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ADHESIVE, PERMEABLE, AND WEARABLE ELECTRONIC SKIN

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PhD

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2024

The Hong Kong Polytechnic University

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**Adhesive, Permeable, and Wearable
Electronic Skin**

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**A thesis submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy**

August 2023

CETIFICATE OF ORIGINALITY

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ABSTRACT

Skin electronics provides remarkable opportunities for non-invasive and long-term monitoring of a wide variety of biophysical and physiological signals that are closely related to health, medicine, and human-machine interactions. Nevertheless, conventional skin electronics fabricated on elastic thin films are difficult to adapt to the wet microenvironments of the skin: elastic thin films are non-permeable, which blocks the skin perspiration; elastic thin films are difficult to adhere to wet skins; most skin electronics are difficult to work stably under wet conditions. In this thesis, these issues are solved by developing state-of-the-art adhesive, permeable and wearable electronic skins.

First, a wet-adaptive electronic skin (WADE-skin) has been investigated, which consists of a next-to-skin wet-adhesive fibrous layer, a next-to-air waterproof fibrous layer, and a stretchable and permeable liquid metal electrode layer. While the electronic functionality is determined by the electrode design, this WADE-skin simultaneously offers superb stretchability, wet adhesion, permeability, biocompatibility, and waterproof property. The WADE-skin can rapidly adhere to human skin after contact for a few seconds and stably maintain the adhesion over weeks even under wet conditions, without showing any negative effect to the skin health. This study demonstrates the use of WADE-skin for the stable recording of electrocardiogram during intensive sweating as well as underwater activities, and as the strain sensor for the underwater operation of virtual reality-mediated human-machine interactions.

Second, a strategy called “nanofibers-to-hydrogel” has been proposed to improve the conformability and reduce the skin impedance for the liquid-metal epidermal electrodes. The liquid-metal PVA fiber mats that are fabricated by electrospinning are easily handled and use-friendly. The hydrophilic PVA fiber mats possess the ability to

rapidly absorb saline water, enabling the on-demand production of ultrathin hydrogel tattoos. These resulting hydrogel tattoos are stretchable, permeable and could conformally adheres to the skin. Furthermore, these hydrogel tattoos display low skin impedance compared to the commercial Ag/AgCl gel electrode. The application of these hydrogel tattoos as biophysiological electrodes for detecting ECG signals for health monitoring, as well as their integration into a 6-channel EMG sensor array for gesture recognition enhanced by machine learning, are demonstrated.

Finally, an all-fiber-mat, permeable, wet-adhesive, and superplastic triboelectric skin (PAST e-skin) has been proposed. The triboelectric fiber mat was fabricated by coaxial electrospinning, resulting in a notable enhancement of stretchability from 200% to 600%, and a reduction in the residue strain from 60% to 30.6% under 100% pre-stretching. The PAST e-skin pertains a wet- and skin-adhesive fiber mat that could seamlessly adheres the PAST e-skin to the wet human skin with an impressive adhesion strength of 80 kPa. The PAST e-skin simultaneously offers high stretchability, low residue strain, textile-like permeability, and wet-adhesive properties. The PAST e-skin exhibits an open-circuit voltage of 96.7 V and a short-circuit current of 4.0 μ A. Furthermore, the on-skin monitoring in different body locations has been also achieved by the PAST e-skin.

In conclusion, this thesis first introduced a pioneering wet-adaptive electronic skin that offers exceptional stretchability, wet adhesion, permeability, biocompatibility, and waterproof properties. Subsequently, an innovative approach, named “nanofibers-to-hydrogel” was developed to produce biophysiological electrodes with permeability, skin adhesion, and low impedance properties. Finally, a type of fibrous triboelectric e-skin was proposed, showcasing permeability, adhesiveness, and stretchability. It could envision that this thesis will bring effective and universal solutions to the development

of wet-adaptive and high-performance on-skin electronics with a more comfortable and user-friendly wearing experience.

LIST OF PUBLICATIONS

Published papers:

1. **Fan Chen**, Qiuna Zhuang, Yichun Ding, Chi Zhang, Xian Song, Zijian Chen, Yaokang Zhang, Quanjin Mei, Xin Zhao, Qiyao Huang, Zijian Zheng, Wet-adaptive electronic skin. *Advanced Materials*, **2023**. 35, 2305630.
2. **Fan Chen**, Qiyao Huang and Zijian Zheng, Permeable conductors for wearable and on-skin electronics. *Small Structures* **2022**, 3, 2100135.
3. Qiuna Zhuang, Kuanming Yao, Mengge Wu, Zhuogui Lei, **Fan Chen**, Jiyu Li, Quanjing Mei, Yingying Zhou, Qiyao Huang, Xin Zhao, Li Ying, Yu Xinge and Zheng Zijian, Wafer-patterned, permeable, and stretchable liquid metal microelectrodes for implantable bioelectronics with chronic biocompatibility. *Science Advances* **2023**, 9, eadg8602.
4. Yaokang Zhang, Yufeng Luo, Lei Wang, Pui Fai Ng, Hong Hu, **Fan Chen**, Qiyao Huang and Zijian Zheng. Destructive-Treatment-Free Rapid Polymer-Assisted Metal Deposition for Versatile Electronic Textiles. *ACS Applied Materials & Interfaces* **2022**, 14, 56193.

Paper in Preparation:

1. **Fan Chen**, Xian Song, jinxing Jiang, jingjing Fu, Qiyao Huang, Zijian Zheng, All-fiber-mat, permeable, wet-adhesive, and superelastic triboelectric skin
2. Yichun Ding, **Fan Chen**, Zijian Zheng, On-demand “nanofibers-to-hydrogel” formation of ultrathin liquid metal hydrogel tattoo for conformable and low-impedance skin electronics.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my sincere gratitude to my supervisor Prof. Zheng Zijian for offering me such a precious opportunity to pursue my Ph.D. study in his group. His wealthy knowledge and meticulous attitude towards scientific research inspired and shaped me a lot. His patient guidance and encouragement support me to move forward progressively. I also appreciate the assistance from Prof. Huang Qiyao.

I am also much grateful to all members of Prof. ZHENG's group for the great lab environment as well as the helping group culture contributed by all of them. I sincerely appreciate to Ms. Zhuang Qiuna, Pro. Ding Yichun, Dr. Song Xian, Dr. Zhang Chi, Dr. Zhang YaoKang, Dr. Zhang Yufei, Dr. Fu Jingjing, Mr. Jiang jinxing, Dr. Hu Hong, Dr. Xu Hailong, Dr. Rong Mingming, Dr. Wang wenshuo, Dr. Wang Chao, Dr. Guo Qianyi, Ms. Zhong Leni, Mr. Chen Zijian, Mr. Zhang Pengxiang, Mr. Wei Zhenyao, Mr. Yu Wancheng, Mr. Fang Lingtao, Ms. Wen Shujing, Mr. Chen Lixi, Mr. Ma Xiaohao, Ms. Shi Yuqing, Dr. Ng Miya, Dr. Luo Yufeng, Dr. Wang Pengwei, Dr. Pei Yi, Dr. Xie Chuan, Dr. Wu Yingsi, Dr. Zhou Junhua, Dr. Wang Huimin, Dr. Gao Yuan, Dr. Wang Lei, Dr. Xu Junling for their intensive training, assistance, discussion, and suggestion during my research activities. Many thanks to all the technicians and partners who are actively engaged in this project. I would like also to thank the technical staffs at Materials Research Center (MRC), University Research Facility in Chemical and Environmental Analysis (UCEA), and industry center. The financial support from the Hong Kong Polytechnic University is well acknowledged.

Finally, I am very much thanks to my parents and all family members for their constant love and support.

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LIST OF ABBREVIATIONS

Carbon nanotubes	CNTs
reduced graphene oxide	RGO
polyaniline	PANI
polypyrrole	PPY
poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)	PEDOT:PSS
Bovine serum albumin	BSA
Liquid Metal	LM
Thermoelastic polyurethane	TPU
Liquid Metal	LM
Eutectic Gallium-Indium alloy	EGaIn
Poly(styrene-butadiene-styrene)	SBS
Thermoplastic polyurethane	TPU
3-[(Ethylimino)methylidene]amino-N,N-dimethylpropan-1-amine	EDC
N-Hydroxy succinimide	NHS
polydopamine	PDA
Polyacrylic acid grafted with NHS and dopamine	PAAND
Wet-adaptive electronic skin	WADE-skin
virtual reality	VR
augmented reality	AR
mixed reality	MR
internet of things	IoTs
analog-to-digital conversion	ADC
degree-of-freedom	DOF
Polyimide	PI
Polycarbonate	PC
Polyethylene terephthalate	PET
Polyvinyl alcohol	PVA
N-hydroxysulfosuccinimide	sulfo-NHS
Polyacrylic acid grafted with sulfo-NHS and dopamine	PAASND

pressure sensitive adhesive	PSA
electrocardiogram	ECG
electrooculogram	EOG
electromyography	EMG
electroencephalogram	EEG
Liquid-metal Hydrogel Tattoo	LMHT
Poly(vinylidene fluoride)	PVDF
Poly(vinylidene fluoride-co-trifluoroethylene)	P(VDF-TrFE)
Permeable, Adhesive, and Stretchable Triboelectric e-skin	PAST e-skin
Triboelectric nanogenerator	TENG
Polytetrafluoroethylene	PTFE
Polydimethylsiloxane	PDMS

CHAPTER 1: INTRODUCTION

1.1 Background and Challenges

Skin-attachable flexible and stretchable electronics show great promises in the applications of non-invasive and imperceptive health monitoring, precision medicine, and human-machine interface^[1-6]. Unlike rigid substrates, skin is soft and dynamic^[7-8]. Therefore, a large number of researches have been focused on the development of soft materials, mechanics, and functions to tackle the mismatch between electronic devices and skin surfaces in the past two decades^[9-15]. With the leverage of advanced technologies such as virtual reality (VR), augmented reality (AR), and machine intelligence, epidermal electronics is recently directed toward a more function-precise, user-friendly, and intelligent direction^[16-21].

Despite those remarkable progresses achieved toward device stretchability, functionality, and biocompatibility^[22-24], the wearing comfort issues induced by the coverage of flexible and stretchable electronics have been largely underestimated^[10, 25-30]. In contrast to the dry environment which conventional electronic applications are in favor of, a constantly changing wet environment occurring on the skin will influence the epidermal electronics^[31]. It is known that skin perspires through “insensible perspiration” by the evaporation of water moisture and “sensible perspiration” by means of sweating^[32]. For providing physiological comfort and reducing uncomfortable sensations and skin allergies and inflammation, the on-skin or wearable electronics should support a microenvironment for human skin to evaporate the sensible or insensible perspiration. The long-term wearing of electronic devices with insufficient permeability to moisture could seriously affect the moisture evaporation of human skin to the outer environment, thus causing uncomfortable sensations and even leading to skin allergies and inflammation^[26, 33-34]. For the urgent demands on comfortable

wearing and functionality, flexible and stretchable electronics with permeability to the air, water moisture, and liquid, called permeable electronics or breathable electronics, has been proposed in recent several years^[25, 33].

Meanwhile, ensuring a strong and conformal adhesion of the device on the skin is crucial to the high performance of epidermal electronics^[35-36]. The adhesion is typically achieved by a combination of van der Waals forces, electrostatic interactions, hydrogen bonds, and covalent bonds^[37-45]. However, the accumulation of water at the device/skin interface tends to significantly weaken the bonding strength between the device and the skin, resulting in unstable device performance and even easy detachment of the device^[46-49]. Developing a strong adhesion strength and more versatile adhesive toward human skin or tissues is still challenging.

Furthermore, epidermal electronics also faces challenges in the wet environment from the daily exposure to foreign water droplets during washing and showering, or in applications that are carried out in the rain or under the water^[50-52]. Although a full encapsulation of the device with another water-impermeable coating may protect the device from foreign water^[53], it will further escalate the negative influence of water at the device/skin interface as discussed above. To date, there is a strong need for an epidermal electronic device that is highly adaptive to different wet environments to ensure the device performance and chronic biocompatibility over long-term attachment.

1.2 Research Objectives

According to the challenges discussed above, this thesis focuses on developing the adhesive, permeable, and wearable electronic skins for wet-adaptive, non-invasive, comfortable, and stable health monitoring and human-machine interactions. The detailed objectives are listed below:

1. To fabricate stretchable, permeable, conductive, and waterproof fibrous substrates by electrospinning for providing physiological comfort during long-term wearing.
2. To fabricate skin-adhesive and permeable fibrous substrates by electrospinning for conformal and strong adhering to the human skin during wet conditions.
3. To fabricate human motion sensors and biophysiological sensors for non-invasive and comfortable health monitoring and human-machine interactions.
4. To investigate liquid-metal-based stretchable and permeable electrodes with higher conformability and lower skin impedance.
5. To investigate intrinsically stretchable, permeable, skin-adhesive triboelectric e-skin for human motion monitoring.

1.3. Research Originality

Electronic skins have been developed for more than one decade. Since they are used as on-skin electronics, electronic skins are always exposed to different kinds of wet scenarios either from the body (such as moisture perspiration and sweat) or the outer environment (such as rainfall and ocean). The adaptability to these wet conditions not only improves the device stability and applicability but also is essential to the long-term biocompatibility of the wearer. However, wet adaptability is often overlooked by the research communities.

Here in Chapter 4, a wet-adaptive electronic skin (WADE-skin) was reported, which consists of a next-to-skin wet-adhesive fibrous layer, a next-to-air waterproof fibrous layer, and a stretchable and permeable liquid metal electrode layer. While the electronic functionality is determined by the electrode design, this WADE-skin might be the first

skin-attachable electronics that simultaneously offers superb stretchability, wet adhesion, permeability, biocompatibility, and waterproof property. The WADE-skin can rapidly adhere to human skin after contact for a few seconds and stably maintain the adhesion and device performance over weeks even under wet conditions. Meanwhile, it does not exhibit negative effects on the human skin. The use of WADE-skin for the stable recording of electrocardiogram during intensive sweating and underwater activities, and as strain sensors for the underwater operation of virtual reality-mediated human-machine interactions have been demonstrated. It is believable that wet adaptability is a milestone in the field of wearable electronics and electronic skins, and this work will appeal to the broad researchers in applied physics, materials science and engineering, soft electronics, polymer science, and interface.

Skin-attachable electrodes, the electrodes adhered to the human skin for the detection of biophysiological signals, are great of importance for health monitoring, gesture recognition, and human-machine interactions. However, fabrication of the electrodes with stretchability, permeability, conformal adhesiveness, and low impedance is still a challenge.

In Chapter 5, a strategy called “nanofibers-to-hydrogel” to fabricate ultrathin liquid metal hydrogel electrodes was investigated for the first time. The liquid-metal PVA fiber mats are easily handled and use-friendly and could instantly absorb saline water thus forming hydrogel tattoos at the surface of the skin. The formed hydrogel tattoo is stretchable and permeable and could conformally adhere to the skin. The hydrogel tattoo displays a low skin impedance compared to the commercial Ag/AgCl gel electrode. The hydrogel tattoos were investigated as a biophysiological electrode to detect ECG signals for health monitoring and assembled to a 6-channel EMG sensor array for gesture recognition assisted by machine learning. This “nanofibers-to-hydrogel” strategy paves the way for the easy and on-demand fabrication of ultrathin

and high-performance hydrogel electrodes and has great potential for next-generation personalized health monitoring, smart gesture recognition, and human-machine interaction.

Triboelectric devices show great potential for skin-attachable bio-mechanical energy harvesting and intimate and noninvasive human motion monitoring. However, to conform during skin deformations, reduce the risks of skin inflammation, and provide stable performance in wet skin, triboelectric devices with permeability, stretchability, low residue strain, and wet adhesion are highly demanded but still challenging.

In Chapter 6, an all-fiber-mat, permeable, wet-adhesive, and superplastic triboelectric skin (PAST e-skin) has been proposed firstly. The triboelectric fiber mat was fabricated by coaxial electrospinning, which significantly enhances the stretchability from 200% to 600% and reduces the residue strain from 60% to 30.6% within 100% pre-stretching. The PAST e-skin pertains a wet- and skin-adhesive fiber mat that could seamlessly adheres the PAST e-skin to the wet human skin with the adhesion strength of 80 kPa. The PAST e-skin simultaneously offers high stretchability, low residue strain, textile-like permeability, and wet-adhesive properties. The triboelectric outputs of the PAST e-skin have been investigated and on-skin monitoring in different body locations using the PAST e-skin has also been conducted. This PAST e-skin offers a new route to design high-performance triboelectric epidermal sensors with permeability, stretchability, and wet adhesion property while putting this field in a more conformal, stable, and comfortable way.

Overall, this study introduced a wet-adaptive electronic skin for the first time, which simultaneously offered superb stretchability, wet adhesion, permeability, biocompatibility, and waterproof property. Afterward, an original strategy “nanofibers-to-hydrogel” has been developed for the fabrication of permeable, skin-adhesive, and

low-impedance biophysiological electrodes. In the end, a type of triboelectric e-skin with permeability, adhesiveness, and stretchability has been proposed. It could envision that this thesis will bring an effective and universal solution to the development of wet-adaptive on-skin electronics with a more comfortable and user-friendly wearing experience.

1.4 Outline of the Thesis

The thesis is organized as follows:

Chapter 1 gives a brief introduction to the general background of permeable electronics and the remaining challenges. Then the research objectives and the originality are also included.

Chapter 2 reviews the design considerations of permeable electronics and the fabrication strategies of nanofiber-mat-based permeable electronics. Furthermore, the adhesive and permeable electronics have been concluded and the wet-adhesive strategies for skin-attachable electronics have been discussed.

Chapter 3 introduces the experimental methodology in detail, including materials, fabrication processes and instruments, and the characterization procedures.

Chapter 4 illustrates the fabrication of a wet-adaptive electronic skin (WADE-skin) that simultaneously offers superb stretchability, wet adhesion, permeability, biocompatibility, and waterproof property and demonstrates the use of WADE-skin for the stable recording of electrocardiogram during wet conditions, and as strain sensors for the underwater operation of virtual reality mediated human-machine interactions.

Chapter 5 introduces a strategy “nanofibers-to-hydrogel” to transform the nanofiber

mats into ultrathin and low-impedance liquid metal hydrogel electrodes and utilizes the transformed hydrogel electrode for precise recording of biophysiological signals.

Chapter 6 investigates an all-fiber-mat, permeable, skin-adhesive, and superplastic triboelectric skin (PAST e-skin) and demonstrates the precise on-skin monitoring of body motions.

CHAPTER 2: LITERATURE REVIEW

In this part, we first discussed the background, significance, and fabrication method of permeable electronics. Then, we introduced the adhesion method for adhering electronics to tissues. Lastly, we discussed the necessity of systematic integration of permeable electronics.

2.1 Development of Permeable Electronics

Flexible and stretchable electronics, a type of electronics which is bendable or stretchable, have attracted intense attention due to their broad applications in various fields, including wearable or on-skin electronics, human-machine interaction, soft robotics, implantable electronics, soft display, flexible energy harvesters, and energy storage devices^[54-67]. Flexible and stretchable electronics usually consist of two types of functional parts: conductive materials and substrates, while the adhesive could be also indispensable for the specific purpose (*e.g.*, on skin). Tremendous advances have been developed in the fabrication of high-performance flexible electronics. Traditional rigid metals (*e.g.*, Cu, Ag, Au) can be engineered with structures to the flexible and stretchable substrates (*e.g.*, PI, PET, PEI, PDMS, Ecoflex, TPU, SBS) to fabricate flexible and stretchable electronics. Metallic nanoparticles, metallic nanowires, as well as carbon-based nanomaterials, could be used as conductive fillers or coating for the fabrication of flexible and stretchable electronics by forming conductive percolation networks. Furthermore, the employment of intrinsically stretchable gallium-based liquid metal alloys has driven the electronics approaching a superelastic state since the room-temperature liquid state property and high conductivity (10^6 S m^{-1})^[68-69].

Unlike rigid substrates, skin is soft and dynamic. The flexibility or stretchability and conductivity make flexible and stretchable electronics highly promising for skin-

attachable health monitoring, personalized medicine, and human-machine interactions. Although plenty of breakthroughs have been developed on flexible to highly stretchable conductors, multi-functional devices, and the integration of flexible and stretchable electronics to the Internet of things, there still have obstacles in the skin-attachable electronics field.

The first is wearing comfort^[25-26]. From the viewpoint of physiological comfort, health skin secretes sweat from day to night, which requires the on-skin or wearable electronics should offer a microenvironment with sufficient permeability for human skin for sensible or insensible perspiration. Long-term covering of impermeable substrates to the human skin inhibits the evaporation of secreted sweat from the skin to the outer environment and may cause skin overhydration and maceration of the stratum corneum^[34]. The changed skin microenvironment may weak the barrier function and further induce skin inflammation or irritant contact dermatitis^[26, 33, 70]. Therefore, the long-term wearing issues of flexible and stretchable electronics should be systematically and dermatologically investigated. On the other hand, permeability to the analytes, for example, exhausted air, electrolytes from the secreted sweat, and so on., which benefits the detection of physiological signals of human beings, greatly facilitates the application of flexible and wearable electronics in multi-functional biological sensing^[55].

For the urgent demands on comfortable wearing and functionality, flexible and stretchable electronics with permeability to the air, water moisture, and liquid, called permeable electronics or breathable electronics, have been proposed in recent several years^[25-26, 33, 71-77]. As shown in Figure 2.1, textiles made by weaving or knitting, films engineered with regular or irregular pores, and micro/nano fiber mats are three kinds of permeable substrates for fabricating permeable electronics^[62, 78-84]. Two routes to render these permeable substrates conductive, that is, direct coating or fabricating conductive

material-substrate composites^[85]. Furthermore, through depositing rigid metals (*e.g.*, Cu, Ag, Au), introducing percolation networks of metallic- and carbon-based nanomaterials, or coating gallium-based liquid metal alloys, permeable electronics can possess conductivity and remain conductive under stretching^[10, 25, 33, 86].

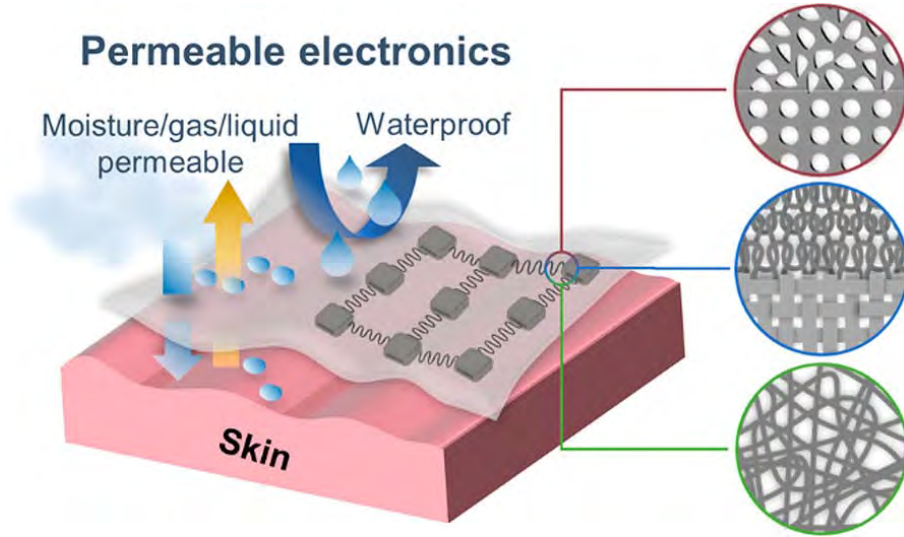


Figure 2.1. Schematic illustration showing the building substrates of permeable electronics^[85].

2.2 Design Considerations for Permeable Electronics

For electronics attached to human bodies, the design of materials and structures needs to take both device functionalities and physiological comfort into consideration^[87-88].

The wearable and on-skin electronics, need to possess such properties: (i) permeability to gas and water to fundamentally ensure a healthy thermal microenvironment of skin/device interface so that the biocompatibility of the electronic systems can be guaranteed; (ii) flexibility or stretchability that can allow the electronic device to accommodate strains induced by the dynamic body or skin deformations without

mechanical failure and noticeably sensational discomfort; (iii) conductivity so that as-made devices can perform their electronic functions; and (iv) adhesiveness to enable stably and intimate attachment to the human skin. **Figure 2.2a** illustrates these key design considerations for wearable and on-skin electronics. The permeability and stretchability of wearable and on-skin electronics will be elucidated below. The conductivity will be introduced during Part 3 of this chapter, while the adhesiveness for wearable and on-skin electronics will be discussed in Part 2.4 of this chapter.

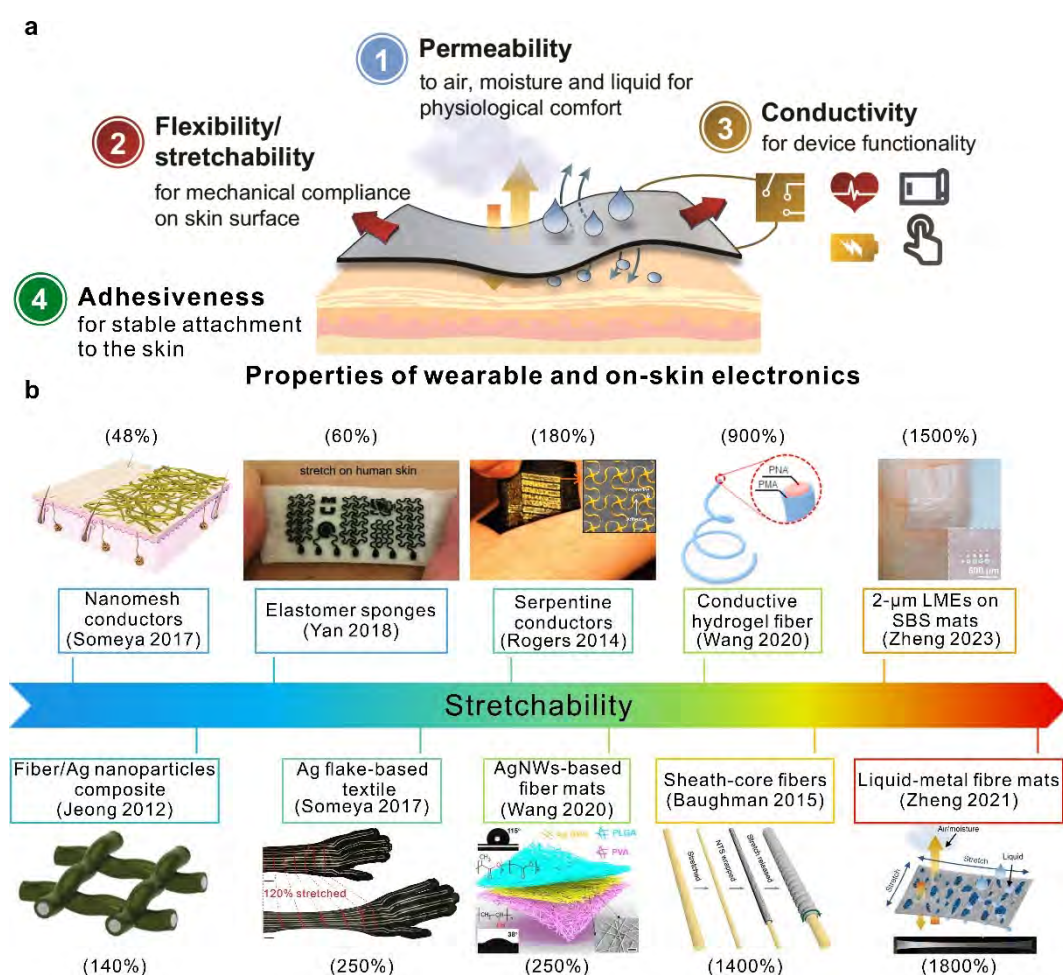


Figure 2.2. **a**, Required properties for wearable and on-skin electronics. **b**, Key advances among the permeable electronics.

2.2.1 Permeability

Skin is the largest organ of the human being with an area of about 1.7 m^2 to 2 m^2 . It performs critical functions for our human beings, including regulating body temperature by sensible or insensible perspiration and as a protective barrier from the outer environment. In general, sweat is constantly secreted from sweat glands to the skin's surface and evaporates to the outer environment. Figure 2.3 graphically illustrates the rates of sensible and insensible perspiration in different body areas of the human being. According to different body areas, the insensible perspiration rate is about $300\text{--}600 \text{ g m}^{-2} \text{ day}^{-1}$ [89]. However, when doing exercises or in a hot environment, the sensible perspiration rate could reach 0.5 L h^{-1} – 1 L h^{-1} [90–92]. The sweaty surfaces of the skin challenge the design of on-skin electronics. On-skin electronics with insufficient permeability will inhibit the evaporation of sweat, thus causing the overhydration and maceration of the skin and weakening the barrier functions of the stratum corneum [34]. The changed skin microenvironment may further induce skin inflammation or irritant contact dermatitis [26, 33, 70]. Therefore, permeability matters in the wearing comfort and safety of flexible and stretchable electronics in a dermatological way. On-skin electronics, which are attached to the surface of the skin, are highly recommended to offer sufficient air/moisture permeability [25, 33].

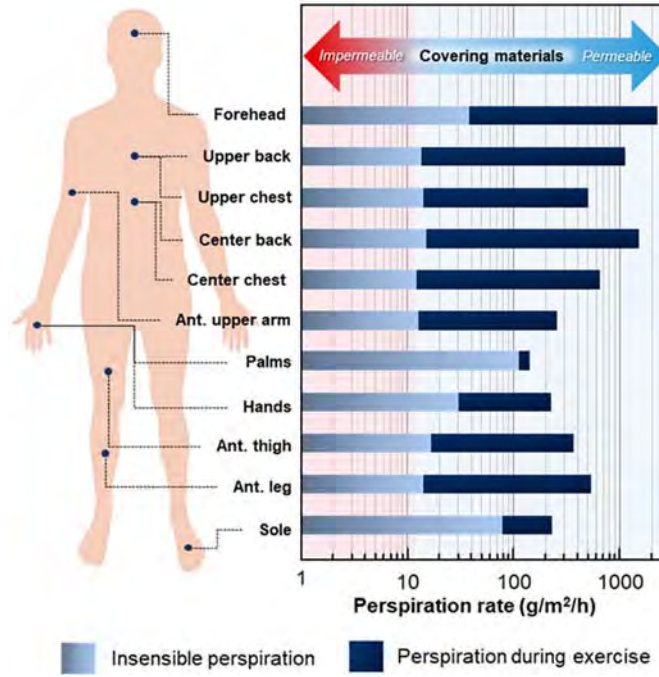


Figure 2.3. Sensible and insensible perspiration rates for the human being in different body areas^[93].

On the other hand, human sweat, containing water metabolites, and electrolytes, is an important body fluid, which provides a lot of information indicating health and fitness conditions^[94]. To analyze human sweat portably, the sweat should reach the target biochemical sensors to induce specific chemical or electrochemical reactions for detection. Apart from making a channel for the transport of sweat, permeable substrates demonstrate intrinsic merits in sweat sensors since the porous structure could allow the flow of sweat to the sensor area^[95].

In consequence, the permeability to gas, moisture, and liquid is highly important for the fabrication of on-skin electronics. Textiles, porous films, and micro/nano fiber mats have been investigated as the idea substrate for fabricating permeable electronics and the permeability of these materials is mainly affected by porosity, thickness, as well as material properties^[96-105]. Therefore, promising strategies to fabricate permeable electronics are to engineer the porous structure and thickness of electronics substrates

to enable permeability to the air, moisture, and liquid^[82-83, 106-107].

The ability of moisture vapor permeability, the amount of moisture vapor penetrated through the materials in a certain period, is reflected in terms of water vapor transmission rate (WVTR). ASTM E96E is the widely-used standard for measuring the WVTR, where the moisture vapor permeability can be measured by covering the materials at the top of a lidless water container and weighting the water loss per hour (or per day) per square meter ($\text{g m}^{-2} \text{h}^{-1}$ or $\text{g m}^{-2} \text{day}^{-1}$). To ensure a healthy thermal and moisture exchange microenvironment, the value of moisture vapor permeability is commended better than $300 \text{ g m}^{-2} \text{day}^{-1}$ for wearable and on-skin electronics^[34]. Air permeability can be measured by measuring the air velocity that passes through materials with a certain area and at a specified differential air pressure between the top and bottom surface of the material and is denoted as $\text{cm}^3 \text{s}^{-1} \text{cm}^{-2}$ (or $\text{m s}^{-1} \text{cm}^{-2}$). Both water vapor transmission rate and air permeability can be directly used for the assessment and comparison of the “breathability” of different kinds of permeable electronics. Higher the values of water vapor transmission rate and air permeability, the better permeability the materials have.

2.2.2 Flexibility and Stretchability

Human skin is soft and dynamic. It will elongate and recover during human motions. The skin stretch varies in different body positions, and its elongation rate can be up to 35~45% strain with an elastic modulus ranging from 10kPa to a few hundred kPa^[87, 108]. Over 100% of strain can even be induced at joint areas of the human body during the movement^[109-110]. Therefore, skin-attachable electronics are required to be flexible, or even elongated and deformed along with the body movement, while maintaining a promising level of performance and reliability that can be comparable to those of well-developed rigid electronic systems^[111]. Due to the wide range of applications of on-

body electronics, flexibility, and stretchability requirements for conductors are largely varied. For example, electronic devices worn by wrists require electronics at least is bendable, while achieving a successful strain sensor device for measuring the movement of body joints primarily requests that the electronics can accommodate the strain of at least 100% without mechanical failure^[109, 112]. Super-stretchable conductors with stretching strain larger than 1,000% could further open up the applications of stretchable electronics in soft robotics or soft human-machine interfaces, in which the conductive stability of conductors over large deformations is highly important^[113-114]. From the other aspect, on-skin sensors built on flexible and stretchable materials with skin-like Young's modulus can be conformably attached to the skin surface, offering a better signal-to-noise ratio and wearing comfort^[108]. Moreover, Researchers in garment comfort have revealed that fabrics with 15~30% elongation can provide minimum resistance to body movements around elbows, knees, and back, which could serve as a reference for designing conductors and devices for wearable and on-skin electronics^[87].

Two main strategies have been proposed to make flexible electronics either extrinsically or intrinsically stretchable, which is illustrated in Figure 2.2b with representative permeable conductors. They are: (i) engineering the conductor structures to achieve extrinsically structural stretchability, and (ii) developing novel conductive materials or composites to make all the components “intrinsically stretchable”. The first approach usually involves implementing ultrathin metallic and semiconductor layers to enable flexibility and then constructing them into wavy, serpentine, kirigami, and/or mesh shapes to yield stretchability^[115-120]. The second approach is to develop new conducting composite materials that can simultaneously have conductive properties and mechanical deformability. A general approach is to load conductive materials into an elastic matrix ((e.g., polydimethylsiloxane (PDMS), polyurethane (PU), polystyrene-block-polybutadiene-block-polystyrene styrene (SBS)) to form intrinsically stretchable

conductors^[121-124].

2.3 Nanofiber mat-based Permeable Electronics

Electrospinning is a very simple but effective and high-throughput method to fabricate fiber mats from the laboratory scale to continuously large-scale commercial production^[125]. Compared to permeable substrates made by textiles or porous films, electrospinning shows ubiquitous advantages for the fabrication of micro/nano fiber-based mats, including 1) versatility, in which a hundred polymers both natural and synthetic can be used, 2) simplicity, experimental setups can be easily constructed in the laboratory scale, 3) capability for large-scale production^[125-128]. The large surface area and high porous volume not only realize the gas and water permeability for the “breath” of the skin but also achieve high mass and area loadings of conductive materials^[128].

The experimental setup of electrospinning is shown in Figure 2.4^[125]. The production process is driven by the high electric field. When a high-voltage field is applied between the spinneret and the collector, the electrostatic charges accumulate at the surface of the polymer solution at the tip of the spinneret. Then, the shape of the solution is changed from a spherical surface to a cone shape (called Taylor Cone) because the increased charge repulsion overcomes the surface tension of the solution, and a jet is extruded from the spinneret in a straight path and then travels with a drastic whipping toward the collector at the electrostatic field. The continuous polymeric fiber is formed during the flying of the jet due to the evaporation of the solvent and the stretching of electrostatic force. Fiber-based mats are obtained after a certain time for collection. The thickness of electrospun mats can be easily adjusted by varying the collection time. In addition, aligned nanofiber-based mats can be realized by the high rotation speed drum and core-sheath nanofibers can also be fabricated by coaxial electrospinning.

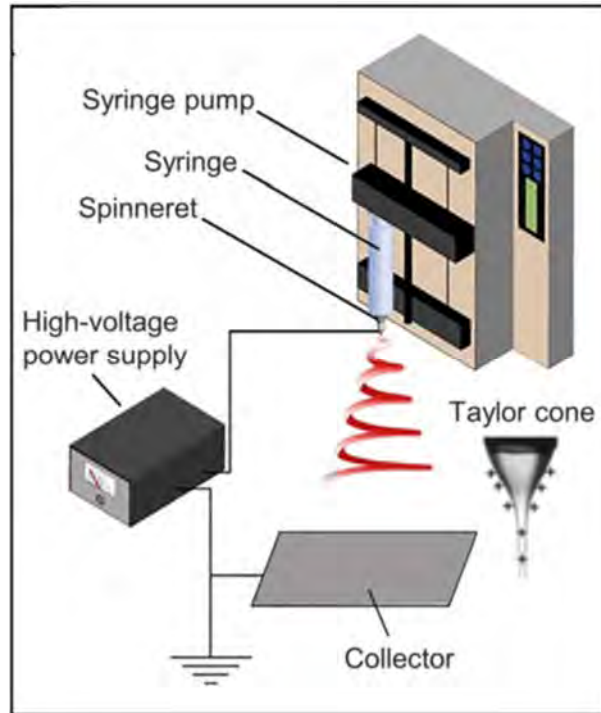


Figure 2.4 Schematic illustration of electrospinning^[125].

The electrospun mats can be used for both the temporary template for the formation of metallic nanostructure networks and stretchable substrates for the construction of breathable and stretchable electronics^[25, 33, 129]. Most conductors can be well employed in electrospun mats for fabrication, while the conductors assembled on the electrospun mats may show unique advantages due to the fiber-shape structure.

The common conductive materials, including metals, liquid metal, nanomaterials, and conductive polymers have been used in the fabrication of electrospun mat-based electronics and classified into structurally stretchable electronics and intrinsically stretchable electronics by flexibility^[25, 71, 77, 129-130]. Methods of introducing these kinds of conductors are mainly included vacuum deposition, sputtering, stencil printing, screen printing, spraying, dip coating, forming conductive material/polymer composite by co-electrospinning the mixed solution, as well as the chemical reduction. Methods of introducing the conductors may be varied due to intrinsic differences, making

electrospun mat extensively applied in many areas spanning from conductors, electrodes, sensors (*i.e.*, photodetectors, strain and pressure sensors, chemical sensors), LEDs to energy harvesters and energy storage devices (Figure 2.5)^[131].

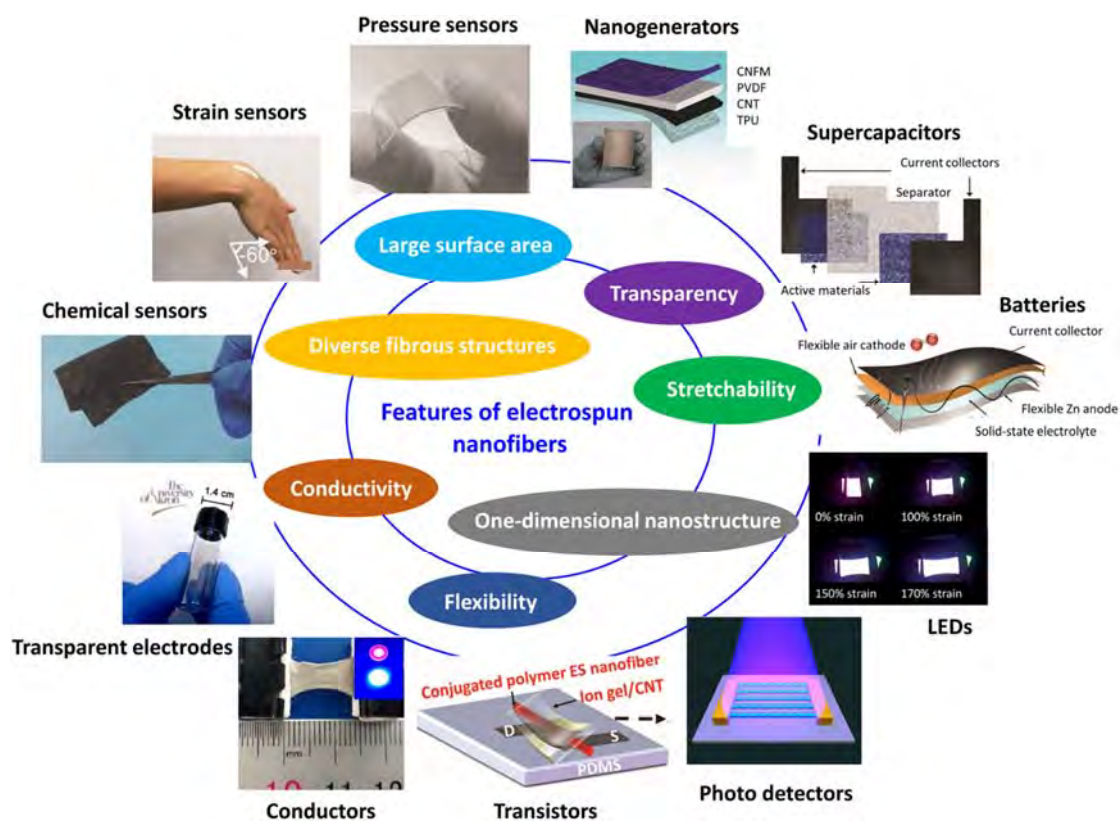


Figure 2.5 Merits and applications for electrospun mats^[131].

2.3.1 Metals

Metals can be introduced into the electrospun mat via vacuum deposition or sputtering. For example, a metal nanotrough network has been fabricated on the PVA electrospun mat by depositing metals (Au, Cu, Ag, Al). By dissolving the PVA electrospun mat, the metallic nanotrough network can be transferred onto various substrates, like PET films, plastic, paper, and curved glass container. The metallic nanotrough-based conductive transparent electrode displayed excellent optoelectronic performance with a sheet

resistance of 2 Ω /square at 90% transmission, considerable flexibility (50 % tensile strain), and durability against 1000 cycles of repeated bending to a 10 mm radius^[129].

For the fabrication of gas-permeable, inflammation-free, comfortable interfacing between human skin and devices to enable long-term health monitoring, this strategy also was employed for on-skin electronics^[33]. The PVA electrospun mat was dissolved by water while the Au nanomesh conductor conformably adhered to the skin, realizing tough, temperature and pressure sensing, and high-precision electromyogram (ECG) recording. The nanomesh conductors show the maximum tensile strain at 48% and a 3 times increase of the resistance after 10,000 cycles of finger bending (about 40% elongation). More notably, due to the highly porous structure, the nanomesh-based electronics presented excellent gas-permeability that is close to the opening conditions, resulting in comfortable wearing and no one case of inflammation observed for one week of wear. Further coating PDMS onto nanofibers, the formed core-sheath polyurethane-PDMS nanomeshes shows enhanced mechanical and electrical stability^[132].

