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ABSTRACT: Achieving high-performance epidermal electrodes for long-term electrophysiological monitoring remains a significant challenge, as it necessitates a delicate balance between high electrical conductivity, optical transparency, mechanical compliance, and environmental stability within a single platform. Herein, we present a multifunctional epidermal bioelectrode (silk/Ag@Au BioE) fabricated by combining a silver-gold core-sheath nanowire (Ag@Au NW) network with a silk fibroin (SF) substrate via direct ink writing and solution-casting transfer techniques. The resulting electrode exhibits superior optical transmittance (up to 94.3%) and a low sheet resistance of 10.9 Ω/sq . A unique hydration-induced plasticization is employed to transform the initially rigid SF film into an ultra-soft, conformal skin interface. This process induces the spontaneous formation of micro-wrinkled architectures, which, in synergy with a meticulously designed second-order serpentine mesh, imparts exceptional omnidirectional stretchability and robust mechanical durability. The electrode also demonstrates high breathability (1591 $\text{g}/(\text{m}^2 \cdot \text{day})$), excellent resistance to sweat and oxidation, and sustainable reusability over multiple hydration-dehydration cycles. This integrated design enables high-fidelity, long-term monitoring of electrocardiogram (ECG), electromyogram (EMG), and electrooculogram (EOG) signals under dynamic and harsh conditions, substantially outperforming conventional Ag/AgCl electrodes. This work provides a versatile and robust material platform for next-generation wearable healthcare diagnostics.

KEYWORDS: epidermal electronics, silk fibroin, Ag@Au nanowire, stretchable, transparent.

1 Introduction

The rise of the Internet of Everything and the surging demand for personalized healthcare have catalyzed significant advancements in flexible electronics [1-6]. Within this field, the development of high-performance epidermal electronic devices is of pivotal importance for applications such as continuous health monitoring, motion rehabilitation, and human-machine interaction. These devices serve as a fundamental interface for acquiring high-fidelity electrophysiological signals, including electrocardiogram (ECG), electromyography (EMG), electrooculography (EOG), and electroencephalography (EEG) [7, 8]. An ideal epidermal electrode must establish a conformal, stable, and imperceptible interface with the soft, dynamic, and irregular topography of human skin [9-13]. This necessitates a synergistic integration of multiple functionalities: high electrical conductivity for sensitive signal acquisition, optical transparency for visual aesthetics, omnidirectional stretchability to accommodate complex body deformations, and sufficient breathability for long-term wearing comfort. Furthermore, excellent environmental stability, particularly resistance to sweat and oxidation, and reusability are essential to enhance practicality and cost-effectiveness. However, conventional Ag/AgCl gel electrodes, despite their

widespread clinical use, suffer from several inherent limitations, including poor breathability leading to skin irritation, signal degradation in humid/sweaty environments, and mechanical rigidity that causes detachment during body motion [14, 15]. These drawbacks underscore a critical challenge in developing a novel epidermal electrode that seamlessly reconciles these often-conflicting properties through integrated design strategies that transcend single-material modification or simple structure engineering [16, 17].

In the fabrication of flexible electrodes, the substrate serves as the mechanical backbone and dictates the interfacial compatibility. Commonly used elastomers, such as polydimethylsiloxane (PDMS), offer adequate stretchability but typically lack sufficient gas permeability, resulting in physiological discomfort [18, 19]. Consequently, there is an urgent need for skin-like substrates that balance functionality with wearability. Silk fibroin (SF), a natural biopolymer, has emerged as a compelling candidate due to its excellent biocompatibility, tunable mechanical properties, and intrinsic breathability [20, 21]. Nonetheless, regenerated SF often demonstrates limited stretchability owing to its high crystallinity [22]. To address this, effective plasticization strategies are vital for achieving conformal contact with the epidermis. For instance, in our previous

work, hygroscopic calcium cations (Ca^{2+}) were incorporated into MXene/silk nanocomposite fibers to induce water-mediated plasticization [23]. This approach enables precise modulation of the SF secondary structure, triggering a transition from a rigid β -sheet conformation to a highly deformable random coil under moisture exposure. As a result, the Young's modulus of the silk matrix can be tuned to match that of human skin, ensuring mechanical compliance and robust cutaneous adhesion [24].

Beyond the flexible polymer substrate, the conductive component is equally critical in determining the performance of high-quality electrodes. Among various candidates, one-dimensional (1D) nanomaterials, particularly silver nanowires (AgNWs), are advantageous because they can form dense percolation networks at low loading densities, thereby achieving high electrical conductivity while maintaining superior optical transparency [25, 26]. Moreover, their high aspect ratio and intrinsic flexibility allow for better adaptation to mechanical strain compared to bulk or two-dimensional (2D) counterparts [27-29]. However, the susceptibility of Ag to oxidation and sulfidation, particularly when exposed to human sweat, limits the long-term reliability of AgNW-based devices [30, 31]. To mitigate this, we employ a core-sheath strategy by conformally growing an Au nanolayer on AgNWs, yielding gold-coated silver nanowires (Ag@Au NWs) [32, 33]. This structure preserves the superior conductivity of the Ag core while leveraging the chemical inertness of the Au sheath to provide excellent resistance to corrosive environments, ensuring sustained electrical stability.

Beyond material selection, the rational design of electrode architecture is critical for enhancing stretchability [34]. The plasticization of SF not only facilitates conformal contact with skin but also exploits modulus mismatch to induce beneficial microstructures. When the Ag@Au NWs conductive network is embedded within the SF substrate, the strong interfacial constraint, arising from the significantly higher modulus of the nanowires compared to the softened silk matrix, triggers the spontaneous formation of 3D wrinkled architectures during water-induced plasticization [35]. These wrinkles act as pre-strained buffers that effectively dissipate tensile stress. To further extend the deformation limits, it is necessary to combine these micro-wrinkles with macro-patterned designs. Second-order serpentine structures, which accommodate strain through out-of-plane bending and extension, offer superior stress distribution and omnidirectional stability compared to conventional first-order patterns [36, 37]. Among various patterning techniques, direct ink writing (DIW) is particularly suitable for its operational simplicity, design versatility, and high material utilization, enabling the precise fabrication of complex second-order serpentine patterns [38-40].

Herein, we present a bioelectrode composed of SF and Ag@Au NWs (silk/Ag@Au BioE) fabricated via DIW and solution-casting transfer techniques for multi-scenario electrophysiological monitoring. The electrode exhibits high electrical conductivity with a sheet resistance (R_s) as low as $10.9 \Omega/\text{sq}$ and excellent optical transmittance (up to 94.3%). Benefiting from the synergy between spontaneous micro-

wrinkling and the second-order serpentine network, the electrode demonstrates remarkable omnidirectional stretchability, maintaining stability over 12,000 cycles at 15% tensile strain. The conformal Au sheath ensures durability under extreme conditions, including 90% relative humidity (RH), exposure to sweat, and even immersion in H_2O_2 solution. Moreover, the electrode demonstrates a high moisture vapor transmission rate ($1591 \text{ g}/(\text{m}^2 \cdot \text{day})$) and tunable adhesion for gentle, residue-free removal. When deployed for ECG, EMG, and EOG monitoring, the electrode delivers stable, high-quality signals across various challenging conditions, including sweating and vigorous motion. This work provides an effective material-to-structure design strategy for the next generation of comfortable, durable, and high-performance wearable medical electronics.

2 Experimental

2.1 Materials

Silver nitrate (AgNO_3 , 99.8%), gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, >99.9%), sodium hydroxide (NaOH, 98%), sodium carbonate (Na_2CO_3 , 99%), sodium sulfite (Na_2SO_3 , 98%), and hydrogen peroxide solution (H_2O_2 , 30% w/w in H_2O) were obtained from Shanghai Aladdin Biomedical Technology Co., Ltd. PVP ($M_w = 40,000$) was purchased from Sigma-Aldrich. Formic acid (FA, 99%) was purchased from Beijing J&K Scientific Co., Ltd. Sodium bromide (NaBr, 99%), ethylene glycol (EG, 98%), sodium alginate (SA, 1000-1200 mPa·s), calcium chloride (CaCl_2 , 99.9%), and polyvinylpyrrolidone (PVP, $M_w = 1,300,000$) were obtained from Shanghai Macklin Biochemical Co., Ltd. PVP ($M_w = 55,000$) was purchased from Shanghai Yuanye Biotechnology Co., Ltd. L-ascorbic acid (L-AA, $\geq 99.7\%$) was purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used as received without further purification.

2.2 Preparation of Silk/ Ca^{2+} /FA Solution

Bombyx mori cocoons were first degummed by boiling in an aqueous solution of Na_2CO_3 (0.02 M) for 30 min to remove sericin. The degummed SF was then thoroughly rinsed with pure water three times (30 min per rinse) to eliminate residual Na_2CO_3 . After rinsing, the SF was allowed to dry naturally in the air. Subsequently, a solvent system was prepared by dissolving 1.8 g of CaCl_2 in 20 g of FA. 3 g of degummed SF was added to the FA/ CaCl_2 solution. The mixture was subjected to stirring and ultrasonication for 1 h, followed by centrifugation at 9000 rpm for 20 min to remove insoluble materials. A silk/ Ca^{2+} /FA solution was finally prepared.

2.3 Preparation of the DIW Ink

The aqueous Ag@Au NWs dispersion, synthesized according to our group's previously reported method [41, 42], was concentrated to 22 mg/mL and ultrasonicated prior to use to ensure homogeneity. The DIW ink was composed of 2 wt.% Ag@Au NWs and 0.5 wt.% SA, and was formulated by mixing a certain amount of 6 wt.% SA aqueous solution, the above Ag@Au NWs dispersion, and deionized water using a mixer (Vortex-Genie 2, USA).

2.4 Preparation of Silk/Ag@Au BioEs

The preparation involved a four-step process: (1) The as-

formulated ink was first printed onto a PET film (thickness: $\sim 38\ \mu\text{m}$) using a robotic deposition system (Nordson EFD, model E2V). The printing was performed with a nozzle inner diameter of $50\ \mu\text{m}$, printing speed of $5\text{--}12.5\ \text{mm/s}$, applied pressure of 6 psi, and needle-to-substrate distance of $80\ \mu\text{m}$. (2) The printed pattern was immersed in artificial sweat ($\text{pH} = 4.7$) for 10 min for post-treatment, followed by rinsing with water and drying. (3) A silk/ Ca^{2+} /FA solution was then cast onto the patterned PET substrate. The sample was dried at $70\ ^\circ\text{C}$ to facilitate the evaporation of FA. After complete evaporation, the silk film, along with the Ag@Au NWs pattern, could be peeled off from the PET substrate. (4) The resulting device was initially rigid but was subsequently plasticized under 60% RH to obtain the final skin-conformal silk/Ag@Au BioEs.

2.5 Environmental Stability Testing of Silk/Ag@Au BioEs

To evaluate environmental stability, both silk/AgNWs and silk/Ag@Au NWs electrodes were fabricated using the same method and cut into samples of identical dimensions. Copper wires with insulation coating were attached to both ends of each electrode and secured using silver paste. After curing, the connection regions were encapsulated with silicone rubber to prevent external interference. For the humidity corrosion test, the two types of electrodes were placed in an environmental chamber maintained at 90% RH, and their electrical resistance was monitored daily. Similarly, to assess chemical stability, the electrodes were immersed separately in artificial sweat ($\text{pH} = 4.7$) and a 5 wt.% H_2O_2 solution, with resistance changes monitored over time to evaluate the impact of each condition on electrode performance.

2.6 Permeability Test

The moisture vapor transmission rate was measured by sealing the identically fabricated electrodes onto bottles containing equal amounts of pure water, with Parafilm ensuring an airtight seal, after which the weight loss was monitored through daily measurements.

