Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

Phase Change Mediated Mechanically Transformative Dynamic Gel for Intelligent Control of Versatile Devices

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Experimental Section

Materials and preparation of phase change gel

Acrylic acid (low water content, AA, 98%, RG, Adamas), *N*,*N'*-methylenebis(acrylamide) (MBA, 99%, RG, Adamas), ammonium persulfate (APS, 90%, RG, TCI) were purchased from Titan technology Inc. (Shanghai, China). Polyethylene glycol (PEG4000, Mn = 4000 g/mol) were purchased from Aladdin Chemicals Inc. (Shanghai, China). All chemicals were used without further purification.

Precursor liquid mixture of PAA network was prepared by mixing AA monomer, MBA crosslinker, APS thermal initiator, and DI water at a weight ratio of 100:5:2:30. The PEG was heated above 80 °C for full melting, and then cooled to 50 °C (Molten PEG will not crystallize at 50 °C because of the supercooling). Phase change gel was prepared by mixing molten PEG liquid and precursor liquid mixture at 50 °C. Once the resulting mixture was homogeneous and clear, it was kept at 90 °C to cure for 30 min. Samples were then cooled to room temperature (approximately 25 °C) before use. Different compositions of phase change gel were made, denoted by P100L#, where # is the weight percentage of precursor liquid mixture relative to the PEG.

Characterization

The network structure of gel was analyzed by a fluorescence microscope (Observer D1/AX10, Zeiss, Germany). Scanning electron microscopy (SEM) images were acquired on a field-emission scanning electron microscope (JSM-5900LV, JEOL, Japan) at an accelerating voltage of 15 kV. The crystalline structures were analyzed by X-ray diffraction (UItima IV, Japan) using Cu Kα radiation ($\lambda = 1.54$ Å) at a scanning speed of 10° min^{-1}. The content of PEG was measured using a TGA2 (METTLER TOLEDO) thermogravimetric analyzer at a heating rate of 10 °C min^{-1} from room temperature to 800 °C in N_2 atmosphere. Crystallization process of gel was visually inspected using both a camera for the macro-scale and an optical microscope (OM, Olympus BX51A, Japan) for the micro-scale. The surface morphology of microstructures gel was done by a laser scanning confocal microscope (LSM700 Carl Zeiss, Germany) using the reflection mode. The crosslinking density was analyzed by the equilibrium swell rate of hydrogel.

Kinetic analysis of phase change

The testbed platforms for kinetic analysis of phase change were prepared by a two-step molding process. First, PDMS (SYLGARD 184, Dow Corning) was casted on a commercial mold. Once curing of PDMS (60 min at 80 °C) was completed, the PDMS layer was delaminated from the mold to use it as a casting mold for phase change gel. All precursor liquid for phase change gel was then casted on the PDMS mold and cured for 30 min at 80 °C. Subsequently, the testbed platform containing phase change gel encapsulated with PDMS was formed. During the phase change process, the surface temperatures of testbed platforms were monitored by a paperless recorder with thermocouples (OMEGA) and an IR thermal imager (Fluke Ti27).

Thermal analysis of phase change

The thermal behaviors of pure PEG and phase change gels were examined using a differential scanning calorimeter (Q20, TA instrument, USA). For each test, the sample was sealed in an aluminum pan and was equilibrated at 40 °C. The sample was then heated to 90 °C and held at 90 °C for 5 min. Then the sample was cooled to -20 °C (using a cooling rate of 10 °C min^{-1}). After kept at -20 °C for 5 min, the sample was heated back up to 90 °C with a heating rate of 10 °C min^{-1}.

Bending stiffness measurement

Stiffness change was measured using a dynamic mechanical analyzer (DMA Q800, TA Instruments). Samples were tested in the DMA chamber for accurate temperature control during the modulus measurements. In this work, the specimens were placed in a double-cantilever clamp, and were applied a sinusoidal force on the moving end of cantilever at a rate of 1 Hz, at a strain of 0.1%. During the measurement, the temperature of the DMA chamber was increased slowly from 30 °C to 90 °C with a rate of 1 °C/min to allow enough heating time for the samples to reach steady state. For cycle testing, the samples were heated to 70 °C and then cooled down to 30 °C with a temperature sweep of 2 °C/min per cycle for a total of five cycles.

