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Supporting Information

Self-Protective, Reproducible Textile Sensor with High Performance towards Human-Machine Interaction

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1. Experimental section

1.1 Materials

The single-walled carbon nanotubes (CNTs) were purchased from Timesnano, Chengdu. Pyrrole, sodium hydroxide, ferric chloride, ethanol and chloroform were purchased from Sinopharm and sodium dodecyl benzene sulfonate (SDBS), 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (PFDS), dopamine hydrochloride and n-hexane from Sigma-Aldrich. The Ni-coated interdigital electrode was prepared as the previously reported method.^[1]

1.2 Fabrication of SPRET

To wrap PET fibers with CNTs, the textile was pretreated by oxygen plasma with 1 min. The CNTs solution was prepared by dispersing 1.6 mg mL⁻¹ CNTs in water with 10 mg mL⁻¹ SDBS by 30 min sonication. Then the PET textile was dipped into the CNTs suspension with 30 min sonication and further dried in a fume cupboard (temperature: 37°C, humidity: 90%). To accelerate the drying process, the textile was gently immersed into ethanol for 1 min after 30 min drying duration. Subsequently, the polymer coating was introduced on the CCET by in-site reaction. The FeCl₃-PDA solution was prepared by mixing 0.1 M dopamine hydrochloride in 1 M ferric chloride water solution. After immersed into FeCl₃-PDA solution for 15 min, the CCET was dipped into 0.2 M pyrrole chloroform solution for 30 min polymerization at 0°C. To remove residual initiator and DA, the textile was rinsed ordinarily by ethanol, deionized water, and 0.1 M sodium hydroxide water solution. It was further annealed in blast drier for 6 h. Before fluorination, CCET-PDA-PPy was wetted by ethanol to increase the effective reaction area. Then it was sucked into n-hexane with 4 vol% concentrated 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane at 60°C for 4 h and finally dried in a fume cupboard.

1.3 Preparation of the control samples

Samples including CCET modified by PFDS, PPy or PPy-PFDS are all fabricated with the methods similar to those for SPRET.

1.4 Fabrication of SPRET sensor, the SPRET glove and the SPRET finger-cot

A piece of 1 cm*1 cm SPRET was stacked onto Ni-coated interdigital textile electrodes attached on a lab glove or a finger-cot. The SPRET was further seamed circularly by waterproof tape.

1.5 Washing test

Having been placed into a laundry bag, the SPRET in 4 cm*4 cm was put into the commercial laundering machine (Haier, XDG70011) together with a lab coat and some detergent (OMO). The washing process lasted 30 min for each cycle.

1.6 Breathability test

The test is carried out with pieces of PDMS, virgin textile and SPRET. All the samples are ~350 μm thick. According to standard ASTM E96,^[2] the test was conducted with the upright cup method in a controlled chamber of 23°C constant temperature and 50% relative humidity. The water vapor transmission rate (WVTR) was calculated with following equation: $WVTR = \Delta m / (A * \Delta t)$. Where the $WVTR$ is the rate of water vapor transfer (g m⁻² h⁻¹), the Δm is the weight difference (g), the Δt is the period of measurement (h), and the A is the exposed sample surface area (m²). All the samples were tested with 6 cycles.

1.7 Characterization

The scanning electron microscope (SEM) (at 2 kV) and energy dispersion spectrum (EDS) images were collected using Verios G4 UC thermal field-emission scanning electron microscope. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Shimadzu Axis Ultra DLD spectroscopy, using Mg Kα as radiation resource. Contact angle pictures and splashing movies were carried out by a contact angle meter (DCAT21 and OCA25), using a 3 μL droplet of water or a 2 μL droplet of oil as an indicator. An electrochemical work station (CHI660E), programmable electrometer (Keithley6514) and tautness meter (Handpi) were used to measure I-t curves at 1 voltage. An Instron 5567 universal tester was used to test the mechanical durability of the SPRET sensor. WVTR was tested with the water vapor transmission rate system (Labthink).

