Supporting Information

Ultra-stretchable Hydrogels with Reactive Liquid Metals as Asymmetric Force-sensors

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Part I: Materials and Methods

1) Materials: Acrylamide (AM) (AR, 99%) and 2-hydroxyethyl acrylate (HEA) (96%) were purchased from Aladdin Industrial Corporation. Ammonium persulfate (APS) (AR, 98%) and potassium iodide (KI) (AR, ≥99%) were supplied by Sinopharm Group Chemical Reagent Co., Ltd. Liquid metal (LM) (Gallium, melting point at 29.13 ^{o}C) was provided by Shenyang Jiabei commercial trading company. Distilled water was supplied by Nanjing Wanqing chemical glassware instrument Co., Ltd. All materials were used without any further purification. 2-Hydroxyethyl methacrylate (HEMA) (99.5%) was provided by Beijing Bailingwei Technology Co., Ltd. Cu foil (Electrodes）was purchased from Hangzhou Biling Architectural Materials Co., Ltd. Copper foil and wires were the eflectrodes used in the sensory applications.

2) Preparation of the control gel*:* 1.4 g AM and 0.6 g HEA were dissolved into 6 mL distilled water in a 20 mL vial. Then, 20 mg APS was added into the solution to initiate the gelation in a 70 ^{o}C oven for 15 min to obtain the colorless transparent cylinder shaped hydrogel. The field emission scanning electron microscopic graphs indicated that net shape structure was formed.

3) Preparation of the LM-hydrogel: The LM-hydrogels were prepared via the similar method, but with the different volume ratios of LM and distilled water. Take the 5 vol% LM-hydrogel as an example: In a 20 mL vial, 0.3 mL LM, 0.6 g HEA and 1.4 g AM were uniformly distributed in the 6 mL distilled water by the ultrasonic crusher for 5 min to form the precursor. Then, 20 mg APS was added into the precursor in sequence to obtain the opaque dark gray LM-hydrogel within 20 seconds at room temperature. In this work, LM-hydrogel loaded 5 vol%, 10 vol% and 20 vol% LM were prepared for experiment.

4) Preparation of the LM-HEMA-hydrogel: The LM-HEMA-hydrogel was prepared via the similar fashion. 20 mg APS was introduced into the 4 mL distilled water which previously dissolved 2.0 g HEMA. Another 10 mL vials, 0.4 mL LM was distributed in 4 mL distilled water by ultrasonic crashing. Then add 2.0 g HEMA and 20 mg APS in turns into the vial.

5) Ultrasonic Crashing: All ultrasonic performances reported in this work are utilized a Biosafer 150-96 ultrasonic crasher, power at 45%. Samples were sonicated for 5 minutes.

6) Field Emission Scanning Electron Microscope (FESEM): FESEM specimen was first dropped into liquid nitrogen by tweezers. Samples were instantly transferred into a freeze-dryer (LC-10N-50A with a 2XZ-2 rotary vane vacuum pump) to freeze-dry for 12 h to remove all water in the hydrogel. The cross-sectional images of the as-prepared specimens were taken under FEI 3D.

7) Mechanical Properties Measurement: The compressive and tensile tests were all conducted on a SANS E42.503 tensile tester at the room temperature with the speed at 30 mm/min. The tensile and compressive samples are long bar ($\Phi = 2.8 \pm 0.2$ mm, $L = 23.4 \pm 3.1$ mm) and cylinders ($\Phi = 23.7 \pm 0.5$ mm, $L = 14.4 \pm 0.6$ mm), respectively. The gauge length used to determine the axial strain is 16.6 ± 0.7 mm. The fixtures on MTS E42 are removable and fixture-choosing depends on test type, tension or compression. All reported values for mechanical properties represent an average over at least three independent measurements for each sample.

8) Resistance Measurement: Specimen was screwed by SANS E42.503 fixtures containg a rubber (act as a buffer and insulator)in a sandwich structure. The Cu foil thickness, 0.12 mm was welded with wires which linked to Keysight 34461A. Rubber or PVDF film was acted as insulator to elimnate any disturbing on resistance parameters from metal fixture conductor. Insulated water-proof PVC tape fixed the sandwich form tightly. In tensile test, while attached by Cu foil and rubber (as a buffer and insulator), two of four fixtures were on the upper and lower ends, respectively. The configuration is a sandwich structure, from inside to outside is Cu foil (electrode), rubber (buffer and insulator), and fixture (a part of MTS E42) in turns. The specimen was adhered on Cu foils by screwing the fixtures at the top and bottom. In the compressive test, PVDF film replaces the rubber as an insulator to prevent the metal fixture touching with Cu foil electrode. The device is also sandwich structure, Cu foil (weld-wired), PVDF film and fixture seats from top to bottom.More details can be seen in the Figure S4, which is the photographs of the setup. The resistance changing with time was monitored by the Keysight 34461A on a two wire mode at room temperature. The number of power line cycles (NPLC) and measurement range is 0.02 and automatic mode while the measurement option is Resistance 2 W. The compressive samples ($\Phi = 23.7 \pm 0.5$ mm, $L = 13.2 \pm 0.7$ mm) and tensile samples ($\Phi = 2.8 \pm 0.2$ mm, $L = 29.7 \pm 2.2$ mm) were measured. Samples were placed between two copper films to connect the device. As shown in Figure 6, LM-hydrogel ($\Phi = 2.8$ mm, $L = 21.5$ mm) was placed on the index finger to sense the finger-bending action, and the responses were monitored by instrument when the finger was bent or stretched. The rectangle specimen (13.6 mm $\times$ 6.1 mm $\times$ 3.1 mm) was used for resistance sensing derived from facial emotions. Devices mounted on human body for movement and facial gesture detection are double-layer structure. A PVDF film was indispensable for prevent the materials directly touching on human body to avoid any toxicity affecting human and insulated the human body conductor and LM-hydrogel conductor. The specimen, adhered on PVDF substrate previously, was wired from its two laterals.In the processes mentioned above, all the wires were fixed firmly by insulating tapes.

