	Highly bendable
60 min	Highly bendable

Table S2. Physical properties of various hydrogel tubes.

Types of SA tubes	Water content	Stability of hollow structure at –70 °C and 120 °C	Mechanical properties at -70 °C	Mechanical properties at 120 °C
H_2O@SA tube	83%	Expansion or shrinking	Inflexible and non-stretchable	Inflexible and non-stretchable
Glycerol/H_2O@SA tube	14%	Intact	Flexible and stretchable	Inflexible and non-stretchable
PEG 400/H_2O@SA tube	7%	Intact	Flexible and stretchable	Flexible and stretchable

Supplementary Movies

Movie S1. Mechanical demonstration of untreated frozen SA hollow hydrogel tube that breaks up upon bending by hand.

Movie S2. Glycerol-treated SA hollow tube shows high flexibility and can be reversibly deformed by hand after freezing at –70 °C.

Movie S3. Verification of hollow structure of Glycerol/H_2O@SA hydrogel tube by liquid transport testing. The result indicates that the tube is capable of keeping its hollow structure at –70 °C.

Movie S4. The demonstration of the movement of dye solution along the channel of the tube, which directly indicated the stability of interconnected hollow or perfusable structures of PEG/Glycerol/H_2O@SA hydrogel tube at 120 °C. The dye solution was injected into the hydrogel tube by a medical syringe.