Electronic Supplementary Information

Volume-invariant Ionic Liquids Microbands as Highly Durable Wearable Biomedical Sensors

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Including: Experimental section, supporting figures and movies

Experimental Section

Materials: Gold (III) chloride trihydrate ($HAuCl_4{\cdot}3H_2O$, 99.9%), Triisopropylsilane (99%), the ionic liquid (1-Methy-3-Octylimidazolium Chloride) and Oleylamine (OA) were purchased from Sigma Aldrich. Ethanol, Hexane and chloroform were obtained from Merck KGaA. All chemicals were used as received unless otherwise indicated. The commercial rubber bands were purchased from local supermarket. Conductive wires were purchased from Adafruit.

Synthesis of ultrathin gold nanowires: 44 mg $HAuCl_4{\cdot}3H_2O$ was added to 40 ml hexane, followed by addition of 1.5 ml OA which acted as a phase-transfer reagent to enable dissolution of gold salts. 2.1 ml Triisopropylsilane was added into the above solution after complete dissolution. The resulting solution was left undisturbed for 2 days at room temperature until the colour turned from yellow into dark red, indicating the formation of gold nanowires. After repeated centrifugation and thorough washing (~ 4 times) using ethanol/hexane (3/1, v/v), the residue chemicals were removed. The AuNWs solution was finally concentrated to a 2 ml stock solution in hexane.

Fabrication of the rubber band sensor: The rubber band mould was designed using 3D Max and printed by an Objet Eden 360 3D printer. The materials used for printing was Fullcure 720. The Ecoflex curable silicone fluid was poured into the mould and cured for 1 hour under 60℃ after which it was peeled off. The grooves in the silicone were then filled with ILs and conductive wires affixed. Following this, a layer of cured Ecoflex was coated on the surface to encapsulate the grooves after spreading a liquid layer of Ecoflex. This assembly was trimmed and cut to achieve a well-shaped rubber band sensor.

Preparation of the wearable wireless patch: A conductive mixture comprising of ILs and the gold nanowires was made. 12.7g 1-Methy-3-Octylimidazolium Chloride was dropped into AuNWs solution (made from 176mg $HAuCl_4$). The mixture was vigorously stirred until hexane fully evaporated, then 35mg of polyaniline was added to achieve a viscous conductive paste. The fabrication of wearable wireless patch was similar to the rubber band sensor which was described in the previous paragraph.

Sensor characterization: To test the electro-mechanical responses, the two ends of the samples were attached to motorized moving stages (THORLABS Model LTS150/M). Then uniform stretching/releasing cycles were applied *via* a computer-based user interface (Thorlabs APT user), while the current changes were measured by the Parstat 2273 electrochemical system (Princeton Applied Research). Similar setups were used for waterproof sensor, thermal sensitivity study, wrist pulse sensing and finger movement tests.

Wireless cervical movements monitoring: A Samsung Galaxy S5 unit was used as a sample information terminal to gather, visualize and transfer data to the cloud service. The wearable patch was integrated with a custom-made data acquisition (DAQ) system which enables personal wireless network communication through Blue-tooth Low Energy (BLE) technology. Moreover, the designed DAQ system is a multifunctional circuit which acquires data from sensors, calibrates the monitored data, and transmits all the data to the information terminal. The DAQ system (power supply: 3.7 V) acquires the resistance changes based on a current between 11 μA (Sleep current) to 4.5mA (Awake current), which provides a long-time operation per battery charge (8.5 h). The resistance of the sensors (provided voltage: 3.3 V) used in this system should be less than 300 KΩ to ensure visualization during monitoring.

Supporting videos:

Mov. S1. Dynamic large strain demonstration using crystal violet staining.

Mov. S2. Waterproofness demonstration of the rubber band like stretchable strain sensor.

Mov. S3. Hand movements detecting.

Mov. S4. Wearable wireless sensor for cervical movement monitoring.