2. Figures

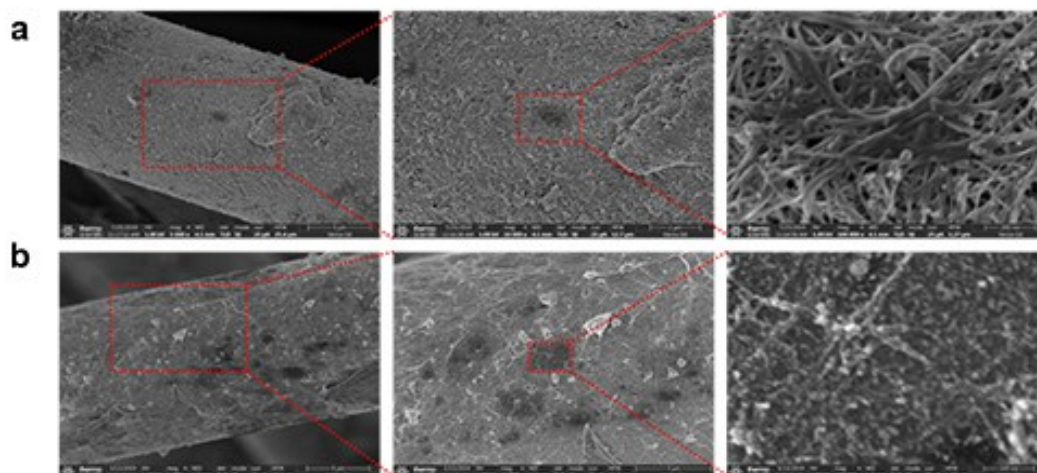


Figure S1. SEM images of the morphology of CCET (a) and SPRET (b) at different magnification.

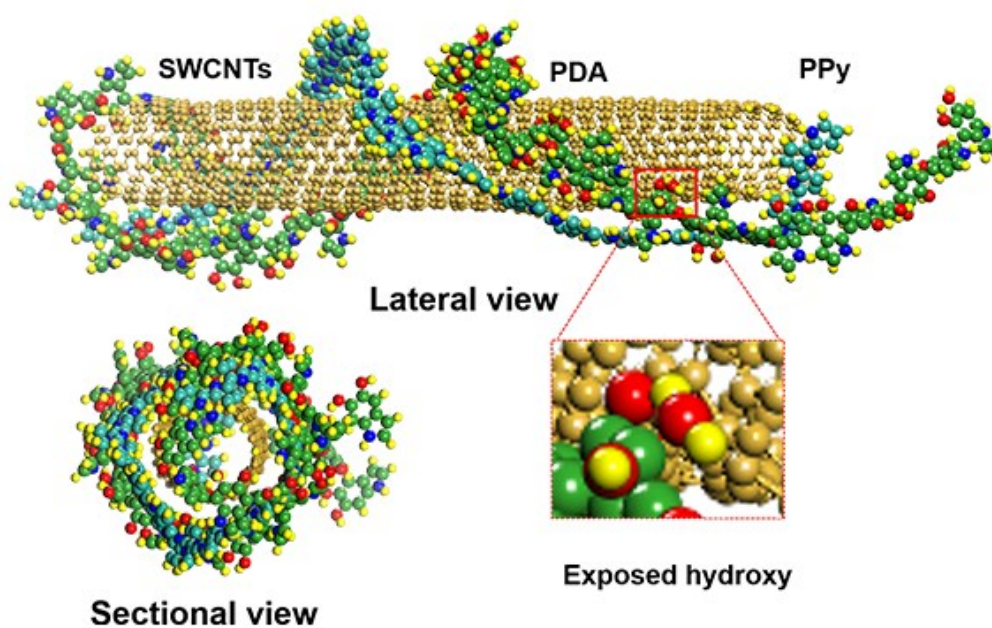


Figure S2. Molecular simulation of CNTs-PDA-PPy. The interaction mechanism of carbon nanotubes (CNTs) with PDA and subsequent formed PPy at molecular level is investigated by molecular simulations as implemented in Materials Studio software. The initial structure of CNT is modeled with a diameter of 9.40Å and a length of 125.46 Å, whereas the models of the PDA and PPy compounds are constructed with 50 repeat units. The geometric minimization and a sufficiently long annealing process are performed to obtain the equilibrium structures. Then, the final structure of CNT covered with PDA and PPy polymers is obtained. Our simulation results show that the strong binding of both PDA and PPy polymers onto CNT is attributed to the π - π and π -H interactions. Meanwhile, the PDA and PPy polymers are coupled mainly through hydrogen bonding. This could result in carbon nanotubes were firmly wrapped by polymer compound as observed experimentally.

