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Ultra-stretchable, bio-inspired ionic skins enable working stably in various harsh environments

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Supporting Information

Experimental Section

Materials. Acrylamide (AAm) as hydrophilic monomer, lauryl acrylate (LA) as hydrophobic monomer, N,N'-methylenebis(acrylamide) (MBAA) as hydrophilic cross-linking agent, 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone as hydrophilic UV initiator, ethylene glycol dimethacrylate as hydrophobic cross-linking agent, 2,2-diethoxyacetophenone as hydrophobic UV initiator and dioctyl terephthalate (DOTP) as hydrophobic dispersion medium were purchased from Aladdin Chemical Co. in China. Agarose (Biochemical reagent), ethylene glycol (EG) and NaCl were purchased from Sinopharm Chemical Reagent Co. in China. All the reagents were used as received. Milli-Q (18.3 M Ω) water was used in all experiments.

Synthesis of organogel-coated hydrogel (OHGel). The hydrophilic reaction solution contained H₂O/EG binary solvent (volume ratio = 1:1), 2 M monomer AAm, 1 M NaCl, 2 wt % agarose

with respect to the weight of the hydrophilic solution, 0.05 mol % MBAA and 0.1 mol % 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone with respect to the monomer. The hydrophobic reaction solution consisted of organic solvent DOTP, 2 M monomer LA, 1 mol % cross-linking agent ethylene glycol dimethacrylate and 0.1 mol % UV initiator 2,2-diethoxyacetophenone with respect to the monomer. Firstly, the hydrophilic reaction solution was heated at 95 °C for 20 min to obtain a transparent pre-hydrogel solution. Then the hot solution was poured into glass molds and cooled at room temperature for 30 min, ensuring the completely gelling of agarose. After that, the pre-shaped agarose hydrogels were immersed in hydrophobic reaction solutions in sealed glass molds, the molds were subsequently irradiated with 365 nm ultraviolet ($\approx 4 \text{ mW cm}^{-2}$) for 4 hours to obtain OHGels. The thickness of organogel coating is about 300 μm , which is controlled by adjusting the thickness difference between the glass mold and the pre-shaped agarose hydrogel.

Synthesis of HGel. In a typical procedure, AAm monomer (2 M), NaCl (1 M), agarose (2 wt %, with respect to the weight of the aqueous solution), MBAA (0.05 mol %, with respect to the monomer) and 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (0.1 mol %, with respect to the monomer) were dissolved in deionized water at 95 °C. Then the homogeneous solution was sealed into glass molds and cooled at room temperature for 30 min, ensuring the completely gelling of agarose. Finally the 365 nm ultraviolet irradiation ($\approx 4 \text{ mW cm}^{-2}$) was applied to the glass molds for 4 h to obtain HGels.

Fabrication of the OHGel ionic skin. Two OHGel sheets with the same thickness of 1 mm were contacted together to form an OHGel ionic skin based on parallel-plate capacitance, in

which inner hydrogels had a thickness of 0.4 mm which were connected to copper wires and organogel coatings had a thickness of 0.3 mm.

Fabrication of the HGel ionic skin. A dielectric layer (PLA organogel with a thickness of 0.6 mm) was sandwiched between two layers of HGel with a thickness of 0.4 mm, and a copper wire was attached to the HGel for electrical connection, resulting in a HGel ionic skin based on parallel-plate capacitance.

Characterization of morphology. The interface of OHGel was observed by scanning electron microscope (FEI, Nova Nano SEM 450, USA). Before this test, the OHGel was brittle failure at liquid nitrogen and then was frozen drying. Finally, the cross-section of OHGel was sputtered gold for 120 s before observation. The surface microstructure of the wrinkled OHGel was observed by an optical microscope (Nikon, LV-LH50PC, Japan).

Method for transmittance measurement. The transmittances of the OHGel and HGel for visible light were measured by an Ultraviolet–Visible Spectrophotometer (Shimadzu, UV-3600, Japan), and the samples were tailored into the same size 20 mm × 20 mm × 2 mm. The measurements were performed in air at room temperature.

Method for mechanical tensile test. The tensile tests of the OHGel and HGel were performed on a universal mechanical test machine (SANS, CMT6350, China). The dumbbell-shaped samples had following dimensions for tensile measurements: total length > 75 mm, effective length = 25 mm, width = 4 mm and thickness = 2 mm. Both ends of the sample were fixed with clamps. The upper clamp was pulled at a constant velocity of 20 mm/min.