Supporting figures:

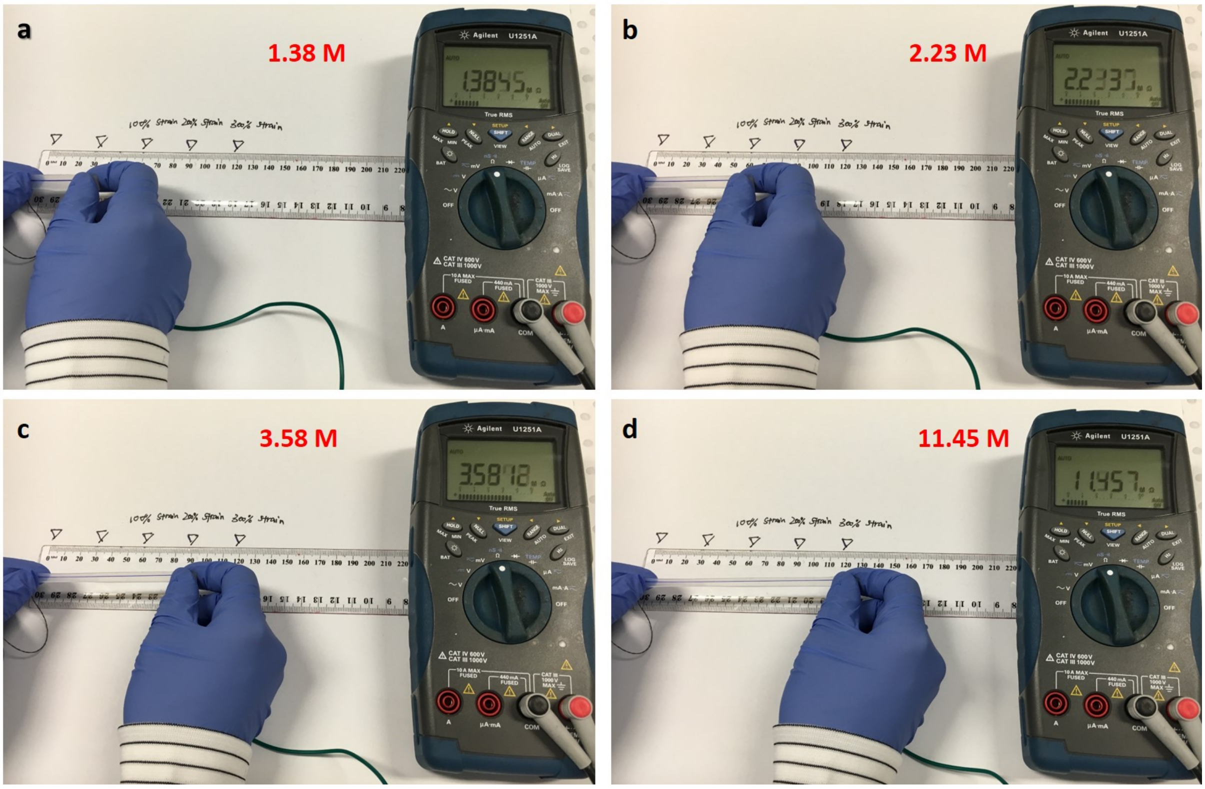

Fig. S1 Stretching demonstration of IL based rubber band-like wearable sensor. Crystal violet is dissolved in the ILs to enable easy observation. (a) Before stretching. (b) 100% strain. (c) 200% strain. (d) 300% strain. Continuous blue flow can be seen during the whole stretching process, indicating good conductivity of the sensor under large strains. Microchannel dimensions: 30mm*0.5mm*0.5mm.