The dissolution of PVA nanofibers not only displayed adhesion to the skin but also enabled the connection between two separate electrospun mats. A nanomesh sensor based on four layers has been reported^[97], which is including the following four layers: a passivation layer based on the polyurethane (PU) nanomesh, a top conductive Au nanomesh, an intermediate parylene-reinforced PU nanomesh layer, and a bottom Au electrode layer. The Au electrode layer formed by the dissolution of the PVA nanofibers, and the layers bonded to each other contributed to the dissolution of PVA nanofibers. The monitoring of finger pressure without interference with human sensation has been demonstrated since the porous structure of the multilayer nanomesh sensor, and the upper thin PU nanomesh-based passivation layer enabled the nanomesh sensors with excellent durability against friction, which could maintain its functionality at over 100

kPa pressure rubbing or after 300 cycles at a 50-g weight rubbing.

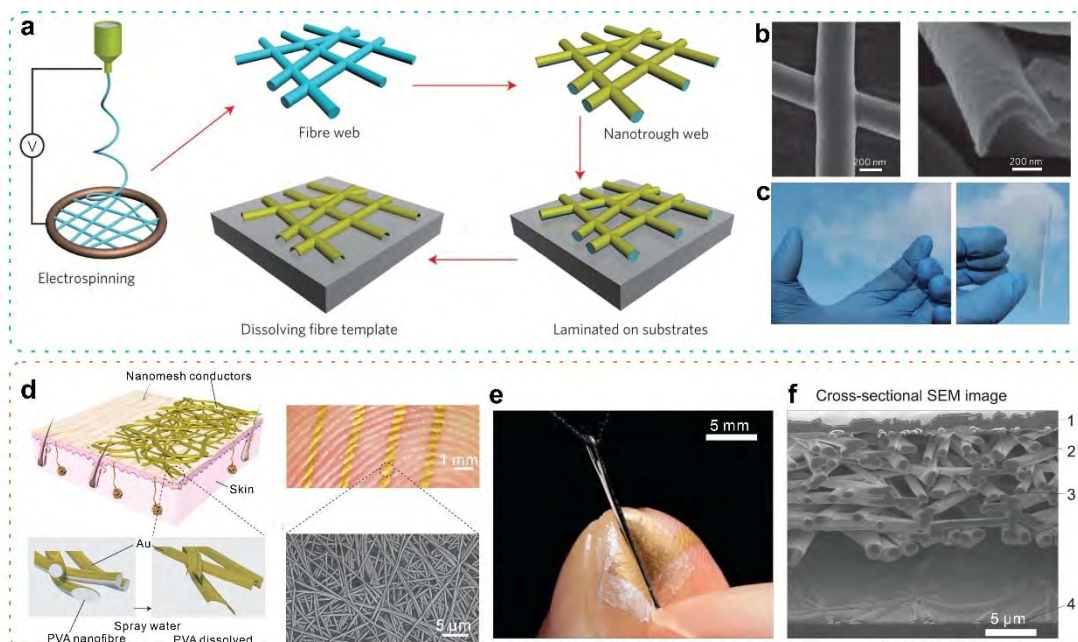


Figure 2.6. **a**, Fabrication and transfer procedures for the metallic nanotrough network. **b**, SEM images of the nanotrough network. **c**, The nanotrough network was transferred onto the glass slide and PET plastic^[129]. **d**, Schematic illustration and images of the nanomesh attached to the skin by spraying water on the skin and dissolving the PVA nanofibers^[33]. **e-f**, Optical image (**e**) and cross-sectional SEM image (**f**) of the nanomesh pressure sensor based on a four-layer structure^[97].

2.3.2 Liquid metal

Galium-based alloys are a kind of conductive liquid metal that perform liquid state at room temperature but are non-toxic and biocompatible compared to the highly toxic mercury^[133]. Due to their high electrical conductivity, thermal conductivity, outstanding biocompatibility, and excellent flexibility, gallium-based liquid metals have been a promising functional material for flexible electronics, soft robotics, biomedical engineering, and catalyst^[34, 69].

Unfortunately, due to the large surface tension, liquid metal will bead up in the absence of the oxidized layer and dewet at the surface of most films before any treatments. Recently, a superelastic and permeable liquid-metal fiber mat (LMFM) has successfully developed via three steps: (i) electrospinning of the stretchable SBS fiber mat, (ii) coating EGaIn at the surface of the fiber mat, and (iii) activation of the EGaIn-coated fiber mat by pre-stretch^[25]. It should be noted that the coated EGaIn layer was shiny and planar and the whole LMFMs were little permeable. To active the permeability, 12 cycles stretching to an 1800% strain and releasing were applied to get a dim and mesh-like porous structure EGaIn layer hanging among the SBS nanofibers. Both the air permeability and the moisture permeability of the 0.8EGaIn-SBS LMFMs (1 cm² with a 0.8 g EGaIn mass loading) were 79.5 mm s⁻¹ and 724 g m⁻² day for, higher than the commercial nylon cloth (11.8 mm s⁻¹ and 621 g m⁻² day) as well as a medical patch (7.0 mm s⁻¹ and 31 g m⁻² day). Such a high permeability completely satisfies the insensible perspiration of a person in daily life. The LMFMs also presented excellent stretchability (1800%) and electrical durability during stretching, in which the conductivity of 0.8EGaIn-SBS was about 10000 S m⁻¹ and only a 4.1% increase after stretching to 1800% strain. This LMFM also exhibited excellent durability at a limited strain (100%), bearing 25,000 stretching cycles with only a small change of resistance (less than 30%). A one-week test attached to the skin showed that the impermeable substrates caused obvious skin inflammation while this LMFM displayed zero negative effects to the skin. The demonstrated devices, including LED arrays, ECG sensor, sweat sensor, temperature sensor, and heater, demonstrated gas-permeability and well performances. Followed by this strategy, a series of research has been developed to further improve this method^[134-135]. For example, a layer of Ag or Cu has been employed to coat the surface of fiber mats by vacuum deposition or chemical reduction. Such Ag/Cu-coated fiber mats showed EGaIn-superlyophilicity and more stable electrical performance^[136-138]. Furthermore, researchers developed high-resolution liquid-metal patterns on fiber

mats via photolithography^[139]. They fabricated Ag micropatterns at Si or SiO₂ wafers by photoetching technique and then electrospun SBS fiber mats to the surface. After peeling off the SBS mat, the Ag micropatterns will be transferred to the SBS mat. Followed by a wetting process with liquid metal, an LMFM with 2- μ m patterning resolution, an ultrahigh density of $\sim 75,500$ electrodes/cm², and a wafer scale (100 mm) can be obtained. This LMFM performed great potential as a neural interface for high spatiotemporal mapping and intervention of electrocorticography signals of living rats.

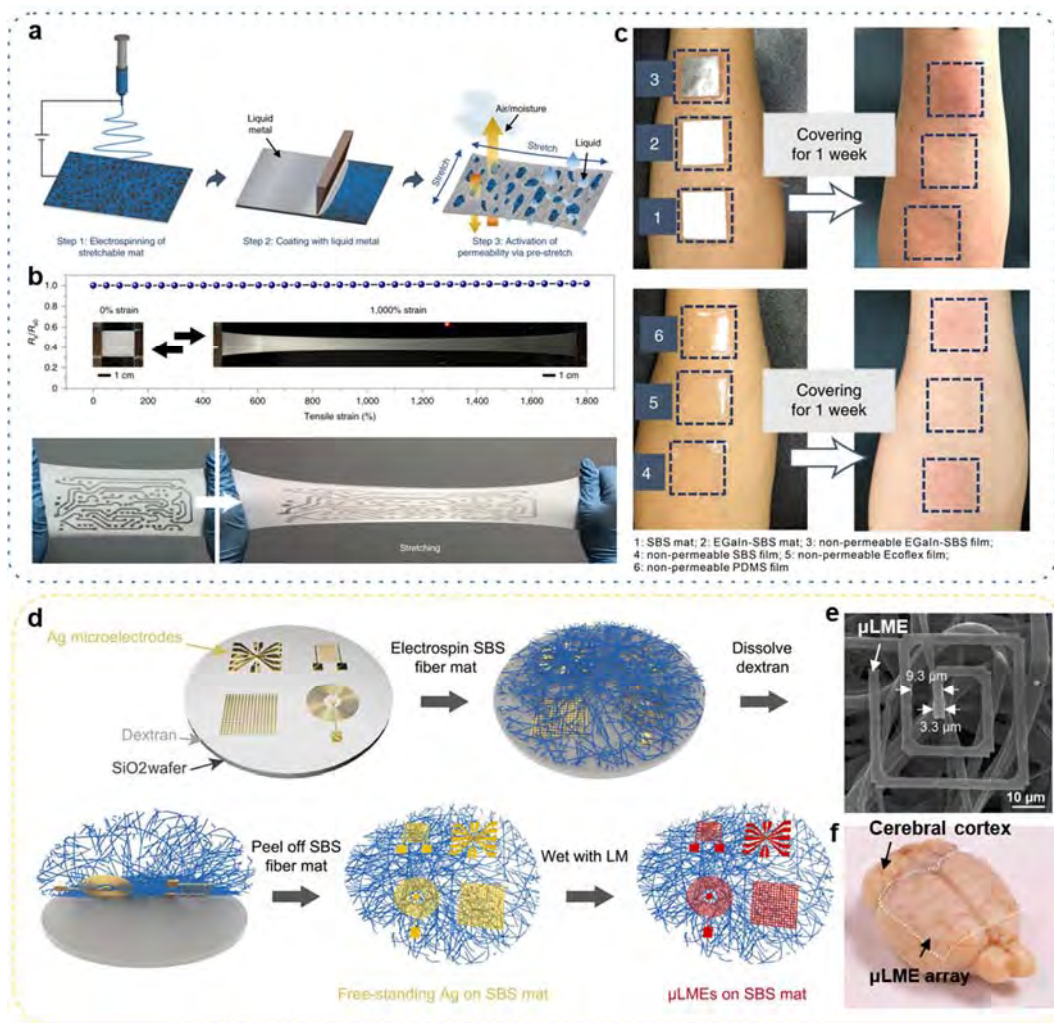


Figure 2.7. **a**, Scheme of the fabrication process of permeable and superelastic liquid-metal fibre mats (LMFMs). **b**, Resistance changes of the LMFMs under stretching and inset images are the LMFM at a strain in 0% and 1800%. **c**, One-week skin attachment

test for the LMFM, non-permeable PDMS film, and non-permeable Ecoflex film^[25]. **d**, Schematic illustration of photolithography process to fabrication of high-resolution liquid-metal patterns on fiber mats. **e**, SEM image of the high-resolution liquid-metal patterns on fiber mats. **f**, Photograph of SBS fiber mat with micro liquid metal bioelectrode array attached to the cerebral cortex^[139].

2.3.3 Nanomaterials

Metallic (Ag or Cu) nanomaterials and Carbon-based nanomaterials (CNTs, graphene) are two kinds of nanomaterial-based conductors widely used in soft and wearable electronics^[130, 140]. The conductive pathways of nanomaterial-based electronics rely on the formation of percolation networks. Different from bulk conductive metals, nanomaterial-based conductors can be optically transparent because light can transmit through the gap between the nanomaterials. Due to the processability to disperse into solution, fabrication of nanomaterial-based conductors can be easily achieved by various methods, including dip-coating, spraying, printing, and mixing.

Silver nanowires (AgNWs) are the most widely used metallic nanomaterials for the fabrication of soft and wearable electronics due to their high electrical conductivity, low cost, and good dispersity to solvent. AgNWs can be embedded into fiber mats to render it conductive by various methods, for example, vacuum filtration, screen printing, and co-electrospinning. Fan *et al.*, presented a robust, transparent, and breathable AgNWs/polyamine electrospun mat, as shown in Figure 2.8 a-d^[130]. Electrospun polyamine mats were used as a filler for the porous structure and permeability, and then AgNWs were embedded into this fiber mat through vacuum filtration. The as-prepared AgNWs-embedded fiber mats show low sheet resistance of $8.2 \, \Omega \, \text{square}^{-1}$ at optical transparency of 84.9%, air-permeability of $6 \, \text{cm}^3 \, \text{s}^{-1} \, \text{cm}^{-2}$ (300 Pa), mechanical durability against 1600 cycles of quick bending, as well as conformal

adhesion to various substrates by van der Waals force. Using biodegradable polymers, such as PVA and poly lactic-co-glycolic acid, as the materials for nanofiber-mat filters, biodegradable and permeable AgNW-embedded nanofiber mats could be obtained (Figure 2.8e) ^[72].

The electrospun mat-based breathable electronics also can be fabricated by the screen printing of AgNWs ink. Wei Yang and his colleagues reported the screen printing method for electrospun mats by utilizing AgNWs ink that was dissolved in ethylene glycol, ethylene glycol butyl ether, and hydroxypropyl cellulose mixture solution^[75]. The prepared lightweight and breathable sensors were built to a layer-by-layer structure with two layers of poly(vinylidene fluoride) electrospun mats for substrates, screen-printed AgNWs for electrodes, and a thermoplastic polyurethane electrospun mat for the dielectric layer. The prepared sensor enabled a fast response time (< 26 ms), an ultralow detection pressure (1.6 Pa), and gas-permeability. Incorporated with the degradable poly lactic-co-glycolic acid and polyvinyl alcohol, the breathable, anti-bacterial, and bio-degradable triboelectric nanogenerator-based e-skin was reported, realizing real-time and self-powered health and human motion monitoring toward the whole body. Moreover, simultaneous electrospinning of polymeric nanofibers and electrospraying of conductive AgNWs were developed to form a hierarchically interactive AgNWs-nanofibers network^[140].

Carbon nanotubes and graphene are two kinds of nanomaterials that attracted extensive attention due to their excellent electrical conductivity and mechanical properties. It has been employed in various applications including electronics, catalysts, energy storage, water desalination, biological engineering, and so on. Methods of incorporation of carbon-based nanomaterials into electrospun mats are similar to the incorporation of AgNWs. The embedding methods of carbon nanotubes and graphene to electrospun mats are mainly including 1) co-electrospinning by dispersing graphene into the

polymeric solution, 2) electrospaying of graphene, and 3) ultrasonic post-decoration^[77, 141-144]. For example, Lijun Lu and his colleagues utilized the ultrasonic post-decoration method to anchor multilayer graphene into polyamide 66 electrospun mats for the preparation of moisture sensors. The electrospun mat-based sensor realized the monitoring of respiration rate in real-time and human-machine interaction^[145-146]. Graphene was interspersed and anchored onto the electrospun polyamide 66 nanofibers under the ultrasonic treatment to construct a 3D conductive network in the nanofiber composite mat^[146].

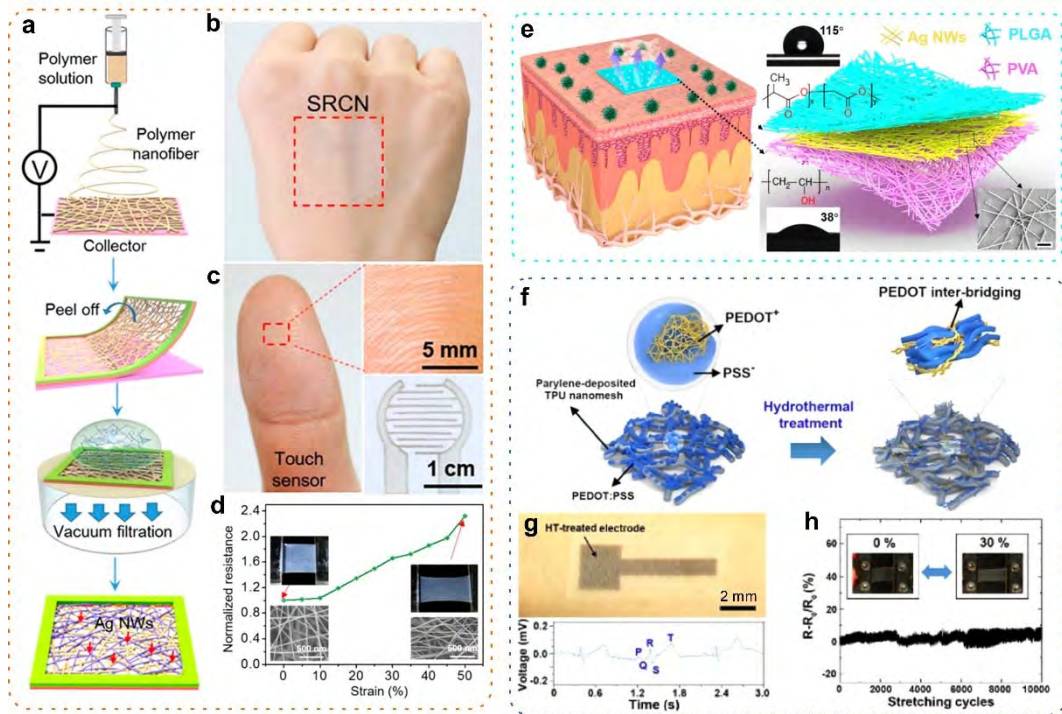


Figure 2.8. Methods to render fiber mats conductive through nano-materials or conductive polymers. **a-d,** (a) Schematic illustration of the fabrication of AgNWs-based electrospun mats; (b) digital image of a transparent device based on AgNWs-based electrospun mats adhered on the skin; (c) digital images of the touch sensor attached to the fingertip; and (d) resistance changes versus the tensile strain of the AgNWs-based electrospun mat^[130]. **e,** Schematic illustration of the breathable, degradable, and conductive e-skin based on three-layer fiber mats^[72]. **f-g,** (f) The PEDOT:PSS

embedded TPU nanomesh fabricated by hydrothermal treatment; (g) real-time monitoring of ECG data and the photograph of a hydrothermal-treated electrode mounted on the chest of a person; and (h) durability of the hydrothermal-treated electrode against loading-unloading cycles at a maximum strain of 30%^[71].

2.3.4 Conductive Polymers

Conductive polymers are another kind of conductor used in soft electronics. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), polyaniline (PANI), polypyrrole (PPY) are three kinds of π -conjugated conductive polymers widely used for building conductive blocks in soft electronics^[147-151]. The construction of conductive pathways for π -conjugated polymers relies on the free movement of delocalized π -electrons in the unsaturated polymeric backbone.

PEDOT:PSS has emerged to be the most promising conductive polymer used for soft electronics since of its flexibility, tunable electrical conductivity, optical transparency, and most importantly electric and ionic conductivity^[38]. PEDOT:PSS-based breathable, flexible, and biocompatible epidermal electrodes also were reported recently (Figure 6.8 f-h). The epidermal electrodes were made by spraying PEDOT:PSS aqueous solution on the polyurethane (TPU) electrospun mats and heating to 110 °C for accelerating the water evaporation. The breathable devices show flexibility with a maximum elongation of 30% and high conductivity at 125.4 S m⁻¹, preventing skin inflammation and irradiation during on-skin health monitoring. The PEDOT:PSS can also be introduced into the electrospun mat by vapor deposition polymerization^[71].

In summary, abundant conductive materials can be used to build permeable and conductive micro/nano fiber mats. Based on the differentiation of intrinsic properties of materials and coating processes, the characters of these electronics can be varied and

show exclusive advantages. In some cases, the synergy of several materials will be the better option to fabricate multifunctional permeable electronics.

2.4 Fabrication of Skin-adhesive Permeable Electronics

2.4.1 Brief Introduction of Adhesion

Adhesion, a process to bond objects together, has been extensively investigated and applied in nearly all materials-related fields^[46, 152-155]. Referring to wearable and on-skin electronics, adhesives also play a critical role in encapsulation, multi-layer-electronics fabrication, and human-electronics interface. The adhesive interface bridging human tissues and biological electronics is critically important for the on-skin or even implanted electronics in the case that the electronics should be firmly attached to the targeted tissues to provide functions like *in-situ* and long-term monitoring biophysiological signals or harnessing the heartbeat by a cardiac pacemaker^[37, 156]. Traditional fixations by surgical sutures have been used for highly stable integration of bioelectronic devices while it could cause tissue damage and localized stress concentration at piercing points, and consequent scar formation^[157]. Thus, biocompatible and strong while damage-free adhesion strategies are highly required.

To design a stable electronics-skin interface, the chemical properties of the tissue should be systematically considered. The properties of the biological tissues are shown in Figure 2.9. Tissues are constructed with liquid (*e.g.*, water and solutes) and solid matter (*e.g.*, proteins and minerals). The liquid components of tissues are hardly employed for adhesion. Proteins, which constitute 20% of the dry mass of the human body in tissues, involve plenty of carboxylic acid/carboxylate (COOH), amine (NH₂), and thiol groups (SH). Forming an adhesive with functional groups that can bond the carboxylic acid/carboxylate (COOH), amine (NH₂), or thiol groups (SH) by hydrogen bondings or

covalent bondings greatly enhance the adhesive performance.

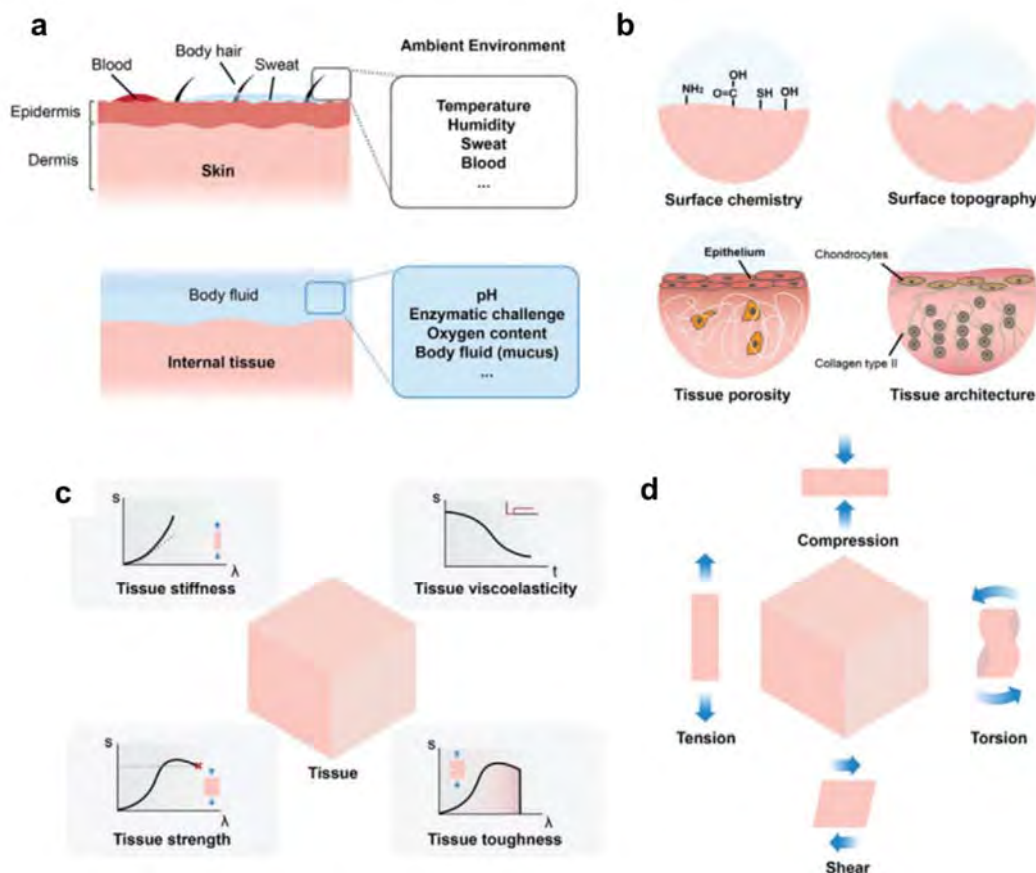


Figure 2.9. The properties of biological tissues. **a**, The microenvironments of the skin and internal tissues. **b**, Chemical and structural properties of biological tissues. **c**, Mechanical properties of the tissues. **d**, Mechanical loading applied onto or exerted by tissues^[46].

To date, there are tremendous polymers, including acrylic-based polymers, protein-based materials, and supermolecules, that have been developed to fabricate adhesives for biological tissues and flexible substrates. The physical interactions, including hydrogen bonding, π - π stacking, dipole-dipole forces, electrostatic interactions, and entanglements as well as covalent bonding are intermolecular interactions employed for bioadhesives to intimately adhere to the adherend (Figure 2.10) ^[39, 158]. Furthermore,

by engineering the structures of substrates, the electronics could be physically entangled to the biological surfaces or attached to the surfaces by van der Waals interactions with adhesive pads inspired by geckos^[159].

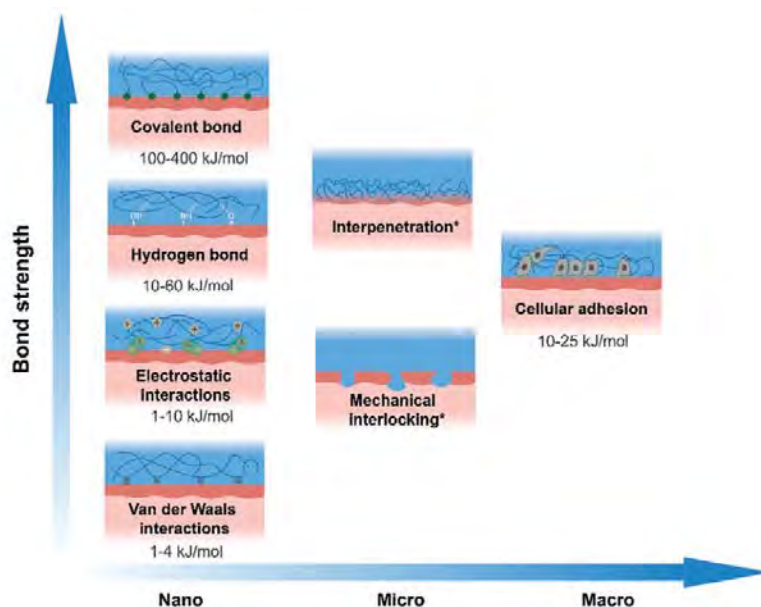


Figure 2.10. Various interactions of both physical and chemical for adhesion^[46].

2.4.2 Fabrication of Adhesive and Permeable Electronics

Electrospun adhesive polymers

To engineer the permeable fiber mat adhesive, hydrophilic polymers (*e.g.*, PVA and PVP) have been engaged in the fabrication of permeable electronics^[26, 33, 129]. Hui Wu *et. al.*, reported a metallic nanotrough network by depositing metals on the surface of electrospun PVA mats^[129]. By dissolving the PVA nanofibers, a super-thin metallic nanotrough network formed, where this nanotrough was adhered to various surfaces like glass, newspaper, and plastics by the dissolved PVA polymer (Figure 2.11). Furthermore, Akihito Miyamoto *et. al.*, performed the same method to adhere conductive nanomesh on the human skin^[26, 33]. The nanomesh conductor demonstrated

ultrahigh conformability to the skin with a 15 mN cm^{-1} adhesion force. This nanomesh was used for non-invasive pressure sensors and as biophysiological electrodes for personalized health monitoring.

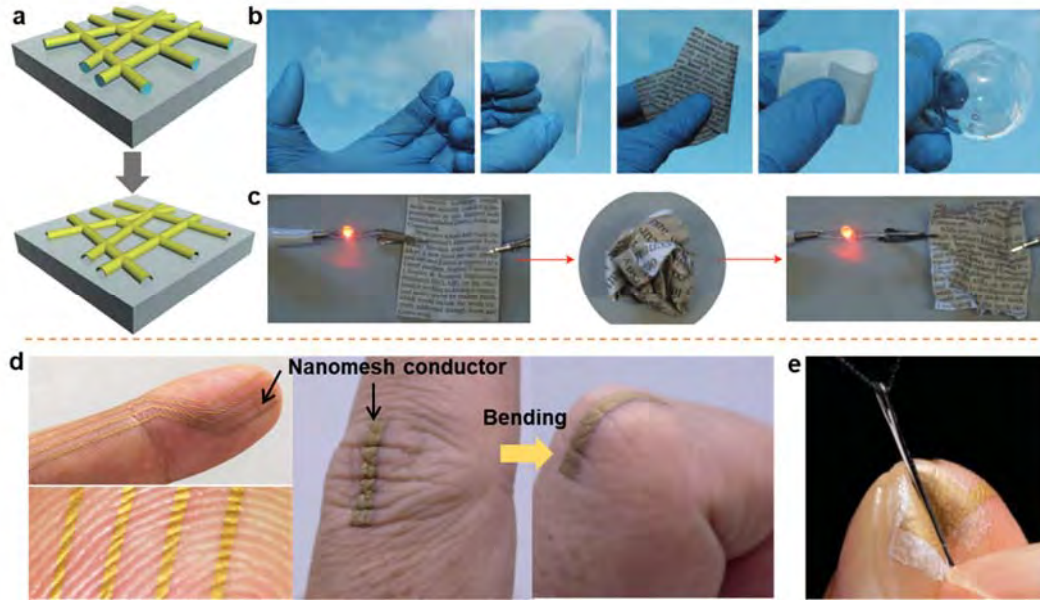


Figure 2.11. Electrospun PVA enables permeable and adhesive electronics. **a-c**, (a) Schematic illustration of the fabrication process of metallic nanotrough network ;(b) it transferred to various substrates, like a glass slide, PET plastic, paper, textile, and a curved glass flask and the nanotrough network-coated paper showed good conductivity even after rubbing^[129]. **d-e**, (d) PVA/Au nanomesh attached to the human finger tip or proximal interphalangeal joint^[33], and the PVA/Au nanomesh-based sensor detected the pressure of a needle^[26].

Additionally, the spider-silk-inspired polyurethane@poly(vinylpyrrolidone) (PU@PVP, core@sheath) nanostructured fibers have been investigated. The high adhesion strength contributed to the dissolved PVP nanosheath while the undissolved PU fibers served as supporting skeleton (Figure 2.12)^[160]. The nanostructured fibers offer a 1.2 N/cm peeling adhesion force to substrates. The bioinspired strategy that constructs core-sheath-nanofiber mats with an undissolved stretchable polymer as the

tough skeleton and the dissolved polymers as the adhesive could be a general method to construct next-generation adhesives.

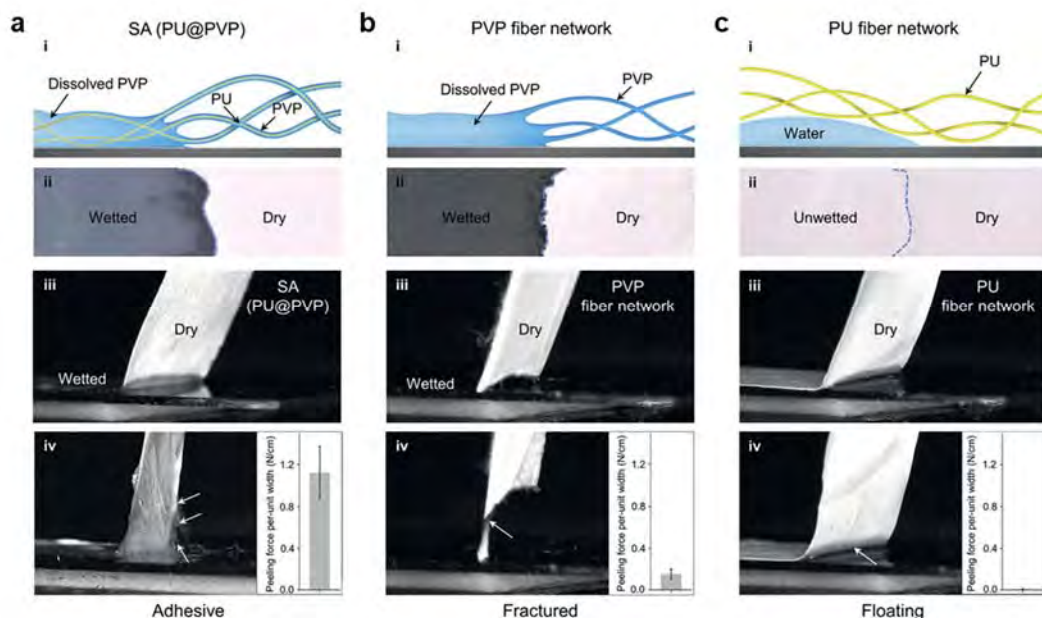


Figure 2.12. Schematic diagram, photograph, and the adhesion strengths showing the adhesion mechanism of PU@PVP core-sheath nanofiber mats (a), PVP fiber network (b), and PU fiber network (c)^[160].

Physical attachment

Physical attachment is a type of adhesion strategy that employs physical interactions to intimately adhered electronics to target substrates, including van der Waals force and electrostatic interactions. Van der Waals force, an undirected, unsaturated, weak interaction between molecules or atoms, acts until the whole thickness of the electronic devices is down to several micrometers (about 5 μm)^[161-162]. With the ultrathin structure, the electronics could be intimately and non-invasively integrated into the soft and curvilinear surfaces of biological tissues, bringing opportunities for skin-attachable human-machine interaction, health monitoring, and diagnosing and treating disease^[162].

Fan et. al., investigated an AgNWs-embedded polyamine electrospun mat with a device thickness of 300 nm. The submicron thickness seamlessly adhered the electrospun mat to the human skin while the electrospun mat demonstrated low sheet resistance of $8.2 \Omega \text{ square}^{-1}$ at optical transparency of 84.9%, air permeability of 6 cm s^{-1} at a pressure drop of 300 Pa, and mechanical durability against 1600 cycles of quick bending^[130]. To simultaneously achieve robustness, permeability, and self-adhesiveness in one ultrathin polymeric nanofilms, wang *et. al.*, developed a PU nanofiber-reinforced PDMS nanofilms (Figure 2.13). They first prepared the ultrathin PU nanofiber mats via electrospinning and then a simple dip-coating process was used to form PDMS coatings with the PU- nanofiber skeleton. The prepared PU nanofiber-reinforced PDMS nanofilms were robust, skin-adhesive, gas-permeable, and free-standing with a thickness of $\sim 95 \text{ nm}$. This nanofilm was robust where it sustained a weight 79,000 times heavier than its one weight. The nanofilm offered a high adhesion energy of $78.4 \pm 11.3 \mu\text{J}/\text{cm}^2$ due to van der Waals forces and it pertained stable as well as robust adhesiveness to the human skin even for 1 week. Such highly robust, stable, and adhesive nanofilms offered great potential for high-fidelity electrocardiogram recording in the long-term, broadening the way toward medicine, healthcare, sports, fitness, virtual reality, and entertainment^[132].

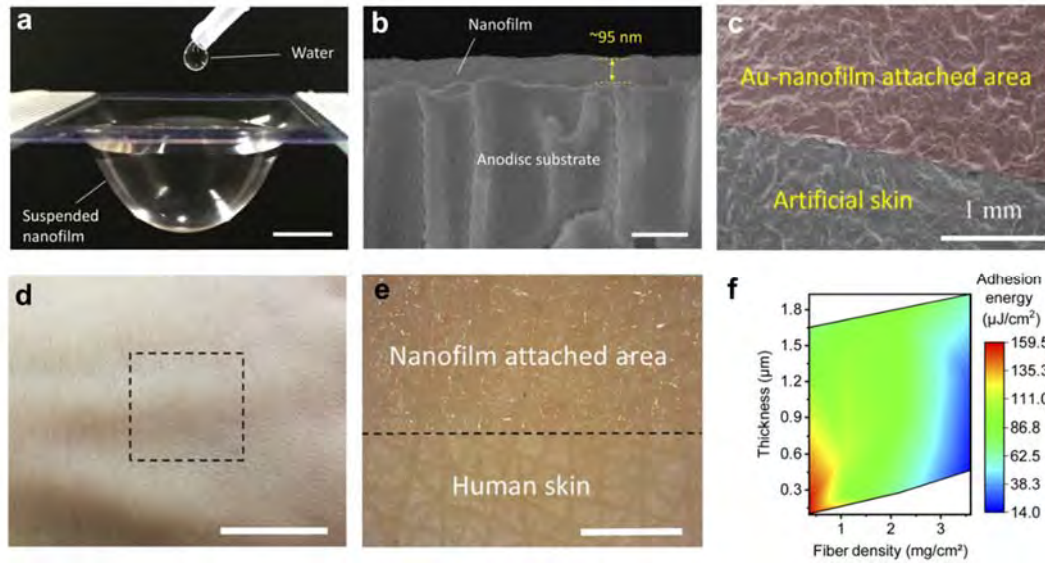


Figure 2.13. Sub-100 nm, robust, permeable, self-adhesive nanofilms. **a**, A nanofilm sustained water with 79,000 times heavier than its one weight. **b-c**, (**b**) Cross-sectional and (**c**) surface SEM images of the nanofilm. **d-e**, (**d**) The nanofilm adhered to the back of the palm, and (**e**) the microscopy image showing the nanofilm attached area. **f**, Adhesion energy of the nanofilm varied by the thickness and the fiber density of the film^[132].

Although great advances have been presented in forming breathable and dry contact between electrodes and human skins via utilizing van der Waals' forces, such types of adhesion mechanisms are only effective for extremely thin epidermal electrodes with a thickness below a few micrometers^[130]. Moreover, the electrospun PVA and PVP mats could also offer skin adhesiveness after the dissolution of mats by water, while the adhesion strength and wet adhesion performance may need to be further improved^[26, 33, 160]. Existing adhesive strategies for permeable electronics-tissues interface are far from the need for complicated conditions when attaching to the human skin. Thus, it is still necessary to develop more effective and versatile adhesion strategies for permeable electronics.

2.4.3 Wet-adhesive Skin-attachable Electronics

The human skin is wet and secretes sweat all the time for body temperature management. Ensuring a strong and conformal adhesion of the device on the skin is crucial to the high performance of epidermal electronics but is a great challenge^[35-37, 156]. The accumulation of water at the device/skin interface tends to significantly weaken the bonding strength between the device and the skin, resulting in unstable device performance and even easy detachment of the device^[46-49]. Furthermore, epidermal electronics also faces challenges in the wet environment from the daily exposure to foreign water droplets during washing and showering, or in applications that are carried out in the rain or under the water^[50-51]. Although a full encapsulation of the device with another water-impermeable coating may protect the device from foreign water^[53], it will further escalate the negative influence of water at the device/skin interface as discussed above. The electronics that can instantly adhere to the skin in various wet conditions is still a challenge and it is hard to find on-skin electronics to meet both needs. To build permeable and wet-adhesive on-skin electronics, the wet-adhesive strategies to fabricate adhesive hydrogels may help to approach this aim.

Adhesive hydrogels, a type of hydrogel with considerable adhesive performance, biocompatibility, and tunable mechanical properties from tough to soft, have been seriously explored as biological adhesives applied in vessel suturing^[157], wound healing^[47], and adhering bioelectronic devices to tissues (Figure 2.13)^[37, 156]. Adhesive hydrogels are commonly constructed by hydrophilic polymers (*e.g.*, PAA, PAM, PEGDA), macromolecules (*e.g.*, dopamine and dopamine-based derivatives), biomacromolecules, or supermolecules that contain abundant carboxy, hydroxy, or amino groups, demonstrating high adhesion strength, conformal adhesion, on-demand detachment, as well as biocompatibility^[47, 163-165]. Adhesive hydrogels could be stably

attached to the wet tissues by special design, for example: synthesize with functional groups or pre-dehydration strategy.

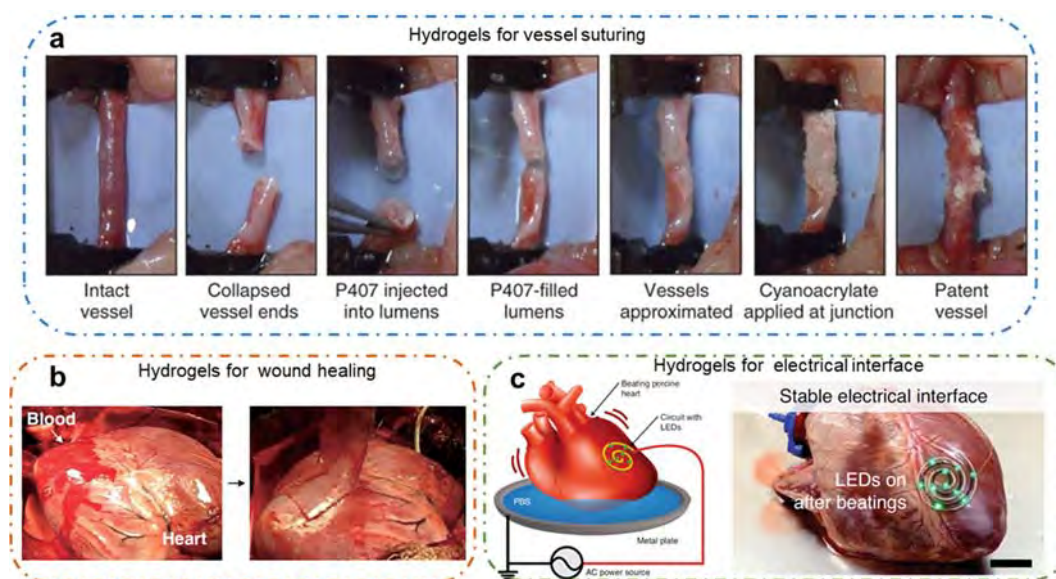


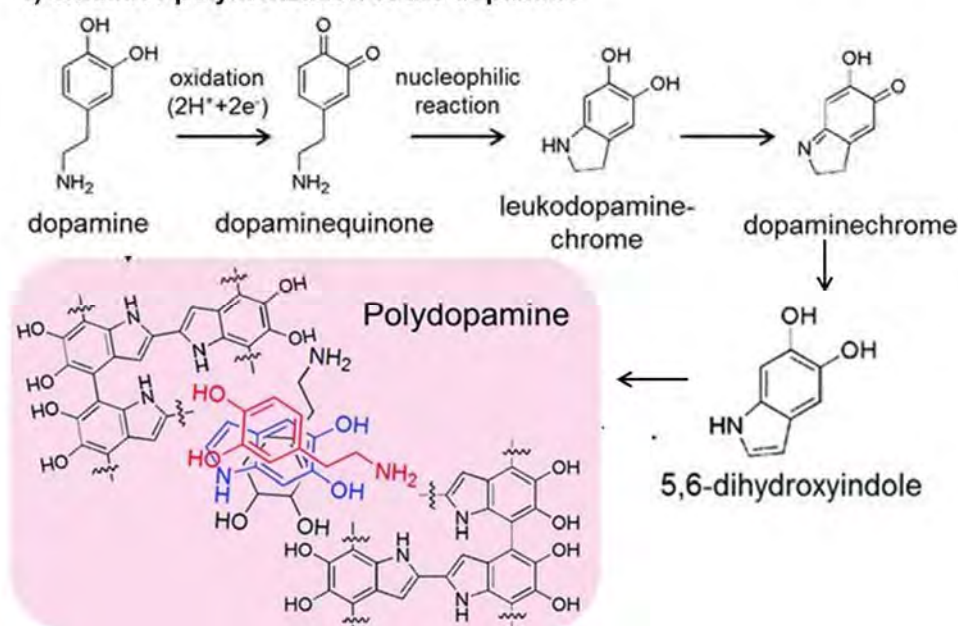
Figure 2.13. Hydrogel-based adhesives for biological applications. **a-c**, Adhesive hydrogels for nurturing a collapsed vessel (**a**), for healing the blood exposure in a beaten porcine heart in vivo (**b**), and (**c**) adhering the electronics to a porcine heart ex vivo.