Grip and adhesion force tests

The home-made test equipment was adapted from a force gauge (HANDPI). A steel cylinder with diameter of 10 mm was connected to the force gauge through thread. The linear stage of the tester lowered and raised the steel cylinder in displacement control, and the force gauge measured the force during the whole process. A hot plate was used to heat the phase change gel samples (20 mm × 20 mm × 5 mm). During the grip force test process, the steel cylinder was embedded into the phase change gel samples under 80 °C at a given embedding depth, then pulled out after the gel samples were cooled down to 25 °C. The adhesion force test apparatus was similar as the grip force test. During the adhesion force test process, the steel cylinder was placed onto the phase change gel samples at 80 °C, then pulled out after the gel sampled were cooled down to 25 °C.

Fabrication of high-temperature warning sensor

The microstructured phase change gel was prepared by a template strategy. First, the flexible PVC membrane with hierarchical microstructures was used as converse template, and the spray-coated CNS electrically conductive layer on the microstructured PVC surface was transferred onto the phase change gel by pouring and further thermal crosslinking of precursor liquid mixture on the surface of PVC, to guarantee sufficient interaction between the conductive layer and gel substrate. The flexible PVC converse template was easily peeled off, leaving a microstructured gel with conductive layer. The high-temperature warning sensor was prepared by assembling two microstructured gels or a microstructured gel with a rigid counter electrode. The electrical resistance and resistance changes of sensors were monitored with a two-electrode digital multimeter (2400S, Keithley Instruments, Inc., Ohio, USA).

Finite element simulation

To investigate the thermal-responsive resistance change of phase change gel microstructure, a sinusoidal convex model was used to simplify the model of the microstructure surface of gel, and the geometric deformation was quantified, which was analyzed by a commercial COMSOL Multiphysics software under an appled pressure of 5kPa, in which the modulus of the gel was assumed to be 576 MPa, 102 MPa, 8 MPa, 0.02 MPa, and 0.002 MPa, respectively, at 50°C, 55°C, 60°C, 65°C, and 70°C.

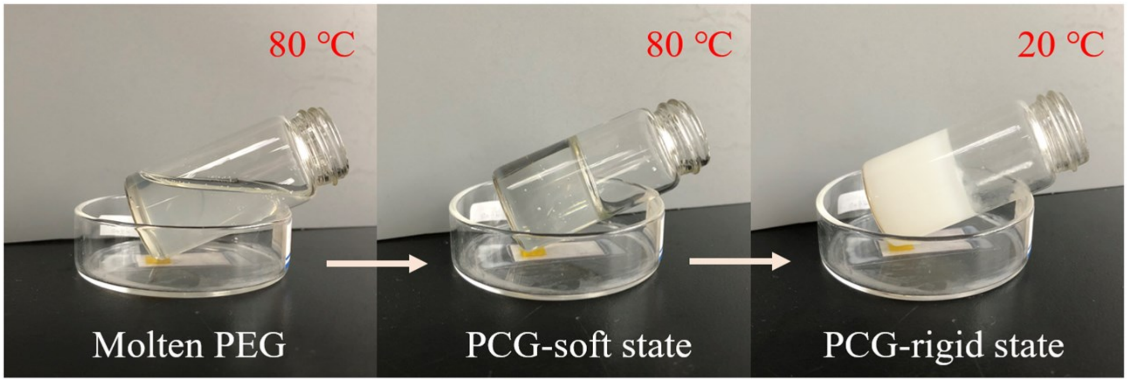

Fig. S1 Digital photographs showing the formation of phase-change gel and the mechanical state change.