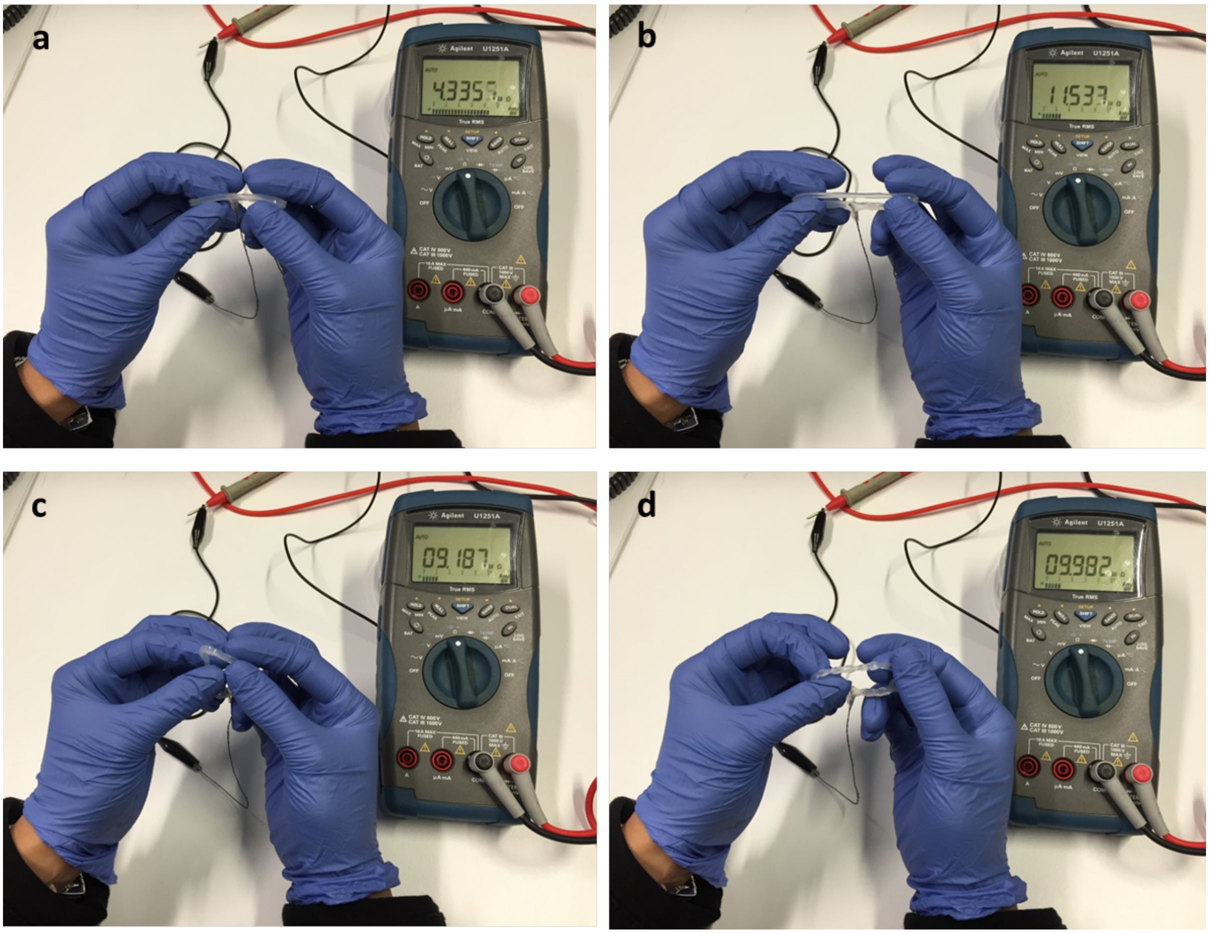

Fig. S2 Stretching, bending, and twisting demonstration of IL based rubber band-like wearable sensor. (a) Before stretching. (b) Stretching. (c) Bending. (d) Twisting.