Characterization of the environmental stability. For the characterization of the anti-dehydration property in arid air, the OHGel and HGel were stored into a container, which was

maintained at constant temperature and humidity ((20 °C, 50 RH% or 80 °C, 30 RH%). The weights of samples (w) as the function of time were recorded. The weight ratios of all samples were calculated by $w/w_0 \times 100 \%$ (w_0 , the original weight of the samples). For the characterization of the anti-swelling and without ions leakage in aqueous environment, the OHGel and HGel were immersed in the same volume of deionized water respectively. The swelling behaviors of the OHGel and HGel in water were determined by the weight change as same as the dehydration behaviors in arid air. The contents of NaCl being released from the samples to deionized water were monitored by a conductivity meter (Mettler Toledo, 731-ISM, Switzerland).

Characterization of the rheological properties. The rheological properties of the OHGel and HGel were investigated by using a modular compact rheometer (TA, Discovery HR-2, USA) at the temperature arrange from -20 to 80 °C. The samples were cut into round plate with a diameter of 25 mm and a thickness of 2 mm. The storage moduli (G') of the samples were measured under small-amplitude oscillatory shear at an applied frequency of $\omega = 10$ rad/s and strain amplitude of $\gamma = 0.1\%$.

Method for pressure-sensitive characterization. The pressure was loaded by a 1×1 cm² glass fixed on the three-dimensional mobile platform and measured by a digital force gauge (ZPS/Z2S-DPU-50, IMADA, Japan). Capacitance was measured by an LCR meter (Agilent, E4980A, USA) with an AC voltage of 1 V and a sweeping frequency of 1 kHz. The mechanical stability testing was tested using a linear motor with straight reciprocating motions.

Supplementary Figures

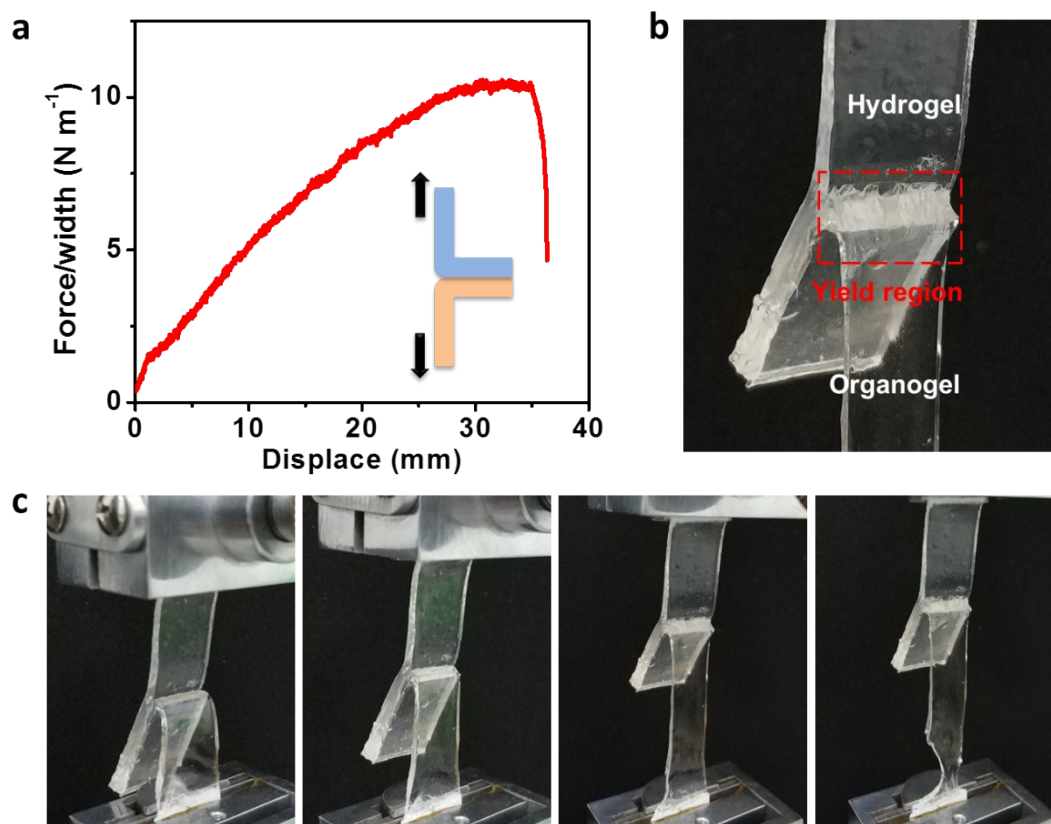


Figure S1. a) The peeling force curve of an OHGel. b) The interface image of an OHGel during peeling process. The yield region was marked in the dashed box. c) Potographs of an OHGel during peeling process.