2.7 Characterization

The morphology and microstructure of the samples were analyzed using scanning electron microscopy (SEM, SU-8000, Hitachi, Japan), transmission electron microscopy (TEM, HT7700, Hitachi, Japan), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, JEM-F200, JEOL, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS). Chemical bonding information was obtained using Fourier-transform infrared (FTIR, Nicolet 6700, Thermo Scientific, USA) with an attenuated total reflection (ATR) accessory. Optical transmittance was measured with an ultraviolet-visible spectrophotometer (UV-vis, Lambda 35, PerkinElmer, USA). The sheet resistance of the electrodes was measured using a digital source meter (Keithley 2450, Tektronix, USA) linked with a four-probe clamp. The tensile tests were performed on the tensile testing machine (ESM 303, Mark-10, USA) at a tensile speed of $10\ \text{mm/min}$. The impedance spectra were acquired using an impedance analyzer (TH2829C, Tonghui, China) over a frequency range from 20 to $1,000\ \text{Hz}$. Biosignal acquisition, including EMG, ECG, and EOG, was carried out with a biosignal acquisition system (BL-420N, Chengdu Taimeng Technology, China). For EMG, three electrodes were attached to the subject's forearm surface, and the subject performed

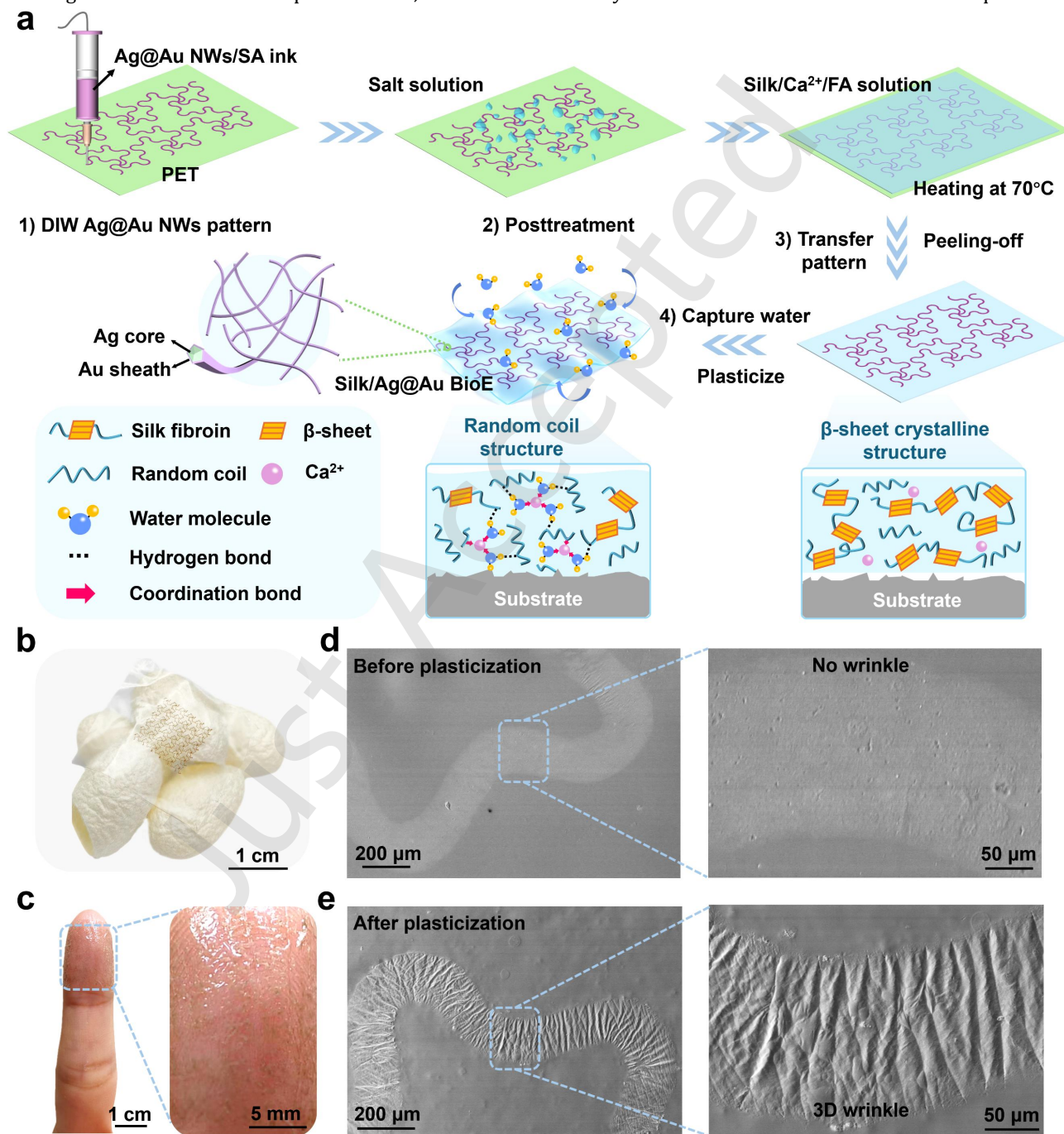
hand movements to trigger muscle activity, with the system synchronously recording the EMG signals at a sampling rate of $2\ \text{kHz}$, a low-pass filter of $100\ \text{Hz}$, and a $50\ \text{Hz}$ notch filter enabled. For ECG, two electrodes were attached to the subject's bilateral wrists with a reference electrode placed on the forearm, and the system recorded ECG signals under different conditions at a sampling rate of $2\ \text{kHz}$, a low-pass filter of $40\ \text{Hz}$, and a $50\ \text{Hz}$ notch filter enabled. For EOG, two electrodes were placed above and below the subject's unilateral eye socket with a reference electrode behind the ear, and the subject performed specific eye movements while the system synchronously recorded the resulting EOG signals at a sampling rate of $2\ \text{kHz}$, a low-pass filter of $100\ \text{Hz}$, and a $50\ \text{Hz}$ notch filter enabled. In addition, to simulate the sweat environment encountered in practical use, artificial sweat was uniformly sprayed onto the skin surface of the electrode attachment area using a sprayer. After forming a stable moist environment, the same signal acquisition procedure was repeated to compare the performance of the electrodes under dry and simulated sweat conditions. All human subject studies were approved by the relevant ethics committee, and written informed consent was obtained from each participant prior to testing. No adverse physical or psychological effects were reported by any volunteer during the experiments.

3 Results and discussion

Figure 1 illustrates the fabrication process and structural characterization of the silk/Ag@Au BioEs for wearable electrophysiological monitoring. The Ag@Au NWs were synthesized by depositing Au atoms onto pre-synthesized AgNWs using a previously reported method, resulting in a double-headed matchstick-like morphology encapsulated by a conformal and dense Au sheath (Figure S1, Supporting Information) [41]. The epitaxial growth of the Au sheath was rigorously confirmed by UV-vis spectroscopy, SEM, and TEM (Figures S2 and S3, Supporting Information). The deposition process increased the average nanowire diameter from $25.6 \pm 4.3\ \text{nm}$ to $34.1 \pm 3.7\ \text{nm}$, corresponding to an Au sheath thickness of approximately $4\ \text{nm}$. High-resolution transmission electron microscopy (HRTEM), HAADF-STEM, and EDS elemental mapping clearly resolve the well-defined core-sheath structure, distinguishing the chemically inert Au sheath from the Ag core (Figure S4, Supporting Information). The fabrication of the silk/Ag@Au BioEs, as depicted in Figure 1a, involves a high-precision transfer of DIW patterns onto a SF substrate through a four-stage process: (1) A second-order serpentine conductive network is patterned on a polyethylene terephthalate (PET) temporary carrier using Ag@Au NWs/SA ink via DIW technology. (2) The patterned electrode is immersed in standardized artificial sweat ($\text{pH} = 4.7$) to facilitate junction welding and reduce contact resistance. (3) Degummed silk cocoons are dissolved in a FA/ Ca^{2+} solution (Figure S5, Supporting Information) and coated onto the patterned PET. Upon the complete evaporation of FA at $70\ ^\circ\text{C}$, the resulting silk film, initially dominated by a crystalline β -sheet secondary structure, spontaneously delaminates from the PET due to its inherent rigidity and poor interfacial adhesion. (4) The brittle silk/Ag@Au BioE is plasticized by leveraging the

hygroscopic nature of Ca^{2+} ions, which can coordinate with up to eight water molecules from the ambient environment [43]. These highly polar water molecules preferentially form hydrogen bonds with the peptide backbone ($\text{C}=\text{O}$, $\text{N}-\text{H}$, $-\text{OH}$), effectively displacing the original intermolecular hydrogen bonds within the β -sheet domains [35]. This process diminishes interchain cross-linking and induces a conformational transition to highly disordered and extensible random coils. Figure 1b displays an optical image of the self-standing silk/Ag@Au BioE after delamination, while Figure 1c demonstrates its conformal adhesion to a human finger after water-induced plasticization, where the

surface appears relatively smooth in its pristine stage (Figure 1d), it develops pronounced 3D micro-wrinkles specifically located within the nanowire-incorporated regions after plasticization (Figure 1e). This phenomenon is ascribed to the in-plane volumetric expansion driven by the conformational transition of SF's secondary structure from β -sheets to random coils. While the pure SF domains expand unimpeded, the nanowire-incorporated regions experience substantial confinement stress due to the strong interfacial bonding between the Ag@Au NWs and the silk matrix and the resulting significant modulus mismatch. Consequently, the system achieves a new mechanical equilibrium by



electrode intricately maps the underlying fingerprint contours. Intriguingly, the electrode exhibits distinct morphological evolution during the plasticization: while the Figure 1 (a) Schematic of the fabrication of the silk/Ag@Au BioEs. (b) Optical image of a silk/Ag@Au BioE (thickness: 60 μm) placed on silkworm cocoons. (c) Optical images of a silk/Ag@Au BioE conformally attached to the finger skin surface. (d, e) SEM images of silk/Ag@Au BioEs before and after plasticization.

releasing internal stress through the spontaneous formation of the micro-wrinkles.

The SF films function as the structural scaffold for the silk/Ag@Au BioEs. By modulating the casting volume of the silk/Ca²⁺/FA solution, the electrode thickness could be precisely controlled within a range of 20 to 100 μm (Figure 2a). High optical transparency is a critical attribute for epidermal electronics, as it ensures seamless integration with the user's skin tone and minimizes visual conspicuousness. As shown in Figure S6 (Supporting Information), all SF films maintained a high transmittance between 82.9% and 87.8% across varying CaCl₂ contents. Notably, the transmittance decreased with reduced CaCl₂ contents, which is attributed to enhanced light scattering from enlarged crystalline domains (composed of β -sheets) that act as scattering centers under calcium-deficient conditions [44]. After plasticization, the structural transition from β -sheets to random coils significantly suppressed scattering and improved transparency. The film with 70 wt.% CaCl₂ achieved an impressive transmittance of 90.26%. The moisture-harvesting capability of the SF films (Figure S7, Supporting Information), driven by the hygroscopic nature of Ca²⁺ cations, could further enhance the secondary structural reorganization. The Ca²⁺-mediated regulation of the secondary structure was elucidated by X-ray diffraction (XRD) and FTIR spectroscopy. XRD patterns (Figure S8, Supporting Information) reveal a characteristic broadening of the β -sheet crystalline diffraction peak (20–30°) with the increase of the Ca²⁺ concentration, signifying a reduction in crystallinity and a concomitant rise in random coil content. In FTIR spectra (Figure 2b), the amide I (C=O stretching) and amide II (N-H bending) bands display blue shifts from 1619.9 and 1515.8 cm^{-1} to 1637.3 and 1542.8 cm^{-1} , respectively. These shifts are primarily attributed to Ca²⁺-coordinated water molecules disrupting the intermolecular hydrogen bonding within β -sheets, thereby promoting a crystalline-to-amorphous transition. Concurrently, the emergence and intensification of O-H stretching vibrations at 3365.2 cm^{-1} with higher Ca²⁺ concentrations confirm the capture of atmospheric water molecules. Meanwhile, the introduction of Ca²⁺ enables precise tuning of mechanical properties, transforming the SF films into soft substrates compatible with human skin. At 60% RH, increasing the CaCl₂-to-silk weight ratio from 20 wt.% to 70 wt.% resulted in a dramatic increase in tensile strain, from 12.32% to a remarkable 3030%, while the Young's modulus plummeted from 3798 MPa to 58.1 kPa (Figure 2c, d). Although the film containing 70 wt.% CaCl₂ exhibits the lowest Young's modulus, its mechanical strength is somewhat compromised. In contrast, the one with 60 wt.% CaCl₂ demonstrates an optimal balance: a tensile strength of 0.1 MPa, an elongation at break of 2878.8%, and a Young's modulus of 126.1 kPa. Notably, this Young's modulus is very close to the reported modulus range of human epidermis (140–600 kPa) [45]. Beyond bulk mechanical properties, the plasticization-induced random coil conformation imparts the SF film with excellent interfacial adhesion. As shown in Figure S9 (Supporting Information), the plasticized film exhibits conformability to porcine skin. Quantitative lap-shear tests

(Figure 2e) were conducted to evaluate the adhesion strength to various substrates. The results are 0.26 MPa to glass, 0.12 MPa to Fe, 0.11 MPa to Al, 0.08 MPa to polytetrafluoroethylene (PTFE), and 0.14 MPa to porcine skin. Collectively, these properties underscore the mechanical matching and robust adhesion between the bioelectrode and biological tissues, establishing the material as a promising candidate for epidermal electronics.

