

Tuning the Rigidity of Silk Fibroin for the Transfer of Highly Stretchable Electronics

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The transfer of stretchable electrodes or devices from one substrate to another thin elastomer is challenging as the elastic stamp often yields a huge strain beyond the stretchability limit of the electrodes at the debonded interface. This will not happen if the stamp is rigid. However, a rigid material cannot be used as the substrate for stretchable electrodes. Herein, silk fibroin with tunable rigidity (Young's modulus can be changed from 134 kPa to 1.84 GPa by controlling the relative humidity) is used to transfer highly stretchable metal networks as highly conformable epidermal electrodes. The silk fibroin stamp is tuned to be rigid during peeling, and then be soft and highly stretchable as a substrate when laminated on moisturized human skin. In addition, the epidermal electrodes exhibit no skin irritation or inflammation after attaching for over 10 d. The high compliance results in a lower interface impedance and lower noises of the electrode in measuring electromyographic signals, compared with commercial Ag-AgCl gel electrodes. The strategy of tuning the rigidity at different stages of transfer is a general method that can be extended to the transfer of other stretchable electrodes and devices for epidermal electronics, human machine interfaces, and soft robotics.

1. Introduction

Stretchable electronics have been attached great significance in recent years.^[1–4] Flexible and transparent electrodes have a wide range of applications in the fields of epidermal electronics,^[5] implantable electronics,^[6] wearable devices and sensors,^[7–9] solar cells,^[10] and soft robotics.^[11] The transfer of electronics from one substrate to another is a key process in electronic industry. Conventional bonding processes work well for the transfer of rigid electronic materials or devices; however, they may not be applied in flexible and stretchable electronics.^[12] The transfer of highly stretchable (stretchability limit > 100%) electronics onto nonplanar or textured surfaces is a big challenge. The transfer often consists of two steps: direct contact of a stretchable elastomeric stamp on the donor substrate, and peeling the electronic materials or devices off from the donor substrate.^[13–15] This requires the stamp to

have a strong adhesion with the electronic materials or devices to ensure a complete transfer. The strong adhesion also exists between two substrates. The tough interface, however, will impose a large strain (ϵ) that might exceed the stretchability limit in the debonded part of the stamp upon peeling. When the materials or devices being transferred are thick and strong, they can be successfully transferred.^[16,17] However, ultrathin and delicate electronics will fully conform with the stamp, and they may fail when ϵ is larger than the stretchability limit of the electronic materials or devices. A method is thus required to significantly reduce the strain to avoid mechanical damage in the soft stamp during the transfer of stretchable electronics.

Here in this work, we show a method that can directly transfer nanoscale stretchable electronics, exemplified by the successful transfer of highly stretchable metal-nanowire-based electrodes, which have gained more and more attention as stretchable electrodes because of their excellent overall electrical, optical, and mechanical performances.^[18–21] In this study, spring-like Au nanotrough networks is used as the stretchable conductor, and silk fibroin adding calcium ions is used as the stamp and also the receiver substrate. During transfer, silk fibroin is tuned to be rigid (elastic modulus > 100 MPa) when peeling the metal network off from the donor substrate because a rigid material will not yield a large strain. After peeling, silk fibroin is tuned to be highly soft (elastic modulus 0.1–2 MPa),

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The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adfm.202001518>.

DOI: 10.1002/adfm.202001518

and its application on human skin is demonstrated. We have demonstrated that the rigid silk fibroin is able to completely transfer the Au nanotrough network without any damage, and the softened silk fibroin/nanotrough electrode can be stably laminated on skin. This epidermal electrode exhibits high conformability with the skin texture and high stability in both electrical and mechanical properties under various mechanical deformation modes, without showing skin irritation after long term attachment. Electromyographic (EMG) signals measured using this silk epidermal electrode exhibits a lower noise amplitude compared with that of conventional Ag-AgCl gel electrodes. The results indicate that our strategy of using rigid fibroin in the electrode transfer stage and softening it as an on-skin stretchable substrate is effective. Such a transfer method is general, and is expected to be applied in the transfer of other stretchable electrodes and devices.

2. Results and Discussion

2.1. The Transfer of Electronics

The transfer of as-fabricated electronics can be realized by attaching a stamp on the original substrate followed by separation. Here we discuss two cases: transfer of electronics using a soft (Figure 1a) and a rigid stamp (Figure 1b). Assume that the original substrate is fixed and the electronic material to be transferred is weakly adhered on it, and the electronic material is thin enough to fully comply with the deformation of the stamp. For the peeling of a top layer on a fixed substrate, according to the classical steady peeling theory,^[22] the strain in the debonded part of the top layer is given by

$$\varepsilon = -(1 - \cos \theta) + \sqrt{(1 - \cos \theta)^2 + \frac{2\gamma}{Etw}} \quad (1)$$

where θ is the peeling angle, γ is the interfacial energy density between the two layers, and E , t , and w are the Young's modulus, thickness, and width of the top layer, respectively. Here the effect of the electronic materials to be transferred is ignored. During peeling, ε should not exceed the stretchability limit of the target electrode, ideally as small as possible. Equation (1) indicates that the strain at the debonded interface of the top layer is a function of θ , γ , E , t , and w . For a given material system, if the dimensions of the layers are fixed, $\varepsilon = f(\theta, \gamma, E)$. In this study, the peeled layer is silk fibroin, the donor substrate is polydimethylsiloxane (PDMS), and γ is determined to be $\approx 65 \text{ J m}^{-2}$ (Figure S1, Supporting Information). If we further fix the peeling angle θ , ε can be simplified to be a function of E because interfacial energy density will not be significantly changed. Our experimental results show that when the peeling angle is fixed to be $\approx 30^\circ$, ε decreases with increasing E —with the increasing of E from 142 kPa to 1.8 GPa, ε decreases from ≈ 13 to ≈ 0 (Figure 1c), covering the elastic limit of most materials and stretchable electronics. Therefore, we can control the maximum strain in the silk fibroin by tuning its rigidity.