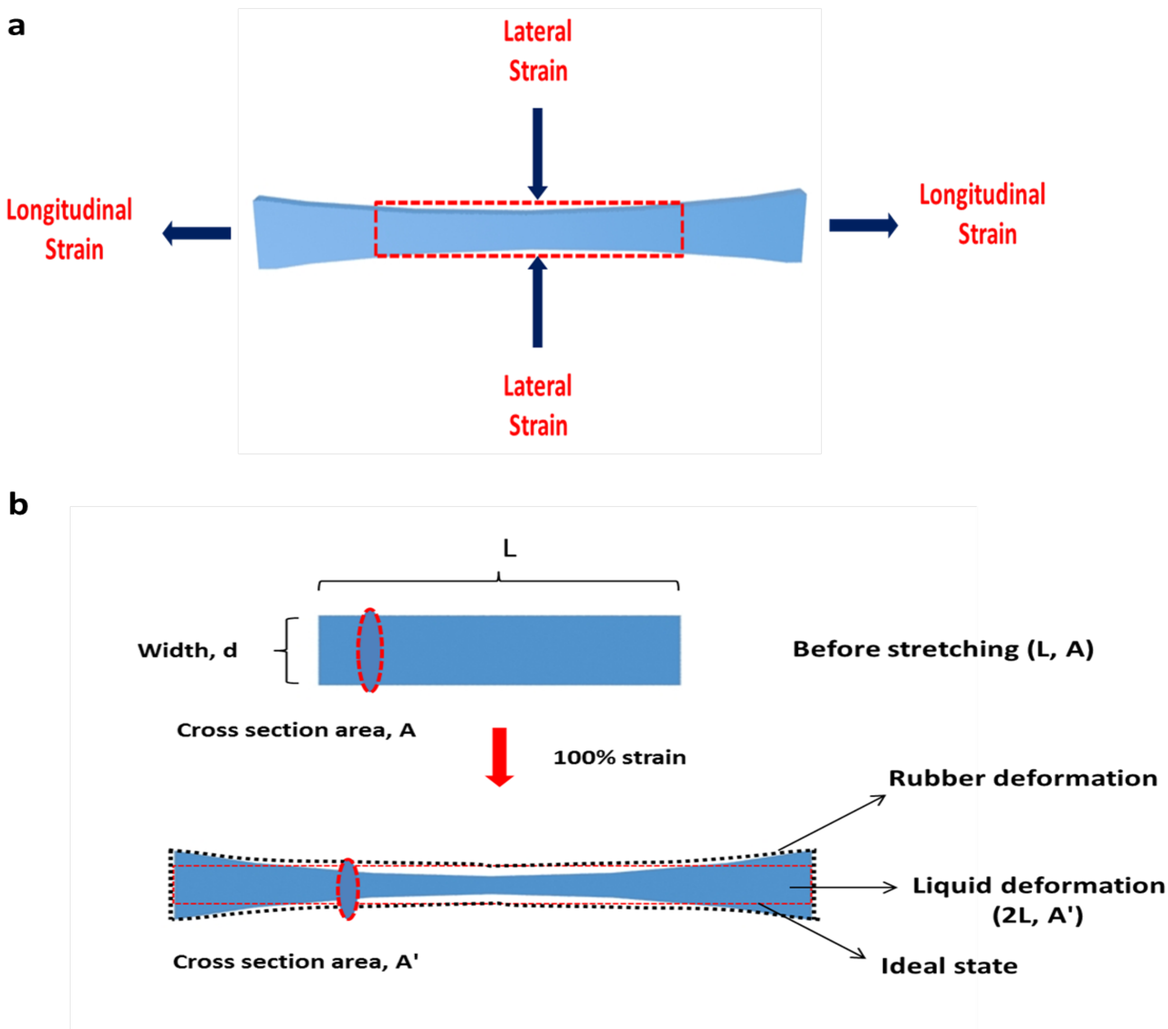

Fig. S3 Conductive liquid deformation during stretching. (a) The rubber band bears bi-directional stress while being stretched. And it will elongate in longitudinal direction and compact in lateral direction. **(b)** The volume of the liquid never changes during stretching. Before stretching, the original length is L, cross section area is A. After being stretched to 100%, the length becomes to 2L. As for the cross section area, in the ideal state it's ½ A, whereas A' in practice. When it comes to pure rubber stretching, the volume of the rubber strip will increased due to Poisson's Ratio (0.48-0.5). Poisson's ratio can be represented as μ=-(Lateral strain/ Longitudinal strain).

