Supplementary Information

Intrinsically Stretchable Nanowire-Based Sensing Patch for Wearable Analysis of Sweat Chloride Ion Composition

Qian Wang,[a] Jinheng Zhang,[a] Junqi Sun,[a] Ting Fang,[a] Cheng Yang[a] and Desheng Kong[a,*]

[a] State Key Laboratory of Analytical Chemistry for Life Science, College of Engineering and Applied Sciences, Nanjing University. Nanjing 210023, China

Experimental Section

Materials

All chemical reagents were used as received from commercial suppliers without further purification. Methanol, dimethyl sulfoxide (DMSO), polyvinyl butyral (PVB), polyvinyl pyrrolidone (PVP), dioctyl sebacate (DOS), sodium chloride (NaCl), potassium chloride (KCl), and iron(III) chloride ($FeCl_3$) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Thermoplastic polyurethane (TPU) was obtained from Asahi Kasei Industrial Co., Ltd. Multi-walled carbon nanotubes (CNTs, XFQ 041, length: 20–100 μm, diameter: 10–20 nm) and an dispersant (XFZ23) were supplied by Nanjing XFNANO Materials Tech. Silver nanowires (Ag NWs) with an average length of ~80 μm were synthesized in-house via a polyol reduction process.

Preparation of Ag NW/AgCl NP Electrodes

Ag NW electrodes were fabricated by spray-depositing a dispersion of Ag NWs in isopropyl alcohol onto a TPU substrate, followed by annealing at 120 °C for 30 min. Shadow masks were employed during deposition to define the desired patterns. An *in situ* oxidation reaction was triggered by immersing the Ag NW electrodes into an aqueous solution bath containing 20 mM PVP and 0.5 mM $FeCl_3$ at room temperature. Fe^{3+} ions oxidize the Ag NWs to produce AgCl nanoparticles, driven by the reduced redox potential of the Ag/AgCl couple. The extent of chloridization was precisely controlled by varying the immersion time. After the desired reaction period, the electrodes were thoroughly rinsed with deionized water and dried in an oven at 60 °C.

Preparation of Reference Membranes

The PVB-based reference membrane was prepared using a solution casting method. First, 0.2 mg of MWCNTs and 2 mg of F127 were dispersed in 1 mL of methanol via probe ultrasonication for 10 minutes. This dispersion was then transferred to a round-bottom flask, followed by the addition of 79.1 mg of PVB and 50 mg of NaCl. The mixture was vigorously stirred on a hot plate at 45 °C for 12 h to ensure complete dissolution. The resulting viscous cocktail was subsequently cast onto a substrate and dried to form the PVB reference membrane. For the TPU-based reference membranes, 0.016 g of CNTs and 0.008 g of a dispersant were added to 26 g of DMSO. After probe sonication for 10 min, 4.2 g of TPU, 5 g of KCl, and 3.49 g of DOS were incorporated. The mixture was ball-milled for 5 h to achieve a homogeneous dispersion. Subsequently, 16 g of methanol was added, and ball milling was continued for another 5 h. The final cocktail dispersion was drop-cast onto an octadecyltrichlorosilane-modified, non-sticky glass wafer and dried at 50 °C to form the TPU reference membrane. This membrane was readily laminated onto the target electrodes at an elevated temperature of 100-120 °C.

Fabrication of the Sweat Sensing Patch

The sensing patch was fabricated on a TPU elastomer substrate. First, silver nanowires (Ag NWs) were spray-deposited onto the substrate through a shadow mask to define the sensing electrodes and electrical interconnects. The entire substrate was then immersed in an aqueous $FeCl_3$/PVP reaction bath for in situ oxidation. A prefabricated TPU-based reference membrane was laminated onto a designated electrode to establish a solid-state reference electrode. A thin TPU encapsulation layer was applied over the electrical interconnects for insulation and encapsulation. A hydrophilic textile layer was placed on top of the electrodes to facilitate continuous sweat uptake. Finally, an adhesive top layer with a skin-compatible interface was used to secure the textile and enable conformal attachment of the patch to the skin. This adhesive consisted of 72.5 wt% styrene-isoprene-styrene (SIS), 27.5 wt% terpene resin/hydrogenated resin (10:3 mixture).