9) Differential Scanning Calorimeter (DSC): The TA DSC25 was used to determine thermal transitions. Specimens were loaded into hermetically-sealed DSC pans. Specimens were quenched to 0 ℃ and subsequently heated to 60 ℃ at a rate of 10 ℃/min. The melting point of LM was determined.

10) The Redox Reaction Experiment of KI, APS and LM: 0.15 mL LM was dispersed in 3 mL distilled water via a 5 min of ultrasonic processing in a 10 mL vial. Then, 1 mg APS was added into the solution to have reactions. After centrifugal separation at 10000 rpm for 10 min, the supernatant was separated from LM. Potassium iodide (10 mg) was added into the centrifuged solution for redox reaction. For the control experiment, in another 10 mL vial, 10 mg KI was added into 3 mL distilled water containing 1 mg APS. Photos were taken after 8 hours reactions of the two vials to observe the colors of the solution.

11) The Dehydration Experimental: A complete regular LM-hydrogel (10 vol%) was halved into two parts. One part was exposed in air while another one encapsulated by PVDF tightly. Weight their mass by analytical balance (SHIMADZU AUY120) every day at the same moment.

12) Statement

Informed consent was obtained from all individual participants included in the study. All procedures performed in studies involving human participants complied with the relevant national laws and regulations, and were performed under the guidance approved by the Laboratory Ethics Committee at Southeast University (Nanjing, China).

Part II: Supplemental data

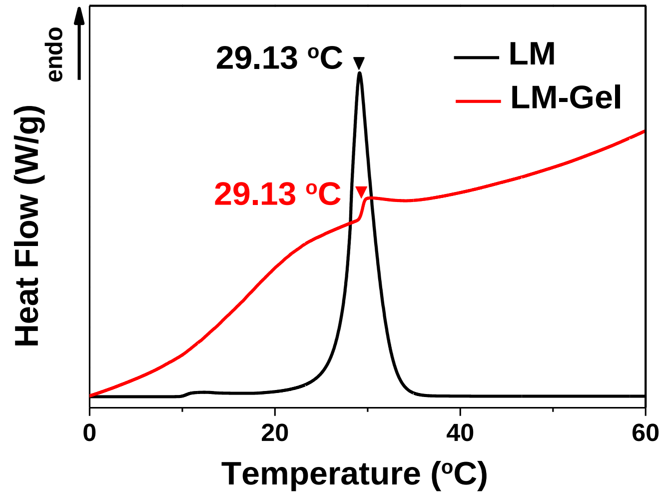

Figure S1. The differential scanning calorimetry (DSC) curves of liquid metal and LM-hydrogel to determine the melting points of liquid metal in LM-hydrogel (10 vol%). It indicated that the melting point of LM had no obvious shifting after gelation.

Scheme S1. The redox reactions of APS, liquid metals and potassium iodide.

$$(NH_4)_2S_2O_8 + 2KI \xrightarrow{\text{Oxidation}} 2(NH_4)_2SO_4 + I_2 \text{ (Brown Solution)}$$

$$(NH_4)_2S_2O_8 \xrightarrow{\text{Liquid Metal}} [SO_4^-]\bullet \longrightarrow SO_4^{2-} \xrightarrow{\text{KI}} \text{No oxidation}$$

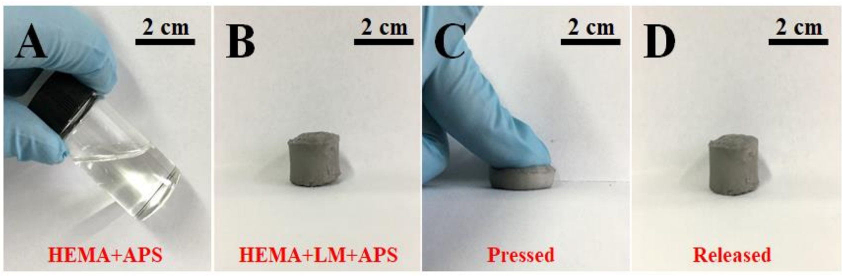

Figure S2. Synthesis of LM-HEMA hydrogel (A) without LM. No gelation was observed without liquid metal. B) The cylinder LM-HEMA hydrogel (10 vol%) was prepared by adding LM to initiate the gelation. Photos of C) pressed and D) released LM- HEMA gel (10 vol%).