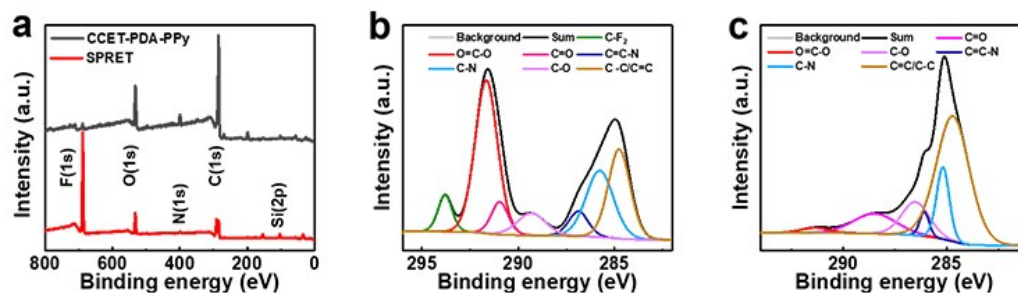


Figure S3. XPS analysis of SPRET and CCET-PDA-PPy. In comparison with CCET-PDA-PPy, the SPRET was characterized by X-ray photoelectron spectroscopy (XPS). As shown in the diagram of (a), a hash peak of fluorine 1s orbital indicates the presence of fluorine on SPRET. The fine spectrum of carbon of SPRET (c) and CCET-PDA-PPy (b) further confirms the fluorine is graft to the surface of SPRET successfully.

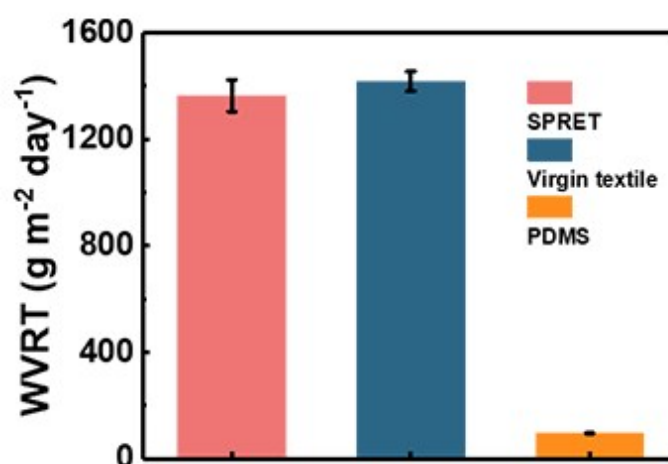


Figure S4. Breathability test of SPRET. The SPRET documents a high WVTR of $\sim 1400 \text{ g m}^{-2} \text{ day}^{-1}$, approaching to the breathability of virgin textile. While PDMS, the most widely used elastic substrate, presents a low WVTR of $\sim 96 \text{ g m}^{-2} \text{ day}^{-1}$.

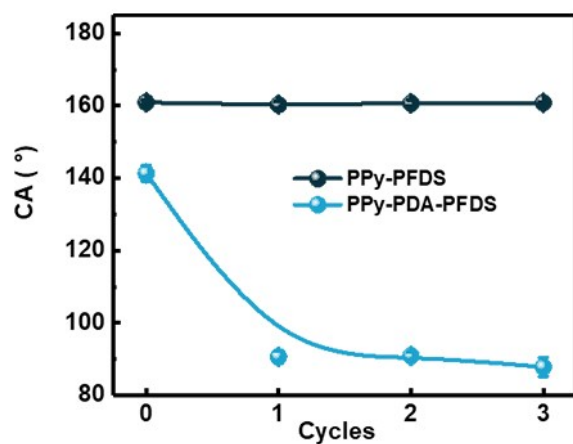


Figure S5. The oil contact angles of CCET modified with PPy-PFDS and PPy-PDA-PFDS after each washing cycles.