2.2. The Transfer of Au Nanotrough Electrode

Silk fibroin has been verified to be a material whose rigidity can be significantly changed by tuning its water content or the relative humidity (RH) of the air.^[23,24] The transition often takes a few hours if silk fibroin is placed in humid air. However, this softening process can also be completed within 1 min by applying a thin layer of water on skin before lamination. Such a soft-rigid transition is reversible. The silk fibroin substrate was prepared using *Bombyx mori* cocoons as the raw material and the fabrication details are described in the Experimental Section. Figure 2a is a schematic illustration showing the transfer of transparent stretchable electrode from an

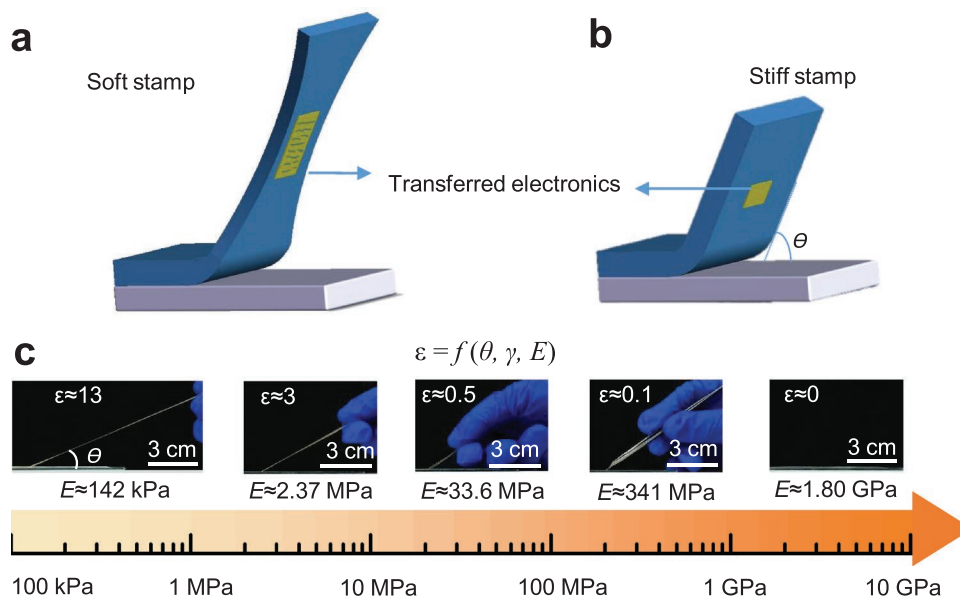


Figure 1. The transfer of electronics. a, b) Schematic illustrations of the transfer of ultrathin electronic materials using a soft and a stiff stamp, respectively. c) Strain as a function of elastic moduli when peeling silk fibroin from a PDMS substrate. The peeling angle is fixed to be $\approx 30^\circ$.