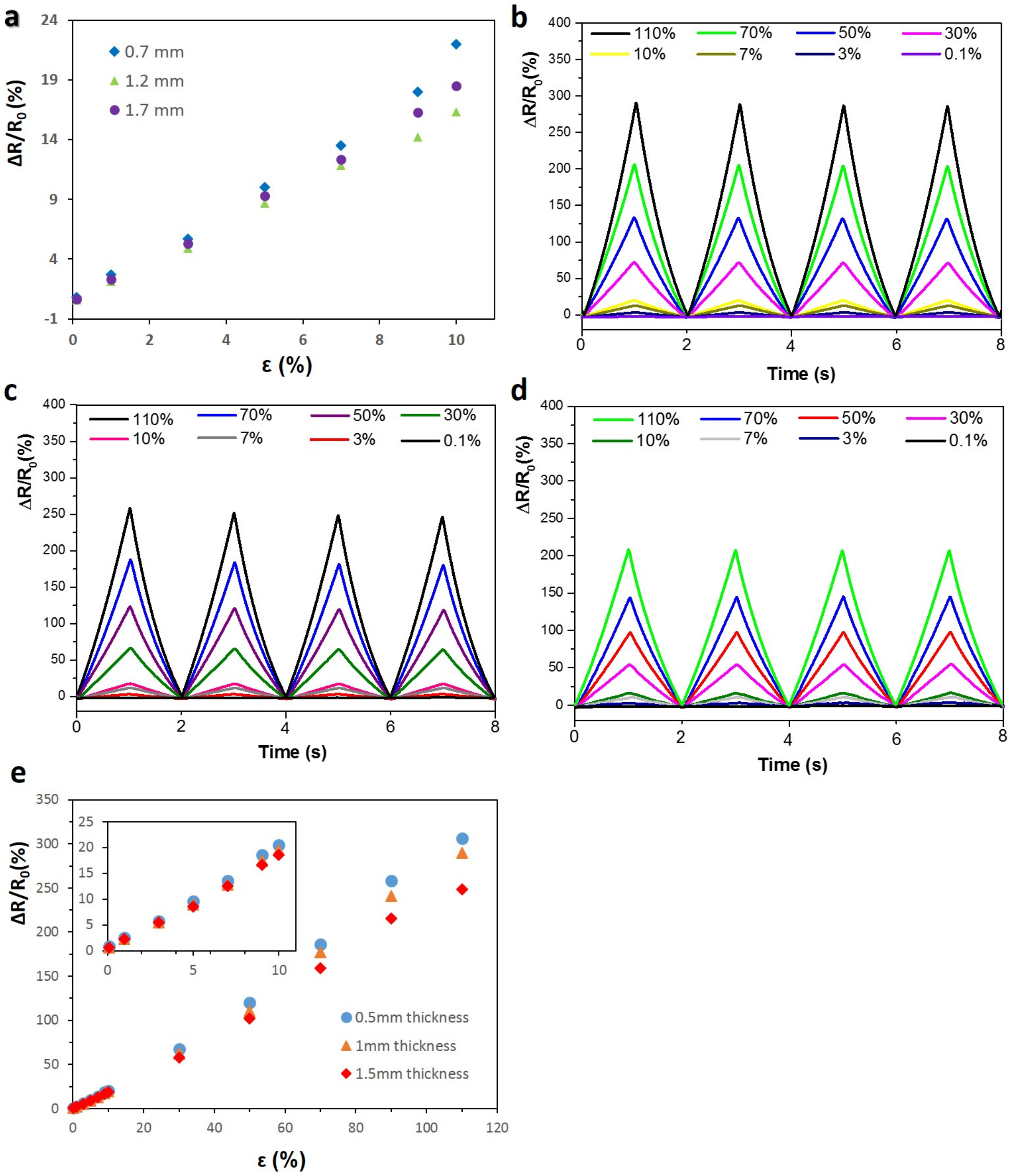

Fig. S4 (a) Plots of resistance change for the sensors with different width under low strain region (0.1%-10%), for the 0.7 mm, 1.2 mm and 1.7 mm, respectively (input voltage: 3v). (b-d) Comparison of sensing performances of three rubber band sensors. The length and height of all the three sensors were the same, namely 25mm and 1mm, respectively; the widths of the sensors are 0.7, 1.2 and 1.7 mm. Voltage: 3 V.