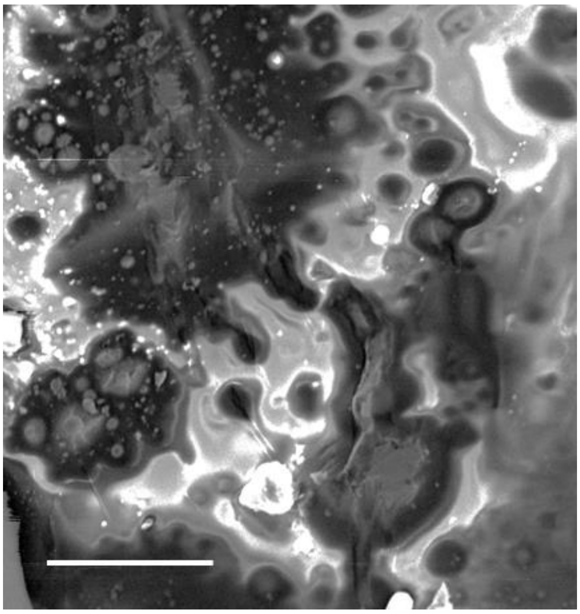

Figure S3. Cross-sectional SEM images for hydrogels with 20 vol% liquid metals. Heavy aggregation was observed in the matrix. Scale bar: 25 μm.

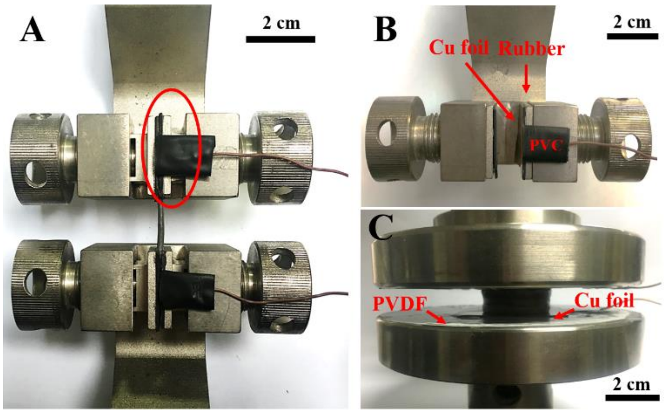

Figure S4. The photographs and illustrations of the configuration applied for mechanical and electrical tests. A) Photo for tensile test and electrical measurement. B) The detailed photo of the tensile fixture attached by Cu foil and rubber (as an insulator). The configuration is a sandwich structure, from inside to outside is Cu foil, rubber, and fixture in turns. The specimen was attached to Cu foil by screwing the fixture. C) The photo of the compressive test and its setup. The fixture adhered by Cu foil and PVDF (as an insulator). The wires connected to Keysight 34461A are associated with Cu foils.

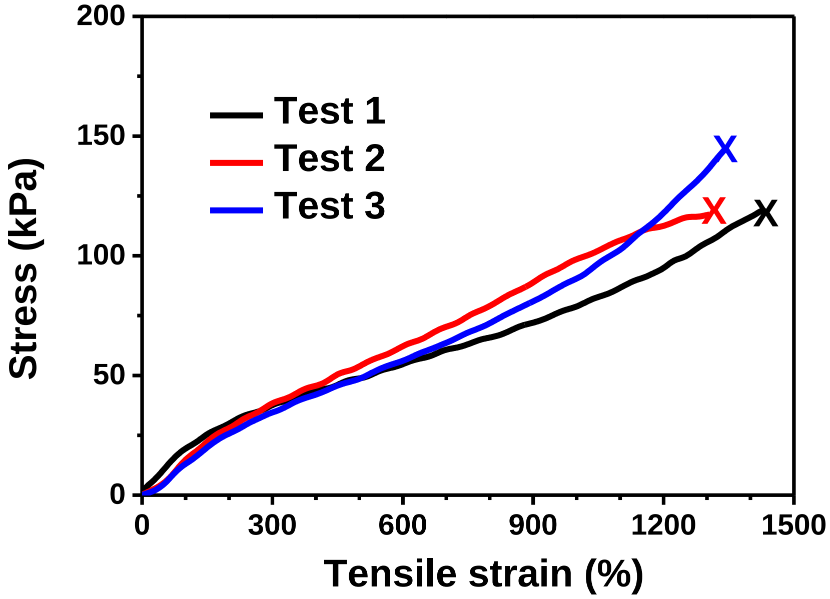

Figure S5. The tensile mechanical curves of LM (eutectic gallium indium, melting point: 10 ^{o}C)-hydrogel (10 vol%).