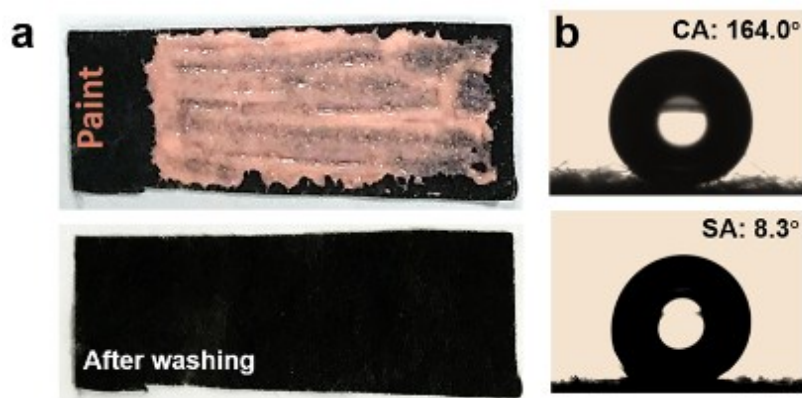


Figure S6. (a) Photographs of SPRET stained by polymer paint (top) and after washing (bottom). CA, SA tests (b) on SPRET after 3 cycles' washing.

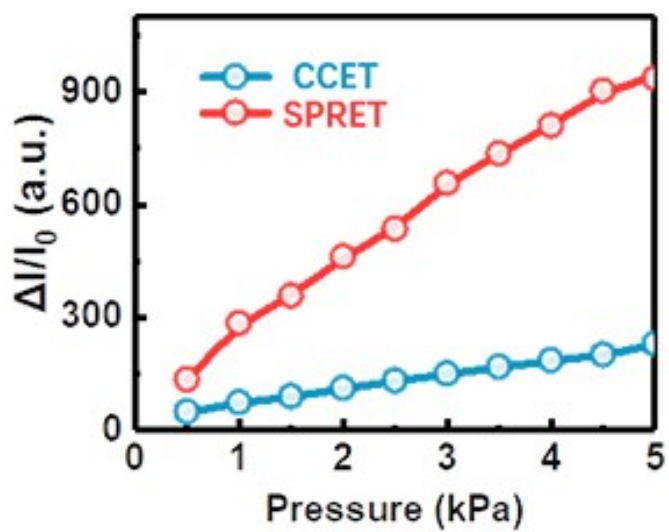


Figure S7. The detail of the pressure-response curves in the low-pressure region (0-5kPa).

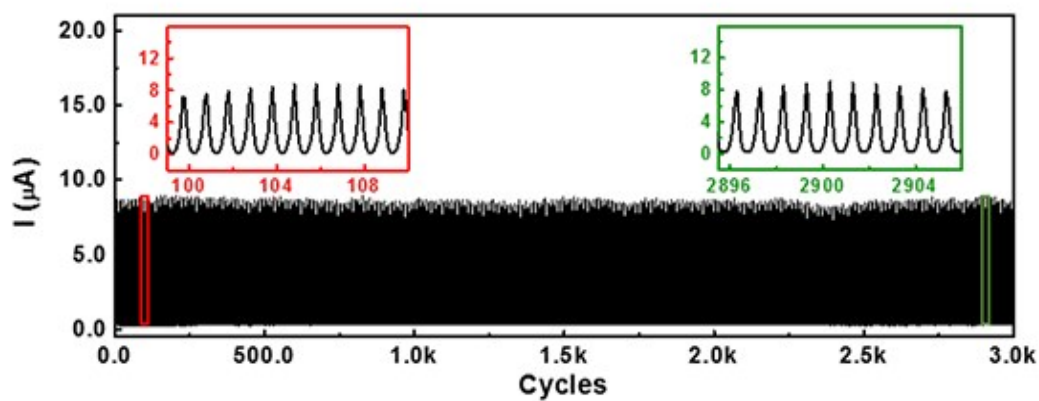


Figure S8. Durability test under ~ 100 Pa pressure and frequency of 1 Hz.