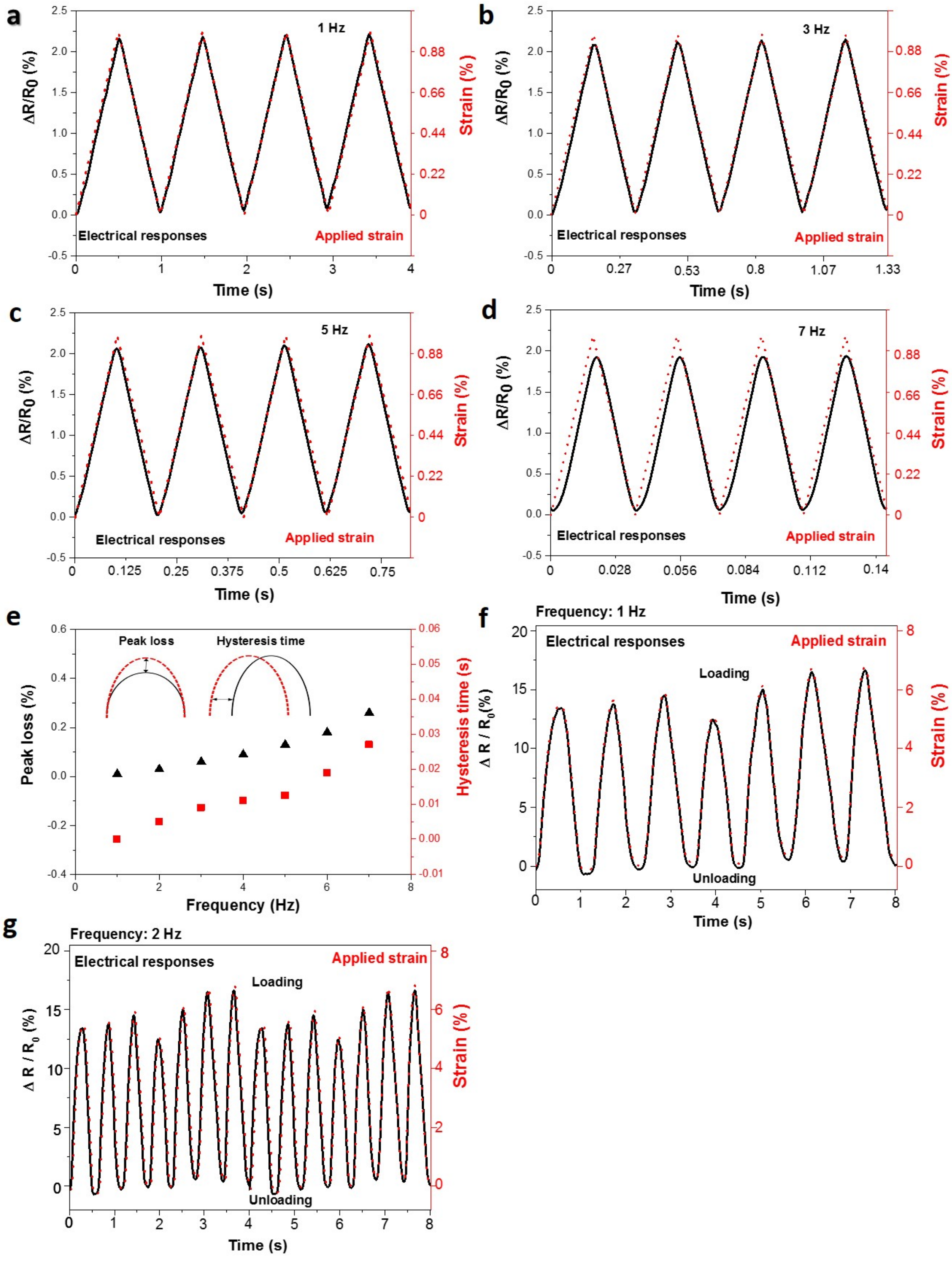

Fig. S5 Hysteresis time and peak loss of the device. (a-d) Electrical responses at the dynamic strain of 1%: strain input frequency of (a) 1 Hz, (b) 3 Hz, (c) 5 Hz and (d) 7 Hz. (e) The peak loss and hysteresis time of the strain sensor under various frequencies. (f. g) Strain-resolved measurements of the output signal as the function of applied strain in the range of 5-7% at the frequency of 1 Hz and 2 Hz, respectively.