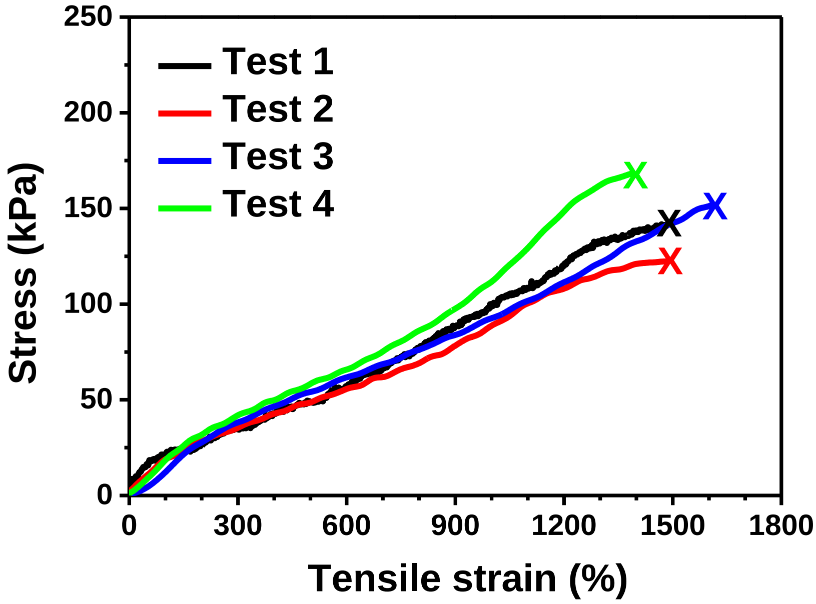

Figure S6. The tensile mechanical curves from three independent LM-hydrogels (10 vol%) and the curve previously reported (black curve of test 1) in **Figure 2c**.

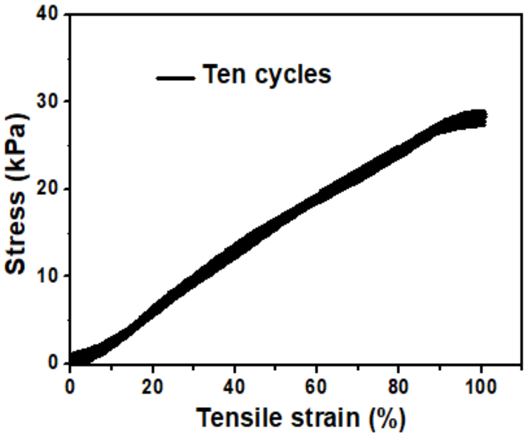

Figure S7. The cyclic tensile curves of LM-hydrogel (10 vol%) at strain of 100% for ten cycles.

Table S1. The mechanical properties of LM-hydrogels.

vol % [a]		0	5	10	20
Compression	σ **(kPa)** [b]	479±18	369±16	351±11	285±21
Tensile	σ_b **(kPa)** [c]	56±1	87±8	130±14	41±3
	ε_b **(%)** [c]	396±20	830±164	1488±182	732±185
	E **(kPa)** [d]	35±3	28±3	24±6	16±2
	Toughness (kJ/m^3) [e]	150	493	982	239

[a] The volume ratio of liquid metal in hydrogels. [b] The compressive stress of LM-hydrogels with the compressive strain at 90%. [c] Elongation and stress at the break of specimen applied on tensile stress. The average values were obtained from three independent samples. [d] Room temperature Young's modulus (E) determined from the slope of the fitting line to the linear region of tensile stress-strain curves. [e] Tensile toughness determined by integrating the area under stress-strain curves up to the specimen braking point.

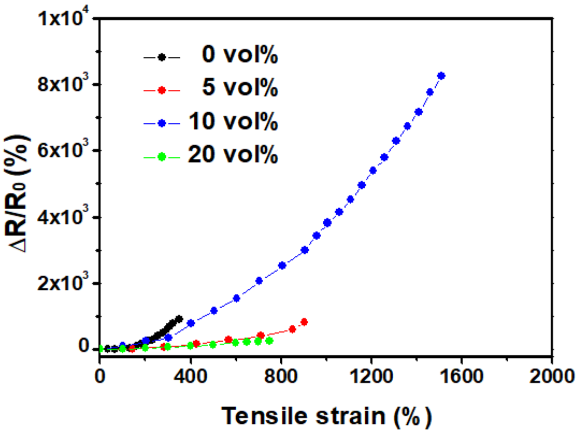

Figure S8. The strain-resistive change curves for tensile strain. The LM-hydrogel is conductive all the time until its breaking.

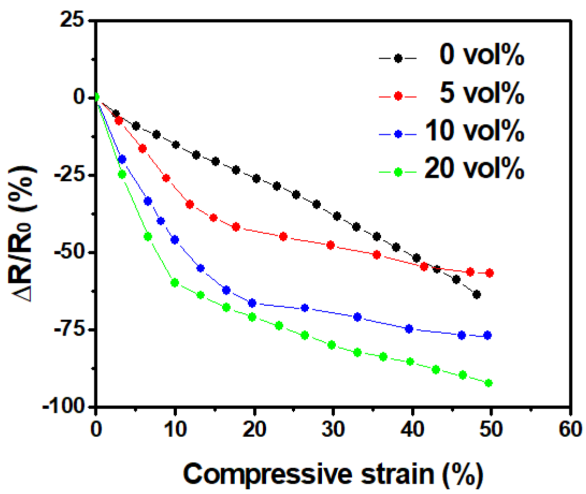

Figure S9. The strain-resistive change curves for compressive strain.

Table S2. The dependence of resistance change ratio of LM-hydrogels under different ranges of applied stress.