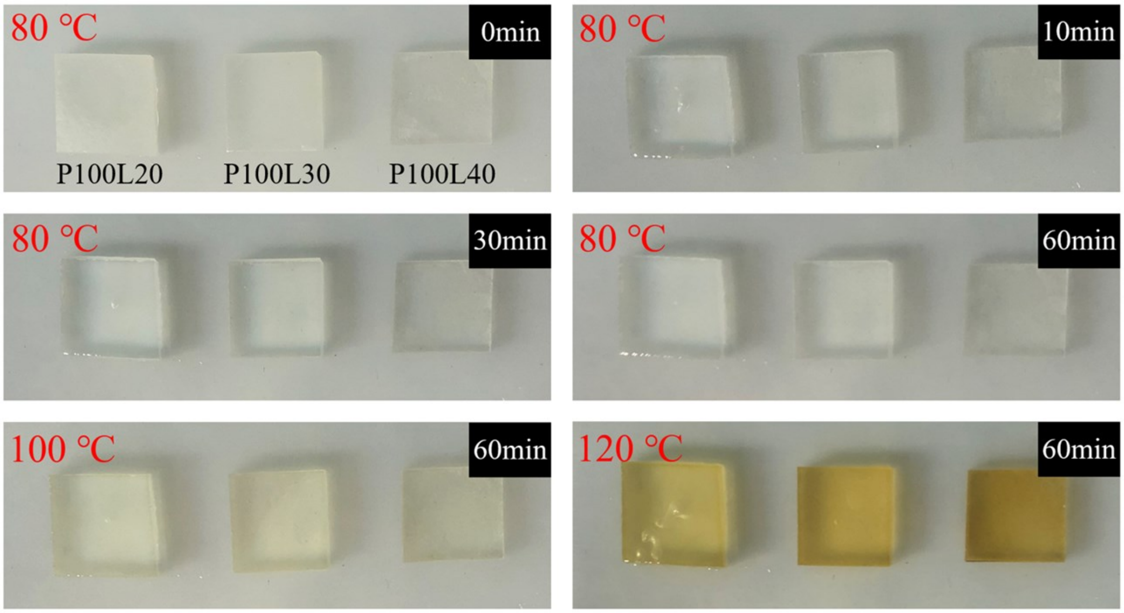

Fig. S2 Digital photographs showing the shape stability of phase-change gel.

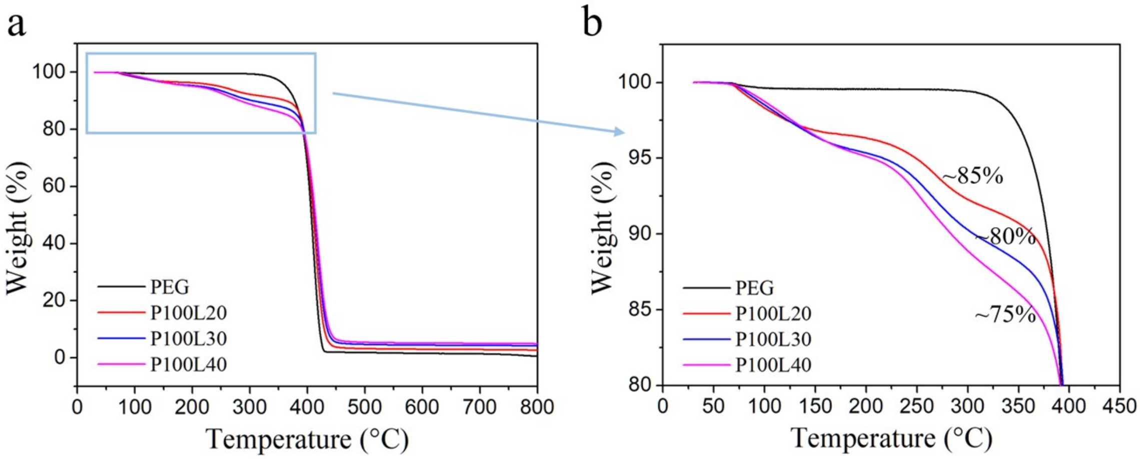

Fig. S3 TGA curves of pure PEG and phase-change gels.

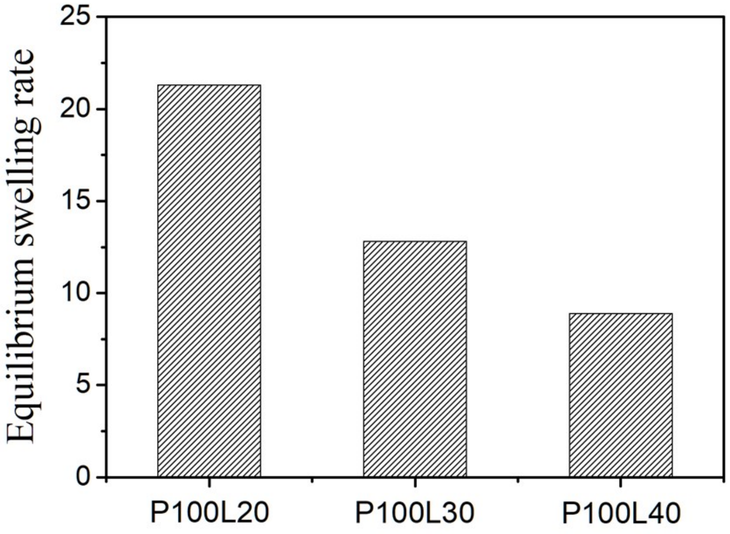

Fig. S4 The equilibrium swelling rates of different phase change gel samples.