Inspired by the mussels that attach to wet surfaces by secreting adhesive proteins, a catecholic acid (dopamine) has been found that significantly contributes to the strong underwater adhesion for mussels^[166-170]. The catechol-containing peptide could be able to penetrate the interfacial water from the adhesive layer to submerged substrates^[154]. The hydroxy and amino groups could form a variety of interactions between the amino groups, carboxy groups, peptide groups as well as thiol groups^[170]. Abundant interactions enabled by the excellent wet adhesion make dopamine and dopamine-based molecules as adhesive moieties for the construction of adhesive hydrogels. As shown in Figure 2.14, the strategies to introduce dopamine into the polymeric networks are mainly including: 1) oxidative polymerization of the dopamine, 2) copolymerization of dopamine-based vinyl monomers, and 3) graft of the dopamine groups into the polymer

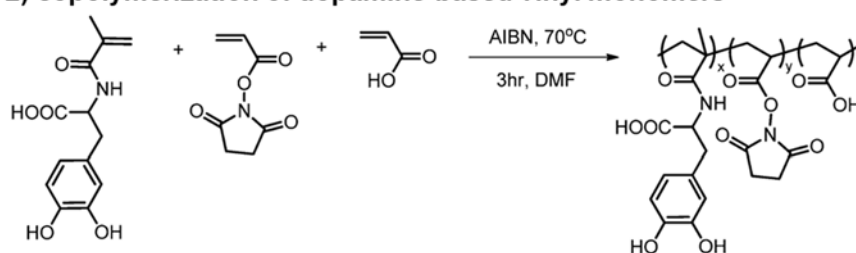
chains.

The oxidative polymerization of dopamine is an intra-molecular cyclization between the catechol side chain and the amine group to form 5,6-dihydroxyindole (DHI). There will be a self-assembly process between the DHI and unpolymerized dopamine to form a stable complex of (dopamine)₂/DHI^[171]. This reaction could be activated by electric field, oxidizing agents (*e.g.*, APS, NaIO₄), or a gentle alkaline environment^[172]. The polydopamine chains formed by oxidized polymerization could be easily grafted to various substrates, like noble metals, oxides, polymers, semiconductors, and ceramics or even nanomaterials (*e.g.*, CNTs), and various hydrogel polymer networks. For example, Lu Han *et al.* oxidized the dopamine and polymerized it on CNT surfaces to form PDA-decorated CNTs which could be uniformly dispersed in an aqueous solution. By incorporating the PDA-decorated CNTs into the hydrogel matrix, the adhesive performance of the hydrogel was significantly enhanced^[173].

1) oxidative polymerization of the dopamine



2) copolymerization of dopamine-based vinyl monomers



3) graft of the dopamine groups into the polymer chains

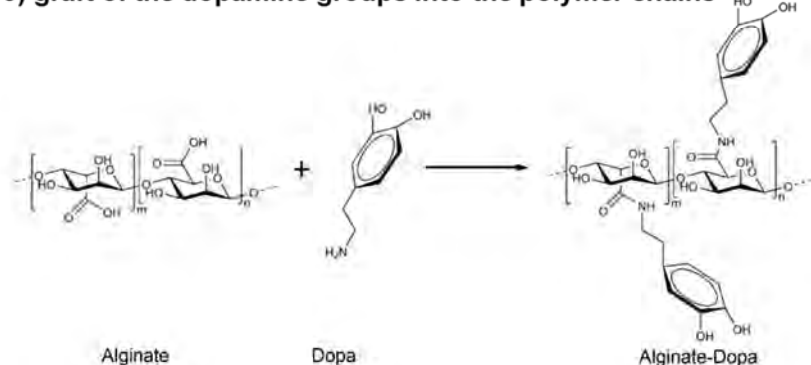


Figure 2.14. Routes to engineer dopamine into polymeric networks^[171, 174].

The copolymerization of strategy utilizes the dopamine-based vinyl monomers, for example, dopamine methacrylamide and *N*-methacryloyl-3,4-dihydroxyl-L-phenylalanine^[175-176]. Dopamine methacrylamide is a type of photopolymerizable monomer that consists of a catechol side chain and a vinyl group. The copolymerization

of dopamine methacrylamide and other hydrophilic photopolymerizable and cross-linkable monomers (*e.g.*, PAA, PAM) could form polymeric networks that could uptake water to form adhesive hydrogels.

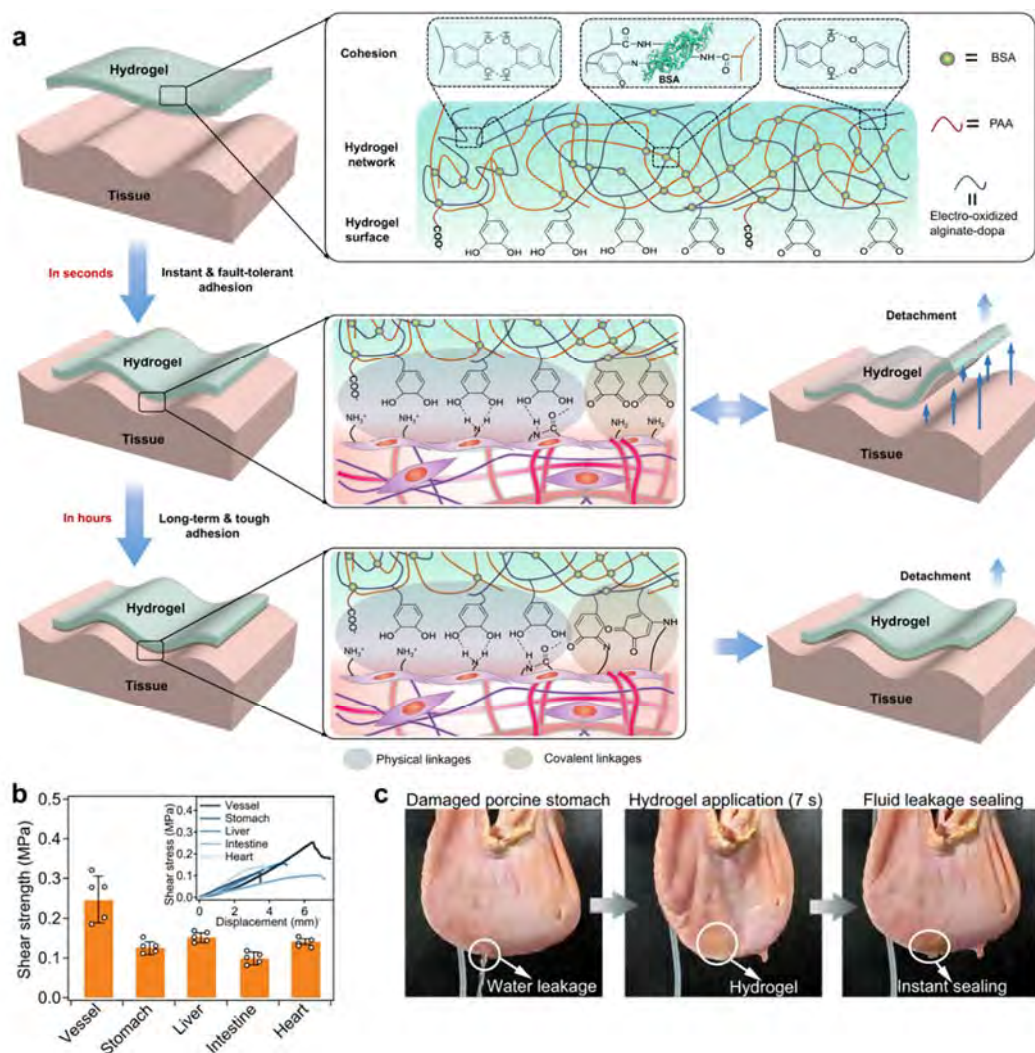


Figure 2.15. Adhesive hydrogel enabled by electrically oxidized dopamine-grafted alginate. **a**, Schematic illustration of the chemical structure and adhesion mechanism of the hydrogel. **b**, Shear strength of the hydrogel for the adhesion of various biological tissues. **c**, Sealing of a water-leaking porcine stomach using hydrogel tape^[174].

Grafting dopamine groups to the polymers with carboxy groups ($-\text{COOH}$) could be

achieved with the assistance of EDC/NHS activation. The EDC could active the carboxyl groups (-COOH) and consequently the NHS groups couples the carbonyl groups (C=O) from carboxyl groups (-COOH), forming an NHS-ester. The formed NHS-ester is not stable and will be further replaced by the polymers with amino groups, that is dopamine^[177]. Based on the EDC/NHS activation, Xue *et al.*, grafted dopamine to the alginate for the formation of adhesive hydrogels (Figure 2.15) ^[174]. The dopamine-grafted alginate was further partially electrically oxidized using a galvanic cell. The electrical oxidation of dopamine-grafted alginate offered high content of dopaquinone as the product. Combining BSA and PAA, the fabricated electro-oxidized hydrogel offered long-term shear adhesion strength over 100 kPa for biological tissues. This strategy enables the formation of long-term and tough adhesive hydrogels for various biomedical applications.

Different from the dopamine-based adhesive monies which could penetrate the interfacial water to submerged substrates, another strategy employs dehydrated hydrogels to absorb the interfacial water of the wet surfaces^[37, 156]. To remove the interfacial water from the tissues, Hyunwoo Yuk *et. al.*, prepared a dry double-sided tape. The fabrication of dry double-sided tape included two steps: 1) fabrication of double-network adhesive hydrogel that consisted of two networks: poly(acrylic acid) grafted with NHS ester (PAA-NHS ester) crosslinked by biodegradable gelatin methacrylate and second biodegradable biopolymers (*e.g.*, gelatin or chitosan); 2) dehydration of the as-prepared hydrogels. The carboxyl groups of PAA-NHS ester chains offer quick hydration and swelling in interfacial water for the dry double-sided tape. The grafted NHS also could be replaced by the amino groups from the proteins in tissues to form covalent peptide bonds. The dry double-sided tape provided stable and strong adhesion to tissues with the maximum interfacial toughness of 710 J m⁻² and adhesion strength over 120 kPa, thus providing a firm and stable adhesion interface for

various applications including sealing of tissue damage, in-situ drug delivery, and electronics-tissue interface (Figure 2.16) [37]. Further studies demonstrated that such a conformal and tough electronics-tissue interface significantly enhanced the durability and stability of the in-planted electronics during the application scenarios[156].

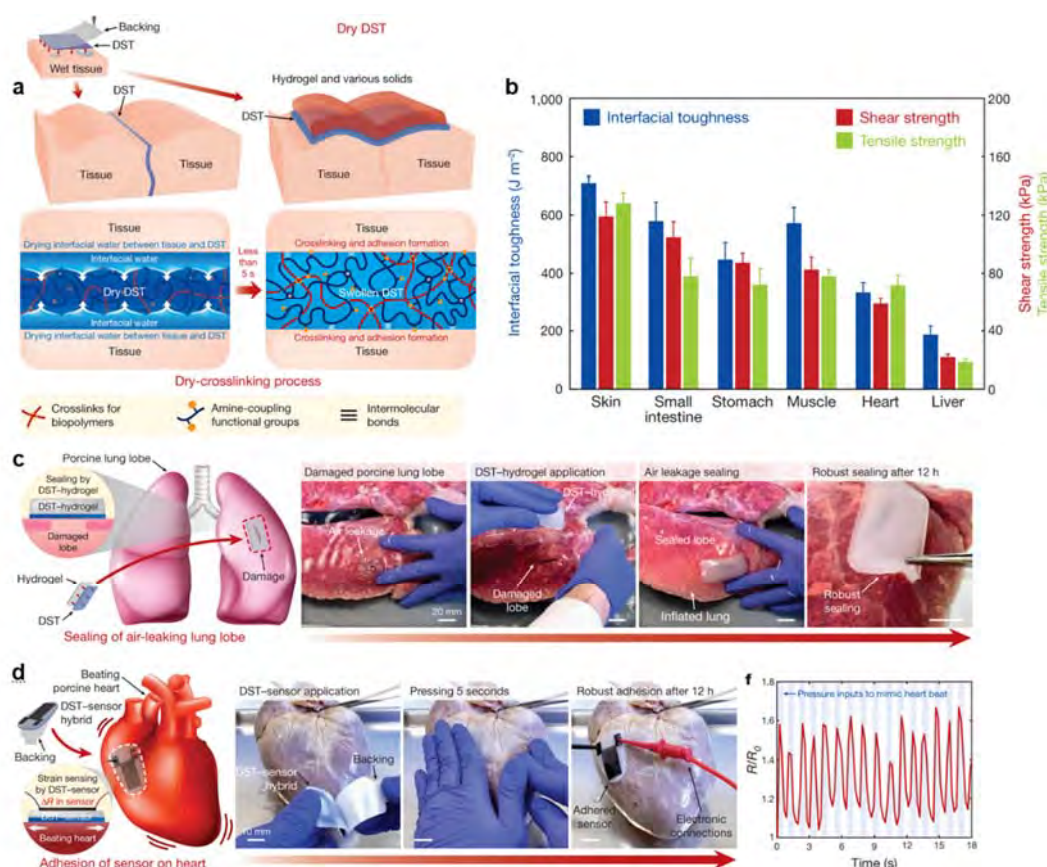


Figure 2.16. Dry double-sided tape to form strong and stable tissue adhesion. **a**, Schematic illustration of the dry double-sided tape. **b**, Adhesive performance of the tape for various biological tissues. **c**, Sealing of the damaged porcine lung by the tape. **d**, Adhering sensor on the heart to monitor the heartbeat[37].

The two strategies, that are dopamine-based moieties and the dehydration strategies, facilitate the adhesion toward wet surfaces for hydrogels. The highly wet-adhesive performance could bring a stable bioelectronics-tissue interface, broadening the applications of bioelectronics in various wet conditions.

2.5 Conclusion and Summary of Research Gaps

Permeability refers to the ability to transport gas and water moisture, which is critical for skin-attachable electronics to reduce the accumulation of interfacial water on the skin and to transport analytes (*e.g.*, glucose, salts) to target sensors^[178-179]. The lack of permeability may cause uncomfortable feelings or even skin irritation and inflammation during long-term use^[85]. Many efforts have been engaged to develop permeable electronics by engineering novel permeable substrate, high-performance and stretchable conductors, and multiple functions^[135, 137, 180-183]. However, few researches focused on the fabrication of the permeable electronics yet pertaining adhesiveness.

The adhesive interface bridging human tissues and biological electronics is critically important for the on-skin or even implanted electronics. These electronics are required to firmly attached to the targeted tissues, functioning in the *in-situ* and long-term monitoring of biophysiological signals^[37, 156]. Thus, the biocompatible and universal adhesion strategies while maintaining the devices' permeability for permeable electronics are highly required.

On the other hand, the human skin is wet and secretes sweat all the time for body temperature management. Ensuring a strong and conformal adhesion of the device on the skin is crucial to the high performance of epidermal electronics but is a great challenge^[35-37, 156]. The accumulation of water at the device/skin interface tends to significantly weaken the bonding strength between the device and the skin, resulting in unstable device performance and even easy detachment of the device^[46-49]. Furthermore, epidermal electronics also faces challenges in the wet environment from the daily exposure to foreign water droplets during washing and showering, or in applications that are carried out in the rain or under the water^[50-51]. Although a full encapsulation of the device with another water-impermeable coating may protect the

device from foreign water^[53], it will further escalate the negative influence of water at the device/skin interface as discussed above. The electronics that can instantly adhere to the skin in various wet conditions is still a challenge and it is hard to find on-skin electronics to meet both needs.

CHAPTER 3: METHODOLOGY

In this chapter, the general methodology of this thesis is elucidated. The method for fabricating electronic skins is illustrated. The equipment and methods that are used for the characterization and evaluation of the electronic skins are elaborated.

3.1 Materials

All the chemicals used in the experiment were used upon received without further purification unless specified. The chemicals used in this report were listed in table 1.

Table 3.1 Chemicals used in experiments.

Name	Brand	Purity	Marks
Polyacrylic acid	Sigma-Aldrich		average Mv ~450,000
N-Hydroxy succinimide		98%	
3-[(Ethylimino)methylidene]amino-N,N-dimethylpropan-1-amine		98%	
Poly(styrene-butadiene-styrene)	SINOPEC Yanshan, 1401		S/B ratio=40/60
Thermoelastic polyurethane	EMOLON, BTE-75A		
Calcium chloride		98%	
Dopamine hydrochloride		98%	
Ammonium persulfate		98%	
Sodium chloride		98%	
Tetrahydrofuran	Aladdin	99%	
N,N-Dimethylformamide	Aladdin	99.8%	
Acetone	Aladdin	99%	
Eutectic gallium-indium alloy	Sigma Aldrich		Ga: In (75.5: 24.5)
Sodium carbonate	Aladdin	99%	
Sodium dodecylbenzenesulfonate	Aladdin	98%	
PVA	Aladdin		1799
P(VDF-TrFE)	Arkema		PVDFKynar Flex 85-15

3.2 Preparation of Electronic Skins

3.2.1 Fabrication of Electrospun Fibrous Mats

The electrospinning is used for the fabrication of flexible porous substrates, porous adhesives, and piezoelectric porous substrates. The experimental setup is shown in Figure 3.1.

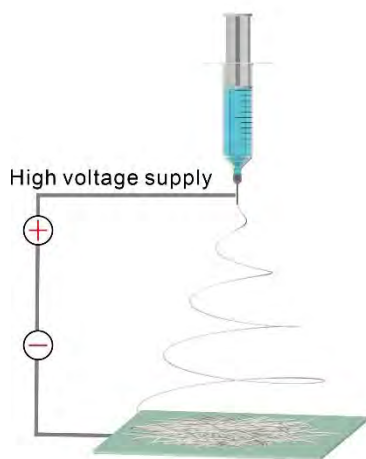


Figure 3.1. Schematic illustration of electrospinning.

The process of electrospinning is driven by electrostatic force. When a high-voltage field is applied between the spinneret and the collector, the electrostatic charges accumulate at the surface of the polymer solution at the tip of the spinneret. Then, the shape of the solution is changed from a spherical surface to a cone shape (called Taylor Cone) because the increased charge repulsion overcomes the surface tension of the solution, and a jet is extruded from the spinneret in a straight path and then travels with a drastic whipping toward the collector at the electrostatic field. The continuous polymeric fiber is formed during the flying of the jet due to the evaporation of the solvent and the stretching of electrostatic force. Fiber-based mats are obtained after a

certain time for collection. The thickness of electrospun mats can be adjusted by varying the collection time. Based on this mechanism, a series of polymeric fibrous mats (e.g., SBS, TPU, PAAND, PVA, P(VDF-TrFE)) were prepared via electrospinning. Furthermore, core-sheath nanofibers have also been fabricated by coaxial electrospinning.

3.2.2 Fabrication of EGaIn electrodes on fibrous mats.

The fabrication of EGaIn electrodes to the fibrous mats was achieved by stencil printing. A stencil mask with the desired patterns was first obtained via laser printing. During the printing of EGaIn, the stencil mask was intimately attached to the surface of the fibrous mat. A brush that absorbed with EGaIn was repeatedly rubbing the surface of the stencil mask. The EGaIn contacted the fibrous mats through the holes of the stencil mask and printed to the surface of the fibrous mats. By controlling the applied weight of EGaIn, a series of mass loading of EGaIn-coated SBS mats could be investigated varied from 3 mg cm^{-2} to 15 mg cm^{-2} or even higher.

3.2.3 Fabrication of Strain Sensors and Systematic Integration of Wheatstone bridges, MCU, and Bluetooth.

The strain sensors were prepared by stencil printing EGaIn-based zig-zag lines ($800\mu\text{m}$) on the surface of SBS mats. The sensors were adhered to the human skin by PAANP mats. To precisely reflect the resistance change of the bending sensor, Wheatstone bridges were employed to measure the electrical resistance change of bending sensors. The schematic diagram of a Wheatstone bridge is shown in Figure 3.2. When the strain or bending degree is zero, the voltage difference between B and C (V_{BC}) is zero, while applying strains or bending the sensors, the resistance of the strain sensor is changed and the voltage difference between B and C can be generated. The relationship between

V_{BC} and the resistance of the strain sensor was concluded by equation 3.1:

$$V_{BC} = \left(\frac{R_x}{R_3 + R_x} - \frac{R_1}{R_1 + R_2} \right) V_{AD} \quad (3.1)$$

where V_{BC} and V_{AD} denote the voltage difference between B and C as well as A and D, respectively, and R_x is the resistance of the strain sensor.

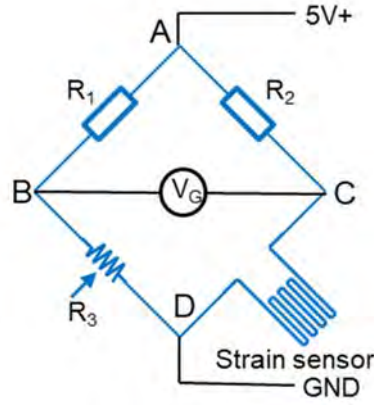


Figure 3.2. Schematic diagram of the Wheatstone bridge to measure the resistance of the strain sensor.

For detecting the strain sensor array, six Wheatstone bridges, an MCU (Arduino nano), and a Bluetooth were soldered together at the same rigid printed circuit board (PCB). A flexible flat cable was made by screen printing of conductive Ag inks to a 50- μ m-thickness polyimide (PI) film and connected the strain sensor array and the PCB. Besides, a robotic hand or an 18-DOF (degree-of-freedom) humanoid was controlled by the communication of MCU through wireless.

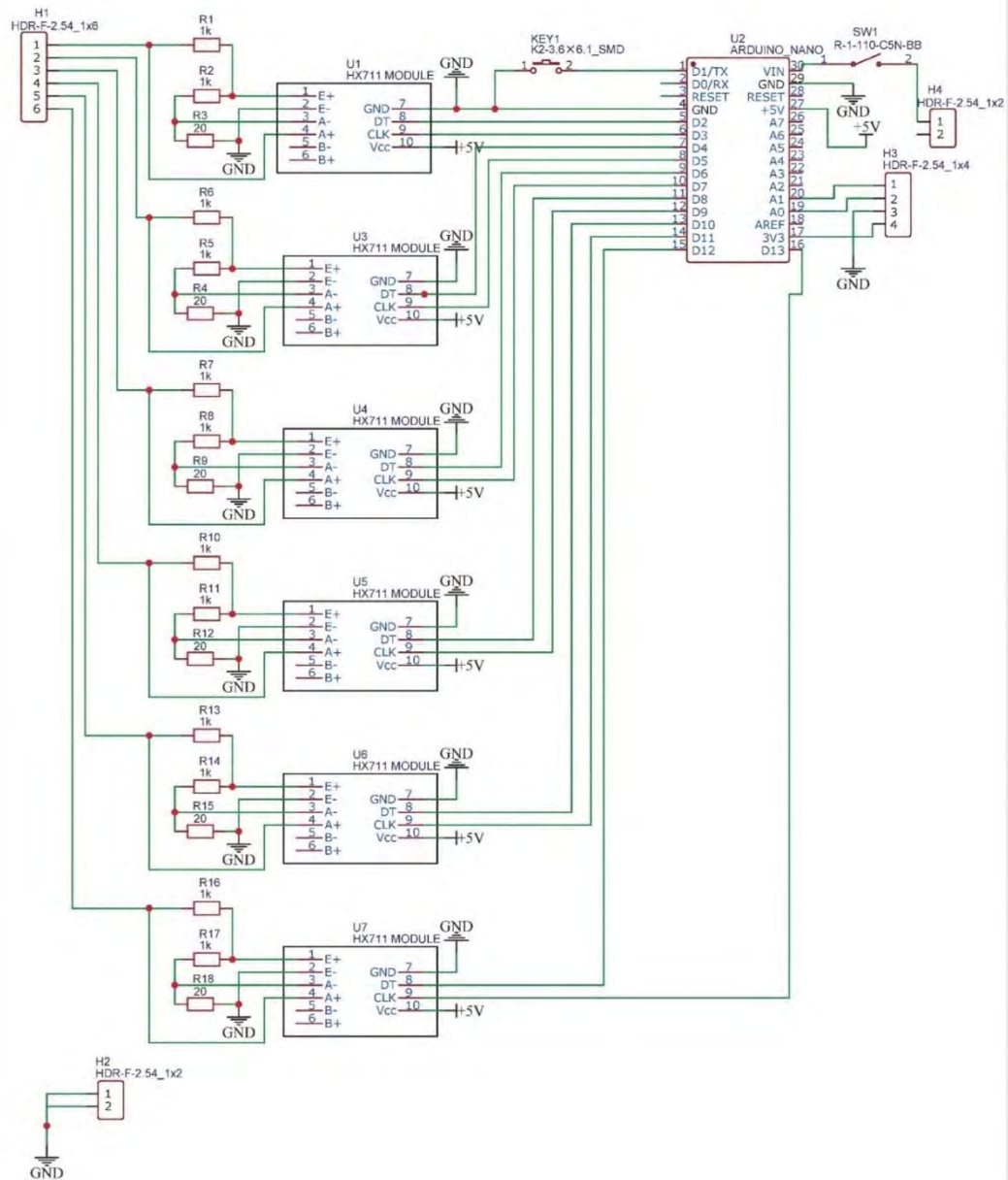


Figure 3.3 Schematic diagram of the printed circuit board (PCB) for the WADE-skin-based strain sensor array. This PCB incorporates 6 Wheatstone bridges and 6 analog-to-digital converters (ADC, HX711), and a microcontroller unit (ADC, Arduino) to convert and transmit signals for controlling the robot. Furthermore, a Bluetooth module (HC-05) is connected to this PCB by the H3 header for wireless communication.

3.3 Characterization

Characterizations include the investigation of chemical structures, physical properties, surface morphology, as well as electrical properties of the materials. The standard deviation was calculated using a minimum of four samples, as per the equation below:

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \bar{x})^2} \dots \dots \dots (3.2)$$

where σ is the standard deviation, x_i is the value of samples, $\bar{x}$ is the sample mean, and N is total number of samples.

3.3.1 Characterization of Structures and Properties

Investigation of the chemical structures: FTIR spectrum and ^1H -NMR spectrum of the samples were characterized by an FTIR spectrometer (Spectrum 100, PerkinElmer, US) and an NMR spectrometer (Jeol ECZ500R 500 MHz Solid-State NMR spectrometer), respectively.

Moisture vapor permeability test: Moisture permeability tests for the samples by using the cup method by the textile standard E96/E96M-13. The moisture transmission rate ($\text{g m}^{-2} \text{day}^{-1}$) was calculated by measuring the weight loss of water, where the water is contained in cups with the openings covered by the tested specimen.

Air permeability test: The air permeability value (mm s^{-1}) of all the samples was tested according to ASTM D737-08 using a MO21S air permeability tester (SDL Americ, Inc.). The output airflow rate (in units of mm s^{-1}) represents the air permeability of samples.

Waterproof test: The water repellent of electronic skins was characterized by an AATCC rain tester following the AATCC test method 35-2006. The test sample (20 cm×20 cm) backed by a 15 cm×15 cm standard paper blotter was clamped in a specimen holder and was positioned into the central position of the water spray at a distance of 30.5 cm from

the face of a spray nozzle. A horizontal water spray was directed against the specimen with a duration time of 5 min. The intensity of the water spray was controlled through a column of water set at 0.6 m. After 5 min test, the paper blotter was carefully removed and weighed. If the increased weight of the paper blotter was higher than 5 g, the test sample will be deemed non-waterproof.

3.3.2 Characterization of Mechanical Properties and Adhesion Strength

Tensile test: A universal tensile test machine (Instron 5566, Lab World Group, USA) was used to test the mechanical properties of SBS mats, where the distance of clamps is about 2 cm and the width and thickness of tested SBS mats is 1cm and 200 μm , respectively. Young's modulus was calculated by the slope of strain-stress curves of the first five percentages. Repeated stretching and releasing cycles were conducted at a displacement platform.

Lap shear test for evaluating the adhesive performance: Substrates (PDMS, glass, PI film, PC film, SBS mats, PET fabric, glass fabric, cotton, pigskin) were cut into small pieces with the dimension of 2.5 cm $\times$ 5 cm. Then, the substrates were plasma-treated and adhered together or other substrates by adhesives with an adhered area of 2.5 cm² (2.5 cm $\times$ 1 cm). For a soft substrate, a stiff backing is adhered to the back of the substrate by cyanoacrylate (Figure 3.4a). Adhered samples were mounted on the tensile test machine (Instron 5566, Lab World Group, USA) with a test speed of 50 mm min⁻¹ (Figure 3.4b). Shear adhesion strength can be calculated by the peak force at the tensile test dividing the adhered area. For mimicking the sweating conditions to assess the adhesive performance against sweat, PET fabrics were chosen as the substrate to secrete sweat due to its porous structure.

Peeling test for evaluating the adhesive performance: Substrates were cut into pieces

with the dimension of $10\text{ cm} \times 5\text{ cm}$. Then, the substrates were plasma-treated and adhered together or other substrates by adhesives with an adhered area of $2.5\text{ cm} \times 7.5\text{ cm}$. For a soft substrate, a stiff backing is adhered to the back of the substrate by cyanoacrylate. Adhered samples were mounted on the tensile test machine (Instron 5566, Lab World Group, USA) with a test speed of 50 mm min^{-1} (Figure 3.5). The plateau force (F) during the peeling test was recorded. Interfacial toughness was used in the peeling test to represent the energy needed to detach the adhesion interface. It can be calculated by the two times plateau force dividing the width of the adhered area.

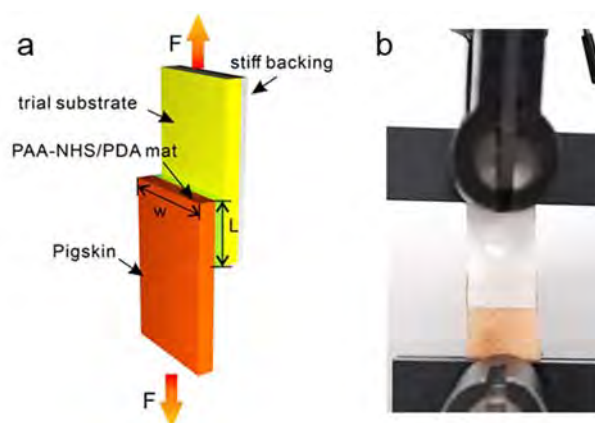


Figure 3.4. a, Schematic illustration of the lap shear test. b, Photograph of a fibrous mat adhered to a pigskin by PAAND mats under lap shear test.

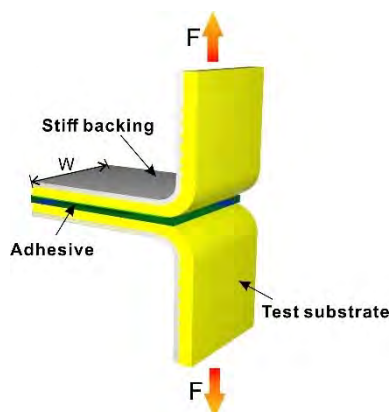


Figure 3.5. Schematic illustration of the peeling test for adhesives.

3.3.3 Measurement of Electrical Properties

The conductivity of EGaIn-coated fibrous mats was performed with a 4-terminal method by a Keithley 2400 Sourcemeter, where a four-terminal method was used for reducing the contact resistance between terminals and specimens. The conductivity of the EGaIn-coated fibrous mats can be calculated by equation 3.2:

$$\sigma = L/((W \times T) \times R) \quad (3.2)$$

Where the measured electrical resistance (R), the length and width of the EGaIn-coated SBS mats (L and W) can be directly measured and the approximate thickness of EGaIn mats (T) can be obtained by equation 3.3:

$$T = m/(\rho \times S) \quad (3.3)$$

where m denotes the weight of EGaIn coated at the surface of fibrous mats; ρ denotes the density of EGaIn, and S denotes the coated area.

The skin impedance of electrodes was conducted via an electrochemical workstation (CHI 660) by the electrochemical impedance spectroscopy (EIS) mode. Two electrodes adhered to the surface of the skin with a distance of 5 cm between each other. Impedance and phase angle as a function of frequency ranging from 1 to 10,000 Hz were recorded by an AC sinusoid signal amplitude of 10 mV.

CHAPTER 4: WET-ADAPTIVE ELECTRONIC SKIN

Permeable electronics with the ability to transport gas and water moisture exhibit exclusive advantages in comfortable and long-term wearing. However, current permeable electronics lack effective adhesion strategies to adhere them firmly and quickly to human skin, especially under wet conditions. In this chapter, a wet-adaptive electronic skin (WADE-skin) that simultaneously pertains good mechanical stretchability, electrical conductivity, permeability, waterproofness, and wet adhesion has been successfully investigated. This WADE-skin is fabricated by layer-by-layer electrospinning of stretchable and permeable SBS fiber mat and NHS and dopamine groups grafted poly(acrylic acid) (PAAND) wet-adhesive fiber mat. This WADE-skin could fast and strongly adhere to the wet skin and pertain adhesion over weeks. Based on such features, the WADE-skin is employed as wireless ECG electrodes for recording electrocardiogram rhythms during wet conditions and long term. Furthermore, the strain sensor array is printed to the surface of WADE-skin, which could adhere to the palm of a human hand as finger-bending sensors to drive VR-mediated human-machine interactions.

4.1 Introduction

Flexible and wearable electronics demonstrate great potential in skin-attachable electronics for health monitoring, human-machine interaction, biological energy harvesting, and so on^[4, 11, 184]. By leveraging the booming technologies such as virtual reality (VR), augmented reality (AR), mixed reality (MR), machine intelligence, and the internet of things (IoTs), flexible and wearable electronics have been brought in a more precise, user-friendly, and intelligent way^[12, 16, 18-20]. Versatile flexible electronics have been designed, for example, wearable sensors for the detection of human physical and chemical signals, soft displays, conductors, and antenna^[2, 6-7]. Even though

extensive research has pushed wearable electronics toward real wearable scenarios with high performances including good flexibility, stretchability, and biocompatibility^[14, 23, 30], while the permeability and adhesion properties are underestimated from the view of wearing comfort and long-term applications.

Permeability refers to the ability to transport gas and water moisture, which is critical for skin-attachable electronics to reduce the accumulation of interfacial water on the skin and to transport analytes (*e.g.*, glucose, salts) to target sensors^[178-179]. For healthy skin, the permeability of on-skin electronics should satisfy the ‘insensible perspiration’ of the skin at the evaporation rate of $600 \text{ g m}^{-2} \text{ day}^{-1}$ for thermoregulation^[89]. The lack of permeability may cause uncomfortable feelings or even skin irritation and inflammation during long-term use^[85]. Therefore, the building blocks including flexible substrates, conductive materials, and adhesives for the fabrication of on-skin wearable electronics are required to be permeable. Many efforts have been engaged to develop permeable materials, for example, porous textiles and electrospun mats^[135, 137, 180-183].

On the other hand, adhesion plays a vital role in bridging biological tissues and flexible electronics^[38, 44, 185-187], which may affect the stability and functionality of devices. An unstable adhesion may cause a lower signal-to-noise (SN) ratio or even loss of function^[3, 35]. Conformal and stable adhesive interfaces can help improve the sensitivity and wearing comfort of electronics but are challenging to achieve. This is because human skin is much soft and more complex than engineering solids^[46, 50]. Human skin deforms under activities, which would be restricted by covering a rigid material/device. Moreover, the rigid cover may even cause device delamination and uncomfortable feelings. The skin is often wet, due to the secretion of interfacial water during sweating, bleeding, and under wet environments (*e.g.*, swimming, washing, showering). The interfacial water tends to destroy the intermolecular bonding between adhesives and adherends, resulting in an unstable adhesion and easy detachment of devices. To

improve the wet-adhesive performance, catechol, and its derivatives, found in the adhesive proteins of marine mussels, have been widely employed in the design of adhesives^[173, 188-189]. Yuk *et al.* also fabricated a dry double-side tape, in which the tape can adsorb the interfacial water and form crosslinking to the adherends fast^[37].

To date, a few attempts have been made to fabricate permeable electronics with good adhesiveness. One strategy is to fabricate ultrathin flexible devices, which adhere to the skin by physical attachment. However, the total thickness of these devices is limited to several microns^[130]. In addition, hydrophilic or adhesive polymers have also been processed into permeable adhesives, for example, by electrospinning them into fibers. However^[31, 45, 97, 190], an adhesive that is universal, robust, and permeable to various substrates and human skin under wet environments is still absent.

To address this challenge, we report a wet-adaptive electronic skin (WADE-skin) that simultaneously offers skin-like stretchability, wet adhesion, permeability, biocompatibility, and waterproof property. The WADE-skin is fabricated based on air- and moisture-permeable multi-layer fibrous fibre mats that are seamlessly stacked vertically with liquid metal electrode patterns. It consists of a next-to-skin fibrous adhesive layer, a next-to-air waterproof fibrous layer, and a stretchable liquid metal electrode layer that is positioned either beneath or above the adhesive layer depending on the targeted electronic functions. The WADE-skin can rapidly adhere to human skin after contact for a few seconds and show a strong adhesion strength of over 150 kPa even in wet conditions. A stretchable electrocardiogram device based on the WADE-skin was demonstrated, which shows a stable device performance and chronic biocompatibility on the skin during exercises and long-term attachment for over one week. The fabrication strain sensor array with WADE-skin that can operate underwater for VR-mediated human-machine interactions was also performed.

4.2 Experiment

4.2.1 Fabrication of WADE-Skin.

Electrospun SBS solutions were prepared by dissolving SBS particles in the mixture solution (THF/DMF =3:1) with a weight ratio of 15 wt%. The PAAND solution was synthesized via two steps of grafting (Figure 4.1). PAA powders were dissolved in the DI water by stirring 12 h at 60 °C to prepare 10 wt% PAA solution. 0.2 g EDC and 0.1g NHS were added to the PAA solution (50 g) to graft NHS groups to the PAA chains since EDC activated the carboxyl groups from the PAA chains. Subsequently, dopamine (30 mg) was added into this solution to further graft dopamine groups into the PAA chains by partial displacement of the grafted NHS groups. Afterward, the as-prepared solution PAAND solution was used for electrospinning.

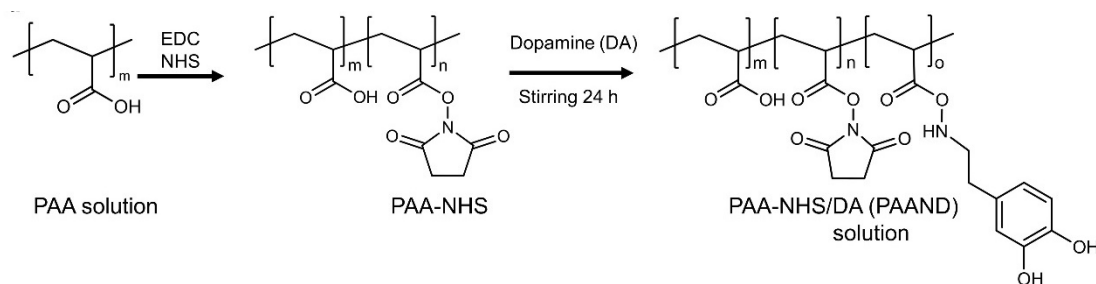


Figure 4.1. Synthesis of the PAAND solution by grafting N-hydroxysuccinimide (NHS) and dopamine groups to the PAA chains.

The substrate of WADE-skin was prepared by layer-by-layer electrospinning (Figure 4.2). PAAND was firstly electrospun to the surface of silicone-oil-coated paper. The feed rate of PAAND solution was 1 ml h^{-1} and a high voltage field was set at 20 kV between the needle tip and collector. The temperature of the electrospinning machine was set at 30-40 °C for accelerating the evaporation of water. Then, the SBS layer was electrospun to the top of the PAAND fiber mat. The feed rate of the SBS solution is at

3 ml h⁻¹ and the electrospinning temperature was ~25 °C. The thickness of this double-layered substrate could be varied from several tens μm to millimeters by controlling the amount of feeding solution. A layer of EGaIn will be printed to the surface of either the PAAND side or the SBS side through a stencil mask. For printing ECG electrodes, the EGaIn will be printed at the surface of the PAAND side of the WADE-skin. For fabricating strain sensor arrays, the EGaIn will be printed at the surface of the SBS side of WADE-skin.

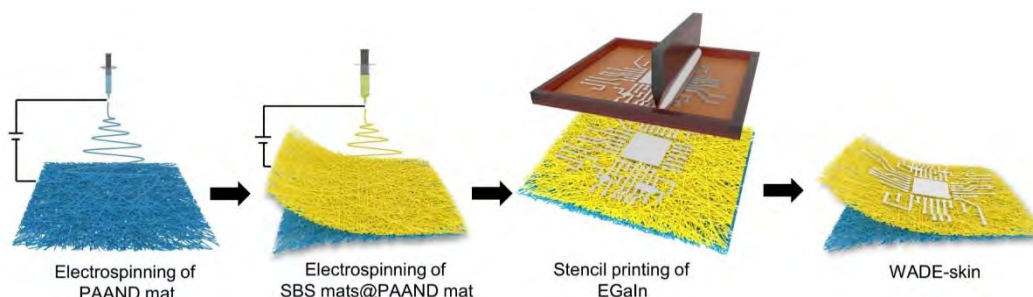


Figure 4.1. Schematic illustration of the fabrication process of WADE-skin through layer-by-layer electrospinning of PAAND and SBS fiber mats and stencil printing of conductive EGaIn onto the surface of the fiber mat.

WADE-skin as ECG electrode

The EGaIn patterns were stencil-printed on the WADE-skin where the templates of stencil printing were obtained by laser printing. For ECG signal capturing, the EGaIn was directly fabricated to the surface of PAAND mats of the WADE-skin, and this WADE-skin was nailed with an Ag/AgCl bottom to connect ECG devices. Two commercial ECG devices (PC-80B and FitPatch H1, Heal force Bio-Meditech Holdings Limited, China) were used for capturing ECG signals. FitPatch was waterproof and used for the 24 h monitoring and swimming and other tests were conducted by the PC-80B device.

WADE-skin as finger bending sensor array

The finger bending sensors contained five individual sensors that were made by patterning the 800- μm zigzag EGaIn line to the surface of SBS mats of the WADE-skin. For encapsulation and waterproofing, another SBS mat was electrospun to the top of the WADE-skin. A self-made flexible flat cable that was made by screen printing of conductive Ag inks to a 50- μm -thickness polyimide (PI) film connected the WADE-skin and a rigid printed circuit board (PCB). This PCB contained 6 Wheatstone bridges, 6 24-bit analog-to-digital converters (ADC, HX711), a Bluetooth (HC-05), and a Microprogrammed Control Unit (Arduino Nano). A robotic hand and an 18-DOF humanoid robot were employed as the controlled machine to realize human-machine interactions and a wide-angle lens was mounted on the humanoid robot to send the robotic vision back to a VR headset through Wi-Fi.