	Sensitivity (Compression, kPa^{-1}) [a]		Sensitivity (Tension, kPa^{-1}) [b]		
Stress range (kPa) [c]	< 10	10 ~ 40	< 35	35 - 100	> 100
0 vol%	-0.012		0.030	0.421	-
5 vol%	-0.145	-0.004	0.033	0.431	-
10 vol%	-0.160	-0.005	0.028	0.478	1.430
20 vol%	-0.251	-0.005	0.030	0.425	-

[a b] The sensitivities were determined from slopes of the fitting lines to the region of different stress in Figure 3, respectively. [c] The stress is separated into several ranges before and after the clear resistive transitions in Figure 3.

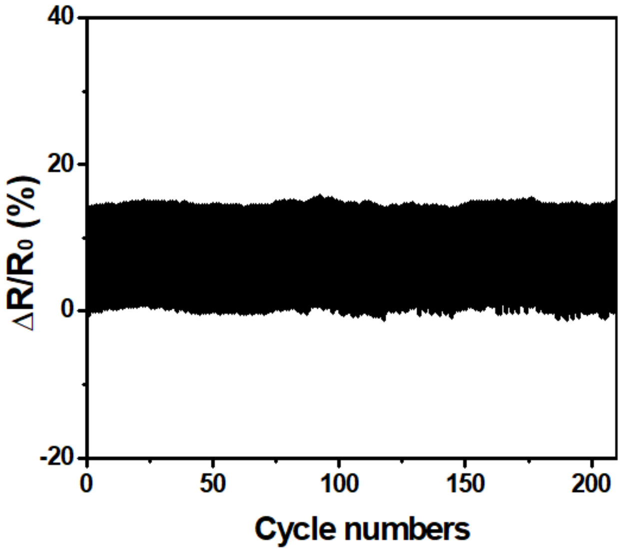

Figure S10. Resistance cycles sensing of 10 vol% LM-hydrogel over 200 times， each cycle applied by tensile strain to 30%. No obvious change of signals was exhibited after more than 200 cycles of tensile deformation, confirming the good electrical stability.

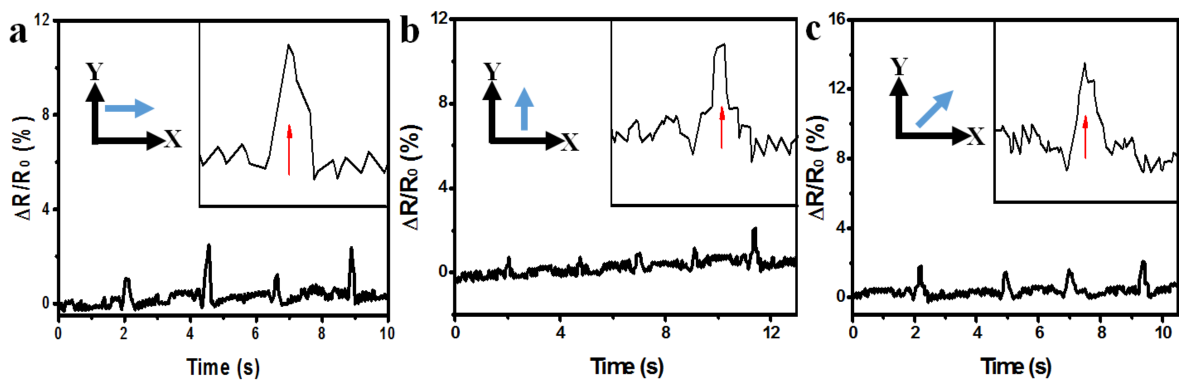

Figure S11. Resistive change of pristine hydrogel in response to object motion on its surface along (a) x direction, (b) y direction and (c) 45^{o} angel along x direction; Each movement in Figure 4a – c was repeated for three times and insets are detailed response for one movement.

Compared with LM-hydrogel, pristine hydrogel lost the ability to discern different object motions.

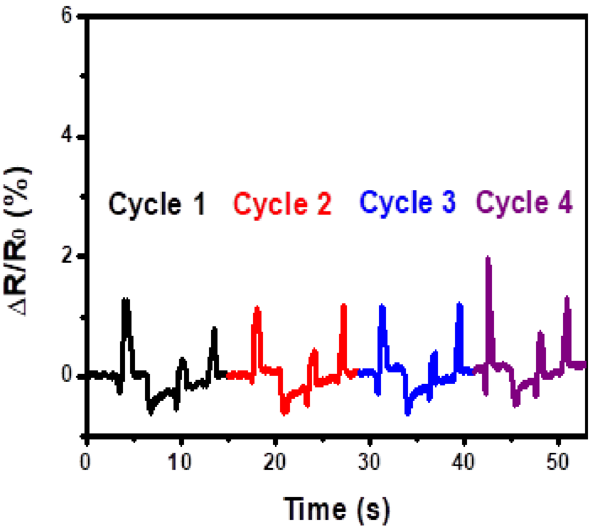

Figure S12. Resistive change for repeated cycles of continuous movement on LM-hydrogel (10 vol%) surface in **Figure 4g**.