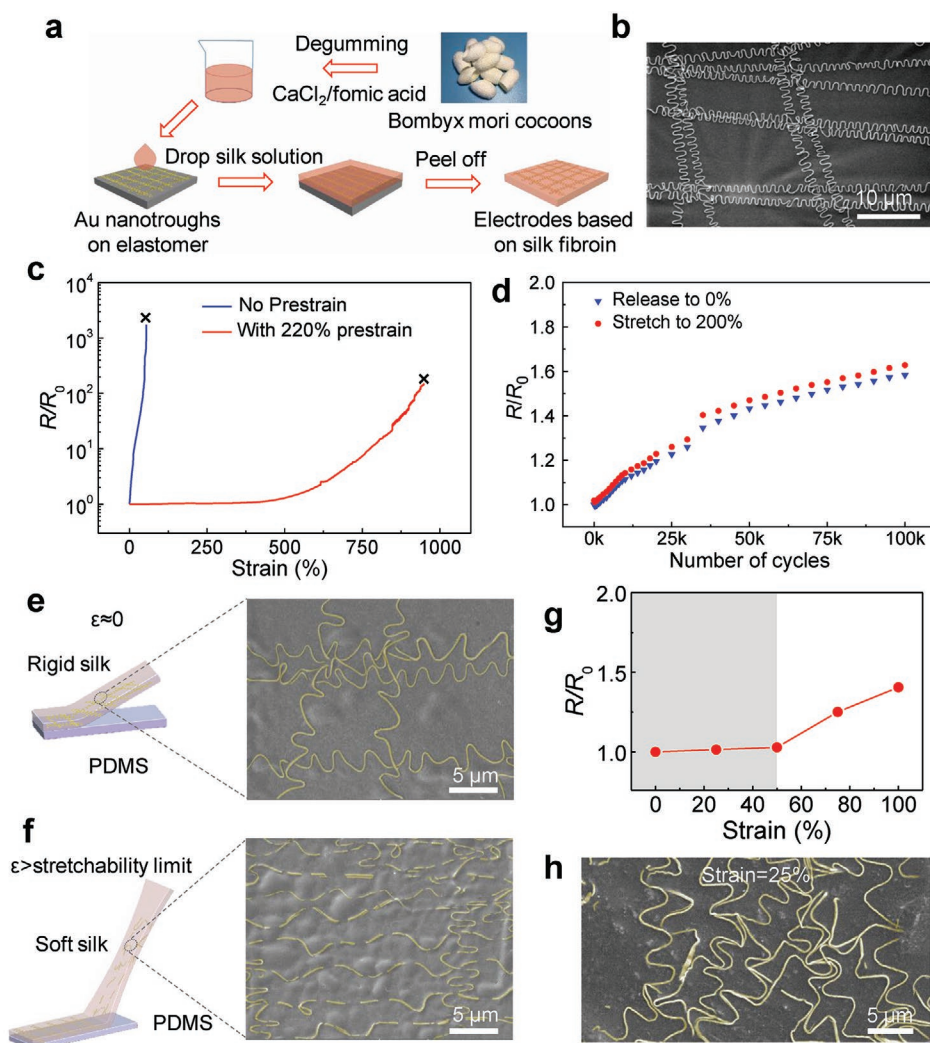


Figure 2. The transfer of highly stretchable Au nanotrough electrode. a) Schematic illustration for the transfer of wavy Au nanotrough electrode using silk fibroin. b) SEM image of the wavy Au nanotroughs. c) Normalized resistance as a function of strain of Au nanotrough electrode with and without a prestrain. d) Normalized resistance over 100 k cycles of loading/unloading to a strain of 200%. e,f) Morphology of the prestrained Au nanotrough electrode under peeling using silk fibroin substrates of 134 kPa and 1.84 GPa in modulus, respectively. g) Normalized resistance as a function of strain for a transferred Au nanotrough electrode. h) SEM image of a transferred Au nanotrough electrode with a silk substrate.

elastomeric substrate (such as Ecoflex and PDMS) to silk fibroin substrate. Silk solution was dropwise casted on the electrode, and peeled off after solidification. The stretchable electrode we used in the work is called Au nanotroughs fabricated by electrospinning and metal deposition,^[25] and then subjected to prestrain ($\approx 220\%$) to form a wave-like geometry. It exhibits a high stretchability and is thus suitable for our study. The width of individual nanotroughs was controlled to be ≈ 100 nm, and at such a small width the nanotroughs do not rupture under large prestrains, but thick nanotroughs broke under large prestrains (e.g., 300 nm in width, Figure S2, Supporting Information). Figure 2b shows the morphology of a biaxially prestrained Au nanotrough electrode, exhibiting periodic in-plane waves which remain conducting until the strain increases to 950% (Figure 2c). At a large strain of less than 400%, the normalized change in resistance (R) of the prestrained Au nanotrough electrode is only 0.1 (Figure S3, Supporting Information), which is

superior to that of a prestrained Au nanomesh with serpentine ligaments.^[26] This electrode also exhibits a high stability in both electrical property and micromorphology over 100 k stretching cycles to 200% strain (Figure 2d and Figure S4, Supporting Information). The in-plane deformation of the waves was verified by atomic force microscopy observation (Figure S5, Supporting Information), and such in-plane waves are critical to the relatively small change in transmittance, otherwise the film will become highly hazy if out-of-plane wrinkles are formed.^[27]

When peeling the silk fibroin from the donor substrate, the strain ϵ in the debonded part of silk decreases with increasing E . In our material system, when the top layer is rigid ($E > 1$ GPa), the strain ϵ will be a quite small value ($\epsilon < 0.1$). As a result, the adhered Au nanotroughs can be safely transferred without damage. This has been verified in our scanning electron microscopy (SEM) observation (Figure 2e). However, when the stamp becomes soft ($E \approx 100$ kPa), ϵ rapidly increases

to a value larger than 10, which is far larger than the stretchability limit of any existing metal electrodes. In this case, the transferred Au nanotroughs form dense localized cracks (Figure 2f) and become nonconducting. We selected silk fibroin with $E = 1.84$ GPa for the transfer.

We call the Au nanotroughs/silk fibroin in this work silk electrode. The transferred Au nanotrough electrode maintains excellent flexibility in terms of bendability and stretchability. The silk electrode was subjected to bends with radii of curvature varying from 72 to 1.3 mm, but little change in resistance was seen (Figure S6, Supporting Information). Moreover, at 69% RH, the resistance of the electrode hardly changes when stretched to strains up to 50% (Figure 2g), which is larger than the maximum strain that can be applied on the human skin.^[28] Therefore, this electrode can satisfy the applications as epidermal electronics in terms of stretchability. The transferred Au nanotrough electrode, however, is not as stretchable as the original Au nanotrough electrode supported on a PDMS or Ecoflex substrate. This is because the Au nanotroughs, although still exhibit a wavy structure, are partially embedded in the silk substrate (Figure 2h) to have a stronger interfacial adhesion. The strong adhesion causes a “stiffening effect” for which the nanotroughs cannot shift and slide freely to relax the imposed strain.^[29] As a result, the stretchability degrades but still keeps a high level due to the well-defined wavy structures.

2.3. Mechanism of the Transfer

The key to transfer Au nanotrough electrode from an elastomeric substrate without destroying the spring-like structure is to decrease the strain ϵ of the debonded silk fibroin. According to Figure 2g, ϵ needs to be smaller than 50% to avoid least damage to the Au nanotrough. The strain as a function of E under various peeling angles of 0°, 30°, 60°, and 90° is shown in Figure 3a as well as in Table S1 (Supporting Information), exhibiting that the strain in the debonded silk decreases with increasing Young's modulus or peeling angle. It is determined that as long as the modulus is larger than 100 MPa, ϵ will be smaller than 50% regardless of the peeling angle, and thus the Au nanotrough can be safely transferred without any electrical property degradation (the dashed area in Figure 3a). When peeling other commonly used soft stamps, such as PDMS and Ecoflex ($E < 2$ MPa), the maximum strain in the debonded interface will be larger than 3 (judged from Figure 3a), which leads to the damage of transferred electronics (assuming that the adhesion condition does not change).