4.2.2 Characterizations

Evaluation of adhesive properties of adhesive PAAND fiber mat

The shear adhesion strength of the adhesive PAAND fiber mat was tested by following the test standard ASTM 2255. Porcine skin that was purchased from the local market was adopted in this adhesion test to mimic human skin. Both porcine skin and WADE-skin were cut into small pieces with the dimension of 2.5 cm $\times$ 5 cm. 1 mol L⁻¹ CaCl₂ solution was then sprayed to the surface of porcine skin for the crosslinking of PAA chains. The WADE-skin was then attached to the porcine skin with the overlapped area of 2.5 cm² (2.5 cm $\times$ 1 cm). Before the adhesion strength test, all the adhered samples were stored for 3 h until reaching the dynamic water equilibrium. To conduct the shear strength test, free ends of the adhered samples were mounted on the tensile test machine (Instron 5566) and separated with a test speed of 50 mm min⁻¹. Peak forces during the separation of samples were recorded. Shear adhesion strength was then calculated by dividing the averaged peak force by the adhered area (*i.e.*, 2.5 cm²). To evaluate the

versatility of PAAND mats, PET fabrics, glass fabrics, cotton, and TPU mats were adhered to the porcine skin by the PAAND mats, and substrates (PDMS, glass, PI film, PC film, TPU mats, PET fabric, glass fabric, cotton, porcine skin) were also adhered to itself by the PAAND mats. As a comparison, commercial fibrin glue (Porcine Fibrin Sealant Kit, Harbin Hanbang Medical Technology Co., LTD.), medical cloth tape (3M), medical PU tape (Jiangsu Hons Bioengineering Co., LTD.) and cyanoacrylate (3M, Vetbond tissue adhesive) were employed to adhere SBS mats to the porcine skin.

For evaluating the wet-adhesive property, the WADE-skin, medical cloth tapes, and medical PU tapes adhered to the porcine skin wetted by water. By comparison, the adhesion strengths to the porcine skin by these adhesives were also measured. To assess the adhesive performance against sweating conditions, PET fabrics were chosen as the substrate to mimic the secretion of sweat by injecting the sweat into the pores of PET fabrics. Artificial sweats (200 g m^{-2}) were injected into the back side of PET fabrics where the front side was adhered with the WADE-skin, medical cloth tape, PU tape, or impermeable WADE-skin (covered with a PET film). The sweat-treated samples were also stored at 35°C for mimicking the evaporation in the human skin.

Long-term on-skin irritation test

The skin irritation test of the WADE-skin was also carried out on human skin. All procedures on human skin followed the ethical guidelines of human subjects and were approved by The Hong Kong Polytechnic University (HSEARS20230101001). One volunteer participated in this study. Four samples, including the WADE-skin, medical cloth tape, medical PU tape, and PDMS/medical PU tape, were adhered to the skin of the forearm of one volunteer. After covering for one week, all testing samples were removed from the skin. The skin was photographed before and after the test so that the appearance could be compared.

***In vitro* cytotoxicity test of the WADE-skin**

3T3 cells (ATCC, US) were used to evaluate the *in vitro* cytotoxicity of the building components of WADE-skin (*i.e.*, PAAND mats, SBS mats, EGaIn) under the ISO 10993-5: 2009(E) standard. 6×10^4 3T3 cells in 1 mL full Dulbecco's Modified Eagle's Medium (DMEM, Hyclone, Hong Kong) supplemented with 10% fetal bovine serum (FBS, Hyclone, Hong Kong) and 1% penicillin/streptomycin (PS, Hyclone, Hong Kong) were seeded in a 24 well plate. Over 24 h incubation time, we refreshed the medium from the culture plate and verified the cell confluency and morphology. After that, 0.2 cm² SBS mats, EGaIn-coated SBS mats, WADE-skin with PAAND (NHS 0.8%, DA0.06%) mat, and WADE-skin with PAAND(NHS 0.8%, DA1.2%) mat were directly added in the 24 well plates to evaluate the cytotoxicity of these materials. The fresh full medium and 20% DMSO/full medium mixture were employed as the blank and positive control. The culture environment of all samples was set at 37°C in the incubator with 5% CO₂ and the incubation time was 24 h. The cell viability was calculated by a Live/Dead assay (Thermo Fisher, Hong Kong). Cells were observed by a fluorescent microscope (Zeiss, Germany).

4.3 Results and Discussion

4.3.1 Fabrication and Characterizations of WADE-Skin

The WADE-skin contains three components: 1) a permeable and stretchable substrate of poly(styrene-butadiene-styrene) (SBS) fiber mat, 2) a wet-adhesive layer of N-hydroxy succinimide (NHS) and dopamine-grafted polyacrylic acid (PAAND) fiber mat, and 3) conductive paths of patterned EGaIn (Figure 4.2). The fabrication process of the WADE-skin is detail described in the experiment section. Briefly, The wet-adhesive PAAND solution is firstly synthesized in two steps: 1) grafting NHS groups to PAA chains by activation of carboxyl groups, 2) grafting dopamine groups to PAA chains by partially replacing the grafted NHS groups. Then, the as-prepared PAAND solution is electrospun to a nanofiber mat. Afterward, a layer of SBS fiber mat is electrospun above the prepared PAAND mat to get a double-layered fiber mat. Finally, the WADE-skin is obtained by printing the EGaIn to the surface of a double-layered fiber mat. Depending on functions, the EGaIn is printed beneath the PAAND fiber mat to be biophysiological electrodes for the direct contact of the skin or above the SBS fiber mat to be strain sensor arrays for monitoring human motions closing to the air side.

The wet adaptivity of this WADE-skin includes: 1) the moisture/air permeability which allows the human skin to breathe and evaporation of sweat, 2) waterproofness to protect the WADE-skin against foreign water from the outer environments, 3) wet adhesion for stable adhesion to the wet skin. The excellent wet adaptivity makes the WADE-skin a platform for health signals monitoring and human-machine interactions toward wet environments and long term.

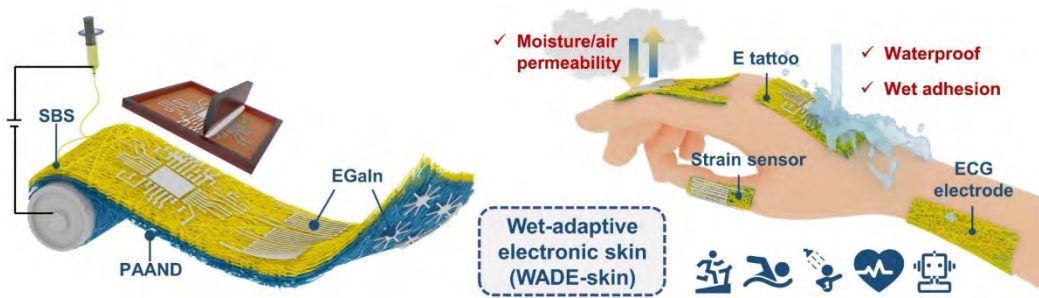


Figure 4.2. Schematic illustration of the fabrication WADE-skin and the application toward skin-adhesive and wet-adaptive applications.

The surface morphology of the WADE-skin had been characterized as shown in Figure 4.3. An EGaln conductive pathway with a width of $\sim 500\ \mu\text{m}$ was printed to the surface of both SBS and PAAND sides of a WADE-skin (Figure 4.3 a and d). This WADE-skin demonstrates a porous structure which allows the penetration of gases and liquids. The average diameters of PAAND and SBS fiber mat are around $2.75\ \mu\text{m}$ and $0.85\ \mu\text{m}$, respectively (Figure 4.3 b-c and e-f).

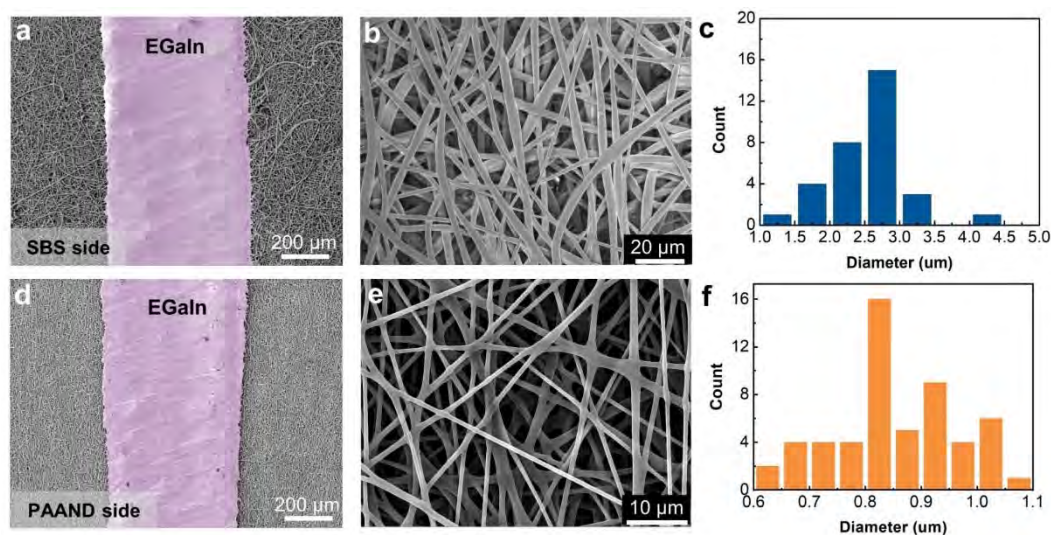


Figure 4.3. Surface morphology SBS fiber mat and PAAND fiber mat for the WADE-skin. **a-c**, SEM image (**a-b**) and the measured diameters (**c**) of the SBS fiber mat of WADE-skin. **d-f**, SEM image (**d-e**) and the measured diameters (**f**) of the PAAND fiber mat of WADE-skin.

The chemical structure of the synthesized PAAND polymeric fiber mats was characterized by the FTIR spectrum and ^1H -NMR spectrum. The IR spectrum is shown in Figure 4.4. The IR peak at 1698 cm^{-1} is assigned as the $-\text{COO}-$ asymmetric stretching mode originating from the carboxyl groups of the PAA chains. The IR peak around 1085 cm^{-1} is assigned as the $-\text{C-N}$ stretching mode. The intensity of the peak of 1085 cm^{-1} rises by improving the weight ratio of NHS, indicating the successful grating of NHS to the PAA chains.

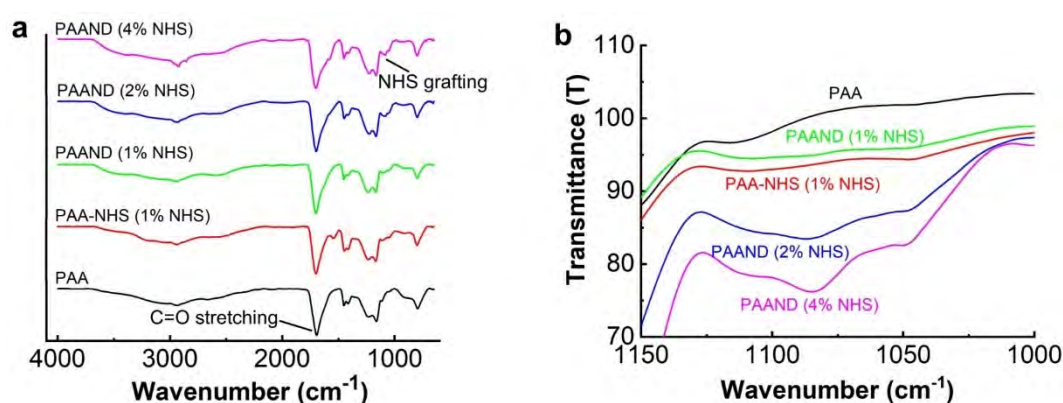


Figure 4.4. Infrared (IR) spectrum of the PAAND fiber mat grafted with different amounts of NHS groups. **a-b**, IR spectrum range from 4000 cm^{-1} to 600 cm^{-1} (**a**) and from 1150 cm^{-1} to 1000 cm^{-1} (**b**).

The ^1H -NMR spectrum of PAA fiber mat, NHS-grafted PAA fiber mat, and PAAND fiber mat is shown in Figure 4.5. The peaks a and b attribute to H in the PAA backbone. From the spectrum of PAA-NHS, and two peaks c and c' at 2.98 and 2.67 ppm attribute to the H from the grafted NHS groups of PAA chains. Peaks d and e attribute to the H from $-\text{CH}_2-$ of the grafted dopamine groups and peaks f, f' as well as f'' attribute to the H from the benzene ring of the grafted dopamine groups. The evidence from the IR and ^1H -NMR spectrums indicates that the PAAND polymers are successfully fabricated and maintained stably after electrospinning.

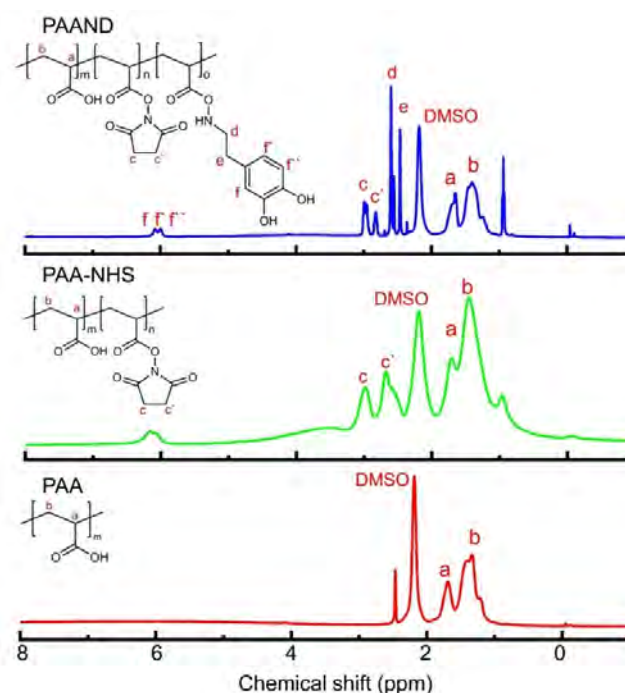


Figure 4.5. Proton nuclear magnetic resonance (¹H-NMR) spectrum of the wet-adhesive polymeric fiber mat.

4.3.2 Stretchability, Conductivity, Permeability, Waterproofness, and Biocompatibility of WADE-Skin

Mechanical properties are key characters for on-skin electronics since the skin deforms during human motions with a maximum of 100% strain. The skin-like Young's modulus at the range of 100 kPa to 1 MPa is also preferred for comfortability and wearing comfort. The effects of the solution concentrations on the mat's mechanical properties have been first investigated (Figure 4.6 a-c). Decreasing the concentration of SBS in the electrospinning solution to 8% could lead to the reduction of the fibre diameters to ~180 nm (Figure 4.6a-b). However, numerous beads appeared and hung on the fibers, resulting in the formation of a fibre mat with rather weak mechanical strength and stretchability (Figure 4.6d). Increasing the concentration of SBS in the electrospinning solution to 15% could result in the formation of the fibre mat with homogeneous fibre

diameter (Figure 4.6c, which in turn could impart the fibre mat with outstanding mechanical strength and stretchability (Figure 4.6d). More importantly, such a fabrication process was highly reproducible. Therefore, the 15 wt% SBS solution was selected as the optimized electrospinning solution for the fabrication of WADE-skin.

Electrospinning offers the simple fabrication of porous fibrous substrates with tunable thicknesses. Via varying the collection time during electrospinning from 15min to 16 h, SBS fibre mats with thicknesses ranging from 30 μm to 2,000 μm could be obtained (Figure 4.6e). The tensile test reveals that all the samples of fibre mats exhibit high breaking strain ($>760\%$) with the skin-like modulus (300 to 850 Pa), demonstrating their suitability to be used as the substrate for WADE-skin (Figure 4.6f).

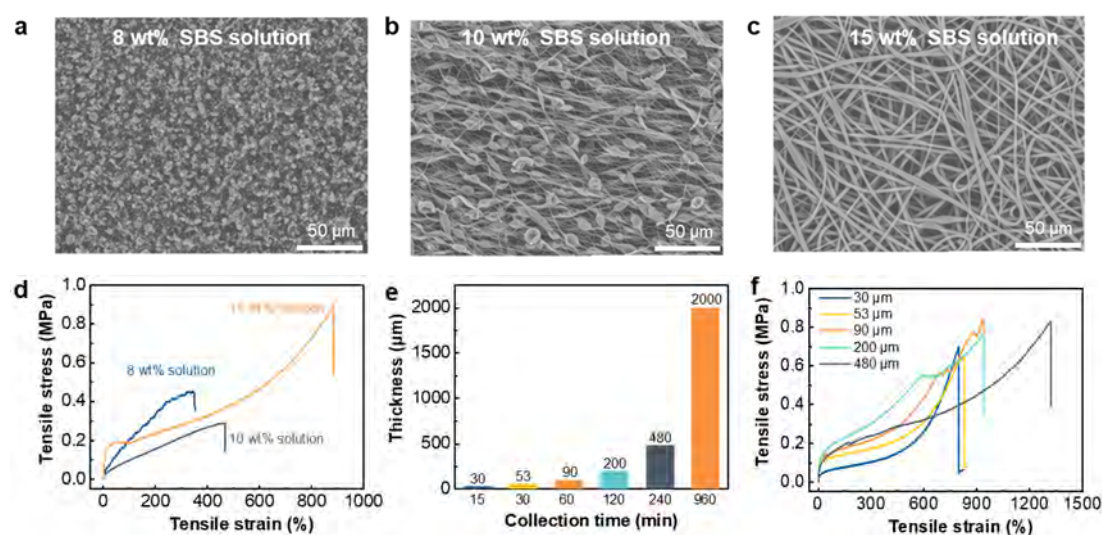


Figure 4.6. Manipulation of electrospinning parameters for the fabrication of SBS fibre mats. **a-c**, Surface morphology of SBS fibre mats fabricated by 8 wt% SBS solution (**a**), 10 wt% SBS solution (**b**), and 15 wt% SBS solution (**c**). **d**, Strain-stress curves of the fibre mats fabricated by 8 wt% SBS solution, 10 wt% SBS solution, and 15 wt% SBS solution. **e**, Dependence of the mat thickness on the collection time during electrospinning. **f**, Strain-stress curves of SBS fibre mats with different thicknesses.

As shown in the optical images of Figure 4.7a, the SBS fibre mats could be stretched to 9 times its original length. The Young's modulus of WADE-skin is ~ 850 kPa, which is similar to the modulus of human skin. The excellent elasticity and skin-like modulus make this WADE-skin a good candidate for epidermal electronics. In Figure 4.7 b, a WADE skin (30×20 cm) was fabricated and stretched over 50% by the human hand.

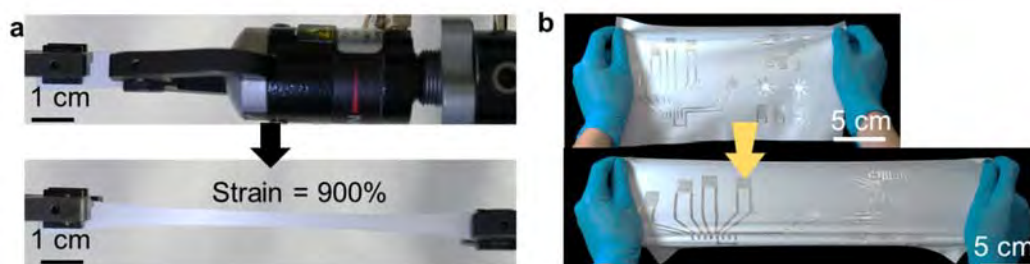


Figure 4.7. **a**, A WADE-skin was stretched by the tensile test machine. **b**, Digital images of a WADE-skin (30×20 cm) stretched by human hands.

WADE-skin exhibits remarkable stretchability, withstanding strains of up to 900%. In contrast, traditional metals fail to meet such high stretchability requirements as they typically fracture at 1%. Herein, eutectic gallium indium (EGaIn) was chosen as the stretchable conductor for preparing the WADE-skin. A series of WADE-skin with EGaIn mass loadings from 3 mg cm^{-2} to 15 mg cm^{-2} were prepared as shown in Figure 4.8a. 10 mg cm^{-2} of EGaIn coating performs the highest conductivity at around $30,000 \text{ S cm}^{-1}$, closing to the conductivity of pure EGaIn metals at $34,000 \text{ S cm}^{-1}$.

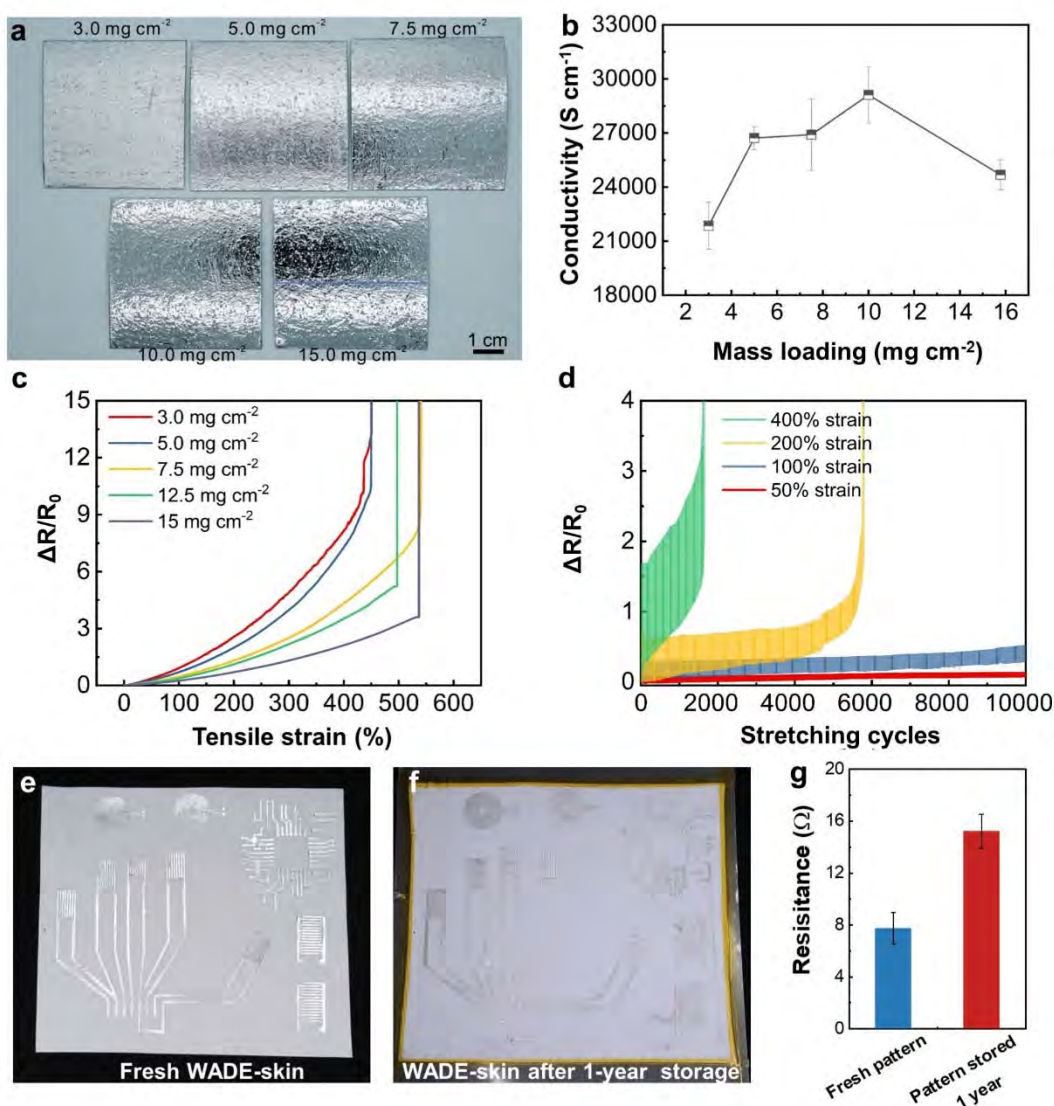


Figure 4.8. Electrical properties of the WADE-skin with different mass loadings of EGaIn. **a-c**, Digital image (**a**), conductivity (**b**), and resistance change under stretching (**c**) of the WADE-skin with different mass loadings of EGaIn. **d**, Resistance change under continuously stretching-releasing cycles at the strains varied from 50% to 400% for the WADE-skin with the EGaIn mass loading at 7.5 mg cm⁻². **e-f**, Digital images of (**e**) freshly prepared WADE-skin and (**f**) the WADE-skin stored after one year. **g**, Resistance changes of the freshly prepared patterns and the patterns stored after one year.

The resistance change of this WADE-skin during stretching was also measured (Figure 4.8c). The higher EGaIn mass loading results in lower resistance increases during stretch. Both EGaIn coatings to the WADE-skin are conductive under the strain range between 0% ~ 400% and the resistance changes of these WADE-skin show nearly linear relativity to the tensile strain. The resistance of these WADE-skin will suddenly go up over 400% since the break of the conductive pathway. 10,000 times consecutive stretching-releasing cycles in different strains for the WADE-skin coated 10 mg cm⁻² EGaIn were performed. This WADE-skin could resist 1800 times stretching cycles at 400% strain or 5000 times at 200% strain. For the stretching strains at 100% or 50%, it could maintain stable over 10,000 times of stretching cycles.

To examine the stability issue of the liquid metal patterns for the WADE-skin, we measured the resistance of the freshly prepared liquid-metal strain sensors and the resistance of the liquid-metal strain sensors that stored after one year (Figure 4.8 e-f). Although the resistance of the liquid-metal patterns increased nearly one times after storage one year from 7.7 Ω to 15.2 Ω , the liquid-metal patterns remained high electrical conductivity, indicating the long-term application potential of the WDE-skin (Figure 4.8g).

Due to the high electrical stability and stretchability, this WADE-skin could seamlessly conform to the human skin during human motions. This makes it highly suitable for use in on-skin electronics. The cross-sectional morphology of the WADE-skin adhered to substrates also was investigated by the SEM (Figure 4.9). A 300- μ m WADE-skin adhered to a PDMS substrate with a thin adhesive interface. A thin layer of the EGaIn conductive pathway was above the SBS fiber mat. The main component Ga of the EGaIn was confirmed by the EDX images (Figure 4.9b).

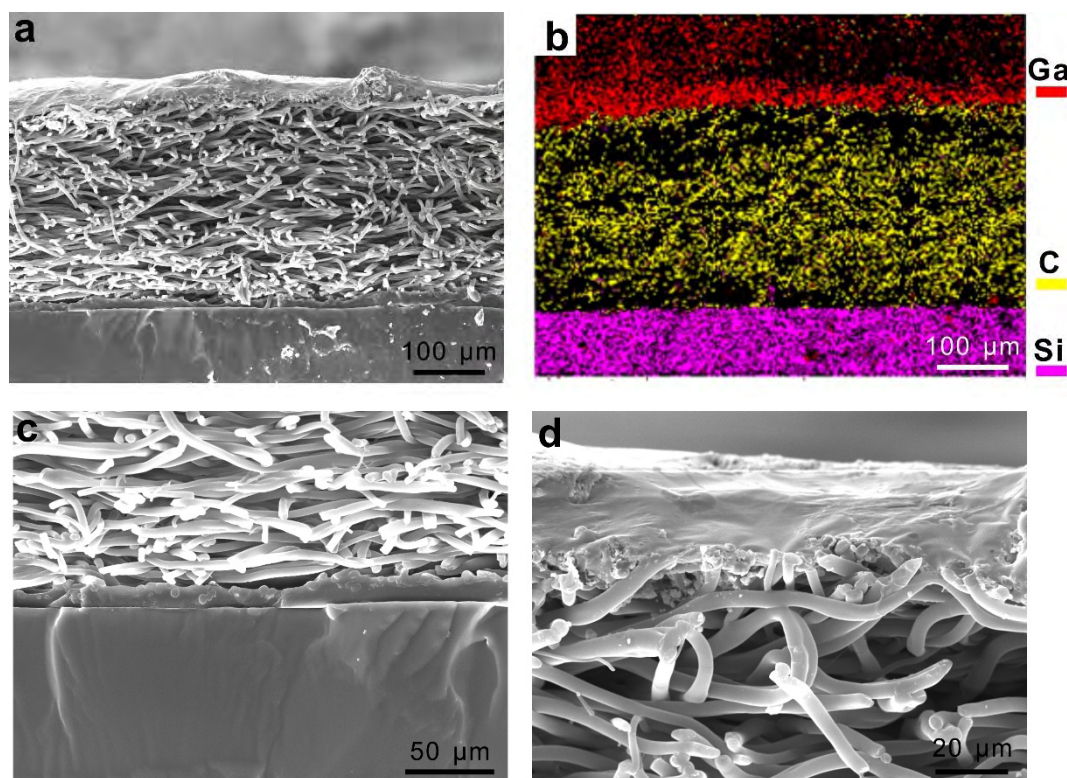


Figure 4.9. a-d, Cross-sectional morphology of a WADE-skin adhered to a PDMS substrate. **a**, Overall perspective, **b**, EDX images showing the distribution of elements, **c**, adhesion interface and **d**, EGaln coating.

The permeability to gases, moisture, and liquids is of utmost importance for ensuring physiological comfort in electronic devices that contact with the skin. The demonstration of gas permeability of the WADE-skin has been first demonstrated, shown in Figure 4.10a. A WADE-skin adhered to a permeable glass fabric and positioned at the opening of a container filled with boiling water. Steam of the boiling water penetrated through the WADE-skin to the opposite side, demonstrating good air permeability of this WADE-skin.

Moisture vapor permeability of the WADE-skin has been conducted, following the ASTM E96E Water Vapor Transmission Rate standard. Bottles covered with the WADE-skin and SBS mat had the same water level drop but were lower than that of the bottle without covers. Bottles covered with a thin layer of PDMS (100 μm), cloth tape,

or thin PU tape pertained the same and miserable water level drop (Figure 4.10b). The moisture permeability of WADE-skin is $852 \text{ g m}^{-2} \text{ day}^{-1}$, satisfying the need for evaporating of insensible perspiration of the human skin ($600 \text{ g m}^{-2} \text{ day}^{-1}$) for thermoregulation (Figure 4.10c). In comparison, the moisture permeability of medical cloth tape, thin polyurethane (PU) tape, and thin PDMS film ($50 \text{ }\mu\text{m}$) are significantly lower than the WADE-skin at $258 \text{ g m}^{-2} \text{ day}^{-1}$, $141 \text{ g m}^{-2} \text{ day}^{-1}$, and $50 \text{ g m}^{-2} \text{ day}^{-1}$, respectively.

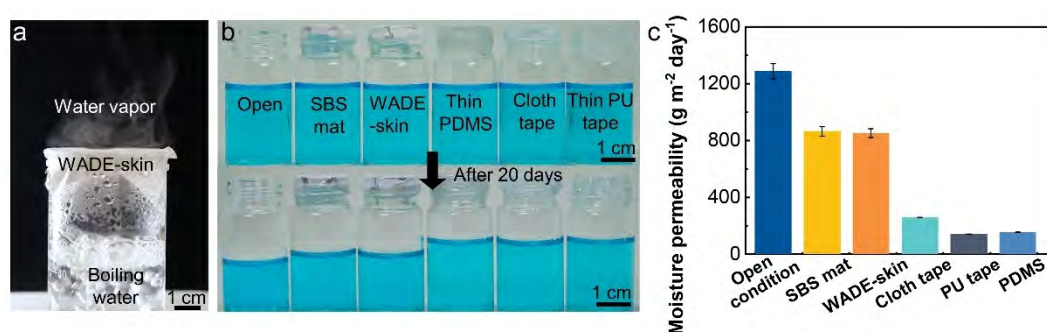


Figure 4.10. Air and moisture permeability of WADE-skin. **a**, Digital image showing the stream permeating through the WADE-skin to the opposite side. **b-c**, Moisture permeability test (**b**) and calculated moisture permeability (**c**) of the control sample, SBS fiber mat, WADE-skin, medical cloth tape, medical PU tape, and PDMS thin film ($50 \text{ }\mu\text{m}$).

Electrospinning offers the simple fabrication of porous fibrous substrates with tunable thicknesses. With varying the collection time during electrospinning, the thicknesses of the SBS fibre mats could be easily turned from $30 \text{ }\mu\text{m}$ to $2,000 \text{ }\mu\text{m}$. The moisture permeability and air permeability for the SBS fibre mats with thicknesses from $30 \text{ }\mu\text{m}$ to $2,000 \text{ }\mu\text{m}$ have been investigated (Figure 4.11). The moisture permeability of the prepared SBS fibre mats ranges from 850 to $900 \text{ g m}^{-2} \text{ day}^{-1}$ (Figure 4.11a). All fibre mats offer a high moisture permeability rate, higher than the required moisture permeability rate at $\sim 600 \text{ g m}^{-2}$ for the “insensible perspiration” of the skin. There is

no evidence that the moisture permeability has been impacted by the mat thickness. Therefore, the selection of mat thickness is more based on the potential applications. For example, conformal skin-attachable electronics prefers thin substrates while robust devices require thicker substrates.

The air permeability of the fibre mats has also been investigated following the ASTM D737-08 standard. As shown in Figure 4.11b, the air permeability of fibre mats dramatically decreases from 575 mm s⁻¹ to 3.7 mm s⁻¹ along with thickness increasing from 30 μm to 2000 μm. Thicker mat shows higher resistance to the gas and restricts the gas transmission.

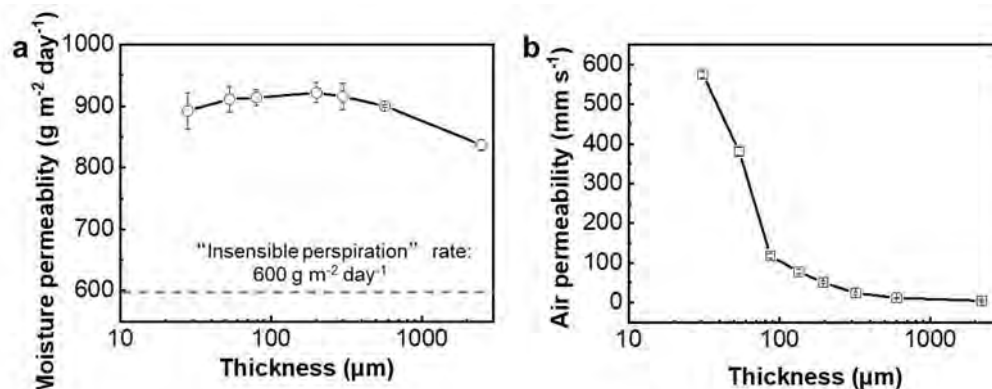


Figure 4.11. a-b, Moisture permeability (a) and air permeability (b) of SBS fibre mats with different thicknesses.

The WADE-skin is waterproof. The waterproof SBS layer of the WADE-skin shows a high water contact angle of 129° and a low water heterosis (Figure 4.12a). The surface of the WADE-skin facilitates the easy sliding off of water droplets and will not absorb the water (Figure 4.12b-c). The waterproofness of the WADE-skin attributes to the waterproof SBS encapsulation layer. Moreover, we systematically assessed the waterproofness of the WADE-skin by the standard rain test following the AATCC Test Method 35-2006 (Figure 4.12.d). This WADE-skin reaches an “excellent” level during

the rain test with only 0.1 g water penetrating through a 20 cm × 18 cm WADE-skin over 5-min heavy water spraying. Such excellent waterproof property safeguards both electrical components and the adhesive interface of the WADE-skin against any foreign water infiltration from external sources.

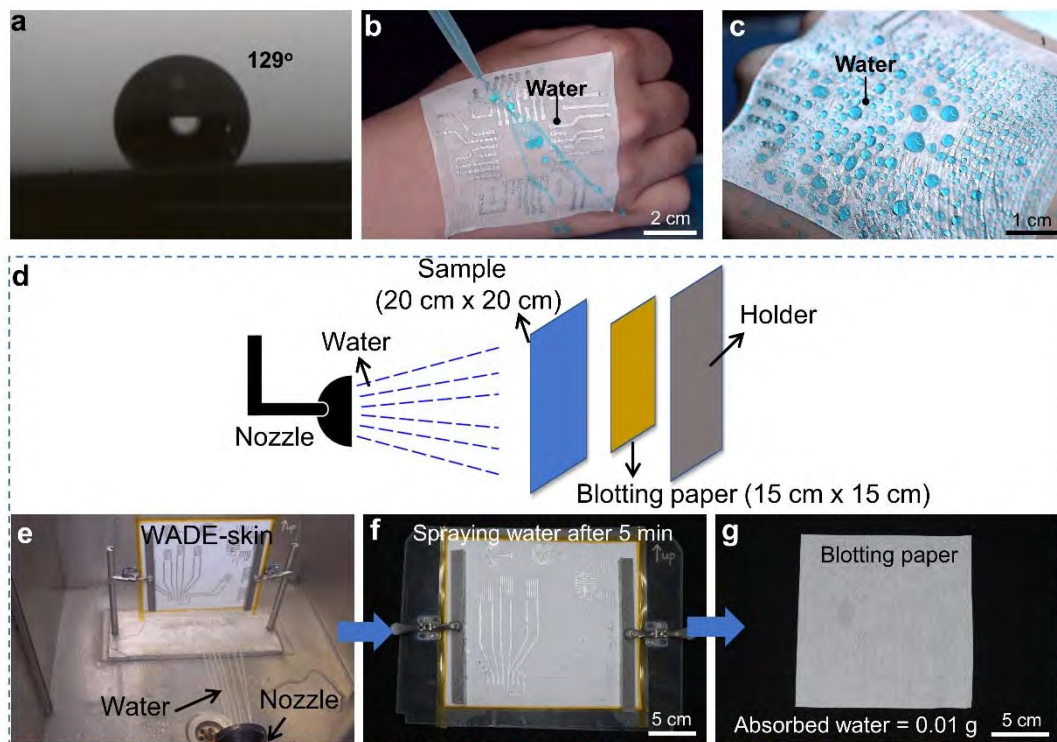


Figure 4.12. Waterproofness of WADE-skin. **a**, Digital image of the water contact angle of the WADE-skin. **b-c**, Digital images demonstrating the waterproofness of WADE-skin; **(b)** water (dyed to blue) flow down from the surface of WADE-skin with no hysteresis and **(c)** water droplets (dyed to blue) hang on the surface of WADE-skin; **d**, Schematic illustration of the rain test, which includes a nozzle to spray the water, the tested sample, a blotting paper at the back of the sample for absorbing the penetrated water, and a holder. **e-g**, Digital images of the rain test **(e)**, the WADE-skin after spraying water over 5 min **(f)**, and the backing blotting paper **(g)**.

Biocompatibility is also an important parameter for skin-attachable electronics. Three key components of the WADE-skin (*i.e.*, SBS mat, PAAND mat, and EGaIn) are non-

cytotoxic confirmed by the *in vitro* cytotoxicity study. The cytotoxicity test used 3T3 cells as the model. All groups during the test exhibited regular cell morphology and scarce dead cells except for the positive control group from bright-field and fluorescent live/dead staining images. All tested groups presented high cell viability of nearly 100% after 24 h of incubation by quantification of live/dead stained cells (Figure 4.13a). The cell has high cell viability and proliferates with the existence of EGaIn, SBS mat, and PAAND mat, indicating that there is no obvious evidence for toxicity of the whole WADE-skin(Figure 4.13b-c).

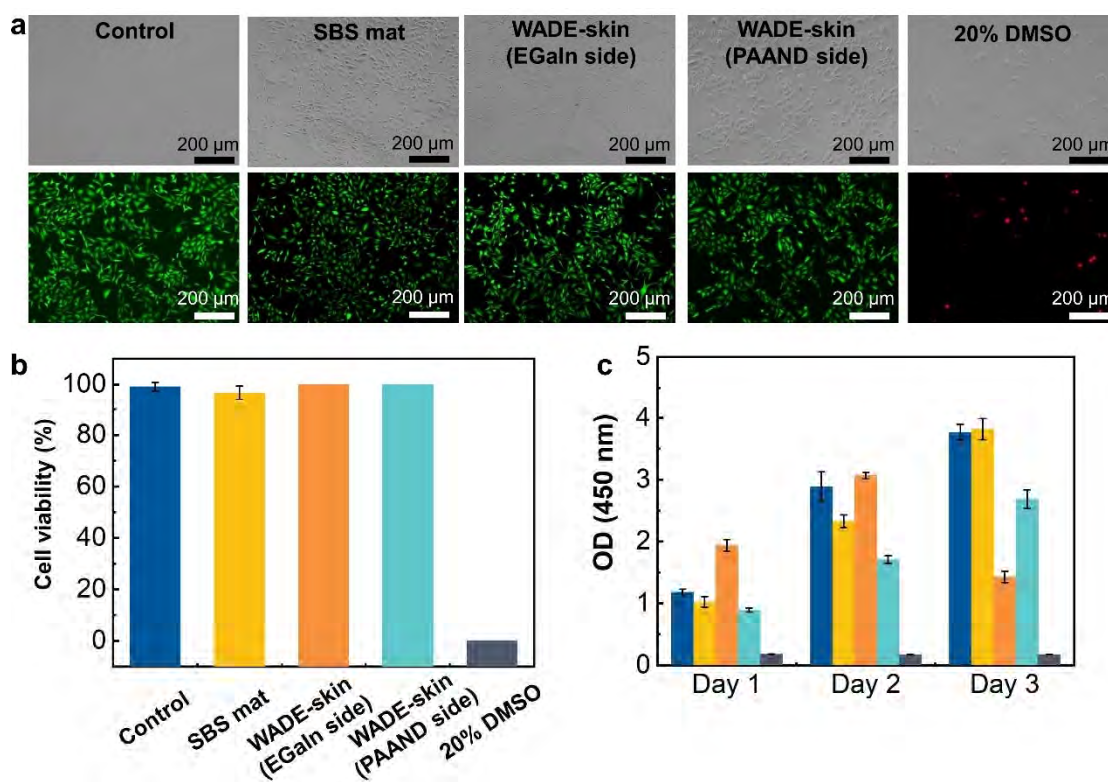


Figure 4.13. Cell cytotoxicity study of the WADE-skin. **a**, Bright-field and fluorescent images of 3T3 cells cultured in the incubation medium with the control sample, SBS, EGaIn side as well as PAAND side of the WADE-skin, and 20% DMSO. **b**, Quantification of 3T3 cell viability in different incubation groups. **c**, Optical density of the cells cultured in the incubation groups for three days.

Furthermore, a long-term on-skin test for identifying the long-term attaching comfort of the WADE-skin was conducted (Figure 4.14). The WADE-skin, medical cloth tape, medical PU tape, and PDMS thin film/PU tape adhered to the human forearm of a volunteer for 7 days. The PU tape and PDMS thin film/PU tape resulted in significant skin erythema at the covered skin and the cloth tape and the PDMS resulted in mild skin maceration since the accumulation of moisture. In contrast, the WADE-skin demonstrated no obvious negative effects on the skin after long-term covering.

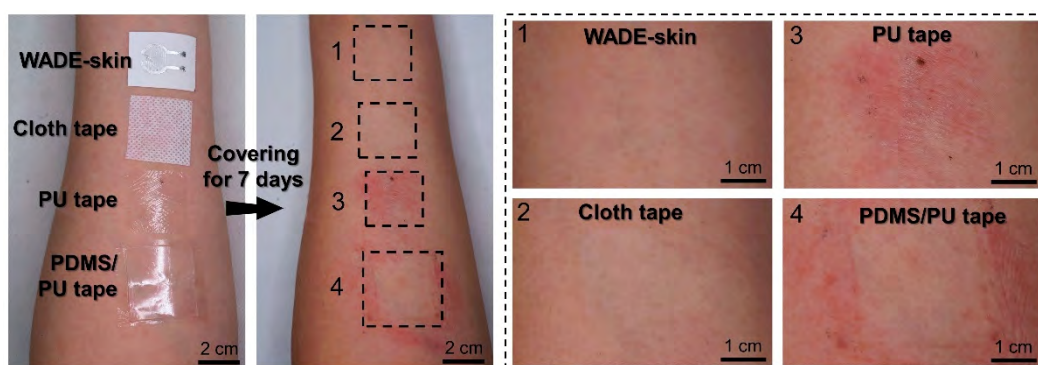


Figure 4.14. Digital images showing the skin irritation results of the adhesive E-patch, cloth tape, PU tape, and PDMS/Pu tape adhered to the forearm of a volunteer.