By controlling the DIW parameters and printing trajectories, conductive networks with tailorable geometric configurations, including pattern layouts (e.g., serpentine) and line widths (ranging from 85 to 250 μm), were fabricated on PET temporary substrates. These networks were subsequently transferred onto the SF films via a solution-casting method without compromising the structural integrity of the conductive pathways (Figures 2f–i, Figures S10, S11, Table S1, Supporting Information). To enhance charge transport, a salt-solution-assisted welding strategy was employed, enabling the Ag@Au NWs network to achieve a superior electrical conductivity of $2.1 \times 10^6 \text{ S/m}$ (Figure 2j). This performance enhancement is attributed to two synergistic mechanisms that effectively minimize NW-NW junction resistance. First, the artificial sweat, serving as a weakly acidic and chloride-rich electrolyte solution, facilitates the dissolution or etching of trace organic residues on the nanowire surfaces via the combined action of Cl[−] and H⁺ ions [46]. The acidic environment triggers the protonation of the pyrrolidone groups in PVP, which improves its hydrophilicity and facilitates its desorption from the NW surfaces. This process thins the insulating PVP layer, thereby reducing the interfacial tunneling barrier (Figure S12, Supporting Information). Second, capillary-force-induced cold welding occurs at room temperature (RT), wherein the Laplace pressure generated by the surface tension of evaporating solvent droplets drives the spontaneous fusion of NW-NW junctions (Figure S13, Supporting Information) [47]. In addition, the thermal conditions during the curing of the SF film play a critical role in the electrical performance. As shown in Figure 2k, curing the SF solution at RT led to a significant increase in the resistance of the Ag@Au NWs conductive network. In contrast, curing at 70 °C resulted in a negligible change in resistance (only a ~5% increase) before and after the transfer process. This disparity is governed by the interfacial infiltration kinetics of the SF macromolecular chains [48]. Prolonged curing at RT allows the polymer chains to penetrate deeply into the interstitial voids of the NW network, which disrupts the conductive junctions and increases electrical resistance. Conversely, accelerated thermal curing at 70 °C rapidly increases the matrix viscosity, effectively inhibiting polymer chain infiltration and thus maintaining the electrical pathways (Figure 2l). Additionally, the hydration-mediated plasticization induced by Ca²⁺ ions was found to have a negligible impact on the resistance of the silk/Ag@Au BioEs, ensuring stable electrical performance during subsequent skin-interfacing applications (Figure S14, Supporting Information).

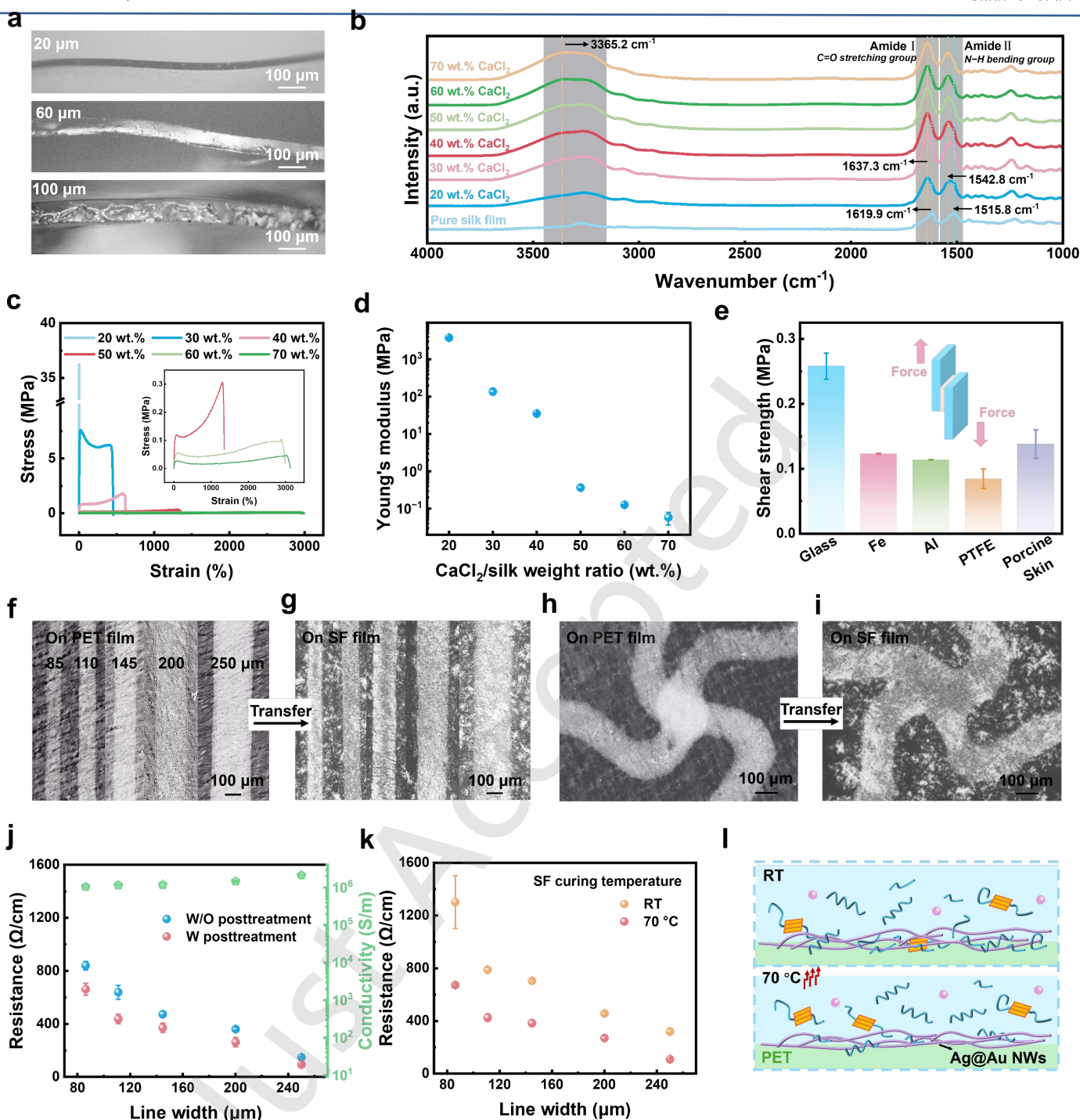


Figure 2 (a) Cross-sectional optical microscopy images of SF films with different thicknesses. (b) FTIR spectra, (c) stress-strain curves, and (d) Young's modulus of SF films with various CaCl_2 weight ratios measured at 60% RH. (e) Adhesion strength of the SF films with 60 wt.% CaCl_2 to different substrates at 60% RH. (f, g) Optical microscopy images of silk/Ag@Au BioEs with varying linewidths on PET and after transfer onto the SF substrate. (h, i) Optical microscopy images of serpentine silk/Ag@Au BioEs on PET and following transfer onto the SF substrate. (j) Resistance and conductivity of Ag@Au NWs lines with different widths printed on PET before and after posttreatment with the salt solution. (k) Resistance of Ag@Au NWs conductive lines treated by SF solution and cured at RT versus 70 $^\circ\text{C}$. (l) Schematic illustration depicting the infiltration of SF molecules into the Ag@Au NWs conductive network under RT and 70 $^\circ\text{C}$ curing conditions.

The geometric configuration of a stretchable electrode is a deterministic factor in its overall stretchability. Among various architectural designs, the serpentine structure is widely employed for its ability to convert global tensile strain into localized bending and twisting, thereby mitigating stress concentrations [34, 49]. As illustrated in Figure 3a, upgrading from a conventional first-order to a

second-order serpentine pattern significantly extends the effective deformable path, providing a higher degree of structural freedom for strain dissipation. The fabricated second-order serpentine silk/Ag@Au BioEs, across various line widths, consistently exhibited high optical transmittance (>80%, up to 94.3%) and a low sheet resistance (down to 10.9 Ω/sq , Figure 3b). Notably, the stretchability of the

electrodes scaled positively with line width (Figure 3c). A comparative analysis confirmed that the second-order pattern achieved enhanced mechanical compliance over its first-order counterpart (Figure 3d). To elucidate the underlying mechanism of resistance stability, the microstructure evolution under controlled strain was characterized via SEM (Figure S15, Supporting Information). A stark contrast was observed: the first-order serpentine pattern developed transverse microcracks at 50% strain, whereas the second-order pattern accommodated the deformation through the graceful unfolding of micro-wrinkles without evidence of structural fracture.

In practical applications, epidermal electrodes are inevitably subjected to unpredictable, multi-directional deformation. Therefore, omnidirectional electromechanical stability is crucial for acquiring stable physiological signals during body movement. To evaluate this key property, the resistance of the silk/Ag@Au BioEs was systematically tested under uniaxial stretching along three different directions. The electrode demonstrated remarkable consistency across all directions, with a relative resistance change ($\Delta R/R_0$) ranging from 16.3% to 22.6% at 30% strain, which corresponds to the typical stretching requirements of human skin (~30%) (Figure 3e) [50]. Furthermore, the electrode successfully endured 12,000 stretching cycles at 15% strain with a modest resistance increase of only ~25% (Figure 3f). To further assess the performance under more complex

deformation, equibiaxial stretching was performed. When subjected to 30% equibiaxial strain along two distinct axes (0° and 45°), the R_s remained remarkably stable, with the total change staying below 1.5-fold (Figure 3g). Moreover, orthogonal biaxial stretching across four measured axes yielded nearly identical resistance profiles, confirming the isotropic electromechanical properties inherent in the second-order design (Figure 3h). Beyond simple elongation, an epidermal electrode attached to the skin may also experience compression or twisting. The interfacial impedance between the electrode and the skin, along with the electrode's electrical performance, remained stable throughout these deformations (Figures 3i and 3j). Finally, the practical robustness of the silk/Ag@Au BioE was demonstrated by mounting an integrated LED-electrode system onto a balloon. As the electrode was subjected to dynamic, omnidirectional, and non-planar strains during the inflation and deflation cycles, the LED maintained stable illumination (Figure 3k). This exceptional working stability arises from the synergistic effect between the electrode's spontaneous micro-wrinkling structure and second-order serpentine network, a unique combination that effectively accommodates large complex deformations, preserves uninterrupted conductive pathways, and imparts outstanding mechanical resilience to the electrode under extreme, real-world dynamic conditions.

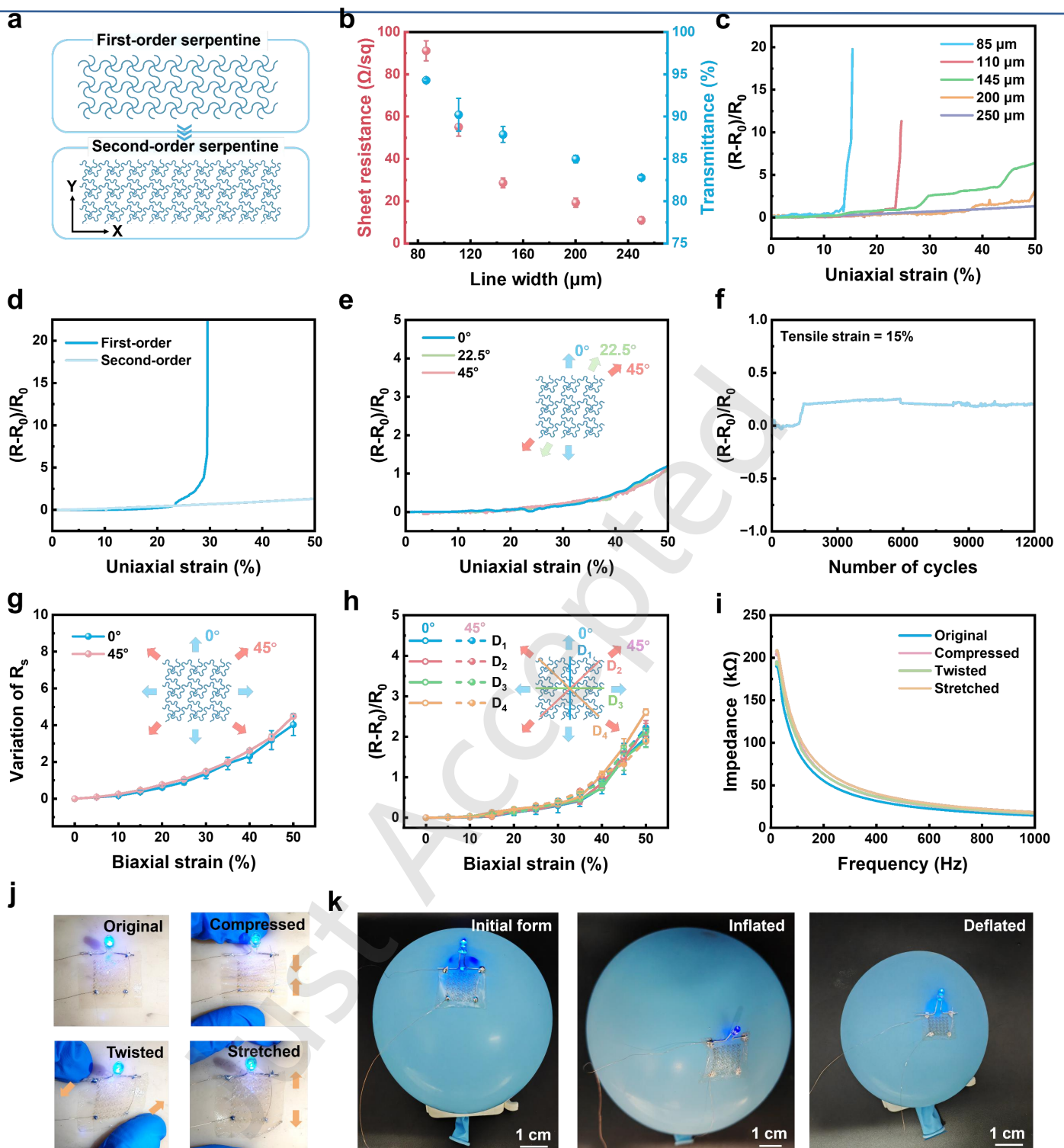


Figure 3 (a) Schematic diagrams of first-order and second-order serpentine structures. (b) Sheet resistance and transmittance of second-order serpentine-patterned silk/Ag@Au BioEs as a function of line widths. (c) Resistance changes of second-order serpentine-patterned silk/Ag@Au BioEs with different line widths under uniaxial stretching along the Y-axis. (d) Comparison of resistance changes between first-order and second-order serpentine-patterned silk/Ag@Au BioEs under uniaxial stretching along the Y-axis. (e) Resistance changes of one second-order serpentine-patterned silk/Ag@Au BioE under uniaxial stretching in different directions. (f) Cyclic stability of resistance variation of the silk/Ag@Au BioE under repeated 15% tensile strain. (g) Changes in sheet resistance of the silk/Ag@Au BioEs during equibiaxial tensile tests. (h) Resistance changes in four different axial directions (D_1 - D_4) during equibiaxial tensile testing. (i) Impedance of the silk/Ag@Au BioE under various skin deformations. (j) Electrical performance of an LED-integrated silk/Ag@Au BioE applied to skin under different deformation conditions. (k) Electrical performance of the silk/Ag@Au BioE under stretching and compression when attached to a balloon.