On the other hand, the silk fibroin needs to mechanically match the human skin for conformable lamination on skin by tuning the RH of the air. Figure 3b depicts the Young's modulus of fibroin as a function of RH. It shows that to avoid damaging the metal nanotroughs, RH should keep to be smaller than 49% (denoted as peeling zone) to ensure that the modulus of the silk fibroin is larger than 100 MPa; while for skin lamination, RH should increase to be larger than 64% (denoted as lamination zone) such that the silk can mechanically match the skin ($E = 0.1$ –2 MPa). Mechanical match has been verified to be critical for the integration of flexible electronics on human skin.^[30] By contrast, a large mechanical mismatch may cause

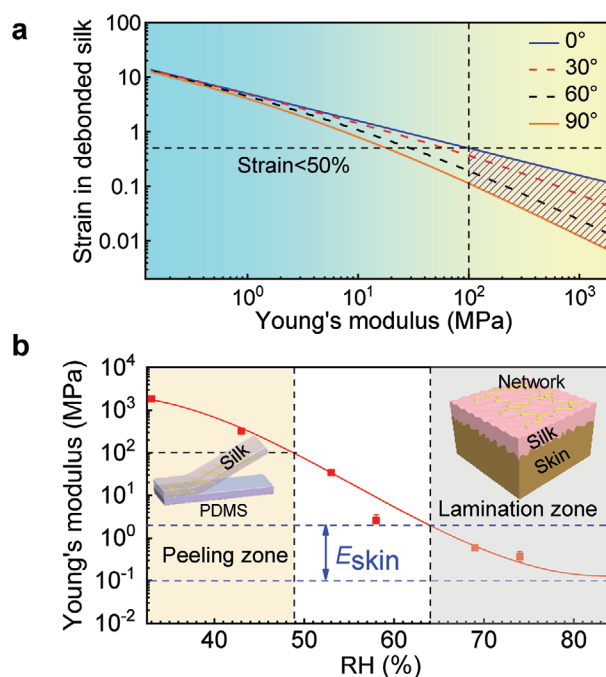


Figure 3. Mechanism of the transfer for the stretchable electrodes. a) Relationship between E and strain in the peeled fibroin at peeling angles of 0°, 30°, 60°, and 90°. b) Relationship between RH and Young's modulus of silk fibroin.

delamination and finally failure of electronics regardless of the interfacial adhesion between two materials.^[31] The high RH may be naturally maintained all the year round in some humid regions, such as in the city of Shenzhen, where the experiment was conducted. However, such an electrode may not be naturally kept soft and stably conformed on skin in arid regions and the control of RH or water content is required.

2.4. Mechanical and Electrical Properties of the Silk Epidermal Electrode

The controllable rigidity of silk fibroin enables a strategy to safely transfer the Au nanotrough electrode to human skin. In the RH range of 33–49%, the fibroin film is hard (E from 100 MPa to 1.84 GPa), and the Au nanotrough electrodes can be transferred to fibroin without damage. The relatively hard fibroin substrate cannot directly adhere on skin (Figure 4a). By contrast, when the hard fibroin is softened by exposing to air with an RH of 63–84% (corresponding E from ≈ 2 MPa to 0.1 MPa) to have a Young's modulus close that of human skin (0.1–2 MPa),^[32] it can be conformably attached on skin (Figure 4b). In our experiment, we attached a piece of silk fibroin on a PDMS skin replica and it shows that the silk well complies with the surface texture of the skin without any gap along the rough interface (Figure 4c). We also conducted direct lamination of the silk electrode (silk supported Au nanotroughs) on human skin, and it shows that the electrode could well follow the profile of surface wrinkles and folds of the skin (Figure 4d). The high conformability lies in the mechanical matching between the materials (close rigidity