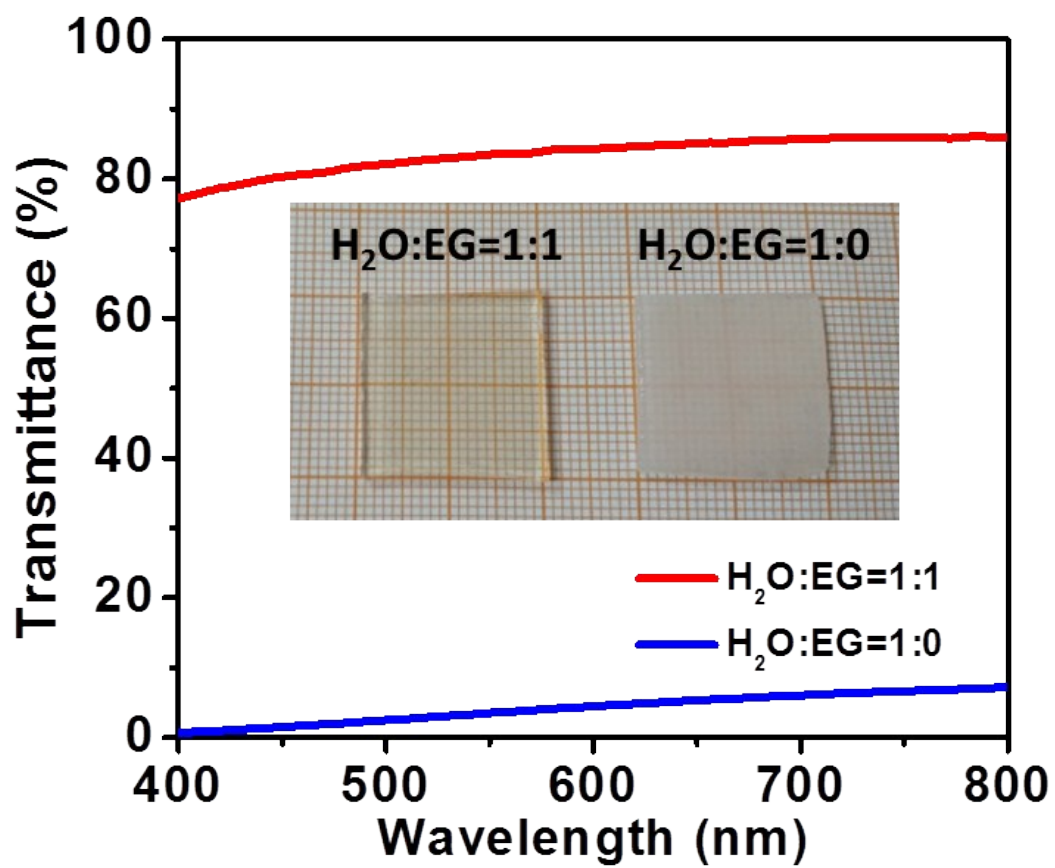


Figure S2. Transmittance in the visible range of the OHGels with H₂O and H₂O/EG (volume ratio=1:1) in inner hydrogels.