Material Characterization

Scanning electron microscopy (SEM) images were acquired using a Zeiss GeminiSEM 500 field emission scanning electron microscope. Electrical resistance was measured using a Keithley 2110 digital multimeter in a four-probe configuration. Tensile strains were applied using a custom-built motorized translational stage. To highlight changes during stretching, the measured resistance was normalized to its value in the relaxed state (R/R_0). Tensile stress-strain curves were measured using a Shimadzu AGS-X universal testing machine equipped with a 50 N load cell. The TPU reference membrane for mechanical testing was fabricated by spray coating to achieve a thickness of approximately 155 μm, which was then laser cut into rectangular specimens with a length of 20 mm and a width of 5 mm.

Electrochemical Measurements

All electrochemical measurements were performed using a ChenHua electrochemical workstation (Shanghai, China). The electrochemical performance of the prepared electrodes was evaluated by measuring open circuit potentials in a two-electrode configuration. A commercial Ag/AgCl electrode (with saturated KCl) was employed as the reference electrode. All measurements were carried out at room temperature under continuous magnetic stirring. Each test began with a 10 mM NaCl solution, and the OCP was recorded continuously in real time. After the baseline stabilized, appropriate volumes of a 2 M NaCl stock solution were successively added to increase the chloride ion concentration stepwise to 20, 40, 80, and 160 mM. The potential was recorded continuously throughout the entire process without interruption, yielding a complete potential–time response curve. Artificial sweat was formulated according to a previously reported procedure to achieve a standard chloride ion concentration of 50 mM.

On-Body Sweat Chloride Analysis

On-body sweat analysis was performed with healthy human subjects following written informed consent. The skin area (e.g., the back of the neck) was cleansed with alcohol swabs prior to patch attachment. The sensing patch was conformally attached to the skin and connected to the electrochemical workstation for real-time open circuit potential measurements. Subjects were asked to perform stationary cycling to induce perspiration. Once sweat accumulation provided a stable ionic bridge between the electrodes, real-time potential data were recorded. Sweat chloride concentrations were subsequently determined based on the pre-established calibration curves.

Supporting Figures

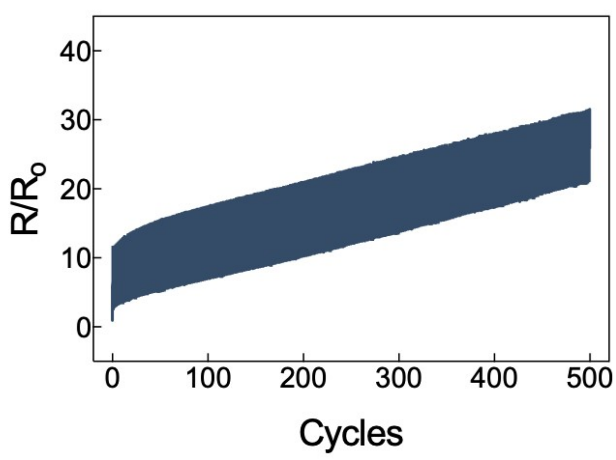

Figure S1. Normalized resistance of an Ag NW/AgCl nanoparticle electrode (reacted to R/R_{Ag} = 2) over 500 stretching cycles to 30% strain. The finite increase in resistance suggests its durability for long-term use.

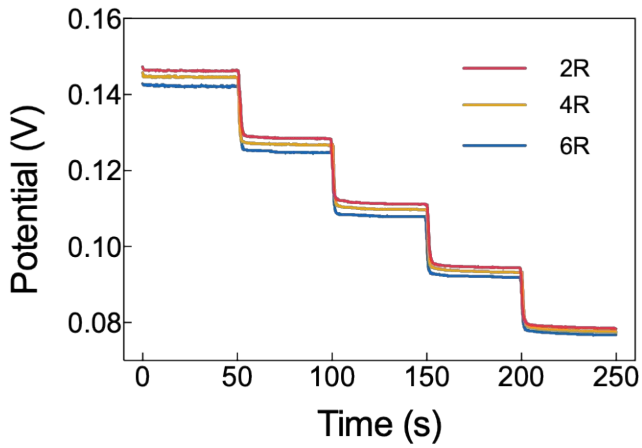

Figure S2. Influence of reaction degree on Cl^- sensing performance. Open circuit potential responses to stepwise increases in Cl^- concentration. All three sensing electrodes show similar sensitivity, despite minor variations in the potential.