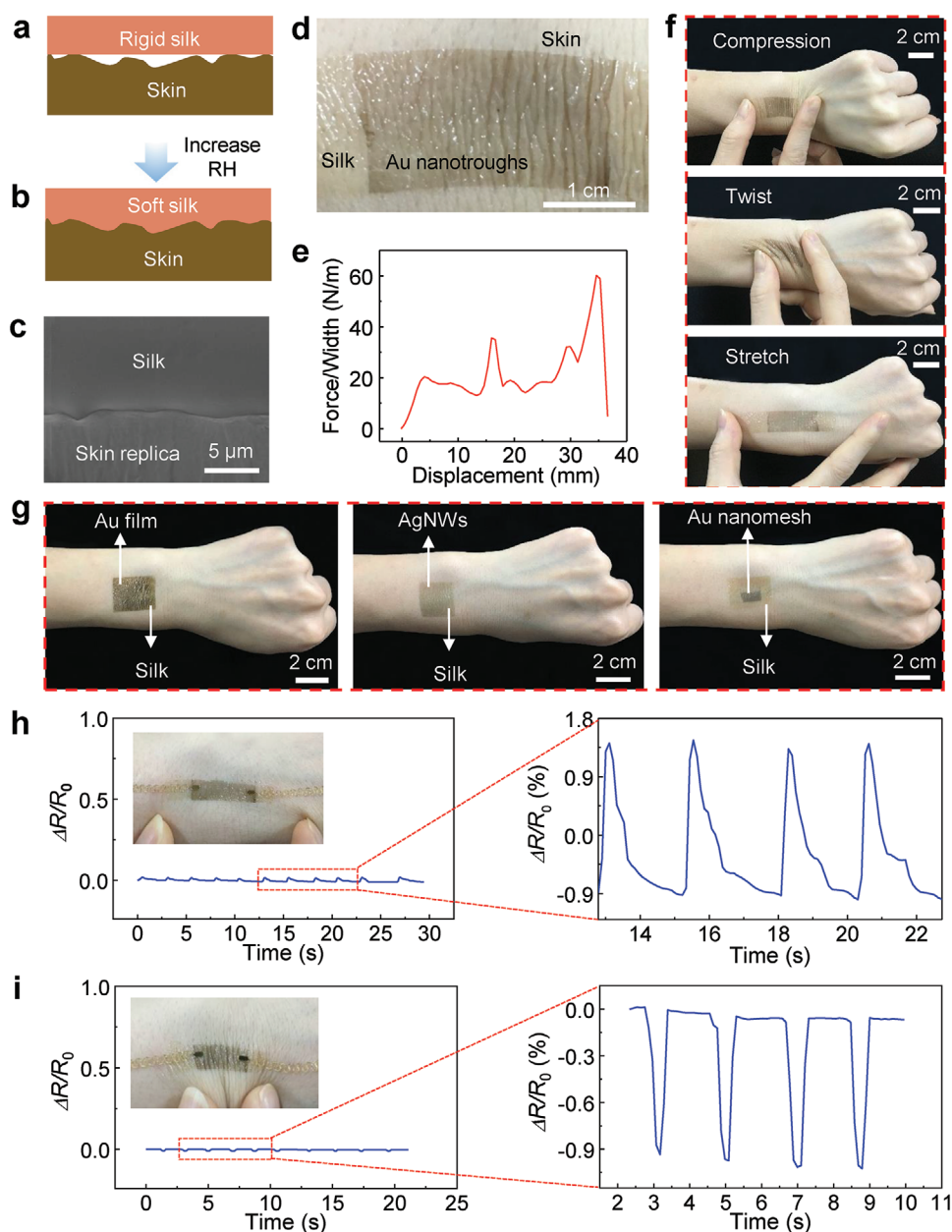


Figure 4. Mechanical and electrical stability of the silk epidermal electrode. a,b) Schematic illustration showing the rigid silk/skin and soft silk/skin interfaces. c) SEM image of an interface between the silk and a skin replica. d) Optical image of a silk electrode on skin, showing that the silk electrode well complies with the skin texture. e) The adhesion strength between silk electrode and toughness was to be 60 N m^{-1} . f) A silk epidermal electrode in different mechanical states of squeezing, twisting, and stretching. g) Photographs of silk electrode with Au film, Ag nanowire (AgNW) electrode, and Au nanomesh electrode laminated on skin. h,i) Normalized change in resistance of the silk epidermal electrodes under repeated skin stretching, and skin squeezing, respectively. Insets show corresponding photographs.

between skin and the silk), as well as the strong interfacial adhesion. The adhesion strength is quantitatively determined to be $\approx 60 \text{ N m}^{-1}$ under a peeling test with a 90° peeling angle (Figure 4e). Such a strong bonding between the skin and the fibroin has also been reported elsewhere for other applications, such as self-healable multifunctional electronic tattoos.^[33] The high conformability as well as the high flexibility of the electrode allows the silk electrode to keep stable under various mechanical modes, such as compression (strain $\approx 22\%$),

stretching (strain $\approx 30\%$), and twisting (strain $\approx 6\%$), as shown in Figure 4f.

This transfer method is general and can also be used to transfer other stretchable electrodes exemplified by Au films, AgNWs, and Au nanomeshes (Figure 4g).^[34] All these electrodes not only exhibit high conformability on skin, but also maintain electrical conductivity after the transfer (Figure S7, Supporting Information). For a specific case of AgNWs, which cannot be in direct contact with the skin because the released Ag^+ is harmful to the

health.^[35] Here in this study, the silk fibroin can separate AgNWs and skin from direct contact and this might offer a possibility to use AgNWs as an epidermal electrode, although the safety of the AgNWs/silk electrode still needs to be further studied.

Apart from the high mechanical stability of the skin-fibroin interface, the silk epidermal electrode also exhibits high stability in electrical properties upon deformation. Our experiment shows that the resistance of the silk epidermal electrodes remains stable after a few cycles of repeated stretching with $\approx 18\%$ strain (Figure 4h) or compression with $\approx 32\%$ strain (Figure 4i). It is interesting that although the resistance of the silk epidermal electrode fully recovers after each cycle, the resistance is found to sensitively respond to deformation during skin motion, enabling the electrode as a potential sensor for human motion monitoring and advanced healthcare.

2.5. On-Skin Electronics Using Silk Epidermal Electrode

The high conformability and high electrical stability allow the silk epidermal electrodes to be used in on-skin electronics. Here we compared our silk electrode with a commercial Ag-AgCl gel electrode in EMG signal measurement. The interfacial impedances of both the silk epidermal electrode and the Ag-AgCl gel electrode on skin were tested. It was found that the silk epidermal electrode has an interfacial impedance a few times lower than that of the Ag-AgCl gel electrodes over a broad test frequency ranging from 10 Hz to 1 MHz (Figure 5a). We used both electrodes with the same area to measure the

EMG signals on the forearm when making a fist, and each test involved repeated fist clenching and relaxing for three times (Figure 5b). A dynamometer was used to control the strength of each fist-clenching. The amplitudes of the EMG signals collected by using both the silk epidermal electrodes and the Ag-AgCl gel electrode were all ≈ 2.38 mV. However, the noise levels of the EMG signals collected by the two types of electrodes are significantly different: the noise amplitude from the silk epidermal electrodes is only 1/10 that collected by using the Ag-AgCl gel electrodes (inset in Figure 5b) because of the high conformability and lower interfacial impedance.^[36] Such a skin-electrode interface with low noise is desired in a variety of physiological signal measurements, such as electrocardiographic and electroencephalographic signals.^[37]

The silk epidermal electrodes need to be irritation-free for safe and long-time attachment on skin. Although silk fibroin is a natural protein that has been worn on human skin for a long history, its long-term attachment on skin still needs to be experimentally confirmed. In our experiment, eleven subjects with forearm skins being attached with a piece of fibroin were involved to test the irritation effect to the skin. No obvious allergic reaction or inflammation was observed on the skin of any subject after attachment for 10 d (Figure 5c,d), indicating that the silk epidermal electrode can be safely attached on the human skin for a variety of applications in epidermal electronics. The result is in line with our expectation that both nanoscale Au and silk fibroin are biocompatible.^[26,38]

The transfer method we studied here is not limited to the direct transfer of stretchable metallic electrodes, but