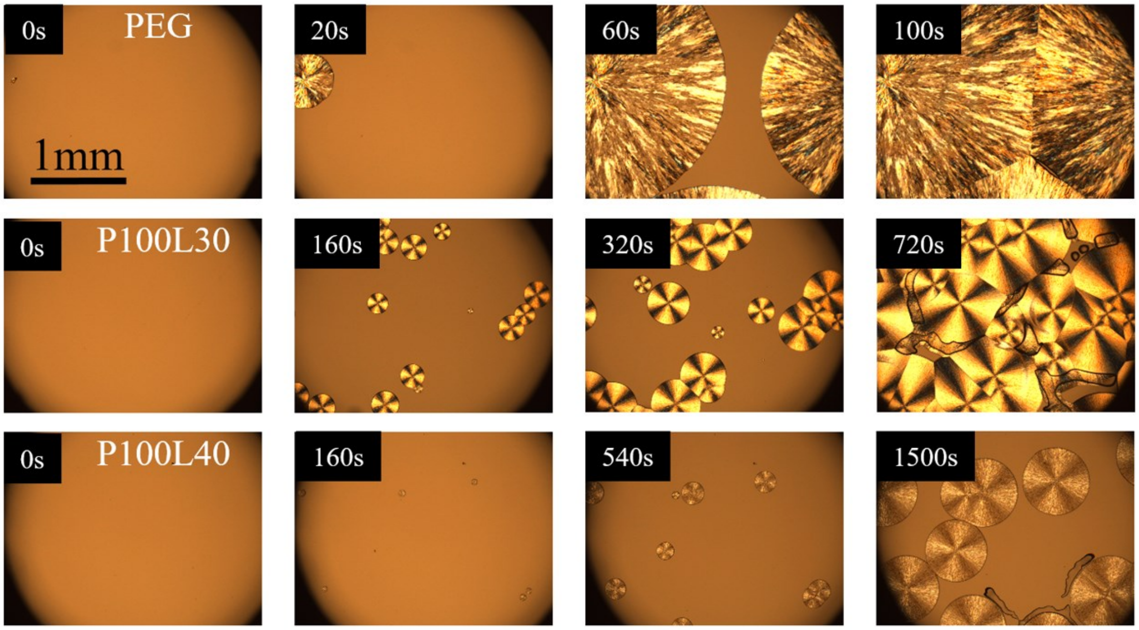

Fig. S5 Polarized microscopic images of crystallization process in PEG and phase-change gels.

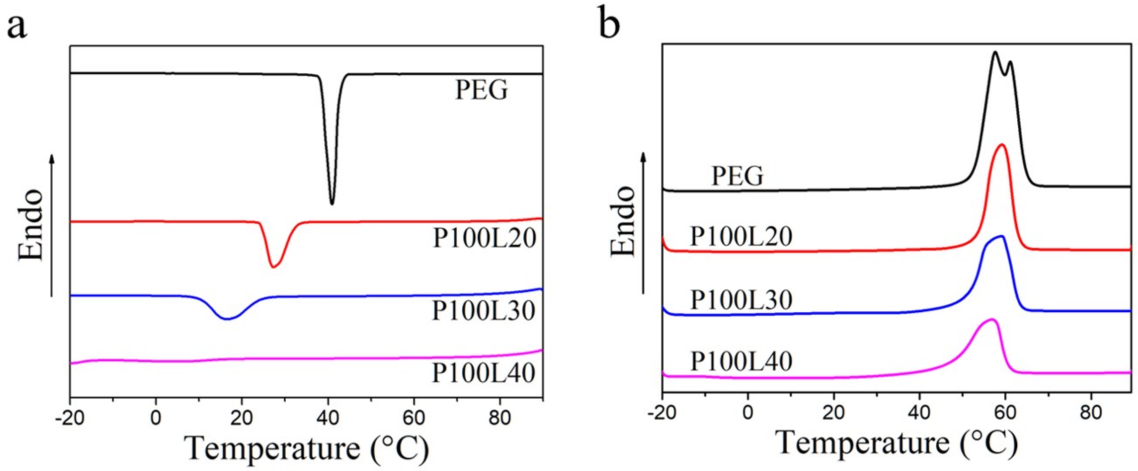

Fig. S6 DSC curves of pure PEG and phase-change gels during crystallization (a) and melting process (b).