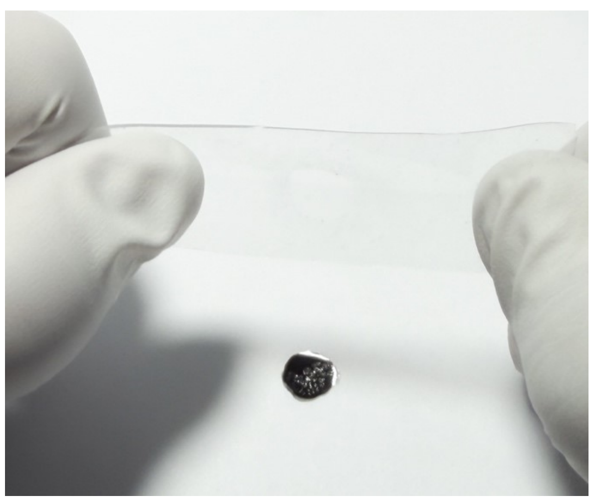

Figure S3. Delamination of the PVB reference membrane. Optical image showing the PVB membrane detaching from the TPU substrate during mechanical deformation, indicating poor interfacial adhesion and mechanical incompatibility with the stretchable substrate.

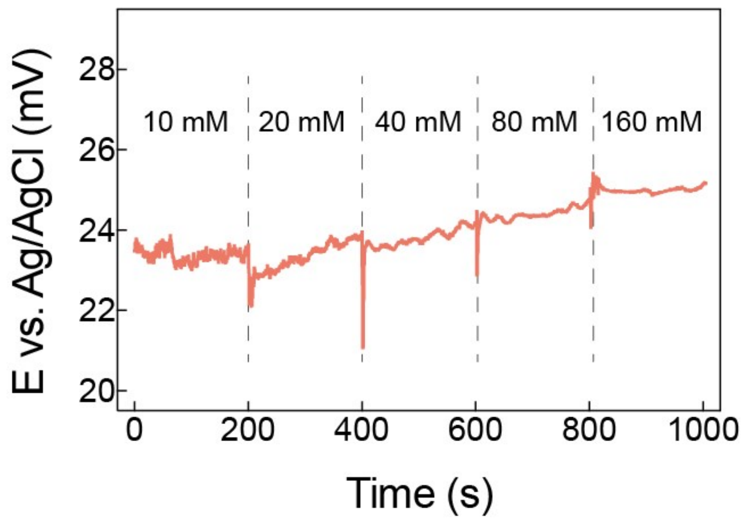

Figure S4. Open-circuit potential response of the PVB-based reference electrode (vs. a commercial Ag/AgCl reference electrode) to stepwise changes in Cl^- concentration.