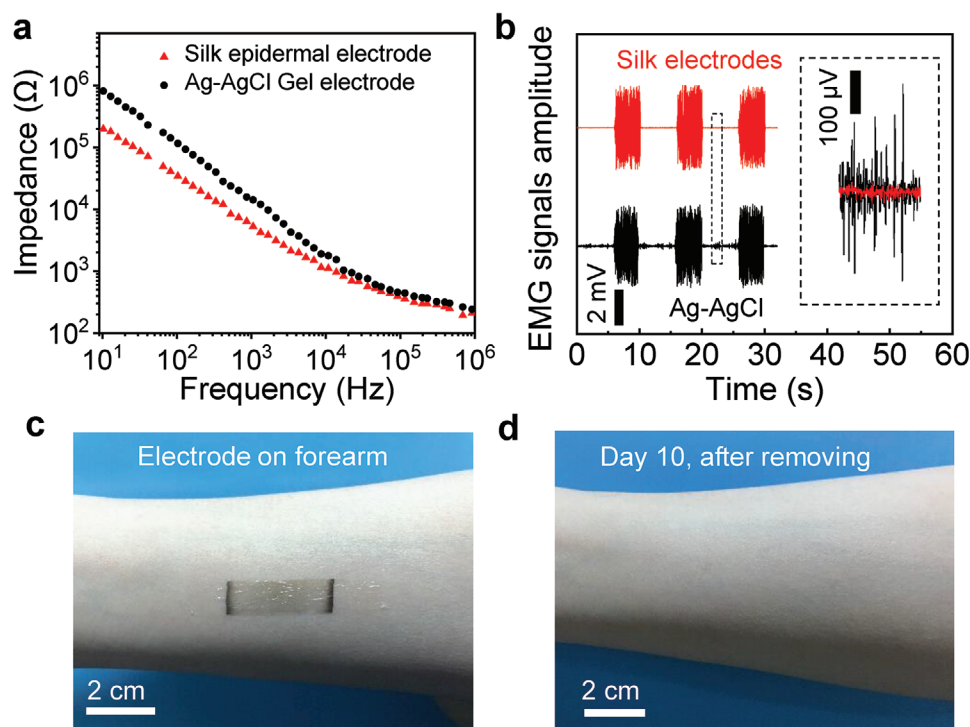


Figure 5. On-skin electronics for silk epidermal electrode. a) On-skin interfacial impedance spectra of silk epidermal electrode and the Ag-AgCl gel electrode. b) EMG signals achieved by using silk epidermal electrode and the Ag-AgCl gel electrode. Inset shows the noise amplitude of the signals collected by the types of two electrodes from 22 to 23 s. c) Photo of silk epidermal electrode on forearm. d) Photo of silk epidermal electrode on forearm at day 10 and was removed.

also expected to transfer other ultrathin flexible electrodes, micro-/nanostructures, and devices. Silk fibroin can be replaced by other elastomeric substrates for which the rigidity can be well tuned in a broad range, such as hydrogels, an ideal biocompatible platform that can merge electronics and human tissue together.^[30] As such, our strategy may be used in implantable electronics because human tissues can offer water to soften the substrate. In addition, this method can also be applied to transfer flexible electronics to other substrates rather than skin, and silk fibroin needs to be dissolved for some specific applications. In this case, no calcium ions should be added to silk fibroin or else it will not be dissolved.

3. Conclusion

In conclusion, we have introduced a method to transfer highly stretchable and ultrathin electronics, which is otherwise too delicate to be successfully transferred, by tuning the rigidity of the silk fibroin receiver substrate at different stage of the transfer. The rigidity of silk fibroin can be changed by four orders of magnitude, from ≈ 100 kPa (that well matches the rigidity of human skin) to ≈ 1 GPa. Hard silk fibroin is first used to safely peel off the stretchable electrodes from a donor substrate, and then softened to form conformable lamination on human skin. This silk electrode causes no skin irritation after 10 d of lamination on skin. We have also demonstrated that our electrode has a much smaller noise level of EMG signals compared with that of commercial Ag-AgCl gel electrodes. Our work provides a new strategy to transfer highly stretchable and delicate electronics to integrate with human body and other nonplanar surfaces.

4. Experimental Section

Fabrication of Au Nanotrough Electrode: Polymeric nanofiber template was fabricated by electrospinning. The raw material used for electrospinning was polyvinyl alcohol (PVA, $M_w = 200\ 500$, Aladdin). Polyvinyl alcohol powders were dissolved in deionized water with a weight ratio of 7 wt% and 10 wt%. Then the mixture was stirred at 90 °C for 1 h until completely dissolved. The conditions for electrospinning were as follows: the high voltage used was 20 kV, the solution injection rate was 8 $\mu\text{L min}^{-1}$, and the needle was No. 20. A square copper frame was used for the collection of the free-standing fibers. The distance between the droplets and the receiving substrates was 19.5 cm, and the humidity should be below 50%. Electrospinning time determined the density of nanofiber networks. Free-standing nanofiber template was deposited with a layer of Au (Nanchang Hanchen New Materials Technology Co., Ltd) with a thickness of 40 nm by (Wuhan Film Technology Co., Ltd). PVA nanofibers deposited with a layer of Au were transferred to a target substrate. More specifically, electrodes were transferred to a biaxially prestretched elastomeric substrates, such as PDMS (KR200, Hangzhou Bald Advanced Materials CO., Ltd.) and Ecoflex.

Fabrication of other Stretchable Electrodes: Au nanomesh electrode was prepared by a previous work.^[34] AgNWs (Nanjing XFANO Materials Tech Co., Ltd) were coated onto PDMS substrates to obtain AgNW electrode. Au film electrode was prepared by depositing a thick layer of Au on PDMS substrates through ion sputtering (MC1000 Ion Sputter, HITACHI).