The sustainability and operational cost-efficiency of epidermal electronics are heavily dependent on their recyclability and reusability. The silk/Ag@Au BioEs enables on-demand detachment from the skin by harnessing the

hydration-dependent secondary structural transitions of the SF film (Figure 4a). In its hydrated (plasticized) state, the electrode maintains strong interfacial adhesion to the skin. Upon dehydration, the electrode preserves its integrity without spontaneous peeling, but it can be completely removed by applying a mild external force (Figure S16, Supporting Information). This reversible adhesion mechanism, governed by the hydration/dehydration cycle, allows the electrode to be reused multiple times. To quantitatively assess the reusability, the electrode was subjected to five full hydration/dehydration cycles. In each cycle, the hydrated film was dehydrated by heating at 75 °C for 10 min, followed by re-hydration under 60% RH. Gravimetric analysis confirmed that the SF film effectively recovered its water content throughout repeated cycles (Figure 4b). Shear adhesion tests on porcine skin revealed that the adhesion strength remained largely unchanged after five cycles (Figure S17, Supporting Information). Crucially, the impact on electrical performance was negligible, with resistance fluctuations no more than 3% (Figure 4c).

The protective efficacy of the Au sheath was investigated by comparing the environmental stability of the silk/Ag@Au NWs electrode against the silk/AgNWs electrode. Since hydration is essential to activate the electrode's excellent stretchability and adhesion, its long-term stability under high humidity (90% RH) is critical. As shown in Figure 4d, the resistance of the silk/AgNWs electrode increased by 53-fold after a single day, whereas the silk/Ag@Au NWs electrode exhibited only a marginal 1.36-fold increase after seven days. This discrepancy highlights the accelerated oxidation of AgNWs in humid environments, which is effectively suppressed by the inert Au coating. Additionally, skin-interfaced electrodes are prone to electrochemical corrosion from sweat. Given that human sweat is typically neutral to slightly acidic [51], the electrodes were immersed in artificial sweat (pH = 4.7) to simulate real-world conditions (Figure 4e, Figure S18, Supporting Information). While the silk/AgNWs electrode suffered catastrophic degradation (5.6-fold resistance increase within 30 min), the silk/Ag@Au NWs electrode exhibited only a 34.5% increase after 24 h. The electrodes were also challenged with an H₂O₂ solution to simulate extreme oxidation (Figure 4f, Figure S19,

Supporting Information). Due to the high oxidative susceptibility of silver, the silk/AgNWs electrode failed within 5 s. In comparison, the silk/Ag@Au NWs electrode demonstrated excellent resistance to H₂O₂-induced oxidation, as confirmed by SEM characterization. These results underscore the critical role of the Au sheath in ensuring operational robustness of the bioelectrode under harsh physiological and environmental conditions.

The cutaneous biocompatibility and long-term wearing comfort of the epidermal electrode are also crucial for continuous health monitoring. A skin irritation test was conducted by attaching both the silk/Ag@Au BioE and a commercial Ag/AgCl gel electrode to a human forearm (Figure 4g). After 10 h of continuous wear, the silk/Ag@Au BioE elicited no adverse cutaneous reactions. In stark contrast, the commercial Ag/AgCl gel electrode induced visible erythema after 5 h of wearing, likely due to its poor gas permeability, which leads to localized sweat accumulation and subsequent skin irritation. The inclusion of Ca²⁺ ions not only plasticizes the SF matrix but also imparts superior breathability, yielding a high moisture vapor transmission rate (MVTR) of 1591 g/(m²·day) (Figure 4h), which is approximately 3.7 times the water vapor evaporation rate of normal human skin (~432 g/(m²·day)) [52]. This ensures that the silk/Ag@Au BioE does not impede natural thermoregulation or sweat evaporation. Moreover, maintaining strong adhesion in sweat-saturated environments is a significant challenge for wearable sensors. Figure 4i compares the adhesion performance of the two electrodes under dry and perspiring conditions. Although the formation of a liquid interlayer at the interface naturally reduces adhesion for both electrodes, the silk/Ag@Au BioE maintained an adhesion strength of 0.096 MPa under sweating conditions, significantly outperforming the commercial benchmark. In summary, the silk/Ag@Au BioE exhibits a superior performance matrix compared to existing literature results, offering a unique synergy of electrical conductivity, transparency, omnidirectional stretchability, reusability, environmental stability, and high breathability, as detailed in the comparative analysis in Table S2 (Supporting Information).

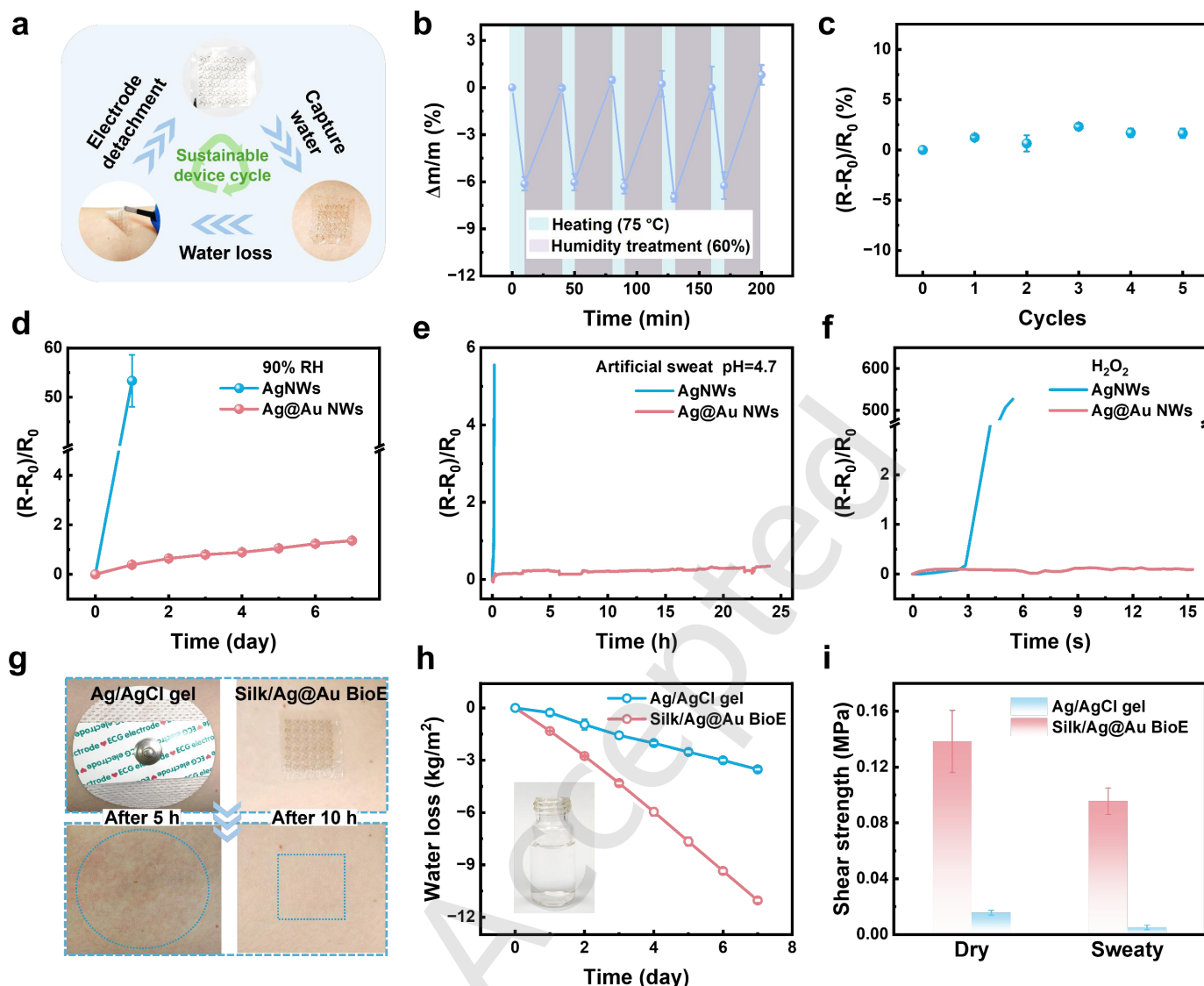


Figure 4 (a) Schematic illustration depicting the reusability of silk/Ag@Au BioEs as wearable electronic devices. (b) Weight changes of SF films during cyclic dehydration (heating at 75 °C for accelerated testing) and rehydration (60% RH). (c) Resistance variation of silk/Ag@Au BioEs during multiple dehydration-rehydration cycles. (d) Long-term resistance stability of the electrodes under static ambient conditions (90% RH, 20 °C). (e) Resistance stability of the electrodes after 24 h of exposure to artificial sweat. (f) The resistance changes upon exposure to H₂O₂ solution. (g) Visual comparison of a commercial Ag/AgCl gel electrode and a silk/Ag@Au BioE attached to skin. (h) Moisture permeability of the silk/Ag@Au BioE and the commercial Ag/AgCl gel electrode. (i) Adhesion strength of the commercial Ag/AgCl gel electrode and the silk/Ag@Au BioE to porcine skin, measured under conditions with and without sweat.

Owing to its superior electromechanical stability and environmental durability, the silk/Ag@Au BioE holds great promise as a high-performance epidermal electronic platform for continuous electrophysiological monitoring (Figure 5a). As shown in Figures 5b and 5c, the electrode was conformally attached to the human forearm to characterize the electrode-skin interfacial impedance over a frequency range of 20 to 1,000 Hz. The silk/Ag@Au BioE exhibited lower impedance than the commercial Ag/AgCl gel electrode under both dry and perspiring conditions. This reduced contact impedance is pivotal for minimizing the noise floor and ensuring high-fidelity electrophysiological recording. To demonstrate its potential for high-performance monitoring, the electrode was rigorously evaluated under various conditions, including dry skin,

sweaty skin, exercising, and skin deformations. First, ECG signals, which are vital for cardiovascular diagnostics, were acquired with the silk/Ag@Au BioE attached to the forearm (Figure 5d). All characteristic P, Q, R, S, and T waves were clearly discernible with a high signal-to-noise ratio (SNR) (Figure S20, Supporting Information). In contrast, the commercial Ag/AgCl gel electrode frequently suffered from interfacial delamination in the presence of sweat, leading to compromised contact and significant signal distortion (Figure 5e). Furthermore, owing to its superior mechanical compliance and adhesion, the silk/Ag@Au BioE maintained stable signal acquisition even during vigorous skin deformation and stretching, effectively suppressing motion artifacts that typically plague wearable sensors (Figure 5f). Subsequently, the silk/Ag@Au BioE was integrated onto the

forearm for high-fidelity EMG signal acquisition (Figures 5g-i). While both the silk-based and commercial electrodes performed comparably on dry skin, the silk/Ag@Au BioE exhibited more stable signal acquisition on sweaty skin, where it maintained its interfacial integrity. Quantitative analysis revealed that the SNR of the silk/Ag@Au BioE consistently surpassed the Ag/AgCl gel electrode across all scenarios, with the most significant advantage observed in perspiring environments (Figure S21, Supporting Information). Furthermore, the silk/Ag@Au BioE demonstrated excellent long-term operational stability during continuous monitoring for up to 10 h (Figure 5j). Throughout this extended period, both the electrode-skin interfacial impedance and the SNR remained stable (Figure S22, Supporting Information). This sustained performance should be attributed to the persistent conformal contact enabled by the plasticized SF substrate. Furthermore, we investigated the resistance stability of the silk/Ag@Au BioE during continuous storage for 5 days at 10 °C and 40 °C, and further recorded EMG signals at three temperatures: 10 °C,

25 °C, and 40 °C. The experimental results demonstrated that the silk/Ag@Au BioE maintained stable resistance characteristics under both high and low temperature conditions, and the recorded EMG signals exhibited clear waveforms and consistent SNRs, without significant performance degradation. Therefore, the electrode shows good applicability within the common environmental temperature range of 10-40 °C (Figure S23, Supporting Information). Moreover, the silk/Ag@Au BioE demonstrated high sensitivity in capturing EOG. When positioned around the eyes, the electrode successfully tracked real-time ocular activities, such as eye closing/opening and directional movements (left/right), with a significantly lower baseline noise compared to the commercial Ag/AgCl gel electrode (Figure 5k and Figure S24 in Supporting Information). These results underscore the significant potential of the silk/Ag@Au BioE for the reliable acquisition of human physiological signals in diverse and dynamic real-world scenarios.