4.3.3 Wet-adhesion of WADE-Skin

Adhesive mechanism

The adhesive PAAND fiber mat of the WADE-skin is meticulously designed to strongly adhered to the wet skin while maintain permeability. Figure 4.15 elucidates the adhesion process and mechanism of the WADE-skin for wet skin. The skin surface is firstly wet by a quick spray of a diluted CaCl_2 aqueous solution. When the WADE-skin approaches the wet skin, the PAAND fiber mat absorbs the interfacial water. The PAAND chains diffuse into the interfacial water and contact the skin, forming multiple bonding to the wet skin. For example, the carboxyl groups and dopamine groups of the

PAAND chains can form intermolecular interactions with the skin and substrates (*e.g.*, hydrogen bonds, electrostatic force, and van der Waals' force) and PAA-NHS could covalently couple the primary amine groups of the skin, facilitating tough adhesion to the wet skin. The PAAND chains could be further ironically crosslinked by Ca^{2+} ions, thus generating an ultrathin hydrogel film adhered to the wet skin. This thin hydrogel film could absorb the secreted body fluids (*e.g.*, sweat) and evaporate them, bringing dynamic moisture balance and long-term comfortable wearing.

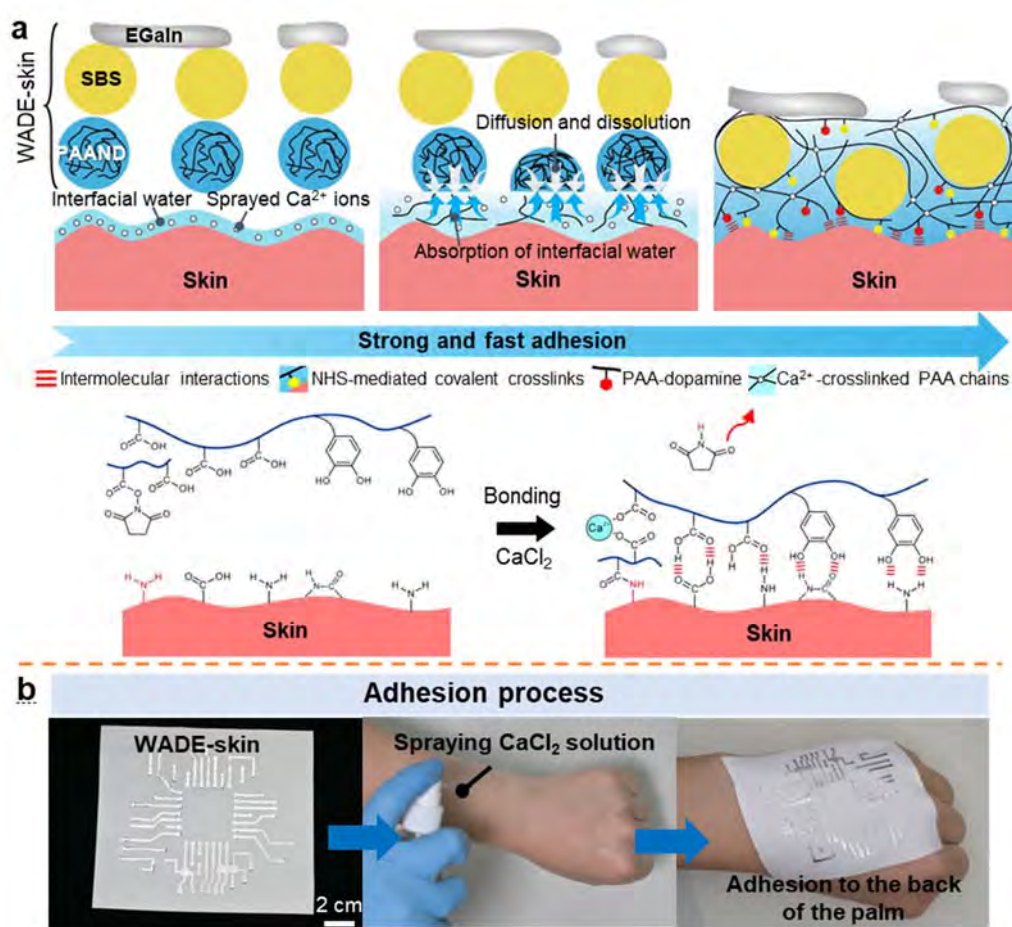


Figure 4.15. Schematic illustration (a) and digital images (b) of the adhesion process and mechanism of the WADE-skin for wet skin.

From the SEM image (Figure 4.16a), this thin hydrogel film embeds the SBS fibers and

adheres to the substrate. Leveraging this PAAN wet-adhesive fiber mat, the WADE-skin could strongly adhere to the wet human skin and hardly be peeled off from the skin (Figure 4.16b).



Figure 4.16. **a**, SEM image showing the adhesion interface of the WADE-skin adhered to a PDMS substrate. **b-c**, Digital images showing the tough wet adhesion between WADE-skin and human skin; a WADE-skin adhered to the human hand (**b**) and was torn apart by stretching the substrate (**c**).

Optimizing parameters

The ionic crosslink densities, molar ratios of the grafted NHS and dopamine groups, and thicknesses of the fabricated PAAND fiber mats have been optimized. The lap shear test was employed for evaluating the adhesion strength, where the shear adhesion strength was equal to the highest adhesion force dividing the adhered area (Figure 4.17a-b). With increasing the ionic crosslink density, the WADE-skin reaches the highest adhesion strength to the wet porcine skin at 75.9 kPa with the crosslinking of 1 mol L⁻¹ CaCl₂ solution. Further increasing the ionic crosslink density causes negative effects on the adhesion strength at the concentration over 1 mol L⁻¹ because of the excessive crosslinks weakening intermolecular interactions between the WADE-skin and the skin (Figure 4.17c).

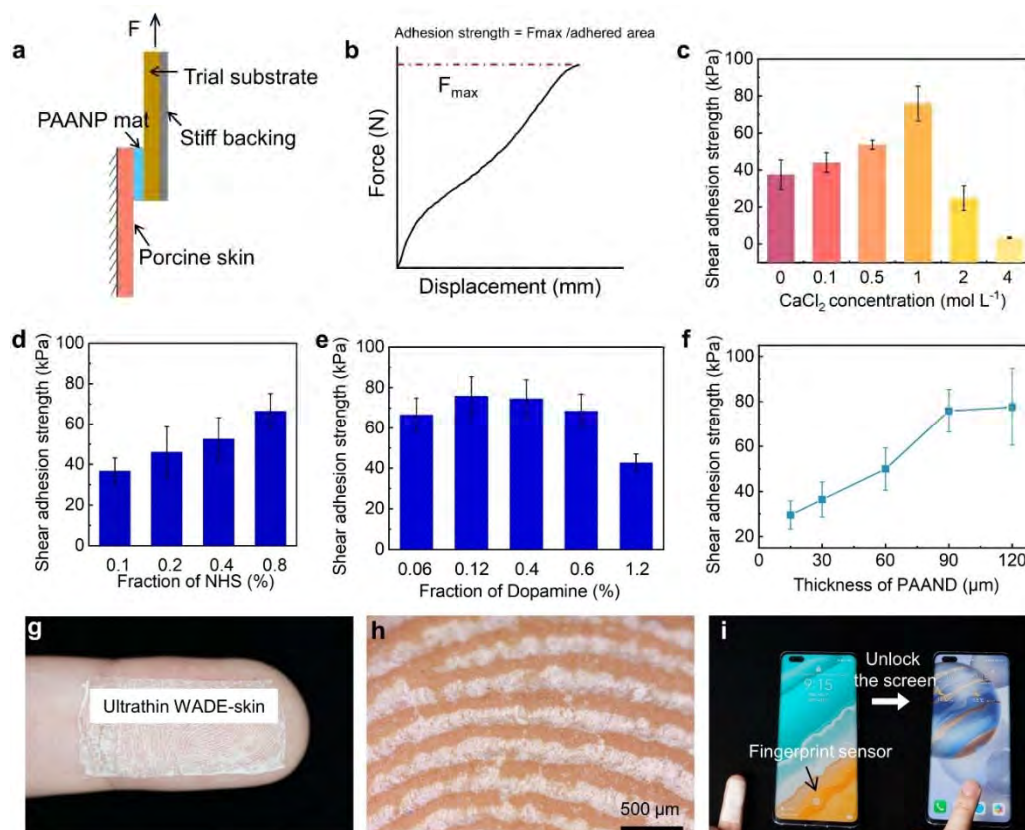


Figure 4.17. Adhesion performance of the PAAND fiber mats with different ionic crosslink densities, molar ratios of NHS and dopamine groups, and thicknesses. **a**, Schematic illustration of the lap shear test for the evaluation of adhesion performance. **b**, Adhesion force versus displacement for the lap shear test; the adhesion strength can be calculated by the peak force dividing the adhered area. **c**, Shear adhesion strengths of the PAAND fiber mats of the WADE-skin with different ionic crosslink densities with the assistance of different concentrations of CaCl_2 solutions. **d**, Shear adhesion strength of the PAAND fiber mats grafted with different amounts of NHS; the grafted dopamine groups were fixed at 0.06 %. **e**, Shear adhesion strength of the PAAND mats grafted with different amounts of dopamine; the grafted NHS groups were fixed at 0.8 %. **f**, Shear adhesion strength of the PAAND fiber mats with different thicknesses for the WADE-skin. **g-i**, Images showing that an ultrathin WADE-skin conformal adhered to the fingertip; **(g)** Digital image of the whole device and **(h)** optical microscope photograph showing the WADE-skin-attached fingerprints; **(i)** The finger attached with

the ultrathin WADE-skin was successfully detected by the fingerprint sensor.

A series of PAAND mats for the WADE-skin with different fractions of NHS and dopamine have been prepared. The shear adhesion strength increases with increasing the fraction of grafted NHS groups while the fraction of NHS could not be higher than 0.8% since the solubility of NHS (Figure 4.17d). The best fraction of grafted dopamine groups is in the 0.12% (Figure 4.17e). A series of PAAND mats with different thicknesses for the WADE-skin were also prepared. The WADE-skin with a 15- μm PAAND fiber mat can reach a considerable adhesion strength (~ 30 kPa) to the skin. As the thickness of PAAND mats exceeds 90 μm , the shear adhesion strength increased to a plateau of around 76 kPa (Figure 4.17f). This character makes the WADE-skin has the potential for the preparation of ultrathin electronics. For example, A ultrathin WADE-skin with a 15- μm SBS layer and a 15- μm PAAND layer has been produced. This ultrathin WADE-skin seamlessly conforms to the fingerprint on a fingertip and even allowed the fingerprint sensor to detect it (Figure 4.17g-i).

Tough wet adhesion performance and on-demand detachment

Because of the multiple interactions, the WADE-skin forms strong adhesion to the wet skin within seconds of contact (Figure 4.18a). The adhesion strength rapidly reaches ~ 25 kPa after contacting for 6 s and continues to rise to ~ 70 kPa until 3 h. Notably, the strong adhesion persists for over one week, showing the potential for long-term wearing applications (Figure 4.18b). Upon replacing the SBS fiber mat substrate with a thermoelastic polyurethane (TPU) fiber mat that has a higher breaking stress (Figure S19a), the adhesion strength of the WADE-skin increases to ~ 150 kPa, similar to that

of a commercial cyanoacrylate adhesive. (Figure 4.18c). In contrast, the adhesion strengths of the medical cloth tape and fibrin glue on a dry surface are only 18 kPa and 35 kPa, respectively (Figure 4.20a). Their adhesion strengths to wet skin dropped by 95.4% (to 840 Pa) and 98.8% (to 400 Pa), respectively (Figure 4.20a). They are easily detached from the porcine skin in the adhesion test (Figure 4.19).

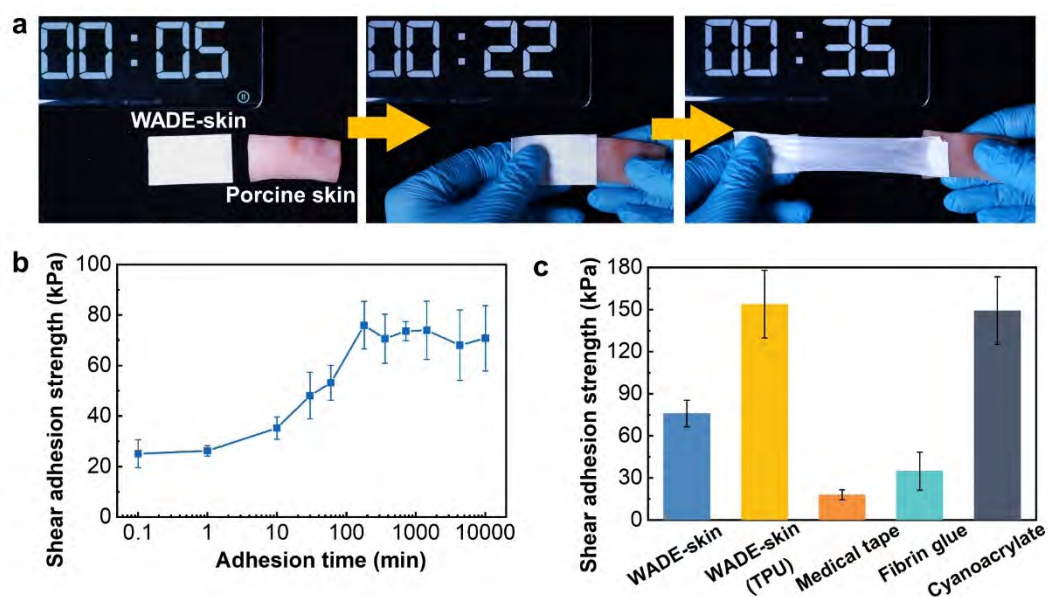


Figure 4.18. **a**, Digital images showing that a WADE-skin rapidly achieves tough adhesion to the wet porcine skin in ten seconds. **b**, Shear adhesion strength of WADE-skin to porcine skin with varying contact times. **c**, Comparison of adhesion performance of WADE-skin and various commercial adhesives.

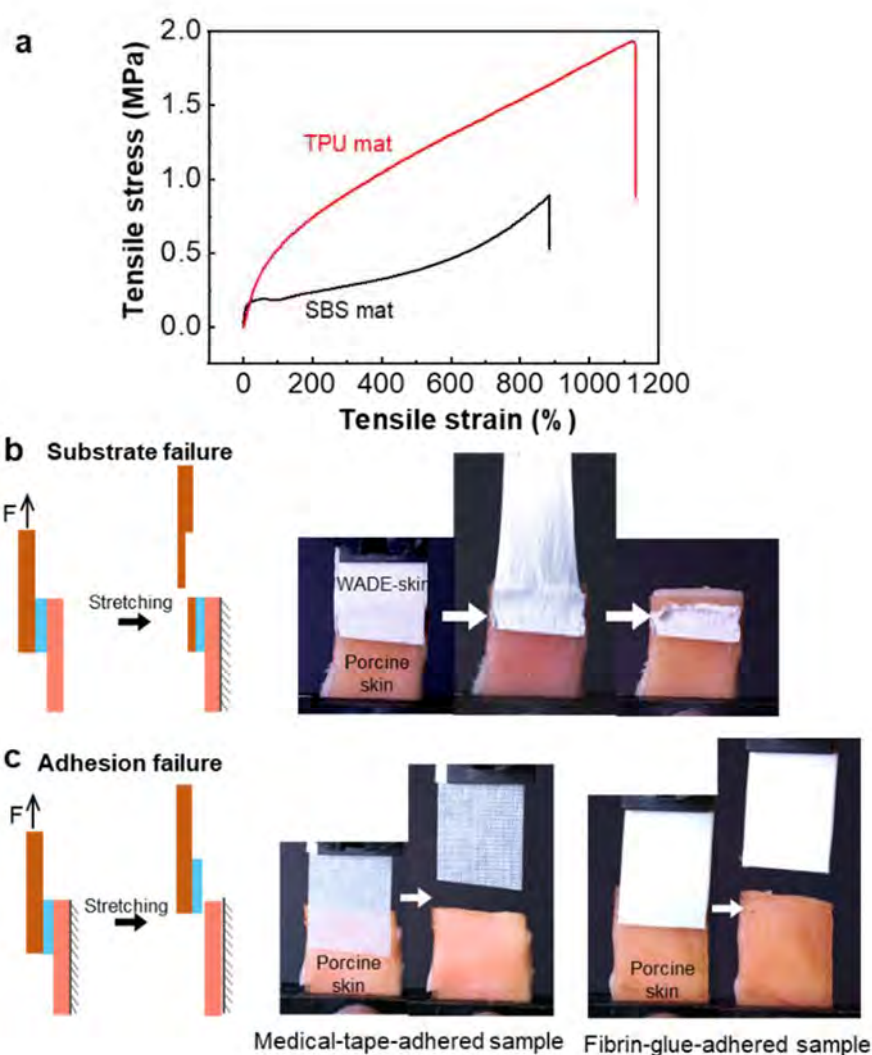


Figure 4.19. Failure types during lap shear test for adhesives. (a) Stress-strain curves of SBS fibre mat and TPU fibre mat. (b) Substrate delamination and fracture during the lap shear test for the WADE-skin adhering to the porcine skin. (c) Adhesion failure of the medical tape and fibrin glue for the adhesion to the porcine skin.

More importantly, after adhesion, the WADE-skin can continue to absorb secreted body fluids (*e.g.*, sweat) and evaporate them via the porous structure, which benefits the dynamic moisture balance and long-term adhesion stability during exercise. We mimic the sweating process by treating different adhered samples with artificial sweat (200 g m^{-2}) and then tested their adhesion strength over periods of time. For thin PU tape, cloth

tape, and impermeable WADE-skin (WADE-skin covered with an impermeable PET film), the adhesion strengths decrease by $\sim 40\%$ after adding the artificial sweat, and the adhesion does not recover. In contrast, the adhesion strength of the WADE-skin also loses by $\sim 40\%$ at the beginning but gradually recovers to its original value in 30 min (Figure 20b). This recovery process is highly reversible. Ten cycles of sweating-evaporation evaluations indicate the excellent stability of the WADE-skin against sweating conditions (Figure 20c).

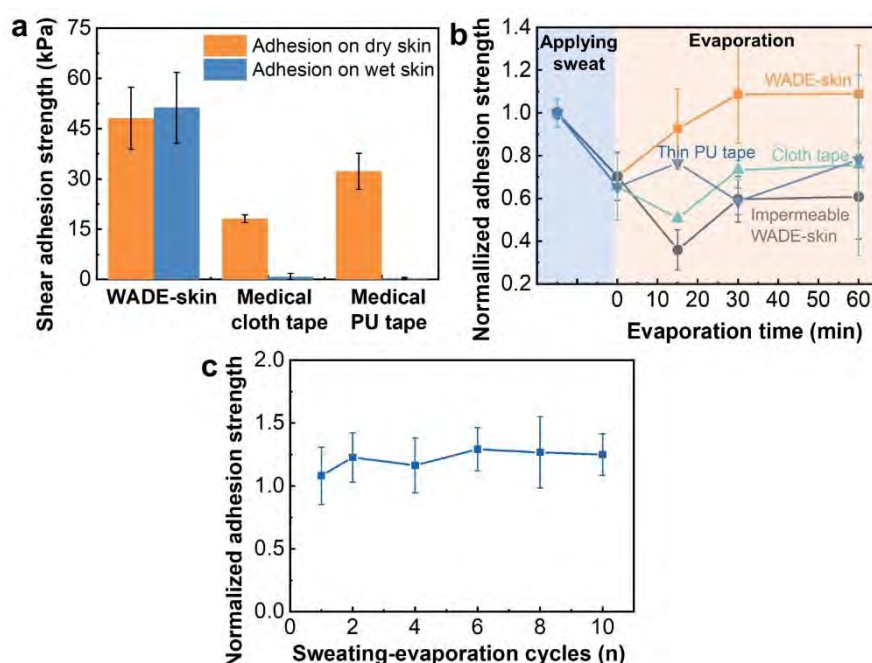


Figure 4.20. Wet-adhesive performance. **a**, Comparison of adhesive performance in dry skin and wet skin for the WADE-skin, medical cloth tape, and medical PU tape. **b**, Comparison of adhesion performance of these adhesives in artificial sweat treating (200 g m^{-2}) as well as the ability to recover the adhesion strength with evaporating the sweat. **c**, Cycles of sweating and evaporation versus the adhesion strength for WADE-skin.

However, the formed strong adhesion can be promptly destroyed by treating it with a biocompatible Na_2CO_3 solution. The triggering solution could break the intermolecular interactions between the skin and the WADE-skin and the ionic crosslinks of PAA

chains, exhibiting on-demand detachment of the WADE-skin from the skin. By introducing this detachment solution for ~ 1 min, the WADE-skin could be easily peeled off from the skin without any damage to both the skin and the device (Figure 4.21a). Na_2CO_3 breaks the intermolecular interactions between the skin and the WADE-skin, as well as the ionic crosslinks of PAA chains (Figure 4.21b), while SDBS can assist the penetration of the solution into the adhesion interface (Figure 4.21c-d). This method provides an on-demand and painless detachment of the epidermal device.

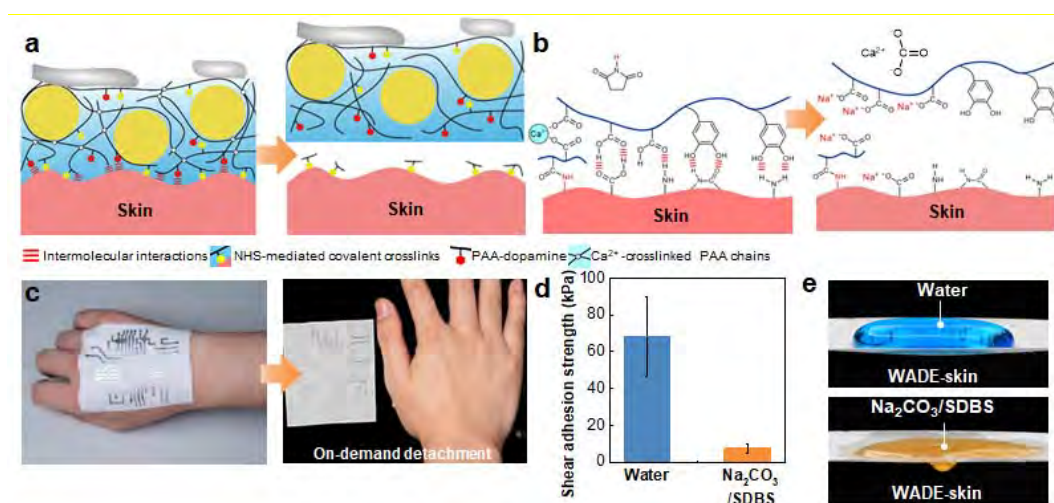


Figure 4.21. On-demand detachment of the WADE-skin from the human skin. **a-b**, Detachment mechanism of the WADE-skin. **c**, On-demand detachment of the WADE-skin from the human skin. **d**, Shear adhesion strength of the sample before and after the treating of Na_2CO_3 /SDBS solution.

The designed PAAND adhesive fiber mat could strongly adhere various permeable substrates to the porcine skin. The shear adhesion strength of WADE-skin (SBS) and WADE-skin (TPU) are ~ 70 kPa and ~ 150 kPa, respectively, while the PAAND could achieve the highest adhesion strength at ~ 200 kPa by adhering the PET fabrics to the porcine skin (Figure 4.22a-c). The differences in adhesion strengths are mainly due to the breaking stress of the substrates (Figure 4.22 h). When adhering tough PET fabrics and cotton to the porcine skin, the adhesion interfaces fail prior to the substrate failure,

indicating that the critical adhesion strength of the PAAND fibre mats is ~ 200 kPa. In contrast, when adhering soft WADE-skin (SBS) and WADE-skin (TPU) to the porcine skin, the substrates delaminate and break prior to the adhesion interface failure (Figure S14a). The breaking stress of WADE-skin (TPU) is ~ 1.93 MPa, higher than ~ 0.89 MPa for WADE-skin (SBS), leading to superior shear adhesion strength compared to WADE-skin (SBS). Whether the WADE-skin (SBS) or WADE-skin (TPU) offers considerable skin-adhesive performances which highly meet the need for stable and tough attachment of the devices to the human skin. However, SBS fibre mats are softer than TPU fibre mats, leading to a comfortable feeling during attachment to the skin.

The PAAND mats could also be used to bond various substrates themselves together. Both impermeable (*i.e.*, PDMS, glass slide, polyimide (PI) film, and polycarbonate (PC) film) and permeable substrates (*i.e.*, cotton, SBS mat, TPU mat, glass fabrics, and PET fabrics) could be strongly adhered by the PAAND mats (Figure 4.22d-g). For rigid substrates, such as glass slide, PI film, PC film, cotton, and PET fabrics, the adhesion strength even reach 600 kPa. For flexible substrates, the substrates themselves failed prior to detachment, proving the tough adhesion of PAAND mats. Such a broad adhesive spectrum makes the PAAND fiber mat a universal but high-performance adhesive for a wide range of application scenarios.

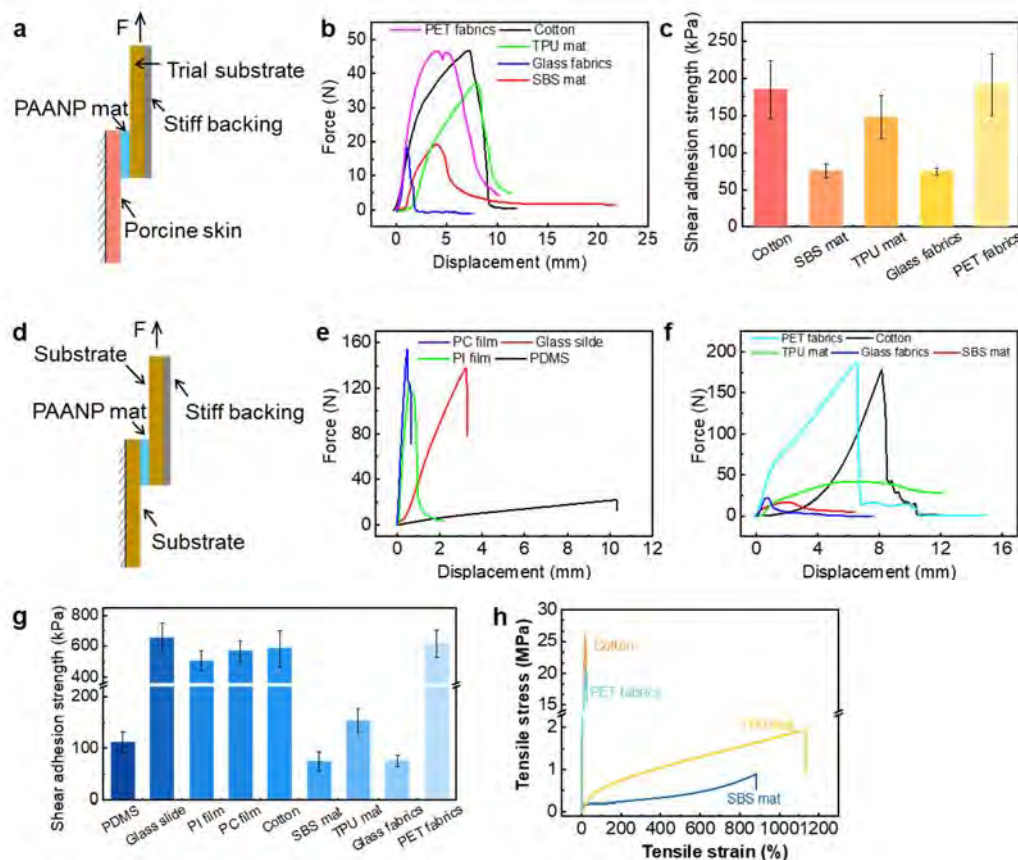


Figure 4.22. Strong adhesion of PAAND fibrous mats toward various substrates. **a**, Schematic illustration of the lap shear test for the evaluation of adhesion performance between substrates and the porcine skin. **b-c**, Adhesion force versus displacement curve (**b**) and the calculated shear adhesion strength (**c**) for various permeable substrates adhered to the porcine skin by PAAND mats. **d**, Schematic illustration of the lap shear test for the evaluation of the adhesion performance of PAAND mats for various substrates. **e-g**, Adhesion force versus displacement curve of the adhesion tests for various dense-film substrates (**e**) and permeable substrates (**f**) adhered by PAAND mats as well as the calculated shear adhesion strengths (**g**) for these substrates. (**h**) Strain-stress curves of permeable substrates.

4.3.4 Wet-adaptive Electrocardiogram (ECG) Signal Monitoring

There has been a strong demand for real-time and long-term ECG monitoring of living bodies in wet environments such as those during sports (*e.g.*, running, swimming) and during work (*e.g.*, underwater operation)^[191-193]. Based on the outstanding wet adaptivity, the WADE-skin was employed to capture ECG signals under various wet conditions. The EGaIn pattern is printed on the PAAND side as ECG electrode for direct contact with the skin surface, while the upper SBS mat serves as the waterproof encapsulation layer (Figure 4.23a-b). The fabricated WADE-skin possesses much lower impedance than commercial Ag/AgCl gel electrodes in the ECG frequency range (1-100Hz), *e.g.*, 22.1 k Ω versus 30.6 k Ω at 10 Hz (Figure 4.23c).

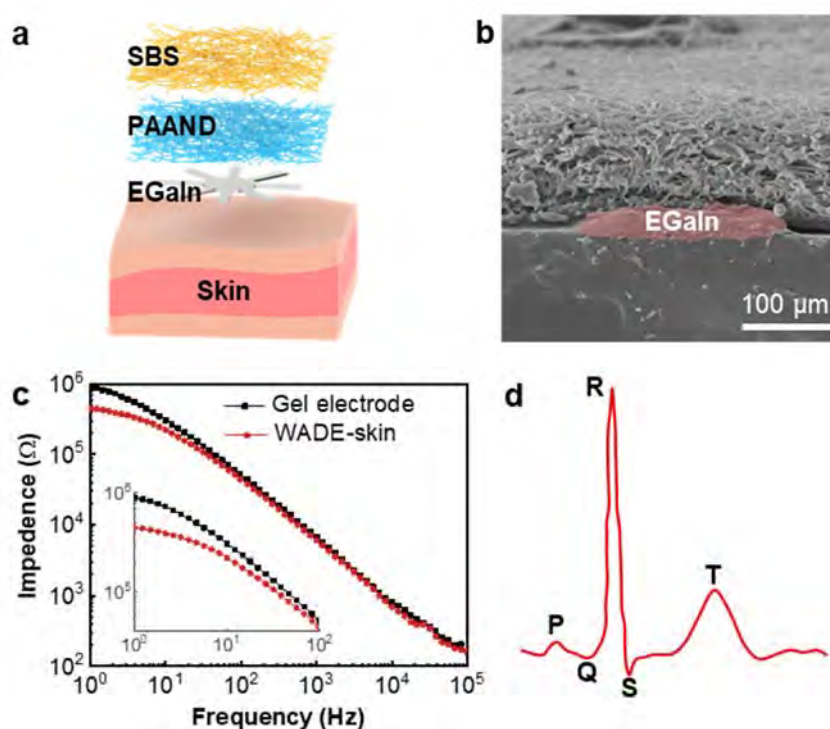


Figure 4.23. WADE-skin as ECG electrode. **a**, Schematic layout of WADE-skin as ECG electrode. **b**, Cross-sectional SEM image of a WADE-skin adhered to PDMS substrate. **c**, Skin impedance-frequency curve of WADE-skin and commercial gel electrode. **d**, One cardiac cycle with P, QRS, and T waves captured by WADE-skin.

The ECG signals captured by WADE-skin after attaching to the human skin show distinct PQRST waveforms (Figure 4.23d). This WADE-skin demonstrates high signal quality at normal state (*i.e.*, static and adhered to the dry skin), which is comparable with commercial Ag/AgCl gel electrode (Figure 4.24a). However, at wet skin, the gel electrode fails to form strong adhesion, leading to partial detachment from the skin and unstable detection of ECG signals, while the WADE-skin could stably detect the ECG signals since the good wet-adhesive property (Figure 4.24b-c). For evaluating the stability of electrodes against sweating, continuous running at an average speed of 6 km/h was carried out for more than 1 h to generate a heavy sweating scenario. While the commercial gel electrode detaches from the sweating skin due to its poor wet adhesion, the WADE-skin pertains stable adhesion and achieves continuous capturing of the ECG signals (Figure 4.24d). For the concern referring that the sweat produced during physical activity could impact the accuracy of measurements, the results also indicate that the sweat will not affect the accuracy of the ECG measurements. The skin moisture (for example, perspiration) could fill the air gaps at the skin-electrode interface and achieve low impedance for the dry-contact electrodes.^[194-195] Therefore, the sweat produced during physical activity will not cause negative effects on the recording of ECG signals as long as the stable adhesion of the dry electrodes.

The WADE-skin also achieves a stable ECG recording and is comfortable over a continuous attaching on the skin over a 7-day period of daily activities (Figure 4.24e and Figure 4.25). When coupled with a Bluetooth device, the WADE-skin can also be used to record the ECG signals when swimming (Figure 4.24f).

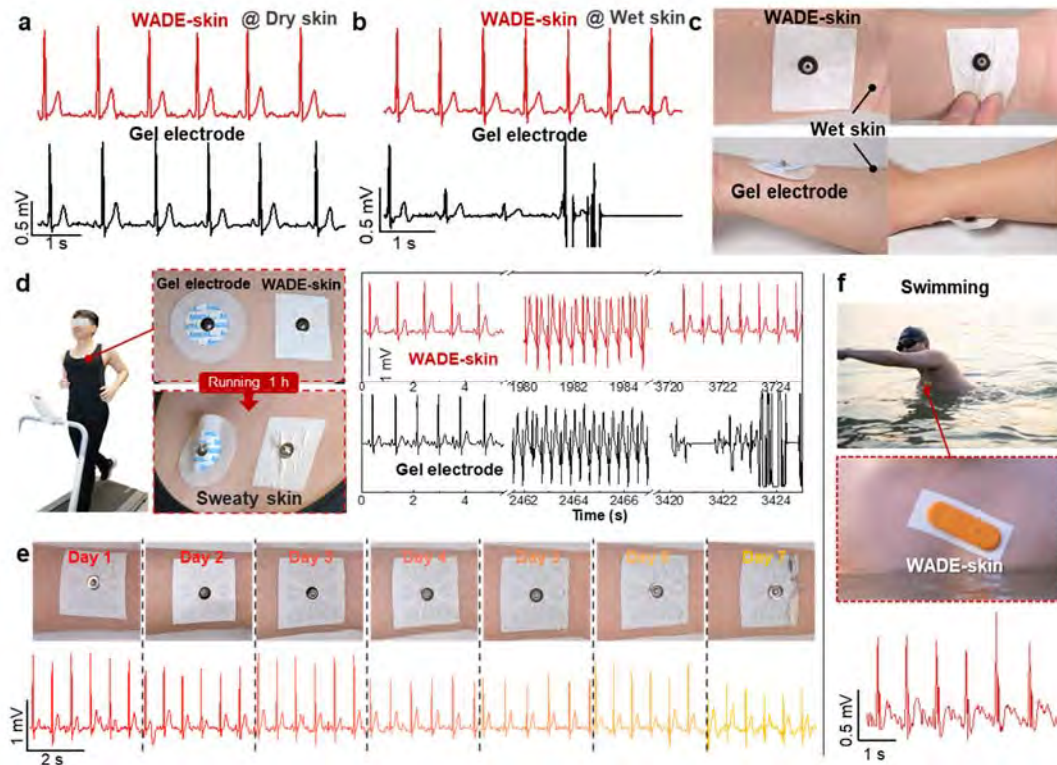


Figure 4.24. ECG monitoring of the WADE-skin. **a**, ECG monitoring at dry skin. **b-c**, ECG signals (**b**) and digital images (**c**) of the WADE-skin and gel electrode adhered to the wet human skin. **d**, Digital images and ECG signals of a volunteer attached to the WADE-skin and gel electrode ran 1 h. **e**, One-week ECG detection by the WADE-skin. **f**, ECG monitoring during swimming in the sea by the WADE-skin connected to a wireless ECG device.

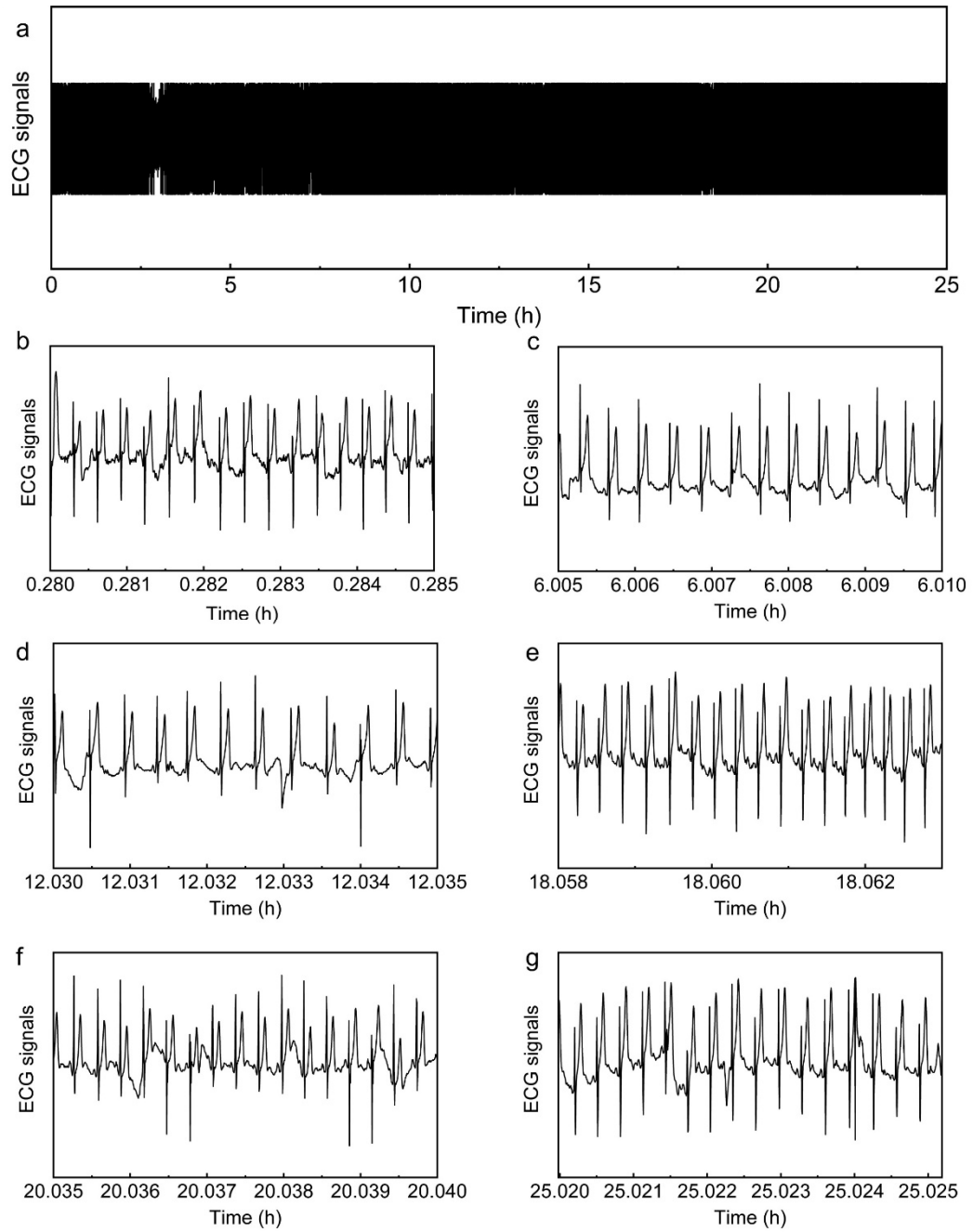


Figure 4.25. Continuous ECG monitoring for 25 hours by WADE-skin. **a.** ECG signals of a 25-h detection by the WADE-skin. **b-g.** Extracted ECG signals in 0 h (**b**), 6 h (**c**), 12 h (**d**), 18 h (**e**), 20 h (**f**), and 25 h (**g**) from the 25-h detection.

4.3.5 Strain Sensor Arrays Using WADE-skin for Human-machine Interactions

The superelastic, conformal, and permeable WADE-skin is highly suitable for applications associated with human-machine interactions. As a proof of concept, strain sensor arrays of WADE-skin have been fabricated, which offers intimate adhesion to the back of the human palm to simultaneously record the finger bending angles for human-machine interactions. To fabricate a strain sensor array, the EGaln paths are first printed on the SBS side of the WADE-skin, as shown in Figure 4.26. Subsequently, a flexible flat cable is used to connect the strain sensor array and the outer printed circuit boards(PCB), as shown in Figure 4.27. Another layer of the SBS fiber mat is then electrospinning to the top of the EGaln patterns serving as an encapsulation layer. The encapsulated strain sensor array will be cut into palm shape for the adhesion to the back of human palm.

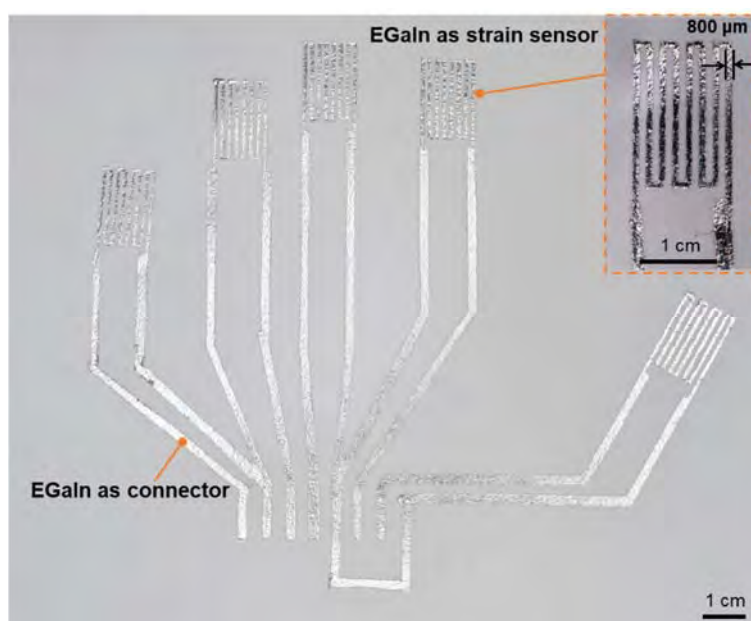


Figure 4.26. Digital image of the EGaln paths for the strain sensor array of the WADE-skin.