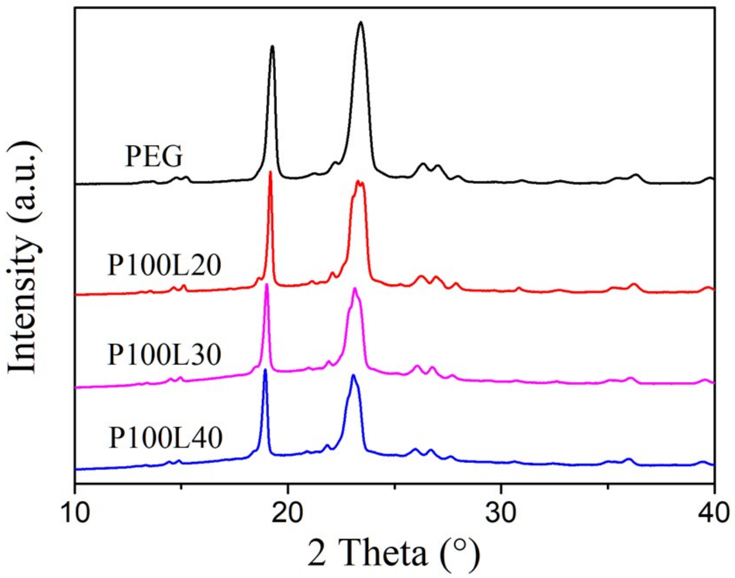

Fig. S7 XRD curves of pure PEG and phase-change gels.

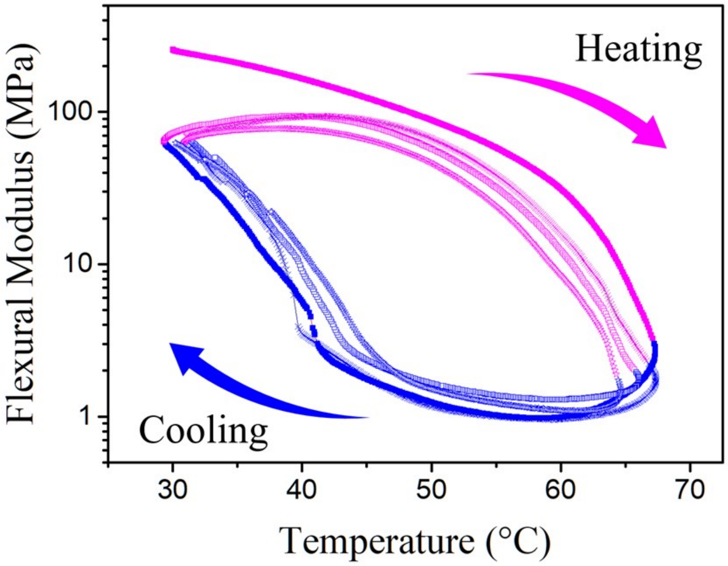

Fig. S8 Flexural modulus evolution of gel sample P100L30 with a temperature sweep of 2 °C/min under heating-cooling cycles.