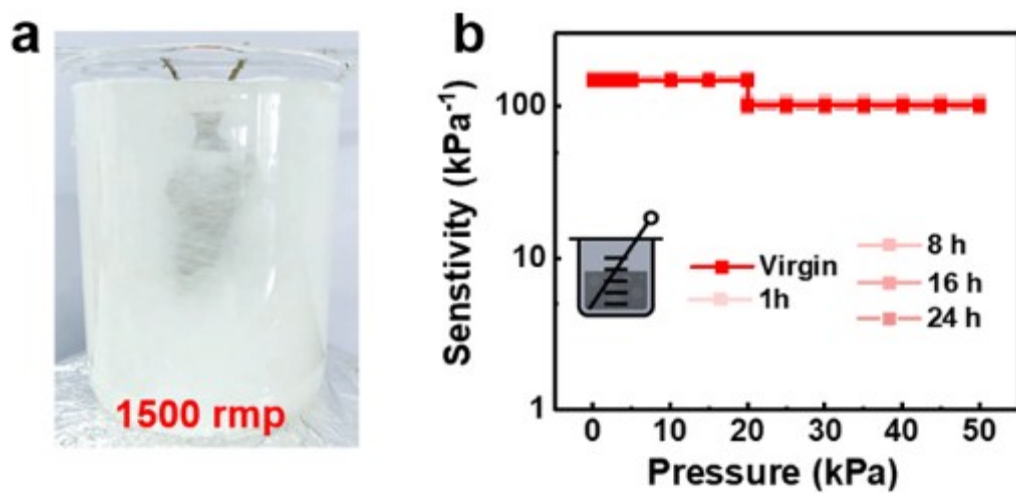


Figure S9. Stir-washing test of SPRET. (a) Photograph of strong stir-washing in a beaker. (b) The sensitivity of SPRET sensors after various washing hours.

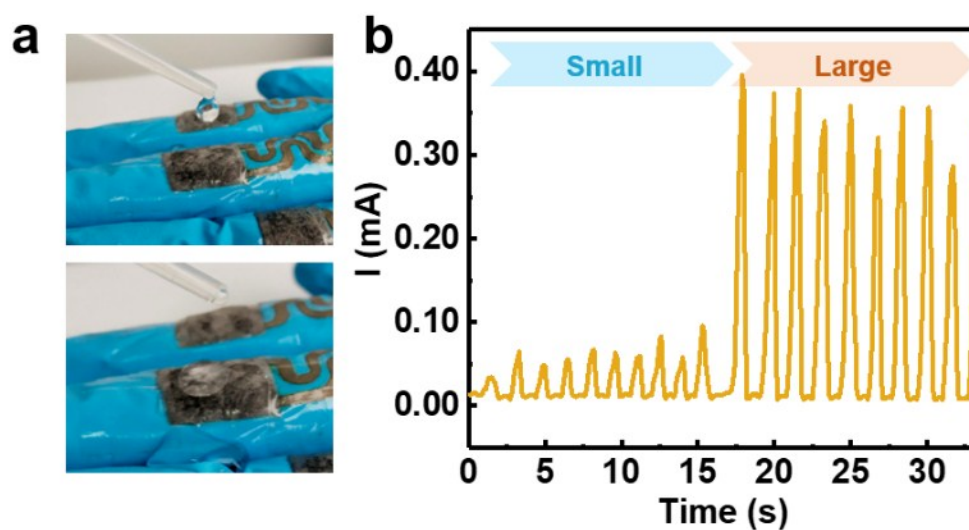


Figure S10. The current curves of SPRET sensors (b) in response to small or large finger bending with consecutive droplet-splashing (a).