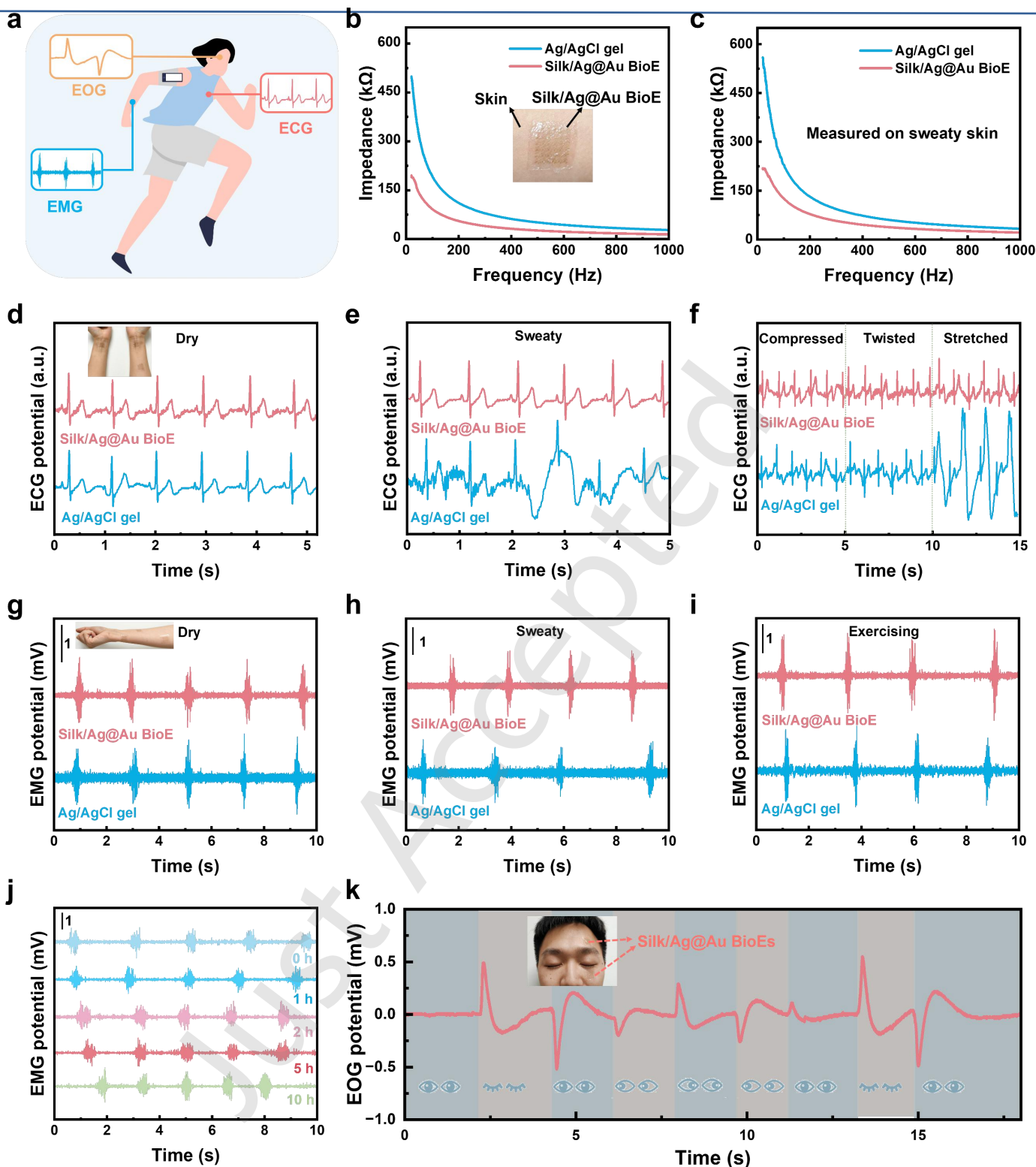


Figure 5 (a) Schematic illustration showing the potential application of the silk/Ag@Au BioE as a skin-conformal electrode for electrophysiological monitoring. (b, c) Electrode-skin interfacial impedance measured on dry forearm skin and sweaty skin. (d-f) ECG signals recorded using the silk/Ag@Au BioE and a commercial Ag/AgCl gel electrode under different skin conditions: dry skin, sweaty skin, and various skin deformations. (g-i) EMG signals recorded by the silk/Ag@Au BioE and the commercial Ag/AgCl gel electrode on dry skin, sweaty skin, and during exercise. (j) EMG signals recorded by the silk/Ag@Au BioE during long-term monitoring. (k) EOG signals recorded by the silk/Ag@Au BioE during eye movements.

4 Conclusion

In summary, we have developed a multifunctional epidermal bioelectrode by integrating an Ag@Au NWs network with a regenerated SF substrate. The resulting silk/Ag@Au BioE simultaneously achieves high electrical conductivity (10.9 Ω/sq), superior optical transparency (94.3%), omnidirectional stretchability, excellent breathability (1591 $\text{g}/(\text{m}^2\cdot\text{day})$), environmental stability, and reusability. The second-order serpentine design of the conductive network, together with the hydration-induced plasticization of the SF substrate, facilitates the spontaneous formation of 3D micro-wrinkled architectures and ensures exceptional mechanical compliance and fatigue resistance (>12,000 cycles). Furthermore, the conformal Au layer of Ag@Au NWs provides robust environmental stability against sweat-induced corrosion and oxidation, while the tunable adhesion of the SF matrix enables residue-free reusability. Therefore, the electrode demonstrated stable, high-fidelity monitoring of ECG, EMG, and EOG signals across diverse dynamic and realistic scenarios, significantly outperforming conventional Ag/AgCl gel electrodes. The material-structure integration strategy can be extended to multimodal wearable systems that combine electrophysiological recording with sweat metabolite sensing or transdermal therapy, and to large-area transparent arrays for high-density electromyography and electroencephalography. The combination of such a breathable, mechanically resilient electrode with wireless electronics holds particular promise for long-term, out-of-clinic cardiac monitoring and neurorehabilitation applications. These concrete directions provide a clear roadmap for translating the current high-performance electrode into a multifunctional, clinically impactful platform for next-generation digital healthcare.

Electronic Supplementary Material: Supplementary material (the preparation and material characterizations of AgNWs and Ag@Au NWs; preparation of the silk/CaCl₂/FA solution; transmittance, water content, and XRD patterns of silk fibroin films with different CaCl₂ weight ratios; SEM image of welded Ag@Au NWs; electrical properties of the silk/Ag@Au BioEs before and after transfer; resistance of silk/Ag@Au BioEs before and after catching water; comparison of SEM morphologies for different patterned silk/Ag@Au BioEs under fixed strain; peeling process of the silk/Ag@Au BioEs; SEM images of AgNWs and Ag@Au NWs after immersion in artificial sweat and H₂O₂ solution; ECG signals recorded by the silk/Ag@Au BioEs; SNR of EMG signals recorded by silk/Ag@Au BioEs and Ag/AgCl gel electrodes; long-term EMG signals recorded by the silk/Ag@Au BioEs; EOG signals recorded by Ag/AgCl gel electrodes; performance comparison of diverse electronic skins reported in literature) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908993>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

L.C.Y.: Conceptualization, Investigation, Visualization, Writing – original draft. M. G.: Data curation, Formal analysis, Visualization. Y.Y.L.: Investigation. J.P.W.: Investigation. L. K. L.: Investigation. X. L.: Formal analysis, Validation. F.X.G.: Writing – review and editing. L.Z.: Writing – review and editing. D.R.W.: Conceptualization, Funding acquisition, Supervision, Writing – review and editing.

Use of AI statement

None

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Electronic Supplementary Material

Hydration-adaptive and omnidirectionally stretchable silk/Ag@Au nanowire epidermal electrodes for unobtrusive long-term electrophysiological monitoring

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Supporting information to <https://doi.org/10.26599/NR.2026.94908993>

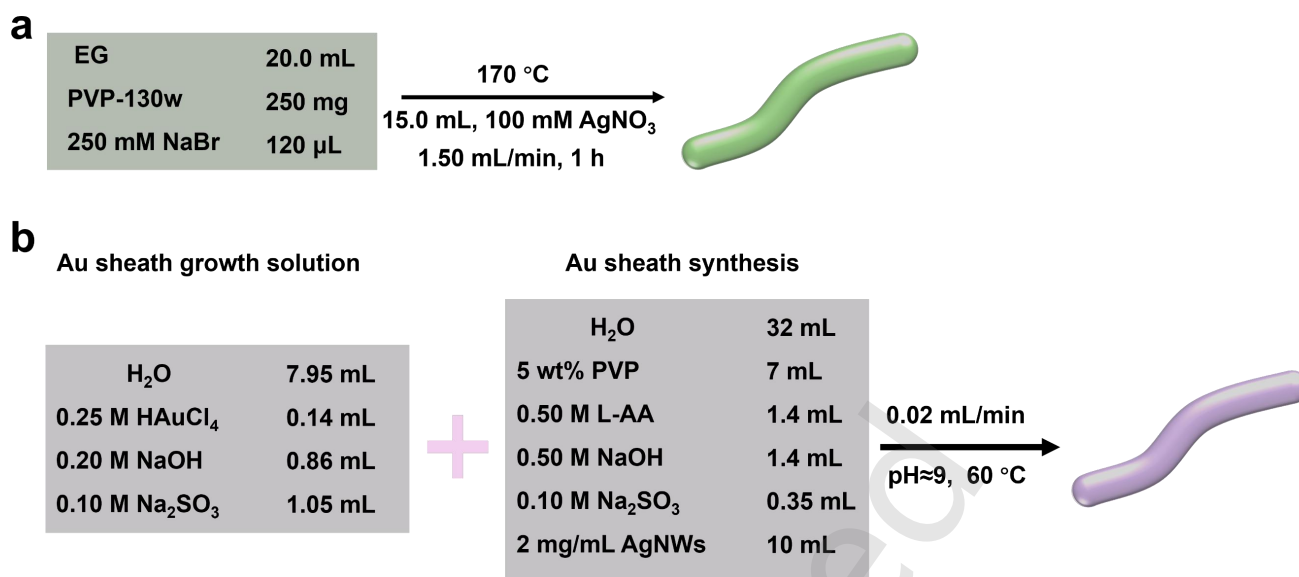


Figure S1. The recipe for the synthesis of Ag NWs (a) and Ag@Au NWs (b).

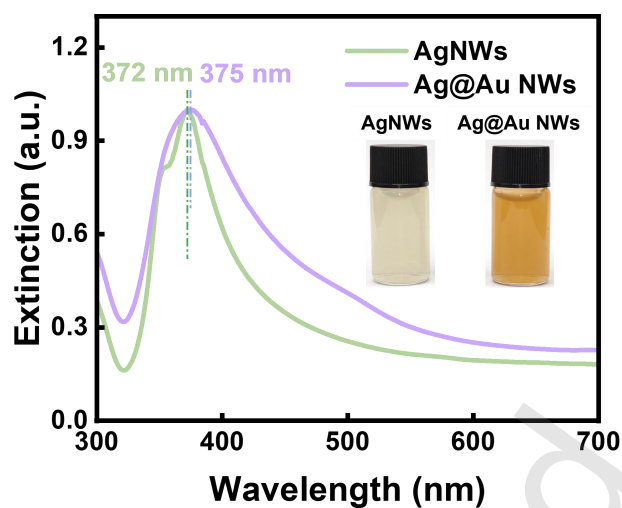


Figure S2. UV-vis extinction spectra of AgNWs and Ag@Au NWs. Inset: photographs of AgNWs and Ag@Au NWs aqueous dispersions.

The extinction peak exhibits a redshift from 372 nm (pristine AgNWs) to 375 nm (Ag@Au NWs), accompanied by peak broadening, which should be attributed to modifications in the dielectric constant of the nanowires owing to the presence of the conformal Au sheath.