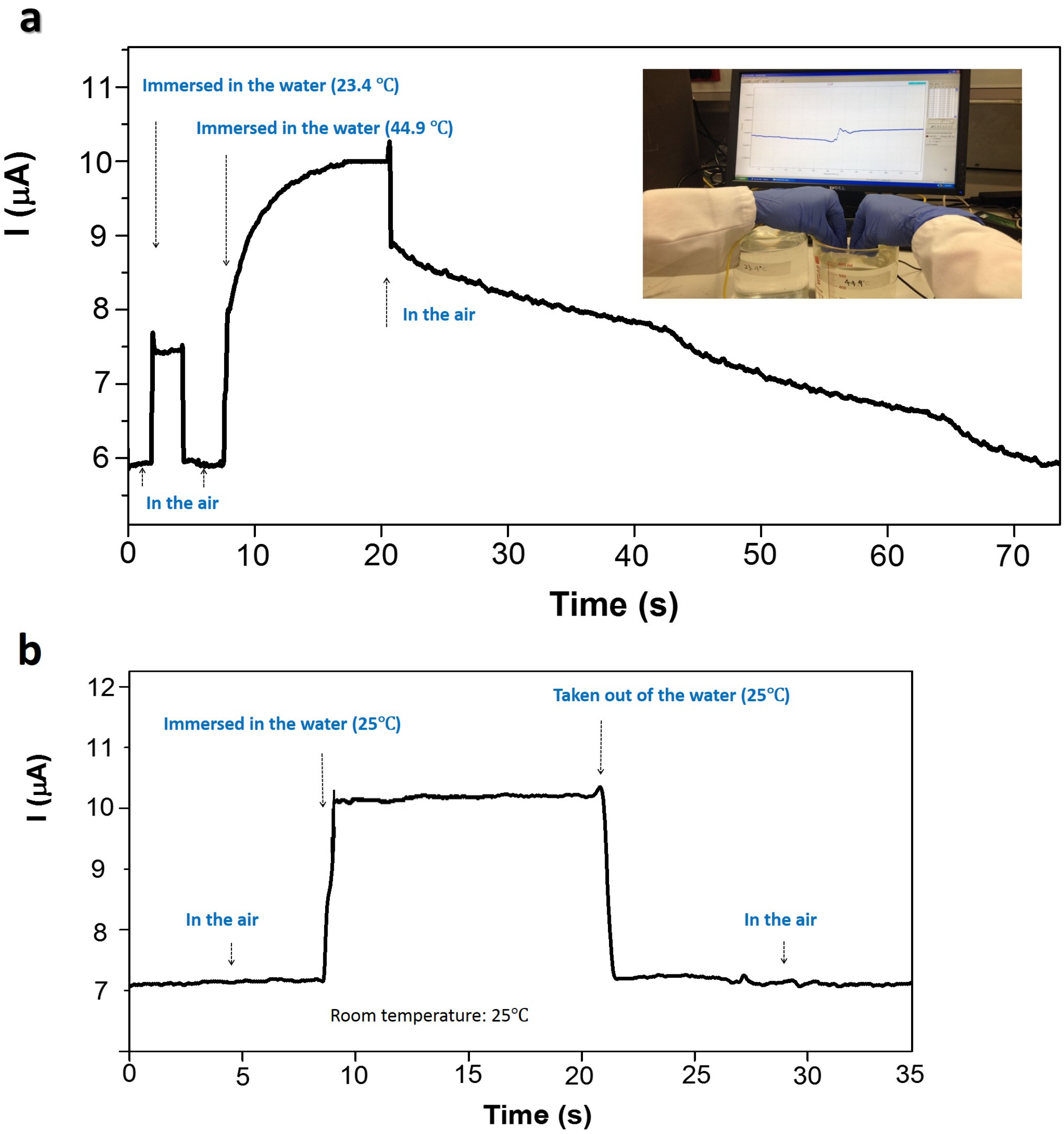

Fig. S6 (a) Waterproofness of IL based rubber band-like wearable sensors under different water temperature (23.4 ^{0}C and 44.9 ^{0}C). Current increases can be seen while the device was immersed in normal and warm water. And it recovered to the background current while the device was brought out of the water. (b) Sudden current increases caused by water pressure. Current increases can be seen while the device was immersed in warm water (25 ^{0}C). The device recovered to the background current while the device was brought out of the water. The room temperature for tests was 25 ^{0}C. Microchannel dimensions: 20mm*0.5mm*0.5mm.