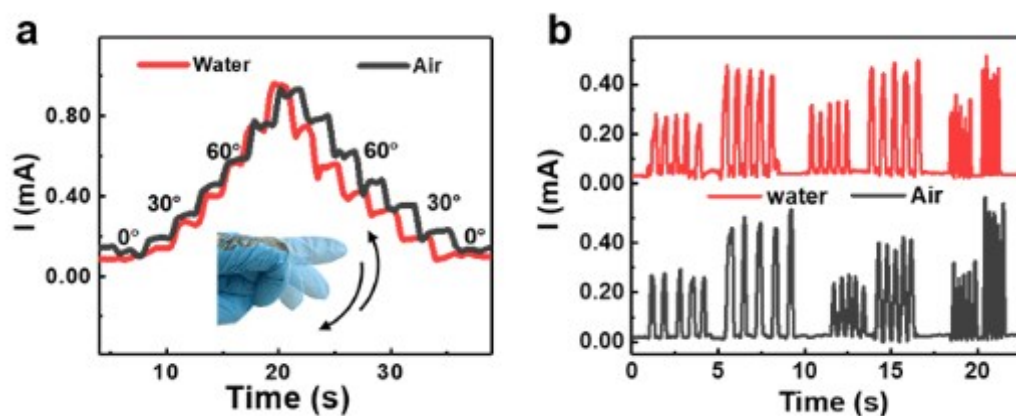


Figure S11. Real-time detection of finger bending at different angles and frequency. Bending of index finger wearing the SPRET glove results in a raise of response current. The current is constant at certain angels (grey curve of image a), thus the bending angel could be monitored through the current signal. Besides, due to the fast response/relax time, the current shows a periodic increase and decrease corresponding to various bending frequency (grey curve of image b). Moreover, capable of self-protection, the SPRET glove presents intact detection under 1 M saline (red curves of image a and b), demonstrating the performance of the SPRET glove was not affected under aqueous condition. Those results indicate the practical potential of SPRET glove in detecting physical signals for human healthcare.