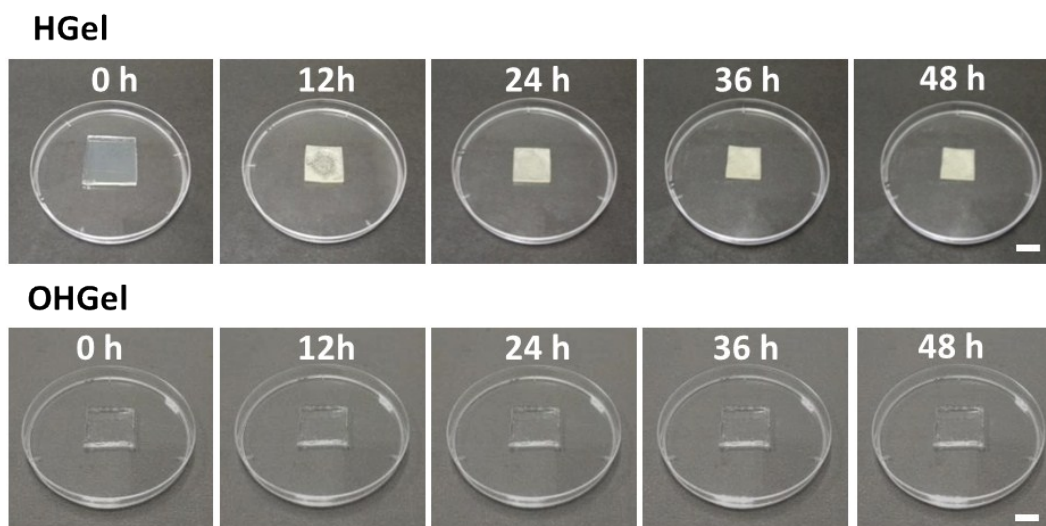


Figure S3. Snapshots of the OHGel and HGel kept in open air at 25 °C and 50 RH%. Scale bar, 10 mm.

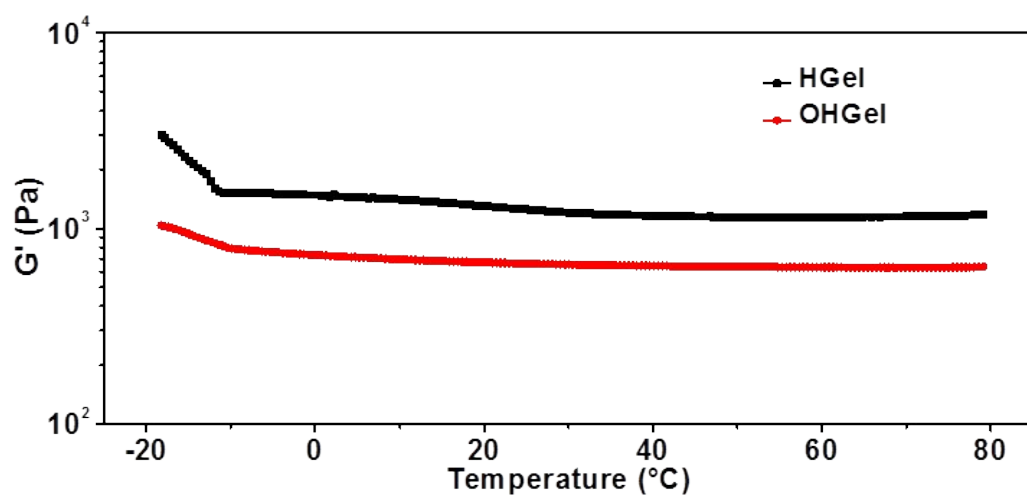


Figure S4. The storage modulus (G') of the HGel composed of pure water system and the anti-freezing OHGel as a function of temperature in the range of -20 to 80 $^{\circ}\text{C}$ at a constant shear strain of 0.1% and frequency of 10 rad/s.