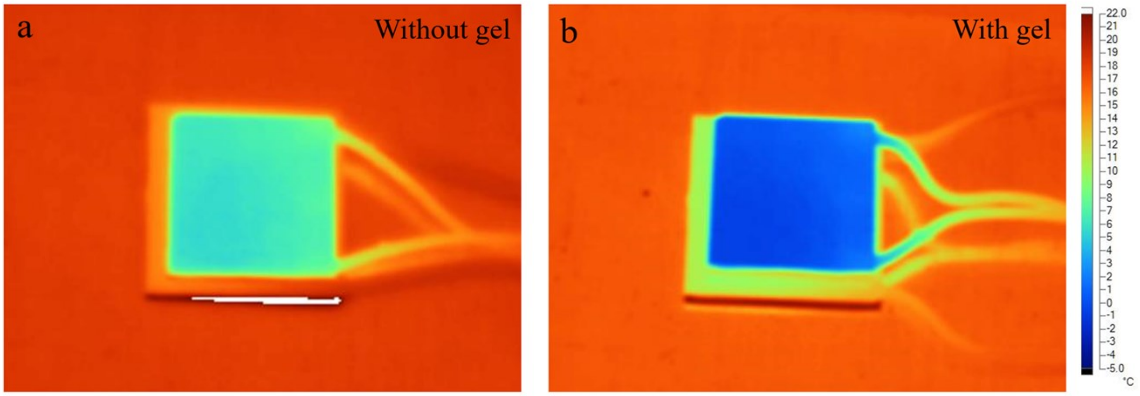

Fig. S9 IR thermal images showing the multistage cooling effect of device without (a) and with phase-change gel (b).

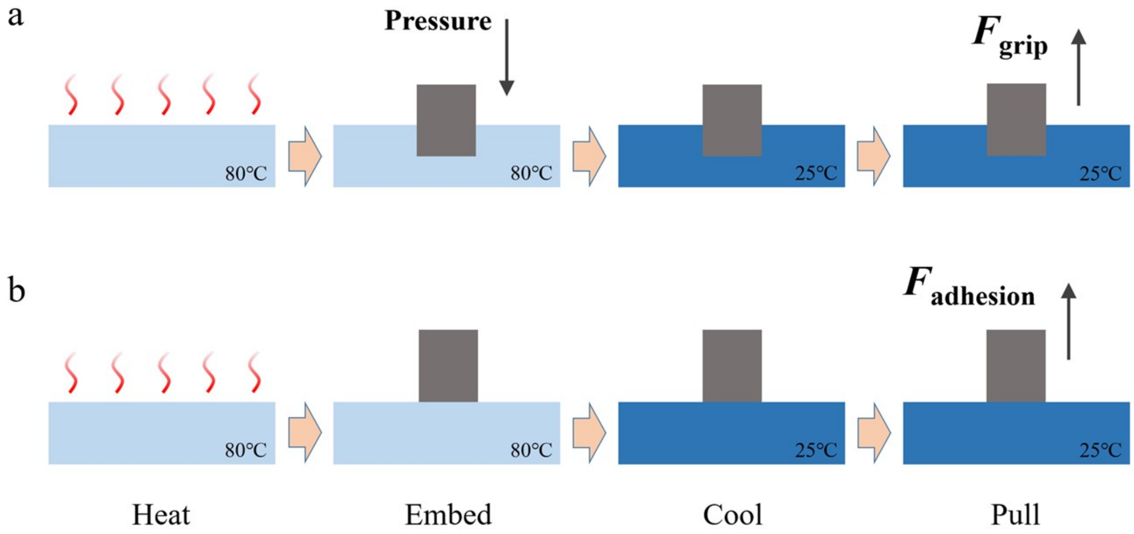

Fig. S10 Schematic illustration for the grip (a) and adhesion (b) force tests.

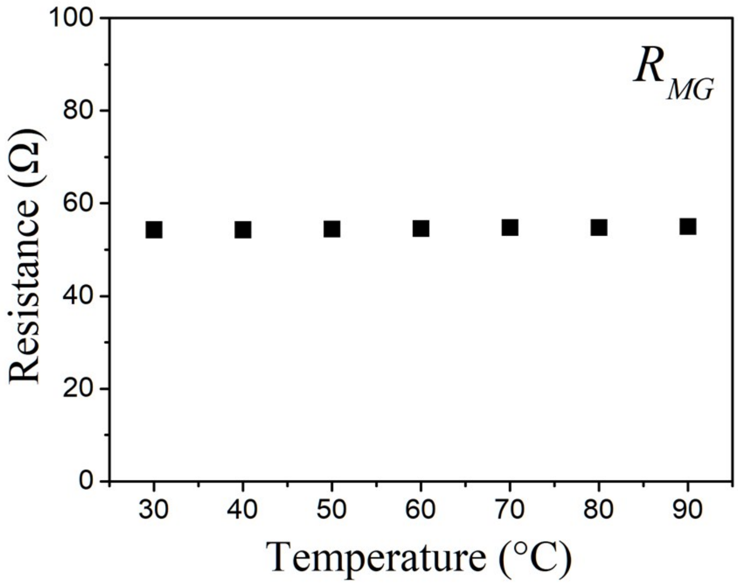

Fig. S11 Electrical resistance change of the microstructured gel as a function of temperature.