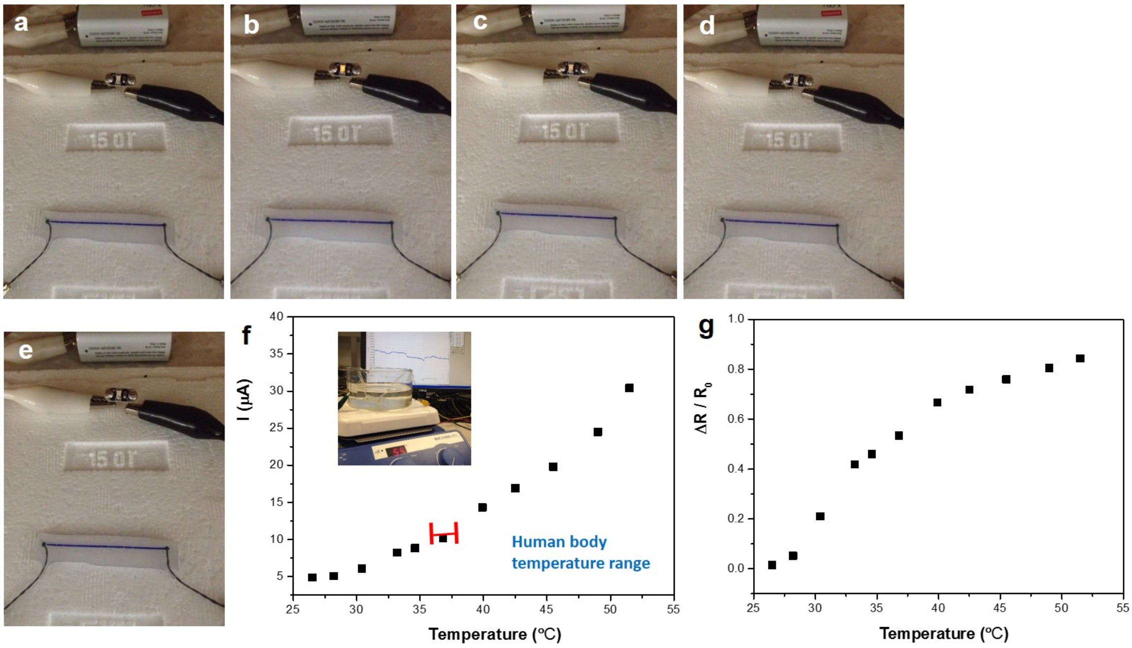

Fig. S7 Thermal sensitivity study of ILs based sensor. (a-e) Optical images of ILs rubber band sensor in a yellow light LED circuit under voltage of 9 V. First heated for 45 s on hot plate (100 ^{0}C) (b), then naturally cooled down for 1 min (c), 2 min (d) and 5 mins (e). (f) Current change under temperature from 26.5 ^{0}C to 51.5 ^{0}C (applied voltage: 3 V), the current in the range of human body temperature is around 10.2 μA. The room temperature was 25 ^{0}C. (g) Measured resistance change of ILs sensor subjected to different temperature values. Microchannel dimensions: 30mm*0.5mm*0.5mm.

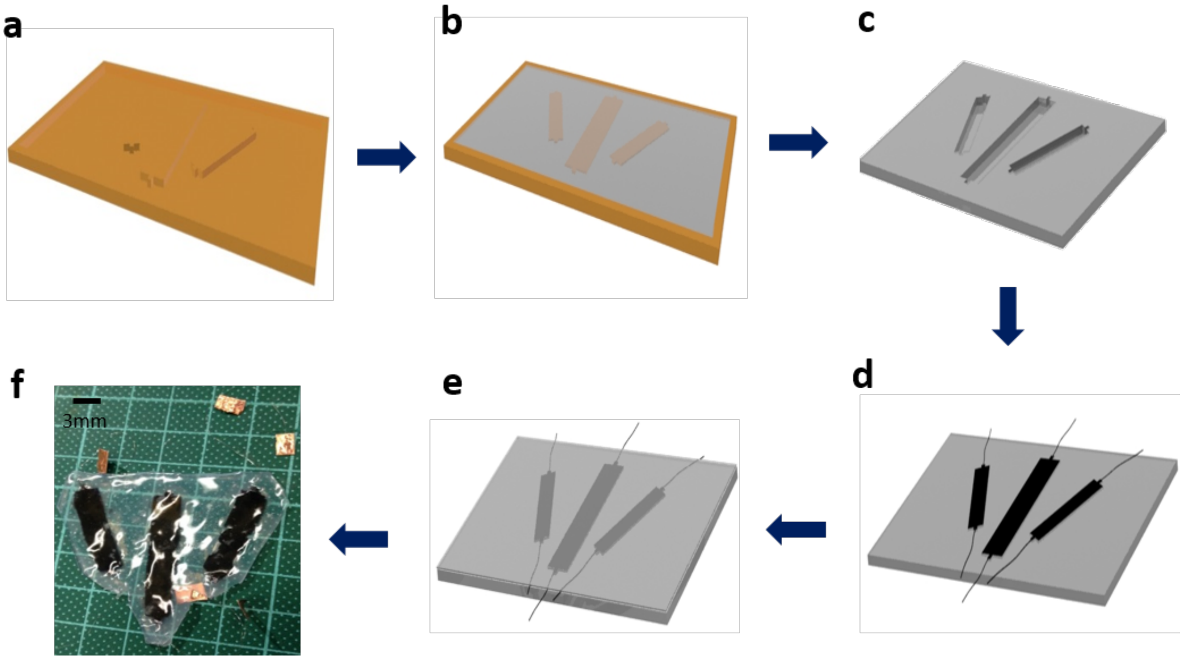

Fig. S8 Fabrication of IL based wearable nanopatch. (a) 3D printing mould designed by 3D Max. (b) The Ecoflex mixture solution is poured into the recessed printed structure, cured for 1 hour under 60 ^{0}C. (c) The cured Ecoflex is removed. (d) The grooves are filled with conductive composite and the conductive wires attached. (e) A layer of Ecoflex mixture solution is spread over the surface of ‘d’, and encapsulated with another layer of cured Ecoflex. (f) It is then trimmed and cut to make well-structured, wearable wireless patch. Groove dimensions: 20mm*10mm*0.5mm, 30mm*10mm*0.5mm.