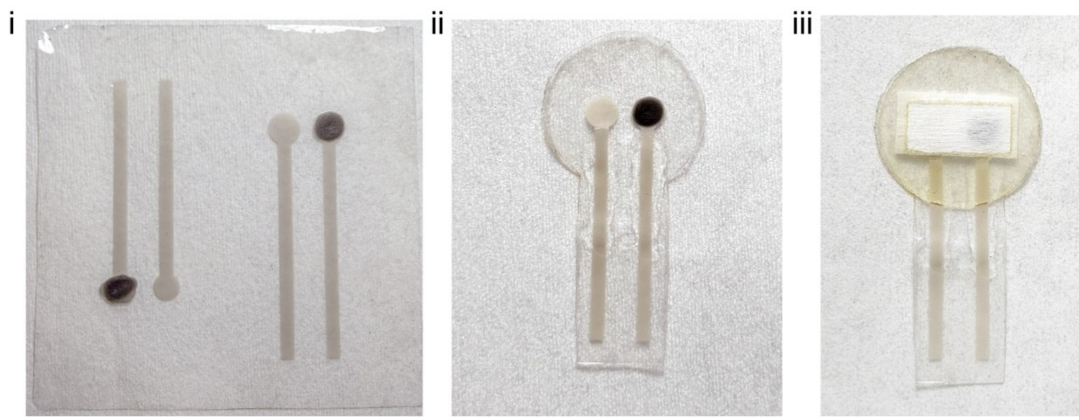

Figure S5. Critical fabrication steps of the sensing patch device. (i) Preparation of the sensing electrodes on the elastomer substrate. (ii) Laser cutting of the patch outline. (iii) Attachment of a sweat-wicking textile and adhesive layer to complete the device.

Figure S6. Optical images demonstrating the reliable adhesion of the patch device to the skin, enabled by the adhesive layer.

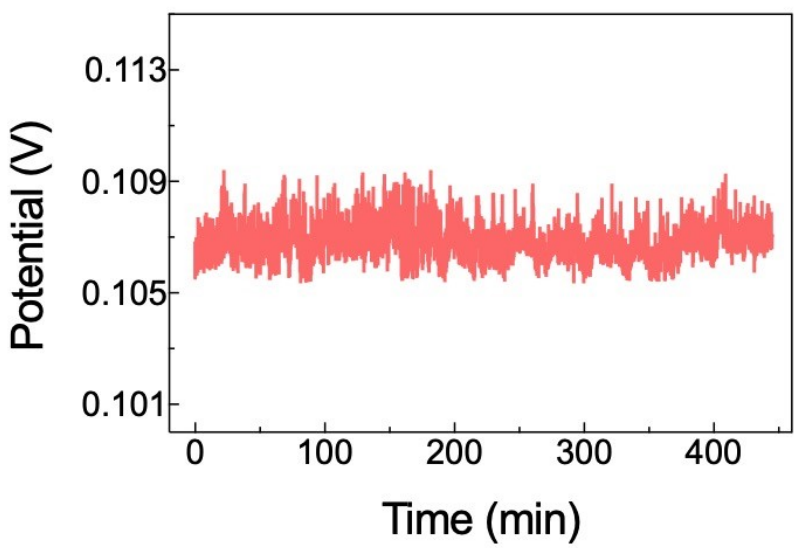

Figure S7. Open-circuit potential profile of a representative sensing patch device in artificial sweat containing 50 mM Cl^- over 420 minutes, exhibiting low drift and demonstrating excellent long-term stability. The chloride concentration extracted from this artificial sweat was determined to be 52.7 ± 1.4 mM based on measurements from multiple sensing patches (n = 5), confirming the reliability of the patches for chloride ion determination.

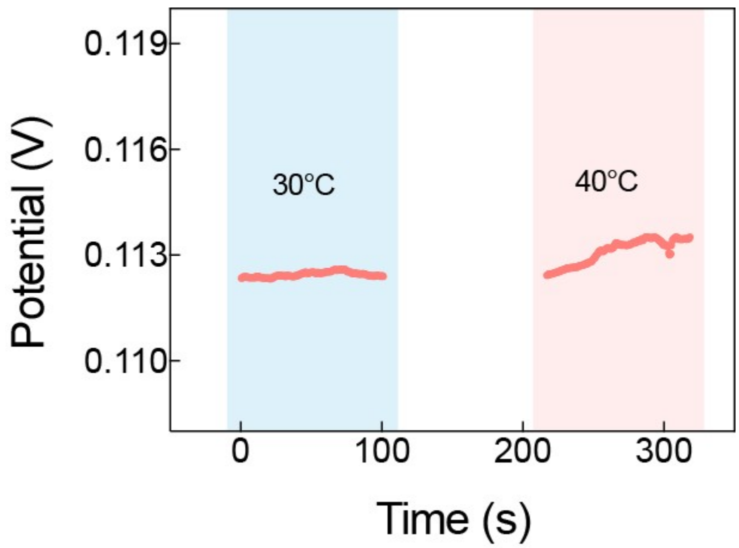

Figure S8. Open circuit potential of a sensing patch device measured at 30 and 40 °C, revealing a minor drift associated with temperature. The results suggest that the temperature influence is rather weak for wearable applications.