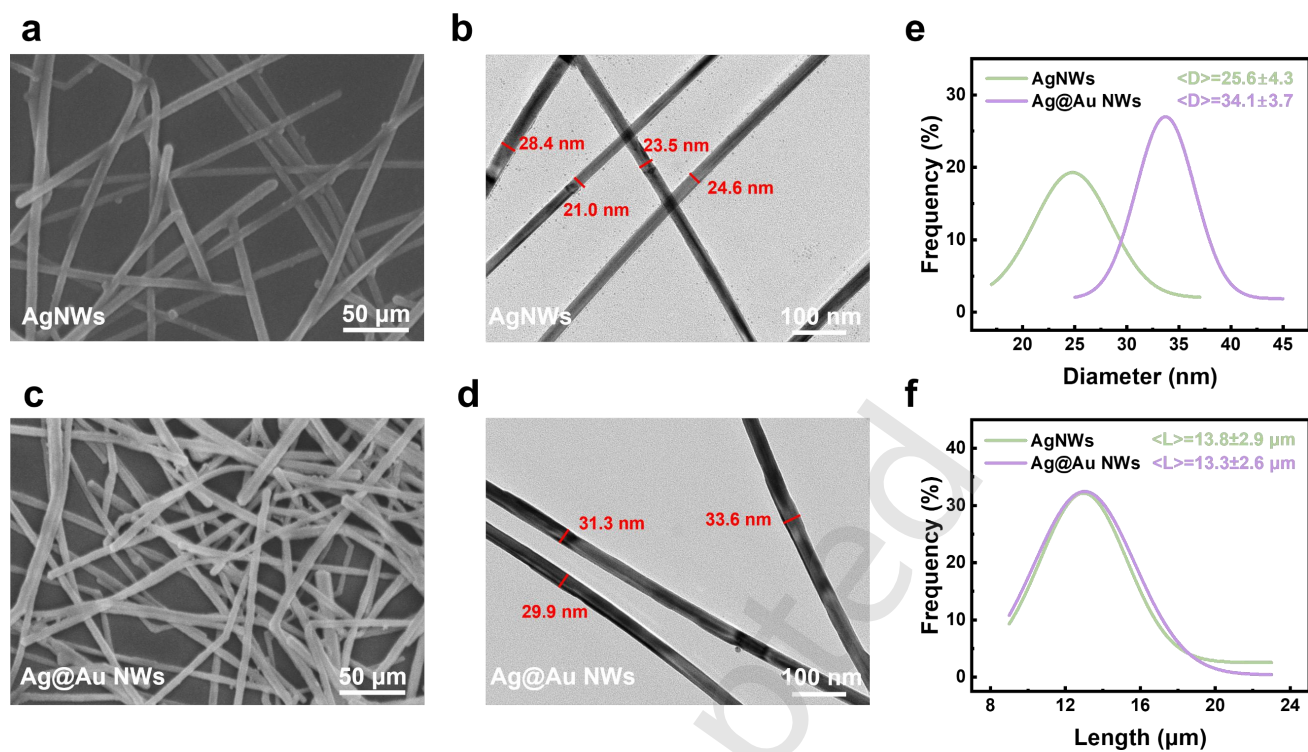


Figure S3. (a) Typical SEM image and (b) TEM image of AgNWs. (c) Typical SEM image and (d) TEM image of Ag@Au NWs. The statistics of diameter (e) and length (f) of AgNWs and Ag@Au NWs.

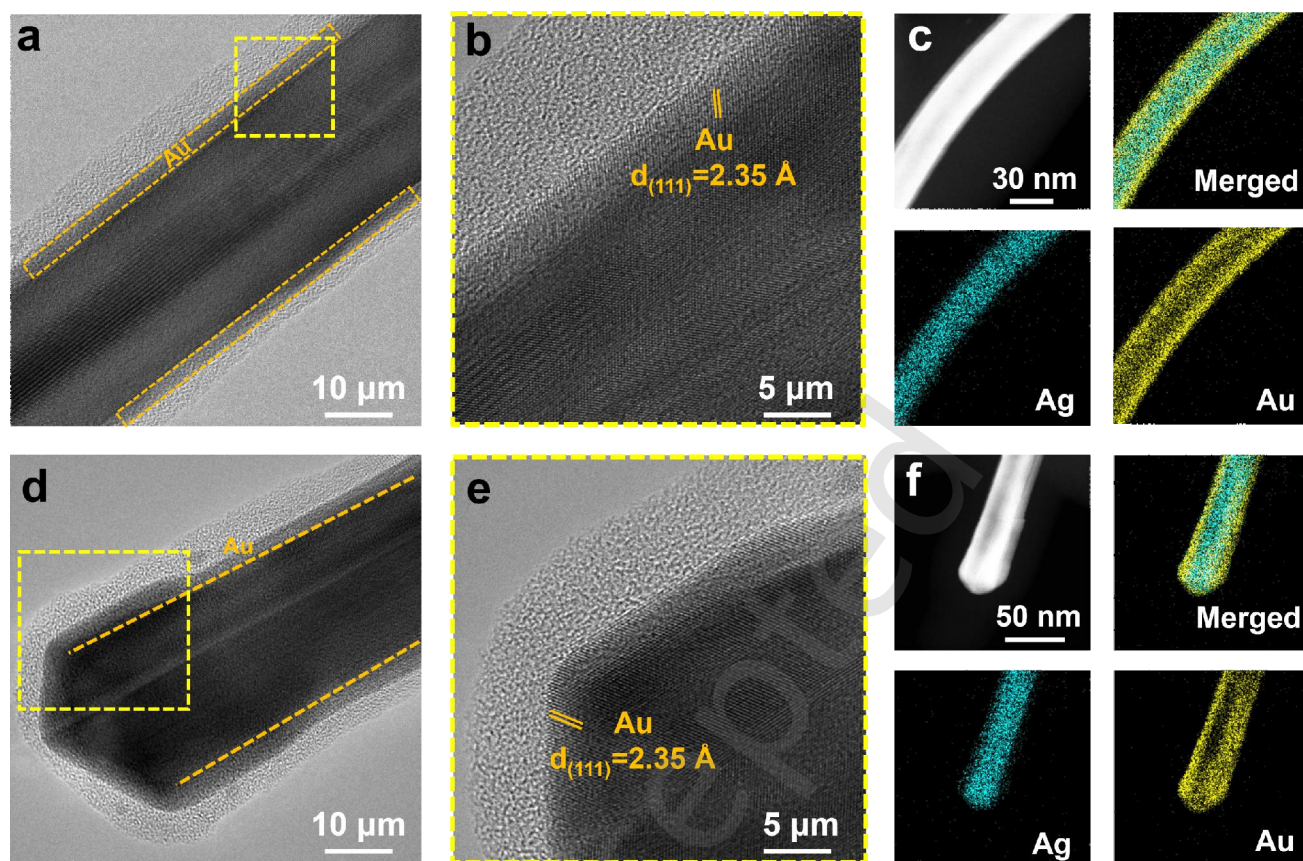


Figure S4. (a, b, d, e) HRTEM images of the Ag@Au NWs with crystalline structure analysis. (c, f) HAADF-STEM and EDS elemental mapping of Ag and Au in the Ag@Au NWs, and the merged images confirming the core-shell structure of the nanowire and the conformal coating of Au layer.



Silk cocoon



Degummed silk



Silk/CaCl₂/FA

Figure S5. Digital photos showing the preparation process of the silk/CaCl₂/formic acid (FA) solution.

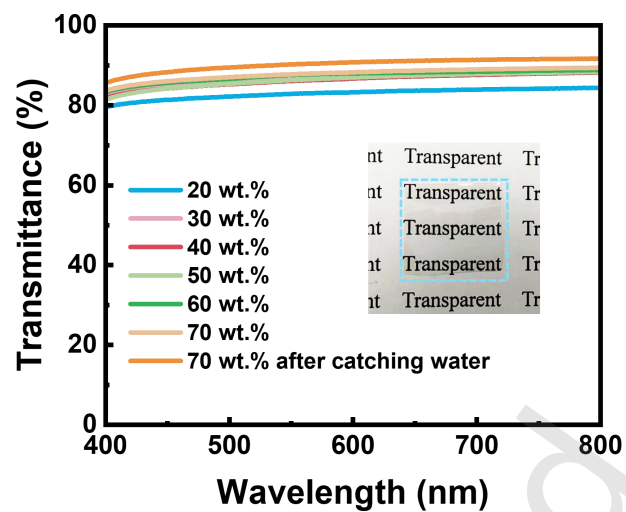


Figure S6. Optical transmittance of silk fibroin films with varying CaCl₂ weight ratios.

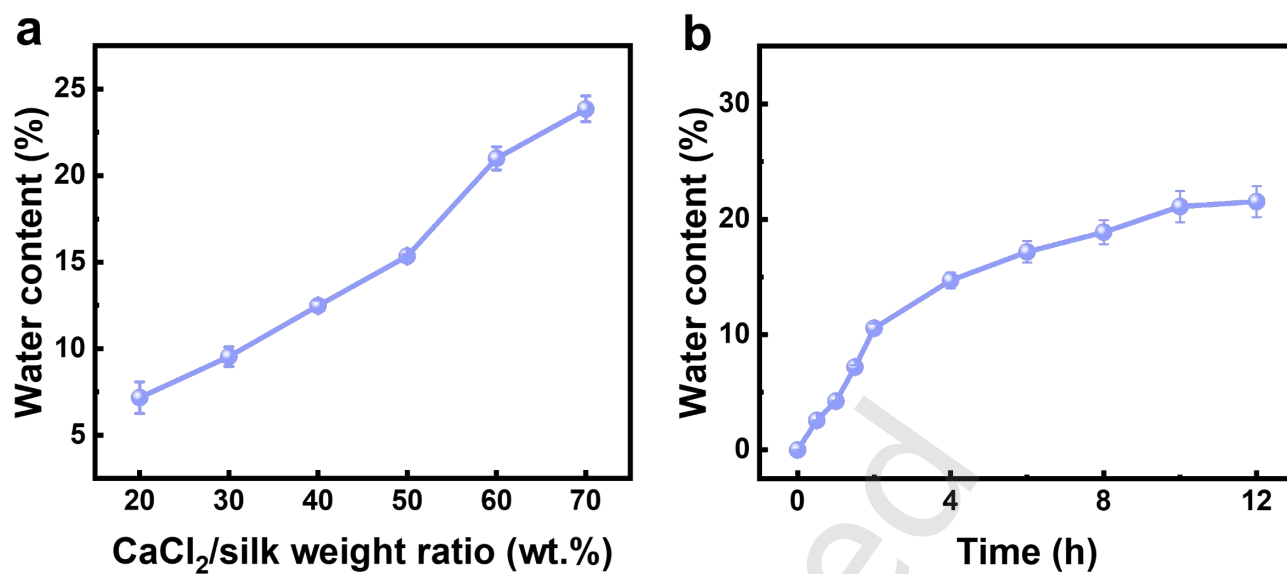


Figure S7. (a) Water content of silk fibroin films with varying CaCl₂ weight ratios at 60% relative humidity. (b) Water content as a function of time for silk fibroin films containing 60 wt.% CaCl₂ under 60% relative humidity. The silk fibroin film exhibits a rapid water absorption rate within the first 2 h, and reaches full hydration equilibrium after approximately 10 h.

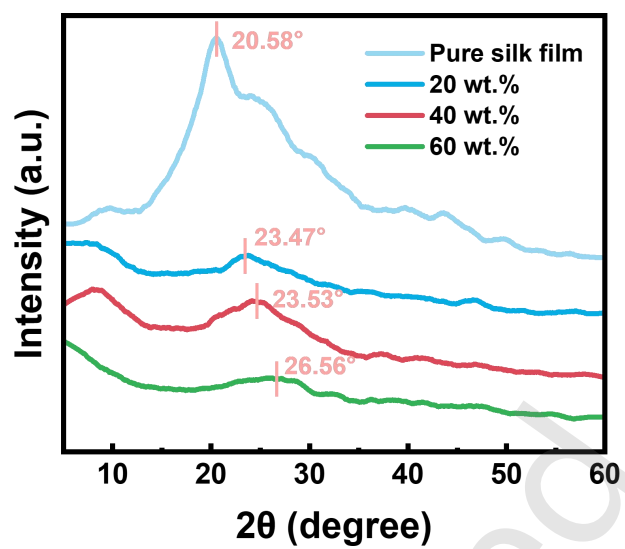


Figure S8. XRD patterns of silk fibroin films with varying CaCl_2 weight ratios.