Transferring of Au Nanotrough Electrode: The purchased natural *Bombyx mori* cocoons were boiled in a Na_2CO_3 (Guangzhou Chemical Reagent Factory) solution for 1 h, and the concentration of the Na_2CO_3 aqueous solution was 0.02 mol L^{-1} . Then the treated *Bombyx mori* cocoons were rinsed repeatedly with deionized water in order to remove

the sericin from the *Bombyx mori* cocoons and leave silk fibroin. The obtained silk fibroin was incubated in an oven at 65 °C for 24 h in order to remove moisture from the silk fibroin. A silk fibroin solution was prepared, including 1 g silk fibroin, 0.15 g CaCl_2 (Shanghai Lingfeng Chemical Reagent Co., Ltd), and 20 g formic acid solution, stirring constantly until the silk fibroin was completely dissolved. The silk fibroin solution was dropped on the electrode and placed in a fume hood over 24 h in order to completely evaporate the formic acid (Aladdin). The controllable relative humidity of a sealed glass vessel was achieved by injecting enough supersaturated aqueous solutions of MgCl_2 , K_2CO_3 , $\text{Mg}(\text{NO}_3)_2$, NaBr, KI, NaCl, and KCl, which yielded about 33%, 43%, 53%, 58%, 69%, 75%, and 84% RH, respectively. It took 24 h for the air in chamber to reach an equilibrium RH.

Peeling Test: Peeling test was conducted by the work of Zhao^[39] and Chen^[24] and the peeling angle was fixed at 90° in this testing section. In order to test the interfacial energy density between silk fibroin and PDMS film, silk fibroin was glued with polyimide sheet by super glue and peeling force was obtained by universal testing machine (XLD-20E, Jingkong Mechanical testing Co., Ltd). Silk fibroin used for this peeling test was at a thickness of 173 μm and a width of 3 cm. To test the adhesion strength between the silk epidermal electrode and the skin, the silk electrode with polyimide sheets was laminated on the moisturizing forearm skin. The width of silk fibroin was 1 cm. Tests were at a speed of 50 mm min^{-1} to measure the peeling force.

Rigidity Measurement: The samples were made into a standard I-shape with a width of 2 mm, a thickness of ≈ 200 μm , and an effective length of 16 mm. The rigidity was figured out using Hooke's law with a strain range of 0–0.5%. Strain–stress curves were collected by using a universal testing machine (XLD-20E, Jingkong Mechanical testing Co., Ltd). Tests were conducted at a rate of 50 mm min^{-1} . Three samples were tested to determine the rigidity of silk fibroin.

Sample Characterizations: The morphology of the spring-like Au nanotroughs, and the gap between silk fibroin and the PDMS skin replica was observed under SEM (TESCAN MIRA3). The morphology of the Au nanotroughs was inspected by atomic force microscope (Bruker Dimension Edge) to verify the in-plane deformation. The in situ morphology change of an Au nanotrough at different strains was observed by optical microscope (Dm 2700M, leica). A homemade device was used for the tensile test at a strain rate of 1 mm s^{-1} , and the resistance change of electrodes under tensile test was measured by Digital Multimeter (Keithley 2100).

Interfacial Impedance Measurement: The interfacial impedance of skin/electrode was measured by a pair of silk electrodes and a pair of commercial Ag-AgCl gel electrodes (CH50RB, Nison Instrument (Shanghai) Limited). All electrodes were round with a diameter of 16 mm and the center-to-center distance was 5 cm on forearm skin. The impedance was measured by electrochemical workstation (CS series, Wuhan CorrTest Instruments Corp., Ltd.) from 10 Hz to 1 MHz.

EMG Signals Measurement: A pair of silk electrodes and a pair of commercial Ag-AgCl gel electrodes were attached to the forearm skin to obtain EMG signals, the same with the interfacial impedance measurement mentioned above, including the size of electrodes, the distance between electrodes from center to center, and the position of attachment. EMG signals were measured by EMG systems (MA300, Motion Lab Systems, Inc.), and the sampling frequency was 500 Hz. An additional gel electrode was placed on the elbow to act as a reference electrode.

Experiments on Human Subjects: All experiments were conducted under approval from the Institutional Review Board at the Southern University of Science and Technology (protocol number: 20190007).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The work was financially supported by the funds of the National Natural Science Foundation of China (grant nos. 51771089 and U1613204), the “Guangdong Innovative and Entrepreneurial Research Team Program” under contract no. 2016ZT06G587, the “Science Technology and Innovation Committee of Shenzhen Municipality” (grant no. JCYJ20160613160524999), and the Shenzhen Sci-Tech Fund (grant no. KYTDPT20181011104007). The authors thank Dr. Siya Huang for her help in electrode preparation.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