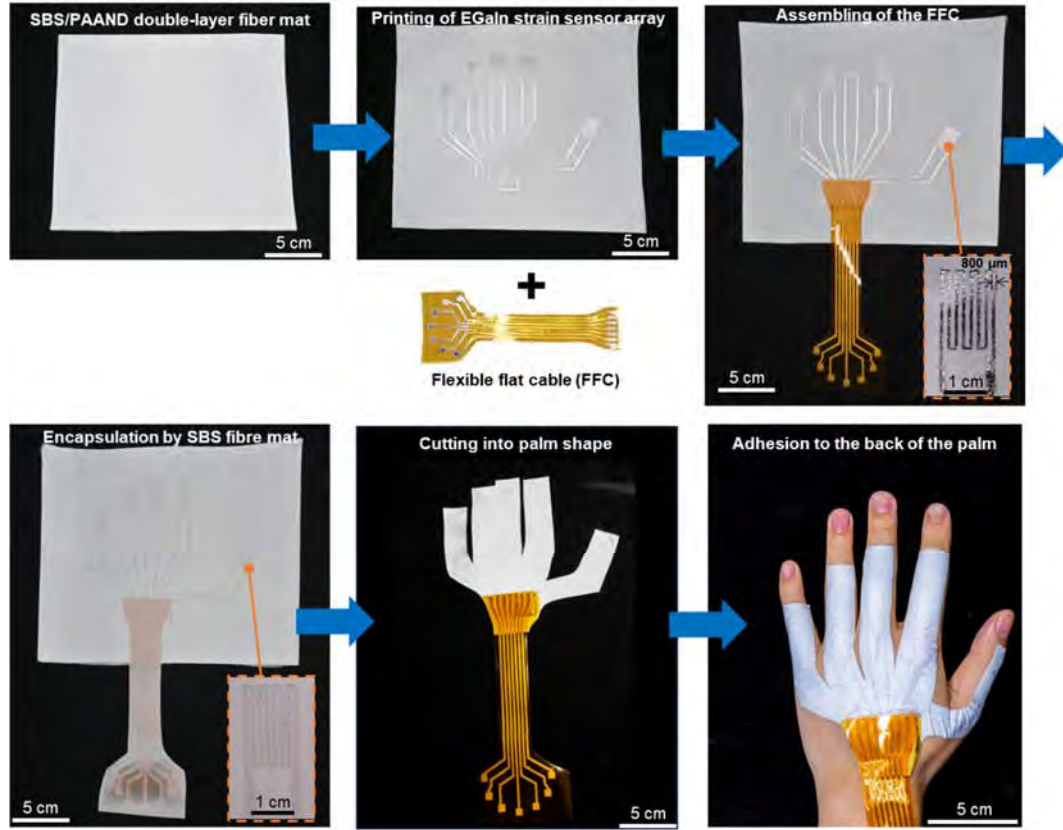


Figure 4.27. Digital images showing the fabrication process for the strain sensor array of the WADE-skin and the adhesion of the strain sensor array to the back of the human palm.

This strain sensor array could achieve tough and conformal adhesion to the hand palm (Figure 4.28a). Individual strain sensor presents an increase of resistance within the stretching strain up to 400% (Figure 4.28b). The gauge factor which represents the sensitivity of strain sensors to strain has been also investigated based on the curve of resistance change versus stretching strain. The gauge factor is defined as the ratio of the fractional change in electrical resistance to the fractional change in strain.

The gauge factor G can be calculated by equation 1:

$$G = \Delta R / R_0 \epsilon \quad (1)$$

where ΔR is the sensor change of resistance, R_0 is initial resistance and ϵ is the

engineering strain.

The electrical resistance of EGaIn paths could be calculated by the definition (Pouille's law):

$$R = \rho L / A \quad (2)$$

where ρ is the resistivity of the EGaIn, A the cross-sectional area of the EGaIn path, and L is the length of the EGaIn path.

The electrical resistance of EGaIn paths with engineering strains (R_x) could be represented by equation 3:

$$R_x = \rho L_x / A_x \quad (3)$$

$$L_x = L_0(1 + \epsilon) \quad (4)$$

where L_x is the length and A_x is the cross-sectional area of the EGaIn paths under stretching.

Based on the definition of Poisson's ratio:

$$A_x = A_0(1 - \nu\epsilon)^2 \quad (5)$$

where ν is the Poisson's ratio of the material.

Therefore:

$$\Delta R / R_0 = \frac{\rho(L_0(1 + \epsilon)) / A_0(1 - \nu\epsilon)^2}{R_0} - 1 \quad (6)$$

$$\Delta R / R_0 = \frac{1 + \epsilon}{(1 - \nu\epsilon)^2} - 1 \quad (7)$$

Equation 7 was used to fit the experimental data (Figure 4.28b). From the fit results, the Poisson's ratio of the material is 0.09895 and the value of the coefficient of determination is 0.99543. The gauge factors continuously increase following the increase of engineering strains. However, for simplification, the strain ranges of the strain sensor were divided into three segments: 0-150%, 150-300%, and 300-400%. The gauge factors are the average value for each segment and it for the strain range of

0-150% is 1.74, for 150-300% is 3.22, and for 300-400% is 4.39, with the coefficient of determinations at 0.9887, 0.9963, and 0.9984, respectively.

The electrical performance of WADE-skin strain sensor arrays is extremely stable, showing negligible resistance change over 5,000 stretching cycles at 100% strain (Figure 4.28c). This sensitive and highly reproducible resistance change allows precise recording of the bending angles of each finger when the WADE-skin adheres to the back of the palm (Figure 4.28d).

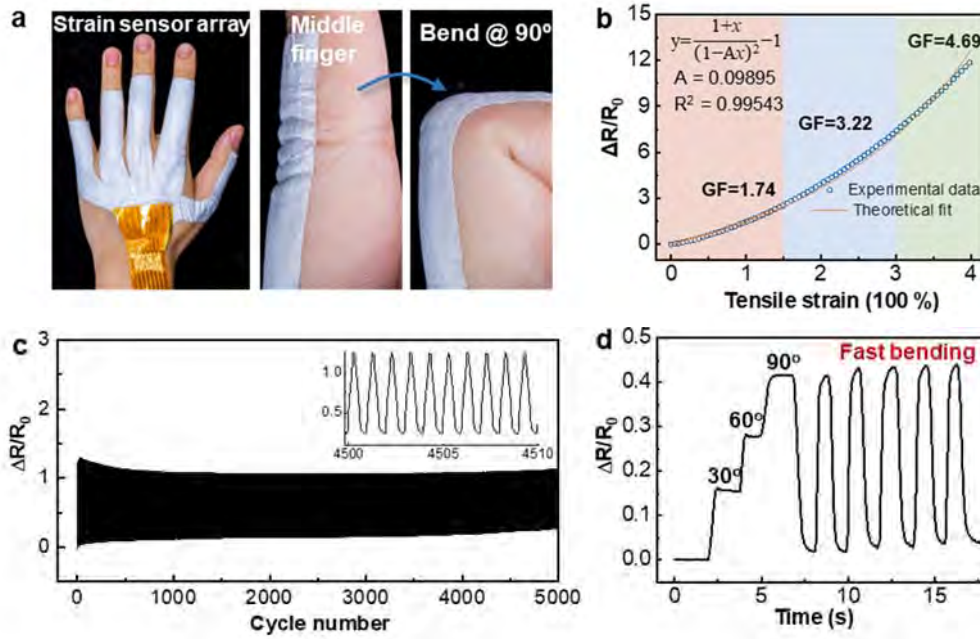


Figure 4.28. Sensing performance of the WADE-skin strain sensor array enabling human-machine interactions. **a**, Digital images of a strain sensor array conformally adhered to the human palm. **b**, Resistance change versus the tensile strain for WADE-skin. **c**, Resistance change under 5000 continuously stretching-releasing cycles at the strain of 100% for WADE-skin. **d**, Resistance change of a WADE-skin adhered to an index finger under different finger bending angles or fast bending-straightening cycles.

Based on such a highly sensitive strain sensor array, the gestures either carried out in the air or under the water can be easily recognized (Figure 4.29a).

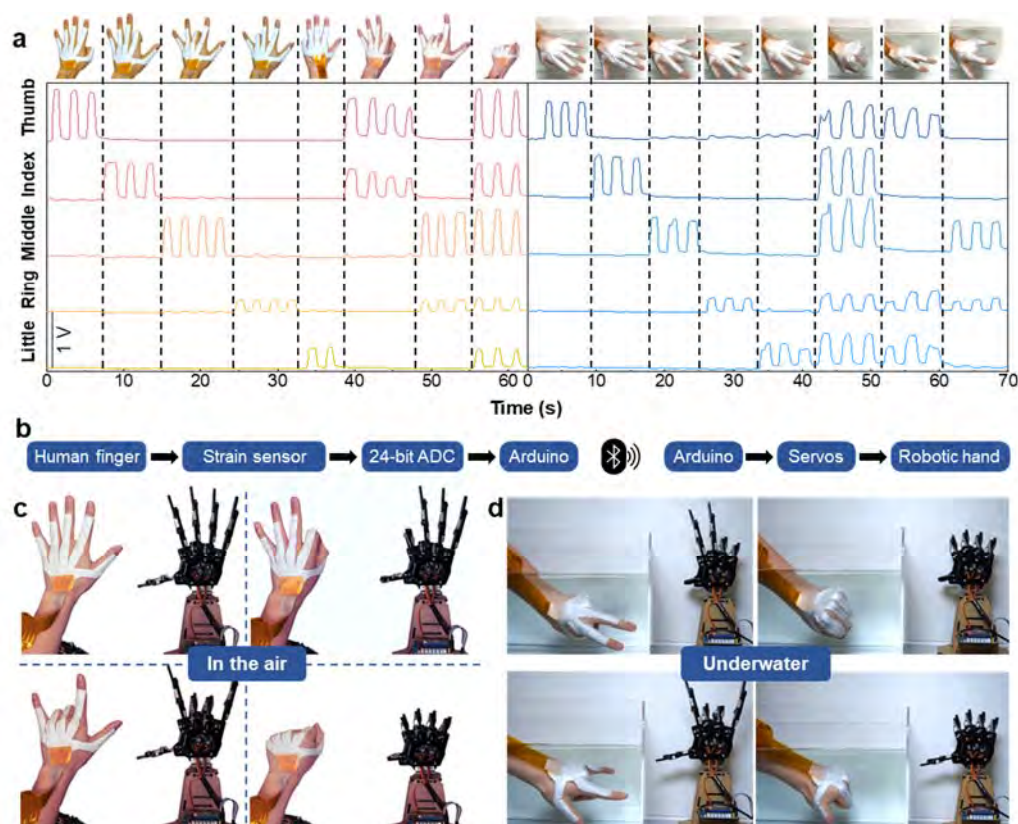


Figure 4.29. WADE-skin strain sensor array enabling human-machine interactions. **a**, Digital data of WADE-skin-based strain sensor array in performing different gestures in the air and underwater, the upper images showing the related hand gestures. **b**, Integration of the robot control system based on WADE-skin. **c-d**, Digital images for demonstrating the real-time robot control in the air (**c**) or underwater (**d**).

The WADE-skin strain sensor arrays were applied as finger-bending sensors to manipulate a robotic hand. We built Wheatstone bridges and 24-bit analog-to-digital converter (ADC) chips to convert electrical signals to digital data. A microcontroller unit (MCU, Arduino Nano) was employed to process the digital data and send commands to the robotic hand wirelessly via a Bluetooth module (Figure 4.29b). Five

bending sensors adhered onto five human fingers could generate stable and accurate digital signals independently either in the air or underwater, enabling the real-time control of robotic fingers by performing different gestures. The robotic hand follows the movements of human fingers by doing different gestures, demonstrating the potential application for human-machine interactions underwater (Figure 4.29c-d).

Remote control of a variety of robotic movements was also performed using the WADE-skin and the VR technology. The VR-integrated WADE-skin system consists of three parts: (i) strain sensor arrays adhered to fingers to detect finger bending degrees and to deliver commands to an 18-DOF (degree of freedom) humanoid robot through Bluetooth; (ii) a camera mounted on the 18-DOF humanoid robot to return the robot vision to a VR headset through wireless fidelity (Wi-Fi); (iii) ECG electrodes adhered to human skin to monitor vital health signals (Figure 4.30a-b).

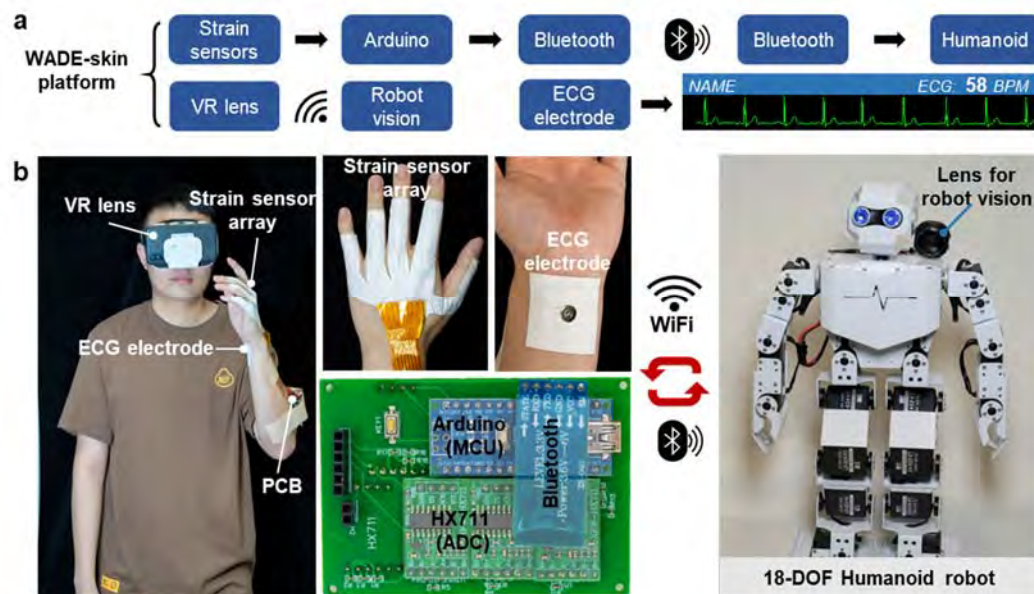


Figure 4.30. WADE-skin platform for Virtual reality (VR)-mediated human-machine interactions. **a**, System integration of WADE-skin platform, including strain sensor array adhered to human palm to wirelessly control a humanoid robot, VR lens to instantaneously receive the robot vision, and ECG electrode to monitor healthy signals.

b, Digital images demonstrating the WADE-skin platform; a volunteer adhered with a bending sensor array and an ECG electrode and wore a VR lens and a printed circuit board (PCB) was used for processing and transmitting the signals; an 18-degree of freedom(DOF) humanoid robot was wirelessly controlled by this system and returned robot version through wireless fidelity (Wi-Fi).

The strain sensors adhered to the thumb finger and index finger were assigned to control the robot to go forward or turn right, respectively. Wireless control of the robot walking and turning in a preset way (yellow line in Figure 4.31a) was achieved by real-time VR view. The ECG electrode also detected the ECG signals simultaneously and the average heartbeat rate was 68 per minute (Figure 4.31a). The strain sensors adhered to the middle finger and ring finger were then assigned to control the robot by grabbing the hand or raising the arm, respectively. The robot was manipulated to grab a swab and raise it approaching a person, performing a contactless throat swab test for the Covid-19 virus (Figure 4.31b). Furthermore, based on the excellent wet adhesion and water repellency of the WADE-skin, underwater health monitoring and human-machine interactions have been realized (Figure 4.31c-d). Therefore, the combination of the WADE-skin platform with VR technology has potential applications in underwater work (such as underwater fixation, transfer, and mineral exploration) with the safety support of vital signal monitoring.

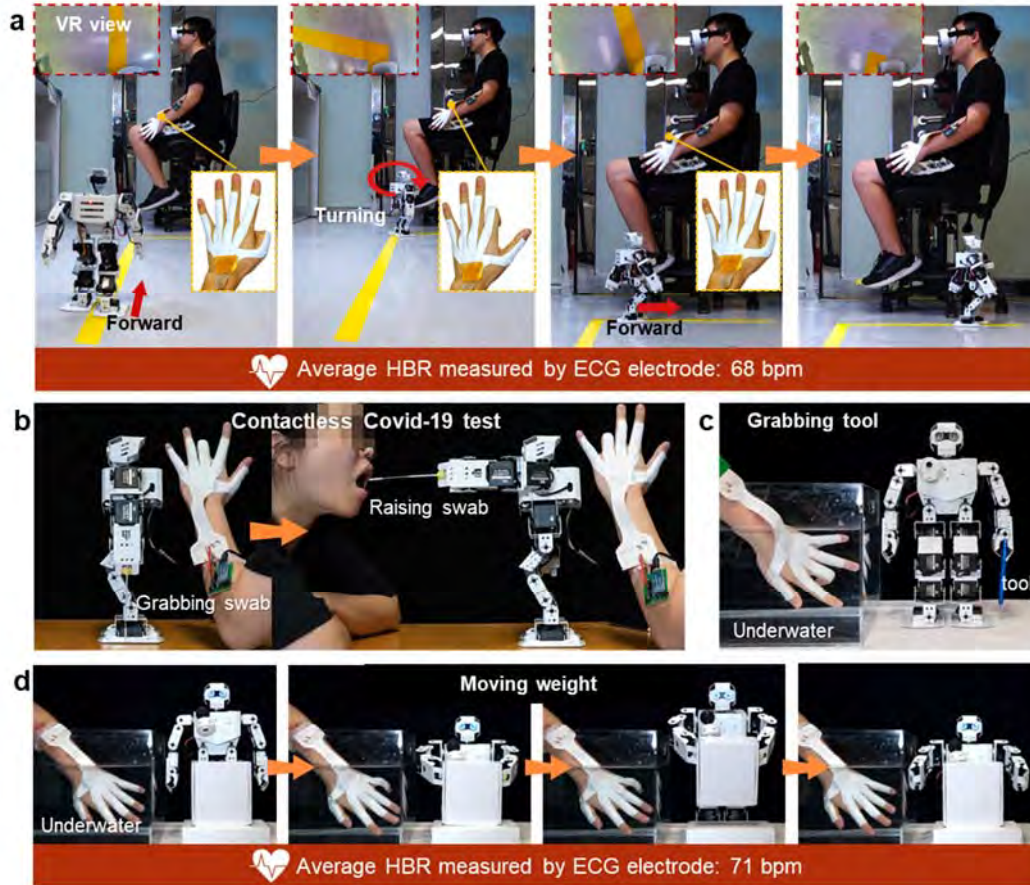


Figure 4.31. Virtual reality (VR)-mediated human-machine interactions. **a**, Digital images showing that a volunteer wirelessly and remotely control a humanoid robot to walk along the fixed route (yellow line) with the assistance of VR view (top inserted images) and the average heartbeat rate (HBR) was also recorded. **b**, Digital images showing the contactless nucleic acid test by controlling the robot to grab the swab and raise the swab. **c-d**, Digital images showing underwater control of the humanoid robot for grabbing tools (**c**) and moving weight (**d**).

4.4 Conclusions

In summary, WADE-skin is a type of wet-adhesive, permeable, and waterproof electronic skin that is fabricated by seamless stacking of LM electrode patterns on multi-layer fibrous fiber mats. WADE-skin offers outstanding adaptability to various wet environments that often occur to wearers. It possesses strong wet adhesion to skins with the fibrous adhesive layer, remarkable air and moisture permeability through the porous fibrous structure, and waterproof property enabled by the next-to-air water-repellent fibrous mat. In comparison to other state-of-the-art functional adhesives and skin-adhesive electronics (Table 4.1), WADE-skin is the only material that simultaneously achieves permeability, waterproofness, stretchability, biocompatibility, and wet adhesion. Using WADE-skin as an electronic platform allows long-term recording of physiological activities such as ECG signals over days, and VR-mediated remote control of robots even under wet or underwater conditions. We envision that this wet-adaptive strategy will bring an effective and universal solution to the development of wet-adaptive on-skin electronics with a more comfortable and user-friendly wearing experience.

Table 4.1. Comparison of wet adhesion, permeability, water repellent property for epidermal electronics.

Adhesive materials	Adhesion performance	Wet adhesion	Permeability	Water repellent	Ref.
PVA nanofibers	15 mN cm ⁻¹	Yes	Permeable	N.A.	¹
PSA electrospun mat	142 J m ⁻²	N.A.	1748 g m ⁻² day ⁻¹ (moisture)	Yes	²
PEG-blended PDMS	30 kPa 0.9 N cm ⁻¹	Yes	N.A.	N.A.	³
PVA/PAA-NHS hydrogel	60kPa 270 J m ⁻²	Wet tissue	N.A.	N.A.	⁴
Gelatin/Hyaluronic acid electrospun mat	1.94 kPa	N.A.	21.94 ml s ⁻¹ cm ⁻¹ (air)	N.A.	⁵
Hydrophobic group- incorporated hydrogel	23 kPa	Underwater adhesion	N.A.	N.A.	⁶
Supramolecular-polymer dry patch	1.8 N cm ⁻¹	Immersion underwater 4 h	N.A.	N.A.	⁷
PDMS/pDAM	~ 2 kPa	Immersion underwater 1 h	N.A.	Yes	⁸
Breathable cellulose substrate	27 kPa	Yes	21.3 g m ⁻² h ⁻¹ (moisture)	N.A.	⁹
This work	150 kPa	Wet skin/ Sweating/ Underwater	852 g m ⁻² day ⁻¹ (moisture)	Excellent	

CHAPTER 5: ON-DEMAND “NANOFIBERS-TO-HYDROGEL” FORMATION OF ULTRATHIN LIQUID-METAL HYDROGEL TATTOO FOR CONFORMABLE AND LOW-IMPEDANCE SKIN ELECTRONICS

Epidermal electrodes, the electrodes adhered to the human skin for the detection of biophysiological signals, are great of importance for health monitoring, gesture recognition, and human-machine interactions. However, fabrication of the electrodes with stretchability, permeability, conformal adhesiveness, and low impedance is still a challenge. In this chapter, a strategy called “nanofibers-to-hydrogel” to fabricate ultrathin liquid metal hydrogel tattoos (LMHT) was investigated. The liquid-metal PVA fiber mats are easily handled and user-friendly and could instantly absorb saline water thus forming hydrogel tattoos at the surface of the skin. The formed LMHT is stretchable and permeable and could conformally adhere to the skin. This LMHT demonstrated a low skin impedance compared to the commercial Ag/AgCl gel electrode. The LMHT were investigated as biophysiological electrode to detect ECG signals for health monitoring and assembled into a 6-channel EMG sensor array for gesture recognition assisted by machine learning.

5.1 Introduction

Skin electronics, a type of soft electronics that could intimately attach to the human skin, have been developed for long-term, continuous, and non-invasive health monitoring and human-machine interactions^[185-186, 194]. Tremendous researches dedicate to investigating state-of-the-art skin electronics with new and outstanding materials, functions, mechanisms, and systems to put the skin electronics in a more intelligent, wireless, miniaturized, and user-friendly way^[3, 10, 68]. Among that, epidermal electrodes are an essential part of the detection of biophysiological signals, for example,

electrocardiogram (ECG), electrooculogram (EOG), electromyography (EMG), and electroencephalogram (EEG) for monitoring health conditions or stimulating the skin surface^[145, 192, 194]. The captured biophysiological signals could be employed for health care, human motion detection, and human-machine interactions.

In all conditions, high-quality physiological signals are preferred for analysis and processing by professionals and machines. Therefore, the skin-electrode interface is strongly required to minimize the noise and crosstalk and amplify the signal levels. However, the interface problem between the electrodes and the skin is a significant challenge^[194]. Due to the high Young's modulus and low interfacial adhesion of the electrodes, there will be air gaps and uncontacted area between the electrodes and the skin, resulting in high contact impedance, and low signal-to-noise ratio. Although increasing the interfacial moisture of the skin could fill the air gaps at the skin-electrode interface^[195], in low moisture conditions, the surface impedance could be as high as over several billion Ω . This limitation could be solved by enhancing the intimate conformal contact of the skin-electrode interface. The contribution of conformal contact to the skin impedance could be represented by equation 5.1^[36]:

$$|Z_c| = \frac{\rho d}{A\sqrt{1+(\omega\rho\epsilon)^2}} \dots\dots\dots(5.1)$$

where ρ denotes the electrical resistivity of the skin, d denotes the distance between the electrodes, A denotes the contact area of the dry electrodes, ω is the signals source frequency, and ϵ is the dielectric constant of the skin. The higher conformal contact area, the lower skin impedance is. The conformal contact for dry electrodes could be approached by decreasing the device thickness. Jae-Woong *et. al.* reported that by decreasing the thickness from 500 μm to below 25 μm , it could reach high conformability to the skin surface and, hence, pertains lower skin impedance and high signal fidelity^[36]. Therefore, enhancing the adhesion, conformal contact, and electrode

conductivity and reducing the device thickness are an efficient way to reduce the skin impedance and bring high-quality biophysiological signals. However, the on-demand fabrication of ultrathin conductive hydrogel for high-performance biophysiological electrodes is still challenging.

Here, a new strategy called “nanofibers-to-hydrogel” to fabricate ultrathin liquid metal hydrogel electrode was investigated. Ultrathin liquid-metal PVA fiber mats were first fabricated and then heated to physically crosslink the PVA molecules. Crosslinked liquid-metal PVA fiber mats could instantly absorb saline water and thus form hydrogel tattoos on the skin. The thickness of liquid-metal PVA fiber mats could be easily turned by varying the collection time during electrospinning. The liquid-metal PVA fiber mats are easily handled and thus facilitate the convenient usage of the LMHT for the on-skin scenario. The formed LMHT is stretchable (breaking strain > 50 %) and permeable (moisture permeability $569 \text{ g m}^{-2} \text{ day}^{-1}$) and could conformally adhere to the skin with interfacial toughness over 44 J m^{-2} .

5.2 Experiment

5.2.1 Fabrication of Liquid-metal and Heat-crosslinked PVA Nanofibrous Mat.

10 wt% PVA solution was prepared by dissolving the PVA powders in the DI water with heating to 90 °C. The PVA solution was injected into a syringe tube and was pumped out to the needle at a speed of 1 ml h^{-1} . A high voltage at 16 kV was applied between the needle tip and the collector where the distance between the needle tip and the collector was 15 cm. A silicone-oil-coated paper was used as the collector. The collection time was varied from 10 min to 10 h for controlling the thickness of the PVA mat. The PVA nanofibrous mat was placed in a vacuum oven for 1 h with the chamber temperature varied from 60 °C to 150 °C for crosslinking of the PVA polymeric chains.

Afterward, liquid metal was printed to the surface of the as-prepared crosslinked PVA nanofibrous mat through a patterned stencil.

5.2.2 On-demand Fabrication of Hydrogels

NaCl solutions with concentrations from 0% to 5% were first prepared. The skin surfaces were quickly wetted by the fast spraying of the NaCl solution and a piece of the prepared liquid-metal PVA nanofibrous mat was attached to the wet skin. After full absorption of the saline water, the PVA nanofibrous mat turned into liquid-metal-coated ionically conductive PVA hydrogel.

5.2.3 Fabrication of Electrophysiological Electrodes

The medical tape was punched with a 1-cm round hole. A piece of liquid-metal PVA nanofibrous mat was cut to disc shape with a diameter of 1.5 cm was attached to the next-to-skin side of the medical tape and the liquid-metal conductive pathway was printed to the air side of the medical tape to connect the liquid-metal PVA nanofibrous mat and the outer rigid metals wires. An additional PU tape is further attached to the surface of the medical tape for encapsulating the electrodes and conductive pathways. For recording ECG signals, 3 electrodes adhered to the left arm, right arm, and left leg, respectively. For recording six-channel EMG signals, 18 electrodes were printed on the medical tape.

5.2.4 Machine Learning for the EMG Signals

The machine learning process was executed using MATLAB 2023 software on a computer equipped with an Inter Core i7 CPU, NVIDIA GTX 1080 GPU, and 16 GB of RAM. The artificial neural network (ANN) model consists of an input layer, multiple

hidden layers with adjustable neuron numbers, and an output layer with 19 neurons corresponding to the 19 hand gesture categories. The network employs the backpropagation (BP) algorithm for error minimization, with weight updates governed by the ADAM optimization method:

$$W_{(t+1)} = \frac{W_{(t)} - \eta \times m_{(t)}}{\varepsilon + \sqrt{V_{(t)}}} \dots\dots\dots 5.1$$

Where $W(t)$ represents the weight at time step t , η is the learning rate, $m(t)$ and $v(t)$ are the first and second moments of the gradients, and ε is a small constant to prevent division by zero.

The activation function used in the hidden layers is the Rectified Linear Unit (ReLU), defined as $f(x) = \max(0, x)$, providing a non-linear transformation to the input data. The output layer employs the softmax function for multi-class classification, converting the output scores into probabilities:

$$Softmax(Z_i) = \frac{\exp(Z_i)}{\sum_j \exp(Z_j)} \dots\dots\dots 5.2$$

Our ANN model's performance is evaluated using the cross-entropy loss function, which measures the difference between the true label distribution and the predicted probability distribution:

$$Loss = - \sum_{i=1}^{size} y_i * \log y_i \dots\dots\dots 5.3$$

15 sets of EMG signals of each gesture were utilized for the training process with a training duration time of 1 min. 5 sets of EMG signals were used to evaluate the recognition accuracy of the model.

5.3 Results and Discussion

5.3.1 On-demand Formation of Ultrathin Liquid-metal Hydrogel Tattoo (LMHT)

To offer a fast and on-demand formation of conformable and low-impedance LMHT, we developed a strategy namely water-triggered “nanofibers-to-hydrogel” transformation. The formation process is shown in Figure 5.1a. The PVA nanofiber mat is firstly fabricated via electrospinning and then heated to 100°C with 1 h for crosslinking. Among that, the interchain hydroxyl groups of the PAA chains dehydrate and covalently couple to form ether groups (Figure 5.1b-c). The liquid-metal PVA nanofiber mat is obtained by seamlessly stacking liquid metals to the surface of crosslinked PVA nanofiber mat. Once the ultrathin LMHT is demanded, the skin surface is quickly sprayed with saline water and then attached with a piece of liquid-metal PVA nanofiber mat. The ultrathin LMHT will be instantly formed in several seconds (~5s) by rapid absorption of the saline water and conformally adhere to the skin surface. Notably, the ultrathin liquid metal hydrogel tattoo pertains ultra-conformability in which this tattoo embeds the skin hair and conforms to the wrinkles of the skin texture. Figure 5.1d shows that a piece of a liquid-metal PVA fibrous mat forms a LMHT that conforms adhered to the human arm. An ultrathin LMHT was also performed to conformally adhere to the fingertip (Figure 5.1e). This LMHT so intimately conforms to the fingerprints of the fingertip and the liquid metal electrode light a small LED lamp. In contrast, conventional fabrication methods rely on chemical polymerization or physical crosslinking, which are time-consuming, tedious, and hard to fabricate ultrathin structures (Figure 5.2a).

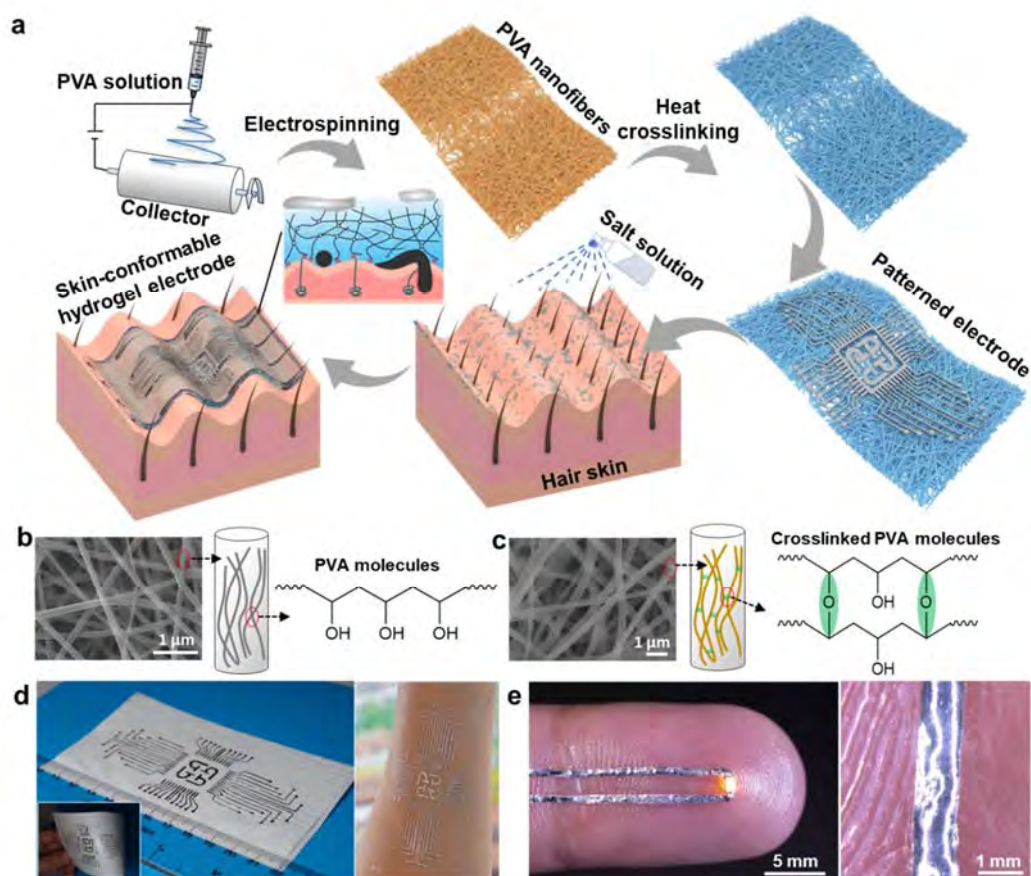


Figure 5.1. On-demand fabrication of ultrathin and superconformal liquid-metal hydrogel tattoo. **a**, Schematic illustration of the on-demand formation of ultrathin liquid metal hydrogel tattoo. **b-c**, Surface morphology and the chemical structure of **(b)** PVA nanofibrous mat and crosslinked PVA nanofibrous mat **(c)**. **d-e**, Liquid-metal PVA nanofibrous mat and on-demand formation of LMHT on the human arm **(d)** and fingertip**(e)**.

We demonstrate the fabrication of a large piece of PVA nanofibrous mat with the size of 30 x 40 cm and this nanofibrous mat could be then fabricated to a transparent liquid-metal hydrogel (Figure 5.2 b-c). The PVA nanofibrous mat swells rapidly at immersion in water; for example, it absorbs 3 times its weight of water in 3s. The absorption reaches equilibrium after 10 s, where the water content of the formed hydrogel is 65%. We also continuously observed the water contact angle(WCA) by dropping a 2-μm

water droplet to the surface of a PVA nanofibrous mat. The WCA dropped dramatically from 72.5° to 35.7° after contacting 1 s to the fibrous surface and further decreased to 0° after 6 s.

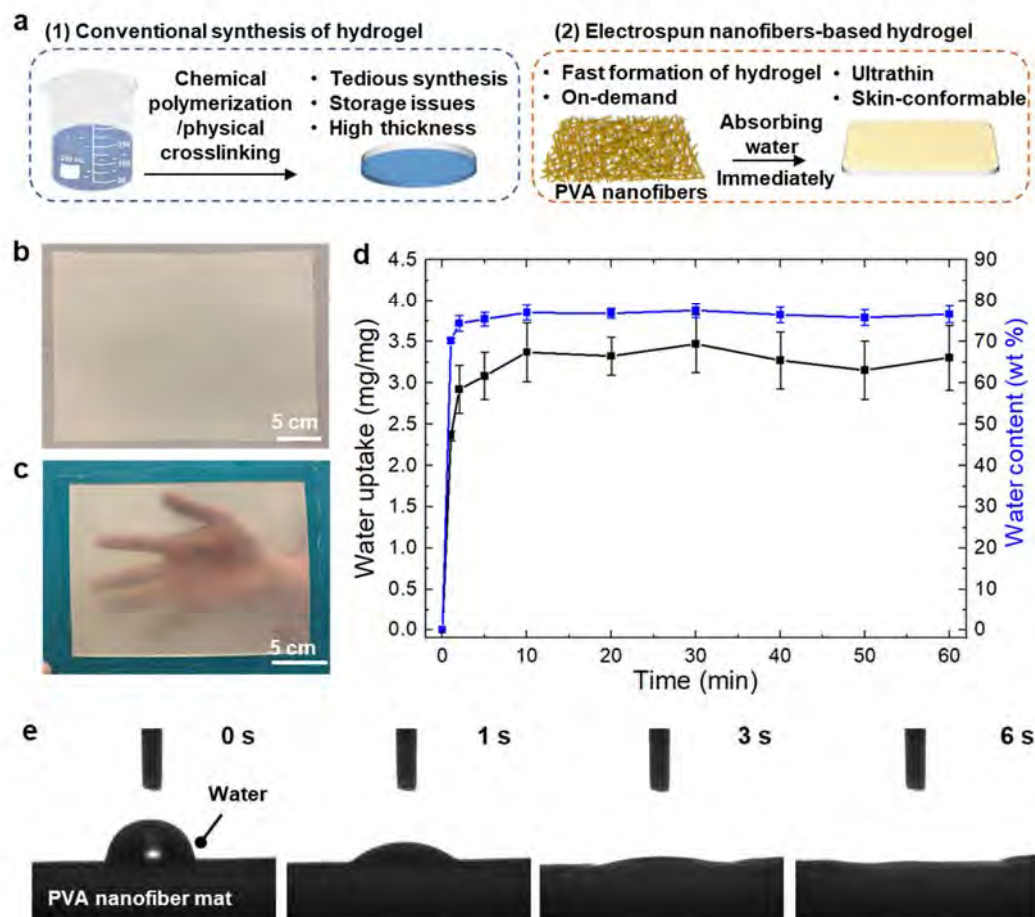


Figure 5.2. On-demand fabrication of hydrogel tattoo. **a**, Comparison of the features of the on-demand “nanofibers-to-hydrogel” method to the conventional fabrication method. **b-c**, A large piece of PVA nanofiber mat (**b**) and it became a PVA hydrogel tattoo (**c**). **d**, Water uptake and the water content during the transform process of “nanofibers-to-hydrogel”. **e**, Water contact angle changes of the PVA nanofiber mat.

The mechanical properties of PVA nanofiber mats and on-demand formed LMHT have been investigated. The higher crosslinking temperature results in higher tensile strength of the nanofiber mat of the high crosslink density (Figure 5.4a) We then employed these

nanofiber mats to form LMHT. Only a curing temperature over 100 °C could form a tough hydrogel tattoo that could be handled or relocated to the tensile test machine after swelling in the saline water. The formed PVA-based LMHT were significantly softer after swelling. The Young's modulus of the PVA hydrogel tattoo (90 μm) was 700 kPa, only 36% of the value of the previous PVA nanofiber mat (1.93 MPa), and the breaking stress was 2.1 MPa versus 12.5 MPa for the PVA LMHT after and before uptake the saline water (Figure 5.3a-b).

On-demand formation of LMHT also renders conformal adhesion to the substrate. Here, the adhesion performance of this hydrogel tattoo has been investigated by the 90° peeling test. The peeling-off force reaches 22 N m^{-1} of the hydrogel tattoo with interfacial toughness over 44 J m^{-2} (Figure 5.3c-d). Such a high adhesion could enable tough and intimate attachment of LMHT to the human skin. Combined with the stretchability, this LMHT could intimately adhere to the human skin and conform even under skin deformations (*e.g.*, stretching, compressing) (Figure 5.3e).

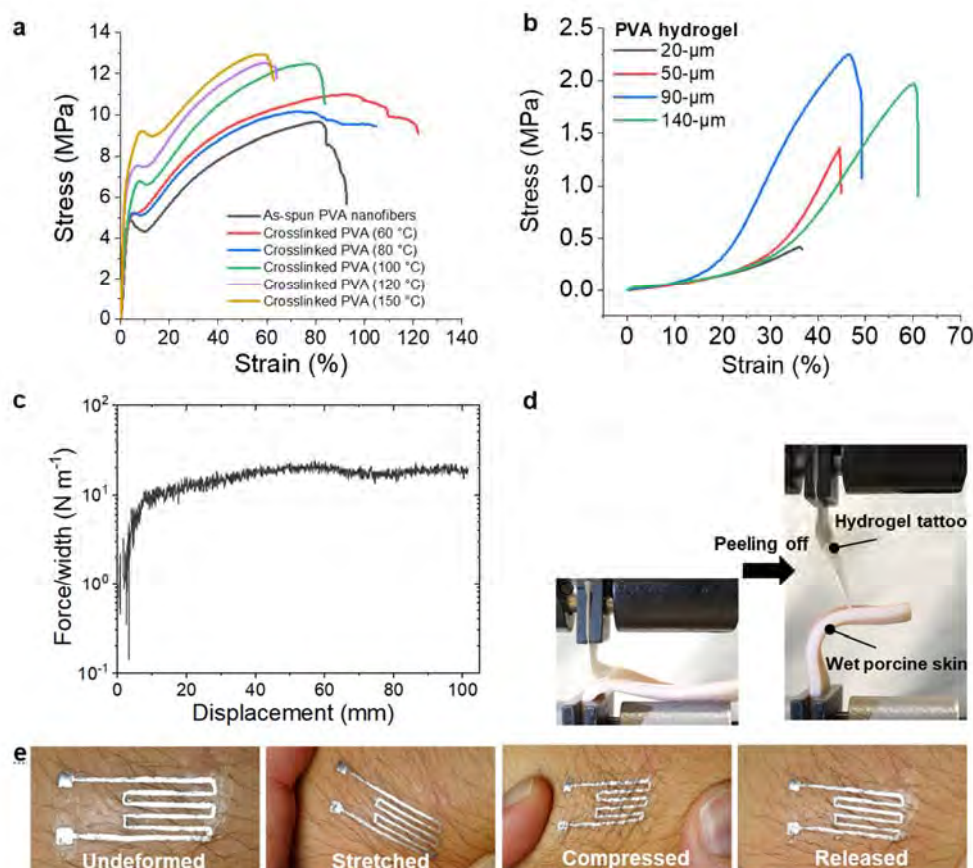


Figure 5.3. Mechanical properties and adhesion performance of the PVA hydrogel tattoo. **a**, Strain-stress curves of PVA nanofiber mat cured in different temperatures. **b**, Strain-stress curves of PVA hydrogel tattoo with different thicknesses. **c-d**, adhesion force (**c**) and the digital images (**d**) of the 90° peeling force for the hydrogel tattoo adhering to the wet porcine skin. **e**, A liquid-metal hydrogel tattoo adhered to the human skin and under deformations.

The formed LMHT inherits the permeability from the porous structure of the PVA nanofiber mat. As shown in Figure 5.4, the moisture permeability of the PVA nanofiber mat is 708 g m⁻² day⁻¹, which is close to the surface without any covering. The moisture permeability of hydrogel tattoos varies from 386 to 588 g m⁻² day⁻¹ according to the thickness of the hydrogel. The thinner hydrogel tattoo, lower moisture permeability has. The permeability of this LMHT satisfies the need for the evaporation of daily insensible

perspiration for human beings at $300\text{--}600\text{ g m}^{-2}\text{ day}^{-1}$. In contrast, the commercial medical TPU tape performs much lower moisture permeability at $149\text{ g m}^{-2}\text{ day}^{-1}$.

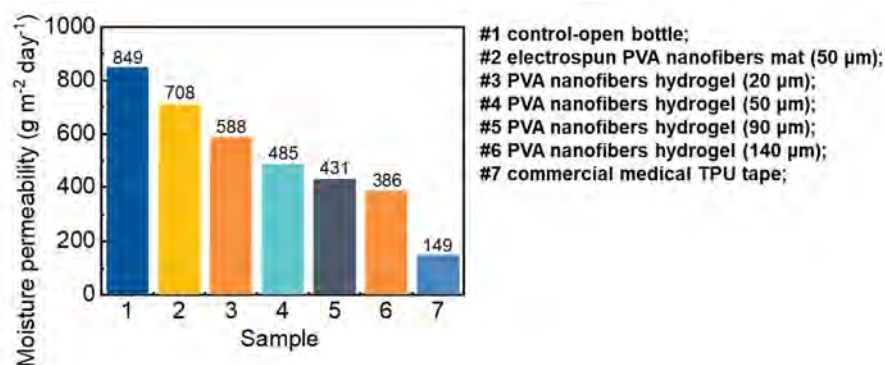


Figure 5.4. Moisture permeability of the PVA nanofiber mat and formed PVA nanofiber hydrogel tattoo.