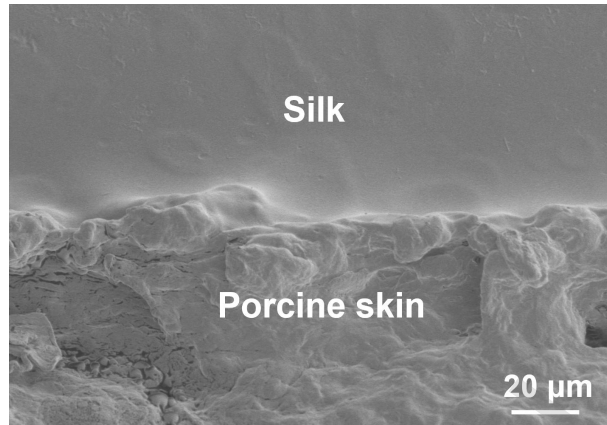


Figure S9. SEM image of the interface between the silk fibroin film and porcine skin.

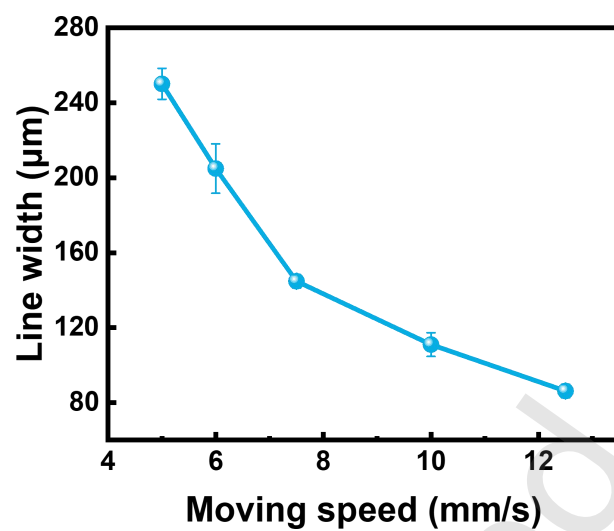


Figure S10. Printed linewidth as a function of the speed of the printing nozzle.

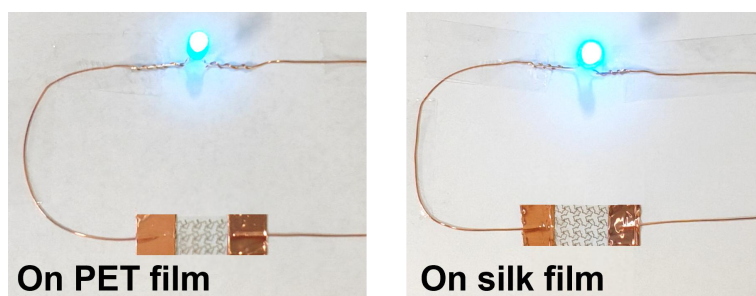


Figure S11. Connection of Ag@Au NWs conductive pathways to a commercial LED on PET substrate (left) and silk fibroin substrate (right), respectively.

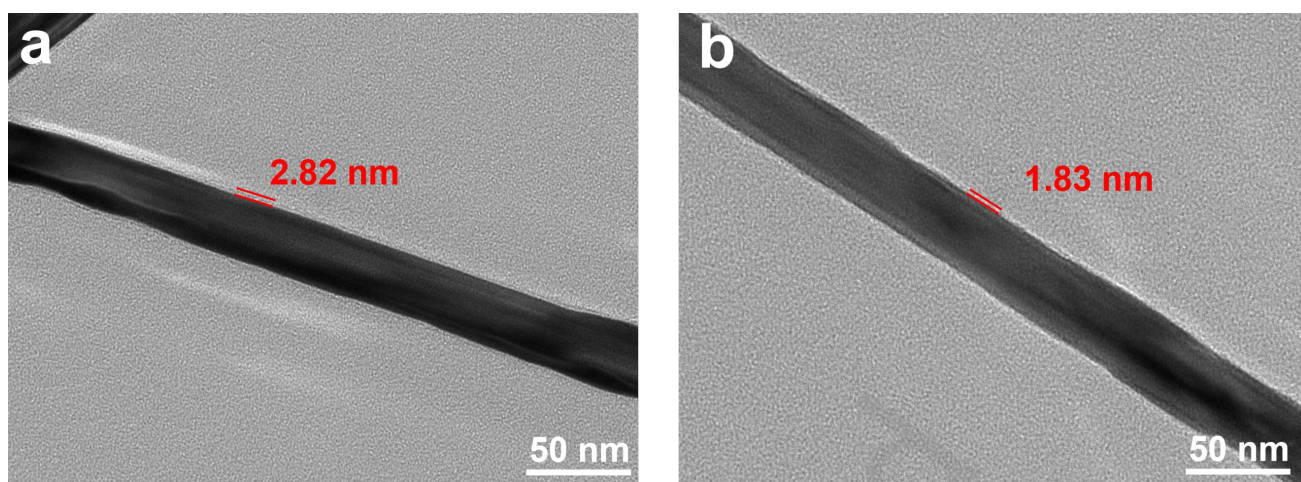


Figure S12. TEM images of single Ag@Au NW before (a) and after (b) cold-welding. The average thickness of PVP on the surfaces of the Ag@Au NW is denoted in the images.

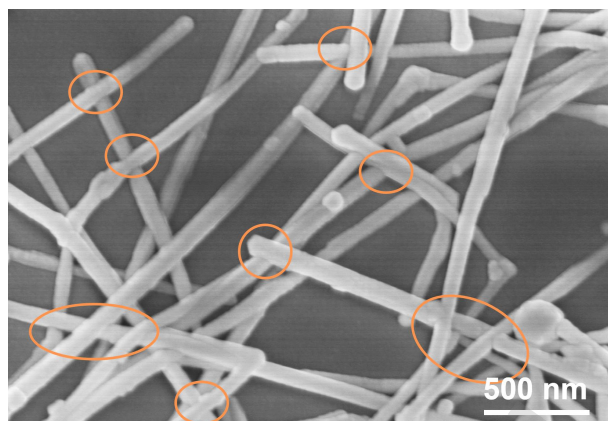


Figure S13. Typical SEM image of Ag@Au NWs network after cold-welding. The circles denote the NW-NW welding points.

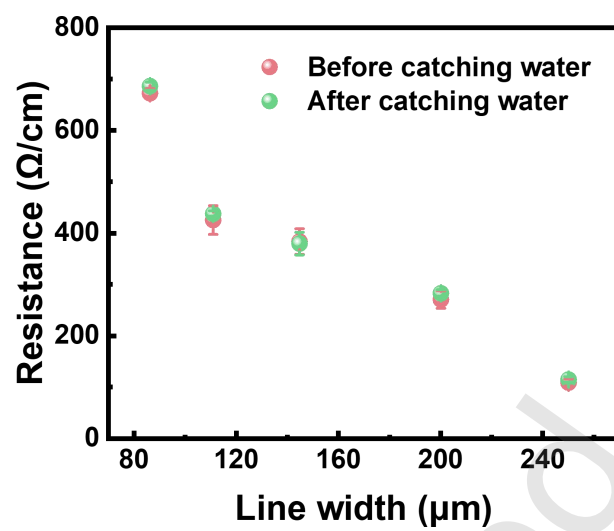


Figure S14. Resistance of silk/Ag@Au BioEs before and after catching water.

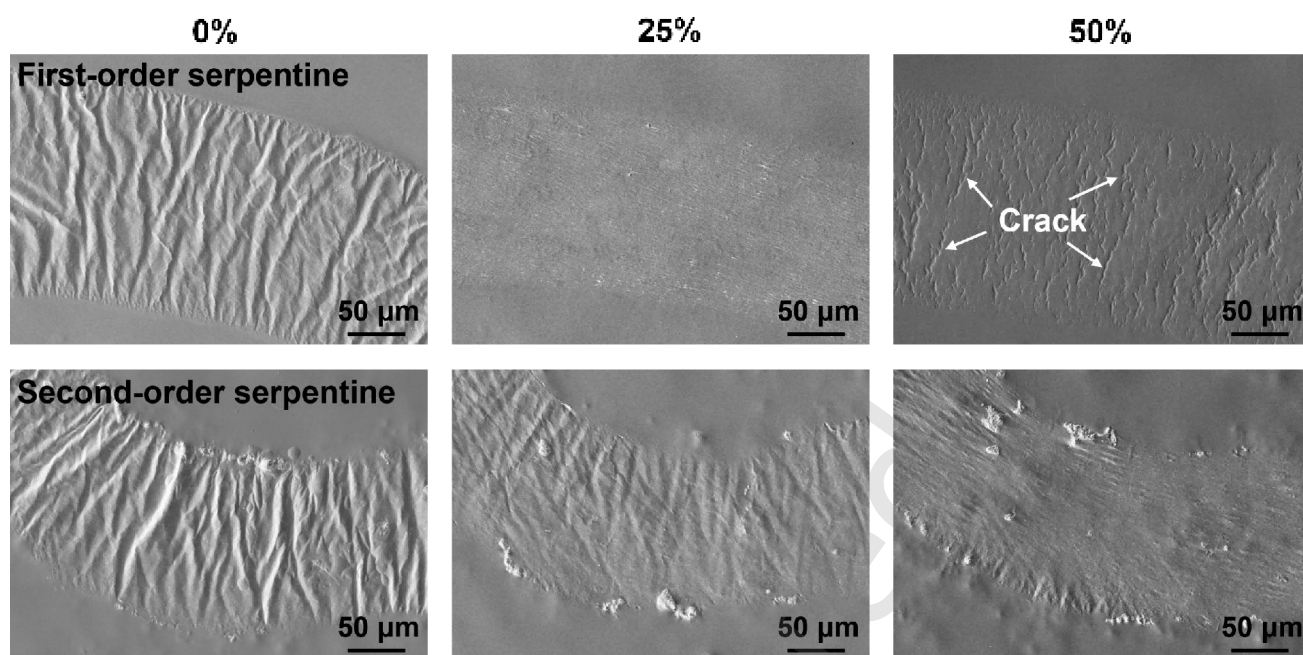


Figure S15. SEM images showing the morphology of wrinkle structures in patterns of first-order serpentine (top row) and second-order serpentine (bottom row) under varying tensile strains (0, 25%, and 50%).

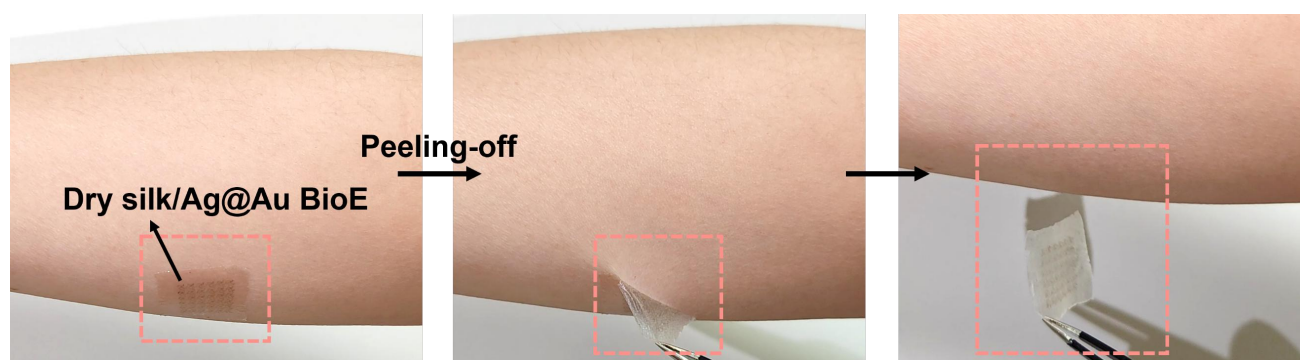


Figure S16. Photos showing the peeling process of a dry silk/Ag@Au BioE from the skin surface.

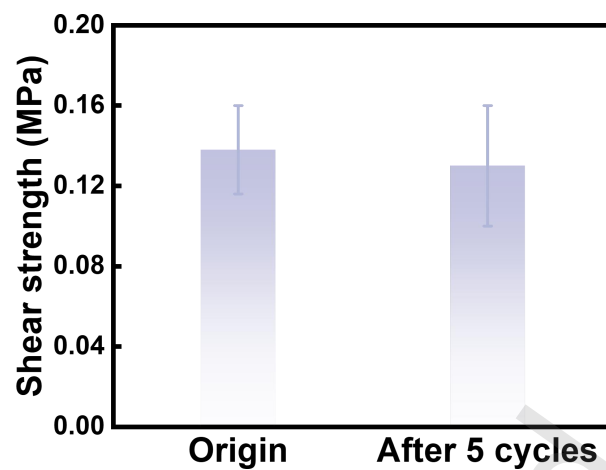


Figure S17. Adhesion strength of the silk fibroin film to porcine skin after 5 cycles of cyclic dehydration and rehydration.