epidermal electrodes, rigidity adjustment, silk fibroin, stretchable electronics

Received: February 18, 2020

Revised: March 17, 2020

Published online: April 20, 2020

- [1] M. Ramuz, B. C. K. Tee, J. B. H. Tok, Z. Bao, *Adv. Mater.* **2012**, 24, 3223.
- [2] D. H. Kim, J. A. Rogers, *Adv. Mater.* **2008**, 20, 4887.
- [3] J. A. Rogers, T. Someya, Y. Huang, *Science* **2010**, 327, 1603.
- [4] Y. Sun, W. M. Choi, H. Jiang, Y. Y. Huang, J. A. Rogers, *Nat. Nanotechnol.* **2006**, 1, 201.
- [5] D.-H. Kim, N. Lu, M. Rui, Y.-S. Kim, R.-H. Kim, S. Wang, W. Jian, M. W. Sang, T. Hu, A. Islam, *Science* **2011**, 333, 838.
- [6] H. C. Ko, M. P. Stoykovich, J. Z. Song, V. Malyarchuk, W. M. Choi, C. J. Yu, J. B. Geddes III, J. L. Xiao, S. D. Wang, Y. G. Huang, J. A. Rogers, *Nature* **2008**, 454, 748.
- [7] Y. Wan, Y. Wang, C. F. Guo, *Mater. Today Phys.* **2017**, 1, 61.
- [8] D. J. Lipomi, M. Vosgueritchian, B. Tee, S. L. Hellstrom, J. A. Lee, C. H. Fox, Z. Bao, *Nat. Nanotechnol.* **2011**, 6, 788.
- [9] Y. Wang, L. Wang, T. Yang, X. Li, X. Zang, M. Zhu, K. Wang, D. Wu, H. Zhu, *Adv. Funct. Mater.* **2014**, 24, 4666.
- [10] Z. Liu, J. Li, F. Yan, *Adv. Mater.* **2013**, 25, 4296.
- [11] N. Lu, D. H. Kim, *Soft Rob.* **2014**, 1, 53.
- [12] J. H. Ahn, H.-S. Kim, K. J. Lee, S. Jeon, S. J. Kang, Y. Sun, R. G. Nuzzo, J. A. Rogers, *Science* **2006**, 314, 1754.
- [13] S. Wagner, S. Bauer, *MRS Bull.* **2012**, 37, 207.
- [14] M. A. Meitl, Z.-T. Zhu, V. Kumar, K. J. Lee, X. Feng, Y. Y. Huang, I. Adesida, R. G. Nuzzo, J. A. Rogers, *Nat. Mater.* **2006**, 5, 33.
- [15] D.-Y. Khang, H. Jiang, Y. Huang, J. A. Rogers, *Science* **2006**, 311, 208.
- [16] P. Peng, K. Wu, L. Lv, C. F. Guo, Z. Wu, *Adv. Mater. Technol.* **2018**, 3, 1700264.
- [17] M. Melzer, D. Karnaushenko, G. Lin, S. Baunack, D. Makarov, O. G. Schmidt, *Adv. Mater.* **2015**, 27, 1333.
- [18] L. Hu, H. Wu, Y. Cui, *MRS Bull.* **2011**, 36, 760.
- [19] L. B. Hu, H. S. Kim, J. Y. Lee, P. Peumans, Y. Cui, *ACS Nano* **2010**, 4, 2955.
- [20] C. F. Guo, Z. Ren, *Mater. Today* **2015**, 18, 143.
- [21] B. Han, K. Pei, Y. Huang, X. Zhang, Q. Rong, Q. Lin, Y. Guo, T. Sun, C. Guo, D. Carnahan, M. Giersig, Y. Wang, J. Gao, Z. Ren, K. Kempa, *Adv. Mater.* **2014**, 26, 873.
- [22] K. Kendall, *J. Phys. D: Appl. Phys.* **1975**, 8, 1449.
- [23] S. Ling, Q. Zhang, D. L. Kaplan, F. Omenetto, M. J. Buehler, Z. Qin, *Lab Chip* **2016**, 16, 2459.
- [24] G. Chen, N. Matsuhisa, Z. Liu, D. Qi, P. Cai, Y. Jiang, C. Wan, Y. Cui, W. R. Leow, Z. Liu, S. Gong, K.-Q. Zhang, Y. Cheng, X. Chen, *Adv. Mater.* **2018**, 30, 1800129.
- [25] H. Wu, D. Kong, Z. Ruan, P. C. Hsu, S. Wang, Z. Yu, Y. Cui, *Nat. Nanotechnol.* **2013**, 8, 421.
- [26] C. F. Guo, Q. Liu, G. Wang, Y. Wang, Z. Shi, Z. Suo, C. Chu, Z. Ren, *Proc. Natl. Acad. Sci. USA* **2015**, 112, 12332.
- [27] Y. Wang, Q. Liu, J. Zhang, T. Hong, W. Sun, L. Tang, E. Arnold, Z. Suo, W. Hong, Z. Ren, C. F. Guo, *Adv. Mater.* **2019**, 31, 1902955.
- [28] N. Lu, C. Lu, S. Yang, J. Rogers, *Adv. Funct. Mater.* **2012**, 22, 4044.
- [29] C. F. Guo, Y. Chen, L. Tang, F. Wang, Z. Ren, *Nano Lett.* **2016**, 16, 594.
- [30] H. Yuk, B. Lu, X. Zhao, *Chem. Soc. Rev.* **2019**, 48, 1642.
- [31] G. Li, Z. Qiu, Y. Wang, Y. Hong, Y. Wan, J. Zhang, J. Yang, Z. Wu, W. Hong, C. F. Guo, *ACS Appl. Mater. Interfaces* **2019**, 11, 10373.
- [32] G. A. Holzapfel, *Mechanics of Biological Tissue*, Springer, Berlin **2006**.
- [33] Q. Wang, S. Ling, X. Liang, H. Wang, H. Lu, Y. Zhang, *Adv. Funct. Mater.* **2019**, 29, 1808695.
- [34] C. F. Guo, T. Sun, Q. Liu, Z. Suo, Z. Ren, *Nat. Commun.* **2014**, 5, 3121.
- [35] Q. Wu, Z. Hao, S. Tao, B. Zhang, R. Liu, *Spectrochim. Acta, Part A* **2015**, 151, 124.
- [36] A. Miyamoto, S. Lee, N. F. Cooray, S. Lee, M. Mori, N. Matsuhisa, H. Jin, L. Yoda, T. Yokota, A. Itoh, M. Sekino, H. Kawasaki, T. Ebihara, M. Amagai, T. Someya, *Nat. Nanotechnol.* **2017**, 12, 907.
- [37] Y. M. Chi, T.-P. Jung, G. Cauwenberghs, *IEEE Rev. Biomed. Eng.* **2010**, 3, 106.
- [38] G. H. Altman, F. Diaz, C. Jakuba, T. Calabro, R. L. Horan, J. S. Chen, H. Lu, J. Richmond, D. L. Kaplan, *Biomaterials* **2003**, 24, 401.
- [39] H. Yuk, T. Zhang, G. A. Parada, X. Liu, X. Zhao, *Nat. Commun.* **2016**, 7, 12028.