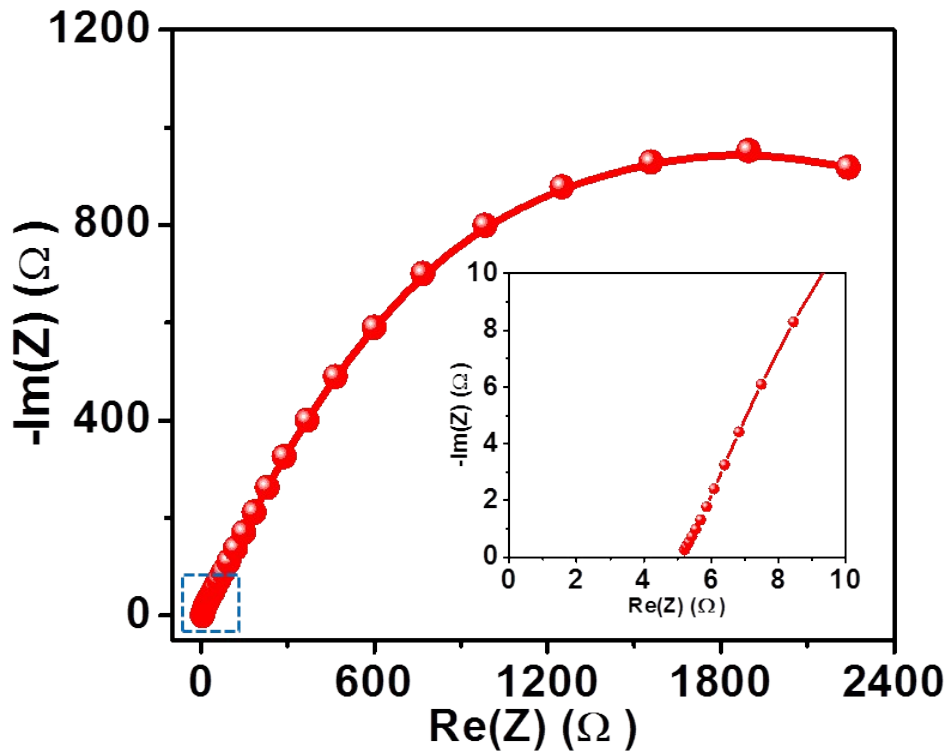


Figure S5. Nyquist plots of the PAAm-NaCl hydrogel electrolyte with a thickness of 1 mm and an area of 1 cm²

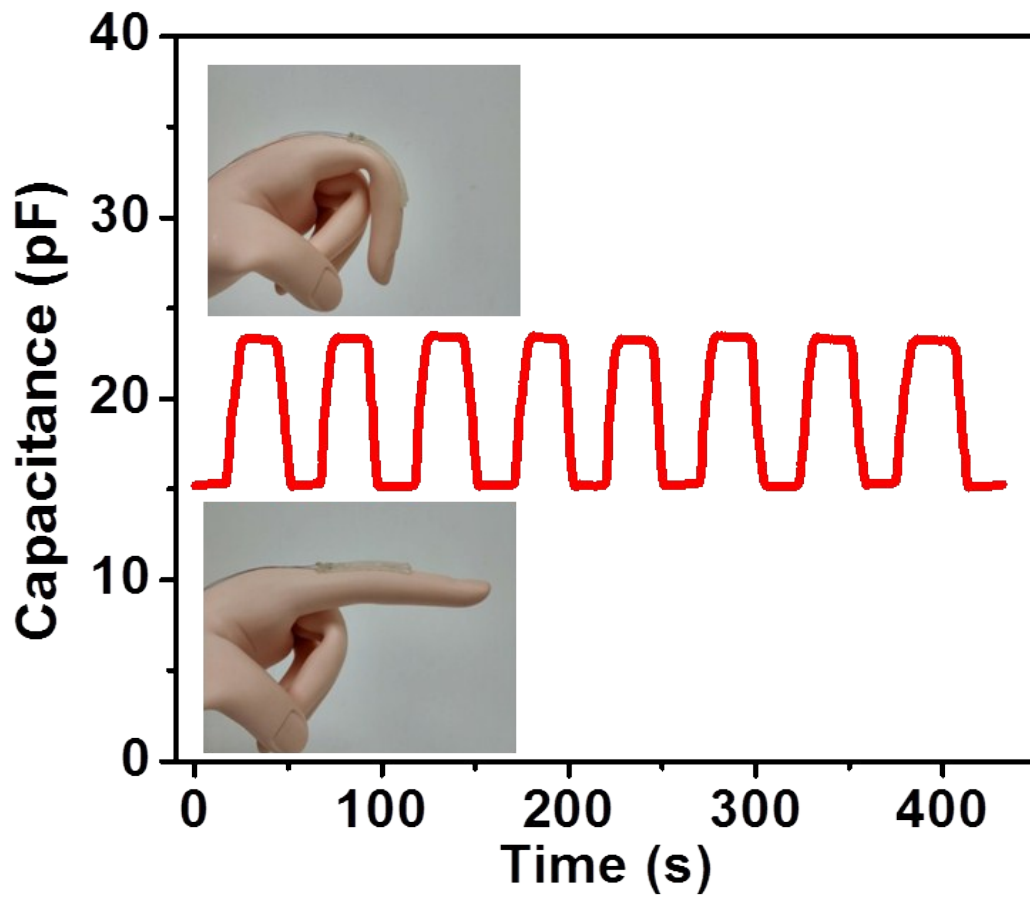


Figure S6. Photos of the finger motion sensor attached to a bent or straight finger and the capacitance signals when the finger bends cyclically.