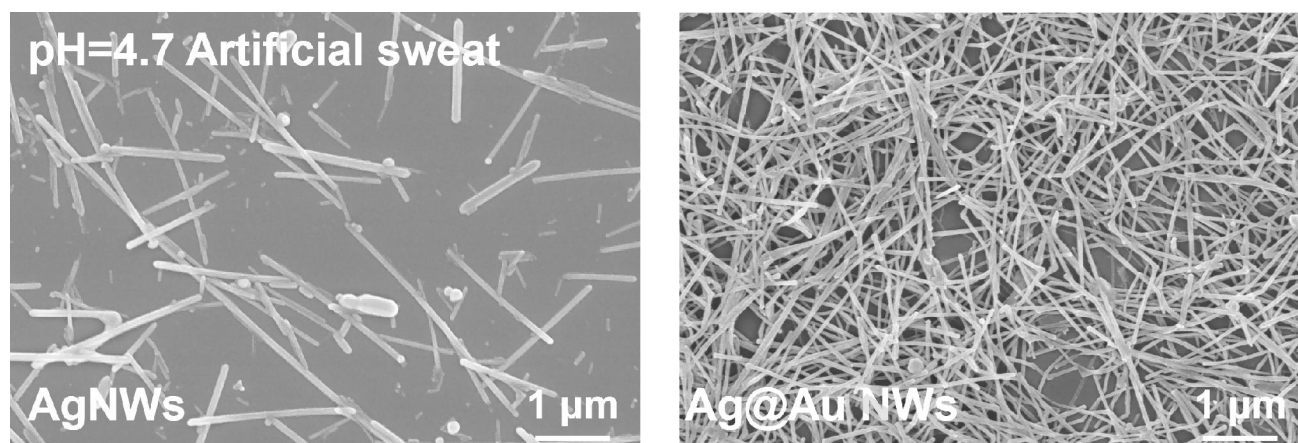


Figure S18. SEM images of AgNWs (left) and Ag@Au NWs (right) after immersion in artificial sweat.

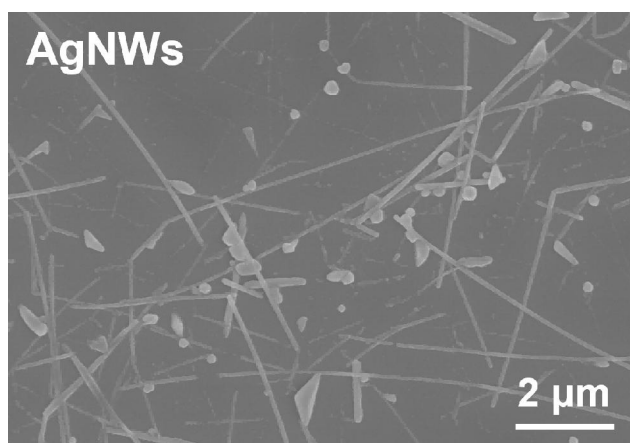


Figure S19. SEM images of AgNWs (left) and Ag@Au NWs (right) after H_2O_2 treatment.

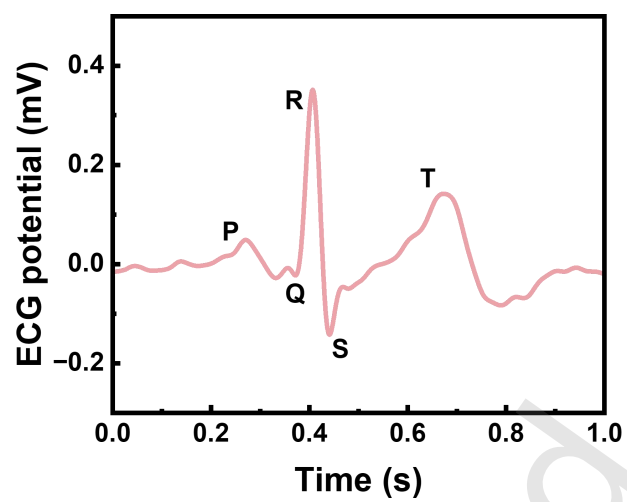


Figure S20. Typical measured ECG signals using the silk/Ag@Au BioE.

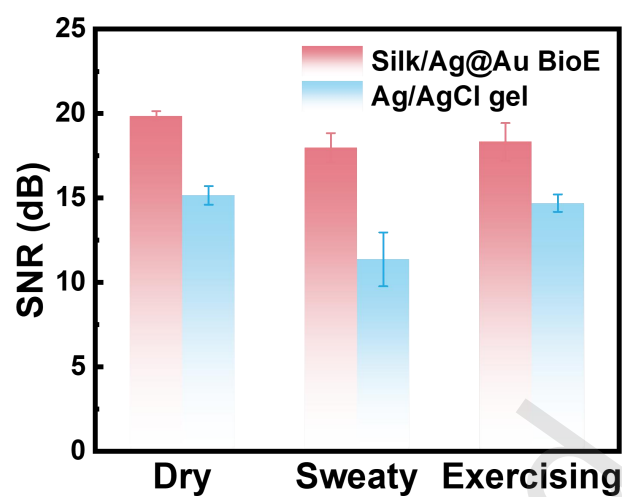


Figure S21. SNRs of the silk/Ag@Au BioE and the Ag/AgCl gel electrode for EMG monitoring under different conditions.

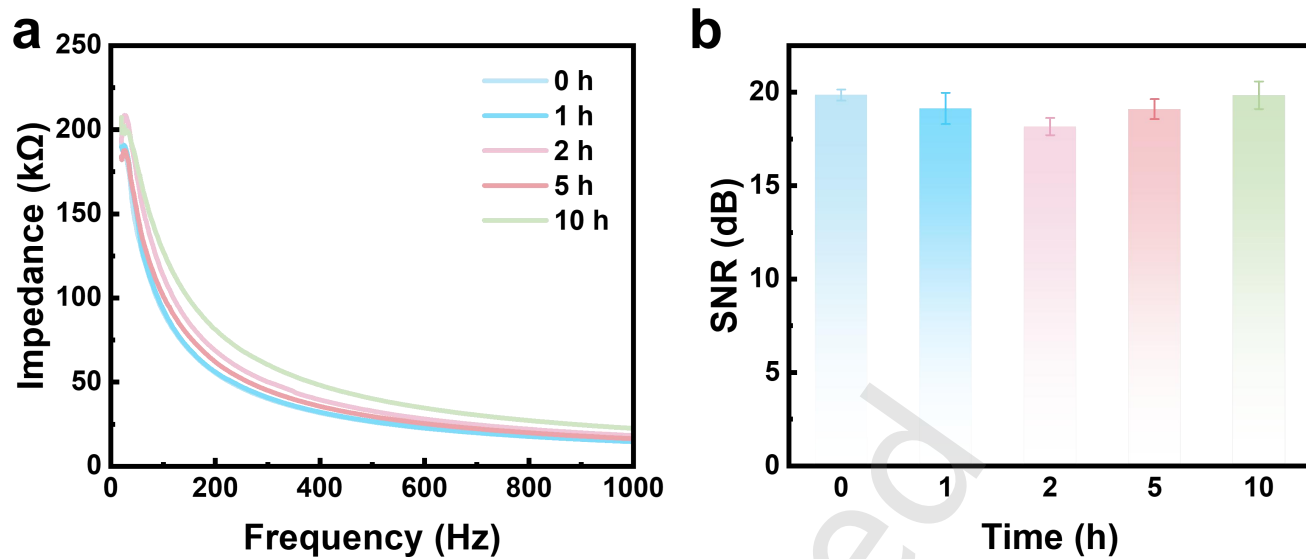


Figure S22. (a) The interfacial impedance between the silk/Ag@Au BioE and the skin during a continuous monitoring of 10 h. (b) SNRs of the silk/Ag@Au BioE in long-term EMG monitoring.

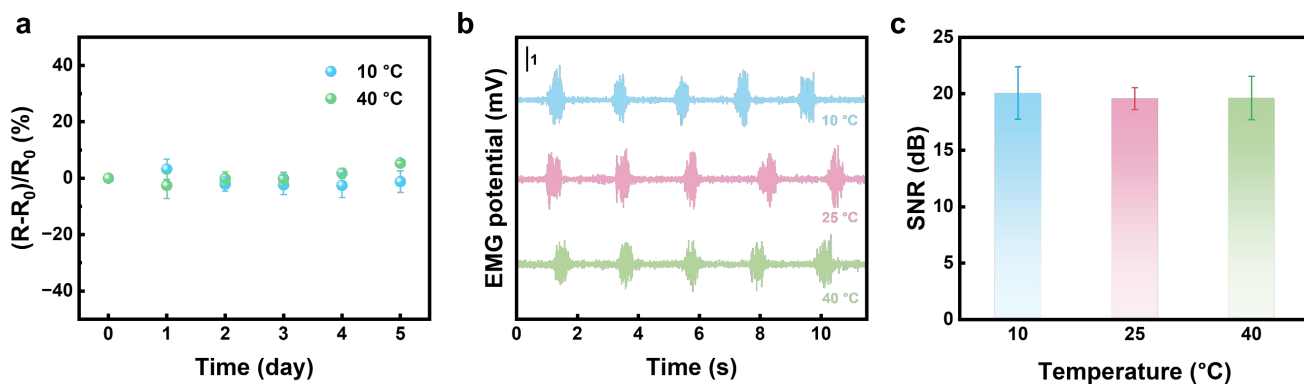


Figure S23. (a) Resistance stability of the silk/Ag@Au BioE at 10 °C and 40 °C. (b) EMG signals recorded by the silk/Ag@Au BioE at 10 °C, 25 °C, and 40 °C and (c) the corresponding SNRs.

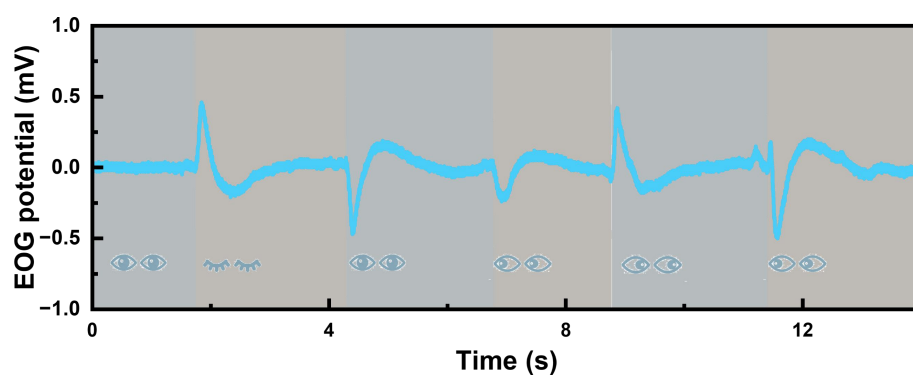


Figure S24. EOG signals recorded by commercial the Ag/AgCl gel electrode when the subject moving eyes.

Table S1. DIW parameters for printing Ag@Au NW patterns with various linewidths.

P (psi)	Z (μm)	V (mm/s)	Line width (μm)
6	80	5.0	250.1 ± 8.2
6	80	6.0	204.9 ± 13.2
6	80	7.5	144.8 ± 3.6
6	80	10	110.9 ± 6.4
6	80	12.5	86.2 ± 3.6

Table S2. Performance matrix of diverse electronic skins reported in literature. Note: “/” indicates that the value was not reported.

Materials	T (%)	R_s (Ω/sq)	$(R-R_0)/R_0$	Number of cycles	Omnidirectionally stretchable	Environmental stability	Breathability	Reusabil ity	Application	Ref.
PPy	×	/	~10% (50% strain)	≥100 (30% strain)	/	/	/	/	ECG (dry, sweaty, running, skin deformation)	[1]
CNT	/	/	40% (100% strain)	≥4500 (50% strain)	/	/	Yes	/	ECG, EMG	[2]
MXene	×	/	/	/	/	/	/	/	EMG, ECG, EOG, EEG (dry, sweaty, exercising)	[3]
AgNS	/	/	~3.5 (50% strain)	≥1200 (30%strain)	Yes	High humidity (90% RH), body temperature (~37 °C), PBS- immersion	/	/	Multi-point pressure mapping and real-time tracking	[4]
AgNWs	87.8	8.4	116.57% (50% strain)	≥50000 (bend)	/	Ambient air	Yes	/	ECG, EMG	[5]
AgNWs	/	≥0.046	~100% (50% strain)	~1000 (50% strain)	/	/	/	/	EMG	[6]

AgNWs	61%	7.3	~10 (20% strain)	≥10000 (bend)	/	/	Yes	/	ECG, EMG	[7]
Au	×	7	2.45 (40% strain)	≥100 (20% strain)	/	/	/	/	EMG	[8]
Ag@Au NWs	/	1	280% (50% strain)	≥1000 (30% strain)	/	/	Yes	/	Epidermal electrochemical biosensor, EMG	[9]
Ag@Au NWs	/	/	~3% (50% strain)	~3000 (30% strain)	/	Ambient air, H ₂ O ₂	/	/	ECG, EMG	[10]
Ag@Au NWs	≤94.3	≥10.9	16.3% (30% strain)	≥12000 (15% strain)	Yes	High humidity (90% RH), artificial sweat, H ₂ O ₂	Yes	Yes	ECG, EMG, EOG (dry, sweaty, exercising, skin deformation)	This work

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