5.3.2 Conformability and Impedance of LMHT

The electrophysiological signals derived from the ionic concentration gradient across cell membranes encompass the use of electrocardiogram (ECG) for diagnosing heart disease and electroencephalography (EEG) as well as electromyography (EMG) for the brain-computer interface. Hydrogel tattoo is one of the important methods to extract the electrophysiological signals. To get high-quality electrophysiological signals, hydrogel tattoos should pertain lower skin impedance.

The impedance of the electrodes is significantly influenced by the ionic conductivity of the electrode. We firstly measured the ionic conductivity of the hydrogel tattoo by electrochemical impedance spectroscopy (Figure 5.5). The ionic conductivity of the hydrogel tattoo absorbing the DI water is 0.1 S m^{-1} and increases with increasing the concentrations of the saline water. Hydrogel tattoo formed by absorbing 5% NaCl water shows high ionic conductivity up to 2.0 S m^{-1} .

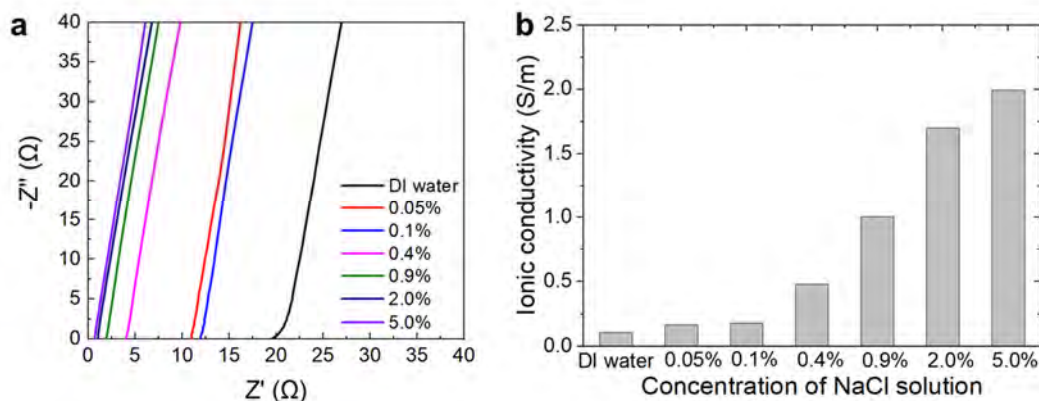


Figure 5.5. Electrochemical impedance spectroscopy (a) and the calculated ionic conductivity (b) of the hydrogel tattoo with the uptake of different saline water.

The skin impedance of the LMHT consists of the impedance of the skin, the impedance of the interface between skin and electrodes, and the impedance of the electrodes, as shown in Figure 5.6a. The ultrathin structure and tissue-like ionic conductivity offered a high conformability and relatively low skin impedance. The skin impedance of the dry liquid-metal electrode, commercial Ag/AgCl gel electrode, and the LMHT with thicknesses from 1 μm to 140 μm were characterized (Figure 5.6b-c and Table 5.1). Commercial Ag/AgCl gel electrode demonstrates the highest impedance during the whole range from 0.1 to 1000 Hz. The impedance of the liquid metal dry electrode is compatible with the impedance of the Ti foil. The LMHT offers the lowest skin impedance, for example: 4.8 $\text{k}\Omega@10$ Hz for the 20- μm LMHT. Decreasing the thickness of the liquid metal gel electrode, the impedance is reduced with an order of magnitude. The 1- μm LMHT exhibited an impedance of about 1.2 $\text{k}\Omega$ (@1 kHz) and 8.16 $\text{k}\Omega$ (@0.1 Hz). The decrease of impedance can be attributed to two aspects: 1) improved conformability as the decrease of thickness; 2) enhanced capacitive coupling capability (*i.e.*, increased capacitance) at the skin-electrode. The LMHT electrodes demonstrated low levels of impedance, which were generally lower than those reported for wet electrodes, dry electrodes, and ultrathin e-tattoos (Figure 5.6c and Table 5.1).

Notably, the impedance of liquid-metal hydrogel tattoo is also stable during deformations (Figure 5.6d). The low and stable impedance makes this liquid-metal hydrogel tattoo ideal electrodes for electrophysiological detection.

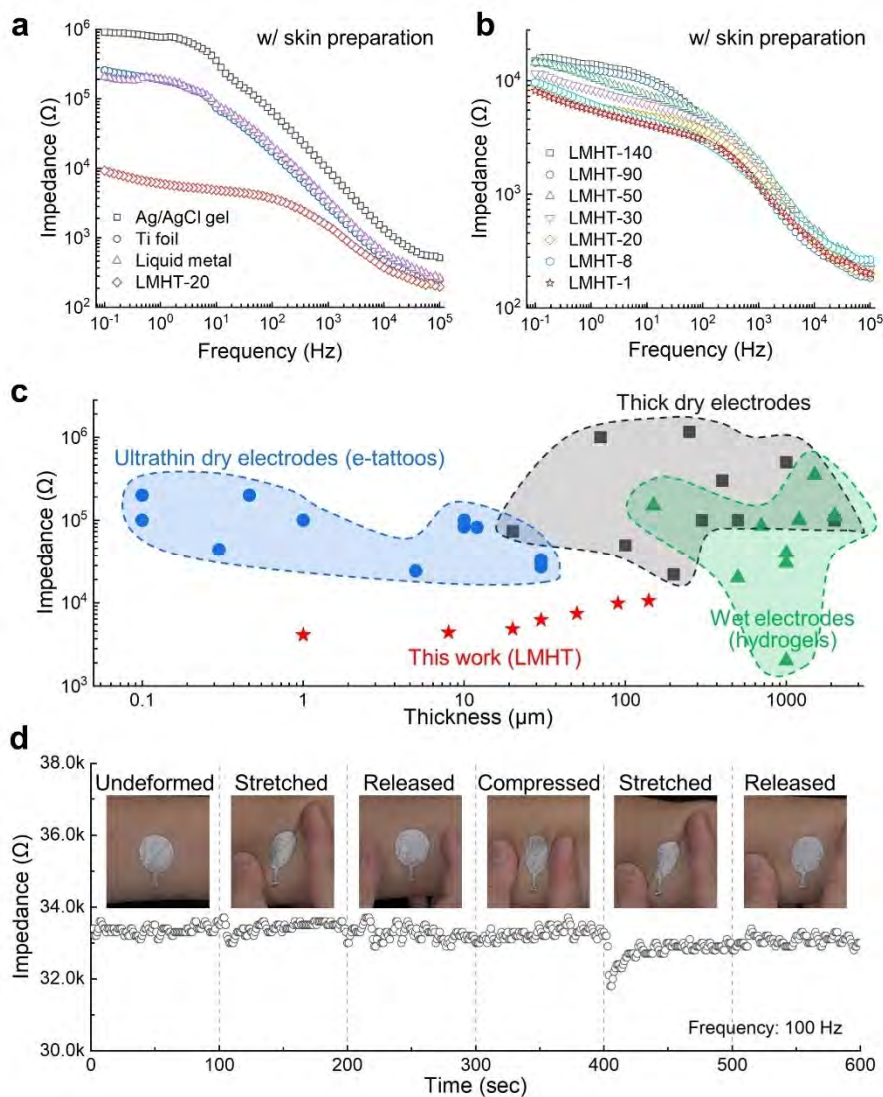


Figure 5.6. Skin impedance of the PVA hydrogel tattoo. **a**, Schematic diagram of the PVA hydrogel attached to the skin and connected with the device by a lead. **b-c**, Skin impedance of different electrodes (**b**) and the PVA hydrogel tattoo with different thickness (**c**). **d**, A comparison of the skin-electrode impedance and thickness of different electrodes: The green area involves reported thick wet electrodes (hydrogels),

the gray area involves reported thick dry electrodes, the blue area involves reported ultrathin dry electrodes (e-tattoos), and the red star markers represent the LMHT electrodes reported in this work. **e**, Skin impedance change of the PVA hydrogel tattoo during deformations.

Table 5.1. Comparison of physiological electrodes in the thickness, skin impedance, and conformability.

Materials	Manufacturing method	Thickness	Skin impedance	Conformability	Ref.
Au/PDMS	Thermal deposition	70 μm	$\sim 1000 \text{ k}\Omega @ 10 \text{ Hz}$	Conformal	[196]
AgNW-embedded PDMS	Spin coating & curing	$\sim 2 \text{ mm}$	$\sim 100 \text{ k}\Omega @ 10 \text{ Hz}$	Conformal	[197]
CNTs/PDMS composite	Mixing & curing	$\sim 250 \mu\text{m}$	$1160 \text{ k}\Omega @ 100 \text{ Hz}$	Adhesive	[198]
Liquid metal/ SEBS fiber mat	Electrospinning & screen printing	$\sim 200 \mu\text{m}$	$22 \text{ k}\Omega @ 10 \text{ Hz}$	Adhesive	[199]
Au mesh	Photolithographic patterning	$\sim 500 \mu\text{m}$	$\sim 100 \text{ k}\Omega @ 10 \text{ Hz}$	/	[200]
PEDOT/WPU composite film	Mould casting & drying	$12 \sim 55 \mu\text{m}$	$82 \text{ k}\Omega @ 10 \text{ Hz}$	Adhesive	[201]
Au nanomesh	Thermal deposition	$< 300 \text{ nm}$	$44 \text{ k}\Omega @ 1000 \text{ Hz}$	Conformal	[202]
Graphene tattoo	CVD	463 nm	$\sim 200 \text{ k}\Omega @ 42 \text{ Hz}$	Conformal	[203]
PEDOT film	Spin coating	100 nm	$\sim 100 \text{ k}\Omega @ 10 \text{ Hz}$	Conformal	[204]
Au-silk	Electrospinning & coating	$10 \mu\text{m}$	$\sim 100 \text{ k}\Omega @ 100 \text{ Hz}$	Conformal	[150]
Sticky liquid metal conductors	Printing & peeling off	$30 \sim 60 \mu\text{m}$	$\sim 30 \text{ k}\Omega @ 10 \text{ Hz}$	Adhesive	[205]
Printable liquid metal ink	Ink (PVA+ liquid metal)	$\sim 30 \mu\text{m}$	$\sim 33 \text{ k}\Omega @ 10 \text{ Hz}$	Adhesive	[206]
PVA-Au nanomesh	Electrospinning & deposition	$1 \mu\text{m}$	$\sim 100 \text{ k}\Omega @ 100 \text{ Hz}$	Conformal	[99]
Alginate-	polymerization	$\sim 500 \mu\text{m}$	$\sim 20 \text{ k}\Omega @ 1$	Adhesive	[207]

PAAm hydrogel with 5 wt% LiCl			Hz		
PEDOT:PSS/PAA m hydrogel	polymerization	150 μ m	~150 k Ω @10 Hz	/	[208]
PAM/salt hydrogel	polymerization	1.2 mm	~100 k Ω @10 Hz	Adhesive	[208]
MXene/PAA hydrogel	polymerization	1 mm	~30 k Ω @10 Hz	/	[209]
Ag/AgCl gel	commercial		~352 k Ω @10 Hz		Control
Ti foil	Commercial	~20 μ m	~74 k Ω @10 Hz		Control
Liquid metal	Painting on skin	~10 μ m	~83 k Ω @10 Hz		Control
LMHT	Electrospinning	1~140 μ m	4.1-10.5 k Ω @10 Hz	Conformal	This work

5.3.3 Ultrathin Liquid-metal Hydrogel Tattoo as Electrophysiological Electrodes

Leverage of the on-demand formation, permeability, good conformability, and low impedance, the ultrathin liquid-metal hydrogel tattoo was employed for ECG signals and EMG signals monitoring and muscle stimulation. Three liquid-metal hydrogel tattoo electrodes attach to the left arm, right arm, and left leg of the human body (Figure 5.7). The liquid-metal hydrogel tattoo electrodes could capture distinguishable ECG signals during the rest condition. The P, QRS, and T waves of the captured ECG data reflect heart rhythms and benefit for analysis of heart diseases. These liquid-metal hydrogel tattoo electrodes also have the potential for long-term monitoring. We performed 1.5-h ECG monitoring by the liquid-metal hydrogel tattoo electrodes (Figure 5.7c). The electrodes pertain good stability from the start to after 1.5 h.

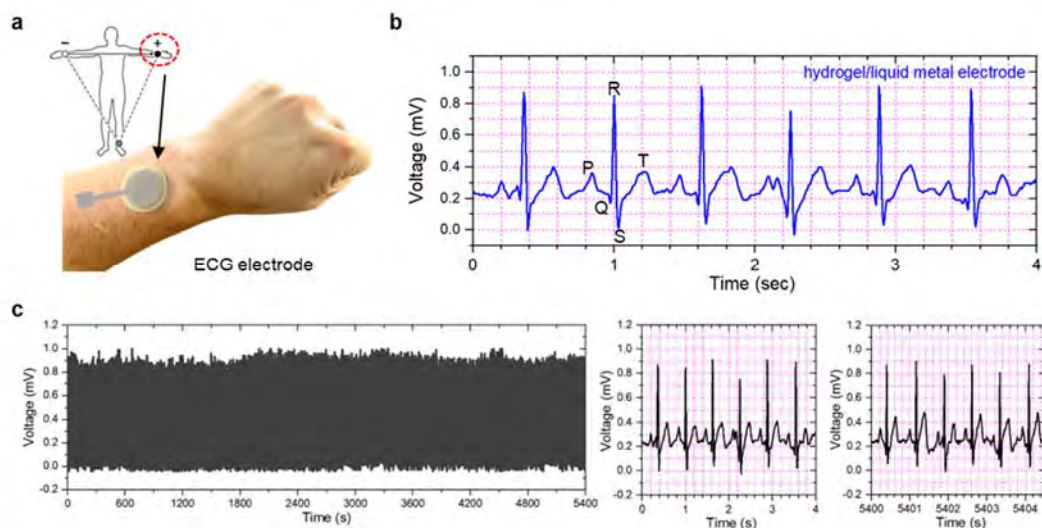


Figure 5.7. ECG monitoring by the liquid-metal hydrogel tattoo electrodes. **a**, Digital image and scheme of the ECG detection employed by liquid-metal hydrogel tattoo electrodes. **b**, ECG monitoring during rest condition. **c**, ECG monitoring over 1.5 h.

We also performed 6-channel surface electromyography (sEMG) monitoring by the hydrogel tattoo electrodes. The 6-channel electrode panel is made as follows: A piece of medical PU tape punched 18 holes (diameter: 1 cm) in six rows with serve as the supporting and adhesive layer of the nanofiber mat electrodes. The distance of holes in the same row is 2 cm and the distance of each row is 2.5 cm. Liquid-metal PVA nanofiber mat is cut to disc shapes with a diameter of 1.5 cm (Figure 5.8). The liquid-metal side of the PVA nanofiber mat will attach to the center of each hole and opposite to the skin. Furthermore, liquid-metal conductive pathways print to the opposite of the adhesive side of this PU tape to connect the PVA nanofiber electrodes and the rigid wires that connect the printed circuit board (PCB). An additional PU tape is further used for encapsulating the electrodes and conductive pathways. After quickly wetting the skin surface of the forearm with the saline water, this PU tape with electrodes adheres to the forearm and aims to detect the forearm muscles including brachioradialis, pronator teres, flexor carpi radialis, flexor carpi ulnaris, extensor carpi radialis longus, extensor carpi radialis brevis, and extensor carpi ulnaris.

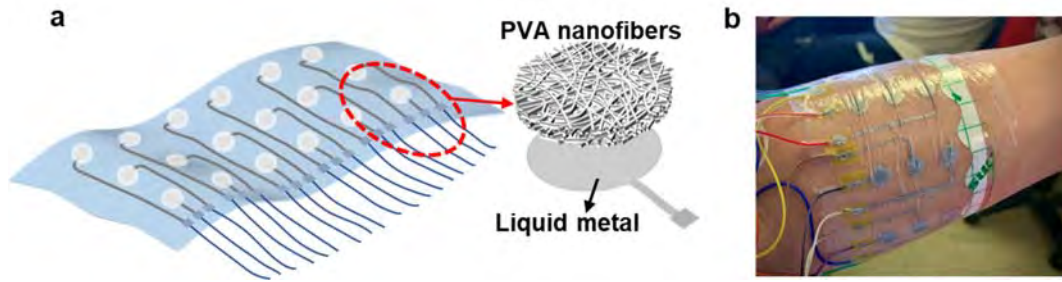


Figure 5.8. **a**, Schematic illustration of the 6-channel EMG monitoring by the hydrogel tattoo electrodes. **b**, Electrodes adhered to the human forearm.

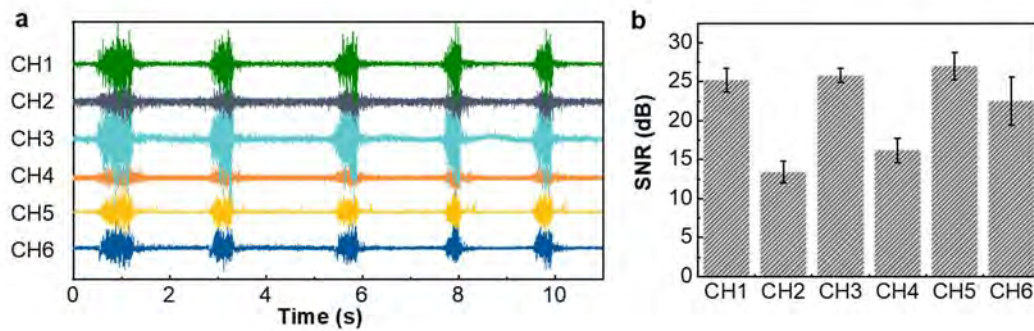


Figure 5.9. EMG waveforms (**a**) and signal-to-noise ratio (SNR) (**b**) of 6 channels of liquid metal hydrogel tattoo during consecutive squeezing and resting of the hand.

The detection of sEMG signals involves placing hands flatly on a table and the palm of the hand grabs a grab dynamometer consecutive squeezing and resting this grab dynamometer to control and maintain a reproducible and consistent level of muscle activity. As shown in Figure 5.9, the sEMG waveforms of 6 channels reveal distinguishable signatures of muscle activation during each hand squeezing and resting. Channel 1, 3, and 5 demonstrate high signal-to-noise ratios (SNR) of around 25 dB. Channel 2, 4, and 6 has lower SNR compared to channel 1, 3, and 5. The differentiation of the SNR of different channels might attributes to the difference in locating muscles.

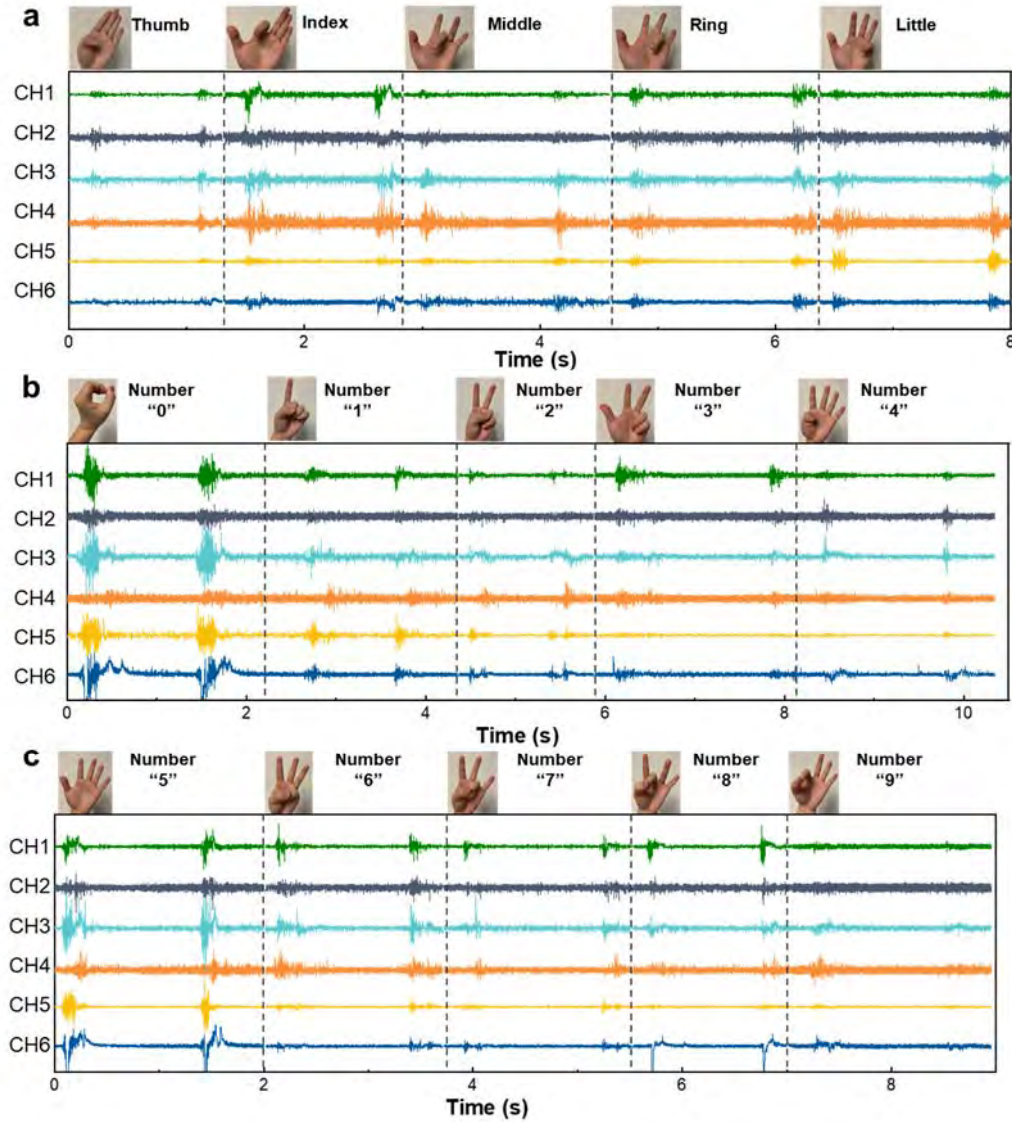


Figure 5.10. 6-channel EMG signals by performing different gestures. a-c, (a) Accordingly bending five fingers from thumb finger to little finger; (b) Performing gestures “Number 0” to “Number 4” and (c) performing gestures “Number 5” to “Number 9”.

The EMG test of bending different fingers from the thumb finger to the little finger was also conducted (Figure 5.10a). Bending fingers requires squeezing and resting muscles of the arm and different muscle groups control different fingers to bend and rest. From Figure 5.10a, when bending the thumb finger, there is no obvious EMG signals

appeared in channel 6(CH6). When bending different fingers, the rhythms and the intensity of different channels are also diverse. Further, EMG signals of gestures of “Number 0” to “Number 9” following the American sign language (ASL) hand gesture were recorded as shown in Figure 5.10b-c. Each gesture was performed at least 6 times but only extracted 2 sections of EMG rhythms in Figure 5.10. Conducting gestures relies on the participation of different muscle groups. Therefore, it will be reflected in the EMG rhythms in the temporal-spatial and intensity way. To clearly distinguish different gestures by the EMG rhythms, the machine learning technique from computer science was employed.

An ANN model is employed to recognize hand gestures based on 6-channel electromyography (EMG) signals, which is illustrated in Figure 5.11. Each EMG channel is characterized by six features: mean, standard deviation, variance, root mean square (RMS), max value, and mean max value. These features are extracted to provide a comprehensive representation of the EMG signals, which are crucial for the accurate recognition of hand gestures. The mean of the EMG signals represents the average activity level of the muscles, while the max value indicates the maximum discharge capacity of muscle activity. Variance and standard deviation reflect the dispersion tendencies of the EMG signals, with higher values indicating greater signal variability. RMS is a measure of the signal's magnitude, providing an overview of the muscle's electrical activity. Finally, the mean max value characterizes the average of the maximum values within the signal, offering insights into the peak muscle activity.

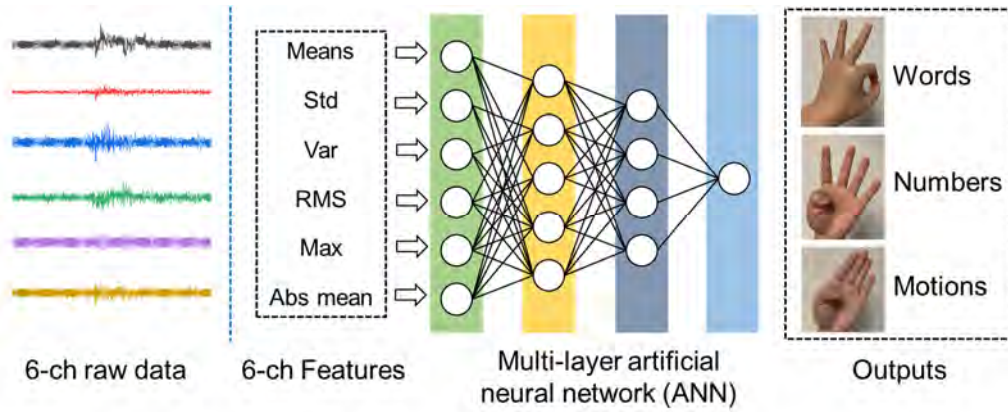


Figure 5.11. Illustration of extracting features of EMG signals for gesture recognition by the multi-layer artificial neural network.

The recognition task involved identifying 19 distinct hand gesture categories, with each category containing five samples for prediction. The proposed ANN model achieved an overall correction rate of 93.69%, with only six categories having false prediction results (Figure 5.12). This high accuracy demonstrates the effectiveness of the proposed system in recognizing hand gestures based on EMG signals.

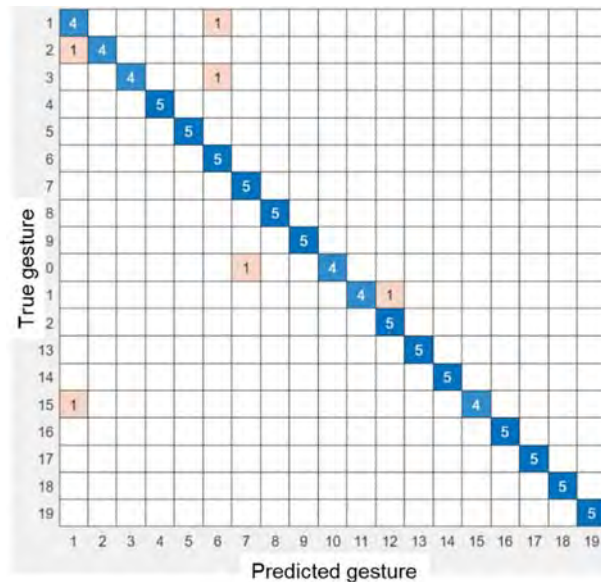


Figure 5.12. Confusion matrix of the verifying results for the 19 types of gestures.

5.4 Conclusion

In summary, the new strategy “nanofibers-to-hydrogel” was investigated to fabricate ultrathin LMHT. The ultrathin PVA fiber mats can be arbitrarily fabricated with tunable thicknesses by the electrospinning. The initial liquid-metal PVA fiber mats are easily handled and thus facilitate the convenient usage of the hydrogel tattoo for the on-skin scenario. With such strategy, it could easily fabricate ultrathin, skin-conformable, adhesive, permeable, stretchable, and biocompatible LMHT on demand. The skin impedance of the hydrogel tattoo decreases with decreasing the hydrogel thickness and, notably, this LMHT demonstrated relatively lower skin impedance and thinner thickness compared to the literatures. The LMHT was further employed as biophysiological electrode to detect ECG signals for health monitoring. A 6-channel EMG sensor array based on the LMHT was also developed for gesture recognition assisted by machine learning. This strategy paves the way for the easy and on-demand fabrication of ultrathin and high-performance hydrogel electrodes and shows great potential for the next-generation personalized health monitoring, smart gesture recognition, and human-machine interaction.

CHAPTER 6: ALL-FIBER-MAT, PERMEABLE, WET-ADHESIVE, AND SUPERELASTIC TRIBOELECTRIC SKIN

Triboelectric devices show great promises for skin-attachable bio-mechanical energy harvesting and intimate and noninvasive human motion monitoring. However, the poor device's permeability, low stretchability of both triboelectric materials and electrodes, and skin adhesiveness hinder the on-skin application of TENG devices in terms of comfortable wearing and stable sensing performance. Here, an all-fiber-mat, permeable, adhesive, and superelastic triboelectric device (PAST E-device) has been developed by the intrinsically stretchable liquid-metal-fiber-mat and highly stretchable core-sheath triboelectric fiber mat enabled by co-axial electrospinning. The core-sheath structure significantly enhanced the stretchability of the triboelectric layer from 200% to 600% while reduces the residue strain from 60% to 30.6% within 100% pre-stretching. The PAST e-skin simultaneously offers high stretchability, low residue strain, textile-like permeability, skin adhesiveness, and long-term wearing biocompatibility. The intrinsically stretchable porous liquid-metal-fiber-mat electrode provides stable and high conductivity even in large deformations. The PAST E-device shows considerable triboelectric outputs with an open-circuit voltage at 90V and stable sensing performance during the strain of 150% and on-skin monitoring. With the leverage of such properties, a machine-learning assisted skin-attachable sensing system has been prepared, showing real-time sign language recognition. It can be envision that this design can not only form great impact to the fabrication of skin-attachable TENG sensors but also provide a new insight to the sign language recognition field.

6.1 Introduction

Skin-attachable flexible electronics have great potential in non-invasive and personalized health monitoring, precision medicine, and smart human-machine

interface^[6, 57, 185, 194]. To date, tremendous efforts have been promoting the development of high-performance flexible substrates, highly conductive conductors, wireless and analysis system integration, and new perspectives as well as new mechanisms of flexible electronics^[10, 58, 68]. Skin-attachable flexible electronics is a tremendous field, including electrical sensors to detect biophysiological signals (ECG, EMG, EEG, *et.al.*), biophysical sensors enabled by resistive, capacitive, iontronic, optical, piezoelectric, and triboelectric models as well as transistors, and biochemical sensors^[20, 59, 72, 126].

Among that, sensors based on piezoelectric and triboelectric effects have been emerging as a promising technology for skin-interfaced electronics. The piezoelectric and triboelectric sensors are self-powered, which harvest the mechanical energy from the human body without the need for external power supplies and even drive the outer loads, thus overwhelming the conventional sensor models^[72, 210]. The working mechanism of TENG combines the effects of contact electrification and electrostatic induction^[210]. Abundant of triboelectric materials, for example, Polytetrafluoroethylene (PTFE), polydimethylsiloxane (PDMS), and polyvinylidene fluoride (PVDF), have been used to fabricate high-performance flexible triboelectric device^[211-212]s. However, there still are several limitations during on-skin applications for the piezoelectric and triboelectric sensors.

The skin is wet and dynamic. Firstly, the skin secretes sweat with insensible perspiration over $600 \text{ g m}^{-2} \text{ day}^{-1}$ ^[89]. Insufficient permeability of skin-interfaced sensors probably results in sweat accumulation and probably causes skin inflammation^[25, 70]. Secondly, the mechanical properties of the skin should be concerned. The skin deforms during human motions with the elongation strains even up 35-45% and the elastic modulus of the skin ranges from 10 kPa to several hundred kPa^[7]. High stretchability and good stability during stretching cycles, called low residue strain are still highly demanded.

The sensors with high permeability and skin-like stretchability could offer highly comfortable wearing experiences for wearers. Thirdly, the piezoelectric and triboelectric sensors should be firmly and intimately attached to the targeted skin area for recording signals or harvesting mechanical energies. Regarding the wet skin surface caused by sweating or outer environments, there is also a strong demand for a wet adhesive layer for the sensors. Plenty of efforts have been involved to develop state-of-the-art permeable piezoelectric and triboelectric sensors^[213-216]. For example, porous yet permeable PVDF fiber mats have been fabricated with a stretchability of 40%, and the copolymer, poly (vinylidene fluoride-trifluoro ethylene) ((P(VDF-TrFE))), could further enhance the stretchability of the fiber mats to 200%^[217-218]. Moreover, the permeable adhesive with the adaptivity to wet skin conditions is still vacant.

Here, an all-fiber-mat, permeable, wet-adhesive, and superplastic triboelectric skin (PAST e-skin) has been developed. This e-skin constitutes two layers of stretchable and permeable liquid-metal fiber mats as electrodes, a layer of core-sheath triboelectric fiber mat, and a layer of wet-adhesive fiber mats. The core-sheath fiber mat of TPU@P(VDF-TrFE) fabricated by coaxial electrospinning significantly enhances the stretchability of P(VDF-TrFE) from 200% to 600% and reduces the residue strain from 60% to 30.6% within 100% pre-stretching. The PAST e-skin pertains a wet- and skin-adhesive fiber mat that could seamlessly adheres the PAST e-skin to the wet human skin with the adhesion strength of 80 kPa. The PAST e-skin simultaneously offers high stretchability, low residue strain, textile-like permeability, and wet-adhesive properties. The open-circuit voltage and the short-circuit current of the PAST e-skin are 96.7 V and 4.0 μ A, respectively. Precise on-skin monitoring of body motions of the finger, wrist, knit, and masticatory muscle have been performed by adhering the PAST e-skin to the target body area.

6.2 Experiment

6.2.1 Fabrication of Core-sheath TPU@P(VDF-TrFE) Fiber Mat

15 wt% P(VDF-TrFE) solution was prepared by dissolving the P(VDF-TrFE) powders in the DMF/Acetone (4/1) mixed solution. 20 wt% TPU solution was prepared by dissolving the TPU powders in the DMF/THF (1/3) mixed solution. TPU@P(VDF-TrFE) nanofibrous mats were fabricated via coaxial electrospinning with stainless-steel needles (23 G for the outer needle and 17G for the inner needle). The distance and high voltage between the needle tip and collector were set as 12 cm and 16 kV, respectively. The feeding rate of the P(VDF-TrFE) solution and TPU solution were varied between 1.5 to 3 ml h⁻¹ to adjust the ratios of TPU/P(VDF-TrFE).

6.2.2 Fabrication of Liquid-metal TPU Fiber Mat and PSA/PAASND Adhesive Fiber Mat

TPU fiber mat was fabricated by electrospinning of the TPU solution with a feeding rate of 3 ml h⁻¹, a high voltage supply of 16 kV, and the distance between the needle tip and collector of 12 cm. Liquid metal was subsequently printed at the surface of TPU mat as the electrode to harvest TENG signals. To adhere the whole device to the skin, an adhesive layer was fabricated opposite the liquid metal at the TPU fiber mat via co-electrospinning of PSA and PAASND solutions. This PSA solution was prepared by diluting the PSA liquid into toluene. PAASND solution was prepared via three steps: (1) dissolving PAA powders into DMF, (2) adding 0.8 g N-hydroxysulfosuccinimide (sulfo-NHS) and 0.4 g EDC into 50 g PAA solution to graft sulfo-NHS to PAA chains, (3) adding 60 mg dopamine hydrochloride to the solution to graft dopamine to PAA chains. During the co-electrospinning process, the feeding rate PSA and PAASND solutions were 2 ml h⁻¹, and the high voltage supply, chamber humidity, chamber

temperature, and the distance between the needle tip and collector were 16 kV, 40%, 30 °C, and 12 cm, respectively.

6.2.3 Assembly of TENG Device

The TENG device used here was a sandwich structure, including a layer of liquid-metal TPU mat, a layer of core-sheath TPU@P(VDF-TrFE) fiber mat, and a layer of liquid-metal TPU mat with a next-to-skin PSA/PAASND adhesive fiber mat.

6.2.4 Triboelectric Performance Test

To apply specific frequencies to the TENG device, a cycling impact apparatus (Impact life tester, Dongguan Huaguo Precise Instruments Co., Ltd., China) was utilized, which was connected to an electrometer (6517, Keithley, America) for detecting the electrical outputs of the TENG device.

6.3 Results and Discussion

6.3.1 Fabrication of Permeable, Adhesive, and Stretchable Triboelectric e-skin (PAST e-skin)

As shown in Figure 6.1, the PAST e-skin consists of four layers: (1) top electrode layer of TPU electrospun fiber mat with EGaIn patterns, (2) second triboelectric layer of TPU@P(VDF-TrFE) core-sheath fiber mat, (3) third electrode layer of TPU electrospun fiber mat with EGaIn patterns, and (4) fourth skin- and wet- adhesive layer of N-hydroxysulfosuccinimide- (sulfo-NHS-) and dopamine-grafted polyacrylic acid

(PAASND) and pressure sensitive adhesive (PSA) electrospun fiber mat. All layers are porous structures fabricated by electrospinning. Notably, the triboelectric layer, which is TPU@P(VDF-TrFE) core-sheath fiber mat, is fabricated by coaxial electrospinning with a stretchable TPU core and a triboelectric P(VDF-TrFE) sheath. The core-sheath structure significantly enhances the stretchability of P(VDF-TrFE) electrospun fiber mat. The liquid-state EGaIn is printed on the top of the TPU fiber mat via a stencil mask, which sandwiches the triboelectric layer and harvests triboelectric signals. Based on such construction, the whole PAST e-skin is permeable and stretchable while the designed adhesive layer provides skin adhesiveness and wet adhesion properties.

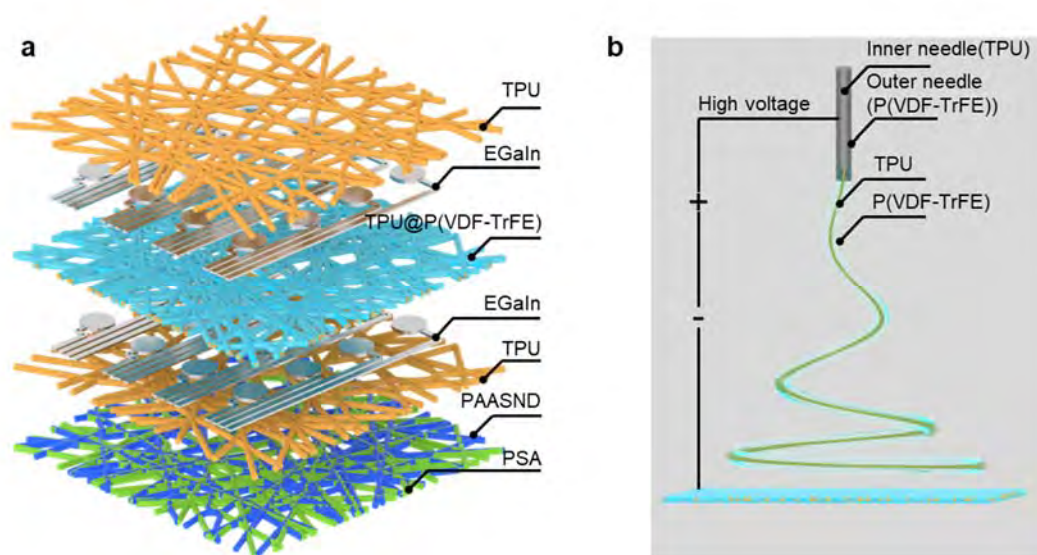


Figure 6.1. a-b, Schematic illustration of the layout of (a) Permeable, Adhesive, and Stretchable Triboelectric skin and (b) of the mechanism of coaxial electrospinning for TPU@P(VDF-TrFE) core-sheath fiber mat.

6.3.2 Characterization of Core-sheath Fiber Mat

The surface morphology of the TPU fiber mat, P(VDF-TrFE), and TPU@P(VDF-TrFE)

core-sheath fiber mat were investigated, as shown in Figure 6.2. All fiber mats demonstrate porous fiber structures. The average diameter of the TPU fiber mat, P(VDF) TPU@P(VDF-TrFE) core-sheath fiber mat is 3.73 μm , 355 nm, and 780 nm, respectively.

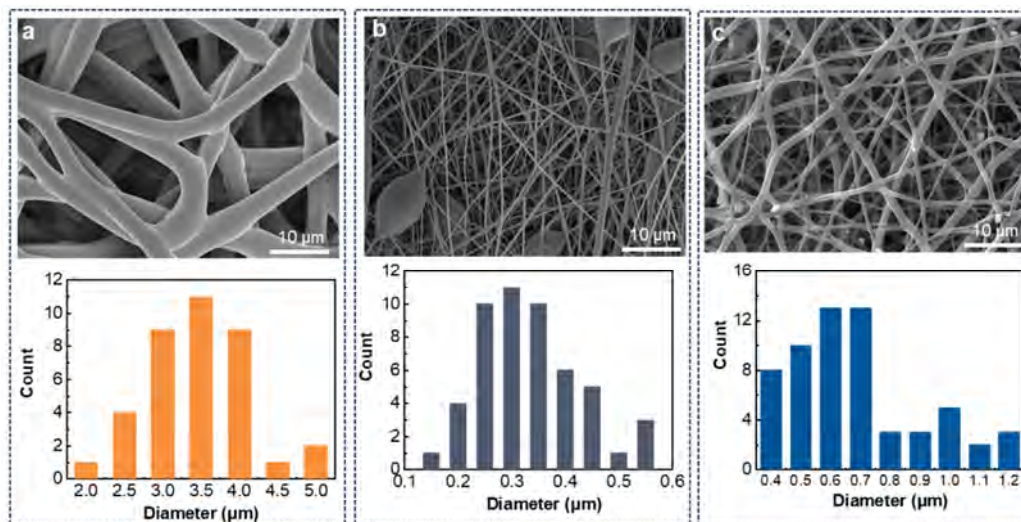


Figure 6.2. a-c, SEM images and diameters of TPU fiber mat (a), P(VDF) (b), and TPU@P(VDF-TrFE) core-sheath fiber mat (c).

To understand the dynamics of the fabricated core-sheath fiber mat, Fourier transform infrared spectroscopy (FT-IR) was employed for the analysis of the vibrational mechanics by monitoring the absorption of infrared energy. FT-IR spectrums of the TPU fiber mat, P(VDF), and TPU@P(VDF-TrFE) core-sheath fiber mat were measured, as shown in Figure 6.2. The absorption bands of the TPU fiber mat at around 1729 cm^{-1} and 1530 cm^{-1} are -N-H deformation and -C=O structure, respectively, indicating the urethane structure.^[219] The absorption bands of P(VDF-TrFE) fiber mat at around 1400 cm^{-1} are assigned to the -CH₂ wagging vibration. The absorption bands at around 1177 cm^{-1} and 841 cm^{-1} are assigned to the CF₂ symmetric stretching. Both three absorption bands at 1400 cm^{-1} , 1177 cm^{-1} , and 841 cm^{-1} associate with the β phase of P(VDF-TrFE) while the absorption band at 761 cm^{-1} links the α phase of P(VDF-

TrFE).

The absorption bands of -N-H (1729 cm^{-1}) and -C=O (1530 cm^{-1}) exist in the spectrums of all TPU@P(VDF-TrFE) core-sheath fiber mat but both bands are significantly weak in the spectrum of TPU@P(VDF-TrFE) fiber mat (66.6% of P(VDF-TrFE)). The absorption bands 1729 cm^{-1} and 1530 cm^{-1} belonging to the CF_2 symmetric stretching also exist during the spectrums of all TPU@P(VDF-TrFE) core-sheath fiber mat and it also weak along the reduction of the ratio of P(VDF-TrFE).