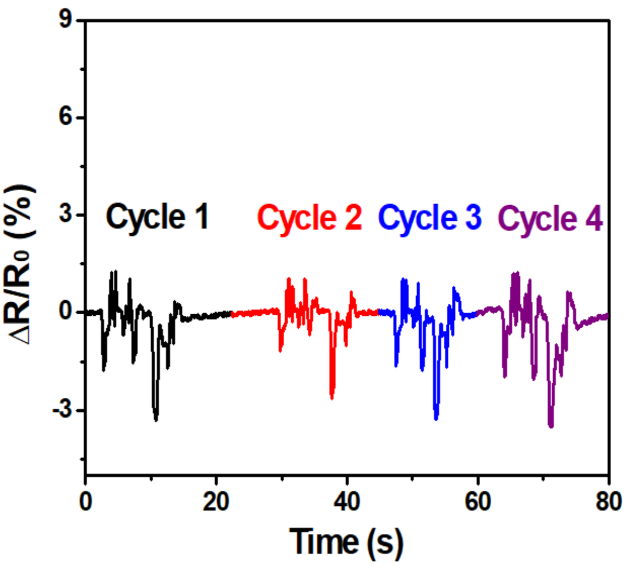

Figure S13. Resistive change of LM-hydrogel (10 vol%) for repeated cycles of writing letters “A”, “B”, “C” and “D”.

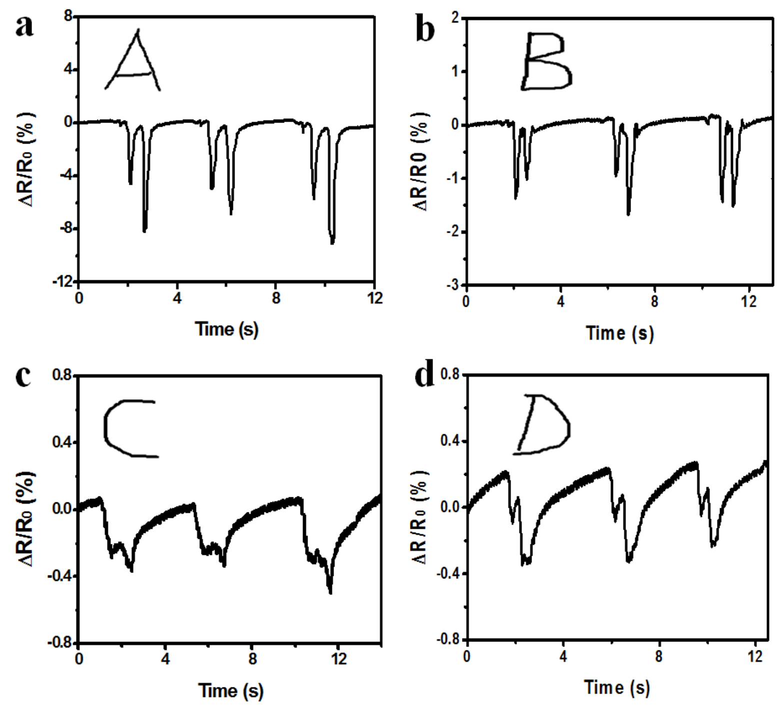

Figure S14. Resistive change of pristine hydrogel pad when writing A, B, C and D; each letter was written for three times to show the repeatability. Compared with LM-hydrogels, peaks from pristine hydrogels are weaker and do not show subtle changes of each letter.

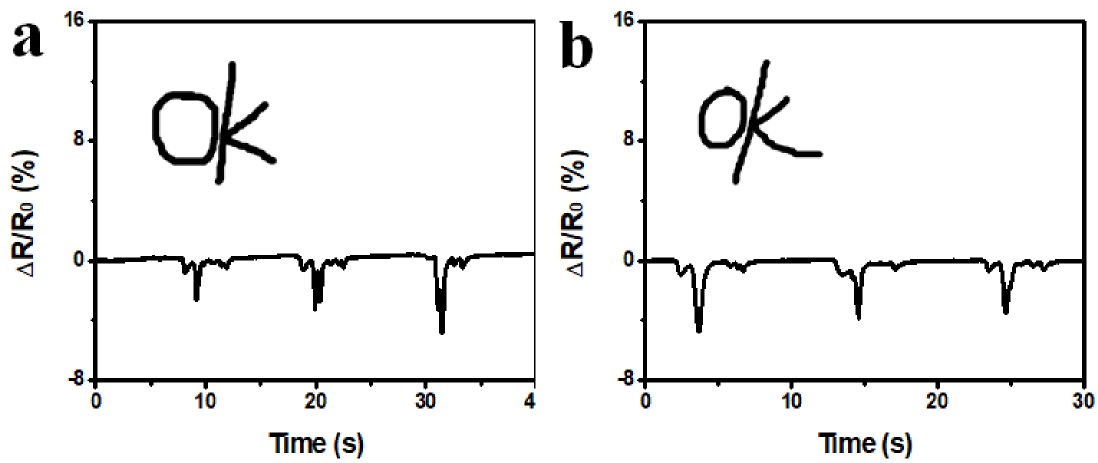

Figure S15. (a-b) The resistive responses of pristine hydrogels to the words "OK" written by two different researchers. Pristine gels lost the ability to discern personal writings.