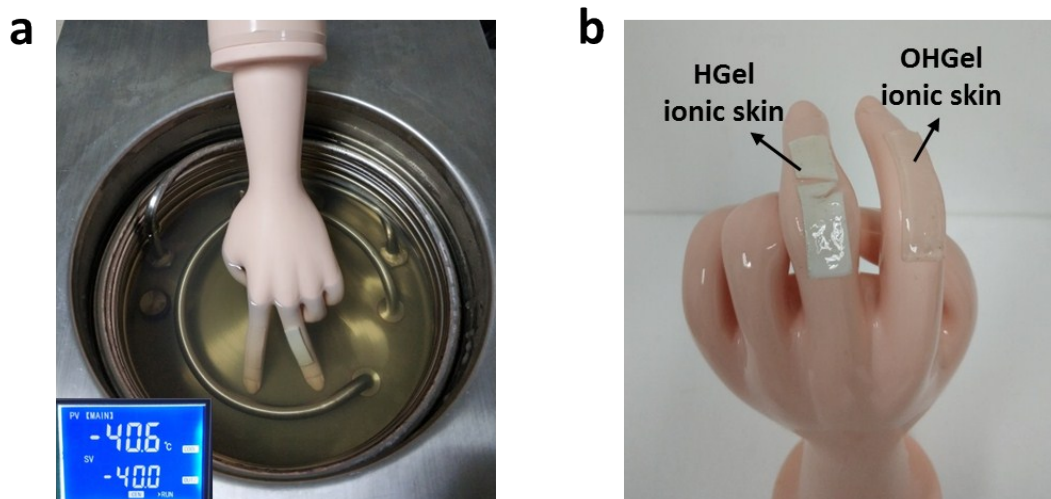


Figure S7. a) Photos of the OHGel ionic skin and HGel ionic skin immersed in the cold alcohol at -40 °C. b) The HGel ionic skin was frozen and could be broken when bending the finger at -40 °C, while the OHGel ionic skin was still stretchable and could adapt the movement of the finger.

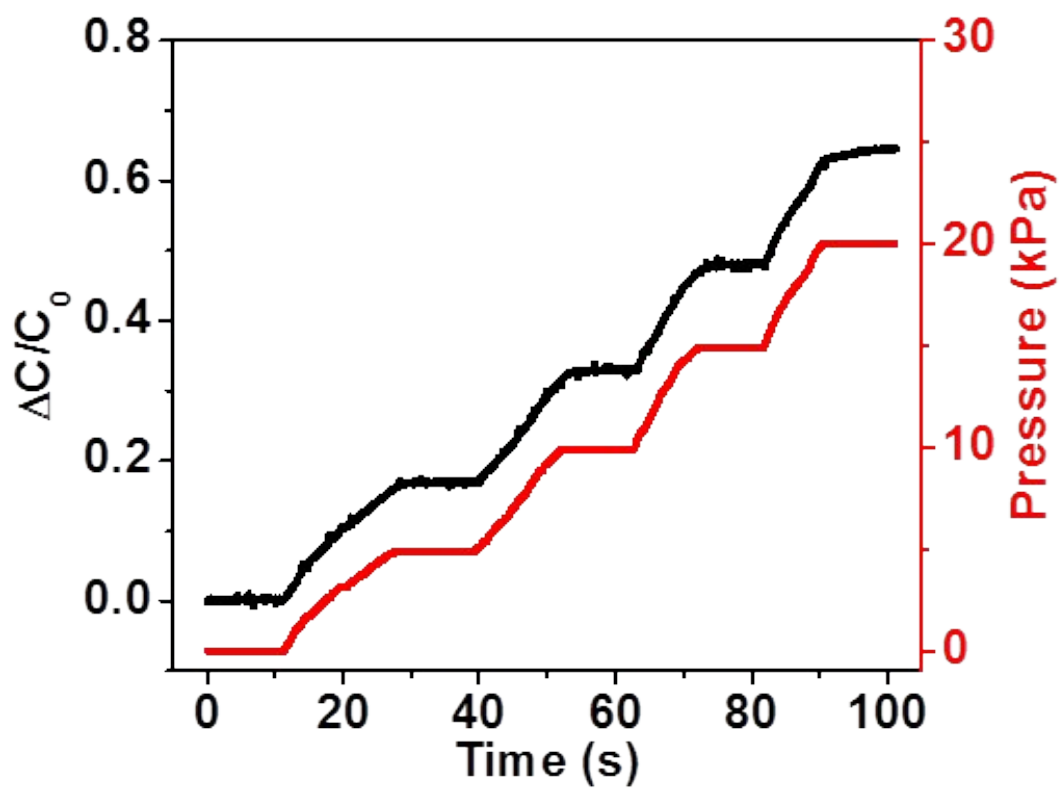


Figure S8. Capacitance signals of the OHGel ionic skin by pressing 1 pixel at increasing pressures.