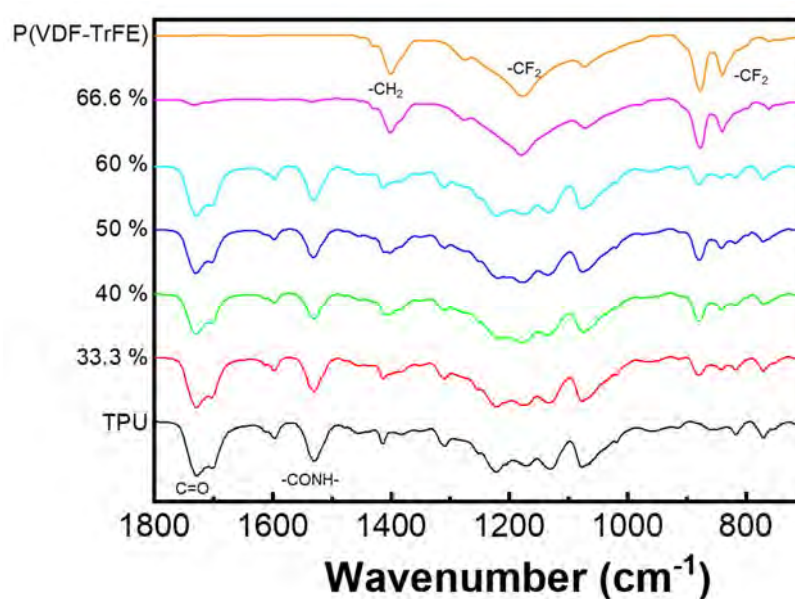


Figure 6.3. FT-IR spectrums of TPU fiber mat, P(VDF), and TPU@P(VDF-TrFE) core-sheath fiber mat.

The content of β phase among these fiber mats can be calculated according to the following equation from Beer-Lambert law:

$$F(\beta) = \frac{A_{\beta}}{1.26A_{\alpha} + A_{\beta}} \quad (6.1)$$

where the A_{α} and A_{β} are the intensities of absorption bands at 761 cm^{-1} and 841 cm^{-1} .

The β -phase content of each fiber mat has been calculated as shown in Table 6.1. The β -phase content of the P(VDF-TrFE) fiber mat is the highest at 84%. The β -phase content of the P(VDF-TrFE) fiber mat decreases to around 40-50% with decreasing the amount of P(VDF-TrFE) in the core-sheath fiber mat.

Table 6.1. Intensities of absorption bands of A(α) at 761 cm^{-1} and A(β) at 841 cm^{-1} and the calculated β phase contents of the fiber mats.

Sample	A(α)	A(β)	F(β) content (%)
Pure P(VDF-TrFE)	0.370	0.056	84.0
P(VDF-TrFE) 66.6%	0.292	0.0855	73.0
P(VDF-TrFE) 60%	0.128	0.14	42.0
P(VDF-TrFE) 50%	0.181	0.12	54.5
P(VDF-TrFE) 40%	0.167	0.106	55.4
P(VDF-TrFE) 33.3%	0.122	0.136	41.5

Water contact angles (WCA) of fiber mats were also investigated (Figure 6.4). The WCAs of the as-prepared P(VDF-TrFE) fiber mat, TPU@P(VDF-TrFE) core-sheath fiber mat, and TPU fiber mat are hydrophilic. The core-sheath fiber mats demonstrate higher WCAs ($>130^\circ$) than the pure P(VDF-TrFE) fiber mat ($>122.5^\circ$) and TPU fiber mat ($>119.1^\circ$). Higher WCA of a fiber mat indicates higher water repellent of materials. Therefore, the core-sheath fiber mats may possess higher waterproof properties.

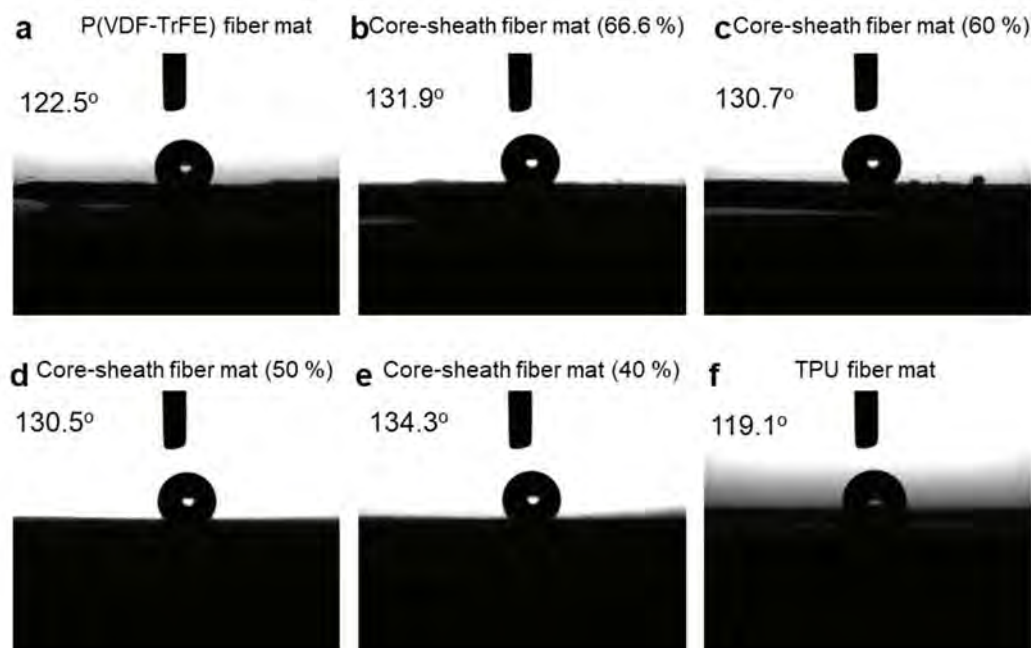


Figure 6.4. Water contact angle of P(VDF-TrFE) fiber mat, TPU@P(VDF-TrFE) core-sheath fiber mat, and TPU fiber mat.

Permeability is a significant character for on-skin electronics since the skin breaths and secretes sweat from day to night. The PAST e-skin is entirely constructed with highly porous fiber mats which enable high permeability. The air permeability test of TPU@P(VDF-TrFE) core-sheath fiber mats was first conducted according to the ASTM D737-08 standard (Figure 6.5). TPU@P(VDF-TrFE) core-sheath fiber mats with 80- μm thickness pertain a high air permeability at the rate of $13.1 \pm 2.0 \text{ mL s}^{-1}$. The air permeability of TPU@P(VDF-TrFE) core-sheath fiber mats displays a negative correlation to the mat thickness. For 600- μm TPU@P(VDF-TrFE) core-sheath fiber mats, the air permeability of the fiber mats decreases to $2.3 \pm 0.2 \text{ mL s}^{-1}$.

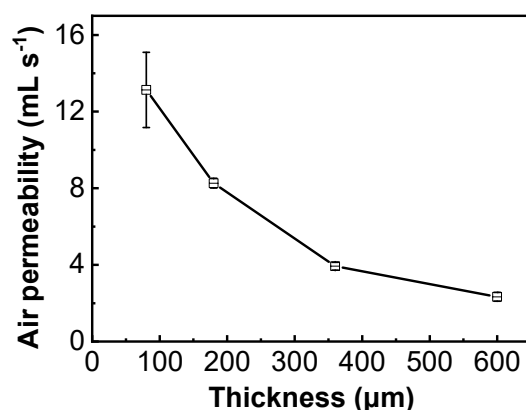


Figure 6.5. Air permeability of TPU@P(VDF-TrFE) core-sheath fiber mats with different thicknesses.

Subsequently, the moisture permeability of PAST e-skin was conducted, as shown in Figure 6.6. The substrates, cotton, TPU@P(VDF-TrFE) core-sheath fiber mats, PAST e-skin, and PDMS, covered in the opening of bottles containing water, and a bottle without any cover was as the control. By measuring the weight loss of the water, the moisture permeability can be calculated. The opening condition demonstrates the highest moisture permeability of $947.5 \text{ g m}^{-2} \text{ day}^{-1}$, while the TPU@P(VDF-TrFE) core-sheath fiber mats assess $867.5 \text{ g m}^{-2} \text{ day}^{-1}$, higher than the value for the cotton. The moisture permeability of the assembled device, PAST e-skin, is $678 \text{ g m}^{-2} \text{ day}^{-1}$, which satisfies the need to evaporate the insensible perspiration of a human.

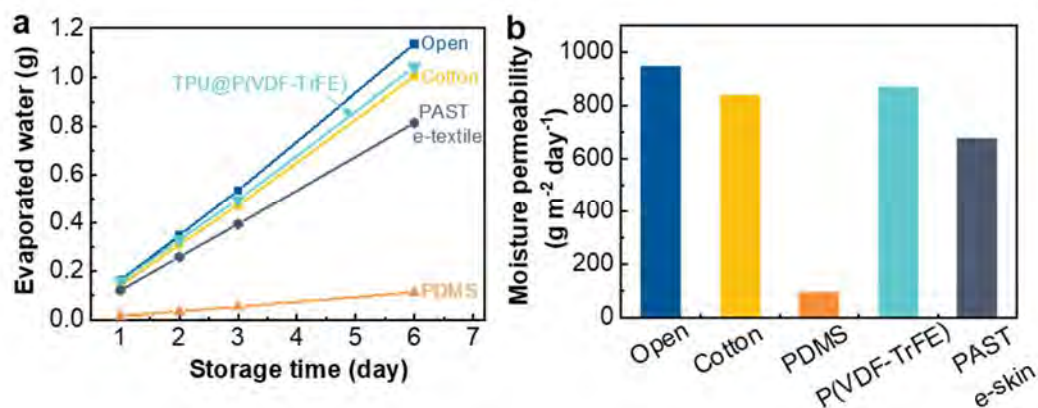


Figure 6.6. a-b, The evaporated water (a) and moisture permeability results (b) of cotton, PDMS, TPU@P(VDF-TrFE) core-sheath fiber mats, and PAST e-skin.

6.3.3 Stretchability and Adhesion of PAST E-skin

To date, PVDF demonstrates high triboelectric and piezoelectric performances among all piezoelectric materials. However, the stretchability of PVDF or PVDF-based electrospun fiber mat is below 40%, hardly satisfying the requirement of stretchable electronics which is attached to the skin and followed the skin deformation (100%). Although the copolymerization of vinylidene fluoride and trifluoro ethylene (P(VDF-TrFE)) could enhance the stretchability to 200%, PVDF-based piezoelectric materials with higher stretchability and lower residue strain after stretching are still highly demanded. Herein, the limitations of stretchability and residue skin of PVDF-based materials are addressed by leveraging the coaxial polymerization to produce TPU@P(VDF-TrFE) core-sheath fiber mat. The core, TPU, provides good mechanical properties while the sheath, P(VDF-TrFE), offers well triboelectric properties. During stretching, the outer sheath of P(VDF-TrFE) breaks while the stretchable TPU core could further sustain a larger deformation, therefore, enhancing the overall stretchability of fiber mats (Figure 6.7). As a result, the as-prepared PAST e-skin demonstrates good stretchability, for example, stretching by hand over 250% strain (Figure 6.7c).

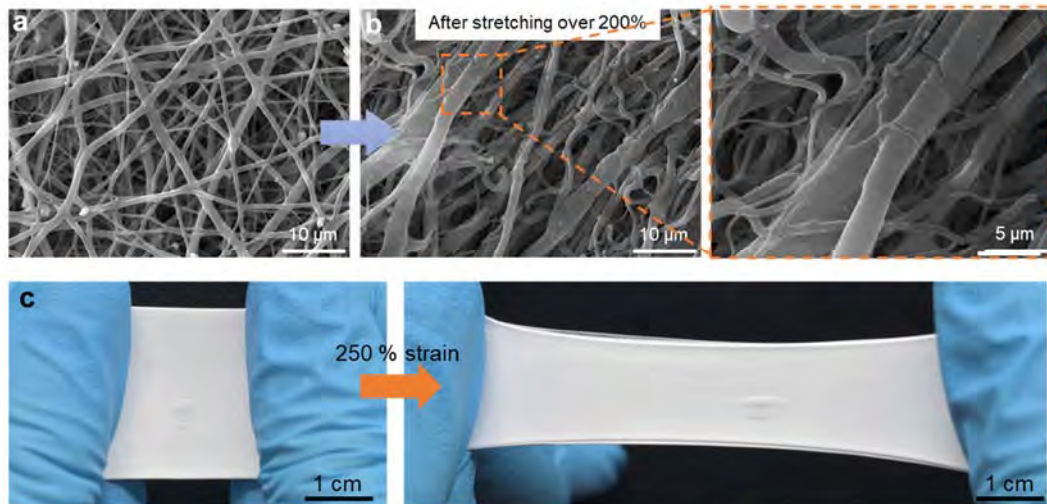


Figure 6.7. a-b, SEM images of TPU@P(VDF-TrFE) core-sheath fiber mat (a) and after stretching (b). c, A piece of PAST e-skin was stretched by hand with 250 % strain.

The mechanical properties of TPU@P(VDF-TrFE) core-sheath fiber mats were identified as shown in Figure 6.8. P(VDF-TrFE) fiber mats break at 200% strain. However, by introducing a stretchable TPU core, the breaking strain significantly rises, for example, 600% for TPU@P(VDF-TrFE) core-sheath fiber mats (P(VDF-TrFE) ratio of 40%). The stretching-releasing cycle at 100 % strain was also conducted. The residue strain after stretching for P(VDF-TrFE) fiber mats is over 60% but it for TPU@P(VDF-TrFE) core-sheath fiber mats (P(VDF-TrFE) ratio: 33.3%) is 31.6%, half lower than the value for P(VDF-TrFE) fiber mats. Ten consecutive stretching-releasing cycles were performed as shown in Figure 6.5 c-f. After 10 cycles, the residue strain of P(VDF-TrFE) fiber mats increases from 63% to 75%. In contrast, the residue strain of the core-sheath fiber mat with a P(VDF-TrFE) ratio of 40% only increased 6.1 % from 32.7 % to 38.6%. Indeed, the core-sheath strategy not only reduces the residue strain after stretching but also increases the stability of stretching cycles.

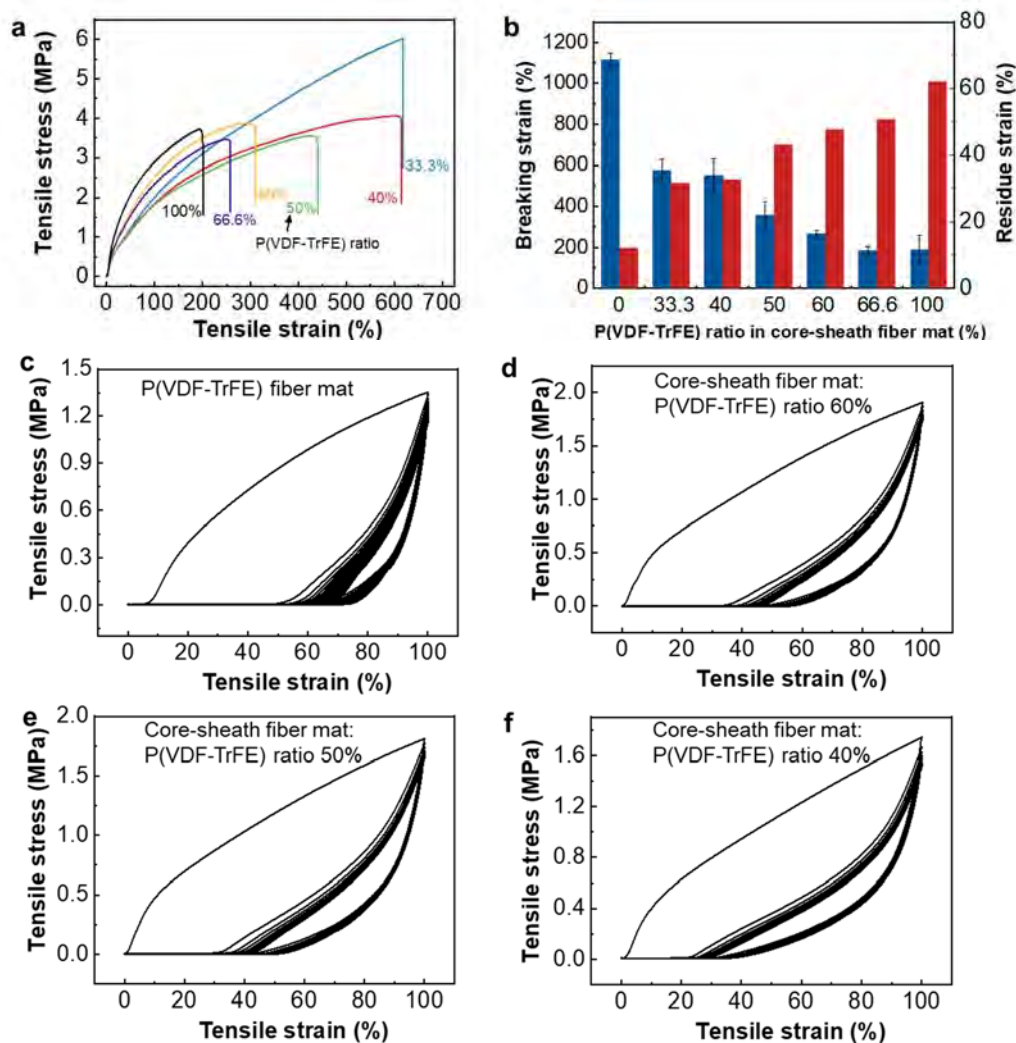


Figure 6.8. Mechanical properties of core-sheath fiber mats. **a-b**, (a) Tensile strain-stress curves and (b) breaking strains and residue strains of core-sheath fiber mats. **c-f**, Ten consecutive stretching-releasing cycles of P(VDF-TrFE) fiber mat (c), core-sheath fiber mats (P(VDF-TrFE) ratio of 60%) (d), core-sheath fiber mats (P(VDF-TrFE) ratio of 50%) (e), and core-sheath fiber mats (P(VDF-TrFE) ratio of 40%) (f).

The PAST e-skin pertains a skin- and wet- adhesive layer of N-hydroxysulfosuccinimide- (sulfo-NHS-) and dopamine-grafted polyacrylic acid (PAASND) and pressure sensitive adhesive (PSA) (PAASND/PSA) electrospun fiber mat. The adhesion performance of this PAASND/PSA fiber mat have been evaluated,

as shown in Figure 6.9. From the lap shear test, the PAST e-skin enables a 20-N adhesion force to the wet porcine skin (Figure 6.9 a-b). The calculated shear adhesion strength of the PAST e-skin for porcine skin is 80 kPa. Therefore, it could offer strong adhesion to the human skin for stable harvesting the human motion energy and stable detect the motion signals (Figure 6.9 c-d).

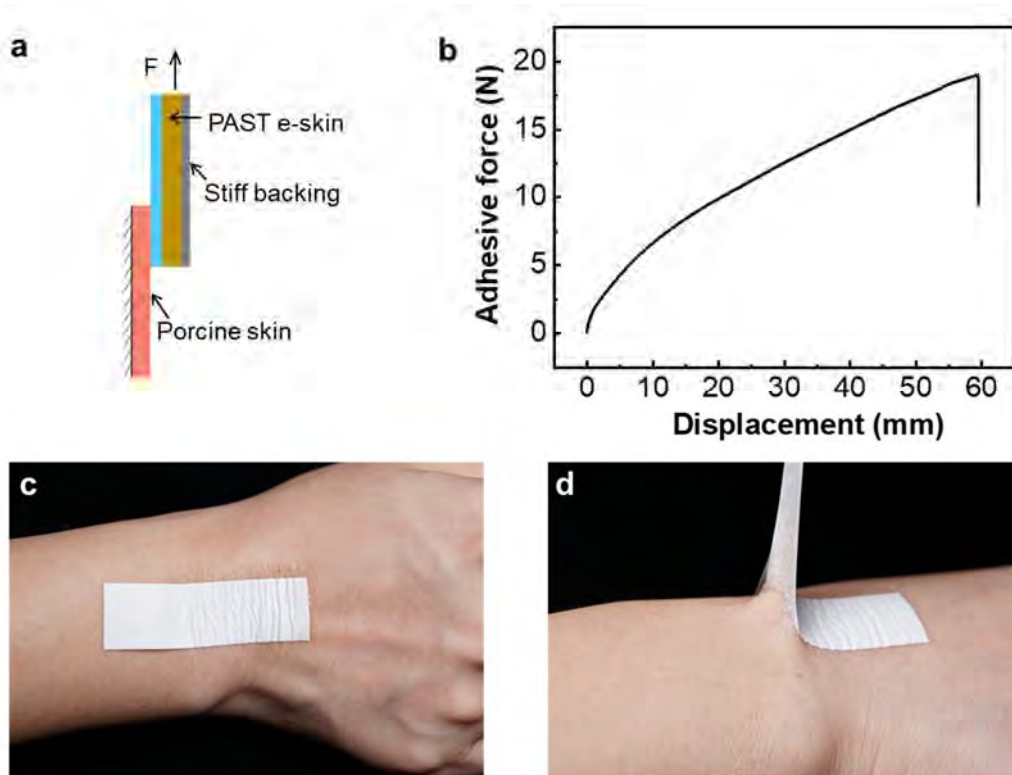


Figure 6.9. Adhesion performance of the PAST e-skin. **a-b**, Schematic illustration of the lap shear test (**a**) and the adhesive force of the PAST e-skin for the wet porcine skin (**b**). **c-d**, The PAST e-skin adhered to the wrist of the human (**c**) and was stretched, showing strong adhesion to the human skin (**d**).

6.3.3 TENG Performance

The TENG performance of the PAST e-skin has been systematically investigated. TPU@P(VDF-TrFE) core-sheath fiber mats were used as triboelectric-active material. Liquid-metal TPU fiber mats were used as the current collector to harvest the

triboelectricity. The working mechanism of the PAST e-skin relies on the combined effects of triboelectrification and electrostatic induction.^[220-221] When the liquid-metal TPU fiber mat electrode approaches contact with the TPU@P(VDF-TrFE) core-sheath fiber mats under external forces, the liquid-metal electrode is positively charged, and the TPU@P(VDF-TrFE) exhibits a negative charge since the triboelectrification effect (1). Once the two materials are separated, a potential difference can be generated and an electron flow from the bottom electrode to the top electrode will be simultaneously produced. This process will approach an equilibrium state after fully separating the two materials. Once the two materials are in contact again, the charges induced by the electrostatic effect will flow back through the external circuit to compensate for the electric potential difference, generating an opposite output.

Firstly, PAST e-skin sandwiched of different TPU@P(VDF-TrFE) core-sheath fiber mats have been fabricated (Figure 6.10a). The open-circuit voltage of pure P(VDF-TrFE) is the highest at over 167.5 V. The open-circuit voltage of TPU@P(VDF-TrFE) core-sheath fiber mats (P(VDF-TrFE) ratio of 66.6%) decreases by 27% to 122 V. Adding the TPU to the TPU@P(VDF-TrFE) core-sheath fiber mats weakens the output voltage of the PAST e-skin since P(VDF-TrFE) is a much better triboelectric material than TPU. However, the open-circuit voltage remains at 73 V decreasing the P(VDF-TrFE) ratio to 33.6%. Both core-sheath fiber mats possess high open-circuit voltage, showing the potential in mechanical energy harvesting and mechanical sensors.

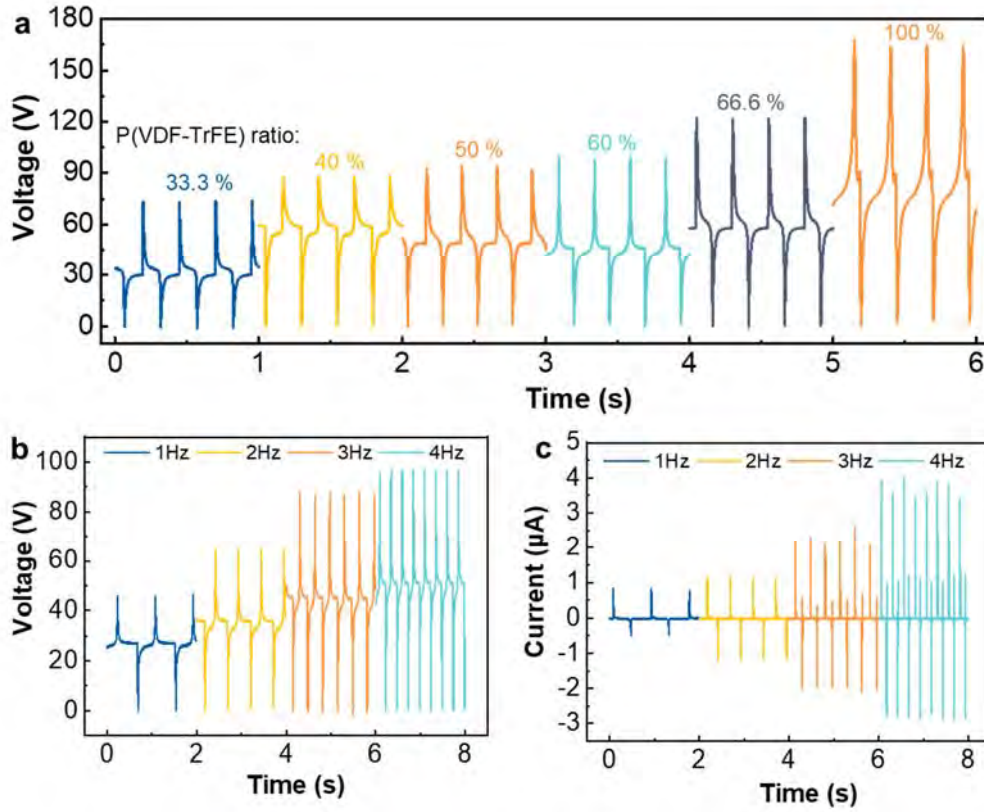


Figure 6.10. Output TENG performance of the PAST e-skin. **a**, The open-circuit voltage of different triboelectric fiber mats varied with the ratio of P(VDF-TrFE). **b-e**, Open-circuit voltage (**b**), short-circuit current (**c**) of the TPU@P(VDF-TrFE) core-sheath fiber mat (P(VDF-TrFE) ratio = 40%) with different contact-release frequencies.

The output signals of the PAST e-skin (40% P(VDF-TrFE)) with different contact-release frequencies have also been investigated (Figure 6.10b). Higher contact-release frequencies can generate higher output signals. The contact-release frequency at 4 Hz has the highest output signals with 96.7 V open-circuit voltage and 4.0 μA short-circuit current. The open-circuit voltage and short-circuit current reduce by 52.7% and 79% by reducing the frequencies to 1 Hz. The potential reason may be that higher impact frequencies can stimulate the electron flow in a short time while boosting the output signals^[213]. Considering the long-term and stable usage of the PAST e-skin, 10,000

continuous contact-release cycles of the PAST e-skin have been conducted (Figure 6.11). The triboelectric performance of the PAST e-skin is highly stable during the 10,000 cycles without any performance degradation. This PAST e-skin could also work during large deformations, for example: 150%, showcasing the stability during large strains (Figure 6.11 b). In comparison to other literature^[77, 217, 222-224], the PAST e-skin is the first self-powered sensor that simultaneously offers high stretchability, textile-like permeability, adhesiveness, and considerable open-circuit voltage (Figure 6.11c).

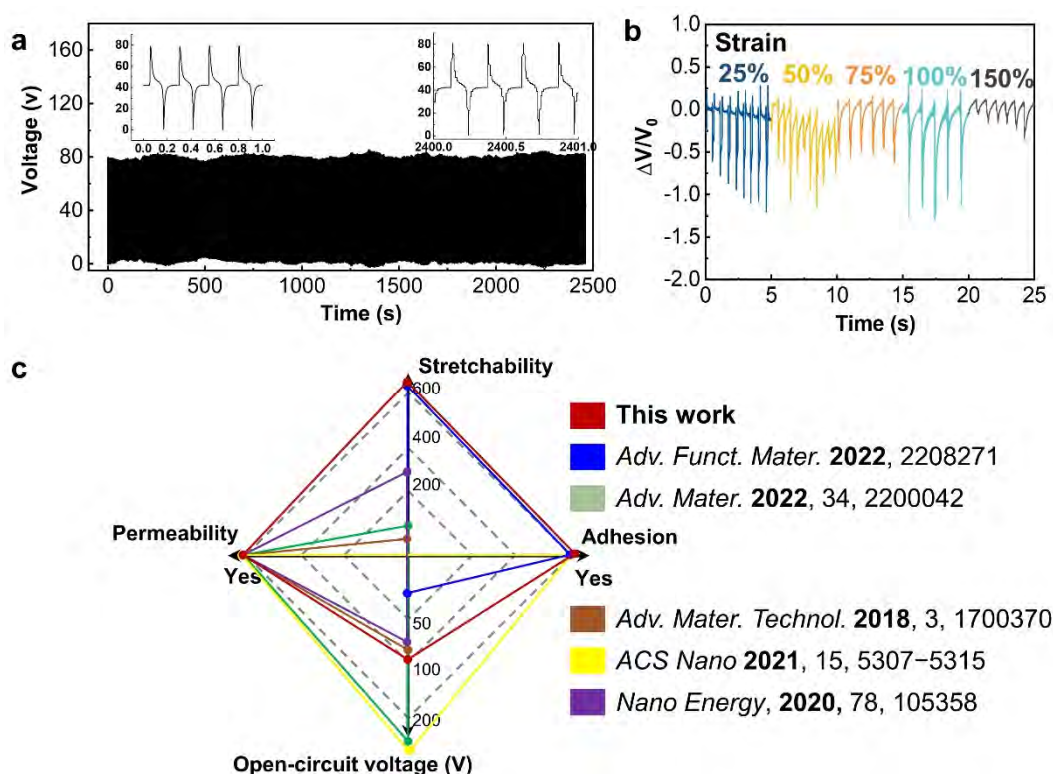


Figure 6.11. Stability and stretching tests for the PAST E-skin. **a**, 10,000 cycles of consecutively contact-detach test for the TPU@P(VDF-TrFE) core-sheath fiber mat (P(VDF-TrFE) ratio = 40%). **b**, Changes of open-circuit voltage during different applied strains. **c**, Comparison of the reported self-powered sensors and this work in the stretchability, permeability, adhesion, and open-circuit output.

Experiments involving the application and release of pressures on the core-sheath TPU@P(VDF-TrFE) triboelectric fiber mats, spanning from 0.25 kPa to 100 kPa, were conducted. The open-circuit voltage exhibited a proportional increase with the applied pressures, rising from 13.1 V at 0.25 kPa to 122 V at 100 kPa (Figure 6.12a). The fiber mats exhibit sensitivities of 5 kPa^{-1} at the pressure range from 0-10 kPa and 0.65 kPa^{-1} at the pressure range from 10-100 kPa. Upon decreasing the applied pressures, the open-circuit voltage declined, stabilizing at a consistent level at a critical pressure, showcasing the high reproducibility and minimal hysteresis of this triboelectric fiber mat in pressure sensing (Figure 6.12).

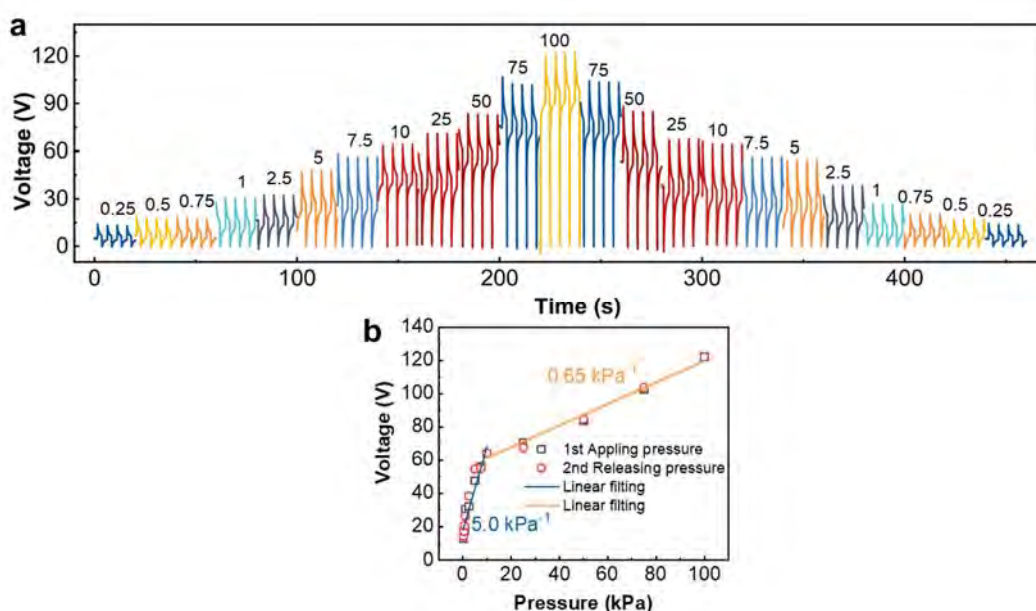


Figure 6.12. Pressure sensing properties of the core-sheath TPU@P(VDF-TrFE) triboelectric fiber mat. **a**, Open-circuit voltage of the triboelectric mat in response to the loaded pressures from 0.25 kPa to 100 kPa and continuously releasing the pressures from 100 kPa to 0.25 kPa. **b**, Open-circuit voltage changes corresponding to the applied pressures.

Combining the high triboelectric performance, excellent stretchability, textile-like permeability, and wet adhesion properties, the PAST e-skin can be a well human motion

sensor to intimately monitor body movements. As shown in Figure 6.13, the PAST e-skin mount on the joint of the index finger generates 2 V output signals during finger bending. The sensors adhered to the skin of the wrist could also produce 1.0 V output signals during wrist movements and those signals are 0.5 V for the knit. The PAST e-skin adhered to the locate of masticatory muscle at the human face and also recorded a 0.2 V output voltage. Although the output voltage of the sensor adhered to the masticatory muscle is the lowest of the small size and low movement stroke of the masticatory muscle, it still indicates the high precision of the PAST e-skin used as the human motion sensors.

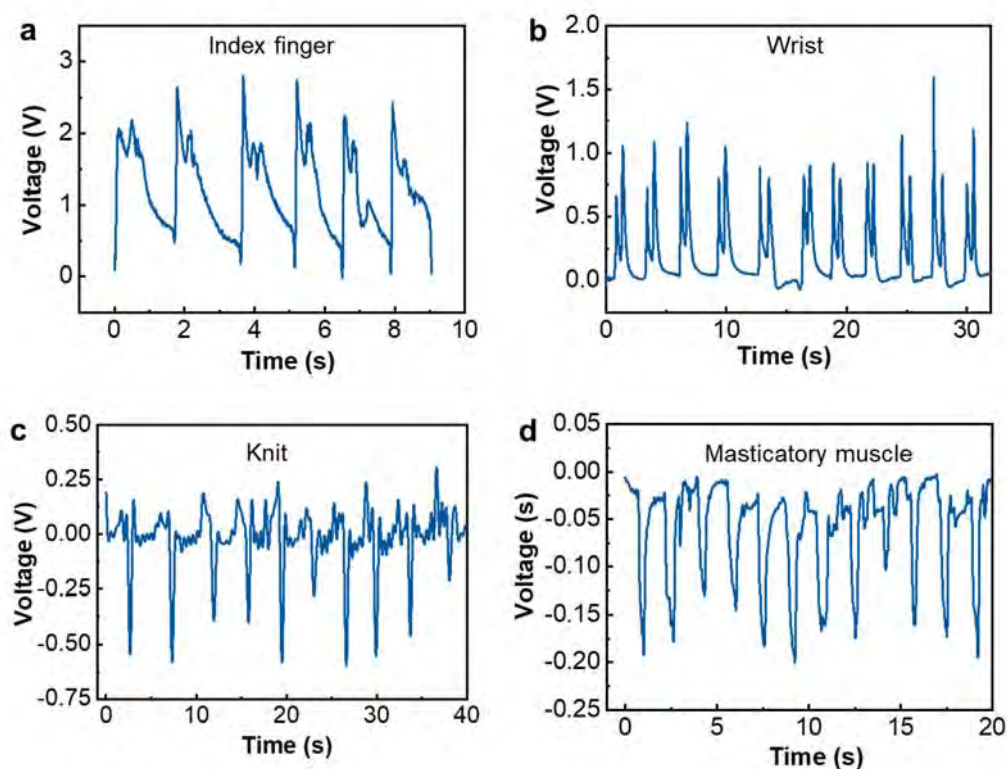


Figure 6.13. PAST e-skin adhered to the human skin for monitoring body motions. **a-d**, Output voltage of the PAST e-skin adhered to the joint of the index finger (**a**), wrist (**b**), knit (**c**), and masticatory muscle (**d**) as the sensors to detect the motions.

6.4 Conclusions

In summary, the all fiber-mat, permeable, wet-adhesive, and superplastic triboelectric e-skin (PAST e-skin) has been developed. Two layers of stretchable and permeable liquid-metal fiber mats as electrodes, a layer of core-sheath triboelectric fiber mat, and a layer of wet-adhesive fiber mats have been stacked together to prepare the PAST e-skin. To enhance the stretchability of the middle-layer triboelectric material, P(VDF-TrFE), the core-sheath TPU@P(VDF-TrFE) fiber mat was developed with a stretchable TPU core, which significantly enhance the stretchability to 600% and reduce the residue strain to 30.6%. The PAST e-skin pertains a wet- and skin-adhesive fiber mat that could seamlessly adheres the PAST e-skin to the wet human skin with the adhesion strength of 80 kPa. The open-circuit voltage and the short-circuit current of the PAST e-skin are 96.7 V and 4.0 μ A, respectively. This PAST e-skin is the first self-powered sensor that simultaneously offers high stretchability, low residue strain, textile-like permeability, and wet-adhesive properties. Precise on-skin monitoring of body motions of the finger, wrist, knit, and masticatory muscles has been achieved by adhering the PAST e-skin to the target body area. This PAST e-skin offers a new route to design high-performance TENG epidermal sensors with permeability, stretchability, and wet adhesion property while putting this field in a more conformal, stable, and comfortable way.

Chapter 7: CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

7.1 Conclusions

In this thesis, adhesive, permeable, and wearable electronic skins have been developed. Electronic skins consist of porous micro/nanofiber mats and EGaIn. The electronic skins could be intimately attached to the human skin, offering stable device performance. The electronic skins also maintain permeability for the perspiration of human skin, providing comfortable sensations and lowering the risks of skin problems. Using electronic skins as an electronic platform allows long-term recording of physiological activities such as ECG signals over days, and VR-mediated remote control of robots even under wet or underwater conditions. The investigation on fabricating low-impedance and ultrathin electrodes has also been achieved via electrospun fibre mats. Furthermore, this thesis also aims to develop triboelectric skin-attachable sensors with permeability, adhesiveness, and stretchability.

Chapter 4 presents the development of a wet-adaptive electronic skin, termed WADE-skin. This WADE-skin incorporates a next-to-skin wet-adhesive fibrous layer, a next-to-air waterproof fibrous layer, and a stretchable and permeable liquid metal electrode layer. The WADE-skin demonstrates exceptional characteristics, including outstanding stretchability, wet adhesion, permeability, biocompatibility, and waterproof properties. Upon contact with human skin, the WADE-skin adheres rapidly within seconds and maintains its performance even when exposed to wet conditions over weeks. Furthermore, its application does not pose any adverse effects on human skin. The versatility of the WADE-skin is demonstrated through applications such as stable electrocardiogram recording during intensive sweating and underwater activities, as well as its use as strain sensor array for wet-adaptive human-machine interactions

mediated by VR.

In Chapter 5, a strategy called “nanofibers-to-hydrogel” to fabricate ultrathin liquid metal hydrogel electrode was investigated for the first time. The liquid-metal PVA fiber mats are easily handled and user-friendly and could instantly absorb saline water thus forming hydrogel tattoos at the surface of the skin. The formed hydrogel tattoo is stretchable and permeable and could conformally adhere to the skin. The hydrogel tattoo displays a low skin impedance compared to the commercial Ag/AgCl gel electrode. The hydrogel tattoos were investigated as biophysiological electrode to detect ECG signals for health monitoring and assembled to a 6-channel EMG sensor array for gesture recognition assisted by machine learning.

In Chapter 6, an all-fiber-mat, permeable, wet-adhesive, and superplastic triboelectric skin (PAST e-skin) has been proposed firstly. The triboelectric fiber mat was fabricated by coaxial electrospinning, which significantly enhances the stretchability from 200% to 600% and reduces the residue strain from 60% to 30.6% within 100% pre-stretching. The PAST e-skin pertains a wet- and skin-adhesive fiber mat that could seamlessly adheres the PAST e-skin to the wet human skin with the adhesion strength of 80 kPa. The PAST e-skin simultaneously offers high stretchability, low residue strain, textile-like permeability, and wet-adhesive properties. The triboelectric outputs of the PAST e-skin have been investigated and on-skin monitoring in different body locations using the PAST e-skin has also been conducted.

7.2 Suggestions for Future Research

It is believed that the wet adaptability is a milestone in the field of wearable electronics and electronic skins, and this work will appeal to the broad readers in applied physics, materials science and engineering, soft electronics, polymer science and interface.

Nevertheless, several bottlenecks still require resolution.

One bottleneck is the reliability of the permeable electronics against repeated and large mechanical deformations. It is highly critical for permeable conductors to maintain stable and reliable conductive performance under different conditions because various types of mechanical deformations and disruption, including but not limited to bending, folding, stretching, shearing, and abrasion motions, occur frequently and irregularly during the practical wearable and on-skin applications. Other than bending and stretching tests that have been widely implemented for the study of conductor performance, attention could also be extended to the ability of the permeable conductors to resist friction, shearing, washing, and low/high temperature, which are largely overlooked in the evaluation of conductors. Additional functionalities, such as self-healing, anti-abrasion, waterproof, and thermal stability, thus may be acquired. This will require more understanding of the interplay among materials, structures, and mechanical strains, and the exploitation of new materials and structures with superior mechanical robustness and environmental stability.

Applications of breathable electronics among long-term healthcare monitoring, human-machine interaction, and energy harvesting have been widely demonstrated based on permeable conductors in research laboratories. However, breathable electronics are still far away from practical applications because of the lack of system integration study and the limitations of scalable fabrication. To date, how to seamlessly integrate different electronic modules, including sensor electrodes, data processing units, and energy harvesting and storage units, into a monolithic patch without affecting the device's functionalities, flexibility/stretchability, and most importantly, permeability is rather challenging. And there are only a few reports on such kinds of highly integrated breathable electronics.^[225-226] On the other hand, the manufacture of these advanced flexible and stretchable electronics largely involves soft substrates with 1D or 2D

architectures, which are not fully compatible with conventional processes for integrated circuit fabrication. Given these research and development gaps, multidisciplinary studies not only with chemical engineering and mechanical sciences, but also with electronic engineering, system integration, machine learning, and mechanical engineering are highly demanding. With enormous efforts kept investing in materials development, structural designs, fabrication optimization, and system integration, we anticipate that permeable conductors with superior mechanical properties and conductivity could be developed for increasingly practical applications of wearable and on-skin electronic systems.

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