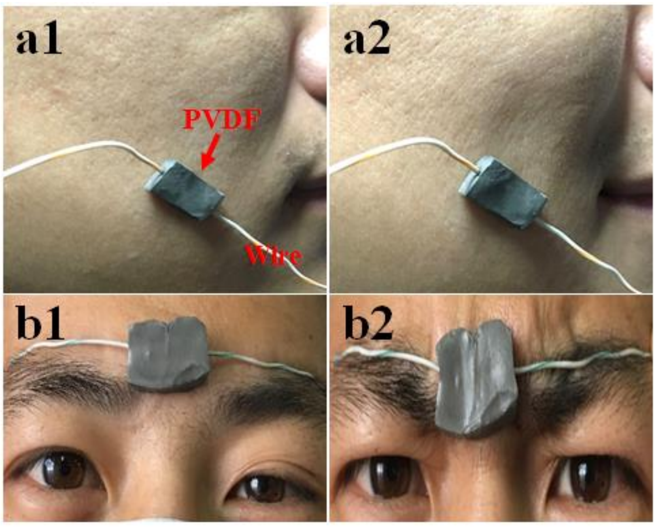

Figure S16. Experimental setup for hydrogels to detect bodily motion from human face (a) Chewing and (b) Frown. The electrodes were copper wires fixing by double-side tape to adhere to skin.

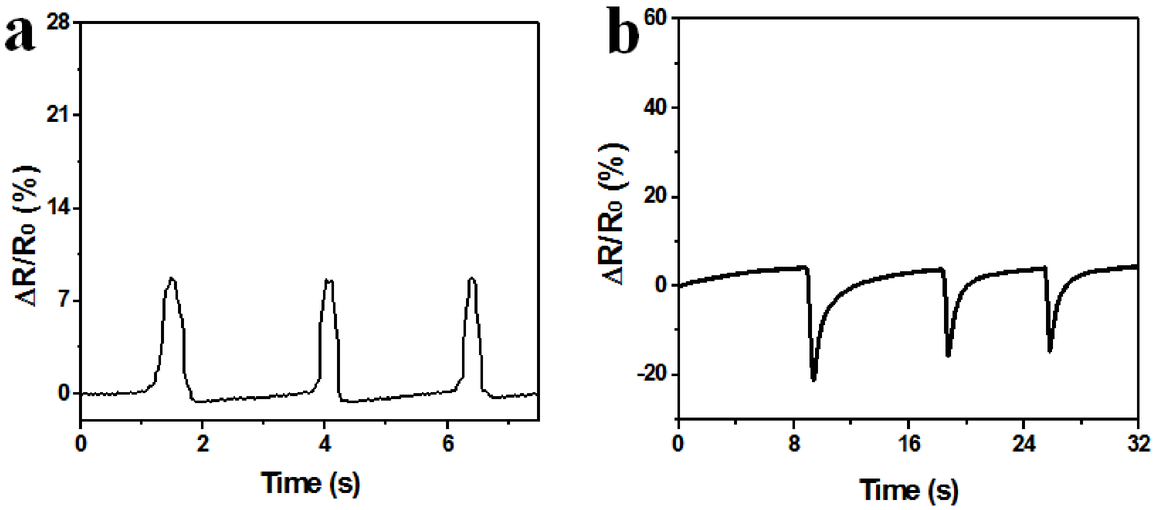

Figure S17. Resistive change of forefinger bending with pristine hydrogel attached outside (a) and inside (b). Pristine hydrogels showed comparable signals as LM-hydrogels under large deformation. Experimental setup was the same as LM-hydrogel as shown in Figure 6a- 6b.

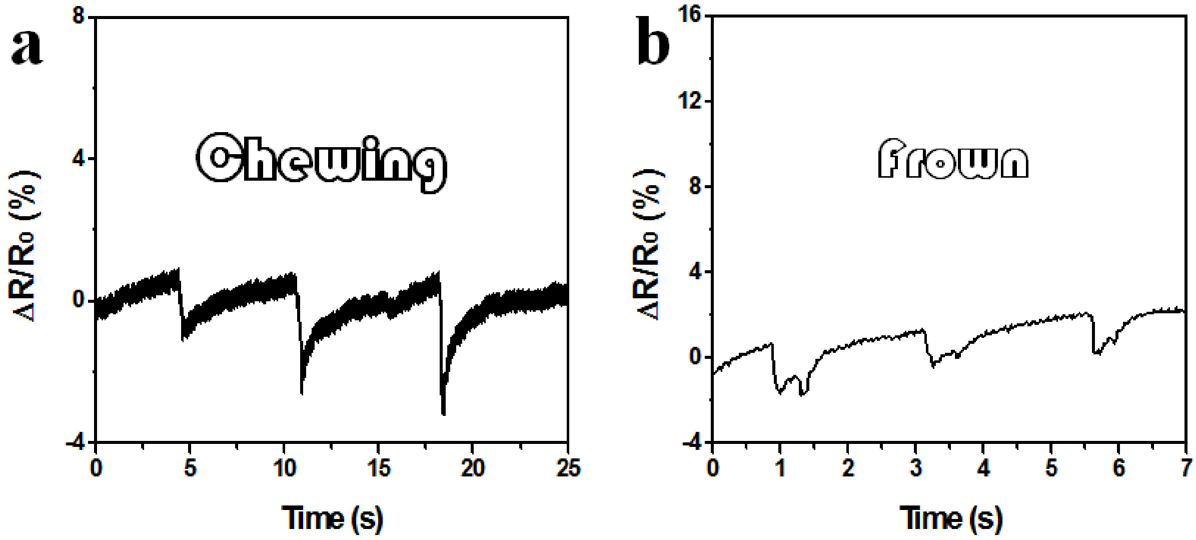

Figure S18. Resistive change from pristine hydrogels of (a) chewing and (b) frown. Hydrogel without liquid metals exhibited weaker signals or lost the detailed information of the motion. Experimental setup was the same as LM-hydrogel as shown in Figure S16.