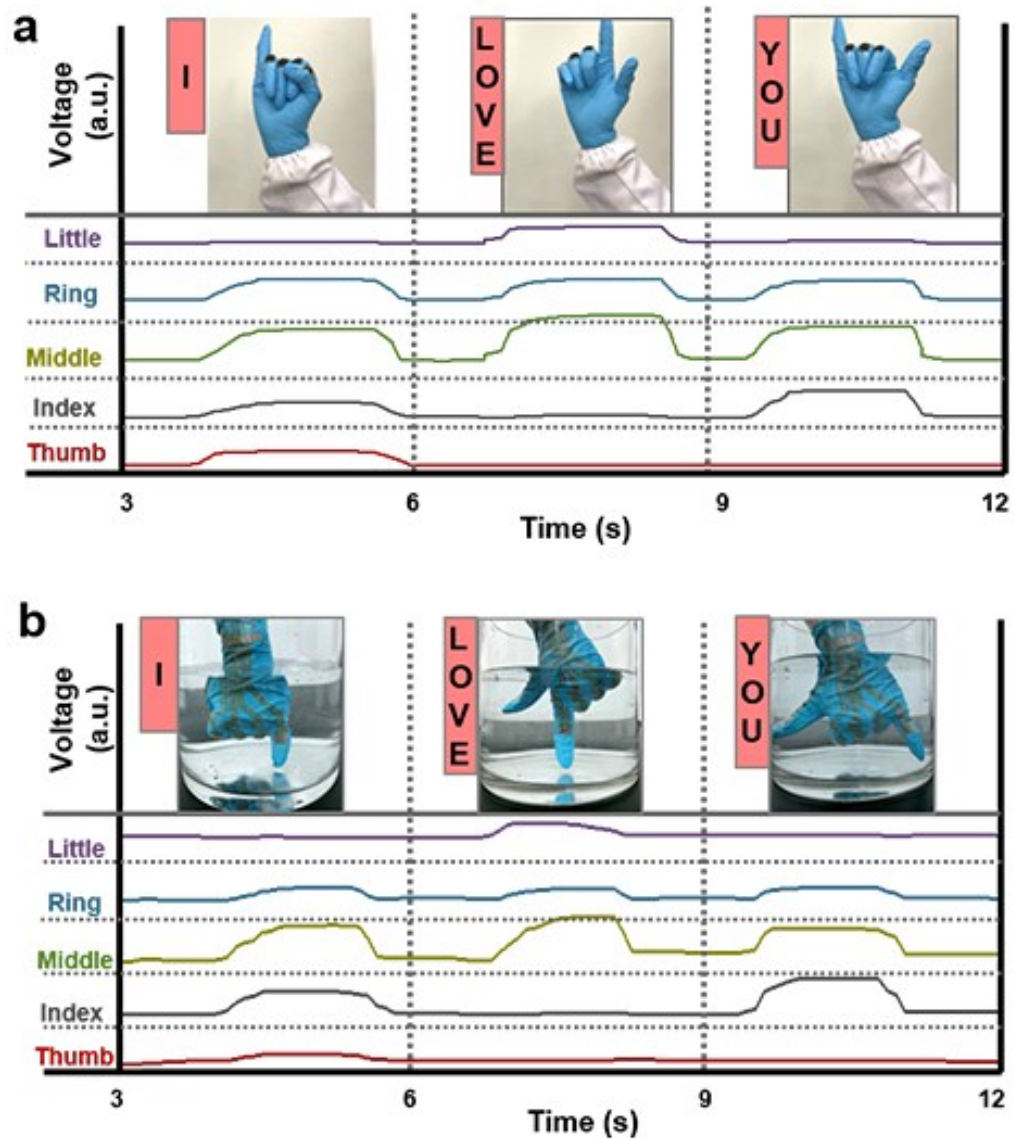


Figure S12. Detection of various gestures performed in air (a) and under saline (b) with a multichannel recorder.

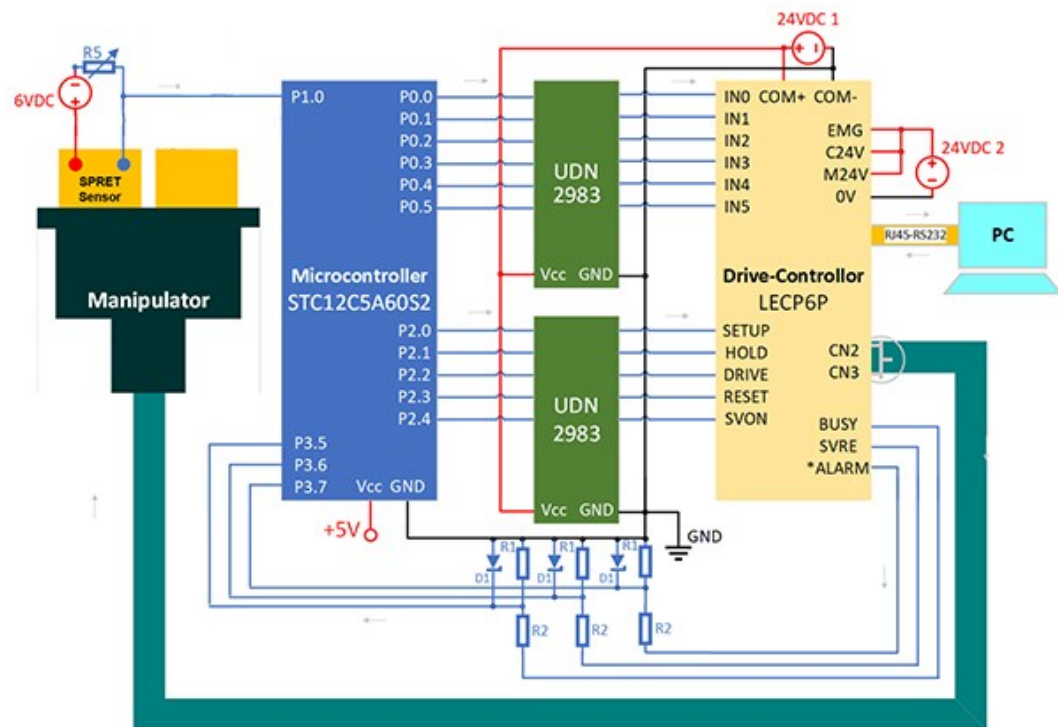


Figure S13. Circuit diagram of the robot-learning system.

3. Reference

1. X. Pu, L. Li, M. Liu, C. Jiang, C. Du, Z. Zhao, W. Hu, Z. L. Wang, *Adv. Mater.* 2016, **28**, 98.
2. E. A. McCullough, M. Kwon, H. Shim, *Meas. Sci. Technol.* 2003, **14**, 1402.