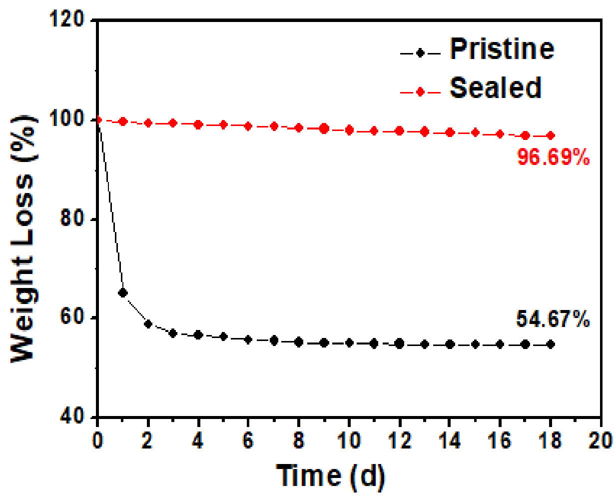

Figure S19. Time-dependent mass changes of LM-hydrogel (10 vol%) with (sealed) or without (pristine) PVDF sealing.

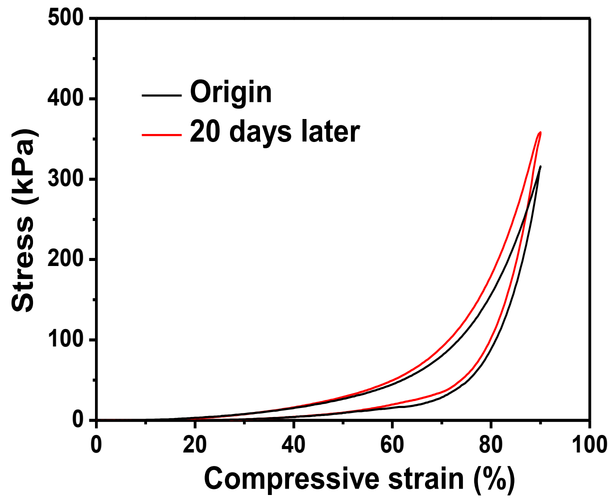

Figure S20. Compressive test for LM-hydrogel (10 vol%) sealed in PVDF films for 20 days. No obvious change was observed after 20 days of dehydration in PVDF films, indicating that the PVDF-sealing strategy was an effective method to protect LM-hydrogel form dehydration. Curve marked with origin was the hydrogel without dehydration.

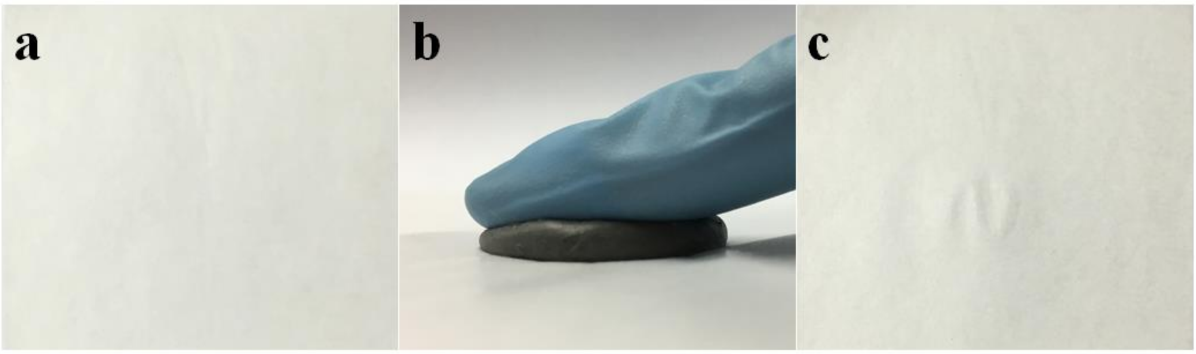

Figure S21. Photo of leaking test for LM-hydrogel (10 vol%) a) A piece of clean paper. b) Pressed LM-hydrogel on paper. c) The paper was only slightly wetted by the hydrogel without leaking of liquid metal.

Video S1. The video of handwriting has been uploaded to SI. The motions in Figure 4a, 4b and Figure 5b were repeated in the video. As shown in the video, the hydrogel and copper electrodes were covered and sealed with PVDF films. The resistance signals monitored by Keysight 34461A displayed on the computer screen. Once the pen moved and gave a stress to the specimen, the signal change was simultaneously displayed on the screen. For easier understanding, we have added subtitles or arrows on the video to explain what kind of action was applied. As shown in video, an object moving vertically (X direction) to the direction of electric current would lead to the quite different signals compared with along the parallel direction (Y direction). The latter "A" was combined two above pattern, expressed a series of turbulence. Similar as the test previously reported in our paper, all the tests were conducted at least three times to ensure the repeatability. These results indicated the excellent ability of LM-hydrogels to discern the different movements on gel surface.